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Sintering Behavior and Microwave Dielectric Properties of BBSZL Glass-doped $ZnTiO_3$ Ceramics for LTCC Applications

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Abstract: A novel low temperature co-fired ceramic (LTCC) material was fabricated by zinc titanate ($ZnTiO_3$) ceramics doped with B_2O_3-BaO-SiO_2-ZnO-Li_2O (BBSZL) glass. The influences of BBSZL glass on wetting behavior, sintering activation energy, phase composition, microstructure and microwave dielectric properties were investigated. The experimental results show that the sintering temperature of $ZnTiO_3$ ceramics can be reduced from 1 100 to 925 ℃, meanwhile the sintering activation energy is decreased from 465.32 to 390.54 kJ·mol^{-1} by BBSZL glass aid, respectively. Moreover, BBSZL glass can inhibit the high $Q\times f$ $ZnTiO_3$ phase decompose into the low $Q\times f$ value Zn_2TiO_4 phase, which is propitious to obtain high $Q\times f$ value LTCC material. The $ZnTiO_3$-BBSZL composite sintered at 925 ℃ displays the excellent microwave dielectric properties with ε_r of 21.8, $Q\times f$ value of 42000 GHz, and τ_f of −75 ppm·℃$^{-1}$.

Key words: $ZnTiO_3$ ceramics; BBSZL glass; sintering behavior; dielectric properties

1 Introduction

With the rapid development of novel microwave technology, such as the Tactile Internet, the intelligent transport systems, the Industrial Internet and so on, low-temperature co-fired ceramics technology (LTCC) has play a more and more important role in the fields of wireless communication systems and military aerospace due to its superior high frequency, integration and sealing[1,2]. There are several parameters taken into account for ideal LTCC materials: low sintering temperature (<900 ℃), an appropriate dielectric constant (ε_r), a high quality factor ($Q\times f \geqslant$ 5000 GHz), a near-zero temperature coefficient of resonant frequency (-10 ppm·℃$^{-1} \leqslant \tau_f \leqslant 10$ ppm ℃$^{-1}$) and the excellent chemical compatibility with Ag inner electrodes[3,4].

Zinc titanate ($ZnTiO_3$)-based systems have been extensively investigated as advanced microwave dielectric ceramic materials due to its good performance ($\varepsilon_r > 15$, $Q\times f > 30000$ GHz)[5]. Sugiura *et al*[6] first discovered the excellent dielectric properties of $ZnTiO_3$ ceramic. However, there are still exit two major problems for the sintering of $ZnTiO_3$ ceramic. One problem is the high sintering temperature 1 150 ℃, which would be a huge barrier for further applying in LTCC technology. The other problem for $ZnTiO_3$ ceramic is that $ZnTiO_3$ is easily decomposed into Zn_2TiO_4 and TiO_2 at low sintering temperature (945 ℃), but Zn_2TiO_4 ceramic possess low $Q\times f$ values ($Q\times f$= 1 000-2 000 GHz, ε_r=19 and $\tau_f = -50$ ppm·℃$^{-1}$), which lead to the deterioration of dielectric properties[7,8]. However, the low-melting oxides or glass were added to lower the sintering temperature of $ZnTiO_3$-based systems[9]. At the same time, it is necessary to introduce some ions (like Mg^{2+}) to stabilize phase $ZnTiO_3$[10]. Wu *et al*[11] sintered $ZnTiO_3$ ceramics at 900 ℃ by adding B_2O_3(ε_r =8.87, $Q\times f$=49,000 GHz, $\tau_f = -32.35$ ppm ·℃$^{-1}$), but the dielectric constant was greatly reduced compared with pure $ZnTiO_3$. Li *et al*[12] investigated the effect of CuV_2O_6 on the sintering temperature and dielectric properties of $(Zn_{0.65}Mg_{0.35})TiO_3$ ceramics. They found that adding CuV_2O_6 reduced the sintering temperature to 930 ℃ and obtained well dielectric properties: ε_r=26.2, $Q\times f$=31,930 GHz, $\tau_f = -0.32$ ppm·℃$^{-1}$. Lee *et al*[13] prepared the $(Zn_{0.95}Mg_{0.05})TiO_3$-$0.25TiO_2$ ceramics and the effect of additive 3ZnO-B_2O_3 on the properties of ceramics was discussed, revealing that the dielectric properties of composites with 1wt% 3ZnO-B_2O_3 addition sintered at 900 ℃ for

