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Oxyfluoride glass-silica ceramic composite for low temperature co-fired ceramics

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Abstract

Glass/ceramic composite materials based on CaF_2–AlF_3–SiO_2 oxyfluoride glass and silica ceramic filler were prepared. The sintering behavior, phase composition and dielectric property of oxyfluoride glass/silica ceramic composites, as well as its compatibility with Ag electrode, were investigated. The results show that the glass/ceramic composite system can be sintered at 825 °C. When the amount of SiO_2 increased from 0 to 20 wt.%, the shrinkage decreased from 17.0 to 14.5%, and the dielectric constant decreased from 5.9 to 5.4, while the thermal expansion coefficient (20–200 °C) increased from 6.0 to 10.1 ppm/°C. The sintered samples had low dielectric losses less than 0.002 and high flexural strengths. This novel glass/ceramic composite system exhibits good sintering compatibility with silver paste, which makes it a promising candidate for low temperature co-fired ceramic application.

Keywords: Glass ceramics; SiO_2; Composites; Dielectric properties; Substrate

1. Introduction

In recent years, low temperature co-fired ceramics (LTCC) have become an attractive technology for electronic components and substrates which have reduced size, light weight, high operating speed and multifunctionality.[1–3] With this technology, passive components (such as capacitors and inductors) can be integrated or embedded into the substrate, by co-firing at a temperature below 900 °C with high-conductive metal electrode (such as silver and copper).[1,3,4] Therefore, it is a key issue for LTCC technology to reduce the sintering temperature to co-fired with metal electrodes. In order to achieve this goal, pure glass or crystallized glass is usually added to ceramic fillers to form glass/ceramic composite systems, in which ceramic fillers mainly play a role in adjusting the dielectric properties of the composites, while glass often acts as a sintering reagent.[3] During the sintering process, the glass becomes softened, then fills the capillary pore channels between the ceramic particles, and as a result, the density of the composite materials gets enhanced.[5,6] Based on this mechanism, one can expect that the transition temperature (T_g) and high-temperature viscosity of the glass are two important factors for the composite systems.

In addition, the selection of ceramic fillers and glass varies with the demands of practical applications. For example, LTCC materials containing ceramic filler with high dielectric constant are desired to reduce the size of capacitors, inductor, filters and antennas.[1,2,7] On the other hand, dielectric materials or substrate materials with low dielectric constant are effective to achieve high speed transmission of signals, for the propagation delay time of the signal is proportional to the square root of the dielectric constant.[3,8,9] Current materials for LTCC substrates usually consist of low dielectric constant ceramic fillers (such as cordierite, SiO_2 and Al_2O_3) and borosilicate glasses or aluminosilicate glasses. However, borosilicate glasses and aluminosilicate glasses usually have a relative high transition temperature (T_g) of 700–800 °C. Moreover, although BaO–B_2O_3–SiO_2 system with large B_2O_3 content had a T_g of 619 °C, the microstructure and the strength of the material were destroyed, and the dielectric loss of the material increased due to the large amount of B_2O_3.[8–12] Thus, it is a key point for LTCC substrate materials to search for new glass systems with low sintering temperature and low dielectric constant.

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In the last years, oxyfluoride glass showed potential capability for its low transition temperature due to the increase in the number of non-bridging bonds during the process of fluorine ions into glass network.[13] In addition, for its large electro-negativity, fluorine incorporation led to the reduction of electronic polarizability and ionic polarizability, as a result, a much lower dielectric constant could be achieved.[14] Therefore, oxyfluoride glass is a promising candidate in constructing glass/ceramic composites with relative low dielectric constant at much lower sintering temperature.

In this paper, LTCC composites consisting of SiO_2 ceramic filler and CaF_2–AlF_3–SiO_2 oxyfluoride glass were prepared. The sintering behaviors, phase composition, microstructure, and dielectric properties of the as-prepared materials, as well as its compatibility with Ag electrode, were investigated. We suggest that the oxyfluoride glass-silica ceramic composites should be a promising candidate for low temperature co-fired ceramic substrate application.

