Microstructure, Thermal, Mechanical, and Dielectric Properties of BaO–CaO–Al₂O₃–B₂O₃–SiO₂ Glass-Ceramics

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Abstract: BaO–CaO–Al₂O₃–B₂O₃–SiO₂ (BCABS) glass-ceramics were prepared via the method of controlled crystallization. The effect of CaO modification on the microstructure, phase evolution, as well as thermal, mechanical, and dielectric properties was investigated. XRD identified that quartz is the major crystal phase; cristobalite and bazirite are the minor crystal phases. Moreover, the increase of CaO could inhibit the phase transformation from quartz to cristobalite, but excessive CaO would increase the porosity of the ceramics. Additionally, with increasing the amount of CaO, the thermal expansion curve tends to be linear, and subsequently the CTE value decreases gradually, which is attributed to the decrease of cristobalite with high CTE and the formation of CaSiO₃ with low CTE. The results indicated that a moderate amount of CaO helps attaining excellent mechanical, thermal, and dielectric properties, that is, the specimen with 9 wt% CaO sintered at 950 °C has a high CTE value (11.5 × 10⁻⁶/°C), a high flexural strength (165.7 MPa), and good dielectric properties (εᵣ = 6.2, tanδ = 1.8 × 10⁻⁴, ρ = 4.6 × 10¹¹ Ω·cm).

1. Introduction

Low temperature co-fired ceramics (LTCC) is a well-known technology, which has been attracted widely for fabrication of multilayer substrates and the application of semiconductor devices packaging, e.g. ceramic ball grid arrays (CBGA) for flip chip packages [1,2]. In order to meet the requirement for LTCC technology, the desired packaging materials need to possess low dielectric constant and loss (εᵣ < 7, tanδ < 1 × 10⁻³), high mechanical strength (≥150 MPa), and a high coefficient of thermal expansion (CTE > 10 × 10⁻⁶/°C) [3,4]. Therefore, the thermal match, to realize the high reliability [5], can be achieved between the packaging substrate and the printed circuit board (PCB, CTE = 12–16 × 10⁻⁶/°C).

Recently, Li et al. [6] reported that BaO–Al₂O₃–B₂O₃–SiO₂ (BABS) glass-ceramics own good dielectric properties and high values of CTE. It was found that the thermal property play an important role in the packaging materials for LTCC applications. Especially, for the BABS glass-ceramic, the occurrence of phase transformation of α–cristobalite/β–cristobalite will lead to the nonlinear variation of thermal expansion [7], which will result in the mechanical failure by the thermal mismatch. In fact, some researchers successfully synthesized the composites with high CTE by using low softening-point glass as the flux agent and quartz powders as the filler [8,9]. Nevertheless, the doping modifications
and the crystalline behaviors of these composites have not been extensively investigated yet. As we know, the calcium borosilicate glass-ceramics not only have a moderate CTE value, but also exhibit a linear trend of the thermal expansion [10]. To improve the mechanical and thermal properties of such material, that CaO partly replacing BaO was applied to research the doping behavior as well as the property change of BCABS glass-ceramics.

In the present work, we focus on the influence of CaO modification on the microstructures and the crystalline phases, as well as the mechanical, thermal, and dielectric properties of BCABS glass-ceramics. More importantly, the aim of this paper is to improve the thermal property and the mechanical property, and finally to achieve a novel glass-ceramic BaO–CaO–Al₂O₃–B₂O₃–SiO₂ (BCABS) as a candidate for CBGA packages.