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2 h were ε_r=23.6, $Q\times f$=30,990 GHz, τ_f=−8 ppm ℃$^{-1}$. Wang *et al*[14] also studied the effect of B_2O_3-SiO_2-ZnO-Na_2O, B_2O_3-SiO_2-ZnO-K_2O and B_2O_3-K_2O-$MnCO_3$ glass on the performance of $(Zn_{0.6}Mg_{0.4})TiO_3$ ceramics, and reported that the $(Zn_{0.6}Mg_{0.4})TiO_3$ with 5wt% BSZK was stable at 1 100 ℃, and exhibited the microwave dielectric properties of ε_r=18, $Q\times f$=29,375 GHz. In addition, the glass phase additions[15-19], such as LBSCA, ZnO-SiO_2-B_2O_3, B_2O_3-SiO_2, CaO-B_2O_3-SiO_2, on $(Zn_xMg_{1-x})TiO_3$ ceramic have been reported in terms of dielectric properties. The properties of other glass doping systems are summarized in Table 1.

Until now, B_2O_3-BaO-SiO_2-ZnO-Li_2O (BBSZL) glass has not been reported in $ZnTiO_3$ ceramic systems. Therefore, the influence of BBSZL sintering aid on phase composition, microstructure, sintering mechanism and microwave dielectric properties were discussed in this study. Moreover, we found that BBSZL glass not only reduced the sintering temperature of $ZnTiO_3$ ceramic, but also effectively suppressed the formation of Zn_2TiO_4 phase without doping Mg^{2+}, which was not reported in other studies.

2 Experimental

The $ZnTiO_3$ phase was fabricated by conventional solid-state reaction method using high-purity oxide powders, ZnO (99.9%) and TiO_2 (99.0%), as raw materials. ZnO and TiO_2 powders were weighed according to chemical formula $ZnTiO_3$, then mixed with in ethanol for 1 h with zirconia balls. The obtained mixtures were dried and calcined at 900 ℃ for 4 h to form $ZnTiO_3$ phase. The 25BaO-35B_2O_3-5SiO_2-25ZnO-10Li_2O glass (in mol%) was prepared by a conventional glass fabrication process: reagent grade powders of H_3BO_3 (99.9%), $BaCO_3$ (99%), SiO_2 (99%), ZnO (99.9%) and Li_2CO_3 (99%) were weighed as the raw materials. The glass batch about 500 g was melted in a platinum crucible at 1 300 ℃ for 2 h, and then the melts were quenched in water. The quenched glass was planetary-milled in aluminum jar with ethyl alcohol and ZrO_2 balls for 2 h. After being dried and screened through a 200-mesh sieve, the BBSZL glass powder was obtained. $ZnTiO_3$ powders with x wt% (x=2, 4, 6, 8, and 10) BBSZL glass powders were mixed together and ball milled in ethanol medium for 1 h to get homogeneously mixed fine powder. After ball re-milled, the mixed powders were mixed with 3wt% polyvinyl alcohol (PVA) solution and then pelleted to 15 mm diameter and 6 mm thick disks at 2 MPa by hydraulic pressing. The disks were sintered at 500 to 950 ℃ for 4 h in air at a heating rate of 5 ℃·min^{-1} and cooled inside the furnace to room temperature.

