

Crystallization, sinterability and dielectric properties of CaO–B₂O₃–SiO₂ glass ceramics with Al₂O₃ additives

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Received: 23 May 2015 / Accepted: 30 July 2015 / Published online: 4 August 2015
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Abstract Glass–ceramic materials of the CaO–B₂O₃–SiO₂ (CBS) system added with various amounts of Al₂O₃ have been prepared by conventional melting and heat treated crystallization method. The effects of Al₂O₃ on the sintering characterization and dielectric properties have been investigated. With increasing the Al₂O₃ content, the bending and stretching vibrations in [SiO₄]²⁻ became weak. XRD patterns of samples with ≥ 3 wt% Al₂O₃ introduce cyclowollastonite (α -CaSiO₃) as single crystallized phase of sintered glass–ceramics. It is found that the optimal sintering temperature for this glass ceramics is 800 °C for 30 min, and the sinterability was obviously improved by Al₂O₃ additive. CBS glass ceramics sample with 5 wt% Al₂O₃ achieved the best sintering characterization and dielectric properties ($\epsilon_r \approx 7$, $\tan \delta = 1.9 \times 10^{-3}$ at 1 MHz), which is proposed to be suitable for LTCC application.

1 Introduction

Low temperature co-fired ceramics (LTCC) technology, because of its excellent electrical, mechanical and thermal properties, is nowadays being increasingly used to make substrates for the production of multilayer ceramic circuits, mainly for telecommunication, automotive and medical applications [1]. The most important parameter

which is expected for LTCC component is the low sintering temperature because of the use of low melting point metals e.g. Cu, Ag and Au. In addition to these basic requirements, the LTCC substrate materials should exhibit a low permittivity ($\epsilon_r < 10$) to reduce the signal propagation delay, and low dielectric losses [2]. The low temperature sintered for LTCC materials can be achieved with use of three main types of materials: glass–ceramics, glass/ceramic and single-phase ceramics. Of these, the glass–ceramic composite system is the most frequently used.

As an attractive glass–ceramic system, CaO–SiO₂–B₂O₃ (CBS) has been investigated as the candidate substrate materials in the electronic packaging filed, because of its low sintering temperature, relatively low dielectric constant (~ 6.5) and low material cost [3–16]. Wang and Zhou [11] studied the effects of the glasses of different compositions, holding time and heating speed on CaO–B₂O₃–SiO₂ system. Zhu et al. [15] reported the effect of temperature, frequency and composition for CBS on the dielectric properties. Zhou et al. [16] found that the La₂O₃–B₂O₃ addition promoted the crystallization of the CaSiO₃ and enhanced flexural strength. However, the large number of pores appeared in CBS system during the crystallization process, which led to low sintering density. Thus, it is difficult to control the proper shrinkage for LTCC application. Many studies indicated that Al₂O₃ is effective material filler for the glass + ceramic composites]. [17, 18]

In this study, a small amounts of Al₂O₃ as additives were mixed with CBS glasses and the sinterability of glass–ceramic increased dramatically. The effects of Al₂O₃ for CBS glasses on the crystalline phases, microstructures and dielectric properties are investigated systematically and discussed in detail.

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2 Experimental procedure

The composition of the glass is 40 wt% CaO, 40 wt% SiO₂ and 20 wt% B₂O₃ and starting materials are analytical reagent-grade CaCO₃, SiO₂ and H₃BO₃ with purities higher than 99 wt%. The raw materials were dry-mixed for 4 h in polyethylene jars. After mixed uniformly, the raw materials were put into an alumina crucible and melted at 1450 °C for 2 h. The molten glass was quenched into distilled water to form cullet. The crushed glass powders were sieved through a 20-mesh screen. Subsequently, the glasses were re-milled in ethyl alcohol for 4 h in a planetary ball mill and then oven-dried at 80 °C. As a next step, Al₂O₃ powders (99.9 %; AR) in a range from 0 to 10 wt% were mixed with the CBS glass frit by ball milling in ethanol for 4 h. The mixtures were added with about 8 wt% of 5 %-PVA solution, and uniaxially pressed under a pressure 80 MPa to obtain green compacts with diameter of 13 mm and thickness of 6 mm. The compacts were then heat treated at 550 °C for 2 h with a heating rate of 2 °C/min to eliminate the PVA, followed by sintering at temperatures between 800 and 900 °C for 15 min–1 h with a heating rate of 5 °C/min.

