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Effects of La_2O_3–B_2O_3 on the flexural strength and microwave dielectric properties of low temperature co-fired CaO–B_2O_3–SiO_2 glass–ceramic

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Abstract

The La_2O_3–B_2O_3 (LB) addition, synthesized using the traditional solid-state reaction process, was chosen as a novel sintering aid of the low temperature co-fired CaO–B_2O_3–SiO_2 (CBS) glass–ceramic. The effects of LB on the flexural strength and microwave dielectric properties have been investigated. The LB addition promotes the crystallization of the $CaSiO_3$ but high amount of the LB addition leads to the formation of more pores. The CBS sample with 4 wt% LB addition sintered at 850 °C for 15 min shows good properties: flexural strength = 193 MPa, $\varepsilon_r = 6.26$ and loss = 9.96×10^{-4} (10 GHz).

Keywords: C. Dielectric properties; LTCC; CBS glass–ceramic; La_2O_3–B_2O_3 (LB) addition; Flexural strength

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1. Introduction

Low temperature co-fired ceramics (LTCC) technology has been playing a significant role in the electronic packaging applications. Due to the limited sintering temperature capability of metal electrodes such as Ag or Cu, LTCC with sintering temperature below 900 °C have been in great demand [1]. LTCC are also of great importance to the electronic industry for building smaller radio frequency (RF) modules, and fulfilling the need for miniaturization of devices in the wireless communication industry. Research on the development of co-fired dielectrics with different dielectric constants ε_r has been carried out for years to fill the need for various RF ranges [2–5]. However, the low ε_r material is still the most popular one, since it provides fast transmission in communication systems [6,7].

Commercially available LTCC systems are glass + ceramics (multiphase ceramics) [8–11] or glass–ceramics (crystallizable glass) [12–15]. The preparation of the former material starts with a mixture of high-melting ceramic filler powders and low-softening glass, which is used to reduce the sintering temperature and enhance the densification. Typical glass + ceramics systems are borosilicate glasses + alumina system developed by Fujitsu [16] and lead borosilicate glasses + alumina system developed by Dupont [17]. However, if the amount of the glass frit is large, the network formers contained in the remaining glass materials, such as B_2O_3 and SiO_2, can deeply absorb the microwave power at high frequencies, causing degradation of the quality factor of the final materials. The preparation of the latter material consists in devitrifying glass system with the consequent formation of crystalline phases during processing. The controlled crystallization in the case of crystallizable glass based glass/ceramic LTCC shows: (1) improved mechanical behavior due to reduction in effective glass content, and (2) lower dielectric constant, loss, and thermal expansion coefficient (TEC) due to crystallization of suitable phase from the glass matrix [18].

As an attractive glass–ceramic system, CaO–B_2O_3–SiO_2 (CBS) glass–ceramic has been investigated as the candidate substrate materials in the electronic packaging field, because of its low sintering temperature and relatively low dielectric constant (6.5), and compatible with Au, Ag or Cu, as the best high frequency conductor. Although the sintering mechanism and characteristics of this material have been reported in detail in references [19–21], for high reliability packaging applications, besides the dielectric, electrical and thermal properties, a high flexural strength is also required, which has been rarely

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developed so far. A novel double layer structure has been designed to enhance the flexural strength, but this design requires the complicated process and gives enlarged size of the production [22].

In this study, La_2O_3–B_2O_3 (LB) was chosen as a novel addition for CBS glass–ceramic and the results showed that the LB effectively enhanced the flexural strength of the CBS glass–ceramic. Furthermore, the underlying mechanisms involved in this process, including how the LB addition and CBS glass–ceramic materials interact with each other and how the microstructures of the sintered composites affect the mechanical and dielectric properties, have been systematically investigated.

