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Influence of Zn substitution on the crystal structures and microwave dielectric properties of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \leq x \leq 0.2$) ceramics

C.H. Yang, H.L. Pan, Y.K. Yang, H.T. Wu*

School of Materials Science and Engineering, University of Jinan, Jinan, 250022, China

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ABSTRACT

A series of Zn-doped $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($x = 0$, 0.05, 0.10, 0.15, 0.2) ceramics were formed via the conventional solid-state process. Influence of Zn^{2+} on the crystal structures, phase compositions, sintering characteristics and properties of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \leq x \leq 0.2$) ceramics were systematically studied. XRD results showed that a single phase with the cubic rock-salt structure was formed for $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \leq x \leq 0.15$) and the second phase of Zn_2TiO_4 could be detected with a further increase of the Zn^{2+} contents. Some intrinsic parameters were calculated in order to investigate the correlations between these parameters of Mg/Zn–O bonds and microwave dielectric properties. As the Zn^{2+} content increases, optimum ε_r values exhibited an increasing trend, which could be explained by the variations of the polarizability and bond ionicity of Mg/Zn–O bonds. The decrease of maximum $Q{\cdot}f$ values for $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($x = 0$, 0.05, 0.10, 0.15, 0.2) ceramics could be predicted by the decrease of the packing fraction and lattice energy of Mg/Zn–O bonds. τ_f values showed close relationship with the bond energy and thermal expansion coefficient of Mg/Zn–O bonds. Excellent combined microwave dielectric properties with $\varepsilon_r = 15.46$ (at 10.9 GHz), $Q{\cdot}f = 125{,}453$ GHz (at 8.6 GHz) and $\tau_f = -32.35$ ppm/°C were obtained for $Li_2(Mg_{0.85}Zn_{0.15})_3TiO_6$ ceramic sintered at 1600 °C.

1. Introduction

Microwave dielectric ceramics or even films have been widely applied to microwave devices such as antennas, resonators and filters due to their excellent microwave dielectric properties [1–3]. An appropriate dielectric constant (ε_r), a high quality factor ($Q{\cdot}f$) and a near-zero temperature coefficient of resonant frequency (τ_f) are required in order to meet the development of wireless communication technology [4]. Recently, $Li_2Mg_3TiO_6$ ceramic has obtained much attention because of its excellent microwave dielectric properties [5–14]. For example, Liu et al. reported that $Li_2Mg_3TiO_6$ ceramic possessed the excellent properties [5,6]. Zhang et al. researched the influences of different divalent ions on the micro-structures and dielectric properties of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$ ceramics [9]. Tang et al. investigated the temperature-stable and high-Q $Li_2Mg_{3-x}Ca_xTiO_6$ ($x = 0.00$–0.18) ceramics [10]. Liu et al. reported that $0.8Li_2Mg_3TiO_6$-$0.2Ca_{0.8}Sr_{0.2}TiO_3$-4 wt% LiF samples sintered at 800 °C possessed good properties [12]. In our previous reports, crystal structure, sintering characteristics and microwave dielectric properties of $Li_2(Mg_{1-x}Co_x)_3TiO_6$ ($0 \leq x \leq 0.4$) ceramics were studied [14]. To the best of our knowledge, effects of Zn-substitution on the crystal structures, sintering characteristics and microwave dielectric properties of $Li_2Mg_3TiO_6$ ceramic have not been investigated.

In the early reports, a small quantity of Zn^{2+} ions could significantly improve the microwave dielectric properties [15–17]. Liu et al. reported that $Q{\cdot}f$ values increased from 103,453 GHz to 138,481 GHz with the increase of x values from 0 to 0.15 for $Mg_{1-x}Zn_xSiO_3$ ($x = 0$–0.3) ceramics [15]. Wang et al. reported that Zn-substitution could enhance $Q{\cdot}f$ values of Li_2MgTiO_4 [16]. Cations displacement were extensively used to enhance the properties, which urged us to prepare $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \leq x \leq 0.2$) ceramics due to the similar ionic radius for Mg^{2+} (0.72 Å) and Zn^{2+} (0.74 Å) [18]. Now in this paper, the effects of Zn-substitution on the crystal structure, sintering characteristics, micro-structures and properties were systematically researched, and the relationship between the intrinsic parameters of Mg/Zn–O bonds and microwave dielectric properties were researched.

* Corresponding author.
E-mail address: mse_wuht@ujn.edu.cn (H.T. Wu).

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2. Experimental procedure

$Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) were prepared through the solid-state process using powders of MgO (Aladdin, 99.99%), Li_2CO_3 (Aladdin, 99.99%), ZnO (Aladdin, 99.9%) and TiO_2 (Aladdin, 99.9%). The raw materials were weighed according to the chemical formulas of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20$) and then ball-milled for 24 h. These wet mixtures were dried in an oven and calcined at 1000 °C for 4 h. The calcined powders were re-ground for 24 h and dried in an oven again. After dried, the powders were mixed with 8 wt% paraffin and pressed into 6 mm thick and 10 mm diameter cylinders. These cylinders were preheated to 500 °C to expel the paraffin and then sintered at 1500–1650 °C in sealed platinum crucibles.

Phase compositions and crystal structures of the sintered specimens were conducted by X-ray diffraction (XRD, D/MAX-B, Rigaku Co., Japan) with Cu K_α radiation. Rietveld refinements were operated to research the crystal structure of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) ceramics using Fullprof software [19]. Archimede's method was used to measure the apparent density of sintered samples. Micro-structure of the specimens was observed by a scanning electron microscopy (SEM, Model JEOL JEM-2010, FEI Co., Japan). A network analyzer (N5234A, Agilent Co., American) was used to measure the properties of sintered samples. ε_r was measured through Hakki-Coleman method [20]. *Q.f* was measured using the cavity method [21]. τ_f was measured and calculated by the Equ. (1).

$$\tau_f = \frac{f_2 - f_1}{f_1(85-25)} \quad (1)$$

where f_1 and f_2 are the resonant frequency at the temperature of 25 °C and 85 °C, respectively.

