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Dielectric properties and crystal structure of $La(Mg_{1/2}Ti_{1/2})O_3$ ceramics with Mg^{2+} substituted by Co^{2+}

Yuan-Bin Chen*

Department of Engineering and Management of Advanced Technology, Chang Jung Christian University, 396 Chang Jung Rd., Sec. 1, Kway Jen, Tainan 71101, Taiwan

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ABSTRACT

Solid solutions of $(1-x)La(Co_{1/2}Ti_{1/2})O_3$–$xLa(Mg_{1/2}Ti_{1/2})O_3$ were used to prepare $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ using solid-state synthesis. X-ray diffraction patterns of the sintered samples revealed single phase formation. A maximum density of 6.01 g/cm^3 was obtained for $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ($x=1$) ceramics sintered at 1375 °C for 4 h. The maximum values of the dielectric constant ($\varepsilon_r=29.13$) and the quality factor ($Q\times f=80{,}000$ GHz) were obtained for $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ with 1 wt% ZnO additive sintered at 1375 °C for 4 h. The temperature coefficient of resonant frequency τ_f was −59 ppm/°C for $x=0.3$.

1. Introduction

High quality devices are important for mobile communication applications. In order to miniaturize the dimensions of devices and for efficiency and stability, microwave resonators materials are required to have the following three dielectric characteristics; high quality factor ($Q\times f$), permittivity ($\varepsilon_r>25$) and a temperature coefficient of resonant frequency ($\tau_f=\pm3$ ppm/°C). Recently, La-modified complex perovskites have attracted a lot of attention as promising microwave dielectrics. It has been shown that $La(B'_{1/2}B''_{1/2})O_3$ perovskites with an oxygen octahedral tilt and B′/B″ ordering have negative TCF whereas alkaline-earth-metal titanates have a positive one [1,2]. In $A(B'B'')O_3$ complex perovskite materials, there are 1:2 and 1:1 orderings according to the arrangement of B site cations. The arrangement of 1:2 and 1:1 orderings means that there are two kinds of B site cation, repeated as B′B″B″B′B″B″ and B′B″B′B″, respectively. In general, the 1:1 ordering and the 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 [3,4]. Among them, $La(Mg_{1/2}Ti_{1/2})O_3$ has a good dielectric constant ($\varepsilon_r\sim29$), a high quality factor ($Q\times f$ value ~73,000 GHz), and a negative τ_f value (−65 ppm/°C). Co is substituted into.

In the present study, Co is substituted into $La(Mg_{1/2}Ti_{1/2})O_3$ to formed $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$. Mg^{2+} (0.72 Å) and Co^{2+} (0.745 Å) have similar ionic radii. The effect of Co^{2+} substituting for Mg^{2+} on the structure and microwave dielectric properties of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ are investigated.

Chemical processing and small particle sizes of the starting materials are generally advantageous for reducing the sintering temperature of dielectric materials. However, they require a flexible procedure which increases the cost and time of fabricating dielectric resonators. Liquid phase sintering with the addition of glass or other low-melting point materials was found to effectively lower the firing temperature of ceramics [5,6]. The microwave dielectric properties of dielectric resonators were also deeply affected by the liquid sintering temperature due to the development of microstructure at low sintering temperature or the reaction between host material and addition. In the present study, ZnO was chosen as a sintering aid to lower the sintering temperature of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics. The crystalline phases, the microstructures, and the microwave dielectric properties of ZnO-doped $La(Mg_{1/2}Ti_{1/2})O_3$ ceramics are investigated.

