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Microwave dielectric properties of $Li_2ZnTi_3O_8$ ceramics doped with Bi_2O_3

Xuepeng Lu, Yong Zheng*, Bin Zhou, Zuowei Dong, Peng Cheng

College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

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Abstract

The effects of Bi_2O_3 on the sintering temperature, phase composition, microstructure and microwave dielectric properties of $Li_2ZnTi_3O_8$ ceramics are investigated. The addition of Bi_2O_3 can effectively reduce the sintering temperature of $Li_2ZnTi_3O_8$ ceramic from 1075 to 950 °C. Only a single phase $Li_2ZnTi_3O_8$ forms in the $Li_2ZnTi_3O_8$ ceramic with less than 1.0 wt% Bi_2O_3 addition sintered at 950 °C. However, when the addition of Bi_2O_3 exceeds 1.0 wt%, the second phase $Bi_2Ti_2O_7$ forms in the $Li_2ZnTi_3O_8$ ceramics. Typically, 2.0 wt% Bi_2O_3-doped $Li_2ZnTi_3O_8$ ceramic sintered at 950 °C can reach a maximum relative density of 97.4% and exhibits good microwave dielectric properties of ε_r =27.8, $Q \times f$=36386 GHz, τ_f=−19.5 ppm/°C.

Keywords: A. Sintering; C. Dielectric properties; Microstructure; Ceramics

1. Introduction

In recent years, along with the rapid growth in wireless communications industry, a variety of microwave devices such as filters, duplexers, resonators and antennas were well developed [1]. Nowadays increased attention has been paid to develop microwave dielectric ceramics with low sintering temperatures for low-temperature cofired ceramics (LTCC) application [2]. To realize cofiring with Ag electrode, the sintering temperatures of these ceramic materials should be lower than 950 °C [3]. However, the sintering temperature of most commercial dielectric ceramic is much higher than the melting point of silver [4–6]. Therefore, it is important to develop the microwave dielectric ceramic with low sintering temperature and good microwave dielectric properties.

Recently, Sebastian et al. [7,8] reported that $Li_2ZnTi_3O_8$ ceramics sintered at 1075 °C for 4 h exhibited good microwave dielectric properties of ε_r=25.6, $Q \times f$=72000 GHz, τ_f=−11.2 ppm/°C. $Li_2ZnTi_3O_8$ ceramics are expected as very competitive ultra-low loss microwave materials compared with the previous materials such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ [9] and $Zr_{0.8}Sn_{0.2}TiO_4$ [10], which have a low cost of raw materials and low bulk density. In order to realize the LTCC applications of $Li_2ZnTi_3O_8$ ceramic, it is essential to reduce the sintering temperature of $Li_2ZnTi_3O_8$ ceramic to 950 °C.

As a common sintering aid, Bi_2O_3 has been reported as a promising sintering aid for the densification at relatively low sintering temperature [11–13]. Tay et al. [12] reported that the addition of 15 mol% Bi_2O_3 can reduce the sintering temperature of the $La(Mg_{0.5}Ti_{0.5})O_3$ ceramics from 1600 to 1325 °C without degradation of the microwave dielectric properties. However, the effect of Bi_2O_3 addition on the sintering temperature and microwave dielectric properties of the $Li_2ZnTi_3O_8$ ceramics has not been studied.

In the present study, the effects of Bi_2O_3 addition on the sintering temperature, densification, phase composition, microstructure and microwave dielectric properties of the $Li_2ZnTi_3O_8$ ceramics were thoroughly investigated. Furthermore, the relationships among densification, microstructure and microwave dielectric properties of the Bi_2O_3-doped $Li_2ZnTi_3O_8$ ceramics were discussed.

2. Experimental procedure

The $Li_2ZnTi_3O_8$ ceramics were prepared by the conventional solid-state ceramic route. Li_2CO_3 (99%), ZnO (99.5%), TiO_2 (99.5%) were used as starting powders. The powders were weighed according to the stoichiometric ratio of $Li_2ZnTi_3O_8$, and milled with zirconia balls in ethanol for 24 h.

*Corresponding author. Tel./fax: +86 25 52112626.
E-mail address: zy_msc@nuaa.edu.cn (Y. Zheng).

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The slurries were dried and sieved and calcined at 900 °C for 4 h, then re-milled with different amounts of Bi_2O_3. With 5 wt % PVA solution as a binder, the granulated mixtures were pressed into disks with 20 mm in diameter and 12 mm in thickness under the pressure of 100 MPa. After debinding, these disks were sintered at temperatures of 925–1000 °C for 4 h.

