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Microwave dielectric properties of the low-temperature-fired $Li_2ZnTi_3O_8$–Li_2TiO_3 ceramics for LTCC applications

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Abstract
In this work, $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ ceramics were prepared through a traditional solid-state process. The effects of Li_2O–B_2O_3–SiO_2–CaO–Al_2O_3 (LBSCA) glass addition on phase formation, microstructure, sintering characteristic and microwave dielectric properties of the ceramics were investigated. A small amount of LBSCA glass addition significantly reduced sintering temperature of the ceramics. X-ray diffraction analysis revealed that $Li_2ZnTi_3O_8$ and Li_2TiO_3 phases coexisted without producing any other crystal phases in the sintered ceramics. Dielectric constant and *Qf* values were related to the amount of LBSCA addition and sintering temperatures. The specimens obtained near-zero temperature coefficient (τ_f) values through the compensation on the positive τ_f of Li_2TiO_3 and the negative τ_f of $Li_2ZnTi_3O_8$. The $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ ceramic with 0.75 wt% LBSCA addition and sintered at 900 °C for 3 h exhibited excellent microwave dielectric properties of $\varepsilon_r = 23.907$, $Qf = 63050$ GHz and $\tau_f = 1.2$ ppm/°C, which was very suitable for LTCC (low temperature co-fired ceramics) applications.

1 Introduction

With the rapid development of wireless communication technology, an increasing number of studies have focused on materials with brilliant microwave dielectric properties. At the same time, to achieve the miniaturisation and integration of microwave devices, many studies have investigated the LTCC technology, which plays an important role in microelectronic applications [1–3]. Ag is widely used as internal-electrode material in LTCC devices to ensure their low cost and high conductivity. Considering that Ag has a melting point of approximately 961 °C, the typical sintering temperature of LTCC materials must be reduced to approximately 900 °C or lower to better co-fire with Ag internal electrodes [4–6]. Low-melting-point glasses were usually used as sintering aids in LTCC materials, which reduced the sintering temperature and achieved optimal microwave dielectric properties. Furthermore, near-zero τ_f of LTCC materials are important to obtain stable LTCC microwave components [7–12]. Near-zero τ_f LTCC materials can be obtained by properly compounding the materials with negative and positive τ_f.

$Li_2ZnTi_3O_8$ ceramics had excellent microwave dielectric properties with ε_r values of ~ 25.8, a Qf value of ~ 74,200 GHz and a τ_f value of − 13 ppm/°C [13]. However, the τ_f value of $Li_2ZnTi_3O_8$ ceramics was negative. On the other hand, Li_2TiO_3 had attracted considerable attention in microwave dielectric ceramics because of its positive τ_f value and relatively outstanding microwave dielectric properties [14]. In the present work, we combined $Li_2ZnTi_3O_8$ with Li_2TiO_3 to obtain materials with near-zero τ_f values. And LBSCA glass was adopted as sintering aid to lower the sintering temperature of $Li_2ZnTi_3O_8$–Li_2TiO_3 compound ceramics because it had very low softening temperature point and efficient help-melting effect [15, 16]. The effects of LBSCA glass addition on the sintering behaviour, microstructure and microwave dielectric properties of the ceramics were investigated and discussed.

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2 Experimental procedure

$Li_2ZnTi_3O_8$–Li_2TiO_3 ceramic samples were prepared by the conventional solid-state reaction. High-purity Li_2CO_3 (99%), ZnO (99.5%) and TiO_2 (99%) were used as starting materials. $Li_2ZnTi_3O_8$ calcined powders were produced by ball-milling Li_2CO_3, ZnO and TiO_2 in a 1:1:3 molar ratio. Then the mixed powders were dried and calcined at 900 °C for 3 h. Li_2TiO_3 calcined powders were produced by ball-milling Li_2CO_3 and TiO_2 in a 1:1 molar ratio. Then the mixed powders were dried and calcined at 820 °C for 3 h. LBSCA glass was prepared by the quenching technology. The oxide raw materials were mixed and melted at 1000 °C for 2 h using an alumina crucible at a Li_2O:B_2O_3:SiO_2:CaO:Al_2O_3 molar ratio of 52.45:31.06:11.99:2.25:2.25 [15, 16]. The solution was removed from the furnace and then poured into cold water to obtain the glass. Then, approximately 0–1.5 wt% of LBSCA glass was added into $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ compounds respectively (0.73:0.27 was the weight ratio of $Li_2ZnTi_3O_8$ and Li_2TiO_3 calcined powders, which was calculated by their respective τ_f to obtain near-zero τ_f in the compound materials). The mixtures were milled in nylon pots with zirconia balls. After drying and granulation, the powders were pressed into cylinders, which were final sintered at 875–950 °C for 3 h.

