Influence of B$_2$O$_3$ content on sintering behaviour and dielectric properties of La$_2$O$_3$–B$_2$O$_3$–CaO/Al$_2$O$_3$ glass-ceramic composites for LTCC applications

F L Wang$^1$, Y W Zhang$^2$, X Y Chen$^1$, H J Mao$^1$ and W J Zhang$^{1,3}$

$^1$ Department of Materials Science and Engineering, National University of Defense Technology, Changsha 410073, China
$^2$ Shandong Institute of Aerospace Electronic Technology, Yantai 264000, China
$^3$ E-mail: zhwjun@nudt.edu.cn

Abstract. La$_2$O$_3$–B$_2$O$_3$–CaO glasses with different B$_2$O$_3$ content were synthesized by melting method to produce glass/ceramic composites in this work. XRD and DSC results revealed that the diminution of B$_2$O$_3$ content was beneficial to increase the crystallization tendency of glass and improve the quality of crystalline phase, while decreasing the effect of glass during sintering process as sintering aids. The choice of glass/ceramic mass ratio was also influenced by the B$_2$O$_3$ content of glass. Dense samples sintered at 875 ºC showed good dielectric properties which meet the requirement of LTCC applications: moderate dielectric constant (7.8–9.4) and low dielectric loss (2.0×10$^{-3}$).

1. Introduction
Low temperature co-fired ceramic (LTCC) technology has been widely used in microelectronic packaging to meet the requirements for miniaturization and high packaging density of highly integrated passive components [1-5]. Generally, the LTCC materials used for high frequency application should have a low sintering temperature (≤900 ºC), low dielectric constant and low dielectric loss [6-8].

Materials based on glass/ceramic systems are popular in LTCC applications for their outstanding designability characteristic. Al$_2$O$_3$ is one of the most common choices of ceramic filler in glass/ceramic systems, for it shows good dielectric properties [9, 10]. As for glass acting as sintering aids, it should have low softening temperature to ensure the sintering temperature of composites meet the requirement of LTCC applications. Several kinds of La$_2$O$_3$–B$_2$O$_3$-based (LB) glass have been studied, for they show good effects in reducing the sintering temperature of glass/ceramic composites. Another attractive character of LB glass is the appearance of some crystalline phases with excellent dielectric properties after the sintering of LB glass based ceramics. Chen et al. [11] found that the sintering temperature of Ca$_0.6$La$_0.268$TiO$_3$ (CLT) dielectric ceramic could be greatly reduced from 1350 ºC to 900 ºC when the La$_2$O$_3$–B$_2$O$_3$–ZnO (LBZ) glass was added. Xiang et al. [12] showed that the addition of La$_2$O$_3$ in CaO–B$_2$O$_3$–SiO$_2$ (CBS) glass could improve the glass-forming ability of the glass, as well as decrease its transition temperature. Tang et al. [13] reported that the sintering temperature of Ba$_{0.75}$Sr$_{0.25}$(Nd$_{0.75}$Bi$_{0.25}$)$_2$Ti$_3$O$_{12}$ (BSNBTE) ceramics doped with glass sintering aids of La$_2$O$_3$–B$_2$O$_3$–ZnO–CaO (LBZC) was decreased to 900 ºC. Jo et al. [14] developed LB glass modified with CaO, MgO and ZnO, and the composites of glass and Al$_2$O$_3$ sintered at 850 ºC showed good dielectric...
performance, i.e., dielectric constant around 8.1–8.3 and \(Q > 1,000\) (at 17.1 GHz). It was also noticed that crystalline phases such as \(\text{LaBO}_3\), \(\text{La(BO}_3)_2\) and \(\text{LaAl}_2\text{O}_3(\text{B}_2\text{O}_3)_0.54\) were detected in the samples after sintering. Jung’s group [15] and Seo’s group [16] reported similar results. Chen et al. [17] researched the dielectric properties of \(\text{LaBO}_3\), which was one of the main crystalline phases precipitated from LB glass and exhibited excellent dielectric properties with a dielectric constant around 11.8 and a quality factor value around 76,869 GHz (at 15 GHz).

In this work, \(\text{La}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot\text{CaO}\) (LBC) glass with different content of \(\text{B}_2\text{O}_3\) was synthesized. These glasses were used as sintering aids in a LBC glass/\(\text{Al}_2\text{O}_3\) system. The sintering behavior and dielectric properties of the composites, and their correlation to the \(\text{B}_2\text{O}_3\) content in LBC glass were discussed.

