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Journal of the European Ceramic Society 32 (2012) 2359–2364

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Effect of Zn^{2+} substitution on the microwave dielectric properties of $LiMgPO_4$ and the development of a new temperature stable glass free LTCC

Dhanesh Thomas, Mailadil T. Sebastian *

Materials Science and Technology Division, National Institute for Interdisciplinary Science and Technology, CSIR, Trivandrum 695019, India

Received 11 December 2011; accepted 31 January 2012
Available online 24 February 2012

Abstract

The $LiMg_{(1-x)}Zn_xPO_4$ ceramics have been prepared by the solid state ceramic route. The $LiMg_{(1-x)}Zn_xPO_4$ ceramic retains the orthorhombic structure up to $x = 0.2$. The compositions with $0.3 \leq x \leq 0.8$ exist as a mixture of orthorhombic and monoclinic phases. When Mg^{2+} is fully replaced with Zn^{2+} ($x = 1.0$) complete transition to monoclinic phase occurs. The ceramic with $x = 0.1$ ($LiMg_{0.9}Zn_{0.1}PO_4$) sintered at 925 °C exhibits low relative permittivity (ε_r) of 6.7, high quality factor ($Q_u \times f$) of 99,700 GHz with a temperature coefficient of resonant frequency (τ_f) of −62 ppm/°C. The slightly large τ_f is adjusted nearly to zero with the addition of TiO_2. $LiMg_{0.9}Zn_{0.1}PO_4$–TiO_2 composite with 0.12 volume fraction TiO_2 sintered at 950 °C shows good microwave dielectric properties: $\varepsilon_r = 10.1$, $Q_u \times f = 52{,}900$ GHz and $\tau_f = -5$ ppm/°C. The ceramic is found to be chemically compatible with silver.

Keywords: Sintering; Porosity; Dielectric properties; Substrates; Glass free LTCC

1. Introduction

The past two decades have witnessed revolutionary changes in wireless communication which stimulated the development of new technologies. Low temperature co-fired ceramic (LTCC) technology has emerged as the paramount technology for the production of miniaturized microwave devices at a relatively low cost. LTCC technology offers high level of passive integration, performance stability and reliability. The ceramic system used for LTCC applications should meet the requirements such as low relative permittivity, low dielectric loss, temperature stability of dielectric properties, low coefficient of thermal expansion and high thermal conductivity. Most importantly the ceramic should be chemically compatible with silver and its sintering temperature must be less than the melting point of silver (961 °C) which is the most commonly used electrode material.[1] Low bulk density of the ceramic is also desirable for the production of light weight electronic modules. These stringent requirements limit the number of materials available for practical applications.

Most of the conventional ceramics with good microwave dielectric properties have very high sintering temperature which is unsuitable for LTCC applications. However, the sintering temperature can be lowered by the liquid phase sintering through the addition of glasses with low melting point.[1] Another method to produce LTCC is through the glass-ceramic route.[2] In both the above mentioned approaches, presence of amorphous phase in the system may degrade the microwave dielectric properties and enhance the possibility of chemical reaction between the substrate and metal electrode.[3] The presence of glass phase may also reduce the ease of processing while tape casting. It is also possible to lower the sintering temperature by using fine powders prepared through wet chemical processing. However, the chemical synthesis is complicated and expensive.[4] Therefore a glass free ceramic with good microwave dielectric properties is desirable for LTCC applications.

Large number of glass free ceramics has been reported in the literature for LTCC applications. Among them Te and Bi based ceramics are found to have very low sintering temperature (<850 °C).[4–13] However, most of the Te-based systems are reactive with silver which limits their practical applications. It should also be noted that any densification of ceramics below 800 °C may prevent the complete evaporation of organics added for tape casting and leave

* Corresponding author. Tel.: +91 471 2515294; fax: +91 471 2491712.
E-mail addresses: mailadils@yahoo.com, mtsebastian@niist.res.in (M.T. Sebastian).

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doi:10.1016/j.jeurceramsoc.2012.01.031

out residual carbon which is detrimental to the microwave dielectric properties.[2] Li_3NbO_4 ceramic sintered at 930 °C is found to have good microwave dielectric properties ($\varepsilon_r = 15.8$, $Q_u \times f = 55{,}009$ GHz and $\tau_f = -49$ ppm/°C). The ceramic is also found to be chemically compatible with silver (Ag).[14] Recently, Bian et al. reported the microwave dielectric properties of $(La_{0.5}Na_{0.5})_{1-x}(Li_{0.5}Nd_{0.5})_xWO_4$ ceramics. The composition with $x = 0.3$ sintered at 800 °C has remarkable dielectric properties: $\varepsilon_r = 12.7$, $Q_u \times f = 23{,}500$ GHz and $\tau_f = -1.4$ ppm/°C at microwave frequency. However, the ceramic is found to be reactive with Ag.[3] $Ca_{1-x}(Li_{0.5}Nd_{0.5})_xWO_4$ scheelites constitute another class of glass-free LTCC. $Ca_{0.8}(Nd_{0.5}Li_{0.5})_{0.2}WO_4$ has an ε_r of 11.7, $Q_u \times f$ of 36,700 GHz, and τ_f of 5.4 ppm/°C and is chemically compatible with Ag.[15]