2. Experimental procedure

Glass–ceramic samples of CBS + x wt% LB, where x = 0, 1, 2, 3 and 4 (denoted as CBS, CBS-LB1, CBS-LB2, CBS-LB3 and CBS-LB4, respectively), were prepared (CBS + 5 wt% LB sample was also prepared, but the sample cracked, which may be due to the excess glass phase). According to our study, the as-received low dielectric constant and low sintering temperature CBS glass ceramics have a preferable composition of, by wt.%, about 40% CaO, 15% B_2O_3 and 45% SiO_2. The starting raw materials were $CaCO_3$, H_3BO_3 and SiO_2 with purity higher than 99%. The batches were dry-milled with zirconia balls for 2 h and then melted in a platinum crucible at 1400 °C for about 2 h. The glass melt was quickly poured and quenched on a copper plate and pulverized in a vibration mill for 4 h. The addition of LB was synthesized using the traditional solid-state reaction process: La_2O_3 and H_3BO_3 were weighed with a ratio of about 45 wt% and 55 wt%, respectively, and then milled with a vibration mill for 3 h in the de-ionized water. Both mixtures were dried and calcined at 650 °C for 2 h. The CBS glass–ceramic powders and LB additions were weighed and milled together by a vibration mill for 3 h in the de-ionized water and then dried. The mixture was then mixed with acrylic acid for making pellets (24 cm in diameter and 1.5 mm in height) by unistatic pressing (under 25 MPa). The pellets were sintered at 850 °C for 15 min with a heating rate of 5 °C/min.

Identification of crystalline phases was carried out by an X-ray diffractometry (XRD, Rigaku Industrial Corporation, Japan). The thermogravitometry (TG) and differential scanning calorimetry (DSC) analyses of the as-prepared pallets were carried out by using a simultaneous thermal analyzer (NETZSCHSTA449c, Germany, heating at a rate of 10 °C/min). The bulk density of the sintered samples was determined by the Archimedes method. The shrinkage rate of the sample was determined by the diameters before and after sintering. The microstructure was examined using a scanning electron microscope (SEM, JSM-6490LV, Japan). The flexural strength was tested in an electromechanical universal testing machine (CMT6104, MTS, China). The relative permittivity and loss were measured by the Hakki-Coleman dielectric resonator method with an HP83752A network analyzer at 10 GHz.

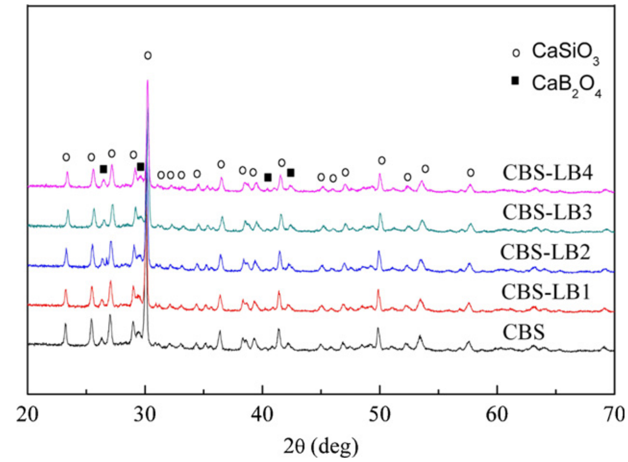

Fig. 1. X-ray diffraction patterns of the CBS samples with different amount of LB additions.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the CBS samples with different amount of LB additions sintered at 850 °C for 15 min. Two phases of wollastonite ($CaSiO_3$, PDF#42-0550) and calcium borate (CaB_2O_4, PDF#32-0155) were observed and no other phases were detected in all the samples, and no different X-ray diffraction patterns can be observed between the CBS and CBS-LB samples. These results are consistent with the phase diagram of CaO–B_2O_3–SiO_2 [23].