2. Experimental procedure

Analytical reagent grade raw materials of $AlF_3{\cdot}3H_2O$, CaF_2 and SiO_2 were used to prepare oxyfluoride glass. Prior to use, $AlF_3{\cdot}3H_2O$ was baked at 550 °C for 1 h to prepare anhydrous AlF_3 in a NH_4F protective atmosphere. The oxyfluoride glass powders had a composition of 45–55 wt.% SiO_2, 35–45 wt.% AlF_3 and 5–15 wt.% CaF_2. After mixed uniformly, the raw materials were melted at 1250–1350 °C for 2 h in an uncovered alumina crucible and quenched in water to form cullet. The cullet was ground to an average particle size of 1–2 μm by ball-milling in ethanol, and then dried completely.

Different amount of SiO_2 filler were mixed with the oxyfluoride glass powders prepared above, and then ball-milled in ethanol for 12 h. After completely dried, the powders were mixed with small amount of polyvinyl alcohol (PVA, 10 wt.%) as organic binder and pressed uniaxially under a pressure of 80 MPa. Then the green compacts were sintered at 750–850 °C for 3 h.

The differential scanning calorimetry (DSC) and thermogravimetric (TG) of the oxyfluoride glass were measured using a thermal analyzer (NETZSCH STA 409 PC/PG) in air up to 1000 °C with a heating rate of 10 °C/min. The densities of the sintered bodies were measured using the Archimedes' method. The shrinkage values of the samples were obtained by measuring the diameters of the sintered samples directly, while the thermal shrinkage curves were measured by a horizontal-loading dilatometer with alumina rams and boats (NETZSCH DIL 402 PC). The crystal structure was identified by X-ray diffraction (XRD, Rigaku X-ray Diffractometer) using Cu Kα radiation, and the microstructure was observed by scanning electron microscopy (SEM, FEI QUANTA 200F). The dielectric properties were measured by HP 4278A impedance analyzer at 1 MHz. The flexural strength and average linear thermal expansion coefficient (TCE) were measured by an electronic universal testing machine (Shimadzu AG-200A) and a thermal mechanical analyzer (NETZSCH DIL 402 PC), respectively.

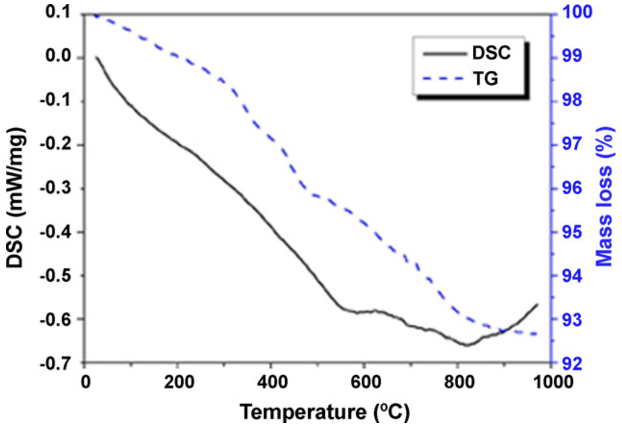

Fig. 1. DSC and TG of the oxyfluoride glass with a heating rate of 10 °C/min.

3. Results and discussion

Fig. 1 shows the DSC and TG curves of the oxyfluoride glass in air up to 1000 °C with a heating rate of 10 °C/min. The base line changing in the DSC trace indicated that the transformation temperature of the glass was about 550 °C and there was no obvious exothermic peak corresponding to crystallization. It is noted that although this oxyfluoride glass contained few low melting-point compounds, the transition temperature was lower in comparison with commonly used glasses in LTCCs. This is mainly due to the fact that the fluorine ions entered into the glass network and one Si–O bond was replaced by two Si–F bonds. As a result, the transition temperature decreased with the increase in the number of non-bridging bonds. The TG trace showed that the weight of the glass powder was unchanged above 850 °C and the final mass loss was about 7–8% which was due to the release of the gas remaining during the process of the glass preparation.