A few glass free phosphates are also reported to be suitable for LTCC applications. Bian et al.[16] studied the microwave dielectric properties of AMP_2O_7 (A = Ca, Sr; M = Zn, Cu). The ceramics can be sintered at a low temperature (≤950 °C) and possess low relative permittivity ($\varepsilon_r < 8$). $SrCuP_2O_7$ sintered at 925 °C has the highest $Q_u \times f$ greater than 100,000 GHz and lowest τ_f of −62 ppm/°C. Nevertheless all the compositions react with silver. Cho et al. reported the microwave dielectric properties of $BiPO_4$ which has a low sintering temperature of 950 °C. The ceramic has an ε_r of 22, $Q_u \times f$ of 32,500 GHz and a τ_f of −79 ppm/°C.[17] The value of τ_f is large and the reactivity with silver has not been reported. In our previous paper we reported the microwave dielectric properties of olivine type $LiMgPO_4$. The ceramic sintered at 950 °C shows an ε_r of 6.6, $Q_u \times f$ of 79,100 GHz and τ_f of −55 ppm/°C.[18] $LiMgPO_4$ sintered at 950 °C with 0.12 volume fraction TiO_2 has good microwave dielectric properties: $\varepsilon_r = 10$, $Q_u \times f = 26{,}900$ GHz and $\tau_f = +1.2$ ppm/°C.

In the present paper we report the effect of Zn^{2+} substitution for Mg^{2+} on the microwave dielectric properties of $LiMgPO_4$ with an objective to develop new low cost, light weight, glass free ceramics having excellent microwave dielectric properties for LTCC applications.

2. Experimental

$LiMg_{(1-x)}Zn_xPO_4$ ceramics were prepared by the solid state ceramic route. High purity Li_2CO_3 (99+%, Sigma–Aldrich, St. Louis, MO), $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ (99%, Sigma–Aldrich), ZnO (99.9%, Sigma–Aldrich) and $NH_4H_2PO_4$ (98+%, Sigma–Aldrich) were used as raw materials. Stoichiometric amounts of the oxides were weighed and ball milled in ethanol for 24 h with yittria stabilized zirconia balls. The slurry was then dried overnight in hot air oven and pre-heated at 500 °C for 4 h. The powder was then ground and calcined at temperatures in the range 700–750 °C for 4 h. Calcined powder was ground into fine powder. The fine powder obtained was mixed with different volume fractions (V_f) of TiO_2 (99.8%, Sigma–Aldrich) in ethanol using an agate mortar and pestle. It was then mixed with 4 wt% PVA (molecular weight 22,000, BDH Lab suppliers, Poole, U.K.). The powder was again dried and ground well. Cylindrical disks having 11 mm diameter and 5–6 mm thickness were prepared by applying a pressure of 100 MPa using a uniaxial press. The samples were then sintered at temperatures in the range 800–1000 °C for 4 h with an intermediate soaking at 600 °C for binder (PVA) burn out. In order to study the chemical compatibility of the ceramic with Ag, the $LiMg_{0.9}Zn_{0.1}PO_4 + 0.12\,V_f$ TiO_2 composite was further mixed with 20 wt% Ag powder (<45 μm, 99.99+%, Sigma–Aldrich) and sintered at 950 °C for 6 h. The bulk density of the sintered samples was measured using the Archimedes method and the sintering temperatures were optimized for maximum densification.

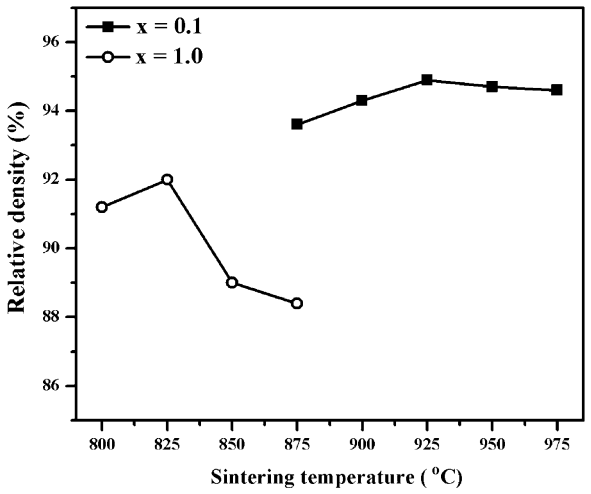

Fig. 1. Variation of relative density with sintering temperature.

