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$(1-x)MgAl_2O_4$-$xTiO_2$ dielectrics for microwave and millimeter wave applications

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ABSTRACT The $MgAl_2O_4$ ceramics were prepared by the conventional solid-state ceramic route and the dielectric properties studied in the microwave frequency region (3–13 GHz). The phase purity and crystal structure were identified using the X-ray diffraction technique. The $MgAl_2O_4$ spinel ceramics show interesting microwave dielectric properties ($\varepsilon_r = 8.75$, $Q_u x f = 68\,900$ GHz (loss tangent = 0.00017 at 12.3 GHz), $\tau_f = -75$ ppm/°C). The $MgAl_2O_4$ has high negative τ_f, which precludes its immediate use in practical applications. Hence the microwave dielectric properties of $MgAl_2O_4$ spinels were tailored by adding different mole fractions of TiO_2. The ε_r and Q factor of the mixed phases were increased with the molar addition of TiO_2 into the spinel to form mixtures based on $(1-x)MgAl_2O_4$-$xTiO_2$ ($x = 0.0 - 1.0$). For $x = 0.25$ in $(1-x)MgAl_2O_4$-$xTiO_2$, the microwave quality factor reaches a maximum value of $Q_u x f = 105\,400$ GHz (loss tangent = 0.00007 at 7.5 GHz) where ε_r and τ_f are 11.035 and -12 ppm/°C, respectively. The microwave dielectric properties of the newly developed $0.75MgAl_2O_4$-$0.25TiO_2$ dielectric is superior to several commercially available low loss dielectric substrates.

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1 Introduction

Recently various wireless communication systems were developed for kilometer-wave to millimeter-wave applications. The increase in the amount of information to be transported necessitated the need for new low loss dielectric materials for high frequency communication. Millimeter-wave telecommunication can transmit a large amount of information at a very high speed. This is important in intelligent transport systems (ITS), ultra high speed wireless LAN and satellite broadcasting. The following are important characteristics required for a dielectric material used in millimeter-wave telecommunication systems: (a) high quality factor (Qxf) to achieve high selectivity (b) low dielectric constant (ε_r) to reduce the delay time of electronic signal transmission and (c) nearly zero temperature coefficient of resonant frequency (τ_f) for frequency stability. This limits the number of materials available for millimeter wave communication [1–4]. Magnesium aluminate ($MgAl_2O_4$) spinel is a potential refractory material with excellent high temperature mechanical, thermal and chemical properties[5]. It has a high melting point (2130 °C) and low thermal expansivity (7.45 ppm/°C).

It has been reported that [6] the addition of a small amount of TiO_2 improves densification of $MgAl_2O_4$. Yu and Hiragushi reported [7] that the sintered density increased with the 1.5 wt% TiO_2 addition. The addition of more than 1.5% of TiO_2 did not further improve the density and they concluded that exsolution of alumina and dissolution of TiO_2 in spinel was probably the reason for improving the densification. Recently Sarkar and Bannerjee [8] confirmed the improvement in the densification for a smaller amount of TiO_2 additive in alumina rich and stoichiometric spinels sintered at 1550 °C and deterioration of the effect at higher percentage of additive was due to grain growth. Many authors studied the low frequency dielectric properties of $MgAl_2O_4$ [9–11]. In 1991, Shannon and Rossman[12] have measured the dielectric loss factor (0.0008 at 1 MHz) and dielectric constant (8.325) of single crystal $MgAl_2O_4$ using a two-terminal method. However no report is available in the literature on the microwave dielectric properties of polycrystalline $MgAl_2O_4$ spinels. Recently Surendran et al. [4] reported that the low loss dielectrics in the $(1-x)ZnAl_2O_4$-$xTiO_2$ system exhibits ideal characteristics for potential applications as microwave substrates and microelectronic packaging materials. The present investigation reports the microwave dielectric properties of $MgAl_2O_4$ spinels and tailoring its properties by making molar mixtures with TiO_2 to form $(1-x)MgAl_2O_4$-$xTiO_2$ in an effort to develop an alternate temperature stable substrate material for applications in microwave and millimeter wave communication systems.

