

Influences of glass content on the microstructure and properties of BaO-CaO-Al₂O₃-SiO₂ glass/alumina composite for LTCC applications

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Abstract. In this paper, a new amorphous Ba-Ca-Al-Si glass was prepared and the composites with different glass/alumina ratios, which ranged from 40 wt. % glass to 60 wt. % glass, have been studied. According to XRD patterns, the main crystalline phases of the composites are Al₂O₃ and BaAl₂Si₂O₈, and BaAl₂Si₂O₈ is generated by the reaction between glass and alumina. With regard to dielectric and mechanical properties, both the dielectric constant and the bending strength of the samples show positive relationships with glass content, and then the values tend to decline when the glass content exceeds 55 wt. %, which can be explained by the results of sintering shrinkage curves, bulk densities and SEM images. The optimal composition of 55 wt. % glass-45 wt. % alumina was developed, exhibiting good dielectric properties ($\epsilon_r=5.882$, $\tan\delta=2.75 \times 10^{-3}$) and high bending strength ($\sigma=169$ MPa). Finally, the 55 wt. % glass/alumina composite was chosen for tape casting, showing a well chemical compatibility with silver.

1. Introduction

Electronic packing is a method of enclosing, protecting or providing physical structure to electronic components and finished electronic devices [1]. In order to get electronic components with smaller size, higher reliability and higher frequency, multilayer cofired ceramics is popular in recent years [2]. Low temperature cofired ceramics (LTCC) adjusts the ceramics with glass to be sintered less than 900 °C, which can be cofired with Au, Ag, Cu and other low melting metal [3]. Because the use of higher conductivity metal gives LTCC substrate materials better performance, LTCC shows good application prospects in computers, aerospace and military communication field.

Generally, LTCC materials can be divided into two categories: glass-ceramic and glass/ceramic [4]. Glass-ceramic is obtained by sintering amorphous glass to make it crystallize [5]. To meet the mechanical and electrical requirements, the crystallization always needs to be accurately manipulated to a certain degree, which makes the sintering process complicated [6]. Glass/ceramic systems are made up of low softening point glass and crystalline ceramics, in which the glass phases wet and connect the ceramic particles to lower the sintering temperature, meanwhile, the ceramic-fillers provide excellent mechanical and electrical properties to the system [7]. Therefore, required performance of the materials can be achieved by designing the composites and the synthetic process is



relatively simple and controllable. On account of these advantages, glass/ceramic materials have been widely used.

In the glass/ceramic systems, alumina is one of the most commonly used ceramics because of its outstanding mechanical and electrical properties. In terms of the glass, lead borosilicate glass with low-softening temperature, low-dielectric constant and low thermal conductivity has attracted much attention, and related commercial products have been developed by the companies of Dupont, Fujitsu and NEC. However, in these systems, the large amounts of residual glassy phases are detrimental to the high-frequency dielectric properties, and lead-based products are not environment-friendly. These disadvantages seriously limit the further application of glass/ceramic systems in the field of LTCC substrate materials. Therefore, based on alumina, a lot of other glass systems have been developed. *Induja et al.* reported [8] a new LTCC composition consisting of $\text{Bi}_2\text{O}_3\text{-ZnO-B}_2\text{O}_3\text{-SiO}_2$ and Al_2O_3 , which had $\epsilon_r=10.9$ and $\tan\delta=0.009$ (at 5 GHz) after sintered at 850 °C. In the research of *Zeng et al.*, the lead-free, low-softening point $\text{ZnO-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glass + Al_2O_3 system were prepared below 850 °C. This system exhibited good dielectric properties: small permittivity of 5.73 and low loss tangent of 8.94×10^{-4} at 1 MHz, and its bending strength was 129.9 MPa [9]. *Xia et al.* obtained a $\text{K}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ glass/alumina + silica composite with the dielectric constant of 6.1 and dielectric loss of 2×10^{-3} at 1MHz, and flexural strength of 168 MPa [10]. The experiment described here attempts to reduce the residual glassy phase in the glass/ceramic system through the avenue of making the glass phases react with the Al_2O_3 ceramics during the sintering process, and then the high-frequency dielectric properties will be improved. The composition of lead-free $\text{BaO-CaO-Al}_2\text{O}_3\text{-SiO}_2$ (BCAS) glass + Al_2O_3 ceramic is selected, the reaction between the two phases is investigated, the effects of the glass/ceramic ratio on the dielectric and mechanical properties are studied, and the microstructure and compatibility of co-firing with Ag electrode are also analyzed.