The crystal structure of the ceramics was studied by recording the X-ray diffraction (XRD) pattern of sintered and powdered samples using Cu Kα radiation (Philips X'Pert PRO MPD X-ray diffractometer; Philips, Almelo, The Netherlands). The surface morphology of the sintered and thermally etched samples was analyzed using a scanning electron microscope (SEM) (JOEL-JSM 5600 LV, Tokyo, Japan). The microwave dielectric properties were measured with a Vector Network Analyzer (Model No. E8362B; Agilent Technologies, Santa Clara, CA). The relative permittivity and the unloaded quality factor (Q_u) of the samples were measured by Hakki–Coleman method modified by Courtney and cavity methods respectively.[19] The τ_f was measured in the temperature range 25–70 °C by noting the temperature at regular intervals while heating and using the equation

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is the resonant frequency at temperature T_1 and f_2 at temperature T_2.

3. Results and discussion

Fig. 1 shows the variation of relative density with sintering temperature for the compositions with $x = 0.1$ and 1.0. The relative density increases with sintering temperature due to grain growth and removal of porosity and reaches a maximum value. Further increase in sintering temperature results in exaggerated grain growth and the relative density decreases as a consequence

of entrapped porosity.[20] For $x = 0.1$, maximum relative density of 94.8% is obtained on sintering at 925 °C and for $x = 1.0$ the sample sintered at 825 °C shows the maximum relative density of 92%.

Fig. 2a–g shows the powder XRD patterns of $LiMg_{(1-x)}Zn_xPO_4$ ($x = 0.1$–1.0) ceramics. The peaks corresponding to $x = 0.1$ are indexed using the standard JCPDS file for $LiMgPO_4$ (file no: 32-0574) with orthorhombic structure and belonging to *Pmnb* space group. Similarly the peaks corresponding to the composition with $x = 1.0$ can be well indexed using the JCPDS file for $LiZnPO_4$ (file no: 84-2136) with monoclinic structure and *Cc* space group. From Fig. 2, it is obvious that the compositions up to $x = 0.2$ form solid solutions having orthorhombic structure. However, for the compositions from $x = 0.3$ onwards, a new peak starts growing at $2\theta \sim 22°$ which corresponds to the major intensity peak of $LiZnPO_4$. As x increases, the peaks of the orthorhombic phase weaken and that of the monoclinic phase becomes stronger. For $x = 0.3$–0.8, the ceramics exist as a mixture of orthorhombic and monoclinic phases and transform completely to monoclinic at $x = 1.0$

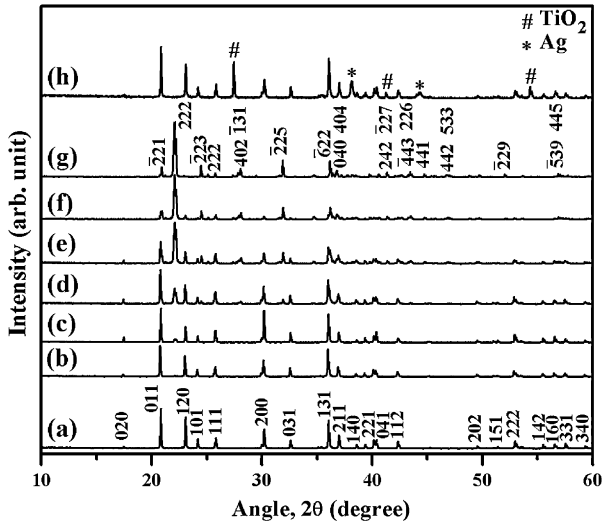

Fig. 2. Powder XRD patterns of $LiMg_{(1-x)}Zn_xPO_4$ ceramics with (a) $x = 0.1$, (b) $x = 0.2$, (c) $x = 0.3$, (d) $x = 0.4$, (e) $x = 0.6$, (f) $x = 0.8$, (g) $x = 1.0$ and (h) $LiMg_{0.9}Zn_{0.1}PO_4 + 0.12\ V_f\ TiO_2 + 20$ wt% Ag.

