SILICATE AND ALUMINATE BASED DIELECTRIC CERAMICS FOR MICROWAVE COMMUNICATION

THESIS SUBMITTED TO COCHIN UNIVERISTY OF SCIENCE AND TECHNOLOGY IN PARTIAL FULFILMENT OF REQUIREMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN PHYSICS

SHERIN THOMAS

Under the guidance and supervision of

Dr. M. T. Sebastian (Supervisor)

NATIONAL INSTITUTE FOR INTERDISCIPLINARY SCIENCE AND TECHNOLOGY (CSIR), THIRUVANANTHAPURAM

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DECLARATION

I hereby declare that the matter presented in the thesis entitled "SILICATE AND ALUMINATE BASED DIELECTRIC CERAMICS FOR MICROWAVE COMMUNICATION" is the outcome of investigations carried out by me under the supervision of Dr. M. T. Sebastian, Scientist 'G', Materials and Minerals Division, National Institute for Interdisciplinary Science and Technology (Formerly Regional Research Laboratory) (CSIR), Thiruvananthapuram, India and the results embodied here has not been submitted elsewhere for the award of any other degree.

Thiruvananthapuram **Sherin Thomas**

Dated:

Dedicated to my family

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CERTIFICATE

This is to certify that this thesis entitled "SILICATE AND ALUMINATE BASED DIELECTRIC CERAMICS FOR MICROWAVE COMMUNICATION" is an authentic record of the investigations carried out by Ms. Sherin Thomas at the Materials and Minerals Division of National Institute for Interdisciplinary Science and Technology (Formerly Regional Research Laboratory) (CSIR), Thiruvananthapuram, India, under my supervision and guidance. This thesis or any part thereof has not been submitted elsewhere for the award of any other degree.

Dr. M. T. Sebastian

Thiruvananthapuram

Dated **(Supervisor)**

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PREFACE

Recently, microwave telecommunication has been developed for a wide range of applications, such as mobile phone, wireless LAN and Intelligent Transport System (ITS). Utilized microwave frequency has also increased from microwave to millimeter range in order to transmit large quantity of information with high speed. Microwave dielectric materials are continuing to play a very important role in the microwave communication systems. As a result, a large number of ceramic dielectric materials have been developed for use as dielectric resonators, capacitors, substrates and electronic packages. The key material requirements for microwave dielectric materials to be used for high frequency applications are: optimum relative permittivity, high quality factor and near-zero temperature coefficient of resonant frequency. The development of low-temperature co-fired ceramics (LTCC) has been stimulated by the benefits offered for the fabrication of miniature multilayer devices and for high level of passive integration involving the co-firing of dielectric and highly conductive metals, such as silver and copper. The present thesis entitled ***"SILICATE AND ALUMINATE BASED DIELECTRIC CERAMICS FOR MICROWAVE COMMUNICATION"*** *is the outcome of a detailed investigation performed on the synthesis, characterization and microwave dielectric properties of some novel rare earth based silicates and aluminate. Accordingly the thesis is divided into seven chapters.*

The first chapter gives a general introduction on low loss microwave dielectric ceramics and its importance in various areas of interest such as dielectric resonators, low temperature cofired ceramics, substrates and electronic packaging. A brief discussion about the relevance of polymer ceramic composites in microelectronic industry is also included. The major scientific and technological aspects, material requirements and applications of the dielectric ceramics are also given.

Chapter 2 presents the details of the preparation techniques adopted for the synthesis of dielectric resonators, LTCC materials and polymer ceramic composites. A brief description about the various characterization techniques used for the structural, microstructural and dielectric characterization in the purview of this thesis is also presented.

Chapter 3 gives a general idea on the importance of silicate materials for microwave applications and throws light into a new group of materials $ARE_4Si_3O_{13}$ *[A=Ca, Sr and Ba; RE=rare earths] belonging to the 'apatite' family for high frequency applications. The synthesizing conditions of these materials are optimized for the best properties. The structural investigations using XRD refinements and TEM revealed that they belong to* $P6_3/m$ *space group with hexagonal symmetry. The materials exhibited a relative density less than 94 % which was improved to certain extent by the addition of a small amount of glass. The microwave dielectric properties of these materials are reported for the first time. The sintered ceramics has a relative permittivity (*ε_r*) less than about 20 and quality factor* Q_u *x f up to 30000 GHz. The high* $_f$ *value (-46 ppm/*^oC*) of* $SrLa_4Si_3O_{13}$ *is tuned to a near zero value by the addition of suitable amount of* TiO_2*. The mixture rules are used to calculate the density,* ε_r *and* $_f$ *of these ceramics and the theoretical values agree well with the experimental ones.*

Chapter 4 highlights the synthesis, characterization and microwave dielectric properties of two novel rare earth based silicates [$Sm_2Si_2O_7$ *and* $RE_2Ti_2SiO_9$ *(RE=La, Pr and Nd)] ceramics. The* $Sm_2Si_2O_7$ *ceramics has a tetragonal symmetry whereas* $RE_2Ti_2SiO_9$ *(RE=La, Pr and Nd) dielectric ceramics possess a monoclinic symmetry. The* $Sm_2Si_2O_7$ *ceramics sintered at 1375*^oC*/2h exhibit excellent dielectric properties:* $\varepsilon_r = 10$ *and tan* $\delta = 0.006$ *measured at 9 GHz. The effect of various low loss glass addition on the sintering, densification and microwave dielectric properties of* $Sm_2Si_2O_7$ *is*

studied. The $Sm_2Si_2O_7$ ceramics mixed with 15 wt% LBS glass lowered the sintering temperature to 975°C, whereas the 15 wt% LMZBS glass addition lowered sintering temperature of 950°C. The pure $Sm_2Si_2O_7$ ceramics and that mixed with 15 wt% LMZBS glass did not show much variation in relative permittivity with temperature. The $RE_2Ti_2SiO_9$ (RE=La, Pr and Nd) ceramics exhibited a relative permittivity less than 20 and relatively low τ_f value. A maximum value of Q_u x f of 33500 GHz is shown by $Pr_2Ti_2SiO_9$ ceramics. It is seen that Pr substitution for La favored the formation of solid solution in the whole range obeying Vegard's law while Nd substitution resulted in the formation of additional phases. As the Pr content increases, an improvement in the quality factor is noted whereas the τ_f value is not much affected.

Chapter 5 discusses in detail the synthesis and characterization of various polymer ceramic composite using $Sm_2Si_2O_7$ ceramics as filler for electronic packaging applications. The polymers used in the investigation are PTFE, Polyethylene and Polystyrene. The dielectric, thermal and mechanical properties of these polymer-ceramic composites has been investigated. The effects of coupling agent and filler particle size on the above properties of PTFE/$Sm_2Si_2O_7$composites are also studied. For a filler loading of 0.5 v_f, PTFE composite has ε_r = 3.82 and tan δ = 0.0136 (at 9 GHz), k_c = 1.76 W/m°C, α_c = 36 ppm/°C, Vickers' microhardness of 13 kgf/mm²; PE composite has ε_r = 5.28 and tan δ = 0.0091 (at 9 GHz), k_c = 2.97 W/m°C, α_c = 60 ppm/°C, Vickers' microhardness of 17 kgf/mm² and PS composite has ε_r = 4.60 and tan δ = 0.0110 (at 9 GHz), k_c = 0.29 W/m°C, α_c = 36 ppm/°C, Vickers' microhardness of 56 kgf/mm². Several theoretical model approaches have been employed to predict the relative permittivity, thermal conductivity and coefficient of linear expansion of the composite systems and the results were compared with that of

experimental data. All theoretical predictions were found to be valid for low filler contents.

Chapter 6 outlines the applicability of 0.83 $ZnAl_2O_4$-0.17 TiO_2 (ZAT) dielectric ceramic based glass and polymer composites for LTCC substrate and electronic packaging applications respectively. The ZAT dielectric ceramic possess excellent thermal and microwave dielectric properties but with a high sintering temperature of 1450°C. The first section of the Chapter 6 discusses the efforts taken to reduce the sintering temperature by glass addition for use as LTCC substrate material. Among the various glasses added, BBSZ is found to lower the sintering temperature without much affecting the microwave dielectric properties. The XRD and SEM of BBSZ glass added ZAT composites suggested the existence of no additional secondary phases. The addition of 10 wt% BBSZ glass reduced the sintering temperature to 950°C with reasonably good microwave dielectric properties. The composites also possessed high chemical compatibility with silver. The results bring out the possibility of using ZAT/10 wt% BBSZ composites for LTCC substrate applications. The second section of this chapter compares the physical, dielectric and thermal properties of ZAT loaded PTFE and PE composites. The PE/ZAT composites possessed a high relative density when compared with the PTFE/ZAT composites. For lower filler content the fillers are uniformly dispersed in the matrix and as the filler content increased the agglomeration also increased and resulted in porosity. The dielectric properties of both the composites showed that ZAT loaded with PE composites exhibited good dielectric properties and also a very low water absorption value of less than 0.1 %. The results show that ZAT filler loaded composites have better properties than that loaded with $Sm_2Si_2O_7$ filler and can be used for electronic packaging applications.

The seventh chapter gives the conclusion of the thesis and scope for future work.

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Sherin Thomas

CHAPTER 1

INTRODUCTION

This chapter gives an introduction and overview of progress of research in dielectric resonators (DR) and low temperature co-fired ceramics (LTCC). The various scientific and technological features of polymer-ceramic composites for substrate and electronic packaging applications are also discussed. The fundamental physical aspects, working principle and some of the practical applications of DR's are briefly depicted. The chapter also cites the important characteristics required for a material for LTCC, electronic packaging and substrate applications.

1.1 INTRODUCTION

COMMUNICATION IS THE FUNDAMENTAL ASPECT OF SOCIAL INTERACTION. THE PI
TECHNOLOGICAL ADVANCES OF THE 19TH CENTURY BROUGHT PROFOUND CHANGES IN C
WHICH WERE PREVIOUSLY LIMITED TO PRIMITIVE HAND-DELIVERY OF MESSAGES
'SEMAPHORE'. THE INTRODUCTION OF ELECTRICITY LED TO THE DEVELOPMENT OF THE T
THE BIRTH OF THE TELECOMMUNICATION WAS IN 1895, WHEN GUGLIELMO MARCONI
OPENED THE WAY FOR MODERN WIRELESS COMMUNICATION BY TRANSMITTING THE THR
CODE FOR THE LETTER 'S' OVER A DISTANCE OF THREE KILOMETERS USING ELECTROM
THAT THE WIRELESS COMMUNICATION DEVELOPED INTO A KEY ELEMENT OF MODERN
LAST FEW DECADES HAVE WITNESSED A PROLIFERATION OF INTERPERSONAL CO
TECHNOLOGIES. DEMAND WITHIN THE ELECTRONICS AND TELECOMMUNICATION INDUST
RAPIDLY WITH CONTINUAL REQUIREMENTS FOR LOWER COST AND BETTER PERFORMAN
THE END USER. THE WIRELESS TECHNOLOGY HAS BEEN THE FASTEST-GROWING INDUSTR
WORLD UNTIL NOW. A PRIME EXAMPLE IS MOBILE TECHNOLOGY, WHICH HAS SEEN A
EXPANSION OVER THE LAST TEN YEARS, AND WITH REDUCTION IN COST OF SYSTEMS, THI
READILY AVAILABLE TO ALL. EVEN OUR COUNTRY HAVE WITNESSED THE RAPID GROWTH
WIZARD THAN ANY OTHER NEW TECHNOLOGICAL INNOVATIONS, BOTH IN RURAL AN
ATTRACTING PEOPLE BY THE AFFORDABILITY AND MANY OTHER RELEVANT FACILITIES
RECENT SURVEY, THE INDIAN TELECOMMUNICATION INDUSTRY IS ONE OF THE WOR
GROWING INDUSTRIES AND THE SECOND LARGEST TELECOMMUNICATION NETWORK IN T
BEING CHINA) WITH ABOUT 654 MILLION TELEPHONE SUBSCRIBERS AND ABOUT 620 MILL
PHONE CONNECTIONS. IT IS PROJECTED THAT INDIA WILL HAVE NEARLY 1.16 BILLI
SUBSCRIBERS BY 2013 [1]. MOBILE PHONE NETWORKS ALLOW COMMUNICATION FROM C
VIA ANTENNAS LOCATED ON MASTS AND ASSOCIATED BASE STATIONS.

TODAY, MICROWAVES ARE EMPLOYED BY TELECOMMUNICATION INDUSTRIES IN TH
BOTH TERRESTRIAL RELAYS AND SATELLITE COMMUNICATIONS. THE TECHNOLOGY USE
COMMUNICATION WAS DEVELOPED IN THE EARLY 1940'S BY WESTERN UNION. TH
MICROWAVE MESSAGE WAS SENT IN 1945 FROM TOWERS LOCATED IN NEW YORK AND PHI
FOLLOWING THIS SUCCESSFUL ATTEMPT, MICROWAVE COMMUNICATION BECAME
COMMONLY USED DATA TRANSMISSION METHOD FOR TELECOMMUNICATIONS SERVIC

FREQUENCIES RANGING FROM 300 MHZ-30 GHZ ARE USUALLY CALLED "MICROW FREQUENCIES ABOVE ABOUT 30 MHZ CAN PASS THROUGH THE IONOSPHERE AND SO AR FOR COMMUNICATING WITH SATELLITES AND OTHER EXTRA-TERRESTRIAL SOURCES. HIGH FREQUENCIES, MICROWAVES HAVE THE ADVANTAGE OF BEING ABLE TO CARRY MO THAN ORDINARY RADIO WAVES AND ARE CAPABLE OF BEING BEAMED DIRECTLY FROM ANOTHER. FIG. 1.1 SHOWS THE MICROWAVE FREQUENCY SPECTRUM AND THE APPLICAT VARIOUS FREQUENCY BANDS [2]. WITH CONTINUING ADVANCES IN MICROWAVE DEV SYSTEMS ARE BEING DEVELOPED FOR MILLIMETER PORTION OF THE MICROWAVE BAND.

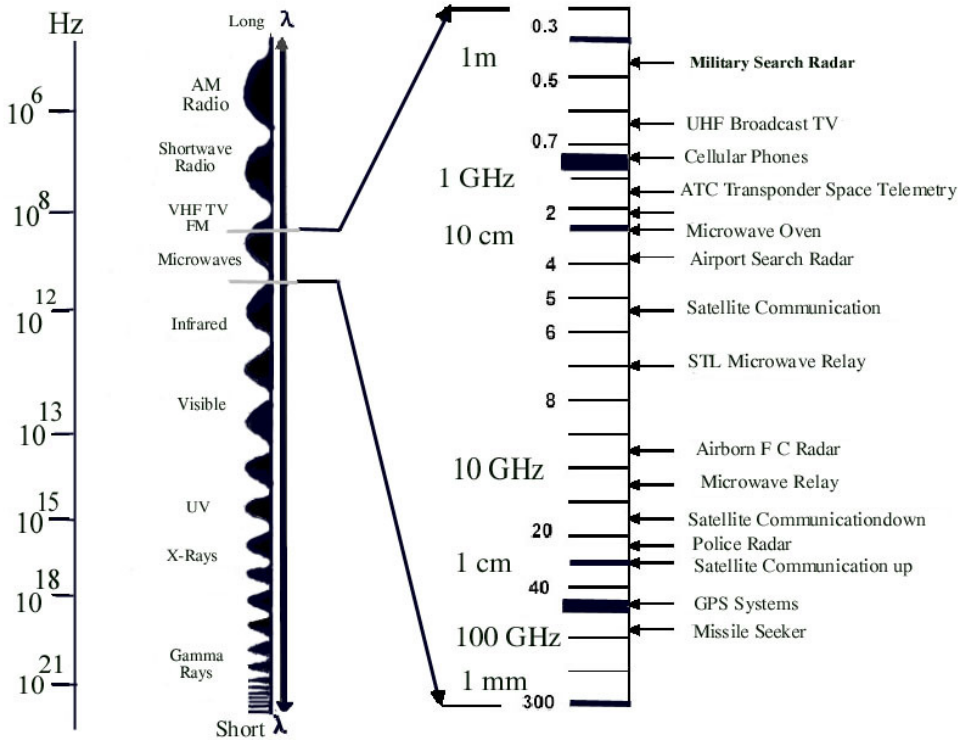

Fig. 1.1 Microwave spectra and its applications.

THE DEMAND FOR CERAMICS IN ELECTRONIC EQUIPMENTS IS GROWING RAPIDLY A OF THEIR SUPERIOR PHYSICAL PROPERTIES AND IMMENSE TECHNOLOGICAL APPLICATIO PAST FIVE YEARS, CERAMICS HAVE UNDERGONE A REVOLUTION ALMOST AS DRAMATI FAMILIAR ONE IN ELECTRONICS. NOVEL APPROACHES FOR PREPARING AND PROCESSING C HAVE BEEN DEVELOPED. TODAY'S ADVANCED CERAMICS REPRESENT DEVELOPMENTS V

THE IMAGINATION OF EVEN THE FEW FARSIGHTED SCIENTISTS OF 25 YEARS AGO WHO FI
THE REMARKABLE POTENTIAL OF CERAMIC SOLIDS AND ESTABLISHED DUCTILE ENGINE
AS A SUITABLE OBJECTIVE FOR MATERIALS RESEARCHERS TO PURSUE. DESIGNERS AR
USING CERAMIC SOLUTIONS IN ELECTRICAL SYSTEMS, AND THE MATERIAL OFTEN
AFFORDABLE SOLUTION TO MANY OF THE ISSUES THAT NEED TO BE OVERCOME. THE W
ORIGINATED FROM THE GREEK WORD 'KERAMOS' CAN BE DEFINED AS,

typically oxides of metals, but may be other inorganic elements in combination with well-defined crystal lattice structures. They are generally hard, brittle and have very high melting points [3].

DIELECTRIC CERAMIC MATERIALS HAVE BEEN STUDIED FOR DECADES DUE TO BOTH TH
IN IMPORTANT TECHNOLOGIES AND THE FUNDAMENTALLY INTERESTING RELATIONSH
CRYSTAL CHEMISTRY, CRYSTAL STRUCTURES AND PHYSICAL PROPERTIES. THE FABR
PERFORMANCE MICROELECTRONIC DEVICES DEPENDS INCREASINGLY ON A SOPHISTICAT
IN WHICH INDIVIDUAL COMPONENTS ARE LOCATED ON COMPLEX SUBSTRATES CON
NECESSARY POWER DISTRIBUTION LINES AND INTERCONNECTS. THESE SUBSTRATES COM
LAYERS OF CERAMIC, METAL AND THIN FILM ORGANIC INSULATORS. THE FABRICAT
SUBSTRATES IS MADE DIFFICULT BY A NUMBER OF PROBLEMS, PROMINENT AMONG WHI
ENSURING ADHESION BETWEEN THE DIFFERENT COMPONENTS. THE MOST COMMONLY U
IN MICROELECTRONICS IS ALUMINA. IT HAS A HIGH RELATIVE PERMITTIVITY WHICH RED
OF THE ELECTRICAL SIGNAL TRANSMISSION. CERAMICS WITH LOWER RELATIVE PERMIT
PREFERABLE BUT NONE OF THE PRESENT ALTERNATIVES IS AS EASILY PROCESSED AS
MICROELECTRONIC PACKAGING REQUIREMENTS FOR LOW TEMPERATURE SINTERING,
PERMITTIVITY AND CONTROLLED THERMAL EXPANSION CANNOT BE MET BY CONVENT
MATERIALS SUCH AS ALUMINA. NEW MULTIPHASE COMPOSITES OFFER MANY OF TH
PROPERTIES, BUT THE RELATIONSHIPS BETWEEN STRUCTURE AND PROPERTY ARE HIG
THUS THE ELECTRONIC CERAMIC INDUSTRY IS MOVING TOWARDS CHEMICALLY SYNTHE
POWDERS IN WHICH SOL-GEL AND OTHER INNOVATIVE TECHNIQUES YIELD MATERIALS
FORM AND SINTER MORE READILY AND YIELD MORE ACCEPTABLE PHYSICAL PROPERTIES

1.2 MICROWAVE DIELECTRIC CERAMICS

1.2.1 INTRODUCTION

THE REVOLUTION IN WIRELESS COMMUNICATIONS AND INFORMATION ACCESS IS
MOST DRAMATIC CHANGES IN TECHNOLOGY IN THE PAST DECADE. AS IN ALL TECHNOLO
THE BASIS OF THESE REVOLUTIONARY CHANGES IS ADVANCES IN MATERIALS. WITH
GENERATION OF MICROELECTRONIC DEVICES NEW AND MORE STRINGENT DEMANDS A
MATERIALS BEING USED. AMONG THE VARIOUS BRANCHES OF FUNCTIONAL CERAMICS, T
CERAMIC INDUSTRY IS OF PRIMARY INTEREST CHARACTERIZED BY RAPID INNOV
TECHNOLOGICAL ADVANCES. ONE OF THE MAJOR ACHIEVEMENTS OF ELECTRONIC CE
RECOGNITION OF POTENTIAL USEFULNESS OF DIELECTRIC MATERIALS AS ENERGY STOR
OSCILLATORS AND FILTERS FOR THE MICROWAVES CARRYING THE DESIRED INFORMA
APPLICATIONS NOW CONSTITUTE THE MAJOR MARKET FOR ADVANCED CERAMICS USED
SUBSTRATES, CAPACITORS, PIEZOELECTRICS AND RESISTORS. THESE MATERIALS A
EMPLOYED AS BULK CERAMICS IN MICROWAVE COMMUNICATION DEVICES; THEY ARE NO
INTO THE MICROELECTRONICS BUT ARE FOUND AS DISCRETE COMPONENTS. SOME OF TH
OF ELECTRONIC CERAMICS IN TELECOMMUNICATION INDUSTRY ARE DISCUSSED BELOW.

1.2.2 MICROWAVE DIELECTRIC RESONATORS

THE NEED FOR COMMUNICATION SYSTEMS USING MICROWAVES ARE INCREASING
INCREASE IN DEMAND FOR EXCHANGE OF INFORMATION VIA WIRELESS COMMUNICATION
ARE IMPORTANT COMPONENTS IN MICROWAVE COMMUNICATION CIRCUITS. THEY FORM
PART OF RADIO RECEIVERS AND CELL PHONES. A MICROWAVE CIRCUIT WORKS WHEN
VIBRATES OR “RESONATES” AT A SPECIFIC FREQUENCY. TYPICALLY MADE OF QUARTZ C
DEVICES PERFORM THE CRITICAL FUNCTION OF PICKING OUT THE FREQUENCY OF THE
SIGNAL FROM THE CACOPHONY OF TRANSMISSIONS IN THE AIRWAVES. HOWEVER, QUAR
ARE UNATTRACTIVE AT MICROWAVE FREQUENCIES DUE TO THE SMALL SIGNAL TO NO
FREQUENCY MULTIPLICATION AND THEIR BULKY NATURE. ONE CAN NO LONGER RELY
CHOICES BUT HAS TO SEARCH FOR ALTERNATIVES. THUS THE METALLIC CAVITY RE
DEVELOPED, WHICH ALSO PROVED TO BE BULKY AND NON-INTEGRABLE FOR MICROWA
CIRCUITS (MIC). LATER ON MICROSTRIP RESONATORS EMERGED WHICH HAD POOR THERM

AND HIGH DIELECTRIC LOSS. THUS THE MINIATURIZATION WAS POSSIBLE IN COMMUNICA
BY COMPROMISING ON THE QUALITY FACTOR AND TEMPERATURE STABILITY. NEXT AT
USE OF CERAMIC PIECES WHICH ARE DESIGNED TO BE DIELECTRIC RESONATORS, RESO
FREQUENCY OF THE CARRIER SIGNAL TO ALLOW THAT SIGNAL TO BE EFFICIENTLY SEPA
SIGNALS IN THE MICROWAVE BAND. THIS LED TO A BOOMING DEVELOPMENT OF NOVI
MICROWAVE DIELECTRIC RESONATORS. A **Dielectric Resonator (DR)** CAN BE DEFINED AS "
electromagnetic component, which is a ceramic puck that exhibits resonance with useful properties for a narrow range of frequencies." THE RESONANT FREQUENCY OF THE DIELECTRIC
COMPONENT DEPENDS ON THE RELATIVE PERMITTIVITY OF THE DIELECTRIC AND THE
RESONATOR [4]. CERAMIC DIELECTRIC MATERIALS ARE USED TO FORM THERMALLY ST
RESONATORS AS KEY COMPONENTS IN A NUMBER OF MICROWAVE SUBSYSTEMS WHICH A
RANGE OF CONSUMER AND COMMERCIAL MARKET PRODUCTS. THE SIZE OF THE RESON
PARTICULAR FREQUENCY DEPENDS ON THE INVERSE OF THE SQUARE ROOT OF THE RELA
(ε_r) OF THE MATERIAL. THUS DIELECTRIC CERAMIC MATERIALS ARE GENERALLY REQUIRE
RELATIVE PERMITTIVITY TO MEET A DEMAND FOR SIZE REDUCTION OF DEVICES, A SM
LOSS IN HIGH FREQUENCY REGIONS AND A SMALL CHANGE IN RESONANT FREQUENCY WI
TEMPERATURE CHANGE. UNTIL RECENTLY, THE OXIDE AND NITRIDE OF SILICON HAVE BE
EXCLUSIVELY FOR DIELECTRIC APPLICATIONS. NOW, BOTH LOW AND HIGH PERMITTIVITY
ARE NEEDED FOR DIFFERENT APPLICATIONS.

1.2.2.1 HISTORICAL DEVELOPMENT OF DIELECTRIC RESONATORS

THE TERM "DIELECTRIC RESONATOR" WAS FIRST USED IN 1939 BY RICHTMEYER
STANDFORD UNIVERSITY WHO SUGGESTED THE POSSIBILITY OF USING UNMETALLIZED
RESONATORS. HE INVESTIGATED THEORETICALLY THE RESONANT PROPERTIES OF TOROI
RING SHAPED DIELECTRIC MATERIALS. HOWEVER, HIS THEORETICAL INVESTIGATIONS FA
SIGNIFICANT INTEREST AND PRACTICALLY NOTHING HAPPENED IN THIS AREA FOR OVE
1953, SCHLICKE [6] REPORTED THE APPLICATION OF SUPER-HIGH RELATIVE PERMITTIVIT
($_r$ ~ 1000) AS CAPACITORS IN LOW RADIO FREQUENCIES. IN THE 1960'S, SEVERAL W
INVESTIGATED THE BEHAVIOR OF DIELECTRICS AT MICROWAVE FREQUENCIES AND TRIE
TO THE MICROWAVE DEVICES. FOR EXAMPLE, THE DIELECTRIC LOSS OF MICROWAVE

FREQUENCY WAS MEASURED AND ITS MECHANISM WAS DISCUSSED. BY SILVERMAN *et al.* [7] AND THE FAR INFRARED DISPERSION WAS INVESTIGATED BY SPITZER AND BARASH REPORTED X-BAND UNLOADED Q OF 9000 AT ROOM TEMPERATURE FOR RUTILE RESONATORS. THE EA STUDIES OF RESONATOR MATERIALS COMMENCED WITH THE WORK OF COHN [9] IN THI RUTILE (TiO_2) CRYSTALS WHICH EXHIBITED RELATIVE PERMITTIVITY OF 100 AND HIGH Q VALUE. HOWEVER, THE FILTER USING TiO_2 WAS NOT PUT INTO PRACTICAL USE BECAUSE OF ITS LAR TEMPERATURE VARIATION OF RESONANT FREQUENCY. LATER, THE PIONEERING INVESTIGATIONS BY BOLTON [10] ON HIGH PERMITTIVITY TUNGSTEN BRONZE-STRUCTU LN_2O_3–TiO_2 ACHIEVED TEMPERATURE STABILITY AND RELATIVE PERMITTIVITIES OF 60–80 Q OF 4500 AT 1 GHZ. *et al.* [11] NOTED THAT THE WORK OF BOLTON WAS RARELY ACKNOWLEDGED IN SUBSEQUE BUT PROVIDED THE TECHNICAL FOUNDATION FOR THE INVESTIGATIONS OF TUNGSTEN B TYPE MATERIALS.

BY THE LATE 1970'S AND EARLY 1980'S THERE WAS INTEREST IN A RANGE OF M INCLUDING $MgTiO_3$–$CaTiO_3$, $(Zr,Sn)TiO_4$ AND $BaTi_4O_9$ [12]. TEMPERATURE STABLE MICROWAVE DRS WERE DEVELOPED BY KONISHI [13] AND PLOUDRE [14] UTILIZING THE CO STRUCTURE OF POSITIVE AND NEGATIVE TEMPERATURE COEFFICIENTS. HOWEVER, T RESONATOR WAS NOT USED IN PRACTICE, BECAUSE OF TOO PRECISE AND CARE NEE MATERIAL PREPARATION PROCESS, MACHINING AND ASSEMBLING. PLOURDE AND REN [REPORTED THAT THE MAXIMUM QUALITY FACTOR (Qxf_0) AVAILABLE WAS AROUND 36,000 GHZ, WITH ε_r MAXIMUM OF 40. LATER, A MODIFIED BARIUM TETRATITANATE WITH IMPROVED PERFORM REPORTED FROM BELL LABORATORIES [16]. THE NEXT MAJOR BREAKTHROUGH CAME WHEN THE MURATA MANUFACTURING COMPANY [17] PRODUCED $(Zr,Sn)TiO_4$ CERAMICS WHICH OFFERED ADJUSTABLE COMPOSITIONS SO THAT THE TEMPERATURE COEFFICIENT CO BETWEEN +10 AND -22 PPM/°C. THESE COMPONENTS BECAME COMMERCIALLY AVAILABLE REASONABLE PRICES. AFTERWARDS, THE EXPERIMENTAL AND THEORETICAL WORK AS W DRS EXPANDED RAPIDLY.

THE GROWTH OF THE MOBILE COMMUNICATIONS MARKET IN THE 1990'S STIM RESEARCH IN MICROWAVE DIELECTRICS, PARTICULARLY FOR HIGH RELATIVE PERMITTIV ε_r ~75–90) FOR MOBILE TELEPHONE HANDSET APPLICATIONS, AND HIGH Q VALUES (3000 AT 3 GHZ) FOR BASE STATION APPLICATIONS. FOR THE FORMER, TEMPERATURE STABLE HIGH-

STRUCTURED MATERIALS (FOR EXAMPLE, $Ba_2Ti_9O_{20}$) REMAINED THE PRIMARY CHOICE, WHILST COMPLEX PEROVSKITES (FOR EXAMPLE, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Nb_{2/3})O_3$, ETC.) HIGHEST Q VALUES FOR THE BASE STATIONS. A STRIKING FEATURE IS THE GAP IN THE MATERIALS WITH ε_R IN THE RANGE 45–75. REANEY AND IDDLES [18] HIGHLIGHTED THE FACT MATERIALS WITH ε_R OF 45–75, WITH HIGH Q VALUE AND ZERO τ_f DO NOT CURRENTLY EXIST. TODAY ABOUT MORE THAN 1500 MICROWAVE DIELECTRIC CERAMICS HAVE BEEN INVESTIGATED APPLICATIONS [2]. CURRENTLY MATERIALS FOR PRACTICAL PURPOSES WHICH POSSE EXCELLENT DIELECTRIC PROPERTIES INCLUDE $Ba_3Nd_3Ti_5O_{24}$ [14], $Ba[(Sn, Mg)_{1/3} Ta_{2/3}]O_3$ [19], $Ba(Mg_{1/3},Ta_{2/3})O_3$ [20], $(Zr,Sn)TiO_4$ [21], $Ba_2Ti_9O_{20}$ [22], $(Ba,Sr)O$-Re_2O_3-TiO_2 [23], $Ba[(Zn_{0.7}Co_{0.3})_{1/3}Nb_{2/3}]O_3$ ETC. IT IS NOTEWORTHY THAT STILL DR MATERIALS ARE NE WITH A WIDE VARIETY OF DIELECTRIC PROPERTIES TO MEET THE EVER-GROWING DEMA WIRELESS DEVICES. HENCE SEARCH IS CONTINUING TO FIND NEW MATERIALS AS WELL AS PROPERTIES OF EXISTING MATERIALS.

AS A RESULT OF THE VAST DEVELOPMENT IN THE TELECOMMUNICATION INDU UTILIZED FREQUENCY HAS ALSO INCREASED FROM MICROWAVE TO MILLIMETER-WAVE LARGE QUANTITY OF INFORMATION MUST BE TRANSPORTED WITH HIGH SPEED. DIELEC MATERIALS FOR MILLIMETER-WAVE USE ARE REQUIRED TO HAVE HIGH QUALITY FACTO $(Q_u \times f_0)$, LOW RELATIVE PERMITTIVITY (ε_r < 15) AND SMALL TEMPERATURE COEFFICIENT OF RESONANT FREQUEN (τ_f). HENCE NEW MATERIALS WITH LOW RELATIVE PERMITTIVITY NEED TO BE EXPLOR PERSPECTIVE MANY ALUMINATE AND SILICATE BASED DIELECTRIC CERAMICS HAVE AT ATTENTION. $ZnAl_2O_4$ [24], $MgAl_2O_4$ [25], Mg_2SiO_4 [26], Zn_2SiO_4 [27-28], Al_2O_3 [29-30], $Mg_4Nb_2O_9$ [31-32] AND $Sr_3Ga_4O_{12}$ [33] GARNET CERAMICS HAVE BEEN INVESTIGATED AS POTENTIAL CANDIDATE MATERIALS FOR MILLIMETER-WAVE DEVICES. THE NEXT GENER SPECTRAL CROWDING AND COMMERCIAL REALITIES CREATE A CONTINUOUS NEED T DIELECTRIC LOSS AND LOWER THE COST OF CERAMIC RESONATORS AND FILTERS. IMPORTANT CHALLENGES TO MATERIALS SCIENTISTS BECAUSE THE FUNDAMENTAL PH RISE TO THE DESIRED PROPERTIES, ESPECIALLY DIELECTRIC LOSS, IS NOT WELL FURTHERMORE, THE DIELECTRIC LOSS OF A MATERIAL, WHICH LIMITS FREQUENCY S HEAVILY INFLUENCED BY EXTRINSIC FACTORS SUCH AS MICROSTRUCTURE, DEFECTS

FUNDAMENTAL UNDERSTANDING OF MICROWAVE CERAMICS IS NEEDED TO IMPROV
MATERIALS AND DISCOVER NEW MATERIALS FOR ADVANCED APPLICATIONS.

1.3 PHYSICS OF DIELECTRIC RESONATORS

1.3.1 POLARIZATION MECHANISMS IN DIELECTRICS

DIELECTRIC PROPERTIES ARE OF SPECIAL IMPORTANCE WHEN CERAMICS OR GLASS
EITHER AS A CAPACITIVE ELEMENT IN ELECTRONIC APPLICATIONS OR AS INSULATION
PERMITTIVITY, DIELECTRIC LOSS AND DIELECTRIC STRENGTH USUALLY DETERMINE TH
PARTICULAR MATERIAL FOR SUCH APPLICATIONS. VARIATION OF DIELECTRIC PRO
FREQUENCY, FIELD STRENGTH AND OTHER CIRCUIT VARIABLES INFLUENCE THE DEVIC
THESE DIELECTRIC PROPERTIES ARE MAINLY CONTROLLED BY THE POLARIZATION MECHANISMS ARISING
FROM THE ELECTRICAL RESPONSE OF INDIVIDUAL MOLECULES OF A MEDIUM. THERE AR
FOUR BASIC KINDS OF POLARIZATION MECHANISMS VIZ. INTERFACIAL, DIPOLAR, IONIC A
EACH DIELECTRIC MECHANISM HAS A CHARACTERISTIC "CUTOFF FREQUENCY." AS
INCREASES, THE SLOW MECHANISMS DROP OUT IN TURN, LEAVING THE FASTER ONES TO
ε_r. THE LOSS FACTOR ($\tan\delta$) WILL CORRESPONDINGLY PEAK AT EACH CRITICAL FREQUENCY
MAGNITUDE AND "CUT OFF FREQUENCY" OF EACH MECHANISM IS UNIQUE FOR DIFFERENT

(i) ***SPACE CHARGE/INTERFACIAL POLARIZATION:*** IN GEOMETRICALLY HETEROGENEOUS MATERIALS T
MOTION OF CHARGE CARRIERS MAY OCCUR MORE EASILY THROUGH ONE PHASE AND
CONSTRICTED AT THE PHASE BOUNDARIES. SPACE CHARGE OR INTERFACIAL POLARIZATI
CHARGE CARRIERS ARE IMPEDED BY PHYSICAL BARRIERS SUCH AS GRAIN BOUNDAR
BOUNDARY ETC. THAT INHIBITS CHARGE MIGRATION LEADING TO PILING UP OF CHA
BARRIERS. WHEN AN AC FIELD OF SUFFICIENTLY LOW FREQUENCY ($< 10^3$ HZ) IS APPLIED, NET
OSCILLATION OF CHARGE IS PRODUCED BETWEEN THE BARRIERS AS FAR APART AS 1 CM
VERY LARGE CAPACITANCE AND RELATIVE PERMITTIVITY. THIS TYPE INVOLVES A LON
MOVEMENT AND MAY EXTEND TO 10^2 HZ.

(ii) ***ORIENTATIONAL/DIPOLAR POLARIZATION:*** THIS TYPE OF POLARIZATION OCCURS ONLY IN POLA
SUBSTANCES. THE DIPOLAR POLARIZATION, OTHERWISE KNOWN AS ORIENTATIONAL
CONTRIBUTES TO THE DIELECTRIC PROPERTIES IN THE SUB-INFRARED RANGE OF FREQU

ELECTRIC FIELD, THE DIPOLES WILL BE RANDOMLY ORIENTED AND THUS CARRY NO NE
WHEN AN ELECTRIC FIELD IS APPLIED, THE DIPOLES WILL TEND TO ALIGN IN THE DIRE
APPLIED FIELD AND THE MATERIALS WILL ACQUIRE A NET MOMENT. IN OTHER WORDS, TH
OF THERMAL MOTION OF THE IONIC OR MOLECULAR DIPOLES, PRODUCES A NET DIPOLAR
THE DIRECTION OF THE APPLIED FIELD. TWO MECHANISMS CAN BE OPERATIVE IN THIS C
LINEAR DIELECTRICS (NON-FERROELECTRICS) DIPOLAR POLARIZATION RESULTS FROM T
CHARGED IONS BETWEEN THE INTERSTITIAL POSITIONS IN IONIC STRUCTURES PARALLE
FIELD DIRECTION. THE MECHANISM IS ACTIVE IN THE 10^{3} TO 10^{6} HZ RANGE. (B) MOLECULES HAVING
PERMANENT DIPOLE MOMENT MAY BE ROTATED ABOUT AN EQUILIBRIUM POSITION AGAI
RESTORING POSITION. ITS FREQUENCY OF RELAXATION IS VERY HIGH, OF THE ORDER OF 10^{11} HZ. DUE
TO THE RANDOMIZING EFFECT OF THE THERMAL VIBRATIONS, ORIENTATIONAL POLAR
EFFECTIVE AS THE TEMPERATURE IS DECREASED AND IT GIVES RISE TO A TEMPERATU
RELATIVE PERMITTIVITY.

(iii) ***IONIC POLARIZATION.*** IONIC POLARIZATION IS DUE TO A RELATIVE DISPLACEMENT OF PO
AND NEGATIVE IONS IN A MATERIAL WITH RESPECT TO EACH OTHER, IN THE PRESENCE
FIELD. IN THIS CASE THE MATERIAL SHOULD HAVE AN IONIC CHARACTER. THE BUILT IN I
CANCEL EACH OTHER AND ARE UNABLE TO ROTATE. THE APPLIED EXTERNAL FIELD DIS
SLIGHTLY FROM THEIR REST POSITIONS AND THEREBY INDUCING NET DIPOLES. THE
CONTRIBUTES TO THE RELATIVE PERMITTIVITY AT INFRARED FREQUENCY RANGE (~10^{12} TO 10^{13} HZ).

(iv) ***ELECTRONIC POLARIZATION.*** ELECTRONIC POLARIZATION IS PRESENT IN ALL MATERIALS A
DOES NOT CONTRIBUTE TO CONDUCTIVITY OR DIELECTRIC LOSS IN MOST DIELECTRICS. T
ARISES FROM A SHIFT OF THE CENTRE OF MASS OF THE NEGATIVE ELECTRON CHARGE CL
THE POSITIVE ATOMIC NUCLEUS UNDER THE INFLUENCE OF AN ELECTRIC FIELD. THIS O
FREQUENCIES OF ABOUT 10^{15} HZ. THE RELATIVE PERMITTIVITY AT OPTICAL FREQUENCIES A
ALMOST ENTIRELY FROM THE ELECTRONIC POLARIZABILITY.

FIGURE 1.2 SHOWS THE VARIATION OF DIELECTRIC LOSS AND PERMITTIVITY WITH
AT MICROWAVE FREQUENCIES THE MECHANISMS DUE TO IONIC AND ELECTRONIC P
CONTRIBUTE TO THE DIELECTRIC PROPERTIES. THE DIELECTRIC PROPERTIES OF A MATER
BY THE TEMPERATURE. THIS DEPENDENCE IS DUE TO THE EFFECT OF TEMPERATURE UPO
POLARIZATION MECHANISMS. ELECTRONIC POLARIZATION IS RELATIVELY UNAFFECTED

HOWEVER, ATOMIC POLARIZATION IS AFFECTED SINCE THE BINDING FORCES BETWEEN I CHANGES WITH TEMPERATURE. IT IS FOUND TO INCREASE WITH TEMPERATURE DUE TO THE CHARGE CARRIERS AND ION MOBILITY. THE ABILITY OF A DIPOLE TO ROTATE IN AN ALSO TEMPERATURE DEPENDENT AND SO ORIENTATIONAL POLARIZATION WILL BE ORIENTATIONAL POLARIZATION IS OPPOSED BY THERMAL AGITATION, SO THE RELATI GOES DOWN AS THE TEMPERATURE INCREASES. FINALLY, SINCE CHARGE MOBILITY IS DEPENDENT, THE INTERFACIAL MECHANISM WILL ALSO BE TEMPERATURE DEPENDENT.

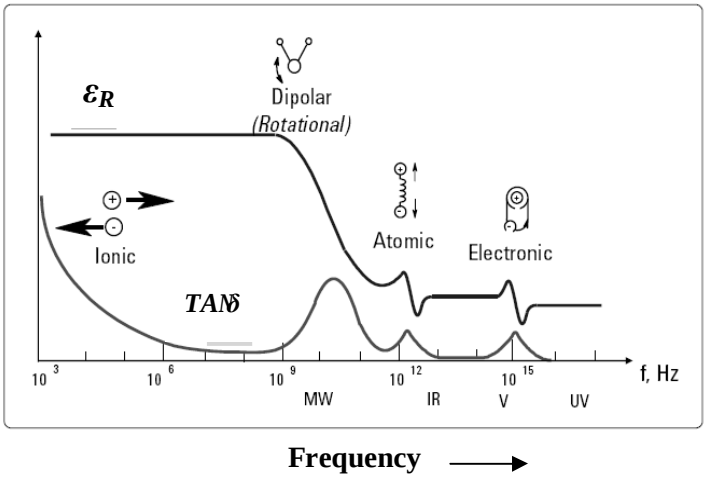

Fig. 1.2 Frequency response of dielectric mechanisms. (en.wikipedia.org/wiki/Dielectric_spectroscopy)

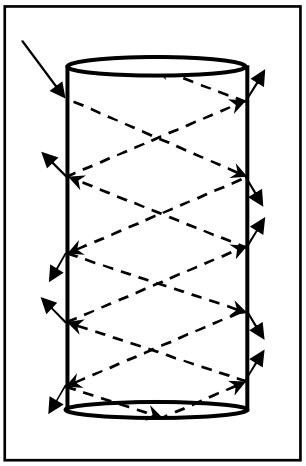

Fig. 1.3 Sketch of multiple total internal reflections in DR.

1.3.2 CLAUSSIUS - MOSSOTTI EQUATION

THE RELATIVE PERMITTIVITY OF AN INSULATOR IS RELATED TO THE POLARIZABI COMPRISING IT. THE PERMITTIVITY, ε_r, CAN BE CALCULATED THEORETICALLY USING CLAUSIUS–MOS EQUATION FOR CUBIC OR ISOTROPIC MATERIALS [34]

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \left(\frac{4}{3}\right)\left(\frac{\alpha_D}{V_m}\right) \tag{1.1}$$

REARRANGING WE GET, $\varepsilon_r = \dfrac{3V_m + 8\alpha_D}{3V_m - 4\alpha_D}$ (1.2)

WHERE V_m IS THE MOLAR VOLUME AND α_D IS THE SUM OF THE DIELECTRIC POLARIZABILITIES O INDIVIDUAL IONS. THE V_m OF THE DIELECTRIC MATERIAL CAN BE OBTAINED FROM X-RAY DIFF STUDIES. THE ε_r DEPENDS ON THE DIELECTRIC POLARIZABILITY OF THE CONSTITUENT ION CRYSTAL STRUCTURE. BASED ON THE ADDITIVITY RULE, SHANNON STATES THAT POLARIZABILITIES α_D OF A COMPLEX MATERIAL CAN BE BROKEN UP INTO THE MOLEC POLARIZABILITIES OF SIMPLER COMPOUNDS BY [35]

$$\alpha_D(A_2A'O_4) = 2\ \alpha_D(AO) + \alpha_D(A'O_2) \qquad (1.3)$$

WHERE A ARE THE CATIONS. FURTHERMORE, IT IS POSSIBLE TO BREAK UP THE MO POLARIZABILITIES OF COMPLEX COMPOUNDS IN TO IONS ACCORDING TO

$$\alpha(A_2A'O_4) = 2\ \alpha(A^{2+}) + \alpha(A^{4+}) + 4\ \alpha(O^{2-}) \qquad (1.4)$$

THE DIELECTRIC POLARIZABILITIES OF SEVERAL IONS ARE REPORTED BY SHANNO CALCULATED ε_r USUALLY AGREE WELL WITH POROSITY-CORRECTED EXPERIMENTAL VALU BEHAVED CERAMICS. IT MAY BE NOTED THAT DEVIATIONS FROM CALCULATED VALUES TO DEVIATIONS FROM CUBIC SYMMETRY, PRESENCE OF IONIC OR ELECTRONIC CONDUCT CO_2 IN CHANNELS, RATTLING OF IONS, PRESENCE OF DIPOLAR IMPURITIES OR FERROELE AND ALSO THE FACT THAT THE SAMPLE IS CERAMIC AND NOT A SINGLE CRYSTAL. THE D REPORTED VALUES OF DIELECTRIC POLARIZABILITY AND EVEN A SMALL ERROR IN DETE VOLUME CAN SIGNIFICANTLY AFFECT THE CALCULATED VALUE OF THE PERMITTIVITY.

1.3.3 WORKING PRINCIPLE OF DIELECTRIC RESONATORS

A PIECE OF DIELECTRIC WITH HIGH RELATIVE PERMITTIVITY CAN CONFINE MICROW AT A FEW DISCRETE FREQUENCIES THROUGH TOTAL MULTIPLE INTERNAL REFLECTIONS A INTERFACE, PROVIDED THAT THE ENERGY IS FED IN THE APPROPRIATE DIRECTION (SEE ELECTROMAGNETIC WAVE MOVING FROM THE ELECTRICALLY DENSE HIGH DIELECTRI ELECTRICALLY THIN AIR MEETS VERY HIGH IMPEDANCE AT THE DIELECTRIC-AIR INTER BACK TO THE DIELECTRIC ITSELF. AS THE RELATIVE PERMITTIVITY INCREASES THE IMP BY THE BOUNDARY ALSO INCREASES TO ALLOW BETTER CONFINEMENT OF ENERGY WITH BODY.

THE REFLECTION COEFFICIENT APPROACHES UNITY WHEN THE RELATIVE PE
APPROACHES INFINITY. THE TRAPPED ELECTROMAGNETIC WAVES WILL FORM STANDI
GENERATE RESONANCE. A HIGH RELATIVE PERMITTIVITY MATERIAL CAN CONFINE MOST
ELECTROMAGNETIC WAVE WITHIN ITS VOLUME. IF THE TRANSVERSE DIMENSIONS OF THE
COMPARABLE TO THE WAVE LENGTH OF THE MICROWAVE, THEN CERTAIN FIELD DISTRIBU
WILL SATISFY MAXWELL'S EQUATIONS AND BOUNDARY CONDITIONS [36] AND ONLY T
SATISFYING THIS CONDITION WILL BE EXCITED. THE FREQUENCY OF THE GENERATE
MODES DEPENDS ON THE DIMENSIONS AND RELATIVE PERMITTIVITY OF THE DIELECTR
FOR MICROWAVES, THE FREE SPACE WAVELENGTH (λ_o) IS OF THE ORDER OF A FEW CENTIMETERS AND
ON ENTERING THE MATERIAL WITH ε_r IN THE RANGE 20-100, THE WAVELENGTH (λ_d) INSIDE THE
DIELECTRIC WILL BE IN MILLIMETERS. THE ELECTROMAGNETIC FIELDS OUTSIDE THE DIELECTRIC SAMPLE
DECAY RAPIDLY. ONE CAN PREVENT RADIATION LOSSES BY PLACING THE DR IN A SMA
ENCLOSURE. SINCE ONLY A SMALL RADIATION FIELD SEES THE METALLIC SURFACE,
CONDUCTION LOSS WILL BE TOO SMALL AND CAN BE NEGLECTED [37].

1.3.4 RESONANCE

A BULK DIELECTRIC MATERIAL EXCITED FOR RESONANCE USING MICROWAVE
EQUIVALENT TO A PARALLEL RLC RESONANT CIRCUIT. HENCE THE ALTERNATING FIELD WILL
INDUCTIVE, CAPACITIVE AND RESISTIVE COMPONENTS. ALL THE THREE (L, C, R) COMPONENTS, C
INDUCTOR (L) AND OHMIC RESISTANCE (R) IN THE CIRCUIT HAVE A COMMON VOLTAGE ($v(t) = |V|$
$\cos \omega t$. FROM THE FUNDAMENTAL RULES OF RESONANT ELECTRICAL CIRCUITS, THE EL
STORED IN THE CAPACITOR IS GIVEN AS [38]

$$W_e(t) = \frac{1}{2} C[v(t)]^2 = \frac{1}{2} C|V|^2 \cos^2(\omega t) \qquad (1.5)$$

AND MAGNETIC ENERGY STORED IN THE INDUCTOR IS

$$W_m(t) = \frac{1}{2} L [I(t)]^2 = \frac{|V|^2}{2\ ^2 L} \sin^2(\ t) \qquad (1.6)$$

THE STORED ELECTRIC ENERGY IS THUS PROPORTIONAL TO $\cos^2 \omega t$ FUNCTION AND THE STORED MAGNETIC ENERGY IS PROPORTIONAL TO $\sin^2 \omega t$ FUNCTION OF TIME. AS FUNCTIONS OF TIME, THE STORED ENERG $W_e(t)$ AND $W_m(t)$ FLUCTUATE BETWEEN ZERO AND THEIR MAXIMUM VALUES $W_{e,max}$ AND $W_{m,max}$. THE AVERAGE VALUES OF W_e AND W_m ARE EQUAL TO ONE HALF OF THE CORRESPONDING MAXIMUM VA AT RESONANCE, CAPACITIVE AND INDUCTIVE REACTANCES BECOME EQUAL AND OPPOS HENCE THE IMPEDANCE OF THE CIRCUIT EQUALS THE OHMIC RESISTANCE AND MAXIM STORAGE TAKES PLACE WITHIN THE BODY OF THE DIELECTRIC RESONATOR.

AT THIS CONDITION,

$$\omega = \omega_{res} = \frac{1}{\sqrt{LC}} \tag{1.7}$$

THE MAXIMUM STORED ENERGY W_{max} WILL BE THE SUM OF THE STORED ENERGY IN CAPACITOR (W_e) AND INDUCTOR (W_m). SINCE THE AVERAGE ENERGY VALUES ARE EQUAL TO ONE HALF OF TH VALUES,

$$W_{max} = 2W_e = 2W_m = W_e + W_m \tag{1.8}$$

IN TERMS OF THE AVERAGE STORED ENERGY, THE QUALITY FACTOR (Q) OF A RESONANCE BECOMES [39]

$$Q = \left[\frac{(W_e + W_m)}{P_d} \right]_{\omega = \omega_{res}} \tag{1.9}$$

WHERE P_d IS THE AVERAGE POWER DISSIPATED IN THE RESONATOR. IF THE OPERATIONAL FREQUENCY IS NOT EQUAL TO THE RESONANT FREQUENCY, THE PEAK OF THE STORED ELECTRIC ENERG THE PEAK OF THE STORED MAGNETIC ENERGY. THEREFORE, THE QUALITY FACTOR IS NOT DEFINED AT ANY FREQUENCY OTHER THAN ω_{res}.

1.3.5 MODES AND MODE NOMENCLATURE

A MICROWAVE RESONATOR HAS INFINITE NUMBER OF MODES, EACH OF THEM CORRESPONDING TO A PARTICULAR RESONANT FREQUENCY, AT WHICH THE ELECTRIC EQUAL TO THE MAGNETIC ONE. THE EXCITED MODES CAN BE CLASSIFIED INTO THREE D

TE, TM AND HYBRID. THE FIELDS FOR *TE* AND *TM* MODES ARE AXISYMMETRIC WHEREAS HYBRID MODES ARE AZIMUTHALLY DEPENDENT. THE HYBRID MODES CAN AGAIN BE CATEGORIZED AS *HE* AND *EH*. ACCORDING TO THE MODE NOMENCLATURE DESCRIBED BY KAJFEZ [40], THE VARIATION OF FIELDS ALONG THE AZIMUTHAL DIRECTION INSIDE THE RESONATOR, ARE DENOTED BY ADDING MODE INDICES AS SUBSCRIPTS TO EACH FAMILY OF MODE. THE NOMENCLATURE IS HISTORICALLY BASED ON THE MODE NOMENCLATURE OF CYLINDRICAL WAVEGUIDES. *TE, TM, HE* AND *EH* MODES ARE CLASSIFIED AS $TE_{nmp+\Delta}$, $TM_{nmp+\Delta}$, $HE_{nmp+\Delta}$, AND $EH_{nmp+\Delta}$ RESPECTIVELY. THE FIRST INDEX DENOTES THE NUMBER OF FIELD VARIATIONS IN AZIMUTHAL DIRECTION ($m = 1, 2, 3 \ldots$) THE INDEX ($n = 0, 1, 2 \ldots$) DENOTES THE ORDER OF VARIATION OF THE FIELD ALONG THE RADIAL DIRECTION AND THE INDEX ($p = 0, 1, 2 \ldots$) DENOTES THE ORDER OF VARIATION OF THE FIELD ALONG THE Z-DIRECTION.

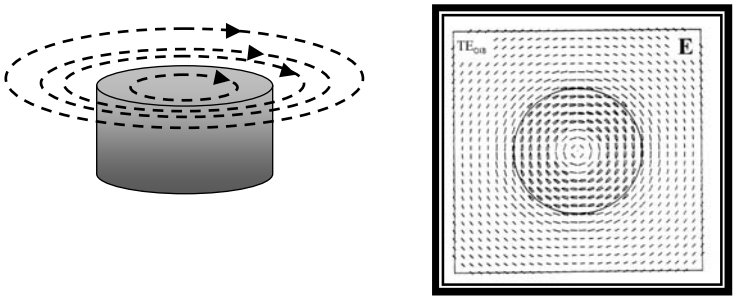

Fig. 1.4 Electric field distribution of $TE_{01\Delta}$ mode in equatorial plane.

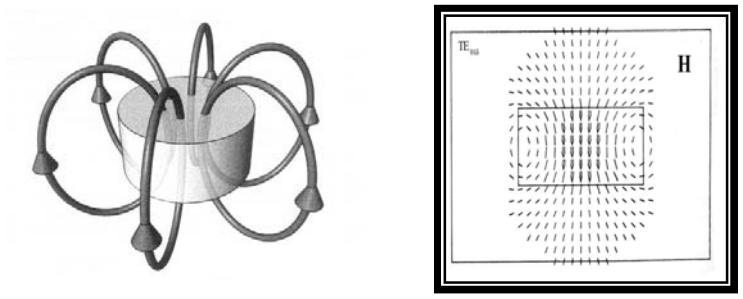

Fig. 1.5 Magnetic field distribution of $TE_{01\Delta}$ in the meridian plane.

THE RESONANT MODE MOST OFTEN USED IN SHIELDED MICROWAVE CIRCUITS IS $TE_{01\Delta}$ WHICH IS A TRANSVERSE ELECTRICAL MODE HAVING AZIMUTHAL SYMMETRY WITH LESS THAN A HALF CYCLE VARIATION IN FIELD IN THE Z-DIRECTION. HERE, THE THIRD INDEX, DENOTES THE

DIELECTRIC RESONATOR IS SHORTER THAN ONE-HALF WAVELENGTH. IT DEPENDS ON THE RELATIVE PERMITTIVITY OF THE RESONATOR AND THE SUBSTRATE, AND ON THE PRO AND BOTTOM CONDUCTOR PLATES. FIGS. 1.4 AND 1.5 RESPECTIVELY SHOWS THE TYP DISTRIBUTIONS FOR THE $TE_{01\delta}$ MODE OF A CYLINDRICAL DIELECTRIC RESONATOR [39]. THE MAGNITUDE O ELECTRICAL FIELD COMPONENT IS ZERO AT THE CENTRE OF THE RESONATOR AND HAS A AT AROUND $r = 2r/3$ WHERE r IS THE RADIUS OF THE DISK. OUTSIDE THE RESONATOR, THE FIELD D EXPONENTIALLY. THE FIELD VARIATION AS A FUNCTION OF RADIAL DISTANCE REMAIN DIFFERENT PLANES PARALLEL TO THE EQUATORIAL PLANE [41].

1.4 MATERIAL REQUIREMENTS FOR DR APPLICATIONS

AS IN ALL TECHNOLOGICAL SYSTEMS, THE BASIS OF THE CHANGES IN WIRELESS COMMUNICATION IS ADVANCES IN MATERIALS. THESE UNIQUE TECHNOLOGIES DEMAN WHICH HAVE THEIR OWN SPECIALIZED REQUIREMENTS AND FUNCTIONS. THE IMPO MINIATURIZATION CANNOT BE OVEREMPHASIZED IN ANY HAND-HELD COMMUNICATION AND CAN BE SEEN IN THE DRAMATIC DECREASE IN THE SIZE AND WEIGHT OF DEVICES. T NEED FOR MINIATURIZATION PROVIDES A CONTINUING DRIVING FORCE FOR THE DISC DEVELOPMENT OF INCREASINGLY SOPHISTICATED MATERIALS TO PERFORM THE SAME FUNCTION WITH DECREASED SIZE AND WEIGHT. THERE ARE THREE KEY PROPERTIES THA THE DIELECTRIC RESONATORS AND THEY ARE DISCUSSED IN DETAIL IN THE FOLLOWING S

1.4.1 RELATIVE PERMITTIVITY (ε_r)

THE RELATIVE PERMITTIVITY CHARACTERIZES THE ABILITY OF A MATERIAL TO STORE CHARGE. A DIELECTRIC RESONATOR (DR) CAN CONFINE ELECTROMAGNETIC WAVES THROUGH TO INTERNAL REFLECTIONS AT THE DIELECTRIC-AIR INTERFACE. IF THE DR IS RESONATING A f_o, THEN THE MAXIMUM WAVELENGTH IT CAN HAVE IS RELATED TO THE RELATIVE PERMI MATERIAL BY THE FOLLOWING EQUATION;

$$f_o \approx \frac{c}{D\sqrt{\varepsilon_r}} \approx \frac{c}{D\sqrt{\varepsilon_r}} \qquad (1.10)$$

WHERE c IS THE VELOCITY OF LIGHT IN VACUUM AND λ IS THE WAVELENGTH OF THE STANDING WAVE ALONG THE DIAMETER (D) OF A RESONATOR. CONSEQUENTLY, IF THE PERMITTIVITY IS INCREAS SIZE OF THE RESONATOR MAY BE DECREASED WHILE STILL MAINTAINING A SPECIF FREQUENCY. IN THE MICROWAVE FREQUENCY RANGE, IONIC POLARIZATION IS THE I CONTRIBUTING TOWARDS THE RELATIVE PERMITTIVITY. HENCE MATERIALS CONTAINING IONIC POLARIZABILITIES ARE NEEDED FOR SUFFICIENTLY HIGH ε_r. ACCORDING TO CLASSICAL DISPERSION THEORY, THE CRYSTAL IS APPROXIMATED AS A SYSTEM OF DAMPED OSCILLATORS APPROPRIATE FREQUENCY AND DIPOLE MOMENT. THE REAL AND IMAGINARY PARTS OF RELATIVE PERMITTIVITY ($\varepsilon_r' - j\varepsilon_r''$) AS FUNCTIONS OF ($\omega$ WHERE $\omega = 2\pi f$) ARE GIVEN BY

$$\varepsilon_r'(\omega) = \varepsilon_\infty + \sum_j \frac{4\pi\alpha_j(\omega_j^2 - \omega^2)\omega_j^2}{(\omega_j - \omega^2)^2 + (\omega_j\omega)^2} \tag{1.11}$$

WHERE $4\pi\alpha_j$ IS THE OSCILLATOR STRENGTH, ω_j IS THE j^{th} RESONANT ANGULAR FREQUENCY OF THE OSCILLATOR, ε_∞ IS THE RELATIVE PERMITTIVITY CAUSED BY ELECTRONIC POLARIZATION FREQUENCIES AND ω_j IS THE DAMPING CONSTANT WHICH IS GIVEN BY THE WIDTH OF THE PEAK SUMMATION IS OVER ALL RESONANCES IN THE SPECTRUM. EACH RESONANCE IS CHARACTERIZED BY ITS DISPERSION PARAMETERS. FOR

$$\varepsilon_r'(\omega) = \varepsilon_\infty + \sum_j 4\pi\alpha_j \tag{1.12}$$

THE ABOVE EQUATION SHOWS THAT RELATIVE PERMITTIVITY IS INDEPENDENT OF FREQ MICROWAVE FREQUENCY REGION. FOR AN IDEAL DIELECTRIC RESONATOR TO BE U MICROWAVE FREQUENCY RANGE, THE RELATIVE PERMITTIVITY MUST BE HIGH IN ORD MINIATURIZATION. HOWEVER, DUE TO THE CROWDING OF CHANNELS, THE APPLICATIONS TO HIGHER FREQUENCIES. THUS LOW RELATIVE PERMITTIVITY IS ESSENTIAL FOR MIL APPLICATIONS.

1.4.2 HIGH QUALITY FACTOR Q OR $Q(f)$

ONE OF THE MOST PERSISTENT PROBLEMS IN MATERIALS IS THE DIELECTRIC
DIELECTRIC LOSS WAS FIRST MEASURED BY RUBENS AND HERTZ [42] IN 1912 AND, TEN Y
EWALD [43] SUGGESTED THAT ITS ORIGIN WAS THE ANHARMONIC INTERACTION BETWEEN
AND THE THERMAL LATTICE VIBRATIONS. WHEN THE ELECTROMAGNETIC FIELD IS CO
LATTICE VIBRATIONS, A MUTUAL PERTURBATION RESULTS AS IN THE COUPLING OF ANY
SYSTEMS. AT MICROWAVE FREQUENCIES, THE COUPLING OF THE FIELD WITH THE LATTIC
FAR FROM RESONANCE. HOWEVER, THE MUTUAL PERTURBATION IS STILL NOTICEABLE
SOME MECHANICAL LATTICE VIBRATIONS ACQUIRE A SMALL FRACTION OF THE EN
ELECTROMAGNETIC FIELD. THEN, DUE TO THE THIRD AND HIGHER ORDER TERMS IN
ENERGY OF THE LATTICE, THIS SMALL FRACTION OF EXTRA ENERGY GRADUALLY DIFFUS
THE MODES IN THE LATTICE AND ULTIMATELY APPEARS AS HEAT.

THE FIGURE OF MERIT FOR ASSESSING THE PERFORMANCE OR QUALITY OF A RESO
Q-FACTOR. IT IS THE EFFICIENCY OF A RESONANT CIRCUIT TO CONFINE ELECTROMAGNETIC
INSIDE A RESONATOR STORE ENERGY AT THE RESONANT FREQUENCY WHERE EQUAL ST
AND MAGNETIC ENERGIES OCCUR. THUS QUALITY FACTOR IS A MEASURE OF ENER
DISSIPATION PER CYCLE AS COMPARED TO THE ENERGY STORED IN THE FIELDS INSIDE TH
Q-FACTOR IS DEFINED BY [44]

$$Q = \frac{Maximum\ \ Energy\ \ Stored\ \ per\ \ cycle}{Average\ \ Energy\ \ Dissipated\ \ per\ \ cycle}$$

$$Q = \frac{2\ W_0}{PT} = \frac{{}_0 W_0}{P} \tag{1.13}$$

WHERE W_0 IS THE STORED ENERGY, P IS POWER DISSIPATION, ω_0 IS RESONANT RADIAN FREQUENCY AND
PERIOD $T = \frac{2}{\omega_0}$. IN THE CASE OF BULK CERAMICS ENERGIZED BY ELECTROMAGNETIC WAVE
FACTOR IS ROUGHLY THE INVERSE OF DIELECTRIC LOSS OF THE MATERIAL. FOR AN ELEC
SYSTEM, THE Q FACTOR REPRESENTS THE EFFECT OF ELECTRICAL RESISTANCE. FOR
ELECTROMECHANICAL RESONATORS SUCH AS QUARTZ CRYSTALS IT REPRESENTS THE M
IN MICROWAVE COMMUNICATIONS, QUALITY FACTOR IS DETERMINED AS THE RESONA

(f_o) DIVIDED BY THE BANDWIDTH, Δf, MEASURED AT 3 DB BELOW THE MAXIMUM HEIGHT AT RESONANCE.

$$Q = \frac{o}{\Delta} = \frac{f_o}{\Delta f} \tag{1.14}$$

IT IS THEREFORE A DIRECT MEASURE OF THE ABILITY OF THE RESONATING BODY TO FREQUENCY. THE DIELECTRIC Q FACTOR, Q_d, FOR HOMOGENEOUS DIELECTRIC MATERIAL IS GIVEN BY

$$Q_d = \frac{1}{\mathrm{TA}\Delta} \tag{1.15}$$

WHEN A RESONANT CIRCUIT OR CAVITY IS USED AS A LOAD IN A MICROWAVE CIRC DIFFERENT Q FACTORS CAN BE DEFINED. FIRST Q ACCOUNTS FOR INTERNAL LOSSES, WHICH IS THE UNLOADED Q FACTOR, Q_u). NEXT EXTERNAL QUALITY FACTOR (Q_e), ACCOUNTS FOR EXTERNAL LOSSES. WHEN THE RESONATOR IS USED OR ATTACHED TO SOME EXTERNAL CIRCUIT THERE ARIS FACTOR (Q_L) WHICH IS THE OVERALL Q FACTOR AND INCLUDES BOTH INTERNAL AND EXTERNAL LOS FOR CAVITY RESONATORS, POWER LOSS BY CONDUCTORS, DIELECTRIC FILLS AND CONTRIBUTE TO UNLOADED Q. THE CONDUCTOR LOSS IS DUE TO THE CONTACT BETWEEN T CAVITY AND DR, RADIATION LOSS IS DUE TO THE EVANESCENT FIELD DECAYING OUT SURFACE AND DIELECTRIC LOSS IS THE INTRINSIC LOSS OF THE MATERIAL.

$$\frac{1}{Q_u} = \frac{1}{Q_c} + \frac{1}{Q_d} + \frac{1}{Q_r} \tag{1.16}$$

WHERE Q_c IS THE CONDUCTOR Q, Q_d IS THE DIELECTRIC Q FACTOR AND Q_r THE RADIATION Q FACTOR. WHEN THE RESONATOR IS CONNECTED TO LOAD

$$\frac{1}{Q_L} = \frac{1}{Q_e} + \frac{1}{Q_o} \tag{1.17}$$

WHERE Q_L IS THE LOADED Q FACTOR, Q_e THE EXTERNAL Q FACTOR AND Q_o THE UNLOADED Q FACTOR. IT SHOULD ALSO BE NOTED THAT IN THE CASE OF DR, $Q_d = Q_o$ AS A GENERAL CONVENTION. HOWEVER, THE QUALITY FACTOR OF A DR CAN ONLY BE MEASURED (Q_L) BY THE LOADED V

KEEPING IN AN EXTERNAL CIRCUIT. HENCE IT IS NECESSARY TO HAVE A RELATION BET
FORMS OF QUALITY FACTOR ( ) AND IS REPRESENTED AS

$$Q_u = Q_L(1+\quad) \tag{1.18}$$

WHERE IS TERMED AS THE COUPLING COEFFICIENT GIVEN BY

$$= \frac{P_e}{P_u} \tag{1.19}$$

P_e IS THE POWER LOSS DUE TO EXTERNAL FACTORS AND P_u IS THE SUM OF THAT DUE TO CONDUCTOR, DIELECTRIC AND RADIATION.

CLASSICAL DISPERSION THEORY [45] PREDICTS THAT AT MICROWAVE FREQUENCI PERMITTIVITY IS INDEPENDENT OF FREQUENCY AND LOSS TANGENT IS PROPORTIONAL TO FREQUENCY ( ).

$$\tan\delta = \left(/ \right)^{2}_{T} f \tag{1.20}$$

WHERE IS THE DAMPING FACTOR, IS THE RESONANT FREQUENCY OF THE OPTICAL MODE OF LATTICE VIBRATION. DECREASES WITH INCREASING FREQUENCY AND IS THEREFORE OFTEN QUOTED WHILE COMPARING CERAMICS.

1.4.3 SMALL TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY ( )

THE TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY IS A MEASURE OF T STABILITY OF THE RESONATOR. IT INDICATES THE "DRIFT" OF RESONANT FREQUENCY WI TEMPERATURE. THE FREQUENCY OF STANDING WAVE WITHIN THE RESONATOR IS GI (1.10). WHEN TEMPERATURE CHANGES, THEN THE RESONANT FREQUENCY ( ) CHANGES DUE TO THE VARIATION IN AND LENGTH OF THE DIELECTRIC MATERIAL. DIFFERENTIATING WITH RESPECT TO TEMPERATURE GIVES

$$\frac{1}{f_0}\cdot\frac{\Delta f_0}{\Delta T} = \frac{-1}{L}\cdot\frac{\Delta L}{\Delta T} - \frac{1}{2}\cdot\frac{1}{\ }\cdot\frac{\Delta\ }{\Delta T} \tag{1.21}$$

WHERE $\frac{1}{f_o}\frac{\Delta f}{\Delta T}$ IS THE TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY (τ_f), $\frac{1}{L}\frac{\Delta L}{\Delta T}$ IS THE LINEAR

EXPANSION COEFFICIENT (α_L) AND $\frac{1}{\varepsilon_r}.\frac{\Delta \varepsilon_r}{\Delta T}$ IS THE TEMPERATURE COEFFICIENT OF PERMITTIVITY (τ_ε).

SUBSTITUTING THESE VALUES IN THE ABOVE EQUATION, WE GET THE EXPRESSION FOR τ_f

$$\tau_f = -\left(\alpha_L + \frac{\quad}{2}\right) \tag{1.22}$$

THE τ_F CAN BE DEFINED MATHEMATICALLY IN TERMS OF RESONANT FREQUENCY AND TEM

$$\tau_f = \frac{1}{f_o} \times \frac{\Delta f}{\Delta T} \tag{1.23}$$

WHERE f_o IS THE RESONANT FREQUENCY, Δf IS THE VARIATION OF RESONANT FREQUENCY WITH ΔT CHANGE IN TEMPERATURE. τ_f IS USUALLY EXPRESSED IN PARTS PER MILLION PER DEGREE CEL (PPM/^{o}C).

THE VALUE OF τ_f SHOULD BE NEAR TO ZERO FOR PRACTICAL APPLICATIONS. IT IS SELF THAT A MATERIAL WITH A SIGNIFICANTLY HIGH VALUE OF τ_f IS USELESS IN A MICROWAVE CIRCUIT AS IT CANNOT MAINTAIN ITS RESONANT FREQUENCY AS THE BASE STATION OPERATING TEMPE HOWEVER, IN REALITY, A SMALL NON-ZERO VALUE OF τ_f IS REQUIRED TO COMPENSATE FOR THERMAL EXPANSION OF THE MICROWAVE CAVITY AND OTHER COMPONENTS IN THE CIRCUIT.

1.5 FACTORS AFFECTING MICROWAVE DIELECTRIC PROPERTIES

MICROWAVE DIELECTRIC PROPERTIES ARE INFLUENCED BY A NUMBER OF FACTO PERMITTIVITY [46], ONSET OF PHASE TRANSITIONS [47-48], PROCESSING CONDITIONS, RAW IMPURITIES [49] AND ORDER/DISORDER BEHAVIOR AND POROSITY [50]. THE DIELECTRIC RESULT OF A COMBINED CONTRIBUTION OF THE DEGREE OF CRYSTAL STRUCTURE MICROSTRUCTURAL INHOMOGENITY AND INTERACTION OF PHONONS. BOTH A HIGH PUR PROCESSING AND THUS GOOD MICROSTRUCTURE ARE REQUIRED FOR A LOW LOSS. C MICROSTRUCTURAL INHOMOGENITIES SUCH AS SPACE CHARGES OR DIPOLES WHICH LIE I

MATRIX GRAINS AND INCLUSIONS OR AT GRAIN BOUNDARIES HAVE HIGHER LO
INHOMOGENITIES MAY ARISE DUE TO SECONDARY PHASES, IMPURITY SEGREGATION,
DENSIFICATION ETC. IT IS FOUND THAT THE QUALITY FACTOR OF A CERAMIC IS INCREASE
IN BULK DENSITY, PROVIDED THE Ddensification IS PROMOTED BY SOLID STATE
MECHANISM. HENCE GLASSY PHASE FORMATION SHOULD BE AVOIDED DURING SINTERIN
QUALITY FACTOR. BECAUSE OF THE NATURAL DIFFICULTIES INVOLVED IN GETTING
REPRODUCIBLE MICROSTRUCTURES, IT IS ESSENTIAL THAT THE CERAMIC IS AT LEAST
SINGLE PHASE WITH HOMOGENEOUS MICROSTRUCTURE AS POSSIBLE. Q_u IS OBSERVED HIGH

THE STRUCTURAL FACTORS THAT ARE INVOLVED IN LOSS MECHANISM INCLUDE L
DISTORTION OF SYMMETRY, MASS OF IONS, CATION ORDERING ETC. THE DIELECTRIC LO
MICROWAVE DIELECTRICS ($\tan\delta$) IS BROUGHT ABOUT BY THE EFFECT OF ANHARMONIC TERMS I
POTENTIAL ENERGY ON THE MEAN SEPARATION OF A PAIR OF ATOMS AND IS INCREAS
IMPERFECTIONS IN THE CRYSTAL. THE DIELECTRIC LOSS CAUSED BY THE ANHARMONIC T
AT HIGHER TEMPERATURES. THE RANDOM DISTRIBUTION OF IONS IS ALSO CONSIDERED T
IMPERFECTION. THE Q FACTOR OF THE ORDERED CERAMICS WOULD BE MUCH GREATER THAN
ORDERED CERAMICS. ANY TYPE OF DEFECTS SUCH AS GRAIN BOUNDARIES, STACKING FA
OR STRUCTURAL DISORDER, POINT DEFECTS, PLANAR DEFECTS, LINE DEFECTS, INCLUS
PHASES, TWINNING, POROSITY ETC. CONTRIBUTE TO DIELECTRIC LOSSES. IN THE MICRO
THE INTRINSIC LOSS IS MAINLY DUE TO THE INTERACTION OF THE APPLIED FIELD WITH
LEADS TO DAMPENING OF THE PHONON MODES OF FUNDAMENTAL LATTICE.

1.5.1 EFFECT OF POROSITY

(a) Relative permittivity

THE VARIATION OF RELATIVE PERMITTIVITY WITH POROSITY HAS BEEN CONSIDERE
NUMBER OF APPROXIMATIONS [51]. THE MODELS CONSIDER THE DIELECTRICS AS A C
SYSTEM OF TWO PHASES (DIELECTRIC MATERIAL AND POROSITY) WITH DIFFERE
PERMITTIVITIES. THE SIMPLEST MODEL IS TO CONSIDER THE DIELECTRIC AS PARALLEL
DIELECTRICS HAVING VOLUME FRACTIONS V_1 AND V_2 AND RELATIVE PERMITTIVITIES
ε_1 ($\varepsilon_1 = \varepsilon_m$, DIELECTRIC PHASE) AND ε_2 ($\varepsilon_2 = 1$, POROSITY) RESPECTIVELY. THEN THERE ARE TWO
POSSIBLE CONFIGURATIONS

(A) ELECTRIC FIELD IS PERPENDICULAR TO THE PLANE OF THE PLATES [51]. THEN

$$' = _m - P(_m - 1) \tag{1.24}$$

(B) IF ELECTRIC FIELD IS PARALLEL TO THE PLANE OF THE PLATES,

$$' = \frac{_m}{P(_m - 1) + 1} \tag{1.25}$$

MAXWELL DERIVED A REALISTIC MODEL OF SPHERICAL PARTICLES, $_d$ OF A RELATIVE PERM
DIELECTRIC MA$_m$RIX. THE RELATIVE PERMITTIVITY OF THE MIXTURE IS GIVEN BY

$$' = \frac{V_m \; _m\left(\frac{2}{3} + \frac{_d}{3\;_m}\right) + V_d \; _d}{V_m\left(\frac{2}{3} + \frac{_d}{3\;_m}\right) + V_d} \tag{1.26}$$

IF THE SPHERES ARE PORES AND APPLYING A LINEARIZED APPR$_m$OXI$'$(\ $_m$),
THEN THE ABOVE EQUATION BECOMES

$$' = _m\left(1 - \frac{3P(_m - 1)}{2\;_m + 1}\right) \tag{1.27}$$

(b) Dielectric loss (tan δ)

THE COMPLEX PERMITTIVITY OF A MATERIAL IS GIVEN BY

$$= ' - i\,'' \tag{1.28}$$

REAL COMPONENT, $'$ IS RELATIVE PERMITTIVITY AND IMAGINARY COMPONENT, $''$ IS KNOWN AS THE
DISSIPATION OF THE ELECTRIC FIELD.

DIELECTRIC LOSS TANGENT, $\tan\Delta = \frac{''}{'}$ (1.29)

QUALITY FACTOR, $Q = \frac{1}{\tan\Delta}$ (1.30)

THE LOSS INCREASES WITH POROSITY AND THEREFORE AN EMPIRICAL TERM IS INTRODUCED. PLOT OF TAN δ AGAINST POROSITY ON A LOG-LOG PLOT SUGGESTED THAT A WOULD GIVE A DEPENDENCE OF THE FORM,

$$\tan\delta = (1-P)\tan\delta_o + AP^n \tag{1.31}$$

$\tan\delta_o$ IS THE LOSS TANGENT OF FULLY DENSE MATERIAL AND P IS THE AMOUNT OF MATERIAL PRESENT IE., IT SHOULD DEPEND ON THE POROSITY. THE ABOVE EQUATION CAN BE PUT IN LAW OF MIXTURES AS

$$\tan\delta = (1-P)\tan\delta_o + P(AP^{n-1}) \tag{1.32}$$

THE LOSS MAY BE RELATED TO THE SURFACE AREA S OF THE PORE VOLUME,

$$\tan\delta = (1-P)\tan\delta_o + P(A'S) \tag{1.33}$$

AS PER THE SINTERING THEORY, SURFACE AREA OF THE PORES VARIES WITH POROSITY AS

$$S \propto \left(\frac{P}{1-P}\right)^{2/3} \tag{1.34}$$

SUBSTITUTING THE ABOVE EQUATION IN EQ. (1.33), WE GET [53]

$$\tan\delta = (1-P)\tan\delta_o + A'P\left[\frac{P}{1-P}\right]^{2/3} \tag{1.35}$$

1.5.2 EFFECT OF HUMIDITY

THE *tan δ* INCREASES WITH INCREASING POROSITY DUE TO MOISTURE IN THE PORES. HUMIDITY EFFECTS ON LOW FREQUENCY DIELECTRIC PROPERTIES OF POROUS M BEEN STUDIED [54]. JONSCHER [55] IDENTIFIED LOW FREQUENCY LOSS MECHANISM IN MATERIALS IN THE PRESENCE OF MOISTURE. *Ku et al.* [56] STUDIED THE EFFECT IN SOME MATERIALS AT MICROWAVES. IT IS CLEAR THAT THE RELAXATION PROCESS CENTERED A IS RESPONSIBLE FOR HIGH DIELECTRIC LOSS OVER A WIDE FREQUENCY RANGE EXTEN MICROWAVE RANGE. THE HUMIDITY EFFECTS ON LOW FREQUENCY DIELECTRIC PROPERT

MATERIALS HAVE BEEN ASSOCIATED TO THE LIBERATION OF IONS BEHAVIOUR FOUND IN THE DRY CONDITION. IN CONTACT WITH AN ADSORBED WATER FILM, THESE IONS BECOME FREE TO MOVE OV REGIONS. THIS MECHANISM WOULD PRODUCE AN INTERFACIAL POLARIZATION PROCESS A LOW FREQUENCY PEAK. CHARGE CARRIERS COULD ALSO BE PRODUCED BY AN ELE PROCESS OF DISSOCIATION OF WATER INTO A PROTON AND A HYDROXYL ION [57].

1.6 APPLICATIONS OF DIELECTRIC RESONATORS

WITH THE ADVENT OF TEMPERATURE STABLE DIELECTRIC MATERIALS, DIELECTRIC RESONATORS HAVE EMERGED AS A HIGH *Q*, CONVENIENTLY SIZED ELEMENT FOR APPLICATIONS IN MICROWAVE INTEGRATED CIRCUITS (MICS) FOR THE ENTIRE MICROWAVE FREQUENCY RANGE. THEY CAN BE USED TO FORM FILTERS, OSCILLATORS, TRIPLEXERS, AND OTHER CIRCUITS DUE TO THEIR RELATIVELY HIGH *Q* (QUALITY FACTOR) VALUES AND GOOD FREQUENCY STABILITY. A FEW OF THE APPLICATIONS OF MICROWAVE DIELECTRIC RESONATORS ARE BRIEFLY DISCUSSED BELOW.

1.6.1 DIELECTRIC RESONATOR OSCILLATORS

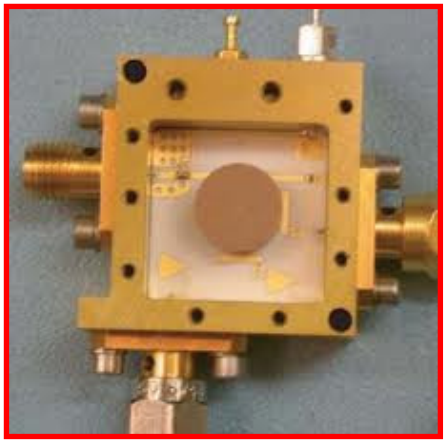

Fig. 1.6 Tuneable dielectric resonator oscillator. (www.londonmet.ac.uk/londonmet/library)

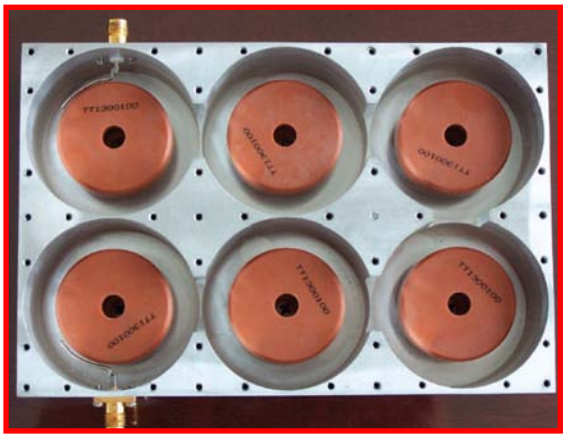

Fig. 1.7 A typical dielectric resonator filter. (BL microwave Ltd.)

OSCILLATORS REPRESENT THE BASIC MICROWAVE ENERGY SOURCE FOR ALL SYSTEMS SUCH AS RADARS, COMMUNICATIONS, NAVIGATION OR ELECTRONIC WARFA MICROWAVE OSCILLATOR CONSISTS OF AN ACTIVE DEVICE (A DIODE OR TRANSISTOR)

FREQUENCY DETERMINING RESONANT ELEMENT. WITH THE RAPID ADVANCEMENT OF TECHNOLOGY, THERE HAS BEEN AN INCREASING NEED FOR BETTER PERFORMANCE. THE EMPHASIS HAS NOISE, SMALL SIZE, LOW COST, HIGH EFFICIENCY, HIGH TEMPERATURE STABILITY AN DIELECTRIC RESONATOR OSCILLATORS (DRO) OFFER THE SYSTEM DESIGNER A VIABLE AL EFFORT TO MEET THESE CHALLENGES. THE APPLICATIONS OF DRO'S INCLUDE LOCAL O COMMUNICATION SYSTEMS, THE LARGEST APPLICATION OF WHICH MAY BE IN DIRECT TV THE APPLICATION OF DR AS OSCILLATOR ELEMENT WAS FIRST PROPOSED BY DAY IN SUBSEQUENTLY, IN 1977, A 4 GHZ GAAS FET OSCILLATOR USING A TiO_2 RESONATOR INTEGRATED WITH SI BIPOLAR TRANSIS WAS USED AS A FIXED FREQUENCY OSCILLATOR. THESE FUNDAMENTAL FIXED FREQUEN ARE SIGNIFICANTLY SIMPLER AND EFFICIENT WITH 10–20 DB LOWER PHASE NOISE THAN C ELECTRONIC OSCILLATORS [59]. FIG. 1.6 SHOWS A TYPICAL TUNABLE DRO.

1.6.2 DIELECTRIC RESONATOR FILTERS

OWING TO THE SUPERIOR PERFORMANCE CHARACTERISTICS OF DIELECTRIC RESONATORS, THE USE OF DIELECTRIC RESONATORS HAS BECOME WIDESPREAD, PARTICULARLY IN HIGHLY SEL FILTERS. DIELECTRIC RESONATOR FILTERS ARE A CLASS OF STABLE MICROWAVE F FREQUENTLY USED IN RADAR AND COMMUNICATION SYSTEMS. A TYPICAL DIELECTRIC R (SEE FIG. 1.7) CONSISTS OF CERAMIC RESONATOR DISCS MOUNTED IN A PARTICULAR W METAL CAVITY. DIELECTRIC RESONATORS ARE OFTEN UTILIZED IN FILTER CIRCUITS INTRINSICALLY HIGH Q VALUE. THE DIELECTRIC RESONATOR, OPERATING AT A FIXED FREQUENCY, IS TUNABLE OVER A NARROW BANDWIDTH AND FREQUENCY FINE TUNING MUST BE A WITHOUT AFFECTING THE HIGH Q OF THE RESONATOR. THESE CHARACTERISTICS ALLOW A E EMPLOYING A DIELECTRIC RESONATOR TO HAVE EXCELLENT FREQUENCY STABILITY W AMOUNT OF FREQUENCY DRIFT OVER A WIDE RANGE OF TEMPERATURES AND EN CONDITIONS. UNLIKE METALLIC RESONATORS, DIELECTRIC RESONATORS YIELD LITTL IMPEDANCE ELECTRIC FIELDS WHEN THEY ARE OPERATED IN DESIRED OPERATING MOD RESONATORS EMPLOYED IN FILTERS COULD BE UTILIZED IN A VARIETY OF MODES, SUC AND HEM (HYBRID ELECTROMAGNETIC) MODES. AT THE PRESENT TIME, DIELECTRIC RESO ARE EMERGING AS THE BASELINE DESIGNS FOR THE MAJORITY OF RF FILTERS USED IN SATELLITE APPLICATIONS. THEY OFFER HIGH Q VALUES WITH A RELATIVELY LOW VOLUME RATIO IN

COMPARISON WITH ANY OTHER KNOWN FILTER TECHNOLOGY. IF RECONFIGURABLE RF F
EMPLOYED IN WIRELESS BASE STATIONS AND SATELLITE SYSTEMS, TUNABLE DIELEC
FILTERS STAND TO BE THE OPTIMUM SOLUTION.

1.6.3 DIELECTRIC RESONATOR ANTENNAS

DIELECTRIC RESONATOR ANTENNAS (DRAS) ARE MADE OF CERAMICS OR
ANOTHER DIELECTRIC MEDIUM FOR MICROWAVE FREQUENCIES. DIELECTRIC RESONATO
FABRICATED ENTIRELY FROM LOW LOSS DIELECTRIC MATERIALS AND ARE TYPICALLY M
PLANES. THEIR RADIATION CHARACTERISTICS ARE A FUNCTION OF THE MODE OF OPERA
THE DRA. THE MODE IS GENERALLY CHOSEN BASED UPON THE OPERATIONAL REQ
DIELECTRIC RESONATOR ANTENNAS OFFER SEVERAL ADVANTAGES OVER OTHER ANTEN
SIZE, HIGH RADIATION EFFICIENCY AND SIMPLIFIED COUPLING SCHEMES FOR VARIOUS T
LINES. THE BANDWIDTH CAN BE CONTROLLED OVER A WIDE RANGE BY THE CHOICE
PERMITTIVITY AND THE GEOMETRIC PARAMETERS OF THE RESONATOR. DIELECTRIC RES
CAN ALSO BE MADE IN LOW PROFILE CONFIGURATIONS, MAKING THEM MORE AESTHETI
THAN STANDARD WHIP, HELICAL, OR OTHER UPRIGHT ANTENNAS.

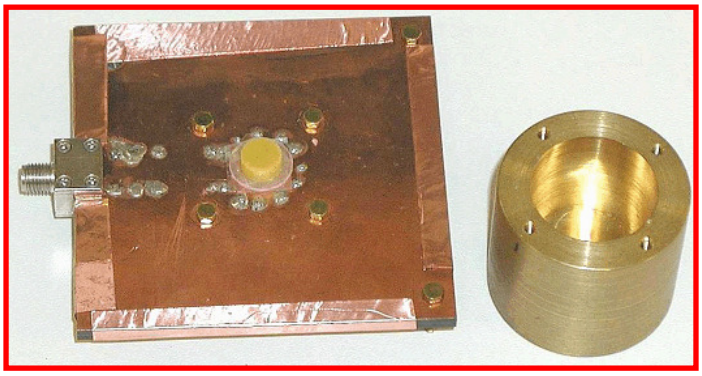

Fig. 1.8 A dielectric resonator antenna with a cap for measuring the radiation efficiency. (www.ee.olemiss.edu/researchbriefs/resonator.bmp)

1.7 SUBSTRATES

SUBSTRATES PROVIDE THE MECHANICAL BASE AND DIELECTRIC MATERIAL ON WHICH
THICK-FILM MATERIALS ARE FABRICATED. THEY MAY FUNCTION AS A SIMPLE PASS

PROVIDING STRENGTH AS IN MANY HYBRID APPLICATIONS OR MAY BE A KEY ACTIVE COMPONENT OF THE CIRCUIT AS IN SILICON SOLAR CELLS. ALL THICK-FILM SUBSTRATES ABILITY TO WITHSTAND HIGH TEMPERATURES AND HAVE HIGH ELECTRICAL RESISTIVI STRENGTH, DIELECTRIC BREAKDOWN VOLTAGE AND THERMAL SHOCK RESISTANCE. IN A GENERAL REQUIREMENTS, OTHER IMPORTANT PROPERTIES THAT DEPEND ON THE APPL THERMAL CONDUCTIVITY, THERMAL EXPANSION, SURFACE SMOOTHNESS, RELATIVE PE DIELECTRIC LOSS. TABLE 1.1 LISTS THE KEY PHYSICAL AND DIELECTRIC PROPERTIES SUBSTRATES.

Table 1.1 Physical properties of selected substrate materials.