2. Experimental Procedures

BCABS glass-ceramics were synthesized by the solid-state method, and the starting materials are analytical reagent Ba(OH)₂·8H₂O, Ca(OH)₂, Al(OH)₃, H₃BO₃, and H₃SiO₃. The chemical compositions of this study were listed in Table 1. The powders were mixed adequately using the deionized water via ball-milling for 7 h. After been dried at 100 °C, these powders were preheated at 700 °C for 3 h in air. Then the powders were pressed into disks (Φ 23.6 mm × 1 mm) and bars (50 mm × 4 mm × 3 mm) at a compressive stress of 25 MPa. Thereinto, 5 wt% acrylic emulsion was used for the previous prilling process. The samples subjected to the controlled crystallization were sintered constantly from room temperature to 400 °C at a heating rate of 2 °C/min for 3 h to remove the organic binder, then heated up to 950 °C and annealed for 1 h at this temperature.

| Sample | BaO | CaO | Al₂O₃ | B₂O₃ | SiO₂ |
|--------|-----|-----|-------|------|------|
| C1     | 32  | 3   | 5     | 12   | 48   |
| C2     | 30  | 5   | 5     | 12   | 48   |
| C3     | 28  | 7   | 5     | 12   | 48   |
| C4     | 26  | 9   | 5     | 12   | 48   |
| C5     | 24  | 11  | 5     | 12   | 48   |
| C6     | 22  | 13  | 5     | 12   | 48   |

X–ray diffractometer (XRD, PANALYTICAL PW3040/60, Netherlands) was employed to identify the crystalline phases of sintered samples, using Cu Kα radiation, in the 2θ range from 20° to 80°. Microstructures of cross–section were characterized by a scanning electron microscopy (SEM, JEOL 6490LV, Japan). The coefficient of thermal expansion of glass-ceramics was measured within the temperature range from 25 to 600 °C at a heating rate of 5 °C/min using a thermal dilatometer (NETZSCH 401 PC, Germany). The bulk density of sintered samples was detected by the precision density balance (AND GF300D, Japan) using Archimedes method. The flexural strength was determined by an electromechanical universal testing machine (MTS CMT6104, China). Dielectric constant and loss of the disk samples with silver electrode were examined at 1 MHz using a precision LCR meter (AGILENT 4284A, USA).

3. Results and Discussions

XRD analysis was used to investigate the effect of CaO addition on the crystallization behavior of BCABS glass-ceramics, and the result of samples sintered at 950 °C for 1 h is presented in figure 1. XRD patterns detected that the major crystal phase is quartz (JCPDS 70-3755), and the minor phases are cristobalite (JCPDS 77-1317) and bazirite (JCPDS 29-0214). Apparently, the bazirite was crystallized from BaO, ZrO₂, and SiO₂. It was found that the intensity of X-ray peaks for each phase has a great relation with the increase of CaO content. Moreover, a new crystal phase wollastonite (JCPDS 75–1396) appears in sample C6 (13 wt% CaO). In the ternary phase system, CaO–B₂O₃–SiO₂,
wollastonite (CaSiO₃) could be formed as a major phase at 800–900 °C [11]. Thus, excessive CaO could react with SiO₂ to generate the CaSiO₃ phase.

The further calculation was figured out by the whole pattern fitting (WPF) method, and the crystal content and the crystallinity of BCABS glass-ceramics were listed in Table 2. The error of calculation was controlled in the range from 1.35% to 3%. It is clearly seen that with the increase of CaO content, the crystallinity of the BCABS glass-ceramic firstly increased from 33.29% to 39.61%, and then decreased to 35.18%. This suggests that only a proper amount of CaO could facilitate the crystallization process of BCABS glass-ceramics. Moreover, the crystal content exhibited a strong dependence as a function of the CaO content. With increasing the amount of CaO, the content of quartz remarkably increased from 86.7 to 94.1 wt%, but that of cristobalite rapidly decreased from 8.5 to 2.0 wt%. The bazirite, in general, behaved the trend of gradual decline. Actually, the cristobalite was not only transformed from the quartz, but also precipitated from the silica glass. The result indicated that the addition of CaO could effectively restrain the transformation from quartz to cristobalite. Also, sample C6 revealed that the excessive CaO will lead to the formation of the new crystal phase CaSiO₃.

Figure 1. XRD patterns of BCABS glass-ceramics with different CaO content sintered at 950 °C.
Figure 2. Bulk density and linear shrinkage of BCABS glass-ceramics as a function of CaO content.