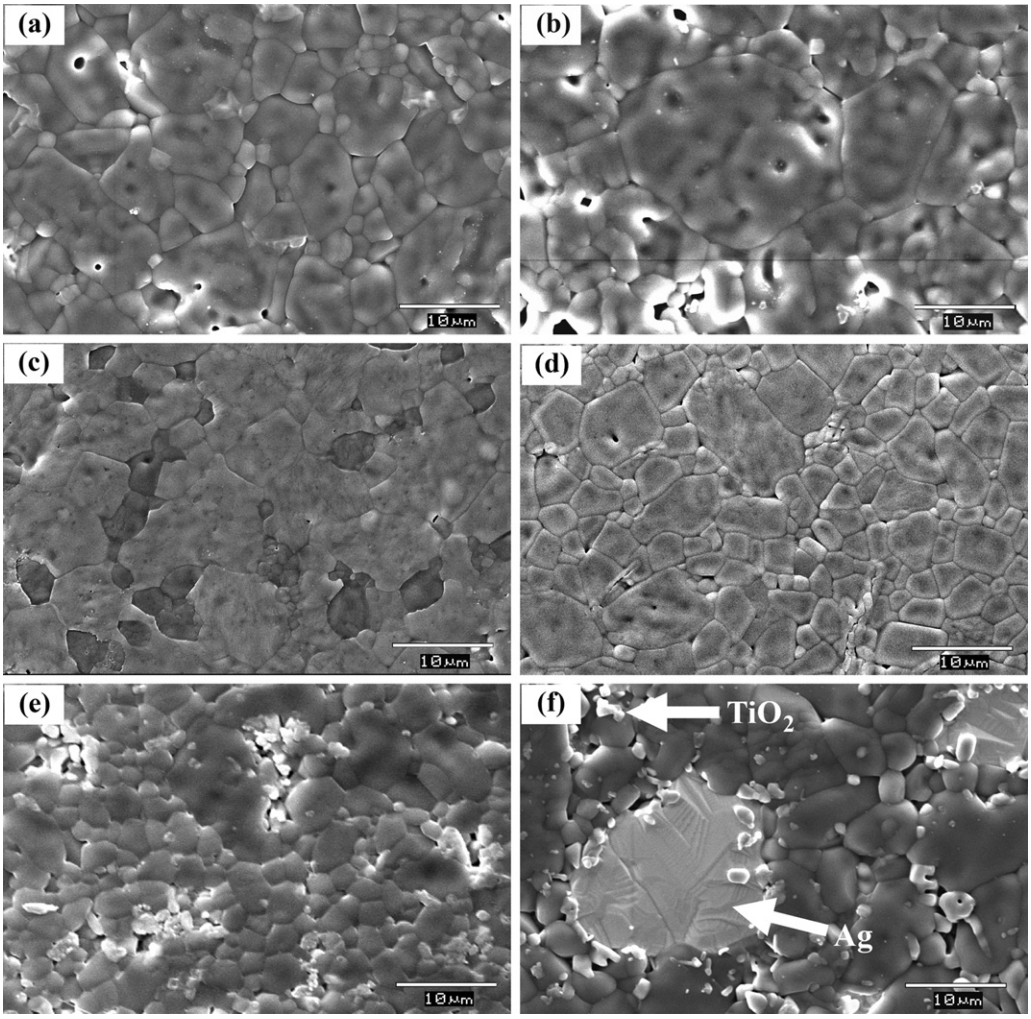

Fig. 3. SEM images of (a) $LiMg_{0.9}Zn_{0.1}PO_4$ ($x = 0.1$) sintered at 925 °C for 4 h, (b) $LiMg_{0.8}Zn_{0.2}PO_4$ ($x = 0.2$) sintered at 900 °C for 4 h, (c) $LiMg_{0.2}Zn_{0.8}PO_4$ ($x = 0.8$) sintered at 850 °C for 4 h, (d) $LiZnPO_4$ ($x = 1.0$) sintered at 825 °C for 4 h, (e) $LiMg_{0.9}Zn_{0.1}PO_4 + 0.12\ V_f\ TiO_2$ sintered at 950 °C for 4 h and (f) $LiMg_{0.9}Zn_{0.1}PO_4 + 0.12\ V_f\ TiO_2 + 20$ wt% Ag sintered at 950 °C for 6 h.

($LiZnPO_4$). The powder XRD pattern of $LiMg_{0.9}Zn_{0.1}PO_4$ ($x = 0.1$) co-fired with 0.12 V_f TiO_2 and 20 wt% Ag at 950 °C for 6 h is shown in Fig. 2h. The peaks corresponding to all the three phases can be well indexed using standard JCPDS files (file no: 21-1276 for TiO_2 and 04-0783 for Ag) and no additional peaks are present.