2 Experimental

The $(1-x)MgAl_2O_4$-$xTiO_2$ ceramics were prepared by the conventional mixed oxide route. High purity $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5\,H_2O$ and Al_2O_3 (Purity 99.9%; Aldrich Chemical Co.) were used as the starting materials for the synthesis of $MgAl_2O_4$ spinels. The chemicals were weighed according to the stoichiometric compositions

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and were ball milled in a polyethylene bottle using zirconia balls in deionized water for 24 hours. The slurry was dried at 100 °C in hot air oven and was calcined at 1100 °C for four hours. The phase purity of the spinel was established through the X-ray diffraction technique. It was then ball milled with Anatase TiO_2 (Aldrich 99.9% pure) according to the formula $(1-x)MgAl_2O_4$-$xTiO_2$ ($x = 0.0, 0.1, 0.12, 0.14, 0.16, 0.18, 0.20, 0.25, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0) for 24 hours using deionized water as the mixing medium. The slurry was dried and was then ground for several hours in agate mortar. Four wt % of poly vinyl alcohol (PVA) was added as the binder and were pressed into cylindrical disks of about 14 mm diameter and 6–8 mm thickness in a tungsten carbide die under a pressure of about 150 MPa. These compacts were fired at a rate of 5 °C/min up to 600 °C and soaked at 600 °C for 1 hour to expel the binder before they were sintered in the temperature range 1400–1460 °C for four hours in air at a heating rate of 10 °C/hour. The sintered samples were annealed at 1000 °C for five hours. The well-polished ceramic pellets with an aspect ratio (D/L) of 1.8 to 2.2 which was found to be the best for maximum separation of the modes, were used for microwave measurements. The bulk density of the sintered samples were measured using Archimedes method. The powdered samples were used for analyzing the X-ray diffraction patterns using Cu K_α radiation (Rigaku - Dmax 1C, Japan).

The dielectric properties ε_r and τ_f of the materials were measured in the microwave frequency range using a network analyzer HP 8510C (Hewlett-Packard, Palo Alto, CA). The dielectric constant ε_r was measured by the post resonator method of Hakki and Coleman [13] and the dielectric sample was end shorted with finely polished copper plates coated with gold. The microwaves are coupled through E-field probes as described by Courtney[14]. The TE_{011} mode of resonance, which is least perturbed by the surrounding field variations was used for measurements. The unloaded quality factor Q_u of the resonance was determined using a copper resonant cavity[15] whose interior was coated with silver; the ceramic dielectric was placed on a low loss quartz spacer. The coefficient of thermal variation of resonant frequency (τ_f) was measured by noting the temperature variation of the resonant frequency of TE_{011} mode in the reflection configuration over a range of temperature 25–75 °C when the sample was kept in the end shorted position.

3 Results and Discussion

The density of sintered pure $MgAl_2O_4$ was measured to be 3.48 g/cm^3 which is about 97% of its theoretical density [16](3.58 g/cm^3). Figure 1 shows the variation of bulk density of $(1-x)MgAl_2O_4$-$xTiO_2$ ceramics as a function of x. The ceramics show a non-linear variation of density with TiO_2 content. Initially the density increases up to $x = 0.15$ and then decreases. The density again increases for $x > 0.4$. This densification behavior of $MgAl_2O_4$-TiO_2 system is different from that of similar [4] $ZnAl_2O_4$-TiO_2 system where the densification is maximum near the zero τ_f region. This is due to the formation of $MgTiO_3$ and Mg_2TiO_4 in the mixed phase region which can severely hinder the densification phenomena. It should be noted that good densification was observed near $x = 0.15$ where the unloaded quality factor reaches its maximum. The theoretical density of TiO_2 (rutile) is 4.26 g/cm^3 It has been reported [17] that the densification behaviour of TiO_2 is hindered due to the anatase to rutile phase transition consequent to the reduction of Ti^{4+} to Ti^{3+}. Hence we doped TiO_2 with 1 mol % additive Fe_2O_3, which improved the densification process. The density reported in Fig. 1 for $x = 1$ in $(1-x)MgAl_2O_4$-$xTiO_2$ corresponds to that of Fe_2O_3 doped titania.

