

Microstructure and microwave dielectric characteristics of CaO–B₂O₃–SiO₂ glass ceramics

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Abstract CaO–B₂O₃–SiO₂ (CBS) glass powders are prepared by traditional glass melting method, whose properties and microstructures are characterized by Differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). It is found that the pure CBS glass ceramics possess excellent dielectric properties ($\epsilon_r = 6.5$, $\tan \delta = 5 \times 10^{-3}$ at 10 GHz), but a higher sintering temperature (>900 °C) and a narrow sintering temperature range (about 10 °C). The addition of a low-melting-point CaO–B₂O₃–SiO₂ glass (LG) could greatly decrease the sintering temperature of CBS glass to 820 °C and significantly enlarge the sintering temperature range to 40 °C. The CBS glass ceramic with 30 wt% LG glass addition sintered at 840 °C exhibits better dielectric properties: $\epsilon_r \approx 6$, $\tan \delta < 2 \times 10^{-3}$ at 10 GHz, and the major phases of the sample are CaSiO₃, CaB₂O₄ and SiO₂.

1 Introduction

Low temperature co-fired ceramics (LTCCs) have been widely investigated due to their applications for the multilayer microwave components which can miniaturize the microwave devices [1]. LTCCs offer low loss dielectric characters and are compatible with Au, Ag or Cu, as the best high frequency conductors. Utilization of low dielectric constant LTCC materials and association with high conductivity metallizations are found to have potential applications in the area of wireless communication [2].

Among several LTCC systems [2–6], CaO–B₂O₃–SiO₂ (CBS) glass ceramics have been reported as a promising material for use in microelectronic fields because of its low sintering temperature and excellent dielectric properties [7, 8]. Chia-Ruey Chang et al. [9] studied the crystallization kinetics and mechanism of a commercial CBS glass ceramic (A6, Ferro Co.). Shao-Hong Wang et al. [10] have found that excessive B₂O₃ in CBS system damages the dielectric properties. Chuang-Chung Chiang et al. [2] studied the compositional effects on the physical properties of CBS glass ceramics.

The pure CBS glass ceramics usually need to be sintered at a higher temperature to achieve high enough density, and the sintering temperatures of CBS in open reports are somewhat too high. How to decline its temperature attracts many researchers' attentions at present. In this paper, a novel CBS glass ceramic preparation method is presented by sintering two devitrifying CBS glasses, and the microstructures of the CBS glass ceramics are investigated systematically and discussed detailedly.

2 Experimental procedure

The compositions of the glass CBS and a low-melting-point CaO–B₂O₃–SiO₂ glass (LG) were marked in the phase diagram of the CBS system, as is shown in Fig. 1. Compared to CBS glass, LG glass contained less SiO₂ but more B₂O₃. Reagent-grade raw materials of CaCO₃, SiO₂ and H₃BO₃ with purities higher than 99 wt% were chosen as the starting materials. After mixed uniformly, the raw materials were put into a platinum crucible and melted by an electric furnace at 1,500 °C for 120 min. The molten glass was quenched into distilled water to form cullet. The cullet was dried and milled with a mixture of agate balls in

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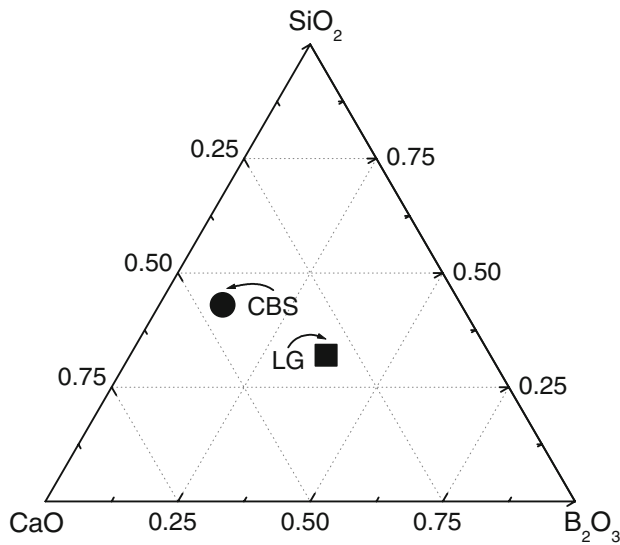


Fig. 1 Compositions of the CBS and LG glasses

different diameters of 5–30 μm to an average particle size of less than 5 μm .

