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# Crystal structure and dielectric properties of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics at microwave frequencies

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## A B S T R A C T

Ceramics in the system $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ with $B_2O_3$ additions (1 wt.%) have been investigated by the conventional solid-state route. The XRD patterns of the sintered samples ($0.3 \le x \le 1.0$) revealed single phase formation with a structure. The unit cell volume slightly increased with increasing Zn content ($x$). $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ were found to form perovskite solid solutions in the whole compositional range. The maximum values of the dielectric constant and the quality factor multiples resonant frequency ($Q \times f$) can be obtained when the $La(Mg_{0.7}Zn_{0.3})_{1/2}Ti_{1/2}O_3$ with 0.5 wt.% $B_2O_3$ additive were sintered at 1475 °C for 4 h. The temperature coefficient of resonant frequency $\tau_f$ (−63 ppm/°C) was measured for $x = 0.7$.

## 1. Introduction

The dielectric properties of perovskite compounds are strongly related to their structural characteristics, such as cation ordering and the orientation of the oxygen octahedral. Recently, the La-modified complex perovskites attracted a great attention as promising microwave dielectrics. It was previously shown that perovskites presenting oxygen octahedral tilt and B′/B″ ordering have negative TCF while alkaline-earth-metal titanates have a positive one [1].

A class of perovskite-related non-ferroelectric materials is known to be appropriate for microwave applications. Owing to their ability to form solid solutions in a wide range of substituting atoms, perovskites are intensively explored as basic compositions to obtain materials with controlled properties. Series of low-loss perovskite system have been investigated and adjusted for microwave applications. However, the most widespread method for producing new materials is still an empirical one and slow progress is observed in discovering and clarifying mechanisms controlling microwave dielectric parameters in complex systems. Correlations between structure and microwave dielectric characteristics of perovskite compounds have only been revealed for some particular compositions [2].

Among many candidates, the complex $A(B'B'')O_3$ perovskite materials have been extensively studied due to their excellent dielectric properties and unique order–disorder behavior. In $A(B'B'')O_3$ complex perovskite materials, there are 1:2 and 1:1 ordering according to the arrangement of B site cations. The arrangement of 1:2 and 1:1 ordering means two kinds of B site cations repeated as B′B″B″B′B″B″and B′B″B′B″, respectively. In general, 1:1 ordering and 1:2 ordering of B sites occur in $A(B_{1/2}{'}B''_{1/2})O_3$ and $A(B_{1/3}{'}B''_{2/3})O_3$-based materials, respectively [1].

Structural changes including cation ordering were suggested as determining factor for the sign of $\tau_f$ in LZT based perovskite systems. Tamura [3] concluded that dielectric loss tangent at microwave frequency is mainly caused by the inharmonic terms in the crystal's potential energy, and increased by lattice defects such as disordered charge distribution.

In this work, $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ the solid solutions were prepared by the solid-state method and its microwave dielectric properties and microstructures were also investigated. Because $Mg^{2+}$ (0.72 Å) and $Zn^{2+}$ (0.83 Å) have a similar ionic radius, it is the intention of this paper to discover the effected Zn substation for Mg on the structures and microwave dielectric properties of the $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$.

## 2. Experimental procedure

The $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ powders were prepared by the solid state reaction method by mixing individual high-purity oxide $La_2O_3$, MgO, $B_2O_3$, ZnO and $TiO_2$. The starting materials were stoichiometrically weighed after drying $La_2O_3$ at 1000 °C for 4 h and MgO at 800 °C for 6 h to remove moisture content and carbonates. The powders were then dry mixed with an agate mortar and pestle and subsequently wet mixed by using distilled water. The calcination temperature was varied between 1100 and 1200 °C for 4 h. The calcined powder with the organic binder polyvinyl alcohol was pressed into pellets by using a uniaxial press and the binder was evaporated at 650 °C for 12 h. Sintering was carried out at 1400–1500 °C for 4 h. The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu Kα radiation (at 30 KV and 20 mA) and a graphite monochrometer in the 2θ

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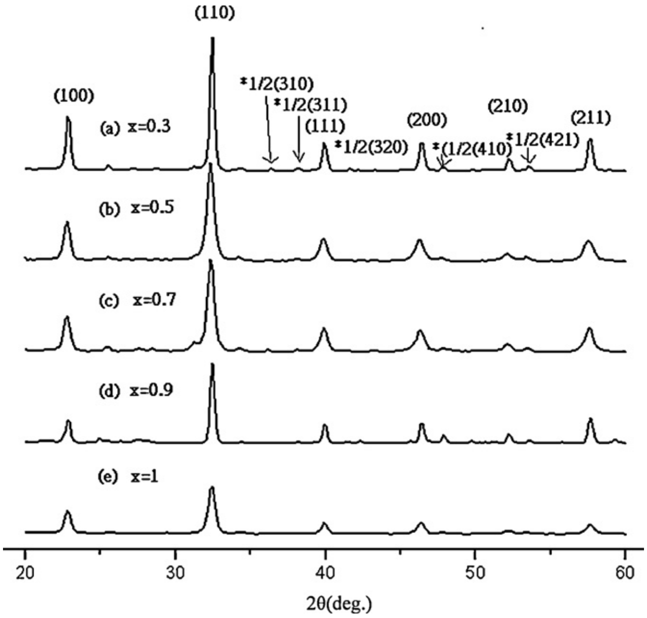

