Tailoring the microwave dielectric properties of BaRE$_2$Ti$_4$O$_{12}$ and BaRE$_2$Ti$_5$O$_{14}$ ceramics by compositional variations

S. SOLOMON, N. SANTHA, I. N. JAWAHAR, H. SREEMOOLANADHAN, M. T. SEBASTIAN
Regional Research Laboratory, Trivandrum-695 019, India
E-mail: mailadils@yahoo.com

P. MOHANAN
Department of Electronics, Cochin University of Science and Technology, Cochin 682022 India

Ceramic dielectric resonators in the BaO-RE$_2$O$_3$-TiO$_2$ (RE = rare earth) system have been prepared by the conventional solid state ceramic route. The dielectric properties have been tailored by substitution of different rare earth oxides and by bismuth oxide addition. The dielectric constants increased with Bi addition whereas the Q decreased. The temperature coefficient of the resonant frequency improved with bismuth addition.
© *2000 Kluwer Academic Publishers*

1. Introduction

Ceramic compositions in the system BaO-RE$_2$O$_3$-TiO$_2$ (RE$_2$O$_3$-rare earth oxide) are extensively used in the manufacture of electronic components. These compositions have high relative permittivity or dielectric constant ($\varepsilon_r \sim 80$) which are useful above 500 MHz, especially for applications like cellular telephones. In pursuit of high-ε ceramics possessing high quality factor (Q) and temperature compensation (zero τ_f), binary oxides of the RE$_2$O$_3$-TiO$_2$ system [1, 2] and ternary oxides of the BaO-RE$_2$O$_3$-TiO$_2$ system [3–20] (RE=La, Pr, Nd, Sm) have been studied by many researchers. The BaO-RE$_2$O$_3$-TiO$_2$ ceramics (RE=Nd, Sm) with stoichiometry near to BaRE$_2$Ti$_5$O$_{14}$ and BaRE$_2$Ti$_4$O$_{12}$ have been widely studied [3–33]. Following earlier reports the BaRE$_2$Ti$_4$O$_{12}$ (BaO : RE$_2$O$_3$: 4TiO$_2$) and BaRE$_2$Ti$_5$O$_{14}$ (BaO : RE$_2$O$_3$: 5TiO$_2$) are represented in this article as 114 and 115 compounds, respectively, for convenience.

Optimization and tailoring of microwave dielectric properties of the ceramics can be achieved by compositional modifications such as doping, partial substitution and solid solution formation to meet the specific needs of the device design engineer. They can also improve the temperature variation of the resonant frequency [8–11]. Several authors [12, 13] reported that substituting Sr for Ba decreased the Q factor and improved the τ_f. Lee and Lin [14] reported that Pb substitution for Ba in BaLa$_2$Ti$_4$O$_{12}$ decreased ε_r, increased Q and improved τ_f. Addition of commercial glass is reported to decrease the sintering temperature, ε_r, Q and τ_f in BaLa$_2$Ti$_4$O$_{12}$ [7]. Valant *et al*. [4] found that addition of WO$_3$ increased the Q but decreased the ε_r whereas Mn addition [5] improved the τ_f keeping ε_r nearly constant. Al-substitution at the Ti site decreased the ε_r, Q and τ_f [6].

Addition of rutile decreased the sintering temperature, and ε_r, and increased the Q and τ_f [6]. Several authors [19, 21, 29–32] reported the effect of Bi$_2$O$_3$ substitution on Nd-based 114 and 115 ceramics. The present study was undertaken to investigate the effect of Bi$_2$O$_3$ addition on the microwave dielectric properties of Nd, Sm, Pr and La-based 114 and 115 ceramics.

2. Experimental

(a) The undoped 114 and 115 ceramics were prepared by weighing high purity (99.9%) BaCO$_3$, RE$_2$O$_3$ (Pr$_6$O$_{11}$ for Pr) in stoichiometric proportions and wet mixed with distilled water and ground in an agate mortar for 1 h and then dried. The dried powders were calcined in platinum crucibles at 1210 °C for 4 h. The calcined powder was again ground well for half an hour and PVA (5%) was added and mixed well. It is then dried and again ground well for half an hour. This fine powder was pressed into cylindrical compacts of about 11 mm diameter and 5–8 mm height under a pressure of about 150 to 175 MPa. The samples were then sintered at appropriate optimized temperatures.

(b) For the Bi-doped 114 and 115 ceramics, the chemicals BaCO$_3$, RE$_2$O$_3$ (Pr$_6$O$_{11}$ for Pr) and TiO$_2$ were weighed in stoichiometric ratios. The powders were mixed well and calcined as described above for undoped ceramics. The calcined powder was then divided into 4 parts. 1 wt % Bi$_2$O$_3$ was added to the first part, 3 wt % of Bi$_2$O$_3$ to the second part, 5 wt % of Bi$_2$O$_3$ to the third and 10 wt % of Bi$_2$O$_3$ to the fourth part. Dielectric resonators were prepared from the powders by the method described above in (a).

(c) For the partial substitution using Bi in $Ba(RE_{1.95}Bi_{0.05})Ti_5O_{14}$ ceramics, stoichiometric amounts of Bi_2O_3 and other oxides were weighed and mixed well. The resonator samples were prepared as described in (a). The samples were sintered at 1320 °C for 4 h.

(d) For the Bi-doped and undoped compositions of $Ba(Nd_xSm_{2-x})Ti_4O_{12}$ and $Ba(Nd_xSm_{2-x})Ti_5O_{14}$ ($x = 0$, 0.5, 1, 1.5, 2), stoichiometric amounts of $BaCO_3$, Nd_2O_3, Sm_2O_3 and TiO_2 were weighed and mixed well. The bismuth-doped samples were prepared by adding 1 wt % of Bi_2O_3 to the calcined powder. The resonator samples were prepared as described in section (a).

The bulk densities of the compacts were measured by the Archimedes method. The sintered pellets were polished and thermally etched near the sintering temperature for 30 min and the surface microstructure studied using scanning electron microscopy (SEM). The phase purities and composition were studied from X-ray diffraction patterns obtained using CuK_α radiation. Microwave dielectric resonator properties such as ε, unloaded Q and τ_f were measured using standard techniques, as explained elsewhere [15].