Property	Al_2O_3	BeO	AlN	Silicon	Borosilicate glass
CTE ($PPM/^0C$)	6.6	7.2-8.0	3.8-4.4	3.5	3.3
THERMAL CONDUC ($WM^{-1}K^{-1}$)	29-37	260-290	140-260	125	1.2
ε_R (AT 1 MHZ)	9.7-10.5	6.5-7.0	8.0-9.2	11.8	4
TAN δ (AT 1 MHZ)	0.0002	0.0004	0.0005	0.005	0.0004

CERAMIC SUBSTRATES ARE THE PREFERRED SUBSTRATE FOR MOST THICK-FILM APP TO DIMENSION STABILITY AND INERTNESS AT TYPICAL THICK-FILM FIRING TEMPERATU HIGH ELECTRICAL RESISTIVITIES IN THE ORDER OF 10^{13} Ω-CM AND DIELECTRIC BREAKDOWN VOLTAGES IN EXCESS OF 500 V/MIL, MAKING THEM IDEAL FOR HIGH-VOLTAGE CIRCUITRY. AMONG TH COMMERCIALLY AVAILABLE SUBSTRATE MATERIALS, ALUMINA HAS BECOME THE MOS ONE BECAUSE IT COMBINES ELECTRICAL, MECHANICAL AND ECONOMICAL ADVANTAG ALUMINA IN ITS PURE FORM HAS A VERY HIGH SINTERING TEMPERATURE ABOVE 1700 ^{0}C. BERYLIA POSSESS A HIGH THERMAL CONDUCTIVITY VALUE (AN ORDER OF MAGNITUDE HIGHER T THE COMBINATION OF HIGH STRENGTH AND THERMAL CONDUCTIVITY GIVE BEO A GO SHOCK RESISTANCE. THE CTE VALUE IS SLIGHTLY HIGHER THAN ALUMINA AND RELATIV IS SLIGHTLY LOWER. THE DISADVANTAGES WITH BERYLIA ARE THE HIGH COST AND POT PROBLEM ASSOCIATED WITH ITS USE. THE HIGH THERMAL CONDUCTIVITY OF ALN CA UTILIZED FOR SUBSTRATE APPLICATIONS, HOWEVER, THEY ALSO POSSESS A HIGH

TEMPERATURE. ALSO, THEY ARE REACTIVE TO SOME GLASS BINDERS THUS CAUSING TO GLASS BINDERS THUS CAUSING DIFFICULTIES IN COFIRING PROCESS. THUS SEARCH FOR NEW MATERIALS WITH GOOD DIELECTRIC PROPERTIES AND ALSO HAVING GOOD COFIRING PROPERTIES ARE STILL IN PR

1.8 LOW TEMPERATURE CO-FIRED CERAMICS

1.8.1 INTRODUCTION

THE CURRENT TREND IN THE MICROELECTRONICS INDUSTRY IS TO REDUCE THE OVERALL SIZE OF ELECTRONIC PACKAGES. THIS MEANS THAT MORE COMPLEX PACKAGES HAVE TO BE HIGHER INTERCONNECT DENSITY, SMALLER COMPONENTS BUT WITH SAME OR GREAT AMONG THE VARIOUS FABRICATION METHODS OF ELECTRONIC DEVICES, LOW TEMPERAT CERAMIC (LTCC) TECHNOLOGY HAS BECOME AN ATTRACTIVE MANUFACTURING PLATFO SPEED AND GOOD FUNCTIONALITY FOR COMPACT, LIGHT WEIGHT AND INTEGRATE COMPONENTS, MODULES, SUBSTRATES AND DEVICES [60-61]. NEXT TO LAMINATES AND PASSIVE INTEGRATION ON HIGH OHMIC SILICON, LTCC IS AN ESTABLISHED TECHNOLOGY FOR TH OF HIGHLY INTEGRATED MODULES FOR MOBILE COMMUNICATION DEVICES. TO REALIZ MINIATURIZED RF MODULES, ONE TECHNOLOGY TREND IS TO DECREASE THE LINEWIDTH OF METAL LINES TO REACH A HIGHER WIRING DENSITY. ANOTHER TREND IS TO INCREAS OF THE PROCESSES IN ORDER TO ENABLE THE SUBSTRATE INTEGRATION OF FUNCTION DEMAND OF ACCURACY. NEXT TO THESE PROCESSING TRENDS LTCC TECHNOLOGY OFFE TO COMBINE DIFFERENT TYPES OF CERAMIC MATERIALS INTO ONE MULTILAYER BOAR TECHNOLOGY HAS THE ABILITY TO INTEGRATE PASSIVE COMPONENTS SUCH AS RESIST AND INDUCTORS INTO A MONOLITHIC PACKAGE [62-64], THEREBY FREEING VALUABLE CI AREAS FOR ACTIVE COMPONENTS. FOR THE MINIATURIZATION OF THESE FUNCTIONS MATERIAL WITH A REASONABLY HIGH RELATIVE PERMITTIVITY, INHERENT LOW LO FREQUENCIES AND EXCELLENT TEMPERATURE STABILITY IS REQUIRED. NEW LOW FI MATERIALS HAVE TO BE COMPATIBLE WITH RESPECT TO FIRING, DIELECTRIC, MAGNETI MECHANICAL PROPERTIES WITH THE COMMERCIAL GLASS CERAMIC LTCC TAPES AND ME THAT MECHANICALLY RELIABLE MULTILAYER STRUCTURES WITH THE DESIRED ELECT CAN BE MANUFACTURED. THE TARGET FIRING TEMPERATURE IS BELOW 900°C. THE RANGE 850-940 IS THE MOST SUITABLE RANGE FOR COMMERCIAL LTCC METAL PASTES AND TAPES.

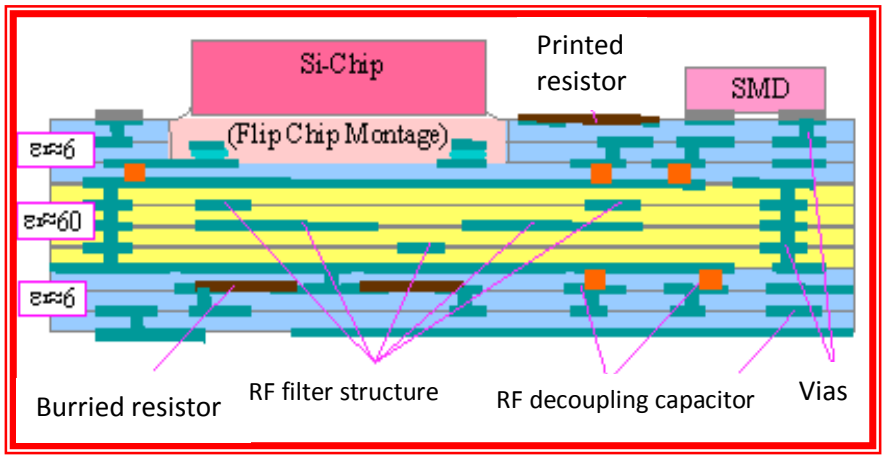

Fig. 1.9 LTCC multilayer module for telecommunication.

THE SIZE, COST AND PERFORMANCE OF INTEGRATION, PACKAGING AND INTERC TECHNOLOGIES ARE CRITICAL FACTORS FOR THE SUCCESS OF A MICROWAVE PRODUC MILITARY AND COMMERCIAL APPLICATIONS, LOWER WEIGHT AND SMALLER SIZE REQ NECESSITATING INCREASED DENSITY IN ELECTRONICS PACKAGING. CROSS-TALK NOISE AND ELECTRIC SIGNAL DELAY ARE SUPPRESSED BY POSITIONING THE ELECTRIC-SIGNAL MATERIAL LAYERS. DOWNSIZING OR LOWERING SUBSTRATES (E.G. DECREASE NUMBER OF CAPACITANCE LAYERS) CAN BE ACHIEVED BY FORMING INTERNAL CAPACITORS ON H LAYERS. ONE WAY TO ACHIEVE GREATER DENSITY IS THROUGH INTEGRATION OF COMPONENTS WITHIN A SINGLE PACKAGE FIG. 1.9 SHOWS THE STRUCTURE OF AN LTCC M MODULE. LTCC HAS THE UNIQUE ABILITY TO INTEGRATE A BROAD VARIETY OF COMPON INDUCTORS, CAPACITORS AND FILTERS INTO A VERY COMPACT ARRANGEMENT.

1.8.2 HISTORICAL DEVELOPMENTS IN LTCC TECHNOLOGY

THE DEVELOPMENT OF MULTI CHIP INTEGRATED CIRCUITS (MCIC) WAS DRIVEN BY THE NEED FOR INCREASED INTERCONNECT DENSITY, HIGHER SIGNAL TRANSMISSION AND CLOCK F AND MICROWAVE ELECTRONICS IN THE EARLY 1990'S. ALTHOUGH MCIC, IN GENERAL, W

MILITARY, SPACE APPLICATIONS ETC., LTCC-BASED TECHNOLOGY MADE ITS OWN BREAKTHROUGH IN THE TELECOMMUNICATION FIELD, WHICH IS ONE OF THE FASTEST GR IN THE CONSUMER ELECTRONICS INDUSTRY. THE HISTORY OF LTCC TECHNOLOGY AC BACK TO EARLY 80'S, WHEN IT WAS FIRST DEVELOPED BY HUGHES AND DUPONT FO SYSTEMS. THE ORIGIN OF MULTILAYER CERAMIC SUBSTRATE TECHNOLOGY IS AT RCA C THE LATE 1950'S AND THE BASES OF CURRENT PROCESS TECHNOLOGIES WERE DISCOVER [66-68]. PROGRESS WAS MADE USING THESE TECHNOLOGIES WITH IBM TAKING THE LEA CIRCUIT BOARD FOR IBM'S MAINFRAME COMPUTER COMMERCIALIZED IN THE EARLY 198 INHERITANCE [69-70]. SINCE THIS MULTILAYER BOARD WAS COFIRED AT THE HIGH TEM 1600^{O}C WITH THE ALUMINA INSULATING MATERIAL AND MO, W, MO-MN), IT IS CALLED HIGH TEMPERATURE COFIRED CERAMIC. FROM THE MIDDLE OF THE 1980'S, E INCREASE THE SPEED OF MAINFRAME COMPUTERS ACCELERATED, AND AS THE KEY T COMPUTER PERFORMANCE, FURTHER IMPROVEMENTS ARE MADE TO MULTILAYER CERA FOR HIGH DENSITY MOUNTING APPLICATIONS. FINE WIRES WERE USED IN ORDER TO INC DENSITY IN CIRCUIT BOARDS FOR HIGH DENSITY MOUNTING. BUT ATTENUATION OF SIG TO THE ELECTRICAL RESISTANCE OF THE WIRING. HENCE IT IS NECESSARY TO USE MAT ELECTRICAL RESISTANCE (LIKE CU OR AU). IN ADDITION, WITH THE FLIP CHIP METHOD O BARE LSI COMPONENTS DIRECTLY, POOR CONNECTION OF THE INTERCONNECTS MAY THERMAL EXPANSION OF THE BOARD IS NOT CLOSE TO THAT OF THE SILICON ($3.5\ PPM/^{O}C$). INSULATING MATERIAL WITH LOW THERMAL EXPANSION (CERAMIC) IS DESIRABLE. FURT HIGH SPEED TRANSMISSION OF SIGNALS, IT IS NECESSARY THAT THE CERAMIC HAS A PERMITTIVITY. IN THE EARLY 1990'S, MANY JAPANESE AND AMERICAN ELECTRONIC AN MANUFACTURERS HAD DEVELOPED MULTILAYER BOARDS THAT MET THESE REQUIREME THEM, FUJITSU AND IBM WERE THE FIRST TO SUCCEED WITH COMMERCIAL APPLIC MULTILAYER SUBSTRATES USING COPPER AS WIRING MATERIAL AND LOW RELATIV CERAMICS. FROM THE LATTER HALF OF THE 1990'S TO THE PRESENT, THE FOCUS OF APP SHIFTED TO HIGH FREQUENCY WIRELESS FOR THE ELECTRONIC COMPONENTS, MODULES IN MOBILE COMMUNICATION DEVICES. FOR THE MULTILAYER CIRCUIT BOARD, THE L EXPANSION OF CERAMICS WAS ITS BIGGEST MERIT FOR THE PURPOSE OF HIGH DENSITY

LSI COMPONENTS. FOR HIGH FREQUENCY APPLICATIONS, LOW TRANSMISSION LOSS IS ITS KEY FEATURE, AND THE LOW DIELECTRIC LOSS OF CERAMIC GIVES IT AN ADVANTAGE OVER O

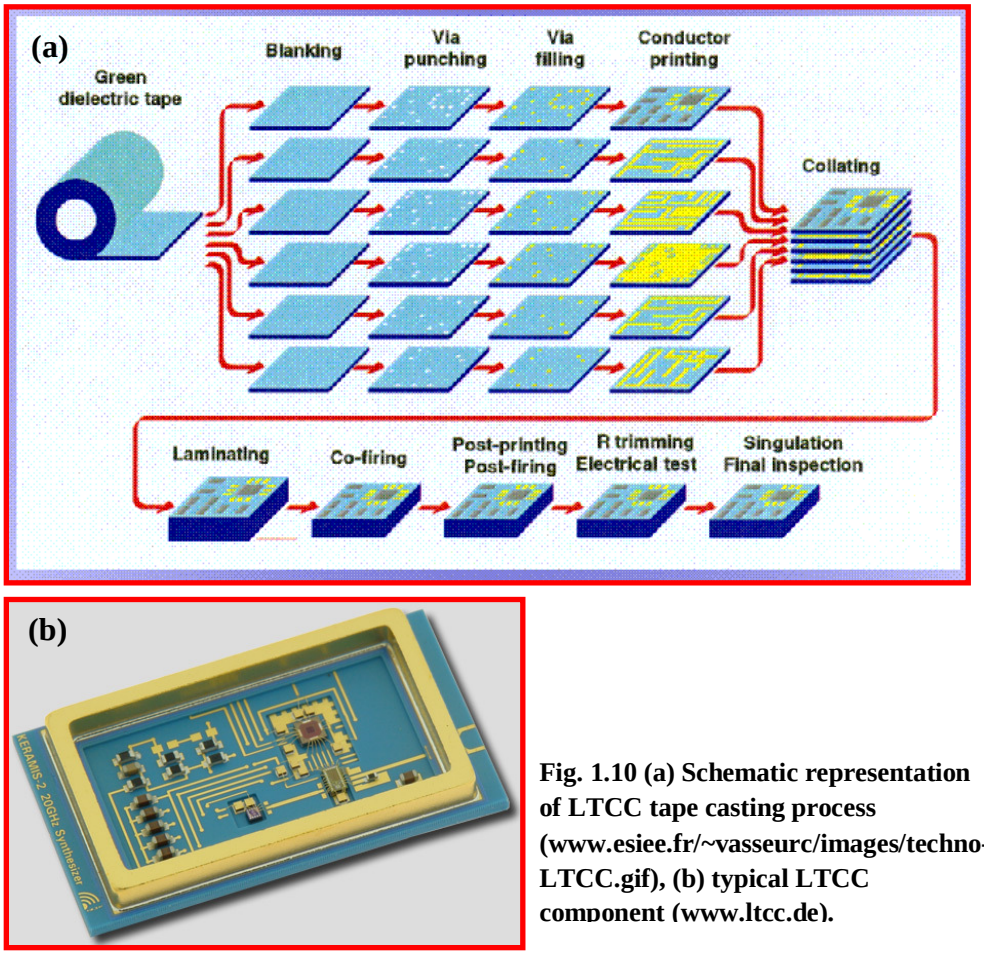

Fig. 1.10 (a) Schematic representation of LTCC tape casting process (www.esiee.fr/~vasseurc/images/techno-LTCC.gif), (b) typical LTCC component (www.ltcc.de).

DURING THE LATE 1980'S, U.S. AND JAPANESE MANUFACTURERS OF COMPUTE CERAMIC MATERIALS CONDUCTED EXTENSIVE RESEARCH AND DEVELOPMENT OF LTCC THAT IS NOW CRUCIAL TO PRESENT DAY AND FUTURE COMMUNICATION TECHNOLOGIES. 15 YEARS SCIENTISTS WORLD OVER HAVE DEVELOPED A LARGE NUMBER OF NEW DIELE (ABOUT 400) FOR HIGH FREQUENCY APPLICATIONS WITH LOW SINTERING TEMPERATURE THE PROPERTIES OF KNOWN MATERIALS. ABOUT 1000 PAPERS AND ABOUT 500 PATENTS A THE AREA OF LTCC MATERIALS AND RELATED TECHNOLOGIES. FOR DETAILS OF THE LTC THE READER IS REFERRED TO THE RECENT REVIEW BY SEBASTIAN AND JANTUNEN

GENERATION ELECTRONICS SYSTEMS WILL DEMAND, THE PERFORMANCE, RELIABILITY, LIGHTER WEIGHT AND AFFORDABILITY THAT LTCC TECHNOLOGY CAN PROVIDE.

1.8.3 MATERIAL SELECTION AND REQUIREMENTS

IN THE DEVELOPMENT OF LTCC APPLICATIONS, SEVERAL PROPERTIES NEED TO BE TAKEN INTO ACCOUNT. THE ELECTRICAL PROPERTIES OF THE DIELECTRIC AND THE CONDUCTOR ARE THE BASIC ISSUE, BUT DESIGNERS SHOULD ALSO BE AWARE OF THE EFFECTS OF THERMOMECHANICAL PROPERTIES, PRODUCTION COSTS AND VARIATION RANGE OF EACH [65]. THE IMPORTANT CHARACTERISTICS REQUIRED FOR AN IDEAL LTCC MATERIAL ARE GIVEN BELOW.

1.8.3.1 DENSIFICATION TEMPERATURE LESS THAN 950 °C

AS THE NAME ITSELF SUGGESTS, LTCC IS A CERAMIC MATERIAL WITH METAL WIRING AT LOW TEMPERATURE, AND ITS CONSTITUENT MATERIALS ARE METAL AND CERAMIC. THE TYPICAL LTCCS ARE THOSE WITH HIGH ELECTRICAL CONDUCTIVITY SUCH AS AG, AU, CU AND THEIR ALLOYS AND THEY ALL POSSESS A MELTING POINT CLOSE TO 1000 °C. IN ORDER TO COFIRE THE CERAMICS MATERIAL WITH THESE METALS, EXTREME PRECISION IS REQUIRED TO KEEP THE SINTERING TEMPERATURE BELOW THEIR MELTING POINT (900 – 1000 °C). IN ORDER TO LOWER THE SINTERING TEMPERATURE SEVERAL METHODS CAN BE ADOPTED SUCH AS ADDITION OF LOW MELTING, LOW LOSS GLASS, CHEMICAL SYNTHESIS OF THE CERAMICS [74] AND USING STARTING MATERIALS WITH SMALL SIZE. AMONG THESE METHODS, LOW LOSS GLASS ADDITION SEEMS TO BE MUCH EFFECTIVE AND ATTRACTIVE DUE TO THEIR EASE OF PREPARATION AND RELATIVELY LOW COST [60, 75-76]. IT IS NOTED THAT ANY DENSIFICATION OR CRYSTALLISATION OF THE COMPOSITE AT LOWER TEMPERATURES SUCH AS BELOW 300 °C IS UNDESIRABLE AS THIS CAN PREVENT THE EVAPORATION OF ORGANICS AND SOLVENTS USED IN CONDUCTIVE PASTES AND BINDER AND PLASTICIZERS CAUSING CARBON TRACES IN THE MICROSTRUCTURE [60, 77]. ANY RESIDUAL CARBON THAT MAY RESULT FROM BINDER DECOMPOSITION IF LEFT IN THE LTCC WOULD ADVERSELY AFFECT THE DIELECTRIC AND THUS THE DENSIFICATION OF THE CERAMIC SHOULD START ABOVE THIS TEMPERATURE.

1.8.3.2 GLASS-CERAMIC COMPOSITES

IN THE FABRICATION OF DESIRABLE LTCC SUBSTRATES, COMPLETE DENSIFICATION AND SUFFICIENT CRYSTALLIZATION ARE GENERALLY NECESSARY TO ACHIEVE THE REQUIRE DIELECTRIC PROPERTIES. POROSITY AND LOW DEGREE OF CRYSTALLINITY WOULD LEA POOR MECHANICAL PROPERTIES AND RESIDUAL GLASS WOULD DECREASE THE QUALITY FACTOR AT HIGH FREQUENCY. ATTEMPTS TO ACHIEVE THE ABOVE REQUIREMENTS ARE THE USE OF GL INCLUDING A HIGH SOFTENING GLASS, NUCLEATING AGENTS, SINTERING AIDS AND PH STRUCTURE MODIFIERS [78-81]. THREE APPROACHES HAVE BEEN USED TO OBTAIN GLA COMPOSITIONS SUITABLE FOR FABRICATING SELF-SUPPORTING LTCC SUBSTRATES. IN TH THE GLASS-CERAMICS (GC), FINE POWDER OF A SUITABLE GLASS COMPOSITION IS USED T ABILITY TO SINTER WELL TO FULL DENSITY IN THE GLASSY STATE AND SIMULTANEOUS BECOME GLASS-CERAMIC. THE CRYSTALLINE PHASES MAKE THE GLASS-CERAMIC VERY S FURTHER TEMPERATURE TREATMENTS SUCH AS POST FIRING PROCESSES. A TYPICAL EX TYPE IS THE GLASS SYSTEM $MgO-Al_2O_3-SiO_2$ HAVING CORDIERITE AS THE PRINCIPAL CRYSTALLI PHASE [82].

THE SECOND TYPE, THE GLASS-CERAMIC COMPOSITES (GCC), CONSISTS OF A MIXTU SUITABLE GLASS AND ONE OR FEW CERAMIC POWDERS, SUCH AS ALUMINA IN NEA PROPORTIONS [83]. USUALLY A VOLUME CONTENT OF MORE THAN 50% OF A GLASS WIT TEMPERATURE OF 20-350 °C BELOW THE SINTERING TEMPERATURE OF THE COMPOSITE I GLASS SERVES AS A FLOW MEDIUM, IE., SINTERING OR DENSIFICATION IS CAUSED BY A VI DISPERSING AND REARRANGING OF THE CRYSTALLINE PARTICLES IN THE GLASS MELT. A PROCESSES SUCH AS DISSOLUTION AND PRECIPITATION OCCUR AT THE GLASS CERAMIC IN ARE NOT ESSENTIAL FOR THE DENSIFICATION PROCESS, IE., DENSIFICATION IS DUE TO LIQUID PHASE SINTERING. IN MOST CASES, THE REACTION BETWEEN THE GLASS AND THE TO THE FORMATION OF NEW CRYSTALLINE PHASES WHICH AFFECTS THE PROPERTIES OF ADVERSELY. IN THE THIRD TYPE, THE GLASS BONDED CERAMICS (GBC), LOW VOLUME CONTENT (5-15%) OF A GLASS WITH A VERY LOW SOFTENING TEMPERATURE (< 400 °C) IS USED TO DENSELY SINTER THE COMPOSITE. IN THIS CASE, IT IS NECESSARY THAT THE PARTICL CRYSTALLINE PHASES BE VERY LOW. COMPARED TO THE SECOND CASE, THE GLASS F WHICH MUST BE MET TO ACHIEVE FULL DENSIFICATION ARE VERY SOPHISTICATED. T

SPECIAL DEVELOPMENT OF SUITABLE GLASSES FOR THIS TYPE OF GLASS BONDED CERAMICS IS ALWAYS NECESSARY. SOME OF THE LTCC MATERIALS BELONGING TO THE ABOVE MENTIONED CAT THEIR PROPERTIES ARE GIVEN IN TABLE 1.2.

Table 1.2 Some of the common LTCC dielectric and their main properties.

LTCC dielectric material	ε_r (1 MHz)	CTE (ppm/°C)	Bending strength (MPa)	T_s (°C)	Cond. material	Company
Glass-ceramics						
$MGO-AL_2O_3-SIO_2$	5.3-5.7	2.4-5.5	180-230	850-950	CU	IBM
$CAO-AL_2O_3-SIO_2-B_2O_3$	6.7	4.8	250	950	CU, NI	TAIYO YUDEN
Glass-ceramic composites						
$SIO_2-B_2O_3 + AL_2O_3$	5.6	4.0	240	1000	CU	FUJITSU
$MGO-AL_2O_3-SIO_2-B_2O_3$ + SILICA	4.3-5.0	3-8	150	850-950	AG, AG/PD	HITACHI
Glass-bonded ceramic						
$BAND_2TI_4O_{12} + BI_2O_3-B_2O_3-SIO_2-ZNO$	60	9-10	300	900	AG, AU, AG/PD/PT	SIEMENS

THE EFFECTIVENESS OF SINTERING AIDS DEPENDS ON SEVERAL FACTORS SUCH A TEMPERATURE, VISCOSITY, SOLUBILITY AND GLASS WETTABILITY [84]. IN ALL THESE C COMPOSITES, THE DENSIFICATION IS ACHIEVED BY THE PROCESS OF LIQUID PHASE SIN MAIN REQUIREMENT FOR LIQUID PHASE SINTERING IS THAT THE LIQUID PHASE SHOULD W OF THE CERAMICS. GENERALLY THE CHEMICAL REACTION BETWEEN SINTERING AIDS AN CAN PROVIDE THE BEST WETTING CONDITION [85]. HOWEVER, A CHEMICAL REACTION RE FORMATION OF THE SECONDARY PHASE. IT WAS SHOWN THAT ONE CAN EXPLOI MECHANISMS OF LIQUID PHASE SINTERING DEPENDING ON THE AMOUNT OF THE GLASS PO COMPOSITE MIXTURE. TO OBTAIN FULL DENSITY IN THE CERAMIC GLASS COMPOSITE, QUANTITY OF GLASS (20-50 %) IS REQUIRED. TOO LITTLE GLASS CAN RESULT IN POOR D

WHICH PRODUCES LOW MECHANICAL STRENGTH AND POOR THERMAL PRODUCTS. TOO
MUCH GLASS (> 50%) IS ALSO UNDESIRABLE, BECAUSE IT CAUSE SHAPE DISTORTION DU
AND ALSO DETERIORATES THE MICROWAVE DIELECTRIC PROPERTIES.

IT HAS BEEN REPORTED THAT THE GLASS MATERIALS FORM PARTICLE-PARTICLE
DISINTEGRATE THE SOLID PARTICLES INTO SMALLER GRAINS BY THE LIQUID PENETRATI
THE INTERACTION AND RESULTANT LIQUID-SOLID INTERFACE PROPERTIES ARE KNOWN
DEPENDENT UPON CHEMICAL COMPOSITION OF THE LIQUID PHASE, IT IS STILL DIFFICU
PRECISE PREDICTIONS ABOUT THE LIQUID PHASE SINTERING MECHANISM. LOW MELTING
AS B_2O_3-ZNO GLASS AND B_2O_3-BAO-SiO_2 GLASS HAVE BEEN CONSIDERED BASED ON SEVERAL
ATTRIBUTES RELATED TO SINTERING TEMPERATURE, VISCOSITY, SOLUBILITY AND WETT
FORM COFIRED CERAMICS. THE CONSTITUENT OXIDES IN GLASS COMPOSITION ARE BROA
INTO OXIDES THAT MAKE NETWORKS, MODIFIER OXIDES THAT BREAK NETWORK AND
OXIDES THAT CAN BECOME OXIDES OF EITHER TYPE. SINCE MODIFIER OXIDES BREAK NE
LOWER THE SOFTENING POINT OF THE GLASS AND INCREASES ITS FLUIDITY. B_2O_3, SiO_2, GeO_2, P_2O_5
AND A FEW OTHERS ARE THE COMMON NETWORK FORMERS. GLASSES MADE SOLELY FR
FORMERS OFTEN HAVE LIMITED UTILITY. FOR EXAMPLE, PURE B_2O_3 GLASS (T$_g$ 450°C) IS NOT WATER
RESISTANT AND PURE SiO_2 GLASS WHILE VALUED FOR ITS CHEMICAL DURABILITY, THERMAL SHOCK
RESISTANCE, POSSESS HIGH PROCESSING TEMPERATURES (ABOVE 1750°C). THE MAJORITY OF USEFUL
GLASSES CONTAIN ADDITIVES THAT SERVE TO ALTER THE PROCESSING AND PROPERTI
COMMONLY TERMED AS NETWORK MODIFIERS AND INTERMEDIATES. NETWORK MODIF
EXTRA OXYGEN IONS BUT DO NOT PARTICIPATE IN THE NETWORK, THEREBY RAISING TH
THE GLASS. THE EXTRA OXYGEN ALLOWS THE BRIDGING OXYGEN BETWEEN TWO TETR
DISRUPTED AND TWO NON-BRIDGING OXYGEN TO TERMINATE EACH TETRAHEDRON. T
MODIFIERS ARE DIRECTLY ANALOGOUS TO THE DECREASING SiO_4 TETRAHEDRAL CONNECTIVITY OBSERVED IN
CRYSTALLINE SILICATES WITH INCREASING O/SI RATIO. IN GLASSES THE LOSS OF CONNE
IN GREATLY DECREASED VISCOSITY FOR MODIFIED SILICATES AND REDUCES THE PROCESSI
TEMPERATURES OF SILICATE GLASSES INTO MORE PRACTICAL RANGES. ALKALINE
LI$_2$O, K$_2$O) ARE VERY EFFECTIVE MODIFIERS, THEY RESULT IN GLASSES THAT ARE NOT CHEMICALLY
DURABLE.

1.8.3.3 DIELECTRIC PROPERTIES

1.8.3.3.1 Relative Permittivity (ε_R)

LTCCS ARE BASICALLY COMPOSITE STRUCTURES AND THEREFORE, IT IS DIFFICULT TO CONTROLLING THEIR RELATIVE PERMITTIVITY DEPENDS LARGELY ON THE COMBINATIO MATERIALS OF THE COMPOSITE AND ITS MATERIAL COMPOSITION. GENERALLY, LO PERMITTIVITY MATERIALS WITH ε_r = 4-10 ARE USED FOR SUBSTRATE LAYERS WHILE HIGH PERMI MATERIALS ARE OPTED TO ENABLE MINIATURISED, EMBEDDED CAPACITORS, INDUCTO ANTENNAS [72, 86]. IN THE CASE OF CERAMIC PACKAGES, THE RELATIVE PERMITTIVI CERAMIC OVER AND WITHIN THE METAL LINES GOVERNS THE PROPAGATION DELAY (t_d), WHICH IS GIVEN BY [69]

$$t_d = \frac{l\sqrt{\varepsilon_r}}{c} \tag{1.36}$$

WHERE l IS THE LINE LENGTH, ε_r THE RELATIVE PERMITTIVITY AND c THE SUBSTRA SPEED OF LIGHT. THUS SUBSTRATES WITH LOW RELATIVE PERMITTIVITY ARE REQUIRED SPEED OF THE SIGNAL.

1.8.3.3.2 Dielectric Loss ($TAN\delta$)

IN ORDER TO REDUCE THE DIELECTRIC LOSS OF LTCC, IT IS EFFECTIVE TO CONSTRUCT THEM WITH LOW DIELECTRIC LOSS MATERIALS. THE DIELECTRIC LOSS VA LTCC MATERIALS, AS EXPRESSED WITH THE Q VALUE ($= 1/\tan\delta$) MULTIPLIED BY THE MEASUREMENT FREQUENCY, WHICH SHOULD BE GREATER THAN 1000. SINCE THE DIELEC GLASSES IS A MAJOR CONCERN IN THESE COMPOSITES, AT LEAST THREE TYPES OF DIEL GLASSES HAVE BEEN DISTINGUISHED: RESONANCE TYPE VIBRATIONAL LOSSES AT VERY H MIGRATION LOSSES CAUSED BY THE MOVEMENT OF MOBILE IONS AND DEFORMATIO DEFECT OR DEFORMATION OF THE BASIC SILICON OXIDE NETWORK [87]. RESONANCE TYP LOSSES ARE PARTICULARLY IMPORTANT IN THE MICROWAVE REGION. AMONG THE GLASS HAS THE LOWEST DIELECTRIC LOSS IN THE MICROWAVE REGION [87-88]. THE DIELECT FUSED QUARTZ IS LESS THAN 0.001 IN THE FREQUENCY RANGE FROM 3×10^{9} TO 2×10^{10} HZ. ALTHOUGH THE LOSS LEVEL IS ATTRACTIVE, SILICA IS NOT AN EFFECTIVE FLUX FOR MICROWAVE DI ALONE. TO LOWER THE MELTING POINT, THE RIGID SiO_2 NETWORK MAY BE BROKEN BY MODIFIERS,

PARTICULARLY ALKALI IONS, BUT THIS RESULTS IN HIGHER LOSSES [89-90]. FOR BINARY GLASSES BASED ON SiO_2, $\tan\delta$ FOR BOROSILICATE IS ABOUT 0.001 AT 3 GHZ. GLASSES BASED ON BOROSILICATES ALSO SHOWS LOW LOSS IN THE MICROWAVE REGION. SOME OF THE ALU BASED GLASSES SUCH AS CORDIERITE AND CELSIAN ALSO SHOW LOW LOSS FACTORS IN REGION. THE MAGNITUDE OF $\tan\delta$ FOR CORDIERITE GLASS CERAMICS AT 10 GHZ INCREASES W DEGREE OF REDUCTION OF THE GLASS-CERAMIC. FOR THE MINERAL CELSIAN WHICH CONTAINS TiO_2, $\tan\delta$ DECREASED AT 10 GHZ WITH INCREASING CRYSTALLIZATION. THIS WAS PROBABLY DUE TO A DECREASE IN THE RESIDUAL GLASSY PHASE WHICH CONTRIB INTERFACIAL POLARIZATION [91]. TABLE 1.3 GIVES THE PHYSICAL AND DIELECTRIC PR VARIOUS GLASSES USED IN THE PRESENT INVESTIGATION.

1.8.3.3.3 Temperature Stability of Dielectric Properties (τ_f AND τ_ε)

THE TEMPERATURE DEPENDENCE OF THE RESONANCE FREQUENCY IS A CRITICAL PARAMETER FOR LTCC'S BECAUSE THE VARIOUS COMPONENTS BASED ON NON-COMPENSATED DIELECTRIC MA ADDITIONAL MECHANICAL AND ELECTRICAL DESIGN TO ENSURE SATISFACTORY ELECTR OF THE DEVICE OVER ITS OPERATING TEMPERATURE [92-93]. THE COEFFICIENT OF TE VARIATION OF THE RESONANT FREQUENCY (τ_f) OF 10 PPM/^{0}C CAUSES A 0.11 % SHIFT OF THE RESONANT FREQUENCY (5.5 MHZ AT 5.2 GHZ) WITHIN THE TEMPERATURE RANGE -30 ^{0}C TO 85 ^{0}C. THOUGH NOVEL LTCC MATERIALS WITH ZERO (τ_f = 0 ± 10 PPM/^{0}C) HAVE BEEN DEVELOPED, THE COMPONENT DESIGNER MUST BE AWARE THAT THE STRUCTUR AFFECT τ_f IS

1.8.3.4 THERMAL PROPERTIES

THE CIRCUIT BOARDS AND PACKAGES UNDERGO THERMAL STRESS DURING ASSEMBLY PROCESSES SUCH AS IN SOLDER REFLOW WHEN LSI COMPONENTS AND OTHER ELECTRONIC PARTS AR THEM AND WHEN RELIABILITY TESTS ARE PERFORMED BEFORE PRODUCT SHIPMENT AN DEVICE OPERATION. THUS IN ADDITION TO THE DIELECTRIC PROPERTIES, DESIGNERS CONSIDER THE THERMAL PROPERTIES OF THE LTCC COMPOSITES.

1.8.3.4.1 THERMAL CONDUCTIVITY

THE THERMAL CONDUCTIVITY OF LTCC MATERIALS SHOULD BE GOOD. THE REMOVAL OF HEAT GENERATED BY THE DEVICE DURING OPERATION IS CRITICAL FOR FUNCTIONING OF THE PACKAGE. IT IS THEREFORE NECESSARY TO MAINTAIN THE TEMP 100^{O}C FOR EFFICIENT AND RELIABLE OPERATION OF THE DEVICE. THE HEAT REMOVAL HAS BECOME EVEN MORE CRITICAL IN RECENT YEARS BECAUSE OF THE EVER-GROWING NEED TO F DENSITY AND HIGH POWER DEVICES THAT CAN OPERATE AT HIGH SPEED. ADVANC TECHNOLOGY AND THE CONTINUING TRENDS TOWARD MINIATURIZATION OF DEVICES IN PLACE EVEN MORE STRINGENT REQUIREMENTS ON HEAT DISSIPATION CHARACTER PACKAGING LTCC. THE THERMAL CONDUCTIVITY OF AN LTCC IS 2 W/MK, VERSUS 0.5 W/ FOR ORGANIC MATERIALS. A COMMON METHOD TO IMPROVE THERMAL DISSIPATION IS T SPREADER, BUT A MORE ADVANTAGEOUS ALTERNATIVE PROVIDED BY LTCC TECHNOLO METALLIC VIA ARRAYS (THERMAL CONDUCTIVITY 50 W/MK) UNDER HIGH POWER COMPON

1.8.3.4.2 THERMAL EXPANSION

THE COEFFICIENT OF THERMAL EXPANSION (CTE) OR α IS A MEASURE OF THE CHARACTERISTIC CHANGE IN ITS DIMENSION FOR EACH DEGREE CHANGE IN TEMPERA MATERIAL IS UNIFORMLY HEATED OR COOLED. THUS, CTE CAN BE WRITTEN AS:

$$= \frac{\Delta l}{l_o \Delta T} \qquad (1.37)$$

WHERE Δl REPRESENTS THE CHANGE IN LENGTH OVER A TEMPERATURE SPAN ΔT, STARTING FROM AN INITIAL LENGTH l_o. IT IS STRONGLY TEMPERATURE DEPENDENT FOR MOST CERAMIC INSULATORS A NEAR LINEAR RANGE CAN BE DEFINED BETWEEN 0^{O}C AND APPROXIMATELY 250^{O}C, WITHIN WHICH THE EXPANSION COEFFICIENT VARIES LITTLE. THE CTE IS AN IMPORTANT PARA AFFECTS THE SI BASED ICS ATTACHED. THEREFORE, THE SUBSTRATE IS EXPECTED TO VALUES CLOSE TO THAT OF SI IN ORDER TO AVOID DEFORMATIONS SUCH AS CRACK, DEL BETWEEN THE SUBSTRATE AND THE ATTACHED COMPONENTS DUE TO SHRINKAGE MISM EXPANSION COEFFICIENT IS A DIRECTIONAL OR ANISOTROPIC FACTOR BECAUSE O DEPENDENCE ON THE CRYSTAL STRUCTURE, BOND STRENGTH AND DENSITY.

1.8.3.5 CHEMICAL COMPATIBILITY WITH ELECTRODE MATERIAL

THE LTCC SHOULD NOT REACT WITH THE CONDUCTIVE METAL DURING THE FORMATION OF ADDITIONAL PHASES IN THE CERAMIC SHOULD BE MINIMISED SINCE THE REACTION OF TH WITH THE CONDUCTING ELECTRODE, DEGRADES THE PERFORMANCE OF THE MICROWAV CRITICAL ISSUE IN MANUFACTURING LTCC MICROELECTRONICS IS THE PRECISE AND R CONTROL OF SHRINKAGE ON SINTERING. IN THE SCREEN-PRINTING OF THE CONDUCT INSTEAD OF PURE METALS, PASTES CONTAINING CONDUCTIVE PARTICLES IN GLASS ADDITIVES ARE USED. THUS WHEN DEVELOPING LTCC MATERIALS, ONE HAS TO TAKE IN REACTIONS NOT ONLY WITH THE CONDUCTIVE MATERIAL LIKE SILVER BUT ALSO WITH C THE CONDUCTOR PASTE.

Table 1.3 Common LTCC glasses and their physical and dielectric properties.

Glass Code	Glass	Density (g/cm^3)	T_s (^oC)	ε_R	$TAN\delta$ (1 MHz)	Ref.
B	B_2O_3	2.46	450	2.5	0.00550	[95]
ZB1	ZNO:B_2O_3 (50:50)	3.65	582	6.9	0.00012	[96]
ZB2	ZNO:B_2O_3 (71:29)	2.19	567	4.2	0.00330	[97]
AS	Al_2O_3:SiO_2 (50:50)	2.60	850	8.1	0.00970	[97]
MAS	MGO-Al_2O_3-SiO_2 (22:22:66)	2.30	1350	4.5	0.00074	[97]
MBS	MGO-B_2O_3-SiO_2 (40:40:20)	3.18	950	5.0	0.00230	[97]
BBS	BAO-B_2O_3-SiO_2 (30:60:10)	3.40	627	7.2	0.00440	[97]
ZBS	ZNO-B_2O_3-SiO_2 (50:40:10)	3.55	611	6.9	0.00950	[97]
LBS	Li_2O-B_2O_3-SiO_2 (35.14:31.66:33.2)	2.34	513	6.4	0.00360	[75]
BBSZ	B_2O_3-Bi_2O_3-SiO_2-ZNO (27:35:6:32)	4.30	950	8.8	0.00130	[98]
LMZBS	Li_2O-MGO-ZNO-B_2O_3-SiO_2 (20:20:20:20:20)	2.75	900	6.9	0.00200	[99]

1.8.4 APPLICATIONS OF LTCC TECHNOLOGY

NOWADAYS THERE ARE MANY NEW MICROELECTRONICS AND MICROSYSTEMS MESO SCALE APPLICATIONS OF THE LTCC TECHNOLOGY. LTCC IS VERY GOOD FOR HIGH VOLT HIGH PRESSURE OR VACUUM APPLICATIONS. THE TECHNOLOGY IS APPLIED TO BUILD M FOR MINIATURE FUEL CELL ENERGY CONVERSION SYSTEMS, DRUG DELIVERY, BIOLOG MONITORING, GAS OR LIQUID CHROMATOGRAPHS, COOLING AND HEAT EXCHANGE SEPARATORS, POLYMERASE CHAIN REACTION (PCR) [101], MICRO TOTAL ANALYSIS S (μTAS), PHOTONIC DEVICES, MOEMS AND MEMS PACKAGING [102]. IMPORTANT NEW APPLICATIONS OF LTCC ARE MICROFLUIDIC SYSTEMS [103] USED MOSTLY FOR CHEMICAL MICRO-HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (μ- HPLC) MADE IN LTCC DEMON VERY GOOD PROPERTIES OF CERAMICS AT HIGH PRESSURES. THE PROPERTIES OF LTCC/CH SMART CHANNELS ARE COMPARABLE TO THE PERFORMANCE OF SILICON-BASED ONE MICRODISCHARGE DEVICE HAS BEEN DEVELOPED AND OPERATED IN NE GAS [104]. THE D BE USED AS UV SOURCE IN BIOMOLECULE ASSAY OPERATIONS WHERE THE TARGET M FLUORESCED IN THE UV LIGHT. LTCC STRUCTURE CAN BE USED AS A FOCUSING ELECT FIELD EMITTER ARRAYS [105]. LTCC MATERIALS ARE APPLIED FOR FIBER OPTIC AND EL PACKAGES [106]. SILICON MEMS PACKAGING IS ANOTHER VERY WIDE FIELD OF L APPLICATION [107]. ANOTHER INTERESTING APPLICATION OF LTCC IS THREE-DIMENSION USED FOR EXAMPLE IN SPHERICAL STEPPER MOTOR [108] OR RADAR SENSOR.

1.9 COMPOSITES

1.9.1 INTRODUCTION

THE TREND FOR MICROELECTRONIC DEVICES HAS BEEN, AND WILL AS HISTORICALLY CONTINUE TO BE, TOWARDS SMALLER FEATURE SIZE, FASTER SPEEDS, MORE COMPLEXITY, HIGHER POW COST. THE MOTIVATING FORCE BEHIND THESE ADVANCES TRADITIONALLY HAS BEEN MI WITH THE TREMENDOUS GROWTH OF WIRELESS TELECOMMUNICATION, RF APPLICA BEGINNING TO DRIVE MANY AREAS OF MICROELECTRONICS TRADITIONALLY LED BY THE THE MICROPROCESSOR. AN INCREASINGLY DOMINANT FACTOR IN RF MICROELECTRONIC PACKAGING AND THE MATERIALS NEEDED TO CREATE THE PACKAGE, BECAUSE TH MATERIALS STRONGLY AFFECT THE PERFORMANCE OF THE RF ELECTRONICS. THE CONT

IN ELECTRONIC PACKAGING DENSITY HAS BEEN INCREASING. THESE TRENDS REQUIRE MATERIALS WITH HIGH THERMAL CONDUCTIVITIES. IN ADDITION, TO MINIMIZE THERMAL STRESSES THAT CAN CAUSE C SOLDER FAILURE, PACKAGING MATERIALS MUST HAVE COEFFICIENT OF THERMAL EXPA WITH THOSE OF CERAMIC SUBSTRATES AND SEMICONDUCTORS. FURTHER, LOW DENSITY MANY APPLICATIONS, INCLUDING PORTABLE SYSTEMS SUCH AS LAP-TOP COMPUTERS TELEPHONES AND AVIONICS. REDUCING WEIGHT ALSO MINIMIZES POTENTIALLY DAMAG RESULTING FROM SHOCK LOADS THAT CAN OCCUR DURING SHIPPING AND FROM OTHE COST IS ALSO A KEY CONSIDERATION. AS TRADITIONAL MATERIALS USED IN ELECTRONI NOT MEET ALL OF THESE REQUIREMENTS, NEW COMPOSITE MATERIALS HAVE BEEN AND A TO BE DEVELOPED.

THE TERM ‘COMPOSITES’ DESCRIBES A MIXTURE OF TWO OR MORE MATERIALS, EACH BEING PRESENT IN SIGNIFICANT QUANTITIES AND EACH IMPARTING A UNIQUE PROPERTY TO TH USE AND POTENTIAL FOR COMPOSITES IN ELECTRONIC PACKAGING IS VERY BROAD. BY C OR MORE CONSTITUENTS, IT IS POSSIBLE TO CREATE MATERIALS WITH UNIQUE COM PROPERTIES THAT CANNOT BE ACHIEVED IN ANOTHER WAY. THE BEST EXAMPLE IS PR BOARDS (PCBS), FOR WHICH DIELECTRIC PROPERTIES AND THE CTE ARE CRITICAL. POLY COMPOSITES IN THE FORM OF E-GLASS FIBER-REINFORCED POLYMER PCBS ARE WELL PACKAGING MATERIALS. SIMILARLY, A VARIETY OF PARTICLES ARE ADDED TO POLYMER CTE AND INCREASE THE THERMAL CONDUCTIVITY, OR BOTH. THESE MATERIALS ARE US TO AS PARTICLE-REINFORCED POLYMER-MATRIX COMPOSITES.

1.9.2 POLYMER-CERAMIC COMPOSITES

THE IMPORTANCE OF POLYMERS IN ELECTRONICS APPLICATION SUCH AS THE FACT THAT, THOUGH THEY ARE NOT INTRINSICALLY FUNCTIONAL, THEY CAN BE DOPED AND MADE FUNCTION OR PLIABLE NATURE ENABLES FLEXIBLE FREE-STANDING SUBSTRATES IN A VARIETY OF UNTIL NOW, THE NEEDS OF SUBSTRATE MATERIALS WERE COVERED BY SOFT THERMOPL POLYTETRAFLUOROETHYLENE (PTFE) OR CERAMIC SUBSTRATES, BUT NEITHER SATIS REQUIRED DIELECTRIC AND MECHANICAL CHARACTERISTICS. THE PRESENCE OF TE FORMULATION OF SUCH POLYMERIC SUBSTRATES MAKES THE METALLIZATION PROCE MANUFACTURE OF LARGE SIZED BOARDS DIFFICULT. IN ADDITION, THERE IS A POLYMER

ROOM TEMPERATURE, SO THE VARIATION OF PERMITTIVITY WITH TEMPERATURE IS NOT LINEAR. RECENTLY, THERE HAS BEEN A HUGE INTEREST IN POLYMER CERAMIC COMPOS THEY ENABLE INEXPENSIVE INDUSTRIAL LEVEL REALIZATION OF 3-D MICROWAVE D PACKAGES WITH ADVANCED ELECTRIC AND MECHANICAL PROPERTIES. PARTICULARI USING THERMOPLASTIC POLYMERS SUCH AS PTFE, POLYETHYLENE, POLYSTYRENE, SILI ETC HAVE DRAWN MUCH INDUSTRIAL AND ACADEMIC INTEREST BECAUSE THEY HAVE ADVANTAGE OF A SIMPLE, 3-D FABRICATION PROCESS SUCH AS INJECTION MOULDING O COMPONENTS.

THE ALMOST LIMITLESS POSSIBILITIES TO COMBINE TWO OR MORE MATERIALS AT OR NANOSCOPIC LEVEL LEAD TO A LARGE RANGE OF PROPERTIES. POLYMER – CERAMI CONSISTING OF CERAMIC PARTICLES FILLED IN A POLYMER MATRIX ARE NOW WIDELY ELECTRONIC INDUSTRY AS SUBSTRATES FOR HIGH FREQUENCY USES, SINCE THEY ELECTRICAL PROPERTIES OF CERAMICS AND THE MECHANICAL FLEXIBILITY, CHEMICA PROCESSING POSSIBILITY OF POLYMERS [109]. THE PRESENCE OF FILLER IN A SEMICR POLYMER CAN CAUSE MANY CHANGES TO THE PHYSICAL PROPERTIES OF THE POLYM REPORTS ARE AVAILABLE WHICH INVESTIGATES THE USE OF SILICA FILLED POLYMER C PACKAGING APPLICATIONS. HOWEVER, BECAUSE OF THE LOW THERMAL CONDUCTIVITY O RESEARCHERS ARE EXTENDING THEIR WORK TO DEVELOP NEW FILLERS WITH HIGH ELECTRICAL PERFORMANCE [110]. THERE ARE MANY POSSIBLE CANDIDATES FOR CER HAVING BOTH HIGH THERMAL CONDUCTIVITY AND HIGH ELECTRICAL RESISTIVITY SUC BERYLLIA, BORON NITRIDE, ALUMINUM NITRIDE ETC. THE THERMAL PROPERTIES OF THE BE IMPROVED WITH A SUFFICIENTLY HIGH (> 40%) VOLUME PERCENTAGE OF FILLE HOWEVER, HIGHER FILLER CONTENT RESULTS IN LOW STRENGTH, POOR FLUIDITY, POOR DEFECTS IN THE COMPOSITE AND HAVE ADVERSE EFFECT ON THE DIELECTRIC PROPERT THE PROPER DESIGN OF THESE COMPOSITES, WE CAN UTILIZE THE EASE OF PROCESSIN RELATIVE PERMITTIVITY OF POLYMERS AND HIGH THERMAL CONDUCTIVITY, LOW THER COEFFICIENT AND THERMAL STABILITY OF CERAMICS.

1.9.3 CONNECTIVITY

MAKING CERAMIC POLYMER COMPOSITES NOT ONLY INVOLVES MIXING OF THE MATERIAL BUT ALSO COUPLING THEM WITH BEST POSSIBLE DESIGN. THE CONCEPT OF CONNECTIVITY ESTABLISHED BY NEWNHAM [112]. CONNECTIVITY IS A KEY FEATURE IN THE DEVELOPMENT OF MULTI PHASE SOLIDS SINCE THE PHYSICAL PROPERTIES CAN BE CHANGED IN DIFFERENT MAGNITUDE DEPENDING ON HOW CONNECTIONS ARE MADE [113]. THE INTERSPATIAL RELATION A MULTIPHASE MATERIAL HAS MAXIMUM IMPORTANCE BECAUSE IT CONTROLS THE ELECTRICAL, MAGNETIC AND THERMAL FLUXES BETWEEN THE PHASES. IN A COMPOSITE MAY BE SELF-CONNECTED IN EITHER ONE, TWO OR THREE DIMENSIONS. IN A TWO PHASE THERE ARE 10 DIFFERENT COMBINATIONS OF CONNECTIVITY AND THEY ARE 0-0, 0-1, 0-2, 0-3, 1-1, 2-2, 1-3, 2-2, 2-3 AND 3-3 CONNECTIVITY. THESE CONNECTIVITY PATTERNS ARE ILLUSTRATED IN 1.11 USING CUBE AS BUILDING BLOCK. THE MOST COMMONLY STUDIED COMPOSITES ARE 0-3 CONFIGURATIONS. 0-3 CONFIGURATION CAN BE EASILY PREPARED AT RELATIVELY LOW

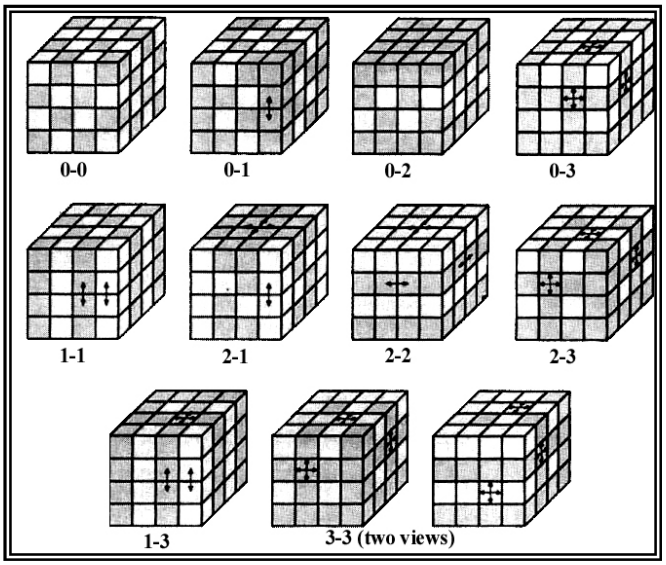

Fig. 1.11 Connectivity patterns in a di-phasic composites systems [112].

1.9.4 MATERIAL REQUIREMENTS FOR ELECTRONIC PACKAGING AND SUBSTRATE APPLICATIONS

THE SELECTION OF A PROPER RF SUBSTRATE IS DRIVEN BY THE MATERIAL CHARACTERISTICS, PARTICULARLY ITS DIELECTRIC PROPERTIES, SINCE THEY SHOULD MA THE OTHER COMPONENTS. IN COMMERCIALLY HIGH-FREQUENCY SUBSTRATES, BASED COMPOSITES OF CERAMIC OR WOVEN QUARTZ FILLERS AND HYDROCARBON RESINS MICROFIBERS MATRICES, IT IS DIFFICULT TO FIND TEMPERATURE-COMPENSATING MA PERMITTIVITIES AROUND 10 AND LOW DIELECTRIC LOSSES [115].

1.9.4.1 DIELECTRIC PROPERTIES

DIELECTRIC PROPERTIES OF PACKAGING MATERIALS SIGNIFICANTLY INFLUENCE THE PERFORMANCE OF HIGH SPEED MICROELECTRONIC DEVICES. ELECTRICAL CHARAC MICROELECTRONIC DEVICES, SUCH AS SIGNAL ATTENUATION, PROPAGATION VELOCITY ARE INFLUENCED BY THE DIELECTRIC PROPERTIES OF THE PACKAGE SUBSTRATE AND MATERIAL. THE ELECTRICAL PROPERTIES IN MATERIAL SELECTION INCLUDE RELATIVE P TANGENT, FREQUENCY AND TEMPERATURE STABILITY OF DIELECTRIC PROPERTIES, DIE AND ELECTRICAL RESISTIVITY. AN IMPORTANT ROLE OF PACKAGING MATERIALS IS T ELECTRICAL INSULATION OF THE SILICON CHIP AND OF CIRCUIT PINS. IDEALLY, A LOW C NEEDED TO AVOID CURRENT LEAKAGE, A LOW RELATIVE PERMITTIVITY TO MINIMIZE T COUPLING EFFECTS AND REDUCE SIGNAL DELAY AND A LOW LOSS FACTOR TO REDUCE [116]. THE TEMPERATURE COEFFICIENT OF THE RELATIVE PERMITTIVITY OF MICROWAVE S VERY IMPORTANT IN MANY OUTDOOR WIRELESS APPLICATIONS FOR THE REDUCTION TEMPERATURE-INDUCED DRIFT IN CIRCUIT OPERATING CHARACTERISTICS [117]. HIG RESISTIVITY AND DIELECTRIC STRENGTH ARE ALSO REQUIRED FOR MICROELECTRONIC AI

1.9.4.2 THERMAL AND THERMO-MECHANICAL PROPERTIES

AN ELECTRONIC MATERIAL EXPERIENCES A WIDE RANGE OF TEMPERATURES, TEMPERATURE GRADIENTS, RATES OF TEMPERATURE CHANGE, TEMPERATURE CYCLE SHOCKS THROUGH MANUFACTURING, STORAGE AND OPERATION. THERMAL PROPER

SIGNIFICANT IN ENDURING SUCH LIFE CYCLE PROBLEMS. THERMAL CONDUCTIVITY/DIFFUSIVITY, SPECIFIC HEAT CAPACITY AND COEFFICIENT OF THERMAL EXPANSION.

1.9.4.3 MECHANICAL PROPERTIES

THE MECHANICAL PROPERTIES AFFECT THE LIFETIME OF THE MATERIAL AS IT IS SUBJECTED TO VIBRATIONS, SHOCK AND THERMOMECHANICAL STRESSES DURING MANUFACTURE, ASS AND OPERATION. KEY PROPERTIES THAT ARE OF IMPORTANCE FOR ELECTRONIC PACKAGI INCLUDE THE MODULUS OF ELASTICITY, TENSILE STRENGTH, POISSON'S RATIO, FLEXU FRACTURE TOUGHNESS, CREEP RESISTANCE AND FATIGUE STRENGTH.

1.9.4.4 CHEMICAL PROPERTIES

CHEMICAL PROPERTIES OF THE SUBSTRATE MATERIAL BECAUSE OF THE NEED TO SURVIVE MANUFACTURING, STORAGE, HANDLING AND OPERATING ENVIRONMENTS. PROPERTIES OF SIGNIFICANCE ARE WATER ABSORPTION, FLAMMABILITY AND CORROS THE ELECTRICAL PROPERTIES OF ELECTRONIC MATERIALS OFTEN CHANGE AS A RE ABSORPTION, SWELLING AND OTHER DIMENSIONAL INSTABILITIES. THE CORROSION I FORMATION OF MORE STABLE COMPOUNDS AND CAN DEGRADE THE PHYSICAL PROPE MATERIALS.

THE KEY PROPERTIES OF THE COMPOSITE MATERIAL VIZ. THE RELATIVE PERMITTIV CONDUCTIVITY AND COEFFICIENT OF THERMAL EXPANSION ARE DEPENDENT ON VARIOU AS THE NUMBER OF COMPONENTS OR PHASES, VOLUME FRACTION OF THE FILLER, TH PROPERTIES OF THE PHASES, PREPARATION METHOD AND THE INTERACTION BETWEEN TH MATRIX. HOWEVER, A LIMITATION FOR CERAMIC LOADING EXISTS FOR POLYMER-CERAM WHICH IS ONE OF THE BIGGEST CONSTRAINTS TO IMPROVE ITS THERMAL, MECHANICAL PROPERTIES. BASED ON THE PRESENT TECHNOLOGY, A CERAMIC LOADING OF ABOVE 80% IMPRACTICABLE. HENCE BY THE PROPER DESIGN OF THESE COMPOSITES, WE CAN UTILIZE PROCESSING AND LOW RELATIVE PERMITTIVITY OF POLYMERS AND HIGH THERMAL CON THERMAL EXPANSION COEFFICIENT AND THERMAL STABILITY OF CERAMICS. VARIOUS AND DISTRIBUTIONS CAN OFFER DIFFERENT SURFACE ENERGIES THAT MAY FACILITATE THE POLYMER CHAINS [60, 119]. THE COUPLING AGENTS PROMOTE A CHANGE OF INT

PROPERTIES OF THE FILLER PARTICLES, GIVING RISE TO BETTER WETTING BETWEEN THE FILLER AND THE POLYMER BINDER AND ULTIMATELY TO THE INCREASED PHYSICAL STRENGTH OF THE C 121].

1.9.5 ADVANTAGES OF POLYMER/CERAMIC COMPOSITES

COMPOSITE MATERIALS ARE TRADITIONALLY USED AS STRUCTURAL MATERIALS. YET, WITH THE RAPID GROWTH OF THE ELECTRONICS INDUSTRY, COMPOSITE MATERIALS ARE AND MORE ELECTRONIC APPLICATIONS. THE DESIGN CRITERIA FOR THESE GROUP OF CO DIFFERENT BECAUSE OF THE VAST DIFFERENCE IN PROPERTY REQUIREMENTS BETWE COMPOSITES AND ELECTRONIC COMPOSITES. WHILE STRUCTURAL COMPOSITES EMPH STRENGTH AND HIGH MODULUS, ELECTRONIC COMPOSITES EMPHASIZE HIGH THERMAL LOW THERMAL EXPANSION, LOW RELATIVE PERMITTIVITY, HIGH/LOW ELECTRICAL COND ELECTROMAGNETIC INTERFERENCE (EMI) SHIELDING EFFECTIVENESS, DEPENDING ON TH ELECTRONIC APPLICATION. THE APPLICATIONS OF POLYMER-CERAMIC COMPO MICROELECTRONICS INCLUDE INTERCONNECTIONS, PRINTED CIRCUIT BOARDS, ENCAPSULATIONS, INTERLAYER DIELECTRICS, DIE ATTACH, ELECTRICAL CONTACTS, CO INTERFACE MATERIALS, HEAT SINKS, LIDS AND HOUSINGS. THE APPLICATIONS OF PR BOARDS CAN BE DIVIDED INTO TWO AREAS: INFORMATION TECHNOLOGY AND COM INDUSTRIES. BOTH APPLICATIONS HAVE IDENTICAL TECHNICAL DEMANDS FOR THE FUTU HIGH-FREQUENCY APPLIANCES. AS THE WORKING FREQUENCY OF ELECTRONIC APPLIAN SIGNAL INTENSITY LOSSES BECOME MORE SENSITIVE. CIRCUIT SUBSTRATES WITH PO PROPERTIES WILL MAINTAIN AN UNFAVOURABLE SIGNAL CONVEYING EFFICIENCY. THER IS HIGH IN HIGH FREQUENCY APPLIANCE MARKETS FOR SMALL RELATIVE PERMITTIV DISSIPATION ENERGY SUBSTRATES. POLYMER-CERAMIC COMPOSITES ALSO OFFER EXCE CHARACTERISTICS INCLUDING LOW TEMPERATURE PROCESSABILITY, FLEXIBILITY, HI RESISTANCE, OUTSTANDING SOLVENT RESISTANCE ETC.

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CHAPTER 2

SYNTHESIS AND CHARACTERISATION

This chapter emphasizes the various steps involved in the synthesis of dielectric ceramics and its composites. A brief description of the instrumentation techniques used for studying the structural, microstructural, microwave dielectric properties and thermal characteristics of low loss materials is also presented.

2.1 CERAMIC PROCESSING

2.1.1 INTRODUCTION

REMARKABLE PROGRESS IN SYNTHETIC CHEMISTRY AND RELATED FIELDS HAS LI
ADVANCES IN MATERIAL SCIENCE. DURING THE PAST 100 YEARS SCIENTISTS AND ENG
ACQUIRED A MUCH BETTER UNDERSTANDING OF CERAMIC MATERIALS AND THEIR PROC
FOUND THAT NATURALLY OCCURRING MINERALS COULD BE REFINED OR NEW COMPOSIT
TO ACHIEVE UNIQUE PROPERTIES. HIGHLY HOMOGENEOUS AND STABLE INDUSTRIAL
EXISTING IN NATURE HAVE BEEN COMMERCIALLY PRODUCED BY THE USE OF ARTIFICIA
STARTING MATERIALS. THE CREATION OF THESE ARTIFICIAL MATERIALS REQUIRED TH
CERAMIC PROCESSING FROM A TECHNOLOGY TO A SCIENCE. THIS DEVELOPMENT HAS S
BASIS OF SO-CALLED ‘FINE OR ADVANCED CERAMICS’. FINE CERAMICS INCLUDES INORGA
METALLIC SOLID MATERIALS OF POLYCRYSTALLINE SINTERED BODIES, FINE POWDERS,
NONCRYSTALLINE MATERIALS, THICK OR THIN FILMS AND FIBERS WITH VARIOUS MOR
FUNCTIONS OF THESE MATERIALS DEPEND ON THEIR MORPHOLOGY, OVER WHICH CON
GAINED THROUGH ADVANCES IN PRODUCTION PROCESSES. CERAMIC FABRICATION IS TH
OF VARIOUS PROCESS TECHNOLOGIES TO PRODUCE MONOLITHIC OR COMPOSITE CERAM
WITHIN A GIVEN SHAPE, SIZE AND MICROSTRUCTURE PROPERTY BOUNDS FOR A GIVEN
[1]. THE CERAMICS ARE IN GENERAL COMPOUNDS OF THE ELECTROPOSITIVE AND ELE
ELEMENTS OF THE PERIODIC TABLE. THEY ARE POLYCRYSTALLINE MATERIALS, WHIC
CRYSTALLINE GRAINS, GRAIN BOUNDARIES, IMPURITIES SEGREGATED IN THE GRAIN BOU
AS THE GRAINS, PORES IN THE GRAINS, GRAIN BOUNDARIES AND IMPERFECTIONS.

MOST OF THE SYNTHESIS METHODS OF ORGANIC AND METALLIC MATERIALS ARE GENERALLY
NOT SUITABLE FOR CERAMICS, DUE TO THE BRITTLENESS AND THE REFRACTORY NA
MATERIALS. THE PROCESSING OF CERAMICS INTO USEFUL PRODUCTS REQUIRES THE TRA
POWDERED RAW MATERIALS TO A DENSE, UNIFORM BODY THROUGH THE APPL
CONSOLIDATION TECHNIQUES AND SUBSEQUENT THERMAL PROCESSING OR SINTERING.
OF GLASS TECHNOLOGY, CERAMIC FORMING TECHNIQUES ARE GENERALLY BASED
PROCESSING WITH POWDER SYNTHESIS, FORMING AND SINTERING. THE SYNTHESIS
POWDERS AND BETTER CONTROL OF CHEMICAL AND PHYSICAL CHARACTERISTICS OF C

ALLOW OBTAINING IMPROVED AND/OR REPRODUCIBLE PROPERTIES. SEVERAL METHO
USED FOR THE PREPARATION OF CERAMIC POWDERS. THE METHODS CAN BE DIVIDED
CATEGORIES: (A) MECHANICAL METHODS AND (B) SOLID STATE REACTION METHODS AN
METHODS. IN THE MECHANICAL METHODS, SMALL PARTICLES ARE PRODUCED FROM L
MECHANICAL FORCES, A PROCESS REFERRED TO AS COMMINUTION. THE PROCESS OF C
INVOLVES OPERATIONS SUCH AS CRUSHING, GRINDING AND MILLING. POWDERS OF
CERAMICS ARE GENERALLY PREPARED BY MECHANICAL METHODS FROM NATURALLY
MATERIALS.

2.1.2 SOLID STATE SYNTHESIS OF CERAMICS

THE SOLID STATE OXIDE ROUTE IS CONSIDERED TO BE ONE OF THE OLDEST A
MATERIALS SYNTHESIZING TECHNIQUES FOR THE SYNTHESIS OF COMPLEX OXIDE MA
OXIDES CONTAINING MORE THAN ONE TYPE OF CATION ARE OF INTEREST FROM BOTH AC
COMMERCIAL POINT OF VIEW. THIS IS BECAUSE COMPLEX METAL OXIDES EXHIBIT A M
FEATURES THAT ARE NOT FOUND IN SIMPLE OXIDES. FOR EXAMPLE, MIXED METAL
STABILIZE BOTH HIGH AND MIXED VOLUME STATES OF TRANSITION METAL ELEMENTS [3

THE CONVENTIONAL CERAMIC APPROACH INVOLVES BASICALLY THREE STEPS (
MIXING OF THE STOICHIOMETRIC OXIDES, (B) HIGH TEMPERATURE FIRING AND (C) IN
GRINDING.

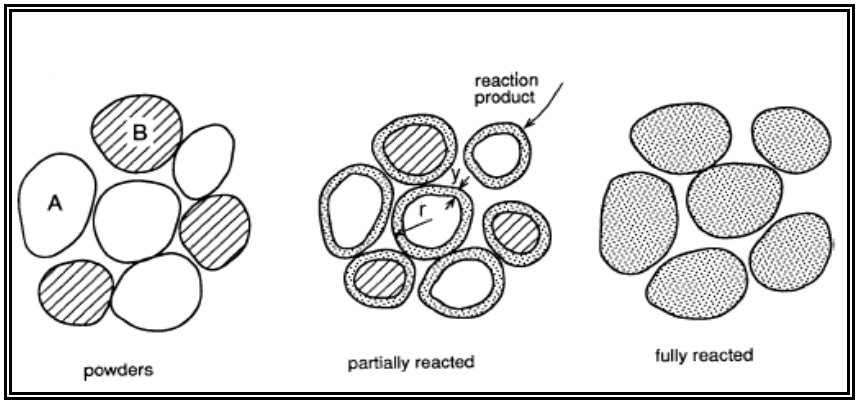

Fig. 2. 1 Reaction between two kinds of particles to form a product at the points of contact.

ON HEATING AT HIGH TEMPERATURES, A NEW MATERIAL IS FORMED (SEE FIG. 2.1) T
THE FREE ENERGY, AT THE POINTS OF CONTACT THROUGH SOLID STATE DIFFUSION. TH
LAYER (OF A FEW Å) EVENTUALLY ACTS AS A POTENTIAL BARRIER BETWEEN TWO GRAINS
IMPEDING FURTHER GRAIN TO GRAIN MATERIAL TRANSPORT. THIS DEMANDS THE NEED
OF CONTACT TO BE INTRODUCED WHICH IS USUALLY ACHIEVED THROUGH GRINDING O
THIS FREQUENT GRINDING COUPLED WITH MULTIPLE CALCINATION MAXIMIZES THE
REACTANT RATIO.

THE REACTANT PARTICLES ARE SCHEMATICALLY ILLUSTRATED TO EMPHASIZE T
MATTER WHAT THE PARTICLE SIZE IS, EACH REACTANT PARTICLE CONTAINS ONLY ONE
THE SEVERE REACTION CONDITIONS ARE NECESSARY TO OBTAIN SINGLE PHASE PRODU
THE DIFFUSIONAL LIMITATIONS OF THE SOLID STATE REACTIONS. INITIAL REACTION IS
REACTION GOES SLOWER AND SLOWER AS THE PRODUCT LAYER BUILDS UP AND THE
BECOME LONGER. A FINE POWDER OF APPROXIMATELY 10,000 Å (OR 1 MICRON) PARTICLE SIZE STILL
REPRESENTS DIFFUSION DISTANCES OF THE ORDER OF 10,000 UNIT CELL DIMENSIONS [4].
SOLUTION SYNTHESIS IMPROVES THE REACTIVITY OF THE COMPONENT OXIDES OR SALT
METHODS CAN GIVE INITIAL CRYSTALLITES OF THE ORDER OF 10 TO 50 Å OR A FEW HUNDRE
THIS MEANS THAT DIFFUSION MUST OCCUR ACROSS 10 TO 50 UNIT CELL DIMENSIONS I
SYNTHESIS TECHNIQUES. COST EFFECTIVENESS AND SIMPLICITY OF SYNTHESIS ARE
ADVANTAGES OF THE SOLID STATE REACTION METHOD. THE MAIN DISADVANTAGE OF SOLID STATE
SYNTHESIS IS OBVIOUSLY THE HIGH TEMPERATURE NEEDED TO FORM THE PRODUCT W
AGGLOMERATED PARTICLES WITH POOR SURFACE AREA [5].

THE SOLID-STATE REACTION METHOD, WHICH IS EMPLOYED IN THE PRESENT WOR
THE FOLLOWING STEPS:

2.1.2.1 SELECTION AND WEIGHING OF RAW MATERIALS

TO SELECT A CERAMIC RAW MATERIAL, IT IS NECESSARY TO KNOW THE FINA
PROPERTIES DEMANDED OF THE CERAMIC PRODUCT. IN ORDER TO PREVENT SEGREG
CERAMICS GREEN BODY, RAW MATERIALS WITH SIMILAR PARTICLE MORPHOLOG
DISTRIBUTIONS SHOULD BE USED. THE NEXT STEP IN THE SOLID-STATE REACTION METH
THE DIFFERENT POWDERS WHICH ACT AS REACTANTS, ACCORDING TO THE STOICH

PRESENCE OF IMPURITIES IN THE RAW MATERIALS CAN AFFECT REACTIVITY AS WEL
PROPERTIES OF THE FIRED CERAMICS. THE RAW MATERIAL PURITY OF GREATER TH
ESSENTIAL FOR OBTAINING PHASE PURE COMPOUNDS. ELECTRONIC BALANCE IS USE
ACCURACY UP TO FOUR DECIMAL PLACES.

2.1.2.2 STOICHIOMETRIC MIXING

THE RAW MATERIALS NEED TO BE INTIMATELY MIXED TO INCREASE THE POINTS
BETWEEN REACTANT OXIDES, WHICH IN TURN ACT AS 'PRODUCT LAYER FORMATION
MIXING AND MILLING ELIMINATES AGGLOMERATES AND REDUCES PARTICLE SIZE. IF AG
PRESENT THEY DENSIFY MORE RAPIDLY RESULTING IN PORES. DURING THE MIXIN
AGGLOMERATES ARE BROKEN AND DEFECTS ARE INTRODUCED INTO THE GRAINS THAT I
MECHANISM. THEREFORE THE MIXTURE OF POWDERS IS GROUND WELL AND THOROU
USING DISTILLED WATER OR ACETONE. BALL MILLS ARE USED FOR THE MIXING PURPOSE
INVESTIGATION, THE MIXTURE OF CONSTITUENT POWDERS TAKEN IN POLYTHENE BOT
MILLED FOR SUFFICIENT DURATION IN DISTILLED WATER MEDIUM USING YTTRIA STAB
(YSZ) BALLS. IN THE MILLING PROCESS, THE PARTICLES EXPERIENCE MECHANICAL STR
CONTACT POINTS DUE TO COMPRESSION, IMPACT OR SHEAR WITH THE MILLING MEDIUM
PARTICLES [6]. THE MECHANICAL STRESS LEADS TO ELASTIC AND INELASTIC DEFORM
STRESSES EXCEED ULTIMATE STRENGTH OF THE PARTICLE, IT WILL FRACTURE THE
MECHANICAL ENERGY SUPPLIED TO THE PARTICLE IS USED NOT ONLY TO CREATE NEW S
TO PRODUCE OTHER PHYSICAL CHANGES IN THE PARTICLE [7]. THE RATE OF MILLING IS D
THE RELATIVE SIZE, SPECIFIC GRAVITY AND HARDNESS OF THE MEDIA AND PARTICLES
THE MILLING MEDIA (BALLS) IS AN IMPORTANT FACTOR IN BALL MILLING AS IT DETERMI
SIZE DISTRIBUTION. USING SPHERICAL BALL THE SIZE DISTRIBUTION IS BROAD SINCE T
ONLY ONE POINT OF CONTACT BETWEEN THEM. ON THE OTHER HAND USING CYLINDRI
'DOME ENDS' THE PARTICLE SIZE DISTRIBUTION IS MORE UNIFORM WITH NARROW DISTR
[8]. THIS IS DUE TO THE FACT THAT CYLINDRICAL BALLS OFFER A LINE OF CONTACT BETW

2.1.2.3 CALCINATION

CALCINATION IS THE INTERMEDIATE HEAT TREATMENT AT A LOWER TEMPERA SINTERING. CALCINATION PROCESSES ARE ENDOTHERMIC DECOMPOSITION REACTIONS OXYSALT, SUCH AS A CARBONATE OR HYDROXIDE, DECOMPOSES, LEAVING AN OXID PRODUCT AND LIBERATING A GAS. THE KINETICS OF SOLID STATE REACTIONS OCC CALCINATION MAY BE CONTROLLED BY ANY ONE OF THE THREE PROCESSES: (I) THE R INTERFACE BETWEEN THE REACTANT AND THE SOLID PRODUCT, (II) HEAT TRANSFER SURFACE OR (III) GAS DIFFUSION OR PERMEATION FROM THE REACTION SURFACE THRO PRODUCT LAYER. THE CALCINATION CONDITIONS SUCH AS TEMPERATURE, DURATION ATMOSPHERE ARE IMPORTANT FACTORS CONTROLLING SHRINKAGE DURING SINTERING. PHASES OF INTEREST MAY NOT BE COMPLETELY FORMED, THE CALCINATION YIELDS PRODUCT.

2.1.2.4 GRINDING

THE CALCINED POWDERS ARE INVARIABLY AGGLOMERATED WHICH NEED TO BE FINE POWDER. GRINDING CAN BE ACCOMPLISHED BY ANY SUITABLE MEANS. IT PREPARES MATERIAL FOR CERAMIC FORMING. THE GRINDING ALSO HELPS TO HOMOGENISE THE C VARIATIONS THAT MAY STILL EXIST OR THAT MAY ARISE DURING CALCINATION. GEN DOWN TO SOMEWHERE AROUND 1 TO 10 μM IS ADVISABLE. IF THE GRIND IS COARSER THE CERAM CAN HAVE LARGER INTERGRANULAR VOIDS AND LOWER FIRED DENSITY. IF GRINDING COLLOIDAL PROPERTIES MAY INTERFERE WITH SUBSEQUENT FORMING OPERATIONS [9]. GRINDING PURPOSE BALL MILL OR MORTAR WITH PESTLE IS USED. THE MILLING P DRAMATICALLY IMPROVE THE QUALITY OF THE POWDER, IMPROVING THE BULK AND AND ENHANCING SINTERING. IN LARGE SCALE OPERATION A GRINDING MEDIUM IS CHOS VERY LITTLE WEAR.

2.1.2.5 ADDITION OF POLYMERIC BINDER

THE PRINCIPAL FUNCTIONS OF A CERAMIC BINDER ARE TO IMPART SUFFICIENT S APPROPRIATE ELASTIC PROPERTIES FOR HANDLING AND SHAPING DURING THE POST F THEY COAT THE CERAMIC PARTICLES AND PROVIDE LUBRICATION DURING PRESSING AN

BOND AFTER PRESSING. THE SELECTION OF BINDER AND OTHER ADDITIVES MUST BE CO
THE CHEMISTRY OF THE CERAMIC AND THE PURITY REQUIREMENTS OF THE APPLICATI
CERAMICS TECHNOLOGY, IN DIE PRESSING, A NARROW RANGE OF WATER-SOLUBLE OR
SUCH AS POLY VINYL ALCOHOL IS MOST OFTEN APPLIED TO IMPROVE THE RHEOLOGICA
THE POWDER COMPACT [10]. THE POLYMERIC DISPERSIONS AND ORGANIC BINDERS PR
PRESSED CERAMIC POWDERS WITH OPTIMAL PROPERTIES FROM THE POINT OF VIEW OF
ABILITIES AND MECHANICAL STRENGTH OF THE PRESSED SAMPLES [11]. THE COMMO
POLYMERS FOR CERAMIC BINDING PURPOSE ARE POLY VINYL ALCOHOL (PVA), POLY ETH
(PEG), CARBOXYMETHYL CELLULOSE ETC. MOST OF WHICH ARE WATER THINNABLE
DISPERSIONS. THE AMOUNT OF ORGANIC BINDER REQUIRED FOR PRESSING IS QUITE LO
RANGING FROM 0.5 TO 5 WT%. THE BINDER CONCENTRATION FOR EACH PROCESS IS ABOU
PROCESS, 3-17 % IN WET PROCESSING AND 7-20 % IN PLASTIC FORMING [12]. THE RE
RESEARCH TRENDS SUGGEST THAT THE PVA AND PEG ARE IDEAL BINDER ADDITIVES FOR
MICROWAVE DIELECTRIC CERAMICS [13].

THE BINDER MUST BE REMOVED PRIOR TO DENSIFICATION OR ELSE CARBON OR CARBIDE
BINDERS CAN BE REMOVED BY THERMAL DECOMPOSITION. FOR EXAMPLE, PVA BURN
HEATING ABOVE 400 °C. IF REACTION BETWEEN THE BINDER AND THE CERAMIC OCCURS BEL
BINDER DECOMPOSITION TEMPERATURE OR IF THE CERAMIC DENSIFIES BELOW THIS TEM
FINAL PART WILL BE CONTAMINATED OR MAY EVEN BE CRACKED OR BLOATED. IF THE
RAISED TOO RAPIDLY OR IF THE ATMOSPHERE IN THE FURNACE IS REDUCING, THE BIN
RATHER THAN DECOMPOSE, LEAVING CARBON.

2.1.2.6 POWDER COMPACTION (UNIAXIAL PRESSING)

MOST CERAMIC-FORMING PROCESSES START WITH A POWDER AND CONSIST OF CO
THE POWDER INTO A DESIRED SHAPE. THE MAIN OBJECTIVE IS USUALLY TO ACHIEVE
DEGREE OF PARTICLE PACKING AND A HIGH DEGREE OF HOMOGENEITY. A TYPICA
OPERATION HAS THREE BASIC STEPS: (I) FILLING THE MOULD OR DIE WITH POWDER (II)
THE POWDER TO A SPECIFIC SIZE AND SHAPE AND (III) EJECTING THE COMPACT FROM T
THE MOST COMMON AND WIDELY USED METHOD OF POWDER COMPACTION IS UNIAXIAL
INVOLVES THE COMPACTION OF POWDER INTO A RIGID DIE BY APPLYING PRESSURE IN A

DIRECTION THROUGH A RIGID PUNCH OR PISTON [15-16]. COMPACTION IS DONE SLOWLY T
THE ESCAPE OF THE ENTRAPPED AIR.

THE PRESSURE GRADIENT IN POWDER COMPACT AS A FUNCTION OF THE DISTANC
UPPER PUNCH IS GIVEN BY THE FORMULA

$$P_x = P_a \, \mathrm{EXP}\left[-4 \; K \frac{L}{D}\right] \qquad (2.1)$$

WHERE P_x IS THE COEFFICIENT OF FRICTION, P_a IS THE APPLIED PRESSURE, L IS THE LENGTH AND D IS
THE DIAMETER OF THE POWDER COMPACT. IT IS EVIDENT THAT THE PRESSURE DISTI
POWDER COMPACT IS MORE UNIFORM WHEN THE LENGTH TO DIAMETER RATIO IS SMALL
MICROWAVE DIELECTRIC MEASUREMENTS WE PREPARE SAMPLES WITH D/L RATIO = 2.0
THE PRESSURE DISTRIBUTION IS MORE OR LESS UNIFORM IN THE POWDER COMPACTS. PR
150 MPA IS IDEAL IN CERAMIC FORMING.

FRICTION BETWEEN THE POWDER AND DIE WALL DECREASES THE PRESSURE AV
COMPACTION WITH INCREASING DISTANCE FROM THE PRESSING PUNCH. SINCE COMPAC
DIRECTLY RELATED TO FORMING PRESSURE, A FORMING PRESSURE GRADIENT BECO
GRADIENT IN THE COMPACTION. EXPACTION IS INFLUENCED BY THE DIE MATERIAL AND ITS LUBRICANTS
NATURE OF THE POWDER AND THE ORGANIC ADDITIVES USED. INTERNAL LUBRICANTS
ACID DISSOLVED IN PROPANE 2-OL, CAN AID PROCESSING.

2.1.2.7 SINTERING

THE FIRING PROCESS OR SINTERING IS USUALLY THE FINAL STAGE IN CERAMIC MA
SINTERING REFERS TO THE DENSIFICATION OF A PARTICULATE CERAMIC COMPACT BY
PORES BETWEEN THE STARTING PARTICLES (ACCOMPANIED BY SHRINKAGE OF THE
COMBINED WITH GROWTH TOGETHER AND STRONG BONDING BETWEEN ADJACENT P
SUBJECTED TO HIGH TEMPERATURES [18]. IT INVOLVES HEAT TREATMENT OF POWDER
ELEVATED TEMPERATURES, WHERE DIFFUSIONAL MASS TRANSPORT IS APPRECIABLE WI
DENSE POLYCRYSTALLINE SOLID [19]. THE CRITERIA THAT SHOULD BE MET BEFORE SINTE
ARE (I) A MECHANISM FOR MATERIAL TRANSPORT MUST BE PRESENT (II) A SOURCE O
ACTIVATE AND SUSTAIN THIS MATERIAL TRANSPORT MUST BE PRESENT. THE PRIMARY M
TRANSPORT ARE DIFFUSION AND VISCOUS FLOW. HEAT IS THE PRIMARY SOURCE O

CONJUNCTION WITH ENERGY GRADIENTS DUE TO PARTICLE-PARTICLE CONTACT AND
THERMODYNAMICALLY, SINTERING IS AN IRREVERSIBLE PROCESS IN WHICH A FREE EN
IS BROUGHT ABOUT BY A DECREASE IN SURFACE AREA. THE PRINCIPAL GOAL OF SIN
REDUCTION OF COMPACT POROSITY. THE DEVELOPMENT OF MICROSTRUCTURE AND
DURING SINTERING IS A DIRECT CONSEQUENCE OF MASS TRANSPORT THROUGH SEVERA
AND ONE OF THESE PATHS IS USUALLY PREDOMINANT AT ANY GIVEN STAGE OF SINTER
ARE (I) EVAPORATION/CONDENSATION (II) SOLUTION/PRECIPITATION (III) LATTICE DIFFU
SURFACE DIFFUSION OR GRAIN BOUNDARY DIFFUSION. SEVERAL VARIABLES INFLUEN
SINTERING. SOME OF THEM ARE INITIAL DENSITY, MATERIAL, PARTICLE SIZE, SINTERIN
TEMPERATURE, TIME AND HEATING RATE. THE SINTERING PHENOMENA ARE OF TWO TYP
SINTERING, WHERE ALL DENSIFICATION IS ACHIEVED THROUGH CHANGES IN PARTICLE
PARTICLE REARRANGEMENT OR THE PRESENCE OF LIQUID AND LIQUID-PHASE SINTERIN
LIQUID THAT IS PRESENT AT SINTERING TEMPERATURES AIDS COMPACTION.

2.1.2.7.1 SOLID STATE SINTERING

SOLID-STATE SINTERING INVOLVES MATERIAL TRANSPORT BY VOLUME DIFFUSIO
MAY CONSIST OF MOVEMENT OF ATOMS OR VACANCIES ALONG A SURFACE OR GRAIN
THROUGH THE VOLUME OF THE MATERIAL. SURFACE DIFFUSION (VAPOUR –PHASE TRAN
RESULT IN SHRINKAGE WHEREAS, VOLUME DIFFUSION ALONG GRAIN BOUNDARIES OR
DISLOCATIONS RESULT IN SHRINKAGE [20]. THE DRIVING FORCE FOR SOLID-STATE SIN
DIFFERENCE IN FREE ENERGY OR CHEMICAL POTENTIAL BETWEEN THE FREE SURFACES
THE POINTS OF CONTACT BETWEEN ADJACENT PARTICLES. THE LINEAR SHRINKAGE C
CAUSED BY THE LATTICE DIFFUSION FROM LINE OF CONTACT BETWEEN TWO PARTICI
REGION CAN BE EXPRESSED AS:

$$\frac{\Delta L}{L_o} = \left(\frac{K\ a^3 D t}{k T d^n} \right)^m \qquad (2.2)$$

WHERE $\Delta L/L_O$ = LINEAR SHRINKAGE (EQUIVALENT TO THE STRAIN); γ = SURFACE ENERGY; A = ATOMIC VOLUME OF THE DIFFUSING VACANCY; D = SELF-DIFFUSION COEFFICIENT; K =

CONSTANT; T = TEMPERATURE; D = PARTICLE DIAMETER; T = TIME AND K = CONSTANT D
GEOMETRY. THE EXPONENT N IS CLOSE TO 3 AND M IS GENERALLY IN THE RANGE OF 0.3 T
FROM EQ. (2.2) IT CAN BE CLEARLY UNDERSTOOD THAT THE PARTICLE DIAMETER HAS A
ON THE RATE OF SINTERING. THE SMALLER THE PARTICLES, THE GREATER THE SINTE
PARTICLE SIZE POWDER CAN BE SINTERED MORE RAPIDLY AT A LOWER TEMPERATUR
POWDER. THE VARIOUS STAGES INVOLVED IN THE SINTERING PROCESS ARE AS FOLLOWS

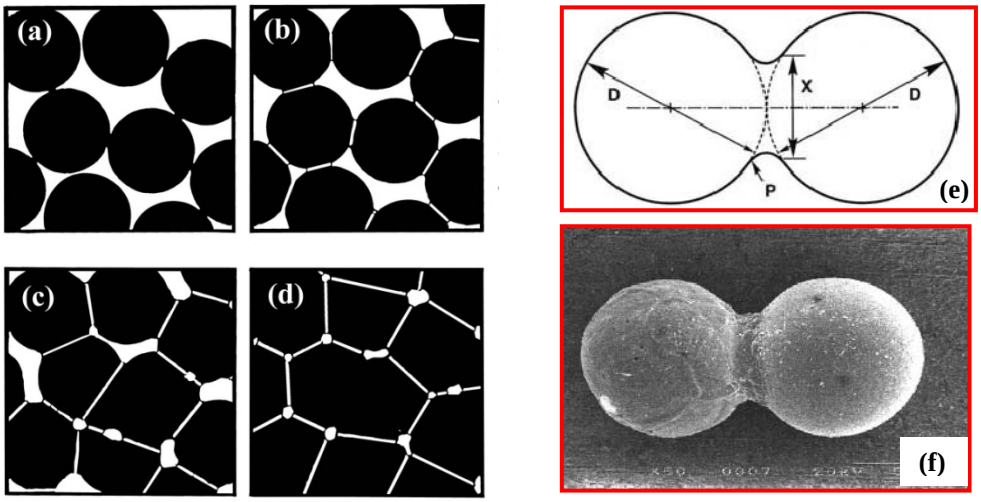

Fig. 2.2 (a) & (b) Initial stage, (c) Intermediate stage and (d) Final stage of sintering (e) Neck formation during first stage and (f) SEM picture of neck formation in sintered alumina.

(A) INITIAl STAGE 0F SINTERING:

IT INVOLVES REARRANGEMENT OF PARTICLES AND INITIAL NECK FORMATION AT TH
BETWEEN EACH PARTICLE. THE REARRANGEMENT CONSISTS OF SLIGHT MOVEMENT O
ADJACENT PARTICLES TO INCREASE THE NUMBER OF POINTS OF CONTACT. BONDING
POINTS OF CONTACT WHERE MATERIAL TRANSPORT CAN OCCUR AND WHERE SURFACE E
AFTER THE INITIAL STAGE, THE DENSIFICATION OF THE SINTERING COMPONENT INCRE
AND IT IS REACHED VERY QUICKLY (SECONDS OR MINUTES) AFTER EXPOSING POWI
TEMPERATURE BECAUSE OF THE LARGE SURFACE AREA AND THE HIGH DRIVING FORC
[21].

(B) INTERMEDIATE STAGE 0F SINTERING:

THE SECOND STAGE OF SINTERING IS REFERRED TO AS INTERMEDIATE SINTERING. T
CHANGES THAT OCCUR AT THIS STAGE ARE: THE SIZE OF THE NECKS BETWEEN THE P
POROSITY DECREASES AND THE CENTERS OF THE ORIGINAL PARTICLES MOVE CLOSEI
GRAIN BOUNDARIES BEGIN TO MOVE SO THAT ONE GRAIN BEGINS TO GROW WHILE THE
IS CONSUMED. THIS ALLOWS GEOMETRY CHANGES THAT ARE NECESSARY TO ACCOMM
NECK GROWTH AND REMOVAL OF POROSITY. INTERMEDIATE SINTERING CONTINUES A
CHANNELS ARE INTERCONNECTED AND ENDS WHEN PORES BECOME ISOLATED. MOST OF
DURING SINTERING OCCURS DURING THIS STAGE. THE SHRINKAGE IN THE INTERMEDI
RESULT IN ADDITIONAL DENSIFICATION BY AS MUCH AS 25%, OR TO A TOTAL OF ABOUT 9
(THEORETICAL DENSITY) [22].

(C) FINAl STAGE 0F SINTERING:

IT INVOLVES THE FINAL REMOVAL OF POROSITY BY VACANCY DIFFUSION ALON
BOUNDARIES. THEREFORE THE PORES MUST REMAIN CLOSE TO THE GRAIN BOUNDARIES
AND VACANCY DIFFUSION ARE AIDED BY THE MOVEMENT OF GRAIN BOUNDARIES AN
GRAIN GROWTH. HOWEVER, IF GRAIN GROWTH IS TOO RAPID, THE GRAIN BOUNDARIES CA
THAN THE PORES AND LEAVE THEM ISOLATED INSIDE THE GRAIN. AS THE GRAIN CONTI
THE PORE BECOMES FURTHER SEPARATED FROM THE GRAIN BOUNDARY AND HAS DECRI
BEING ELIMINATED. THEREFORE, GRAIN GROWTH MUST BE CONTROLLED TO ACHIEV
REMOVAL OF POROSITY.

THE FINAL SINTERING STAGE BEGINS AT ABOUT 93-95% OF THEORETICAL DENS
POROSITY IS ALREADY ISOLATED [23]. IDEALLY, AT THE END OF THIS STAGE ALL POROSIT
THE COMPLETE ELIMINATION OF POROSITY IN THE FINAL STAGE OF SINTERING CAN ONLY
ALL PORES ARE CONNECTED TO FAST, SHORT DIFFUSION PATHS ALONG GRAIN BO
EQUIVALENTLY, IF THE GRAIN BOUNDARIES REMAIN ATTACHED TO THE PORES).

OTHER FACTORS WHICH AFFECT THE RATE OF SINTERING ARE PARTICLE PACKING,
AND PARTICLE SIZE DISTRIBUTION. IF PARTICLE PACKING IS NOT UNIFORM IN THE GREE
BE DIFFICULT TO ELIMINATE ALL THE POROSITY DURING SINTERING. IF THE CONCENTRA
PARTICLES IS HIGH, IT CAN RESULT IN BRIDGING DURING THE FORMING PROCESS PRO

IRREGULARLY SHAPED PORES THAT ARE DIFFICULT TO REMOVE AFTER SINTERING. PART
ARE DIFFICULT TO PACK EFFICIENTLY AND THEY FORM COMPACTS WITH LARGE POR
VOLUME PERCENTAGE OF POROSITY. HOWEVER, COMMONLY AVAILABLE POWDER HA
PARTICLE SIZES FROM SUBMICRON UPWARD. BETTER OVERALL PACKING CAN BE ACH
COMPACTION, BUT ISOLATED PORES DUE TO BRIDGING AND AGGLOMERATION ARE USU
AND RESULT EITHER IN POROSITY OR LARGE GRAIN SIZE AFTER SINTERING.

