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Microstructure and dielectric properties of Ca-Al-B-Si-O glass/Al$_2$O$_3$ composites with various alkali oxides contents

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Abstract: The effects of alkali oxides (Na$_2$O and K$_2$O) addition on both the sintering behavior and dielectric properties of Ca-Al-B-Si-O glass/Al$_2$O$_3$ composites were investigated by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimeter (DSC), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The results show that the increasing amount of alkali oxides in the glass causes the decrease of [SiO$_4$], which results in the decrease of the continuity of glass network, and leads to the decrease of the softening temperature T_f of the samples and the increasing trend of crystallization. And that deduces corresponding rise of densification, dielectric constant, dielectric loss of the low temperature co-fired ceramic (LTCC) materials and the decrease of its thermal conductivity. By contrast, the borosilicate glass/Al$_2$O$_3$ composites with 1.5% (mass fraction) alkali oxides sintered at 875 °C for 30 min exhibit better properties of a bulk density of 2.79 g/cm^3, a porosity of 0.48%, a λ value of 2.28 W/(m·K), a ε_r value of 7.82 and a tanδ value of 9.1×10^{-4} (measured at 10 MHz).

Key words: borosilicate glass; alkali oxides; Ca-Al-B-Si-O glass; Al$_2$O$_3$; microstructure; thermal properties; dielectric properties

1 Introduction

With the development of the co-fired multilayer circuits (CMC), low temperature co-fired ceramic (LTCC) played a decisive role as a base material in producing various modules and substrates [1−2]. The glass matrix easily enabled low temperature co-fired with low-resistance metals such as silver, glass crystallization was utilized to ensure post-firing stability, and the large variety of utilizable glasses and ceramic fillers in different ratios permitted the continuous tuning of LTCC properties in wide ranges [3−4]. SEO et al reported that the optimum case of 3 μm filler size with 35% Al$_2$O$_3$ (mass fraction) exhibited a desirable performance, a high density of 2.89 g/cm^3, a dielectric constant of 8.1, and a quality factor of 160, as a result of firing at 850 °C for 30 min [5]. The system of borosilicate glass/Al$_2$O$_3$ ceramic composites belonged to liquid-phase sintering

with partial reaction since 5% by volume of the alumina amount was left out in the alumina-riched glass [6]. ZHANG et al [7] reported that AlN/borosilicate glass composites were fabricated through hot-press sintering at low temperature (850−1 000 °C), with thermal conductivity as high as 10 W/(m·K). However, glass/Al$_2$O$_3$ composites had been paid much attention due to its meeting a lot of performance of requirements of physical, electrical and thermal properties [8]. Particularly, the addition of alkali oxides into the glass was known to be beneficial in producing homogeneous melts at a relatively low temperature [9]. The proper ratio of Na$_2$O and K$_2$O could decrease the dielectric loss of samples.

Though previous researches have referred to different particles size, different fillers and the influence of alumina dissolution on sintering and crystallization, no general conclusion could be made on the effect of glass composition with various alkali oxides (Na$_2$O and K$_2$O) content on Ca-Al-B-Si-O glass/Al$_2$O$_3$. The main

objective of this work was to investigate the effect of glass composition with various alkali oxides (Na_2O and K_2O) content on the sintering behavior, thermal properties, dielectric properties and microstructures of samples. The relationships between the sintering temperatures, microstructure evolution and microwave dielectric properties of Al_2O_3/borosilicate glass with various alkali oxides content were also presented.

2 Experimental

The composition chosen for the experimental samples is given in Table 1. The composition 17.5CaO-14Al_2O_3-8.5B_2O_3-58SiO_2 (mass fraction, %) was used as basic glass, and different amounts of alkali oxides (1.5%−9%, mass fraction) were introduced. Reagent-grade $CaCO_3$, Al_2O_3, H_3BO_3, SiO_2, Na_2CO_3, and K_2CO_3 were chosen as the raw materials. The constituents were mixed and blended uniformly, and then put into platinum crucible, which were then placed in the high-temperature furnace heated at 1 400−1 500 °C for about 1−20 h. After the last melts were quenched into distilled water, borosilicate glass crushed was acquired. Then the glass frit after drying and crushed was milled using planetary mill for 5−10 h with a mixture of agate balls. The resulting glass powders and Al_2O_3 powders were mixed and blended at the mass ratio of $m(Al_2O_3):m(glass)=$ 40:60 for about 20 h. In this work, the average median size of borosilicate glass was 1.86 μm, and for Al_2O_3 powders is 2.63 μm according to NSKC-1 Photo Size.