Crystalline phase structures were analysed through X-ray diffraction (XRD:DX-2700) using Cu Kα radiation. Bulk densities of the sintered samples were measured using the Archimedes method, and the densities were obtained by the ratio of mass and volume. Sample micrographs were examined by scanning electron microscopy (SEM:JEOL JSM6490LV). The microwave dielectric properties of the sintered ceramics in microwave frequency were measured using the Hakki–Coleman method and Agilent N5230A network analyser (300 MHz–20 GHz) in a resonant cavity. τ_f values were measured at a temperature range of 20–80 °C. The values were calculated from the following formula:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \times 10^6$$

where f_T and f_0 are the resonant frequencies at 80 and 20 °C, respectively.

3 Results and discussion

Figure 1 shows the XRD patterns of $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ ceramics with different LBSCA glasses and sintered at 900 °C for 3 h. All samples contained $Li_2ZnTi_3O_8$ and Li_2TiO_3 phases, no other phases were detected. All peaks were indexed in terms of $Li_2ZnTi_3O_8$

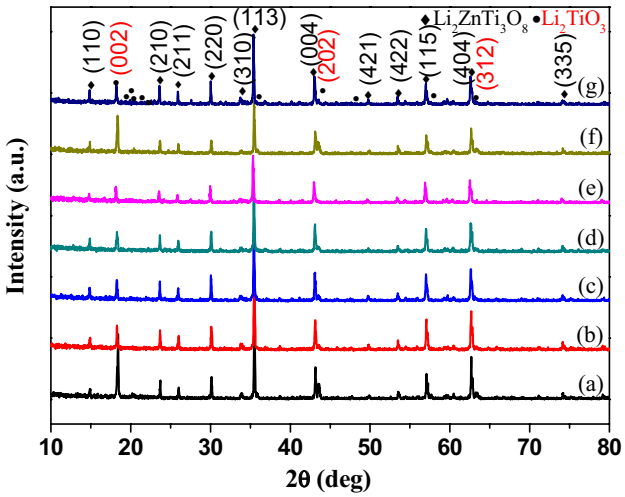

Fig. 1 XRD patterns of $Li_2ZnTi_3O_8$–Li_2TiO_3 ceramics with x wt% LBSCA additive and sintered at 900 °C for 3 h. (*a*) x = 0, (*b*) = 0.25, (*c*) = 0.5, (*d*) = 0.75, (*e*) = 1, (*f*) = 1.25, and (*g*) = 1.5

(PDF #44-1037) and Li_2TiO_3 (•, #33–0831). $Li_2ZnTi_3O_8$ is a cubic structure which belongs to the P4332 space group. Zn^{2+} and 1/2 of the Li^+ are located in the centre of [ZnO_4] and [LiO_4] tetrahedral units [17]. Ti^{4+} and the remaining 1/2 Li^+ are located in the [TiO_6] and [LiO_6] octahedron centre. Li_2TiO_3 is a monoclinic structure which belongs to the C2/c(15) space group [18]. Ti^{4+} is located in the centre of [TiO_6] octahedron, and the octahedrons are connected to each other through six-coordinated Li^+. Due to the large crystal structure difference between $Li_2ZnTi_3O_8$ and Li_2TiO_3, the Li_2TiO_3 phase beneficially coexisted with the $Li_2ZnTi_3O_8$ phase in the $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ ceramics. LBSCA addition was undetectable, which indicated that LBSCA existed in the amorphous phase.

Figure 2 shows the SEM micrographs of $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ ceramics with different LBSCA glasses. LBSCA addition significantly influenced the densification and average grain size of the compound ceramics. Figure 2a presented a porous microstructure with many intergranular pores. Figure 2b, c showed that the intergranular pores decreased, the grain size increased and the samples became dense with the increase of LBSCA glass content. This phenomenon was due to that LBSCA glass formed a liquid phase during sintering, which accelerated mass transfer and promoted sintering [19]. Figure 2d showed that the sample obtained a dense and uniform microstructure, which was doped with 0.75 wt% LBSCA glass. Figure 2e–g showed that the microstructure of the samples did not change significantly with further increasing LBSCA glass content.