The SEM images of the sintered and thermally etched surfaces of the ceramics with $x = 0.1$, 0.2, 0.8 and 1.0 are shown in Fig. 3a–d, respectively. The images reveal a microstructure containing grains of size randomly varying from ~1 μm to >10 μm. From the surface morphology of the composition with $x = 0.8$ (Fig. 3c) it is obvious that the ceramic is mixture of two phases. From Fig. 3d it can be observed that the grain boundaries of $LiZnPO_4$ are sharper. Fig. 3e shows the microstructure of $LiMg_{0.9}Zn_{0.1}PO_4$ co-fired with 0.12 V_f TiO_2 at 950 °C for 4 h. Large grains of $LiMg_{0.9}Zn_{0.1}PO_4$ and small particles of TiO_2 can be observed in the image. The sintering temperature of TiO_2 is very high (~1500 °C) and hence no substantial grain growth occurs for TiO_2 at 950 °C. The SEM image of the composite of $LiMg_{0.9}Zn_{0.1}PO_4$ with 0.12 V_f TiO_2 and 20 wt% Ag sintered at 950 °C for 6 h is shown in Fig. 3f. In Fig. 3f, all the constituent phases can be separately identified which indicates that no significant reaction occurs between these phases.

The optimized sintering temperature (T_s), bulk density and the dielectric properties at 1 MHz of the ceramics are given in Table 1. The sintering temperature decreases gradually from 950 °C to 825 °C as the value of x increases from 0.0 to 1.0. The relative densities of the compositions from $x = 0.3$ to $x = 0.8$ are not calculated as they are found to contain more than one phase. The relative permittivity at 1 MHz increases gradually from 7.1 at $x = 0$ to 7.4 at $x = 0.2$ and saturates up to $x = 0.4$, then goes on decreasing from $x = 0.6$ onwards. The initial increase in ε_r may be attributed to the large ionic polarizability of Zn^{2+} (2.04 Å^3) compared to Mg^{2+} (1.32 Å^3)[21] and to the fact that Zn^{2+} gets partially substituted for Mg^{2+} in the orthorhombic lattice. However, as the value of x increases further the amount of monoclinic phase in the sample also increases and causes to reduce the value of ε_r. Lowest value of 5.2 is obtained for ε_r at $x = 1.0$ which is purely monoclinic in structure. The ceramics show very low dielectric loss ($\tan\delta$) of the order of 10^{-4} at 1 MHz (Table 1). It is also noteworthy that the compositions with $x = 0.1$ and 0.2 exhibit lowest dielectric loss ($\tan\delta = 2 \times 10^{-4}$).

Fig. 4 depicts the microwave dielectric properties of $LiMg_{(1-x)}Zn_xPO_4$ ceramics. The values of ε_r and $Q_u \times f$ as a function of x are shown in Fig. 4a. The variation in ε_r follows somewhat similar trend as that obtained at 1 MHz. The values of ε_r obtained at microwave frequencies are slightly lower than that at 1 MHz. This may be due to the fact that some of the polarization mechanisms become inactive as the frequency increases from MHz to GHz range.[22] From Fig. 4a it can be observed that the quality factor ($Q_u \times f$) increases from 79,100 GHz at $x = 0.0$ to 99,700 GHz at $x = 0.1$. Some of the early reports show such an increase in $Q_u \times f$ due to Zn^{2+} substitution.[23–25] From $x = 0.2$ onwards $Q_u \times f$ decreases gradually up to $x = 0.8$ and then increases for $x = 1.0$. The value of $Q_u \times f$ depends largely on the extrinsic factors like porosity and phase purity.[26] In the present study, the decrease in $Q_u \times f$ as the value of x increases from 0.1 to 0.2 may be due to the decrease in relative density (Table 1). Further, as the value of x increases from 0.2 to 0.8, the amount of secondary phase (monoclinic phase) in the sample also increases which is evident from the XRD patterns as well as SEM images (Figs. 2 and 3) and this may be the reason for the decrease in $Q_u \times f$ up to $x = 0.8$. At $x = 1.0$, the material becomes purely monoclinic $LiZnPO_4$ and hence $Q_u \times f$ increases. Highest $Q_u \times f$ of 99,700 GHz is obtained for $x = 0.1$ ($LiMg_{0.9}Zn_{0.1}PO_4$) which is greatly appreciable for microwave applications. The variation of τ_f with x is shown in Fig. 4b. The value of τ_f increases steadily from −55 ppm/°C for $x = 0.0$ to −80 ppm/°C for $x = 1.0$.

