Research Article

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Preparation of low-permittivity $K_2O-B_2O_3-SiO_2-Al_2O_3$ composites without the addition of glass

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Abstract: In the field of low temperature co-fired ceramic (LTCC), it remains a challenge to design the performance of LTCC with low permittivity less than 5. Here, the $K_2O-B_2O_3-SiO_2-Al_2O_3$ composites are prepared without the preparation of prior glass. Meanwhile, the factors of the CaO content on microstructure, phase structure and properties of the composites are considered systematically. The crystal structure measured by X-ray diffraction (XRD) shows that there are quartz and alumina as the crystal phases. The results reveals that the tailoring CaO content benefits sintering densification, low dielectric loss, great mechanical properties and low thermal expansion coefficient. As CaO content increases up to 2.8 wt%, the composites sintered at 850°C have a dielectric constant of 4.94 and tanδ of $8 \times 10^{-4}$ at 1 MHz, thermal expansion coefficient (CTE) of 8.5 ppm/°C, and flexural strength of 150 MPa. As the mass fraction of CaO increases up to 3.2 wt%, the maximum flexural strength of 173 MPa is achieved. The above study provides an effective approach for preparing the novel composites as a promising candidate for LTCC applications.

Keywords: Low permittivity, Low loss, High flexural strength, LTCC applications

1 Introduction

For light and integrated electron devices in microwave communication, low temperature co-fired ceramic (LTCC) technology has been widely applied due to its superior properties and low cost. In wireless telecommunication and microwave integrated circuits, low permittivity (low for fast signal transmission) and high quality factor ($Q$) are critical for practical applications. Beyond that, high flexural strength provides outstanding supporting for the electronic packaging. The matched thermal expansion coefficient (CTE) effectively promotes the reliability of the system designs [1, 2]. However, most conventional ceramics materials have a high sintering temperature of over 1000°C. Attention is therefore focused on the role of glasses because of the effects they reduce the sintering temperature of ceramics materials. There are two approaches to obtaining ceramic composites with the sintering temperature of below 1000°C [1].

The first approach is to add glasses prepared via high temperature melting technique. For glasses compositions, borosilicate glasses have drawn a lot of attention due to its excellent comprehensive performance. As a promising material, $Al_2O_3$ has $e_r$ of 9.8, making $Al_2O_3$ ceramic-filler a potential glass/ceramic candidate. In addition, $Al_2O_3$ is chosen due to its high mechanical strength and high surface energy, which is able to provide hydrodynamic lubrication for sintering densification [3]. The typical borosil-
Table 1: Composition of different CaO content (mass fraction, wt %)

| Sample | CaO | SiO<sub>2</sub> | Al<sub>2</sub>O<sub>3</sub> | B<sub>2</sub>O<sub>3</sub> | K<sub>2</sub>O | Na<sub>2</sub>O | BaO |
|--------|-----|----------------|-----------------|-----------------|--------|--------|------|
| A1     | 0.5 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A2     | 0.9 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A3     | 1.3 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A4     | 1.7 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A5     | 2.1 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A6     | 2.5 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A7     | 2.8 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A8     | 3.2 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |
| A9     | 3.6 | 63             | 23              | 11              | 2.5    | 1.5    | 0.5  |

indicate glasses are listed as following: SiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub>–CaO–MgO [4], ZnO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> [5], CaO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–Na<sub>2</sub>O–K<sub>2</sub>O [6], B<sub>2</sub>O<sub>3</sub>–Bi<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–ZnO [7], BaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> [8], K<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> [9] etc. Qin Xia et al. [9] prepared K<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> glass ceramics, showing a high dielectric constant of 6.1 and a heavy dielectric loss of 2×10<sup>−3</sup> at 1 MHz. Xianfu Luo et al. [10] reported the properties of CaO–Al<sub>2</sub>O<sub>3</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass/Al<sub>2</sub>O<sub>3</sub> composite with different CaO contents. They found that an appropriate addition of CaO into CABS glass enhances glass/ceramic density.

However, melting glasses are prepared at high temperature, leading to large energy consumption. And boron oxide (melting point of 450°C) evaporates rapidly at high temperature, making it difficult for borosilicate glasses to control their composition. Hence, as a novel and low-cost method, another approach is via the glass–ceramic route. Heli Jantunen et al. [11] investigated the possibility of preparing a similar LTCC ceramic without the preparation of prior glass. Xueming Cui et al. [12] reported an effective pre-sintering method to fabricate BaO–TiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass–ceramic, which was a simple approach that the whole mixed solid oxides were sintered at 750°C instead of preparing melting glass over 1000°C. There were few reports about low-permittivity K<sub>2</sub>O–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> glass-ceramic prepared via pre-sintering method.