**Fig. 1.** X-ray diffraction patterns of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics with 1 wt.% $B_2O_3$ addition sintered at 1500 °C.

range of 20–60°. The microstructural observations and analysis of sintered surface were performed by a scanning electron microscopy (SEM, Philips XL-40FEG).

The bulk densities of the sintered pellets were measured by the Archimedes method. Microwave dielectric properties such as dielectric constant and unloaded Q were measured at 6–12 GHz by the post-resonant method as suggested by Hakki and Coleman [4]. This method consisted of parallel conducting plates and coaxial probes on the $TE_{011}$ mode. TE means transverse electric waves and the first two subscript integers denote the wave guide mode, while the third integer denotes the order of resonance in an increasing set of discrete resonant lengths. The temperature coefficient of resonant frequency was measured in the temperature range of 20–80 °C. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement.

## 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of 1 wt.% $B_2O_3$-doped $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics at various sintering temperatures (1400–1500 °C). In Fig. 1, no secondary phases can be observed since detection of a minor phase by X-ray is extremely difficult. The existence of some superlattice peaks with low intensities needed to be confirmed by using high resolution XRD patterns. These results illustrated that with the replacement of Mg by Zn, $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ($0.3 \le x \le 1$) ceramics would form a solid solution. The diffraction peaks slightly shift to a lower angle as $x$ increases due to the incorporation of big $Zn^{2+}$ (0.83 Å) in place of $Mg^{2+}$ (0.72 Å). The evidence of anti-phase tilting was found for all compositions particularly from the (3 1 1) reflections [5]. The (3 3 1) reflections also corresponding to the anti-phase tilting began to appear of 1 wt.% $B_2O_3$-doped $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$. Fig. 1 XRD patterns of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramic systems form solid solution, and all peaks match with $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ compound. Lee [6] refinement of these neutron diffraction data indicate that the true symmetry is probably $P21/n$ ($0.3 \le x \le 1$), this structure is essentially very similar to those of $La(Mg_{1/2}Ti_{1/2})O_3$ and $Nd(Mg_{1/2}Ti_{1/2})O_3$ proposed previously [6]. In perovskite compounds, two mechanisms are commonly responsible for unit-cell doubling: cation ordering and tilting of oxygen octahedra. According to Glazer [7,8], the superlattice reflections, with specific combinations of odd (*o*) and even (*e*) Miller indices, point to definite types of deviation of the structure from the undistorted cubic one, such as octahedral in-phase tilting (*ooe*, *oeo*, *eoo*), anti-phase tilting (*ooo*, $h+k+l>3$), chemical ordering (*ooo*) and anti-parallel displacement of A-cations (*eeo*, *eoe*, *oee*). In the studied system all these features are present for all the compositions.

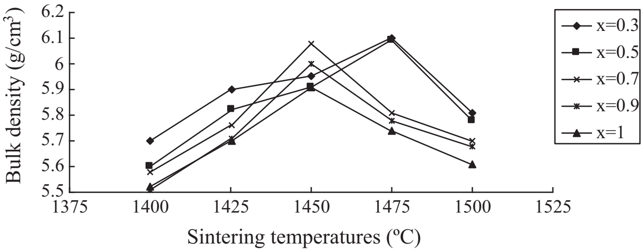

**Fig. 2.** Bulk density of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with 1 wt.% $B_2O_3$ addition.

**Table 1**
Structural data for sintered $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$.

| $x$ | Tolerance factor | In-phase tilting 1/2(3 1 0) | Anti-phase tilting 1/2(3 1 1) |
|---|---|---|---|
| 0 | 0.946237438 | o | o |
| 0.3 | 0.944863092 | o | o |
| 0.5 | 0.943949077 | o | o |
| 0.7 | 0.943036828 | o | o |
| 0.9 | 0.942126341 | o | o |
| 1 | 0.941671757 | o | o |

The density of the $B_2O_3$-doped $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics sintered at various temperatures as shown in Fig. 2. It indicated that densities of 5.52–6.09 (g/cm$^3$) were obtained for $B_2O_3$-doped $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics at sintering temperatures from 1400 °C to 1500 °C. The sintering temperatures were determined on the basis of the apparent densities of the solid solutions. The densities of specimen for $x = 0.3–0.1$ are shown in Fig. 2. All specimens have high relative densities over 96% sintering above 1450 °C. Bulk densities are decreased with decrease of $x$ because of the effect of ZnO evaporation at higher sintering temperatures.