Furthermore, the CBS glass and LG glass powders were used as precursors and mixed in accordance with $(1-x)$ CBS- x LG system ($0.05 \leq x \leq 0.6$) by ball milling with deionized water for 2 h. After drying, the powders prepared above were mixed with an amount of polyvinyl alcohol (PVA, 12 wt%), uniaxially pressed under a pressure of 100 MPa to obtain the green compacts with diameter of 13 mm and thickness of 4–10 mm, and then sintered in air at different temperatures for 15 min. The physical properties of those sintered bodies were measured, such as dielectric constant, dielectric loss and microstructure. The phase compositions of the samples were determined by X-ray diffraction with $\text{CuK}\alpha$ radiation (XRD ARL X'TRA). The crystal structures were examined by scanning electron microscopy (SEM JSM-5900). The dielectric properties were measured at 10 GHz by Agilent 8722ET network analyzer.

3 Results and discussion

3.1 Characterization of CBS glasses

Figure 2 shows the results of DTA measurement of the CBS, LG and 70 wt% CBS + 30 wt% LG glass powders. The DTA curves are obtained in air up to 900 $^{\circ}\text{C}$ by a heating rate of 10 $^{\circ}\text{C min}^{-1}$ using a STA 449C/6/F analyzer. The exothermic peaks for CBS, LG and the glass composite are at about 870, 825 and 860 $^{\circ}\text{C}$, respectively. Thus, the crystallization temperature (T_c) of the glass composites is just between that of CBS and that of LG glass.

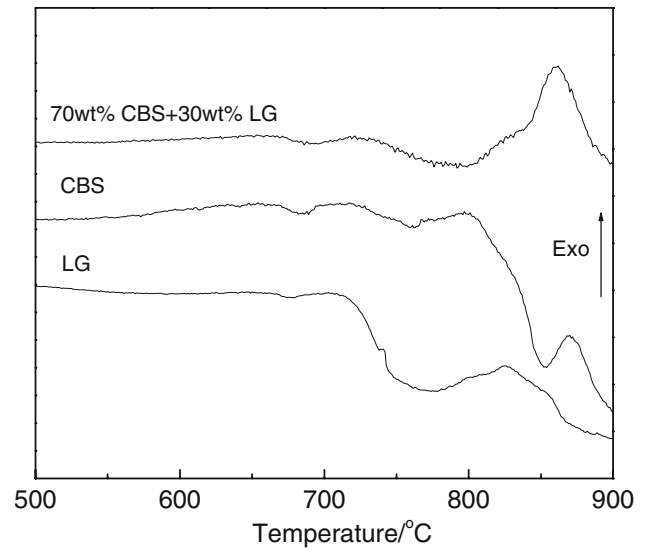


Fig. 2 DTA curves of the CBS glass powders

It is found in experiment that the sintering temperature of pure CBS glass is high than 900 $^{\circ}\text{C}$ and the sintering range is about 10 $^{\circ}\text{C}$. For LG glass, samples become serious deformation when the sintering temperature reaches to 750 $^{\circ}\text{C}$. This is mainly caused by the formation of too much liquid phase.

3.2 Sintering characterization of CBS glass ceramics

Figure 3 displays the relationship between the bulk densities of CBS glass ceramics and the sintering temperatures. The bulk densities of pure CBS specimens increase from 1.87 to 2.15 g cm^{-3} , and water absorptions decrease only from 12 to 8%, as the sintering temperatures increase from 840 to 880 $^{\circ}\text{C}$. The CBS glass ceramics doped by 20–50 wt% LG glass exhibit high enough densities at

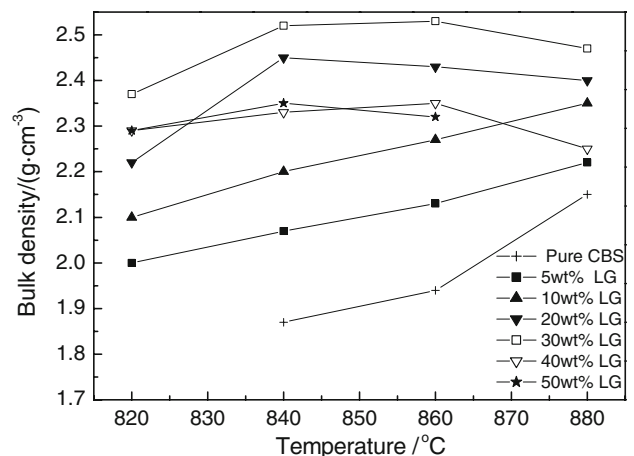


Fig. 3 Relationship between the bulk densities of CBS glass ceramics and sintering temperatures

840–880 °C, because the water absorptions of these samples are all less than 0.8%. The sinterabilities of the green compacts improve dramatically with the increasing amount of LG glass from 5 to 30 wt%, whereas the bulk densities of the glass ceramics all enhance with the rising sintering temperatures.