Density measurements on the CBS glass with Al₂O₃ were done using the Archimedes method. X-ray diffraction with CuK_α radiation was used to determine the phase composition of these samples. FTIR spectra of the powdered samples were recorded at room temperature in the range 400–4000 cm⁻¹ using Nicolet 5700. Glass transition and crystallization temperature of samples were determined by differential scanning calorimeter (DSC) at N₂ atmosphere with a heating rate of 10 °C/min.

(NETZSCH-STA 449F3, α -alumina reference material). Scanning electron microscopy (SEM) was used to reveal the microstructures of sintered samples. The dielectric properties were measured at 1 MHz by Agilent4278A impedance analyzer at 20 °C.

3 Results and discussions

3.1 Crystallization and structure of glass

Figure 1 illustrates XRD patterns of all samples sintered at 750–850 °C for 30 min. No crystallization occurred at 750 °C because sintering temperature was below crystallization temperature (illustrated in Fig. 4). At 800 °C, pure CBS sample is composed of main crystallization phase of cyclowollastonite (α -CaSiO₃) and minor crystallization phase of wollastonite (β -CaSiO₃), phase transition from β -CaSiO₃ to α -CaSiO₃ happened for sample with <3 wt% Al₂O₃, resulting in the decrease of β -CaSiO₃ phase;

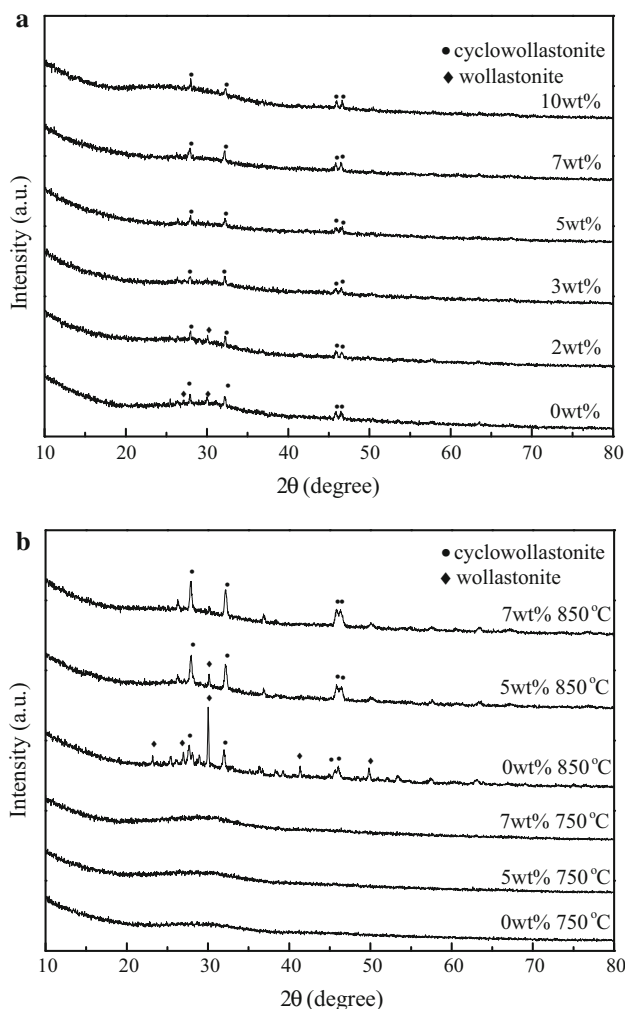


Fig. 1 XRD patterns of CBS glass with different contents of Al₂O₃ sintered for 30 min at **a** 800 °C and **b** 850 and 750 °C