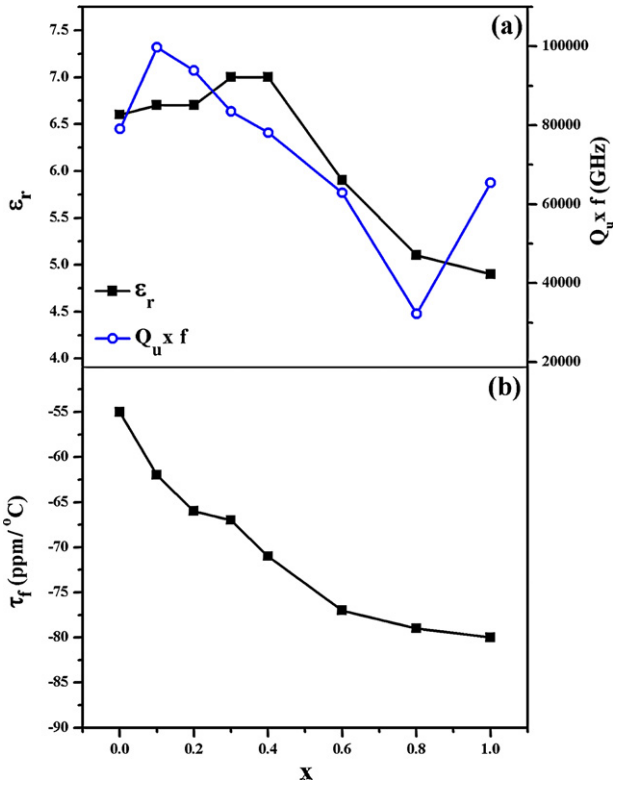

Fig. 4. Variation of (a) ε_r and $Q_u \times f$ and (b) τ_f of $LiMg_{(1-x)}Zn_xPO_4$ ceramics with the value of x.

The ceramics developed in the present study have good microwave dielectric properties suitable for LTCC applications. The composition with $x = 0.1$ ($LiMg_{0.9}Zn_{0.1}PO_4$) is interesting since it has very high quality factor ($Q_u \times f = 99{,}700$ GHz). However the temperature stability of resonant frequency is poor ($\tau_f = -62$ ppm/°C) for practical applications. The value of τ_f can be tuned nearly to zero by making composite with a suitable ceramic having large positive τ_f like TiO_2 ($\tau_f = +450$ ppm/°C). In the present study, rutile type TiO_2 is used since it has been reported more effective in improving the microwave dielectric properties compared to the anatase.[27] The microwave dielectric properties of $LiMg_{0.9}Zn_{0.1}PO_4$–TiO_2 composites are given in Table 2. With the addition of TiO_2, the sintering temperature increases slightly due to the high sintering temperature of TiO_2 (≈1500 °C). The sintering temperature for the composite with 0.15 V_f TiO_2 is 975 °C which is not suitable for LTCC applications. On the other hand, composites containing up to 0.12 V_f TiO_2 can be well sintered below the melting

Table 1
Sintering temperature, density and dielectric properties at 1 MHz of $LiMg_{(1-x)}Zn_xPO_4$ ceramics.

x	T_s (°C)	Bulk density (g cm^{-3})	Relative density (%)	ε_r	tan δ
0.0	950	2.825	95.0	7.1	7×10^{-4}
0.1	925	2.916	94.9	7.3	2×10^{-4}
0.2	900	2.968	93.9	7.4	2×10^{-4}
0.3	900	3.075	–	7.4	6×10^{-4}
0.4	875	3.129	–	7.4	7×10^{-4}
0.6	850	3.116	–	6.1	7×10^{-4}
0.8	850	2.986	–	5.6	9×10^{-4}
1.0	825	3.050	92.0	5.2	7×10^{-4}

Table 2
Microwave dielectric properties of $LiMg_{0.9}Zn_{0.1}PO_4$–TiO_2 composites.

Volume fraction of TiO_2	T_s (°C)	Bulk density (g cm^{-3})	Relative density (%)	ε_r	$Q_u \times f$ (GHz)	Experimental τ_f (ppm/°C)	Calculated τ_f (ppm/°C)
0.00	925	2.916	94.9	6.7	99,700	−62	−62
0.05	925	3.009	96.0	8.2	80,200	−39	−36
0.10	950	3.051	95.6	9.5	69,500	−15	−11
0.12	950	3.072	95.5	10.1	52,900	−5	−1
0.15	975	3.097	95.3	11.7	49,800	17	15

point of Ag. Form Table 2 it is clear that the relative densities of the composites are higher than the pure $LiMg_{0.9}Zn_{0.1}PO_4$ ceramic. It has been reported earlier that TiO_2 acts as a sintering aid to improve the sinterability of the ceramic co-fired with it.[26] The value of ε_r increases with the volume fraction of TiO_2 due to the large relative permittivity of TiO_2 ($\varepsilon_r \approx 100$). The quality factor decreases gradually from 99,700 GHz for $LiMg_{0.9}Zn_{0.1}PO_4$ to 49,800 GHz for the composite with 0.15 V_f TiO_2. The observed reduction in $Q_u \times f$ may be mainly attributed to the low quality factor ($Q_u \times f < 30{,}000$ GHz)[28] of TiO_2 compared to $LiMg_{0.9}Zn_{0.1}PO_4$. Inhomogeneity in mixing may also be deleterious to $Q_u \times f$. The value of τ_f varies from −62 ppm/°C to +17 ppm/°C as the V_f of TiO_2 increases from 0 to 0.15. The values of τ_f for the composites can be theoretically calculated using the mixture rule[29]