Fig. 2 shows the effects of the SiO_2 content and sintering temperature on the shrinkage behaviors of the samples. When the sintering temperature rose, the shrinkages of the samples increased first, and then reached their maximal values at about 825 °C. In addition, when the amount of SiO_2 increased

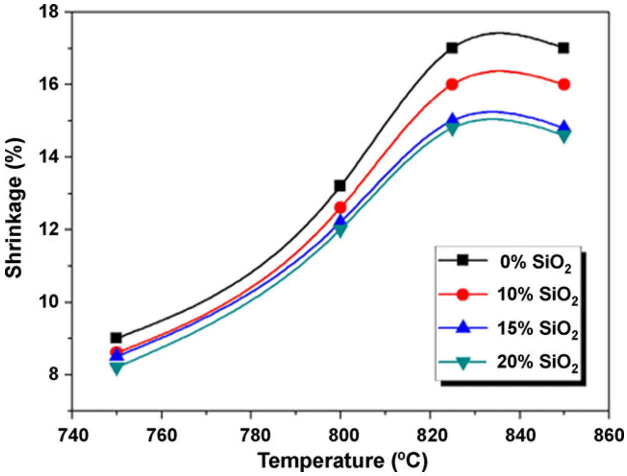

Fig. 2. Effects of the SiO_2 content and sintering temperature on the shrinkage behaviors of the samples.

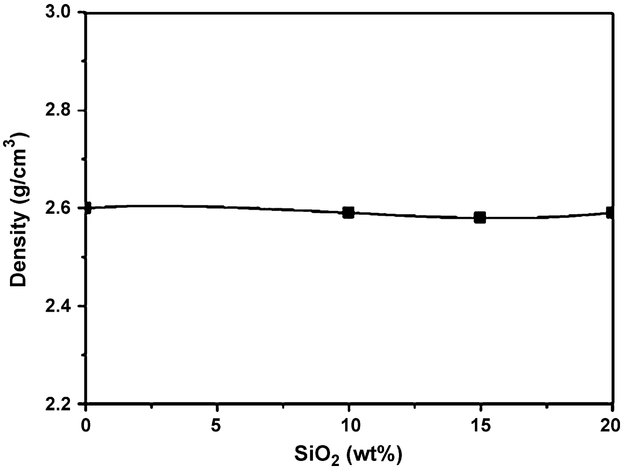

Fig. 3. Variation in densities of the samples with different SiO_2 content sintered at 825 °C for 3 h.

from 0 to 20 wt.%, the shrinkages of the samples sintered at 825 °C decreased from 17.0 to 14.5% accordingly. Fig. 3 shows the dependence of density on the SiO_2 content for the specimens sintered at 825 °C for 3 h. The SiO_2 content affected little on the densities of the samples because the density of SiO_2 (2.5–2.7 g/cm^3) is close to that of the oxyfluoride glass (~2.6 g/cm^3).

Fig. 4 shows the SEM images of the fractured surfaces of the samples with different SiO_2 amount sintered at 825 °C for 3 h. The fractured surfaces of the samples were covered by large amount of glass phase, and all the samples were densified effectively, only a few pores were left. With the increase of SiO_2 content from 10 to 20 wt.%, the pores became small and dispersive.