2.1.2.7.2 LIQUID PHASE SINTERING

LIQUID-PHASE SINTERING (LPS) IS AN IMPORTANT MEANS OF MANUFACTURING
CERAMIC COMPONENTS FROM POWDER COMPACTS. IT INVOLVES THE PRESENCE OF A VI
AT THE SINTERING TEMPERATURE AND IS THE PRIMARY DENSIFICATION MECHANISM FO
SYSTEMS. IN TWO PHASE SYSTEMS INVOLVING MIXED POWDERS, LIQUID FORMATION
BECAUSE OF DIFFERENT MELTING RANGES FOR THE COMPONENTS OR THE FORMATION
PHASE, INCLUDING A GLASSY PHASE. THE MAJOR ADVANTAGES OF LPS ARE ENHANCE
KINETICS AND TAILORED PROPERTIES. HOWEVER, APART FROM THESE MERITS, THE CER
BY LPS ARE SUSCEPTIBLE TO SHAPE DEFORMATION. IN ORDER TO ATTAIN DENSIFICAT
CERTAIN CRITERIA MUST BE SATISFIED. THEY ARE (I) A LIQUID MUST BE PRESENT AT
TEMPERATURE, (II) THERE MUST BE GOOD WETTING OF THE LIQUID ON SOLID OR THE
MUST BE LOW AND (III) THERE MUST BE APPRECIABLE SOLUBILITY OF SOLID IN LIQUID.
CERAMICS TEND TO HAVE A SMALL AMOUNT OF REACTIVE LIQUID THAT ACCELERATES
RATHER THAN FACILITATE VISCOUS FLOW. WHEN THE LIQUID COATS EACH GRAIN, TH
OFTEN BE SINTERED TO A HIGHER DENSITY AT A LOWER TEMPERATURE WITH LESS OF
EXAGGERATED GRAIN GROWTH. LESS THAN 1 VOLUME % OF THE LIQUID PHASE IS SUFFI
THE GRAINS IF THE LIQUID IS DISTRIBUTED UNIFORMLY AND THE GRAIN SIZE IS ABOUT 1
THE LIQUID MUST HAVE A SOLUBILITY FOR THE SOLID. FINALLY, THE DIFFUSIVE TRANSP
ATOMS DISSOLVED IN THE LIQUID SHOULD BE HIGH ENOUGH TO ENSURE RAPID SIN
WETTING LIQUID CONCENTRATES AT THE PARTICLE CONTACTS AND FORMS A MENISCU
EFFECTIVE COMPRESSIVE PRESSURE ON THE COMPACT RESULTING IN A RAPID REARR
PARTICLES INTO A HIGHER DENSITY CONFIGURATION.

DENSIFICATION DURING LPS CAN BE ACHIEVED BY THE FOLLOWING THREE RATE-
MECHANISMS:

PARTICLE REARRANGEMENT: IN THE INITIAL STAGES OF LIQUID PHASE SINTERING, A NUMBE
CONSECUTIVE AND SIMULTANEOUS PROCESSES SUCH AS MELTING, WETTING, SPREA
REDISTRIBUTION ETC. MAY OCCUR. BOTH SOLID AND LIQUID ARE SUBJECTED TO RI
BECAUSE OF THE UNBALANCED CAPILLARY FORCES. LIQUID FILMS BETWEEN THE PAR
LUBRICANT AND THE PARTICLE REARRANGEMENT TAKES PLACE IN THE DIRECTION OF R
THE DRIVING FORCE FOR THE REARRANGEMENT ARISES DUE TO THE IMBALANCE IN CA
AS A RESULT OF PARTICLE SIZE DISTRIBUTION, IRREGULAR PARTICLE SHAPE, LOCAL DEN
THE POWDER COMPACT AND ANISOTROPIC MATERIAL PROPERTIES. AS THE DENSIT
PARTICLES EXPERIENCE INCREASING RESISTANCE TO FURTHER REARRANGEMENT DUE
NEIGHBORING PARTICLES UNTIL THE FORMATION OF A CLOSE PACKED STRUCTURE.

SOLUTION-PRECIPITATION: WHEN THE REARRANGEMENT BECOMES INSIGNIFICANT, ADDIT
DENSIFICATION CAN BE ACHIEVED BY DISSOLUTION OF THE SOLID AT GRAIN CONTACTS
THE CENTER-TO-CENTER APPROACH OF PARTICLES. THE MAIN DRIVING FORCE FOR T
CAPILLARY FORCES. THE DISSOLVED SOLUTE TRANSFERS TO THE UNCOMPRESSED PA
STRUCTURE BY DIFFUSION THROUGH A LIQUID PHASE. THIS MASS TRANSFER RESULTS I
FLATTENING AND CORRESPONDING LINEAR SHRINKAGE IN THE POWDER COMPACT. THE I
OF THE SOLID DECREASES AS THE CONTACT AREA INCREASES DUE TO SIMULTANEOU
EFFECTIVE STRESS AT THE CONTACT AREA. AT THE LATER STAGE OF SOLUTION PR
INTERCONNECTED PORE STRUCTURES PINCH OFF TO FORM ISOLATED OR CLOSED PORES.

PORE REMOVAL: THIS IS THE FINAL STAGE OF LPS WHICH STARTS AFTER PORE CLOSURE.
THIS STAGE A MAXIMUM RELATIVE DENSITY UPTO 95% IS ATTAINED. THE CLOSED PO
CONTAIN GASEOUS SPECIES FROM SINTERING ATMOSPHERE, VAPORIZED LIQUID AND
SOLID. SEVERAL PROCESSES CAN OCCUR SIMULTANEOUSLY DURING THE FINAL STAG
INCLUDES GROWTH AND COALESCENCE OF GRAINS AND PORES, DISSOLUTION OF LIQU
PHASE TRANSFORMATIONS AND FORMATION OF REACTION PRODUCTS BETWEEN LIQUID A

2.2 PREPARATION OF GLASS

MOST OF THE CERAMICS POSSESS HIGH SINTERING TEMPERATURES (ABOVE 120^{0}C). AS DISCUSSED IN CHAPTER 1, THE MOST EFFECTIVE METHOD TO LOWER THE PROCESSING T THE CERAMIC IS TO ADD LOW MELTING, LOW LOSS GLASSES. TRADITIONALLY, GLASSES A COOLING A LIQUID FAST ENOUGH TO PREVENT DETECTABLE CRYSTALLIZATION. FROM T OF VIEW, GLASS FORMATION CAN BE CONSIDERED AS THE *avoidance of crystallization*. IN THE PRESENT INVESTIGATION, MULTI COMPONENT GLASSES SUCH AS ZBS, BBSZ, LBS, BBS, LMZBS ETC. ARE SELECTED. INITIALLY HIGH PURITY OXIDES SUCH AS ZnO, B_2O_3, SiO_2, $BaCO_3$, Bi_2O_3 AND $(MgCO_3)_4Mg(OH)_2 5H_2O$ (99.9 % ALDRICH CHEMICAL COMPANY, U.S.A) ARE ACCURATELY WEIGHED AND THOROUGHLY MIXED. AFTER MIXING THEY ARE DRIED PLATINUM CRUCIBLES ABOVE THEIR MELTING POINTS. THE HIGH TEMPERATURE FAVOUR TO REACT WITH ONE ANOTHER AND ALSO ENCOURAGES THE ESCAPE OF GAS BUBBLES WHICH IS USUALLY REFERRED TO AS REFINING THE GLASS. UPON COMPLETION OF PROCESS, THE GLASS IS SUDDENLY COOLED FROM THE MELTING TEMPERATURE TO ROO (PROCESS KNOWN AS QUENCHING) WHERE THE GLASS HAS HIGHER VISCOSITY. FINALLY T GLASS IS POWDERED FOR FURTHER MIXING WITH CERAMICS.

2.3 SYNTHESIS OF POLYMER-CERAMIC COMPOSITES

2.3.1 POWDER PROCESSING METHOD

IN THE PRESENT STUDY, PTFE/CERAMIC COMPOSITES WERE PREPARED BY P PROCESSING TECHNOLOGY. DIFFERENT VOLUME FRACTIONS (0 TO 0.5) OF CERAMICS POWDERS WERE DISPERSED IN ETHYL ALCOHOL USING ULTRASONIC MIXER FOR ABOUT DRY POWDER MIXTURE WAS OBTAINED BY REMOVING THE SOLVENT AT 70^{0}C. THESE HOMOGENEOUSLY MIXED PTFE/CERAMIC COMPOSITE POWDERS WERE THEN COMPACT UNIAXIAL PRESSURE OF 50 MPA FOR 1 MINUTE. THE CYLINDRICAL AND RECTANGULAR OBTAINED WERE KEPT AT 310^{0}C FOR 12 HRS.

2.3.2 SIGMA BLEND METHOD

THIS METHOD IS USED FOR LOW MELTING, LOW VISCOUS POLYMERS POLYETHYLENE/POLYSTYRENE. THE POLYMER AND CERAMIC WERE MIXED THORO KNEADING MACHINE. THE KNEADING MACHINE CONSISTS OF VARIABLE SPEED MIXER COUNTER ROTATING SIGMA BLADES WITH A GEAR RATIO OF 1:1.2 AND HEATING FACILIT THE COUNTER ROTATING SIGMA BLADES ENSURE FINE MIXING BY APPLYING HIGH SHEA DOUGH-LIKE MIXTURE. INITIALLY THE DESIRED AMOUNT OF POLYMER IS MELTED A POINT. DIFFERENT VOLUME FRACTIONS CERAMICS WERE ADDED TO THE MELTED P BLENDED AT SUITABLE TEMPERATURE FOR 30 MINUTES. THUS OBTAINED COMPOSITES LAMINATED UNDER A PRESSURE OF 200 MPA AND OPTIMIZED TEMPERATURE FOR 15 M THERMOLAMINATION, THE COMPOSITES WITH DESIRED SHAPES WERE POLISHED FO MEASUREMENTS. FIG. 2.3 SHOWS THE PICTURE OF THE KNEADING MACHINE AND THE SI USED FOR MIXING.

Fig. 2.3 Kneading machine used in melt mixing technique. Inset figure shows the sigma blades.

2.4 STRUCTURAL AND MICROSTRUCTURAL CHARACTERIZATION

2.4.1 X-RAY DIFFRACTOMETER

X-RAY DIFFRACTION (XRD) IS A VERSATILE, NON-DESTRUCTIVE TECHNIQUE TH DETAILED INFORMATION ABOUT THE CHEMICAL COMPOSITION AND CRYSTALLOGRAP MATERIALS. AN X-RAY INCIDENT UPON A SAMPLE WILL EITHER BE TRANSMITTED, IN W WILL CONTINUE ALONG ITS ORIGINAL DIRECTION, OR IT WILL BE SCATTERED BY THE ATOMS IN THE MATERIAL. ALL THE ATOMS IN THE PATH OF THE X-RAY BEAM SCATT GENERAL, THE SCATTERED WAVES DESTRUCTIVELY INTERFERE WITH EACH OTHER, WIT SPECIAL ORIENTATIONS AT WHICH BRAGG'S LAW IS SATISFIED. THE PHENOMENON OF OCCURS WHEN PENETRATING RADIATION, SUCH AS X-RAYS, ENTERS A CRYSTALLINE S SCATTERED. THE DIRECTION AND INTENSITY OF THE SCATTERED (DIFFRACTED) BEAMS ORIENTATION OF THE CRYSTAL LATTICE WITH RESPECT TO THE INCIDENT BEAM [24]. CRYSTAL LATTICE CONSISTS OF PARALLEL ROWS OF ATOMS SEPARATED BY A UNIQ SPACING), WHICH ARE CAPABLE OF DIFFRACTING X-RAYS. IN ORDER FOR A BEAM TO DIFFRACTED, THE DISTANCE IT TRAVELS BETWEEN ROWS OF ATOMS AT THE ANGLE OF I EQUAL TO AN INTEGRAL MULTIPLE OF THE WAVELENGTH OF THE INCIDENT BEAM [25].

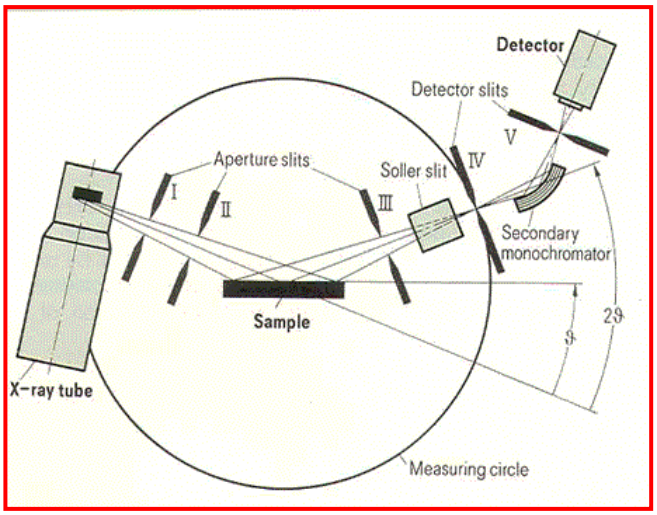

Fig. 2.4 Schematic diagram of an X-ray diffractometer.

AN X-RAY DIFFRACTOMETER UTILIZES A POWDERED SAMPLE, A GONIOMETER, AN
POSITION DETECTOR TO MEASURE THE DIFFRACTION PATTERNS OF UNKNOWNS (SEE
POWDERED SAMPLE PROVIDES (THEORETICALLY) ALL POSSIBLE ORIENTATIONS OF THE
THE GONIOMETER PROVIDES A VARIETY OF ANGLES OF INCIDENCE, AND THE DETECTO
INTENSITY OF THE DIFFRACTED BEAM. THE RESULTING ANALYSIS IS DESCRIBED GRAPHIC
PEAKS WITH % INTENSITY ON THE Y-AXIS AND GONIOMETER ANGLE ON THE X-AXIS.
ANGLE AND INTENSITY OF A SET OF PEAKS IS UNIQUE TO THE CRYSTAL STRUCTURE E
[26]. THE X-RAY DIFFRACTION METHOD IS MOST USEFUL FOR QUALITATIVE, RAT
QUANTITATIVE, ANALYSIS (ALTHOUGH IT CAN BE USED FOR BOTH). THE MONOCHROMA
ENSURE THAT A SPECIFIC WAVELENGTH REACHES THE DETECTOR, ELIMINATING FLUOR
THE RESULTING TRACE CONSISTS OF RECORDING THE INTENSITY VS. DETECTOR ANGLE
CAN THEN BE USED TO IDENTIFY THE PHASES PRESENT IN THE SAMPLE. DIFFRACTION DA
MATERIALS HAVE BEEN RECORDED IN A COMPUTER SEARCHABLE POWDER DIFFRACTIO
FILE). MATCHING THE OBSERVED DATA IN THE PDF ALLOWS THE PHASES IN THE SAM
IDENTIFIED [27-28].

2.4.2 SCANNING ELECTRON MICROSCOPE

THE SCANNING ELECTRON MICROSCOPE (SEM) IS THE MOST WIDELY USED FO
ELECTRON MICROSCOPE IN THE FIELD OF MATERIAL SCIENCE. IN LIGHT MICROSCOPY, A
VIEWED THROUGH A SERIES OF LENSES THAT MAGNIFY THE VISIBLE-LIGHT IMAGE. H
SCANNING ELECTRON MICROSCOPE DOES NOT ACTUALLY VIEW A TRUE IMAGE OF THE
RATHER PRODUCES AN ELECTRONIC MAP OF THE SPECIMEN THAT IS DISPLAYED ON A CA
THE SEM IS A MICROSCOPE THAT USES ELECTRONS INSTEAD OF VISIBLE LIGHT TO FOR
THE SCANNING ELECTRON MICROSCOPE HAS MANY ADVANTAGES OVER T
MICROSCOPES. THE SEM HAS A LARGE DEPTH OF FIELD, WHICH ALLOWS MORE OF A SPEC
IN FOCUS AT ONE TIME [29]. THE SEM ALSO HAS MUCH HIGHER RESOLUTION, SO CLOSE
SPECIMENS CAN BE MAGNIFIED AT MUCH HIGHER LEVELS. BECAUSE THE SEM
ELECTROMAGNETS RATHER THAN LENSES, THE RESEARCHER HAS MUCH MORE CONTRO
MAGNIFICATION.

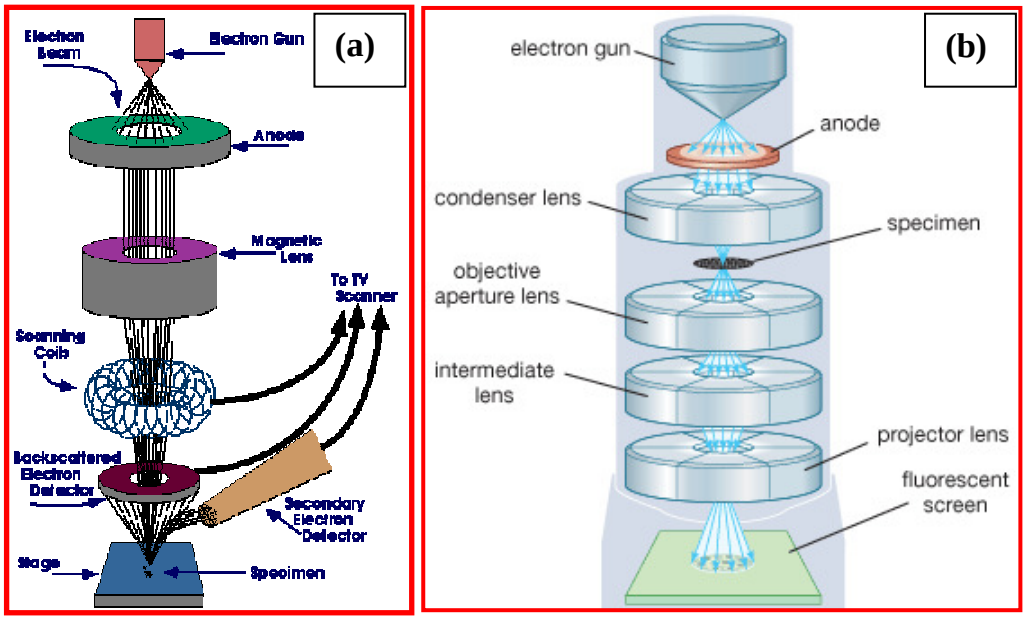

Fig. 2.5 Schematic diagram of (a) SEM (www.purdue.edu/REM/rs/sem.htm) (b) TEM (www.britannica.com)

A BEAM OF ELECTRONS IS PRODUCED AT THE TOP OF THE MICROSCOPE BY AN GUN. THE ELECTRON BEAM FOLLOWS A VERTICAL PATH THROUGH THE MICROSCOPE, WITHIN A VACUUM. THE BEAM TRAVELS THROUGH ELECTROMAGNETIC FIELDS AND FOCUS THE BEAM DOWN TOWARD THE SAMPLE. ONCE THE BEAM HITS THE SAMPLE, ELEC RAYS ARE EJECTED FROM THE SAMPLE (SEE FIG. 2.5 (A)). DETECTORS COLLECT THE BACKSCATTERED ELECTRONS, AND SECONDARY ELECTRONS AND CONVERT THEM INT SENT TO A SCREEN SIMILAR TO A TELEVISION SCREEN. THIS PRODUCES THE FINAL IMA ARE CONDUCTIVE AND REQUIRE NO PREPARATION BEFORE BEING USED. ALL NON-MET MADE CONDUCTIVE BY COVERING THE SAMPLE WITH A THIN LAYER OF CONDUCTIVE GOLD [30].

2.4.3 TRANSMISSION ELECTRON MICROSCOPY

IN TRANSMISSION ELECTRON MICROSCOPY (TEM) A THIN SLICE OF THE MATER STUDIED (0.1 TO 0.5 μM THICK) IS USED AND AN ENERGETIC ELECTRON BEAM IS PASSED DI THROUGH THE SAMPLE. ON THE EXIT SIDE OF THE SPECIMEN SEVERAL DIFFRACTED BEA IN ADDITION TO THE TRANSMITTED BEAM AND ARE FOCUSED BY AN OBJECTIVE LENS TO

ITS BACK FOCAL PLANE. THIS DIFFRACTION PATTERN IS ALSO MAGNIFIED BY OTHER TV
ELECTRON DIFFRACTION PATTERN CAN BE USED TO GAIN QUANTITATIVE INFORMATION
OF PHASES AND THEIR ORIENTATION, SPACE GROUPS, ORDER/DISORDER, MAGNETIC DOM
FIG. 2.5 (B) SHOWS THE SCHEMATIC DIAGRAM OF TEM. ONE OF THE DISADVANTAGES
ELECTRON DIFFRACTION IS THE SECONDARY DIFFRACTION WHICH OCCURS COMMON
DIFFRACTION OCCURS WHEN THE DIFFRACTED BEAMS BECOMES INCIDENT BEAM AND
ANOTHER SET OF PLANES. THE TWO UNDESIRABLE CONSEQUENCES OF SECONDARY D
OCCURRENCE OF EXTRA SPOTS IN THE DIFFRACTION PATTERN AND THE INTENSITIES O
BEAM ARE UNRELIABLE AND CANNOT BE USED FOR CRYSTAL STRUCTURE DETERMINATI

SELECTED AREA (ELECTRON) DIFFRACTION, ABBREVIATED AS SAD (SAED),
CRYSTALLOGRAPHIC EXPERIMENTAL TECHNIQUE THAT CAN BE PERFORMED INSIDE A
ELECTRON MICROSCOPE. IN A TEM, A THIN CRYSTALLINE SPECIMEN IS SUBJECTED TO A PARALLE
OF HIGH-ENERGY ELECTRONS. AS TEM SPECIMENS ARE TYPICALLY ~100 NM THICK,
ELECTRONS TYPICALLY HAVE ENERGY OF 100-400 KILOELECTRON VOLTS, THE ELECTRO
THE SAMPLE EASILY. THE WAVELENGTH OF HIGH-ENERGY ELECTRONS IS A FRACTION O
AND THE SPACINGS BETWEEN ATOMS IN A SOLID IS ONLY SLIGHTLY LARGER, THE AT
DIFFRACTION GRATING TO THE ELECTRONS. THAT IS, SOME FRACTION OF THEM WILL
PARTICULAR ANGLES, DETERMINED BY THE CRYSTAL STRUCTURE OF THE SAMPLE, WHIL
TO PASS THROUGH THE SAMPLE WITHOUT DEFLECTION. AS A RESULT, THE IMAGE ON TH
TEM WILL BE A SERIES OF SPOTS, THE SELECTED AREA DIFFRACTION PATTERN, SADP,
CORRESPONDING TO A SATISFIED DIFFRACTION CONDITION OF THE SAMPLE'S CRYSTAL
SAMPLE IS TILTED, THE SAME CRYSTAL WILL STAY UNDER ILLUMINATION, BUT DIFFE
CONDITIONS WILL BE ACTIVATED, AND DIFFERENT DIFFRACTION SPOTS WILL APPEAR
THE PRESENT INVESTIGATION SELECTED AREA DIFFRACTION PATTERN HAS BEEN EMPL
THE CORRECT SPACE GROUP OF THE CERAMICS. SAMPLES FOR TEM IN THE PRESENT
PREPARED BY THINNING PELLETS TO ELECTRON TRANSPARENCY BY CONVENTIONAL
TECHNIQUES FOLLOWED BY ION THINNING (MODEL 600, GATAN, PLEASANTON, CALIFOR
ELECTRON TRANSPARENCY FOR OBSERVATION IN THE TEM (JEM-2100 HR, JEOL, JAPAN).

2.5 MICROWAVE CHARACTERIZATION

2.5.1 INTRODUCTION

MICROWAVE MEASUREMENTS AND THE DIELECTRIC PROPERTIES OF MATERIALS INCREASING APPLICATION IN MANY AREAS OF SOLID-STATE PHYSICS, MATERIALS ELECTRONIC ENGINEERING. THE INCREASING DEMAND FOR THE DEVELOPMENT OF HIGH FREQUENCY CIRCUITS AND SYSTEMS REQUIRE A COMPLETE UNDERSTANDING OF THE MATERIALS FUNCTIONING AT MICROWAVE FREQUENCIES. IN GENERAL, THE MICROWAV MATERIALS CHARACTERIZATION FALL INTO TWO CATEGORIES: NON-RESONANT METH METHODS. NON-RESONANT METHODS ARE OFTEN USED TO GET A GENERAL KNO ELECTROMAGNETIC PROPERTIES OVER A FREQUENCY RANGE, WHILE RESONANT METH GET ACCURATE KNOWLEDGE OF DIELECTRIC PROPERTIES AT A SINGLE FREQUENCY OR A FREQUENCIES. THE GENERALLY ADOPTED METHODS FOR MEASURING THE MICROWA PROPERTIES OF MATERIALS ARE (I) PERTURBATION METHODS, (II) OPTICAL MET TRANSMISSION LINE METHODS, (IV) REFLECTION METHODS AND (V) EXACT RESONANCE CHOICE OF METHOD OR COMBINATION OF METHODS WILL DEPEND ON THE VALUE OF R_s AND LOSS FACTOR, THE AMOUNT OF MATERIAL AVAILABLE, THE ACCURACY REQUIRED AND WHET IS REQUIRED FOR RESEARCH OR ROUTINE MEASUREMENTS.

Perturbation Technique: THE PERTURBATION METHODS ARE HIGHLY SUITABLE MATERIALS OF SMALL SIZE SINCE THE MATERIAL SHOULD NOT ALTER THE FIELD CONSIDERABLY. THESE TECHNIQUES ARE SUITABLE FOR RELATIVE PERMITTIVITIES ALTHOUGH THIS RANGE CAN BE EXTENDED BY AN EXACT SOLUTION OF THE RESONATO SPECIMEN [32]. HENCE THIS TECHNIQUE IS NOT COMMONLY USED FOR DR CHARACTERISA

Optical Methods: OPTICAL METHODS ARE APPLICABLE FOR WAVELENGTH BELOW CENTIMETRE. SINCE THIS METHOD REQUIRES LARGE AMOUNT OF MATERIAL IT IS NOT SU [33].

Transmission line techniques: THIS TECHNIQUE HAS A SERIOUS DISADVANTAGE OF TH VERY SMALL WAVEGUIDE SIZE USED BELOW 4 MM, WHICH GIVES RISE TO PRACTICAL [34]. MORE OVER IMPERFECTIONS IN THE SAMPLE DIMENSIONS PRODUCE ERRORS

MEASUREMENT. IT WAS REPORTED THAT THE ACCURACY OF TRANSMISSION MODE ME
THE DIELECTRIC PROPERTIES IS MORE IN WEAK COUPLING CONDITIONS [35].

Reflection methods: IN REFLECTION METHODS, WAVES REFLECTED FROM THE DIEL
ARE STUDIED. WHEN THE RELATIVE PERMITTIVITY BECOMES LARGE, THERE OCCURS CO
IN THE MEASUREMENT OF COMPLEX VOLTAGE REFLECTION COEFFICIENT [36].

Resonance methods: EXACT RESONANCE METHOD IS THE MOST ACCURATE METHO
COMPARED TO THE ABOVE-MENTIONED METHODS FOR THE MEASUREMENT OF DRS. IN T
THE EXACT RESONANT FREQUENCY OF THE RESONATOR IS MEASURED USING DIFFERENT
FROM THE RESONANT CHARACTERISTICS, PARAMETERS LIKE f_0, Q ETC ARE DETERMINED. SPECIAL
TECHNIQUES OF EXACT RESONANCE METHODS ARE USED IN THE PRESENT STUDY, WHICH
IN DETAIL IN THE FOLLOWING SECTIONS.

2.5.2 NETWORK ANALYZER

IN MICROWAVE ENGINEERING, NETWORK ANALYZERS ARE THE BASIC INSTRUM
ANALYZE A WIDE VARIETY OF MATERIALS, COMPONENTS, CIRCUITS AND SYSTEMS. A ME
THE REFLECTION FROM AND/OR TRANSMISSION THROUGH A MATERIAL ALONG WITH K
PHYSICAL DIMENSIONS PROVIDES THE INFORMATION TO CHARACTERIZE THE PERM
PERMEABILITY OF THE MATERIAL. NETWORK ANALYZER IS A SWEPT FREQUENCY M
EQUIPMENT TO COMPLETELY CHARACTERIZE THE COMPLEX NETWORK PARAMETERS IN
LESS TIME, WITHOUT ANY DEGRADATION IN ACCURACY AND PRECISION. TWO TYPES
ANALYZERS ARE AVAILABLE, SCALAR AND VECTOR NETWORK ANALYZERS. SCALAR
MEASURES ONLY THE MAGNITUDE OF REFLECTION AND TRANSMISSION COEFFICIENTS W
NETWORK ANALYZER MEASURES BOTH THE MAGNITUDE AND PHASE. BOTH THE MAGNIT
BEHAVIOR OF A COMPONENT CAN BE CRITICAL TO THE PERFORMANCE OF A COMMUNICA
A VECTOR NETWORK ANALYZER CAN PROVIDE INFORMATION ON A WIDE RANGE OF I
ACTIVE DEVICES SUCH AS AMPLIFIERS AND TRANSISTORS, TO PASSIVE DEVICES SUCH
AND FILTERS.

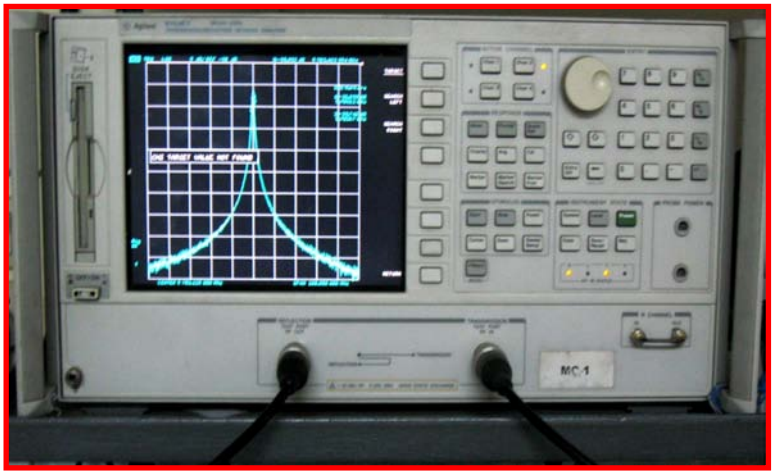

Fig. 2.6 Picture of HP 8753 ET Vector Network Analyzer.

A BASIC NETWORK ANALYZER IS DESIGNED TO SHOW GRAPHICALLY, A PLOT OF GAIN OR LOSS OF A NETWORK VERSUS FREQUENCY. THE NETWORK ANALYZER M MAGNITUDE, PHASE, AND GROUP DELAY OF TWO-PORT NETWORKS TO CHARACTERIZ BEHAVIOUR. A NETWORK ANALYZER CONSISTS OF A SWEPT FREQUENCY SOURCE TH NETWORK UNDER TEST AND TWO RECEIVERS. THE FIRST RECEIVER IS USED TO ACCURAT REFLECTION OR INPUT VOLTAGE TO THE NETWORK. THE SECOND RECEIVER IS CALLED TH CHANNEL AND IS USED TO MEASURE THE OUTPUT OF THE NETWORK UNDER TEST. TH OUTPUT TO THE INPUT LEVEL IS DISPLAYED AS DB AND IS THE VOLTAGE GAIN OR LOSS O THE NETWORK ANALYZER USED IN THE PRESENT STUDY IS SHOWN IN FIG. 2.6.

2.5.3 MEASUREMENT OF RELATIVE PERMITTIVITY (ε_r)

IN THIS METHOD DEVELOPED BY HAKKI AND COLEMAN [38] A CIRCULAR DISC OF MATERIAL TO BE MEASURED IS INSERTED BETWEEN TWO MATHEMATICALLY INFINITE CONDUCTI SHOWN IN FIG 2.7. IF THE DIELECTRIC MATERIAL IS ISOTROPIC THEN THE CHARACTERIST THIS RESONANT STRUCTURE OPERATING IN TM_{0n0} MODE IS WRITTEN AS

$$\frac{J_0(\ )}{J_1(\ )} = - \frac{K_0(\ )}{K_1(\ )} \qquad (2.3)$$

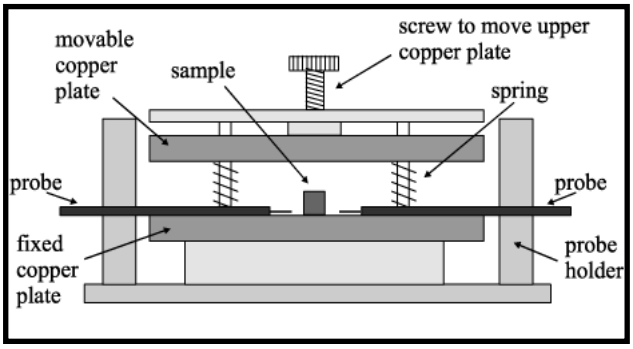

Fig. 2. 7 A dielectric rod kept end shorted between two mathematically infinite conducting plates

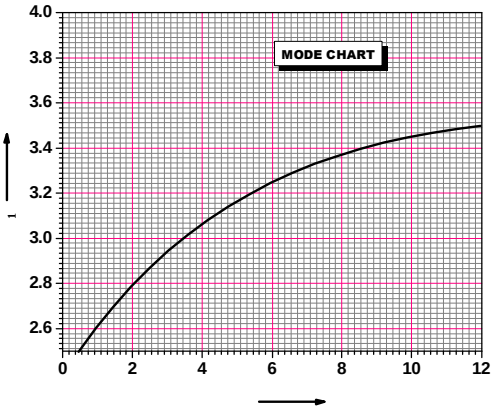

Fig. 2.8 Mode charts of Hakki and Coleman giving $_1$ as functions of .

WHERE$_0$(J) AND$_1$( ) ARE BESSEL FUNCTIONS OF THE FIRST KIND OF ORDERS ZERO AN RESPECTIVELYK_0( ) ANDK_1( ) ARE THE MODIFIED BESSEL FUNCTIONS OF THE SECOND KIN ORDER ZERO AND ONE RESPECTIVELY. THA PARAMETER ON THE GEOMETRY, THE RESONANT WAVELENGTH INSIDE AND OUTSIDE THE DR RESPECTIVELY AND DIELECT THUS,

$$\alpha = \frac{D}{o}\left[_r - \left(\frac{l_o}{2L}\right)^2 \right]^{1/2} \qquad (2.4)$$

$$\beta = \frac{D}{o}\left[\left(\frac{l_o}{2L}\right)^2 - 1 \right]^{1/2} \qquad (2.5)$$

WHERE

l = THE LONGITUDINAL VARIATIONS OF THE FIELD ALONG THE AXIS

L= LENGTH OF THE DR

D= DIAMETER OF THE DR

$_0$ = FREE SPACE RESONANT WAVE LENGTH

THE CHARACTERISTIC EQUATION IS A TRANSCENDENTAL EQUATION AND HENC
SOLUTION IS NECESSARY. CORRESPONDING TO EACH VALUE OF n THERE ARE INFINITE NUMBER OF ($
THAT SOLVES THE CHARACTERISTIC EQUATION. HAKKI AND COLEMAN OBTAINED A
SHOWING THE VARIATION OF λ_0/l VALUES AS A FUNCTION OF D/l AND ARE SHOWN IN FIG. 2.7. THE
RELATIVE PERMITTIVITY OF THE RESONATOR CAN BE CALCULATED USING THE MODE C
(β_1 AND α_1), THE RESONANT FREQUENCY (f_R) AND THE DIMENSIONS OF THE DIELECTRIC PUCK USING T
EQUATION

$$\varepsilon_R = 1 + \left[\frac{c}{Df_r}\right]^2 \left(\beta_1^2 + \alpha_1^2\right) \qquad (2.6)$$

THE HORIZONTALLY ORIENTED E-FIELD PROBES FOR COUPLING MICROWAVES TO T
PROPOSED BY COURTNEY [39] WHICH ENABLED TO SPAN A WIDE RANGE OF FREQUENCIES, S
THERE IS NO CUT-OFF FREQUENCY FOR TE_{011} MODES. IT IS USED FOR THE
MEASUREMENTS SINCE THIS MODE PROPAGATES INSIDE THE SAMPLE BUT IS EVANESCEN
THEREFORE A LARGE AMOUNT OF ELECTRICAL ENERGY CAN BE STORED IN THE HIG
RESONATORS [40]. HOWEVER, IN THE OPEN SPACE POST RESONATORS SETUP, A PART O
ENERGY IS RADIATED OUT AS EVANESCENT FIELD AND HENCE THE AXIAL MODE NUM
EXPRESSED AS δ SINCE IT IS LESS THAN 1 ($\delta_{01\delta}$). IN THE END SHORTED CONDITION THE E FIELD
BECOMES ZERO CLOSE TO THE METAL WALL AND ELECTRIC ENERGY VANISHES IN THE AI

IN THE EXPERIMENTAL SETUP, A VECTOR NETWORK ANALYZER (MODEL 8753 ET, A
TECHNOLOGIES, HEWLETT-PACKARD, PALO ALTO, CA) IS USED FOR TAKING MEASUR
MICROWAVE FREQUENCIES. THE HP 9000, 300 SERIES INSTRUMENTATION COMPUTER, IN
WITH NETWORK ANALYSER MAKES THE MEASUREMENT QUICKER AND ACCURATE. TH
PLACED APPROXIMATELY SYMMETRICAL WITH THE TWO PROBES. THE RESONANT
VISUALISED BY GIVING A WIDE FREQUENCY RANGE BY ADJUSTING THE NETWORK A
SELECT THE TE_{011} RESONANCE FROM THE SEVERAL MODES HAVING COMPONENTS IN THE
UPPER METAL PLATE IS SLIGHTLY TILTED TO INTRODUCE AN AIR GAP. AS THE PLATE IS T
TM MODES MOVE RAPIDLY TO THE HIGHER FREQUENCIES WHEREAS TE_{011} MODE REMAINS ALMOST
STATIONARY. IT IS WELL KNOWN THAT IN EXACT RESONANCE TE_{011} MODE IS UNAFFECTED BY
THE SURROUNDINGS. AFTER IDENTIFYING TE_{011} RESONANT FREQUENCY OR CENTRAL FREQUENCY (f_0),

THE SPAN AROUND β_0 IS REDUCED AS MUCH AS POSSIBLE TO GET MAXIMUM RESOLUTION. THE BANDWIDTH OF THE CURVE DECREASES AND A STAGE OF SATURATION IS REACHED WHE REMAIN THE LEAST POSSIBLE. THE COUPLING LOOPS ARE FIXED AT THIS POSITION AN FREQUENCY CAN BE NOTED CORRESPONDING TO f_0. BY KNOWING THE DIAMETER 'D' AND LENGTH 'L' OF THE SAMPLE ε_r CAN BE CALCULATED USING EQ. (2.5). FROM THE MODE CHART TH VALUE OF p_1 CORRESPONDING TO f_0 IS NOTED. THE RELATIVE PERMITTIVITY IS CALCULATED USING EQ. (2.6).

2.5.4 MEASUREMENT OF UNLOADED QUALITY FACTOR (Q_u)

THERE ARE VARIOUS METHODS WHICH ENABLES MEASUREMENTS OF THE Q-FACTORS OF THE MICROWAVE RESONATORS [42-45]. HOWEVER, NOT ALL OF THEM TAKE INTO ACCOUN EFFECTS INTRODUCED BY A REAL MEASUREMENT SYSTEM SUCH AS NOISE, CROSSTALK, C TRANSMISSION LINE DELAY, AND IMPEDANCE MISMATCH. INADEQUATE ACCOUNTING OF MAY LEAD TO SIGNIFICANT UNCERTAINTY IN THE Q-FACTOR OBTAINED.

FOR A DR, THE QUALITY FACTOR MEASUREMENT USING THE $TE_{01\delta}$ MODE IS DIFFICULT SINCE THE PARALLEL PLATE MOD RESONATOR IS VERY LOW SINCE THERE OCCURS LOSSES DUE TO CONDUCTING PLATI UNDER END SHORTED CONDITION. IN ORDER TO REDUCE THESE EFFECTS, IN THE PRES UNLOADED QUALITY FACTOR (Q_u) OF THE DRS IS MEASURED USING A TRANSMISSION MODE CAVI PROPOSED BY KRUPKA *et al.* [46]. THE SPECIMEN WAS PLACED ON A LOW LOSS QUARTZ SPACER HEIGHT 8 MM INSIDE A COPPER CAVITY OF INNER DIAMETER 40 MM AND HEIGHT 22 MM INNER SIDE WAS FINELY POLISHED AND SILVER PLATED TO REDUCE RADIATION LOSS. T LOSS SINGLE CRYSTAL QUARTZ SPACER REDUCES THE EFFECT OF LOSSES DUE TO THE S OF THE CAVITY. SAMPLES WITH DIAMETER TO HEIGHT (D/L) RATIO OF 1.8 - 2.2 IS PREFERABLE TO GET MAXIMUM MODE SEPARATION AND TO AVOID INTERFERENCE FROM OTHER MODES. ALS FIELD IS SYMMETRIC WITH THE GEOMETRY OF THE SAMPLE AND THE CAVITY, WHICH HE THE SOURCES OF LOSS DUE TO CAVITY. AS SEEN IN FIG. 2.9 (A), THE SAMPLE IS ISOLATE QUARTZ SPACER, FROM THE EFFECTS OF LOSSES DUE TO THE FINITE RESISTIVITY OF T PLATES. MICROWAVES ARE FED INTO THE SAMPLE USING TWO LOOP COAXIAL ANTE PROVIDES A MAGNETIC COUPLING TO EXCITE THE TRANSMISSION MODE RESONANCE

DIELECTRIC CYLINDER. THE COUPLING IS ADJUSTED TO BE OPTIMUM (WEAK COUPLING Q_u AND STRONG COUPLING FOR LOSSY SAMPLES). OBSERVE S_{21} PARAMETER IN FREQUENCY SPECTRUM. IN PRINCIPLE THE CAVITY HAS INFINITE NUMBER OF MODES, WHEN EXCITED WITH M SPECTRUM OF FREQUENCIES. $TE_{01\Delta}$ MODE IS IDENTIFIED AS THE FUNDAMENTAL MODE WITH LE PERTURBATION WHEN THE TUNABLE TOP LID IS ADJUSTED PROPERLY. AFTER IDENTIFY MODE, THE LID IS FINE TUNED TO GET MAXIMUM SEPARATION BETWEEN $TE_{01\Delta}$ AND ANY NEARBY CAVITY MODES, TO ATTAIN MAXIMUM POSSIBLE Q_u. MEASURE THE $TE_{01\Delta}$ MODE FREQUENCY AND THE 3 DB BANDWIDTH FROM THE RESONANCE SPECTRUM (B)) TO CALCULATE THE Q FACTOR USING THE EQ. 1.14.

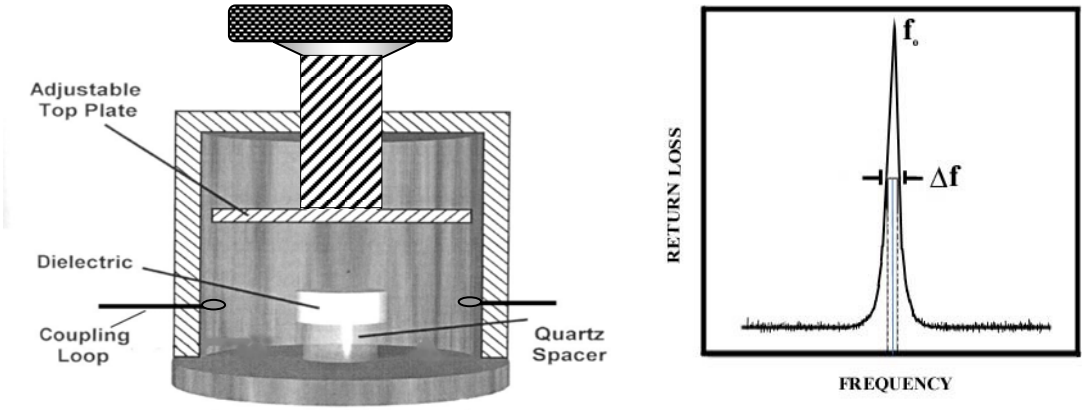

Fig. 2. 9 (A) The cavity set up for the measurement of *Q* factor and (B) the method of calculating from resonant mode using Eq. 1.14.

2.5.5 MEASUREMENT OF TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY (τ_f)

THE TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY (τ_f) IS AN IMPORTANT PARAMETER THAT DETERMINES THE PERFORMANCE OF THE DEVICE. SINCE RESONATORS AR COMMUNICATION SYSTEMS TEMPERATURE STABILITY IS AN IMPORTANT FACTOR AND SE ZERO.

THE $_f$ CAN BE MEASURED BY THE CAVITY METHOD USED FOR MEASURING THE FACTOR. THE USE OF INVAR CAVITY CAN MINIMIZE THE INACCURACY CAUSED DUE TO EXPANSION OF THE CAVITY WHILE HEATING. THE CAVITY IS KEPT IN AN OVEN AND THE ENTIRE SYSTEM IS INSULATED IN AN ISOTHERMAL ENCLOSURE. THE SET UP IS THEN SLOWLY (~1^{o}C/MINUTE) IN THE RANGE 25 TO 80^{o}C. THE PROBE OF THE THERMOCOUPLE IS KEPT JUST INSIDE THE ISOTHERMAL ENCLOSURE SO THAT IT DOES NOT DISTURB THE RESONANT FREQUENCY. THE RESONANT FREQUENCY OF $TE_{01\delta}$ MODE IS NOTED AT EVERY 2^{o}C INCREMENT IN TEMPERATURE. THE VARIATION OF RESONANT FREQUENCY IS PLOTTED AS FUNCTION OF TEMPERATURE. $_f$ IS CALCULATED FROM THE SLOPE OF THE CURVE USING THE EQ. (2.7).

$$_f = \frac{1}{f}\frac{\Delta f}{\Delta T} \qquad (2.7)$$

2.5.6 CAVITY PERTURBATION METHOD

IT IS KNOWN THAT THE COMPLEX PERMITTIVITY OF MATERIALS USUALLY CHANGES ON THE FREQUENCY, TEMPERATURE AND COMPOSITIONS. THEREFORE, IN DESIGNING OF MICROWAVE DEVICES, IT IS VERY IMPORTANT TO STUDY THE TEMPERATURE DEPENDENCE PERMITTIVITY OF MATERIALS OVER THE WIDE TEMPERATURE RANGE. ONE OF THE USUAL OBTAIN COMPLEX PERMITTIVITY OF MATERIALS IS THE PERTURBATION METHOD U RESONATOR. CAVITY PERTURBATION METHODS ARE WIDELY USED IN THE STU ELECTROMAGNETIC PROPERTIES OF DIELECTRICS, SEMICONDUCTORS, MAGNETIC M COMPOSITE MATERIALS. IT WORKS WELL FOR THE DETERMINATION OF THE DIELECTRIC OF THIN SHEET SAMPLES OF LOW AND MEDIUM DIELECTRIC LOSS [47]. WHEN THE PE METHOD IS APPLIED, IT IS NECESSARY TO SATISFY TWO CONDITIONS. ONE OF THEM IS TO DIELECTRIC MATERIAL COMPARED WITH THE VOLUME OF THE CAVITY RESONATOR, AND THAT THE ELECTROMAGNETIC FIELD DISTRIBUTION IS NOT CHANGED AFTER INSERTI MATERIAL INTO THE CAVITY. IN A RESONANT PERTURBATION METHOD, THE SAMPLE INTRODUCED TO A RESONANT CAVITY, AND THE ELECTROMAGNETIC PROPERTIES OF DEDUCED FROM THE CHANGE OF RESONANT FREQUENCY AND QUALITY FACTOR OF CAVITY.

IN THE CAVITY PERTURBATION TECHNIQUE, A SMALL PIECE OF THE MATERIAL U
FORM OF A DISK OR SHEET IS PLACED IN A METALLIC RESONANT CAVITY OPERATING IN A
THE MATERIAL CHARACTERISTICS ARE ESTIMATED FROM THE SHIFT IN THE RESONANT
CHANGE IN THE Q OF THE SYSTEM [48]. THIS TECHNIQUE WAS PIONEERED BY SLATER [49] AN
SUITABLE METHOD FOR MEASURING THE DIELECTRIC PROPERTIES OF MATERIALS WITH
THAN 10. THE CAVITY PERTURBATION METHOD IS NOT A SWEPT FREQUENCY MEASUREM
MEASUREMENT FREQUENCIES ARE DETERMINED BY THE CAVITY AS WELL AS THE DR
HENCE IT CAN BE USED ONLY FOR DISCRETE FREQUENCY MEASUREMENTS. IN THIS
RECTANGULAR WAVE GUIDE WITH A SMALL SLOT AT THE BROADER WALL AT THE MID
CAVITY IS EXCITED WITH OPTIMUM IRIS COUPLING AND THE RESONANT FREQUENCY
FACTOR OF THE EMPTY CAVITY IS DETERMINED FOR DIFFERENT CAVITY MODES. THEN
SAMPLE IS INSERTED AND POSITIONED AT THE E-FIELD ANTINODE. IF THE SAMPLE IS PUR
THE MAXIMUM ELECTRIC FIELD CAN BE EASILY DETERMINED BY SIMPLY MOVING THE SA
THE SLIT. THE MODE WILL SHIFT TO LOW FREQUENCY SIDE AND RETRACES FROM THERE
KEPT AT THE RETRACING POSITION, THIS IS THE ELECTRIC FIELD MAXIMUM POSITION. I
MAGNETIC THE PERMITTIVITY CAN BE MEASURED ONLY FOR THE ODD MODES BY KEE
MIDDLE OF THE CAVITY. THE NEW RESONANT FREQUENCY AND Q FOR THE SAMPLE IS AGAIN MEASURED.
THE COMPLEX RELATIVE PERMITTIVITY OF THE SAMPLE IS CALCULATED [47, 50] USING T
EQ. (2.8 - 2.10) [51].

$$\varepsilon_r' = 1 + \left[\frac{V_c (f_o - f_s)}{2 V_s f_s} \right] \tag{2.8}$$

$$\varepsilon_r'' = \frac{V_c (Q_o - Q_s)}{4 V_s Q_o Q_s} \tag{2.9}$$

$$\text{TAN}\,\delta = \frac{\varepsilon_r''}{\varepsilon_r'} \tag{2.10}$$

WHERE f_o = RESONANT FREQUENCY OF THE EMPTY CAVITY, f_s = RESONANT FREQUENCY OF THE CAVITY
WITH SAMPLE, V_c = VOLUME OF THE CAVITY, V_s = VOLUME OF THE SAMPLE, Q_o IS THE QUALITY
FACTOR OF THE EMPTY CAVITY AND Q_s IS THE QUALITY FACTOR OF THE CAVITY WITH SAMPLE.

EXPERIMENTAL ERROR WAS FOUND TO BE LESS THAN 2 % IN CASE OF PERMITTIVITY ANI
CASE OF DIELECTRIC LOSS. THE MAIN ADVANTAGE OF THIS METHOD IS THE EASINESS O
THE PERMITTIVITY AND LOSS USING SIMPLE DEVICE WITH MODERATE ACCURACY.

2.5.7 SPLIT-POST DIELECTRIC RESONATOR METHOD

SPLIT- RESONATOR METHODS ARE SUITABLE FOR THE CHARACTERIZATION OF DI
SAMPLES, INCLUDING DIELECTRIC SUBSTRATES FOR PLANAR CIRCUITS [52]. THE RESC
CONSISTS OF TWO DIELECTRIC DISCS IN A METAL ENCLOSURE. THE DIELECTRIC DISCS A
HEIGHT OF METAL ENCLOSURE IS RELATIVELY SMALL, SO THE EVANESCENT ELECTR
CHARACTER IS STRONG NOT ONLY IN THE AIR-GAP REGION FOR RADII GREATER THAN
DIELECTRIC RESONATOR. IN A SPLIT-POST DIELECTRIC RESONATOR (SPDR) METHO
MEASUREMENT FIXTURE USUALLY HAS A CYLINDRICAL STRUCTURE WORKING AT A TE
RESONATOR IS SPLIT INTO TWO PARTS AT THE ELECTRIC CURRENT NODE ALONG A PLAN
THE CYLINDER AXIS. THE SAMPLE UNDER TEST IS PLACED IN THE GAP BETWEEN THE TW
RESONATOR, AND USUALLY THE SAMPLE IS AT THE PLACE OF MAXIMUM ELECTRIC FIEL
OF A DIELECTRIC SHEET SAMPLE CHANGES THE RESONANT PROPERTIES OF A SPLIT RES
DIELECTRIC PROPERTIES OF THE SAMPLE CAN BE DERIVED FROM THE RESONANT PRO
RESONATOR LOADED WITH SAMPLE AND THE DIMENSIONS OF THE RESONATOR AND THE

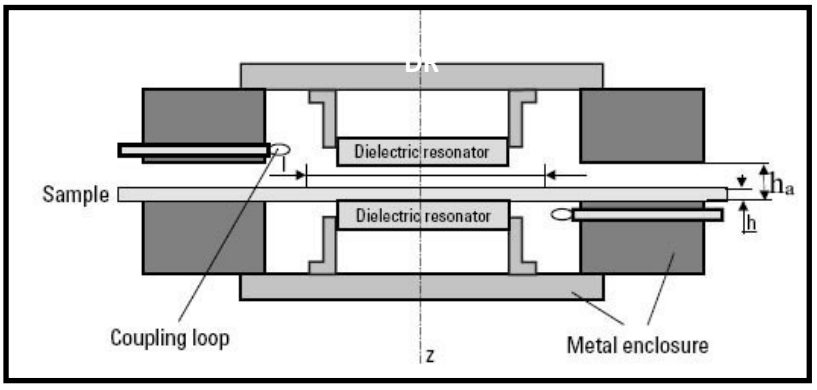

Fig. 2.10 Schematic representation of SPDR.

THE PROPOSED GEOMETRY OF A SPLIT-DIELECTRIC RESONATOR FIXTURE FOR THE
OF THE COMPLEX PERMITTIVITY OF DIELECTRIC SHEET SAMPLES IS SHOWN IN FIG. 2.10.
DIELECTRIC RESONATOR USUALLY OPERATES IN THE $TE_{01\delta}$ MODE, WHICH HAS ONLY AZHIMUTHAL
ELECTRIC FIELD COMPONENT, SO THE ELECTRIC FIELD REMAINS CONTINUOUS ON T
INTERFACES. THE FIELD DISTRIBUTIONS ARE AFFECTED BY THE INTRODUCTION OF THE S
TURN CHANGES THE RESONANT FREQUENCY, AND THE UNLOADED QUALITY FACTOR OF THE SAMPLE. THE
DIELECTRIC PROPERTIES OF THE SAMPLE ARE DERIVED FROM THE CHANGES OF RESON
AND UNLOADED QUALITY FACTOR DUE TO THE INSERTION OF THE SAMPLE. FOR LOW-LO
INFLUENCE OF LOSSES ON THE RESONANT FREQUENCIES IS NEGLIGIBLE, SO THE F
PERMITTIVITY OF THE SAMPLE UNDER TEST IS RELATED TO THE RESONANT FREQUENC
DIMENSIONS OF THE CAVITY AND SAMPLE ONLY. IN THIS METHOD, CALIBRATION TECH
AND WE COMPARE THE DIFFERENCE OF RESONANT FREQUENCY OF THE SPLIT DIELEC
BEFORE AND AFTER THE SAMPLE IS INSERTED. THE RELATIVE PERMITTIVITY OF THE
ITERATIVE SOLUTION TO THE FOLLOWING EQUATION [54]

$$\varepsilon_r = 1 + \frac{f_o - f_s}{h f_o K(\varepsilon_r, h)} \tag{2.11}$$

WHERE h IS THE THICKNESS OF THE SAMPLE UNDER TEST, f_o IS THE RESONANT FREQUENCY OF EMPTY
RESONANT FIXTURE, f_s IS THE RESONANT FREQUENCY OF THE RESONANT FIXTURE WITH DIELECTRIC W
SAMPLE, K IS A FUNCTION OF ε_r AND h. THE DIELECTRIC LOSS TANGENT OF THE SAMPLE CAN
DETERMINED BY

$$\tan\delta = \frac{1}{p_{es}}\left(\frac{1}{Q} - \frac{1}{Q_{DR}} - \frac{1}{Q_c}\right) \tag{2.12}$$

WITH

$$p_{es} = h\,\varepsilon_r K_1(\varepsilon_r, h) \tag{2.13}$$

$$Q_c = Q_{c0} K_2(\varepsilon_r, h) \tag{2.14}$$

$$Q_{DR} = Q_{DR0} \cdot \frac{f_o}{f_s} \cdot \frac{p_{eDR0}}{p_{eDR}} \tag{2.15}$$

WHERE p_{es} AND p_{eDR} ARE THE ELECTRIC-ENERGY FILLING FACTORS FOR THE SAMPLE AND FO
RESONATOR RESPECTIVELY, p_{eDR0} IS THE ELECTRIC-ENERGY FILLING FACTOR OF THE DIELECTR
RESONATOR FOR EMPTY RESONANT STRUCTURE, Q_{c0} IS THE QUALITY FACTOR DEPENDING ON METAL
ENCLOSURE LOSSES FOR EMPTY RESONANT STRUCTURE, Q_{DR0} IS THE QUALITY FACTOR DEPENDING ON
DIELECTRIC LOSSES IN DIELECTRIC RESONATORS FOR EMPTY RESONANT STRUCTURE; AND Q_s IS THE UNLOADED
QUALITY FACTOR OF THE RESONANT FIXTURE CONTAINING THE DIELECTRIC SAMPLE. THE p_{eDR}, p_{es} AND Q_c FOR A GIVEN RESONANT STRUCTURE CAN BE CALCULATED USING NUMERICAL T
TERMS OF SAMPLE GEOMETRY, THE REQUIREMENTS ARE THAT THE SAMPLE MUST EXTE
DIAMETER OF THE TWO CAVITY SECTIONS AND THE SAMPLE MUST BE FLAT. THIS P
ACCURACY OF A RESONATOR TECHNIQUE WITHOUT HAVING TO MACHINE THE SAM
UNCERTAINTY OF THE PERMITTIVITY MEASUREMENTS OF A SAMPLE OF THICKNESS h CAN BE ESTIMATED
AS $\Delta\varepsilon'/\varepsilon' = \pm(0.0015+\Delta h/h)$ AND UNCERTAINTY IN LOSS TANGENT MEASUREMENTS $\Delta\tan\delta = 2\times10^{-5}$.

2.6 RADIO FREQUENCY DIELECTRIC MEASUREMENTS

LCR METERS ARE GENERALLY USED FOR MEASURING CAPACITANCE AND
DISSIPATION FACTOR OF CAPACITORS IN THE RADIO FREQUENCY REGION BY THE WELL
PLATE CAPACITOR METHOD. THIS WILL GIVE AN APPROXIMATE VALUE OF ε' WHICH IN TURN
HELPS TO CALCULATE THE APPROXIMATE RESONANT FREQUENCY AND SIZE OF THE DR T
Q-FACTOR. THE PARALLEL PLATE CAPACITOR METHOD INVOLVES SANDWICHING A TH
MATERIAL BETWEEN TWO ELECTRODES TO FORM A CAPACITOR. THE CAPACITANCE OF
CAPACITOR IN VACUUM IS COMPARED WITH ONE IN THE PRESENCE OF THE MATERIAL F
DIELECTRIC PROPERTIES ARE TO BE MEASURED. THEN RELATIVE PERMITTIVITY IS CALCU
EQ. (2.16) [21].

$$C = \frac{\varepsilon_r \varepsilon_o A}{d} \tag{2.16}$$

WHERE C IS THE CAPACITANCE OF MATERIAL, ε_r AND ε_o ARE THE RELATIVE PERMITTIVITIES OF MATERIA
AND FREE SPACE RESPECTIVELY. IN THE PRESENT STUDY, THE DIELECTRIC PROPER
FREQUENCY ARE MEASURED USING LCR METER (HIOKI 3532-50 LCR HI TESTER, JAPAN).

2.7 ERROR CALCULATIONS IN DIELECTRIC PROPERTY MEASUREMENTS

THE MEASUREMENT OF MICROWAVE DIELECTRIC PROPERTIES OF MATERIALS WITH TWO DECIMAL POINT ACCURACY. USUALLY THREE SAMPLES WERE PREPARED IN A BATCH CORRESPONDING TO A PARTICULAR COMPOSITION AND THE MEASUREMENTS WERE MADE AT LEAST TWICE ON EACH SPECIMEN. THE ERROR IS CALCULATED USING THE ROOT SUM OF SQUARES (RSS) METHOD. THE ACCURACY OF MEASUREMENT IS RESTRICTED TO THE ACCURACY IN MEASUREMENT OF FREQUENCY AND DIMENSIONS OF THE SAMPLE. THE ERROR IN ε_r IS LESS THAN THE POSSIBLE ERRORS IN THE MEASURED VALUES OF L, r AND f_r. THE ERROR IN ε_r MAY INCLUDE THE ERROR ASSOCIATED WITH THE SAMPLE HOLDER AND RESONANT FREQUENCY GIVEN BY

$$\Delta\varepsilon_r = \left[\left(\frac{\partial \varepsilon_r}{\partial L}\Delta L\right)^2 + \left(\frac{\partial \varepsilon_r}{\partial r}\Delta r\right)^2 + \left(\frac{\partial \varepsilon_r}{\partial f_r}\Delta f_r\right)^2\right]^{1/2} \tag{2.17}$$

IF THE INDEPENDENT SOURCES OF ERROR CORRESPONDS TO ONE STANDARD DEVIATION, THEN THE ERROR IN ε_r WILL ALSO CORRESPONDS TO ONE STANDARD DEVIATION [55]. THE ERRORS IN QUALITY FACTOR (Q_u) AND TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY (τ_f) ARE CALCULATED USING RSS METHOD BY TAKING PARTIAL DERIVATIVE OF THESE PARAMETERS WITH INDEPENDENT VARIABLES.

2.8 THERMAL CHARACTERIZATION TOOLS

THERMAL ANALYSIS INCORPORATES THOSE TECHNIQUES IN WHICH A PHYSICAL PARAMETER OF THE SYSTEM IS DETERMINED AND RECORDED AS A FUNCTION OF TEMPERATURE. THERMAL CHARACTERIZATION METHODS ADOPTED IN THE PRESENT INVESTIGATION ARE GIVEN BELOW.

2.8.1 THERMO GRAVIMETRIC ANALYSIS (TGA)

THERMO GRAVIMETRIC ANALYSIS IS A TECHNIQUE IN WHICH THE MASS OF A SUBSTANCE, IN AN ENVIRONMENT HEATED OR COOLED AT A CONTROLLED RATE, IS RECORDED AS A FUNCTION OF TEMPERATURE. THUS THE BASIC REQUIREMENTS FOR THE MEASUREMENT ARE A HEATING UP AND A MEANS OF WEIGHING. THE TG CURVE GIVES INFORMATION ABOUT

(I) THE THERMAL STABILITY OF THE MATERIAL.

(II) THE PROCEDURAL DECOMPOSITION TEMPERATURE, I.E., THE TEMPERATURE AT WHICH THE CUMULATIVE MASS CHANGE REACHES A MAGNITUDE THAT THE THERMO DETECT.

(III) THE TEMPERATURE AT WHICH THE REACTION IS COMPLETE AND THE REACTION IN

2.8.2 THERMO MECHANICAL ANALYSIS (TMA)

IN THIS TECHNIQUE, DIMENSIONAL CHANGES IN THE SAMPLE ARE PRIMARILY MEASURED, WITH NEGLIGIBLE FORCE ACTING ON IT, WHILE THE SAMPLE IS HEATED, COOLED, OR STU TEMPERATURE. IT IS PARTICULARLY SUITED TO POLYMER MATERIALS BUT A WIDE RAN CAN BE EXAMINED [56]. IN THE PRESENT STUDY, TMA (TMA- 60 H, SHIMADZU, KYOTO, JAP IS USED TO DETERMINE THE THERMAL EXPANSION COEFFICIENT AND SOFTENING TEM APPLICATION OF LOAD AND HEMISPHERE-PLUGS) OF COMPOSITES. TMA IS ALSO USED T THE SOFTENING AND MELTING TEMPERATURE OF GLASS-CERAMIC COMPOSITES US TEMPERATURE CO-FIRED CERAMIC APPLICATIONS.

2.8.3 THERMAL CONDUCTIVITY MEASUREMENT

AN IMPROVED PHOTOPYROELECTRIC TECHNIQUE [57-58] WAS USED TO DETERM THERMAL CONDUCTIVITY OF THE POLYMER COMPOSITES. A 70 MW HE-CD LASER OF W 442 NM, INTENSITY MODULATED BY A MECHANICAL CHOPPER (MODEL SR540) WAS USE OPTICAL HEATING SOURCE. A PVDF FILM OF THICKNESS 28 M, WITH NICKEL COATING ON BOTH SIDES, IS USED AS PYROELECTRIC DETECTOR. THE OUTPUT SIGNAL IS MEASURED USI AMPLIFIER (MODEL SR 830). MODULATION FREQUENCY IS KEPT ABOVE 60 HZ TO ENSURE DETECTOR, THE SAMPLE AND BACKING MEDIUM ARE THERMALLY THICK DURING MEAS THERMAL THICKNESS OF THE COMPOSITES WAS VERIFIED BY PLOTTING PHOTOPYROE AMPLITUDE AND PHASE WITH FREQUENCY AT ROOM TEMPERATURE. THE THERMAL DIFFUS THERMAL EFFUSIVITY (E) WERE ALSO MEASURED FROM PPE SIGNAL PHASE AND AMPL FROM THE VALUES OF D AND E THE THERMAL CONDUCTIVITY AND SPECIFIC HEAT CAPACITY SAMPLES WERE OBTAINED. IN THE PRESENT INVESTIGATION THERMAL CONDUCTIVITY I POLYMER CERAMIC COMPOSITES USED FOR MICROWAVE SUBSTRATES AND ELECTRO APPLICATIONS.

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CHAPTER 3

STRUCTURE AND MICROWAVE DIELECTRIC PROPERTIES OF $ARE_4Si_3O_{13}$ [A=Sr, Ca, Ba; RE=Rare Earths] CERAMICS

This chapter deals with the synthesis, characterization and microwave dielectric properties of a series of rare earth silicate based materials $ARE_4Si_3O_{13}$ [A=Ca, Sr and Ba; RE=rare earths] with apatite structure. The structure and microstructure of these compounds were confirmed using XRD and SEM analysis. All of them belong to $P6_3/m$ with a hexagonal symmetry. A detailed structural analysis was performed for $SrRE_4Si_3O_{13}$ series using refinement studies and TEM analysis. The microwave dielectric properties of $ARE_4Si_3O_{13}$ materials showed a relative permittivity in the range 10-20, reasonably good quality factor and relatively low value of τ_f. The τ_f value of $SrLa_4Si_3O_{13}$ was tailored by the addition of proper amount of TiO_2. The microwave dielectric properties of these compounds were investigated for the first time.

3.1 INTRODUCTION

THE RAPID DEVELOPMENT IN THE MICROELECTRONIC TECHNOLOGIES SUCH AS WIR
INTELLIGENT TRANSPORT SYSTEM (ITS) AND MICROWAVE INTEGRATED CIRCUITS (MIC) H
INCREASING DEMAND FOR NOVEL CERAMIC MATERIALS FOR BEING USED AS DIELECTRIC
MICROWAVE FREQUENCIES. TO MEET THIS REQUIREMENT MATERIALS WITH RELATIVE PE
> 10 ARE PREFERRED DUE TO THE SMALL SIZE OF THESE MATERIALS AT HIGH FREQUENC
CROSS COUPLING EFFECT AS WELL AS HIGH SIGNAL PROPAGATION VELOCITY [1-3]. WI
PROGRESS OF MICROWAVE DEVICES, THE DIELECTRIC MATERIALS USED FOR HIGHER FRE
HAVE ATTRACTED MUCH ATTENTION. MANY MICROWAVE CERAMICS WITH LOW DIELEC
RELATIVE PERMITTIVITY AS WELL AS LOW TEMPERATURE COEFFICIENT OF RESONANT
BEEN EXTENSIVELY STUDIED FOR SPECIFIC APPLICATIONS [3-5]. HOWEVER, THE S
REQUIREMENTS ON DIELECTRIC PROPERTIES LIMIT THE NUMBER OF MATERIALS AVAIL
FREQUENCY APPLICATIONS. THE DETAILED RESEARCH ON FLUORITE AND PEROVSKITE
ESSENTIALLY REACHED THE STATE OF ART THAT CAN BE ACHIEVED IN SUCH STRUCTU
NEW HIGH PERFORMANCE MATERIALS, SILICATES ARE CATCHING MUCH ATTENTION [4, 6
FORM THE LARGEST SINGLE GROUP OF MINERALS. IT IS COMMON PRACTICE TO CLASSIF
WELL AS OTHER MINERALS ACCORDING TO THE KINDS OF THEIR COORDINATION POLYHE
THESE POLYHEDRA ARE LINKED. BY CONTRAST, SiO_4 TETRAHEDRA AND SiO_6 OCTAHEDRA ARE THE
ONLY $[SiO_n]$ POLYHEDRA KNOWN TO EXIST IN SILICATES. MANY STUDIES WERE REPORTE
MICROWAVE DIELECTRIC PROPERTIES OF VARIOUS SILICATE BASED SYSTEMS [8-11] FOR S
MILLIMETER WAVE APPLICATIONS.

3.2 APATITE STRUCTURE

AMONG THE VARIOUS SILICATES INVESTIGATED SO FAR, RARE EARTH BASED OXY
RECEIVED MUCH ATTENTION DUE TO THE WIDE VARIETY OF PROPERTIES POSSESSED BY T
FORM A LARGE FAMILY OF ISOMORPHOUS COMPOUND WITH GENERAL FORMULA $A_{10}(MO_4)_6B_2$, WHERE
A REPRESENTS A DIVALENT CATION, M A TRIVALENT OR TETRAVALENT ANION. ONE OF THE M
CHARACTERISTICS OF THE APATITE STRUCTURE IS THAT IT ALLOWS A LARGE NUMBER O
ALL THE THREE SITES. SOME OF THESE SUBSTITUTIONS CAN BE REALIZED WITHOUT A
CATIONIC OR ANIONIC CHARGE. IT IS POSSIBLE TO SUBSTITUTE THE BIVALENT CATION W

CATION AND TRIVALENT ANION (PO$_4^{3-}$) WITH A TETRAVALENT ANION (SIO$_4^{4-}$). THIS EARLIER REPORT ALSO CONFIRMS THAT A SOLID SOLUTION EXISTS BETWEEN PHOSPHATE AND SILICATE A MINERALS OF THE APATITE GROUP ARE CHARACTERIZED BY A HIGH RESISTANCE TO CHE IN NEUTRAL TO ALKALINE ENVIRONMENTS AND BY THEIR POTENTIAL FOR RESTORING DAMAGES. FIG. 3.1 SHOWS A TYPICAL APATITE STRUCTURE. IN THE APATITE STRUCTU CATIONS ARE LOCATED IN TWO DIFFERENT SITES: 4F WITH 9-FOLD COORDINATION AND COORDINATION [14-15]. THE LARGE DIFFERENCE BETWEEN THESE TWO SITES IS THAT THE POSITION IS COORDINATED TO AN O(4) OXYGEN ION THAT IS PRESENT IN THE CHANN SOMETIMES CALLED 'FREE OXYGEN ION'. THIS OXYGEN ATOM DOES NOT BELONG TO A GROUP AND THE BINDING STRENGTH OF THE O(4) ION IS NOT SATURATED. THE NINE O COORDINATED TO THE 4F SITE ALL BELONG TO THE SILICATE GROUP. THIS DIFFERENCE INCREASE OF THE AVERAGE COVALENCY OF THE 6H SITE. ACCORDING TO FELSCHE [15], DIOXYAPATITE LN$_8$(SIO$_4$)$_6$O$_2$ [ME=MG, CA, SR AND BA; LN=LANTHANIDES), THE MG^{2+} IONS ARE ASSUMED TO BE IN 6H, BA^{2+} IN 4F. ON THE OTHER HAND, BLASSE [16] PROPOSED THAT THE ALKALINE EARTH METALS MAY BE FOUND IN 4F, EXCEPT TOO LARGE AND ME^{2+} IONS WHICH ARE TOO SMALL. IONS ARE ALSO EXPECTED TO BE FOUND IN 6H. HE ALSO PREDICTED THAT BY DOPING THESE COMPOUNDS WITH LN^{3+} IONS, THEY WILL ENTER THE 6H SITES IN ME$_2$LA$_8$(SIO$_4$)$_6$O$_2$ AND 4F SITES IN ME$_2$Y$_8$(SIO$_4$)$_6$O$_2$ [ME=MG, CA] RESPECTIVELY. THIS IS DUE TO THE FACT THAT LA^{3+} IS SMALLER THAN Y^{3+} AND LARGER THAN Y^{3+}. IN LATER REPORTS, THE DOPING RARE EARTH IONS (RE^{3+}) HAVE BEEN FOUND TO OCCUPY BOTH THE 4F AND 6H SITES I ME$_2$Y$_8$(SIO$_4$)$_6$O$_2$ [ME=MG, CA, SR] BY LUMINESCENCE SPECTROSCOPY [17-18].

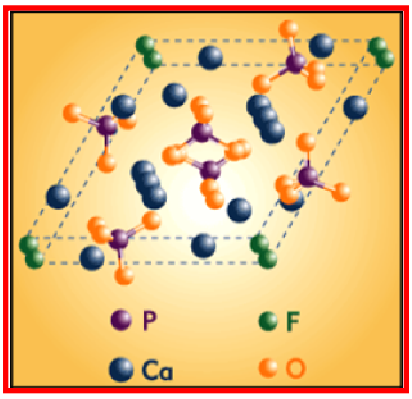

Fig. 3.1 The crystal structure of apatite.
(www.cea.fr/.../Clefs46/pagesg/clefs46_52.html)

THE AREAS OF POTENTIAL APPLICATION FOR APATITE MATERIALS ARE WIDE
BIOCERAMICS, LUMINESCENT HOST LATTICES, ETC. IN RECENT TIMES, CONSIDERABLE AT
TO THE RARE EARTH CONTAINING SILICATE AND GERMINATE APATITES DUE TO THEIR
CONDUCTIVITY. THE APATITE BASED SILICATES FIND MUCH INTEREST IN TECHNOLOGICA
SUCH AS FUEL CELLS, OXYGEN SENSORS AND IMPROVED ELECTROLYTES FOR USE IN SO
CELLS [19-22]. THE DOPED APATITE COMPOUNDS HAVE BEEN ESTABLISHED AS PRO
CANDIDATES FOR USE IN FLUORESCENT LAMP PHOSPHORS AND LASER TECHNOLOGY
BECAUSE OF THE NUMEROUS SUBSTITUTIONS OFFERED BY THE APATITE STRUCTURES,
HAVE ALREADY DEALT WITH THE OXYAPATITE MATERIALS. SOME OF THEM REPORT TH
CATIONIC SUBSTITUTIONS WITH SEVERAL LANTHANIDES OR DIVALENT CATIONS. THESE
THAT THE HIGHEST IONIC CONDUCTIVITY VALUES IN OXYAPATITES ARE CAUSED BY T
OXYGEN MIGRATION ALONG A NON-LINEAR PATHWAY. HOWEVER, NO ATTEMPT HAS BE
EXPLORE THE MICROWAVE DIELECTRIC PROPERTIES OF THIS GROUP OF MATERIALS. IN
STUDY WE FOCUS OUR ATTENTION ON THE SINTERABILITY, STRUCTURE AND DIELECTR
$ARE_4SI_3O_{13}$ [A = SR, CA AND BA; RE = RARE EARTHS] CERAMICS.

3.3 EXPERIMENTAL

THE $ARE_4SI_3O_{13}$ [A = SR, CA AND BA; RE = RARE EARTHS] CERAMICS WERE PREPARED B
THE CONVENTIONAL SOLID STATE CERAMIC ROUTE. $CACO_3$, $BACO_3$, $SRCO_3$
(ALDRICH CHEMICAL COMPANY INC., MILWAUKEE, WI; 99.9%), SI_2O_3 (99.9%, ALDRICH INC., ST.
LOUIS, MO; 99.9%), RARE EARTH OXIDES, PR_6O_{11}, ND_2O_3, EU_2O_3, GD_2O_3, TB_2O_3, DY_2O_3,
ER_2O_3, TM_2O_3, TB_2O_3 AND YB_2O_3 (TREIBACHER INDUSTRIES AG–9330, AITHOFEN, AUSTRIA;
99.99%;), LA_2O_3 AND SM_2O_3 (IRE, 99.9 %) CHEMICALS WERE MIXED BY BALL MILLING FOR 24
HOURS IN DISTILLED WATER MEDIUM USING ZIRCONIA BALLS. AFTER DRYING THE SLURR
POWDERS WERE CALCINED AT 1250 °C AND THEN GROUND WELL IN AN AGATE MORTAR. THE
POWDERS WERE THEN MIXED WITH 4 WT % POLYVINYL ALCOHOL (PVA), DRIED AND
UNIAXIALLY UNDER 150 MPA PRESSURE INTO PELLETS OF 20 MM DIAMETER AND 10 MM T
FOR MICROWAVE MEASUREMENTS. THE SINTERING WAS DONE IN THE TEMPERATURE R
1650 °C FOR 4 HOURS. THE BULK DENSITIES OF THE POLISHED SAMPLES WERE MEASURE
DIMENSIONAL METHOD. IN THE CASE OF THOSE SAMPLES WITH POOR SINTERABILITY, A S

(0.5 WT %) OF ZINC BOROSILICATE (50ZnO-40B_2O_3-10SiO_2) GLASS WAS ADDED TO THE CALCINED POWDER AND THE PELLETS WERE PREPARED AS BEFORE.

THE SINTERED SAMPLES WERE POWDERED AND USED TO ANALYZE THE CRYSTAL S PHASE PURITY BY X-RAY DIFFRACTION METHOD USING CU-Kα RADIATION. THE SAMPLES TO BE EXAMINED VIA THE TRANSMISSION ELECTRON MICROSCOPE (JEOL JEM-2100HR,) WERE PREPARE THINNING PELLETS TO ELECTRON TRANSPARENCY USING CONVENTIONAL CERAMOGRA FOLLOWED BY PRECISION ION POLISHING (GATAN MODEL 691). RIETVELD STRUCTURE WAS CONDUCTED USING THE BRUKER DIFFRACPLUS TOPAS 4.2 PROGRAM. SILICON 6 STANDARD POWDER FROM NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY WAS THE INSTRUMENT PARAMETERS USING A SIMPLE AXIAL MODEL. BACKGROUND WAS RE USING CHEBYCHEV FUNCTION, FOLLOWED BY REFINEMENT ON PEAK SHIFTS, INTENSITY SAMPLE CONVOLUTIONS, CELL PARAMETERS, CRYSTAL SIZE AND ATOMIC POSITIO PARAMETERS AND SITE OCCUPANCIES WERE FIXED DURING THE REFINEMENT PROCESS D OF SENSITIVITY ON OXYGEN SITES FOR XRD DATA. THE SINTERED SAMPLES WERE ET TEMPERATURE 25^{0}C BELOW THE SINTERING TEMPERATURE FOR 30 MINUTES AND THE SU MORPHOLOGY WAS RECORDED USING SCANNING ELECTRON MICROSCOPE. THE SINT POLISHED SAMPLES WERE USED FOR MICROWAVE DIELECTRIC PROPERTY MEASUREME AGILENT NETWORK ANALYZER AS DESCRIBED IN CHAPTER 2.

3.4 RESULTS AND DISCUSSION

3.4.1 MICROWAVE DIELECTRIC PROPERTIES OF $LnSr_4Sn_3O_{13}$ [Ln= LA, PR, ND, SM, EU, GD, TB, DY, ER, TM, YB AND Y]

THE CALCINATION AND SINTERING TEMPERATURES OF THE $LnSr_4Sn_3O_{13}$ CERAMICS ARE OPTIMIZED FOR THE BEST DENSIFICATION AND MICROWAVE DIELECTRIC PROP CALCINATION TEMPERATURE IS OPTIMIZED AT 1250^{0}C. FIG. 3.2.5 SHOWS THE OPTIMIZATION OF SINTERING TEMPERATURE OF A REPRESENTATIVE MATERIAL $LaSr_4Sn_3O_{13}$ (FIG. 3.2.5(A)) IT IS SEEN THAT AS THE SINTERING TEMPERATURE INCREASES, THE DENSITY INCREASES, REACHI VALUE AT 1325^{0}C AND THEREAFTER DECREASES. AT THIS TEMPERATURE THE RELATIVE DENS IT WAS REPORTED EARLIER THAT APATITE BASED MATERIALS ARE DIFFICULT TO SINTER PERMITTIVITY VARIATION WITH THE SINTERING TEMPERATURE ALSO SHOWS A SIMILA

RELATIVE PERMITTIVITY IS DEPENDENT ON THE RELATIVE DENSITY. THUS A MAXIM
PERMITTIVITY OF 14.2 IS EXHIBITED AT 1325 °C. FIG. 3.2 (B) SHOWS THE DEPENDENCE OF QUALITY
FACTOR OF $SrLa_4Si_3O_{13}$ CERAMICS WITH SINTERING TEMPERATURE. IT WAS REPORTED BY IDDL
[28] THAT ABNORMAL GRAIN GROWTH WAS MORE IMPORTANT FACTOR THAN THE PORE
QUALITY FACTOR OF MICROWAVE CERAMICS OVER 90% RELATIVE DENSITY. THE EXT
CAUSED BY THE DEFECTS IN CERAMICS EG. CRYSTAL DEFECTS, PORE, SUBSTITUTION OR
BOUNDARIES, SECONDARY PHASES ETC DOMINATES IN DETERMINING THE Q_u VALUE AS
A FUNCTION OF SINTERING TEMPERATURE IN THE MICROWAVE REGION. WHEN THE TE
INCREASED THE $Q_u \times f$ INCREASES INITIALLY AND THEN DECREASES. WITH THE INCREASE
SINTERING TEMPERATURE, FIRST THE PORES SHRINK AND THE GRAINS GREW LARGER
INCREASE IN THE QUALITY FACTOR. $SrLa_4Si_3O_{13}$ SHOWS A MAXIMUM QUALITY FACTOR OF NEARLY
26300 GHZ AT A SINTERING TEMPERATURE OF 1325 °C. THUS THE SINTERING TEMPERATURE OF
$SrLa_4Si_3O_{13}$ IS OPTIMIZED AT 1325 °C. IN A SIMILAR MANNER THE SINTERING TEMPERATURES
OTHER MATERIALS IN THE SERIES ARE ALSO OPTIMIZED. TABLE 3.1 GIVES THE OPTIMISE
TEMPERATURES OF THE SERIES $RELa_4Si_3O_{13}$ [RE = LA, PR, ND, SM, EU, GD, TB, DY, ER, TM, YB AND
Y] CERAMICS. THE SINTERING TEMPERATURES ARE FOUND TO BE IN THE RANGE 1325 – 165
TO BE NOTED THAT FOR RARE EARTH IONS HAVING LOWER IONIC RADIUS THE MATERIAL
SINTERING TEMPERATURE (°C) > 1500

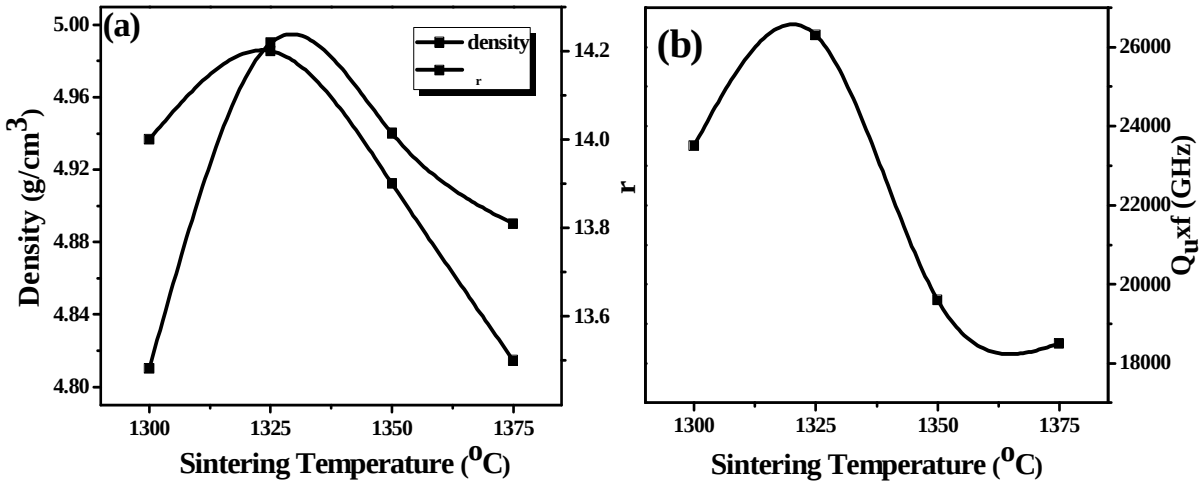

Fig. 3.2 The variation of (a) density, ε_R and (b) $Q_U XF$ of $SrLa_4Si_3O_{13}$ with sintering temperature.

FIGURE 3.3 SHOWS THE XRD PATTERNS OF $SrRE_4Si_3O_{13}$ [RE = LA, PR, ND, SM, EU, GD, TB, DY, ER, TM, YB AND Y] CERAMICS SINTERED AT THEIR RESPECTIVE OPTIMIZED SI TEMPERATURES. THE STRUCTURAL REFINEMENTS FOR $SrRE_4Si_3O_{13}$ BASED ON XRD DATA HAVE BEEN REPORTED [29-30], AND THEY HAVE HEXAGONAL SYMMETRY IN $P6_3/m$ SPACE GROUP AS SUCH, A SIMILAR HEXAGONAL UNIT CELL WAS ASSUMED HERE, AND DIFFRACTION INDEXED ACCORDINGLY.

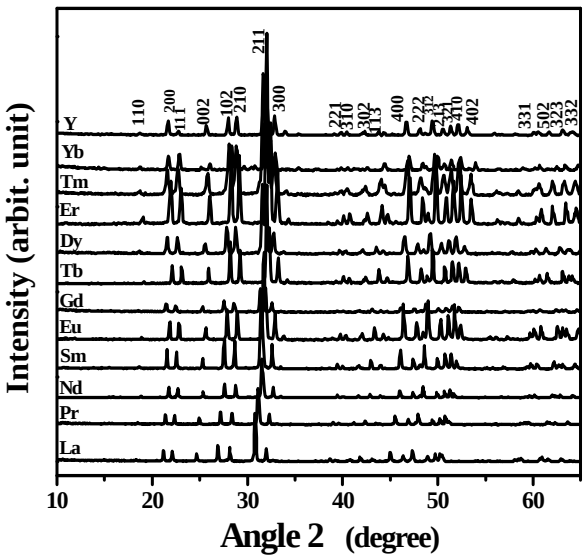

Fig. 3.3 XRD patterns of $SrRE_4Si_3O_{13}$ [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb and Y] ceramics.

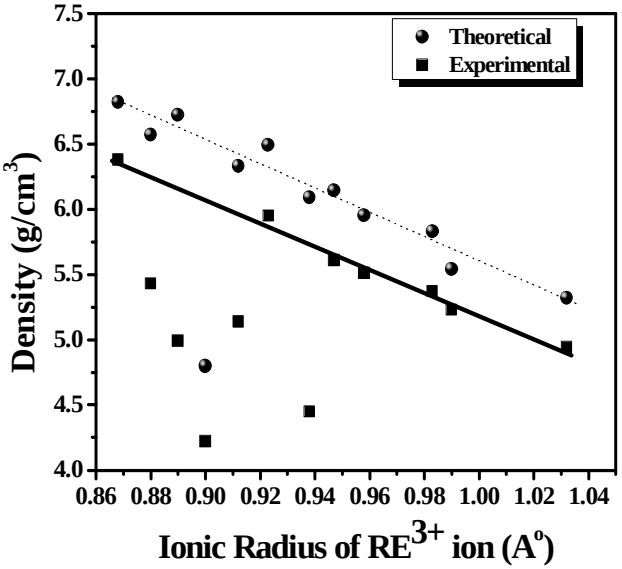

Fig. 3.4 The variation of theoretical and experimental density of $SrRE_4Si_3O_{13}$ [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb and Y] ceramics with the RE^{3+} ionic radius.

THE LATTICE PARAMETERS CALCULATED FROM THE XRD PATTERNS ARE TABULA 3.1. IT CAN BE SEEN THAT THE 'A' AND 'C' VALUES VARY FROM 9.6752 Å TO 9.2875 Å AND 7 Å TO 6.816 Å RESPECTIVELY WITH NO APPRECIABLE DEPENDENCE ON THE IONIC RADIUS O EARTH ION. A GRADUAL DECREASE IN THE LATTICE PARAMETER WITH THE IONIC RADIU ION IS EXPECTED. THE VARIATION IN 'C' IS SEEN TO BE MUCH MORE REGULAR THAN THE HOWEVER, THE RESULTS OBTAINED IN THE PRESENT STUDY ARE, TO SOME EXTENT, NOT WITH THE EARLIER REPORTS ON THE DEPENDENCE OF THE LATTICE PARAMETERS ON THE THE RARE EARTH IONS [15]. ONE OF THE REASONS FOR THIS ANOMALY MAY BE DUE TO T IN THE COORDINATION NUMBER EXHIBITED BY THE RE^{3+} IONS. THE EFFECTIVE RADIUS OF ANY ION DEPENDS ON BOTH THE COORDINATION NUMBERS OF THE CATION AND ANION. I

APATITE BASED MATERIALS THE IONS CAN OCCUPY DIFFERENT SITES EXHIBITIN COORDINATION NUMBERS [14-15]. HOWEVER, MORE DETAILED STRUCTURAL STUDIES AR EXPLAIN THIS PHENOMENON.

Table 3.1 The optimised sintering temperature, relative density and lattice parameters of $SrRE_4Si_3O_{13}$ [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb and Y] ceramics.

$SrRE_4Si_3O_{13}$	Sintering Temp. (^oC)	Ionic Radius of RE^{3+} (Å)	Relative Density (%)	Lattice parameters (Å)	
				a	c
$SrLa_4Si_3O_{13}$	1325 °C/4H	1.032	93	9.6752	7.1983
$SrPr_4Si_3O_{13}$	1325 °C/4H	0.990	94	9.5885	7.1072
$SrNd_4Si_3O_{13}$	1400 °C/4H	0.983	92	9.4698	7.0207
$SrSm_4Si_3O_{13}$	1375 °C/4H	0.958	93	9.4962	7.0071
$SrEu_4Si_3O_{13}$	1450 °C/4H	0.947	91	9.4073	6.9657
$SrGd_4Si_3O_{13}$	1525 °C/4H	0.938	73	9.5232	7.0087
$SrTb_4Si_3O_{13}$	1500 °C/4H	0.923	92	9.3327	6.8903
$SrDy_4Si_3O_{13}$	1475 °C/4H	0.912	81	9.4699	6.9551
$SrY_4Si_3O_{13}$	1575 °C/4H	0.900	85	9.2875	6.8160
$SrEr_4Si_3O_{13}$	1500 °C/4H	0.890	74	9.3501	6.8493
$SrTm_4Si_3O_{13}$	1650 °C/4H	0.880	83	9.4544	6.8874
$SrYb_4Si_3O_{13}$	1525 °C/4H	0.868	92	9.4109	6.8057

FIG. 3.4 SHOWS THE VARIATION OF THEORETICAL AND EXPERIMENTAL DENSITY WI RADIUS OF THE RARE EARTH IONS. THE THEORETICAL AND EXPERIMENTAL DENSITIES INCREASE IN THE IONIC RADII DUE TO (I) THE REPLACEMENT OF THE RARE EARTH ION WI AND (II) THE INCREASE IN THE UNIT CELL VOLUME. THE DENSITY OF $SrY_4Si_3O_{13}$ IS LOWER THAN THAT OF OTHER RARE EARTH SILICATES. THIS IS DUE TO THE FACT THAT YTTRIUM IS LIGHTER THE RARE EARTH ELEMENTS AND DOES NOT BELONG TO THE LANTHANIDE GROUP. FROM BE SEEN THAT $SrRE_4Si_3O_{13}$ [RE=LA, PR, ND, SM, EU, TB, YB] SHOWS A RELATIVE DENSITY ABOVE 90 % WHILE $SrRE_4Si_3O_{13}$ [RE=GD, DY, ER, TM, Y] SHOWS LOW VALUE OF RELATIVE DENSITY (< 85 %). NUMEROUS REPORTS ARE AVAILABLE BASED ON THE EFFECT OF GLASS

THE SINTERABILITY OF DIELECTRIC MATERIALS [31-32]. ADDITION OF SMALL AMOUNT (0
ZINC BOROSILICATE (ZBS) GLASS IMPROVED THE DENSITY OF THESE MATERIALS CONSIDE

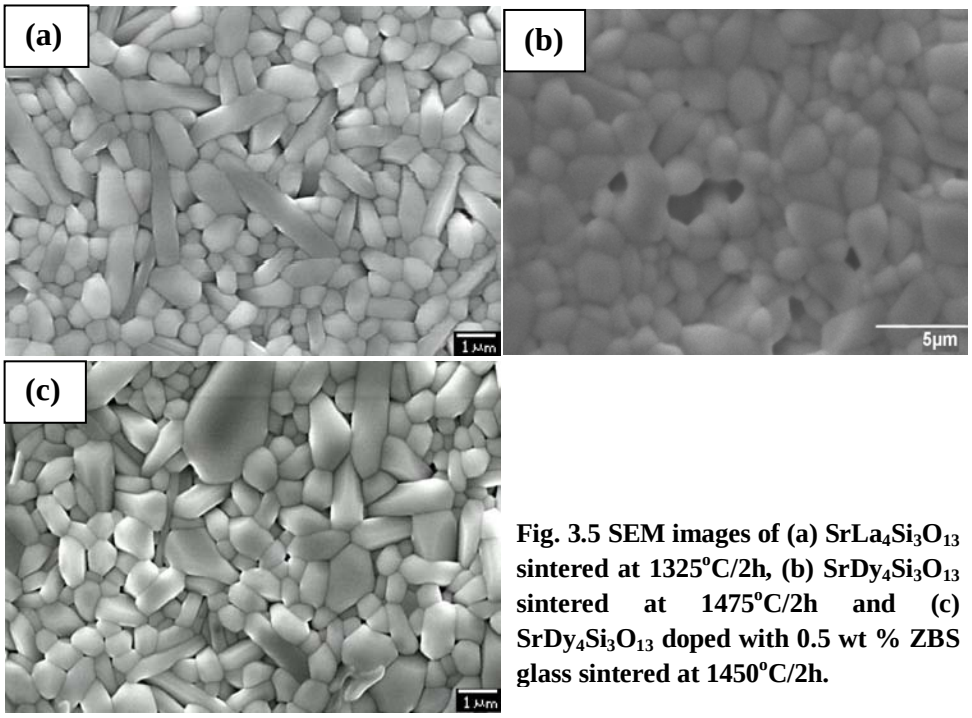

Fig. 3.5 SEM images of (a) $SrLa_4Si_3O_{13}$ sintered at 1325°C/2h, (b) $SrDy_4Si_3O_{13}$ sintered at 1475°C/2h and (c) $SrDy_4Si_3O_{13}$ doped with 0.5 wt % ZBS glass sintered at 1450°C/2h.