$$\tau_{f\,mixture} = V_{f1}\tau_{f1} + V_{f2}\tau_{f2} \quad (2)$$

where V_{f1} and V_{f2} are the volume fractions of $LiMg_{0.9}Zn_{0.1}PO_4$ and TiO_2 and τ_{f1} and τ_{f2} are their respective temperature coefficients of resonant frequency. The calculated values of τ_f are given in Table 2. The experimentally observed values of τ_f are found to be in agreement with the theoretical ones. $LiMg_{0.9}Zn_{0.1}PO_4$ co-fired with 0.12 V_f TiO_2 at 950 °C shows the best microwave dielectric properties with $\varepsilon_r = 10.1$, $Q_u \times f = 52{,}900$ GHz and $\tau_f = -5$ ppm/°C. The excellent microwave dielectric properties and the glass-free nature make this composition competitive with the commercially available LTCC substrates.[1]

4. Conclusions

The effect of Zn^{2+} substitution on the microwave dielectric properties of $LiMg_{(1-x)}Zn_xPO_4$ ($x = 0.0$–1.0) have been investigated. The compositions with $x \geq 0.3$ show a mixture of orthorhombic and monoclinic phases. As the value of x increases, the amount of monoclinic phase increases. At $x = 1.0$, the structure is completely transformed from orthorhombic to monoclinic. $LiMg_{0.9}Zn_{0.1}PO_4$ has $\varepsilon_r = 6.7$, $Q_u \times f = 99{,}700$ GHz and $\tau_f = -62$ ppm/°C. The $LiMg_{0.9}Zn_{0.1}PO_4$–TiO_2 composite containing 0.12 V_f TiO_2 has got good microwave dielectric properties with $\varepsilon_r = 10.1$, $Q_u \times f = 52{,}900$ GHz and $\tau_f = -5$ ppm/°C. The analysis of XRD pattern and microstructure reveals the chemical compatibility between the composite and the commonly used electrode material Ag. The excellent microwave dielectric properties of $LiMg_{0.9}Zn_{0.1}PO_4$–TiO_2 composite developed in the present study makes it a potential candidate for LTCC applications. The glass-free nature and low bulk density makes the composite more attractive.

Acknowledgments

Dhanesh Thomas is grateful to the Council of Scientific and Industrial Research (CSIR), India for the award of Senior Research Fellowship. The authors are thankful to Dr. P. Prabhakar Rao and Mr. M.R. Chandran for recording XRD patterns and SEM. The authors are grateful to DRDO, New Delhi for financial support.

References

1. Sebastian MT, Jantunen H. Low loss dielectric materials for LTCC applications: a review. *Int Mater Rev* 2000;**53**:57–90.
2. Tummala RR. Ceramic and glass-ceramic packaging in the 1990. *J Am Ceram Soc* 1991;**74**:895–908.
3. Bian JJ, Wang L. Glass-free LTCC microwave ceramic-$(La_{0.5}Na_{0.5})_{1-x}(Li_{0.5}Nd_{0.5})_xWO_4$. *J Am Ceram Soc* 2011:1–4.
4. Li Y, Bian J, Yuan L. A new glass-free low-temperature fired microwave ceramic. *J Mater Sci* 2009;**44**:328–30.