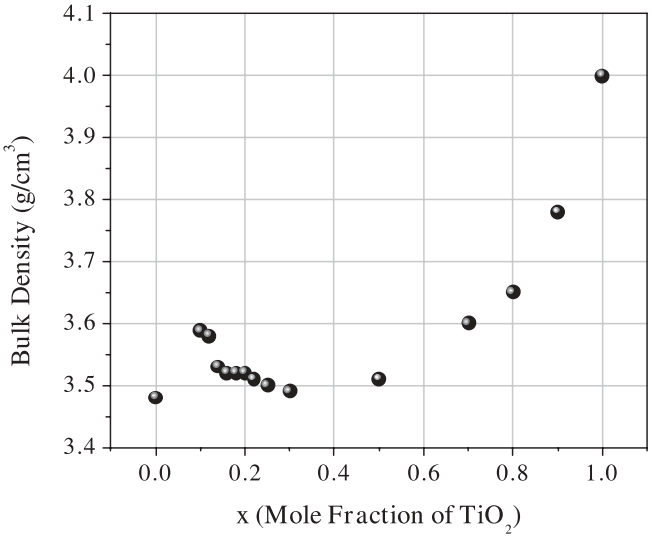

FIGURE 1 Variation of bulk density of $MgAl_2O_4$ with a TiO_2 addition

The X-ray diffractograms recorded from $x = 0.0, 0.12, 0.14, 0.16, 0.18, 0.2, 0.3, 0.5, 0.7, 0.9$ and 1.0 in $(1-x)MgAl_2O_4$-$xTiO_2$ are given in Fig. 2. The crystal structure of $MgAl_2O_4$ is cubic fcc [16] which can be indexed using the JCPDS File Card No. 33-853. As the concentration of TiO_2 in $MgAl_2O_4$ increases, an additional phase $MgTiO_3$ (JCPDS File Card No. 6-494) was formed consequent to the reaction between spinel and rutile. For 20 and 30 mole % of TiO_2 additions, the presence of another magnesium titanate, Mg_2TiO_4 (JCPDS File Card No. 25-1157) was also detected in the XRD-patterns. It is worthwhile to note that the detrimental effects of spinel structured Mg_2TiO_4 in $MgAl_2O_4$-TiO_2 mixtures cannot be ruled out, as a recent study[18] pointed out that a stable solid solution is possible between similar structured $MgAl_2O_4$ and Mg_2TiO_4. A previous investigation [8] revealed that presence of a low melting phase formed at the grain boundary during excess doping of TiO_2 caused micro cracks, which could degrade the densification of spinel. The formation of low dielectric constant phases like $MgTiO_3$ and Mg_2TiO_4 on adding TiO_2 to $MgAl_2O_4$ was reported by Yu and Hiragushi [7]. Though anatase TiO_2 was used in this investigation as starting material, it converts into rutile (JCPDS File Card No. 21-1276) at temperature above 700 °C whose XRD is shown in Fig. 2.

The dielectric constant of pure $MgAl_2O_4$ is measured to be 8.75. The dielectric constant of pure TiO_2 is 93.8 and that doped with Fe_2O_3 is 105. The dielectric constant of a mixture can be calculated using the general Maxwell–Wagner formula [19] for the calculation of the dielectric constant of

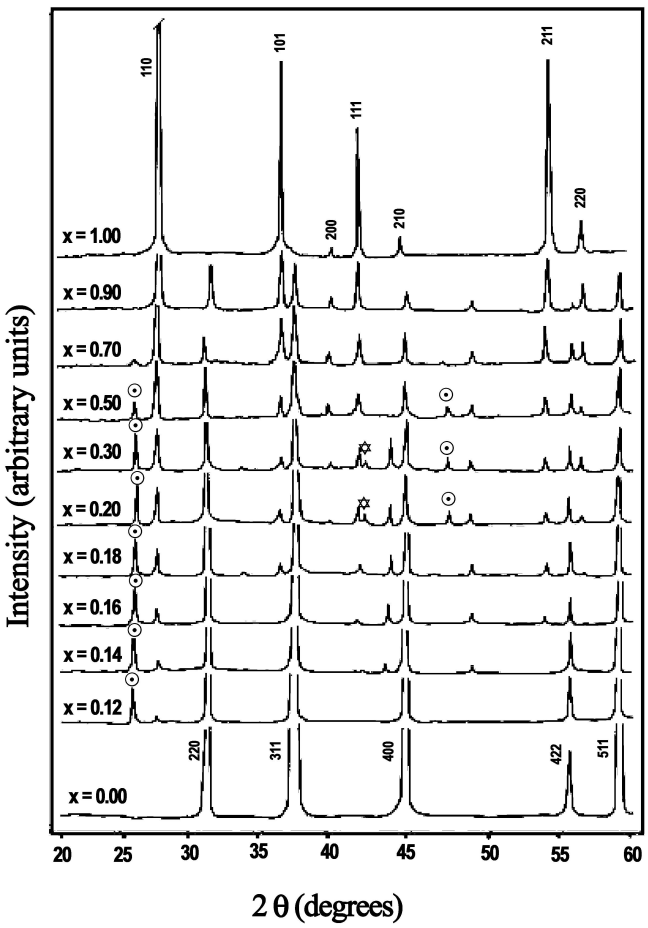

FIGURE 2 Powder diffraction pattern of $(1-x)MgAl_2O_4$-$xTiO_2$ system for $x = 0.0$, 0.12, 0.14, 0.16, 0.18, 0.20, 0.30, 0.50, 0.70, 0.90 and1.0. ⊙ represents $MgTiO_3$ and ✡ represents Mg_2TiO_4 phases