The bulk densities of the ceramics were measured by the Archimedes method. The crystal phases of the sintered samples were identified by X-ray diffraction pattern (Cu K_α radiation, Advance D8, Bruker). The microstructures of the samples were observed by a scanning electron microscope (Quanta 200, Eindhoven, Holland). Microwave dielectric properties of dielectric constant (ε_r), quality factors ($Q \times f$) and temperature coefficients of resonant frequency τ_f between 25 °C and 85 °C were measured in the TE011 mode by the Hakki–Coleman method [14] using a microwave network analyzer (Advantest R3767C, Tokyo, Japan).The temperature coefficients of resonant frequency (τ_f) were defined as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \times 10^6 \ (\mathrm{ppm}/^{\circ}\mathrm{C}) \quad (1)$$

where f_{85} and f_{25} represent the resonant frequencies at 85 °C and 25 °C, respectively.

3. Results and discussions

The X-ray diffraction patterns of the $Li_2ZnTi_3O_8$ ceramics doped with different Bi_2O_3 additions sintered at 950 °C are shown in Fig. 1. Only a cubic spinel structure $Li_2ZnTi_3O_8$ phase (space group P4332, a=8.3710 Å, JCPDS file No. 86-1512) appears in the XRD patterns of the specimens with 1.0 wt% Bi_2O_3 addition. However, when the addition of Bi_2O_3 exceeds 1.0 wt%, the $Li_2ZnTi_3O_8$ and $Bi_2Ti_2O_7$ phase which is formed at 800 °C [15] co-exist in the specimens sintered at 950 °C. With increasing Bi_2O_3 additions, the peak intensities of $Bi_2Ti_2O_7$ phase increase gradually.

The crystal parameters of $Li_2ZnTi_3O_8$ with different Bi_2O_3 additions are calculated and summarized in the Table 1. It is noteworthy that the lattice parameters and cell volumes of $Li_2ZnTi_3O_8$ ceramics with Bi_2O_3 additions are larger than that of pure $Li_2ZnTi_3O_8$ ceramics. These results indicate that the Bi^{3+} ions substituted the Zn^{2+} or Ti^{4+} ions of $Li_2ZnTi_3O_8$ lattice, Since the ion radius of Bi^{3+} (1.03 Å, CN=6) is larger than that of Zn^{2+} (0.74 Å, CN=6) or Ti^{4+} (0.61 Å, CN=6) [16]. The crystal parameters increase with increasing Bi_2O_3 additions and then decrease after reaching the maximum values. With 2.5 wt% Bi_2O_3 addition, the decrease of the lattice parameters and cell volumes are caused by the solubility limit of Bi^{3+} and the formation of $Bi_2Ti_2O_7$ phase in $Li_2ZnTi_3O_8$ ceramic.

Fig. 2 shows the densities of the $Li_2ZnTi_3O_8$ ceramics doped with different amounts of Bi_2O_3 sintered at various sintering temperatures. Addition of Bi_2O_3 can effectively reduce the sintering temperature of $Li_2ZnTi_3O_8$ ceramics. The densities of $Li_2ZnTi_3O_8$ ceramics increase with increasing Bi_2O_3 additions and then decrease after reaching their respective maximum values. In fact, the ceramics with 1.0 wt%, 1.5 wt%, 2.0 wt% and 2.5 wt% Bi_2O_3 additions reach their maximum densities at 975 °C, 950 °C, 950 °C and 950 °C, respectively. It is obvious that the densification temperature tends to shift down

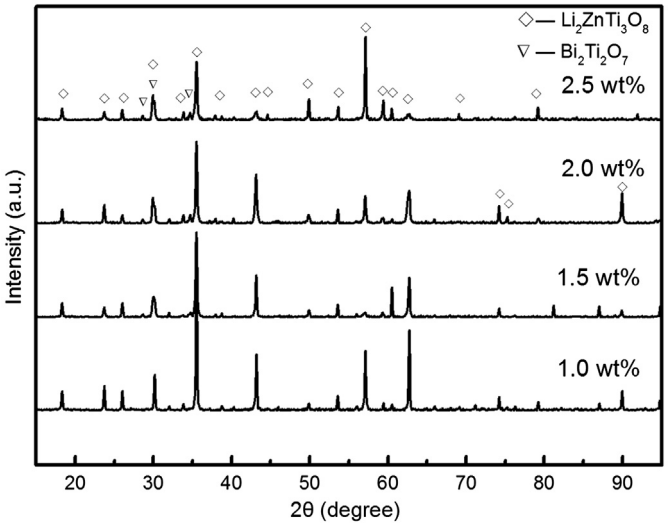

Fig. 1. XRD patterns of $Li_2ZnTi_3O_8$ ceramics doped with different Bi_2O_3 additions sintered at 950 °C.