Table 1 Composition of different borosilicate glasses (mass fraction, %)

Sample	CaO	Al_2O_3	B_2O_3	SiO_2	K_2O	Na_2O
L1	17.5	14	8.5	60	0	0
L2	17.5	14	8.5	60	0.5	1
L3	17.5	14	8.5	60	1.5	3
L4	17.5	14	8.5	60	3	6

The solvent was composed of ethanol, xylene and isopropyl, castor oil as the dispersant, polyvinyl butyral (PVB) as the binder, dibutyl phthalate (DBP) as the plasticizer. In order to investigate the LTCC slurry for tape casting, solvents, dispersant, plasticizers and binder were first mixed for 12 h, and then the composite powders composed of glass powders and Al_2O_3 powders were added and mixed for another 12 h to obtain a homogeneous slurry, so that the mass ratio of solid to liquid was about 55/45. The tape casting was done with

caster (LYJ-240), at a slurry viscosity of 1 800 mPa·s. In general, ceramics slurries with viscosity of 1 000−2 000 mPa·s would be suitable for the tape casting progress [10]. The resulting mixture was then degassed and the thin film tape was dried and cut off into a given size then Ag electrode circuit was screen-printed on every sheet. The sheets were stacked and laminated, dried at 70 °C for 10 min at 11.070 MPa. Figure 1 shows the SEM micrographs of prepared green tape for sample L2+40% Al_2O_3.
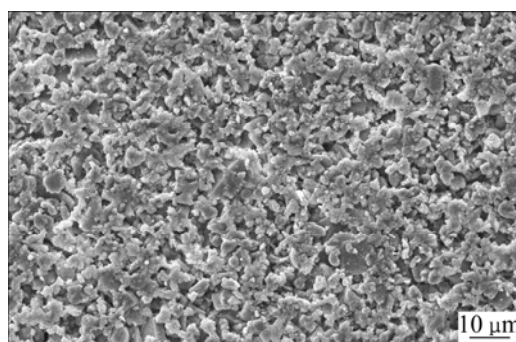

Fig. 1 SEM micrograph of green tape for sample L2+40%Al_2O_3

The organic matters in the laminated sheets were removed at a heating rate of 2 °C/min from room temperature to 450 °C. To remove the organic completely, the laminates were held at 450 °C for 5 h, and then followed by sintering at temperatures ranging from 800 °C to 925 °C for 30 min with a heating rate of 5 °C/min.

The granularity of the powders was measured by NSKC-1 Photo Size using distilled water as media. The slurry viscosity was tested by NDJ-11 rotational viscometer, while its rotational speed was 176 s^{-1}. The FTIR spectroscopy of the glass samples were recorded at room temperature ranging from 400−1 500 cm^{-1} according to NEXUS870 Infrared Spectrometer. Glass transition and crystallization temperature of samples were determined by differential scanning calorimeter (DSC) with a heating rate of 10 °C/min (NETZSCH-STA 449C, α-alumina as reference material). The phase composition of the samples was determined by X-ray diffraction with Cu/K_α radiation (XRD ARL X/TRA). The microstructures of fractograph of the samples were examined by scanning electron microscopy (SEM JSM-5900). Bulk density and porosity of the fired samples were measured by Archimedean immersion method using water as media with an accuracy of ±0.01 g/cm^3. The dielectric properties such as dielectric constant (ε_r), dielectric loss (tanδ) were measured by Agilent 4294A+16047E impedance analyzer at 10 MHz.