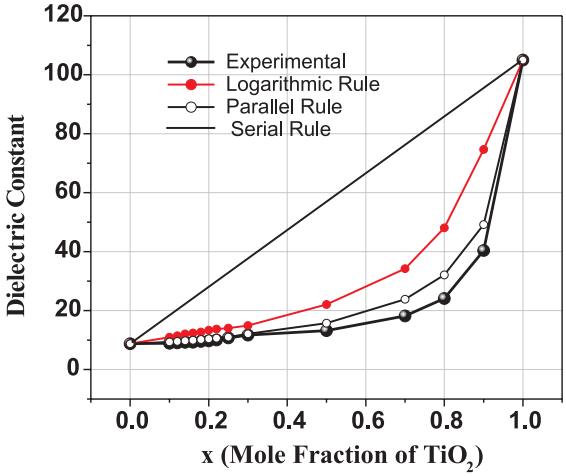

FIGURE 3 Variation of ε_r of $MgAl_2O_4$ with a TiO_2 addition

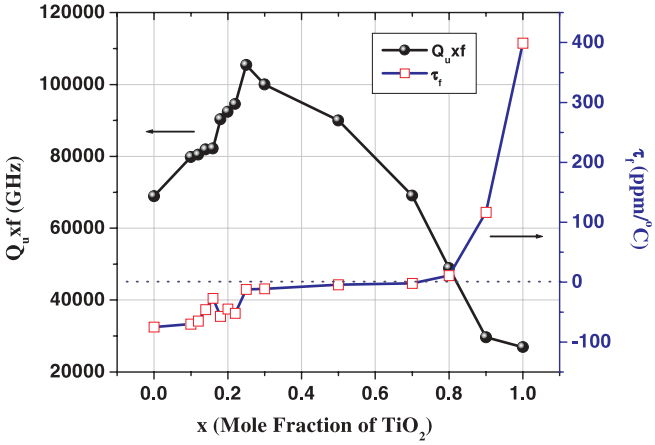

FIGURE 4 Variation of Q_u and τ_f of $MgAl_2O_4$ with a TiO_2 addition

the compound

$$\varepsilon_r^{\alpha} = \Sigma V_i \varepsilon_{ri}^{\alpha} \quad (1)$$

where V_i and ε_{ri} are the volume fraction and relative dielectric constant of the ith material and α is a constant which depends on the type of the mixing rule.

$\alpha = 1$ (serial mixing model)
$\alpha = -1$ (parallel mixing model)
$\alpha = 0$ (logarithmic mixing model)

It must be noted that such plots are made by curve fitting and do not have any physical significance in the two-phase region. Using the rule of mixtures, the dielectric constant of the mixture is calculated and is plotted as function of the mole fraction of TiO_2 addition as shown in Fig. 3. The deviation from the ideal curve fitting plots are believed to be due to the presence of additional phases. It is interesting to note that the dielectric constant is ~ 20 for the mixture phases between $x = 0.7$ and 0.8 in $(1-x)MgAl_2O_4$-$xTiO_2$ ceramics where the τ_f approaches zero value.

The unloaded quality factor and τ_f of $MgAl_2O_4$ are plotted in Fig. 4 with as a function of TiO_2 content. The quality factor $Q_u xf$ of pure $MgAl_2O_4$ is 68 900 GHz (loss tangent = 0.00017 at 12.3 GHz), which is higher than that of many of the conventional spinels with low dielectric constants. As the TiO_2 concentration in $MgAl_2O_4$ increases, the microwave quality factor also increases, reaching a maximum value of $Q_u xf$ =105 400 GHz (loss tangent = 0.00007 at 7.5 GHz) for $x = 0.25$ in $(1-x)MgAl_2O_4$-$xTiO_2$. For higher TiO_2 contents, the quality factor decreases as is evident from

Fig. 4. Compositions in the mixture region between $x = 0.7$ and 0.8 in $(1-x)MgAl_2O_4$-$xTiO_2$ where the τ_f approaches minimum values, have reasonably good quality factors ($Q_u xf$ = 49 000 to 69 000 GHz). It must be remembered that the quality factor, which depends considerably on the synthesizing conditions, purity of the chemicals and densification of the samples during sintering, does not follow any mixture rule in the entire range of spinel-rutile mixtures. Moreover, the quality factor of the intermediate phases is more than the end members which we have observed in another rutile-spinel [4] mixture too.