2. Experimental procedure

$La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ powders were prepared using the solid-state reaction method by mixing individual high-purity oxides La_2O_3, MgO, ZnO, CoO, and TiO_2. The starting materials were stoichiometrically weighed after La_2O_3 was dried 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 using distilled water. The calcination temperature was varied between 1100 and 1200 °C for 4 h. The calcined powder with organic binder polyvinyl alcohol was pressed into pellets using a uniaxial press. The binder was evaporated at 650 °C for 12 h. Sintering was carried out at 1350–1450 °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 monochromator in the 2θ range of 20–60°. The microstructural observations and analysis of the sintered surface were performed using 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 the dielectric constant and unloaded Q were measured at 6–12 GHz by the post-resonant method, as suggested by Hakki and Coleman [7]. This method utilizes parallel conducting plates and coax-

* Tel.: +886 6 2785123 6112.
E-mail address: cubnck@yahoo.com.tw

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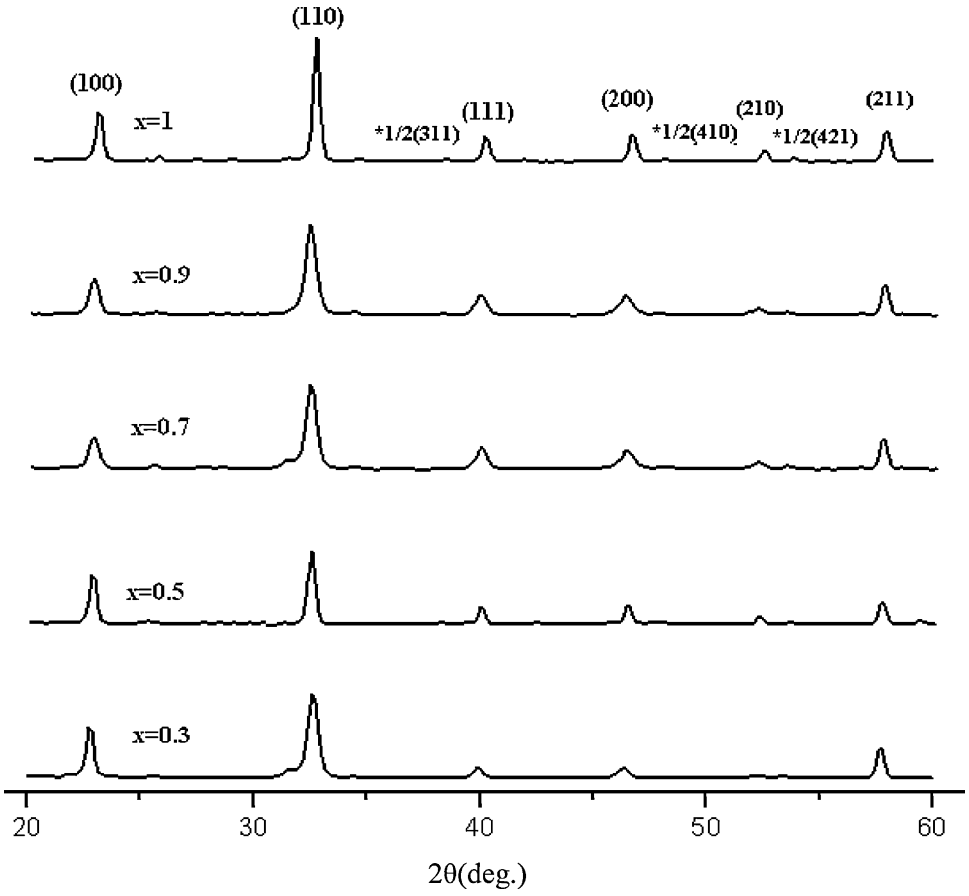

Fig. 1. X-ray diffraction patterns of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics with 1 wt.% ZnO addition sintered at 1375 °C.

ial probes in TE_{011} mode, where TE means transverse electric waves and the first two subscript integers denote the wave guide mode, and the subscript 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 HP8757D network analyzer and a HP8350B sweep oscillator were employed in the measurement.

3. Results and discussion

XRD patterns of 1 wt% ZnO-doped $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics sintered at 1375 °C are shown in Fig. 1. No secondary phases can be observed since the detection of a minor phase by XRD is extremely difficult. The existence of some superlattice peaks with low intensities was confirmed by high-resolution XRD patterns. With the replacement of Mg by Co, $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics formed a solid solution. The diffraction peaks slightly shift to a lower angle as x increases due to the incorporation of relatively large Co^{2+} (0.745 Å) in place of Mg^{2+} (0.72 Å). In perovskite compounds, two mechanisms are commonly responsible for unit-cell doubling: cation ordering and tilting of oxygen octahedra. According to Glazer [8,9], 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.