2. Experimental procedures

The starting materials were high purity powders (>99%, Sinopharm Chemical Reagent Co., Ltd.) of BaCO_3 , CaO , Al_2O_3 , SiO_2 , B_2O_3 , ZrO_2 and TiO_2 . The designed composition of Ba-Ca-Al-Si glass is shown in table 1. After the homogeneous mixture process, the powder was melted in a platinum crucible at 1500°C for 2 hours. Then the frits were obtained by pouring the liquid directly into deionized water for quenching. The glass powder was finally obtained after milling the frits in agate jars with absolute ethanol at the speed of 500 r/h for 12 hours.

Table 1. Composition of Ba-Ca-Al-Si glass (mol%).

BaO	CaO	SiO ₂	Al ₂ O ₃	B ₂ O ₃	ZrO ₂	TiO ₂
15	11	54	7	10	2	1

Different glass/ceramic samples were prepared by mixing 40 wt. %, 45 wt. %, 50 wt. %, 55 wt. % and 60 wt. % glass (D50=2 µm) with Al_2O_3 (D50=5 µm). For homogeneous mixing, the samples were ball milled with absolute ethanol at 300 r/h for 3 hours. After drying the slurries up, the powders were well mixed with 5 wt. % polyvinyl alcohol (PVA) separately and pressed into pellets and bars. Finally the samples were continuously sintered at 450 °C for 2 h, 750 °C for 1 h and 875 °C for 1 h with a heating rate of 2 °C /min.

The identification of crystalline phases was carried out by X-ray diffraction analysis (XRD, Bruker AXS D8 Advance device, Germany). The microstructures were studied by a scanning electron microscopy (SEM, Quanta FEG 250, US). The sintering shrinkage curves were determined in the temperature range from 10 °C to 1000 °C at 5 °C /min (Netzsch DIL 402C, Germany). The densities of the sintered samples were measured using Archimedes method. The dielectric constants ϵ_r and dielectric losses $\tan\delta$ of the composites were tested using a network analyser (N5230C, Agilent Co.).

3. Results and discussion

Figure 1(a) shows the XRD patterns of original BCAS glass, sintered glass and the composite of 50 wt. % glass-50 wt. % alumina. It indicates that the designed BCAS glass has amorphous nature with small amount of quartz, regardless of whether the glass is sintered, while the composition with alumina generates new crystalline phases. According to the number and intensity of the peaks, we can determine that the main crystalline phases of the composites are Al_2O_3 and $\text{BaAl}_2\text{Si}_2\text{O}_8$. Moreover, the disappearance of broad peak with the addition of Al_2O_3 into the BCAS glass suggests the reduction of the glass phases. Therefore, it can be concluded that the emerging $\text{BaAl}_2\text{Si}_2\text{O}_8$ phase is generated from the reaction between the BCAS glass and Al_2O_3 . Further analyses of the samples with different amounts of glass content are demonstrated in figure 1(b). It can be seen that the content of glass from 40 wt. % to 60 wt. % doesn't affect the main type of crystalline phases.