α -CaSiO₃ as single crystallized phase was observed for sample with ≥ 3 wt% Al₂O₃. When the sintering temperature is increased to 850 °C, the diffraction peaks intensities of samples increased, indicating that the crystallization is more complete; as 7 wt% Al₂O₃ was introduced, the β -CaSiO₃ phase disappeared. In addition, no Al₂O₃ or containing Al₂O₃ crystallization phase is detected in all samples. It indicates that Al₂O₃ has already melted, becoming glass network former in CBS glasses. Normally, the phase transformation from β -CaSiO₃ to α -CaSiO₃ is 1125 °C. In this study, more Al₂O₃ are favorable to α -CaSiO₃ being crystallized. The reason may due to high field strength of Al³⁺ ions resulting in the reduction of activation energy of crystallization.

Figure 2 depicts the FT-IR spectra of CBS glass–ceramic in the presence of variable amounts of Al₂O₃ additives. All spectra exhibit four broad transmittance bands in the region of 400–2000 cm⁻¹. The IR features

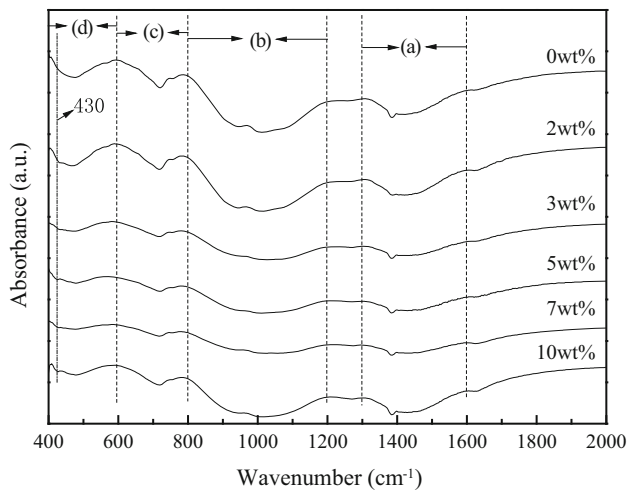


Fig. 2 FT-IR spectra of CBS glass-ceramic with various Al₂O₃ sintered at 800 °C for 30 min

located in the first region that range between 1300 and 1600 cm⁻¹ are attributed to the asymmetric stretching relaxation of B–O bonds of from the [BO₃] trigonal units (Fig. 2a). The second region range between 800 and 1200 cm⁻¹ and its spectral features are related to the presence of the B–O bonds stretching vibrations of [BO₄] tetrahedral units and the Si–O–Si bonds stretching vibrations [9] (Fig. 2b). The bands in the 600–800 cm⁻¹ region are due to the stretching vibrations of Al–O bond in [AlO₂]⁻ tetrahedral and the bending vibration of the B–O–B bonds in the borate network [8, 14] (Fig. 2c). The band in 400–600 cm⁻¹ can be attributed to O–Si–O bending vibrations and Al–O stretching vibrations in [AlO₃]³⁻ octahedral [19](Fig. 2d). The reason may due to Al replacing Si as a glass network former, resulting in the weaker bending and stretching intensity in [SiO₄]. The band located at about 430 cm⁻¹ results from Al–O stretching vibrations in [AlO₃]³⁻ octahedral. As the amount of Al₂O₃ increased, the band at about 430 cm⁻¹ became stronger because more [AlO₃]³⁻ octahedral formed. However, the absorbance of the sample with 10 wt% Al₂O₃ is higher than that of the sample with 5 wt% Al₂O₃, which is caused by more [AlO₃]³⁻ octahedral forming and less [SiO₄] being destroyed.