3. Results and discussion
3.1. Sintered density and sintering temperature
Fig. 1 shows the variation of bulk densities and sintering temperatures of different 115 ceramics as a function of the percentage addition of Bi_2O_3. The addition of Bi_2O_3 decreased the sintering temperature and increased the density. Fig. 2 shows the variation of bulk densities and sintering temperatures of different 114 ceramics as a function of the percentage addition of Bi_2O_3. It can be seen from the figure that the sintered densities of all the compounds increased when a small percentage of Bi_2O_3 is added. The densities of La and Pr-based 114
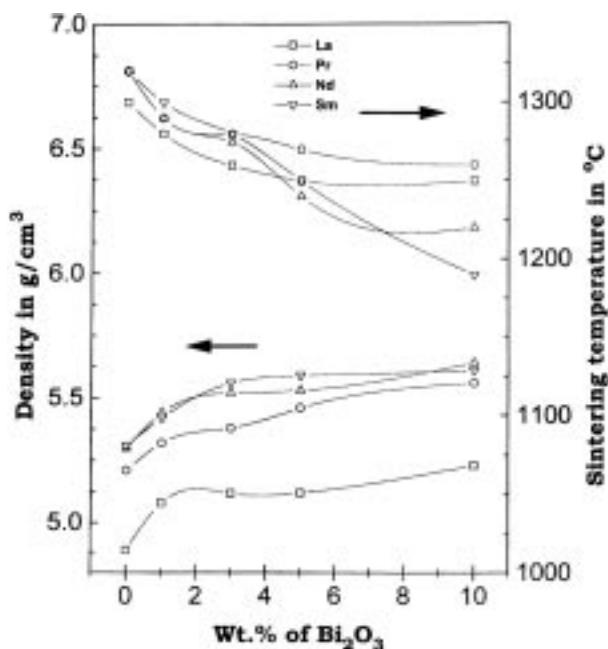

Figure 1 Variation of bulk densities and sintering temperatures of 115 ceramics due to the addition of Bi_2O_3.
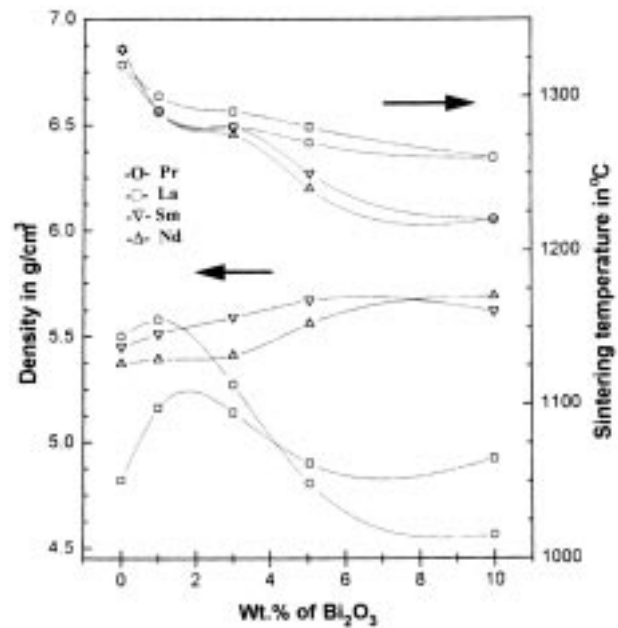
Figure 2 Variation of bulk densities and sintering temperatures of 114 ceramics due to the addition of Bi_2O_3.

compounds showed a decrease in density beyond 1 or 3 wt % addition of Bi_2O_3. This may be due to the porosity that larger amounts of Bi_2O_3 produces.

Table I shows that the variation in densities of $BaRE_{1.95}Bi_{0.05}Ti_5O_{14}$ ceramics due to Bi_2O_3 substitution is relatively small; the values in between those of respective undoped 115 ceramics and those doped with 1% of Bi_2O_3. The sintering temperature of $BaRE_{1.95}Bi_{0.05}Ti_5O_{14}$ ceramics also decreased by a small factor only. In general, addition of a small amount of Bi_2O_3 increased the density of the sintered samples and lowered the sintering temperature.

3.2. X-ray diffraction and electron microscopy
The X-ray diffraction (XRD) patterns obtained for the representative compounds of Bi_2O_3 doped 115 and 114 ceramics using CuK_α radiation are shown in Fig. 3 and Fig. 4, respectively. The patterns are in agreement with earlier reports [16–18]. Kolar *et al.* [19] had observed faint super-structure reflections in their XRD due to doubling of the *c*-axis. Rawn *et al.* [20] have taken into account the super-structure reflections in the refinement of the data. It has been reported that these ceramics may contain many secondary phases such as $Ba_2Ti_9O_{20}$, TiO_2, $RE_2Ti_2O_7$, $BaTi_4O_9$, $RE_4Ti_9O_{24}$, $Ba_4Ti_{13}O_{30}$, etc. [5, 6, 12, 14, 19, 21–26] and it is difficult to get a single phase material. Among these, $Ba_2Ti_9O_{20}$ and TiO_2 are found to be present as secondary phases more frequently.

The crystal system of these ceramics is reported to be tungsten-bronze type orthorhombic. Rawn *et al.* [20] also arrived at an orthorhombic crystal system with doubling of the lattice parameter and space group Pnma. It can be described as consisting of an infinite network of TiO_6 corner-shared octahedra. The RE ions are in the perovskite-like columns surrounded by TiO_6 octahedra. The addition of Bi_2O_3 to 115 and 114 ceramics does not show any significant variation in the XRD patterns. Matveera *et al.* [27] were the first to make an XRD study

T A B L E I Microwave dielectric resonator properties of Ba$\{$RE$_{1.95}$Bi$_{0.05}\}$Ti$_5$O$_{14}$ ceramics

	Density (g/cc)	TE$_{011}$ (GHz)	ε	$Q \times f$ (GHz)	τ_f (ppm$^\circ$C^{-1})
La	5.01	3.8197	89	3290	330
Pr	5.29	3.5286	86	7190	134
Nd	5.35	3.7248	80	10 800	69
Sm	5.40	3.6097	73	6200	$-$30

of the structure of these types of compounds. They reported the crystal structure of Ba$_{3.75}$Pr$_{9.5}$Ti$_{18}$O$_{54}$ single crystals as made up of corner-sharing perovskite-like TiO$_6$ octahedra. Further to that, pentagonal and rhombic channels existed in this framework of linked TiO$_6$ octahedra, which can be occupied by Ba or RE ions. The occupancies of the pentagonal and rhombic sites are found to be different in different reports [20]. Accordingly [28], a solid solution, described by the general formula Ba$_{6-x}$RE$_{8+2/3x}$Ti$_8$O$_{54}$ extends from $x = 0$ through to $x = 3$ for La-containing compounds have been proposed. The solid solutions can have different cations, large size Ba^{2+} and/or RE^{3+}. The variations in composition occur due to possible replacement of Ba^{2+} with RE^{3+}. Thus, to maintain charge neutrality three Ba^{2+} ions should be replaced with two RE^{3+} ions and a vacancy. The concentration of vacancies and ratio of Ba/Sm in the shared channel depend on the composition (x) of the solid solution.