Figure 3 presents the variation in sintered densities of the samples with different LBSCA contents. The sintered densities initially increased and reached their maximum with x = 0.75 wt% and then gradually decreased. The first

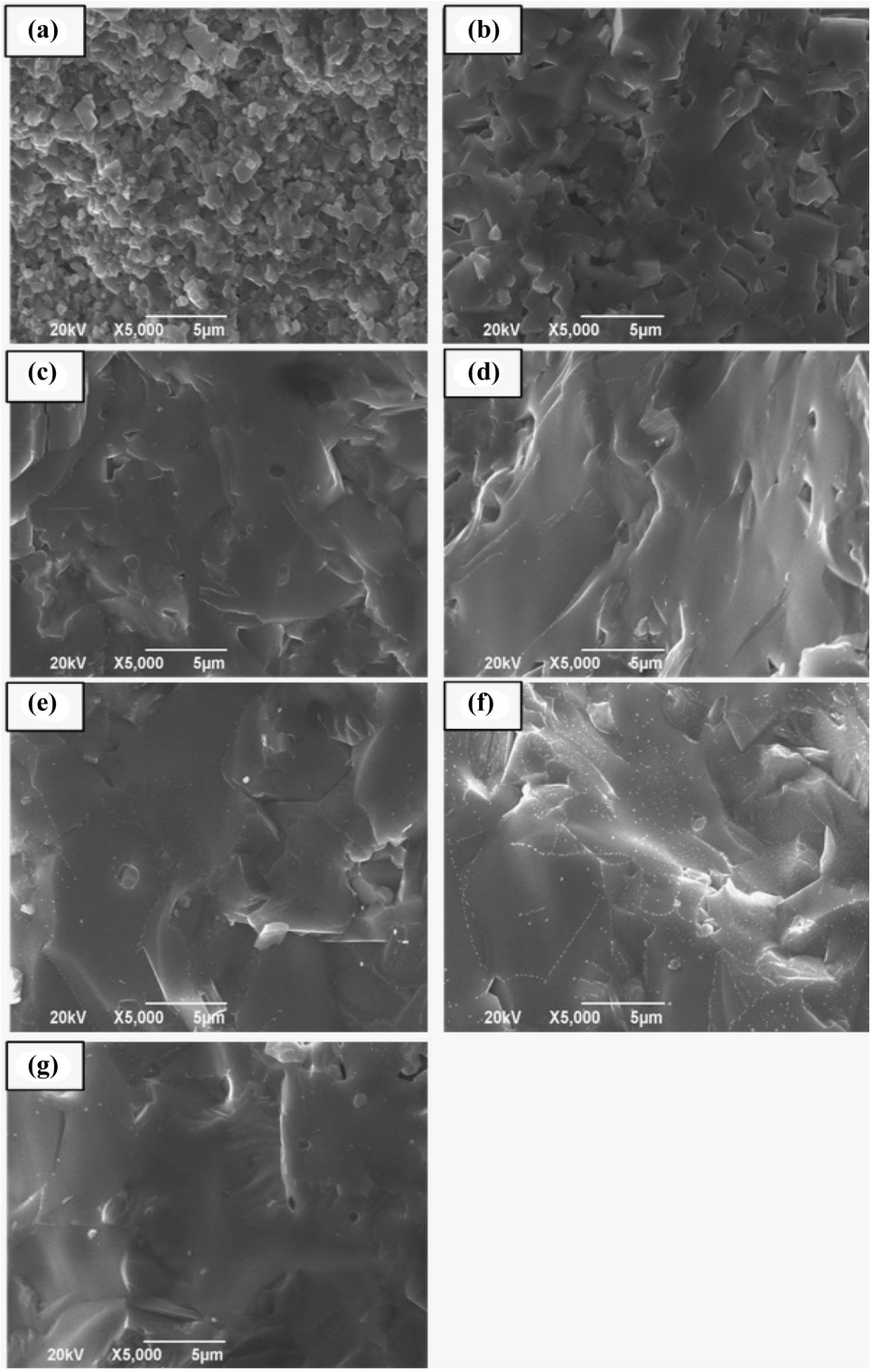

Fig. 2 SEM micrographs of $Li_2ZnTi_3O_8$–Li_2TiO_3 ceramics with x wt% LBSCA additive and sintered at 900 °C for 3 h. **a** x = 0, **b** = 0.25, **c** = 0.5, **d** = 0.75, **e** = 1, **f** = 1.25, and **g** = 1.5

increase in densities was due to the liquid phase of LBSCA formed during sintering effectively promoted the densification of the materials [20]. The densities monotonously decreased with further increasing LBSCA content, which could be attributed to two reasons. One reason was that excessive grain boundary amorphous LBSCA glass hindered the further densification of the materials. The other reason was that the content ratio of low-density glass addition contributed to the decrease in densities of the samples.