3.2 Sinterability and microstructure

Figure 3 displays the bulk densities of CBS glass ceramic with various Al₂O₃ content sintered at 800–900 °C for 30 min and sintered at 800 °C for 15 min–1 h. It was obvious that the densification strongly depends on the sintering temperature, time and Al₂O₃ content. Among these factors, the Al₂O₃ content was the most important factor in the densification process of the composites. As the Al₂O₃ content from 0 to 3 wt%, the bulk density increased markedly; and further

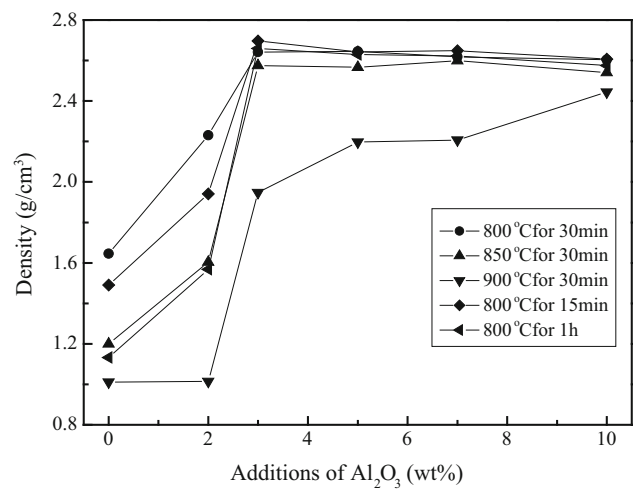


Fig. 3 Relationship between the bulk densities of samples sintered at 800–900 °C for 15 min–1 h and its compositions

increasing the Al₂O₃ content, the bulk density change little. Moreover, it is found that the appropriate sintering temperature and holding time are 800 °C and 30 min, respectively. According to the previous work [1], densification mechanisms for the glass/ceramic system can be divided into two categories: owing to the coexistence of filler and glass in LTCC, liquid-phase sintering can be considered; due to the large amount of glass, viscous sintering can be assumed [1]. For the present study, it is considered to be the latter mechanism that dominates the densification process, because small amount of Al₂O₃ was added in CBS glass and melted in it. Generally, the crystallizing in the compacts will increase the relative amount of B₂O₃ in CBS glass, leading to the decrease of the viscosity of CBS glass which contributes to densification [20]. In this study, the higher temperatures (≥800 °C) and longer holding time (≥30 min) can promote the crystallization and densification of CBS glass; however, the samples possessed lower densities. This cause is probably attributed to the boron-rich