The surface microstructure of typical Bi$_2$O$_3$-added 115 and 114 ceramics obtained using scanning electron microscopy (SEM) are shown in Fig. 5 a to d. The figures show the secondary electron images of polished and thermally etched surfaces of sintered ceramics. Most of the ceramics had columnar grains up to 5 μm in size. The SEM pictures showed relatively low levels of porosity in the ceramics. Ceramics doped with larger amounts of Bi$_2$O$_3$ show secondary phases.

3.3. Dielectric resonator properties
3.3.1. 115 Ceramics
The relative dielectric constants (ε_r) of the ceramics are obtained using the TE$_{011}$ resonant frequencies and dimensions of the resonator. The samples showed sharp TE$_{011}$ resonances in the 3–5 GHz range. Table II lists the TE_{011} mode resonant frequencies and ε_r of these ceramics. It can be seen that Bi$_2$O$_3$ addition increases the ε_r of the ceramics. Fig. 6 shows the variation of ε_r with respect to the percentage of Bi$_2$O$_3$ addition. The increase in ε_r with Bi$_2$O$_3$ addition showed a behavior similar to the increase in density with Bi$_2$O$_3$ addition. The ε_r increases with Bi$_2$O$_3$ doping up to 10 wt %. In the case of Sm-based ceramics the ε increased up to 5 wt % addition of Bi$_2$O$_3$ and further addition decreased ε_r. The BaRE$_{1.95}$Bi$_{0.05}$Ti$_5$O$_{14}$ ceramics show a small increase in the dielectric constant (see Table I). This can be supported by the fact that the increase in density by the Bi-substitution is also very small.
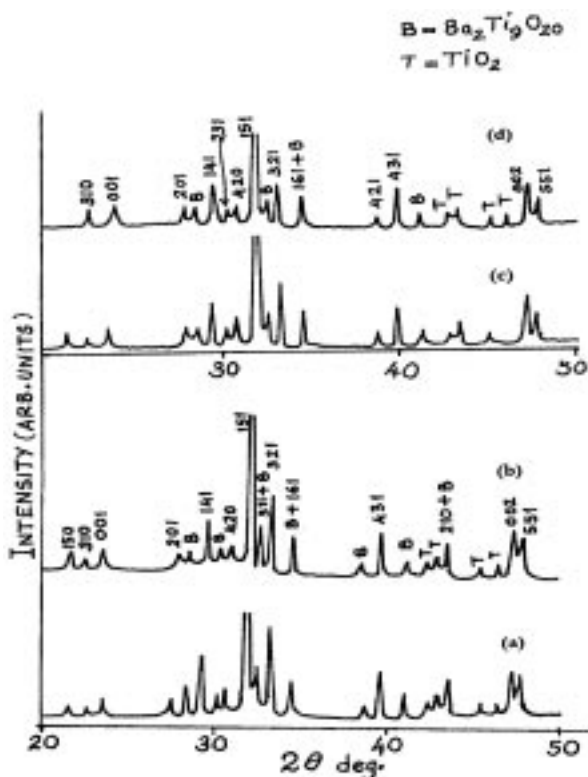

Figure 3 X-ray diffraction (XRD) patterns of typical 115 ceramics (a) La-compound, (b) La-compound with 5% Bi$_2$O$_3$ added (c) Nd-compound and (d) Nd-compound with 5% Bi$_2$O$_3$ added.
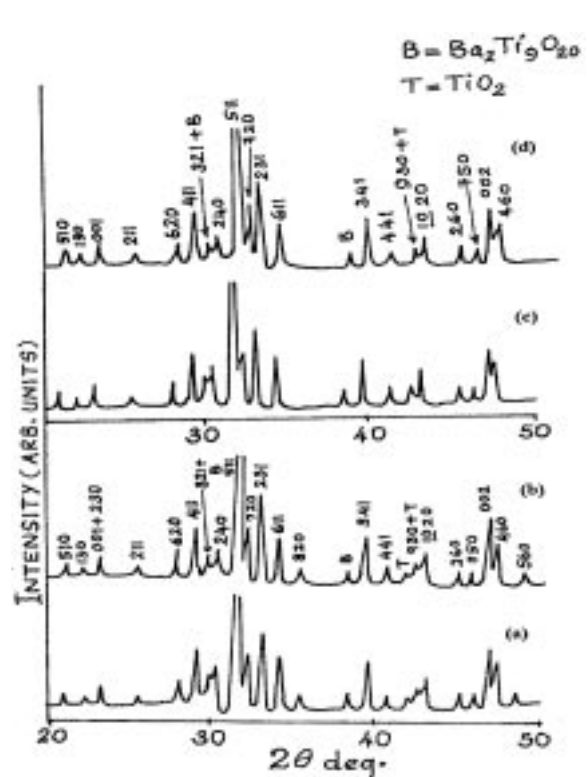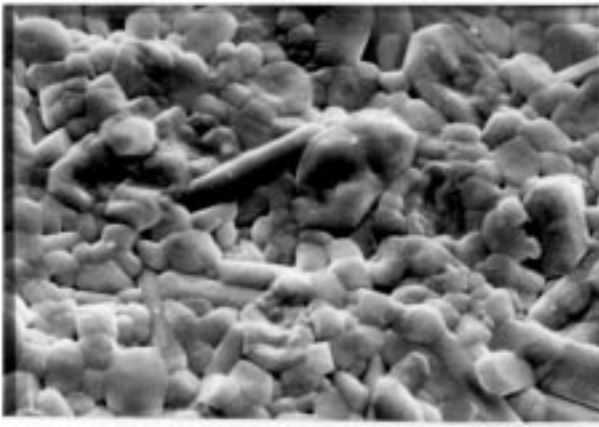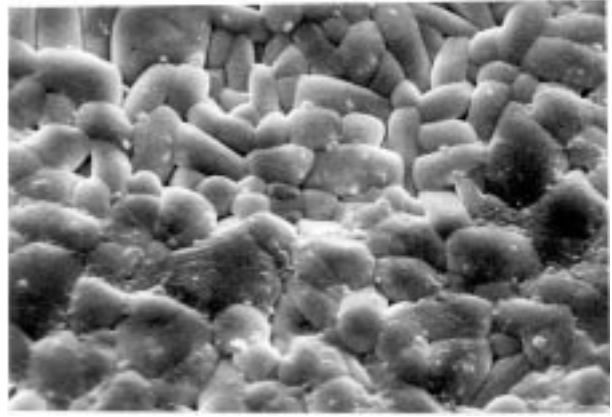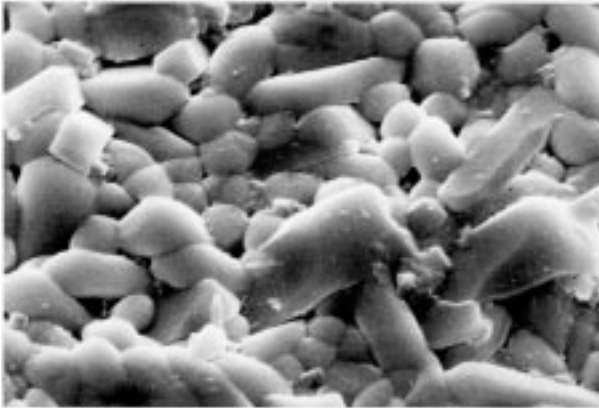