The dielectric properties of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ with 1 wt.% $B_2O_3$ addition are illustrated in Fig. 3. As the $x$ value increased from 0.3 to 1, the dielectric constants decreased from 28.97 ($x = 0.3$ sintered at 1475 °C) to 27.5 ($x = 1$ sintered at 1450 °C).

The variation in the relative permittivity with composition is often explained using the Claussius–Mossotti relation, which shows how the relative permittivity depends on the composition and crystal structure through polarizability and molar volume.

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_m}{3V_m - 4\pi\alpha_m} \tag{1}$$

Here $\varepsilon_r$, $V_m$, and $\alpha_m$ represent the relative permittivity, molar volume, and macroscopic polarizability, respectively. Using the experimental relative permittivity data and unit-cell volume data, the macroscopic polarizability, $\alpha_m$, was calculated. The theory polarizability data show an almost sigmoidal increase with an increase in Zn content while the unit-cell volume increased with

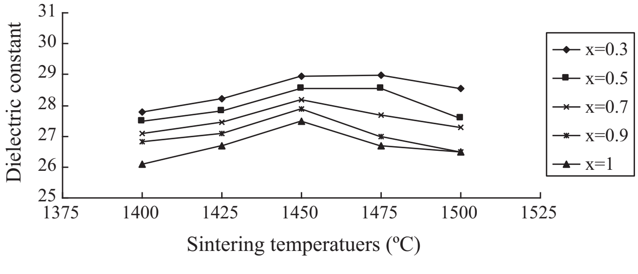

**Fig. 3.** $\varepsilon_r$ values of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with 1 wt.% $B_2O_3$ addition.

**Table 2**
Lattice parameter, cell volume, ionic polarizabilities, $\varepsilon_r$ data for sintered $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$.

| $x$ | 0 | 0.3 | 0.5 | 0.7 | 0.9 | 1 |
|---|---|---|---|---|---|---|
| $a$ (Å) | 7.8410 | 7.8691 | 7.8712 | 7.8709 | 7.8811 | 7.8950 |
| $b$ (Å) | 5.5308 | 5.5680 | 5.5711 | 5.5789 | 5.5821 | 5.5964 |
| $c$ (Å) | 5.6110 | 5.5752 | 5.5763 | 5.5781 | 5.5801 | 5.5809 |
| $V_m$ (Å$^3$) | 241.4711 | 244.2751 | 244.5481 | 245.1918 | 245.4827 | 246.5841 |
| $\alpha_m$(theory) | 56.78 | 57.212 | 57.5 | 57.788 | 58.076 | 58.22 |
| $\alpha_m$(exp) | 52.45 | 52.85 | 52.9 | 53.01 | 53.05 | 53.2 |
| Dielectric (measured) | 29 | 28.93 | 28.81 | 28.79 | 28.73 | 28.69 |

$x$. The relative permittivity increases with $\alpha_m$, and that as the value of $\alpha_m$ approaches $3V_m/4\pi$ the relative permittivity increases very rapidly. It has also been reported that the macroscopic polarizability of complex systems having an ideal symmetry can be determined from the summation of the polarizability of the

constituent cations such that, $\alpha_m = \sum \alpha(\text{ions})$ (2)

Table 1 includes the tolerance factor ($t$) of each composition and the 1/2(3 1 1) superlattice reflection due to the 1:1 ordering. The tolerance factor $t$, which is given by $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$ in the $ABO_3$ perovskite, was calculated after taking the average ionic sizes of each site for $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$. The tolerance factor decreased with increasing $Zn^{2+}$ content, which can be expected from the main contribution of the relatively large size of $Zn^{2+}$ ion at the B site. The tolerance factor is known correlated with structural symmetry and tilting of the octahedral in perovskites [5,9].