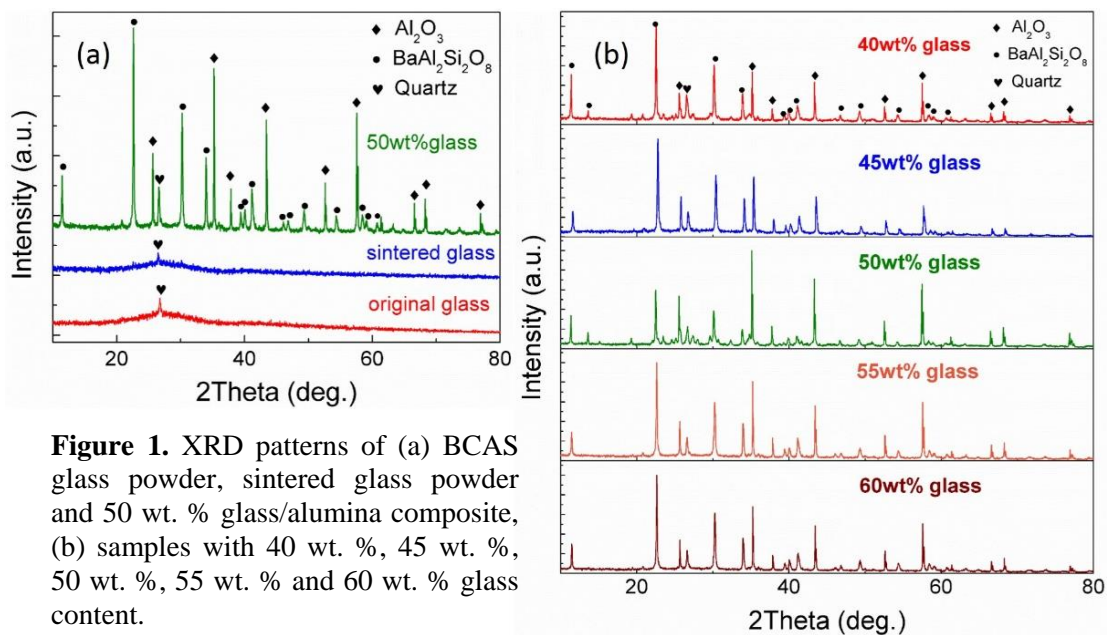


Figure 1. XRD patterns of (a) BCAS glass powder, sintered glass powder and 50 wt. % glass/alumina composite, (b) samples with 40 wt. %, 45 wt. %, 50 wt. %, 55 wt. % and 60 wt. % glass content.

We now turn towards the dielectric and mechanical properties of the series of samples. For the design of advanced electronic packaging in integrated circuits, signal transmission quality is one of the most important aspects, and dielectric constant can be a direct measure for it. For substrates, the dielectric constant and the delay time t_d has the following relationship:

$$t_d = l \times (\epsilon_r)^{1/2} / c \quad (1)$$

Where l is the wiring length, ϵ_r is the dielectric constant and c is the velocity of light. The equation indicates that reducing the dielectric constant makes the signal transmission speed up. Therefore, a low dielectric constant is an essential prerequisite for the commercial application of an LTCC substrate material. Figure 2(a) shows the dielectric data of the samples. It can be found that all the samples have a dielectric constant lower than 6 at ~ 10 GHz. Furthermore, the dielectric constant increases with the increase of glass content. When it comes to a critical value, the dielectric constant begins to decrease if the glass content continues to increase. The maximum dielectric constant 5.882 of the samples can be achieved when the composite contains 55 wt. % glass. Besides, the absorption of electric signal by the dielectric material is inevitable during its propagation process, thus, in order to get better performance, low dielectric loss is also an essential element. As shown in figure 2(a), all the samples display a dielectric loss less than 0.003 at ~ 10 GHz. Bending strength is another key performance indicator for the LTCC substrate materials, determining the service life of the related commercial products. The variation of the bending strength illustrating in figure 2(b) displays the similar tendency as the dielectric constant. The optimal composite is 55 wt. % glass/alumina and the bending strength achieves 169 MPa.

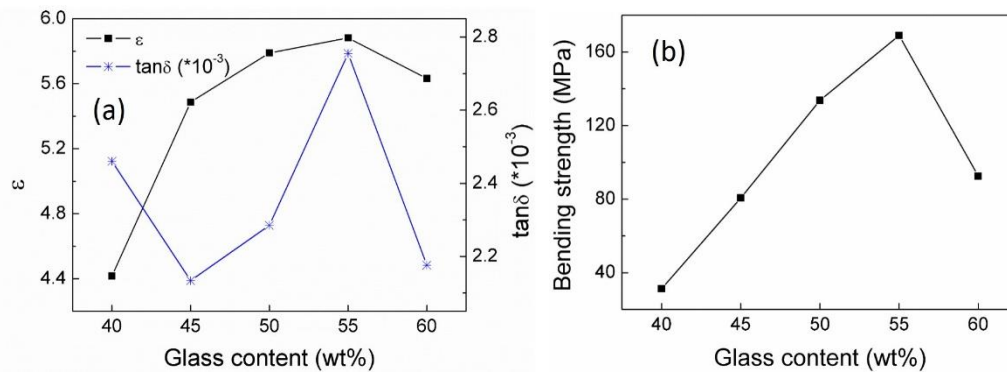


Figure 2. (a) Dielectric constants and dielectric losses measured at ~10 GHz and (b) bending strength of the BCAS /Al₂O₃ systems.