Herein, we propose a novel perspective on the role of CaO, which is significant to develop a low-cost process on account of avoiding melting glass. The effects of CaO content on dielectric properties, thermal expansion coefficient, and flexural strength are presented separately.

2 Experimental procedures

The composites were prepared by the conventional solid-state ceramic route. According to the composition shown in Table 1, the K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, CaO, Ba(OH)<sub>2</sub>·8H<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> (the purity of all the raw materials is 99.9%) with different CaO contents (mass fraction, %) (0.5, 0.9, 1.3, 1.7, 2.1, 2.5, 3.2, 3.6) were directly mixed and blended for 4 h by the planetary ball mill. After completely dried off, the powders were sifted at the pre-sintering temperature of 750°C for 2 h and then we sifted the pre-sintered powders using 100 mesh sieve to guarantee uniform particle size. The uniform powers (about 150 µm) were added into the planetary ball mill at 280 r/min for 6h. Later, the slurry was dried off at 100°C for 24 h. Then we ground down the powers by adding Acrylic acid as the binder until we made it uniform and fluid. At the end, the powders were formed via pressing process at 20MPa and the samples were respectively sintered at 850°C for 2 h.

The phase analysis of the samples sintered at 850°C was carried out by XRD using Cu Ka radiation (Philips...
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Figure 2: XPS patterns of the composite with CaO content of 2.8 wt.% sintered at 850°C

Table 2: Properties of the composites in comparison with commercial LTCC materials

| Material       | \(\varepsilon_r\) | Loss \((10^{-3})\) | Strength (MPa) | CTE (ppm/°C) | Sintering temperature (°C) |
|----------------|-------------------|-------------------|----------------|---------------|---------------------------|
| DuPont 951     | 7.8               | 1.5@1KHz         | 320            | 5.8           | <900                      |
| Ferro A6       | 5.9               | 2@10MHz          | 130            | 7             | <900                      |
| Heraeus CT700  | 7                 | 2@1KHz           | 240            | 6.7           | <900                      |
| This work      | 4.94              | 0.8@1MHz         | 150            | 8.3           | 850                       |

X'Pert Pro MPD). The microstructures of the samples were examined via electron microscopy (SEM, FEI Inspect F, UK). X-ray Photoelectron Spectroscopy (XPS) measurements were performed on an AXIS ULTRA spectrometer (Kratos Analytical Ltd., Japan) using a monochromatic Al source. The densities of the samples were measured using a GF-3000D Density Meter. A network analyzer (Agilent Technologies E5071C, USA) and a temperature chamber (DELTAC 9023, Delta Design, USA) were used to measure the microwave dielectric properties. Flexural strengths and TEC values were measured using a CMT6104 microcomputer control electronic universal testing machine and a NETZSCH DIL402PC, respectively.
3 Results and discussion

XRD patterns of the composites shown in Figure 1. From XRD results, it can be seen that SiO₂ (quartz) is the main crystalline phase, and the additional crystalline phase is Al₂O₃. As CaO content increases, it has no significant effects on phase structure. However, the intensity of quartz phase slightly decreases. Chung Chiang et al. [13] reported CaO–B₂O₃–SiO₂ system glass–ceramics which only consists of SiO₂ (quartz structure) after sintering. Compared with the work of Chung Chiang et al. [13], the main crystalline of the composites is also SiO₂ (quartz) phase due to its abundant silica. Second, and more importantly, low pre-fired temperature provides insufficient energy for forming largely an amorphous glass structure of Si-O network, resulting in the crystallization of SiO₂ (quartz).

The XPS measurements is widely applied for confirming chemical state of composites [14]. In order to deepen our understanding of chemical state of composites, the XPS results are presented in Figure 2. The photoelectron binding energy peaks for each element are as follows: Al2p is at 74.17 eV, O1s is at 532.03 eV, and Si2p is at 102.86 eV. From the comparison between our experimental data and the XPS standard database [15], the XPS measurements results (Figure 2) further confirm the presence of SiO₂ and Al₂O₃. The individual spectra of Ca shows the resolution of Ca2p spectrum into two peaks 2p1/2 and 2p3/2 at 350.85 and 348.02 eV, respectively. Ca2p spectrum possesses two
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Figure 4: Elemental map distributions measured by back scattered electron mode: A) S1; B) S4; C) S8; D) S9

peaks, which is also confirmed by this study of Aneela Anwar et al. [16].

Figure 3 shows the microstructures of K$_2$O–B$_2$O$_3$–SiO$_2$–Al$_2$O$_3$ composites sintered at 850°C for 2h. The research of SEM indicates that porosity, the heterogeneity of grain size as well as detectable amorphous phases are the typical microstructure of the composites. As CaO content increases up to 2.8 wt.% Figure 3C reveals crystalline grains firmly embedded within a homogeneous liquid phase, showing a dense microstructure.