2. Experimental Procedure
LBC glasses were prepared by the melting method, and the chemical compositions were shown in table 1. The molar ratios of \(\text{La}_2\text{O}_3\), \(\text{B}_2\text{O}_3\) and \(\text{CaO}\) were set to be 1:2:1, 2:5:2 and 1:3:1 (noted as LBC21, LBC252 and LBC131, respectively). All raw materials were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The batches were mixed and melted in a platinum crucible at 1500 °C for 2h at a heating rate of 10 °C/min. The melt was rapidly quenched into deionized water, ball-milled with agate balls for 12h, and later dried at 120 °C.

| Sample | \(\text{La}_2\text{O}_3\) (wt%) | \(\text{B}_2\text{O}_3\) (wt%) | \(\text{CaO}\) (wt%) |
|--------|-----------------|-----------------|-----------------|
| LBC121 | 62.45           | 26.82           | 10.73           |
| LBC252 | 58.53           | 31.42           | 10.05           |
| LBC131 | 55.07           | 35.47           | 9.46            |

The next step was to prepare glass/ceramic composites. High pure \(\text{Al}_2\text{O}_3\) powder in the range from 30 to 50 wt% was mixed with three types of LBC glass by ball-milling in deionized water for 4 hours and dried at 120 °C. The powders were then admixed with 5 wt% polyvinyl alcohol (PVA) binder solution and pressed into disks (20 mm in diameter and 2 mm in height) at 20MPa. The samples were heat treated at 450 °C for 1h at a heating rate of 3 °C/min, then sintered at 875 °C for 2h. Disk samples only containing three types of glass were prepared using the same method.

The bulk densities of sintered samples were examined by the Archimedes method. The shrinkage values of samples were calculated by comparing the diameters of samples before and after sintering. Differential scanning calorimeter (DSC) analyses of glass samples were performed by a Netzsch STA 449F3 analyzer up to 1100 °C under 10 °C/min heating rate. Glass transition temperatures (\(T_g\)) and softening temperatures (\(T_s\)) of glass were obtained by thermo-mechanical analysis (TMA) via a dilatometer (Netzsch DIL 402C, Germany) with an alumina sample holder. The crystalline phases of samples were recorded using an X-ray diffractometer (XRD, Bruker AXS D8 Advance device, Germany), which employed Cu-Ka radiation (\(\lambda = 1.5418 \, \text{Å}\)). The microstructures of samples were observed by a field emission scanning electron microscopy (FE-SEM, Hitachi SU8010, Japan). The dielectric constant and dielectric loss of samples at 1 MHz were measured by a precision impedance analyzer (Wayne-Kerr 6500B, England).

3. Results and Discussion
3.1. The crystalline, microstructure and sintering behavior of glasses and composites
Figure 1a shows the XRD patterns of LBC glass samples before and after heat treated at 875 °C. No obvious crystalline phase can be identified from the original LBC131 glass sample. However, the crystalline phase of \(\text{LaBO}_3\) (JCPDS card no. 12-0762) is detected in the original LBC252 and LBC121 samples, while the original LBC121 sample also contains another kind of \(\text{LaBO}_3\) phase (\(\text{LaBO}_3^\prime\)), also reported as low temperature forming \(\text{LaBO}_4\) [18], JCPDS card no. 72-0074). In the samples been heat treated, the major crystalline phase is \(\text{LaBO}_3\), and the secondary phase is \(\text{CaB}_2\text{O}_4\) (JCPDS card no. 32-1234567890).
0155). With the decrease of \(B_2O_3\), the less crystalline phase of \(CaB_2O_4\) can be observed. The results indicate that the reducing of \(B_2O_3\) will improve the amount and purity of \(LaBO_3\) phase, as well as increasing the crystallization tendency of LBC glass. The spontaneous crystallization of \(LaBO_3\) and \(LaBO_3^*\) phases before heat treatment will increase the viscosity of melted glass, which could have negative influence on the effect of glass as sintering aids.

The XRD patterns of composite samples containing 60 wt% glass and 40 wt% \(Al_2O_3\) sintered at 875 °C are shown in figure 1b. The crystalline phases of \(LaBO_3\) and \(Al_2O_3\) (JCPDS card no. 10-0173) are identified as major ones in all three samples. And new crystalline phases of \(CaB_2O_7\) (JCPDS card no. 31-0253) and \(La_2CaB_{10}O_{19}\) (JCPDS card no. 54-0033) are found in LBC131 + \(Al_2O_3\) sample. These two phases can be regarded as B-rich phases and their developments might be involved with the high content of \(B_2O_3\) in LBC131 glass.