The sinterability of pure CBS glass is poor with the lack of open porosity, but LG glass could act as the fluxes and increase the liquid fluidity during viscous flow. With the liquid formation, there is a rapid densification due to capillary force exerted by the liquid on the glass particles and filled liquid fluidity to the pores in the samples. In addition,

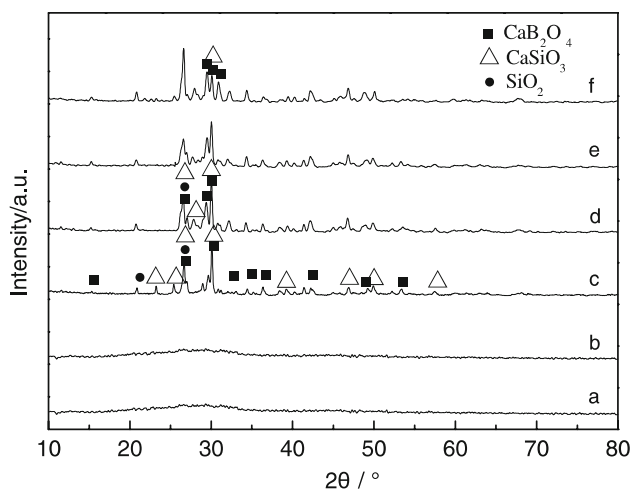
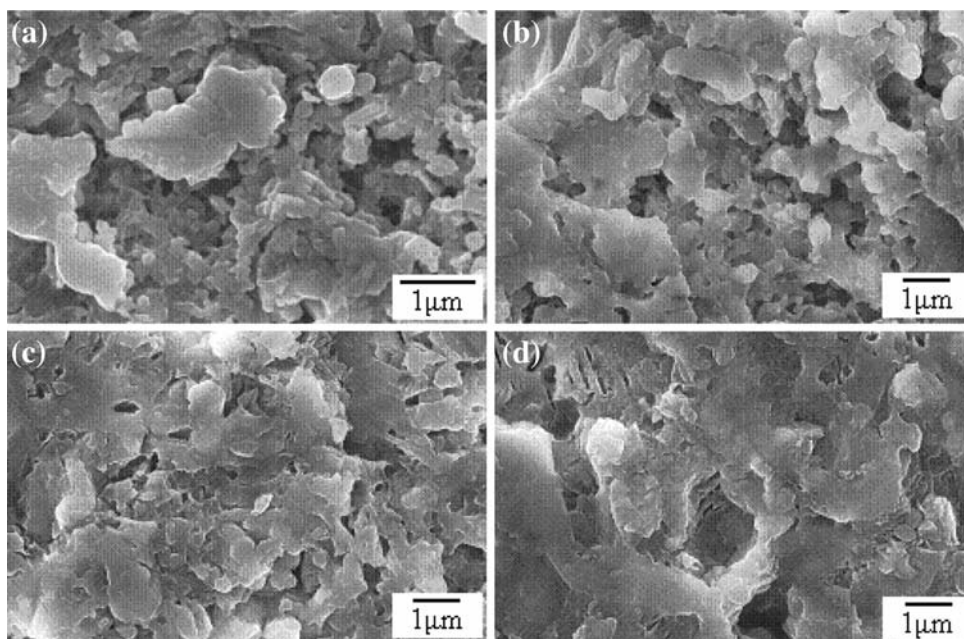


Fig. 4 XRD patterns of the glass powders and CBS glass ceramics: (a) CBS glass, (b) LG glass, (c) CBS glass sintered at 900 °C, (d) with 20 wt% LG glass sintered at 840 °C, (e) with 30 wt% LG glass sintered at 840 °C, (f) with 40 wt% LG glass sintered at 840 °C

Fig. 5 SEM images of CBS samples etched surfaces (2%HF for 30 s): **a** CBS glass sintered at 900 °C, **b** with 20 wt% LG glass sintered at 840 °C, **c** with 30 wt% LG glass sintered at 840 °C, **d** with 40 wt% LG glass sintered at 840 °C



the T_c of the LG glass is only 825 °C and about 50 °C lower than that of the CBS glass. Thus, the former crystallization phases of LG glass could induce CBS glass to crystallize. However, when the amount of LG glass is more than 30 wt%, the bulk densities of the glass ceramics decline with the increasing amount of LG glass. For example, the bulk densities of CBS specimens sintered at 840 °C decrease from 2.52 to 2.35 g cm⁻³, as the amount of LG glass increases from 30 to 50 wt%. It is attributed to the small density of the LG glass, only about 2.23 g cm⁻³.

3.3 XRD analysis results and SEM observations

Figure 4 shows the XRD patterns of the glass powders and CBS glass ceramics. The XRD patterns of CBS and LG glass powders are basically composed of amorphous glassy phases and no crystalline phases, while the CBS samples sintered at 840 or 900 °C for 15 min are mainly composed of crystalline phases of CaSiO₃ (JCPDS no. 75–1,396), CaB₂O₄ (JCPDS no. 76–747) and SiO₂ (JCPDS no. 78–1,252). The maximum peak intensities of samples with 20, 30 and 40 wt% LG glass appear at $2\theta = 30, 30$ and 27° , respectively. Major crystalline phases of the three samples do not change, but the amount of each crystalline phase varies greatly.