It is well known that the dielectric constant and bending strength are fairly interrelated to the densification of the samples. We now focus on the shrinkage process, density and microstructure of the samples to analyze the densification process and unravel the reason of the aforementioned phenomena. The sintering curves of different glass-content samples are shown in figure 3(a). It can be seen that the temperature range of shrinkage in all the samples is from ~700 °C to ~875 °C, which means the densification process starts at ~700 °C and ends at ~875 °C. Moreover, it is obviously detected that the shrinkage intensity is enlarged as the glass content elevates. And the shrinkage percentages are ~8 %, ~10 %, ~11.3 %, ~12.6 % and ~16.6 % for the samples with glass content of 40 %, 45 %, 50 %, 55 % and 60 %, respectively. This phenomenon can be explained by the role of glass phases in the composites. In glass/ceramic systems, glass phases wet and connect the ceramic particles, so that the more glass is contained, the larger the shrinkage percentage will be. In addition, we can find that the slope of the shrinkage curve gradually increases with the increase of the glass content, implying that the samples with larger amount of glass appear to have a high shrinkage speed. The differential curves in figure 3(a) also prove this view. It should be noted that too low shrinkage rate may be detrimental to the densification of the sample, and excessively high shrinkage speed may lead to the formation of more pores. The experiment results of the sample density and microstructure below provide evidences to this deducing.

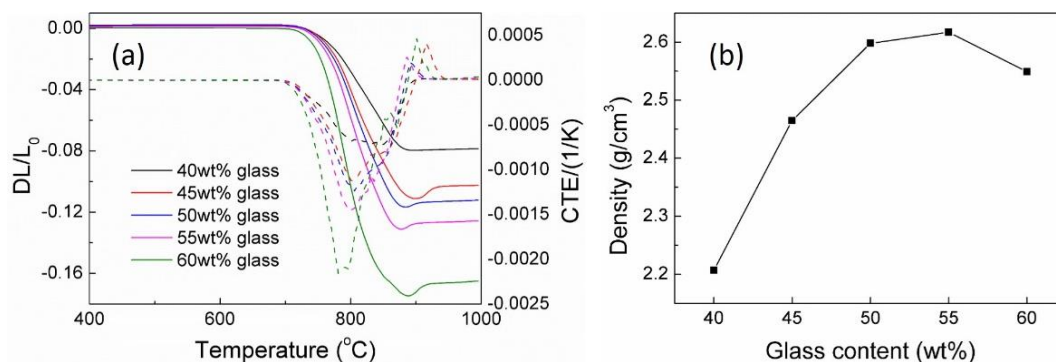


Figure 3. (a) sintering shrinkage curves, and (b) densities of the BCAS /Al₂O₃ systems.

The measured density data in figure 3(b) reveal that the maximum value of 2.617 is obtained when the glass content reaches 55 wt. %, and further increase of the glass content induces the decline of the density. This feature is nearly consistent with the variation of the dielectric constant and bending strength. As mentioned before, the increase of the glass content is accompanied by enlarged shrinkage intensity, which directly results in the enhancement of the density and then improves the dielectric and mechanical properties. As to the lower density of the sample with 60 % glass, the too fast shrinkage

speed bringing about more pores is the critical factor, which will be discussed later. More visualized and detailed proofs are given by the detection of the cross-section morphology.

Figure 4 shows the cross-section images of the samples with different content of glass measured by SEM.