Figure 4 X-ray diffraction (XRD) patterns of typical 114 ceramics (a) La-compound, (b) La-compound with 5% Bi$_2$O$_3$ added (c) Nd-compound and (d) Nd-compound with 5% Bi$_2$O$_3$ added.
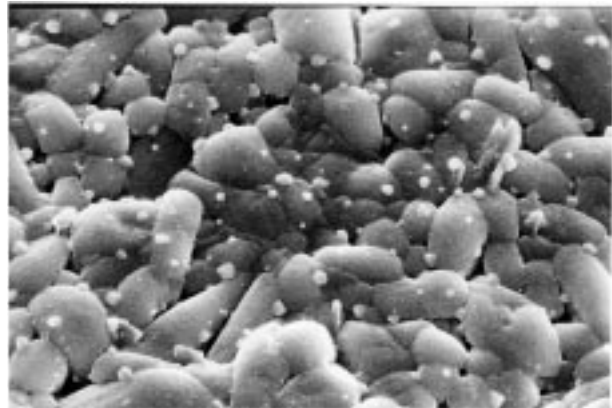
(a)

(b)

(c)

(d)

Figure 5 Secondary electron images of the etched surfaces of 115 ceramics (a) Nd-compound (b) Nd-compound with 10% Bi_2O_3 added. Similar images obtained for 114 ceramics (c) Nd-compound, (d) Nd-compound with 10% Bi_2O_3 added.

3.3.2. 114 ceramics

In the case of 114 ceramics ε_r also gradually increased with Bi_2O_3 addition (see Fig. 7 and Table III). However, $BaLa_2Ti_4O_{12}$ showed a decrease in ε from 97 to 82 when 10% of Bi_2O_3 was added. In addition to this, $BaPr_2Ti_4O_{12}$ ceramics showed a drastic decrease in ε beyond 1 wt % addition of Bi_2O_3. These variations appeared to be dependent on the density (see Fig. 2), although this can also occur due to the change in the composition.

The $Ba(Nd_xSm_{2-x})Ti_5O_{14}$ $(0 < x < 2)$ ceramics have the dielectric constant values in the range 61 to 80 (see Table IV). The dielectric constants of these samples are less than 78 for $BaNd_2Ti_5O_{14}$ and 72 for $BaSm_2Ti_5O_{14}$ ceramics. The experiment was repeated after adding 1% of Bi_2O_3. The Bi_2O_3-added (1%) ceramics have higher ε and lower τ_f (see Fig. 8).

The XRD pattern (Fig. 4) shows the presence of $Ba_2Ti_9O_{20}$ and a small amount of rutile. The SEM studies also show the presence of secondary phases. The ε and τ_f of ceramics containing two phases can be given by the expression [1]

$$\ln \varepsilon = V_1 \ln \varepsilon_1 - V_2 \ln \varepsilon_2$$
$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2}$$

where V_1 and V_2 are the volume fractions of the two phases and ε_1 and ε_2 are their dielectric constants. The

presence of $Ba_2Ti_9O_{20}$ with $\varepsilon_r = 39$ lowers the dielectric constant. The dielectric constant of rutile is 104, $Q \sim 10\,000$ and, $\tau_f = +400$ ppm. Hence, small amounts of rutile as a secondary phase increases ε, Q and τ_f. In the case of ceramics with negative τ_f the presence of rutile changes the τ_f to a positive value. Thus the resultant τ_f and ε depend on the amount of secondary phases. The amount and type of secondary phases depend on the processing conditions and purity of the chemicals used. This is one of the reasons why the results of different investigators are slightly inconsistent.

3.4. The quality factor (Q)

The Q is calculated from the $TE_{01\delta}$ mode of band-rejection filter obtained by coupling the resonators to the stripline. The Q factors are normalized to 1 GHz ($Q \times f$) and are given in Tables I–IV. In the case of 115 ceramics the $Q \times f$ decreased with Bi_2O_3 addition. However, a small increase in $Q \times f$ is observed for La-based ceramics up to 3 wt % of Bi_2O_3 and then it decreased. In 114 ceramics the $Q \times f$ increased initially for small amounts of Bi_2O_3 and then decreased for La, Pr and Nd-based ceramics. The $BaRE_{1.95}Bi_{0.05}Ti_5O_{14}$ ceramics show $Q \times f$ in the range 3300 to 10 800. Partial substitution of Bi^{3+} for RE increased the Q (see Table I). $Ba(Nd_xSm_{2-x})Ti_5O_{14}$ ceramics possess high Q (see Table IV) with $Q \times f$ in the range 7000 to 11 000. The

TABLE II Microwave dielectric resonator properties of Bi_2O_3-doped $BaRE_2Ti_5O_{14}$ ceramics

	Wt % Bi_2O_3	D (mm)	L (mm)	TE_{011} (GHz)	ε	$Q \times f$ (GHz)	τ_f (ppm°C^{-1})
La	0	9.91	11.37	3.2163	85	2800	345
	1	9.43	6.48	3.8979	92	3000	324
	3	9.42	7.71	3.62265	95	3250	213
	5	9.44	7.61	3.618	96	3000	160
	10	9.41	8.2	3.3167	106	1900	139
Pr	0	9.77	8.87	3.6388	78	7090	147
	1	9.48	9.35	3.652	79	5830	132
	3	9.70	9.92	3.428	82	5300	109
	5	9.69	9.31	3.373	90	3400	98
	10	9.71	10.08	3.1499	96	2870	80
Nd	0	9.5	8.83	3.731	78	8900	82
	1	9.47	6.87	4.07875	80	8800	74
	3	9.34	8.37	3.736	84	7400	60
	5	9.38	8.14	3.7046	86	6500	45
	10	9.38	6.51	3.883	93	4400	41
Sm	0	9.56	7.18	4.1872	72	8750	-42
	1	9.75	5.58	3.835	74	7800	-18
	3	9.42	7.52	3.9894	78	8000	-2
	5	9.48	6.37	4.2185	80	6200	-5
	10	9.48	9.39	3.775	74	2000	*

compounds containing $Bi_2O_3 > 10$ wt % did not show resonance. This may be due to the very low quality factor of the samples.