Various microstructures of above samples are examined and the results are illustrated in Fig. 5. The pure CSB glass sintered at 900 °C is more porous (Fig. 5a). With the increasing addition of LG glass, the pore size and porosity decline obviously (Fig. 5b–d) and the grain sizes are all less than 1 μm. Softening and fluidizing of crystal grains bonding each other and filling of liquid phase to the pores

are also observed. The more LG glass addition, the more glassy phase formation. The sample with 40 wt% LG glass has the least porosity and the largest glass phase (Fig. 5d). This can be accompanied by the variation of densification (shown in Fig. 3). When the amount of LG glass is less than 30 wt%, the values of densities rise rapidly with the increasing amount of LG glass. However, when the amount of LG glass is more than 30 wt%, values of densities decline caused by the formation of too much liquid phase.

3.4 Dielectric properties of CBS glass ceramics

The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of pure CBS glass ceramics sintered at 900 °C are 6.5 and 5×10^{-3} at 10 GHz, respectively. Fig. 6 summarizes ϵ_r and $\tan \delta$ of the CBS samples with different sintering temperatures. The values of ϵ_r and $\tan \delta$ vary greatly with increasing of sintering temperatures and amount of LG. The values of ϵ_r and $\tan \delta$ of CBS glass ceramics decline and the values of ϵ_r are all less than 6.3, as the amount of LG glass increases from 10 to 30 wt%. The ϵ_r of the well-sintered CBS samples are mainly influenced by the major crystalline phases (CaSiO_3 , CaB_2O_4 and SiO_2) and glassy phases. In this study, the ϵ_r of CaSiO_3 , CaB_2O_4 , SiO_2 and glass phase are about 5.4, 7, 3.8 and 7, respectively. At low LG glass content, the ϵ_r of the samples are primarily affected by crystalline phases. The ϵ_r values of CBS glass ceramics would decrease with the increasing major crystalline phases or the decreasing glass phases, according to the dielectric constant mixing rules [11]:

$$\ln \epsilon = x_1 \ln \epsilon_1 + x_2 \ln \epsilon_2$$

where x_1 , x_2 is the volume fraction of the major crystalline phases and glass phases ($x_1 + x_2 = 1$), respectively. ϵ_1 , ϵ_2 is the dielectric constant of the major crystalline phases and glass phases, respectively. However, when LG glass content is more than 40 wt%, glass phases dominate in the ϵ_r of the samples. The ϵ_r values enhance with the increasing

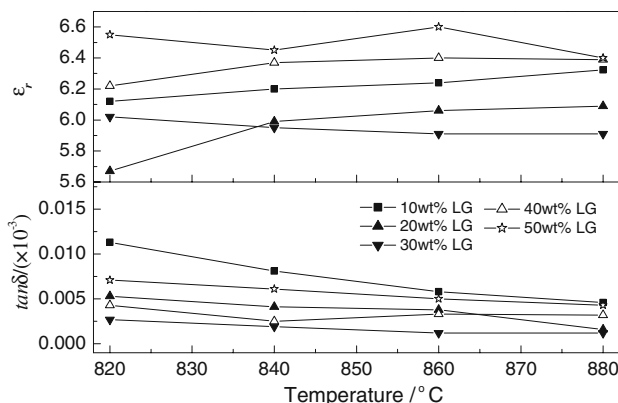


Fig. 6 Relationship between dielectric properties of CBS glass ceramics and sintering temperatures

amount of LG glass and are high than 6.3. But much poorly conducting glass phases in the dielectric damage the dielectric properties, leading to the $\tan \delta$ rising with the increasing LG glass content.

4 Conclusions

The pure CBS glass ceramics possess excellent dielectric properties ($\epsilon_r = 6.5$, $\tan \delta = 5 \times 10^{-3}$ at 10 GHz), but a higher sintering temperature (>900 °C) and a narrow sintering temperature range (about 10 °C). The addition of a low-melting-point $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ glass (LG) could greatly decrease the sintering temperature of CBS glass to 820 °C and significantly enlarge the sintering temperature range to 40 °C. The CBS glass ceramic with 30 wt% LG glass addition sintered at 840 °C exhibits better dielectric properties: $\epsilon_r \approx 6$, $\tan \delta < 2 \times 10^{-3}$ at 10 GHz, and the major phases of the sample are CaSiO_3 , CaB_2O_4 and SiO_2 . This material is suitable to be used as the LTCC material for the application in wireless communications.

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