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2735

3 Results and discussion

3.1 Effect of alkali oxides on FTIR absorption spectra of Ca-Al-B-Si-O glasses

FTIR spectroscopy is used to obtain essential information concerning the arrangement of the structural units from the studied glasses. The experimental FTIR spectra of the Ca-Al-B-Si-O glasses with various alkali oxides content show five main bands (Fig. 2). The IR features located in the first region between 1 200 and 1 600 cm^{-1} are due to the asymmetric stretching relaxation of B—O bonds of the [BO$_3$] trigonal units. The second region between 800 and 1 200 cm^{-1} and its spectral features are due to the B—O bond stretching of [BO$_4$] tetrahedral units. In the third region ranging from 600 to 800 cm^{-1}, there is an important band located around 703 cm^{-1} assigned to the bending vibrations of various borate segments [11−15]. The band at about 460 cm^{-1} is due to Si—O—Si asymmetric bending vibration and the band in the region 800−850 cm^{-1} for α-SiO$_2$ is commonly assigned to the anti-symmetric stretching vibration of Si—O—Si in [SiO$_4$] tetrahedral [16].
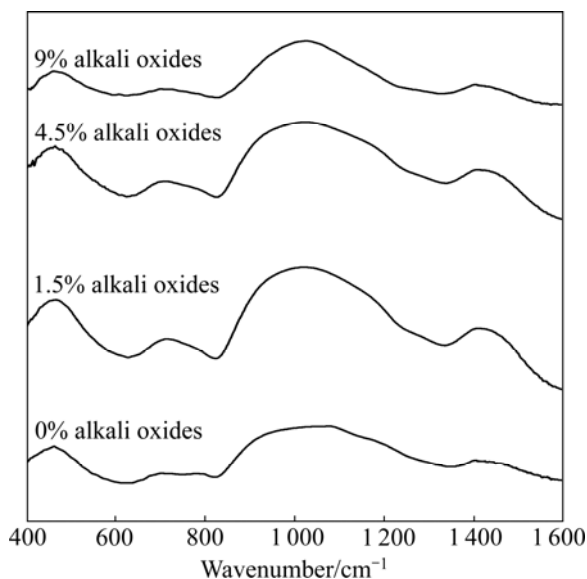

Fig. 2 FTIR spectroscopy of Ca-Al-B-Si-O glass samples with various alkali oxides contents (mass fraction)

With increasing alkali oxides content, the relative intensity of the band at about 796 cm^{-1} seems to decrease. Especially, the intensity of L3 and L4 sample in the same position nearly disappears. The results show that increasing amount of alkali oxides causes the decrease of [SiO$_4$]. The addition of Na$_2$O and K$_2$O as a network modifier, can offer free oxygen. With increasing alkali oxides content, the content of free oxygen increases. So,

the main reason is that when the free oxygen is full enough, [BO$_3$] has priority to associate itself with free oxygen to form [BO$_4$]. The rest free oxygen can associate with SiO$_2$, the free oxygen mainly serves to destroy Si—O—Si and to form non-bridging oxygen. This can result in a larger number of non-bridge oxygen in the network structure of the glass, which leads to the decrease in the continuity of glass network and consequently results in the increasing trend of crystallization.

3.2 Effect of alkali oxides on sintering behavior of borosilicate glass/Al$_2$O$_3$ composites

Figure 3 shows the DSC curves of glass/Al$_2$O$_3$ ceramic samples. It can be seen that an increase of alkali oxides leads to a decrease of softening temperature (T$_f$) of samples. While the alkali oxides content is 1.5%, the sample starts to show the peak of secondary re-crystallization. Exothermic peaks corresponding to crystallization (as indicated in Fig. 3) strongly depend on the alkali oxides content in the glass, which matches well with the tendency of the crystalline phases in the XRD patterns. This means that increasing alkali oxides content into the glass affects the samples stability and increases the trend to crystallization. The crystallization peaks are believed to be correlated to the crystallization of CaAl$_2$Si$_2$O$_8$ as identified in the results of the XRD patterns.
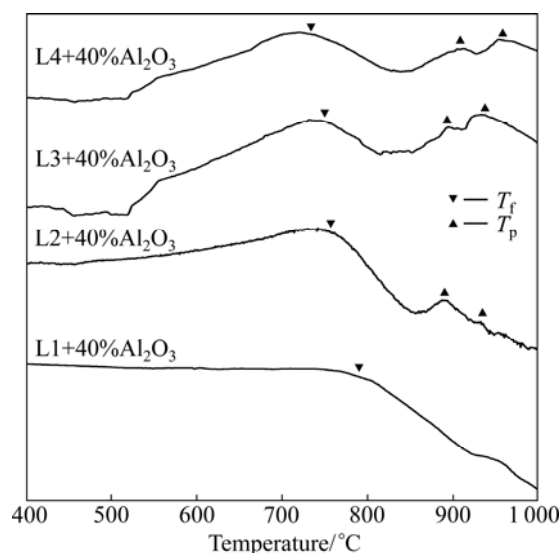