The shrinkage curves of the ceramic with different heating rate of 5, 10, and 15 K·min^{-1} were researched by Thermomechanical Analyses (TMA) (DIL 402C, Netzsch Instruments, Germany). The sintered pellets were ground into powder to study the phase composition by X-Ray diffractometer (XRD, Uitima, Rigaku, Japan) using Cu/Kα radiation. The microstructure observations of the sintered surfaces were performed by field emission scanning electron microscope (FESEM, Magellan 400, FEI Company, USA). The bulk density of the samples was measured by the Archimedes method. Dielectric constant and the quality factor measurements were carried out using an Agilent E8363A PNA network analyzer in a wide frequency (1-20 GHz). The temperature coefficients of resonant frequency (τ_f) were measured with changing temperatures from 25 to 85 ℃ defined as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \times 10^6 \,(\text{ppm/℃}) \qquad (1)$$

where, f_{25} and f_{85} represent the resonant frequency at 25 and 85 ℃, respectively.

3 Results and discussion

For the study of wetting behavior of BBSZL glass on the $ZnTiO_3$ ceramics, a piece of green BBSZL glass compact is putted on top of the dense $ZnTiO_3$ substrate and followed by sintering between 700 and 800 ℃ at a heating rate of 10 ℃·min^{-1} recorded by an optical camera as shown in Fig.1(a). It can be found that the BBSZL glass cylinder slightly shrinks at 700 ℃. However, there is just a slight expansion of glass cylinder at 790 ℃, and it may be due to the expansion of closed pores at high sintering temperature[26]. When

Table 1 The properties of other glass doping systems

System	Additive	Sintering temperature/℃	Dielectric constant	$Q\times f$/GHz	τ_f / (ppm/℃)
$ZnTiO_3$[20]	B_2O_3-SiO_2 glass	850	22.2	52 460	
$ZnTiO_3$[21]	Li_2CO_3-B_2O_3-V_2O_5	870	24	22 900	−4
$ZnTiO_3$[22]	B_2O_3	900	8.87	49 000	−32.35
$ZnTiO_3$[23]	CuO-MoO_3	975	28.6	12 150	+17.8
$ZnTiO_3$-0.25TiO_2[24]	CuO-V_2O_5-Bi_2O_3	850	30	32 000	+12
$ZnTiO_3$[25]	ZnO-V_2O_5	800	25.3	15 200	−16

the sintering temperature is 800 ℃, the wetting angle is less than 90°, suggesting that the glass addition could wet the $ZnTiO_3$ ceramic particles when temperature higher than 800 ℃. The result is further supported by the SEM micrograph of the cross-section between BBSZL glass and $ZnTiO_3$ substrate sintered at 800 ℃ in Fig.1(b). It can be seen that the interface between BBSZL glass and $ZnTiO_3$ substrate is difficult to distinguish due to good wetting. The results indicate that the BBSZL glass will provide a large amount of liquid phase at about 800 ℃ and the liquid phase could wet the $ZnTiO_3$ ceramic particles well, which facilitate the densification process of $ZnTiO_3$ ceramic according to the liquid-phase sintering mechanism.

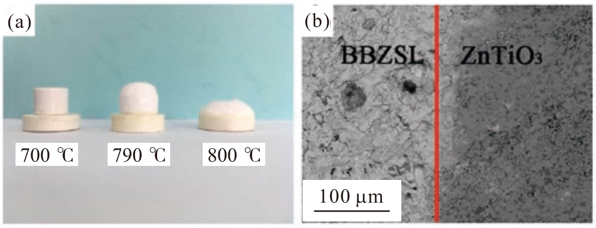


Fig.1 (a) Wetting behavior of BBSZL glass on the $ZnTiO_3$ substrates at different temperatures; (b) SEM image of the cross-section between BBSZL glass and $ZnTiO_3$ substrate sintered at 800 ℃

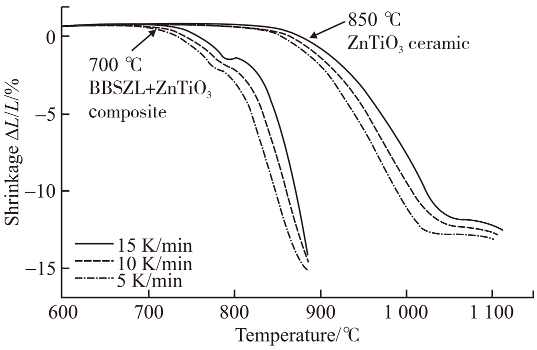


Fig.2 The shrinkage curves of pure $ZnTiO_3$ ceramic and $ZnTiO_3$ with BBSZL glass composites at different heating rates of 5, 10, and 15 $K\cdot min^{-1}$