![XRD patterns of composite samples](image)

**Figure 1.** XRD patterns of (a) LBC glass samples before and after heat treatment, (b) 60 wt% LBC glass + 40 wt% \(Al_2O_3\) composites sintering at 875 °C.
The DSC curves of three types of LBC glass are shown in figure 2. And table 2 summarizes the characteristic temperatures of glass samples based on the DSC and TMA results. The softening points of all kinds of LBC glass are around 650 °C, which just meet the requirement of LTCC applications. The change of peak positions in DSC curves suggests that the sintering behavior of LBC glass is influenced by the content of B₂O₃. For glass containing more B₂O₃, the T_g and T_s tend to be a bit higher. The major crystalline peak temperatures (T_c1) are around 700-740 °C, which correspond to the report of Jo et al. [14]. These peaks are presumably associated with the crystallization of the LaBO₃ phase. The secondary crystalline peak temperatures (T_c2) are around 800 °C, which are likely corresponding to the crystallization of CaB₂O₄. Moreover, an exothermic peak at 698 °C has shown in the DSC curve of LBC121 glass. According to the researches of Takada’s group [19] and Jung’s group [15], this peak could be attributed to the crystallization of a transient phase, such as LaBO₃* or La(BO₃)ₓ, which would transform into the LaBO₃ phase at higher temperature.

Table 2. Characteristic temperatures of LBC glass samples.

| Glass   | T_g (°C) | T_s (°C) | T_C1 (°C) | T_C2 (°C) |
|---------|----------|----------|-----------|-----------|
| LBC121  | 636      | 642      | 737       | 809       |
| LBC252  | 648      | 652      | 709       | 794       |
| LBC131  | 656      | 669      | 740       | 803       |

Figure 2. DSC curves of the LBC glass.

Figure 3 shows the SEM images of four selected samples, which performs the microstructures of their surface. As shown in figure 3, for samples having a LBC glass/Al₂O₃ ratio of 1:1, with the increase of B₂O₃ content in LBC glass, less pores can be observed. Figure 3d has clearly exhibited the porous structures of 70 wt%/30 wt% Al₂O₃ sample.
Figure 3. SEM images of samples containing (a) 50 wt% LBC121/50 wt% Al₂O₃, (b) 50 wt% LBC252/50 wt% Al₂O₃, (c) 50 wt% LBC131/50 wt% Al₂O₃ and (d) 70 wt% LBC131/30 wt% Al₂O₃.

Figure 4a and figure 4b present the shrinkage values and bulk densities of all samples containing three different kinds of LBC glass with 30 wt%, 40 wt% and 50 wt% Al₂O₃. Especially, the properties of samples containing 50 wt% Al₂O₃ are shown in Table 3. Most samples show appropriate shrinkage values of about 12% with bulk densities around 3.2-3.3 g/cm³. The shrinkage values of composite samples containing 50 wt% Al₂O₃ suggest that LBC glass with higher content of B₂O₃ shows more positive effect on the sintering process of sample at this glass/ceramic ratio, which could also be proved by the SEM results shown in figure 3. However, the composites of 70 wt%/30 wt% Al₂O₃, 70 wt% LBC252/30 wt% Al₂O₃ and 60 wt% LBC131/40 wt% Al₂O₃ show unusually low shrinkage values and bulk densities. Similar phenomenon has been reported by Thieme et al. [20]. Their glass-ceramic samples in the system BaO-SrO-ZnO-SiO₂ show obvious foaming at temperature above 900 °C, resulting in reducing shrinkage values and bulk densities. When the sintering temperature is higher than the crystalline temperature of low-melting-point glass in a high glass/ceramic ratio system, the release of gases inside the samples during the densification process could be blocked because of the viscosity rising of glass due to crystallization. Subsequently, these gases will lead to the formation of porous structures, just as figure 3d shows. Foaming is not observed in samples containing LBC121 glass, for the spontaneous crystallization in LBC121 glass could be regarded as a reducing in glass/ceramic ratio. However, this might have bad effect on the densification processes of composite samples, which could be proved by the decrease of shrinkage value and bulk density when the B₂O₃ content get lower in table 3.

Table 3. Characteristics of glass/ceramic compositions with 50 wt% Al₂O₃.

| Glass  | Shrinkage (%) | Density (g/cm³) | Dielectric constant | Dielectric loss (×10⁻³) |
|--------|--------------|----------------|---------------------|------------------------|
| LBC121 | 12.1         | 3.221          | 9.1                 | 7.98                   |
| LBC252 | 12.3         | 3.247          | 7.9                 | 1.92                   |
| LBC131 | 12.9         | 3.304          | 7.7                 | 1.69                   |
3.2. The dielectric properties of sintered glass/ceramic composites
The dielectric properties of samples containing 50 wt% Al$_2$O$_3$ measured at 1 MHz is shown in Table 3. With the decrease of B$_2$O$_3$ content in LBC glass, the dielectric constant of samples increases gradually, which is associated with the increase of crystalline phase having high dielectric constant, e.g. LaBO$_3$ phase shown in XRD results. And the dielectric loss shows an opposite variation tendency. This could be ascribed to the formation of more pores suggested by the reducing of shrinkage values and bulk densities.