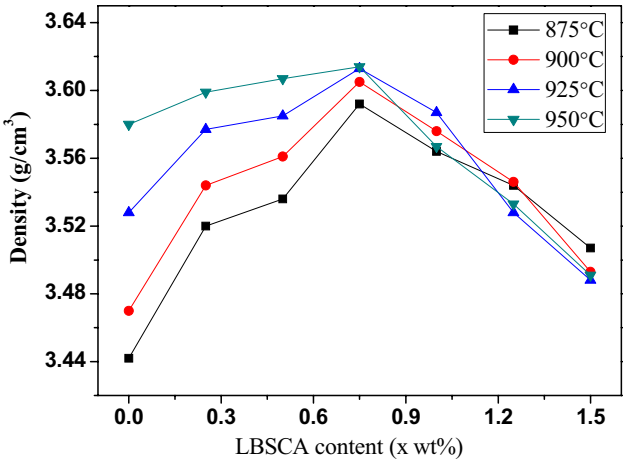

Fig. 3 Sintered densities of $Li_2ZnTi_3O_8$–Li_2TiO_3 ceramics with different LBSCA glass and sintered from 875 to 950 °C

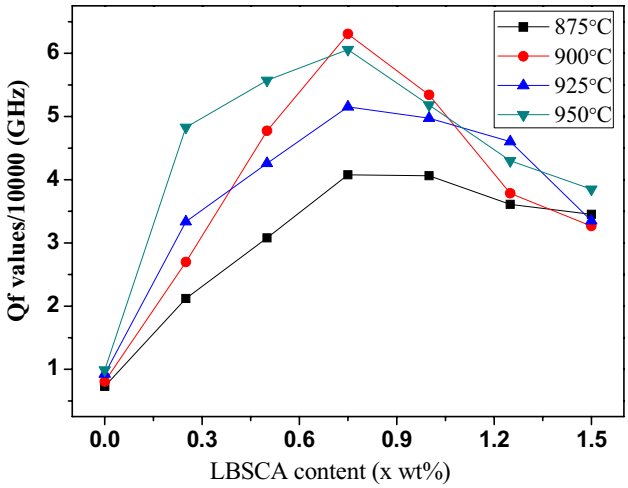

Fig. 5 *Qf* values of $Li_2ZnTi_3O_8$–Li_2TiO_3 ceramics with different LBSCA glass and sintered from 875 to 950 °C

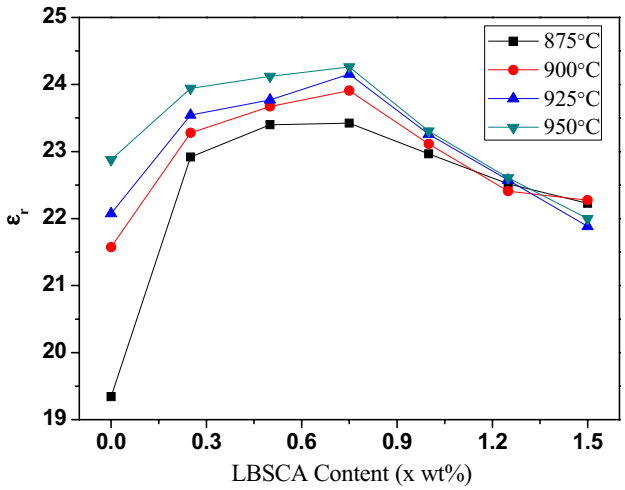

Fig. 4 Permittivity of $Li_2ZnTi_3O_8$–Li_2TiO_3 ceramics with x wt% LBSCA glass and sintered from 875 to 950 °C