5. Kwon DK, Lanagan MT, Shrout TR. Microwave dielectric properties and low-temperature cofiring of $BaTe_4O_9$ with aluminum metal electrode. *J Am Ceram Soc* 2005;**88**:3419–22.
6. Kwon DK, Lanagan MT, Shrout TR. Microwave dielectric properties of BaO–TeO_2 binary compounds. *Mater Lett* 2007;**61**:1827–31.
7. Subodh G, Sebastian MT. Glass-free $Zn_2Te_3O_8$ microwave ceramic for LTCC applications. *J Am Ceram Soc* 2007;**90**:2266–8.
8. Udovic M, Valant M, Suvorov D. Dielectric characterisation of ceramics from the TiO_2–TeO_2 system. *J Eur Ceram Soc* 2001;**21**:1735–8.
9. Zhou D, Randall CA, Wang H, Pang LX, Yao X. Ultra-low firing high-k Scheelite structures based on $[(Li_{0.5}Bi_{0.5})_xBi_{1-x}][Mo_xV_{1-x}]O_4$ microwave dielectric ceramics. *J Am Ceram Soc* 2010;**93**:2147–50.
10. Udovic M, Valant M, Suvorov D. Phase formation and dielectric characterization of the Bi_2O_3–TeO_2 system prepared in an oxygen atmosphere. *J Am Ceram Soc* 2004;**87**:591–7.
11. Valant M, Suvorov D. Processing and dielectric properties of sillenite compounds $Bi_{12}MO_{20-\delta}$ (M = Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$). *J Am Ceram Soc* 2001;**84**:2900–4.
12. Valant M, Suvorov D. Glass-free low-temperature cofired ceramics: calcium germanates, silicates and tellurates. *J Eur Ceram Soc* 2004;**24**:1715–9.
13. Zhou D, Wang H, Pang LX, Randall CA, Yao X. Bi_2O_3–MoO_3 binary system: an alternative ultralow sintering temperature microwave dielectric. *J Am Ceram Soc* 2009;**92**:2242–6.
14. Zhou D, Wang H, Pang LX, Yao X, Wu XG. Microwave dielectric characterization of a Li_3NbO_4 ceramic and its chemical compatibility with silver. *J Am Ceram Soc* 2008;**91**:4115–7.
15. Bian JJ, Wu JY. Designing of glass-free LTCC microwave ceramic-$Ca_{1-x}(Li_{0.5}Nd_{0.5})_xWO_4$ by crystal chemistry. *J Am Ceram Soc* 2011:1–6.
16. Bian JJ, Kim DW, Hong KS. Glass-free LTCC microwave dielectric ceramics. *Mater Res Bull* 2005;**40**:2120–9.
17. Cho IS, Kim JR, Kim DW, Hong KS. Phase transformation and microwave dielectric properties of $BiPO_4$ ceramics. *J Electroceram* 2006;**16**: 379–83.
18. Thomas D, Sebastian MT. Temperature-compensated $LiMgPO_4$: a new glass-free low-temperature cofired ceramic. *J Am Ceram Soc* 2010;**93**:3828–31.
19. Sebastian MT. *Dielectric materials for wireless communication*. Oxford, UK: Elsevier; 2008. p. 16–24.
20. Lal R, Gokhale NM, Krishnan R, Ramakrishnan P. Effect of sintering parameters on the microstructure and properties of strontium modified PZT ceramics prepared using spray-dried powders. *J Mater Sci* 1989;**24**:2911–6.
21. Shannon RD. Dielectric polarizabilities of ions in oxides and fluorides. *J Appl Phys* 1993;**73**:348–66.
22. Joseph T, Sebastian MT. Microwave dielectric properties of alkaline earth orthosilicates M_2SiO_4 (M = Ba, Sr, Ca). *Mater Lett* 2011;**65**:891–3.
23. Zheng CW, Wu SY, Chen XM, Song KX. Modification of $MgAl_2O_4$ microwave dielectric ceramics by Zn substitution. *J Am Ceram Soc* 2007;**90**:1483–6.
24. George S, Sebastian MT. Microwave dielectric properties of novel temperature stable high Q $Li_2Mg_{1-x}Zn_xTi_3O_8$ and $Li_2A_{1-x}Ca_xTi_3O_8$ (A = Mg, Zn) ceramics. *J Eur Ceram Soc* 2010;**30**:2585–92.
25. Yokoi A, Ogawa H, Kan A, Nakamura Y. Relationship between crystal structure and microwave dielectric properties of melilite-type ceramic. *J Eur Ceram Soc* 2007;**27**:2989–93.
26. Guo Y, Ohsato H, Kakimoto K-I. Characterization and dielectric behavior of willemite and TiO_2-doped willemite ceramics at millimeter-wave frequency. *J Eur Ceram Soc* 2006;**26**:1827–30.
27. Tsunookaa T, Androua M, Higashidaa Y, Sugiurab H, Ohsato H. Effects of TiO_2 on sinterability and dielectric properties of high-Q forsterite ceramics. *J Eur Ceram Soc* 2003;**23**:2573–8.
28. Templeton A, Wang XR, Penn SJ, Webb SJ, Cohen LF, Alford NM. Microwave dielectric loss of titanium oxide. *J Am Ceram Soc* 2000;**83**:95–100.
29. Dong MZ, Yue ZX, Zhuang H, Meng SQ, Li LT. Microstructure and microwave dielectric properties of TiO_2-doped Zn_2SiO_4 ceramics synthesized through the sol–gel process. *J Am Ceram Soc* 2008;**91**:3981–5.