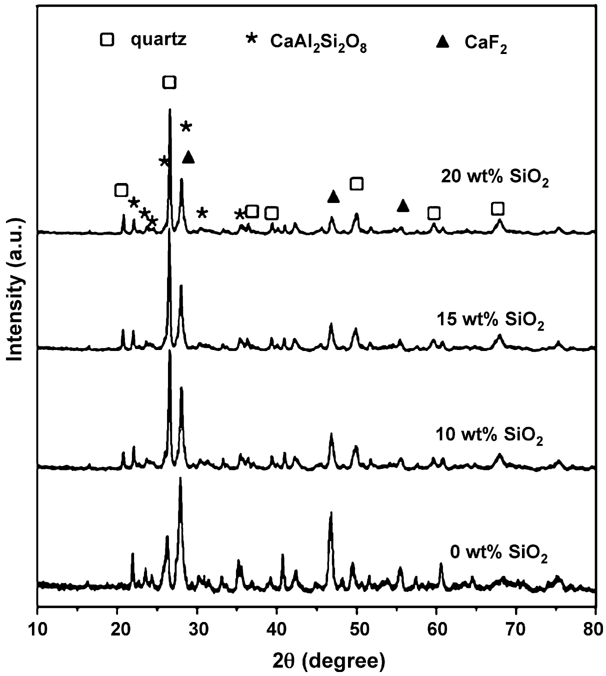

Fig. 5. XRD patterns of the samples containing different amount of SiO_2 filler sintered at 825 °C for 3 h.

Table 1
A summary of the properties of flexural strength and TCE of the samples sintered at 825 °C for 3 h

SiO_2 filler content (wt.%)	0	10	15	20
Flexural strength (3 point bend) (MPa)	150	190	184	194
TCE (ppm/°C) (20–200 °C)	6.0	8.5	9.7	10.1

Fig. 5 shows the XRD patterns of the samples sintered at 825 °C for 3 h with different amount of SiO_2 filler. The sample without SiO_2 addition was mainly composed of crystalline phases of $CaAl_2Si_2O_8$ (anorthite) and CaF_2. When the addition of SiO_2 filler increased from 0 to 20 wt.%, the diffraction peaks of quartz appeared and no noticeable reaction was observed between the oxyfluoride glass and SiO_2 ceramic filler, only the relative intensity of the peaks corresponding to quartz phase got enhanced. The dielectric constants and dielectric losses of the samples with different SiO_2 content sintered at 825 °C for 3 h are shown in Fig. 6. For the large electro-negativity of fluorine ions, the dielectric constant of oxyfluoride glass itself lowered to about 5.9. When the amount of SiO_2 filler with low dielectric constant increased from 0 to 20 wt.%, the dielectric constants of the samples decreased linearly from 5.9 to 5.4. In addition, the samples with different SiO_2 amount all exhibited low dielectric loss (tan δ) less than 0.002.

Table 1 lists the values of flexural strength and TCE of the samples sintered at 825 °C for 3 h with different SiO_2 content. The flexural strengths of the samples with SiO_2 filler were

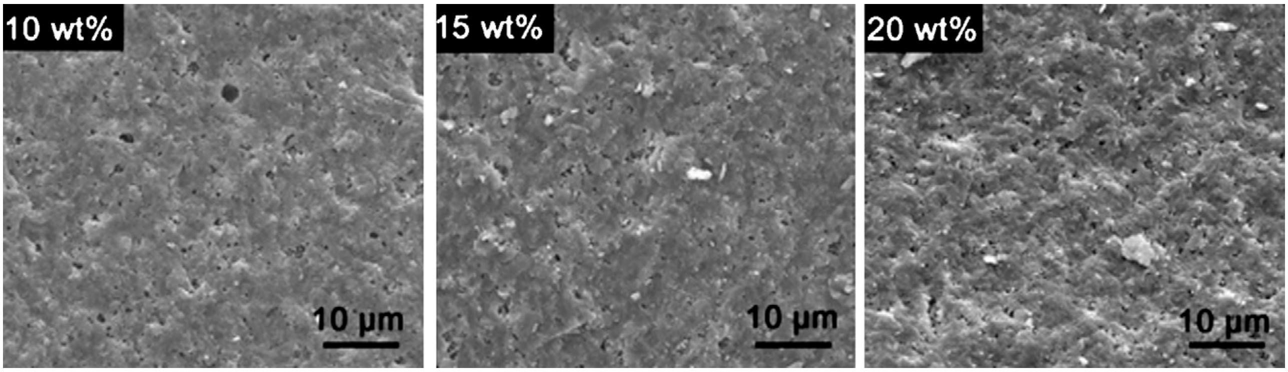

Fig. 4. SEM images of the samples with different amount of SiO_2 sintered at 825 °C for 3 h.