Fig.2 shows the linear shrinkage curves of the $ZnTiO_3$ ceramic and the $ZnTiO_3$ with 4wt% BBSZL glass composites at different heating rates of 5, 10, and 15 $K\cdot min^{-1}$. It can be found that the pure $ZnTiO_3$ ceramic start to shrink at 850 ℃ and a linear shrinkage of 12% at 1 050 ℃, while the onset of shrinkage dramatically decreases about 700 ℃ for BBSZL glass doped composites and the shrinkage reached 12% at 870 ℃. It is obviously that the BBSZL glass can efficiently reduce the sintering temperature of the $ZnTiO_3$ ceramic because of the presence of the glass liquid phase.

To further understand the sintering behavior, the activation energy (E_a) of the $ZnTiO_3$ ceramic and the $ZnTiO_3$ with 4wt% BBSZL glass composite can be calculated by the follow Arrhenius equation:

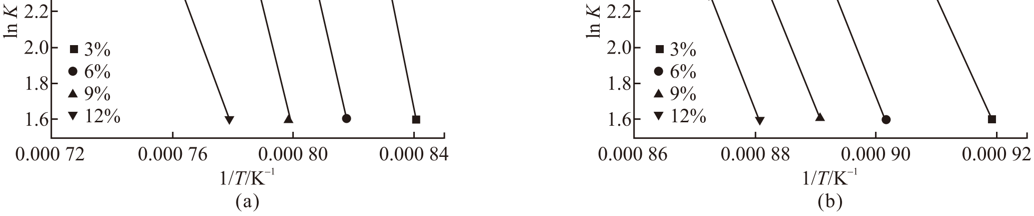
$$\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln z \tag{2}$$

where, k is the heating rate, E_a is the activation energy, T is the absolute temperature, R is the universal gas constant (=8.3145 $J\cdot K^{-1}\cdot mol^{-1}$) and ln z is a constant. The E_a values can be obtained by calculating the slope of ln k against $1/T$. By formula (2), ln K and $1/T$ function curve as shown in the Fig.3 and it can be calculated that the average E_a of the pure $ZnTiO_3$ ceramic and the $ZnTiO_3$-BBSZL composite were 465.32 $kJ\cdot mol^{-1}$ and 390.54 $kJ\cdot mol^{-1}$, respectively. It can be known from the E_a results, adding liquid-phase sintering mechanism can reduce the sintering activation energy of $ZnTiO_3$ ceramics and achieve the purpose of reducing the sintering temperature.

Fig.4 shows XRD patterns of $ZnTiO_3$ ceramics with 4wt% BBSZL glass sintered at temperatures ranging from 500 to 950 ℃ for 4 h. It can be seen that the samples sintered at less than 750 ℃ included the major crystalline phase $ZnTiO_3$ (JCPDS No. 26-1500), two second phases Zn_2TiO_4 (JCPDS No. 25-1164) and TiO_2 (JCPDS no. 21-1276). The production of Zn_2TiO_4 and TiO_2 phases is mainly due to the decomposition of $ZnTiO_3$ during calcination. The phase transformation reaction process can be summarized as Eq.(3):

$$ZnO+TiO_2 \xrightarrow{700℃} ZnTiO_3 \xrightarrow{900-950\ ℃} Zn_2TiO_4+TiO_2 \tag{3}$$

$$Zn_2TiO_4 + TiO_2 \xrightarrow{BBZ\text{ glass}} ZnTiO_3 \tag{4}$$



(a) (b)

Fig.3 The ln K as a function of $1/T$ at different shrinkages of (a) $ZnTiO_3$ with 4wt% BBSZL glass composites; (b) $ZnTiO_3$ ceramic