Fig. 3 DSC records of glass/Al$_2$O$_3$ ceramic composites with various alkali oxides contents

Figure 4 displays the shrinkage curves of glass/Al$_2$O$_3$ composites with various alkali oxides contents. For sintering process at temperatures ranging from 550 °C to 925 °C for 30 min with a setting heating rate of 5 °C/min, the linear shrinkage of samples can be measured using micro-calipers. It is obtained by measuring
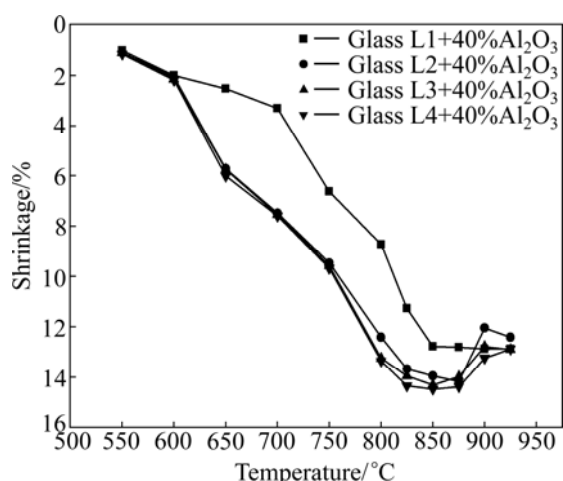
Fig. 4 Shrinkage curves of glass/Al_2O_3 composites with various alkali oxides contents

more than 10 points then averaging. The sintering process for glass/Al_2O_3 composites is controlled by viscosity flow. Al_2O_3 particles are coated by glass phase through viscous sintering. Glass/Al_2O_3 densification is almost completed before the crystallization starts, and that results in a significant shrinkage within a narrow temperature range. It is manifested that the densification proceeds simultaneously with crystallization (Fig. 3 and Fig. 4). However, the maximum linear shrinkage rates of samples with various alkali oxides contents in samples L1+40%Al_2O_3, L2+40%Al_2O_3, L3+40%Al_2O_3, L4+40%Al_2O_3 are evaluated to be 12.87% (900 °C/30 min), 14.17% (875 °C/30 min), 14.32% (850 °C/30 min), 14.48% (850 °C/30 min), respectively. Increasing the alkali oxides content in the glass results in the decrease of the glass softening temperature, and that brings about the best sintered temperature ahead of time. Above the best sintered temperature, the linear shrinkage rate of samples starts to decrease due to over-burning.

3.3 Effect of alkali oxides on properties of borosilicate glass/Al_2O_3 Composites

Table 2 gives the compositions and characteristics of LTCC with various alkali oxides contents. Porous body leaves over with burning out the organic matters. Glass phase softens into the viscosity fluid at the glass transition temperature. Then glass fluid phase fills in the pores, wets Al_2O_3 ceramic particles and tauts ceramic particles to slide and rearranges under the action of capillary attraction, and that results in densification.