The density of the ZnO-doped $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics with various Co content levels sintered at various temperatures as shown in Fig. 2. It indicated that densities of 5.6–6.01 g/cm^3 were obtained for ZnO-doped $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics at sintering temperatures of 1350–1450 °C. The sintering temperatures were determined based on the apparent densities of the solid solutions. All specimens sintered above 1375 °C have high relative densities of over 96%. Bulk density increased with increasing Co, because the mass of Co has a larger mass than that of Mg.

The dielectric constant of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ with 1 wt.% ZnO addition are illustrated in Fig. 3. When the x was value

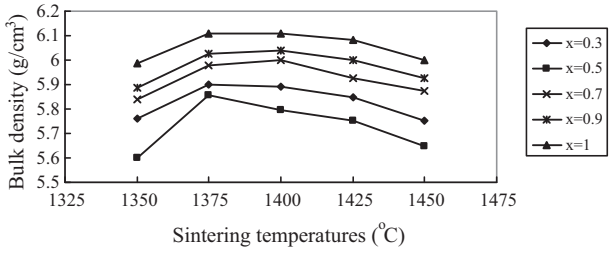

Fig. 2. Bulk density of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with 1 wt.% ZnO_3 addition.

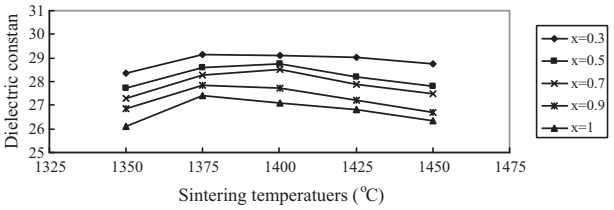

Fig. 3. ε_r values of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with 1 wt.% ZnO addition.

Table 1
Lattice parameter, cell volume, ionic polarizablities, ε_r data for sintered $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$.

x =	0	0.3	0.5	0.7	0.9	1
A (Å)	7.8411	7.8384	7.8358	7.8332	7.8306	7.867
b (Å)	5.6	5.6062	5.6122	5.6184	5.6241	5.6601
c (Å)	5.5382	5.5292	5.52	5.5116	5.5203	5.4945
V_m (Å^3)	241.47	242.9557	242.7393	242.548527	243.0969051	244.6325
α_m(theory)	56.9	57.098	57.23	57.362	57.494	57.5
α_m(exp)	52.45	52.85	52.9	53.01	53.05	53.2
Dielectric (cal.)	30.18	29.1	28.73	28.7	27.8	27
Dielectric (measured)	29	28.87	28.4	27.95	27.1	26.8
Tolerance factor	0.946237	0.94452	0.943378	0.94224	0.941104	0.940537

increased from 0.3 to 1, the dielectric constant decreased from 29.13 (x = 0.3 sintered at 1375 °C) to 27.4 (x = 1 sintered at 1375 °C).

Table 1 shows the tolerance factor (t) of each composition. 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 size of each site for $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$. Where R_A and R_B are the average ionic radii of the A and B sites, respectively, and R_O is the radius of O^{2-} in the appropriate coordinations.

The tolerance factor decreased with increasing Co^{2+} content, which is expected from the main contribution of the relatively large size of Co^{2+} ion at the B site. The tolerance factor is known to be correlated with structural symmetry and the tilting of the octahedra in perovskites [10,11].