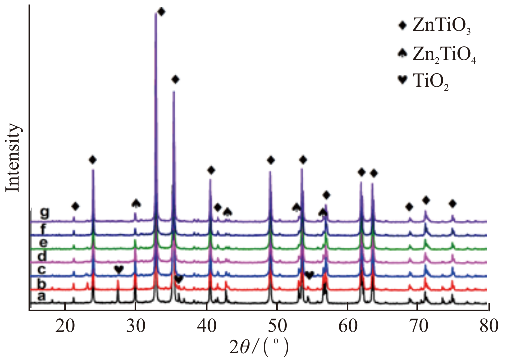


Fig.4 XRD patterns of the ZnTiO$_3$ with 4wt% BBSZL composite sintered at different temperatures: (a) 500 ℃, (b) 750 ℃, (c) 800 ℃, (d) 875 °C, (e) 900 ℃, (f) 925 ℃, and (g) 950 ℃

With the increase of sintering temperature to 800 ℃, the diffraction peak of Zn$_2$TiO$_4$ and TiO$_2$ phases disappear, which liquid phase coming from BBSZL glass at 800 ℃ not only promote the sintering process of ZnTiO$_3$ ceramic through the liquid-phase sintering mechanism, but also lead to a chemical reaction between Zn$_2$TiO$_4$ and TiO$_2$ form ZnTiO$_3$ phase again in equation (4). On the other hand, there are no obvious additional peaks observed when the sintering temperature increased from 875 to 950 ℃, which means that the phase composition has no variations after sintering at 875 ℃.

Fig.5 shows the variation in microstructures of ZnTiO$_3$ added with different content of BBSZL glass sintered at 925 ℃ for 4 h. As shown in Fig.5(a), when BBSZL glass was added 2wt%, the grains size was small and there are more pores between grains. With the increasing of BBSZL, the grain size of ceramics raised gradually and the number of pores were reduced. But the uniformity of the grains got worsened and the large grains begin to appear.

The bulk density of ZnTiO$_3$ ceramics are demonstrated in Fig.6(a). It can clearly see that with the increasing sintering temperature from 875 to 950 ℃, the density gradually increased to the highest value at 925 ℃. That's mainly due to the grain growth and BBSZL glass phase in-filled. Then the density dropped because the pores increased. At different glass contents, the maximum relative density (D = 4.68 g·cm^{-3}) was obtained with 4wt% BBSZL. The dielectric constant (ε_r), quality factor ($Q \times f$) and temperature coefficient of the resonant frequency values (τ_f) of ZnTiO$_3$ composites with 4wt% BBSZL are shown in Figs.6(b) and 6(c), respectively. This is well known that microwave dielectric ceramics are mainly relative to phase composition, grains and pores[27,28]. The variations of ε_r and $Q \times f$ had similar a trend to density. The ε_r and $Q \times f$ value increased to the maximum value at x = 4 and then decreased. The saturated ε_r and $Q \times f$ value of 21.8 and 42 000 GHz, respectively.

Fig.7 shows the τ_f of ZnTiO$_3$ composites added with BBSZL glass sintered at 925 ℃ for 2 h, from which it is found that as BBSZL glass addition increases, the τ_f values firstly increase and reach the maximum at 6wt% content of BBSZL glass, and then decreased. This result can be interpreted as the content