FIGURES 3.5 (A) AND (B) SHOW THE SEM IMAGES OF $SrLa_4Si_3O_{13}$ AND $SrDy_4Si_3O_{13}$ SINTERED AT 1325 AND 1475°C RESPECTIVELY. BOTH THE MICROSTRUCTURES REVEAL THE S PHASE NATURE OF THE MATERIALS. $SrLa_4Si_3O_{13}$ SHOWS A DENSE MICROSTRUCTURE WITH GRAIN SIZE VARYING FROM 1 TO 3 µM. THE MICROSTRUCTURE OF $SrDy_4Si_3O_{13}$ SHOWS A RELATIVELY POROUS BEHAVIOUR WHICH IS IN AGREEMENT WITH THE MEASURED DENSITY. FIG. 3.5 (C) SHOWS IMAGE OF 0.5 WT% ZINC BOROSILICATE (ZBS) GLASS ADDED $SrDy_4Si_3O_{13}$ CERAMICS. IT CAN BE SEEN THAT THE PORES HAVE BEEN ELIMINATED BY LIQUID PHASE SINTERING RESULTING IN THE DENSITY. NO SECONDARY PHASES ARE OBSERVED WHILE AN INCREASE IN THE G NOTED BY THE ADDITION OF GLASS FRITS.

FIGURE 3.6 SHOWS THE TEM IMAGES OF $SrLa_4Si_3O_{13}$ AND $SrDy_4Si_3O_{13}$ CERAMICS. THESE SAMPLES SHOW LARGE GRAINS AND CLEAR GRAIN BOUNDARIES, ALTHOUGH THERE I INTERGRANULAR POROSITY (FIG. 3.6 (B)), WHICH REFLECTS A SOMEWHAT POOR DENSIFIC AGREES WELL WITH THE RESULTS IN TABLE 3.1.

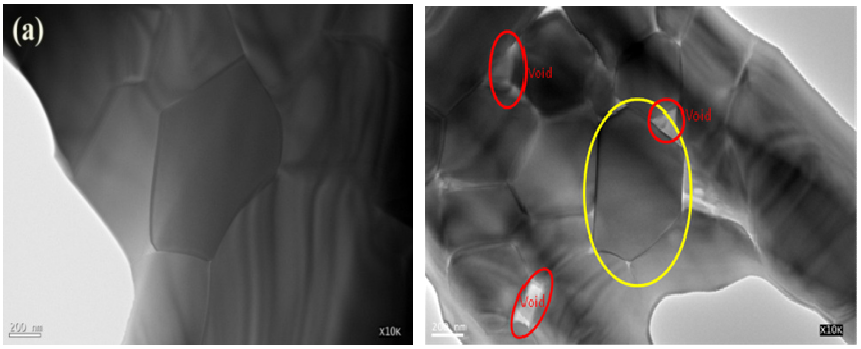

Figure 3.6 TEM images of (a) $SrY_4Si_3O_{13}$ and (b) $SrPr_4Si_3O_{13}$.

FIGURE 3.7 SHOWS SELECTED AREA ELECTRON DIFFRACTION PATTERNS (SADP) OF REPRESENTATIVE MATERIAL, $SrY_4Si_3O_{13}$, OBTAINED WITH THE BEAM PARALLEL TO (A) [110], (B) [011], (C) [120] AND (D) [001]. THE DIFFRACTION PATTERNS ARE IDENTICAL FOR ALL THE MATERIALS. SIX-FOLD SYMMETRY SHOWN IN THE [001] ELECTRON DIFFRACTION PATTERN SUGGESTS A HEXAGONAL CRYSTAL SYSTEM. CUBIC SPACE GROUPS ARE NOT CONSIDERED BECAUSE OF THE FOURFOLD SYMMETRY IN CUBIC PATTERNS. THERE ARE 25 TRIGONAL SPACE GROUPS AND 27 HEXAGONAL ONES. THE DIFFRACTION PATTERNS TAKEN PARALLEL TO [100] AND [120] SHOW CONSISTENT SYSTEMATIC ABSENCE:

$$00l: l = 2n$$

THE XRD OF THESE SAMPLES INDICATES THAT THE SELECTED REFLECTION SHOULD BE EXCLUDED SINCE {111} REFLECTIONS ARE ALLOWED AND KINEMATICALLY PRESENT, AS SHOWN IN 3.7 (B). MOREOVER, THE SYSTEMATIC PRESENCE OF $\bar{h}h0l: l = 2n$ REFLECTION [FIG. 3.7 (C) & (D)] LEAVES ONLY THE POSSIBLE SPACE GROUP, $P6_3$ (NO. 173), $P6_3/m$ (NO.176) OR $P6_322$ (NO.182). OF THESE GROUPS ONLY $P6_3/m$ (NO. 176) IS CENTROSYMMETRIC. AS DIELECTRIC LOSS MEASUREMENTS DO NOT SUGGEST PIEZOELECTRICITY, A CENTROSYMMETRIC SPACE GROUP IS THE MOST PROBABLE SOLUTION. TO FURTHER CONFIRM THE CRYSTAL STRUCTURE, RIETVELD REFINEMENTS WERE CARRIED OUT ON THE POWDER X-RAY DIFFRACTION DATA.

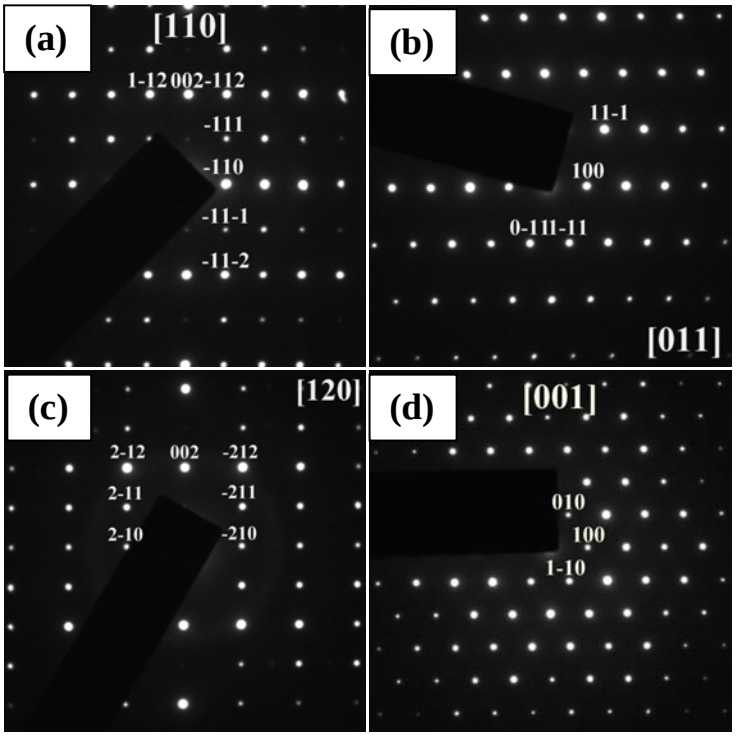

Fig. 3.7 Electron diffractions of $SrY_4Si_3O_{13}$ taken at (a) [110], (b) [011], (c) [120] and (d) [001].

THE FINAL REFINEMENT PARAMETERS AND ATOMIC COORDINATES FOR SAMPLES S$_4$Si$_3$O$_{13}$ (RE = Y, LA, PR, TB OR YB) ARE SUMMARIZED IN TABLES 3.2 AND 3.3. THE CORRESPOND FITTED DIFFRACTION PROFILES ARE SHOWN IN FIG. 3.8. THE RESULTS SUGGEST A HEXAG STRUCTURE IN $P6_3/m$ (NO.176) AND ARE IN GOOD AGREEMENT WITH THOSE OF MASUBUCHI *et al.* [33] AND SHEN *et al.* [29]. BOTH a AND c LATTICE CONSTANTS SHOW A LINEAR RELATIONSHIP W THE IONIC RADIUS OF THE RARE-EARTH ELEMENT (La^{3+}=1.032 Å, Pr^{3+}=1.0 Å, Y^{3+}=0.9 Å [39]). AS SUCH, THE CELL VOLUME INCREASES WITH INCREASING IONIC RADIUS. THE SUMMARY LENGTH AND BOND VALENCE FOR RE^{I}, SR^{II} AND SI-O POLYHEDRA AND BOND ANGLE OF O-SI-O TETRAHEDRA FROM RIETVELD REFINEMENT IS GIVEN IN TABLE 3.4. RE AND SR CATIONS S SITES AND FORM OCTAHEDRA WITH 6 OXYGEN IONS, INCLUDING THREE O1^{II} AND THREE SITE OCCUPIED ENTIRELY BY RE IONS IS COORDINATED TO SEVEN OXYGEN IONS, INCLUD ONE O2, FOUR O3 AND ONE O4. THE SI ION IS COORDINATED TO FOUR OXYGEN IONS, WHIC TETRAHEDRON WITH TWO OXYGEN IONS RESIDING ON O3 SITES AND THE OTHERS AT O1 DETAIL OF THE CRYSTAL STRUCTURE IS SHOWN IN FIG. 3.9. NOTE THAT RE IONS ARE ALL U

(TABLE 3.4), WHEREAS MOST SR IONS (EXCEPT IN THE CASE OF $SrLa_4Si_3O_{13}$) AND SR IONS (EXCEPT IN THE CASE OF $SrY_4Si_3O_{13}$) ARE OVER-BONDED. THESE DISCREPANCIES MIGHT BE ATTRIBUTED TO THE LACK OF ACCURACY IN THE REFINEMENT OF OXYGEN POSITIONS VIA XRD; HOWEVER, REFINEMENTS PRESENTED HERE ARE BASED ON THE ATOMIC COORDINATES OF $SrLa_4Si_3O_{13}$ OBTAINED FROM NEUTRON DIFFRACTION DATA BY MARSH [33], AND THE RESULTS ARE IN GOOD AGREEMENT WITH THE MODEL.

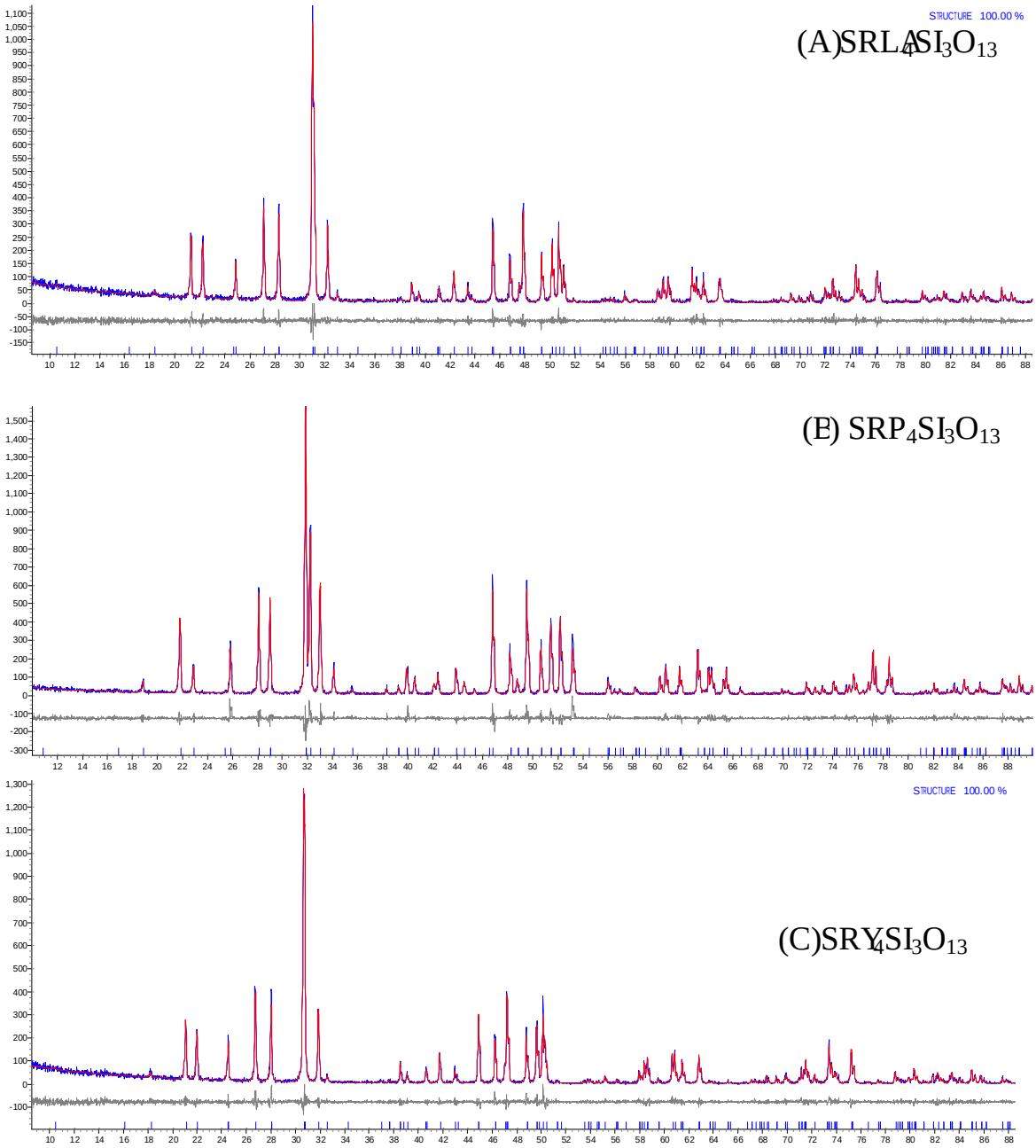

Fig. 3.8 Fitted diffraction profiles of (a) $SrLa_4Si_3O_{13}$ (b) $SrPr_4Si_3O_{13}$ and (c) $SrY_4Si_3O_{13}$, showing observed (blue), calculated (red), and difference (lower) profiles.

Table 3.2 Refined structure parameters for $SrRE_4Si_3O_{13}$ (RE=La, Pr and Y) at room temperature.

Compound	$SrLa_4Si_3O_{13}$	$SrPr_4Si_3O_{13}$	$SrY_4Si_3O_{13}$
R_{WP}(%)	19.53	19.84	18.76
R_{BRAG} (%)	3.787	3.757	4.557
GOF	1.10	1.09	1.20
SPACE GROUP	$P6_3/m$	$P6_3/m$	$P6_3/m$
CELL MASS (G)	1870.98	1887.01	1470.98
CELL VOLUME (Å^3)	590.12 (2)	571.15 (2)	524.26 (2)
CRYSTALLITE SIZ	1741.9	1837.3	1624.8
CRYSTALLITE D (G/CM^3)	5.2648 (2)	5.4863 (2)	4.6592 (2)
LATTICE PARAM			
A (Å)	9.7035 (2)	9.6098 (2)	9.3825 (1)
C (Å)	7.2369 (2)	7.1415 (2)	6.8767 (1)

Table 3.3 Refined atomic positions for $SrRE_4Si_3O_{13}$ (RE= La, Pr and Y) at room temperature.

Compound	$SrLa_4Si_3O_{13}$	$SrPr_4Si_3O_{13}$	$SrY_4Si_3O_{13}$
RE1/SR1, 4F (1/3, 2/3, Z)			
X	0.3333	0.3333	0.3333
Y	0.6667	0.6667	0.6667
Z	0.0007 (9)	0.0012 (11)	-0.0008 (7)
SITE OCCUPAN (RE/SR)	(0.5/0.5)	(0.5/0.5)	(0.5/0.5)
RE2, 6H (X, Y, 1/4			
X	0.0135 (4)	0.0102 (4)	0.0053 (4)
Y	0.2445 (3)	0.2431 (3)	0.2376 (3)
Z	0.2500	0.2500	0.2500
SITE OCCUPAN	1	1	1
SI, 6H (X, Y, 1/4			
X	0.4033 (13)	0.3987 (14)	0.3953 (8)
Y	0.3686 (14)	0.3710 (15)	0.3697 (8)
Z	0.2500	0.2500	0.2500
SITE OCCUPAN	1	1	1
O1, 6H (X, Y, 1/)			
X	0.3243 (29)	0.3201 (30)	0.3132 (16)
Y	0.4773 (27)	0.4788 (29)	0.4839 (16)
Z	0.2500	0.2500	0.2500
SITE OCCUPAN	1	1	1
O2, 6H (X, Y, 1/4			
X	0.5973 (29)	0.5871 (29)	0.5926 (16)
Y	0.4675 (29)	0.4634 (30)	0.4753 (16)
Z	0.2500	0.2500	0.2500
SITE OCCUPAN	1	1	1
O3, 12I (X, Y, Z			

TABLE 3.3 CONTINUED...

Compound	**$SrLa_4Si_3O_{13}$**	**$SrPr_4Si_3O_{13}$**	**$SrY_4Si_3O_{13}$**
X	0.3475 (18)	0.3409 (19)	0.3352 (11)
Y	0.2587 (20)	0.2555 (20)	0.2466 (11)
Z	0.0777 (20)	0.0688 (21)	0.0661 (11)
SITE OCCUPANCIES	1	1	1
O4, 2A (0, 0, 1/4			
X	0	0	0
Y	0	0	0
Z	0.2500	0.2500	0.2500
SITE OCCUPANCIES	1	1	1

Table 3.4 Selected bond lengths, bond valence and bond angles for $SrRE_4Si_3O_{13}$ (RE=La, Pr and Y).

Compound	**$SrLa_4Si_3O_{13}$**	**$SrPr_4Si_3O_{13}$**	**$SrY_4Si_3O_{13}$**
BOND LENGTH (Å) ^{I} (4F)-O			
A^{I}-O1 X 3	2.545 (21)	2.492 (22)	2.372 (12)
A^{I}-O2 X 3	2.513 (24)	2.510 (25)	2.473 (13)
BOND LENGTH (Å) ^{II} (6H) - O			
A^{II}-O1 X 1	2.718 (21)	2.704 (22)	2.648 (12)
A^{II}-O2 X 1	2.535 (24)	2.550 (24)	2.386 (13)
A^{II}-O3 X 2	2.536 (15)	2.426 (16)	2.337 (9)
A^{II}-O3 X 2	2.612 (17)	2.569 (18)	2.415 (10)
A^{II}-O4 X 1	2.310 (3)	2.288 (4)	2.205 (3)
BOND LENGTH (Å) OF SI-			
SI-O1	1.585 (37)	1.555 (38)	1.602 (20)
SI-O2	1.630 (27)	1.557 (27)	1.605 (20)
SI-O3 X 2	1.551 (17)	1.615 (17)	1.612 (9)
BOND ANGLES (º) OF O-			
O1-SI-O2	114.1 (15)	115.5 (16)	112.3 (8)
O1-SI-O3	109.8 (11)	110.1 (11)	111.5 (6)
O2-SI-O3	107.9 (11)	106.9 (11)	108.9 (6)
O3-SI-O3	106.9 (14)	107.1 (14)	103.3 (7)
BOND VALENCE OF			
RE-O ON A^{I}(4F)	1.144	1.125	1.018
SR-O ON A^{I}(4F)	0.989	1.066	1.330
RE-O ON A^{II} (4F)	2.649	2.754	2.691
SI-O	4.531	4.453	4.180

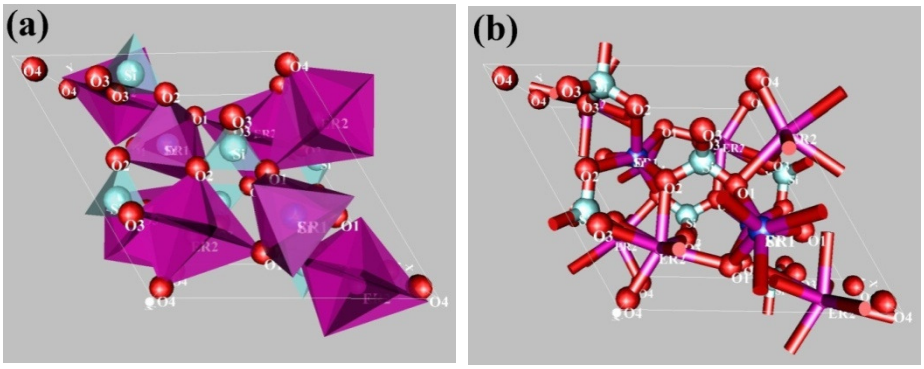

Fig. 3.9 The crystal structure of $SrRE_4Si_3O_{13}$ showing (a) polyhedral and (b) cation-oxygen bonds.

TABLE 3.5 GIVES THE MICROWAVE DIELECTRIC PROPERTIES OF $SrRE_4Si_3O_{13}$ [RE = LA, PR, ND, SM, EU, GD, TB, DY, ER, TM, YB AND Y] CERAMICS. FROM THE TABLE IT IS SEEN THAT EXPERIMENTAL RELATIVE PERMITTIVITY VARIES FROM 9.6 TO 15.6. THE CERAMIC COMPO EARTHS WITH HIGHER IONIC RADIUS EXHIBITED A HIGHER RELATIVE PERMITTIVITY TH ONE. AT MICROWAVE FREQUENCY, THE RELATIVE PERMITTIVITY IS DEPENDENT ON POLARIZABILITY, DENSITY AND PRESENCE OF SECONDARY PHASES. THE ε_r IS SYMMETRIC FOR $SrPrSi_3O_{13}$ AND MINIMUM FOR $SrDyRE_4Si_3O_{13}$ CERAMICS. $SrLaRE_4Si_3O_{13}$ CERAMIC HAS A LOW RELATIVE PERMITTIVITY WHEN COMPARED TO THAT OF $SrRE_4Si_3O_{13}$ DUE TO THE HIGH IONIC POLARIZABILITY VALUE OF La^{3+} WITH RESPECT TO RE^{3+}. VILLARS *et al*. REPORTED [34] THAT A MORE CORRECT VALUE OF THE DIELECTRIC POLARIZABILITY OF LA IS 4.82 IN REPORTED BY SHANNON [35]. IN ORDER TO NULLIFY THE EFFECT OF POROSITY ON THE REL PERMITTIVITY VALUES, *et al*. [36] PROPOSED A CORRECTION FACTOR WHICH IS GIVEN AS:

$$\varepsilon_m = \varepsilon_c\left[1-\frac{3P(\varepsilon_c-1)}{2\varepsilon_c+1}\right] \qquad (3.1)$$

WHERE ε_c IS THE RELATIVE PERMITTIVITY OF THE COMPOSITE WHICH CONTAINS A POROSITY P, ε_m IS THE ACTUAL RELATIVE PERMITTIVITY OF THE DIELECTRIC. THE RELATIVE PERMITTIVITIE CONSIDERED ARE CORRECTED FOR POROSITY AND ARE GIVEN IN TABLE 3.5. THE POROSI RELATIVE PERMITTIVITY OF THESE MATERIALS VARIES FROM 12.9 TO A MAXIMUM VALUE RELATIVE PERMITTIVITY IS NOT ONLY DEPENDENT ON THE IONIC POLARIZABILITIES, BU RATTLING EFFECT WHICH COULD BE EXPLAINED BASED ON THE BOND VALENCE OF THE

THE BASIS OF THE REFINED CRYSTAL STRUCTURE PARAMETERS AND BOND VALENCE T
STRENGTH AND COVALENCE OF THE CATION-OXYGEN BONDS ARE DETERMINED USING
EQUATIONS [37]:

$$V_{ij} = \sum_j S_{ij} \tag{3.2}$$

$$S_{ij} = \mathrm{EXP}\left[\left(R_{ij} - d_{ij}\right)/b\right] \tag{3.3}$$

$$f_c = aS_{ij}^{M} \tag{3.4}$$

WHERE R_{ij} IS THE BOND VALENCE PARAMETER, d_{ij} IS THE BOND LENGTH, $b = 0.37$ Å IS THE UNIVERSAL CONSTANT, f_c IS THE COVALENCE, AND 'a' AND 'M' ARE EMPIRICALLY DETERMINED PARAMETERS AND DEPEND ON THE NUMBER OF CORE ELECTRONS IN THE CATION. PREVIOUSLY REPOR BOND VALENCE PARAMETERS 'a' AND 'M' ARE USED [37]. THE AVERAGE BOND STRENGTH CAN BE CALCULATED WITH THE AVERAGE BOND VALENCE SUM DIVIDED BY THE AVERAGE CATIO NUMBER. THE AVERAGE BOND STRENGTH AND COVALENCE OF $SrY_4Si_3O_{13}$, $SrLa_4Si_3O_{13}$ AND $SrY_4Si_3O_{13}$ ARE SHOWN IN TABLE 3.6. IT IS CLEAR FROM THE TABLE THAT THE SI-O BOND ST MUCH LARGER WHEN COMPARED WITH THE RE-O AND SR-O. THE BOND VALENCE IS NO MEASURE OF NUMBER OF ELECTRONS ASSOCIATED WITH A BOND, BUT ALSO THE DEGREE THE COVALENCE OF THE VARIOUS BONDS ARE CALCULATED BY THE METHOD PROPOSED SHANNON [38]. FROM THE TABLE IT IS SEEN THAT THE SI-O BOND SHOWS A COVALENCE C ABOUT 59% FOR $SrLa_4Si_3O_{13}$ WHICH DECREASES GRADUALLY ON CHANGING La^{3+} IONS WITH RE IONS THUS DECREASES.
THUS WITH THE DECREASE IN COVALENCE AN INCREASE IN RELATIVE PERMITTIVITY HOWEVER, THIS IS NOT SATISFIED BY $SrLa_4Si_3O_{13}$ EVEN IF WE CONSIDER THE POROSITY CORRECTED VALUE. THUS IT CAN BE CONCLUDED THAT BOTH THE POLARIZABILITY AND BOND CONTRIBUTING TO THE RELATIVE PERMITTIVITY OF THESE MATERIALS.

Table 3.5 The optimised microwave dielectric properties of $SrRE_4Si_3O_{13}$ [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb and Y] ceramics.

$SrRE_4Si_3O_{13}$	$Q_u \times f$ (GHz)	Relative permittivity (ε_R)	Corrected Relative permittivity (ε_{RCORR})	τ_f (ppm/°C)
$SrLa_4Si_3O_{13}$	26300	14.2	15.7	-46
$SrPr_4Si_3O_{13}$	12200	15.6	17.0	-9
$SrNd_4Si_3O_{13}$	21000	15.5	17.4	-29
$SrSm_4Si_3O_{13}$	20800	13.5	14.9	-28
$SrEu_4Si_3O_{13}$	20700	14.8	17.8	-24
$SrGd_4Si_3O_{13}$	8800	12.6	18.2	-20
$SrTb_4Si_3O_{13}$	19300	14.3	16.1	6
$SrDy_4Si_3O_{13}$	9200	9.6	12.9	28
$SrY_4Si_3O_{13}$	20500	12.6	15.8	-18
$SrEr_4Si_3O_{13}$	18100	10.4	16.1	-24
$SrTm_4Si_3O_{13}$	14400	11.2	14.5	-20
$SrYb_4Si_3O_{13}$	11400	13.1	14.7	-25

Table 3.6 The average bond strength and covalence of RE-O, Sr-O, Si-O bonds in $SrRE_4Si_3O_{13}$ [RE=La, Pr and Y] ceramics.

Material	Average bond strength				Covalence (v. u)*			
	$\langle S^I_{RE-O} \rangle$	$\langle S^{II}_{RE-O} \rangle$	$\langle S_{SR-O} \rangle$	$\langle S_{Si-O} \rangle$	f_c^I, $_{RE-O}$	f_c^{II}, $_{RE-O}$	f_c, $_{SR-O}$	f_c, $_{Si-O}$
$SrLa_4Si_3O_{13}$	0.1271	0.3784	0.1099	1.1328	0.0192 (15.1%)	0.1066 (28.2%)	0.0153 (13.9%)	0.6625 (58.5%)
$SrPr_4Si_3O_{13}$	0.1250	0.3934	0.1184	1.1133	0.0187 (15%)	0.1133 (28.8%)	0.0172 (14.5%)	0.6439 (57.8%)
$SrY_4Si_3O_{13}$	0.1131	0.3844	0.1478	1.045	0.0160 (14.2%)	0.1092 (28.4%)	0.0244 (16.5%)	0.5804 (55.5%)

*THE PERCENTAGE COVALENCIES ARE SHOWN IN PARENTHESES.

$SrRE_4Si_3O_{13}$ (RE=LA, ND, SM, EU AND SM) SHOWED A REASONABLY GOOD $Q_u \times f$ (> 20000 GHZ) WITH A MAXIMUM VALUE OF 26300 GHZ FOR $SrLa_4Si_3O_{13}$ CERAMIC. THE

DIELECTRIC LOSSES AT MICROWAVE FREQUENCIES ARISE MAINLY FROM THREE MECHAN
DUE TO ANHARMONIC LATTICE FORCES IN PERFECT CRYSTAL, (II) EXTRINSIC LOSSES DU
SECONDARY PHASES, GRAIN BOUNDARIES AND INCLUSIONS IN REAL INHOMOGENEOUS
(III) LOSSES IN REAL BUT HOMOGENEOUS CRYSTALS CAUSED BY POINT DEFECTS SUCH
ATOMS AND VACANCIES [39]. AMONG THESE THE FORMER IS RELATED TO THE CRYSTAL
BONDING CHARACTER OF THE MATERIAL. IN GENERAL, STRONGER BOND INDICATES
CONSTANT IF THE NATURE OF BOND IS SIMILAR IN THE SAME SERIES. A LARGER FORCE C
IMPLIES A LOWER DAMPING CONSTANT RESULTING IN A LOWER DIELECTRIC LOSS. ALSO
BY SCHLOMANN [40] SHOWS THAT THE RANDOM DISTRIBUTION OF DIVALENT AND TRIVA
EQUIVALENT SITE CONTRIBUTES TO THE DIELECTRIC LOSSES EVEN WHEN ELECTRO
CONDUCTION ARE COMPLETELY SUPPRESSED. THESE MATERIALS WITH APATITE STRU
RANDOM DISTRIBUTION OF IONS IN THE 4F AND 6H SITES WHICH MAY CONTRIBUTE T
LOSSES. IN THE PRESENT CASE ALMOST ALL MATERIALS EXCEPT $SrLa_4Si_3O_{13}$ AND $Sr_4La_6Si_6O_{26}$ SHOW
A $Q_u \times f$ OF NEARLY 20000 GHZ WITH A LOW RELATIVE DENSITY LESS THAN 94 %. HOW
$SrGd_4Si_3O_{13}$ AND $SrDy_4Si_3O_{13}$ EXHIBIT LOW $Q_u \times f$ OF 8800 AND 9200 GHZ RESPECTIVELY. ONE
OF THE REASONS MAY BE DUE TO THE POOR DENSIFICATION OF THESE COMPOUNDS (SEE T

IT IS WELL KNOWN THAT THE TEMPERATURE COEFFICIENT OF RESONANT FREQUE
TEMPERATURE DEPENDENCE OF RELATIVE PERMITTIVITY AND THERMAL EXPANSION C
42]. LOW PERMITTIVITY MATERIALS GENERALLY HAVE A POSITIVE τ_ε VALUE AND HIGH PERMITTIVITY
MATERIALS (> 20) HAVE A MORE NEGATIVE τ_ε VALUE [40]. *et al.* [40] WAS PROPOSED THAT THE ION
COORDINATION NUMBER AND BONDING CHARACTER ARE THE MAIN SOURCES OF THE DI
ADDITIONALLY, *et al.* [43] REPORTED LOWER VALENCE AND MORE UNDERBONDED (SMA
BOND VALENCE SUM) IONS INFLUENCE A MORE NEGATIVE τ_f VALUE IN THE PEROVSKITE SYSTEM. FROM
TABLE 3.6 IT IS CLEAR THAT $SrLa_4Si_3O_{13}$ CERAMICS EXHIBITS A HIGH VALUE OF BOND VALENCE SU
WHEN COMPARED TO THAT OF $SrGd_4Si_3O_{13}$ AND $SrDy_4Si_3O_{13}$ CERAMICS AND IT EXHIBITS A LOW τ_f
VALUE OF -9 PPM/ AS FAR AS THE DIELECTRIC CERAMICS ARE CONCERNED, τ_f IS MAINLY
DEPENDENT ON τ_ε VALUE OWING TO THE NEGLIGIBLE MAGNITUDE OF THERMAL EXPA
COEFFICIENT. ACCORDING TO BOSMAN AND HAVINGA [44, 45], TWO MAIN EFFECTS
CONTRIBUTE TO THE TEMPERATURE DEPENDENCE OF RELATIVE PERMITTIVITY. AMO
VOLUME-DEPENDENT CONTRIBUTION PLAYS A DOMINATING ROLE. AS CELL VOLUME I
NUMBER OF POLARIZABLE PARTICLES PER UNIT VOLUME DECREASES LEADING TO THE

POLARIZABILITY. HENCE THE RELATIVE PERMITTIVITY AND τ_ε INCREASES AND τ_f SHIFTS TO POSITIVE SIDE.

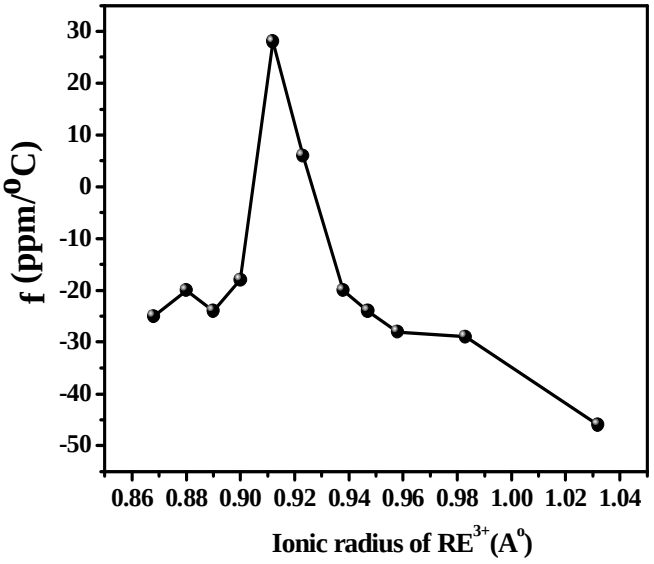

Fig. 3.10 The variation of τ_F of $SrRE_4Si_3O_{13}$ with ionic radius of rare earth ions.

THE TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY OF $SrRE_4Si_3O_{13}$ IS PLOTTED AS A FUNCTION OF THE RE^{3+} IONIC RADIUS IN FIG. 3.10. τ_f VALUE INCREASES TO POSITIVE VALUE (-25 TO +28 PPM/°C) WITH THE RE^{3+} IONIC RADII UPTO r_{Dy} = 0.912 Å AND THEN INCREASES TO NEGATIVE VALUE (+6 TO -46 PPM/°C) UPTO r_{La} = 1.032 Å. THIS IS IN ACCORDANCE WITH THE VARIATION OBSERVED IN $CA(B'_{1/2}TA_{1/2})O_3$ [B'=LANTHANIDES, Y AND IN] BY *KHALYAM ET AL* [45] WHERE THEY NOTED AN INTERSUBSTITUTION BETWEEN THE CA AND THE B' IONS. IN THE PRESENT CASE THE DI CAN OCCUPY DIFFERENT SITES AS MENTIONED EARLIER. THE REFINEMENT STUDIES ALS INTERSUBSTITUTION BETWEEN THE Sr^{2+} AND RE^{3+}.

THE DENSITIES OF THESE SAMPLES BY THE ADDITION OF DIFFERENT (0.2, 0.5, 1, 3) W VARIOUS GLASSES SiO_2, ZBS, LBS ARE MEASURED. IT WAS OBSERVED THAT THE SAMPLE SHOWED A MAXIMUM DENSIFICATION AND GOOD DIELECTRIC PROPERTY FOR 0.5 WT% ADDITION. FURTHER INCREASE IN THE AMOUNT OF GLASS DETERIORATED THE QUALI ADDITION OF SMALL WEIGHT % OF ZBS GLASS IMPROVED THE DENSITY OF THE MATERI EXTENT. THE SINTERING TEMPERATURE, RELATIVE DENSITY AND MICROWAVE DIELECTR GLASS ADDED CERAMICS ARE GIVEN IN TABLE 3.7. THE SINTERING TEMPERATURE LOWE 100°C BY GLASS ADDITION. A MARKABLE INCREASE IN DENSITY IS NOTED FOR SRTM $SRY_4SI_3O_{13}$ WHICH CAN BE ATTRIBUTED TO THE LIQUID PHASE SINTERING OCCURRING

COMPOSITES. HOWEVER, ONLY A MARGINAL RISE IS OBTAINED FOR $SrRE_4Si_3O_{13}$ (RE = LA, SM, EU AND ER). THE RELATIVE PERMITTIVITY OF THE GLASS ADDED COMPOSITES ALSO SHO INCREASE DUE TO THE INCREASE IN RELATIVE DENSITY. IN THE CASE OF $SrRE_4Si_3O_{13}$ (RE = LA, SM AND RELATIVE PERMITTIVITY IS NOTED WHICH MAY BE DUE TO THE DECREASE IN DENSITY. IT NOTED THAT GLASSES IN GENERAL HAS A LOW RELATIVE PERMITTIVITY [47]. FROM THE T SEEN THAT $Q_u x f$ FOR $SrLa_4Si_3O_{13}$ INCREASES FROM 19300 TO 23500 GHZ AND THAT FOR $SrNd_4Si_3O_{13}$ INCREASES FROM 14400 TO 16500 GHZ. IT MAY BE NOTED THAT IN THE CASE MATERIALS WITH ONLY SLIGHT IMPROVEMENT IN DENSITY, THE QUALITY FACTOR IMPROVED. THE RELATIVE DENSITY OF $SrEu_4Si_3O_{13}$ INCREASES FROM 74 TO 77 % WITH AN IMPROVEMENT IN $Q_u x f$ VALUE FROM 18100 TO 21000 GHZ. HOWEVER, THE τ_f OF THE MATERIALS ARE NOT MUCH AFFECTED BY THE GLASS ADDITION.

Table 3.7 The optimised sintering temperature, density and microwave dielectric properties of glass added $SrRE_4Si_3O_{13}$ [RE = La, Nd, Sm, Eu, Tb, Dy, Er, Tm, Yb and Y] ceramics.

$SrRE_4Si_3O_{13}$ + 0.5 wt% ZBS	Sintering Temp. (^oC)	Relative Density (%)	$Q_U X F$ (GHz)	Relative permittivity (ε_R)	τ_F (ppm/^oC)
$SrLa_4Si_3O_{13}$	1300 ^{C}C/4H	95	25800	14.7	-40
$SrNd_4Si_3O_{13}$	1350 ^{C}C/4H	90	20500	13.9	-33
$SrSm_4Si_3O_{13}$	1350 ^{C}C/4H	92	21800	13.9	-28
$SrEu_4Si_3O_{13}$	1425 ^{C}C/4H	92	19800	14.2	-22
$SrTb_4Si_3O_{13}$	1425 ^{C}C/4H	92	23500	14.3	10
$SrDy_4Si_3O_{13}$	1425 ^{C}C/4H	86	9500	13.0	28
$SrY_4Si_3O_{13}$	1475 ^{C}C/4H	90	21500	13.5	-18
$SrEr_4Si_3O_{13}$	1475 ^{C}C/4H	77	21000	11.2	-20
$SrTm_4Si_3O_{13}$	1575 ^{C}C/4H	92	16500	12.8	-26
$SrYb_4Si_3O_{13}$	1425 ^{C}C/4H	92	12000	12.9	-27

3.4.1.1 TAILORING THE τ_f BY TiO_2 ADDITION

IT IS EVIDENT FROM TABLE 3.2 THAT $SrLa_4Si_3O_{13}$ CERAMICS HAS A RELATIVELY HIGH $Q_u x f$ OF 26300 GHZ, ε_r OF 14.2 AND A HIGH τ_f OF -46 PPM/^oC. IT IS POSSIBLE TO TUNE THE τ_f TO ZERO

BY THE ADDITION OF SUITABLE AMOUNT OF MATERIALS SUCH AS THE TiO_2. THE $SrLa_4Si_3O_{13}$ HAS ε_r OF 10[illegible], $Q_u \times f$ OF 26900 GHZ AND τ_f OF +411 PPM/°C [3]. SINCE TiO_2 IS WELL KNOWN AS A SINTERING AID TO IMPROVE THE SINTERABILITY OF THE BASE CERAMIC MATE[illegible] SINTERING TEMPERATURE OF $SrLa_4Si_3O_{13}$ CERAMIC DECREASES FROM 1325 TO 1225°C WITH INCREASE IN TiO_2 CONTENT. THE XRD PATTERNS OF $SrLa_4Si_3O_{13}$ MIXED WITH 8 WT % TiO_2 AND SINTERED AT 1225°C/4H IS SHOWN IN FIG. 3.11. THE FIGURE INDICATES THE NON-REACTIVITY OF SRLA[illegible] WITH TiO_2. THE TiO_2 PHASES ARE INDEXED BASED ON THE JCPDS FILE NO. 76-1934. THE DENSITY OF THE MIXTURE IS CALCULATED ACCORDING TO THE EQUATION:

$$\rho_{mixture} = V_1 \rho_1 + V_2 \rho_2 \qquad (3.5)$$

WHERE $\rho_{mixture}$ IS THE CALCULATED THEORETICAL DENSITY OF THE MIXTURE, V_1, V_2 AND ρ_1, ρ_2 ARE THE VOLUME FRACTIONS AND DENSITIES OF $SrLa_4Si_3O_{13}$ AND TiO_2 RESPECTIVELY. THE VARIATION OF THEORETICAL AND EXPERIMENTAL DENSITIES OF THE MIXTURE AS A FUNCTION OF THE A[illegible] IS SHOWN IN FIG. 3.12. THE THEORETICAL DENSITY DECREASES WITH THE ADDITION OF TiO_2 DUE TO THE LOWER DENSITY POSSESSED BY TiO_2 (4.23 G/CM^3) COMPARED TO THAT OF $SrLa_4Si_3O_{13}$ (5.32 G/CM^3). HOWEVER, A SMALL INCREASE IN THE EXPERIMENTAL DENSITY IS ADDITIONALLY OBTAINED FOR 5 WT% TIO[illegible] THE RELATIVE DENSITY REACHES A MAXIMUM VALUE OF 95 % AT THIS COMPOSITION AN[illegible] DECREASES.

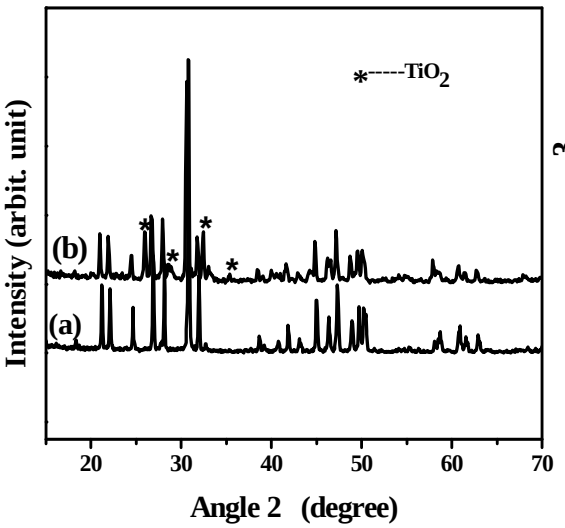

Fig. 3.11 XRD patterns of (a) $SrLa_4Si_3O_{13}$ ceramics sintered at 1325°C and (b) $SrLa_4Si_3O_{13}$ + 8 wt% TiO_2 sintered at 1225°C.

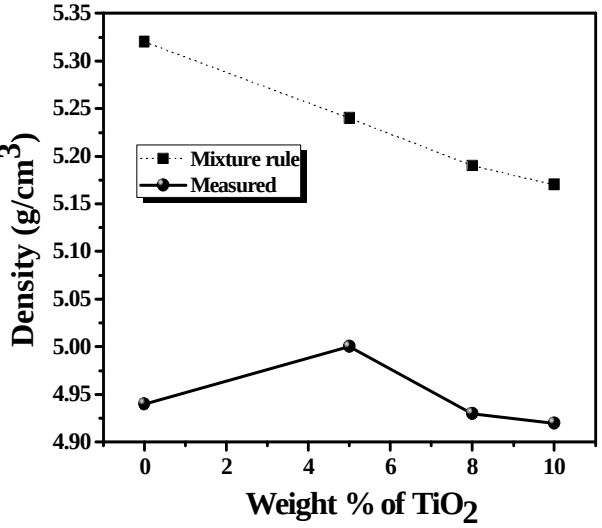

Fig. 3.12 The variation of theoretical and experimental densities of $SrLa_4Si_3O_{13}$ with TiO_2 addition.

FIGURE 3.13 SHOWS THE VARIATION OF THE MICROWAVE DIELECTRIC PROPE
$SrLa_4Si_3O_{13}$ AS A FUNCTION OF THE AMOUNT OF TiO_2 ADDITION. THE RELATIVE PERMITTIVITY OF THE
MIXTURE SHOWS A LINEAR INCREASE AS THE TiO_2 CONTENT INCREASES AS SHOWN IN FIG.
3.13 (A). THIS IS EXPECTED SINCE THE ε_r OF TiO_2 IS MUCH HIGHER AS COMPARED WITH
$SrLa_4Si_3O_{13}$. THE ε_r INCREASES FROM 14.2 TO 23.4 AS THE AMOUNT OF TiO_2 INCREASES AND
REACHES 10 WT%. THE ε_r OF THE MIXTURE IS CALCULATED USING THE SERIAL MIXING RUL
GIVEN AS:

$$\varepsilon_{mixture} = V_1 \varepsilon_1 + V_2 \varepsilon_2 \qquad (3.6)$$

WHERE $\varepsilon_{mixture}$, ε_1 AND ε_2 ARE THE RELATIVE PERMITTIVITY OF THE MIXTURE, $SrLa_4Si_3O_{13}$ AND TiO_2
RESPECTIVELY. FIG. 3.13 (A) ALSO COMPARES THE CALCULATED AND MEASURED
PERMITTIVITIES OF THE MIXTURE AS A FUNCTION OF TiO_2 ADDITION. THE CALCULATED VALUES ARE
FOUND TO DEVIATE SLIGHTLY FROM THE EXPERIMENTAL VALUES. THIS IS BECAUSE THE
DOES NOT INCLUDE THE POROSITY IN THE COMPOSITE. THE UNLOADED QUALITY
$SrLa_4Si_3O_{13}$ IS PLOTTED AS A FUNCTION OF TiO_2 CONTENT IN FIG. 3.13 (A). AS THE TiO_2 CONTENT
INCREASES FROM 0 TO 10 WT%, THE $Q_u \times f$ GRADUALLY DECREASES FROM 26000 TO 12000 GHZ. IT
IS TO BE NOTED AT THIS POINT OF DISCUSSION THAT THE $Q_u \times f$ VALUE DEPENDS ON THE SYNTHESIZING
CONDITIONS, PURITY OF CHEMICALS AND Ddensification OF THE SAMPLES DURING SINTE
FOLLOW ANY MIXTURE RULE.

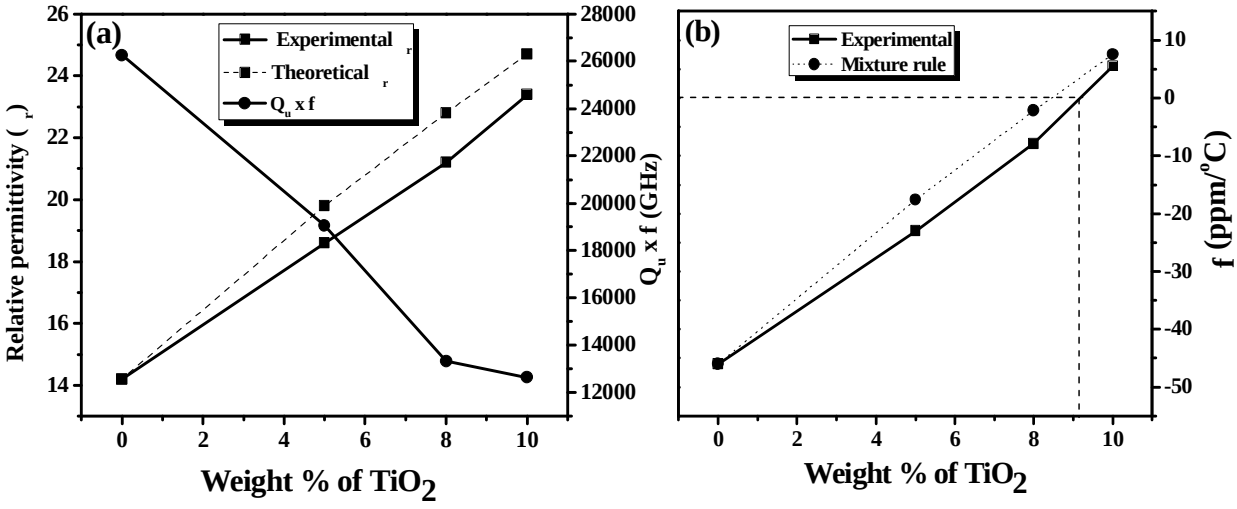

Fig. 3.13 The variation of (a) relative permittivity, $Q_U \times f$ and (b) τ_f of $SrLa_4Si_3O_{13}$ with TiO_2 addition.

THE DEPENDENCE OF τ_f ON THE AMOUNT OF TiO_2 IS SHOWN IN FIG. 3.13 (B). THE τ_f OF $SrLa_4Si_3O_{13}$ BECOMES LESS NEGATIVE WITH THE INCREASE IN THE TiO_2 CONTENT DUE TO THE HIGH POSITIVE τ_f VALUE OF TiO_2 (+400PPM/°C). THE τ_F OF THE MIXTURE PHASES IS COMPUTED USING THE GENERAL MIXING FORMULA [48]:

$$\tau_{f,mixture} = V_1 \tau_{f1} + V_2 \tau_{f2} \qquad (3.7)$$

WHERE $\tau_{f,mixture}$, τ_{f1} AND τ_{f2} ARE THE TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY OF MIXTURE, $SrLa_4Si_3O_{13}$ AND TiO_2 RESPECTIVELY. THE EXPERIMENTAL AND THE MEASURED τ_f VALUES ARE COMPARED IN FIG. 3.13 (B). BOTH ARE FOUND TO BE MATCHING. THE τ_f OF THE MIXTURE VARIES FROM -46 PPM/°C TO A MAXIMUM OF +7.5 PPM/°C FOR 10 WT% TiO_2 ADDITION. FROM THE CURVE IT CAN BE INFERRED THAT τ_f IS OBTAINED ZERO FOR TiO_2 CONTENT OF 9 WT%.

3.4.2 MICROWAVE DIELECTRIC PROPERTIES OF $(CaSrBa)RE_4Si_3O_{13}$ [RE = RARE EARTHS]

FIGURES 3.14 (A) AND (B) RESPECTIVELY SHOW THE X-RAY DIFFRACTION PATTERNS OF $CaRE_4Si_3O_{13}$ [RE = LA, PR, ND, SM, EU, TB, DY, TM, YB AND Y] AND $SrRE_4Si_3O_{13}$ [RE = LA, PR, ND, SM] CERAMICS. ALL THE PEAKS ARE INDEXED COMPARING WITH THAT OF THE PEAKS OF $CaLa_4Si_3O_{13}$ (JCPDS 71-1368) WITH HEXAGONAL SYMMETRY. IT CAN BE SEEN THAT ALL THE COMPOUNDS IN THE SERIES BELONG TO THE HEXAGONAL SYMMETRY WITH SPACE GROUP $P6_3/m$ AS SEEN IN THE CASE OF $SrLa_4Si_3O_{13}$. HOWEVER, IT IS INTERESTING TO NOTE THAT AS THE IONIC RADIUS OF A-SITE ION DECREASES FROM BA TO CA, DEFINITE CHANGES ARE VISIBLE FOR THE XRD MATERIALS. THE INTENSITY OF ONE OF THE REFLECTIONS (110) IN THE XRD PATTERN DECREASES FROM $BaRE_4Si_3O_{13}$ SERIES TO SR SERIES AND FINALLY DISAPPEARS IN $CaRE_4Si_3O_{13}$. EVEN THOUGH THE PRESENT STUDY REVEALS THAT SINGLE PHASE COMPOUNDS ARE OBTAINED IN THIS SYSTEM, STUDIES ARE CLEARLY NEEDED TO ELUCIDATE THE EXACT CRYSTAL STRUCTURE OF THESE COMPOUNDS. THE LATTICE PARAMETERS OF $CaRE_4Si_3O_{13}$ [RE = LA, PR, ND, SM, EU, TB, DY, TM, YB AND Y] AND $BaRE_4Si_3O_{13}$ [RE = LA, PR, ND, SM] CERAMICS ARE DETERMINED FROM THE XRD PATTERNS AND ARE GIVEN RESPECTIVELY IN TABLES 3.8 AND 3.9. IT IS EXPECTED THAT AS THE IONIC RADIUS OF THE RARE EARTH DECREASES FROM LA TO YB, THE LATTICE PARAMETERS (*a* AND *c*) ALSO DECREASE. HOWEVER, THE *a* VALUES DEVIATE CONSIDERABLY FROM THE LINEAR TREND WHILE *c*

SHOWS AN ALMOST REGULAR DECREASE WITH THE IONIC RADIUS. THIS CAN BE DUE TO SITE OCCUPANCY OF VARIOUS IONS WHICH IS FOUND IN APATITE TYPE STRUCTURES AS CONFIRMED IN $SrRE_4Si_3O_{13}$ SERIES IN THE PREVIOUS SECTION.

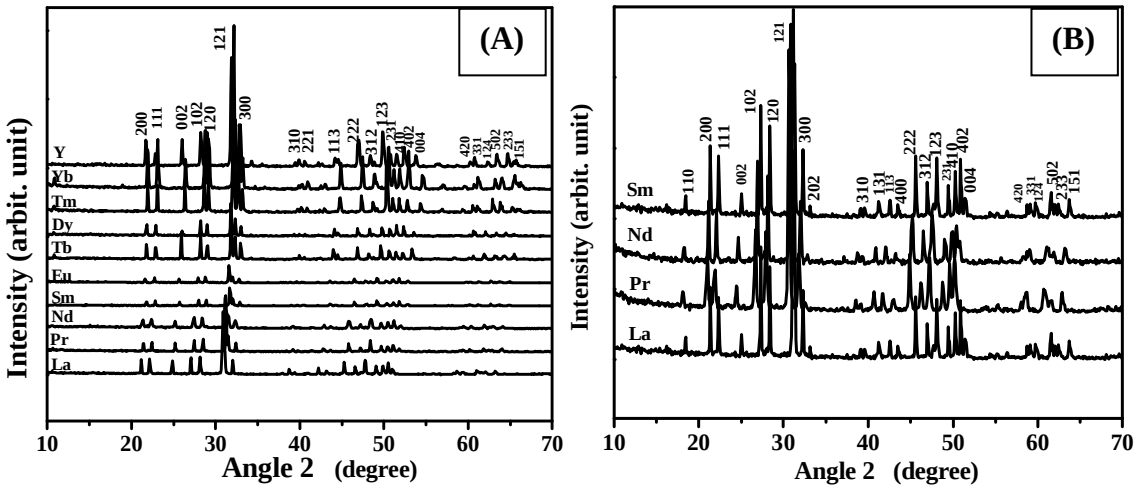

Fig. 3.14 XRD patterns of (A) $CaRE_4Si_3O_{13}$ [RE = La, Pr, Nd, Sm, Eu, Tb, Dy, Tm, Yb and Y] and (B) $BaRE_4Si_3O_{13}$ [RE = La, Pr, Nd, Sm] ceramics.

THE DENSITY DEPENDENCE ON RE^{3+} IONIC RADIUS IS SIMILAR TO THAT OBSERVED IN THE CA OF $SrRE_4Si_3O_{13}$. AS THE IONIC RADIUS OF THE RARE EARTH ION DECREASES, THE THEORETIC AS THE EXPERIMENTAL DENSITIES INCREASES. HOWEVER, THE RELATIVE DENSITIES OF $CaRE_4Si_3O_{13}$ SERIES EXHIBITED A BETTER VALUE WHEN COMPARED TO THAT OF $SrRE_4Si_3O_{13}$. ALL OF THEM HAVE A RELATIVE DENSITY VALUE GREATER THAN 90% EXCEPT FOR $CaYb_4Si_3O_{13}$ AND $CaTm_4Si_3O_{13}$. A MAXIMUM VALUE OF RELATIVE DENSITY OF ABOUT 94% IS EXHIBITED BY $CaEu_4Si_3O_{13}$ AND $CaNd_4Si_3O_{13}$. A RELATIVELY LOWER RELATIVE DENSITY OF ABOUT 87 % IS SHOWN BY $CaTm_4Si_3O_{13}$. THE ATTEMPTS TO IMPROVE THE DENSIFICATION BY GLASS ADDITION RESULTED IN AN INCREASE IN THE DIELECTRIC LOSS AND RESULTED IN NON-RESONATING IT IS CLEAR FROM THE TABLES THAT THE BA-COMPOSITIONS EXHIBIT HIGHER DENSITY WHEN WITH THAT OF SR AND CA BASED COMPOSITIONS, WHICH IS DUE TO THE HIGHER MASS OF BA. ALSO A COMPARATIVE STUDY ON THE RELATIVE DENSITIES SHOWS THAT $BaRE_4Si_3O_{13}$ COMPOSITIONS POSSESS A HIGHER RELATIVE DENSITY WITH A MAXIMUM OF 98% FOR $BaPr_4Si_3O_{13}$ EXCEPT FOR BALA

Table 3.8 The optimized sintering temperature, physical and microwave dielectric properties of $CaRE_4Si_3O_{13}$ [RE = La, Pr, Nd, Sm, Eu, Tb, Dy, Tm, Yb and Y] ceramics.

$CaRE_4Si_3O_{13}$	Sintering Temp. (°C)	Lattice parameter		Theor. Density (g/cm^3)	Relative density (%)	$Q_u X F$ (GHz)	ε_R	ε_{RCORR}	τ_F (ppm /°C)
		a (Å)	c (Å)						
$CAL_4SI_3O_{13}$	1350/4H	9.6481	7.1343	5.13	93.2	24800	14.9	16.4	-20
$CAP_4SI_3O_{13}$	1375/4H	9.5437	7.01473	5.38	93.0	17800	14.9	16.4	4
$CANI_4SI_3O_{13}$	1325/4H	9.5465	7.0337	5.44	94.0	21100	14.3	15.6	-23
$CASM_4SI_3O_{13}$	1350/4H	9.4336	6.9303	5.81	93.5	22000	14.2	15.4	-39
$CAEI_4SI_3O_{13}$	1400/4H	9.4646	6.9314	5.81	94.1	20000	14.2	15.4	-35
$CATI_4SI_3O_{13}$	1625/4H	9.3783	6.8645	6.15	89.6	20100	13.1	15.3	-12
$CAD'_4SI_3O_{13}$	1550/4H	9.3784	6.8483	6.25	89.8	13300	14.0	16.3	10
$CAY_4SI_3O_{13}$	1625/4H	9.3863	6.8329	4.38	91.8	30500	12.8	14.4	-36
$CATM_4SI_3O_{13}$	1550/4H	9.3382	6.7511	6.57	87.4	17000	11.9	15.7	-32
$CAYI_4SI_3O_{13}$	1625/4H	9.3232	6.7249	6.72	91.2	23500	13.2	15.0	-13

Table 3.9 The optimized sintering temperature, physical and microwave dielectric properties of $BaRE_4Si_3O_{13}$ [RE = La, Pr, Nd and Sm] ceramics.

$BaRE_4Si_3O_{13}$	ST (°C)	Lattice parameter		Theor. Density (g/cm^3)	Relative density (%)	$Q_u X F$ (GHz)	ε_R	ε_{RCORR}	τ_F (ppm/° C)
		A (Å)	*C* (Å)						
$BAL_4SI_3O_{13}$	1325/4H	9.6024	7.0888	5.78	87.4	26100	14.2	17.2	-38
$BAP_4SI_3O_{13}$	1325/4H	9.7250	7.2466	5.56	98.7	19700	16.8	17.2	-8
$BANI_4SI_3O_{13}$	1250/4H	9.6733	7.1779	5.77	96.5	16000	15.1	15.9	-19
$BASM_4SI_3O_{13}$	1325/4H	9.5768	7.0827	6.09	94.6	16200	15.5	16.7	-27

THE RELATIVE DENSITY MAXIMA OF BA COMPOSITIONS APPEAR AT A LOWER TEMPERATU
AND CA COUNTERPARTS. IN THE CASE OF COMPOUNDS CONSISTING OF Ba^{2+} IONS WITH THE SAME A-

SITE ION OCCUPANCIES, THE RELATIVE DENSITY MAXIMA APPEARED AT DIFFERENT TEMP
INDICATES THAT THE SINTERING BEHAVIOUR OF THESE CERAMICS IS SIGNIFICANTLY A
RARE EARTH IONS. IT IS CLEAR THAT SIMILAR TO THE $LaCa_4Si_3O_{13}$ SERIES, AS THE RARE EARTH IONIC
RADIUS INCREASES, THE SINTERING TEMPERATURE DECREASES IN THE CASE OF
COMPOSITIONS. IN THE CASE OF $BaCa_4Si_3O_{13}$ THE SINTERING TEMPERATURE REMAINS CONSTANT F
ALL THE COMPOSITIONS EXCEPT FOR $LaCa_4Si_3O_{13}$ WHERE THE BEST PROPERTIES ARE ATTAINED AT A
TEMPERATURE OF 1250°C.

FIGURES 3.15 (A) AND (B) SHOW THE MICROSTRUCTURE OF $LaCa_4Si_3O_{13}$ AND $CaY_4Si_3O_{13}$
SINTERED AT 1325°C AND 1475°C RESPECTIVELY. BOTH OF THEM REVEALED A UNIFORM SING
PHASE AND A WELL PACKED MICROSTRUCTURE. HOWEVER, THE PRESENCE OF SLIGHT
POROSITY IS ALSO NOTED. THE $LaCa_4Si_3O_{13}$ CERAMICS HAS AN AVERAGE GRAIN SIZE LESS THAN
µM WHEREAS $CaY_4Si_3O_{13}$ SHOWS A COMPARATIVELY HIGHER GRAIN SIZE (~ 2-3 µM). FIG. 3.15
(C) SHOWS THE MICROSTRUCTURE OF $BaCa_4Si_3O_{13}$ SINTERED AT 1325°C. FROM THE SEM IMAGE IT
CAN BE INFERRED THAT THE MATERIAL POSSES A HIGHLY DENSE MICROSTRUCTURE.
RELATIVE DENSITY SHOWS A LOW VALUE OF 87%. ALSO PRESENCE OF SOME UNIDENTIFIE
PHASE WHICH IS ABSENT IN THE XRD PATTERN IS ALSO NOTED. THE LOW VALUE OF DE
ACHIEVED MAY BE DUE TO THE PRESENCE OF THIS UNEXPECTED PHASE.

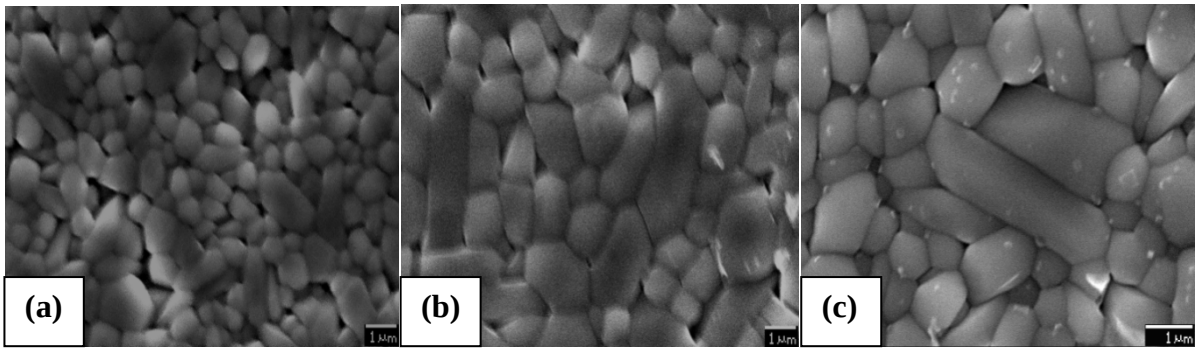

Fig. 3.15 SEM images of (a) $CaLa_4Si_3O_{13}$ sintered at 1325°C/2 h, (b) $CaY_4Si_3O_{13}$ sintered at 1475°C/2 h and (c) $BaLa_4Si_3O_{13}$ sintered at 1325°C/2 h.

THE MICROWAVE DIELECTRIC PROPERTIES OF THE $LaCa_4Si_3O_{13}$ AND $CaLn_4Si_3O_{13}$ SERIES ARE
SHOWN IN TABLE 3.8 AND 3.9. NO REGULAR DEPENDENCE OF MICROWAVE DIELECTRIC P
WITH IONIC RADIUS IS NOTED FOR CA BASED COMPOSITIONS. GENERALLY, A DECREAS
PARAMETERS PROMOTES SHRINKAGE OF THE TETRAHEDRA AND DECREASES THE IONIC

THIS WILL IN TURN DECREASE THE RELATIVE PERMITTIVITY OF THE MATERIALS. A MAX
PERMITTIVITY VALUE OF 14.9 IS EXHIBITED BY $Ca_4Si_3O_{13}$ AND A MINIMUM VALUE OF 11.9 BY
$CaTm_4Si_3O_{13}$. THIS CAN BE WELL EXPLAINED BY THE RELATIVE DENSITY VALUES OF THESE
AS GIVEN IN TABLE 3.8 SINCE RELATIVE PERMITTIVITY IS VERY MUCH DEPENDENT ON T
DENSITY. IN THE CASE OF BA SERIES ONLY FOUR OF THE RARE EARTH BASED SILICATES
EXHIBIT RESONANCE AT MICROWAVE FREQUENCY. VERY FEW REPORTS ARE AVAIL
EXISTENCE OR FORMATION OF PHASE POSSIBILITIES. IT IS SEEN FROM TABLE 3.9 THAT
$BaRe_4Si_3O_{13}$ POSSESS A HIGH VALUE OF RELATIVE PERMITTIVITY (CORRECTED FOR PORO
COMPARED WITH THAT OF THE RESPECTIVE CA AND SR BASED RARE EARTH SILICATES.
THE HIGH IONIC POLARIZABILITY VALUE ($6.24 Å^3$) OF Ba^{2+} HAS A MAXIMUM VALUE OF RELATIVE
PERMITTIVITY OF ABOUT 16.8 IS OBTAINED FOR BAPR $_4Si_3O_{13}$.

THE QUALITY FACTOR OF $CaRe_4Si_3O_{13}$ VARIES FROM 13000-31000 GHZ AS SEEN FROM
TABLE 3.8. IT IS A WELL KNOWN FACT THAT APART FROM THE INTRINSIC FACTORS, QU
AFFECTED BY MANY EXTRINSIC FACTORS SUCH AS THE CONCENTRATION OF DEFECTS, IN
SIZE, POROSITY ETC. IT IS CLEAR FROM THE TABLE THAT THE QUALITY FACTOR IS NOT I
WITH THE RELATIVE DENSITY FOR CERTAIN COMPOSITIONS. EVEN THOUGH $CaEu_4Si_3O_{13}$ HAS THE HIGH
MAXIMUM RELATIVE DENSITY, A MAXIMUM QUALITY FACTOR OF NEARLY 30500 GHZ IS
$CaY_4Si_3O_{13}$. FROM EARLIER REPORTS IT CAN BE POINTED OUT THAT A LARGE GRAIN SIZE C
GRAIN BOUNDARY INDICATES A REDUCTION IN LATTICE IMPERFECTIONS RESULTING IN
LOSS MATERIALS [49]. IN THE PRESENT CASE ALSO ONE OF THE REASONS FOR THE HIGH $Q_u f$ VALUE FOR
$CaY_4Si_3O_{13}$ MAY BE THE INCREASE IN GRAIN SIZE. ALSO THE IONIC RADII DIFFERENCE BET
Ca^{2+} AND RE^{3+} IONS MAY REDUCE THE LATTICE STRAIN THEREBY INCREASING THE QUAL
HOWEVER, THE LOW QUALITY FACTOR VALUE FOR $CaSm_4Si_3O_{13}$ AND $CaTm_4Si_3O_{13}$ CAN BE PURELY
ATTRIBUTED TO THE LOW VALUE OF RELATIVE DENSITY. CONSIDERING THE $CaEu_4Si_3O_{13}$ CERAMICS, IT
IS QUITE SURPRISING TO NOTE THAT $CaEu_4Si_3O_{13}$ WITH A LOW RELATIVE DENSITY EXHIBITS THE
MAXIMUM QUALITY FACTOR IN THE SERIES. SIMILAR TO THE $CaRe_4Si_3O_{13}$ AND $BaRe_4Si_3O_{13}$ SERIES AS THE
RE^{3+} IONIC RADII DECREASES, THE QUALITY FACTOR IS FOUND TO DECREASE GRADUALL
DUE TO THE INCREASING IONIC CHARACTER AS OBSERVED IN THE CASE OF $CaRe_4Si_3O_{13}$. IT IS CLEAR
FROM THE TABLES THAT $CaLa_4Si_3O_{13}$ SHOWS τ_f VALUE LESS THAN -40 PPM/°C AND A MAXIMUM VALUE
OF -39 PPM/°C IS SHOWN BY $CaSm_4Si_3O_{13}$ AND A LOW VALUE OF -4 PPM/°C BY $CaLu_4Si_3O_{13}$.
HOWEVER, THE ATTEMPT TO TUNE THE τ_f BY THE TiO_2 ADDITION RESULTED IN A NON-

RESONATING OR HIGH DIELECTRIC LOSS COMPOSITION WHICH MAY BE DUE TO THE FORM
SECONDARY PHASES. IN THE CASE OF BA-SERIES, $Ba_4Sr_3Ca_3Si_4O_{13}$ SHOWS A MINIMUM VALUE OF τ_f
OF ABOUT -8 PPM/°C. THE τ_f OF A MATERIAL IS VERY MUCH DEPENDENT ON THE STRUCTU
EXPLAINED EARLIER. SINCE IN THE PRESENT CASE NO PHASE TRANSITION IS OBSE
STRUCTURAL STUDIES ARE REQUIRED FOR EXPLAINING THE τ_f VARIATION.

3.5 CONCLUSIONS

- THE $AR_4Si_3O_{13}$ [A=CA, SR AND BA; RE=RARE EARTHS] ARE SYNTHESIZED BY SOLID ST CERAMIC METHOD. THE PHASE AND STRUCTURAL ANALYSIS USING XRD AN CONFIRMED A HEXAGONAL SYMMETRY FOR THESE GROUP OF MATERIALS ALL BEL $P6_3/M$ SPACE GROUP. THE LATTICE PARAMETERS SHOW A DECREASE WITH DECREAS RADII OF BOTH A-SITE AND RE-SITE IONS.

- THE CALCINATION AND SINTERING TEMPERATURES ARE OPTIMIZED AND THE M DIELECTRIC PROPERTIES ARE MEASURED IN THE FREQUENCY RANGE 5-6 GH $SRRE_4Si_3O_{13}$ CERAMICS SHOWED POOR DENSIFICATION WITH A MAXIMUM R $SRLa_4Si_3O_{13}$. THE DENSIFICATION OF THE MATERIALS IS IMPROVED BY THE ADDITI SMALL WEIGHT PERCENTAGE OF ZBS GLASS. HOWEVER, THE MICROWAVE DI PROPERTIES ARE NOT IMPROVED MUCH. THE $CaRE_4Si_3O_{13}$ COMPOSITIONS ALSO EXHIBIT RELATIVE DENSITY LESS THAN 94%, BUT BETTER THAN THE $SrRE_4Si_3O_{13}$ SERIES. THE BA ANALOGUE SHOWS A VERY HIGH DENSIFICATION OF GREATER THAN 95% EX $BaLa_4Si_3O_{13}$.

- THE $SrRE_4Si_3O_{13}$ EXHIBITED RELATIVE PERMITTIVITY IN THE RANGE 10-19. A MAXIM $Q_u \times f$ OF ABOUT 26000 GHZ IS EXHIBITED BY $Ba_4Sr_3Ca_3Si_4O_{13}$ WITH ε_r = 14.2 AND A RELATIVELY HIGH τ_f OF -46 PPM/°C. THE MICROWAVE DIELECTRIC PROPERTIES OF THE COMPOSITIONS ARE CORRELATED WITH THE BOND VALENCE AND BOND STRENGTH τ_f OF $SrLa_4Si_3O_{13}$ IS TUNED BY THE ADDITION OF SUITABLE AMOUNT OF TiO_2. IT IS FOUND THE ADDITION OF NEARLY 8 WT% OF TiO_2 REDUCED THE τ_f VALUE TO ZERO, THE $Q_u \times f$ IS REDUCED TO 13300 GHZ WITH AN INCREASE IN ε_r TO NEARLY 21.

- THE BOND VALENCE, BOND STRENGTH AND COVALENCE OF $Ln_4Si_3O_{13}$ REFINED SRRE COMPOSITIONS ARE CALCULATED AND CORRELATED WITH THE MICROWAVE PROPERTIES. IT IS SEEN THAT AS THE BOND STRENGTH DECREASES, THE RELATIVE AND DIELECTRIC LOSS ARE FOUND TO INCREASE.
- THE $CaLn_4Si_3O_{13}$ AND $BaLn_4Si_3O_{13}$ CERAMICS HAVE A RELATIVE PERMITTIVITY LESS THA 20. THE $CaYb_4Si_3O_{13}$ CERAMICS SHOWS A MAXIMUM QUALITY FACTOR OF 30500 GHZ WITH ε_r =12.8 AND τ_f = -36 PPM/^{0}C. THE $BaLn_4Si_3O_{13}$ SERIES SHOWS A RELATIVELY HIGH ε_r AND A LOW $Q_u x f$ VALUE. A MAXIMUM $Q_u x f$ OF 26100 GHZ IS EXHIBITED BY $BaLa_4Si_3O_{13}$ WITH ε_r =14.2 AND τ_f = -38 PPM/^{0}C.

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CHAPTER 4

MICROWAVE DIELECTRIC PROPERTIES OF NOVEL RARE EARTH SILICATE CERAMICS

The structure and microwave dielectric properties of two novel rare earth silicate based ceramics: $Sm_2Si_2O_7$ and $RE_2Ti_2SiO_9$ [RE=La, Pr and Nd] are presented in this chapter. The dielectric properties of these materials are investigated for the first time. The $Sm_2Si_2O_7$ exhibited a low relative permittivity and dielectric loss which makes it suitable for substrate applications. The influence of several low loss glasses on the sintering temperature, densification and dielectric properties of $Sm_2Si_2O_7$ ceramics is discussed in detail. Attempts are also made to synthesis and characterize $Sm_2Si_2O_7$ ceramics by sol-gel method. The microwave dielectric properties of $RE_2Ti_2SiO_9$ [RE=La, Pr and Nd] ceramics and the effect of solid solution formation on the densification, lattice parameters and microwave dielectric properties are also presented. The results bring out its potential for dielectric resonator applications.

4.1 SYNTHESIS AND MICROWAVE DIELECTRIC PROPERTIES OF $SM_2SI_2O_7$

4.1.1 INTRODUCTION

COMMERCIAL INTEREST IN HIGHLY SOPHISTICATED, RELIABLE AND CONVENIENT DEVICES HAS ESTABLISHED A PERMANENT NEED FOR COMPLEX, ROBUST AND MINIATU SUBSTRATES. NEW PACKAGING TECHNOLOGY REQUIRES SUBSTRATES WITH LOW INTERCONNECTIONS MADE OF HIGH-CONDUCTIVITY METALS, HIGH WIRING DENSITY AN PASSIVE CIRCUIT ELEMENTS. IMPORTANT PROPERTIES OF SUBSTRATE MATERIALS INCLUD LOSS, HIGH THERMAL CONDUCTANCE, LOW THERMAL EXPANSION AND HIGH INTERFACI THE METAL SURFACES OR OTHER FILMS. IN SEARCH OF NEW HIGH PERFORMANCE M MILLIMETER WAVE DEVICES, SILICATES ARE PROPOSED TO BE GOOD CANDIDATES BEC LOW ε_r. GENERALLY SILICATES ARE FORMED BY SiO_4 TETRAHEDRAL FRAMEWORK WITH 45% IONIC BOND AND 55% COVALENT BOND. THE COVALENT BOND IN SILICATES ε_r BECAUSE LARGE BOND STRENGTH DUE TO WHICH THE ATOMS CANNOT RATTLE AROUND. [1-2]. RECENTLY OSHAT SUCCESSFULLY DEVELOPED FORSTERITE AND WILLEMITE CERAMICS FOR SUBSTRAT HOWEVER, THE POSSIBILITY OF RARE EARTH BASED SILICATES FOR USE IN MICROELECT HAS NEVER BEEN INVESTIGATED.

BINARY SYSTEMS CONTAINING SiO_2 ARE VERY IMPORTANT IN VARIOUS FIELDS OF TECHNOLOGY, INCLUDING LASER AND OPTICAL FIBRE APPLICATIONS, MICROELECTRONIC THE ANALYSIS OF RE_2O_3-SiO_2 PHASE DIAGRAMS BY FELSCHE [3] SHOWED THAT VARIOUS BINA SILICATE COMPOUNDS SUCH AS MONOSILICATES RE_2SiO_5, APATITE LIKE COMPOUNDS $RE_{9.33}(SiO_4)_6O_2$ AND DISILICATES $RE_2Si_2O_7$ MAY FORM AT NORMAL PRESSURE. CRYSTAL CHEMISTR OF DISILICATES IS PARTICULARLY COMPLEX, SINCE SEVERAL POLYMORPHIC STRUCTU REPORTED. THE RARE EARTH SILICATES RE_2SiO_5 AND [$RE_2Si_2O_7$] ARE FORMED AS THE MAJOR SECONDARY PHASES IN Si_3N_4 AND SiC HIGH-PERFORMANCE CERAMICS SINTERED WITH RARE E OXIDES AS SINTERING ADDITIVES [4]. DIFFERENT STRUCTURE TYPES (A-L) HAVE BEEN REPORTED FOR THE SINGLE RE DISILICATES [5-7]. THIS DIVERSITY IN STRUCTURE TYPE RE THE MONOTONIC DECREASE IN SIZE OF RE^{3+} CATIONS THROUGH THE LANTHANIDE SERIES AND CRYSTAL CHEMICAL RESPONSE TO CHANGE IN TEMPERATURE AND PRESSURE. IN EIG STRUCTURE TYPES (A, B, C, D, E, F, G, H AND K) THE SiO_4 TETRAHEDRA ARE ASSOCIATED INTO THE DIORTHOSILICATE, $[Si_2O_7]^{6-}$ IONS, AND THE STRUCTURES ESSENTIALLY REPRESENT DIFFERENT

PACKING DIORTHOSILICATE ANIONS AND $Si_2O_7^{6-}$ IONS ARE PRESENT IN THE RATIO 1:2. THE NINTH, TENTH AND ELEVENTH STRUCTURE TYPES ARE NOT DIORTHOSILICATES. INSTEAD, LINEAR TRIS $(Si_3O_{10}^{8-})$ IONS OCCUR WITH ORTHOSILICATE (SiO_4^{4-}) IONS IN THE TYPE B AND L STRUCTURES AND A HORSESHO SHAPED CATENA-TETRASILICATE $(Si_4O_{12}^{8-})$ ION OCCURS WITH TWO ORTHOSILICATE IONS PER FORMU UNIT IN THE TYPE I STRUCTURE. THE TYPE B STRUCTURE HAS BEEN REPORTED FOR TH Si_2O_7. DISILICATES OF EU, GD, TB, DY, HO AND ER AT THE LOWEST TEMPERATURES INVESTIGA 1450°C) AT 1 BAR AND FOR TM DISILICATE AND 200°C AT LOW PRESSURE, AS WELL AS FOR THE DISILICATES OF YB AND LU AT HIGHER PRESSURE *(7 GPA)*. [8]. IT WAS SUGGESTED THAT THE PHASE TRANSITION SEQUENCE C → X → B IS ACCOMPANIED BY THE CLOSURE OF THE DIH O-SI) BOND ANGLE WITH INCREASE IN PRESSURE. THIS SUGGESTION IS SUPPORTED BY TH THE HIGH-PRESSURE (10 GPA, 1600°C) TYPE K STRUCTURE FOR THE DISILICATES OF ND, SM, EU AND GD [5], WHERE COMPRESSION IS ACCOMPLISHED MAINLY BY CLOSURE OF THE BOND ANGLE TO 123-124° THROUGH RIGID BODY ROTATION OF THE SiO_4 TETRAHEDRA IN THE DIORTHOSILICATE ION.

THE PHASE RELATIONSHIPS IN THE Y_2O_3-SiO_2 SYSTEM HAVE BEEN STUDIED EXTENSIVELY WHERE THE EXISTENCE OF TWO DOUBLE OXIDES WITH COMPOSITIONS Y_2SiO_5 AND $Y_2Si_2O_7$ HAS BEEN PROVED. $Y_2Si_2O_7$ HAS BEEN ALSO INVESTIGATED FROM A STRUCTURAL POINT OF VIEW D COMPLEX HIGH-T POLYMORPHISM [9]. SO FAR SIX DIFFERENT MODIFICATIONS (α, β, γ, δ, ε AND ζ) HAVE BEEN REPORTED. ACCORDING TO ITO AND JOHNSON [10] THE TRANSITION SEQUE RECONSTRUCTIVE TRANSFORMATIONS BETWEEN THE FIRST FOUR FORMS IS AS FOLLOW $\alpha \xrightarrow{1225^{\circ}C} \beta \xrightarrow{1445^{\circ}C} \gamma \xrightarrow{1535^{\circ}C} \delta$. THESE FOUR MODIFICATIONS CAN BE SYNTHESIZED FRO APPROPRIATE REAGENTS BY SOLID STATE REACTIONS IN THE RESPECTIVE STABILITY RA *et al.* [11] MADE AN ATTEMPT TO IMPROVE THE SINTERING BEHAVIOR AND STRENGTH R SILICON NITRIDE (Si_3N_4) USING RARE EARTH DISILICATES $(RE_2Si_2O_7$ WHERE RE: ND, SM, Y AND YB) AS ADDITIVES. WITH THESE IN MIND THE ATTEMPTS TO SYNTHESIZE $RE_2Si_2O_7$ CERAMICS PAVED WAY FOR A NEW LOW LOSS DIELECTRIC MATERIAL. THE OTHER MEMBERS SYNTHESIZED IN THIS FAMILY FAILED TO FORM AT ORDINARY CONDITIONS AND EXHIBITED POOR DIELECT

IN THIS SECTION THE SYNTHESIS AND DIELECTRIC PROPERTIES OF $RE_2Si_2O_7$ ARE DESCRIBED IN DETAIL. A BRIEF DESCRIPTION ON THE SOL-GEL SYNTHESIS OF $RE_2Si_2O_7$ CERAMICS AND ITS PROPERTIES ARE ALSO DESCRIBED. EFFORTS ARE ALSO MADE TO LOWER THE SINTERING THE CERAMIC BY THE ADDITION OF VARIOUS LOW LOSS GLASSES.

4.1.2 EXPERIMENTAL

4.1.2.1 SOLID STATE SYNTHESIS OF $Sm_2Si_2O_7$ CERAMICS

THE $Sm_2Si_2O_7$ CERAMICS WAS PREPARED BY CONVENTIONAL SOLID STATE CERAMIC
HIGH PURITY Sm_2O_3 (IRE, 99.9%) AND SiO_2 (ALDRICH CHEMICAL COMPANY, 99.9%) WERE
USED AS STARTING MATERIALS FOR THE SYNTHESIS OF SAMARIUM SILICATE. THE CH
STOICHIOMETRICALLY WEIGHED AND BALL MILLED IN DISTILLED WATER USING ZRO
HOURS. THE SLURRY WAS DRIED IN HOT AIR OVEN AND CALCINED AT 1250 °C
CALCINED POWDER WAS GROUND WELL, MIXED WITH POLYVINYL ALCOHOL (PVA),
PRESSED INTO PELLETS OF 14 MM DIAMETER AND 1-2 MM THICKNESS FOR LOW FR
MEASUREMENTS. TO STUDY THE DIELECTRIC PROPERTIES IN THE MICROWAVE FREQU
RECTANGULAR SHEETS OF DIMENSIONS (40X12X1 MM^3) WERE ALSO MADE AND WERE SINTERED IN THE
TEMPERATURE RANGE 1325-1400 °C FOR 2H.

IN ORDER TO STUDY THE EFFECT OF GLASS ADDITION ON THE SINTERING ANI
PROPERTIES OF SAMARIUM SILICATE, VARIOUS LOW LOSS GLASSES (ZBC), SUCH AS 50ZNO-50B
60ZNO-30B_2O_3-10SiO_2 (ZBS), 27B_2O_3-35Bi_2O_3-6SiO_2-32ZNO (BBSZ), 22.2MGO-
22.2Al_2O_3-55.5SiO_2 (MAS), 35.1Li_2O-31.7B_2O_3-33.2SiO_2 (LBS) AND 20Li_2O-20MGO-
20ZNO-20B_2O_3-20SiO_2 (LMZBS) WERE SELECTED. THESE GLASSES WERE PREPARED AS
EXPLAINED IN CHAPTER 2 SECTION 2.2. THE CALCINED $Sm_2Si_2O_7$ POWDERS SUBSEQUENTLY
MIXED WITH GLASS IN DIFFERENT WEIGHT PERCENTAGE RANGING FROM 0.2 TO 15. THI
POWDERS WERE MIXED WITH PVA, GROUND WELL AND PRESSED TO FORM PELLETS AS
EARLIER. THE PELLETS WERE SINTERED IN AIR AT 900-975 °C WITH A HEATING RATE OF 5
COOLING RATE OF 2 °C/MIN.

4.1.2.2 CHEMICAL SYNTHESIS OF $Sm_2Si_2O_7$ CERAMICS

NANO-CRYSTALLINE SAMARIUM SILICATE POWDER WAS SYNTHESIZED BY SOL-G
THE SOL-GEL PROCESS IS AN EXCELLENT TECHNIQUE FOR NANO POWDER SYNTHESIS. IT
THE POSSIBILITY OF CONTROLLING THE STOICHIOMETRY AND HOMOGENEITY OF THE RES
MOREOVER, IT OFFERS THE ADVANTAGES OF BOTH OBTAINING FINE GRAINS AND PROC
TEMPERATURES, WHICH CAN HELP TO ENHANCE THE MICROWAVE DIELECTRIC PROPE
CERAMICS. $Sm(CH_3COO)_3.NH_2O$ (ALDRICH CHEMICALS, 99.9%), TETRA ETHYL ORTHOSILICAT
(TEOS) (98%, ALDRICH CHEMICALS) WERE USED AS STARTING MATERIALS ALONG WITH A

AND ETHYL ALCOHOL (MERCK CHEMICALS, INDIA) AS SOLVENTS. INITIALLY, STOICHIOM
OF TEOS WAS REFLUXED IN ETHYL ALCOHOL FOR 30 MIN TO GET A CLEAR S
$SM(CH_3COO)_3.NH_2O$ SEPARATELY DISSOLVED IN ACETIC ACID WAS THEN MIXED WITH THE
SOLUTION AT ROOM TEMPERATURE UNDER CONSTANT STIRRING TO OBTAIN A STABLE SO
HOMOGENEOUS PRECURSOR WAS THEN TRANSFERRED TO A GLASS PETRI DISH AND KEPT
ROOM TEMPERATURE FOR ONE WEEK. TRANSPARENT DRY GEL OBTAINED WAS POW
SUBJECTED TO CALCINATION AT 900 ^{0}C FOR 4 HRS. THE PELLETS WERE PREPARED AND SINTERING WA
CARRIED OUT AS EXPLAINED ABOVE. THE SPECIFIC SURFACE AREA OF THE SAMPLES WAS
NITROGEN ADSORPTION MEASUREMENT (BET) IN MICROMERITICS (GEMINI III 2375) SURFA
ANALYZER.

CRYSTALLINE PHASES OF THE SINTERED CERAMICS WERE INVESTIGATED FROM XR
THE MICROSTRUCTURES OF THE SINTERED, ETCHED SAMPLES WERE OBSERVED USIN
ELECTRON MICROSCOPE. THE DENSIFICATION BEHAVIOR OF THE CERAMICS WAS EV
DETERMINING THE BULK DENSITY BY ARCHIMEDES METHOD. THE THIN PELLETS WERE EL
UNIFORMLY COATING WITH SILVER PASTE ON BOTH SIDES IN THE FORM OF CERAMIC CA
THE LOW FREQUENCY (50 HZ - 5 MHZ) DIELECTRIC MEASUREMENTS WERE MADE USING
METER. THE MICROWAVE DIELECTRIC PROPERTIES OF THESE CERAMIC COMPOSITES WE
AT 9 GHZ AT ROOM TEMPERATURE USING THE CAVITY PERTURBATION TECHNIQUE AS
CHAPTER 2 SECTION 2.5.7. THE TEMPERATURE VARIATION OF RELATIVE PERMITTIVITY
AT LOW FREQUENCY (1 MHZ) WAS ALSO MEASURED IN THE TEMPERATURE RANGE 25 ^{0}C TO 200 ^{0}C USING
THE EQUATION:

$$= \frac{1}{} \times \frac{\Delta}{\Delta T} \qquad (4.1)$$

WHERE Δ IS THE VARIATION IN THE RELATIVE PERMITTIVITY FROM ROOM TEMPERATURE A
DIFFERENCE IN TEMPERATURE.

4.1.3 RESULTS AND DISCUSSION

4.1.3.1 STRUCTURE AND DIELECTRIC PROPERTIES OF $Sr_2Sm_2O_5$ CERAMIC

THE CALCINATION AND SINTERING TEMPERATURES OF THE MATERIAL ARE OPTIMIZ
THE TEMPERATURE AT WHICH MAXIMUM DENSITY IS ATTAINED. FOR THIS THE MATERIAL

A TEMPERATURE RANGE OF 1200-1275°C AND SINTERED AT AN ARBITRARY TEMPERATURE 1375°C/2H. THE DENSITY VARIATION IS AS SHOWN IN FIG. 4.1 (A). IT IS SEEN THAT THE DEN MAXIMUM AT A CALCINATION TEMPERATURE OF 1250°C. AT LOWER CALCINATION TEMPERATURES THE COMPOUND FORMATION MAY NOT BE COMPLETED. IT IS ALSO NOTED THAT THE RELATIV HAS A MAXIMUM VALUE AND DIELECTRIC LOSS EXHIBITED A MINIMUM VALUE (SEE FIG. 4 A CALCINATION TEMPERATURE OF 1250°C/4HR. THUS THE CALCINATION TEMPERATURE IS OPTIMIZED A 1250°C/4H. NOW, IN ORDER TO OPTIMIZE THE SINTERING TEMPERATURE, THE DRY PO CALCINED AT 1250°C/4H AND SINTERED IN THE TEMPERATURE RANGE 1325-1400°C.

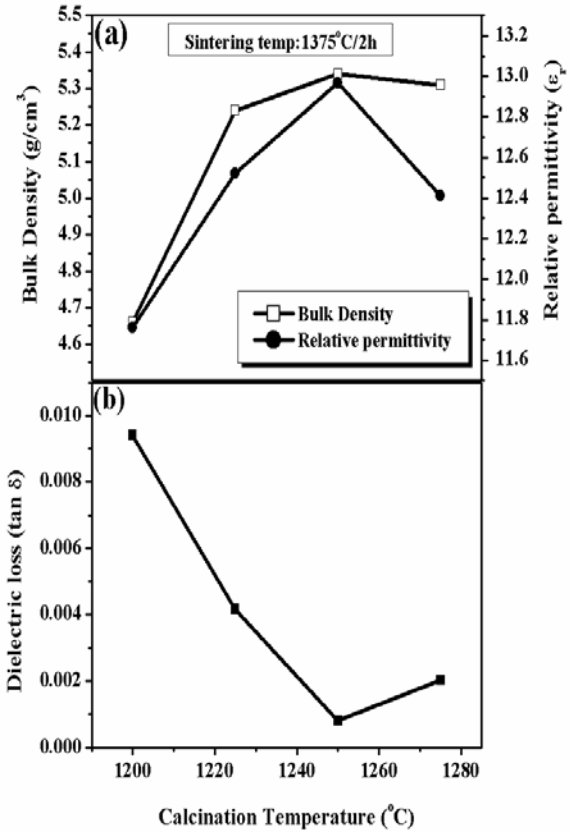

Fig. 4.1 The optimization of calcination temperature.