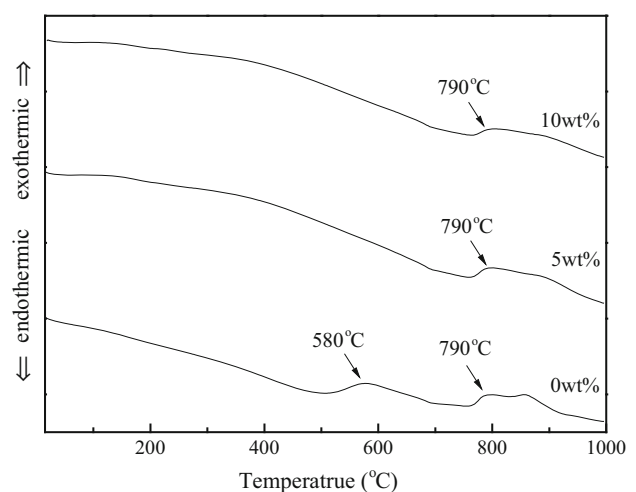


Fig. 4 DSC curves of CBS glass with different contents of Al₂O₃

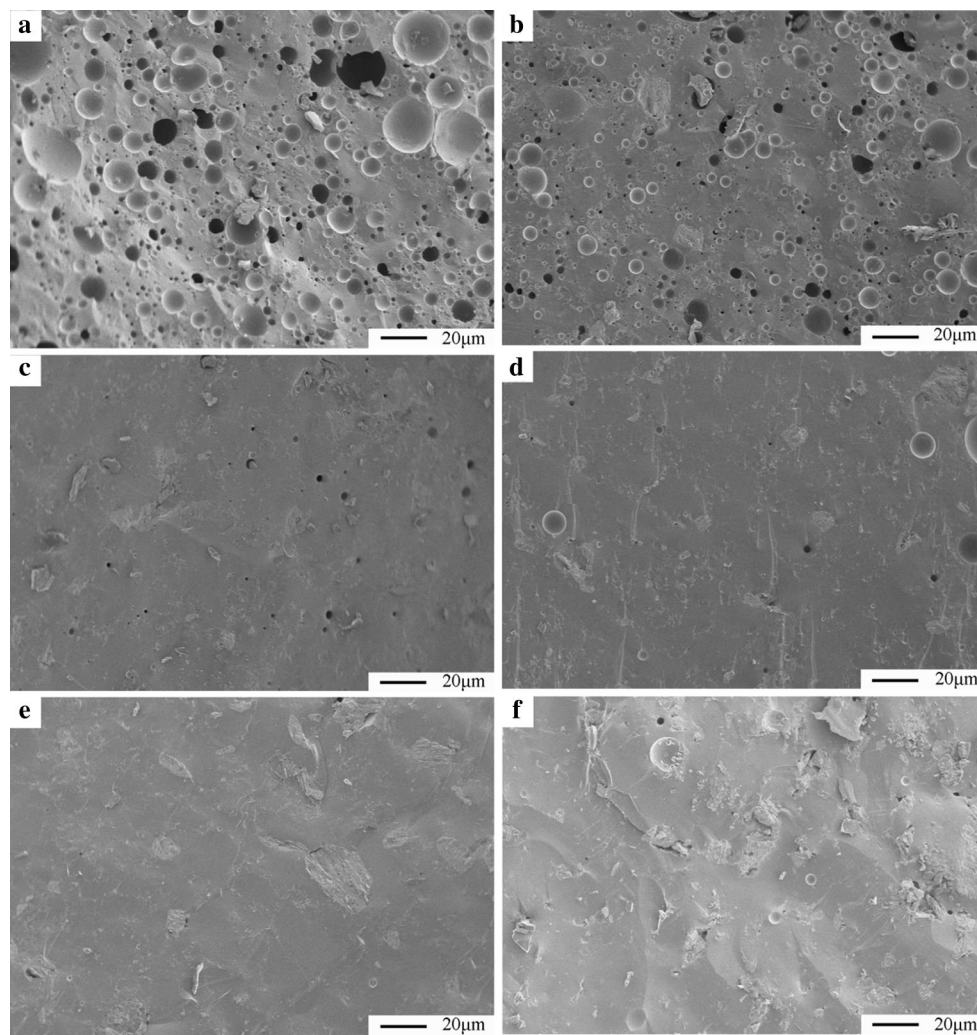


Fig. 5 SEM images of CBS glass with different contents of Al_2O_3 sintered at 800 °C for 30 min: **a** 0 wt%, **b** 2 wt%, **c** 3 wt%, **d** 5 wt%, **e** 7 wt% and **f** 10 wt%

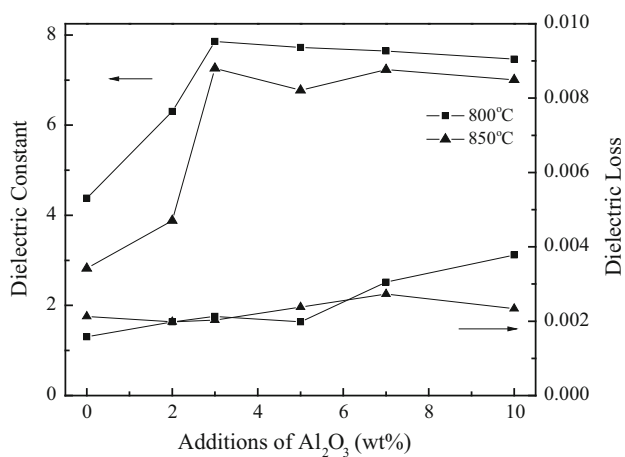


Fig. 6 Dielectric properties of CBS glass with various Al_2O_3 sintered at 800–850 °C for 30 min

CBS glass volatilization. Besides, the shorter holding time (<30 min) also achieved the low densities, which is due to high viscosity of CBS glass restraining further densification. This above results indicated that the addition of Al_2O_3 dramatically improved the sinterability of CBS, which acted as the fluxes and increased the liquid fluidity during viscous flow [21].