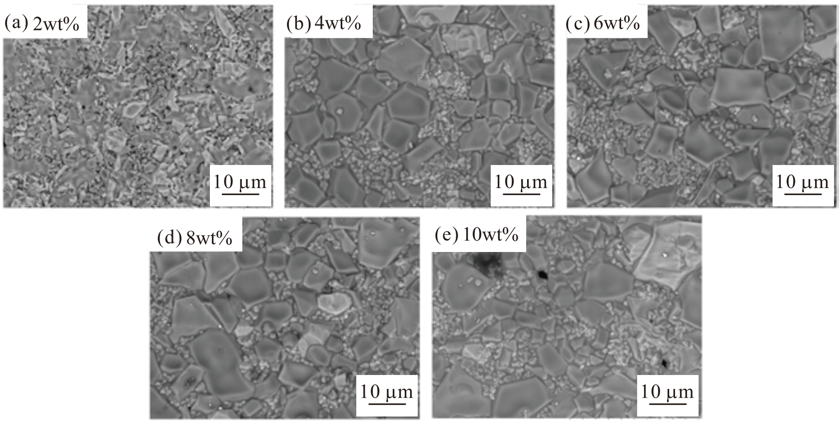


Fig.5 SEM images of the ZnTiO$_3$ ceramics doped with different BBSZL glasses sintered at 925 ℃ for 4 h

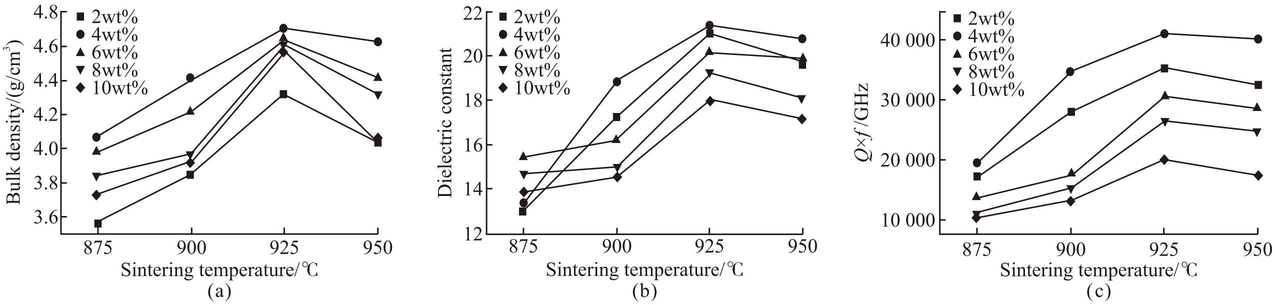


Fig.6 The bulk density (a), ε_r (b), and $Q \times f$ (c) values of the ZnTiO$_3$ ceramics with different BBSZL glass contents at different temperatures

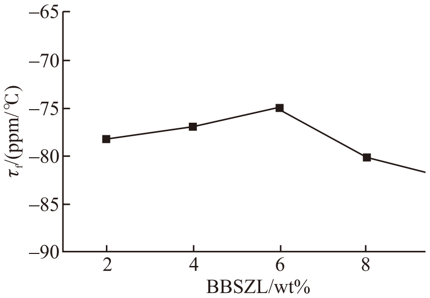


Fig.7 The τ_f valve of the $ZnTiO_3$ ceramics with different BBSZL glass contents sintered at 925 ℃ for 4 h

of BBSZL glass increased from 2wt% to 4wt% caused the grain growth and increased density, so the dielectric performance was improved. However, as the BBSZL glass content continues to increase, the microstructure of the $ZnTiO_3$ ceramic begins to grow abnormally large grains and pores seriously affect the dielectric properties. In addition, too much glass liquid phase also has an impact on dielectric performance.

4 Conclusions

As mentioned above, dense $ZnTiO_3$-BBSZL composites are synthesized using solid state reaction, and the phase evolution, structural characteristic, sintering mechanism and microwave dielectric properties are examined. The introduction of BBSZL glass can not only effectively improve the density, but also lower the sintering temperature and sintering activation energy of $ZnTiO_3$ to 925 ℃ and 390.54 $kJ\cdot mol^{-1}$, respectively. In addition, BBSZL glass can reduce the generation of harmful phase Zn_2TiO_4 and improve dielectric properties. The $ZnTiO_3$ ceramic with 4wt% BBSZL glass sintered at 925 ℃ in air for 4 h shows obvious microwave dielectric properties of $\varepsilon_r = 21.8$, $Q\times f = 42\ 000$ GHz, and τ_f of approximately -75 ppm·℃$^{-1}$.

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