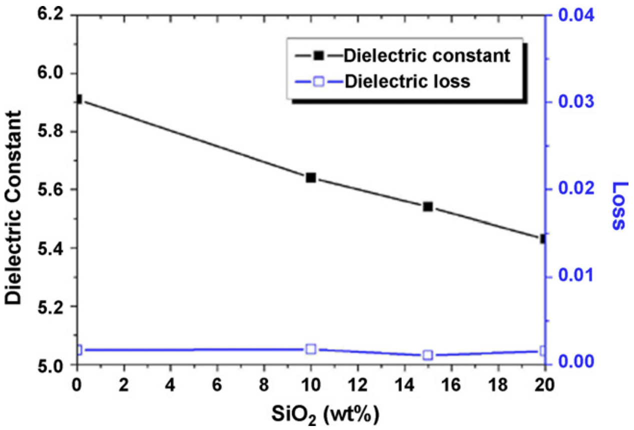

Fig. 6. Dielectric constants and dielectric losses of the samples sintered at 825 °C for 3 h as a function of SiO_2 filler content.

higher than that of the sample without SiO_2 filler. This was because that the dispersed SiO_2 ceramic particles can prevent the cracking growth in the glass/ceramic composites and enhance the mechanical strengths. However, on the other hand when the amount of SiO_2 filler increased further, more dispersive small pores were left, as shown in Fig. 4, which can damage the strengths at same time, therefore when the SiO_2 content increased further, the strength values kept almost constant. The TCE value of the sample without SiO_2 was about 6.0 ppm/°C. With the rise of SiO_2 amount, the TCE values increased linearly from 6.0 to 10.1 ppm/°C due to the large TCE value of SiO_2 ceramic itself (∼12 ppm/°C).

Cylindrical green compacts were prepared with a diameter of 5 mm and a thickness of 3–4 mm for shrinkage analysis during heating. Fig. 7 shows the thermal shrinkage curves of silver, oxyfluoride glass and oxyfluoride glass with 15 wt.% SiO_2 filler. The start point of dimensional shrinkage of Ag compact was about 250 °C. The shrinkage ratio varied slowly in the range of 250–800 °C and got a peak value at about 800 °C. The oxyfluoride glass without and with 15 wt.% SiO_2 started to be densified at about 650 °C, and then shrank rapidly to the peak values at about 800 and 820 °C, respectively. The sintering temperatures of the three samples nearly matched, and the maximal shrinkage difference between silver conductor and the glass/ceramic sample was about 10% at around 680 °C, while it became very small around 800 °C. The shrinkage values of Ag, oxyfluoride glass and oxyfluoride glass with 15 wt.% SiO_2 filler sintered at 825 °C were 13.5, 17.0 and 16.0%, respectively, which implied a good co-firing match between Ag and the glass/ceramic samples.

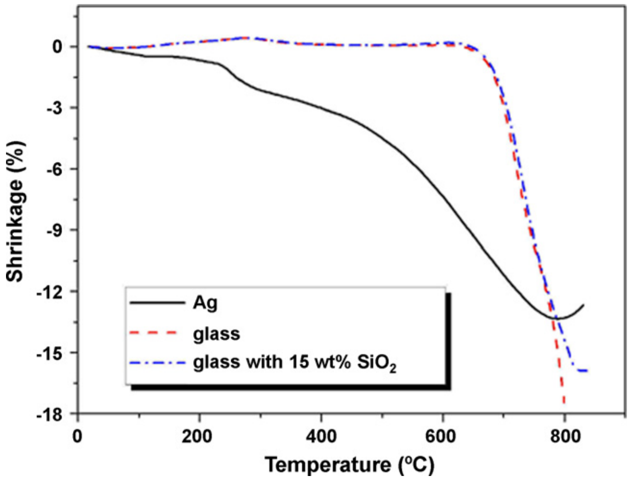

Fig. 7. Shrinkage behaviors of silver conductor, oxyfluoride glass and oxyfluoride glass with 15 wt.% SiO_2 filler measured at a heating rate of 10 °C/min.