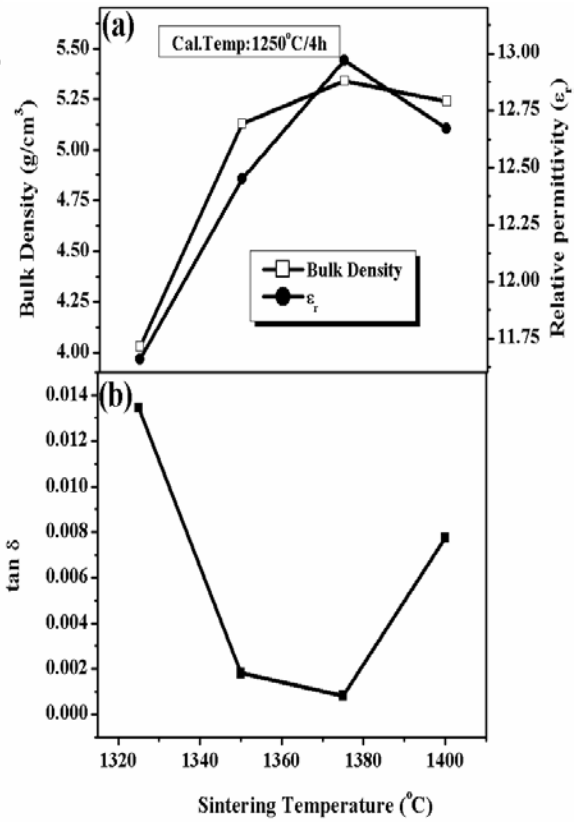

Fig. 4.2 The optimization of sintering temperature.

FIGURE 4.2 (A) SHOWS THE VARIATION OF RELATIVE DENSITY WITH SINTERING TEMP $SM_2SI_2O_7$ CALCINED AT 1250°C. THE DENSITY INCREASES GRADUALLY WITH THE SINTER TEMPERATURE REACHING A MAXIMUM AT 1375°C AND THEREAFTER DECREASES. THE $SM_2SI_2O_7$ HAS A THEORETICAL DENSITY 5.69 G/CM^3. THE RELATIVE DENSITY REACHES TO ABOUT 94 % (5.35 G/CM^3)

OF THE THEORETICAL DENSITY. GENERALLY SILICATES HAVE LOW DENSITY. THE INCREASE DENSITY WITH THE SINTERING TEMPERATURE IS DUE TO THE DECREASE IN POROSITY OF T ALSO DUE TO THE ENHANCED GRAIN GROWTH. HOWEVER, SINTERING AT VERY HIGH WOULD CAUSE ABNORMAL GRAIN GROWTH RESULTING IN A DECREASE IN THE DENSITY. TO AN INCREASE IN THE CLOSED POROSITY WHICH ADVERSELY AFFECTS THE DENSITY A DIELECTRIC PROPERTIES. MOREOVER, INCREASE IN THE SINTERING TIME WOULD ENHA GROWTH RESULTING IN AN INCREASE IN THE DENSITY. HOWEVER, PROLONGED SINTERI LEAD TO ABNORMAL GRAIN GROWTH THEREBY REDUCING THE DENSITY AND DIELECTR THE PRESENT CASE THE SINTERING TEMPERATURE IS OPTIMIZED AS 1375 °C/2H.

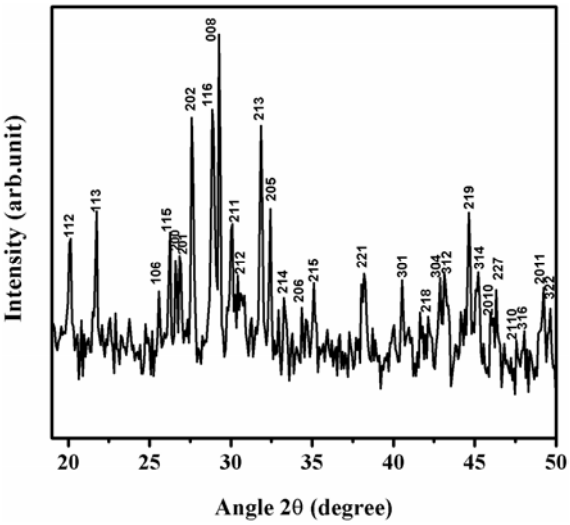

Fig. 4.3 XRD pattern of pure $Sm_2Si_2O_7$ (CT: 1250°C/4h; ST: 1375°C/2h).

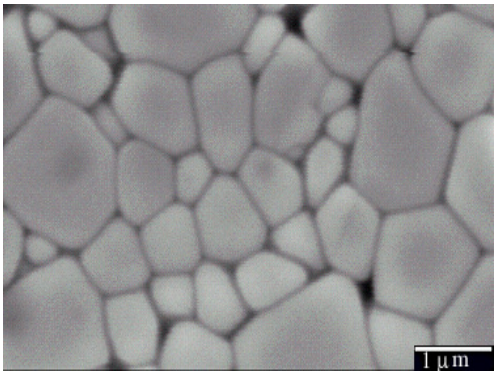

Fig. 4.4 The scanning electron micrographs of pure $Sm_2Si_2O_7$ calcined at 1250°C/4h and sintered at 1375°C/2h.

FIGURE 4.3 SHOWS THE XRD PATTERN OF $Sm_2Si_2O_7$ CERAMIC CALCINED AT 1250 °C/4H AND SINTERED AT 1375 °C/2H. THE DIFFRACTION PEAKS ARE INDEXED BASED ON JCPDS FILE NO 24-711. EARLIER REPORTS SHOWS THAT RARE EARTH BASED DISILICATES ARE FOUN POLYMORPHISM AND ARE DIFFICULT TO FORM UNDER ORDINARY CONDITIONS [6]. SM TETRAGONAL CRYSTAL SYMMETRY BELONGING TO SPACE GROUP $I4_1/amd$ (141). THE LATTICE PARAMETERS CALCULATED FROM THE XRD PATTERNS ARE: A = 6.70 Å AND C = 24.35 Å. THEY ARE FOUN IN GOOD AGREEMENT WITH THE REPORTED VALUES. THE MICROSTRUCTURE OF POLISHED ETCHED $Sm_2Si_2O_7$ CERAMIC SINTERED AT 1375 °C FOR 2 HOURS IS SHOWN IN FIG. 4.4. IT INDICATES THAT SAMARIUM SILICATE IS SINGLE PHASE AND HAS A RELATIVELY SMALLER GRAIN SIZ

AVERAGE GRAIN SIZE. IT IS THE VARIATIONS IN THE SINTERING CONDITIONS ARE CONSIDERED TO
IMPORTANT ROLE IN IMPROVING THE GRAIN-TO-GRAIN CONNECTIVITY OF THE CERAMIC
PORES AND ABNORMAL GRAINS ARE OBSERVED WHICH CONFIRMS GOOD DENSIFICA
HOMOGENEOUS MICROSTRUCTURE.

THE DIELECTRIC PROPERTIES OF THE SAMPLES ARE DEFINED BY THE CRYSTALLINE
WHICH ARE IN TURN DETERMINED BY THE SINTERING TEMPERATURE. FROM FIG. 4.2 IT I
THE RELATIONSHIP BETWEEN RELATIVE PERMITTIVITY AND SINTERING TEMPERATURE SI
SAME TREND AS THAT BETWEEN DENSITY AND SINTERING TEMPERATURE. THE HIGHES
RELATIVE PERMITTIVITY ARE FOUND FOR SAMPLES SINTERED AT 1375°C. AT THIS OPTIMIZED
TEMPERATURE THE RELATIVE PERMITTIVITY IS 12.5 MEASURED AT 1 MHZ. THE VAR
DIELECTRIC LOSS MEASURED AT 1 MHZ WITH SINTERING TEMPERATURE IS ALSO SHOWI
(B). THE DIELECTRIC LOSS IS FOUND TO DECREASE WITH INCREASE IN THE SINTERING TEM
REACHES A MINIMUM VALUE OF 0.0008 AT 1375°C. THIS MAY BE DUE TO THE ESTABLISHED FACT
THAT HIGH DIELECTRIC LOSS IS MAINLY CAUSED BY THE INSUFFICIENT DENSIFICATIO
GROWTH AND IMPROVEMENT OF THE GRAIN CONNECTIVITY OF THE CERAMICS WITH TE
EXPECTED TO DECREASE THE DIELECTRIC LOSS. A UNIFORM GRAIN MORPHOLOGY ALSO
DIELECTRIC LOSS VALUE [12] WHICH IS EVIDENT FROM THE SEM IMAGE.

TABLE 4.1 SUMMARIZES THE MICROWAVE DIELECTRIC PROPERTIES OF SM
MICROWAVE FREQUENCY (9 GHZ). MEASUREMENTS AT 1 MHZ INDICATE THAT SM
12.5 AND $\tan\delta = 8\text{X}10^{-4}$. AT THE MICROWAVE FREQUENCY THE VALUES ARE
$6\text{X}10^{-3}$. IT IS SEEN THAT THE RELATIVE PERMITTIVITY HAS A LOW VALUE WHEN COMPA
MEASURED AT 1 MHZ. THIS IS DUE TO THE DIFFERENCE IN THE POLARIZATION MECHANIS
FREQUENCIES WHICH CONTRIBUTES TO THE RELATIVE PERMITTIVITY. AT LOW FREQUENC
PERMITTIVITY IS ATTRIBUTED TO ALL THE FOUR POLARIZATIONS WHICH ARE ACTIVE AT
BUT IN THE MICROWAVE FREQUENCY RANGE ONLY ELECTRONIC AND IONIC POLARIZATI
TO THE NET RELATIVE PERMITTIVITY AND THEREFORE A REDUCTION IN THE RELATIVE PE
THE LOSS TANGENT AT 9 GHZ IS AN ORDER OF MAGNITUDE HIGHER THAN THAT MEASUR
IT MAY BE NOTED THAT AT LOW AND MICROWAVE FREQUENCY RANGE TWO DIFFERENT
DIFFERENT SHAPE AND SIZE WERE USED FOR MEASUREMENTS BY TWO DIFFERENT MI
SAMPLES FOR MICROWAVE MEASUREMENTS WERE LARGE, THIN RECTANGULAR STRIPS A
DENSITY AS COMPARED TO THE SMALL PELLETS MADE FOR RADIO FREQUENCY ME

MOREOVER, IT MAY BE NOTED THAT THE DIELECTRIC LOSS INCREASES WITH INCREASE I
THE MICROWAVE REGIME [5].

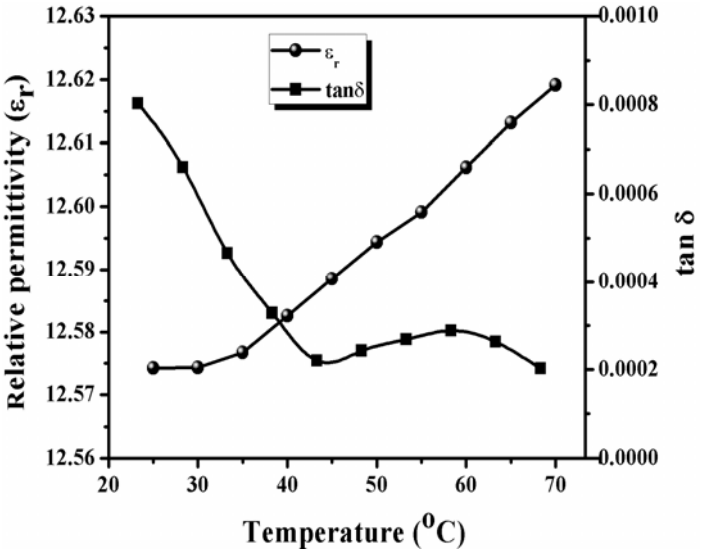

Fig. 4.5 The variation of relative permittivity and dielectric loss (at 1 MHz) of $Sm_2Si_2O_7$ with temperature.

THE STABILITY OF DIELECTRIC PROPERTIES WITH TEMPERATURE IS THE MAIN CON
OF THE PRACTICAL CIRCUITS. FIG. 4.5 SHOWS THE VARIATION OF RELATIVE PERMITTIVIT
WITH TEMPERATURE IN THE RANGE 25 – 70 °C. IT IS CLEAR FROM THE FIGURE THAT THE RELATIV
PERMITTIVITY INCREASES IN A REGULAR MANNER WITH RISE IN TEMPERATURE. T
PERMITTIVITY VARIES FROM ABOUT 12.57 TO 12.62 SHOWING A RELATIVE DEVIATION OF C
$SM_2SI_2O_7$ HAS A τ_ε OF +63 PPM/°C IN THE MEASURED TEMPERATURE RANGE. THIS IS WELL I
AGREEMENT WITH THE OBSERVATIONS BY BOSMAN AND HAVINGA [13] WHERE THEY NO
TEMPERATURE DEPENDENCE OF RELATIVE PERMITTIVITY IS POSITIVE FOR MATERIALS W
ABOUT 20 AND NEGATIVE FOR LARGER VALUES OF ε_r. THE VARIATION OF DIELECTRIC LOSS OF THE
CERAMICS WITH TEMPERATURE IS ALSO SHOWN IN FIG. 4.5. THE DIELECTRIC LOSS INITIAL
FROM 0.0008 AT ROOM TEMPERATURE TO NEARLY 0.0002 AT ABOUT 50 °C. WITH FURTHER RISE IN
TEMPERATURE THE DIELECTRIC LOSS ALMOST REMAINS CONSTANT AT THIS VALUE. IT
TABLE 4.1 THAT THE DIELECTRIC PROPERTIES OF $Sm_2Si_2O_7$ ARE COMPARABLE TO THE CONVENTIONAL
SUBSTRATE MATERIALS AND IT IS A PROMISING MATERIAL FOR ELECTRONIC SUBSTRATE

4.1.3.2 PROPERTIES OF NANO $Sm_2Si_2O_7$ CERAMIC

THIS SECTION GIVES A BRIEF DESCRIPTION ON THE CHARACTERISTICS OF SOL-GEL $SM_2SI_2O_7$ CERAMICS. THE TYPICAL TG CURVE OF THE $Sm_2Si_2O_7$ GEL IS SHOWN IN FIG. 4.6. THE RESULT INDICATES THAT THE WEIGHT LOSS BEGAN AT ABOUT 63°C AND ALL CHEMICAL REACTIONS INVOLVING WEIGHT LOSSES, SUCH AS DECOMPOSITION OF POLYMERIC NETWORK WITH THE EVOLUTION OF H_2O AND CO_2 WERE COMPLETED BELOW THIS TEMPERATURE. BEYOND 550°C, THE MASS OF THE DRIED GEL EXHIBITED ALMOST NO CHANGE. HOWEVER, THE FORMATION TEMPERATURE OF SOL-GEL SYNTHESIZED $Sm_2Si_2O_7$ CERAMICS WAS 900°C WHICH IS CONFIRMED FROM THE XRD PHASE ANALYSIS SHOWN IN FIG. 4.7. TABLE 4.1 GIVES THE OPTIMIZED CALCINATION AND SINTERING TEMPERATURES OF $Sm_2Si_2O_7$ PREPARED BY SOLID STATE AND SOL-GEL ROUTE.

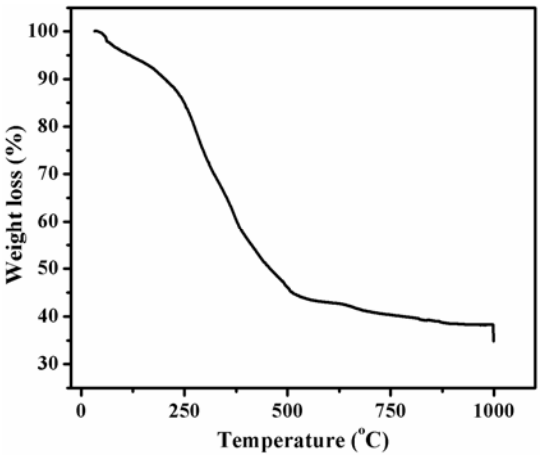

Fig. 4.6 TGA curve of sol-gel synthesized $Sm_2Si_2O_7$.

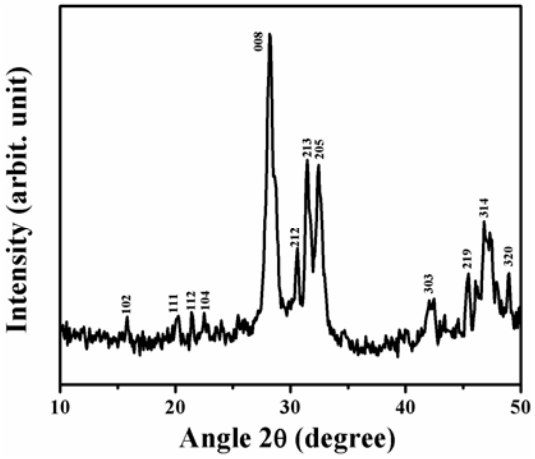

Fig. 4.7 XRD pattern of sol-gel synthesized $Sm_2Si_2O_7$ calcined at 900°C/4h.

Table 4.1 The physical and dielectric properties of $Sm_2Si_2O_7$ ceramics synthesized by different methods.

Synthesis method	CT	ST	Relative Density (%)	BET Surface area (m^2/g)	Dielectric Properties (1 MHz)	
					ε_r	$TAN\delta$
SOLID STATE	1250°C/4H	1375°C/2H	94.02	0.15	12.5	0.0008
SOL-GEL	900°C/4H	1325°C/2H	70.50	20.94	7.6	0.0010

FIGURE 4.8 SHOWS THE TEM IMAGE OF SOL-GEL DERIVED $Sm_2Si_2O_7$ POWDER HEATED AT 900°C/4H. THE PARTICLE SIZE VARIES FROM ABOUT 40-70 NM. ALSO THE NANO PARTIC FOUND TO AGGLOMERATE AND THEY SEEM TO BE INDISTINGUISHABLE. THE LOWER TEMPERATURE WILL RESULT IN A LESS AGGREGATED POWDER. THE SPECIFIC SU MEASUREMENTS SHOW THAT THE MICRON SIZED $Sm_2Si_2O_7$ POSSESS A VERY SMALL AVERAGE SURFACE AREA VALUE (0.16 m^2/g) AS COMPARED TO THE NANO SIZED ONE (20.94 m^2/g). THIS MAY INCREASE THE SINTERING ACTIVITY OF THE POWDER, WHICH WILL IN TURN REDUCE THE SINTERIN HOWEVER, IN THE PRESENT CASE EVENTHOUGH A REDUCTION IN CALCINATION TEMPERA THE SINTERING TEMPERATURE IS REDUCED BY ARROUND 50°C SIMILAR RESULTS ARE OBSERVED IN THE CASE OF SOL-GEL SYNTHESIZED $SrZrO_3$ CERAMICS WHERE AN ADDITIONAL REDUCTION IN THE SINTE TEMPERATURE IS ACHIEVED WITH THE ADDITION OF TiO_2 [14].

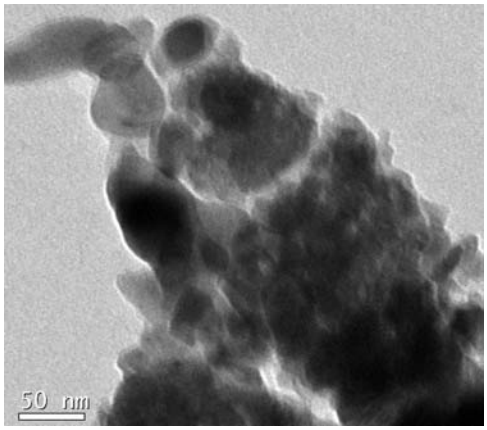

Fig. 4.8 TEM image of $Sm_2Si_2O_7$ heated at 900°C/4h.

A COMPARISON OF THE DIELECTRIC PROPERTIES OF BOTH THE SAMPLES MEASUREI SHOW THAT SOL-GEL SYNTHESIZED $Sm_2Si_2O_7$ CERAMIC EXHIBITS A LOW RELATIVE PERMITTIVITY AN HIGH DIELECTRIC LOSS WHEN COMPARED TO THAT PREPARED THROUGH SOLID STATE R BE PROBABLY DUE TO THE VERY LOW RELATIVE DENSITY ACHIEVED BY THE FORMER E TEMPERATURE OF 1325°C. THUS IT CAN BE CONCLUDED THAT $Sm_2Si_2O_7$ CERAMIC SYNTHESIZED BY SOLID STATE METHOD POSSESS PROMISING DIELECTRIC PROPERTIES FOR SUBSTRATE APP

4.1.3.3 EFFECT OF GLASS ADDITION ON $Sm_2Si_2O_7$ CERAMIC

THE PURE $Sm_2Si_2O_7$ CERAMICS HAS A HIGH SINTERING TEMPERATURE OF ABOUT 1375 °C IS IMPERATIVE TO LOWER THE SINTERING TEMPERATURE OF $Sm_2Si_2O_7$ FOR PRACTICAL APPLICATIONS. ADDITION OF LOW MELTING POINT GLASSES, CHEMICAL PROCESSING AND SMALLER PA THE STARTING MATERIALS ARE THE THREE METHODS TO REDUCE THE PROCESSING TEM DIELECTRIC AS EXPLAINED IN CHAPTER 1. THE PRESENT SECTION DEALS WITH THE EFFE LOW MELTING GLASSES ON THE SINTERING AND DIELECTRIC PROPERTIES OF $Sm_2Si_2O_7$ CERAMICS

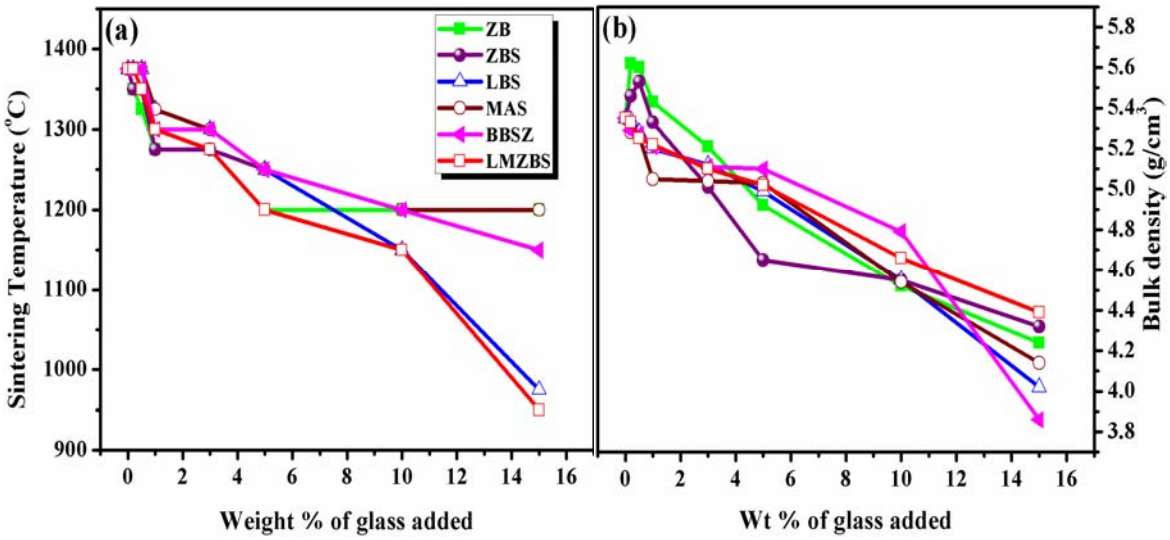

Fig. 4.9 The variation of (a) sintering temperature and (b) bulk density with the amount of glass addition in $Sm_2Si_2O_7$ ceramics.

FIGURE 4.9 (A) SHOWS THE OPTIMIZED SINTERING TEMPERATURE OF VARIOUS GLA $SM_2SI_2O_7$ CERAMICS. THE SINTERING TEMPERATURES ARE OPTIMIZED FOR THE MAXIMUM AND BEST DIELECTRIC PROPERTIES. IT MAY BE NOTED THAT THE ADDITION OF DIFF PERCENTAGE OF VARIOUS GLASSES LOWERS THE SINTERING TEMPERATURE GRADUALL THE WELL KNOWN LIQUID PHASE SINTERING TAKING PLACE IN THE CERAMIC-GLASS COM IS WELL EXPLAINED IN CHAPTER 2 SECTION 2.1.2.7.2. THESE GLASSES ARE HAVING LOW POINT AS GIVEN IN TABLE 1.3 IN CHAPTER 1.THE BOROSILICATE GLASSES ARE REPORTED ADDITIVE TO LOWER THE SINTERING TEMPERATURE FOR MANY DIELECTRIC MATERIALS THE VARIOUS GLASSES USED IN THE PRESENT STUDY ARE BASED ON TiO_2-B_2O_3-ZnO-SiO_2 GLASSES (ZB, ZBS, BBSZ,

LMZBS) REDUCES THE SINTERING TEMPERATURE MUCH EFFECTIVELY. THIS MAY BE DUE
THAT ZNO IN THE RESPECTIVE GLASS COMPOSITION ACT AS A MODIFIER OXIDE WHICH
NETWORK STRUCTURE OF THE GLASS THEREBY REDUCING THE SOFTENING POINT OF
INCREASING ITS FLUIDITY [17]. Al_2O_3 IS RECOGNIZED AS A TYPICAL GLASS NETWORK FORM
THAT HAS A LOW GLASS TRANSITION TEMPERATURE [18]. THE SINTERING TEMPERATU
FROM 1375-1275 °C WITH THE ADDITION OF 3 WT% OF THE ABOVE GLASSES EXCEPT FOR B
HOWEVER, IT IS INTERESTING TO NOTE THAT ADDITION OF HIGHER WEIGHT PERCENTAGE
THESE GLASSES HAS NO EFFECT ON THE SINTERING TEMPERATURE. EVEN WITH THE ADDI
OF THESE GLASSES, THE SINTERING TEMPERATURE IS LOWERED ONLY BY 100-200 °C. THIS MAY BE DUE
THE FORMATION OF SOME HIGH TEMPERATURE STABLE SECONDARY PHASES. A SIMILAR
OBSERVED FOR MAS GLASS WHICH MAY BE DUE TO ITS HIGH SOFTENING POINT AS A RE
ABSENCE OF B_2O_3. THE LITHIUM BASED BOROSILICATE GLASSES IS VERY EFFECTIVE IN LOWE
SINTERING TEMPERATURE. THE LITHIUM BASED GLASSES HAVE A LOW MELTING POINT
EFFECTIVE IN LOWERING THE SINTERING TEMPERATURE [19]. IT IS SEEN THAT WITH TH
BOTH LBS AND LMZBS GLASS CONTENT, THERE IS A REGULAR REDUCTION IN THE
TEMPERATURE OF THE COMPOSITE. HOWEVER, THE LMZBS GLASS IS MORE EFFICIENT IN
THE TEMPERATURE.

THE THEORETICAL DENSITY OF THE GLASS ADDED, Li_2SiO_3, IS CALCULATED USING EQ. (4.2)
[20]:

$$D = \frac{W_1 + W_2}{W_1/D_1 + W_2/D_2} \qquad (4.2)$$

WHERE W_1 AND W_2 ARE THE WT% OF THE Li_2SiO_3 AND GLASS WITH DENSITIES D_1 AND D_2
RESPECTIVELY. TABLE 4.2 GIVES THE DENSITIES AND OPTIMIZED SINTERING TEMPER
VARIOUS GLASS ADDED TO Li_2SiO_3. THE THEORETICAL DENSITY OF THE CERAMIC-GLASS COMPOS
DECREASES WITH THE INCREASE IN THE AMOUNT OF GLASS CONTENT. THIS IS DUE TO TH
POSSESSED BY THE GLASSES. FIG. 4.9 (B) SHOWS THE DEPENDENCE OF THE BULK DENSI
COMPOSITE ON THE AMOUNT OF VARIOUS GLASSES ADDED. IT IS FOUND THAT ADDITI
SMALL AMOUNT (0.2 WT%) OF ZB, ZBS AND LBS GLASSES IMPROVE DENSIFICATION. A MAX
RELATIVE DENSITY OF ABOUT 99% IS OBTAINED WITH THE ADDITION OF 0.2 WT% OF ZB. C
THE EFFECTIVENESS OF SINTERING AIDS DEPENDS ON SEVERAL FACTORS SUCH A

TEMPERATURE, VISCOSITY, SOLUBILITY AND GLASS WETTABILITY [21]. THE DENSIFICATIO
THE CERAMIC-GLASS COMPOSITES IS EXPLAINED BY THE VISCOUS FLOW OF THE GLASS I
EARLIER JHOU AND JEAN [22] NOTED THAT THE WETTING BEHAVIOR IS GREATLY IMP
INCREASING BAO CONTENT IN THE B_2O_3-ZNO GLASS SINCE BOTH THE SOFTENING AND MELTING
POINTS DECREASES. A COMPLETE WETTING BETWEEN GLASS AND CERAMICS IS NOTE
CONTACT ANGLE AND IT IS VERY MUCH DEPENDENT ON THE AMOUNT OF SINTERING AID.
IN THE CASE OF MAS GLASS ADDITION THE RELATIVE DENSITY IS FOUND TO INCREASE
WHICH MAY BE DUE TO THE ABOVE FACT. THE DRIVING FORCE FOR THE DENSIFICATIO
FROM THE CAPILLARY PRESSURE OF THE LIQUID PHASE LOCATED BETWEEN THE FINE S
WHEN THE LIQUID PHASE WETS THE SOLID PARTICLES, EACH INTER-PARTICLE SPACE
CAPILLARY, IN WHICH A SUBSTANTIAL CAPILLARY PRESSURE DEVELOPS [23]. IT SHOULD
DENSIFICATION MAY BE RETARDED DUE TO THE INSUFFICIENT AMOUNT OF GLASS DURIN
SINTERING. THE INCREASE IN ADDITION OF ZB GLASS DECREASES THE DENSITY AND T
DENSITY REACHES 92% WITH 15 WT% ADDITION OF THE GLASS. THE ZBS GLASS ALSO F
SIMILAR TREND SHOWING A MAXIMUM RELATIVE DENSITY OF 96% WITH 0.2 WT% ADDI
THERE IS A FASTER REDUCTION IN THE DENSITY FOR HIGHER WT% OF ZBS GLASS AS COM
GLASS. IT HAS BEEN REPORTED EARLIER [24-25] THAT ZINC BORATE GLASS IMPROVES THE
OF THE GLASS/CERAMIC COMPOSITES. FOR ALL OTHER GLASSES THE DENSITY SHOW
DECREASE WITH THE GLASS CONTENT AND THEY DO NOT ASSIST IN DENSIFICATION OF TI
TO BE NOTED THAT EVEN THOUGH LITHIUM BASED GLASSES LOWER THE SINTERING TEM
EFFECTIVELY, THE DENSIFICATION IS ADVERSELY AFFECTED. ADDITION OF 15 WT% O
LMZBS GLASSES REDUCES THE RELATIVE DENSITY TO ABOUT 84% AND 88% RESPECTIVE
OPTIMIZED SINTERING TEMPERATURES. THIS IS DUE TO THE LOW DENSITY POSSESSE
GLASSES WHEN COMPARED TO OTHERS (SEE TABLE 1.3 IN CHAPTER 1).

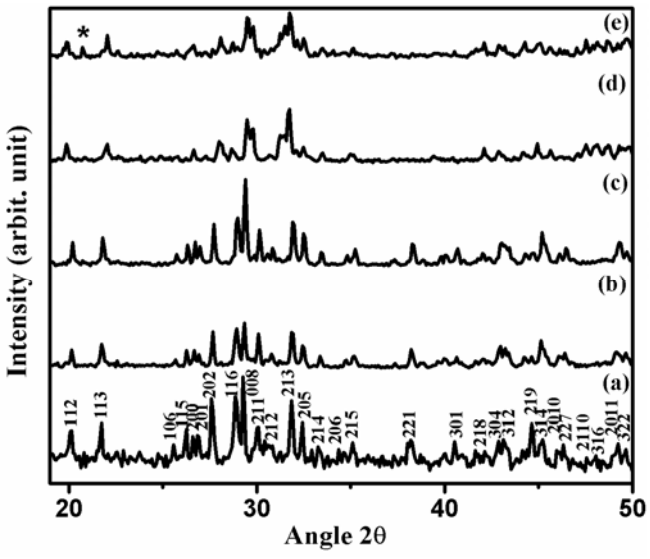

Fig. 4.10 XRD pattern of (a) pure $Sm_2Si_2O_7$ (ST: 1375 ^oC), (b) $Sm_2Si_2O_7$ + 3 wt% LBS (ST: 1300 ^oC), (c) $Sm_2Si_2O_7$ + 3 wt% LMZBS (ST: 1275 ^oC), (d) $Sm_2Si_2O_7$ + 15 wt% LBS (ST: 975 ^oC) and (e) $Sm_2Si_2O_7$ + 15 wt% LMZBS (ST: 950 ^oC). (* represents $SmBO_3$ phase).

FIGURE 4.10 (B)-(E) SHOWS THE XRD PATTERNS OF $Sm_2Si_2O_7$ SINTERED WITH DIFFERENT WEIGHT PERCENTAGE OF LBS AND LMZBS GLASSES. IT IS OBSERVED THAT WITH THE AI SMALL WEIGHT PERCENTAGE OF BOTH THE GLASSES NO SECONDARY PHASES ARE OBSE OF LARGER AMOUNT (UPTO 15 WT%) OF LBS GLASS DOES NOT PRODUCE ANY ADDITIONAL X-RAY DIFFRACTION PEAKS. THIS INDICATES THE NON – REACTIVITY OF LBS GLASS WITH $Sm_2Si_2O_7$ ABSENCE OF ADDITIONAL DIFFRACTION PEAKS IN THE XRD PATTERNS OF SAMPLES CON AMOUNT OF GLASSES MAY BE DUE TO THE FACT THAT THE GLASS IS IN THE AMOR ALTHOUGH, THE SAMPLES ARE SINTERED AT 1275 ^oC AND THEN SLOWLY COOLED AT A RATE OF 2 ^oC/MINUTE, LBS LIQUID PHASE IS NOT CRYSTALLIZED RETAINING ITS AMORPHOUS NATU CAN BE CONCLUDED THAT LBS GLASS EXISTED DURING LIQUID PHASE SINTERING AND DENSIFICATION OF $Sm_2Si_2O_7$ CERAMIC. HOWEVER, ADDITION OF 15 WT% LMZBS GLASS RESULTS AN ADDITIONAL PEAK OF $SmBO_3$ AS SEEN IN FIG. 4.10 (E).

Table 4.2 Sintering, densification and microwave dielectric properties of pure $Sm_2Si_2O_7$ and that treated with various glass additives.

$Sm_2Si_2O_7$ +Glass	Wt % of glass	Sintering Temp. (^oC)	Theoretical Density (g/cm^3)	Relative Density (%)	At 9 GHz	
					ε_r	$\tan\delta$
PURE $SM_2SI_2O_7$	0	1375	5.69	94.02	10	0.006
ZB	0.2	1350/2H	5.67	99.12	10.01	0.0034
	0.5	1325/2H	5.64	99.29	9.70	0.0031
	1	1275/2H	5.60	96.96	9.64	0.0030
	3	1275/2H	5.43	95.95	9.05	0.0019
	5	1200/2H	5.29	93.01	8.10	0.0019
	10	1200/2H	4.97	90.95	8.03	0.0017
	15	1200/2H	4.71	90.02	7.58	0.0023
ZBS	0.2	1350/2H	5.68	96.13	9.05	0.0039
	0.5	1350/2H	5.67	97.53	9.07	0.0035
	1	1275/2H	5.65	94.34	8.45	0.0029
	3	1275/2H	5.59	89.62	8.37	0.0022
	5	1250/2H	5.54	83.94	8.10	0.0028
	10	1200/2H	5.41	84.10	8.09	0.0022
	15	1200/2H	5.29	81.66	6.37	0.0016
LBS	0.2	1375/2H	5.67	94.18	9.58	0.0043
	0.5	1375/2H	5.65	93.45	9.08	0.0040
	1	1325/2H	5.61	92.69	8.99	0.0036
	3	1300/2H	5.46	93.77	8.78	0.0032
	5	1250/2H	5.33	93.80	8.35	0.0034
	10	1150/2H	5.03	90.46	6.91	0.0022
	15	975/2H	4.79	83.92	6.06	0.0025
MAS	0.2	1375/2H	5.67	93.12	9.14	0.0044
	0.5	1375/2H	5.65	93.09	8.59	0.0037
	1	1325/2H	5.61	90.02	8.58	0.0036
	3	1300/2H	5.46	92.31	8.72	0.0034
	5	1250/2H	5.32	94.55	8.28	0.0031
	10	1200/2H	5.02	90.44	8.26	0.0026
	15	1200/2H	4.77	86.79	7.07	0.0025
BBSZ	0.2	1375/2H	5.69	92.97	9.07	0.0029
	0.5	1375/2H	5.68	92.78	9.07	0.0035
	1	1300/2H	5.67	91.89	8.92	0.0037
	3	1300/2H	5.64	90.60	8.53	0.0030
	5	1250/2H	5.61	90.91	8.32	0.0026
	10	1200/2H	5.55	86.31	7.79	0.0021
	15	1150/2H	5.48	70.44	6.89	0.0022
LMZBS	0.2	1375/2H	5.68	93.84	12.17	0.0038
	0.5	1350/2H	5.66	92.76	10.10	0.0030
	1	1300/2H	5.63	92.72	9.47	0.0031
	3	1275/2H	5.52	92.39	8.84	0.0025
	5	1200/2H	5.41	92.79	7.75	0.0022
	10	1150/2H	5.19	89.79	7.29	0.0033
	15	950/2H	4.99	87.98	6.91	0.0026

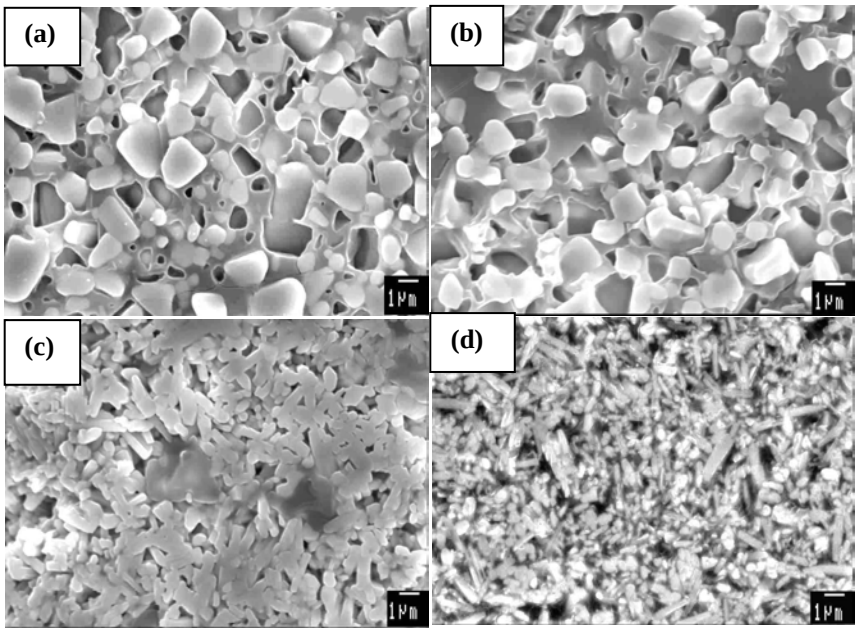

Fig. 4.11 The scanning electron micrographs of $Sm_2Si_2O_7$ (a) doped with 3wt% LBS sintered at 1300°C, (b) doped with 3wt% LMZBS sintered at 1275°C, (c) treated with 15wt% LBS sintered at 975°C and (d) treated with 15wt% LMZBS sintered at 950°C.

THE COMPOSITIONAL DEPENDENCE OF MICROSTRUCTURE WITH DIFFERENT AMOU
FOR $SM_2SI_2O_7$ CERAMIC IS SHOWN IN FIG. 4.11 (A)-(D). FIG. 4.11 (A) AND (B) SHOWS THE SEM
PICTURES OF $SM_2SI_2O_7$ WITH 3 WT% OF LBS AND LMZBS GLASS RESPECTIVELY. THE GLASS MEL
AND FORMS A LIQUID PHASE AND THE EXCESS AMOUNT OF GLASS CAN BE CLEARLY OBSE
SEM IMAGES. BOTH THE GLASSES DID NOT REACT WITH THE CERAMIC BUT FORMS A G
OVER THE GRAIN LEADING TO LIQUID PHASE FORMATION. AS THE AMOUNT OF GLASS
PORES APPEAR IN THE MICROSTRUCTURE. FIG. 4.11 (C) AND (D) ILLUSTRATES THE SEM P
$SM_2SI_2O_7$ DOPED WITH 15 WT% OF LBS AND LMZBS GLASS RESPECTIVELY. IT IS FOUND THA
ADDITION OF GLASS REDUCES THE GRAIN SIZE OF THE COMPOSITE INDICATING THAT A
SINTERING PROCESS PRODUCES SMALLER GRAIN SIZE THAN SOLID STATE SINTERING. TH
GRAIN SIZE AND INCREASE IN POROSITY ARE DUE TO THE LOWERING OF SINTERING TEMP
BY THE INCREASED GLASS CONTENT. THE PRESENCE OF TRACES OF SECONDARY PHASE
IN THE CASE OF 15 WT% LMZBS GLASS ADDED $Sm_2Si_2O_7$ (FIG. 4.11 (D)). B_2O_3-RICH
COMPOUNDS GENERALLY HAVE LOW MELTING POINT AND GROW INTO ABNORMALLY
DURING SINTERING. IT IS CONSIDERED TO ENHANCE $Sm_2Si_2O_7$ SINTERING AND INTERACTS

WITH OTHER IONS IN THE MATRIX PHASE. THIS SUGGEST THAT ALTHOUGH EXCESSIVE B_2O_3 CONTENT WOULD IMPROVE THE DENSITY OF THE SAMPLES, IT WOULD INTRODUCE A LARGE AMOUNT OF UNWANTED SECONDARY PHASES WHICH COULD DEGRADE THE PHYSICAL PROPE SAMPLES [26-28].

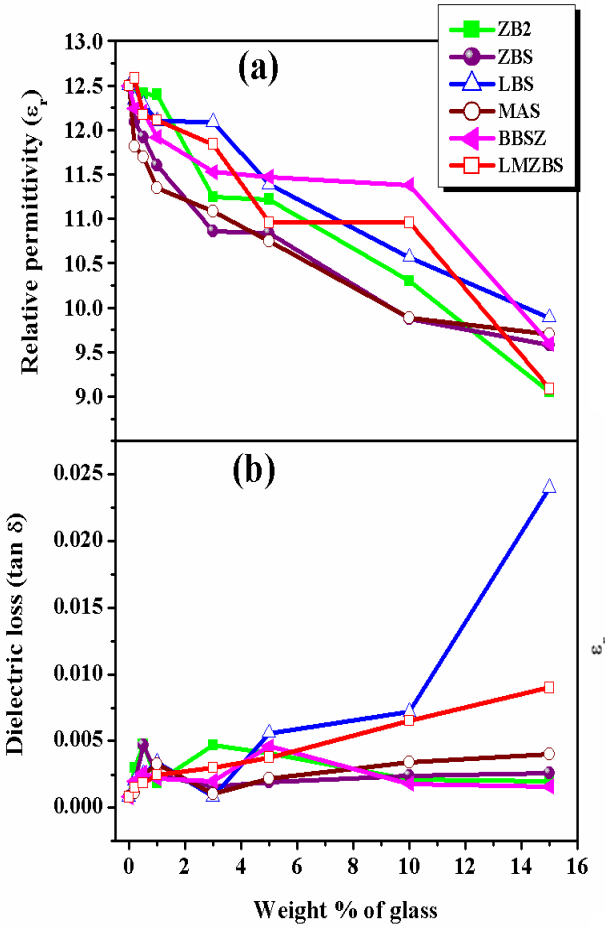

Fig. 4.12 Variation of dielectric properties of $Sm_2Si_2O_7$ as a function of glass addition.

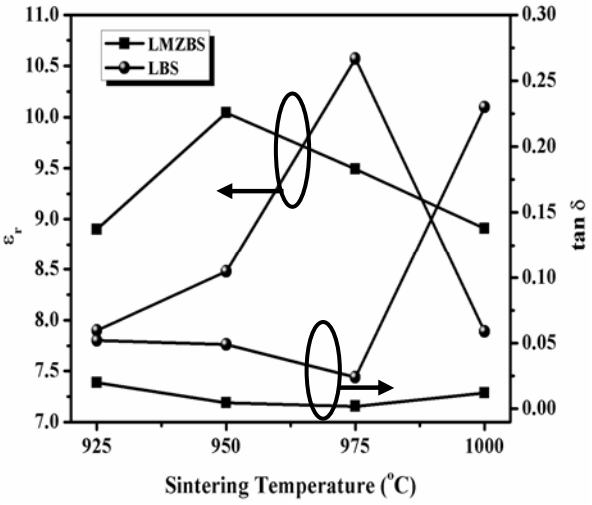

Fig. 4.13 The variation of dielectric properties with sintering temperature for $Sm_2Si_2O_7$ doped with (a) 15 wt% LBS glass and (b) 15 wt% LMZBS.

ACCORDING TO *et al.* [29] THE MICROWAVE DIELECTRIC LOSS AND THE RELATI PERMITTIVITY OF GLASS DEPEND ON THE IONIC SIZE, IONIC DIELECTRIC POLARIZA CONCENTRATION OF THE CATION IN THE NETWORK MODIFYING OXIDE IN THE GLASS. FI SHOWS THE VARIATION OF RELATIVE PERMITTIVITY MEASURED AT 1 MHZ WITH WEIGHT VARIOUS GLASS ADDED $Sm_2Si_2O_7$ CERAMICS. THE ε_r GRADUALLY DECREASES WITH INCREASE IN THE AMOUNT OF GLASSES. GENERALLY AN INCREASE IN RELATIVE DENSITY RESULTS IN AN

RELATIVE PERMITTIVITY VALUE. HOWEVER, IN THE CASE OF $Sm_2Si_2O_7$ CERAMICS WITH LOW WEIGHT PERCENTAGE OF GLASS, EVEN THOUGH AN INCREASE IN THE DENSIFICATION IS NOTED PERMITTIVITY SEEMS TO DECREASE. THIS MAY BE DUE TO THE LOW RELATIVE PERM GLASSES. THUS THE PRESENCE OF EXCESS GLASS IN THE MATRIX MAY CONTRIBUTE TO PERMITTIVITY OF THE COMPOSITE. FIG. 4.12 (B) SHOWS THE VARIATION OF DIELECTRIC FUNCTION OF DIFFERENT GLASS CONTENT. IT IS SEEN THAT THERE IS NOT MUCH VARIATION UPTO ABOUT 10 WT% OF THE GLASSES. HOWEVER, FURTHER ADDITION OF GLASS INCREASES *tan δ* VALUES.

IN ALKALI BORATE GLASS [30], THE OSCILLATION OF THE ALKALI ION WAS LIMITE BONDING WHILE IN THE VITREOUS STATE THEY WERE LOOSELY HELD IN THE INTERSTICI NETWORK WHICH WERE RELATIVELY FREE TO OSCILLATE WITH EXTERNAL FIELD, WHI EXTENSIVE DIELECTRIC LOSSES. WHEN SUCH LOSSY AMORPHOUS MATERIAL IS INCORPO LOW LOSS MATERIAL, THE DIELECTRIC LOSS OF THE LATTER CAN INCREASE. IN OR ACCEPTABLE DENSIFICATION AND DIELECTRIC PROPERTIES AT LOW TEMPERATURES, IT DESIGN GLASS COMPOSITIONS WITH A LOW GLASS TRANSITION TEMPERATURE AND A LOSS. IN THE PRESENT INVESTIGATION IT IS SEEN THAT B_2O_3 IS AN APPROPRIATE SINTERING AIDS FOR $Sm_2Si_2O_7$ DIELECTRIC CERAMICS. FIG. 4.13 SHOWS THE VARIATION OF RELATIVE PERM AND DIELECTRIC LOSS WITH SINTERING TEMPERATURE FOR $Sm_2Si_2O_7$+15 WT% LBS AND LMZBS GLASSES. IT IS OBSERVED THAT FOR BOTH THE GLASSES THE RELATIVE PERMITTI WITH THE SINTERING TEMPERATURE UP TO A PARTICULAR TEMPERATURE AND THERE THE $Sm_2Si_2O_7$+15 WT% LBS AND $Sm_2Si_2O_7$+15 WT % LMZBS COMPOSITES HAVE A MAXIMUM RELATIVE DENSITY OF 84% AT 875 °C AND 88% AT 950 °C RESPECTIVELY. BEYOND THESE RESPECTIVE TEMPERATURES THE DENSITY IS FOUND TO DECREASE. THE RELATIVE PER THESE COMPOSITIONS ALSO FOLLOW A SIMILAR TREND. IT IS WELL KNOWN [31] THAT AIDS CONTAINING BORON OXIDE AND LITHIUM OXIDE PROMOTES DENSIFICATION BY L SINTERING UP TO A PARTICULAR TEMPERATURE AND AS THE TEMPERATURE INCREASES THESE OXIDES MAY TAKE PLACE. THIS MAY LEAD TO THE FORMATION OF PORES THEREB THE DENSITY AND THE RELATIVE PERMITTIVITY. FIG. 4.13 ALSO COMPARES THE DIELEC $Sm_2Si_2O_7$ + 15 WT% LBS AND $Sm_2Si_2O_7$ + 15 WT% LMZBS MEASURED AT 1 MHZ AS A FUNCTION OF SINTERING TEMPERATURE. FROM THE FIGURE IT IS NOTED THAT THE DIEL LMZBS ADDED $Sm_2Si_2O_7$ IS LESS THAN THAT FOR LBS ADDED ONE. THE LMZBS ADDED SAMPL SHOWS ALMOST A STEADY VARIATION IN THE DIELECTRIC LOSS EXHIBITING A RELATIVE

0.009 AT 950°C WHEREAS THE LBS ADDED $Sm_2Si_2O_7$ HAS A HIGH LOSS OF 0.024 AT 975°C. THIS MAY BE ATTRIBUTED TO THE FACT THAT THE ADDITIONAL B_2O_3 IN THE FORM OF (SMBO $Sm_2Si_2O_7$/LMZBS COMPOSITE HAS A LOW DIELECTRIC LOSS IN THE RANGE OF 10^{-4} AND A RELATIVE PERMITTIVITY OF 9 [32]. AS THE SINTERING TEMPERATURE INCREASES THE DIELECTRIC LO REACHING A MINIMUM AT THEIR RESPECTIVE TEMPERATURES AND THEN INCREASES. THI TO THE INCREASED POROSITY PRODUCED DUE TO THE EVAPORATION OF THE VOLATILE B_2O_3 AND Li_2O AT HIGHER TEMPERATURES.

TABLE 4.2 GIVES THE MICROWAVE DIELECTRIC PROPERTIES OF VARIOUS GLAS $Sm_2Si_2O_7$ COMPOSITES. A COMPARISON OF THE DIELECTRIC PROPERTIES OF THE COMPOSIT AND MICROWAVE FREQUENCY POINTS TO THE FACT THAT THE DIELECTRIC LOSS IS MICROWAVE REGION. ONE OF THE MAIN REASONS MAY BE THAT THE NETWORK FORMERS THE REMAINING GLASS CAN PROFOUNDLY ABSORB THE MICROWAVE POWER AT HIGH WHICH INCREASES THE DIELECTRIC LOSS OF THE COMPOSITES [33]. THE DIELECTRIC LOSS IS DEPENDENT ON VARIETY OF FACTORS WHICH ARE EXPLAINED IN CHAPTER 1 SECTION1.

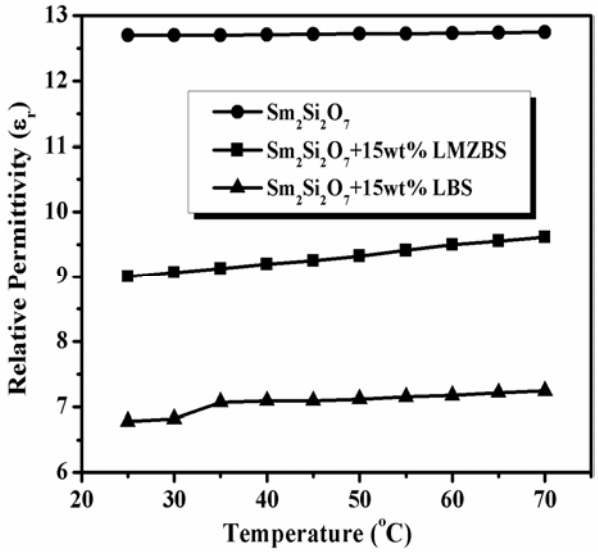

Fig. 4.14 The variation of relative permittivity with temperature of $Sm_2Si_2O_7$ treated with 15 wt% LBS glass and 15 wt% LMZBS.

FIGURE 4.14 SHOWS THE VARIATION OF RELATIVE PERMITTIVITY WITH TEMPER $Sm_2Si_2O_7$ TREATED WITH 15 WT% LMZBS AND 15 WT% LBS. THE RELATIVE PERMITTIVITY O GLASS ADDED $Sm_2Si_2O_7$ VARIES FROM 9 TO 9.61 IN THE TEMPERATURE RANGE 25-70°C.

VALUE INCREASES TO 79.3 WITH THE ADDITION OF 15 WT% LMZBS GLASS SHOWING A PERCENTAGE DEVIATION OF NEARLY 0.36%. HOWEVER, A VERY GOOD VALUE OF τ_ε IS NOTED IN THE CASE OF LBS GLASS WHERE THE RELATIVE PERMITTIVITY VARIES FROM 6.78-7.24 IN THE TEMPERATURE RANGE. THE PERCENTAGE DEVIATION FOR THE LBS GLASS IS NOTED AS (THE ADDITION OF GLASS INCREASES THE K_ε VALUE. THIS IS DUE TO THE HIGH POSITIVE τ_ε VALUE POSSESSED BY THE GLASSES. THE RESULTS SHOW THAT SiO_2 WHEN MIXED WITH SUITABLE AMOUNT OF GLASS CAN EFFECTIVELY LOWER THE SINTERING TEMPERATURE AND CAN BE EXPLOITE APPLICATIONS.

4.2 MICROWAVE DIELECTRIC PROPERTIES OF NOVEL RARE EARTH BASED SILICATES: $RE_2TI_2SIO_9$ [RE = LA, PR, ND]

4.2.1 INTRODUCTION

THE GROWING IMPORTANCE OF CERAMICS DIELECTRICS FOR APPLICATIONS AS M OSCILLATORS, FILTERS ETC HAS LED TO GREAT ADVANCES IN THE MATERIAL RESEARCH OF NEW DIELECTRIC CERAMIC SYSTEMS. MANY MICROWAVE DIELECTRIC MATERIALS DEVELOPED AND MODIFIED ACCORDING TO THE NEEDS OF THE SPECIFIC APPLICATIONS RESPECT TO THE SPECIFIC MICROWAVE APPLICATIONS, THEY SHOULD POSSESS A RANGE PROPERTIES, INCLUDING APPROPRIATE RELATIVE PERMITTIVITY, HIGH QUALITY FACT TEMPERATURE COEFFICIENT OF RESONANT FREQUENCY [34]. THE NEED TO PRODUCE THE TO GET CERAMIC MATERIALS HAVING HIGH RELATIVE PERMITTIVITY (>20), HIGH QUALIT SMALL τ_f VALUE. RECENTLY AVAILABLE QUALITY MATERIALS WILL EXTEND COMMERCIAL APPLICATIONS OF DIELECTRIC RESONATORS TO MUCH HIGHER FREQUENCIES, BUT FU DEVELOPMENT IS NEEDED.

NOW-A-DAYS, CONSIDERABLE ATTENTION HAS BEEN PAID ON MANY SILICATE MA USE IN MICROWAVE APPLICATIONS [2, 16, 35-36]. SILICATES GENERALLY EXHIBIT LOW PERMITTIVITY AND ALSO A NEGATIVE VALUE OF TEMPERATURE COEFFICIENT OF RESON CERAMIC DIELECTRIC MATERIALS BASED ON TITANATES ARE IMPORTANT FOR VARIETY O COMMUNICATION SYSTEMS [37]. SEVERAL TITANIUM BASED COMPOSITIONS WERE DEVELO SHOWS A LOW Q_f ALSO FOR CERTAIN LOW LOSS DIELECTRIC MATERIALS SUITABLE AMOUN ADDITION COULD TUNE τ_f TO NEAR ZERO VALUE. IN GENERAL TiO_2 BASED COMPOSITIONS ARE MUCH EFFECTIVE FOR DEVELOPING MATERIALS WITH TEMPERATURE STABLE DIELECT

CONTINUING THE RESEARCH ON SILICATE BASED DIELECTRIC MATERIALS, A STRONG INT
NEW CLASS OF MATERIALS- RARE EARTH TITANOSILICATES [$RE_2TI_2SIO_9$] BELONGING TO THE CRYSTAL
STRUCTURE TRIMOUNSITE WITH MONOCLINIC SYMMETRY. IT INCLUDES A NETWORK OF
TETRAHEDRA CONNECTED BY TWO TYPES OF OCTAHEDRA [38-39]. AN IDEAL TRIMOUNSITE
CRYSTAL STRUCTURE IS SHOWN IN FIG. 4.15.

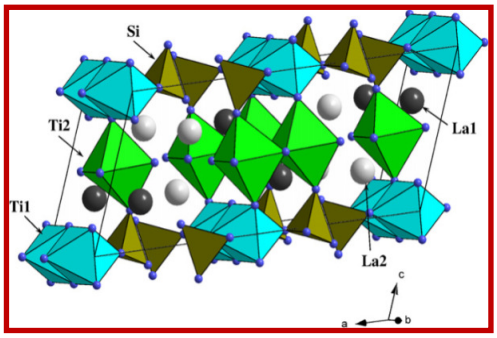

Fig. 4.15 Crystal structure of trimounsite.

UNLIKE PEROVSKITE TYPE STRUCTURES WHERE ALL OCTAHEDRAL ARE CORNER
EQUIVALENT TO POLYHEDRA IN $RE_2TI_2SIO_9$ SHARE THEIR EDGES. TWO NON-EQUIVALENT RE SITES
EXISTING IN THIS STRUCTURE ARE LOCATED BETWEEN TWO LAYERS. ALSO, THE LATTICE
COMPRISES RELATIVELY LARGE CAVITIES BETWEEN METAL OXYGEN POLYHEDRAL, W
OCCUPIED BY INTERSTITIAL IONS. EARLIER REPORTS BY SWANSON *et al.* [40-43] SUGGESTED THREE MIXED
VALENCE LA-TITANOSILICATES. HOWEVER, THE DIELECTRIC PROPERTIES OF THESE COMP
UNKNOWN. THE PRESENT STUDY THROWS LIGHT INTO THE MICROWAVE DIELECTRIC
$RE_2TI_2SIO_9$ [RE=LA, PR AND ND]. THE EFFECT OF SUBSTITUTION IN THE RE-SITE ON THE STR
AND PROPERTIES ARE ALSO INVESTIGATED.

4.2.2 EXPERIMENTAL

THE $RE_2TI_2SIO_9$ [RE = LA, PR AND ND] (NAMED AS LTS, PTS AND NTS
RESPECTIVELY) CERAMICS WERE PREPARED BY THE CONVENTIONAL SOLID STATE CER
EXPLAINED IN CHAPTER 2, SECTION 2.1.2. THE STARTING MATERIALS WERE HIGH PU
(ALDRICH CHEMICAL COMPANY INC., MILWAUKEE, WI; 99.9%), TiO_2 (99.9%-ALDRICH INC., ST.
LOUIS, MO; 99.9%), RARE EARTH OXIDES La_2O_3, Pr_6O_{11}, Nd_2O_3 (IRE, 99.9 %) CHEMICALS.
THE MIXED AND DRIED POWDERS WERE CALCINED AT 1100 °C FOR 4 HRS AND THEN GROUND WELL IN AN

AGATE MORTAR. AFTER PELLETIZING, SINTERING WAS DONE IN THE TEMPERATURE RANG
FOR 2 HOURS. THE BULK DENSITIES OF THE POLISHED SAMPLES WERE MEASURED USING I
METHOD.

THE SINTERED SAMPLES WERE POWDERED AND USED TO ANALYZE THE CRYSTAL S
PHASE PURITY BY X-RAY DIFFRACTION METHOD AND THE SURFACE MORPHOLOGY OF
SAMPLES WAS RECORDED USING SCANNING ELECTRON MICROSCOPE. THE DIELECTRIC P
$Q_u xf$ AND $_f$ OF SINTERED AND POLISHED MATERIALS WERE MEASURED IN THE MICROWAVE
RANGE USING RESONANCE TECHNIQUE [42-44] AS DESCRIBED IN CHAPTER 2, SECTIONS
2.5.5.

4.2.3 RESULTS AND DISCUSSION

THE CALCINATION AND SINTERING TEMPERATURES OF $La_2Ti_2SiO_9$ [RE=LA, PR AND ND]
DIELECTRIC CERAMICS ARE OPTIMIZED AT THE MAXIMUM DENSITY POINT AS DESCRI
PREVIOUS SECTION. THE OPTIMIZED SINTERING TEMPERATURES OF THE RESPECTIVE M
GIVEN IN TABLE 4.3. FIG. 4.16 SHOWS THE X-RAY DIFFRACTION PATTERNS OF $RE_2Ti_2SiO_9$ [RE=LA,
PR AND ND] SINTERED AT THEIR RESPECTIVE SINTERING TEMPERATURES. THE DIFFRACT
INDEXED BASED ON THE EARLIER REPORTS ON $La_2Ti_2SiO_9$ [JCPDS FILE NO. 82-1490]. THEY
BELONG TO THE SPACE GROUP C2/M (12) WITH MONOCLINIC SYMMETRY. THE CRYSTAL ST
LTS HAS BEEN REPORTED BY *et al.* [39]. EARLY REPORTS BY KOLITSCH [38] POINTED OUT THAT
IT IS DIFFICULT TO SYNTHESIZE $La_2Ti_2SiO_9$, HOWEVER, IN THE PRESENT CASE NO SECONDARY PHASE
ARE IDENTIFIED.

FIGURE 4.17 SHOWS THE XRD PATTERNS OF $Sm_2Ti_2SiO_9$ [SMTS] AND $Ln_2Ti_2SiO_9$
[LNTS] CERAMICS SINTERED AT 1275 . IT IS NOTED THAT $(La_{2-x}Nd_x)Ti_2SiO_9$ [X=0-2] FORMS
SINGLE PHASE COMPOSITION IN THE WHOLE RANGE. NO ADDITIONAL PHASES ARE DETEC
DIFFRACTION DATA. ALL THE PEAKS CAN BE INDEXED BASED ON THE PARENT MATERIA
CAN BE CONCLUDED THAT THESE COMPOSITIONS FORM A SOLID SOLUTION. HOWEVER, I
ND SUBSTITUTION FOR LA, THE PRESENCE OF ADDITIONAL PHASES OF $Nd_2Ti_2O_7$ IS NOTED

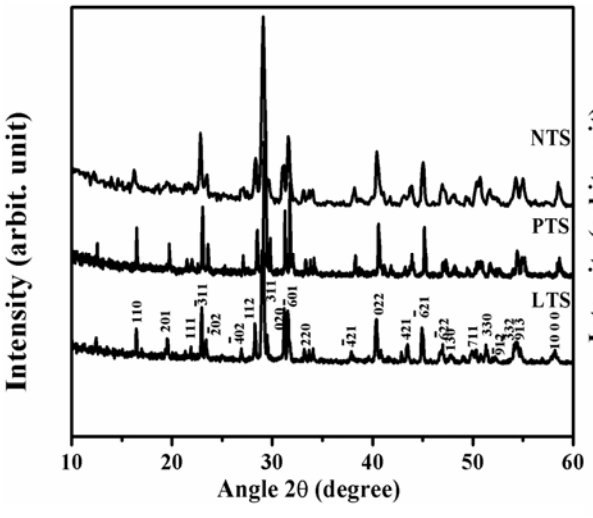

Fig. 4.16 XRD patterns of $La_2Ti_2SiO_9$, $Pr_2Ti_2SiO_9$ and $Nd_2Ti_2SiO_9$.

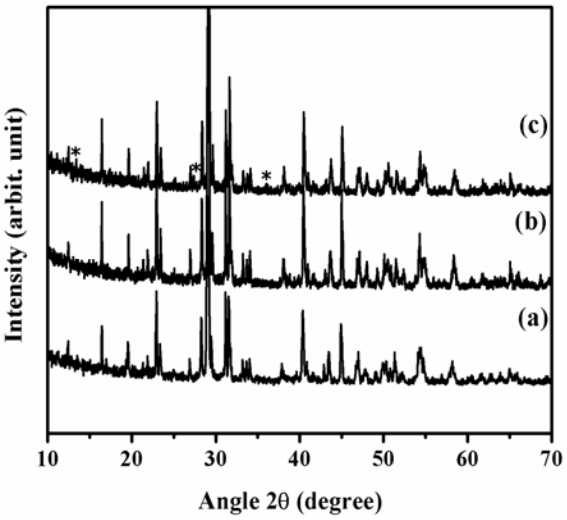

Fig. 4.17 XRD patterns of (a) $La_2Ti_2SiO_9$, (b) $LaPrTi_2SiO_9$ and (c) $LaNdTi_2SiO_9$ (* represents the $Nd_2Si_2O_7$ phase).

Table 4.3 The optimized sintering temperatures, lattice parameters and the microwave dielectric properties of $RE_2Ti_2SiO_9$ [RE = La, Pr and Nd].

Material	Sint. Temp	Theo. density (g/cm^3)	Lattice parameters				Microwave Dielectric Properties		
			a (Å)	b (Å)	c (Å)	β (^{o})	$Q_U X F$ (GHz)	ε_R	τ_F (ppm/^{o}C)
LTS	1325^{C}C	5.21	16.998	5.745	7.625	111.19	29500	28.3	22.6
PTS	1325^{C}C	5.36	16.888	5.718	7.569	111.42	33700	29.2	19.5
NTS	1275^{C}C	5.31	17.029	5.737	7.638	111.23	19600	30.1	9.6

THE LATTICE PARAMETERS OF LTS, PTS AND NTS ARE CALCULATED FROM THE PATTERNS USING X'PERT PLUS SOFTWARE PACKAGE AND THE VALUES OBTAINED ARE L 4.3. SINCE THE IONIC RADIUS DECREASES FROM LA TO ND, IT IS EXPECTED THAT TH PARAMETERS MUST SHOW A REGULAR VARIATION IE., A DECREASE IN THE LATTICE PAR HOWEVER, IN THE PRESENT CASE EVEN THOUGH A DECREASE IS NOTED IN THE CASE O PARAMETERS SHOW AN INCREASE FOR NTS. FIG. 4.18 SHOWS THE VARIATION OF TH PARAMETERS OF THE $La_{2-x}A_xTi_2SiO_9$ [A=PR, ND; X=0, 0.5, 1, 1.5, 2] SOLID SOLUTIONS AS A FUNCTION OF X. THE LATTICE PARAMETERS VARY LINEARLY AS THE X VALUE INCREASE

$La_{2-X}PR_XTI_2SIO_9$ COMPOSITIONS WHICH CONFIRM THAT THE PR SUBSTITUTED SOLID SO
SATISFIES THE VEGARD'S LAW. IT IS SEEN THAT AS PR SUBSTITUTION FOR LA INCREASE
PARAMETERS (A, B AND C) DECREASES AND β INCREASES IN A LINEAR FASHION WHICH IS DUE TO TH
LOW VALUE OF IONIC RADIUS OF PR WHEN COMPARED WITH THAT OF LA [45-46]. HOWEV
CASE OF ND CONTAINING SOLID SOLUTION, A LINEAR VARIATION IN THE LATTICE PARAM
IN THE RANGE $0 \leq X \leq 1.5$. THUS UPTO THIS COMPOSITION (X = 1.5) VEGARD'S LAW IS OBEYED AN
BEYOND THAT AN INCREASE IN THE VALUES ARE NOTED.

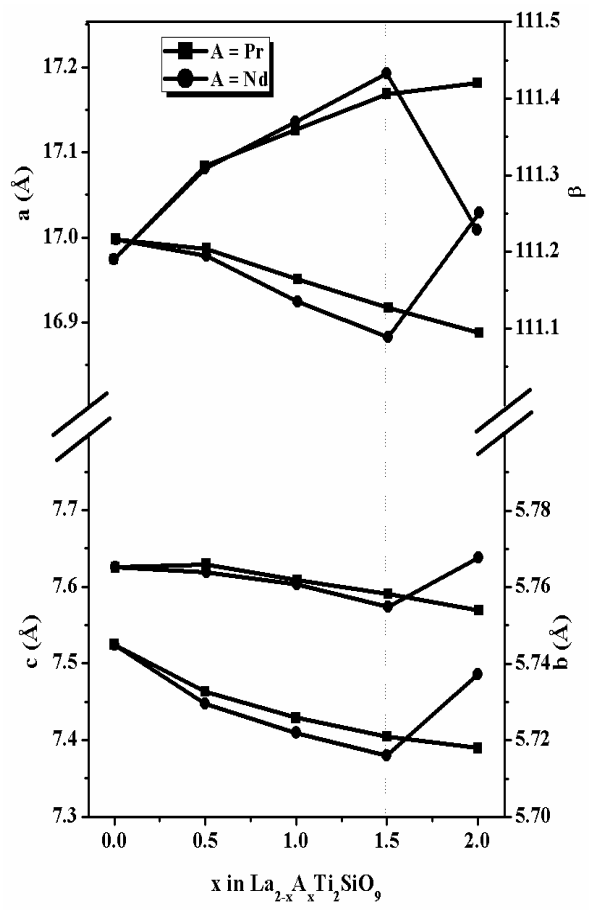

Fig. 4.18 Variation of lattice parameters of $La_{2-x}A_xTi_2SiO_9$ [A= Pr and Nd] with x.

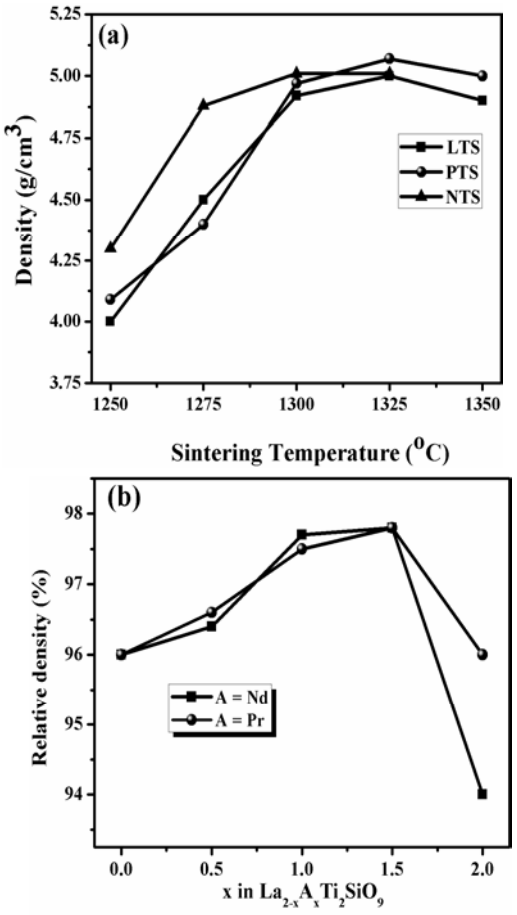

Fig. 4.19 The variation of (a) density of $RE_2Ti_2SiO_9$ [RE=La, Pr and Nd] with sintering temperature and (b) relative density with composition x.

FIGURE 4.19 (A) SHOWS THE VARIATION OF THE BULK DENSITY OF $La_2Ti_2SiO_9$ [RE=LA, PR AND ND] CERAMICS WITH SINTERING TEMPERATURE. IT IS SEEN THAT AS THE SINTERING

INCREASES THE DENSITY ALSO INCREASES, REACHES A MAXIMUM AND THEN DECREAS
THIS IS DUE TO THE ELIMINATION OF PORES WITH INCREASE IN THE SINTERING TEMPE
THEORETICAL DENSITIES OF THE MATERIALS ARE GIVEN IN TABLE 4.3. THE SINTERING TE
THE RESPECTIVE COMPOUNDS ARE OPTIMIZED AT THEIR MAXIMUM DENSITY POINT. TH
DENSITY INCREASES TO ABOUT 96%, 95% AND 94% OF THE THEORETICAL DENSITIES FOR
AND NTS CERAMICS RESPECTIVELY AT THEIR OPTIMIZED SINTERING TEMPERATURES. FR
(B) IT IS SEEN THAT THE RELATIVE DENSITY INCREASES GRADUALLY WITH INCREASE IN X
AND PR. THE RELATIVE DENSITY INCREASES FROM 96 - 97.8 % IN THE CASE OF BOTH PR
BASED SOLID SOLUTIONS IN THE RANGE $X \leq 1.6$. HOWEVER, AT X = 2, FOR PTS AND NTS A
SUDDEN DECREASE IN THE RELATIVE DENSITY IS NOTED.

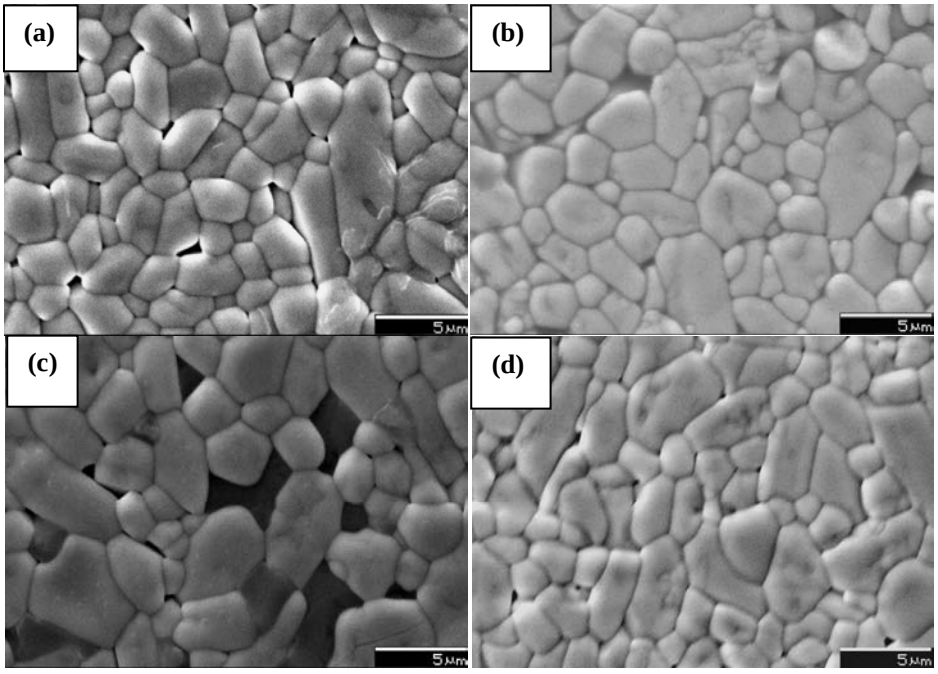

Fig. 4.20 The SEM pictures of (a) LTS, (b) PTS, (c) LNTS and (d) LPTS sintered at 1325^{o}C.

FIGURES 4.20 (A) AND (B) SHOW THE SEM IMAGES OF THE POLISHED AND THERM
ETCHED LTS AND PTS RESPECTIVELY SINTERED AT 1325^{o}C. BOTH THE IMAGES SHOW A WELL
PACKED SYSTEM WITH GRAIN SIZE VARYING FROM 1-5µM. NO OBVIOUS PORES AND A
GRAINS ARE OBSERVED IN THE SEM IMAGES WHICH CONFIRM GOOD DENSIFICATION. FIG
AND (D) RESPECTIVELY SHOWS THE MICROSTRUCTURES OF LNTS AND LPTS SINTERED A^{o}C

THE PRESENCE OF SECONDARY PHASE IN LNTS IS EVIDENT FROM THE SEM IMAGE (FIG. 4.2
IT IS ALSO NOTED THAT THE LOW MELTING Y_2SiO_5 PHASE FORMED APPEARED AS A LIQUID PHASE
WHICH IN TURN IMPROVED THE DENSIFICATION OF THE MATERIAL. FIG. 4.20 (D) SHOW
PACKED ARRANGEMENT OF GRAINS FOR THE SOLID SOLUTION LPTS.

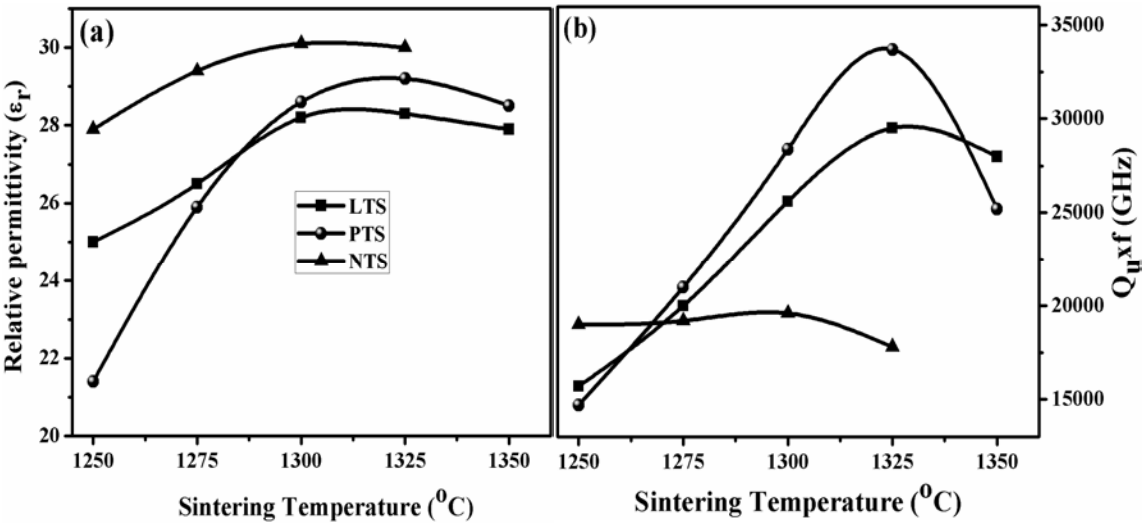

Fig. 4.21 The variation of (a) relative permittivity and (b) $Q_U X F$ of $RE_2Ti_2SiO_9$ [RE=La, Pr and Nd] with sintering temperature.

FIGURE 4.21 SHOWS THE VARIATION OF THE DIELECTRIC PROPERTIES OF $RE_2Ti_2SiO_9$
[RE=LA, PR AND ND] CERAMICS WITH THE SINTERING TEMPERATURE. THE RELATIVE PERM
THE CERAMICS INCREASES WITH INCREASE IN THE SINTERING TEMPERATURES AND SAT
FROM FIG. 4.21 (A). THE RELATIONSHIP BETWEEN RELATIVE PERMITTIVITY AND S
TEMPERATURES REVEAL THE SAME TENDENCY WITH THAT BETWEEN DENSITY VALUES A
TEMPERATURES, BECAUSE HIGHER SINTERING TEMPERATURES WILL CAUSE THE GRAI
MINIMUM PORES LEADING TO HIGHER ε_r VALUES. THE RELATIVE PERMITTIVITY IS MAXIMUM AT
THE TEMPERATURE WHERE THE BULK DENSITY SHOWED A MAXIMUM OR CONSISTENT VA
PTS AND NTS RESPECTIVELY SHOW A RELATIVE PERMITTIVITY OF 28.3, 29.2 AND 30.1 AT
OPTIMIZED SINTERING TEMPERATURES. SINCE NO ADDITIONAL SECONDARY PHASES ARE
XRD, THIS IS CORRELATED WITH THE DECREASE IN DENSITY AT HIGHER TEMPERATURES.
SHOWS THE $Q_u \times f$ VALUES OF LTS, PTS AND NTS CERAMICS AS A FUNCTION OF SINTERI
TEMPERATURES. AS THE SINTERING TEMPERATURE INCREASES, THE QUALITY FACTOR AL

REACHES A MAXIMUM VALUE AND FURTHER INCREASE IN THE SINTERING TEMPERATURE
Q-FACTOR. THE MICROWAVE DIELECTRIC LOSS IS AFFECTED BY BOTH INTRINSIC AND EX
[47]. THE MICROWAVE DIELECTRIC LOSS INCREASES DRASTICALLY WHEN THE LATTICE DI
A DISORDERED DISTRIBUTION OF THE CHARGES WHICH DEVIATE FROM PERFECT LATT
[48]. A MAXIMUM $Q_u \times f$ VALUE OF 33700 GHZ IS SHOWN BY PTS AT A SINTERING TEMPERATU
OF 1325^{O}C. THE NTS CERAMICS EXHIBITED THE LOWEST QUALITY FACTOR OF 19600 GH
1275^{O}C.

FIGURE 4.22 SHOWS THE VARIATION OF MICROWAVE DIELECTRIC PROPERTIES
$_{X}A_{X}TI_{2}SIO_{9}$ [A=PR, ND; X=0, 0.5, 1, 1.5, 2] AS A FUNCTION OF X. IT IS CLEAR FROM FIG. 4.22 (A)
THAT THE RELATIVE PERMITTIVITY IS LINEARLY DEPENDENT ON THE X VALUE IE.,
PERMITTIVITY INCREASES WITH INCREASE IN X FOR BOTH PR AND ND. THE RELATIVE
INCREASES FROM 28.3 TO 29.2 AND 28.3 TO 30.1 RESPECTIVELY FOR PR AND ND BASED
SOLUTIONS. THE RELATIVE PERMITTIVITIES OF THE CERAMICS DEPEND ON THE RELATIV
ALSO ON THE IONIC POLARIZABILITY (α). ACCORDING TO THE IONIC POLARIZABILITY VALUE REPORTE
VINEIS, THE OF LA^{3+} ION (4.82 Å^3) IS SMALLER THAN THAT OF PR^{3+} ION (5.22 Å^3) AND ND^{3+} ION
(5.01 Å^3) [49]. THUS WITH THE SUBSTITUTION OF PR OR ND FOR LA, AN INCREASE IN THE
PERMITTIVITY IS NOTED WHICH IS DUE TO THE INCREASE IN THE IONIC POLARIZABILIT
RELATIVE PERMITTIVITY OF A CERAMIC IS VERY MUCH AFFECTED BY EXTRINSIC FAC
POROSITY. THE RELATIVE PERMITTIVITY IS CORRECTED FOR POROSITY USING EQ. (3.3
CHAPTER 3. THE POROSITY CORRECTED RELATIVE PERMITTIVITY (ε_{corr}) USING THE ABOVE
EQUATION IS PLOTTED AS A FUNCTION OF X IN FIG. 4.22 (A). THE ε_{corr} VARIES FROM 30 - 31.7 IN THE
CASE OF $_{2-x}$PR$_x$TI$_2$SIO$_9$ AND FROM 30 - 32.8 FOR $_{2-x}$ND$_x$TI$_2$SIO$_9$. THE DIFFERENCE BETWEEN
ε_r AND ε_{corr} DECREASES WITH X UPTO X=1 AND BEYOND THIS VALUE THE DEVIATION IN
SHOWING THE DOMINANT EFFECT OF POROSITY ON THE RELATIVE PERMITTIVITY OF THE

FIGURE 4.22 (B) SHOWS THE COMPOSITIONAL DEPENDENCE OF QUALITY FACTOR (Q_u)
$_{X}A_{X}TI_{2}SIO_{9}$ [A=PR, ND; X=0, 0.5, 1, 1.5, 2] CERAMICS. IT IS TO BE NOTED THAT AT X = 0.5, THE
QUALITY FACTOR DECREASES FOR BOTH A=PR AND ND IN $_{2-x}$PR$_x$TI$_2$SIO$_9$ [X = 0.5] AND $_{2-x}$ND$_x$TI$_2$SIO$_9$ [X = 0.5] CASE OF LA
THE QUALITY FACTOR GRADUALLY INCREASES AND REACHES A MAXIMUM AT X = 2 W
VALUE OF 33700 GHZ. IT IS INTERESTING TO NOTE THAT THE $Q_u \times f$ VALUE INCREASED WITH X DESPITE
THE FACT THAT A DECREASE IN THE DENSITY IS NOTED AT X = 2. HOWEVER, THE LA$_{2-x}$ND$_x$TI$_2$SIO$_9$
CERAMICS EXHIBIT ALMOST A CONSTANT $Q_u \times f$ VALUE IN THE RANGE 0.5 < X < 2. IN VIEW OF THE

CRYSTAL PHASES AND MICROSTRUCTURES, THE VARIATIONS OF THE DIELECTRIC PRO
CONTENT MAY BE ATTRIBUTED TO THE CHANGE OF PHASE RELATIONS AND MICROSTRUC
THE SUBSTITUTION OF ND FOR LA. THE DIELECTRIC LOSS OF THE PERFECT CRYSTALS
FREQUENCY IS CONSIDERED TO ORIGINATE FROM THE ANHARMONIC LATTICE FORCES T
INTERACTION BETWEEN CRYSTAL'S PHONONS.

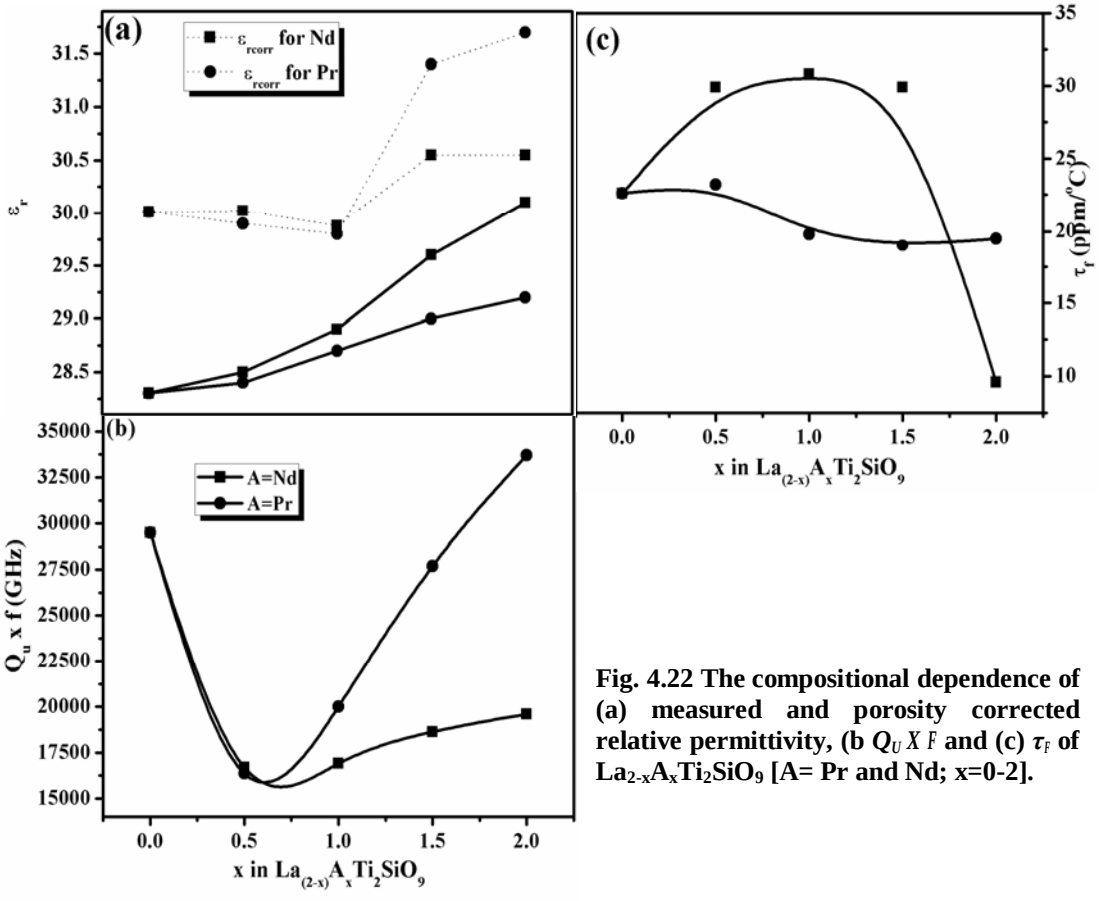

Fig. 4.22 The compositional dependence of (a) measured and porosity corrected relative permittivity, (b $Q_U X F$ and (c) τ_F of $La_{2-x}A_xTi_2SiO_9$ [A= Pr and Nd; x=0-2].

FIG. 4.22 (C) SHOWS THE VARIATION OF τ_f WITH X FOR BOTH PR AND ND SUBSTITUTION FOR LA. IN THE CASE OF PR SUBSTITUTED COMPOSITIONS, τ_f SEEMS TO REMAIN ALMOST CONSTANT WITH X WHILE FOR ND SUBSTITUTION, A NONLINEAR REDUCTION IN τ_f IS NOTICED. IN GENERAL, τ_f IS KNOWN TO BE RELATED WITH THE TEMPERATURE COEFFICIENT OF RELATIVE PERMITTIVITY (τ_ε) AND THE THERMAL EXPANSION COEFFICIENT OF WHICH THE VALUE IS APPROXIMATELY NEGATIVE ONE HALF OF τ_ε [56]. IN THE MICROWAVE DIELECTRIC CERAMICS, Kolodiazhnyi *et al.* [57] HAVE INVESTIGATED THE INTERRELATIONSHIP BETWEEN $Q_U \times f$ AND CRYSTAL STRUCTURE IN Ln_2O_3-TiO_2 CERAMICS AND SUGGESTED THAT τ_ε OF THE CERAMICS VARIES LINEARLY AS A FUNCTION OF UNIT CELL VOLUME AND REACHES A MINIMUM VALUE OF ABOUT 9.6 PPM/

FOR X = 2. THUS IT CAN BE CONCLUDED THAT WHILE PR BASED SOLID SOLUTION IMP
QUALITY FACTOR, THE ND SUBSTITUTION IMPROVED THE τ_f VALUE.

4.3 CONCLUSIONS

- THE SYNTHESIS AND MICROWAVE DIELECTRIC PROPERTIES OF TWO NEW RARE E
  SILICATES ($Sm_2Si_2O_7$ AND $RE_2Ti_2SiO_9$ [RE=LA, PR AND ND]) ARE INVESTIGATED IN THIS
  CHAPTER. THE DIELECTRIC CERAMICS ARE PREPARED BY SOLID STATE CERAMIC R
  STRUCTURE AND MICROSTRUCTURE ARE DETERMINED USING XRD AND SEM TE
  RESPECTIVELY. THE $Sm_2Si_2O_7$ CERAMICS IS ALSO SYNTHESIZED BY SOL-GEL TECHNIQUE
  OBTAIN NANO POWDERS. $Sm_2Si_2O_7$ CERAMICS REVEALED A TETRAGONAL SYMMETR
  WHEREAS $RE_2Ti_2SiO_9$ HAS A MONOCLINIC STRUCTURE.

- THE DIELECTRIC PROPERTIES OF THESE TWO SILICATE BASED SYSTEMS ARE INVES
  THE FIRST TIME. THE $Sm_2Si_2O_7$ CERAMIC POSSESS A RELATIVE PERMITTIVITY OF 12.5 AN
  DIELECTRIC LOSS OF 0.0008 AT 1 MHZ AT A SINTERING TEMPERATURE OF 1375 °C. AT
  MICROWAVE FREQUENCY, A LOW RELATIVE PERMITTIVITY OF 10 AND A LOSS FACT
  IS OBTAINED.

- THE SINTERING TEMPERATURE OF $Sm_2Si_2O_7$ IS LOWERED BY THE ADDITION OF SEVERAL LOW
  LOSS GLASSES. IT IS FOUND THAT B_2O_3 BASED GLASSES ARE MORE EFFECTIVE IN
  LOWERING THE SINTERING TEMPERATURE WITHOUT AFFECTING THE DIELECTR
  ADDITION OF 15 WT% LBS GLASS REDUCES THE SINTERING TEMPERATURE TO 975 °C WITH ε_r
  OF 9.89 AND $\tan\delta$ OF 0.024 WHEREAS 15 WT% LMZBS GLASS ADDITION DECREASES THE
  SINTERING TEMPERATURE OF $Sm_2Si_2O_7$ TO 950 °C WITH ε_r = 9.09 AND $\tan\delta$ = 0.009.

- THE SOL-GEL SYNTHESIZED $Sm_2Si_2O_7$ CERAMICS RESULTED IN NANO POWDERS WHOSE
  CALCINATION TEMPERATURE IS MUCH LOWER (900 °C). HOWEVER, THE DIELECTRIC PROPERTIES OF
  NANO $Sm_2Si_2O_7$ CERAMICS ARE NOT MUCH PROMISING WHICH IS DUE TO THE L
  DENSIFICATION ACHIEVED.

- THE $RE_2Ti_2SiO_9$ [RE = LA, PR AND ND] CERAMICS HAVE A RELATIVE PERMITTIVITY L
  THAN 20 AND RELATIVELY LOW τ_f VALUE. A MAXIMUM VALUE OF $Q_u \times f$ OF 33700 GHZ IS
  SHOWN BY $Pr_2Ti_2SiO_9$ CERAMICS WITH ε_r = 29.2 AND τ_f = 19.5 PPM/°C. THE
  MICROWAVE DIELECTRIC PROPERTIES OF $RE_2Ti_2SiO_9$ [RE= LA, ND] CERAMICS ARE

RESPECTIVELY. $Q_u \times f$ = 29500 GHZ AND 19600 GHZ, τ_f = 28.3 AND 30.1 AND ε_r = 22.6 AND 9.6 PPM/°C.