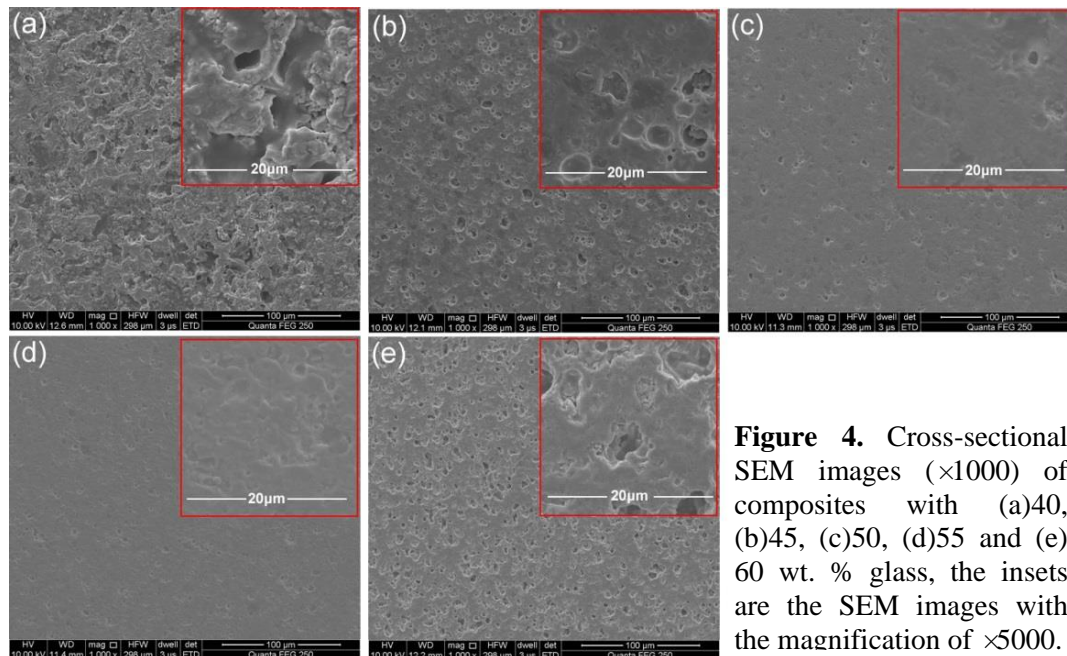


Figure 4. Cross-sectional SEM images ($\times 1000$) of composites with (a)40, (b)45, (c)50, (d)55 and (e) 60 wt. % glass, the insets are the SEM images with the magnification of $\times 5000$.

A typical glass/ceramic behavior, with large Al_2O_3 grains embedded within an amorphous glass matrix, is observed in all the samples. However, the details in the microstructure images are distinct. For the 40 wt. % glass sample, there are plenty of uncoated Al_2O_3 phases and large pores displayed in figure 4(a), resulting in lower density, dielectric constant and bending strength as mentioned before. As the increase of glass content, the size of the pores is scaled down and the structure becomes more homogenous, and the most dense morphology can be obtained when the glass content is 55 wt. %, seen from figure 4(b) to (d). Whereas, figure 4(e) indicates that excess glass has negative effect, leading to the emergence of numerous large pores. This is ascribed to the excessively fast shrinkage speed analyzed in figure 3(a). So it is easy to understand that the 55 wt. % glass sample possesses the optimal dielectric and mechanical properties.

In order to confirm whether the BCAS glass / Al_2O_3 ceramic is suitable for LTCC substrate application, the properties of the samples laminated with green tapes and the chemical compatibility of this composition and silver are evaluated. The 55 wt. % glass/alumina composite was chosen for tape casting. From figure 5(a), we can see that the laminated sample after the same sinter process as aforementioned samples demonstrates a denser and more homogeneous microstructure, but inevitable pores still exist. Additionally, the density is enhanced to 2.74, the dielectric constant increases to 6.53, and the bending strength is improved to 210 Mpa. Figure 5(b) shows the backscattered-electron diffraction (BSED) image of the samples with the printing of silver paste on to the layered green tapes. After co-fired at 875 °C, a silver layer with the thickness of $\sim 10 \mu\text{m}$ is formed, accompanied with the formation of a $\sim 50 \mu\text{m}$ buffer layer. The EDS results in figure 5(c) and (d) reveal that the bright white layer is pure silver, and the dark gray part in the buffer layer is abundant with the element of Al, Si and Ba. These results imply that the reaction between the Ag and BCAS glass / Al_2O_3 ceramic is not taken place, showing a well chemical compatibility. The segregation of the phases with the Al, Si and Ba elements and the pores at the buffer layer may be due to the mismatching between the silver paste and green tape, and our later work will devote to the development of the better matched silver paste.