Figure 4 shows the DSC curves for CBS glass with different Al_2O_3 contents. All of these samples have exothermic peaks corresponding to crystallization (as indicated in Fig. 1) at about 790 °C. The crystallization peaks are believed as correlated to the crystallization of α - CaSiO_3 and β - CaSiO_3 as identified in the results of the XRD patterns in Fig. 1. The exothermic peak at about 580 °C is the softening temperature of pure CBS glass. The samples with Al_2O_3 found no peaks at about 580 °C. The

possible reason is that the temperature of Al_2O_3 melting in CBS glass was at about 580 °C.

Figure 5 shows the microstructures of the cross section of sintered CBS glass ceramic with different Al_2O_3 contents at 800 °C for 30 min. The CBS specimen with no Al_2O_3 exhibited large number of open pores as shown in Fig. 5a. Both the amount and the size of pores decreased with increase of Al_2O_3 . Dense structure with a few pores with small size were observed for the samples with 3–10 wt%. However, their densities didn't absolutely agree with the change of pores. It can be explained by the fusion of Al_2O_3 . When Al_2O_3 melted in CBS glass, it formed $[\text{AlO}_2]^-$ tetrahedral or $[\text{AlO}_3]^{3-}$ octahedral. The $[\text{AlO}_3]^{3-}$ octahedral as glass network intermediate can reduce the density of CBS glass. With Al_2O_3 adding, there are more $[\text{AlO}_3]^{3-}$ octahedral formed in CBS glass.

3.3 Dielectric properties

Dielectric properties of CBS samples with various Al_2O_3 content sintered at 800–850 °C for 30 min are shown in Fig. 6. The changed trends of dielectric constants of specimens agree with the trends of their densities in Fig. 3. The dielectric constant of the sample sintered at 800 °C first increased, reached the maximum value at 3 wt%, and then decreased with increasing Al_2O_3 content. However, the dielectric constant of the sample sintered at 850 °C shows a little different changing tendency. The sample with 5 wt% Al_2O_3 has a lower dielectric constant than the one with 7 wt% Al_2O_3 , which is caused by its lower density. It is concluded that the porosities play decisive role in the variations of dielectric constants in specimens with relative low densities. With the addition of Al_2O_3 increasing, the dielectric loss of samples sintered at 850 °C increases firstly and then decreases. However, the dielectric loss of samples sintered at 800 °C increases with the rising of addition, except the one with 5 wt% Al_2O_3 . Pure CBS sample sintered at 800 °C for 30 min have lower dielectric loss. Overall, the addition of Al_2O_3 would cause the dielectric loss to increase. Many factors are believed to affect the dielectric loss and these factors can be divided into two categories: the intrinsic loss and the extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification or porosity [14]. In this study, it can be concluded that the dielectric properties of the samples in this study are mainly affected by $[\text{AlO}_3]^{3-}$ stretching vibrations.

4 Conclusions

In this study, the crystallization, sintering and dielectric properties of CBS glass ceramic containing Al_2O_3 were investigated. With increasing the Al_2O_3 content, the

bending and stretching vibrations in $[\text{SiO}_4]^{2-}$ became weak. XRD patterns of samples with ≥ 3 wt% Al_2O_3 introduce cyclowollastonite (α - CaSiO_3) as single crystallized phase of sintered glass–ceramics. It is found that the optimal sintering temperature for this glass ceramics is 800 °C for 30 min, and the sinterability was obviously improved by Al_2O_3 additive. CBS glass ceramics sample with 5 wt% Al_2O_3 achieved the best sintering characterization and dielectric properties ($\epsilon_r \approx 7$, $\tan \delta = 1.9 \times 10^{-3}$ at 1 MHz), which is proposed to be suitable for LTCC application.

Acknowledgments The authors gratefully acknowledge the financial support from the national high technology research and development program of China (863 programs) (No. 2013AA030701).

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