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

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

where ε_r, V_m, and α_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, α_m, was calculated. The theoretical polarizability data show an almost sigmoidal increase with increasing Co content. The unit-cell volume increased with x. The relative permittivity increases with α_m. When the value of α_m approaches $3V_m/4\pi$, the relative permittivity increases very rapidly. It has also been reported that the macroscopic polarizability of complex systems with an ideal symmetry can be determined from the summation of the polarizability of the constituent cations such that

$$\alpha_m = \sum \alpha(\text{ions}) \quad (2)$$

The theoretical polarizability denoted as α_m(theory) values calculated using Eq. (2) are compared with the "experimental" polarizabilities (determined using Claussius–Mossotti relation, Eq. (2) in Table 1). It is noted that α_m(exp) for the $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ end member is less than the α_m(theory) value. Shannon [12] 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 α_m(exp) value for $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ may thus be due to compression effects because of the large difference between the sizes of the Mg^{2+} and Co^{2+} cations in the octahedral sites. By a similar argument the larger α_m(exp) for Co^{2+} can 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 the 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 [13]. 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. [14].

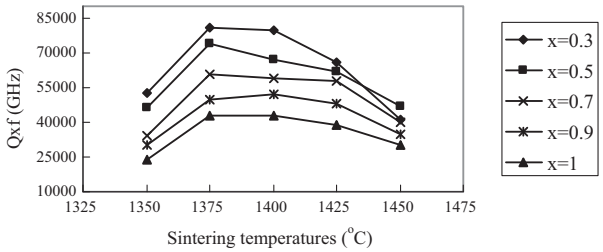

Fig. 4. $Q \times f$ values of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with various 1 wt.% ZnO addition.

Fig. 4 shows the $Q \times f$ values of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics with 1 wt.% ZnO additives for various sintering temperatures as a functions of the x value. The $Q \times f$ value decreases with increasing of Co^{2+} content and sintering temperature. Many factors can 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 the $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics system was dominated by the bulk density decreased due to the weight loss in the samples can be ascribed to ZnO evaporation. The maximum $Q \times f$ value of 80,000 (GHz) for x = 0.3 was achieved at the sintering temperature of 1375 °C.

The temperature coefficient of resonant frequency (τ_f) of ZnO-doped $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics for various sintering temperatures is shown in Fig. 5. The temperature coefficient of resonant frequency is related to the composition, additives, and the second phase of the material. Higher Co^{2+} content would shift the τ_f value to more positive. It varied from −59 to −35 ppm/°C as the amount of x values increased from 0.3 to 1 for sintering at 1375 °C. In general, the temperature coefficient of resonant frequency is related to the composition and the decrease of t (Table 1) with increasing Co^{2+} content is correlated to the increase of τ_f, as

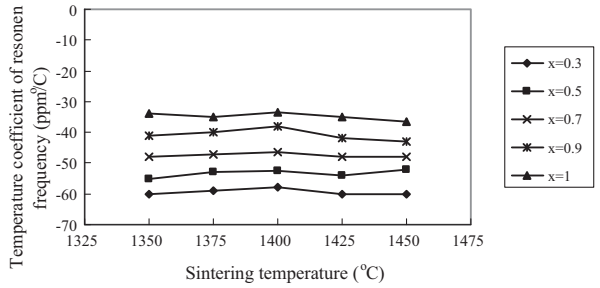

Fig. 5. Temperature coefficient values of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics system sintered at different temperatures with 1 wt% ZnO addition.

shown in Fig. 5. In the tilted region, the increasing thermal energy is completely absorbed to recover tilting. TCF values were found to increase with Co^{2+} content, as shown in Fig. 5.

4. Conclusions

The dielectric properties of ZnO-doped $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics were investigated by conventional the solid-state oxide methods. The microwave dielectric properties of $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics were improved by substituting Mg^{2+} ions with Co^{2+} ions. With 1 wt% ZnO addition, a dielectric constant of 29.13, a $Q \times f$ value of 80,000 (GHz), and a τ_f value of -59 ppm/°C were obtained for $La(Mg_{0.7}Co_{0.3})_{1/2}Ti_{1/2}O_3$ ceramics sintered at 1375 °C for 4 h. Actually in $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics systems increasing Co content lowered $Q \times f$ and τ_f.

ZnO-doped $La(Mg_{1-x}Co_x)_{1/2}Ti_{1/2}O_3$ ceramics are suitable for applications in microwave dielectric resonators and microwave devices due to their its excellent microwave dielectric properties.

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