Figure 4c and figure 4d show the dielectric properties of more samples with different Al$_2$O$_3$ content as well as different types of LBC glass. Samples containing LBC glass with high B$_2$O$_3$ content have lower dielectric constant. The varying tendency of dielectric loss of samples match well with that of shrinkage value and bulk density shown in figure 4a and figure 4b. Four samples with the contents of 70 wt% LBC121/30 wt% Al$_2$O$_3$, 60 wt% LBC252/40 wt% Al$_2$O$_3$, 50 wt% LBC252/50 wt% Al$_2$O$_3$, and 50 wt% LBC131/50 wt% Al$_2$O$_3$ show excellent combination dielectric properties, i.e., dielectric constant about 7.8-9.4 and dielectric loss about 2.0×10^{-3}.

Based on the above results, we believe that the LBC glass/Al$_2$O$_3$ composite has the potential to be chosen as the substrate material in LTCC applications. Our further study will concentrate on the thermal properties and mechanical properties of the composite, e.g. coefficient of thermal expansion (CTE), thermal conductivity and bending strength, etc. In addition, we will also investigate the compatibilities of the composite with the low-melting and highly conductive silver and gold electrodes.

4. Conclusions
La$_2$O$_3$-B$_2$O$_3$-CaO glass with different B$_2$O$_3$ content and glass/ceramic composites based on LBC glass/Al$_2$O$_3$ had been fabricated. The decrease of B$_2$O$_3$ content would increase the crystallization tendency of LBC glass as well as improve the quality of crystalline LaBO$_3$ phase. But it would damage the effect of glass during sintering process of glass/ceramic composite. LBC glass with high
B₂O₃ content should be chosen for a low glass/ceramic ratio system, while low B₂O₃ content glass suited high ratio system better. Composites following this rule showed superior dielectric properties: moderate dielectric constant about 7.8-9.4 and low dielectric loss about 2.0×10⁻³.

References
[1] Mohanram A, Lee S H, Messing G L and Green D J 2006 J. Am. Ceram. Soc. 89 1923-29
[2] Valant M, Suvorov D, Pullar R C, Sarma K and Alford N M 2006 J. Eur. Ceram. Soc. 26 2777-83
[3] Sayyadi-Shahraki A, Taheri-Nassaj E, Hassanzadeh-Tabrizi S A and Barzegar-Bafrooei H 2014 J. Mater. Sci-Mater. El. 25 355-60
[4] Chen X, Zhang W, Bai S and Du Y 2013 Ceram. Int. 39 6355-61
[5] Wilhelm S P, Kay R W, Mohammed M I, Lacrotte Y and Desmulliez M P 2013 Microsyst. Technol. 19 801-7
[6] Tummalala R R 1991 J. Am. Ceram. Soc. 74 895-908
[7] Sebastian M T and Jantunen H 2008 Int. Mater. Rev. 53 57-90
[8] Chang C R and Jean J H 1999 J. Am. Ceram. Soc. 82 1725-32
[9] Lee Y H Aand Wei W C J 2005 Key Eng. Mater. 280 935-40
[10] Müller R, Reinsch S, Eberstein M, Deubener J, Thiel A and Schiller W A 2008 Adv. Mater. Res. 39 373-8
[11] Chen Y, Li E, Zou M, He H and Zhang S 2017 J. Mater. Sci-Mater. El. 28 13132-8
[12] Xiang Y, Han J, Lai Y, Li S, Wu S, Xu Y, Zeng Y, Zhou L and Huang Z 2017 J. Mater. Sci-Mater. El. 28 9911-8
[13] Tang B, Xiong Z, Li H, Long M and Zhang S 2015 J. Mater. Sci-Mater. El. 26 8017-21
[14] Jo Y H, Kang M S, Chung K W and Cho Y S 2008 Mater. Res. Bull. 43 361-9
[15] Jung B H, Hwang S J and Kim H S 2005 J. Eur. Ceram. Soc. 25 3187-93
[16] Seo Y J, Shin D J and Cho Y S 2006 J. Am. Ceram. Soc. 89 2352-55
[17] Chen X, Bai S, Li M and Zhang W 2013 J. Eur. Ceram. Soc. 33 3001-6
[18] Hwang S J, Kim Y J and Kim H S 2007 J. Electroceram. 18 121-8
[19] Takada T and Kageyama K 2005 Jpn. J. Appl. Phys. 44 6629-35
[20] Thieme C, Schlesier M, Bocker C, Buzatto de Souza G and Rüssel C 2016 ACS Appl. Mat. Inter. 8 20212-19