The theoretical polarizability [denoted as $\alpha_m$(theory)] values calculated according to Eq. (2) are compared with the "experimental" polarizabilities [determined using Claussius–Mossotti relation, Eq. (2) in Table 2. It is noted that $\alpha_m$(exp) for the $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ end member is less than the $\alpha_m$(theory) value, the $\alpha_m$(exp) values are smaller than $\alpha_m$(theory). Shannon [10] suggested that deviations from additivity of ionic polarizability arise when compression or rattling of cations occur in the structural sites as the cation sizes are varied. The lower $\alpha_m$(exp) value for $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ may thus be due to compression effects because of the large difference between the sizes of the $Mg^{2+}$ and $Zn^{2+}$ cations in the octahedral sites. By a similar argument the larger $\alpha_m$(exp) in $Zn^{2+}$ would be attributed to the rattling of the smaller $Mg^{2+}$ cations in the oxygen octahedra, characteristic of ferroelectric materials. The reduction in the lattice stress effectively induces a decrease in restoring force constant with a resultant increase in the vibrational anisotropy leading to an increase in the relative permittivity and its temperature dependence. This correlation also agrees with the harmonic-oscillator model [11]. Indeed, the unique relationship between permittivity and internal lattice stress is analogous to the reversible changes in permittivity with applied external stress reported by Steiner et al. [12].

Fig. 4 shows the $Q \times f$ values of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics with 1 wt.% $B_2O_3$ additions at different sintering temperatures as functions of the $x$ value and with different $x$ value had a maximum value at 1500 °C. The $Q \times f$ value decrease with the increase of $Zn^{2+}$ content and sintering temperature. Many factors could affect the microwave dielectric loss of dielectric resonators such as the lattice vibration modes, the pores and the secondary phases. Generally, a larger grain size, i.e., a smaller grain boundary, indicates a reduction in lattice imperfection and the dielectric loss was thus reduced. It seems that the dielectric loss of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics system was dominated by the bulk density decreased due to the weight loss in the samples can be ascribed to ZnO evaporation. The highest $Q \times f$ value of 74,000 (GHz) for $x = 0.3$ is achieved at the sintering temperature 1475 °C.

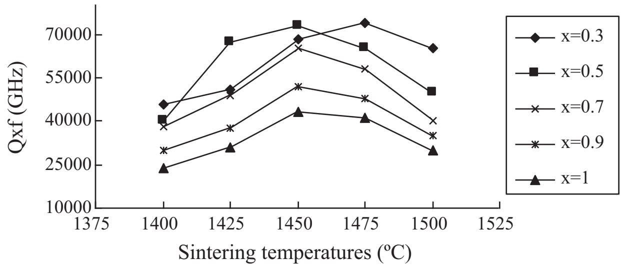

**Fig. 4.** $Q \times f$ values of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with various 1 wt.% $B_2O_3$ addition.

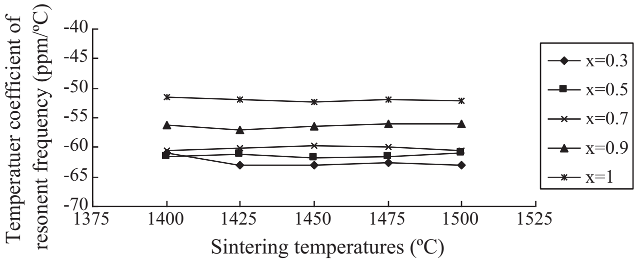

**Fig. 5.** Temperature coefficient values of $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with 1 wt.% $B_2O_3$ addition.

The temperature coefficients of the resonant frequency ($\tau_f$) of $B_2O_3$-doped $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics at different sintering temperatures are illustrated in Fig. 5. The temperature coefficient of resonant frequency is well known related to the composition, the additives and the second phase of the material. It seemed that higher $Zn^{2+}$ content would shift the $\tau_f$ value to more positive. It varied from −62.5 to −52 ppm/°C as the amount of $x$ values increased from 0.3 to 1 sintered at 1475 °C. In general, the temperature coefficient of the resonant frequency was found to be related to the composition and the decrease of $t$ (Table 1) with increasing $Zn^{2+}$ contents is correlated to the increase of $\tau_f$ as shown in Fig. 5. In the tilted region, generally the increasing thermal energy is completely absorbed to recover the tilting. TCF values were found to increase with the content of $Zn^{2+}$ as shown in Fig. 5.

## 4. Conclusions

The dielectric properties of $B_2O_3$-doped $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics were investigated. $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramics exhibited perovskite structure. With 1 wt.% $B_2O_3$ addition, a dielectric constant of 28.97, a $Q \times f$ value of 74,000 (GHz) and a $\tau_f$ value of −62.5 ppm/°C were obtained for $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ($x = 0.3$) ceramics at 1475 °C for 4 h. The decrease in $Q \times f$ value at higher sintering temperature and more $Zn^{2+}$ content was owing to that the grain boundary phases were pronounced product and ZnO evaporation. Therefore, the $B_2O_3$-doped $La(Mg_{1-x}Zn_x)_{1/2}Ti_{1/2}O_3$ ceramic is suitable for applications in microwave dielectric resonators and microwave device because of its excellent microwave dielectric properties.

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