Table 1
Crystal parameters of $Li_2ZnTi_3O_8$ ceramics with different Bi_2O_3 additions.

Addition of Bi_2O_3 (wt%)	a (Å)	V (Å^3)	Ref
0	8.3738	587.17	[7]
1.0	8.3794	588.35	–
1.5	8.3816	588.82	–
2.0	8.3830	589.11	–
2.5	8.3818	588.86	–

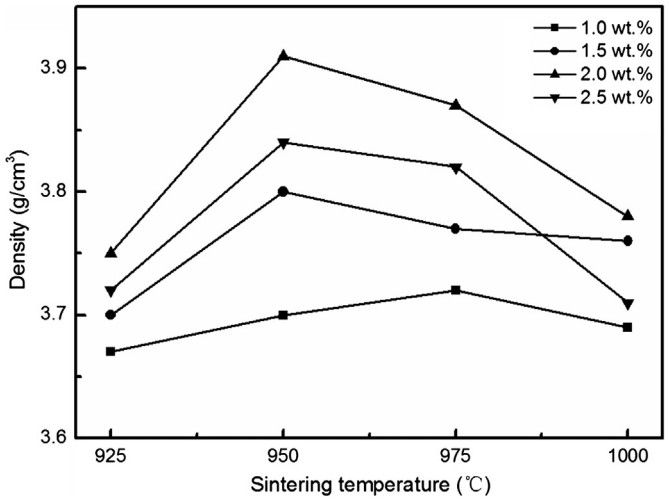

Fig. 2. Density of the $Li_2ZnTi_3O_8$ ceramics as a function of the Bi_2O_3 content and sintering temperature.

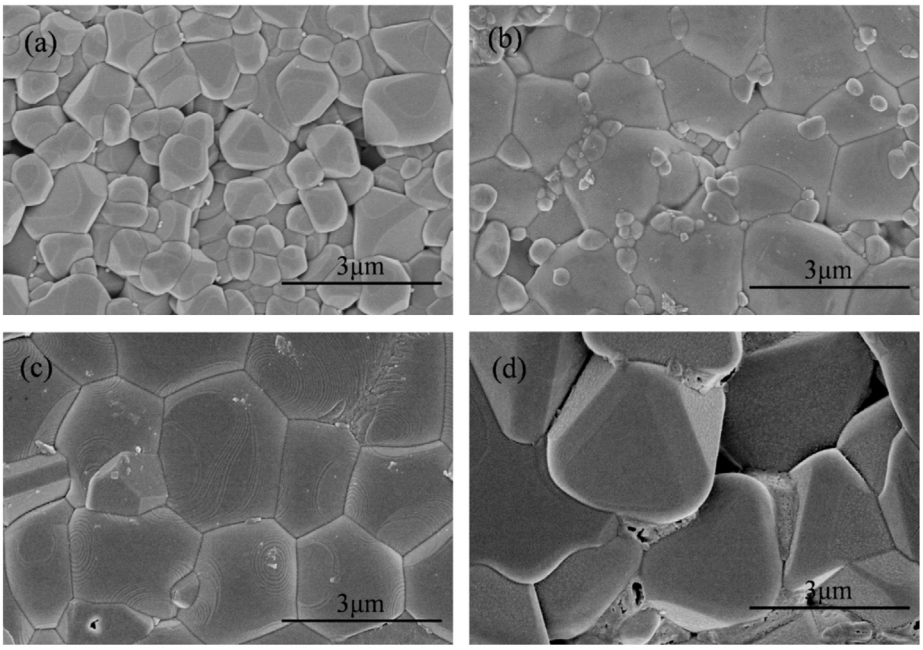

Fig. 3. SEM micrographs of $Li_2ZnTi_3O_8$ ceramics sintered at 950 °C doped with (a) 1.0 wt%, (b) 1.5 wt%, (c) 2.0 wt% and (d) 2.5 wt% Bi_2O_3.

with increasing Bi_2O_3 addition. Typically, the $Li_2ZnTi_3O_8$ ceramic with 2.0 wt% Bi_2O_3 addition sintered at 950 °C can reach a maximum density of 3.91 g/cm^3, which is equivalent to a relative density of 97.4%. This maximum density is obtained by the elimination of the pores and the high density of second phase $Bi_2Ti_2O_7$ (6.68 g/cm^3) [17].