Figure 3. Cross-section SEM (SE mode) images of BCABS glass-ceramics with various CaO content sintered at 950 °C (a) 3 wt%, (b) 5 wt%, (c) 7 wt%, (d) 9 wt%, (e) 11 wt%, (f) 13 wt% CaO.
Table 2. Phase content and crystallinity calculated from XRD

| Sample | Phase content (wt%) | Crystallinity (%) |
|--------|---------------------|-------------------|
| C1     | 86.7 8.5 4.8 –     | 33.3              |
| C2     | 91.3 4.5 4.2 –     | 33.9              |
| C3     | 92.9 3.4 3.7 –     | 34.7              |
| C4     | 93.6 2.1 4.3 –     | 39.6              |
| C5     | 94.1 2.0 4.0 –     | 35.3              |
| C6     | 87.3 3.1 2.5 7.1   | 35.2              |

Figure 4. CTE (25 - 600 °C) of BCABS glass-ceramics as a function of CaO content.

Figure 5. Flexural strength and coefficient of thermal expansion (at 400 °C) of BCABS glass-ceramics versus CaO content.

In order to study the influence of CaO contents on the sintering behavior in detail, the bulk density and the linear shrinkage at 950 °C was shown in figure 2. For the specimens with ≤9 wt% CaO, the linear shrinkage slightly increased from 19.8% to 20.02%, while the bulk density almost kept in the range of 2.84–2.89 g/cm³. However, both shrinkage and density decreased suddenly when the CaO content was more than 9 wt%. For specimen C6 (13 wt% CaO), the bulk density and the linear shrinkage reached the minimum value of 2.547 g/cm³ and 16.7%, respectively. In fact, the crystal phase transformation from quartz to cristobalite is accompanied by a volume increase of approximate 17% [12]. As a result, the density and the shrinkage decreased markedly after extra CaO being added. Therefore, this result also proved that excessive CaO cannot promote the densification process of such system.

Figure 3 shows the cross-section SEM microphotographs (SE mode) of BCABS specimens with different CaO contents sintered at 950 °C. It is observed that the BCABS glass-ceramics is mainly composed of the crystal phase (dark gray particles) and the glass phase (light gray matrix). A few pores are randomly distributed in the microstructure. To a certain degree, the number of grains increased first and then decreased as the CaO addition increased, which is accordance with the crystallinity in Table 2. However, the number of pores in specimens C5-C6 (11-13 wt% CaO) is clearly more than that in specimens C1-C4 (3-9 wt% CaO). This finding indicates that BCABS samples with > 9 wt% CaO completed their sintering at higher temperatures, which also lead to the occurrence of their insufficient crystallization. Hence, the SEM image for Sample C4 (9 wt% CaO) demonstrated that an appropriate amount of CaO in BCABS will advantage the formation of the best microstructure.

To avoid the thermal mismatch between substrates and PCB, it is very important to investigate the thermal properties of BCABS glass-ceramics. Figure 4 illustrates the temperature dependence of CTE values from 25 to 600 °C for samples with various amount of CaO. Clearly, the nonlinear variation
emerged on these curves for samples C1-C2, and the changing slope was observed around 220–270 °C [7]. In a previous study [12], BCABS glass-ceramic was found as a high expansion system because of the major crystal phases with high CTE value i.e. quartz (13 × 10⁻⁶/°C) and cristobalite (50 × 10⁻⁶/°C). Accordingly, this phenomenon can be explained reasonably through the phase transformation: α–cristobalite/β–cristobalite, which is accompanied by a dramatic expansion in volume. Nevertheless, with further increase of CaO content, the thermal expansion curves of samples became increasingly linear (samples C3-C6). This means that CaO could suppress the nonlinearity of the thermal expansion for the BCABS glass-ceramics, and thus decrease the thermal stress produced by the great volume change originated from the transformation of cristobalite, which will guarantee it to meet the requirements of IC package, such as thermal shock resistance and mechanical strength. Thus, it is believed that the increase of CaO content can effectively improve the thermal property of BCABS glass-ceramics. At the same time, the CTE values at 400 °C as a function of CaO content was shown in figure 5. Apparently, CTE values versus CaO content presents the tendency of gradual decrease from 12.26 to 11.09 ppm/°C. As we know, the value of CTE is directly related to the proportion of crystal phases and residual glass in specimens. As mentioned above, CaO additions can suppress the occurrence of phase transition from quartz to cristobalite. Consequently, the decrease in CTE of glass-ceramics was certainly caused by the reduction in the proportion of cristobalite with higher CTE, which also verified the XRD result. In addition, the lowest CTE of sample C6 could be attributed to the formation of new phase CaSiO_3 having a lower CTE value of 6.5 ppm/°C [13,14].