- IT IS SEEN THAT PR SUBSTITUTION FOR LA FAVORED THE FORMATION OF SOLID SO WHOLE RANGE WHILE ND SUBSTITUTION RESULTED IN THE FORMATION OF ADDITI AS THE PR CONTENT INCREASES, AN IMPROVEMENT IN THE QUALITY FACTOR IS NOT τ_f VALUE IS NOT MUCH AFFECTED.

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CHAPTER 5

POLYMER-CERAMIC COMPOSITES FOR MICROELECTRONIC APPLICATIONS

This chapter describes in detail the synthesis and characterization of various polymer-ceramic composites with $Sm_2Si_2O_7$ as filler. The polymers used for the present study are Polytetrafluoroethylene (PTFE), Polyethylene (PE) and Polystyrene (PS). These composites are prepared by two different methods:- powder processing and melt mixing methods. The dielectric properties (at 1 MHz and 9 GHz), thermal and mechanical properties of these composites are investigated. The effect of coupling agent and the filler size on these properties are also investigated for PTFE/$Sm_2Si_2O_7$ composites. Various theoretical models are used to calculate the effective relative permittivities of the composites and are compared with the experimentally observed results.

5.1 INTRODUCTION

THE EVER INCREASING DEMAND FOR HIGH PERFORMANCE ELECTRONIC DEVICES N
NEW MATERIALS TO BE USED AS CIRCUIT BOARD LAMINATES THAT POSSESS SUPERIOR PE
COMPARED TO THE CONVENTIONALLY USED ONES. THESE MATERIALS SHOULD SATISFY C
REQUIREMENTS SUCH AS LOW RELATIVE PERMITTIVITY TO REDUCE THE SIGNAL PROPAGA
DIELECTRIC LOSS FOR BETTER DEVICE PERFORMANCE, HIGH THERMAL CONDUCTIVITY T
HEAT GENERATED, LOW OR MATCHING THERMAL EXPANSION COEFFICIENT WITH TH
MOISTURE ABSORPTION RESISTANCE, HIGH DIMENSIONAL STABILITY AND MECHANICAL
2]. IN COMMERCIALLY HIGH FREQUENCY SUBSTRATES, BASED ON COMPLEX COMPOSITES
OR WOVEN QUARTZ FILLERS AND HYDROCARBON RESINS OR GLASS MICROFIBERS MATRIC
TO FIND TEMPERATURE COMPENSATING MATERIALS WITH LOW RELATIVE PERMITTIVITY
LOW DIELECTRIC LOSS [3-4]. THEY ARE BRITTLE AND NEED TO BE SINTERED AT HIGH TEMI
THESE REASONS, THE APPLICATION OF AN INDIVIDUAL CERAMIC IS GREATLY RESTRI
ASPECTS. POLYMERIC MATERIALS PLAY A VITAL ROLE IN ELECTRONIC PACKAGES AS A
EASE OF PROCESSING, LOW COST, LOW RELATIVE PERMITTIVITY, ADHESIVE PROPERTIES
POOR THERMAL AND MECHANICAL PROPERTIES. THUS THE POLYMER/CERAMIC COMPOSI
THE CERAMIC FILLERS ARE DISPERSED IN THE POLYMER MATRIX PROVIDE A NEW ROUTE
THE MERITS OF CERAMICS AND THE POLYMERS. THEY UTILIZE THE THERMAL PROPERTI
AND PROCESSABILITY OF POLYMERS.

AMONG THE VARIOUS POLYMERS USED COMMERCIALLY, POLYTETRAFLUOROETHYLENE (PTFE)
HOLDS A RELEVANT POSITION DUE TO THE SUPERIOR DIELECTRIC PROPERTIES AND EXC
INERTNESS [2, 5]. PTFE HAS A HIGH VIRGIN CRYSTALLINE MELTING POINT (T_m) OF 342
HIGH SHEAR VISCOSITY (10^{11} POISE AT 380 ^{o}C) IN THE MELT [6]. IT HAS A LOW RELATIVE PERMITTIVIT
OF NEARLY 2.1 AND EXTREMELY LOW DIELECTRIC LOSS (10^{-4}) WHICH IS ORDERED OVER A
WIDE RANGE OF FREQUENCIES [7]. THE LOW LOSS TANGENT IS A CONSEQUENCE OF THE S
CONFORMATION OF THE POLYMER BACKBONE, WHICH EFFECTIVELY NEUTRALIZES THE D
THE C-F BONDS YIELDING A NET ZERO DIPOLEMOMENT [8]. HOWEVER, THE HIGH VA
COEFFICIENT OF THERMAL EXPANSION (CTE, 100 PPM/^{o}C), LOW THERMAL CONDUCTIVITY AND POOR
STRESS RELIEF RESTRICT THE WIDER USAGE OF PTFE AS SUCH FOR MICROELECTRONI
MANY STUDIES WERE CONDUCTED TO IMPROVE BOTH THE MECHANICAL AND DIELECTRIC
PTFE BY SUITABLE FILLER INCORPORATION [6, 9-15]. IT IS REPORTED THAT PTFE FILLED WITH

60 WT% SiO_2 FILLER LOWERED THE COEFFICIENT OF THERMAL EXPANSION WITH DESIRABL
PROPERTIES [17]. THE ADDITION OF ZnO-$Zn_3Nb_2O_8$ AND ZnO-Nb_2O_5 FILLERS INTO THE PTFE MATRIX SHOWED
GOOD FREQUENCY STABILITY OF RELATIVE PERMITTIVITY OVER A WIDE RANGE AND A C
WITH THE PERCOLATION THEORY [14]. IN ORDER TO DEVELOP SUITABLE COMPOSITES FO
APPLICATIONS, THE PRIME REQUIREMENT IS A FILLER HAVING LOW RELATIVE PERM
DIELECTRIC LOSS, HIGH THERMAL CONDUCTIVITY AND GOOD THERMAL STABILITY.

ALTHOUGH THE POWDER PROCESSING METHOD FOR THE SYNTHESIS OF PTFE
COMPOSITES IS SIMPLE, THE FINAL DENSITY OF THE COMPOSITES IS RATHER POOR DUE
AMOUNT OF POROSITY. THIS CAN BE IMPROVED BY ADOPTING NEW PREPARATION METH
MELT MIXING OR SIGMA BLENDING TECHNIQUE. HOWEVER, IN ORDER TO FABRICATE P
COMPOSITES, HIGH TEMPERATURE ($> 250\ ^{o}C$) IS REQUIRED, ALSO PTFE HAS VERY HIGH VISCOSITY
COMPARED TO OTHER THERMOPLASTIC POLYMERS LIKE POLYETHYLENE OR POLYSTYRE
AND POLYETHYLENE ARE NON POLAR POLYMERS WITH A LOW MELTING POINT OF AR
^{o}C.
THESE POLYMERS POSSESS A LOW RELATIVE PERMITTIVITY OF 2.6 AND 3.2 RESPECTIVELY
DIELECTRIC LOSS OF 0.0006 AND 0.0004 RESPECTIVELY AT 1 MHZ [18]. EVENTHOUGH STUDI
REPORTED ON THE CERAMIC FILLED POLYSTYRENE COMPOSITES [19-21], ONLY A FEW RE
AVAILABLE WHICH EXPLORE THE APPLICABILITY OF POLYETHYLENE COMPOSITES FO
PACKAGING. POLYETHYLENE IS ALSO A WELL KNOWN POLYMERIC INSULATING MATER
HIGH DIELECTRIC STRENGTH, LOW DIELECTRIC LOSS AND GOOD MECHANICAL PROPERT
NUMBER OF REPORTS [18, 22-24] SHOWING THE DIELECTRIC PROPERTIES OF BOTH METAL
CERAMIC FILLED POLYETHYLENE COMPOSITES. VARIOUS RESEARCHERS HAVE PUT CONSI
TO IMPROVE THE PROPERTIES OF POLYETHYLENE BY VARYING THE FILLER PARTICL
COUPLING AGENTS ETC. [25-27]. THE EFFECTS OF BORON NITRIDE CONTENT, PARTICLE SIZ
AND TEMPERATURE ON THE THERMAL CONDUCTIVITY OF HDPE-BORON NITRIDE COMP
BEEN INVESTIGATED BY *Yu et al.* [28]. THERE ARE REPORTS ON THE PROCESSING AND MECHANIC
PROPERTIES OF MULTIWALLED NANOTUBE (MWNT)-HDPE COMPOSITES [29]. THE EFFE
MATERIAL PARAMETERS AND PROCESSING CONDITIONS ON THE FOAM MORPHOLOGIES AN
PROPERTIES OF HDPE-CLAY NANOCOMPOSITES HAVE BEEN STUDIED BY *Lee et al.* [30]. EVEN JO
THOUGH THE MECHANICAL PROPERTIES OF HDPE COMPOSITES ARE WELL STUDIED [31
ATTENTION HAS BEEN PAID TO ITS ELECTRICAL AND THERMAL PROPERTIES.

DUE TO THE DIFFERENCE IN THE SURFACE CHARACTERISTICS BETWEEN THE INO
AND THE ORGANIC MATRIX, IT IS DIFFICULT TO DISPERSE THE FILLER HOMOGENEOUSLY
ESPECIALLY FOR HIGHER VOLUME FRACTION OF FILLER WHICH RESULTS IN HIGH POROS
ABSORPTION LEADING TO UNDESIRABLE CHANGES IN THE DIELECTRIC PROPERTIES A
MECHANICAL INTEGRITY. IN ORDER TO IMPROVE THE PROPERTIES OF FILLED POLYM
COUPLING AGENTS ARE DEVELOPED [33-34]. COUPLING AGENTS POSSESS SPECIAL STRU
TWO DIFFERENT FUNCTIONAL GROUPS, ONE THAT IS ATTACHED TO THE POLYMER MATR
ONE ATTACHED TO THE INORGANIC FILLER. VARIOUS STUDIES HAVE BEEN REPORTED O
COUPLING AGENTS ON THE THERMAL, MECHANICAL AND DIELECTRIC PROPERTIES OF PO
COMPOSITES [16, 34-36]. EARLIER *et al.* CHEN [36] INVESTIGATED THE EFFECT OF PHENYL
TRIMETHOXY SILANE CONTENT ON THE THERMAL AND DIELECTRIC PROPERTIES O
COMPOSITES. THE COUPLING AGENT CHANGES THE NATURE BY WHICH POLYMER INTERA
FILLER LEADING TO A DECREASE IN THE POROSITY AND ALSO THE HYDROPHILICITY OF T
THEY ALSO PREVENT THE FORMATION OF FILLER AGGLOMERATION THEREBY P
HOMOGENEOUS DISPERSION OF FILLER IN THE MATRIX. THE DIELECTRIC PROPERTIES O
ARE VERY MUCH DEPENDENT ON THE SIZE AND SHAPE OF THE FILLERS AND THE INTERA
THE FILLER AND THE POLYMER MATRIX. NOW-A-DAYS POLYMER/NANO COMPOSITES A
TECHNOLOGICAL INTEREST DUE TO THEIR INTERESTING ELECTRICAL, MECHANICA
PROPERTIES WHEN COMPARED WITH THAT OF THE CONVENTIONAL MICROMETER SIZE F
COMPOSITES. WHEN THE FILLER SIZE REDUCES TO NANOMETER LEVEL, THE SURFACE TO
INCREASES THEREBY A SIGNIFICANT ENHANCEMENT IN THE ELECTRIC AND THERMAL PRO
COMPOSITES IS ACHIEVED EVEN AT LOWER FILLER CONTENT. DURING THE LAST FEW
RESEARCHERS HAVE EXPLORED THE OPTICAL, THERMAL, MECHANICAL AND DIELECTR
POLYMER/NANO COMPOSITES [23, 35, 37-38]. GOOD AMOUNT OF EFFORT HAS BEEN P
DEVELOPING HIGH K POLYMER/NANO COMPOSITES FOR CAPACITOR APPLICATIONS [3
HOWEVER, A FEW REPORTS ARE AVAILABLE WHICH EXPLOITS THE APPLICABILITY OF P
COMPOSITES FOR ELECTRONIC PACKAGING APPLICATIONS [37-38, 41-42].

THE PRESENT CHAPTER GIVES A DETAILED INVESTIGATION ON THE THERMOMECHANICAL AND
DIELECTRIC PROPERTIES OF $SM_2SI_2O_7$ LOADED PTFE, POLYETHYLENE AND POLYSTYRENE
COMPOSITES. THE EFFECT OF COUPLING AGENT AND PARTICLE SIZE OF THE FILLER ON TH
PTFE/$SM_2SI_2O_7$ COMPOSITES IS ALSO STUDIED. THE EXPERIMENTAL VALUES OBTAINED FOR

PERMITTIVITY, THERMAL CONDUCTIVITY AND COEFFICIENT OF THERMAL EXPANSION WITH VARIOUS THEORETICAL MODELS.

5.2 THEORETICAL MODELLING

5.2.1 RELATIVE PERMITTIVITY

THE PRECISE PREDICTION OF RELATIVE PERMITTIVITY OF THE COMPOSITE FROM T PERMITTIVITY OF THE COMPONENTS AND THE VOLUME FRACTION OF THE FILLER IS VER THE DESIGN OF COMPOSITES FOR ELECTRONIC APPLICATIONS. SINCE THE COMPOSITES A MIXTURES OF TWO OR MORE COMPONENTS, THE EFFECTIVE RELATIVE PERMITTIVITY BETWEEN THE VALUES OF THE INDIVIDUAL COMPONENTS. THE DIELECTRIC PROPER COMPOSITES ARE INFLUENCED NOT ONLY BY THE RELATIVE PERMITTIVITIES OF THE CO ALSO BY OTHER FACTORS SUCH AS THE MORPHOLOGY, DISPERSION AND THE INTERACTI TWO PHASES AND HENCE THE PREDICTION OF RELATIVE PERMITTIVITY IS A DIFFICU FOLLOWING EQUATIONS ARE USED TO CALCULATE THE RELATIVE PERMITTIVITY OF TH LOW FILLER CONTENT:

(a) Jayasundere-Smith equation [43]:

$$\varepsilon_{eff} = \frac{\varepsilon_m(1-v_f)+\varepsilon_f v_f\left[\frac{3\varepsilon_m}{\varepsilon_i+2\varepsilon_m}\right]\left[1+\left(\frac{3v_f(\varepsilon_f-\varepsilon_m)}{\varepsilon_i+2\varepsilon_m}\right)\right]}{1-v_f+v_f\left[\frac{3\varepsilon_m}{\varepsilon_f+2\varepsilon_m}\right]\left[1+\left(\frac{3v_f(\varepsilon_f-\varepsilon_m)}{\varepsilon_f+2\varepsilon_m}\right)\right]} \qquad (5.1)$$

(b) Lichtenecker equation [44] :

$$\ln\varepsilon_{eff} = (1-v_f)\ln\varepsilon_m + v_f \ln\varepsilon_f \qquad (5.2)$$

(c) Modified Lichtenecker equation [43]:

$$\log\varepsilon_{eff} = \log\varepsilon_m + v_f(1-k)\log\left(\frac{\varepsilon_f}{\varepsilon_m}\right) \qquad (5.3)$$

(d) Maxwell – Wagner equation [45] :

$$\varepsilon_{eff} = \varepsilon_m \frac{2\varepsilon_m + \varepsilon_f + 2v_f(\varepsilon_f - \varepsilon_m)}{2\varepsilon_m + \varepsilon_f - v_f(\varepsilon_f - \varepsilon_m)} \quad (5.4)$$

(e) Effective Medium Theory [46] :

$$\varepsilon_{eff} = \varepsilon_m \left[1 + \frac{v_f(\varepsilon_f - \varepsilon_m)}{\varepsilon_m + n(1-v_f)(\varepsilon_f - \varepsilon_m)}\right] \quad (5.5)$$

WHERE ε_{eff}, ε_f, ε_m ARE THE RELATIVE PERMITTIVITY OF THE COMPOSITES, FILLER AND RESPECTIVELY AND v_f IS THE VOLUME FRACTION OF THE FILLER. k AND n ARE EMPIRICALLY DETERMINED PARAMETERS IN THE MODIFIED LICHTENECKER AND EMT MODELS RESPECTIVELY.

THE RELATIVE PERMITTIVITY OF COMPOSITES DEPENDS ON THE DISTRIBUTION OF SHAPE AND SIZE OF FILLERS AND INTERFACE BETWEEN CERAMICS AND POLYMERS. RECENTLY *et al.* [46] PROPOSED AN EFFECTIVE MEDIUM THEORY (EMT) TO PREDICT THE EFFECTIVE RELATIVE PERMITTIVITY OF THE COMPOSITE BY CONSIDERING THESE FACTORS. IN THIS MODEL, THE PROPERTY OF THE COMPOSITE IS TREATED AS AN EFFECTIVE MEDIUM WHOSE RELATIVE PERMITTIVITY IS OBTAINED BY AVERAGING THE PERMITTIVITIES OF THE CONSTITUENTS. EMT MODEL IS A CONSISTENT MODEL WHICH ASSUMES A RANDOM UNIT CELL CONSISTING OF EACH FILLER SURROUNDED BY A CONCENTRIC MATRIX LAYER. THIS RANDOM UNIT CELL WHEN EMBEDDED IN THE EFFECTIVE MEDIUM MUST NOT BE DETECTED IN AN EXPERIMENT USING ELECTROMAGNETIC MEASUREMENTS. IT INCLUDES A MORPHOLOGY FACTOR 'n' WHICH IS DETERMINED EMPIRICALLY. THIS CORRECTION FACTOR 'n' COMPENSATES FOR THE SHAPE OF THE FILLER USED IN THE POLYMER-CERAMIC COMPOSITE. A HIGH VALUE OF 'n' INDICATES A NEAR SPHERICAL SHAPE FOR THE FILLER, WHILE A LOW VALUE OF 'n' SHOWS A LARGELY NON-SPHERICALLY SHAPED PARTICLE. EARLIER REPORTS [46] SHOWED THAT FOR WELL DISPERSED POLYMER CERAMIC COMPOSITES, THE VALUE OF 'N' IS 0.35.

5.2.2 COEFFICIENT OF THERMAL EXPANSION (CTE)

THERMAL EXPANSION COEFFICIENTS OF COMPOSITES ARE VERY IMPORTANT IN RELATION TO DIMENSIONAL STABILITY AND THE MECHANICAL COMPATIBILITY WHEN USED WITH OTHER

CONSIDERABLE AMOUNT OF WORK HAS BEEN DONE TO PREDICT THE THERMAL EXPANSIO
OF COMPOSITES [47-48]. THE RULE OF MIXTURES SERVES AS THE FIRST-ORDER APPROXIMA
OVERALL CALCULATION OF THE CO-EFFICIENT OF THERMAL EXPANSION OF THE COMPOS
EXPRESSED AS

$$_c = v_f \quad _f + \left(1 - v_f\right) \quad _m \qquad (5.6)$$

WHERE $_c$, $_m$ AND $_f$ ARE COEFFICIENT OF THERMAL EXPANSION OF THE COMPOSITE, MATE
FILLER RESPECTIVELY.

5.2.3 THERMAL CONDUCTIVITY

MATERIALS FOR ELECTRONIC PACKAGING REQUIRE HIGH THERMAL CONDUCTIVIT
DISSIPATE THE HEAT GENERATED IN THE DEVICES. THUS IT IS A NEED TO MODEL AND
THERMAL CONDUCTIVITY OF THE COMPOSITES IN A NUMBER OF INDUSTRIAL PRO
PREDICTION OF THERMAL CONDUCTIVITY OF THE COMPOSITES COMPRISES A SIGNIFICA
THE HEAT TRANSFER LITERATURE. MANY REPORTS CONCERNING THE THERMAL CONDUC
COMPOSITES, ASSOCIATED WITH VARIOUS MODELS OR EQUATIONS FOR PREDICTING
CONDUCTIVITY HAVE BEEN PUBLISHED [49-50]. THEY ARE EITHER THEORETICALLY BA
EMPIRICAL WHICH MEANS TO INCLUDE ONE OR MORE EXPERIMENTALLY DETERMINED
FOR A TWO COMPONENT COMPOSITE, THE SIMPLEST MODEL WOULD BE WITH THE MATERIALS
ARRANGED IN EITHER PARALLEL OR SERIES WITH RESPECT TO HEAT FLOW, WHICH GIVE
LOWER BOUNDS (ALSO REFERRED TO AS WEINER BOUNDS) OF EFFECTIVE THERMAL CON
IN THE PRESENT STUDY, FOLLOWING MODELS ARE USED TO PREDICT THE THERMAL CON
COMPOSITES:

1. Geometric Mean Model:

$$k_c = k_f^{\,v_f} k_m^{\,1-v_f} \qquad (5.7)$$

WHERE k_c, k_f AND k_m ARE THE THERMAL CONDUCTIVITIES OF COMPOSITE, FILLER AND
RESPECTIVELY AND v_f IS THE VOLUME FRACTION OF THE FILLER IN THE COMPOSITE.

2. Agari Model:

AGARI DEVELOPED A MODEL BASED ON THE GENERALIZATION OF MODELS OF S
PARALLEL CONDUCTION IN COMPOSITES. THE MODEL PROPOSED BY AGARI *et al.* [52-53]
CONSIDERED THE EFFECT OF DISPERSION STATE BY INTRODUCING TWO FACTORS C_1 AND C_2

$$\log k_c = v_f C_2 \log k_f + (1 - v_f C_1) \log k_m \qquad (5.8)$$

WHERE k_c, k_m AND k_f ARE THE THERMAL CONDUCTIVITY OF COMPOSITES, POLYMER AND
RESPECTIVELY, AND v_f IS THE VOLUME FRACTION OF FILLER.

IN COMPOSITES, EACH PHASE CANNOT BE RESTRICTEDLY ARRANGED IN A BLOCK BUT O
DISCONTINUOUS NETWORK OF FILLER IN THE MATRIX. THE CONSTANT C_2 IS INTRODUCED TO DEFINE
THE ABILITY OF FORMING CONTINUOUS NETWORK OF FILLER IN THE MATRIX. CONSIDE
PREPARATION PROCEDURE OF THE COMPOSITES CAN AFFECT THE CRYSTALLINITY OF T
THEREBY THE THERMAL CONDUCTIVITY, THE CONSTANT C_1 IS INTRODUCED. ACCORDING TO AGARI, THE
VALUES OF C_1 AND C_2 SHOULD BE IN BETWEEN 0 AND 1, THE CLOSER THE VALUES ARE TO 1, THE MORE
EASILY CONDUCTIVE CHAINS ARE FORMED IN COMPOSITES.

3. Maxwell - Eucken Model

MAXWELL, USING POTENTIAL THEORY [54], OBTAINED AN EXACT SOLUTION
CONDUCTIVITY OF RANDOMLY DISTRIBUTED AND NON INTERACTING HOMOGENEOUS
HOMOGENEOUS MEDIUM AND IS GIVEN BY

$$k_c = k_m \left[\frac{k_f + 2k_m + 2v_f (k_f - k_m)}{k_f + 2k_m - v_f (k_f - k_m)} \right] \qquad (5.9)$$

4. Cheng - Vachon Model

BASED ON TSAO'S MODEL WHICH GIVES THE THERMAL CONDUCTIVITY OF TWO PH
MIXTURE [55], CHENG AND VACHON ASSUMED A PARABOLIC DISTRIBUTION OF THE DIS
PHASE IN THE CONTINUOUS PHASE. THE CONSTANTS OF THIS PARABOLIC DISTRIBU
DETERMINED BY ANALYSIS AND PRESENTED AS A FUNCTION OF THE DISCONTINUOUS P
FRACTION. THUS, THE EQUIVALENT THERMAL CONDUCTIVITY OF THE TWO PHASE SOLI
DERIVED IN TERMS OF THE DISTRIBUTION FUNCTION, AND THE THERMAL CONDUCT
CONSTITUENTS FOR $k_f > k_m$

$$\frac{1}{k_c} = \frac{1}{\sqrt{C(k_m - k_f)[k_m + B(k_f - k_m)]}} \mathrm{LN} \frac{\sqrt{[k_m + B(k_f - k_m)]} + \frac{B}{2}\sqrt{C(k_m - k_f)}}{\sqrt{[k_m + B(k_f - k_m)]} - \frac{B}{2}\sqrt{C(k_m - k_f)}} + \frac{1 - B}{k_m} \quad (5.10)$$

WHERE $B = \sqrt{3v_f/2}$ $C = -4\sqrt{2/3v_f}$

5. Nielson Model

LEWIS AND NIELSON [56] MODIFIED HALPIN-TSAI EQUATION [57] TO INCLUDE THE E OF THE SHAPE OF THE PARTICLES AND THE ORIENTATION OR TYPE OF PACKING FOR SYSTEM.

$$k_c = k_m \left[\frac{1 + ABv_f}{1 - Bv_f} \right] \quad (5.11)$$

WHERE $B = \dfrac{\frac{k_f}{k_m} - 1}{\frac{k_f}{k_m} + A}$ $= 1 + \left(\dfrac{1 - v_{fm}}{v_{fm}^2} \right) v_f$

A(-3) IS A FUNCTION OF GEOMETRY OF THE FILLER PARTICLES AND v_{fm} IS THE MAXIMUM FILLER CONTENT.

5.3 EXPERIMENTAL

THE $Sm_2Si_2O_7$ CERAMICS WERE PREPARED BY CONVENTIONAL SOLID STATE CERAM AS DESCRIBED IN CHAPTER 4, SECTION 4.1.2.1. THE POWDER CALCINED AT 1375 °C WAS GROUND WELL AND SINTERED AT 1375 °C. AGAIN THE POWDER WAS FINELY GROUND AND SIEVED USING μM SIEVES. THE PTFE/$Sm_2Si_2O_7$ COMPOSITES WERE PREPARED BY POWDER PROCESSING TECHNIQUE AS EXPLAINED IN CHAPTER 2, SECTION 2.3.1. DIFFERENT VOLUME FRACTIONS $Sm_2Si_2O_7$ CERAMICS AND PTFE (HINDUSTAN FLUOROCARBONS, HYDERABAD, INDIA) PO WERE DISPERSED IN ETHYL ALCOHOL USING ULTRASONIC MIXER FOR ABOUT 1 H. A MIXTURE WAS OBTAINED BY REMOVING THE SOLVENT AT 70 °C WITH STIRRING. THE HOMOGENOUSLY MIXED PTFE/$Sm_2Si_2O_7$ POWDERS WERE THEN HOT PRESSED IN THE FORM OF CYLINDRICA RECTANGULAR PELLETS UNDER A UNIAXIAL PRESSURE OF 30 MPA AT 310 °C FOR 30 MINUTES

IT IS WELL KNOWN THAT GENERALLY THE CERAMIC FILLERS ARE HYDROPHILIC I
THIS PROPERTY OF THE FILLER MAY ADVERSELY AFFECT THE PERFORMANCE OF THE COM
IS RECOMMENDED TO USE SUITABLE COUPLING AGENT TO COAT THE FILLER SURFACE.
STUDY THE COUPLING AGENT USED WAS PHENYL TRIMETHOXY SILANE (PTMS). INI
AQUEOUS SOLUTION WAS PREPARED BY ADJUSTING THE PH OF THE WATER TO 3 WITH TH
ACETIC ACID. AFTER THAT A VOLUME EQUIVALENT TO 1 WT% OF PTMS WAS ADDED TO T
WATER FOLLOWED BY VIGOROUS STIRRING FOR ABOUT 15 MIN. BEFORE IT HYDROLYSED
CLEAR AND HOMOGENEOUS SOLUTION. THE CERAMIC FILLERS WERE MIXED WITH SILANE
FOR 24 H. WITHOUT ADDITIONAL SOLVENT. THE RESULTING MIXTURE WAS DRIED AT 120 ^{O}C FOR 6 HRS TO
OBTAIN THE SILANE COATED FILLER.

THE POLYSTYRENE-$SM_2SI_2O_7$ (PS-$SM_2SI_2O_7$) AND POLYETHYLENE-$SM_2SI_2O_7$ (PE-
$SM_2SI_2O_7$) COMPOSITES WERE PREPARED BY SIGMA-BLEND TECHNIQUE AS EXPLAINED IN
2.3.2 IN CHAPTER 2. THE POLYMERS WERE FIRST MELTED IN KNEADING MACHINE AT 150 ^{O}C FOR 15 MIN.
DIFFERENT VOLUME FRACTIONS (0 TO 0.5) OF CERAMIC FILLER WERE ADDED TO THE MEL
AND BLENDED AT 150 ^{O}C FOR 30 MINUTES. THUS OBTAINED COMPOSITES WERE THERMO - LAMIN
USING SUITABLE DIE UNDER A PRESSURE OF 200 KG/CM^2 AT 150 ^{O}C FOR 15 MIN. AFTER THERMO-
LAMINATION, THE COMPOSITES WITH DESIRED SHAPES WERE POLISHED FOR CHARACTERI

THE DENSITY OF THE COMPOSITES WAS MEASURED USING ARCHIMEDES METHO
MICROSTRUCTURE OF THE COMPOSITES WAS RECORDED USING SEM. THE LOW FREQUENC
PROPERTIES AND THE VARIATION IN RELATIVE PERMITTIVITY WITH TEMPERATURE IN T
60 ^{O}C WERE MEASURED BY LCR METER (HIOKI 3532-50). THE DIELECTRIC PROPERTIES
MICROWAVE FREQUENCIES WERE CHARACTERIZED USING HP 8510 VECTOR NETWORK AN
THE CAVITY PERTURBATION TECHNIQUE WHICH IS DISCUSSED IN DETAIL IN CHAPTER 2, SE

THE FILLER PARTICLE SIZE IS MEASURED USING PHOTON CORRELATION SPEC
(CILAS 930 PARTICLE SIZE ANALYZER - FRANCE). THE SPECIFIC SURFACE AREA OF THE S
WAS MEASURED BY NITROGEN ADSORPTION MEASUREMENT (BET) IN MICROMERITICS (C
2375) SURFACE AREA ANALYZER. THE COEFFICIENT OF THERMAL EXPANSION (CTE)
COMPOSITES WAS MEASURED USING A THERMO - MECHANICAL ANALYZER (TMA – 60H, SH
IN THE RANGE 25 – 250 ^{O}C. A PHOTOPYROELECTRIC (PPE) TECHNIQUE [58] (DISCUSSED IN SECTIO
2.8.3 IN CHAPTER 2) WAS USED TO DETERMINE THE THERMAL CONDUCTIVITY OF THE C
THERMAL DIFFUSIVITY (α) AND THERMAL EFFUSIVITY (e) WERE ALSO MEASURED FROM PPE SIGNAL

PHASE AND AMPLITUDE [59]. FROM THE VALUES OF THERMAL CONDUCTIVITY AND SPECIFIC HEAT CAPACITY OF THE SAMPLES WERE OBTAINED.

THE VICKER'S MICROHARDNESS OF PTFE AND PS-$SM_2SI_2O_7$ COMPOSITES WERE MEASURED USING MICRO HARDNESS TESTER (CLEMEX 4, GERMANY). BOTH THE SURFA SAMPLES WERE POLISHED TO HAVE OPTICALLY FLAT SURFACE FOR INDENTATION. THE SUBJECTED TO A LOAD OF 100 G AND DWELL TIME OF 10 S. A TOTAL OF 5 READINGS WE GET THE AVERAGE HARDNESS. THE WATER ABSORPTION MEASUREMENTS WERE CONDU ASTM D570. THE SAMPLES WERE WEIGHED AND SUBMERGED IN DISTILLED WATER AT 25 °C FOR 24 H. THE SAMPLES WERE REMOVED, WIPED, DRIED AND THE AMOUNT OF WATER ABSO CALCULATED BASED ON THE WEIGHT GAIN OF THE SAMPLES.

5.4 RESULTS AND DISCUSSION

5.4.1 PTFE/$SM_2SI_2O_7$ COMPOSITES

FIGURE 5.1 SHOWS THE PARTICLE SIZE DISTRIBUTION OF $SM_2SI_2O_7$ CERAMICS. FROM THE FIGURE IT IS CLEAR THAT $SM_2SI_2O_7$ POSSESS A VERY SMALL PARTICLE SIZE WITH AN AVERAGE VAL 1.4 µM.

Ultrasounds	: 60	s
Obscuration	: 18 %	
Diameter at 10%	: 0.22	µm
Diameter at 50%	: 0.87	µm
Diameter at 90%	: 3.19	µm
Mean diameter	: 1.44	µm

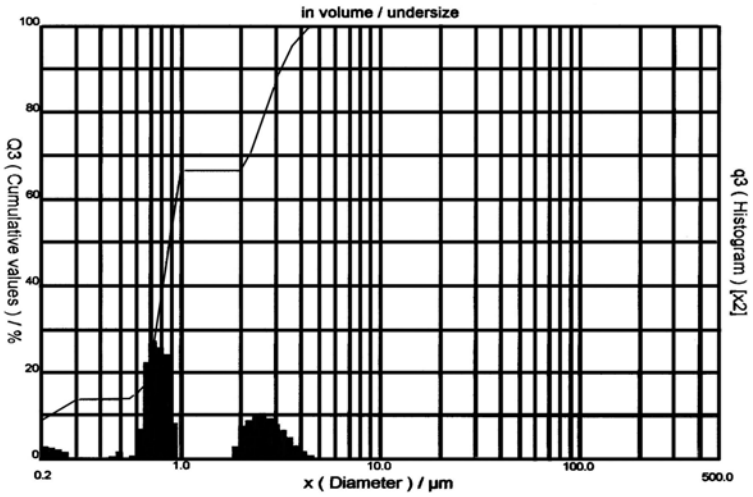

Fig. 5.1 Particle size distribution of $Sm_2Si_2O_7$ filler.

FIGURE 5.2 (A) SHOWS THE SEM IMAGES OF $Sm_2Si_2O_7$ POWDER. FROM THE FIGURE IT CAN BE INFERRED THAT THE $Sm_2Si_2O_7$ CERAMIC SHOWED A PARTICLE SIZE VARYING FROM 1-3 µM WHI CONFIRMS THE RESULT OBTAINED FROM THE PARTICLE SIZE ANALYZER. FIGURE 5.2 (B)-(D) SHOW THE MICRO STRUCTURAL IMAGES OF $Sm_2Si_2O_7$ POLYMER – CERAMIC COMPOSITES FOR DIFFERENT VOLUME FRACTION OF CERAMIC LOADING. IT CAN BE SEEN THAT AT LOWER CERAMIC LO A GOOD ADHESION IS OBSERVED BETWEEN THE POLYMER AND CERAMIC WITH MINIMU AND THE $Sm_2Si_2O_7$ CERAMIC PARTICLES ARE UNIFORMLY DISPERSED THROUGHOUT THE MATRIX. HOWEVER, AS THE FILLER CONTENT INCREASES THE PACKING OF THE PARTICL LEADING TO PARTICLE AGGLOMERATION. THESE AGGLOMERATES MAY INCREASE THE EF SIZE THEREBY RESTRICTING THE VOID FILLING BETWEEN BIGGER PARTICLES. FROM FIG SEEN THAT AS THE CERAMIC CONTENT (v_f), THE POROSITY OF THE COMPOSITES INCREASES WHICH ADVERSELY AFFECTS THE DIELECTRIC, THERMAL AND MECHANICAL PROPE COMPOSITES.

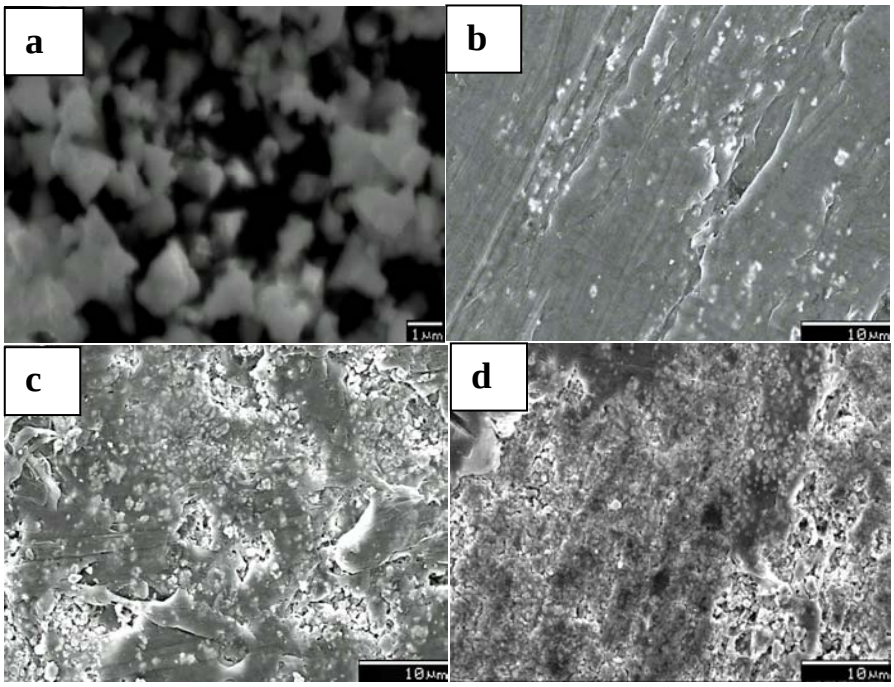

Fig. 5.2 SEM images of PTFE loaded with (a) $Sm_2Si_2O_7$ powder, (b) 0.1 v_f $Sm_2Si_2O_7$, (c) 0.3 v_f $Sm_2Si_2O_7$ and (d) 0.5 v_f $Sm_2Si_2O_7$.

THE THEORETICAL DENSITY OF THE COMPOSITE (ρ_{comp}) IS CALCULATED USING THE MIXTURE RULE [44]:

$$\rho_{comp} = V_1\rho_1 + V_2\rho_2 \quad (5.12)$$

WHERE ρ_1, ρ_2, V_1 AND V_2 RESPECTIVELY ARE THE DENSITY OF THE FILLER, DENSITY OF THE VOLUME OF THE FILLER AND VOLUME OF THE MATRIX. THE DENSITIES OF PTFE AND $Sm_2Si_2O_7$ MEASURED BY ARCHIMEDES METHOD ARE FOUND TO BE 2.15 AND 5.35 g/cm^3 RESPECTIVELY. TABLE 5.1 GIVES THE RELATIVE DENSITY AND POROSITY OF THE PTFE/$Sm_2Si_2O_7$ COMPOSITES WITH VARYING FILLER CONTENT. THE DENSITY OF THE COMPOSITE INCREASES AS THE FILLER LOADING I THE HIGHER DENSITY OF THE CERAMIC. HOWEVER, THE RELATIVE DENSITY GRADUALLY INCREASE IN FILLER CONTENT. THIS BEHAVIOR IS MAINLY DUE TO THE PRESENCE OF PRODUCED DURING THE SYNTHESIS PROCESS WHEN AIR LIBERATION IS RESTRICTED DU VISCOSITY OF THE MATRIX. A MONOTONIC INCREASE IN THE POROSITY IS OBSERVE INCREASE IN THE CERAMIC CONTENT. POROSITY GENERALLY ARISES FROM AGGLOMER SOLVENTS AND ALSO BECAUSE OF THE LOW POLYMER CONTENT WHICH IS INSUFFICIE PARTICLE NETWORK. THE PRESENCE OF AGGLOMERATION AND PORES IS ALSO EVIDENT I IMAGES (SEE FIG. 5.2 (C) AND (D)). THE POROSITY REACHES A MAXIMUM VALUE OF 24.7 % FILLER CONTENT OF 0.5 V_f.

Table 5.1 The density, relative density and porosity of PTFE/$Sm_2Si_2O_7$ composites.

Volume fraction filler	Density (g/cm^3)	Relative density (%)	Porosity (%)
0.1	2.45	97.8	2.2
0.2	2.78	97.3	2.7
0.3	2.95	91.8	8.2
0.4	2.94	82.4	17.6
0.5	2.95	75.3	24.7

THE VARIATION OF THE DIELECTRIC PROPERTIES OF THE PTFE/$Sm_2Si_2O_7$ COMPOSITE WITH THE VARYING FILLER DISTRIBUTION AS A FUNCTION OF FREQUENCY IS SHOWN IN FIG. 5. THE DIELECTRIC RESPONSE IS STUDIED OVER THE FREQUENCY RANGE 1 KHZ – 1 MHZ. I THAT THE RELATIVE PERMITTIVITY IS ALMOST INDEPENDENT OF FREQUENCY. AS THE INCREASES THE RELATIVE PERMITTIVITY ALSO INCREASES DUE TO THE HIGHER RELATIV THE CERAMIC COMPARED TO THE POLYMER. FROM FIG. 5.3 (B) IT IS CLEAR THAT THE DIE

IS VERY MUCH FREQUENCY DEPENDENT. IN THE REGION OF LOW FREQUENCIES, THE DI
ATTAINS A HIGH VALUE WHICH DECREASES AS THE FREQUENCY INCREASES. THIS CAN
BASED ON THE INTERFACIAL POLARIZATION, KNOWN AS MAXWELL-WAGNER-SILLARS (
WHICH APPEARS IN HETEROGENEOUS SYSTEMS DUE TO THE ACCUMULATION OF CHA
INTERFACES [60]. THIS POLARIZATION IS PREDOMINANT AT THE LOWER FREQUENCIES A
WITH THE FILLER CONTENT. GENERALLY IN POLYMER COMPOSITES INTERFACIAL POLAR
OPERATIVE AT LOW FREQUENCY, IS ALWAYS PRESENT DUE TO THE PRESENCE OF ADDIT
IMPURITIES HAVING LARGER MASSES THAN THE LOW MOLECULAR WEIGHT DIPOLES TH
SYSTEMS HETEROGENEOUS. THE INTERFACIAL POLARIZATION RELATED TO THE LARGE D
INTERFACE IS LESS ACTIVE AS THE ELECTRIC FIELD CHANGES RAPIDLY. HOWEVER, A SLI
THE RELATIVE PERMITTIVITY AND AN INCREASE IN DIELECTRIC LOSS IS NOTED BOT
FREQUENCY REGION (177 KHZ). THIS MAY BE PROBABLY DUE TO CERTAIN RELAXATION
THE POLYMER. SIMILAR RELAXATION MECHANISM WAS OBSERVED AND STUDIED IN DET
et al. [61].

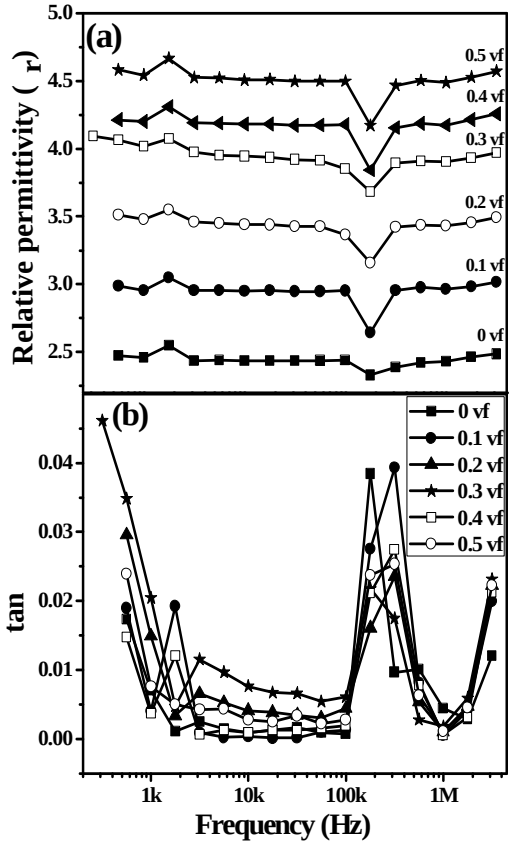

Fig. 5.3 The variation of (a) relative permittivity and (b) dielectric loss with frequency for PTFE/$Sm_2Si_2O_7$ composites.

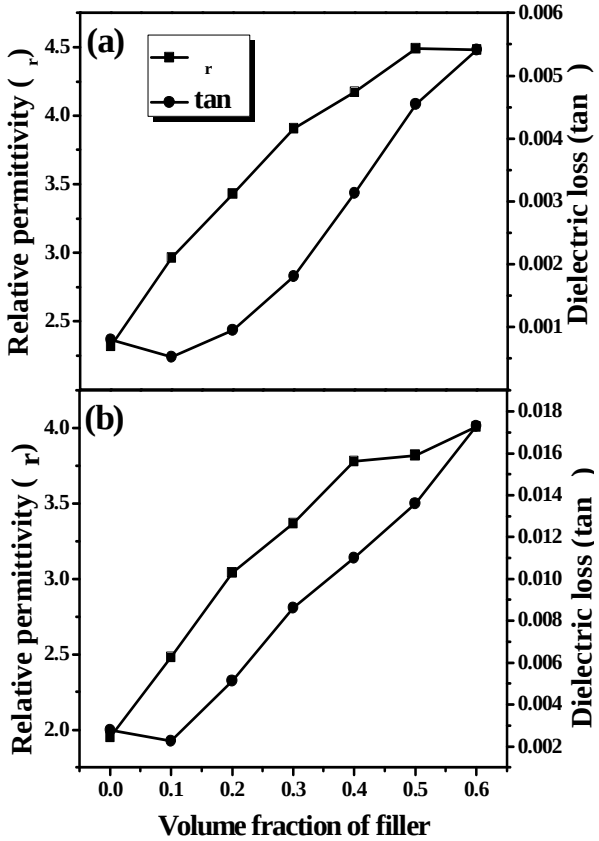

Fig. 5.4 The variation of dielectric properties with filler content for PTFE/$Sm_2Si_2O_7$ composites at (a) 1 MHz and (b) 9 GHz.

IN A HETEROGENEOUS POLYMER SYSTEM, THE INCLUSION OF FILLER WILL NORMA
PROPERTIES OF THE POLYMER MATRIX. FIG. 5.4 GIVES A COMPARISON OF THE DIELECTRI
OF THE PTFE/SM_2O_7 COMPOSITES WITH VARYING FILLER CONTENT AT 1 MHZ AND 9 GHZ.
BOTH THE FREQUENCIES THE RELATIVE PERMITTIVITY INCREASES WITH INCREASE IN TH
THIS IS DUE TO THE RELATIVELY HIGH PERMITTIVITY OF THE FILLER (ε_r = 12.5 AT 1 MHZ AND 10
AT 9 GHZ) COMPARED TO THAT OF THE MATRIX (ε_r = 2.32 AT 1 MHZ AND ε_r = 1.95 AT 9 GHZ).
WHEN THE CERAMIC FILLER CONTENT IS SMALL, IT FORMS A DISPERSED PHASE IN THE CO
DIELECTRIC RESPONSE IS MAINLY CONTRIBUTED BY THE CONTINUOUS MATRIX, DUE
RELATIVE PERMITTIVITY HAS A LOW VALUE. BUT AS THE FILLER CONTENT INCREASE
PARTICLES COME CLOSE TOGETHER LEADING TO AN INCREASE IN THE DIPOLE – DIPOL
THEREBY INCREASING THE RELATIVE PERMITTIVITY [62]. THE EFFECTIVE RELATIVE PERM
COMPOSITE MAY BE DEPENDENT ON THE INTERPHASE CHARACTERISTICS. THESE
CHARACTERISTICS ARE AFFECTED BY A CHANGE IN THE FILLER PARTICLE SIZE AND / OR
BY A CHANGE IN THE CHEMICAL STRUCTURE OF THE INTERPHASE REGION. SINCE TH
STRUCTURE OF THE INTERPHASE REGION IS A FUNCTION OF THE POLYMER AND ITS INTE
FILLER PARTICLES, A CHANGE OF THE BONDING BETWEEN THESE TWO PHASES WILL ALT
RELATIVE PERMITTIVITY OF THE COMPOSITE. THE DIELECTRIC LOSS WHICH IS THE
AFFECTING THE FREQUENCY SELECTIVITY OF A MATERIAL IS INFLUENCED BY MANY F
POROSITY, MICROSTRUCTURE AND DEFECTS [63]. FROM THE FIGURE IT IS OBSERVED THA
CONTENT INCREASES THE DIELECTRIC LOSS ALSO INCREASES FOR BOTH 1 MHZ AND 9 G
ATTRIBUTED TO THE INCREASED POROSITY (SEE TABLE 5.1) OF THE MATERIAL AND ALSO DUE
TO THE INTERFACIAL POLARIZATION BETWEEN THE POLYMER AND CERAMIC AT HIGHER
THE DIELECTRIC LOSS VARIES FROM 0.00052-0.00455 AT 1 MHZ WITH THE FILLER ADDITION
- 50 VOL %. THIS IS A MUCH SATISFACTORY RESULT WHEN COMPARED WITH SOME OF T
REPORTS ON SEVERAL POLYMER-CERAMIC COMPOSITES [64-65]. AT 9 GHZ, AS THE VOLUM
OF FILLER INCREASES (0 - 50 VOL%), THE RELATIVE PERMITTIVITY AND DIELECTRIC LO
FROM 1.95 TO 3.82 AND 0.0024 TO 0.0136 RESPECTIVELY. THIS LOW VALUE OF RELA
PERMITTIVITY WHEN COMPARED WITH THAT AT 1 MHZ IS DUE TO THE DIFFERENC
POLARIZATION MECHANISMS. ALL THE FOUR POLARIZATION MECHANISMS (DESCRIBED
ARE ACTIVE AT LOW FREQUENCIES BUT AS THE FREQUENCY INCREASES ONLY IONIC A
POLARIZATION DOMINATES. AT LOWER FREQUENCIES, ALL THE FREE DIPOLAR GROUPS

CHAIN CAN ORIENT THEMSELVES RESULTING IN THE HIGHER VALUE OF RELATIVE PERM
THE FREQUENCY INCREASES, THE BIGGER DIPOLES FIND IT DIFFICULT TO ALIGN IN THE
RESULTING IN A NET DECREASE IN THE RELATIVE PERMITTIVITY.

THE PTFE MATRIX POSSESSES A LOW VALUE OF THERMAL CONDUCTIVITY OF NE
$WM^{-1}K^{-1}$. THE THERMAL CONDUCTIVITY OF THE FILLER IS MUCH HIGHER (18.13 WM
MATRIX AND THEREFORE THERE IS AN EXPECTED INCREASE IN THE THERMAL CONDUC
FILLER ADDITION. THE INFLUENCE OF THE VOLUME FRACTION OF FILLER ON THE THERM
OF PTFE/$Sm_2Si_2O_7$ COMPOSITES IS SHOWN IN FIG. 5.5. IT IS OBSERVED THAT THE THERM
CONDUCTIVITY GRADUALLY INCREASES WITH INCREASING FILLER CONTENT. WHEN T
HEATED, THE HEAT WILL FLOW THROUGH THE FILLER PARTICLES, JUST AS ELECTRIC CHA
A SMALL RESISTANCE PATH. FOR HIGHER FILLER CONTENT, THE PARTICLES BEGIN TO T
AND FORM CONDUCTIVE CHANNELS IN THE DIRECTION OF HEAT FLOW CAUSING AN EXPO
THE THERMAL CONDUCTIVITY. IT IS SEEN THAT FOR A MAXIMUM FILLER CONTENT OF 0.5
CONDUCTIVITY SHOWS A VALUE AS HIGH AS 1.764 WM

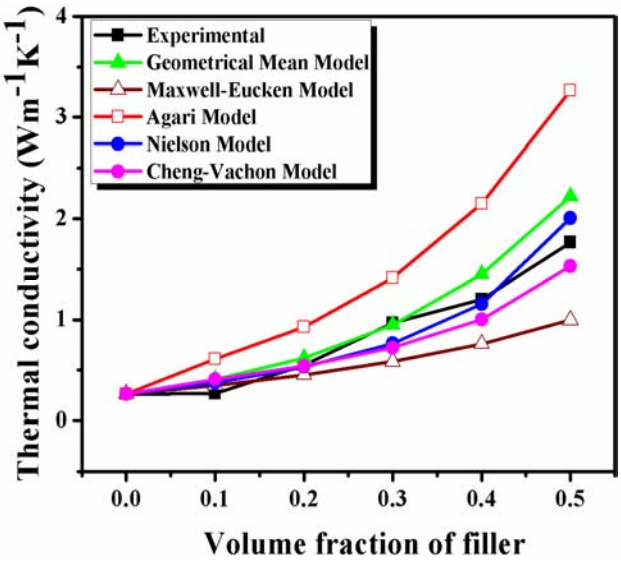

Fig. 5.5 Variation of the thermal conductivity of PTFE-$Sm_2Si_2O_7$ and comparison with the theoretical models.

FIGURE 5.5 ALSO COMPARES THE EXPERIMENTAL THERMAL CONDUCTIVITY W
PREDICTED USING VARIOUS THEORETICAL MODELS. GENERALLY ALL THE THEORETICA
VALID ONLY FOR LOWER FILLER CONCENTRATIONS. AS THE FILLER CONTENT INCREAS

INHOMOGENITY AND DEFECTS IN THE COMPOSITES INCREASES WHICH ARE NOT CONSID
MODELS AND THEREFORE THE DEVIATION FROM THE PREDICTED VALUES ALSO INCREA
CLEARLY SHOWS THAT THE GEOMETRIC MEAN MODEL AND NIELSON MODEL HOLDS GO
AND 0.4 V_F RESPECTIVELY. EARLIER HASSELMAN AND JOHNSON [66] DEVELOPED A THEOR
EFFECTIVE THERMAL CONDUCTIVITY OF THE COMPOSITES CONSISTING OF A CONTINUOU
WITH DILUTE CONCENTRATIONS OF FILLER, WITH A THERMAL BARRIER RESISTANCE OR K
WHICH MAY ARISE FROM POOR MECHANICAL OR CHEMICAL ADHERENCE AT THE INTERFA
OF NIELSON MODEL ALSO THE COMPOSITE SYSTEM IS CONSIDERED TO BE HOMOGENEO
IDEAL INTERFACE. HOWEVER, WITH THE INCREASE IN THE VOLUME FRACTION OF TH
MISMATCH BETWEEN THE MATRIX AND THE FILLER IN THE FORM OF INTERFACIAL GAP
SERIOUS WHICH ADVERSELY AFFECTS THE HEAT CONDUCTION. THUS THE MODEL NEEDS
BY CONSIDERING THE INTERFACIAL THERMAL RESISTANCE. THE EXPERIMENTAL VALUES
HIGHER THAN THAT PREDICTED USING MAXWELL-EUCKEN AND CHENG-VACHON MODEL
BE DUE TO THE FACT THAT THESE MODELS ASSUME THAT THE SHAPE OF THE FILLER IS
DISPERSION STATE OF THE FILLER IN COMPOSITES, IE., FILLER MIXED INTO MELTED MAT
EFFECT OF POROSITY IS NOT CONSIDERED WHICH WILL AFFECT THE EFFECTIVE THERMAL
THE COMPOSITES DUE TO THE POOR THERMAL CONDUCTIVITY OF AIR.

5.4.1.1 EFFECT OF COUPLING AGENT ON THE PROPERTIES OF PTFE/SiO_2 COMPOSITES

THE COUPLING AGENTS ARE GENERALLY EMPLOYED TO ENHANCE THE COMPATIBIL
THE POLYMER PHASE AND FILLER PHASE OF THE COMPOSITE SYSTEMS. FIG. 5.6 S
COMPARISON OF THE SEM MICROGRAPH OF PTFE FILLED WITH 30 VOL% SiO_2
AND UNTREATED COMPOSITE. IT CAN BE SEEN THAT THE CERAMIC PARTICLES TREATED
MORE UNIFORMLY DISTRIBUTED IN THE POLYMER MATRIX AND THERE IS NO AGGREGAT
PARTICLES IN THE COMPOSITES (ALSO SEE FIG. 5.6 (A)). THUS THE PTMS COUPLING AG
EFFECTIVE IN IMPROVING THE DISPERSION OF THE SiO_2 IN THE POLYMER MATRIX.

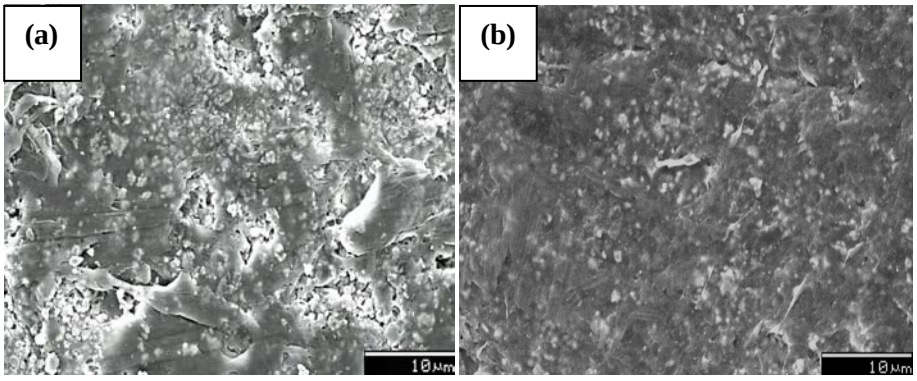

Fig. 5.6 SEM images of PTFE loaded with 0.3 v_f (a) untreated and (b) silane treated $Sm_2Si_2O_7$.

TABLE 5.2 GIVES THE RELATIVE DENSITY AND POROSITY OF THE COMPOSITES WIT
AMOUNT OF SILANE TREATED FILLER CONTENT. IT IS SEEN THAT THE SILANE TREATME
ADHESION BETWEEN THE MATRIX AND THE FILLER THEREBY IMPROVING THE DENSIFIC
EVIDENT FROM FIG. 5.6. THE SILANE TREATED COMPOSITES SHOW HIGHER RELATIVE DE
COMPARED WITH THAT OF THE UNTREATED ONE. A COMPARISON OF UNTREATED AND
COMPOSITES SHOW THAT THE POROSITY CONTENT IS MUCH REDUCED BY COUPLING. THI
WITH A HIGHER FILLER CONTENT (v_f = 0.5) SHOWS A HIGH POROSITY OF 24.7 % IN THE CASE OF
UNTREATED FILLER WHEREAS THE SILANE TREATED COMPOSITION EXHIBITS A MUCH RE
18.1 %.

Table 5.2 The relative density, porosity and microwave dielectric properties of silane treated PTFE/$Sm_2Si_2O_7$ composites.

Volume fraction filler	Relative density (%)	Porosity (%)	Microwave dielectric properties (9 GHz)	
			ε_R	$TAN\delta$
0.1	99.6	0.4	2.55	0.0040
0.2	98.5	1.5	3.04	0.0031
0.3	92.8	7.2	3.51	0.0043
0.4	86.7	13.4	3.92	0.0054
0.5	81.9	18.1	4.29	0.0105

FIGURE 5.7 SHOWS THE COMPARISON OF THE VARIATION OF THE DIELECTRIC PROP
VOLUME FRACTION OF FILLER CONTENT OF SiO_2 COMPOSITES AT 1 MHZ, FOR FILLERS
TREATED WITH SILANE COUPLING AGENT AND THAT WHICH IS UNTREATED. IT IS CLEAR
COATED COMPOSITES SHOWS A HIGHER RELATIVE PERMITTIVITY WHEN COMPARED WITH
ONE WHICH IS IN AGREEMENT WITH EARLIER STUDIES [33]. THE IMPROVEMENT IN THE
PROPERTIES IS DUE TO THE ENHANCEMENT IN THE RELATIVE DENSITY OF SILANE TREAT
ALSO THE SILANE COUPLING AGENT ACT AS A MOLECULAR BRIDGE BETWEEN THE MATR
THEREBY FORMING A COVALENT BOND ACROSS THE INTERFACE. HAWRYLO *et al.* [33]
EXPLAINED THE ROLE OF COUPLING AGENTS IN DETERMINING THE EFFECTIVE INTERF
PERMITTIVITY. THE COUPLING AGENTS EFFECTIVELY CHANGE THE MEANS BY WHICH T
PHASE CHEMICALLY INTERACTS WITH THE SURFACE OF THE FILLER PARTICLES. THUS THI
CHANGING THE CHARACTERISTICS OF THE INTERPHASE REGION OF POLYMER-CERAMIC C
COUPLING AGENT FORMS COVALENT CHEMICAL BONDS WITH THE FILLER SURFACE, TH
THE BOND BETWEEN THE POLYMER MATRIX AND THE CERAMIC FILLER. THIS WILL I
MOLECULAR POLARIZABILITY OF THE INTERPHASE THEREBY LEADING TO AN INCREASE
PERMITTIVITY. ALSO FROM THE MICROSTRUCTURE A GOOD HOMOGENEOUS DISPERSION O
POLYMER IS OBTAINED WHICH ALSO ENHANCES THE DIELECTRIC PROPERTIES. SIMIL
OBSERVED IN THE MICROWAVE FREQUENCY ALSO (SEE TABLE 5.2). FIG. 5.7 ALSO SHO
VARIATION OF DIELECTRIC LOSS OF BOTH THE UNTREATED AND SILANE TREATED C
DIELECTRIC LOSS INCREASES WITH THE FILLER CONTENT AS EXPECTED. THE DIELECT
RESPECTIVELY FROM 0.00052-0.00455 AND 0.00055-0.00678 FOR THE UNTREATED AND SIL
TREATED COMPOSITES FOR FILLER CONTENTS VARYING FROM 1 TO 30 VOL%. IT IS EVIDENT FROM THE FIGURE FOR
LOWER FILLER (UPTO 03 VOL%) CONTENT, THE DIELECTRIC LOSS SHOWS NO CLEAR DIFFERENCE F
COMPOSITES. HOWEVER, FOR HIGHER FILLER CONCENTRATIONS (>3 VOL%) THE DIELECTRIC LOSS VALUES
EXHIBIT A SIGNIFICANT CONTRAST. THE SILANE COUPLED COMPOSITES POSSESS A HIG
DIELECTRIC LOSS COMPARED TO THE UNTREATED ONE. SIMILAR OBSERVATION IS REPORT
[35] FOR ALUMINIUM/EPOXY COMPOSITES. THIS MAY BE DUE TO THE INCREASE IN THE IN
POLARIZATION CAUSED DUE TO THE INTRODUCTION OF ADDITIONAL PHASES. SINCE THE
IS QUITE SENSITIVE TO POLAR IMPURITIES OR POLAR OXIDATIVE PRODUCTS FROM POLY
DURING COMPOUNDING, THIS INCREMENT IN LOSSES SHOULD BE CONSIDERED CARE
TARGETING INDUSTRIAL APPLICATIONS. HOWEVER, AT 9 GHZ SILANE TREATED COMPOS

LOWER DIELECTRIC LOSS WHEN COMPARED WITH THAT OF THE UNTREATED ONE WHICH
THE REDUCED POROSITY. AT 9 GHZ, PTFE LOADED WITH 0.3 VOLUME FRACTION OF $Sm_2Si_2O_7$ HAS ε_r =
3.51 AND $\tan\delta$ = 0.0043.

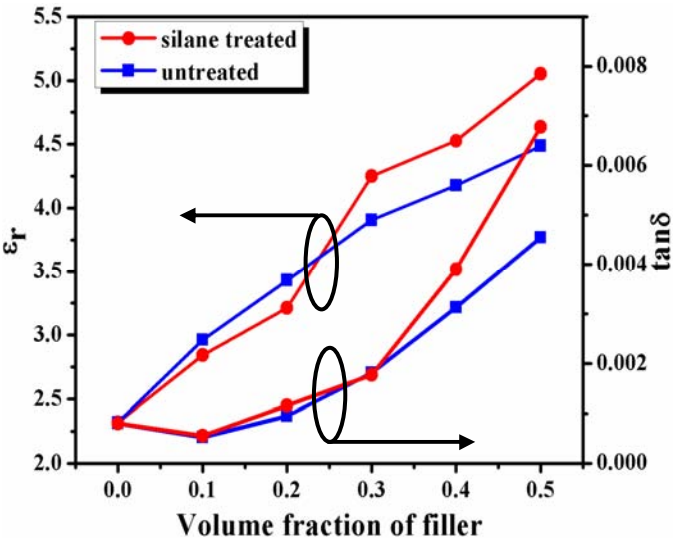

Fig. 5.7 Variation of relative permittivity and tan δ of untreated and silane treated PTFE/$Sm_2Si_2O_7$ composites with volume fraction of filler at 1MHz.

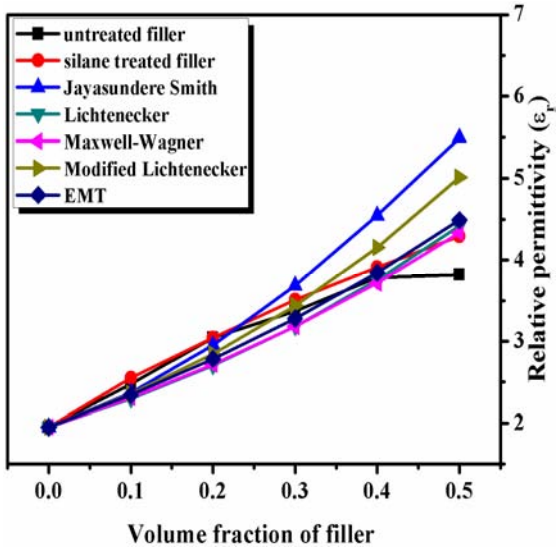

Fig. 5.8 Comparison of experimental and theoretical relative permittivity of PTFE/$Sm_2Si_2O_7$ composites with volume fraction of filler at 9 GHz.

FIGURE 5.8 SHOWS THE COMPARISON BETWEEN THE EXPERIMENTAL AND THEORETICAL VALUES OF RELATIVE PERMITTIVITY AT 9 GHZ FOR BOTH UNTREATED AND SILANE TREATED PTFE/$Sm_2Si_2O_7$ COMPOSITES. THE MEASURED RELATIVE PERMITTIVITIES ARE WELL MATCHED WITH THE PREDICTIONS FOR LOWER FILLER CONTENT ONLY AND DEVIATIONS OCCUR AT HIGHER FILLER LOADINGS DUE TO THE IMPERFECT DISPERSION OF CERAMIC PARTICLES AND ALSO DUE TO THE AIR ENTRAPMENTS IN THE COMPOSITES WHICH IS NOT CONSIDERED IN THE THEORETICAL EQUATIONS. AS THE FILLER CONTENT OF UNTREATED FILLER INCREASES (> 0.3 V_f), THE RELATIVE PERMITTIVITY SHOWS A WIDE VARIATION FROM THE THEORETICAL VALUES. THE MODIFIED LICHTENECKER EQUATION IS REPORTED TO BE WELL SUITED FOR CERAMIC COMPOSITES [13, 67] WHERE A FITTING FACTOR 'K' IS ALSO INCLUDED WHICH REPRESENTS THE INTERACTION BETWEEN THE FILLER AND THE MATRIX. BUT IN THE PRESENT CASE A PERCENTAGE DEVIATION OF NEARLY 21% IS NOTED IN THE CASE OF UNTREATED COMPOSITES WITH 0.3 V_f FILLER. THIS IMPLIES THAT THE FITTING FACTOR 'K' MUST BE MODIFIED CONSIDERING THE NATURE OF THE

FILLER AND MATRIX. HOWEVER, THE SILANE TREATED COMPOSITES SHOWS GOOD AGREE
HIGHER FILLER CONTENT DUE TO THE HOMOGENEITY IN DISPERSION AND ALSO THE RE
WHICH IS EVIDENT FROM TABLE 5.2. IT IS INTERESTING TO NOTE THAT BOTH THE UNTREA
TREATED COMPOSITES HOLD A GOOD MATCH WITH THE EMT MODEL FOR LOW FILLER C
0.3 V_F). IN THE PRESENT CASE THE *n* VALUE OBTAINED AS 0.3 WHICH IS IN AGREEMENT WITH
THE REPORTED VALUE [46]. HOWEVER, FOR HIGHER FILLER LOADING THE UNTREATE
EXHIBIT A LARGER DEVIATION WHEN COMPARED WITH THE SILANE COUPLED COMPOSIT
NOTED THAT WHILE THE UNTREATED $Sm_2Si_2O_7$ 0.5 COMPOSITE SHOW A PERCENTAGE
DEVIATION OF 19 % THE SILANE COATED $Sm_2Si_2O_7$ COMPOSITE SHOW ONLY A SMALL
DEVIATION OF NEARLY 9 % WHICH IS QUITE SATISFACTORY. THIS IS A STRONG EVIDENCE FOR THE
UNIFORM DISPERSION OF THE CERAMIC FILLER IN THE POLYMER MATRIX WITH THE A
COUPLING AGENT.

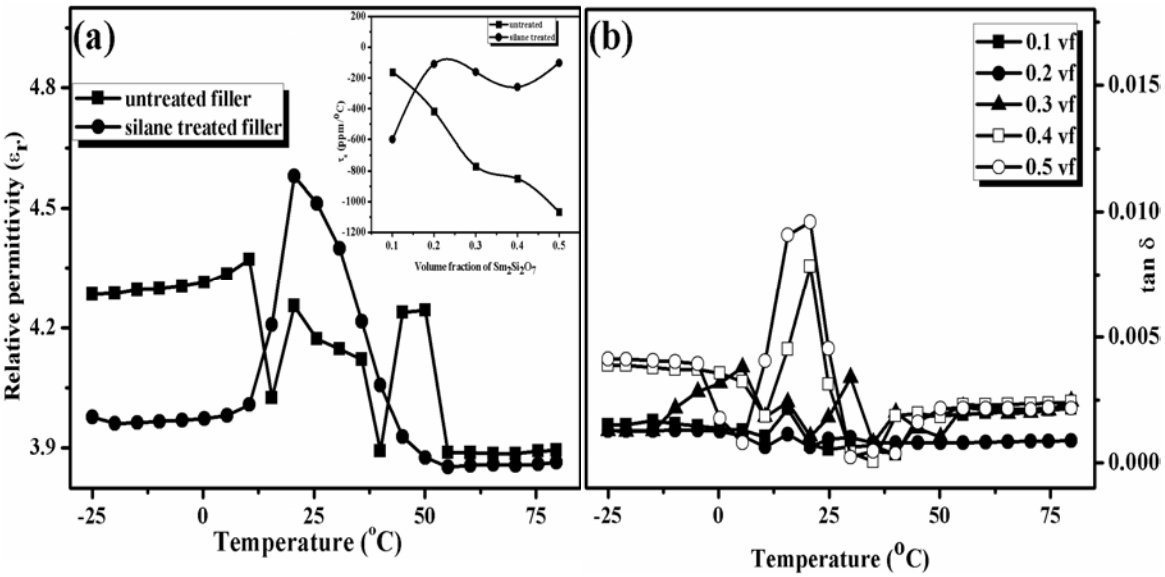

Fig. 5.9 Variation of (a) relative permittivity of untreated and silane coupled PTFE/0.4 v_f $Sm_2Si_2O_7$ composite (b) dielectric loss with temperature for various volume fractions of filler at 1 MHz. Inset of (a) shows the variation of τ_ε with volume fraction of PTFE/$Sm_2Si_2O_7$ composites.

THE TEMPERATURE DEPENDENCE OF DIELECTRIC PROPERTIES OF THE COMPOSI
IMPORTANT FACTOR WHICH JUDGES THE OVERALL PERFORMANCE OF THE MATERIAL. FIG
(B) SHOW THE VARIATION OF DIELECTRIC PROPERTIES OF BOTH UNTREATED AND S
PTFE/0.4 V_F $SM_2SI_2O_7$ COMPOSITE WITH TEMPERATURE IN THE RANGE -25 TO +80 ^{0}C. IN BOTH
CASES A STEADY INCREASE IN THE RELATIVE PERMITTIVITY AND DIELECTRIC LOSS VAL

TEMPERATURE AROUND 20 °C. THIS JUMP IS PRESENT IN THE CASE OF ALL THE COMPOSITIONS CONSIDERED IN THE PRESENT STUDY. THIS MAY BE DUE TO THE PHASE CHANGE OF PTFE FROM TRICLINIC TO HEXAGONAL STRUCTURE AT AROUND 19 °C [68]. LEARDINI *et al.* [69] HAS ALSO NOTED SIMILAR VARIATION IN THE $SM_2SI_2O_7$ COMPOSITES.

THE TEMPERATURE COEFFICIENT OF RELATIVE PERMITTIVITY (τ_ε) IS CALCULATED USING EQ. (4.1) GIVEN IN CHAPTER 4. THE INSET OF FIGURE 5.9 (A) SHOWS THE VARIATION OF τ_ε WITH FILLER CONTENT FOR UNTREATED AND SILANE COUPLED COMPOSITES. IT IS CLEAR FROM THE FIGURE, IN THE CASE OF UNTREATED FILLER, τ_ε BECOMES MORE NEGATIVE WITH THE AMOUNT OF FILLER CONTENT DESPITE THE FACT THAT THE $SM_2SI_2O_7$ FILLER HAS A τ_ε VALUE OF +63 PPM/°C. WANG *et al.* [70] ALSO OBSERVED A SIMILAR VARIATION IN THE CASE OF COPPER PHTHALOCYANINE/BATIO$_3$ COMPOSITES. GENERALLY, IN COMPOSITES THE DIELECTRIC RESPONSE WITH TEMPERATURE CAN BE EXPLAINED ON THE FOLLOWING TWO COMPETITIVE MECHANISMS [70]. THE SEGMENTAL MOBILITY OF POLYMER IS IMPROVED BY THE INCREASE IN TEMPERATURE. THIS WILL ENHANCE THE POLARIZATION OF THE FILLER THEREBY LEADING TO AN INCREASE IN THE RELATIVE PERMITTIVITY. THE SECOND MECHANISM IS RELATED TO THE DIFFERENCE IN THE THERMAL EXPANSION COEFFICIENTS OF POLYMER AND THE FILLER. THE LARGE DIFFERENCE IN THESE VALUES MAY PREVENT THE AGGREGATION OF POLAR COMPONENTS AND THIS MIGHT LEAD TO A REDUCTION IN RELATIVE PERMITTIVITY WITH RISE IN TEMPERATURE. IN THE PRESENT CASE THE COEFFICIENT OF THERMAL EXPANSION OF PTFE AND $SM_2SI_2O_7$ ARE 93 PPM/°C AND 1.61 PPM/°C RESPECTIVELY. THUS THE PARTICLE AGGLOMERATION IS DISRUPTED AND SUBSEQUENTLY THE RELATIVE PERMITTIVITY DECREASES.

FIGURE 5.10 SHOWS THE VARIATION OF THE COEFFICIENT OF THERMAL EXPANSION OF PTFE/$SM_2SI_2O_7$ COMPOSITES WITH DIFFERENT VOLUME FRACTION OF BOTH UNTREATED AND SILANE TREATED FILLER. IT IS SEEN THAT WITH THE INCREASE IN FILLER CONTENT THE CTE DECREASES GRADUALLY. THIS IS QUITE EXPECTABLE DUE TO THE LOW VALUE OF CTE POSSESSED BY $SM_2SI_2O_7$ WHEREBY THE EXPANSION OF THE MATRIX IS CONSTRAINED [38]. GENERALLY IN PARTICULATE COMPOSITES, THE FILLER PARTICLES CAN BE CONSIDERED TO BE SURROUNDED BY TWO REGIONS (I) TIGHTLY BOUND POLYMER OR CONSTRAINED POLYMER CHAIN AND (II) BY LOOSELY BOUND OR UNCONSTRAINED POLYMER CHAIN. WHEN THE FILLER CONTENT INCREASES, THE INTERPARTICLE DISTANCE DECREASES AND THE UNCONSTRAINED POLYMER CHAINS GET TRANSFORMED INTO CONSTRAINED POLYMER CHAINS. THIS INCREASED CONCENTRATION OF CONSTRAINED PTFE POLYMER CHAINS SUPPRESSES THE THERMAL EXPANSION OF THE COMPOSITES. THE CTE DECREASES FROM

TO 36 PPM/°C WITH THE ADDITION OF 50 VOL% UNTREATED $Sm_2Si_2O_7$ CERAMIC. HOWEVER, THE CTE VALUES OF THE COMPOSITES ARE MUCH REDUCED TOWARDS LOWER VALUES ON ADDITION OF SILANE COUPLED $Sm_2Si_2O_7$ CERAMIC INTO THE PTFE MATRIX. THIS IS IN CONTRADICTION WITH EARLIER REPORT BY *et al.* [36] WHERE AN INCREASE IN THE CTE VALUE IS NOTED WITH TH ADDITION OF SILANE COATED $Sm_2Si_2O_7$. THE DECREASE IN THE CTE VALUE OF SILANE TREATED PTFE/$Sm_2Si_2O_7$ COMPOSITES IS DUE TO THE INCREASING WETTABILITY AND DISPERSION FILLER PARTICLES. THE UNTREATED PTFE/$Sm_2Si_2O_7$ COMPOSITES CONTAIN TINY GAPS BETWEEN THE FILLER AND THE MATRIX WHICH IS THE REASON FOR THE INCREASED CTE WHEN COMPA OF THE COUPLED COMPOSITES.

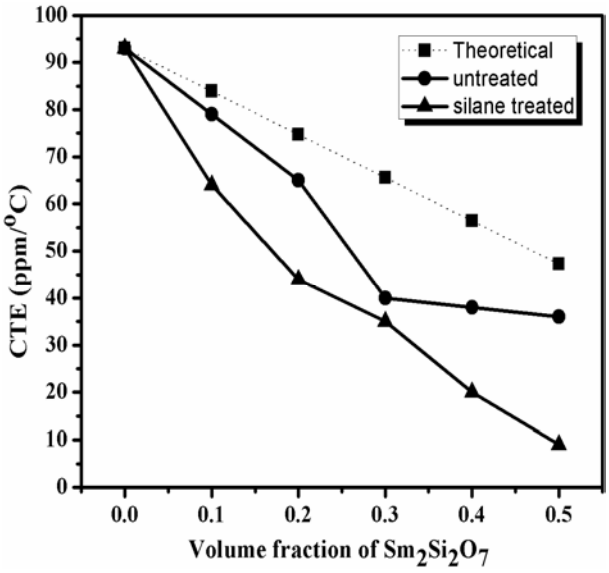

Fig. 5.10 Variation of the coefficient of thermal expansion of PTFE/$Sm_2Si_2O_7$ composites and comparison using rule of mixtures.

THE EXPERIMENTAL CTE VALUES OF BOTH THE UNTREATED AND THE SILANE PTFE/$Sm_2Si_2O_7$ COMPOSITES ARE COMPARED WITH THE THEORETICAL PREDICTION USING MIXTURES AND ARE SHOWN IN FIG. 5.10. ACCORDING TO THE RULE OF MIXTURES THE CTE PHASE COMPOSITE IS DEPENDENT LINEARLY ON THE VOLUME FRACTION OF THE EXPERIMENTAL VALUES SHOW A WIDE VARIATION FROM THE CALCULATED ONES. THIS I THE FACT THAT THE EQUATION DOES NOT CONSIDER THE MECHANICAL CONSTRAINTS MATRIX DUE TO THE FILLERS.

TABLE 5.3 GIVES THE MICROHARDNESS AND WATER ABSORPTION OF PTFE/$Sm_2Si_2O_7$ COMPOSITES WITH FILLER CONTENT VARIATION. THE VICKER'S MICROHARDNESS OF MATRIX IS NEARLY 7 kg/mm^2. AS THE FILLER CONTENT INCREASES, THE MICROHARDNESS INCREASES AS EXPECTED DUE TO THE FACT THAT CERAMICS GENERALLY POSSESS A H MICROHARDNESS. IT IS SEEN THAT WITH THE INCREASE IN THE FILLER CONTENT THE INCREASES TO VALUE OF 13 kg/mm^2 IN THE CASE OF UNTREATED FILLER AND 16 kg/mm^2 FOR SILANE COUPLED FILLER.

Table 5.3 The Vicker's hardness and water absorption of PTFE/$Sm_2Si_2O_7$ composites.

Composite	Volume fraction of filler (v_f)	Vickers microhardness (kg/mm^2)	Water absorption (%)
UNTREATED PTFE/$SM_2SI_2O_7$	0.0	7	0.53
	0.1	9	0.15
	0.3	10	0.22
	0.5	13	13.05
SILANE TREATED PTFE/$SM_2SI_2O_7$	0.1	8	0.02
	0.3	12	0.68
	0.5	16	2.17

FROM THE TABLE IT IS ALSO EVIDENT THAT THE WATER ABSORPTION OF THE INCREASES WITH THE FILLER CONTENT. THIS IS PROBABLY DUE TO THE HYDROPHILIC CERAMICS. A COMPARISON OF THE WATER ABSORPTION OF THE COMPOSITES UNTREATE WITH COUPLING AGENT SHOWS THAT THE SILANE TREATED COMPOSITES POSSESS A LOW DUE TO THE REDUCED POROSITY (SEE TABLES 5.1 AND 5.2). IN THE CASE OF UNTREATED THE WATER ABSORPTION SHOWS A VALUE AS HIGH AS 13% FOR V_f = 0.5 WHERE AS ON THE OTHER HAND THE ONE TREATED WITH SILANE SHOWS A VERY LOW VALUE OF NEARLY 2 VOLUME FRACTION. THE SILANE COUPLING AGENT REDUCES THE HYDROPHILICITY OF FILLER AND ALSO DISPERSES THE CERAMIC UNIFORMLY IN THE MATRIX THEREBY REDU ABSORPTION.

5.4.1.2 EFFECT OF PARTICLE SIZE ON THE PROPERTIES OF $Sm_2Si_2O_7$ PTFE/SM COMPOSITES

THE SPECIFIC SURFACE AREA MEASUREMENTS SHOW THAT THE MICRON SIZED $Sm_2Si_2O_7$ POSSESS A VERY SMALL AVERAGE SURFACE AREA ($2.1 m^2/g$) AS COMPARED TO THE NANO SIZED ONE ($20.94 m^2/g$). FIGURES 5.11 (A) AND (B) SHOW THE MICROSTRUCTURAL IMAGES OF P FILLED WITH 0.05 v_f AND 0.25 v_f OF NANO SIZED $Sm_2Si_2O_7$ CERAMICS. IT IS TO BE NOTED THAT AT LOWER FILLER CONTENT THE NANO SIZED PARTICLES ARE ALMOST UNIFORMLY DISPERS WHILE HIGHER CERAMIC LOADING FACILITATES THE FORMATION OF CLUSTERS. THE DIS PARTICLES INTO A POLYMER MATRIX IS VERY MUCH DEPENDENT ON THE KINETICS O PREPARATION. AT LOWER FILLER CONTENT THE ATTRACTIVE VAN DER WAALS FORCES B PARTICLES ARE WEAK DUE TO THE LONG INTERPARTICLE DISTANCE. THUS THE AGGLOM CAN BE EASILY BROKEN BY APPLYING THE FORCE PROVIDED BY THE MIXING DEVICE. H HIGHER FILLER LOADING THE INTERPARTICLE DISTANCE DECREASES EXPONENTIALLY STRONG FORCE OF ATTRACTION THE PARTICLES GET AGGLOMERATED. THUS IT IS DIFF COMPOSITES WITH HIGHER FILLER LOADING OF NANO SIZED POWDER. IN THE PRESE MAXIMUM FILLER LOADING OF 0.25 v_f COULD BE OBTAINED.

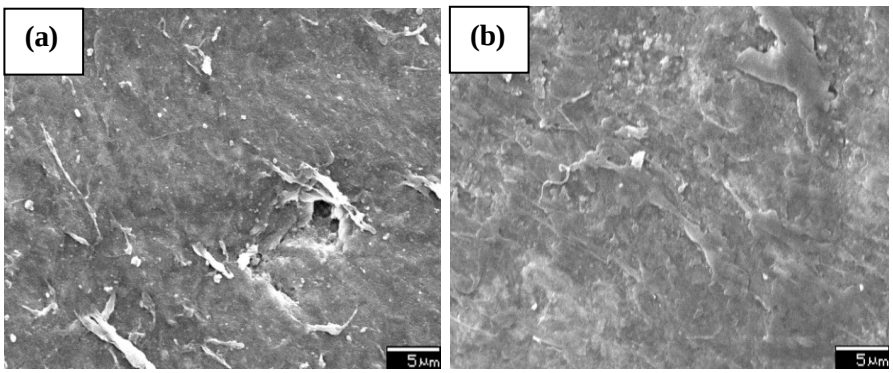

Fig. 5.11 SEM images of PTFE loaded with (a) 0.05 v_f nano $Sm_2Si_2O_7$, (b) 0.25 v_f nano $Sm_2Si_2O_7$.

IN ELECTRONIC PACKAGING APPLICATIONS, THE PROPOSED MATERIAL MUST W TEMPERATURE UP TO 300 °C AND SHOULD MAINTAIN THEIR PROPERTIES [71]. THE THERMAL STA AND WEIGHT LOSS OF THE COMPOSITES ARE ANALYZED USING TGA. FIG. 5.12 SHOWS T THERMOGRAMS OF PURE PTFE, PTFE LOADED WITH MICRO AND NANO SIZED $Sm_2Si_2O_7$ FILLER

DECOMPOSITION OF PTFE STARTS AT CA. 500 °C AND THE MATERIAL RESIDUE WAS ZERO AT A TEMPERATURE OF 597 °C.

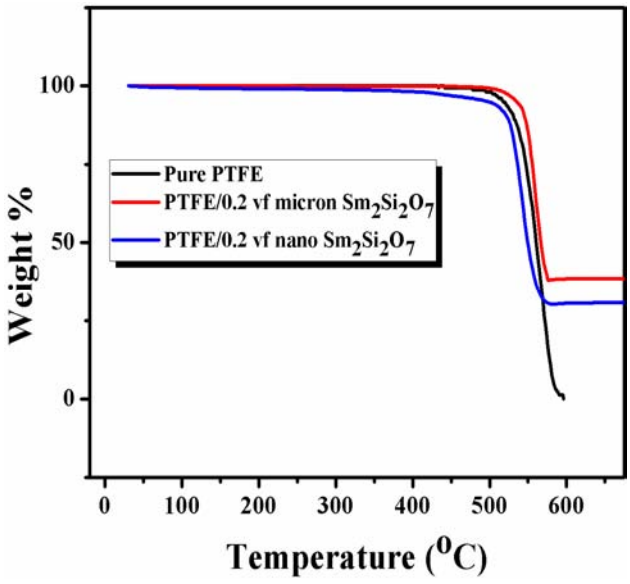

Fig. 5.12 TGA curves of PTFE/$Sm_2Si_2O_7$ composites.

Table 5.4 TGA parameters of pure PTFE and PTFE loaded with micro and nano $Sm_2Si_2O_7$.

Material	T_{10} (°C)	Filler added (wt%)	Filler residue (wt%)
PURE PTF	531.9	0	0
PTFE/0.2V_F MSM$_2$SI$_2$O$_7$	545.7	38.4	34.8
PTFE/0.2V_F NSM$_2$SI$_2$O$_7$	522.9	38.4	27.9

T_{10} IS THE TEMPERATURE AT WHICH 10% WT OF THE SAMPLE IS LOST AFTER HEATING IN NITROGEN ATMOSPHERE.

TABLE 5.4 GIVES THE PARAMETERS OBTAINED FROM THE TGA CURVE. IT IS SEEN THAT P SHOWS A T_{10} VALUE OF 531.9 °C AND AN INCREASE OF MORE THAN 10 °C IS NOTED WITH THE ADDITION OF 0.2 V_F MICRON SIZED FILLER. THIS INCREASE IN THE DECOMPOSITION TEMPE MAY BE DUE TO THE INCREASED INTERACTION BETWEEN THE MATRIX AND THE FILLE SEGMENTAL MOBILITY OF THE POLYMER IS REDUCED. THUS THE THERMAL STABILITY IS FILLER ADDITION. THE RESIDUE FILLER IN THE PTFE-MICROSTM AT 800 °C IS

NEARLY CLOSE TO THE AMOUNT INITIALLY ADDED. HOWEVER, IN CONTRAST TO THE EAR
72] THE NANO-COMPOSITE SHOWS A LOW DECOMPOSITION TEMPERATURE THAN THE PU
IN THE CASE OF NANO FILLER LOADED COMPOSITE, A SLIGHT DECREASE IN WEIGHT A
TEMPERATURE IS NOTED WHICH MAY BE DUE TO THE LOSS OF VOLATILE BY-PRODUCTS. T
FROM TABLE 5.4 WHERE THE RESIDUE FILLER FOR NANO-COMPOSITE IS ONLY 27.9 %.

TABLE 5.5 GIVES THE MICROWAVE DIELECTRIC PROPERTIES OF THE PTFE/SM_2O_7
COMPOSITES LOADED WITH MICRON AND NANO SIZE FILLERS. IN BOTH CASES IT IS CL
RELATIVE PERMITTIVITY INCREASES WITH FILLER CONTENT WHICH IS QUITE EXPECT
INCREASED RELATIVE PERMITTIVITY OF SM_2O_7 COMPARED WITH THAT OF THE PTFE MATRIX. AN
INCREASE IN THE NANO FILLER CONCENTRATION TENDS TO INCREASE THE RELATIVE PE
THE INCREASE IN THE NUMBER OF NANO PARTICLE FILLERS CONTRIBUTING TO THE EF
PERMITTIVITY WHICH OVERHEADS THE EFFECT OF IMMOBILIZATION OF POLYMER CHAIN
HIGHER FILLER CONTENT WHICH HAS A TENDENCY TO LOWER THE RELATIVE PERMITTIV
FILLER LOADING LEVEL, THE COMPOSITES FILLED WITH SMALLER PARTICLES WILL
INTERFACIAL AREA WHICH PROMOTES THE INTERFACIAL POLARIZATION MECHANISM
INCREASING THE EFFECTIVE RELATIVE PERMITTIVITY. THE NUMBER OF PARTICLES I
COMPOSITE IS GREATER THAN THAT IN THE MICRON SIZE COMPOSITES FOR THE SAME F
SIMILAR OBSERVATIONS WERE EARLIER REPORTED IN THE CASE OF PTFE/$ZrTiO_4$
COMPOSITES [37]. IT IS ALSO NOTED THAT THE DIELECTRIC LOSS INCREASES WITH THE INC
CONTENT FOR BOTH MICRON AND NANO SIZE SM_2O_7 FILLERS AND A HIGH DIELECTRIC LOSS IS
EXHIBITED BY THE NANO SIZED FILLED COMPOSITES. THE REASON FOR THIS INCREASE I
DUE TO THE LARGE INTERACTION ZONE AND THE INCREASE IN THE LATTICE STRAIN CA
INCREASE IN THE SURFACE AREA. MOREOVER, SEVERAL OTHER FACTORS SUCH AS C
POLYMER MORPHOLOGY, SPACE CHARGE DISTRIBUTION, REDUCTION IN THE INTERNAL F
THE DECREASE IN THE PARTICLE SIZE AND SCATTERING MECHANISMS MAY ALSO AFFEC
PROPERTIES SIGNIFICANTLY [74].

Table 5.5 The density, microwave dielectric properties and water absorption of PTFE/$Sm_2Si_2O_7$.

Volume fraction filler	Density (g/cm^3)	Microwave dielectric properties (9 GHz)		Water absorption (%)
		ε_R	$TAN\delta$	
micron				
0.05	2.21	2.37	0.0009	0.08
0.10	2.32	2.48	0.0023	0.15
0.15	2.49	2.92	0.0026	0.17
0.20	2.79	3.04	0.0051	0.19
0.25	2.98	3.49	0.0057	0.23
nano				
0.05	2.01	2.33	0.0046	0.05
0.10	2.20	2.52	0.0130	0.12
0.15	2.40	2.71	0.0219	0.14
0.20	2.47	3.06	0.0161	0.54
0.25	2.53	3.39	0.0315	0.68

FIGURES 5.13 (A) AND (B) RESPECTIVELY SHOW THE COMPARISON BETWEEN EXPERIMENTAL AND THEORETICAL VALUES OF RELATIVE PERMITTIVITY AT 1 MHZ FOR BOTH MICRON AND NANO SIZE FILLER LOADED PTFE/$Sm_2Si_2O_7$ COMPOSITES. IT CAN BE OBSERVED THAT THE NANO FILL COMPOSITES SHOW A BETTER AGREEMENT WITH THE THEORETICAL PREDICTIONS. FROM CLEAR THAT NANO COMPOSITES ARE FOUND TO BE IN GOOD AGREEMENT WITH TH LICHTENECKER EQUATION IMPLYING A GOOD DISPERSION OF THE NANO PARTICLES IN T TWO-PHASE MODELS, BOTH THE CONSTITUENTS OF THE COMPOSITE SYSTEM ARE CO DIFFERENT PHASES RATHER THAN CONSIDERING ONE CONSTITUENT OF THE COMPOSITE IN A CONTINUOUS PHASE OF ANOTHER. THE RELATIVE PERMITTIVITY OF COMPOSITES AL THE DISTRIBUTION OF THE FILLER, SHAPE AND SIZE OF FILLERS AND INTERFACE BETWEE POLYMERS. THE COMPOSITES WITH LOWER NANO FILLER CONTENT SHOWS A GOOD MA EMT MODEL WHILE THE HIGHER VOLUME FRACTIONS DEVIATE MORE FROM THE PREDI MAY BE DUE TO THE HIGHER AMOUNT OF POROSITY IN THE COMPOSITES. IN THE CAS COMPOSITES MORE PRECISE MODEL WHICH CONSIDERS THE INTERFACIAL CONTRIBUT INTERPHASE POWER LAW NEED TO BE CONSIDERED.