The SEM micrographs of the $Li_2ZnTi_3O_8$ ceramics with different amounts of Bi_2O_3 sintered at 950 °C are shown in Fig. 3. The porosity of the $Li_2ZnTi_3O_8$ ceramics decreases with increasing Bi_2O_3 addition, while the average grain sizes of the $Li_2ZnTi_3O_8$ ceramics increase with increasing Bi_2O_3 addition. It illustrates that the Bi_2O_3 additions accelerate the grain growth due to the formation of second phase $Bi_2Ti_2O_7$ during sintering. However, with the 2.5 wt% Bi_2O_3 addition, the abnormally bigger grain and the phenomenon of partial over-sintering are observed in the $Li_2ZnTi_3O_8$ ceramic. An uniform and dense microstructure is observed in the $Li_2ZnTi_3O_8$ ceramics with 2.0 wt% Bi_2O_3 additions.

Fig. 4 shows the microwave dielectric properties of the $Li_2ZnTi_3O_8$ ceramics as a function of the Bi_2O_3 addition and sintering temperature. It is noticed that the variation of dielectric constant (ε_r) is very similar to that of the density. The ε_r values of $Li_2ZnTi_3O_8$ ceramics both increase initially and then reduce with increasing of Bi_2O_3 content and sintering temperature. The dielectric constant is dependent on the density, molecular volume, ionic polarizability, second phase and structural characteristics such as the distortion and tilting spaces of oxygen octahedron in the unit cell [18]. In present study, the density and second phase are the two main factors that may change the ε_r value. According to the Lichtenecker law [19], the $Li_2ZnTi_3O_8$ ceramics with 1.0 wt% Bi_2O_3 addition have lower ε_r values, which is caused by the lower density (the dielectric constant of pore equals 1.0). The maximum ε_r value (27.8) of $Li_2ZnTi_3O_8$ ceramic with 2.0 wt% Bi_2O_3 addition sintered at 950 °C is larger than the ε_r value (25.6) of pure $Li_2ZnTi_3O_8$ ceramic, which is related to the large ε_r value (125.5) of the second phase $Bi_2Ti_2O_7$ [17].

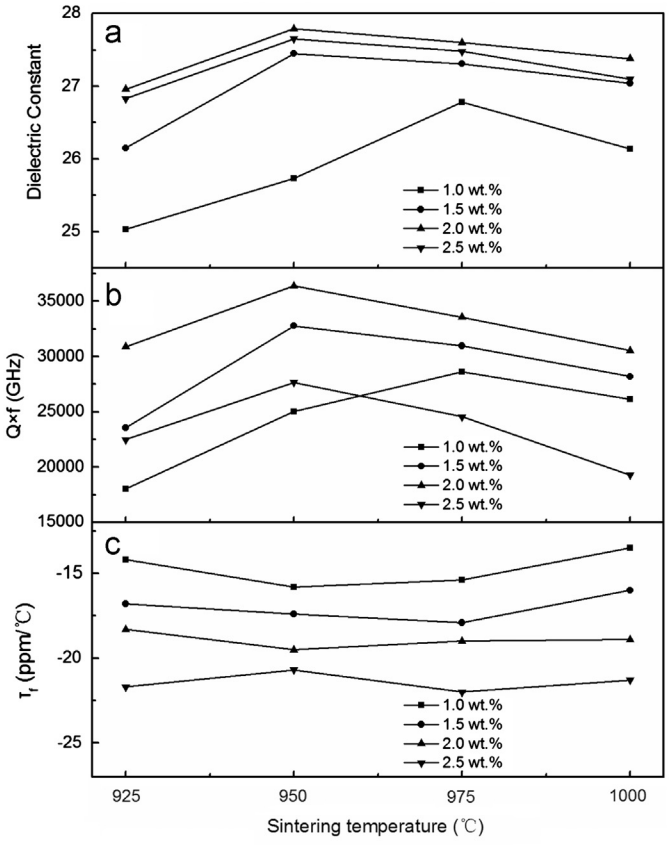

Fig. 4. Microwave dielectric properties of $Li_2ZnTi_3O_8$ ceramics as a function of the Bi_2O_3 addition and sintering temperature.