Table 1 compares the dielectric properties of $0.75MgAl_2O_4$-$0.25TiO_2$ substrate with other commercially important substrates such as Fused Silica, Teflon (or PTFE), Cordierite, Alumina, Aluminum Nitride and Beryllia. It is evident that even though the newly developed dielectric has a slightly higher dielectric constant (11.03), it is superior to a number of commercial dielectrics due to its extremely lower

Substrate	Density	Dielectric Constant ε_r	Dielectric Loss Tanδ (at frequency)	Reference
Sintered Alumina (Al_2O_3)	3.97	8.9	0.00002 (10 GHz)	20
Aluminium Nitride (AlN)	3.26	8.8	0.0001 (1 MHz)	21
Beryllium Oxide (BeO)	3.01	6.5	0.0005 (1 MHz)	21
Fused Silica (SiO_2)	2.20	3.8	0.0001 (10 GHz)	22
Teflon (PTFE)	2.16	2.1	0.0002 (1 MHz)	23
Cordierite ($2MgO\text{-}2Al_2O_3\text{-}5SiO_2$)	2.30	4.5	0.0007 (1 MHz)	24
Spinel-Rutile (new) ($0.75MgAl_2O_4\text{-}0.25TiO_2$)	3.50	11.03	0.00007 (7.5 GHz)	Present Paper

TABLE 1 Comparison of dielectric properties of the new spinel-rutile composition with commercial dielectric substrates

dielectric loss factor in the microwave region (0.00007 at 7.5 GHz) (see Table 1).

The temperature coefficient of resonant frequency (τ_f) of pure $MgAl_2O_4$ is -75 ppm/°C. The TiO_2 known to have a high temperature coefficient of resonant frequency of 398 ppm/°C. As the TiO_2 content in $MgAl_2O_4$ increases the τ_f must assume less negative values owing to a general mixture rule. But it can be seen from Fig. 4 that for $x = 0.16$ τ_f is -27 ppm/°C but for $x = 0.18$ it again shifted to -57 ppm/°C. The fluctuating nature of the temperature coefficient of TiO_2 added $MgAl_2O_4$ might be attributed to the formation of $MgTiO_3$ which is also a low loss dielectric. The zero τ_f region of the mixture is expected to be between $0.3ZnAl_2O_4\text{-}0.7TiO_2$ and $0.2ZnAl_2O_4\text{-}0.8TiO_2$ compositions. In $(1-x)ZnAl_2O_4\text{-}xTiO_2$ mixture, the zero τ_f region is in the spinel rich region [4] where as in $(1-x)MgAl_2O_4\text{-}xTiO_2$, it occurs in the rutile rich region of the mixture.

From the above discussion it reveals that unlike in $ZnAl_2O_4\text{-}TiO_2$ mixtures, $MgAl_2O_4$ spinels react with TiO_2 to form secondary phases, which affect the unloaded quality factor of the mixed phases. The properties of the temperature compensated low loss dielectrics (1-x) $MgAl_2O_4\text{-}xTiO_2$ could be improved by suppressing the formation of additional phases such as $MgTiO_3$ and Mg_2TiO_4 using suitable modification of the synthesizing conditions or doping.

4 Conclusions

The microwave dielectric properties of $(1-x)MgAl_2O_4\text{-}xTiO_2$ mixtures were investigated for possible applications as substrates and microelectronic packages in microwave and millimeter wave communication systems. The samples were synthesized using mixed oxide route. Pure $MgAl_2O_4$ dielectrics have $\varepsilon_r = 8.75$, $Q_u x f = 68\,900$ GHz (loss tangent = 0.00017 at 12.3 GHz), $\tau_f = -75$ ppm/°C in the microwave frequency range. The dielectric constant increased with the molar addition of TiO_2 into the spinel to form mixtures based on $(1-x)MgAl_2O_4\text{-}xTiO_2$ ($x = 0.0 - 1.0$). The microwave quality factor increases with TiO_2 addition reaching a maximum value of $Q_u x f = 105\,400$ GHz (loss tangent = 0.00007 at 7.5 GHz) for $0.75MgAl_2O_4\text{-}0.25TiO_2$ where ε_r and τ_f are 11.035 and -12 ppm/°C, respectively. The low loss dielectrics in the mixture region between $x = 0.7$ and 0.8 in $(1-x)MgAl_2O_4\text{-}xTiO_2$ where the τ_f approaches minimum values, have high quality factors ($Q_u x f = 49\,000$ to 69 000 GHz). The properties of the temperature compensated low loss dielectrics $(1-x)MgAl_2O_4\text{-}xTiO_2$ could be improved by suppressing the formation of additional phases such as $MgTiO_3$ and Mg_2TiO_4 using suitable modification of the synthesizing conditions or doping.

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