3.5. Temperature coefficient of resonant frequency (τ_f)

The temperature variation of resonant frequencies of Bi_2O_3 added 115 and 114 ceramics, obtained from the slope of the variation of resonant frequency versus temperature are given in Tables II and III respectively.

The τ_f values decrease with increase in the percentage of addition of Bi_2O_3. Valant et al. [19] also have reported that Bi_2O_3 addition up to 6.5 wt % lowers τ_f and further addition increases the τ_f in $BaNd_2Ti_5O_{14}$ ceramics.

In the case of $BaSm_2Ti_5O_{14}$, τ_f improves from -42 ppm °C^{-1} to -5 ppm °C^{-1}. Figs 9 and 10 show the variation in τ_f with respect to the addition of Bi_2O_3 in 115 and 114 ceramics, respectively. Bi^{3+} added compounds show lower τ_f when compared to their corresponding undoped samples (see Table II and III).

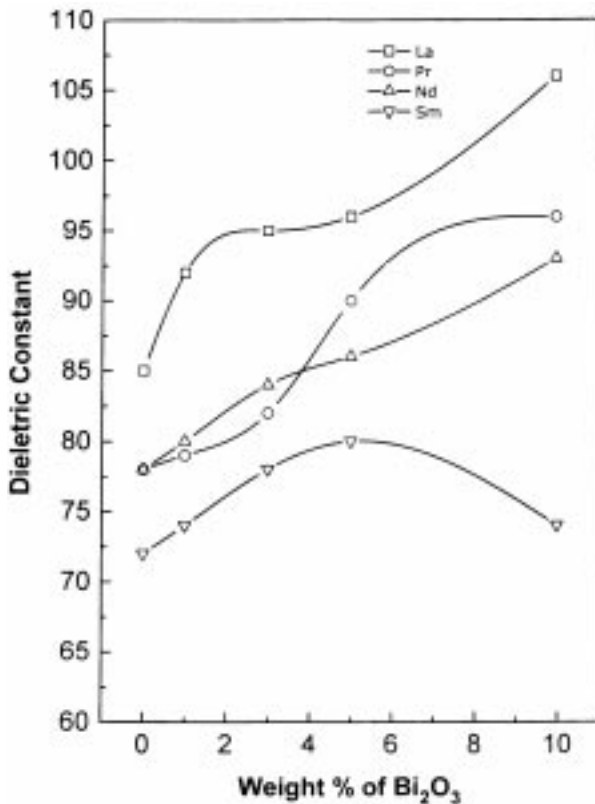Fig. 11 shows the variation in the resonant frequency

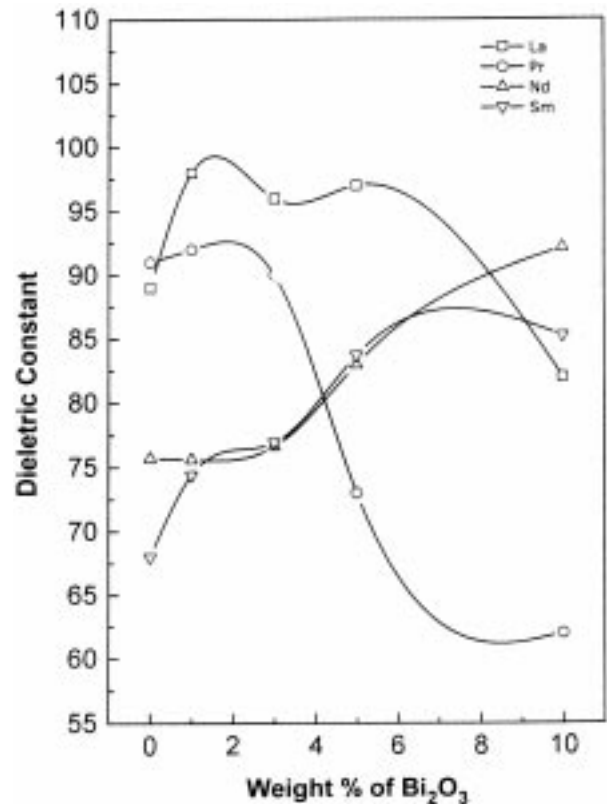Figure 6 Effect of Bi_2O_3 addition on the dielectric constants (ε_r) of 115 ceramics.

Figure 7 Effect of Bi_2O_3 addition on the dielectric constants (ε_r) of 114 ceramics.

TABLE III Microwave dielectric resonator properties of Bi_2O_3-doped $BaRE_2Ti_4O_{12}$ ceramics

	Wt % Bi_2O_3	D (mm)	L (mm)	TE_{011} (GHz)	ε	$Q \times f$ (GHz)	τ_f (ppm°C^{-1})
La	0	9.65	6.14	4.04097	89	1900	301
	1	9.53	6.11	3.8807	98	2100	286
	3	9.55	5.97	3.935	96	2450	197
	5	9.53	8.38	3.4211	97	2250	169
	10	9.91	8.32	3.6121	82	1650	144
Pr	0	9.32	8.35	3.5883	91	5600	135
	1	9.47	5.8	4.1555	92	5650	118
	3	9.59	5.86	4.1385	90	5350	89
	5	9.81	10.16	3.5753	73	4850	75
	10	10.04	9.44	3.939	62	4200	72
Nd	0	9.7	7.19	4.0584	75.7	5600	77
	1	9.79	5.9	4.4575	75.6	6350	63
	3	9.85	8.25	3.778	76.6	4950	56
	5	9.83	9.64	3.4396	83	3100	39
	10	9.77	6.08	3.9604	92.1	2300	28
Sm	0	9.69	6.59	3.429	68	3600	-21
	1	9.65	7.64	4.0303	74.4	3150	-30
	3	9.59	8.04	3.8733	76.9	2000	-52
	5	9.54	7.34	3.8797	83.7	1950	-25
	10	9.7	8.14	3.6375	85.2	2300	-27

with respect to temperature for the Bi^{3+}-substituted $BaRE_{1.95}Bi_{0.05}Ti_5O_{14}$ compounds. The values of τ_f are lower than that of the pure samples.