The remarkable changes in the element distributions of the composites sintered at 850°C are shown in Figure 4A-D. Al$_2$O$_3$ crystals with maximal sizes of up to 7 µm are clearly discernable in the mappings C and D. Meanwhile, increasing enrichment of all the elements can be detected, indicating that it favors to efficiently increase the enrichment of elements by tailoring the addition of CaO.

The common structure of borosilicate glass is a structure of Si-O network modified by alkali ions and alkaline earth metal ions. These four metallic oxides have significant effects on breaking the network and promoting the formation of glass phase [17]. The movement of the mobile K$^+$ and Na$^+$ causes heavy dielectric loss but proportionate content of K$^+$ and Na$^+$ help the reduction of loss according to the mixed alkali effect in glass [18]. As the radius of Ba$^{2+}$ is larger than other ions, it favors to efficiently suppress the migration of K$^+$ and Na$^+$ [17]. In this work, the powders sintered at 750°C result in a certain volume fraction of liquid phase, which is available for low temperature sintering by liquid phase sintering theory.

Figure 5A shows the change trend of density as a function of CaO content. The increasing density corresponds to elements enrichment reflected by the mappings in Figure 3. The results also show that the composites without melting glass addition can achieve a better density. As
Figure 5: Properties of composites: A) density; B) dielectric loss; C) dielectric constant; D) density and dielectric constant with different temperatures; E) strength; F) CTE
CaO content increases up to 3.2 wt%, the higher density of 2.57 g/cm³ with reasonably excellent characteristics of microstructures in Figure 3C is acceptable for the LTCC applications. Figure 4B represents dielectric loss of samples sintered at 850°C. It appears that dielectric loss decreases as CaO content increases. In this work, dielectric loss most likely results from the movements of the mobile K⁺ and Na⁺ [17]. The effective radius of Ca²⁺ is close to barium ion, which shows a limited mobility in glass structure, thus preventing the migration of the alkali ions [19, 20]. Hence an increasing CaO content obviously leads to low loss and the dielectric loss is considerably below 10⁻³ when the addition of CaO is more than 1.5 wt%.

With respect to Figure 5C and D, it is generally believed that there is a clear relation between dielectric properties and densification [21, 22]. It can be seen in Figure 5 A and C that increasing density corresponds to the permittivity rising. In addition, permittivity is also influenced by the constituent phases. SiO₂ has the low dielectric constants of 3.8, indicating that Si-rich composites have lower dielectric constant [22]. As shown in Figure 5C, the present composites emerge a low permittivity around 5 at 1 MHz and 5.5 at 14 GHz with the CaO content of 3.2 wt%.

As for physical properties shown in Figure 5E, flexural strength increases first and then decreases. In this work, the density is deemed to dominate the flexural strength of composites. The flexural strength of the composites firstly increases to 173 MPa, and then slightly decreases to 156 MPa as CaO content increases, closely corresponding to the density as shown in Figure 4 A. According to the theory of liquid phase sintering [1], the densification occurs through the viscous flow mechanism. When the composites are sintered at 850°C, SiO₂ and Al₂O₃ crystal particles dissolve easily in liquid phase and then rearrangement of grain availability makes samples compact [1, 23]. The results indicate that an excellent physical properties can be attained by the addition of CaO, showing a promising approach to preparing glass-ceramics without the addition of melting glass.

As for the thermal properties of the composites sintered at 850°C, Figure 5F indicates that the CTE values of the composites ranging between temperatures of 25°C–300°C are 8~9 ppm/°C. The CTE value of composites obviously decreases with the addition of CaO content. The reason is that tailoring CaO content contributes to densification, thus resulting in forming less pores. Because pores possess a higher CTE value (= 10³ ppm/°C), high densification corresponds to a decreasing thermal expansion. Obviously, the composites with CTE of 8~9 ppm/°C is available for applications between the LTCC module and the alumina substrate [1, 24].

Finally, we make a comparison between the commercial LTCC materials and the K₂O–B₂O₃–SiO₂–Al₂O₃ composites in this work. As shown in Table 2, the composites we prepared possess higher CTE, lower permittivity, and lower dielectric loss, which provides a good reliability for electronic packaging [25].

4 Conclusions

Without melting glass, the K₂O–B₂O₃–SiO₂–Al₂O₃ composites were prepared through the simple solid state synthesis methods. The addition of CaO in the composites exhibits superior effects on dielectric properties, thermal expansion coefficient and flexural strength. As CaO content increases up to 2.8 wt%, the composites show a dielectric constant of 4.94 and tanδ of 8 × 10⁻⁴ at 1 MHz, thermal expansion coefficient of 8.5 ppm/°C and flexural strength of 150 MPa, providing a useful thought for electronic packaging that K₂O–B₂O₃–SiO₂–Al₂O₃ composites with dielectric constant less than 5 can be prepared by tailoring the addition of CaO.

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