The increase of alkali oxides content leads to the decrease of glass softening temperature, which can promote the arrival of sintered temperature of samples ahead of time, and that deduces the decrease of porosity of samples and the increase of the bulk density of samples. Increasing alkali oxides content, results in the increase in the ions migration rate, and that can provoke dielectric loss to rise dramatically. The increase of alkali oxides content results in the decrease in the continuity of glass network (Fig. 2), brings about the rising of ionic polarization, and that deduces the increase in dielectric constant of samples. Also, increasing the alkali oxides content leads to the decrease of the continuity of glass network (Fig. 2), deduces the rise of phonon scattering, and results in the decrease of its thermal conductivity. Especially, a bulk density of 2.79 g/cm^3, a porosity of 0.48%, a λ value of 2.28 W/(m·K), a ε_r value of 7.82 and a $\tan\delta$ value of $9.1×10^{-4}$ (measured at 10 MHz) are obtained for 1.5% alkali oxides (mass fraction) in the samples sintered at 875 °C for 30 min.

3.4 Effect of alkali oxides on microstructures of borosilicate glass/Al_2O_3 composites

Figure 5(a) shows the XRD patterns of the L1−L4 glass powders. It is found that all the samples do not

Table 2 Compositions and characteristics of LTCC with different compositions

Samples	Sintering parameter	Bulk density/(g·cm^{-3})	Porosity/ %	Dielectric constant (10 MHz)	Dielectric loss/ 10^{-3} (10MHz)	Thermal conductivity/ (W·m^{-1}·K^{-1})
Glass L1		2.37	0.31	4.01	1.64	0.86
Glass L2	750 °C / 30 min	2.33	0. 19	4.25	1.71	0.84
Glass L3		2.29	0. 12	4.40	1.99	0.78
Glass L4		2.24	0. 10	4.54	2.96	0.75
60% L1+40% Al_2O_3		2.76	1.04	7.76	1.49	2.38
60% L2+40% Al_2O_3	875 °C / 30 min	2.79	0.48	7.82	0.91	2.28
60% L3+40% Al_2O_3		2.85	0.42	8.21	1.63	2.07
60% L4+40% Al_2O_3		2.86	0.39	8.26	2.57	2.04

exhibit any crystalline phase, which demonstrates that all raw materials used for preparing glass have formed amorphous matters. Figure 5(b) represents the XRD patterns of Al_2O_3 powders and glass/Al_2O_3 composites sintered at 875 °C/30 min. It is found that all the samples exhibit the crystalline phase of $CaAl_2Si_2O_8$, and the peak intensity at about $2\theta=28°$ increases with the increase of alkali oxides content in the glass.

Figure 6 depicts the SEM photographs of glass/Al_2O_3 composites at 875 °C/30 min. The sample L2+40% Al_2O_3 shows a uniformly dense microstructure. The irregular Al_2O_3 particles are coated with glass phase, and the fractograph is smooth (Fig. 6(a)). With the increase of alkali oxides content in the glass, the trend of glass crystallization starts to rise, and that results in the increasingly rough fractograph (Fig. 6).

Figure 7 shows the SEM micrographs of green compact section of sample L2+40%Al_2O_3 heated at different temperatures. The section of the green compact is porous and the average particle size is less than 5 μm (Fig. 1). Uniformly, dense microstructures are observed for the samples sintered at 850 °C (Fig. 7(d)) and 900 °C (Fig. 7(e)). Glass phase starts to exhibit a crystalline of anorthite at 850 °C (Fig. 3). Crystal phase with order structure, compared with the disorder structure of glass phase has higher density, and that can further promote the densification of samples. But the sample sintered at 950 °C (Fig. 7(f)) has slightly more rough fractograph and more pores than that sintered at 900 °C. That might be due to over heat-treatment.
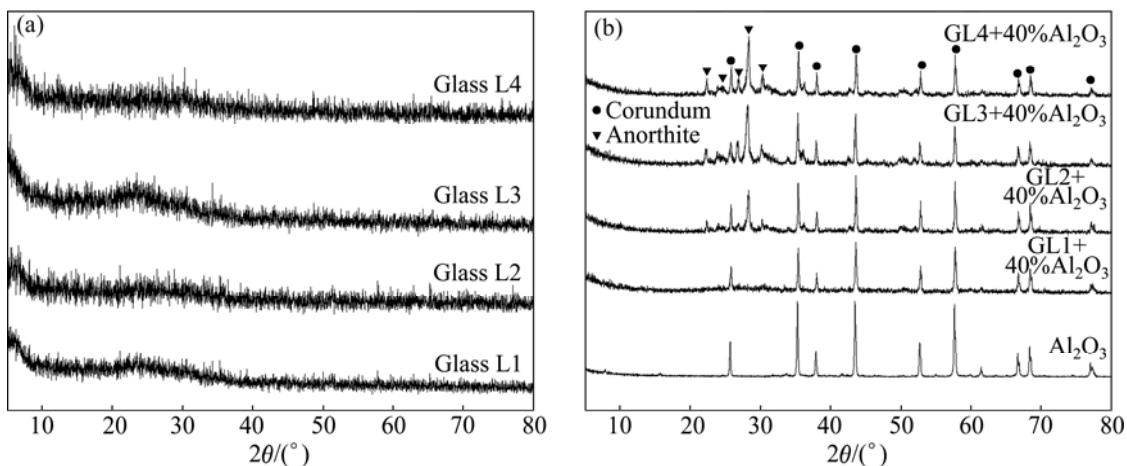