The τ_f of $BaNd_2Ti_5O_{14}$ is 82 and that of $BaSm_2Ti_5O_{14}$ is -42. Therefore it should be possible to tune τ_f by making solid solution between these compounds. The solid solutions with the general formula $Ba(Nd_xSm_{2-x})Ti_5O_{14}$ have τ_f values between those of the above two compounds. When $x = 0.5$, i.e. $Ba(Nd_{0.5}Sm_{1.5})Ti_5O_{14}$ $\tau_f = +5$ ppm°C^{-1}. The τ_f for $x = 1$, i.e. $Ba(NdSm)Ti_5O_{14}$ is $+10$ ppm°C^{-1}. When 1 wt % of Bi_2O_3 is added to this compound, the τ_f value is reduced to 0.4 and this is useful for practical applications. Fig. 12 shows the variation in the resonant frequency with respect to temperature for

$Ba(Nd_xSm_{2-x})Ti_5O_{14}$ ceramics. Table IV shows the microwave dielectric resonator properties of $Ba(Nd_xSm_{2-x})Ti_5O_{14}$ ceramics. The variation in τ_f and ε_r with respect to x for pure and 1% Bi_2O_3-added $Ba(Nd_xSm_{2-x})Ti_5O_{14}$ ceramics are given in Fig. 8. The $Ba(Nd_xSm_{2-x})Ti_4O_{12}$ ceramics have a very low Q and hence the τ_f could not be measured.

The beneficial influence of bismuth addition on the dielectric properties of the ceramics with ternary compositions from the $BaO-Nd_2O_3-TiO_2$ system was first reported by Kolar et al. [19]. They noticed that by increasing the Bi content, the ε_r and τ_f increased. Several authors [29–32] confirmed the observations of Kolar.
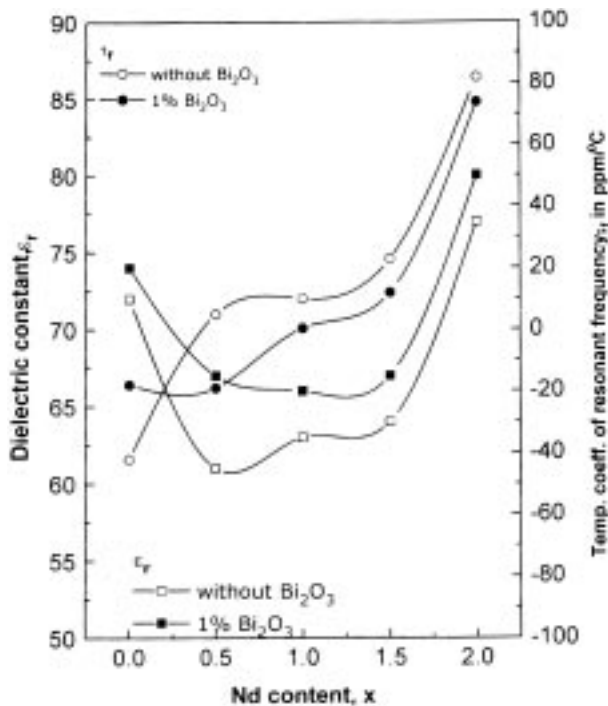

Figure 8 Influence of substitution (x) and Bi_2O_3 addition on the dielectric constants (ε_r) of $Ba(Nd_xSm_{2-x})Ti_5O_{14}$ ceramics.
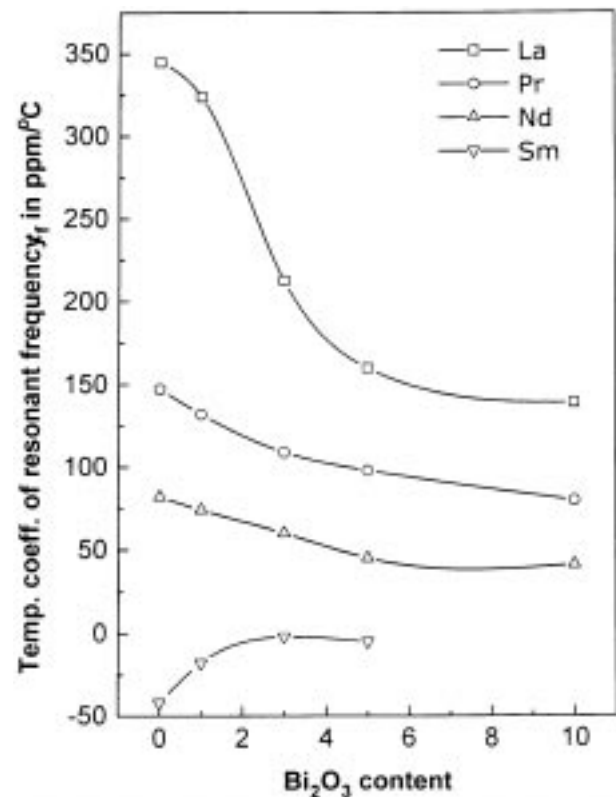

Figure 9 Effect of Bi_2O_3 addition on the temperature coefficient of resonant frequencies (τ_f) of 115 ceramics.

TABLE IV Microwave dielectric resonator properties of Ba{Nd$_x$Sm$_{2-x}$}Ti$_5$O$_{14}$ ceramics

X	Wt % Bi$_2$O$_3$	D (mm)	L (mm)	ρ(g cm^{-3})	TE$_{011}$ (GHz)	ε	Q × f (GHz)	τ$_f$(ppm°C^{-1})
0.0	–0–	9.56	7.18	5.31	4.19	72	8750	− 42.0
	1.0	9.75	5.58	5.42	3.38	74	7450	− 18.0
0.5	–0–	9.44	5.66	5.31	5.05	61	8200	5.0
	1.0	9.39	6.72	5.39	4.35	67	7200	− 19.0
1.0	–0–	9.31	7.35	5.33	4.48	63	8800	10.0
	1.0	9.28	6.46	5.36	4.68	66	9000	0.4
1.5	–0–	9.24	7.67	5.31	4.38	64	11 000	23.0
	1.0	9.36	7.37	5.37	4.38	67	9200	12.0
2.0	–0–	9.50	8.83	5.30	3.73	78	8900	82.0
	1.0	9.47	6.87	5.44	4.08	80	8800	74.0

However, the role of Bi in optimizing the dielectric properties is still a matter of discussion. Recently, it has been reported [32] that Bi^{3+} substitutes for Nd^{3+} in the crystal structure of the BaNd$_2$Ti$_4$O$_{12}$ up to the solubility limit, which was determined to be 2.5 mol %. After exceeding the solubility limit, additional Bi$_2$O$_3$ concentrates as a Bi-enriched phase at the grain boundaries, causing considerable reduction in the Q and increases τ$_f$. Moreover, Valant et al. [33] made a detailed EXAFS (extended X-ray absorption time spectroscopy) study on Ba$_{4.5}$Nd$_{9-y}$Bi$_y$Ti$_{18}$O$_{54}$ (y = 0, 0.5, 1). Due to very similar environments of the equivalent sites in the subcells, only EXAFS can distinguish the different channels. Their results indicate that Bi^{3+} do not substitute for Nd^{3+} randomly on all possible sites. The Bi^{3+} selectively enters one of the following possible channels i.e., R: x = 0.9484, y = 0.2500, z = 0.2939 and/or x = 0.0455, y = 0.2500, z = 0.6928 previously occupied by Nd^{3+}.