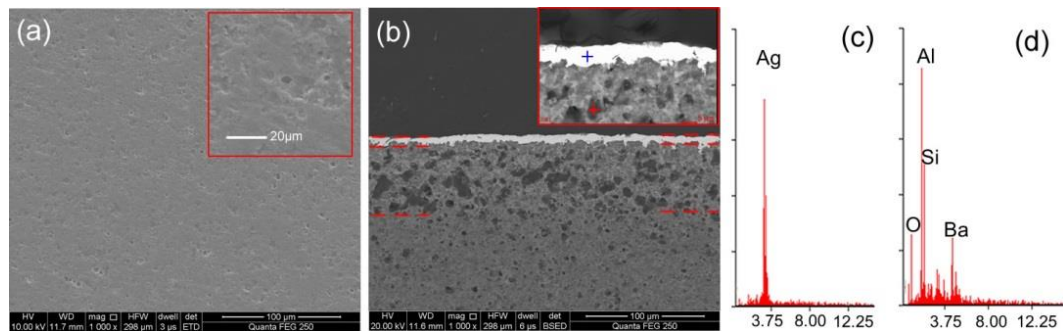


Figure 5. Cross-sectional SEM images ($\times 1000$) of (a) the laminated tape and (b) the tape with silver paste, (c) and (d) SEM-EDS results of the tape with silver paste, the blue and red crosses in the inset of (b) correspond to (c) and (d), respectively. Both the inset in (a) and (b) are the SEM images with the magnification of $\times 5000$.

4. Conclusions

The amorphous Ba-Ca-Al-Si glass was prepared and synthesized with alumina. The XRD patterns show that the reaction between the BCAS glass and alumina can generate $\text{BaAl}_2\text{Si}_2\text{O}_8$ crystalline phases. Moreover, the content of glass from 40 % to 60 % doesn't affect the main type of crystalline phases. All the samples have dielectric losses less than 0.003, which can meet the commercial requirement. As the glass content increases from 40 wt. % to 55 wt. %, both the dielectric constant and the bending strength show an upward tendency. When the glass content exceeds 55 wt. %, the dielectric constant and the bending strength begin to decline. The results of sintering shrinkage curves, density and SEM images can well explain this phenomenon. With the increase of glass content, the shrinkage intensity and the shrinkage speed are elevated. Low shrinkage rate is detrimental to the densification process, while high shrinkage speed may lead to the formation of more pores. The optimal composite, which consists of 55 wt. % glass and 45 wt. % alumina, can achieve the dielectric of 5.882, the bending strength of 169 MPa. The optimal composition was chosen for tape casting. The tape has better properties and more homogeneous microstructures, and shows chemical compatibility with silver. Finally, further research needs to be carried out to develop suitable silver paste matching better with the tape.

Reference

- [1] Wessely H, Fritz O, Horn M, Klimke P, Koschnick W and Schmidt K H 1991 Electronic packaging in the 1990s: the perspective from europe *IEEE Transactions on Components Hybrids & Manufacturing Technology* **14** 272-84
- [2] Sebastian M T and Jantunen H 2008 Low loss dielectric materials for LTCC applications: a review *International Materials Reviews* **53** 57-90
- [3] Berglund M, Persson A and Thornell G 2015 Evaluation of Dielectric Properties of HTCC Alumina for Realization of Plasma Sources *Journal of Electronic Materials* **44** 3654-60
- [4] Shimada Y, Utsumi K, Suzuki M, Takamizawa H, Nitta M and Watari T 2003 Low firing temperature multilayer glass-ceramic substrate *IEEE Transactions on Components Hybrids & Manufacturing Technology* **6** 382-8
- [5] Shimada Y, Yamashita Y and Takamizawa H 2002 Low dielectric constant multilayer glass-ceramic substrate with Ag-Pd wiring for VLSI package *Micronanoelectronic Technology* **11** 163-70
- [6] Li B, Qing Z, Li Y, Li H and Zhang S 2016 Crystallization, microstructures and properties of low temperature co-fired $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramic *Journal of Electroceramics* 1-6
- [7] Induja I J, Surendran K P, Varma M R and Sebastian M T 2017 Low κ , low loss alumina-glass composite with low CTE for LTCC microelectronic applications *Ceramics International* **43** 736-40

- [8] Induja I J, Abhilash P, Arun S, Surendran K P and Sebastian M T 2015 LTCC tapes based on Al_2O_3 -BBSZ glass with improved thermal conductivity *Ceramics International* **41** 13572-81
- [9] Zeng D, Xu J, Chen Y, Chen W, Yu Y, Wang H and Zeng R 2015 Novel lead-free glass/ceramics system with low permittivity, low loss for ltcc application *International Journal of Applied Ceramic Technology* **12** E112-6
- [10] Xia Q, Zhong C W and Luo J 2014 Low temperature sintering and characteristics of K_2O - B_2O_3 - SiO_2 - Al_2O_3 , glass /ceramic composites for LTCC applications *Journal of Materials Science Materials in Electronics* **25** 4187-92