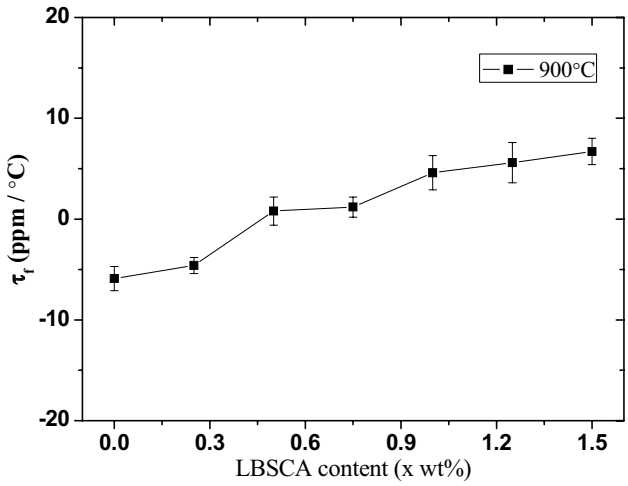

Fig. 6 τ_f values of $Li_2ZnTi_3O_8$–Li_2TiO_3 ceramics with different LBSCA glass and sintered at 900 °C for 3 h

Figure 4 shows the variation in ε_r values of the ceramics with different LBSCA glass contents and sintered under different temperatures. Obviously, the tendency of ε_r variation was consistent with that of density. As LBSCA content increased, ε_r gradually increased and reached the maximum with 0.75 wt% LBSCA. After that, ε_r slightly decreased with further increasing LBSCA content. Similar to the variation of density, this trend remained the same under different sintering temperatures. Therefore, sintered density was the main factor determining the ε_r value of the ceramics.

Figure 5 shows the *Qf* values of $0.73Li_2ZnTi_3O$–$0.27Li_2TiO_3$ ceramics with different LBSCA contents and sintered at 875–950 °C. The *Qf* values initially increased and then decreased with increasing LBSCA content. The maximal *Qf* values were obtained with 0.75 wt% LBSCA content, in spite of different sintering temperatures. After that, *Qf* values gradually decreased with further increasing LBSCA content. This phenomenon was very close to the variation of density. The microwave dielectric losses can be divided into internal and external losses [21]. Internal losses are related to the internal crystal structure of the dielectric material and are mainly caused by the lattice vibration modes, whereas extrinsic losses are associated with many factors, such as second phases, oxygen vacancies, grain size and densification. Therefore, the initial increase in *Qf* values might be attributed to the increase in densification and average grain size. The subsequent decrease in *Qf* values was mainly due to the reduced density. Furthermore, the relatively high loss of glassy phase was also responsible for the decrease of *Qf* values.

Figure 6 shows the τ_f values of $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ ceramics sintered at 900 °C for 3 h. τ_f can be tuned by the mixtures of dielectrics with opposite τ_f values. A previous report showed that $Li_2ZnTi_3O_8$ has a negative τ_f value of − 13.75 ppm/°C, whereas Li_2TiO_3 had a positive τ_f value of 35.78 ppm/°C. Therefore, the expected near-zero τ_f values could be achieved by the compensation of the positive τ_f of Li_2TiO_3 and the negative τ_f of $Li_2ZnTi_3O_8$ in $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$. Furthermore, τ_f altered from − 6 to 7 ppm/°C with increasing LBSCA content in this study. This fact might due to the influence of the glass's τ_f and the variation of sintered densities. The specimen with 0.75 wt% LBSCA and sintered at 900 °C could obtain very high *Qf* value (which was 63,050 GHz) and near-zero τ_f of 1.2 ppm/°C, which was considered suitable for LTCC applications.

4 Conclusion

In this study, the effects of LBSCA addition on the phase formation, sintering characteristic, microstructure and microwave dielectric properties of the $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ ceramics were investigated. Proper LBSCA glass addition could effectively densify the samples and improve the microwave dielectric properties. No chemical reaction occurred between the $Li_2ZnTi_3O_8$ and Li_2TiO_3 ceramics. A near-zero τ_f value was obtained through the compensation of the positive τ_f of Li_2TiO_3 and the negative τ_f of $Li_2ZnTi_3O_8$. The $0.73Li_2ZnTi_3O_8$–$0.27Li_2TiO_3$ sample with 0.75 wt% LBSCA glass addition and sintered at 900 °C presented excellent dielectric properties with $\varepsilon_r = 23.907$, $Qf = 63{,}050$ GHz and $\tau_f = 1.2$ ppm/°C. The proposed ceramic was a perfect candidate material for LTCC applications.

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