A practical problem in the synthesis of these bismuth-substituted materials is related to the conditions necessary to maintain exact stoichiometry and reproducibility due to the vaporization of Bi$_2$O$_3$ at elevated temperatures. Slight changes in stoichiometry can lead to large changes in the microstructure development during sintering. Incomplete substitution of Bi^{3+} for Nd^{3+} due to the evaporation of Bi$_2$O$_3$ during sintering leads to the formation of multiphase ceramics. In such ceramics, the additional phases can increase or decrease ε$_r$ and τ$_f$ of 114 and 115 ceramics and hence the microwave dielectric properties vary according to the contributions of each phase. This is one of the reasons for different dielectric properties reported by different research groups.

4. Conclusion
BaRE$_2$Ti$_5$O$_{14}$ and BaRE$_2$Ti$_4$O$_{12}$ ceramics have been prepared with different trivalent ions for RE and also using different percentages of Bi$_2$O$_3$ as additive and sintered into dense ceramics. The dielectric resonator
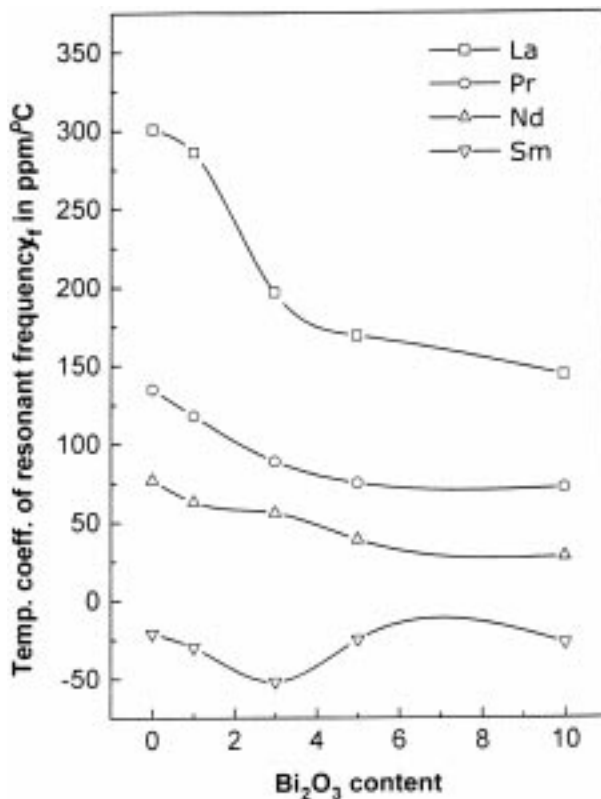

Figure 10 Effect of Bi$_2$O$_3$ addition on the temperature coefficient of resonant frequencies (τ) of 114 ceramics.
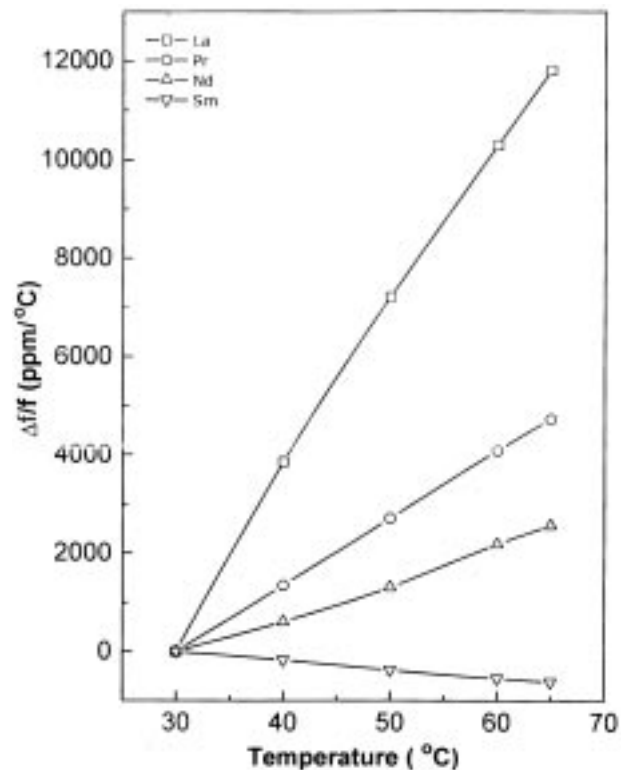

Figure 11 Variation of (Δf/f) as a function of temperature in Ba(RE$_{1.95}$Bi$_{0.05}$)Ti$_5$O$_{14}$ ceramics.
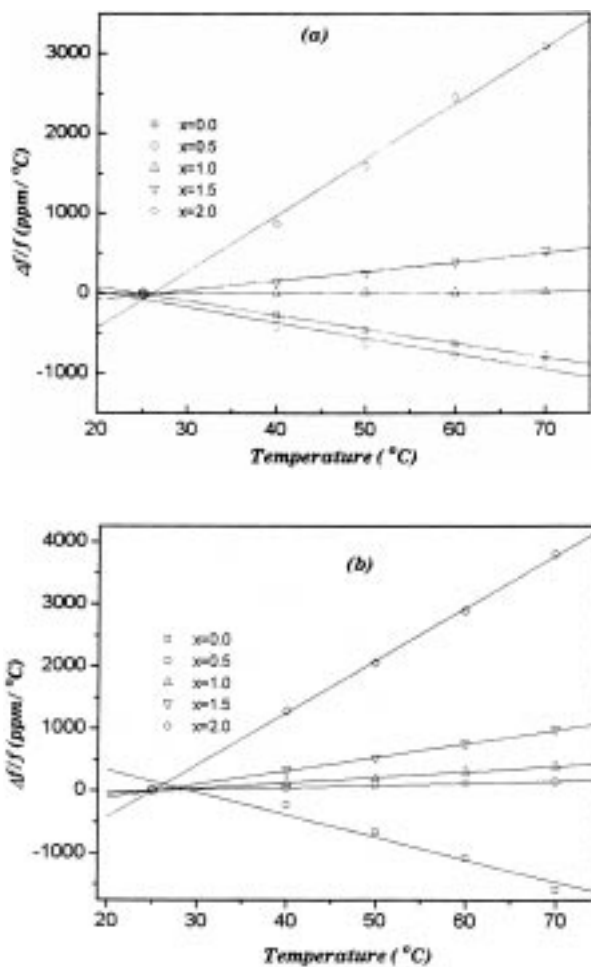
601