The $Q \times f$ values of the $Li_2ZnTi_3O_8$ ceramics as a function of the Bi_2O_3 addition and sintering temperature are shown in Fig. 4(b). The $Q \times f$ value variation revealed similar tendency with the density of the $Li_2ZnTi_3O_8$ ceramics. The microwave dielectric loss is caused not only by the lattice vibrational modes, but also by the density, oxygen vacancies, second phases, grain sizes, etc. [11]. Larger grain resulted in less grain boundary which meant less lattice mismatch and lower dielectric loss. When Bi^{3+} ions substitute for Zn^{2+} sites of $Li_2ZnTi_3O_8$ ceramics, the electrons are generated by the following equation:

$$Bi_2O_3 \rightarrow 2Bi^{\bullet}_{Zn} + 3O_o + 2e' \quad (2)$$

The produced electrons promote the transformation of Ti^{4+} ions to Ti^{3+} ions, which increases the dielectric losses of $Li_2ZnTi_3O_8$ ceramics. On the other hand, the existence of oxygen vacancies in $Li_2ZnTi_3O_8$ ceramics is due to the Ti^{4+}sites substituted by Bi^{3+} ions, which can be expressed as

$$Bi_2O_3 \rightarrow 2Bi^{'}_{Ti} + 3O_o + V^{\bullet\bullet}_o \quad (3)$$

The appearance of oxygen vacancies in $Li_2ZnTi_3O_8$ ceramics increased the anharmonic interaction, which also increases the dielectric losses of $Li_2ZnTi_3O_8$ ceramics.

The $Li_2ZnTi_3O_8$ ceramic with 2.0 wt% Bi_2O_3 addition sintered at 950 °C has the maximum $Q \times f$ value of 36386 GHz. The decrease of $Q \times f$ values of $Li_2ZnTi_3O_8$ ceramics with 1.0 wt% and 1.5 wt% Bi_2O_3 additions is correlated with the relatively low density, the substitution of Bi^{3+} ions and the small grain sizes. Excessive Bi_2O_3 addition leads to the reduction of the $Q \times f$ value, which can be explained by the high dielectric losses of the $Bi_2Ti_2O_7$ phase [17] and the presence of pores.

The τ_f values of the $Li_2ZnTi_3O_8$ ceramics as a function of the Bi_2O_3 addition and sintering temperature are shown in Fig. 4(c). The τ_f values of $Li_2ZnTi_3O_8$ ceramics do not considerably change with the sintering temperature, while it decrease with increasing the Bi_2O_3 addition. It is well known that the temperature coefficient of composite ceramic was obtained from the Lichtenecker empirical logarithmic rule [20]:

$$\tau_f = V_1\tau_{f1} + V_2\tau_{f2} \quad (4)$$

where the τ_{f1} and τ_{f2} are the τ_f values of the $Li_2ZnTi_3O_8$ and $Bi_2Ti_2O_7$ phase, respectively. As the τ_f value of $Bi_2Ti_2O_7$ phase is −239 ppm/°C [17], so the τ_f values of $Li_2ZnTi_3O_8$ ceramics decrease with increasing the Bi_2O_3 addition.

4. Conclusion

The sintering temperature, densification, microstructure and microwave dielectric properties of the $Li_2ZnTi_3O_8$ ceramics with Bi_2O_3 addition are investigated. Only a single phase $Li_2ZnTi_3O_8$ forms in the $Li_2ZnTi_3O_8$ ceramic with less than 1.0 wt% Bi_2O_3 addition sintered at 950 °C. However, when the addition of Bi_2O_3 exceeds 1.0 wt%, the second phase $Bi_2Ti_2O_7$ forms in the $Li_2ZnTi_3O_8$ ceramic. The lattice parameters and cell volumes of $Li_2ZnTi_3O_8$ ceramics with Bi_2O_3 additions are larger than that of pure $Li_2ZnTi_3O_8$ ceramics, which is caused by the substitution of Bi^{3+} ions. The lattice parameters and cell volumes of $Li_2ZnTi_3O_8$ ceramics sintered at 950 °C increases with increasing Bi_2O_3 additions and then decrease after reaching the maximum values at 2.0 wt% Bi_2O_3 addition. The relative density of $Li_2ZnTi_3O_8$ ceramics with 2.0 wt% Bi_2O_3 addition sintered at 950 °C is up to 97.4%, which is attributed to the elimination of the pores and the high density of second phase $Bi_2Ti_2O_7$. The average grain sizes of the $Li_2ZnTi_3O_8$ ceramics sintered at 950 °C increases with increasing Bi_2O_3 addition. The $Li_2ZnTi_3O_8$ ceramic with 2.0 wt% Bi_2O_3 addition sintered at 950 °C has a uniform and dense microstructure. The $Li_2ZnTi_3O_8$ ceramics with 2.0 wt% Bi_2O_3 addition sintered at 950 °C exhibit good microwave dielectric properties of $\varepsilon_r = 27.8$, $Q \times f = 36386$ GHz, $\tau_f = -19.5$ ppm/°C, which is promising for LTCC applications.

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