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 $\tan\delta$ of 8×10^{-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 ϵ_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-

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Table 1: Composition of different CaO content (mass fraction, wt %)

Sample	CaO	SiO ₂	Al ₂ O ₃	B ₂ O ₃	K ₂ O	Na ₂ 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

icate glasses are listed as following: SiO₂–B₂O₃–CaO–MgO [4], ZnO–B₂O₃–SiO₂ [5], CaO–Al₂O₃–B₂O₃–SiO₂–Na₂O–K₂O [6], B₂O₃–Bi₂O₃–SiO₂–ZnO [7], BaO–B₂O₃–SiO₂ [8], K₂O–B₂O₃–SiO₂ [9] etc. Qin Xia *et al.* [9] prepared K₂O–B₂O₃–SiO₂–Al₂O₃ glass ceramics, showing a high dielectric constant of 6.1 and a heavy dielectric loss of 2×10^{-3} at 1 MHz. Xianfu Luo *et al.* [10] reported the properties of CaO–Al₂O₃–B₂O₃–SiO₂ glass/Al₂O₃ 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–TiO₂–B₂O₃–SiO₂ 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 K₂O–B₂O₃–SiO₂–Al₂O₃ 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

Figure 1: XRD patterns of samples with different CaO contents

in Table 1, the K₂CO₃, Na₂CO₃, CaO, Ba(OH)₂·8H₂O, B₂O₃, SiO₂, Al₂O₃ (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, 2.8, 3.2, 3.6) were directly mixed and blended for 4 h by the planetary ball mill. After completely dried off, the powders were sintered 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 grinded 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 Kα radiation (Philips

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	ϵ_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 (DELTA 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.

Figure 3: SEM micrograph of composites measured by secondary electrons mode A) S1; B) S4; C) S8; D) S9

3 Results and discussion

XRD patterns of the composites shown in Figure 1. From XRD results, it can be seen that SiO_2 (quartz) is the main crystalline phase, and the additional crystalline phase is Al_2O_3 . 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 $\text{CaO-B}_2\text{O}_3\text{-SiO}_2$ system glass-ceramics which only consists of SiO_2 (quartz structure) after sintering. Compared with the work of Chung Chiang *et al.* [13], the main crystalline of the composites is also SiO_2 (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 SiO_2 (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: $\text{Al}2p$ is at 74.17 eV, $\text{O}1s$ is at 532.03 eV, and $\text{Si}2p$ 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 SiO_2 and Al_2O_3 . The individual spectra of Ca shows the resolution of $\text{Ca}2p$ spectrum into two peaks $2p_{1/2}$ and $2p_{3/2}$ at 350.85 and 348.02 eV, respectively. $\text{Ca}2p$ spectrum possesses two

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 $K_2O-B_2O_3-SiO_2-Al_2O_3$ composites sintered at $850^\circ C$ 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 $850^\circ C$ are shown in Figure 4A-D. Al_2O_3 crystals with maximal sizes of up to $7\ \mu m$ 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 contents 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 $750^\circ C$ 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/cm^3 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 Ca^{2+} 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. SiO_2 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 1MHz 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 173MPa, and then slightly decreases to 156MPa 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 , SiO_2 and Al_2O_3 crystal particles dissolve easily in liquid phase and then rearrangement of grain availably 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/ $^\circ\text{C}$. 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 ($\approx 10^3$ ppm/ $^\circ\text{C}$), high densification corresponds to a decreasing thermal expansion. Obviously, the composites with CTE of 8–9 ppm/ $^\circ\text{C}$ 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 $K_2O-B_2O_3-SiO_2-Al_2O_3$ 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 $K_2O-B_2O_3-SiO_2-Al_2O_3$ composites were prepared through the simple solid state synthesis methods. The addition of CaO in the composites exerts superior effects on dielectric properties, thermal expansion coefficient and flexural strength. As CaO content increases up to 2.8wt%, the composites show a dielectric constant of 4.94 and $\tan\delta$ of 8×10^{-4} at 1 MHz, thermal expansion coefficient of 8.5 ppm/ $^\circ\text{C}$ and flexural strength of 150 MPa, providing a useful thought for electronic packaging that $K_2O-B_2O_3-SiO_2-Al_2O_3$ composites with dielectric constant less than 5 can be prepared by tailoring the addition of CaO.

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