Fig. 5 XRD patterns of samples: (a) L1−L4 glass powders; (b) Al_2O_3 powders and glass/Al_2O_3 composites at 875 °C for 30 min

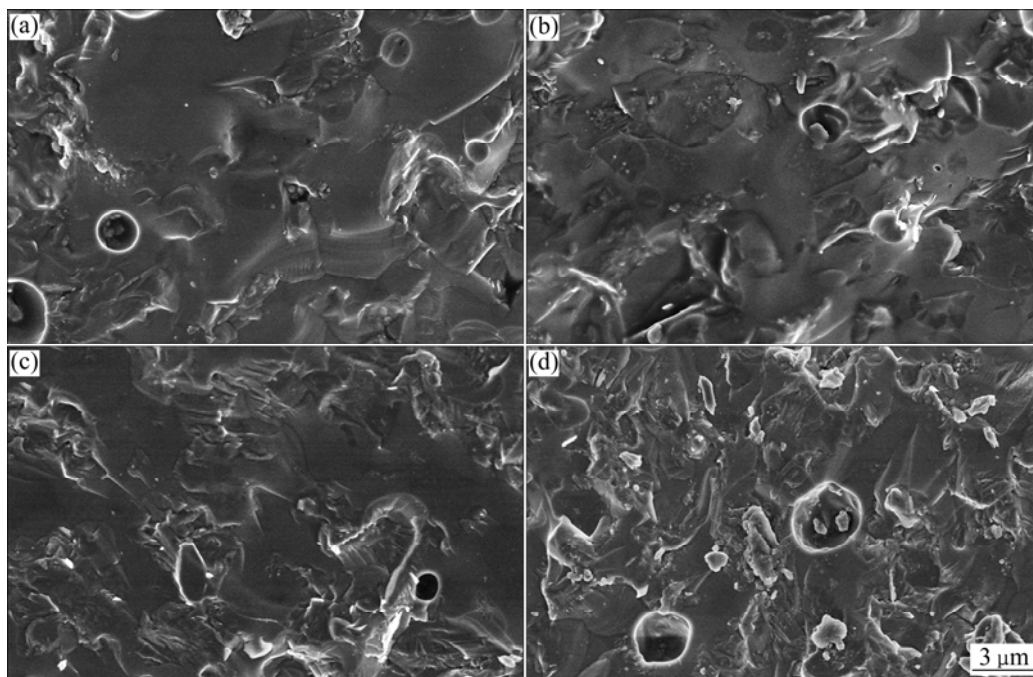**Fig. 6** SEM photographs of glass/Al_2O_3 composites at 875 °C/30 min: (a) L1+40% Al_2O_3; (b) L2+40% Al_2O_3; (c) L3+40% Al_2O_3; (d) L4+40% Al_2O_3
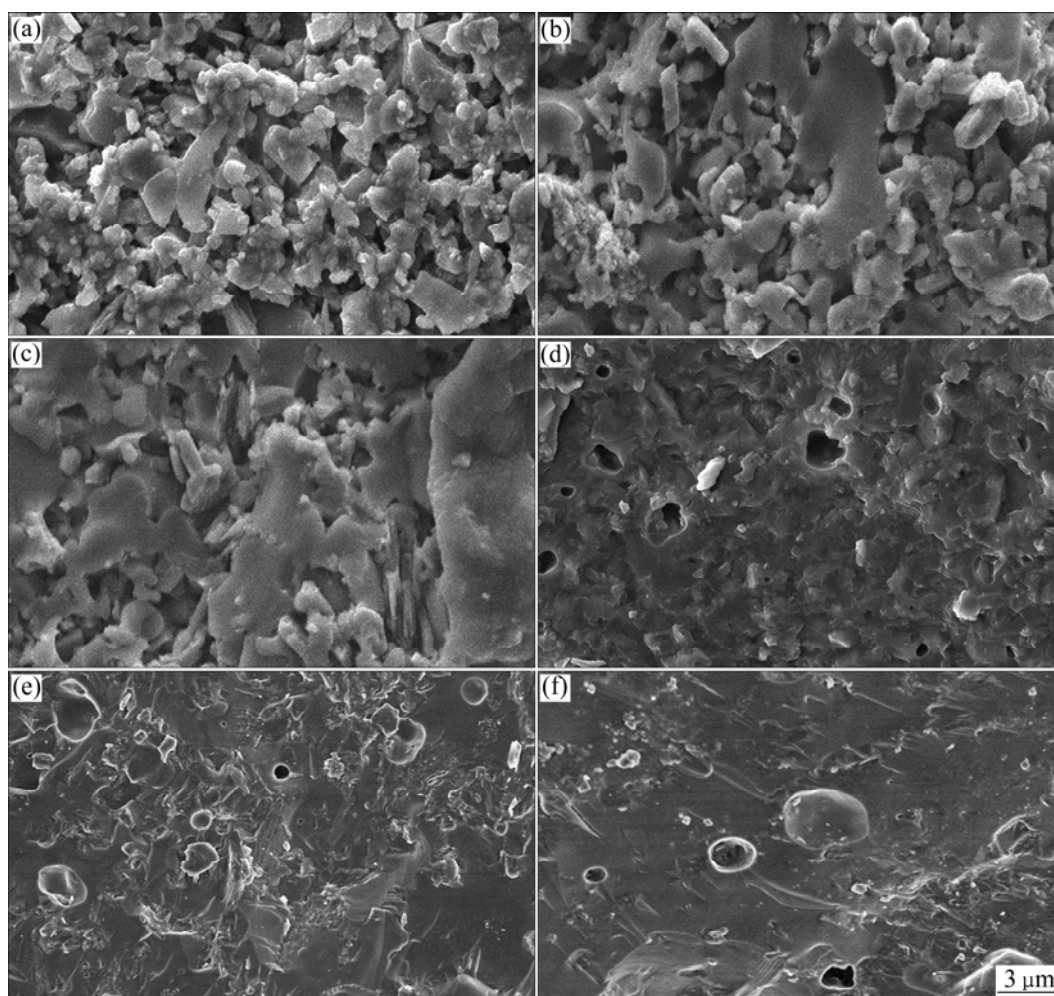
Fig. 7 SEM micrographs of green compact section of sample L2+40%Al$_2$O$_3$ heated at different temperatures: (a) 600 °C; (b) 700 °C; (c) 800 °C; (d) 850 °C; (e) 900 °C; (f) 950 °C

4 Conclusions

1) The increase of alkali oxides (Na$_2$O and K$_2$O) content in the glass results in the decrease of [SiO$_4$], and that leads to the decrease in the continuity of glass network.

2) Increasing alkali oxides content in the glass results in the decrease of the glass softening temperature, and that deduces the best sintered temperature ahead of time.

3) Densification and dielectric constants increase with the increase of alkali oxides content, but dielectric loss and the thermal conductivity worsen. The borosilicate glass/Al$_2$O$_3$ composites with 1.5% alkali oxides sintered at 875 °C for 30 min exhibit a better performance of a bulk density of 2.79 g/cm^{-3}, a porosity of 0.48%, a λ value of 2.28 W/(m·K), a ε_r value of 7.82 and a tanδ value of 9.1×10^{-4} (measured at 10 MHz).

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