3. Results and discussion

3.1. Phases refinement

XRD patterns of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) specimens sintered at 1600 °C are illustrated in Fig. 1. A single-phase is observed for $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.15$), which is identified to be the rock-salt structure with Fm-3m space group (No. 225) according to the $Li_2Mg_3SnO_6$ (JCPDS PDF#39-0932). When the substitution increase to 0.2, the second phase Zn_2TiO_4 (JCPDS PDF#25-1164) can be detected. As shown in the insert of Fig. 1, the main peak (at $2\theta = 43°$) shifts to the low angles with the increase of the x values from 0 to 0.2, which can be explained by the substitution of larger Zn^{2+} ion (0.740 Å) for Mg^{2+} ion (0.720 Å) and indicates the increase of the cell volumes.

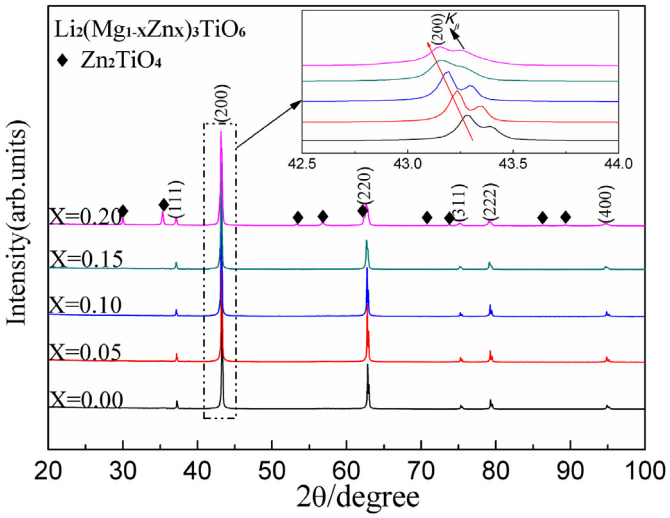

Fig. 1. XRD patterns of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) ceramics sintered at 1600 °C.

Fig. 2(a–e) shows the refinement patterns of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) ceramics sintered at 1600 °C $LiFeO_2$ [22] was selected as the original model for Rietveld refinement due to the similar crystal structure such as the same Fm-3m space group (No. 225), nearly cell volumes and lattice constants. The measured patterns match well with the calculated ones for different components. The refinement results of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) ceramics are illustrated in Table 1. Fig. 2(f) exhibits the variations of cell volumes and lattice constants of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ sintered at 1600 °C. With the x values increasing from 0 to 0.2, the cell volumes increase from 73.1790 $Å^3$ to 73.5840 $Å^3$, which corresponds with the XRD results.

Fig. 3 exhibits the schematic representation of the crystal structure for $Li_2Mg_3TiO_6$ super-cell. $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) show a cubic rock-salt structure, wherein cations (Li^+, Mg^{2+}/Zn^{2+}, Ti^{4+}) and anion (O^{2-}) occupy 4a and 4b Wyckoff positions, respectively. The occupancies of Li^+, Mg^{2+}/Zn^{2+}, Ti^{4+} and O^{2-} are 0.3333, 0.5000, 0.1667 and 1.000, respectively. On the basis of these results and refinement results, the bond lengths are calculated and shown in Table 2. In the early reports, there is a close connection between *Q.f* values and the packing fraction (*P. F.*) [23,24]. Based on the refinement results, the packing fraction is calculated using Equ. 2 [23] and the results are shown in Table 2.

$$Packing\ fraction = \frac{volume\ of\ packedions}{volume\ of\ unitcell} \times Z \quad (2)$$

3.2. Sintering characteristics and micro-morphology

Apparent densities of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) ceramics sintered at 1500–1650 °C are shown in Fig. 4. Apparent densities increase first due to the growth of grains and the lack of pores from 1500 °C to 1600 °C, and then slightly decrease due to the abnormal grain growth. The maximum apparent densities are obtained at 1600 °C for different components. At the same sintering temperatures, the apparent densities gradually increase with the increase of Zn^{2+} contents, which can be explained by the higher atomic mass of Zn^{2+} (65.41) in comparison with that of Mg^{2+} (24.31) with the unit cell volume (Table 1) shows no significant change. For example, the maximum densities increase from 3.35 g/cm^3 to 3.49 g/cm^3 for different Zn^{2+} contents.

Fig. 5 illustrates microstructures of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) ceramics sintered at 1600 °C. With the increase of Zn^{2+} contents from 0 to 0.2, the grain size exhibits no significant change. The grains exhibit homogeneous state and the average grain size is about 60 μm. It can be concluded that dense micro-structures of $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.2$) ceramics can be obtained at 1600 °C, which corresponds with the results of apparent densities.

3.3. Complex bond theory and bond energy calculation

Microwave dielectric properties are influenced by both extrinsic factors and intrinsic factors [25,26]. In this paper, a relative dense microstructure with pure phase is achieved at 1600 °C for $Li_2(Mg_{1-x}Zn_x)_3TiO_6$ ($0 \le x \le 0.15$) ceramics, which implies that the influence of extrinsic factors can be neglected and the influence of intrinsic factors should be further studied. According to the refinement