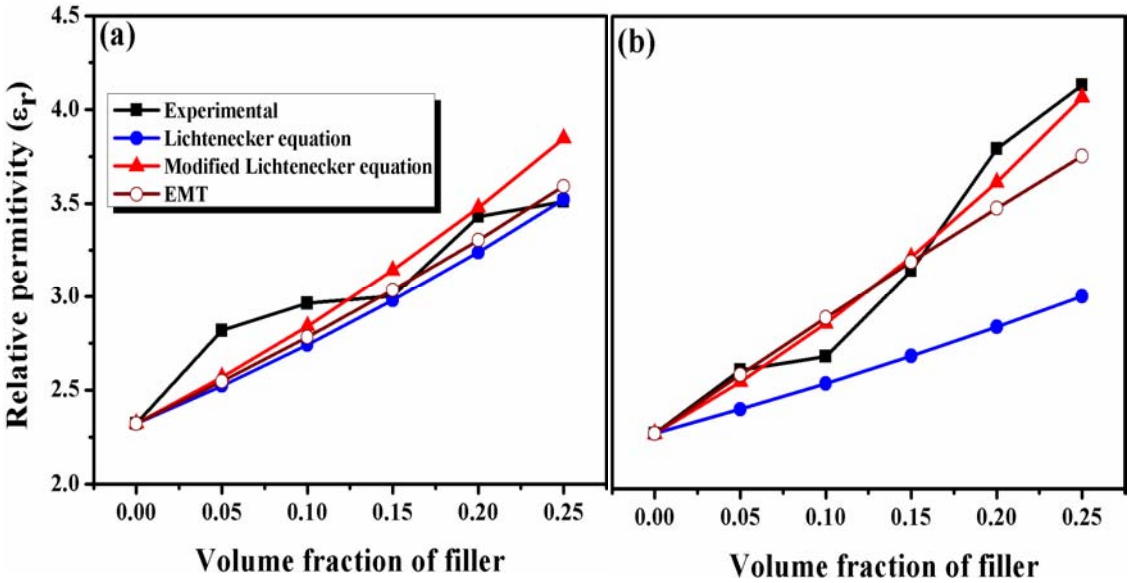

Fig. 5.13 Comparison of experimental and theoretical relative permittivity of (a) PTFE/micro $Sm_2Si_2O_7$ (b) PTFE/nano $Sm_2Si_2O_7$ composites with volume fraction of filler at 1MHz.

FIGURE 5.14 SHOWS THE VARIATION OF τ_ε WITH THE FILLER CONTENT FOR PTFE/$Sm_2Si_2O_7$ COMPOSITES. IT IS CLEAR FROM THE FIGURE THAT IN THE CASE OF MICRON SIZE FILLER, τ_ε BECOMES MORE NEGATIVE WITH THE AMOUNT OF FILLER CONTENT DESPITE THE FACT THAT THE $Sm_2Si_2O_7$ FILLER HAS A τ_ε VALUE OF +63 PPM/°C. THE FIGURE CLEARLY SHOWS THAT THE COMPOSITES WITH SM SIZE FILLER HAVE A LOWER τ_ε VALUE. IN THE CASE OF NANO-COMPOSITES, THE SEGMENTAL MOBILITY OF THE POLYMER IS MUCH REDUCED SINCE MORE PARTICLES SURROUND EA CHAIN THEREBY INHIBITING THE FREE MOVEMENT. THE LARGE DIFFERENCE IN THE CTE V MATRIX AND THE FILLER MAY PREVENT THE AGGREGATION OF THE POLAR COMPONENTS LEAD TO A REDUCTION IN RELATIVE PERMITTIVITY WITH INCREASE IN TEMPERATURE. T 5.14 SHOWS THE VARIATION OF RELATIVE PERMITTIVITY WITH TEMPERATURE IN THE +80°C FOR 0.2 V_F OF PTFE/NANO $Sm_2Si_2O_7$ COMPOSITE. IT IS EVIDENT FROM THE FIGURE THAT TH VARIATION OF RELATIVE PERMITTIVITY IS ALMOST REGULAR EXCEPT FOR AN INCREAS PERMITTIVITY VALUE AT A TEMPERATURE AROUND 20°C. THIS IS DUE TO THE PHASE CHANGE ASSOCIATED WITH PTFE POLYMER AS DISCUSSED EARLIER.

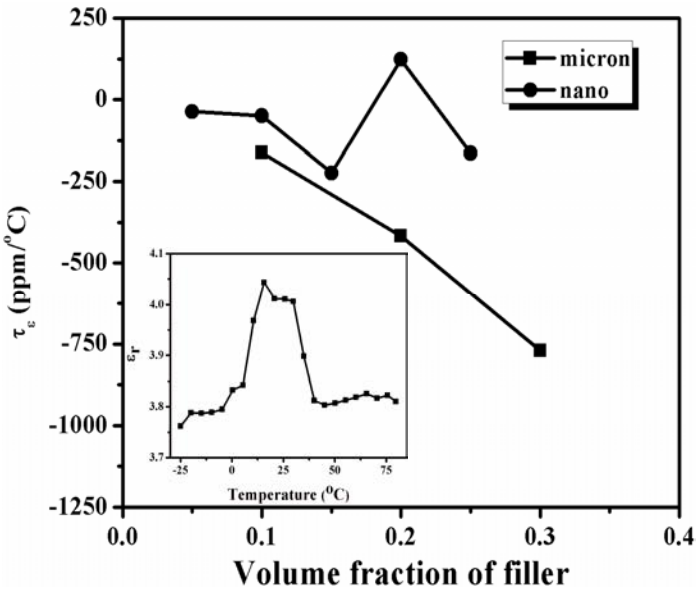

Fig. 5.14 Variation of temperature coefficient of relative permittivity of PTFE/$Sm_2Si_2O_7$ composites with volume fraction of micron and nano size fillers.

FIGURE 5.15 SHOWS THE VARIATION OF CTE OF PTFE/$Sm_2Si_2O_7$ COMPOSITES WITH DIFFERENT VOLUME FRACTION OF BOTH MICRON AND NANO SIZE FILLERS. IT IS FOUND INCREASE IN BOTH TYPE OF FILLER CONTENT, THE CTE DECREASES GRADUALLY. T EXPECTABLE DUE TO THE LOW VALUE OF CTE POSSESSED BY $Sm_2Si_2O_7$ (SEE FIG 5.12) WHEREBY THE EXPANSION OF THE MATRIX IS CONSTRAINED. IT IS TO BE NOTED THAT FOR THE S FRACTION OF FILLER, NANO-COMPOSITE EXHIBITS A MUCH LOWER VALUE OF CTE WHEN THE MICRO COMPOSITES. THE CTE OF PTFE/MICRO $Sm_2Si_2O_7$ AND NANO $Sm_2Si_2O_7$ LOADED COMPOSITES HAS A CTE VALUE OF 65 PPM/°C AND 40 PPM/°C RESPECTIVELY. THIS MAY BE DUE TO THE FACT THAT, FOR THE SAME FILLER CONTENT, NANO PARTICLES HAVE LARGE SURFACE AREA HIGH PARTICLE DENSITY. THIS REDUCES THE FREE VOLUME OF THE MATRIX WHICH IN T MATRIX EXPANSION. ALSO THE NANO PARTICLES ARE WELL DISPERSED IN THE POLYMER COMPARED TO THE MICRON SIZED PARTICLES. THIS WILL CREATE GOOD INTERFACIAL AR NANO $Sm_2Si_2O_7$ AND PTFE AND REPORTS SHOW THAT COMPOSITES WITH STRONG INTERFAC A VERY LOW VALUE OF CTE [75]. IN THE CASE OF NANO-COMPOSITES THE CONCENTI CONSTRAINED PTFE POLYMER CHAINS IS MUCH HIGHER WHICH SUPPRESSES THE EXPANSION OF THE COMPOSITES.

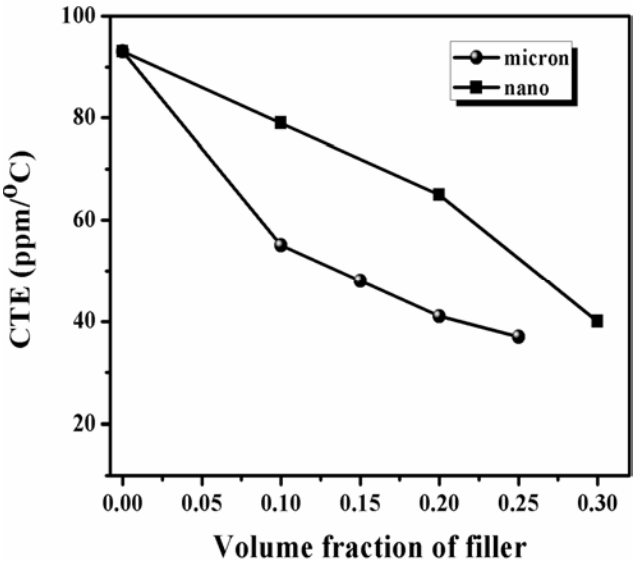

Fig. 5.15 Variation of the coefficient of thermal expansion of micron and nano PTFE/$Sm_2Si_2O_7$ composites.

TABLE 5.5 ALSO GIVES THE WATER ABSORPTION OF $Sm_2Si_2O_7$ FILLED PTFE COMPOSITES WITH MICRON AND NANO FILLER CONTENT VARIATION. THE COMPOSITES CONSIST OF TW MATERIALS, ONE HYDROPHILIC AND THE OTHER HYDROPHOBIC IN NATURE. FROM TH EVIDENT THAT THE WATER ABSORPTION OF BOTH THE COMPOSITES INCREASES WITH TH WHICH IS DUE TO THE HYDROPHILIC NATURE OF THE CERAMICS. A COMPARISON OF ABSORPTION OF THE COMPOSITES WITH VARYING FILLER SIZE SHOWS THAT SMALLER HIGHER IS THE WATER ABSORPTION TENDENCY. IN THE CASE OF PTFE FILLED WITH 0.2 V $SM_2SI_2O_7$ SHOWS A WATER ABSORPTION OF 0.19 % WHEREAS ON THE OTHER HAND THAT F SAME VOLUME FRACTION OF $Sm_2Si_2O_7$ SHOWS A HIGH VALUE OF 0.54%. THIS IS DUE TO THE HIGHER SURFACE AREA OF $Sm_2Si_2O_7$ CERAMIC FILLER.

5.4.2 $SM_2SI_2O_7$ FILLED POLYETHYLENE AND POLYSTYRENE COMPOSITES

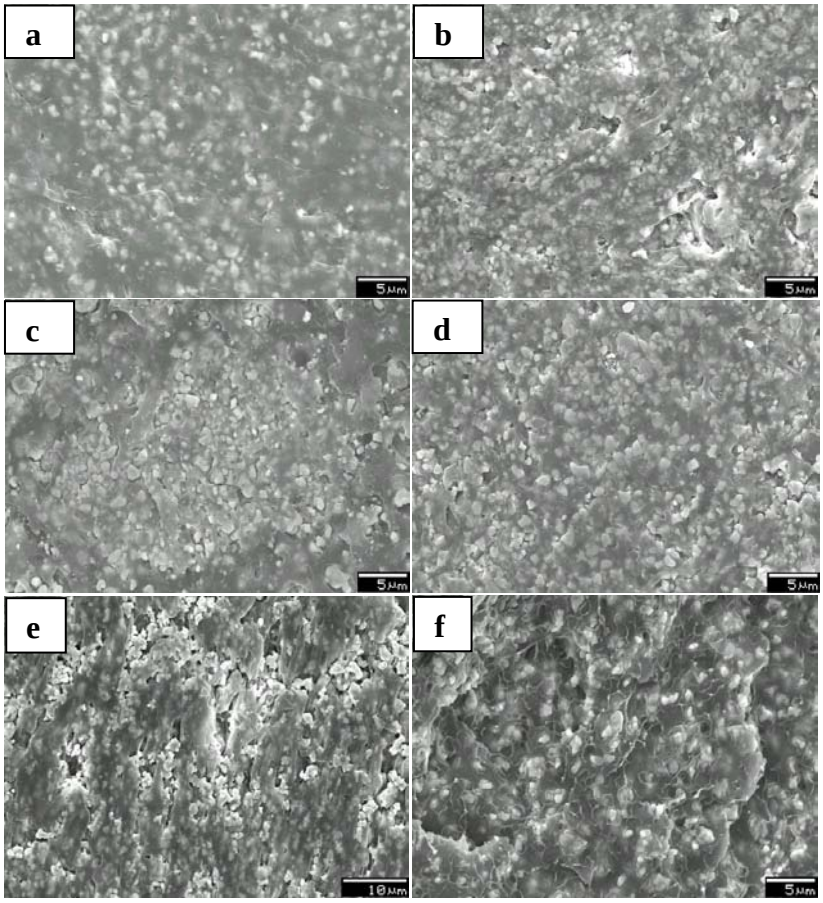

Fig. 5.16 SEM images of (a) PE-0.3 v_f $Sm_2Si_2O_7$, (b) PE-0.5 v_f $Sm_2Si_2O_7$, (c) PS-0.3 v_f $Sm_2Si_2O_7$, (d) PS-0.5 v_f $Sm_2Si_2O_7$, (e) fractured surface of PE-0.3 v_f $Sm_2Si_2O_7$ and (f) PS-0.3 v_f $Sm_2Si_2O_7$.

FIGURES 5.16 (A)-(D) SHOW THE MICROSTRUCTURAL IMAGES OF PE-$SM_2SI_2O_7$ AND PS-$SM_2SI_2O_7$ POLYMER – CERAMIC COMPOSITES FOR DIFFERENT VOLUME FRACTION OF LOADING. FROM FIG. 5.16 (A) AND 5.16 (B) IT IS CLEAR THAT THE $SM_2SI_2O_7$ FILLERS IS UNIFORMLY DISTRIBUTED IN THE POLYETHYLENE MATRIX. AS THE FILLER CONTENT INCREASES THE CERAMIC PARTICLES GREW DENSER INDICATING EXCELLENT COMPATIBILITY BETWEEN POLYETHYLENE MATRIX. HOWEVER, IN THE CASE OF PS-$SM_2SI_2O_7$ COMPOSITES (FIGS. 5.16 (C) AND 5.16 (D)) A HOMOGENEOUS PARTICLE DISTRIBUTION ALONG WITH SMALL TRAILS OF AGGLOMERATES WERE OBSERVED. IT IS ALSO FOUND THAT THE POROSITY OF THE COMPOSITES INCREASES WITH INCREASE IN THE FILLER LOADING. FIGS. 5.16 (E) AND (F) SHOW THE FRACTURED SURFACES OF PE-$SM_2SI_2O_7$ AND

PS-$SM_2SI_2O_7$ FOR 0.3 VOLUME FRACTION OF CERAMIC. THESE MICROSTRUCTURES INDIC
HOMOGENEOUS DISTRIBUTION OF THE CERAMIC PARTICLES IN BOTH THE POLYMER MELT

Table 5.6 The physical and dielectric properties (at 1 MHz) of polyethylene-$Sm_2Si_2O_7$ and polystyrene-$Sm_2Si_2O_7$ polymer ceramic composites.

Material	Filler Volume Fraction	Density (g/cm^3)	Relative density (%)	Porosity (%)	At 1 MHz	
					ε_R	$TAN\delta$
POLYETHYLENE-$SM_2SI_2O_7$ COMPOSITE	0.0	0.95	99.6	0.4	2.62	0.0006
	0.1	1.40	98.6	1.4	3.17	0.0008
	0.2	1.87	98.9	1.1	3.48	0.0014
	0.3	2.29	96.6	3.4	4.35	0.0027
	0.4	2.75	96.5	3.5	5.02	0.0059
	0.5	3.14	94.6	5.4	5.39	0.0091
POLYSTYRENE-$SM_2SI_2O_7$ COMPOSITE	0.0	1.04	98.3	1.7	3.20	0.0017
	0.1	1.44	96.0	4.0	3.51	0.0012
	0.2	1.79	90.9	9.0	4.19	0.0014
	0.3	2.21	90.9	9.1	4.41	0.0034
	0.4	2.65	90.9	9.1	5.12	0.0078
	0.5	3.05	90.8	9.2	6.11	0.0087

TABLE 5.6 GIVES THE RELATIVE DENSITY AND POROSITY OF PS-$SM_2SI_2O_7$ AND PS-$SM_2SI_2O_7$ COMPOSITES WITH THE VOLUME FRACTION OF THE FILLER. THE DENSITIES OF PO AND POLYSTYRENE MEASURED BY ARCHIMEDES METHOD ARE FOUND TO BE 0.95 G/CM^3 AND 1.04 G/CM^3 RESPECTIVELY. IT IS FOUND THAT THE DENSITY OF THE COMPOSITE INCREASES WIT THE FILLER CONTENT AS EXPECTED DUE TO THE HIGHER DENSITY OF $SM_2SI_2O_7$. IT IS OBSERVED THAT THE RELATIVE DENSITY IS MORE IN THE CASE OF PS-$SM_2SI_2O_7$ COMPOSITES THAN PE-$SM_2SI_2O_7$ COMPOSITES SHOWING GOOD ADHESION BETWEEN THE POLYMER AND THE CERAMIC PARTICLES. MAXIMUM FILLER LOADING OF PE-$SM_2SI_2O_7$ SHOWS A RELATIVE DENSITY OF 94.6% WHEREAS PS-$SM_2SI_2O_7$ HAS ONLY ABOUT 91% DENSIFICATION. THIS MAY BE DUE TO THE PRES

OF VOIDS INSIDE THE COMPOSITE WITH THE INCREASED FILLER CONTENT. THIS IS A CLEA
THE STRONG ADHESION BETWEEN THE POLYETHYLENE MATRIX AND $Sm_2Si_2O_7$ FILLER WHICH IS ALSO
CLEAR FROM THE SEM IMAGES.

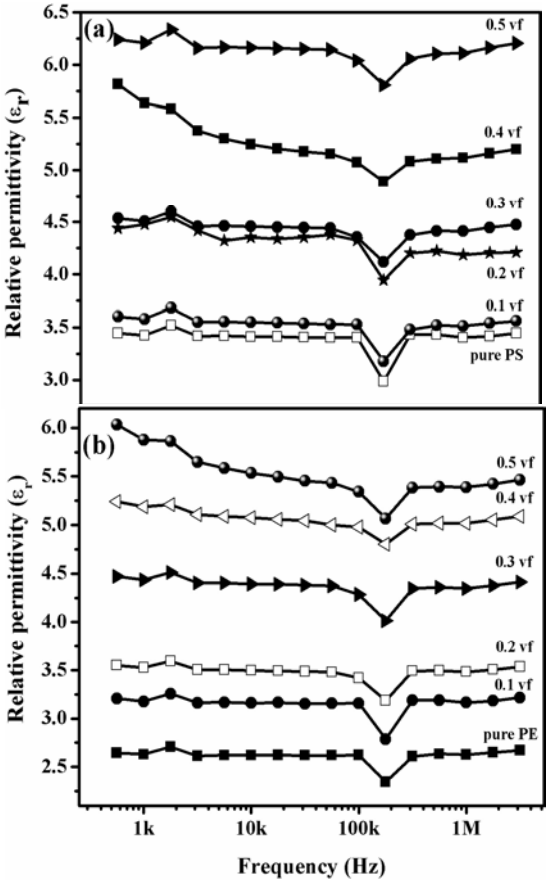

Fig. 5.17 The variation of relative permittivity with frequency for (a) PS/$Sm_2Si_2O_7$ and (b) PE/$Sm_2Si_2O_7$ composites.

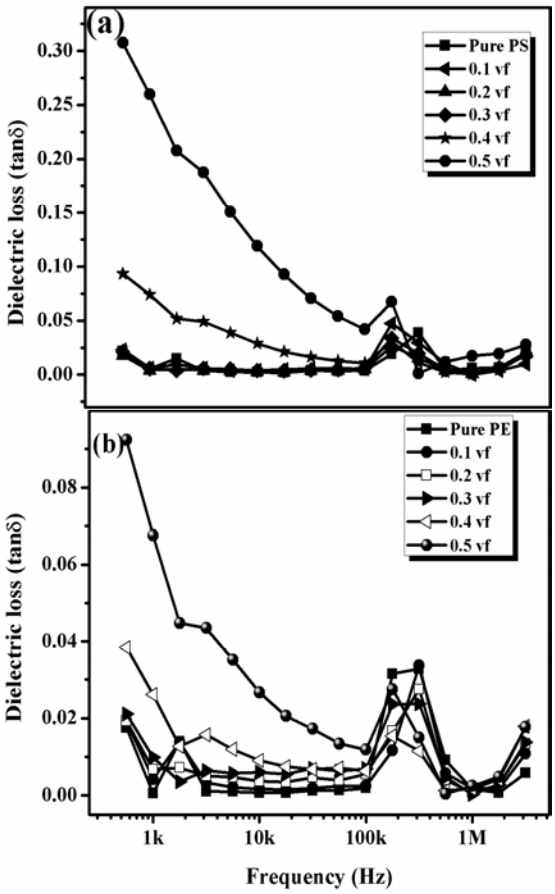

Fig. 5.18 The variation of dielectric loss with frequency for (a) PS/$Sm_2Si_2O_7$ and (b) PE/$Sm_2Si_2O_7$ composites.

THE RELATIVE PERMITTIVITY VARIATION OF THE COMPOSITES WITH THE FILLER D
A FUNCTION OF FREQUENCY IN THE RANGE 1 KHZ – 1 MHZ AND PS/$Sm_2Si_2O_7$
COMPOSITES ARE SHOWN IN FIGS. 5.17 (A) AND (B). IT IS FOUND THAT THE RELATIVE PERM
THE COMPOSITES REMAIN NEARLY A CONSTANT IN THE WHOLE MEASURED FREQUENC
RELATIVE PERMITTIVITY IS FOUND TO BE NEARLY INDEPENDENT OF FREQUENCY FOR
LOADING. HOWEVER, FOR HIGHER FILLER CONTENTS (ABOVE 0.4 VF) IT IS FOUND TO BE MORE FREQUENCY
DEPENDENT. IN POLYMERS THE DIPOLAR ORIENTATION COMES FROM THE MOTION O

GROUPS. BUT THE CROSS LINKING NATURE OF THE POLYMERS HINDERS THE MOLECULAR
POLAR GROUPS. THUS THE POLYMER MOLECULES WITHIN THE INTERPHASE REGION ARE R
DIPOLAR POLARIZATION WHEN COMPARED TO THE MOLECULES IN THE BULK MATRIX R
TO A REDUCTION IN THE RELATIVE PERMITTIVITY.

FIGS. 5.18 (A) AND (B) RESPECTIVELY SHOW THE VARIATION OF DIELECTRIC LO
FREQUENCY. THE DIELECTRIC LOSS INCREASES GRADUALLY WITH THE FILLER CONTENT
HOWEVER, A SLIGHT DECREASE IN RELATIVE PERMITTIVITY IS NOTED FOR BOTH THE COM
KHZ. THIS MAY BE PROBABLY DUE TO THE DIPOLAR RELAXATION PROCESS ASSOCIAT
MATRICES [41, 76]. AT THE SAME FREQUENCY AN INCREASE IN THE DIELECTRIC LOS
OBSERVED. IT HAS BEEN REPORTED EARLIER THAT THE POLYSTYRENE AND POLYETHY
RELAXATION PEAK IN THE RANGE 1 HZ-100 KHZ AT VERY LOW AND HIGH TEMPERATURE
76]. HOWEVER, IN THE PRESENT CASE THE INCREASE IN THE DIELECTRIC LOSS AT ROOM
MAY BE DUE TO THE NON-ACTIVATED CHARGE MOTION SUCH AS TUNNELLING.

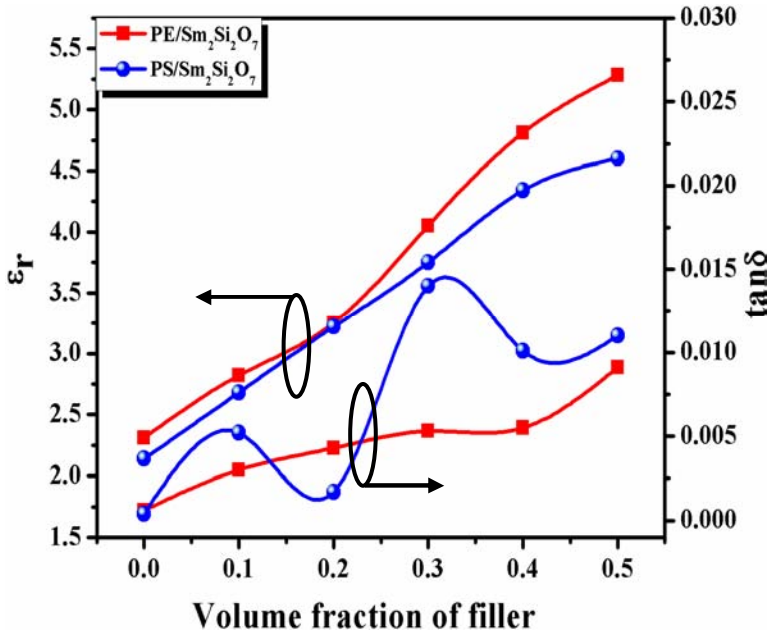

Fig. 5.19 Variation of relative permittivity and tan of polystyrene-$Sm_2Si_2O_7$ and polyethylene-$Sm_2Si_2O_7$ composites with volume fraction of filler at 9 GHz.

FIGURE 5.19 SHOWS THE VARIATION OF RELATIVE PERMITTIVITY AND DIELECTRI
VOLUME FRACTION OF $Sm_2Si_2O_7$ AT 9 GHZ FOR PE-$Sm_2Si_2O_7$ AND PS-$Sm_2Si_2O_7$ COMPOSITES
RESPECTIVELY. IN BOTH THE CASES THE RELATIVE PERMITTIVITY INCREASES WITH THE

DUE TO THE HIGH RELATIVE PERMITTIVITY OF $Sm_2Si_2O_7$ COMPARED WITH THAT OF THE RESPECTIVE MATRICES. FROM THE FIGURE IT IS ALSO OBSERVED THAT AS THE FILLER CONTENT DIELECTRIC LOSS ALSO INCREASES DUE TO THE INCREASED POROSITY OF THE COMPOSI ALSO DUE TO THE INTERFACIAL POLARIZATION BETWEEN THE POLYMER AND CERAMIC LOADINGS. AT 9 GHZ, A LOW VALUE OF RELATIVE PERMITTIVITY = 3.28 AND DIELECTRIC LOSS ($\tan\delta$ = 0.0091 FOR PE-$Sm_2Si_2O_7$ COMPOSITES AND = 4.6 AND $\tan\delta$ = 0.011 FOR PS-$Sm_2Si_2O_7$ COMPOSITES) ARE OBTAINED EVEN FOR A HIGHER FILLER CONTENT (0.5 V

FIGURES 5.20 (A) AND (B) RESPECTIVELY SHOW THE COMPARISON BETWEEN EXPERIMENTAL AND THE THEORETICAL VALUES OF RELATIVE PERMITTIVITY AT 9 GHZ VARIOUS THEORETICAL PREDICTIONS FOR PE-$Sm_2Si_2O_7$ AND PS-$Sm_2Si_2O_7$ COMPOSITES. IT IS SEEN THAT FOR BOTH THE COMPOSITES THE LICHTENECKER AND MAXWELL – WAGNER EQUA WIDE DEVIATION FROM THE EXPERIMENTAL VALUES. THE PERCENTAGE DEVIATIO EXPERIMENTAL VALUES FROM THESE PREDICTIONS IS FOUND TO INCREASE FROM 5.3 % F MAXIMUM OF 9 % FOR THE FILLER CONTENT IN THE CASE OF PE-$Sm_2Si_2O_7$. GENERALLY ALL THE THEORETICAL PREDICTIONS ARE VALID FOR LOW FILLER CONTENTS DUE TO THE IMP OF CERAMIC PARTICLES AT HIGHER FILLER CONTENTS AND ALSO DUE TO THE AIR EN COMPOSITES. ALSO THESE PREDICTIONS DO NOT CONSIDER THE MATRIX/FILLER INTERACTIONS AND IS VALID FOR COMPOSITES WITH NEAR VALUES OF RELATIVE PERMIT AND MATRIX. RECENTLY *Tan et al.* [67] REPORTED THAT MODIFIED LICHTENECKER EQUATION SHO A BETTER FIT WITH THE EXPERIMENTAL RESULTS FOR BST-CYCLIC OLEFIN COPOLYM COMPOSITES BUT EXHIBITED A SIGNIFICANT DISCREPANCY BEYOND A FILLER CONTENT EARLIER REPORTS [43] SHOW A VALUE OF -0.455352 AND -0.477392 FOR CYANATE ESTER/BATIO$_3$ EPOXY/BATIO$_3$ POLYMER-CERAMIC COMPOSITES RESPECTIVELY [35]. IN THE PRESENT STU OBTAINED A VALUE -0.2365 FOR PE-$Sm_2Si_2O_7$ AND -0.2272 FOR PS-$Sm_2Si_2O_7$ COMPOSITES. THE CALCULATED RELATIVE PERMITTIVITY VALUES USING THE MODIFIED LICHTENEC SHOW GOOD CORRESPONDENCE WITH THE EXPERIMENTAL VALUES FOR BOTH THE COMPO VOLUME FRACTION OF FILLER (V_f) CONTENT WITH A PERCENTAGE DEVIATION LESS THAN 3 FOR PE-$Sm_2Si_2O_7$ AND 5 % FOR PS-$Sm_2Si_2O_7$. HOWEVER, IT IS FOUND THAT FOR THE 0.5 V PREDICTIONS DEVIATE FROM THE EXPERIMENTAL VALUE SHOWING A VALUE AS HIGH A $Sm_2Si_2O_7$ AND NEARLY 20 % FOR PS-$Sm_2Si_2O_7$. THIS LARGE DEVIATION OBSERVED FOR PS-

$Sm_2Si_2O_7$ COMPOSITES MAY BE DUE TO THE SLIGHT INHOMOGENITY IN THE PARTICLE DIST
THE POLYSTYRENE MATRIX WHEN COMPARED TO THAT OF POLYETHYLENE.

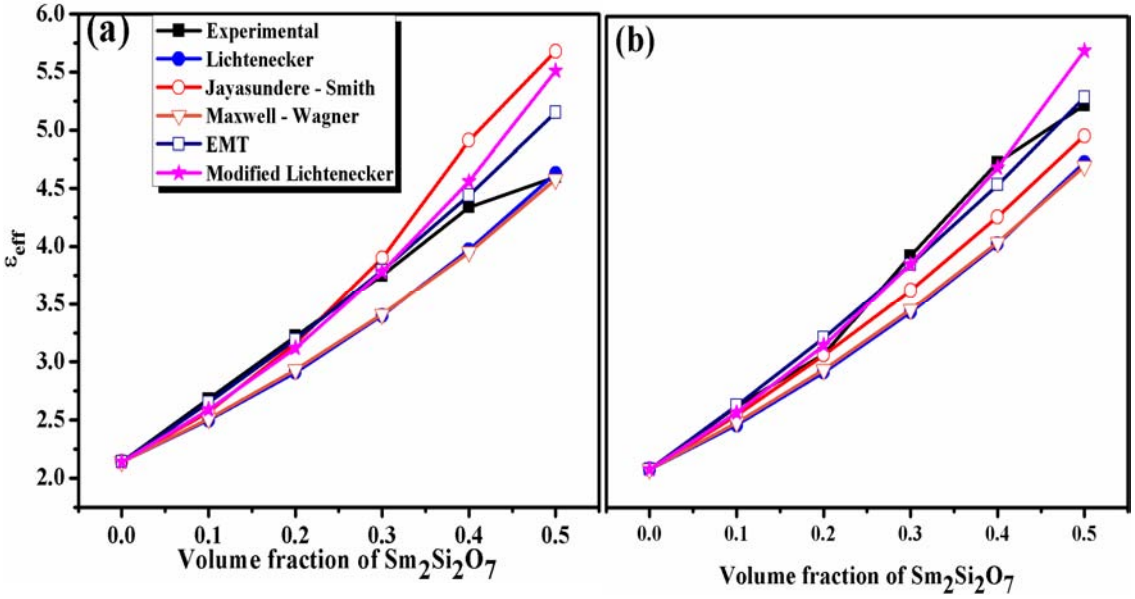

Fig. 5.20 Comparison of experimental and theoretical relative permittivity of (a) polystyrene-$Sm_2Si_2O_7$ and (b) polyethylene-$Sm_2Si_2O_7$ composites at 9 GHz.

THE RELATIVE PERMITTIVITY OF COMPOSITES ALSO DEPENDS ON THE DISTRIBUT
FILLER, SHAPE AND SIZE OF FILLERS AND INTERFACE BETWEEN CERAMICS AND POLYMER
THE EXPERIMENTAL VALUES ARE COMPARED WITH THOSE PREDICTED USING EMT MO
PRESENT WORK WE FOUND THE 'A' VALUE OF 0.16 FOR BOTH PE-$Sm_2Si_2O_7$ AND 0.16 FOR PS-
$Sm_2Si_2O_7$ COMPOSITES WHICH IS IN AGREEMENT WITH THE EARLIER REPORTS [36]. IT IS C
THAT THE EMT MODEL HOLDS GOOD FOR PE-$Sm_2Si_2O_7$ COMPOSITES EVEN FOR A HIGHER FILLER
LOADING OF 0.5 V$_f$. HOWEVER, IN THE CASE OF PS-$Sm_2Si_2O_7$ COMPOSITES THE EMT MODEL IS
FOUND TO BE WELL MATCHED ONLY UP TO 0.4 V$_f$ FILLER LOADING. FOR A HIGHER FILLER CONTE
OF 0.5 V$_f$ THE MODEL DEVIATES CONSIDERABLY FROM THE EXPERIMENTAL VALUE. COM
FIGS. 5.20 (A) AND (B) SHOWS THAT THE PREDICTIONS ARE IN GOOD AGREEMENT W
EXPERIMENTAL RESULTS FOR PE-$Sm_2Si_2O_7$ COMPOSITES THAN FOR PS-$Sm_2Si_2O_7$ COMPOSITES. THIS
MAY BE DUE TO THE FACT THAT THE PE-$Sm_2Si_2O_7$ SHOWS A BETTER DENSIFICATION THAN THE PS-
$Sm_2Si_2O_7$ COMPOSITES AS EVIDENT FROM TABLE 5.6.

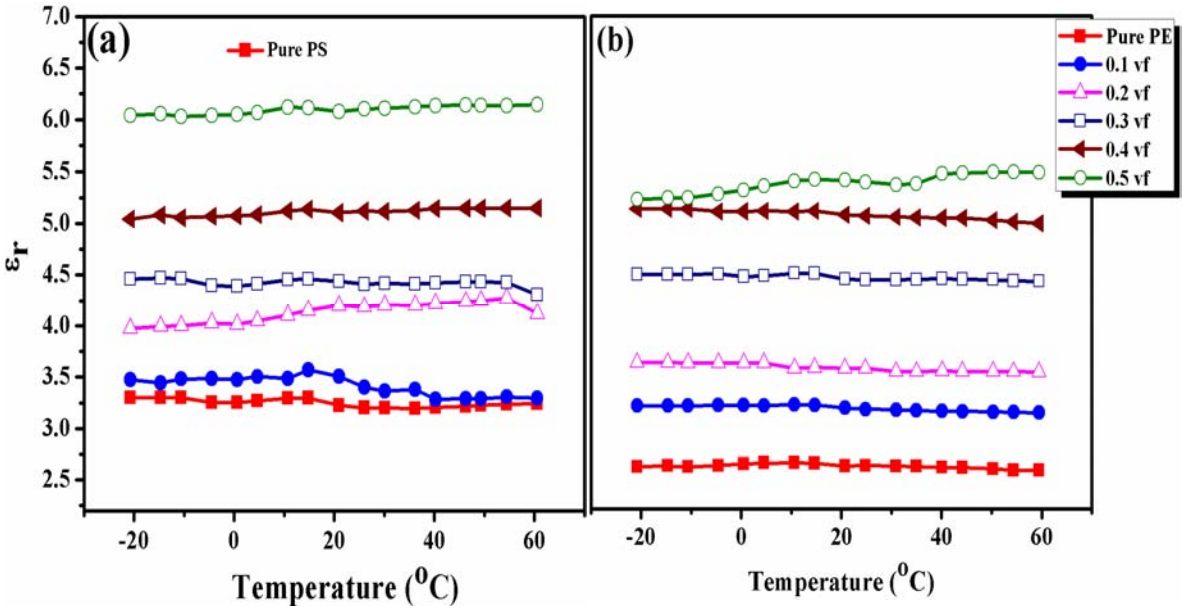

Fig. 5.21 The variation of relative permittivity with temperature for (a) polystyrene-$Sm_2Si_2O_7$ and (b) polyethylene-$Sm_2Si_2O_7$ composites.

FIGURES 5.21 (A) AND (B) RESPECTIVELY REPRESENT THE TEMPERATURE DEPENDENCE OF RELATIVE PERMITTIVITY OF PS-$SM_2SI_2O_7$ COMPOSITES AND PE-$SM_2SI_2O_7$ COMPOSITES MEASURED AT 1 MHZ. IT IS CLEAR FROM THE FIGURES THAT PS-$SM_2SI_2O_7$ COMPOSITES SHOW NEARLY A STEADY VARIATION IN RELATIVE PERMITTIVITY WITH TEMPERATURE SHOWING A POSITIVE VARIATION OF 1.5 % FOR 0.5 V_F OF FILLER LOADING. ON THE OTHER HAND FOR PE-$SM_2SI_2O_7$ COMPOSITES, THE VARIATION IS MUCH MORE PRONOUNCED. IT CAN BE OBSERVED THAT THESE COMPOSITES SHOW DECREASE IN RELATIVE PERMITTIVITY WITH INCREASE IN TEMPERATURE FOR LOWER FILLER LOADINGS (UP TO 0.4 V_F). HOWEVER, FOR HIGHER FILLER LOADINGS (0.5 V_F) AN INCREASE IN RELATIVE PERMITTIVITY IS OBSERVED WITH TEMPERATURE. THE DEVIATION IS FOUND TO BE AS HIGH AS 5 %. AT HIGH TEMPERATURE AND FOR HIGH FILLER CONTENT, THE SEGMENTAL MOBILITY FACTOR INCREASES CAUSING AN INCREASE IN RELATIVE PERMITTIVITY. THUS FROM THE FIGURES IT CAN BE CONCLUDED THAT PS-$SM_2SI_2O_7$ COMPOSITES EXHIBIT BETTER TEMPERATURE STABILITY OF RELATIVE PERMITTIVITY COMPARED TO THAT OF PE-$SM_2SI_2O_7$ COMPOSITES.

FIGURE 5.22 SHOWS THE VARIATION OF COEFFICIENT OF THERMAL EXPANSION (CTE) OF PE-$SM_2SI_2O_7$ COMPOSITES AS A FUNCTION OF FILLER CONTENT. THE CTE OF POLYETHYLENE AND POLYSTYRENE ARE 250 PPM/^{0}C AND 100 PPM/^{0}C RESPECTIVELY. THE COEFFICIENT OF THERMAL EXPANSION OF

THE COMPOSITES DECREASES WITH THE INCREASE IN CERAMIC LOADING. THIS IS DUE
CTE OF $Sm_2Si_2O_7$ WHICH WILL CONSTRAINT THE EXPANSION OF THE MATRIX. ALSO COM
WITH STRONG INTERFACE EXHIBIT AN ADDITIONAL REDUCTION IN CTE [75]. IT IS NOTED T
OF PE-$Sm_2Si_2O_7$ COMPOSITES DECREASES DRASTICALLY FROM 250 TO 60 PPM/^oC IS A
GRADUAL REDUCTION FOR PS-$Sm_2Si_2O_7$ COMPOSITES FROM 100 PPM/^oC TO 36 PPM/^oC. THE
EXPERIMENTAL RESULTS WERE COMPARED WITH THE THEORETICAL PREDICTION USING
GIVEN IN EQ. (5.6).

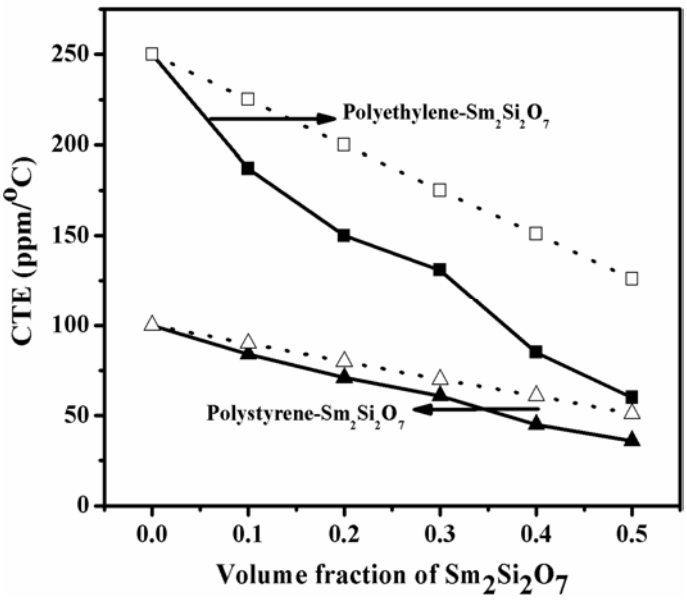

Fig. 5.22 Variation of the coefficient of thermal expansion of polystyrene-$Sm_2Si_2O_7$ and polyethylene-$Sm_2Si_2O_7$ composites and comparison using rule of mixtures.

THE DOTTED LINE REPRESENTS THE CTE VALUES CALCULATED USING THE RULE OF
IS OBSERVED THAT THE PREDICTION SHOWS A GOOD AGREEMENT WITH THE OBSERVED V
$Sm_2Si_2O_7$ COMPOSITES WHILE IT SHOWS A WIDE DEVIATION FOR PE-$Sm_2Si_2O_7$ COMPOSITES. IT IS
ALSO CLEAR FROM THE FIGURE THAT THE CALCULATED CTES ARE HIGHER THAN THE
RESULTS. THIS MAY BE DUE TO THE DIFFERENCES IN THE MICROSTRUCTURE, BULK M
THERMAL SOFTENING OF THE COMPONENTS WHICH ARE NOT TAKEN INTO ACCOUNT I
MODEL.

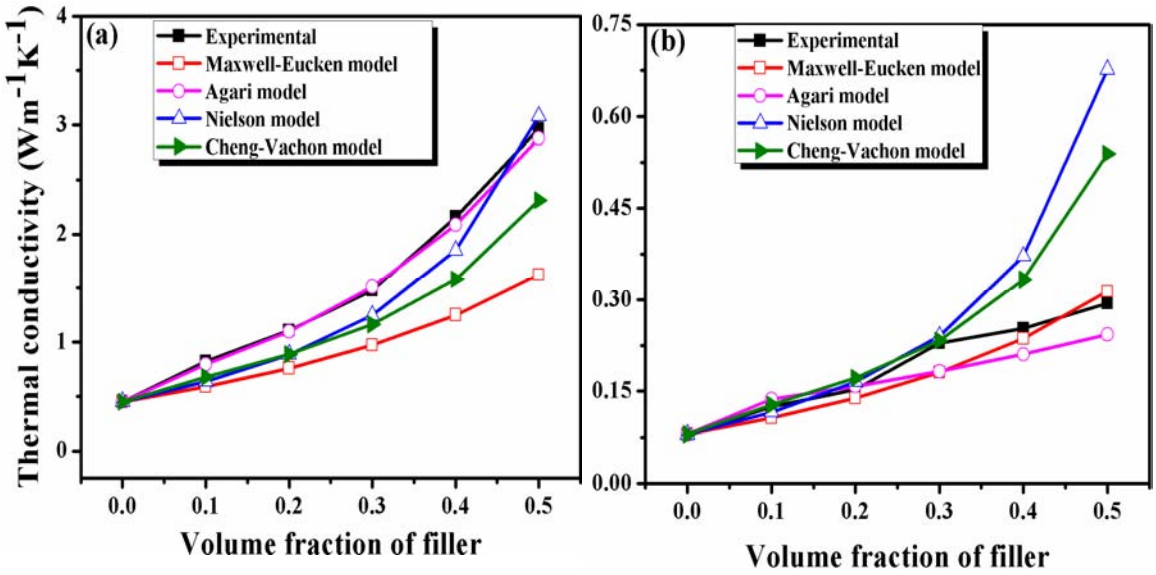

Fig. 5.23 Variation of the thermal conductivity of (a) polyethylene-$Sm_2Si_2O_7$ and (b) polystyrene-$Sm_2Si_2O_7$ composites with the filler content.

FIGURE 5.23 SHOWS THE VARIATION OF THERMAL CONDUCTIVITY OF PE-SM$_2$SI$_2$O$_7$ AND PS-SM$_2$SI$_2$O$_7$ COMPOSITES WITH THE VOLUME FRACTION OF THE FILLER. THE THERMAL CONDUCTIVITY OF BOTH THE POLYMER COMPOSITES INCREASE WITH THE FILLER CONTENT. THE PE-SM$_2$SI$_2$O$_7$ COMPOSITES SHOW A HIGH RATE OF INCREASE IN THERMAL CONDUCTIVITY THAN THE PS-SM$_2$SI$_2$O$_7$ COMPOSITES WHICH IS DUE TO THE RELATIVELY HIGH THERMAL CONDUCTIVITY OF POLYETHYLENE (0.38 WM^{-1}K^{-1}) COMPARED TO THAT OF POLYSTYRENE (0.08 WM^{-1}K^{-1}). IN THE CASE OF PE-SM$_2$SI$_2$O$_7$ COMPOSITES A SUDDEN INCREASE IN THERMAL CONDUCTIVITY IS NOTED BEYOND 0.3 V$_f$ WHICH IS DUE TO THE FACT THAT AT HIGHER FILLER CONTENT THE CERAMIC PARTICLES GET CONNECTED TO FORM CONDUCTIVE PATHS IN THE COMPOSITES. FROM SEM IMAGES IT IS CLEAR THAT THE POLYMER MATRIX (PE AND PS) ARE ESSENTIALLY SURROUNDED BY THE FILLER PARTICLES. THE MOST PROBABLE WAY IS THAT SM$_2$SI$_2$O$_7$ PARTICLES CAN TOUCH EACH OTHER AND FORM THERMALLY CONDUCTIVE PATHS IN THE COMPOSITES. FOR A FILLER CONTENT OF 0.5 V$_f$, THE THERMAL CONDUCTIVITY OF PE-SM$_2$SI$_2$O$_7$ COMPOSITES BECOMES NEARLY 7 TIMES THAT OF PURE POLYETHYLENE, WHEREAS 2.97 WM^{-1}K^{-1} THAT OF PS-SM$_2$SI$_2$O$_7$ COMPOSITES OF SAME VOLUME FRACTION IS ONLY ABOUT 1.94 WM^{-1}K^{-1}. AGARI AND CO-WORKERS [77] PROVED THAT THE THERMAL CONDUCTIVITY OF THE COMPOSITES IS DEPENDENT ON THE PROCESSING METHOD ADOPTED. THEY FOUND THAT FOR A GIVEN VOLUME FRACTION OF FILLER, THE THERMAL CONDUCTIVITY OF COMPOSITES OBTAINED FROM

DISPERSION METHOD IS HIGHER THAN THAT OBTAINED BY MELT MIXING TECHNIQUE. FI
COMPARES THE EXPERIMENTAL VALUES WITH VARIOUS THEORETICAL PREDICTIONS OBT
(5.7) – (5.11). THE AGARI EQUATION IS FOUND TO BE IN GOOD AGREEMENT WITH THE EXPE
VALUES IN THE CASE OF PE/$SM_2SI_2O_7$ COMPOSITES WHILE IT SHOWS CONSIDERABLE DEVIATION I
PS/$SM_2SI_2O_7$. THIS MAY BE DUE TO THE BETTER DENSIFICATION ACHIEVED BY THE PE/$SM_2SI_2O_7$
COMPOSITES (SEE TABLE 5.6) THEREBY REDUCING THE POROSITY WHICH IMPROVES TH
CONDUCTIVITY. FIG. 5.23 (B) SHOWS THAT FOR PS/$SM_2SI_2O_7$ COMPOSITES, ALL THE PREDICTIONS
HOLD GOOD FOR LOWER CONCENTRATION OF FILLER (v_f). AS THE FILLER CONTENT INCREASES
THE EXPERIMENTAL VALUES SHOW CONSIDERABLE DEVIATION FROM THE THEORETICAL

Table 5.7 The Vickers hardness and water absorption of polyethylene-$Sm_2Si_2O_7$ and polystyrene-$Sm_2Si_2O_7$ polymer ceramic composites.

Composite	Volume fraction of filler (v_f)	Vicker's microhardness (kg/mm^2)	Water absorption (%)
PE-$SM_2SI_2O_7$	0.0	10	0.03
	0.1	10	0.20
	0.3	14	0.25
	0.5	17	0.30
PS-$SM_2SI_2O_7$	0.0	21	0.14
	0.1	28	0.27
	0.3	33	0.30
	0.5	56	0.41

TABLE 5.7 GIVES VICKER'S MICROHARDNESS AND WATER ABSORPTION OF PE-SM
PS-$SM_2SI_2O_7$ COMPOSITES WITH FILLER VARIATION. THE VICKER'S HARDNESS OF
POLYETHYLENE AND POLYSTYRENE ARE FOUND TO BE 10 KG/MM^2 AND 21 KG/MM^2 RESPECTIVELY.
THE MICRO HARDNESS OF THE COMPOSITES IS FOUND TO INCREASE WITH THE FILLER
MAXIMUM OF 56 KGF/MM^2 IS OBSERVED FOR PS-$SM_2SI_2O_7$ AT V_F = 0.5 WHEREAS A MUCH LOWER
VALUE OF 17 KGF/MM^2 IS OBTAINED FOR PE-$SM_2SI_2O_7$ FOR THE SAME VOLUME FRACTION OF
CERAMIC. IT IS EVIDENT FROM THE TABLE THAT AS THE FILLER CONTENT INCREAS

ABSORPTION OF BOTH THE COMPOSITES INCREASES WITH $SM_2SI_2O_7$ CONTENT. PE-SM
WATER ABSORPTION THAN THE PS-$SM_2SI_2O_7$ COMPOSITES. THIS IS DUE TO THE HIGHER POROSITY OF
THE PS-$SM_2SI_2O_7$ COMPOSITES COMPARED TO THAT OF PE-$SM_2SI_2O_7$ COMPOSITES (TABLE 5.6).
HOWEVER, THE WATER ABSORPTION IS FOUND TO BE LOW FOR PE-$SM_2SI_2O_7$ AND
PS-$SM_2SI_2O_7$ COMPOSITES EVEN FOR A HIGHER FILLER CONTENT OF 0.5 V

5.5 CONCLUSIONS

- THE EFFECT OF $SM_2SI_2O_7$ FILLER ON THE DIELECTRIC AND THERMO-MECHANICAL PROP
  OF VARIOUS POLYMERS SUCH AS PTFE, POLYETHYLENE AND POLYSTYRENE ARE IN
  THE INFLUENCE OF COUPLING AGENT AND FILLER PARTICLE SIZE ON THE PERF
  PTFE/$SM_2SI_2O_7$ IS ALSO STUDIED IN DETAIL. THE PTFE/$SM_2SI_2O_7$ COMPOSITES ARE
  PREPARED BY POWDER PROCESSING TECHNIQUE AND PE/$SM_2SI_2O_7$ AND PS/$SM_2SI_2O_7$
  COMPOSITES BY THE MELT MIXING METHOD.
- THE MICROSTRUCTURE OF THE COMPOSITES SHOWS A UNIFORM DISPERSION FOR L
  CONCENTRATION AND AS THE FILLER CONTENT INCREASES A SMALL AMOUNT OF
  IS NOTICED. IT IS FOUND THAT ADDITION OF SILANE TREATED FILLER REDUCED
  AGGLOMERATION RESULTING IN GOOD HOMOGENEITY IN THE CASE OF PTFE/$SM_2SI_2O_7$
  COMPOSITES.
- THE DIELECTRIC PROPERTIES OF THE COMPOSITES ARE MEASURED AT 1 MHZ AN
  MICROWAVE FREQUENCY RANGE. IT IS SEEN THAT THE RELATIVE PERMITTIVITY A
  LOSS OF THE COMPOSITES INCREASES WITH INCREASE IN THE FILLER CONTENT. F
  FILLER CONTENT OF 0.5 V, MICROWAVE DIELECTRIC PROPERTIES OF THE COMPOSITES
  PTFE COMPOSITE, ε_r = 3.82 AND $\tan\delta$ = 0.0136, PE COMPOSITE, ε_r = 5.28 AND $\tan\delta$
  = 0.0091 AND PS, ε_r = 4.60 AND $\tan\delta$ = 0.0110. HOWEVER, THE SILANE TREATED AND
  NANO PTFE/$SM_2SI_2O_7$ COMPOSITES SHOWED A HIGHER VALUE OF RELATIVE PERMITT
  AND DIELECTRIC LOSS WHEN COMPARED WITH THE UNTREATED ONE.
- IT IS ALSO OBSERVED THAT THE THERMAL CONDUCTIVITY AND VICKER'S MICRO
  THE COMPOSITES IMPROVED WITH FILLER CONTENT WHEREAS THE THERMAL EXP
  DECREASED WHICH IS REQUIRED. ALSO THE ADDITION OF COUPLING AGENT TO
  IMPROVED THE THERMO-MECHANICAL PROPERTIES OF PTFE/$SM_2SI_2O_7$ COMPOSITES. THE

NANO-COMPOSITES EXHIBITED A MUCH LOWER CTE VALUE WHEN COMPARED V
MICRON COUNTERPART WHEREAS THEY SHOWED A HIGH WATER ABSORPTION VAL

- VARIOUS THEORETICAL PREDICTIONS ARE EMPLOYED TO FIT THE EXPERIMENTA
  RELATIVE PERMITTIVITY, THERMAL CONDUCTIVITY AND THERMAL EXPAN
  EXPERIMENTAL AND THEORETICAL VALUES ARE FOUND TO BE IN GOOD AGREEME
  FILLER CONTENT. THE RESULTS SUGGEST THAT SiO_2 FILLED PI POLYMER COMPOSITES ARE
  GOOD CANDIDATES FOR ELECTRONIC PACKAGING APPLICATIONS.

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CHAPTER 6

ALUMINATE BASED COMPOSITES FOR LTCC AND ELECTRONIC PACKAGING APPLICATIONS

This chapter is divided into two sections. The first section describes the synthesis and properties of aluminate based ceramic glass composites for LTCC substrate applications. The ceramic used for the study is 0.83 $ZnAl_2O_4$ - 0.17 TiO_2 (ZAT) with excellent microwave dielectric properties. The effect of various low melting and low loss glasses on the densification, microstructure and microwave dielectric properties of ZAT is discussed in detail. The second section gives a comparative study of PTFE/ZAT and PE/ZAT composites for electronic packaging applications. The dielectric properties of the composites are measured at low and microwave frequencies and the effective relative permittivity obtained are compared with the theoretical predictions.

6.1 SYNTHESIS AND CHARACTERIZATION OF 0.83 $ZNAl_2O_4$-0.17 TIO_2/GLASS COMPOSITES FOR LTCC APPLICATIONS

6.1.1 INTRODUCTION

DEVELOPMENT OF VERY LARGE-SCALE INTEGRATION (VLSI) CONTINUOUSLY DEM CERAMIC MANUFACTURERS PROVIDE SUBSTRATE MATERIALS WITH HIGH SIGNAL TRAN HIGH WIRING DENSITY, HIGH RELIABILITY AND LOW COST [1-2]. TO MAKE A PACKAGE E FASTER, LOW RELATIVE PERMITTIVITY CERAMICS CO-FIRABLE WITH HIGHLY CONDUCTIV AG, PD AND AU ARE DESIRABLE. LOW TEMPERATURE CO-FIRED CERAMIC (LTCC) MU SUBSTRATES HAVE RECENTLY BEEN PROPOSED FOR APPLICATIONS IN THE WIRELESS FIE LOW DIELECTRIC LOSS AND RAPID SIGNAL PROPAGATION AT HIGH FREQUENCIES [3]. DESCRIPTION ON THE LTCC TECHNOLOGY, ITS ADVANTAGES, MATERIAL REQUIRE APPLICATIONS ARE GIVEN IN CHAPTER 1 SECTION 1.8. GENERALLY SPEAKING, ADDITI SOFTENING TEMPERATURE GLASS IS AN EFFECTIVE AND CHEAP APPROACH TO LOWER TH TEMPERATURE OF CERAMICS [4]. HOWEVER, IN MANY CASES, THEY MAY INDUCE A SI DEGRADATION OF DIELECTRIC PROPERTIES BECAUSE OF THE LARGE AMOUNT OF ADD REQUIRE A COMPLICATED PROCESSING. TO WEAKEN THE DESTRUCTIVE EFFECT OF THE G ON THE INTRINSIC MICROWAVE PROPERTIES OF THE CERAMICS, RESEARCHERS HAVE TO F FLUX WHICH COULD DECREASE THE SINTERING TEMPERATURE GREATLY WITH SMA ADDITIVES WITHOUT INFLUENCING THE MICROWAVE DIELECTRIC PROPERTIES OF THE CONSIDERABLY. FOR LTCC, IN ADDITION TO THE LOW SINTERING TEMPERATURE, APPROP PERMITTIVITY, HIGH QUALITY FACTOR AND A NEAR ZERO TEMPERATURE COEFFICIEN FREQUENCY ARE ALSO CRITICAL REQUIREMENTS FOR COMMERCIAL APPLICATIONS. THU THE NEW MATERIALS WITH INTRINSIC LOW SINTERING TEMPERATURES AND GOOD DIELECTRIC PROPERTIES IS STILL IN RAPID PROGRESS.

A NUMBER OF MATERIAL-RESEARCH LABORATORIES HAVE FOCUSED THEIR AT REDUCING THE SINTERING TEMPERATURES OF FUNCTIONAL MATERIALS. ALTHOUGH *et al.* [5] REPORTED THE MICROWAVE DIELECTRIC PROPERTIES OF LOW TEMPERATURE SINTERE QUALITY FACTOR OF THE CERAMIC WAS TOO LOW TO USE IN THE MICROWAVE APPLIC FREQUENCY. SEVERAL MICROWAVE DIELECTRIC COMPOSITIONS INCLUDING (ZR,SN)TIO_4 [6], $BAMG_{1/3}TA_{2/3}O_3$ [6], $BAZN_{1/3}TA_{2/3}O_3$ BAO-TIO_2-WO_3 [7], $CA[(LI_{1/3}NB_{2/3})_{1-X}TI_X]O_{3-\delta}$ [8], CEO_2 [9] AND BAO-RE_2O_3-TIO_2 [10] SYSTEMS HAVE BEEN STUDIED FOR THE DEVELOPMENT O

THE MIDDLE-K LTCC BY USING GLASS FRITS. MANY LOW LOSS GLASSES AND LOW MELT
HAVE BEEN SUGGESTED AS SINTERING AIDS FOR SEVERAL MATERIALS TO BE USED
APPLICATIONS. *ZHOU* [11] PROPOSED $0.83ZnO-0.17V_2O_5$ AS AN EFFECTIVE ADDITIVE TO
LOWER THE SINTERING TEMPERATURE OF $ZnO-Nb_2O_5-TiO_2$ (LNT) CERAMICS, BUT THE
INTERACTION BETWEEN V AND AG LIMITED IT FOR LTCC APPLICATIONS. LATER THE SA
SUGGESTED B_2O_3 AND CUO AS SUITABLE SINTERING AIDS FOR LNT. THESE WERE ALSO FOUND
EFFECTIVE IN REDUCING THE SINTERING TEMPERATURES OF $BaTi_4O_9$, $Ba(Zn_{1/3}Ta_{2/3})O_3$
AND $Ba(Zn_{1/3}Nb_{2/3})O_3$ CERAMICS TO BELOW 900°C [12]. $ZnO-B_2O_3-SiO_2$ [13] AND $ZnO-B_2O_3-Bi_2O_3$
[14] BASED GLASS HAVE BEEN REPORTED TO BE EFFECTIVE LOW TEMPERATURE PROMO
TITANATE CERAMICS. EARLIER REPORTS BY *CHOU ET AL* [15] SHOWS THAT $ZnO-La_2O_3$ (BZL)
GLASS WHICH IS USED AS OPTICAL GLASS CAN SERVE AS A SINTERING AID FOR $BaTi_4O_9$ CERAMICS FOR
LTCC APPLICATION. *KIM ET AL.* [16-17] USED B_2O_3 TO LOWER THE SINTERING TEMPERATURE OF
$Ba_5Nb_4O_{15}$ AND DECREASED THE τ_f VALUE THROUGH THE FORMATION OF COMPOSITE CERAMICS
$Ba_5Nb_4O_{15}$ AND $Ba_2Ti_9O_{20}$.

6.1.1.1 SPINELS

OXIDE SPINELS COMPRISE A VERY LARGE GROUP OF STRUCTURALLY RELATED
MANY OF WHICH ARE OF CONSIDERABLE TECHNOLOGICAL OR GEOLOGICAL SIGNIFICANC
EXHIBIT A WIDE RANGE OF ELECTRONIC AND MAGNETIC PROPERTIES [19], IN
SUPERCONDUCTIVITY IN $Li_2Ti_3O_4$. THE IRON CONTAINING AND ZINC CONTAINING SPINELS ARE OF C
IMPORTANCE PRIMARILY DUE TO THEIR MAGNETIC AND INSULATING PROPERTIES, I
AMONG THE VARIOUS SPINEL OXIDES INVESTIGATED, THE MAGNESIUM AND ZINC DIA
OXIDES HOLDS GREAT IMPORTANCE AS IT HAS ATTRACTED A GREAT DEAL OF ATTENTION AS
TECHNOLOGICALLY IMPORTANT ADVANCED CERAMIC MATERIAL OWING TO ITS HIGH
(2135°C), HIGH MECHANICAL STRENGTH AT ELEVATED TEMPERATURE, LOW ELECTRICA
CHEMICAL INERTNESS AND THERMAL SHOCK RESISTANCE. BECAUSE OF THESE PROPE
APPLICATIONS RANGING FROM TRADITIONAL REFRACTORIES TO SOME ADVANCED USA
AND HUMIDITY SENSORS, ARMOUR MATERIALS, EXCELLENT TRANSPARENT MATERIAL F
ENVELOPES AND ALKALI-METAL VAPOUR DISCHARGE DEVICES. VARIOUS METHODS HAVE REPORTED THE
PREPARATION OF SPINEL BY DIFFERENT CHEMICAL ROUTES LIKE SOL-GEL [20], SPRAY PY
CO-PRECIPITATION, PRECIPITATION FROM ORGANOMETALLIC PRECURSORS, AUTO-IG

MICROWAVE-ASSISTED SYNTHESIS [23] ETC. THESE SPINEL OXIDES ARE WIDE GAP SEMIC
WITH NUMEROUS OPTICAL, GEOPHYSICAL AND MAGNETIC APPLICATIONS. IT IS ALSO FOU
MATERIALS ARE HIGHLY RESISTANT AT ELEVATED TEMPERATURE AND HIGHLY
WAVELENGTHS IN UV REGION, WHICH MAKE THEM CANDIDATE MATERIALS FOR REFLE
COATINGS IN AEROSPACE APPLICATIONS.

THE CRYSTAL STRUCTURE OF SPINEL WAS DETERMINED INDEPENDENTLY BY
NISHIKAWA [24-25]. THEY BELONG TO THE FACE CENTERED CUBIC SYMMETRY WITH SPA
F*d*3M. THE CUBIC CELL CONSISTS OF A CLOSE - PACKED ARRAY OF 32 OXYGEN ATOMS WI
IN THE TETRAHEDRAL AND OCTAHEDRAL SITES. IN THE NORMAL SPINEL STRUCTURE, TH
OCCUPY THE TETRAHEDRAL SITES AND THE TRIVALENT CATIONS OCCUPY THE OCTAHE
TYPICAL SPINEL STRUCTURE IS AS SHOWN IN FIG. 6.1.

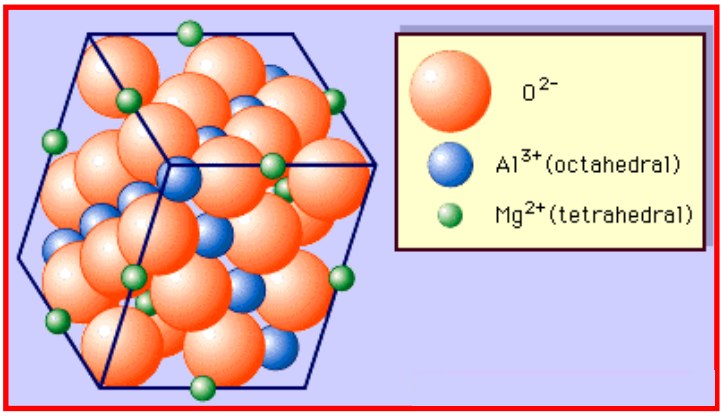

Fig. 6.1 The crystal structure of $MgAl_2O_4$ spinel. (www.britannica.com)

EARLIER INVESTIGATIONS REVEALED THAT ZNAL$_2$O$_4$ [27] AND MGAL$_2$O$_4$ [28] ARE POSSIBLE CANDIDATES FOR PACKAGING APPLICATIONS DUE TO THE LOW RELATIVE PERMITTIVITY (ε_r) VALUE. HOWEVER, THE HIGH NEGATIVE (-79 PPM/°C) τ_f VALUE OF ZNAL$_2$O$_4$ PRECLUDES ITS USE IN PRACTICAL APPLICATIONS. MANY RESEARCHERS HAVE TRIED TO TUNE THE τ_f VALUE OF ZNAL$_2$O$_4$ CERAMICS [29-31]. RECENTLY SUREN *et al.* [27] STUDIED THE EFFECT OF TIO$_2$ ON THE DIELECTRIC PROPERTIES OF ZNAL$_2$O$_4$ AND TUNED THE τ_f TO A NEARLY ZERO VALUE. THEY PROPOSED ZN(AL$_{1-X}$TI$_X$)$_2$O$_4$ [X = 0.17] (NAMED AS ZAT HEREAFTER) AS AN IDEAL COMPOSITION FOR SUBSTRATE APP HOWEVER THE SINTERING TEMPERATURE OF ZAT WAS ABOVE 1400 °C AND HAS TO BE REDUCED FOR LTCC APPLICATIONS. IN THE PRESENT SECTION ATTEMPTS HAVE BEEN MADE TO

SINTERING TEMPERATURE OF 0.83 $ZnAl_2O_4$-0.17 TiO_2 (ZAT) CERAMICS THROUGH SUITABLE GLASS ADDITION FOR LTCC APPLICATIONS.

6.1.2 EXPERIMENTAL

THE 0.83 $ZnAl_2O_4$-0.17 TiO_2 (ZAT) CERAMICS WERE PREPARED BY THE CONVENTIONAL SOLID STATE CERAMIC ROUTE. HIGH PURITY ZNO [ALDRICH CHEMICAL COMPANY, 99.9 Al_2O_3 [ALCOA A16SG] WERE TAKEN AS STARTING MATERIALS FOR THE SYNTHESIS OF $ZnAl_2O_4$. THE VARIOUS STEPS INVOLVED IN THE SYNTHESIS ARE EXPLAINED IN CHAPTER 2 SECTION 2.1. $ZnAl_2O_4$ WAS CALCINED AT 1400 °C FOR 4H. IT WAS THEN BALL MILLED WITH ACETONE AND MIXED INTO THE COMPOSITION (0.83 $ZnAl_2O_4$-0.17 TiO_2) FOR 24H. THE SLURRY WAS DRIED AND GROUND WELL. 4 WT% PVA WAS ADDED AS BINDER, MIXED AND AGAIN GROUND INTO FINE POWDER AND I FORM CYLINDRICAL DISKS OF 20 MM DIAMETER AND 10 MM THICKNESS UNDER A UNIAXI OF ABOUT 100 - 150 MPA. THIN PELLETS OF THE ZAT WITH DIAMETER 14 MM AND THICKN MM WERE MADE FOR LOW FREQUENCY MEASUREMENTS. THE GLASSES USED IN TH INVESTIGATION ARE ZB1, ZB2, ZBS, BBSZ, BBS, AS, BB, MBS AND ABS. DIFFERENT WEIGHT PERCENTAGES OF THESE GLASSES WERE ADDED TO THE PURE ZAT. THE PELLETS WERE DESCRIBED ABOVE. THE PURE SAMPLE WAS SINTERED AT 1450 °C FOR 4H. GLASS ADDED SAMPLES WERE SINTERED AT DIFFERENT TEMPERATURE RANGING FROM 850 °C TO 950 °C FOR 4H. THE SINTERED SAMPLES WERE WELL POLISHED AND THEIR BULK DENSITIES WERE CALCULATED BY METHOD. STRUCTURAL, MICROSTRUCTURAL AND MICROWAVE CHARACTERIZATIONS WERE PERFORMED AS EXPLAINED IN CHAPTER 2.

6.1.3 RESULTS AND DISCUSSION

THE EFFECT OF NINE DIFFERENT GLASSES (ZB1, ZB2, ZBS, BBSZ, BBS, ABS, MBS, AS AND BB) ON THE SINTERING TEMPERATURE, DENSIFICATION AND MICROWAVE PROPERTIES OF ZAT IS STUDIED. THE PHYSICAL AND ELECTRICAL PROPERTIES OF THE VA USED ARE GIVEN IN TABLE 1.3 IN CHAPTER 2. INITIALLY, A SMALL WEIGHT PERCENTAGE (THESE GLASSES ARE ADDED TO THE PARENT MATERIAL. TABLE 6.1 GIVES THE OPTIMIZ TEMPERATURE AND MICROWAVE DIELECTRIC PROPERTIES OF 0.1 WT% GLASS AD COMPOSITES. THE SINTERING TEMPERATURE OF THESE COMPOSITES IS OPTIMIZED FO DENSITY AND MICROWAVE DIELECTRIC PROPERTIES. IT IS TO BE NOTED THAT THE ADDIT

OF VARIOUS GLASSES REDUCED THE SINTERING TEMPERATURE CONSIDERABLY. THE PU
SINTERING TEMPERATURE OF 1450 °C. IT IS KNOWN [32] THAT BORON BASED GLASSES ARE MOR
EFFECTIVE IN LOWERING THE SINTERING TEMPERATURE DUE TO THE LOW SOFTENIN
(450 °C) OF B_2O_3. FROM THE TABLE IT IS CLEAR THAT ZINC BORATE BASED GLASSES AR
EFFECTIVE IN REDUCING THE SINTERING TEMPERATURE WITHOUT AFFECTING THE DI
MICROWAVE DIELECTRIC PROPERTIES. THE ZB2, BBSZ AND BBS GLASS LOWERED THE S
TEMPERATURE TO 1400 °C WHERE AS ZB1 AND ZBS ARE FOUND TO BE MUCH MORE EFFECTIVE SI
THE SINTERING TEMPERATURES ARE REDUCED TO 1350 °C RESPECTIVELY. WITH THIS VIEW
WE HAVE CONSIDERED ONLY FIVE GLASSES (ZB1, ZB2, ZBS, BBSZ AND BBS) FOR FURT
STUDIES.

Table 6.1 The optimized sintering temperature and microwave dielectric properties of 0.1 wt% glass added ZAT ceramics.

Glass added	Sintering temp: (°C/h)	Microwave Properties				Loss at 1MHz
		Relative Density (%)	$Q_u \times f$ (GHz)	τ_f (ppm/°C)	ε_R	
PURE ZAT	1450/4	97.0	91000	1.4	11.7	0.0010
ZB1	1375/4	97.4	71000	-4.0	11.9	0.0007
ZB2	1400/4	98.3	73200	2.6	11.9	0.0004
ZBS	1350/4	97.8	70100	2.3	11.9	0.0016
BBSZ	1400/4	97.6	92500	-3.7	11.8	0.0019
BBS	1400/4	97.3	103000	-0.7	11.8	0.0029
AS	1425/4	97.1	65000	3.0	11.7	0.0025
BB	1400/4	97.0	66300	1.8	11.8	0.0033
MBS	1400/4	97.3	68500	-6.3	11.8	0.0046
ABS	1400/4	97.1	55400	2.3	11.6	0.0050

6.1.3.1 PHASE ANALYSIS

FIGURE 6.2 (A) SHOWS THE XRD PATTERNS OF PURE ZAT. THE POWDER DIFFRAC
PATTERNS OF $ZnAl_2O_4$ AND TiO_2 ARE INDEXED BASED ON JCPDS FILE CARD NUMBERS 5-669 AND
21-1276 RESPECTIVELY. THE XRD PATTERN OF ZAT SHOWS THAT TiO_2 AND ZnAl
SOLUTION WITH TiO_2 AS REPORTED EARLIER [31]. FIGS. 6.2 (B), (C), (D) AND (E) SHOW THE XRD
PATTERNS OF ZAT SINTERED WITH DIFFERENT WEIGHT PERCENTAGES OF BBSZ GLASS. M
ON THE CERAMIC GLASS COMPOSITES [33-34] REPORT THE FORMATION OF LOSSY SECON
WHICH ADVERSELY AFFECT THE PHYSICAL AND MICROWAVE DIELECTRIC PROPERTI
PRESENCE OF SECONDARY PHASES IN THE LTCC COMPOSITE SIGNIFICANTLY INCRE
POSSIBILITY OF A CHEMICAL REACTION WITH THE METAL ELECTRODE WHICH IN TURN AF
PERFORMANCE. IN THE PRESENT CASE NO ADDITIONAL PEAKS ARE OBSERVED FOR ZAT
10, 12, 15 WT% OF BBSZ. THIS MAY BE DUE TO THE FACT THAT THE BBSZ DID NOT REACT
THE PARENT MATERIAL TO FORM ADDITIONAL PHASES THEREBY REMAINING AS GL
RETAINING ITS AMORPHOUS NATURE. THIS IS A CLEAR EVIDENCE FOR THE CHEMICAL S
PARENT MATERIAL.

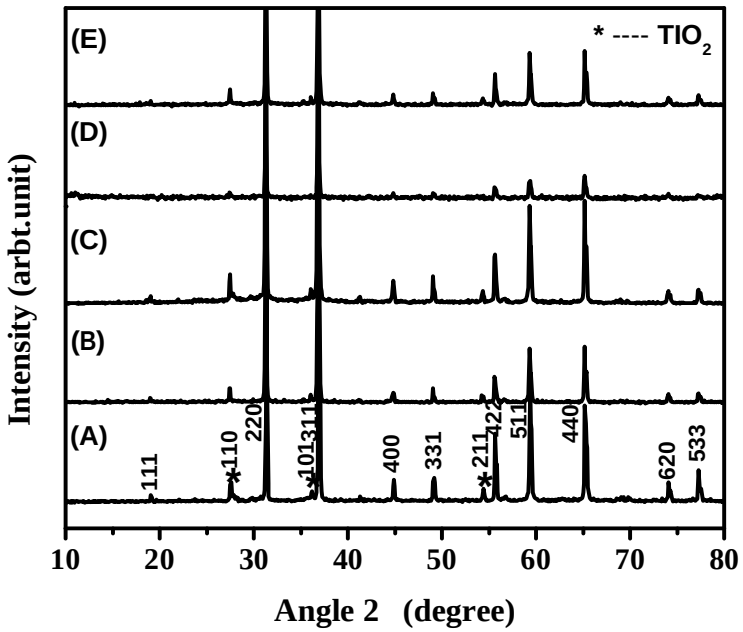

Fig. 6.2 The powder diffraction patterns of (a) $0.83ZnAl_2O_4$-$0.17TiO_2$ (ZAT) (b) ZAT + 10 wt% BBSZ (c) ZAT + 12 wt% BBSZ (d) ZAT + 15 wt% BBSZ (e) ZAT + 10 wt% BBSZ + 0.3 wt% LiF.

6.1.3.2 SINTERING AND DENSIFICATION

THE PURE ZAT HAS A SINTERING TEMPERATURE OF 1450 °C. IT IS A WELL ESTABLISHED FACT THAT ADDITION OF SMALL AMOUNT OF GLASS TO THE CERAMIC LOWERS THE PROCESSI WITH IMPROVED DENSIFICATION AND PROPERTIES. FIG. 6.3 SHOWS THE VARIATION OF SINTERING TEMPERATURE AS A FUNCTION OF DIFFERENT WEIGHT PERCENTAGE OF ZB1, ZB2, ZBS, BI BBS GLASS. THE SINTERING TEMPERATURE GRADUALLY DECREASES WITH INCREASE IN FROM 0.1 WT% - 3 WT% BUT THE RATE OF DECREASE VARIES WITH THE NATURE OF GLASS GLASSES ZB1 AND ZB2 SHOWS SIMILAR TREND. EVENTHOUGH A SUDDEN DECREASE IS NO WT% ADDITION OF THESE GLASSES, HIGHER GLASS CONTENT SHOWS ONLY A SLIGHT D SINTERING TEMPERATURE. ADDITION OF 3 WT% OF THESE GLASSES REDUCED THE TEMPERATURE TO 1325 °C.

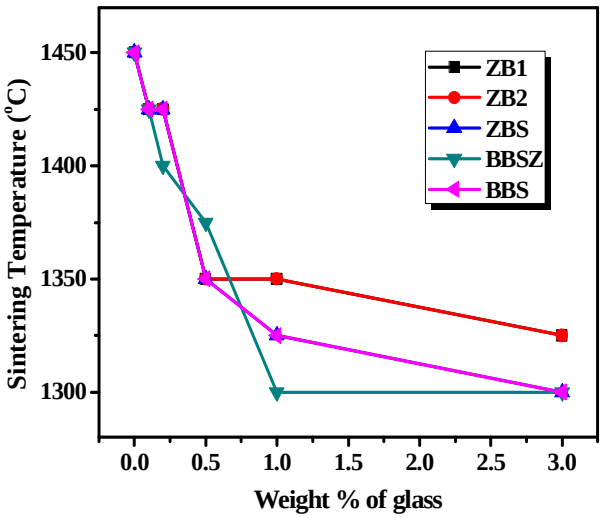

Fig. 6.3 The variation of sintering temperature with weight percentage of various glasses.

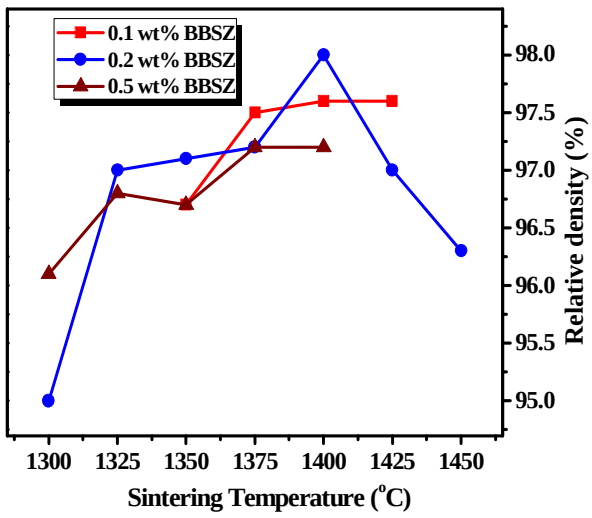

Fig. 6.4 The variation of relative density with sintering temperature with 0.1, 0.2 and 0.5 wt% of BBSZ glass addition to ZAT.

THE THEORETICAL DENSITY OF ZAT MEASURED USING THE MIXTURE RULE IS FO 4.58 G/CM^3. THE MEASURED DENSITY OF THE SAMPLE SINTERED AT 1450 °C IS 97 % OF THE THEORETICAL DENSITY. THE THEORETICAL DENSITY OF ZAT DOPED GLASS (ADDED ZAT IS CALCULATED USING THE EQ. (4.2) IN CHAPTER 4. TABLE 6.1 GIVES THE OPTIMIZED RELATIVE DENSITY OF ZAT WITH 0.1 WT% VARIOUS GLASSES. A SLIGHT IMPROVEMENT IN DENSITY IS NOTED FO

COMPOSITES WITH 0.1 WT% GLASS ADDITION. FIG. 6.4 SHOWS THE RELATIVE DENSITY
DOPED WITH 0.1, 0.2 AND 0.5 WT% BBSZ GLASS AS A FUNCTION OF SINTERING TEMPERATU
OBSERVED THAT THE RELATIVE DENSITY INCREASES WITH THE SINTERING TEMPERAT
MAXIMUM AND THEN DECREASES. LOW CONTACT ANGLE, LOW DIHEDRAL ANGLE AND H
OF THE SOLID IN THE LIQUID ARE ESSENTIAL FOR ACHIEVING HIGH SINTERED DENSITY
CERAMICS. IN SUCH CASES, THE TRANSIENT GLASSY PHASE FORMED AT A LOWER TEMPE
ACT AS A SHORT CIRCUIT MEDIUM FOR GRAIN TO GRAIN MATERIALS TRANSPORT [35]. T
THIS VARIATION IS EXPLAINED BY THE PRESENCE OF SECONDARY PHASES IN SEVERAL
SYSTEMS [9, 36]. HOWEVER, THE XRD AND SEM RESULTS CONFIRM THE ABSENCE OF
SECONDARY PHASES. THUS THE REASON FOR THE INITIAL INCREASE IN THE DENSITY
ELIMINATION OF PORES AS TEMPERATURE INCREASES. THE TEMPERATURE AT WHICH
DENSITY IS ACHIEVED DEPENDS ON THE GLASS CONTENT. THE LARGER THE AMOUNT OF G
THE LOWER THE SINTERING TEMPERATURE. WHEN THE GLASS ADDITION EXCEEDS 20
SINTERING IS INITIATED [7]. A MAXIMUM RELATIVE DENSITY OF NEARLY 98% IS REAC
SINTERING TEMPERATURE FOR 1400 °C 0.2 WT% BBSZ ADDITION WHICH IS HIGHER THAN THAT FO
0.1 WT% BBSZ. THIS TEMPERATURE MAY BE THE OPTIMUM FOR THE OCCURRENCE OF LIQU
SINTERING. FURTHER INCREASE IN THE SINTERING TEMPERATURE MAY FACILITATE THE
THE VOLATILE COMPONENTS FROM THE GLASS FRIT FROM GRAIN BOUNDARIES, CAUSI
WETTING RESULTING IN TRAPPED POROSITY ASSOCIATED WITH GRAIN GROWTH AT HIGH
IT HAS BEEN REPORTED THAT THE SINTERING AIDS CONTAINING BORON OXIDE PROMOTE
BY LIQUID PHASE SINTERING AND THEN EVAPORATED [37]. IN THE CASE OF 0.1 WT% AND
BBSZ GLASS ADDITION THE RELATIVE DENSITY CAN REACH 97% AND 98% AT 1375 °C AND 1425 °C RESPECTIVELY AND
FURTHER INCREASE IN SINTERING TEMPERATURE DID NOT AFFECT THE DENSIFICATION.

FIGURE 6.5 SHOWS THE VARIATION OF SINTERING TEMPERATURE AND BULK DEN
COMPOSITES WITH WEIGHT PERCENTAGE OF BBSZ GLASS ADDITION. IT IS CLEAR THAT T
TEMPERATURE GRADUALLY DECREASES WITH INCREASE IN THE AMOUNT OF GLASS. E
RATE OF DECREASE IS SUDDEN TILL 0.5 WT%, BEYOND THIS LIMIT THE SINTERING T
DECREASES VERY SLOWLY. THE SINTERING TEMPERATURE FOR 0.5 WT % AND 3 WT% B
ADDITION IS 1300 °C AND BEYOND THIS THE TEMPERATURE AGAIN DECREASES TO ABOUT 950 °C WITH
THE ADDITION OF 10 WT% BBSZ GLASS. ADDITION OF HIGHER AMOUNT OF GLASS (> 10 W

NO EFFECT ON THE SINTERING TEMPERATURE, IE., THE SINTERING TEMPERATURE SATU
THIS IS DUE TO THE FACT THAT THE BBSZ GLASS MELTS AT 950 °C.

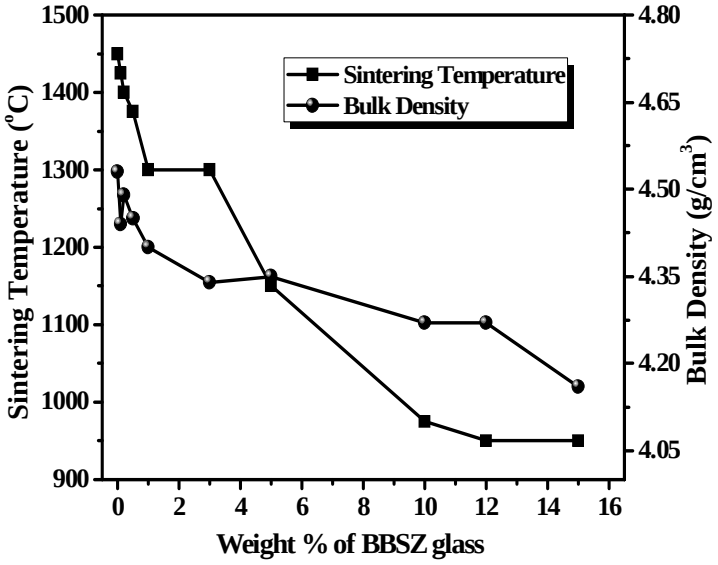

Fig. 6.5 The variation of sintering temperature and bulk density with weight percentage of BBSZ glass.

THE BULK DENSITY ALSO DECREASES WITH THE AMOUNT OF GLASS ADDITION. IT IS
THAT THE 0.2 WT% GLASS ADDED COMPOSITE EXHIBITED A BETTER DENSIFICATION WH
TO THE LOWER WEIGHT PERCENTAGE. THIS MAY BE DUE TO THE FACT THAT AT LOWER
THE AMOUNT OF MELTED GLASS MAY NOT BE SUFFICIENT ENOUGH TO FILL THE PORES
DENSIFICATION. HOWEVER, FURTHER INCREASE IN THE GLASS CONTENT (0.5 WT%) DE
RELATIVE DENSITY DUE TO THE LOW DENSITY OF THE GLASS WHEN COMPARED TO T
FURTHERMORE HIGHER GLASS CONTENT MAY INDUCE POROSITY WHICH ADVERSELY
DENSITY. THE RELATIVE DENSITY DECREASES FROM 96% TO 91% AS THE BBSZ GLASS
INCREASES FROM 1 WT% TO 15 WT%.

6.1.3.3 MICROSTRUCTURAL ANALYSIS

FIGURE 6.6 (A) SHOWS THE SEM PICTURES OF ZAT SINTERED AT 1450 °C. IT INDICATES THAT
$ZNAl_2O_4$ AND TiO_2 DO NOT REACT TO FORM ANY SECONDARY PHASE. FIG. 6.6 (B) SHOWS THE
PICTURE OF ZAT TREATED WITH 0.2 WT% BBSZ GLASS SINTERED AT 1400 °C. THE PARTICLES SEEM
TO COALESCE TOGETHER DECREASING THE SURFACE POROSITY. IT IS BELIEVED THAT T

POINT OF THE BBSZ GLASS PROMOTES LIQUID PHASE SINTERING AND RESULTS IN GOOD D
(SEE ALSO TABLE 6.2). FIG. 6.6 (C) SHOWS THE SEM PICTURE OF ZAT DOPED WITH 10 WT
BBSZ FROM WHICH THE PRESENCE OF SLIGHT POROSITY IS OBSERVED. DUE TO THE MUC
SINTERING TEMPERATURE OF THE COMPOSITE, THE GRAIN SIZE IS SMALLER WHEN COMP
HIGH TEMPERATURE SINTERED ZAT. THE GLASS DID NOT REACT WITH ZAT BUT FORMS A C
OVER THE GRAIN LEADING TO EXCESS LIQUID PHASE FORMATION. THE SEM PICTURE OF
WITH BBSZ AND LIF [FIG. 6.6 (D)] IS SIMILAR TO THAT TREATED WITH 10 WT% BBSZ. FIG.
SHOWS THE BACK SCATTERED IMAGE OF PURE ZAT AND THAT TREATED WITH 10 WT% B
FIG. 6.7 (A) CLEARLY SHOWS TWO AREAS (DARK AND LIGHT) INDICATING THE PHASES OF $ZrTiO_4$ AND
TiO_2. IN THE CASE OF BBSZ ADDED COMPOSITE (FIG. 6.7 (B)), THE WHITE AREA SHOWS
PRESENCE OF UNREACTED GLASS.

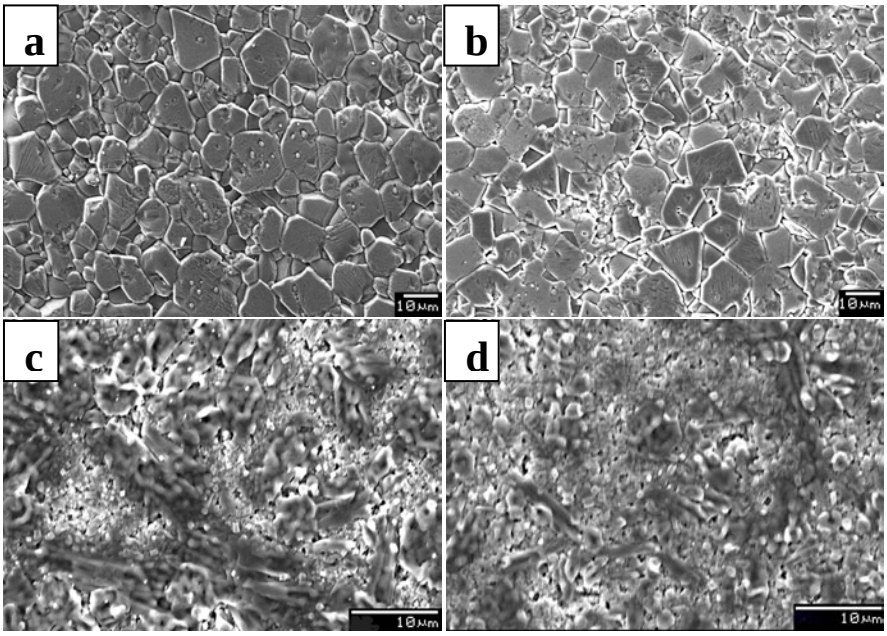

Fig. 6.6 The scanning electron micrographs of (a) pure ZAT, (b) doped with 0.2 wt% BBSZ sintered at 1400°C, (c) doped with 10 wt% BBSZ sintered at 950°C and (d) doped with 10 wt% BBSZ and 0.3 wt% LiF sintered at 925°C.

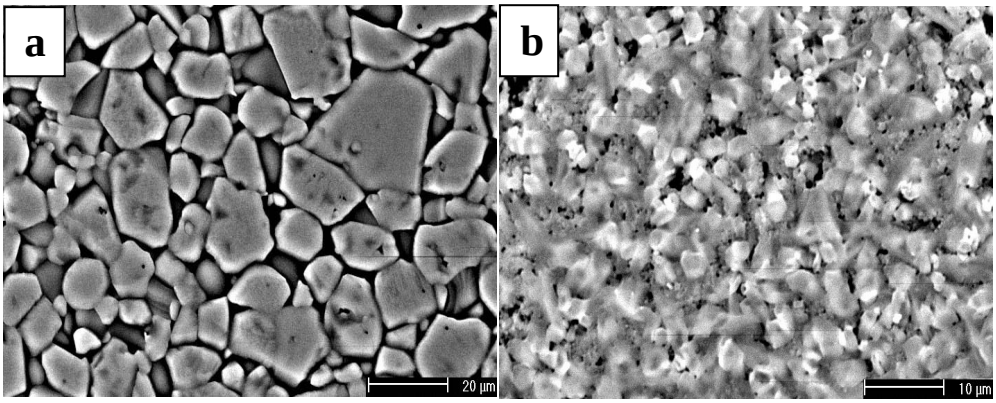

Fig. 6.7 The backscattered electron image of (a) pure ZAT and (b) doped with 10 wt% BBSZ sintered at 950°C.

6.1.3.4 MICROWAVE DIELECTRIC PROPERTIES

THE MICROWAVE DIELECTRIC PROPERTIES OF UNDOPED ZAT SINTERED AT 1450°C SHOWS $Q_u xf$=91000 GHZ, ε_r = 11.7 AND τ_f = 1.4 PPM/°C. THE EFFECT OF GLASS ADDITION ON THE MICROWAVE DIELECTRIC PROPERTIES IS DEPENDENT ON THE CHEMISTRY OF THE GLA REACTIONS, PHASE CHANGES DURING SINTERING AND FINAL DENSITY. TABLE 6.1 SHOWS PROPERTIES OF ZAT DOPED WITH 0.1 WT% OF DIFFERENT LOW LOSS GLASSES. IT IS CLEAR THE GLASSES ARE EFFECTIVE IN IMPROVING THE SINTERABILITY AND THE DIELECTRIC P WITH THE ADDITION OF SMALL WT% OF SOME OF THE GLASSES SUCH AS AS, ABS, MBS A THE QUALITY FACTOR IS FOUND TO DECREASE CONSIDERABLY. THIS MAY BE DUE TO HIGH DIELECTRIC LOSS EXHIBITED BY THESE GLASSES (SEE TABLE 1.3 CHAPTER 1). DUE SINTERABILITY AND POOR PROPERTIES EXHIBITED BY THESE GLASS COMPOSITES, THE FROM FURTHER STUDIES.