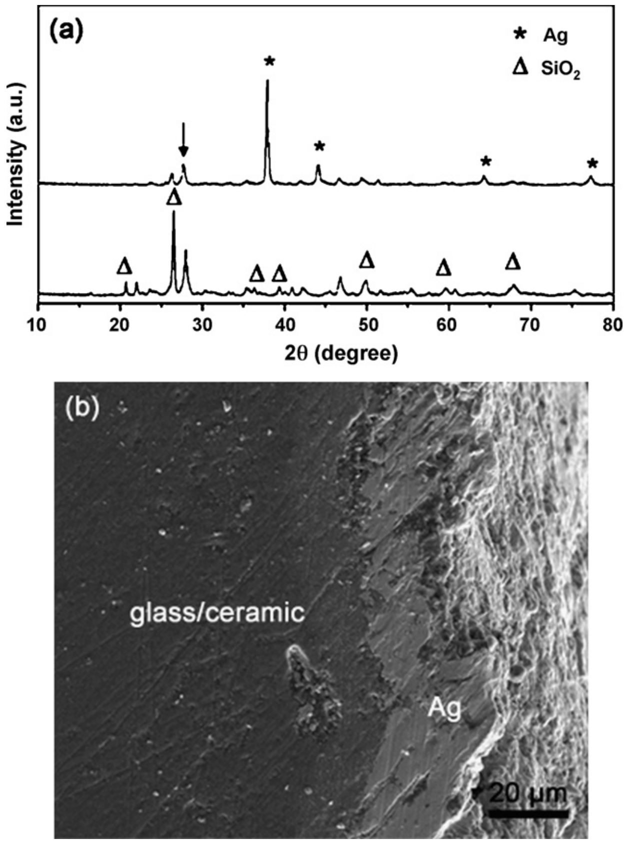

Fig. 8. Oxyfluoride glass with 15 wt.% SiO_2 filler co-fired with silver at 825 °C for 3 h. (a) XRD patterns of the samples with (top) and without (bottom) 15 wt.% silver powders. (b) SEM of oxyfluoride glass with 15 wt.% SiO_2 filler co-fired with silver paste in air.

Fig. 8(a) shows the XRD patterns of oxyfluoride glass with 15 wt.% SiO_2 filler co-fired with silver powders. There was no new phase appeared which meant that the glass/ceramic composite did not react with the Ag conductor. At same time, compared the XRD patterns of the samples with and without Ag powder, the addition of Ag promoted the crystallization of oxyfluoride glass, which resulted in a rise of the relative intensity of the diffraction peak corresponding to oxyfluoride glass as marked with arrows in Fig. 8(a). Fig. 8(b) shows the SEM result of oxyfluoride glass with 15 wt.% SiO_2 filler co-fired with silver paste. It indicated that the sample had good compatibility with silver paste, and the interface between the glass/ceramic composite and Ag electrode matched well and got good adherence.

4. Conclusions

LTCC glass/ceramic composites of CaF_2–AlF_3–SiO_2 oxyfluoride glass and SiO_2 ceramic filler were prepared. The sintering behavior, microstructures, phase composition, and dielectric properties were studied. The composites can be sintered at 825 °C. As the amount of SiO_2 filler increased from 0 to 20 wt.%, the shrinkage decreased from 17.0 to 14.5%, dielectric constant decreased from 5.9 to 5.4, while the strength increased from 150 to 190 MPa and TCE value increased from 6.0 to 10.1 ppm/°C. The sintered samples had low dielectric losses less than 0.002. In addition, this material system exhibited good co-fired compatibility with Ag electrode. This glass/ceramic composite system should be an ideal candidate of LTCC dielectric material for electronic substrates or passive integration.

Acknowledgments

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