Figure 12 Variation of $(\Delta f/f)$ as a function of temperature in Ba(Nd$_x$Sm$_{2-x}$)Ti$_5$O$_{14}$ ceramics. (a) undoped (b) lwt % Bi$_2$O$_3$.

properties of these ceramics have been measured in the microwave frequency range. The ceramics have been characterized using XRD and SEM. It is found that:

1. The dielectric constant (ε) and density increase with increase in the additive content. However, the Q value is found to be good for ceramics with low Bi$_2$O$_3$ content only. Addition of larger amounts of Bi$_2$O$_3$ reduced the Q value considerably.

2. The temperature coefficient of resonant frequency (τ_f) improved with increase in weight percentage of Bi$_2$O$_3$ addition. This shows that Bi$_2$O$_3$ can be added to BaRE$_2$Ti$_5$O$_{14}$ and BaRE$_2$Ti$_4$O$_{12}$ ceramics to adjust ε and τ_f to be useful for practical applications.

3. The τ_f can also be reduced to a desired value by making solid solutions between compositions with positive and negative τ_f.

4. The addition of Bi$_2$O$_3$ lowered the sintering temperature and increased the sintered density up to a certain level and further addition decreased the density.

References

1. A. E. PALADINO, *J. Am. Ceram. Soc.* **54** (1971) 168.
2. J. TAKAHASHI, K. KAGEYAMA and K. KODAIRA, *Jpn. J. Appl. Phys.* **32** (1993) 4327.
3. D. KOLAR, Z. STADLER, S. GABERSCEK and D. SUVOROV, *Ber. Dt. Keram. Ges.* **55** (1978) 346.
4. M. VALANT, D. SUVOROV and D. KOLAR, Proc. III Euro-Ceramics, edited by P. Duran and J. F. Fernandez, Faenza Editrice Iberica S.L. **2** (1993) 235.
5. M. MIZATE, K. UENOYAMA, H. OHSATO, S. NISHIGAKI and T. OKUDA, *Jpn. J. Appl. Phys.* **35** (1996) 5065.
6. H. OHSATO, A. KOMURA, Y. TAKAGI, S. NISHIGAKI and T. OKUDA *ibid.* **37** (1998) 5357.
7. C. C. LEE and P. LIN, *ibid.* **37** (1998) 6048.
8. H. SREEMOOLANADHAN, PhD Thesis, University of Kerala (1997).
9. H. TAKAHASHI, Y. BABA, K. EZAKI, V. OKAMOTA, K. SHIBATA and K. KUROTO, US Patent 5244851 (1993).
10. H. TAKAMI, S. YANO and M. ABE, US Patent 5185304 (1993).
11. T. FUJIMURA, T. YONEDA and H. TAKI, US Patent 5256639 (1993).
12. J. S. SUN, C. C. WEI and L. WU, *J. Mater. Sci.* **27** (1992) 5818.
13. S. NISHIGAKI, KATO, YANO and R. KAMIMURA, *Am. Ceram. Soc. Bull* **66(9)** (1987) 1405.
14. C. C. LEE and P. LIN, *Jpn. J. Appl. Phys.* **37** (1998) 779.
15. R. RATHEESH, H. SREEMOOLANDHAN, P. MONAHAN and M. T. SEBASTIAN, *Ferroelectrics* (1998) 211.
16. JCPDS file 35-331.
17. J. TAKAHASHI, T. IKEGAMI and K. KAGAYEMA, *J. Am. Ceram. Soc.* **74** (1991) 1873; *ibid.* 1868.
18. H. OHSATO, T. OHHASHI, H. KATO, S. NISHIGAKI and T. OKUDA, *Jpn. J. Appl. Phys.* **34** (1993) 187.
19. M. VALANI, D. KOLAR, and D. SUVOROV, Proc. III Euro-Ceramics, edited by P. Duran and J. F. G. Fernandez **2** (1993) 235.
20. C. J. RAWN, D. P. BIRNICA, M. A. BRUCK, J. H. ENEMARK and R. S. ROTH, *J. Mater. Res.* **13** (1998) 187.
21. J. M. DURAND and J. P. BOILOT, *J. Mater. Sci. Lett.* **6** (1987) 134.
22. J. M. WU, M. C. CHANG and P. C. YAO, *J. Am. Ceram. Soc.* **73** (1990) 1599.
23. P. LAFFEZ, G. DESGARDIN and B. RAVEAU, *J. Mater. Sci.* **27** (1992) 5229.
24. H. OHSATO, T. OHHASHI, S. NISHIGAKI, T. OKUDA, K. SUMIYA and S. SUZUKI, *Jpn. J. Appl. Phys.* **32** (1993) 4323.
25. X.M. CHEN, Y. SUZUKI and N. SATO, *J. Mater. Sci. Mater. Electron.* **6** (1995) 10.
26. H. SREEMOOLANATHAN, M. T. SEBASTIAN and P. MOHANAN, *Br. Ceram. Trans.* **95** (1996) 79.
27. R. G. MATVEERA, M. B. VARFOLOMEEV and L. S. IL'YUSHCHENKO, *Zh. Neogan. Khim.* **29** (1984) 31.
28. M. B. VORFOLOMEEV, A. S. MIRONOVA, U. S. KOSTOMAROV, L. A. GOLUBCOVA and T. A. ZOLOTOVA, *ibid.* **33** (1988) 1070.
29. F. AZOUGH, P. SETASWAN and R. FREER, ''Materials and Processes for Wireless Communications,'' edited by T. Negas and H. Ling. *Ceram. Trans.* **53** (The American Ceramic Society, 1995) p. 215.
30. T. NEGAS and P. K. DAVIES, *ibid.* p. 179.
31. D. SUVOROV, M. VALANT and D. KOLAR, *ibid.* p. 197.
32. M. VALANT, D. SUVOROV and D. KOLAR, *J. Mater. Res.* **11** (1996) 928.
33. M. VALANT, I. ARCON, D. SUVOROV, A. KODRE, T. NEGAS and R. FRAHN, *ibid.* **12** (1997) 799.