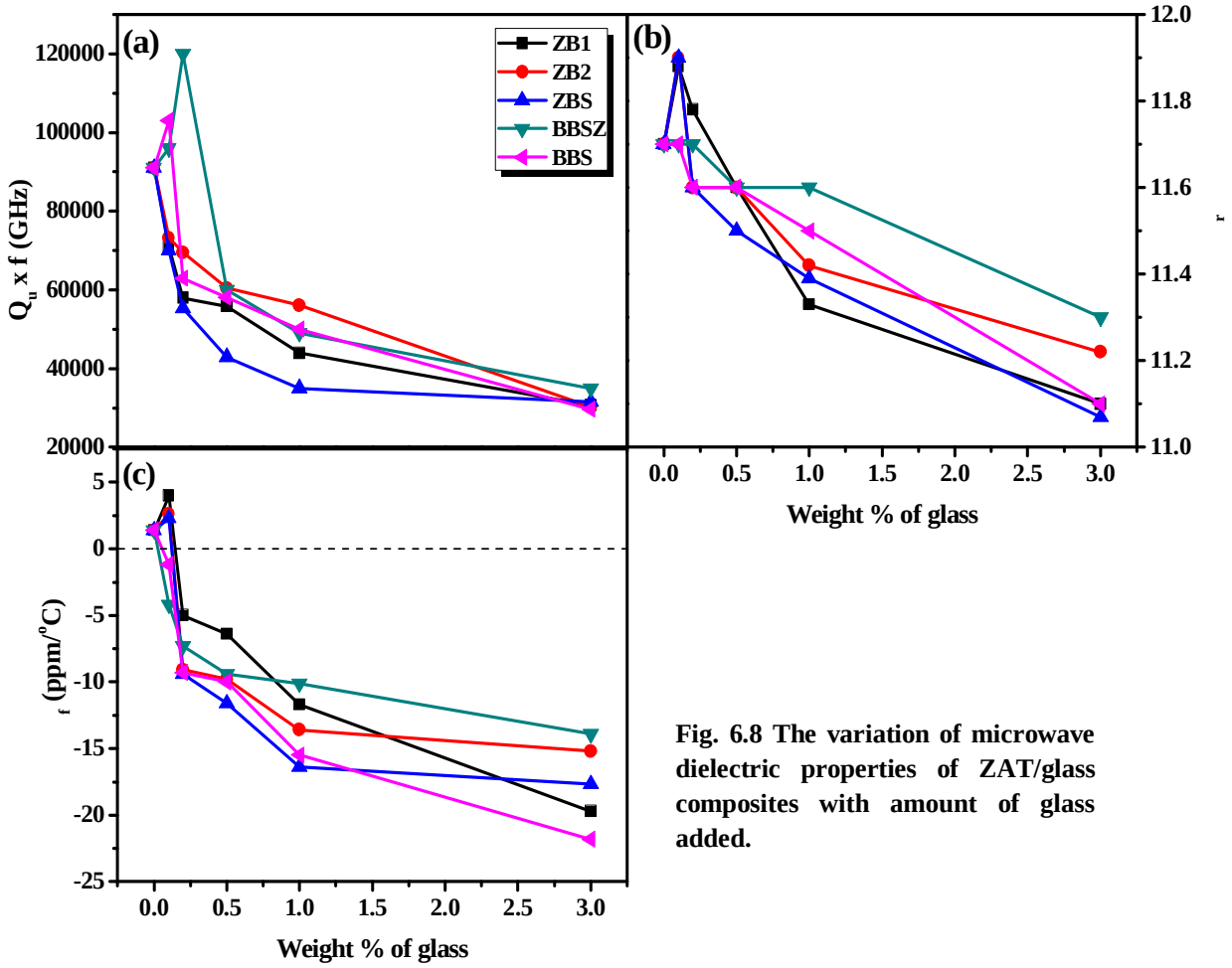

Fig. 6.8 The variation of microwave dielectric properties of ZAT/glass composites with amount of glass added.

FIGURE 6.8 SHOWS THE MICROWAVE DIELECTRIC PROPERTIES OF VARIOUS GLASS A COMPOSITES. FROM FIG. 6.8 (A) IT IS CLEAR THAT ADDITION OF SMALL WEIGHT PERCENTA AND BBS GLASS IMPROVED THE QUALITY FACTOR. THE ADDITION OF BINARY GLASSES (ZI SHOWED ALMOST SIMILAR VARIATION IN THE DIELECTRIC PROPERTIES (TABLE 6.1). E ADDITION OF SMALL AMOUNT (0.1, 0.2 WT%) OF THESE GLASSES INCREASED THE PERMITTIVITY DUE TO THE INCREASE IN RELATIVE DENSITY, THE QUALITY FACTOR IS RE 70000 GHZ. THE GLASS IN THE GRAIN BOUNDARY MAY BE RETAINED DURING SINTERING HAVE INCREASED THE VOLUME WHEN THE EUTECTIC LIQUID FORMATION TOOK PLACE. TH REASON FOR THE DECREASE IN THE QUALITY FACTOR EVEN THOUGH THE DENSIFICATI SIMILAR TREND IS EXHIBITED BY ZBS GLASS WHERE THE QUALITY FACTOR IS FOUND T GHZ. IT IS EVIDENT FROM THE FIG. 6.3 THAT THE GLASSES HAVING MORE COMPONENTS AR AS SINTERING AIDS. A COMPARISON OF THE MICROWAVE DIELECTRIC PROPERTIES OF V

ADDED ZAT COMPOSITES SHOWED THAT BBSZ AND BBS IMPROVED THE QUALITY FACTOR
GHZ AND 103000 GHZ RESPECTIVELY FOR 0.1 WT % GLASS. HOWEVER, THE ADDITION OF 0
0.5 WT% OF BBS DECREASED THE QUALITY FACTOR. IN THE CASE OF BBSZ GLASS IT IS F
ADDITION OF 0.2 WT% IMPROVED THE QUALITY FACTOR TO NEARLY 120000 GHZ WITH $Q_u f$ AND
τ_f OF -7.3 PPM/°C. THIS IS DUE TO THE ENHANCED DENSIFICATION DUE TO LIQUID PHASE SIN
THE ZNO IN BBSZ GLASS ACTS AS A MODIFIER OXIDE AND THE ADDITIONAL INCREASE OF
OF CERAMICS WITH SUCH ADDITIVES INCREASE THE DENSIFICATION [82]. ALSO THE LOSS
OF BBSZ GLASS IS RELATIVELY LOW (0.001) AS COMPARED TO OTHER GLASSES [6] (SEE TA
CHAPTER 1). THE VARIOUS LOSS MECHANISMS ASSOCIATED WITH GLASSES IN THE MICRO
ARE ALSO DISCUSSED IN CHAPTER 1, SECTION 1.8.3.3.2. FROM FIG. 6.8 (B) IT IS CLEAR TH
RELATIVE PERMITTIVITY SHOWS AN IMPROVEMENT ONLY FOR LOWER GLASS CONTENT A
CONTENT INCREASES, THE RELATIVE PERMITTIVITY GRADUALLY DECREASES WHICH IS D
VALUES POSSESSED BY THE GLASSES. IT IS SEEN FROM FIG. 6.8 (C) THAT THE ε_r BECOMES MORE
NEGATIVE WITH HIGHER GLASS CONTENT WHICH IS DUE TO THE HIGHER POSITIVE τ_f VALUE OF GLASSES

THE DIELECTRIC PROPERTIES OF THE MATERIALS ARE DEFINED BY THEIR C
COMPONENTS WHICH IN TURN ARE DETERMINED BY THE SINTERING TEMPERATURE. FI
SHOWS THE VARIATION OF RELATIVE PERMITTIVITY OF DIFFERENT WEIGHT PERCENTAGE
ZAT COMPOSITE WITH SINTERING TEMPERATURE. THE VARIATION IS SIMILAR TO TH
VARIATION WITH TEMPERATURE AS IN FIG. 6.4. THE RELATIVE PERMITTIVITY INITIALLY I
INCREASE IN THE SINTERING TEMPERATURE, ATTAINS A MAXIMUM VALUE AND THEN D
FURTHER INCREASE IN TEMPERATURE. THIS IS BECAUSE THE RELATIVE PERMITTIVIT
DEPENDENT ON THE DENSITY. AS THE AMOUNT OF GLASS INCREASES TO 0.2 WT% TH
PERMITTIVITY ATTAINS THE MAXIMUM VALUE OF 1196 AT 1400°C. FURTHER INCREASE IN THE GLASS
CONTENT DECREASES THE RELATIVE PERMITTIVITY GRADUALLY DUE TO THE LOW DENSI
AND ALSO DUE TO THE FACT THAT GLASSES HAVE LOW RELATIVE PERMITTIVITY. THE Q
THE COMPOSITE IS STRONGLY DEPENDENT ON BOTH THE SINTERING TEMPERATURE AND
BBSZ GLASS ADDED AS SHOWN IN FIG. 6.9 (B). IN THE CASE OF VARYING GLASS CONTE
INCREASING SINTERING TEMPERATURE, $Q_u f$ VALUES FOUND TO INCREASE TO A MAXIMUM VALUE
AND THEREAFTER DECREASES. FOR ZAT CERAMICS WITH 0.1, 0.2 AND 0.5 WT% OF BBSZ
ADDITIONS, THE MAXIMUM $Q_u f$ VALUES ARE 96000, 120000 AND 60000 GHZ RESPECTIVELY AT
THEIR OPTIMIZED SINTERING TEMPERATURES. EVENTHOUGH, POROSITY IS ONE OF THE FA

THE MICROWAVE DIELECTRIC LOSS [38-39], SOME INVESTIGATORS ALSO REPORTED THA
FACTOR IS INDEPENDENT OF POROSITY FOR A THEORETICAL DENSITY > 90% [40]. THE INC
QUALITY FACTOR AT LOW TEMPERATURE IS DUE TO THE INCREASE IN DENSITIES AND
WHERE THE MAXIMUM $Q_u \times f$ CORRESPONDS TO MAXIMUM DENSIFICATION. THE VARIATION O
WITH SINTERING TEMPERATURE IS SHOWN IN FIG. 6.9 (C). IT IS SEEN THAT THE τ_f IS MORE
NEGATIVE VALUE WITH INCREASE IN TEMPERATURE.

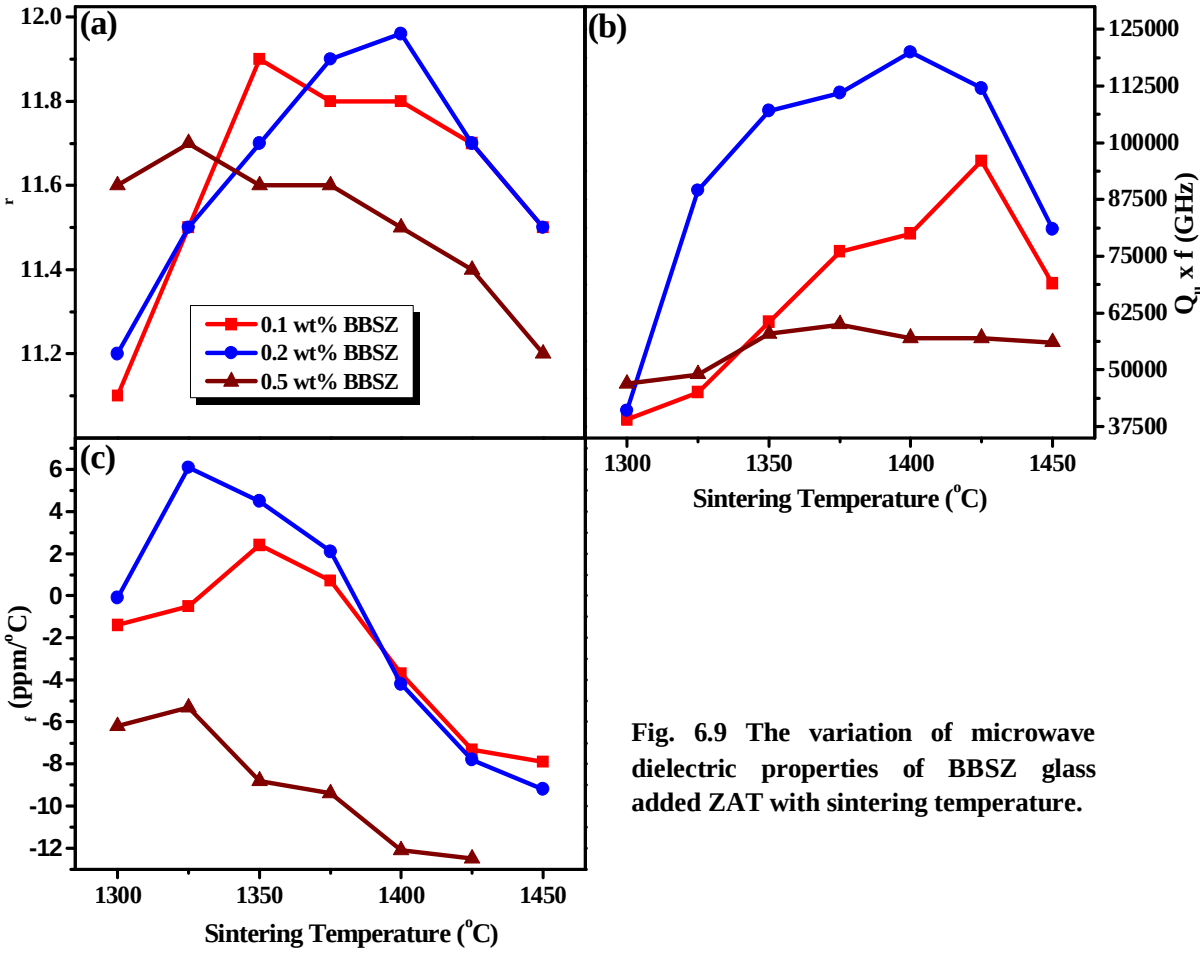

Fig. 6.9 The variation of microwave dielectric properties of BBSZ glass added ZAT with sintering temperature.

Table 6.2 The sintering temperature, relative density and dielectric properties of ZAT doped with different weight percentage of BBSZ glass.

Weight % of BBSZ added	Sintering temp. (^oC/h)	Microwave Properties				Loss at 1MHz
		Relative Density (%)	$Q_U X F$ (GHz)	τ_F (ppm/^oC)	ε_R	
0	1450/4	97	91,000	1.4	11.7	0.0010
0.1	1425/4	97	96,000	-4.2	11.7	0.0007
0.2	1400/4	98	120,000	-7.3	11.9	0.0004
0.5	1375/4	97	60,000	-9.4	11.6	0.0016
1	1300/4	96	49,000	-10.1	11.6	0.0019
3	1300/4	95	35,000	-13.9	11.3	0.0029
5	1150/4	95	21,000	-19.7	11.2	0.0035
10	950/10	93	12,000	-23.2	10.9	0.0058
12	950/10	93	11,500	-25.2	10.9	0.0155
15	950/10	91	9,300	-29	10.6	0.0307
10+0.3LIF	925/10	94	14,500	-28	10.5	0.0046

TABLE 6.2 SUMMARIZES THE PROPERTY OF ZAT/BBSZ GLASS COMPOSITES FOR DIF
WEIGHT PERCENTAGES OF GLASS CONTENT. THE INCREASE IN GLASS CONTENT DECREA
FACTOR. FOR 5 WT% GLASS ADDITION THE MICROWAVE DIELECTRIC PROPERTIES ARE $Q_U x f$
= 21000 GHZ, ε_r = 11.2 AND τ_f = -19.7 PPM/^oC. THE QUALITY FACTOR IS REDUCED TO NEARLY
10000 GHZ BY THE ADDITION OF 12 WT% AND 15 WT% BBSZ. SINCE NO SECONDARY PHAS
DETECTED IN THE PRESENT SYSTEM, THE VARIATION IN THE QUALITY FACTOR CAN BE
THE BULK DENSITY OF THE SYSTEM. THE RELATIVE PERMITTIVITY DECREASES TO ABO
WT% GLASS ADDITION WHICH IS DUE TO THE REDUCED DENSIFICATION (94%). THE τ_f
VALUE OF NEARLY -30 PPM/^oC. IN ORDER TO IMPROVE THE DENSIFICATION OF THE MATERIAL A
AMOUNT (0.3 WT%) OF LITHIUM FLUORIDE (LIF) IS ADDED TO THE COMPOSITION ZAT+1
BBSZ. FIG. 6.10 SHOWS THE VARIATION OF QUALITY FACTOR AND τ_f WITH SINTERING TEMPERATURE
FOR BOTH ZAT TREATED WITH 10 WT% BBSZ GLASS AND THAT TO WHICH LIF IS ADD
QUALITY FACTOR INCREASED GRADUALLY WITH SINTERING TEMPERATURE FOR BOTH
HOWEVER, τ_f ALSO SHIFTED TO MORE NEGATIVE VALUE. IT IS OBSERVED THAT AT A

TEMPERATURE OF 950 ^{o}C. THE A MAXIMUM QUALITY FACTOR IS ABOUT 12000 GHZ AND τ_f
23 PPM/^{o}C FOR THE COMPOSITION UNTREATED WITH LIF. THE COMPOSITE TREATED W
DECREASED THE SINTERING TEMPERATURE TO 925 ^{o}C WITH AN ENHANCEMENT IN THE
DIELECTRIC PROPERTIES WITH Q_u x f OF 14500 GHZ AND ε_r OF 10.5. THE τ_f, HOWEVER, INCREASED
TO A VALUE OF -28 PPM/^{o}C. THE LOW RELATIVE PERMITTIVITY OF THE GLASS AND THE PRESE
POROSITY DECREASED THE RELATIVE PERMITTIVITY OF THE CERAMIC-GLASS COMPOSI
ALSO GIVES THE DIELECTRIC LOSS OF VARIOUS ZAT/BBSZ COMPOSITES AT LOW FREQ
MHZ). AT LOW FREQUENCY, THE DIELECTRIC LOSS IS ATTRIBUTED TO THE STRUCTURAL
POLARIZATION LOSS WHILE AT THE MICROWAVE FREQUENCIES, THE DECREASE IN THE
MAY BE CAUSED BY THE DISAPPEARANCE OF IONIC POLARIZATION LOSS. IN ADDITION, T
STRUCTURE ALSO AFFECTS THE DIELECTRIC PROPERTY. THE DIELECTRIC STRUCTURE
COMPRISE THE WELL CONDUCTING CRYSTAL GRAINS WHICH ARE SEPARATED BY POOR
GLASSY PHASE. THE GLASS PHASE OF LOWER CONDUCTIVITY MAY BE EFFECTIVE AT LO
WHILE CRYSTAL GRAINS OF HIGH CONDUCTIVITY MAY BE EFFECTIVE AT HIGH FREQUENC
THE HIGHER VALUES OF DIELECTRIC LOSS ARE OBTAINED AT LOWER FREQUENCIES. TH
RELATIVE PERMITTIVITY (MEASURED AT 1 MHZ) OF ZAT AND THAT DOPED WITH 10 WT
WITH TEMPERATURE IS SHOWN IN FIG. 6.11. IT IS NOTED THAT THE RELATIVE PERMITTIV
ALMOST A CONSTANT IN THE TEMPERATURE RANGE 20-75 ^{o}C.

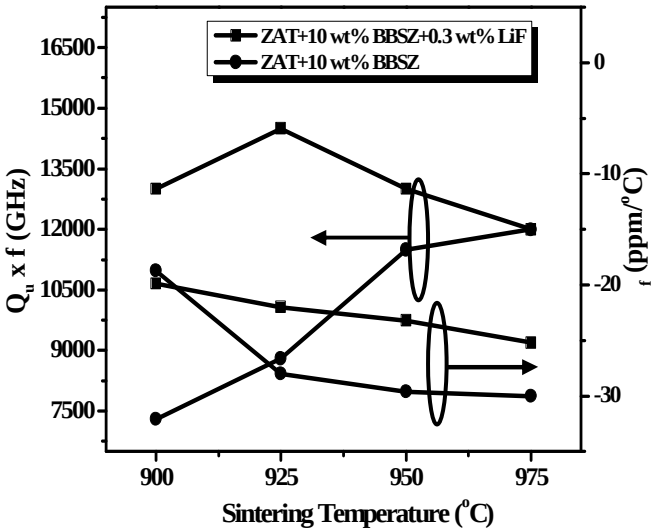

Fig. 6.10 The variation of quality factor and tauf with sintering temperature for ZAT doped with 10 wt% BBSZ glass.

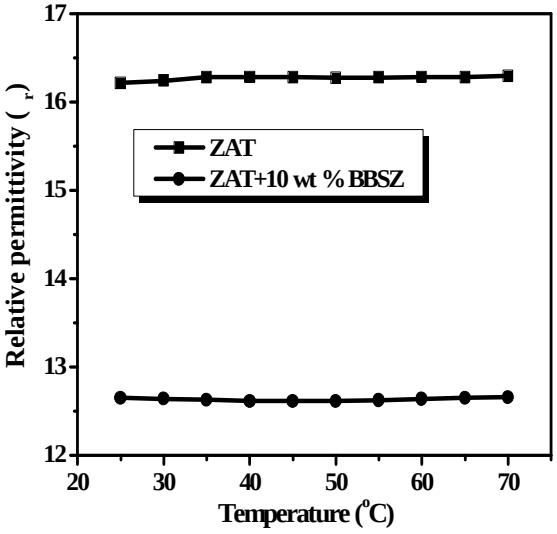

Fig. 6.11 The variation of relative permittivity (1 MHz) with temperature for ZAT and 10 wt% BBSZ added ZAT.

THE SHRINKAGE OF PURE ZAT, ZAT +10 WT% BBSZ AND ZAT +10 WT% BBSZ + 0.3 WT% LIF CERAMICS DURING FIRING PROCESS ARE MONITORED USING DILATOMETRIC ME AND THE RESULTS ARE AS SHOWN IN FIG. 6.12. IT IS SEEN THAT PURE ZAT EXHIBITS N SHRINKAGE IN THE MEASURED TEMPERATURE RANGE. THIS IS BECAUSE THE SINTERING T THE MATERIAL IS AS HIGH AS 1450 °C.

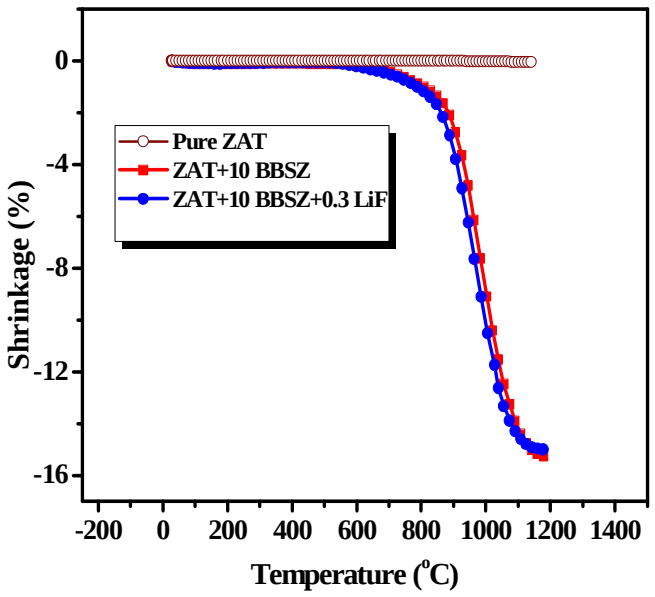

Fig. 6.12 The shrinkage curves of pure ZAT and that doped with 10 wt% BBSZ and 10 wt% BBSZ + 0.3 wt% LiF.

IT IS SEEN THAT WITH THE ADDITION OF 10 WT% BBSZ GLASS THE SHRINKAGE STARTS LOWER TEMPERATURE (~760 °C). THE SAMPLE SINTERED WITH LIF SHRINKS AT A SLIGHTLY LOW TEMPERATURE THAN THAT ADDED WITH BBSZ GLASS ALONE. HOWEVER, IN BOTH THE SHRINKAGE IS COMPLETE ONLY BEYOND 1400 °C. AT THIS TEMPERATURE BOTH THE COMPOSITES EXHIBIT PERCENTAGE SHRINKAGE OF ABOUT 10 %. HOWEVER, SINTERING THE SAMPLES A DECREASED THE QUALITY FACTOR AS SHOWN IN FIG. 6.10.

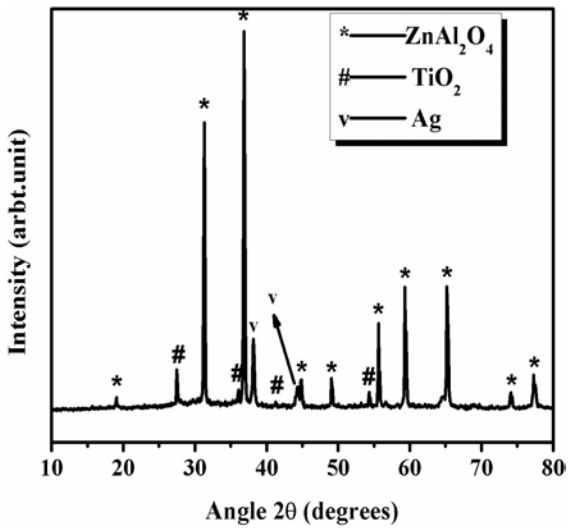

Fig. 6.13 The XRD pattern of 10 wt% BBSZ added ZAT treated with 20 wt% of silver.

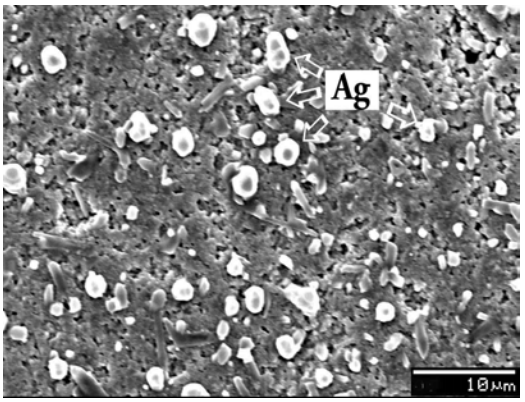

Fig. 6.14 The scanning electron micrograph of ZAT treated with 10 wt% BBSZ glass and 20 wt% silver.

IN ORDER TO USE ZAT/GLASS COMPOSITES FOR LTCC APPLICATIONS, IT IS NECESS FULFILL THE REQUIREMENT OF CHEMICAL COMPATIBILITY WITH A METAL ELECTRO COMMON MATERIAL FOR LTCC ELECTRODES IS SILVER. THUS, TO STUDY THE REACTIV WITH THE GLASS ADDED CERAMICS, 20 WT% AG IS ADDED TO ZAT + 10 WT% BB COMPOSITION. FIGS. 6.13 AND 6.14 SHOW THE POWDER DIFFRACTION PATTERN AND T PICTURE OF THE ABOVE COMPOSITION RESPECTIVELY. THE POWDER DIFFRACTION PAT WERE INDEXED BASED ON JCPDS FILE CARD NUMBER 4-783. IT IS EVIDENT FROM THESE F THAT SILVER REMAINS UNREACTED WITH THE CERAMIC-GLASS COMPOSITE, WHICH IS REQUIREMENTS OF LTCC.

THIS SECTION GIVES A BRIEF DISCUSSION ON THE DEVELOPMENT OF AN LTCC COMP BASED ON ZAT AND BBSZ GLASS WITH IMPROVED MICROWAVE DIELECTRIC PROPERT CHEMICAL COMPATIBILITY. THE NEXT SECTION DEALS WITH THE SYNTHESIS AND CHARA ZAT BASED POLYMER – CERAMIC COMPOSITES FOR ELECTRONIC PACKAGING AND APPLICATIONS.

6.2 POLYMER/0.83ZNAl$_2$O$_4$-0.17TIO$_2$ COMPOSITES FOR ELECTRONIC PACKAGING APPLICATIONS

6.2.1 INTRODUCTION

THE RECENT DEVELOPMENTS IN ELECTRONICS AND CIRCUIT ASSEMBLY DEMA PERMITTIVITY MATERIALS FOR THE PACKAGING OF RADIO FREQUENCY, MICROWAVE PRODUCTS [42]. THESE SUBSTRATE MATERIALS MUST POSSESS LOW RELATIVE PERMITTI DIELECTRIC LOSS TO REDUCE THE SIGNAL PROPAGATION DELAY WHICH IN TURN PROVID PERFORMANCE. THEY SHOULD ALSO HAVE GOOD THERMAL PROPERTIES SUCH AS H CONDUCTIVITY TO DISSIPATE THE HEAT GENERATED AND LOW OR MATCHING THERM COEFFICIENT WITH SILICON [43-44]. POLYMERS, ESPECIALLY POLYTETRAFLUOROETHYLEN POLYETHYLENE (PE), ARE WIDELY USED IN PACKAGING AND SUBSTRATE INDUSTRIES DU RELATIVE PERMITTIVITY AND EXCELLENT CHEMICAL INERTNESS [45]. HOWEVER, THE HI LINEAR COEFFICIENT OF THERMAL EXPANSION AND LOW THERMAL CONDUCTIVITY VA PRACTICAL USE [46]. THESE DIFFICULTIES CAN BE OVERCOME TO A CERTAIN EXTENT BY OF INORGANIC FILLERS SUCH AS CERAMIC PARTICLES INTO THE POLYMER MATRIX. CER COMPOSITES CONSISTING OF CERAMIC PARTICLES FILLED IN A POLYMER MATRIX FORM GROUP OF MATERIALS FOR PRODUCING DEMANDING AND FUNCTIONAL PACKAGES, SINCE THE ELECTRICAL PROPERTIES OF CERAMICS AND THE MECHANICAL FLEXIBILITY, CHEMIC PROCESSING POSSIBILITY OF POLYMERS. THE KEY PROPERTIES OF THE COMPOSITE VIZ. T PERMITTIVITY, THERMAL CONDUCTIVITY AND COEFFICIENT OF THERMAL EXPANSION AR VARIOUS FACTORS SUCH AS THE NUMBER OF COMPONENTS OR PHASES, VOLUME FRACTIO INDIVIDUAL PROPERTIES OF THE PHASES, PREPARATION METHOD AND THE INTERACTIO FILLER AND THE MATRIX [47-48]. HOWEVER, HIGH FILLER CONTENT RESULTS IN LOW ST FLUIDITY, POOR FLEXIBILITY AND DEFECTS IN THE COMPOSITE. THUS WITH THE PROPE THESE COMPOSITE ONE CAN UTILIZE THE EASE OF PROCESSING AND LOW RELATIVE PE POLYMERS AND HIGH THERMAL CONDUCTIVITY AND THERMAL STABILITY OF CERAMICS.

MANY STUDIES WERE CONDUCTED TO IMPROVE BOTH THE MECHANICAL AND PROPERTIES OF PTFE AND PE AS DISCUSSED EARLIER IN CHAPTER 5. ONE OF THE IMPORTA REGARDING THE DESIGN OF COMPOSITE MATERIALS FOR PRACTICAL APPLICATION IS TH RELATIVE PERMITTIVITY. MANY THEORETICAL MODELS HAVE BEEN PROPOSED FOR SI

ELECTRICAL AND THERMAL PROPERTIES OF THE COMPOSITES AND SOME OF THE PREDIC
THE STUDY ARE GIVEN IN CHAPTER 5.

EARLIER STUDIES [31] SHOWED THAT $0.83ZnAl_2O_4$-$0.17TiO_2$ (ZAT) CERAMICS POSSESS GOOD TEMPERATURE STABLE MICROWAVE DIELECTRIC PROPERTIES. IT HAS A RELATIVE 12 AND DIELECTRIC LOSS LESS THAN 0.001 AT 5 GHZ AND A HIGH THERMAL CONDUCTI $WM^{-1}K^{-1}$. THUS THE ADDITION OF PROPER VOLUME FRACTION OF ZAT AS FILLER INTO TH MATRIX CAN IMPROVE ITS PROPERTY TO CERTAIN EXTENT. THE PRESENT SECTION IS FO DIELECTRIC PROPERTIES OF ZAT/PTFE AND ZAT/PE COMPOSITES FOR ELECTRONIC PAC APPLICATIONS.

6.2.2 EXPERIMENTAL

THE $0.83\ ZnAl_2O_4$-$0.17\ TiO_2$ (ZAT) CERAMICS WERE PREPARED AS EXPLAINED IN SECTION 6.1.2. ZAT/PTFE (HINDUSTAN FLUOROCARBONS, HYDERABAD, INDIA) AND ZA COMPOSITES WERE PREPARED BY POWDER PROCESSING METHOD AND MELT MIXING T RESPECTIVELY AS DESCRIBED IN CHAPTER 2. THE POWDERED ZAT WAS MIXED WITH AC SOLUTION FOR 1H AND DRIED. THIS PROVIDED AN ACTIVE SURFACE FOR BINDING WITH P ACRYLIC ACID IS A WELL-KNOWN POLYMERIZING AGENT. THE HOMOGENOUSL POLYMER/ZAT COMPOSITES WERE THEN COMPACTED USING HOT PRESS FURNACE AT A PRESSURE OF 50 MPA FOR 30 MINUTE.

THE COMPOSITES WERE CHARACTERIZED USING XRD AND SEM. THE THIN PELLET DIAMETER 14 MM AND THICKNESS LESS THAN 1 MM WERE ELECTRODED BY UNIFORMLY C SILVER PASTE ON BOTH SIDES IN THE FORM OF CERAMIC CAPACITORS. THE LOW FREQUE PROPERTIES WERE MEASURED BY LCR METER. THE VARIATION IN RELATIVE PERMITT TEMPERATURE WAS ALSO INVESTIGATED FOR THE COMPOSITES IN THE TEMPERATURE R ^{0}C THE MICROWAVE DIELECTRIC PROPERTIES WERE MEASURED BY THE CAVITY PERTURBA WHICH IS DISCUSSED IN DETAIL IN CHAPTER 2, SECTION 2.5.6. THE COEFFICIENT OF EXPANSION (CTE) OF THE COMPOSITES WAS MEASURED USING A THERMO - MECHANICAL IN THE RANGE 25 – 250 ^{0}C. THE WATER ABSORPTION MEASUREMENTS WERE CONDUCTED FOLL ASTM D570 AS DESCRIBED IN CHAPTER 5, SECTION 5.3.

6.2.3 RESULTS AND DISCUSSION

FIGURE 6.15 SHOWS THE XRD PATTERNS OF PURE PTFE, ZAT AND THAT FILLED WIT
V_F AND 0.3 V_F ZAT RESPECTIVELY. PTFE IS A SEMI-CRYSTALLINE POLYMER AND IT CAN CRYS
MORE EASILY AND FASTER THAN ANY OTHER POLYMERS [49]. THE XRD CHARACTERIZA
THAT PTFE HAS A STRONG CRYSTALLINE PEAK AT $2\theta = 18^\circ$ AS OBSERVED EARLIER BY *Ref.* [50].
FROM THE PREVIOUS SECTION IT IS CLEAR THAT ZNO AND Al_2O_3 DO NOT FORM A SOLID SOLUTION WITH TIO$_2$
IN THE COMPOSITION 0.83ZnO-0.17TiO_2 (ZAT) AND REMAIN AS A MIXTURE. THE POWDER
DIFFRACTION PATTERNS OF ZAT AND TiO_2 ARE INDEXED BASED ON JCPDS FILE CARD
NUMBERS 5-669 AND 21-1276 RESPECTIVELY. IT IS SEEN THAT AS THE VOLUME FRACTION
INCREASES, THE INTENSITY OF PTFE PHASE DECREASES. ALSO NO ADDITIONAL PHASES A
FOR PTFE/ZAT COMPOSITE INDICATING GOOD CHEMICAL STABILITY.

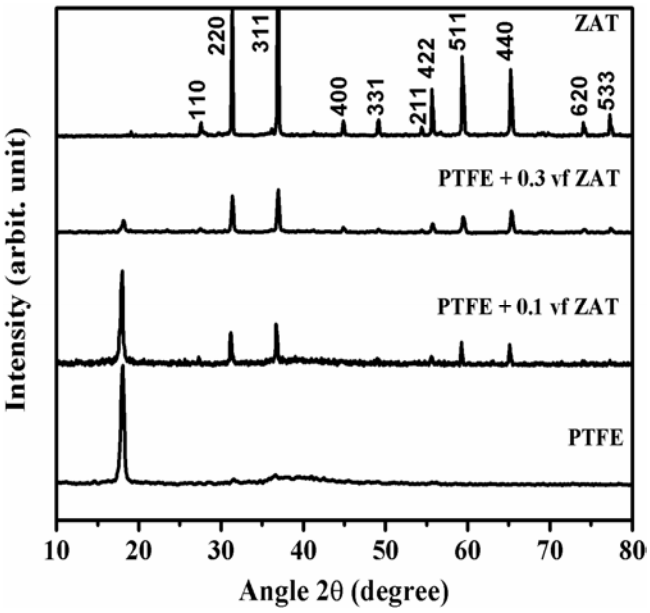

Fig. 6.15 XRD patterns of pure PTFE, ZAT and PTFE/ZAT composites.

THE SURFACE MORPHOLOGIES OF THE DIFFERENT VOLUME FRACTION OF ZAT LOA
AND PE COMPOSITES ARE SHOWN IN FIG. 6.16. IT IS CLEAR FROM THE FIGURES THAT FOR L
CONTENT THE CERAMIC PARTICLES ARE UNIFORMLY DISTRIBUTED IN THE POLYMER MA
PARTICLES ARE DISTRIBUTED THROUGHOUT THE PTFE MATRIX WITH RELATIVELY HIGH
DISTANCE FOR LOWER LOADING OF CERAMICS. WITH THE INCREASE IN THE ZAT CONTENT
PARTICLES WERE WELL EMBEDDED IN THE MATRIX AND ALSO RESULTED IN THE AGGR

CERAMIC PARTICLES. HOWEVER, A HIGHER DEGREE OF HOMOGENEITY IN DISPERSION IS N
PE/ZAT COMPOSITES WHICH MAY BE DUE TO THE DIFFERENCE IN THE PROCESSING TE
ADOPTED. THE FRACTURED SURFACE OF THE COMPOSITES ALSO CONFIRMS A GOOD BIN
THE MATRIX AND THE FILLER. HOWEVER, PTFE/ZAT COMPOSITE EXHIBITS SOME DEG
PARTICLE AGGLOMERATION AND POROSITY.

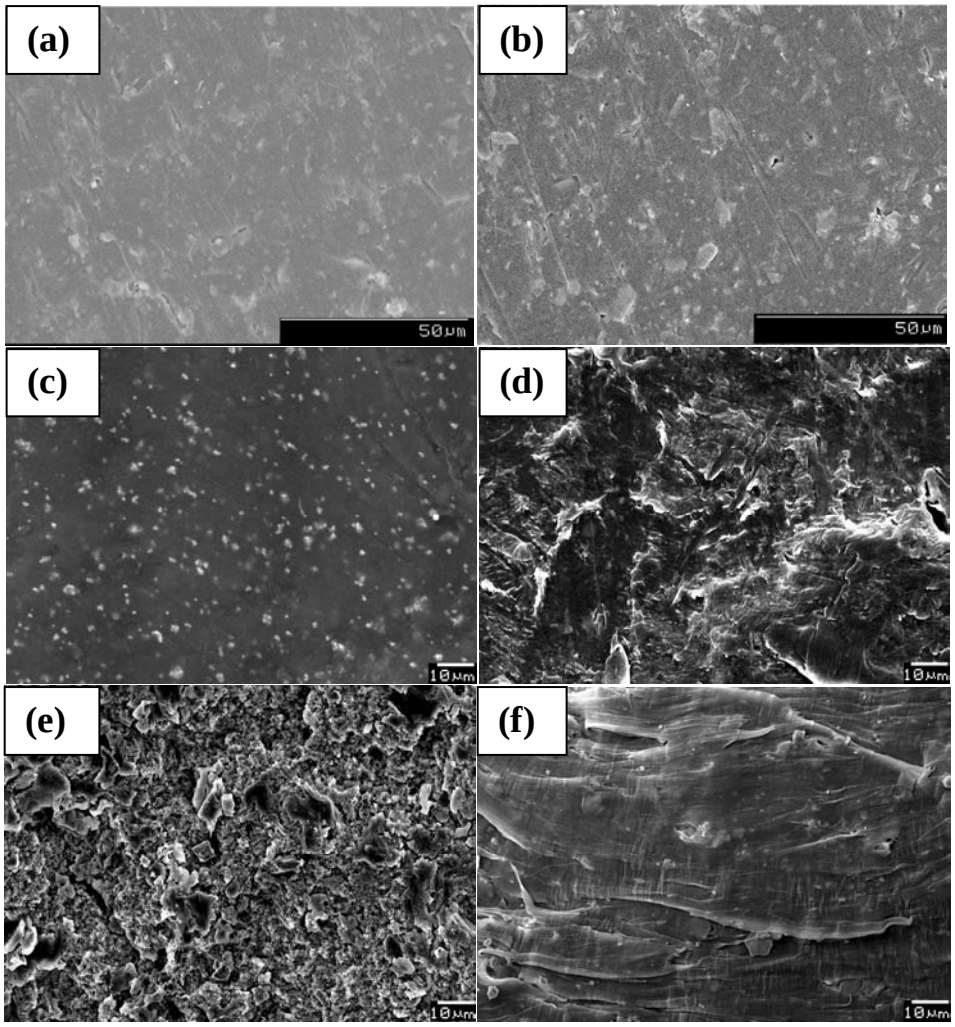

Fig. 6.16 SEM images of (a) PTFE-0.1 v_f ZAT, (b) PTFE-0.3 v_f ZAT, (c) PE-0.1 v_f ZAT, (d) PE-0.3 v_f ZAT and fractured surface of (e) PTFE-0.3 v_f ZAT, (f) PE-0.3 v_f ZAT.

THE THEORETICAL DENSITY OF BOTH THE COMPOSITES (ρ_{comp}) CALCULATED USING THE MIXTURE RULE GIVEN IN EQ. (5.12) IN CHAPTER 5.

Table 6.3 The physical and dielectric properties of PTFE/ZAT and PE/ZAT composites.

Volume fraction filler		ρ (%)	V_{filler} (%)	V_{matrix} (%)	V_{air} (%)	Dielectric properties at 1 MHz		
						ε_R	$TAN\delta$	τ_ε (ppm/^{o}C)
PTFE/ZAT	0.1	97.5	9.75	87.75	2.5	2.63	0.0017	-98
	0.2	95.0	19.00	76.00	5.0	2.79	0.0032	-120
	0.3	94.8	28.44	66.36	5.2	3.35	0.0063	-350
	0.4	90.1	36.04	54.06	9.9	3.87	0.0063	-396
	0.5	89.3	44.65	44.65	10.7	4.22	0.0065	-580
PE/ZAT	0.1	98.9	9.89	89.01	1.1	2.96	0.0012	-38
	0.2	97.7	19.54	78.16	2.3	3.53	0.0033	-53
	0.3	95.2	28.56	66.64	4.8	4.04	0.0044	-82
	0.4	92.3	36.92	55.38	7.7	4.63	0.0046	-187
	0.5	91.1	45.55	45.55	8.9	5.39	0.0052	-400

THE DENSITIES OF PTFE, PE AND ZAT MEASURED BY ARCHIMEDES METHOD ARE FO
TO BE 2.15, 0.95 AND 4.58 G/CM^3 RESPECTIVELY. TABLE 6.3 GIVES THE RELATIVE DENSITY A
POROSITY OF THE COMPOSITES WITH VARYING FILLER CONTENT. THE RELATIVE DENSITY
97.5 % OF THE THEORETICAL VALUE FOR 0.1 VOLUME FRACTION LOADING WHICH DECREASED GRADUALLY W
THE INCREASE IN FILLER CONTENT AND REACHED A VALUE OF 89.3% FOR 0.5 VOLUME FRACTION. THIS DECREASE
IN THE RELATIVE DENSITY INDICATES THE PRESENCE OF POROSITY. ON THE OTHER HA
COMPOSITES SHOW A BETTER DENSIFICATION AS COMPARED WITH THE PTFE COMPOSIT
EVIDENT FROM THE SEM IMAGES WHERE A GOOD ADHESION BETWEEN THE PE MATRIX
FILLER. EVEN FOR A HIGHER FILLER LOADING (0.5 VOLUME FRACTION) THE RELATIVE DENSITY IS ABOUT 91%. THE
POROSITY IS FOUND TO EXHIBIT A MUCH LOWER VALUE (LESS THAN 10%) EVEN FOR A
FILLER CONTENT OF 0.5. IT SHOULD BE NOTED THAT THE POROSITY HAS A LOWER VALUE AS C
TO THAT REPORTED BY XIANG AND SUN FOR $Sr_3Ti_2O_7$ COMPOSITES [51]. A COMPARISON OF THE
POROSITY VALUES OF PTFE/ZAT AND PTFE/Sr_2TiO_4 COMPOSITES SHOW THAT THE FORMER HAS A
LOWER POROSITY CONTENT WHICH IS HIGHLY ENCOURAGING.

FIGURES 6.17 (A) AND (B) RESPECTIVELY SHOW THE FREQUENCY DEPENDENCE OF PERMITTIVITY OF THE PTFE/ZAT AND PE/ZAT COMPOSITES WITH DIFFERENT VOLUME FRA FILLER IN THE FREQUENCY RANGE 1 KHZ-1 MHZ. IT IS FOUND THAT THE RELATIVE PE REMAIN NEARLY A CONSTANT IN THE ENTIRE FREQUENCY RANGE. THIS SHOWS TH FREQUENCY STABILITY OF THE COMPOSITES. THIS INDICATES THAT THESE COMPO PROMISING CHARACTERISTICS FOR POTENTIAL APPLICATIONS IN A WIDE RANGE O FREQUENCIES.

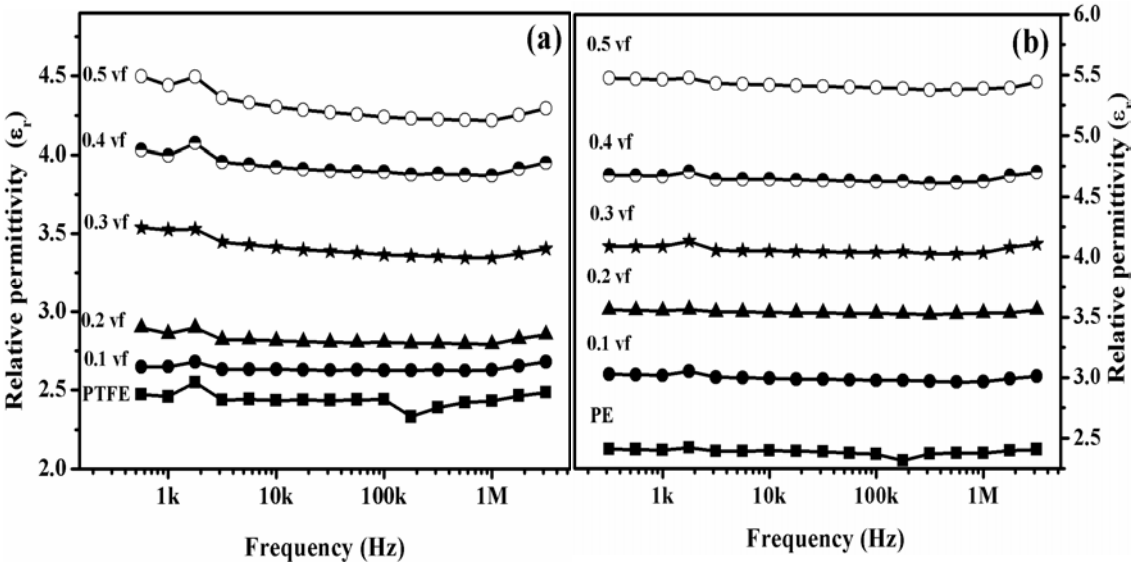

Fig. 6.17 The variation of relative permitttivity of (a) PTFE/ZAT and (b) PE/ZAT composites with frequency.

FIGURE 6.18 SHOWS THE VARIATION OF RELATIVE PERMITTIVITY AND DIELECTRI VOLUME FRACTION OF ZAT FOR BOTH PTFE/ZAT AND PE/ZAT COMPOSITES AT 9 GHZ. FOR THE COMPOSITES THE RELATIVE PERMITTIVITY INCREASES WITH INCREASE IN THE FILLE IS DUE TO THE RELATIVELY HIGH PERMITTIVITY OF THE ZAT FILLER (ε_r = 34 AT 1 MHZ AND 12 AT 9 GHZ) COMPARED TO THAT OF THE MATRIX. THE DIELECTRIC LOSS ALSO INCREASES O THE FILLER CONTENT. THIS IS DUE TO THE FACT THAT AS THE FILLER CONTENT INCREA PARTICLES COME CLOSE TOGETHER LEADING TO AN INCREASE IN THE DIPOLE – DIPOL THEREBY INCREASING THE RELATIVE PERMITTIVITY [52]. THE SAME TREND IS OBSER FREQUENCY ALSO. THE DIELECTRIC PROPERTIES OF THE COMPOSITES AT 1 MHZ FOR VA CONCENTRATION ARE GIVEN IN TABLE 6.3. THE RELATIVE PERMITTIVITY SHOWS A DECRE

MICROWAVE FREQUENCY WHEN COMPARED WITH THAT AT 1 MHZ. IN THE MATRIX A D
DIPOLAR POLARIZATION MAY BE RESPONSIBLE FOR THIS BEHAVIOR WHEREAS IN CO
HETEROGENEOUS SYSTEMS, INTERFACIAL OR MAXWELL-WAGNER-SILLARS POLARIZA
CONTRIBUTING TO THE DIELECTRIC PROPERTIES. THE DIELECTRIC LOSS WHICH IS TH
AFFECTING THE FREQUENCY SELECTIVITY OF A MATERIAL IS INFLUENCED BY MANY F
POROSITY, MICROSTRUCTURE AND DEFECTS [33]. THE INCREASED DIELECTRIC LOSS MAY BE ATTRIBUTE
TO THE INCREASED POROSITY (SEE TABLE 6.3) OF THE COMPOSITE MATERIAL AND ALSO
INTERFACIAL POLARIZATION BETWEEN THE POLYMER AND CERAMIC AT HIGHER FILLE
DIELECTRIC LOSS VARIES FROM 0.0017-0.0065 AND 0.0012-0.0052 AT 1 MHZ WITH THE FIL
ADDITION FROM 0.1 TO 0.5 V_F FOR PTFE/ZAT AND PE/ZAT COMPOSITES RESPECTIVELY. THIS IS A
MUCH SATISFACTORY RESULT WHEN COMPARED WITH SOME OF THE EARLIER REPOR
POLYMER-CERAMIC COMPOSITES [44, 54-55]. BY COMPARING THE DIELECTRIC PROPERTIE
THE COMPOSITES, IT CAN BE CONCLUDED THAT THE PTFE/ZAT COMPOSITES EXHIBIT A LO
PERMITTIVITY WHEN COMPARED TO THAT OF THE PE/ZAT COMPOSITES. HOWEVER, THE
LOSS OF THE FORMER IS HIGH IN COMPARISON WITH THE PE COUNTERPART.

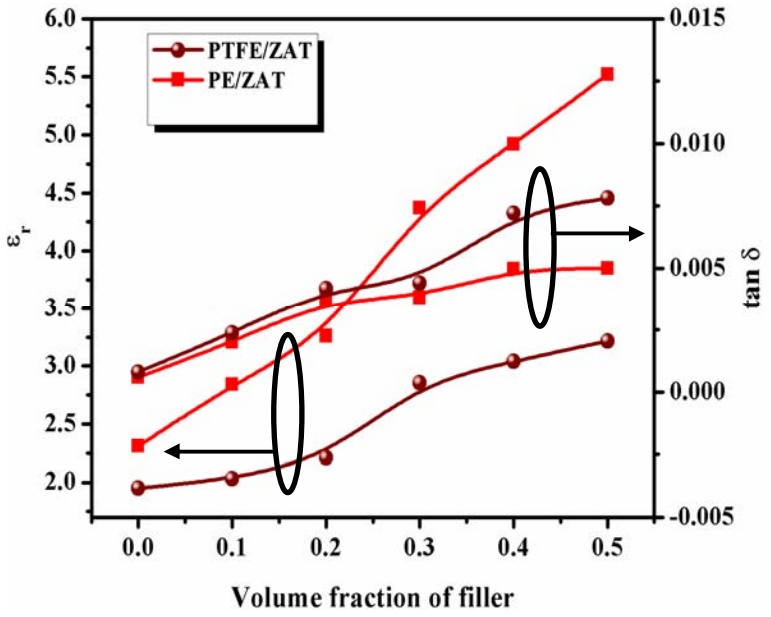

Fig. 6.18 Variation of ε_r and tan δ (at 9 GHz) of PTFE/ZAT and PE/ZAT composites with volume fraction of filler.

AT 9 GHZ, AS THE VOLUME FRACTION OF FILLER INCREASES (0.1 TO 0.5), THE RELATIVE PERMITTIVITY AND DIELECTRIC LOSS INCREASES FROM 1.95 TO 3.24 AND 0.0008 TO 0.0089 RESPECTIVE PTFE/ZAT COMPOSITES. ON THE OTHER HAND, FOR PE/ZAT COMPOSITES THE RESPEC VARIATIONS ARE FROM 2.32 TO 5.52 AND 0.0006 TO 0.005. THE REDUCED DIELECTRIC LOSS PE COMPOSITES CAN BE WELL UNDERSTOOD FROM THE LOW POROSITY VALUE OF THES (SEE TABLE 6.3). THE DIELECTRIC LOSS OF THE COMPOSITES AT MICROWAVE FREQUENC THAN THAT AT 1 MHZ. AT HIGHER FILLER CONTENT THE LOWER CONNECTION BETWEEN THE FILLER MAY LEAD TO MORE AIR AND MOISTURE CONTENT IN THE COMPOSITES. A FREQUENCY, THERE IS A LARGE DIELECTRIC LOSS DUE TO THE LARGE LOSS FROM THE D OF WATER [56].

THE PREDICTION OF RELATIVE PERMITTIVITY OF THE COMPOSITES FROM THE RELATIVE PERMITTIVITIES OF THE CONSTITUENT COMPONENTS AND THE VOLUME FRACTION OF THE IMPORTANT FACTOR FOR ELECTRONIC PACKAGING APPLICATIONS. THE EXPERIMENT RELATIVE PERMITTIVITY OF BOTH THE COMPOSITES ARE COMPARED WITH THE THEO PREDICTED USING JAYASUNDERE-SMITH, LICHTENECKER, MAXWELL WAGNER, M LICHTENECKER AND EMT MODELS GIVEN IN EQS. (5.1) TO (5.5) IN CHAPTER 5.

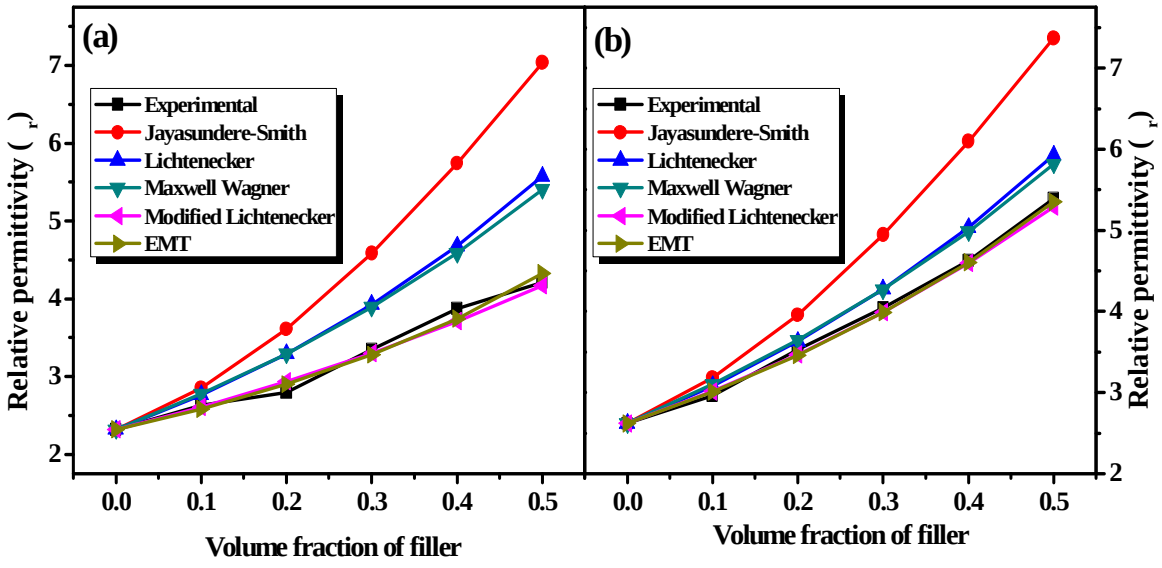

Fig. 6.19 Comparison of experimental relative permittivity with theoretical predictions of (a) PTFE/ZAT and (b) PE/ZAT composites at 1 MHz.

FIGURES 6.19 (A) AND (B) RESPECTIVELY SHOW THE COMPARISON BETWEEN EXPERIMENTAL AND THE THEORETICAL VALUES OF RELATIVE PERMITTIVITY OF PT PE/ZAT COMPOSITES AT 1 MHZ. IT IS CLEAR FROM THE FIGURES THAT FOR PTFE/ COMPOSITES, JAYASUNDERE-SMITH, LICHTENECKER, MAXWELL WAGNER MODELS DEV FROM THE EXPERIMENTAL VALUES WHEREAS FOR PE/ZAT COMPOSITES THE LICHT MAXWELL WAGNER MODELS ARE FOUND TO BE IN AGREEMENT AT LOWER FILLER CONT V_f). GENERALLY ALL THE THEORETICAL PREDICTIONS ARE VALID FOR LOW FILLER CO AMOUNT OF THE FILLER INCREASES, THE DEVIATION FROM THE PREDICTED VALUE IS OB DUE TO THE IMPERFECT DISPERSION OF CERAMIC PARTICLES AT HIGHER FILLER CONTENT THE AIR ENCLOSED BY THE COMPOSITES WHICH REDUCES THE EFFECTIVE RELATIVE PER CLEAR FROM THE FIGURES THAT THE MODIFIED LICHTENECKER EQUATION AND EFFEC THEORY ARE FOUND TO BE IN GOOD MATCH WITH THE EXPERIMENTAL VALUES FO COMPOSITES. THE FITTING FACTOR k OBTAINED IN THE PRESENT STUDY FOR PTFE/ZAT AND PE/ZAT COMPOSITES ARE 0.13 AND 0.14 RESPECTIVELY WHICH IS IN AGREEMENT WITH EARL REPORT FOR WELL-DISPERSED POLYMER-CERAMIC COMPOSITES [57]. IN THE CASE OF LICHTENECKER EQUATION EVEN FOR HIGHER VOLUME FRACTION OF THE FILLER, THE PTFE/ZAT AND PE/ZAT ARE 4.1 % AND 1.9 % RESPECTIVELY. THE EFFECTIVE MEDIUM THEORY WHICH ASSUMES THE FILLER AS A RANDOM UNIT CELL EMBEDDED IN THE EFFEC IS FOUND TO BE WELL SUITED FOR A NUMBER OF POLYMER CERAMIC COMPOSITES. THE DEVIATION FROM EMT MODEL IS FOUND TO BE 2.6 % AND A VERY LOW VALUE OF 0 RESPECTIVELY FOR PTFE/ZAT AND PE/ZAT COMPOSITES. THE RELATIVELY LOW PERC DEVIATION FOR THE PE/ZAT COMPOSITES IS DUE TO THE LOW POROSITY CONTENT COMPOSITES.

THE TEMPERATURE COEFFICIENT OF RELATIVE PERMITTIVITY IS ONE OF THE PROPERTIES WHICH CONTROL THE OVERALL PERFORMANCE OF THE SUBSTRATE MATERIA AND (B) RESPECTIVELY SHOWS THE VARIATION OF RELATIVE PERMITTIVITY OF PTFE PE/ZAT COMPOSITES WITH TEMPERATURE AT 1 MHZ. IT IS CLEAR THAT FOR ALL THE FRACTIONS THE RELATIVE PERMITTIVITY IS NEARLY INDEPENDENT OF TEMPERATUR AVERAGE NEGATIVE PERCENTAGE DEVIATION OF ABOUT 0.46 %. THE TEMPERATURE CO RELATIVE PERMITTIVITY OF BOTH ZAT/PTFE AND ZAT/PE COMPOSITES ARE GIVEN IN TABLE 6.3. THE τ_ε VALUE BECOMES MORE AND MORE NEGATIVE WITH THE INCREASE IN THE FILL

FOR BOTH THE COMPOSITES. THIS IS QUITE UNEXPECTED SINCE THE FILLER POSSESS A VALUE. THUS THE DECREASE IN RELATIVE PERMITTIVITY WITH TEMPERATURE MAY BE D DIFFERENCE IN THERMAL EXPANSION COEFFICIENT OF POLYMER MATRIX AND THE ZAT WOULD DISTURB THE AGGREGATION OF THE POLAR COMPONENTS CAUSING A DECREASE PERMITTIVITY [58-59] WHICH HAS BEEN EXPLAINED EARLIER IN CHAPTER 5. ALSO FROM T IS CLEAR THAT THE PTFE/ZAT COMPOSITES EXHIBIT A LOWER τ_ε VALUE WHEN COMPARED WITH THAT OF THE PE/ZAT COMPOSITES WHICH MAY BE DUE TO THE POOR ADHESION BETWEEN PTFE FILLER WHEN COMPARED WITH THE LATTER AT HIGHER FILLER CONTENTS.

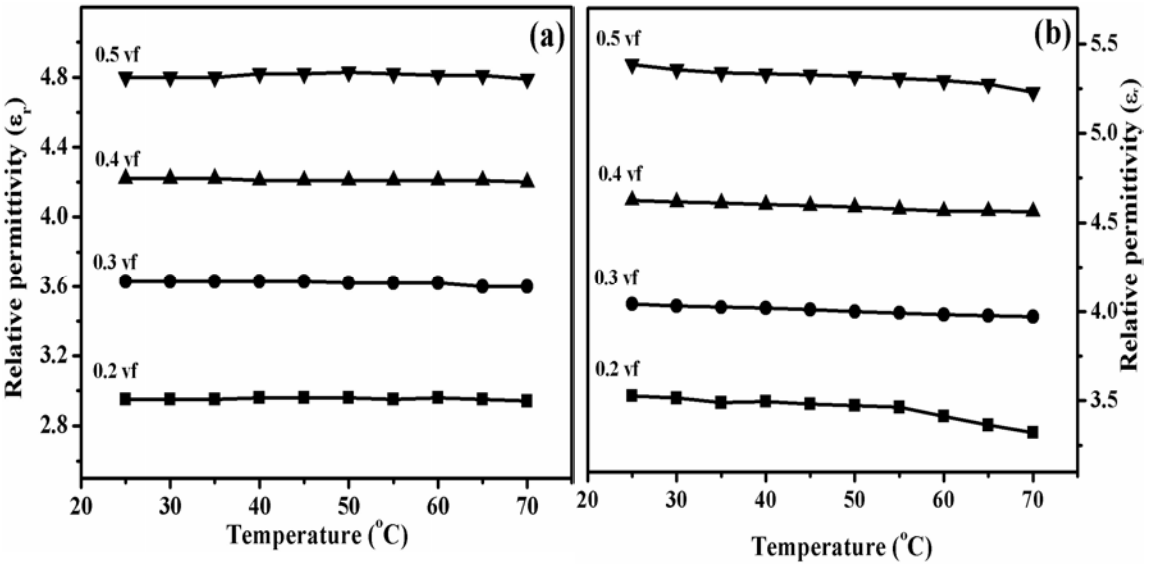

Fig. 6.20 Variation of relative permittivity of (a) PTFE/ZAT and (b) PE/ZAT composites with temperature in the range 25-70^{o}C.

FIGURE 6.21 SHOWS THE VARIATION OF THE COEFFICIENT OF THERMAL EXPA PTFE/ZAT AND PE/ZAT COMPOSITES AS A FUNCTION OF FILLER CONTENT. IT CAN BE SEEN CTE VALUE DECREASES GRADUALLY AS THE FILLER CONCENTRATION INCREASES W EXPECTED DUE TO THE VERY LOW CTE VALUE POSSESSED BY THE ZAT FILLER (6.3 PPM/^{o}C) COMPARED WITH THAT OF THE POLYMERS USED. FOR A FILLER CONTENT OF 0.5 V AND PE/ZAT COMPOSITES EXHIBIT A CTE VALUE OF 28 AND 58 PPM/^{o}C RESPECTIVELY. THE CTE VALUES OBTAINED FOR POLYMER/ZAT COMPOSITES ARE HIGHER WHEN COMPARED W POLYMER/$SrTiO_3$ COMPOSITES. THE DOTTED LINES IN FIG. 6.21 REPRESENT THE THEORE

CTE VALUES OF BOTH THE COMPOSITES PREDICTED USING THE MIXTURE RULE GIVEN IN
LARGE DEVIATION FROM THE PREDICTED VALUE IS NOTED FOR PE/ZAT COMPOSITES W
EXPERIMENTAL VALUES ARE IN GOOD AGREEMENT WITH THE THEORETICAL PREDICTION
COMPOSITES. THIS IS BECAUSE THE MIXING RULE IS A SIMPLE PREDICTION WHICH CONS
THE CTE VALUES OF THE INDIVIDUAL COMPONENTS AND OTHER FACTORS SUCH AS POR
INTERACTION, STRAINS ETC ARE NOT TAKEN INTO ACCOUNT. HOWEVER, PTFE/ZAT COMP
A GOOD CORRESPONDENCE WITH THE PREDICTION UPTO A FILLER CONTENT OF 0.4 V

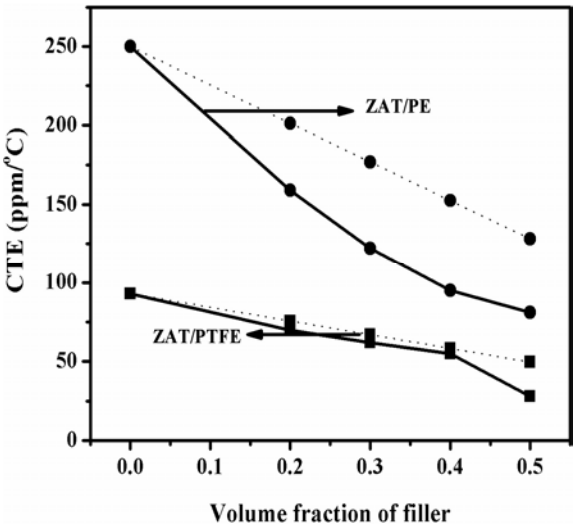

Fig. 6.21 Variation of CTE values of PTFE/ZAT and PE/ZAT composites with filler content.

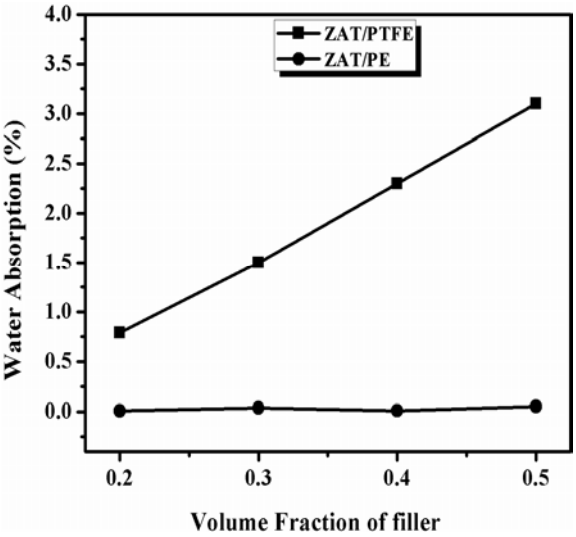

Fig. 6.22 The variation of water absorption of PTFE/ZAT and PE/ZAT composites with filler content.

FIGURE 6.22 SHOWS THE AMOUNT OF WATER ABSORBED BY THE COMPOSITES AS A
OF THE FILLER CONTENT. IN BOTH THE CASES, AN INCREASE IN WATER ABSORPTION IS NO
AMOUNT INCREASES. A COMPARISON OF THE WATER ABSORPTION VALUES OF ZAT/P
ZAT/PE COMPOSITES SHOW THAT THE FORMER EXHIBIT A HIGHER VALUE WHICH MAY BE
SURFACE CHARACTERISTICS OF THE MATRIX UNDER CONSIDERATION. IT IS HIGHLY ENCO
THAT EVEN FOR A HIGHER FILLER CONTENT, THE ZAT/PE COMPOSITES HAS A VERY
LOW VALUE OF WATER ABSORPTION (0.052 %) WHEN COMPARED WITH ITS ZAT/PTFE (3.
COUNTERPART. THIS MAY LEAD TO AN INCREASE IN THE DIELECTRIC LOSS AS OBSERVED
PTFE/ZAT COMPOSITES.

THE POLYMER CERAMIC COMPOSITES INVESTIGATED IN THIS SECTION HAVE PHYSICAL AND DIELECTRIC PROPERTIES AND CAN BE WELL OPTED FOR ELECTRON APPLICATIONS.

6.3 CONCLUSION

➢ ZAT/GLASS COMPOSITES

- ❖ THE EFFECT OF VARIOUS LOW MELTING AND LOW LOSS GLASSES SUCH AS ZB1, ZB BBSZ, BBS, ABS, MBS, AS AND BB ON THE SINTERING AND THE MICROWAVE DIELECTRIC PROPERTIES OF $0.8ZrTiO_4$-$0.2SnTiO_4$ (ZAT) CERAMICS FOR LTCC APPLICATION HAVE BEEN STUDIED.
- ❖ AMONG THE VARIOUS GLASSES STUDIED, BOROSILICATE GLASSES ARE FOUND TO IN LOWERING THE SINTERING TEMPERATURE WITHOUT ADVERSELY AFFECTING PROPERTIES. THE ADDITION OF 10 WT% BBSZ GLASS LOWERED THE SINTE TEMPERATURE TO ABOUT 950^{O}C. THE SINTERING TEMPERATURE IS FURTHER REDUCED 925^{O}C WITH THE ADDITION OF LIF TO THE ABOVE COMPOSITE.
- ❖ THE XRD AND SEM ANALYSIS INDICATES THE ABSENCE OF ADDITIONAL PHASES COMPOSITE EVEN FOR HIGHER AMOUNT OF GLASS ADDITION.
- ❖ ADDITION OF 0.2 WT% BBSZ GLASS IMPROVED THE DIELECTRIC PROPERTIES OF ZA $Q_u \times f$ OF 120000 GHZ, τ_f OF -7.3 PPM/^{O}C AND A RELATIVE PERMITTIVITY OF 11.7 AT 1400^{O}C. THE MICROWAVE DIELECTRIC PROPERTIES OF ZAT+10WT% BBSZ ARE 12000 GHZ, ε_r = 10.9 AND τ_f = -23 PPM/^{O}C. THE ADDITION OF 0.3 WT% LIF TO THE ABOVE COMPOSITION SLIGHTLY IMPROVED THE QUALITY FACTOR TO 14000 GHZ INCREASED THE τ_f VALUE TO -28 PPM/^{O}C.
- ❖ THE NON-REACTIVITY OF THE LTCC COMPOSITION WITH AG REVEALED THA COMPOSITION SHOWS EXCELLENT CHEMICAL STABILITY AND CAN BE PROPOSED CANDIDATE FOR LTCC SUBSTRATE APPLICATIONS.

➢ ZAT/POLYMER COMPOSITES

- ❖ THE PHYSICAL AND DIELECTRIC PROPERTIES OF PTFE/ZAT AND PE/ZAT COMPOSITE ELECTRONIC PACKAGING APPLICATIONS ARE COMPARED AND STUDIED.

- ❖ THE PTFE/ZAT AND PE/ZAT COMPOSITES ARE PREPARED BY POWDER PROCESSING A MELT MIXING TECHNIQUES RESPECTIVELY. THE PE/ZAT COMPOSITES EXHIBITED A LEVEL OF POROSITY AND LOW WATER ABSORPTION VALUE WHEN COMPARED W PTFE/ZAT COMPOSITES.

- ❖ THE DIELECTRIC PROPERTIES OF THE COMPOSITES ARE MEASURED AT 1 MHZ ANI BOTH THE COMPOSITES POSSESS A LOW VALUE OF RELATIVE PERMITTIVITY AND LOSS. AT 9 GHZ, THE PTFE/ZAT AND PE/ZAT COMPOSITE WITH 0.3 V_F 2.85 AND 4.37 AND $\tan\delta$ = 0.0038 AND 0.0044 RESPECTIVELY. ALSO THEY POSSESS NEARLY STABLE TEMPERATURE VARIATION OF RELATIVE PERMITTIVITY.

- ❖ THE CTE VALUES OF BOTH THE COMPOSITE IS FOUND TO DECREASE WITH INCREAS CONTENT AND REACHES A MINIMUM VALUE OF 28 AND 82 PPM/^{O}C AT 0.5 V_F RESPECTIVELY FOR ZAT WITH PTFE AND PE COMPOSITES. THE RESULTS SUGGEST THAT THE PROPERTIES OF PTFE AND PE CAN BE IMPROVED AND CAN BE USE SUBSTRATE AND ELECTRONIC PACKAGING APPLICATIONS WITH THE AID OF SUIT OF ZAT FILLER.

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CHAPTER 7

CONCLUSIONS AND SCOPE FOR FUTURE WORK

This chapter summarizes the results obtained in various chapters in the thesis and suggests the possibility of further extension of the work.

THE RAPID DEVELOPMENT IN THE MICROELECTRONIC TECHNOLOGIES SUCH AS WIR
INTELLIGENT TRANSPORT SYSTEM (ITS) AND MICROWAVE INTEGRATED CIRCUITS (MIC) H
INCREASE IN THE UTILIZED FREQUENCY FROM KILOMETRE WAVE TO MILLIMETRE WAVE.
FOR CERAMICS IN ELECTRONIC EQUIPMENTS IS GROWING RAPIDLY AS A RESULT OF TH
PHYSICAL AND ELECTRICAL PROPERTIES AND IMMENSE TECHNOLOGICAL APPLICATION
REPORTS THE SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF SOME RARE EARTH
AND ALUMINATE AND THEIR COMPOSITES FOR VARIOUS MICROWAVE APPLICATIONS SUCH
RESONATORS, LOW TEMPERATURE CO-FIRED CERAMICS (LTCC) AND AS ELECTRONIC PA
MATERIALS. THE INVESTIGATIONS PERFORMED ARE DIVIDED INTO SEVEN CHAPTERS.

THE FIRST CHAPTER IS A GENERAL INTRODUCTION TO THE DIELECTRIC RESONATO
SUBSTRATES, LTCC, ELECTRONIC PACKAGING MATERIALS AND THEIR CURRENT TRENDS. IT
MATERIAL REQUIREMENTS FOR THE ABOVE APPLICATIONS AND PRESENT CHALLENGE
DISCUSSES IN DETAIL VARIOUS PREPARATION TECHNIQUES USED FOR THE SYNTHESIS OF C
POLYMER CERAMIC COMPOSITES. A BRIEF ACCOUNT OF STRUCTURAL AND MICRO
CHARACTERIZATION TECHNIQUES LIKE, XRD, ELECTRON DIFFRACTION AND SEM AND
CHARACTERIZATION METHODS USED ARE ALSO INCLUDED. A DETAILED ACCOUNT OF
CHARACTERIZATION OF THE CERAMICS AND POLYMER CERAMIC COMPOSITES ARE ALSO
CHAPTER 2.

CHAPTER 3 STARTS WITH A BRIEF INTRODUCTION TO THE APATITE BASED MATE
STRUCTURAL ASPECTS AND APPLICATIONS, GIVING SPECIAL EMPHASIS TO THE SILI
OXYAPATITES. THE CHAPTER DEALS WITH THE SYNTHESIS AND CHARACTERIZATION O
$A_4RE_6Si_6O_{26}$
[A=CA, SR AND BA; RE = RARE EARTHS] CERAMICS. A DETAILED INVESTIGATION ON THE
USING XRD REFINEMENTS AND TEM REVEALED THAT THE $Ca_4RE_6Si_6O_{26}$ SERIES BELONG TO THE
HEXAGONAL SYMMETRY. HOWEVER, ALL OF THEM EXHIBITED A LOW RELATIVE DENS
95%) EXCEPT FOR BA-SERIES. THE $Sr_4RE_6Si_6O_{26}$ EXHIBITED RELATIVE PERMITTIVITY IN THE RANGE
10-19. A MAXIMUM $Q_u \times f$ OF ABOUT 26000 GHZ IS EXHIBITED BY $Sr_4Sm_6Si_6O_{26}$ WITH ε_r = 14.2
AND A RELATIVELY HIGH τ_f OF -46 PPM/°C. THE MICROWAVE DIELECTRIC PROPERTIES OF THE
COMPOSITIONS ARE CORRELATED WITH THE BOND VALENCE AND BOND STRENGTH VA

THAT AS THE BOND STRENGTH DECREASES, THE RELATIVE PERMITTIVITY AND DIELECTR
TO INCREASE. THE τ_f OF $SrLa_4Si_3O_{13}$ IS TUNED BY THE ADDITION OF SUITABLE AMOUNT OF TiO_2
EVEN THOUGH THE ADDITION OF TiO_2 REDUCES THE $Q_u \times f$ VALUE, THE $Q_u \times f$ IS REDUCED
TO 13300 GHZ WITH AN INCREASE IN τ_f TO NEARLY 21. THE $CaLa_4Si_3O_{13}$ AND $BaLa_4Si_3O_{13}$
CERAMICS HAVE A RELATIVE PERMITTIVITY LESS THAN 20. THE $CaLa_4Si_3O_{13}$ CERAMIC SHOWS A
MAXIMUM QUALITY FACTOR OF 30500 GHZ WITH ε_r = 17.8 AND τ_f = -36 PPM/^{O}C. THE
$BaLa_4Si_3O_{13}$ SERIES SHOWS A RELATIVELY HIGH ε_r AND LOW $Q_u \times f$ VALUE. A MAXIMUM $Q_u \times f$
OF 26100 GHZ IS EXHIBITED BY $SrLa_4Si_3O_{13}$ WITH ε_r =14.2 AND τ_f = -38 PPM/^{O}C.

THE SYNTHESIS, CHARACTERIZATION AND MICROWAVE DIELECTRIC PROPERTIES OF TWO NOVEL RARE EARTH BASED SILICATES, $Sm_2Si_2O_7$ AND $RE_2Ti_2SiO_9$ (RE=LA, PR AND ND) CERAMICS ARE DISCUSSED IN CHAPTER 4. THE STRUCTURAL AND MICROSTRUCTURAL STUDIES REVEALED T OF SINGLE PHASE MATERIALS. THE $Sm_2Si_2O_7$ CERAMICS HAS A TETRAGONAL SYMMETRY WHERE A $RE_2Ti_2SiO_9$ (RE=LA, PR AND ND) DIELECTRIC CERAMICS POSSESS A MONOCLINIC SYMMETRY CALCINATION AND SINTERING TEMPERATURES OF THE ABOVE CERAMICS ARE OPTIMI DENSIFICATION AND MICROWAVE DIELECTRIC PROPERTIES. THE $Sm_2Si_2O_7$ CERAMICS SINTERED AT 1375^{O}C/2H EXHIBIT EXCELLENT DIELECTRIC PROPERTIES, ε_r = 6.8, $Q_u \times f$ = 6 X 10^3 MEASURED AT 9 GHZ. IN ORDER TO REDUCE THE SINTERING TEMPERATURE OF $Sm_2Si_2O_7$ CERAMICS, THE MOST EFFECTIVE METHOD OF GLASS ADDITION IS ADOPTED. SEVERAL LOW LOSS GLASSES SUC $50B_2O_3$ (ZB), $60ZnO\text{-}30B_2O_3\text{-}10SiO_2$ (ZBS), $27B_2O_3\text{-}35Bi_2O_3\text{-}6SiO_2\text{-}32ZnO$ (BBSZ), $22.2MgO\text{-}22.2Al_2O_3\text{-}55.5SiO_2$ (MAS), $35.1Li_2O\text{-}31.7B_2O_3\text{-}33.2SiO_2$ (LBS) AND $20Li_2O\text{-}20MgO\text{-}20ZnO\text{-}20B_2O_3\text{-}20SiO_2$ (LMZBS) ARE ADDED IN DIFFERENT WEIGHT PERCENTAGE TO THE $Sm_2Si_2O_7$ CERAMICS. IT IS NOTED THAT LITHIUM BASED GLASSES ARE MUCH EFFEC REDUCING THE DENSIFICATION TEMPERATURE WITHOUT DEGRADING THE DIELECTRIC P $Sm_2Si_2O_7$ CERAMICS TREATED WITH 15 WT% LBS GLASS LOWERED THE SINTERING TEMPE 975^{O}C, WHEREAS THE 15 WT% LMZBS GLASS ADDITION LOWERED SINTERING TEMPERA 950^{O}C. THE MICROWAVE DIELECTRIC PROPERTIES OF $Sm_2Si_2O_7$ CERAMICS TREATED WITH 15 WT% LBS GLASS AND THAT TREATED WITH 15 WT% LMZBS GLASS ARE ε_r = 6.6, 5.8 AND $\tan\delta$ = 2.5 X 10^3, 2.2 X 10^3 RESPECTIVELY. THE PURE $Sm_2Si_2O_7$ CERAMICS AND THAT MIXED WITH 15WT% LMZBS GLASS DID NOT SHOW MUCH VARIATION IN RELATIVE PERMITTIVITY WITH TEMPE $RE_2Ti_2SiO_9$ (RE=LA, PR AND ND) CERAMICS EXHIBITED A RELATIVE DENSITY ABOUT OF

THESE MATERIALS HAVE A RELATIVE PERMITTIVITY LESS THAN 20 AND τ_f VALUE IS RELATIVELY L
MAXIMUM VALUE OF $Q \times f$ IS SHOWN BY THE $Pr_2Ti_2SiO_9$ CERAMICS. IT IS SEEN THAT PR SUBSTITUTION
FOR LA FAVORED THE FORMATION OF SOLID SOLUTION IN THE WHOLE RANGE OBEYING
WHILE ND SUBSTITUTION RESULTED IN THE FORMATION OF ADDITIONAL PHASES. AS TH
INCREASES, AN IMPROVEMENT IN THE QUALITY FACTOR IS NOTED WHEREAS THE τ_f VALUE REMAINS
AFFECTED. A MAXIMUM QUALITY FACTOR OF ABOUT 34000 GHZ IS OBTAINED IN THE C
$Pr_2Ti_2SiO_9$ WITH ε_r = 29.2 AND τ_f = 19.5 PPM/^{O}C.

CHAPTER 5 DISCUSSES IN DETAIL THE SYNTHESIS AND CHARACTERIZATION OF VARI
CERAMIC COMPOSITE USING $Sr_2Si_2O_7$ CERAMICS AS FILLER FOR ELECTRONIC PACKAGIN
APPLICATIONS. THE POLYMERS USED IN THE INVESTIGATION ARE PTFE, POLYETHYL
POLYSTYRENE. THE PTFE/$Sr_2Si_2O_7$ COMPOSITES ARE PREPARED BY POWDER PROCESSING METH
WHEREAS $Sr_2Si_2O_7$ LOADED POLYETHYLENE AND POLYSTYRENE COMPOSITES BY MELT
TECHNIQUE. THE RELATIVE PERMITTIVITY, DIELECTRIC LOSS ($\tan\delta$) AND VICKERS'
MICROHARDNESS INCREASED WITH INCREASE IN FILLER CONTENT. THE THERMAL CON
INCREASED AND COEFFICIENT OF THERMAL EXPANSION (α_c) DECREASED WITH INCREASE IN FILLER
LOADING FOR ALL THE COMPOSITES. FOR A FILLER FRACTION OF 0.55 PTFE COMPOSITE HAS ε_r = 3.82
AND $\tan\delta$ = 0.0136 (AT 9 GHZ), k_c = 1.76 W/M^{O}C, α_c = 36 PPM/^{O}C, MICROHARDNESS OF 13
KGF/MM^2. PE COMPOSITE HAS ε_r = 5.28 AND $\tan\delta$ = 0.0091(AT 9 GHZ), k_c = 2.97 W/M^{O}C, α_c
= 60 PPM/^{O}C, VICKERS' MICROHARDNESS OF 17 KGF/MM^2. PS COMPOSITE HAS ε_r = 4.60 AND
$\tan\delta$ = 0.0110 (AT 9 GHZ), k_c = 0.29 W/M^{O}C, α_c = 36 PPM/^{O}C, VICKERS' MICROHARDNESS OF
56 KGF/MM^2. THE EFFECT OF COUPLING AGENT AND FILLER PARTICLE SIZE ON THE ABOVE
OF PTFE/$Sr_2Si_2O_7$ COMPOSITES ARE ALSO STUDIED. THE COMPOSITES MODIFIED USING COUP
AGENT AND NANO SIZED FILLER COMPOSITES SHOWS AN INCREASED VALUE FOR BO
PERMITTIVITY AND DIELECTRIC LOSS. HOWEVER, BOTH OF THEM EXHIBITED ENHANCED
MECHANICAL PROPERTIES COMPARED WITH THAT OF THE UNTREATED MICRON SIZED
SEVERAL THEORETICAL MODEL APPROACHES HAVE BEEN EMPLOYED TO PREDICT
PERMITTIVITY, THERMAL CONDUCTIVITY AND COEFFICIENT OF LINEAR EXPANSION OF
SYSTEMS AND THE RESULTS ARE COMPARED WITH THAT OF EXPERIMENTAL DATA. G
THEORETICAL PREDICTIONS ARE FOUND TO BE VALID FOR LOW FILLER CONTENTS.

CHAPTER 6 OUTLINES THE APPLICABILITY OF ZrO_2-TiO_2-Al_2O_3 (ZAT) DIELECTRIC CERAMIC BASED GLASS AND POLYMER COMPOSITES FOR LTCC SUBSTRATE AND E PACKAGING APPLICATIONS RESPECTIVELY. THE FIRST SECTION OF THE CHAPTER 6 DIS EFFORTS TAKEN TO REDUCE THE SINTERING TEMPERATURE BY GLASS ADDITION. THE EFF GLASSES SUCH AS ZnO-BaO-B_2O_3-SiO_2, ZNO-B_2O_3-SiO_2 AND B_2O_3-ZNO-B_2O_3-SiO_2 ON THE MICROSTRUCTURE, DENSIFICATION AND MICROWAVE DIELECTRIC PROPERTIES LTCC APPLICATIONS IS INVESTIGATED. AMONG THE VARIOUS GLASSES ADDED, BBSZ IS F LOWER THE SINTERING TEMPERATURE WITHOUT MUCH AFFECTING THE MICROWAV PROPERTIES. THE XRD AND SEM OF BBSZ GLASS ADDED ZAT COMPOSITES SUGGESTED EXISTENCE OF NO ADDITIONAL SECONDARY PHASES. THE ADDITION OF 10 WT% BBSZ GLA THE SINTERING TEMPERATURE TO 875 °C WITH REASONABLY GOOD MICROWAVE DIELECTRIC PROPER THE QUALITY FACTOR IS FOUND TO INCREASE TO A MAXIMUM VALUE OF ABOUT 120000 GI THE ADDITION OF SMALL WEIGHT PERCENTAGE (0.2 WT%) OF BBSZ GLASS. FURTHER INCR GLASS CONTENT REDUCED THE SINTERING TEMPERATURE BUT ALSO THE DENSITY A PROPERTIES. THE MICROWAVE DIELECTRIC PROPERTIES OF ZAT+10 WT% BBSZ ARE $Q_u \times f$ = 12000 GHZ, ε_r = 10.9 AND τ_f = -23 PPM/°C. THE ADDITION OF 0.3 WT% LIF TO THE ABOVE COMPOSITION SLIGHTLY IMPROVED THE QUALITY FACTOR TO 14000 GHZ BUT ALSO INCRE τ_f VALUE. THE COMPOSITES ALSO POSSESSED HIGH CHEMICAL COMPATIBILITY WITH SILVER BRING OUT THE POSSIBILITY OF USING ZAT/10 WT% BBSZ COMPOSITES FOR LTCC SUBST APPLICATIONS.

THE SECOND SECTION OF THIS CHAPTER COMPARES THE PHYSICAL, DIELECTRIC A PROPERTIES OF ZAT LOADED PTFE AND PE COMPOSITES. THE PE/ZAT COMPOSITES POSSE HIGH RELATIVE DENSITY WHEN COMPARED WITH THE PTFE/ZAT COMPOSITES. FOR LOW CONTENT THE FILLERS ARE UNIFORMLY DISPERSED IN THE MATRIX AND AS THE FILLER C THE AGGLOMERATION ALSO INCREASED AND RESULTED IN POROSITY. THE DIELECTRIC BOTH THE COMPOSITES SHOWS THAT ZAT LOADED WITH PE COMPOSITES EXHIBITED GOO PROPERTIES AND ALSO A VERY LOW WATER ABSORPTION VALUE OF LESS THAN 0.1%. SHOWS THAT ZAT FILLER LOADED COMPOSITES HAVE BETTER PROPERTIES THAN THAT $SM_2SI_2O_7$ FILLER AND CAN BE USED FOR ELECTRONIC PACKAGING APPLICATIONS.

THE MAJOR RESULTS DRAWN FROM THE THESIS ARE PRESENTED IN THE FOLLOV
(TABLE 8.1 TO 8.2).

Table 8.1 The microwave dielectric properties of selected materials proposed for dielectric resonator and LTCC substrate applications.

Material	ST (°C)	ε_R	$Q_U X F$ (GHz)/ *TAN*δ	τ_F (ppm/°C)
$SRLA_4SI_3O_{13}$	1325°C/4H	14.2	26300	-46.0
$SRPR_4SI_3O_{13}$	1325°C/4H	15.6	12200	-9.0
$SRLA_4SI_3O_{13}$ + 10 WT% TIO_2	1225°C/4H	23.4	12000	7.5
$CALA_4SI_3O_{13}$	1350°C/4H	14.9	24800	-20.0
$CAY_4SI_3O_{13}$	1625°C/4H	12.8	30500	-36.0
$CAYB_4SI_3O_{13}$	1625°C/4H	13.2	23500	-13.0
$BALA_4SI_3O_{13}$	1325°C/4H	14.2	26100	-38.0
$LA_2TI_2SIO_9$	1325°C/4H	28.3	29500	22.6
$PR_2TI_2SIO_9$	1325°C/4H	29.2	33700	19.5
$ND_2TI_2SIO_9$	1275°C/4H	30.1	19600	9.6
0.83 $ZNAL_2O_4$-0.17 TIO_2 (ZAT)	1450°C/4H	11.7	91000	1.4
ZAT + 0.2 WT% BBSZ	1400°C/4H	11.9	120000	-7.3
ZAT + 10 WT% BBSZ	950°C/10H	10.9	12000	-23.2
ZAT + 10 WT% BBSZ + 0.3 LIF	925°C/10H	10.5	14500	-28.0
$SM_2SI_2O_7$	1375°C/2H	10.0	0.0060	-----
$SM_2SI_2O_7$+ 15 WT% LBS	975°C/2H	6.1	0.0025	-----
$SM_2SI_2O_7$+ 15 WT% LMZBS	950°C/2H	6.9	0.0026	-----

Table 8.2 The physical and microwave dielectric properties of polymer/ceramic composites for substrate and electronic packaging applications.

Material	Relative Density (%)	Water absorption (%)	Dielectric properties (9 GHz)		*CTE* (ppm/^{o}C)
			ε_R	*TAN*δ	
PTFE/0.5 V_F $SM_2SI_2O_7$	75.3	13.05	3.82	0.0136	36
PTFE/0.5 V_F SILANE TREATED $SM_2SI_2O_7$	81.9	2.17	4.29	0.0105	10
PE/0.5 V_F $SM_2SI_2O_7$	94.6	0.30	5.28	0.0091	60
PS/0.5 V_F $SM_2SI_2O_7$	90.8	0.41	4.60	0.0110	36
PTFE/0.5 V_F ZAT	89.3	3.1	3.24	0.0089	28
PE/0.5 V_F ZAT	91.1	0.05	5.52	0.0050	81

THE SCOPE FOR THE EXTENSION OF THE WORK DESCRIBED IN THIS THESIS LIES MAI
FOLLOWING AREAS. THE FIRST ONE IS TO IMPROVE THE DENSIFICATION AND MICROWA
PROPERTIES OF THE PROPOSED APATITE SILICATES BY SUITABLE DOPANT ADDITION AND
IS SEEN FROM THE RESULTS THAT EVEN THOUGH GLASS ADDITION LOWERS THE SINTERIN
THE MICROWAVE DIELECTRIC PROPERTIES ARE ADVERSELY AFFECTED. HENCE CHEMICA
TECHNIQUES LIKE HYDROTHERMAL, CO-PRECIPITATION, CITRATE-GEL, SOL-GEL ETC. WO
CHALLENGING AREA TOWARDS THE DEVELOPMENT OF THESE SILICATES. VARIOUS POL
COMPOSITES DEVELOPED IN THE PRESENT STUDY MAY BE USED TO FABRICATE SUBSTRATE
AND PRINTED CIRCUIT BOARD APPLICATIONS. MOREOVER EFFORTS MAY BE MADE TO
THERMAL CONDUCTIVITY OF THESE COMPOSITES BY THE ADDITION OF SUITABLE AMO
BROADBAND DRAS OF DIFFERENT GEOMETRIES AND DRA ARRAY USING TEMPERATURE S
CAN ALSO BE FABRICATED USING THE DEVELOPED DR MATERIALS.

LIST OF PUBLICATIONS

Publications in SCI Journals

1. L. A. KHALAM, **Sherin Thomas** AND M. T. SEBASTIAN, "TEMPERATURE-STABLE AND LOW-LOSS DIELECTRICS IN THE $Ba_3B'_2TaO_9$ [B′ = LANTHANIDES, Y, AND IN] SYSTEM", *J. Am. Ceram. Soc.* **90**, 2476-2483 (2007).

2. L. A. KHALAM, **Sherin Thomas** AND M. T. SEBASTIAN, "TAILORING THE MICROWAVE DIELECTRIC PROPERTIES OF $Ba_6Ln_2Ti_4Nb_4O_{30}$ CERAMICS", *Int. J. Appl. Ceram. Tech.* **4**, 359-366 (2007).

3. **Sherin Thomas** AND M. T. SEBASTIAN, "EFFECT OF B_2O_3-SiO_2-ZnO GLASS ON THE SINTERING AND MICROWAVE DIELECTRIC PROPERTIES OF $Ba_5Nd_2Ti_4Nb_4O_{30}$ CERAMICS", *Mater. Res. Bull.* **43**, 843-851 (2008).

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