The flexural strength of BCABS glass-ceramics was measured and the result was also drawn in figure 5. For specimens C1-C3 (3-7 wt% CaO), the flexural strength was enhanced from 143.5 to 153.6 MPa. And sample C4 with 9 wt% CaO obtained a maximum strength of 165.7 MPa. As shown in Table 2, the highest crystallinity of sample C4 may be one of the most important reasons for the highest flexural strength. As is well known, the fluctuation of volume generated by the rapid and reversible structural transformation of cristobalite is disadvantage to the mechanical property. XRD results say that the addition of CaO restrained the precipitation of the cristobalite phase [15,16]. Hence, the improvement of flexural strength is ascribed to the decrease in the mass fraction of cristobalite. However, when further increasing CaO content (11 wt%), specimen C5 has the lowest flexural strength of 93 MPa. It was considered that the appearance of pores resulted in the remarkable decline of the mechanical property. The similar trend was also observed for the bulk density and the linear shrinkage in figure 2. Generally, the mechanical property is correlated with the crystal phases in the materials. It was notable that the flexural strength of sample C6 (13% CaO) rebounded to 110.6 MPa, which is contributed to the presence of CaSiO_3 phase.

**Figure 6.** Dielectric properties of BCABS glass-ceramics as a function of CaO content.
Figure 6 shows the dielectric properties at 1 MHz, including dielectric constant, dielectric loss, and insulation resistivity, for BCABS glass-ceramics versus the amount of CaO. The dielectric constant remained stable around 6.0–6.2 when the CaO content within 3–9 wt%, whereas it decreases to 5.4 for CaO contents > 11–13 wt% due to the porous microstructure. Accordingly, the variation of dielectric constant is attributed to the emergence of the remaining pores in the microstructure of BCABS. Besides, independent of CaO content, the dielectric loss always maintained at the same magnitude of 10⁻⁴. Obviously, the insulation resistivity first enhanced and then declined, which is coincident with the tendency of bulk density. Generally, sample C4 (9 wt% CaO) possesses the good dielectric properties: $\varepsilon_r = 6.2$, $\tan\delta = 1.8 \times 10^{-4}$, $\rho = 4.6 \times 10^{11}$ Ω·cm, meeting the requirement of the substrate materials.

4. Conclusions

BaO–CaO–Al₂O₃–B₂O₃–SiO₂ (BCABS) glass-ceramics were prepared for the LTCC application: CBGA package. The research indicated that the amount of CaO addition significantly affected the sinterability, structure, thermal, mechanical, and dielectric properties of BCABS system. The crystal phases Quartz (major) as well as Cristobalite and Bazirite (minor) were detected by XRD. Due to the phase transformation of quartz to cristobalite restrained by the CaO addition efficiently, the thermal property, especially the linearity, was improved evidently. However, an excess of CaO deteriorated the bulk density, bending strength, and dielectric properties, which was mainly attributed to the formation of more pores during the sintering process. 9 wt% CaO doped BCABS glass-ceramics sintered at 950 °C achieved high flexural strength (165.7 MPa), high CTE value (11.50 × 10⁻⁶/°C), low dielectric constant ($\varepsilon_r = 6.2$), low dielectric loss ($1.8 \times 10^{-6}$).

5. References

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