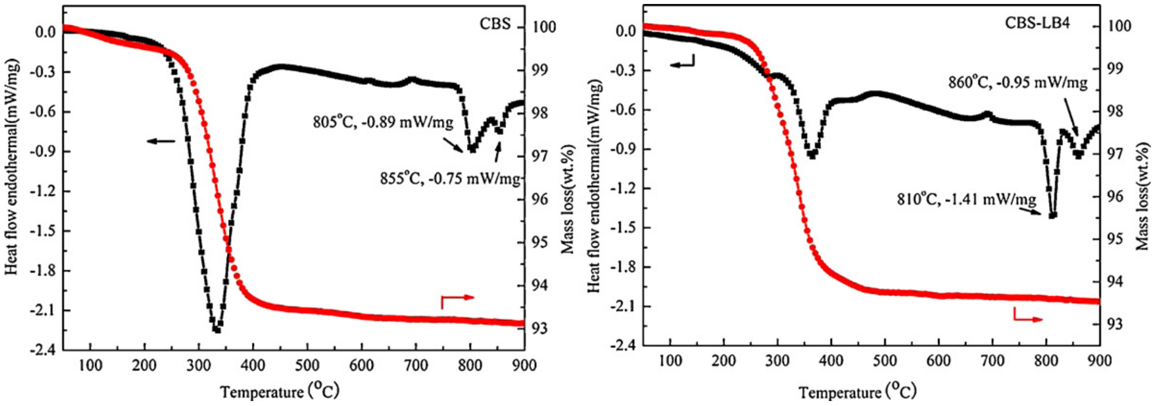

Fig. 2. The DSC and TG curves of the CBS and CBS-LB4 samples.

As $CaSiO_3$ has excellent dielectric properties and reliable thermal stability [24], it is supposed to be the desired phase in the CBS glass ceramic and widely applied to LTCC technology.

The DSC and TG curves of the CBS and CBS-LB4 samples are shown in Fig. 2. The peaks may shift slightly with changing the heating rate. The exothermic peak at around 330 °C with about 7% mass loss is caused by the decomposition reaction of acrylic acid added for when making pellets. There are two other exothermic peaks at around 800 °C and 850 °C, which correspond to the crystallization of $CaSiO_3$ and CaB_2O_4, respectively. It can be seen that the exothermic peak of $CaSiO_3$ is obviously sharpened in the presence of LB, indicating that the LB addition promotes the crystallization of $CaSiO_3$.

The dependence of the bulk density and shrinkage rate of the CBS samples with different amount of LB additions is shown in Fig. 3. The densities slightly decrease with the LB additions and all the samples show high volume densities of about 2.7 g/cm^3. It can be seen from Fig. 3 that the CBS glass–ceramic has a high shrinkage rate of 17.4%. In practical application, however, the shrinkage rate of around 15% is usually required. It can be seen that the shrinkage rate decrease with LB addition, reaching a minimum value of 15.5% with 2 wt% LB, and then increase with more LB addition. As mentioned above, the LB addition promotes the crystallization of $CaSiO_3$, and leads to the decrease of the shrinkage rate. However, with larger amount of LB addition, the shrinkage rate increase again and more pores are formed (see discussion below).

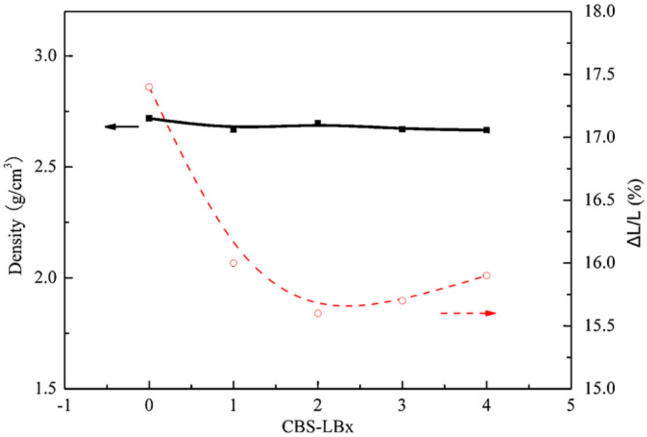

Fig. 3. The volume density and shrinkage rate of the CBS samples with different amount of LB additions.

In the comparison of the cross-section microstructures of the CBS samples with different amount of LB additions, as presented in Fig. 4, the trend of more pore formation with more LB addition can been seen. These results are consistent with the change of shrinkage rate in Fig. 3. Usually, the physical properties of ceramic materials depend on the microstructures and their major crystal phases. The flexural strength properties of the CBS-LB ceramics are shown in Fig. 5. The enhancement

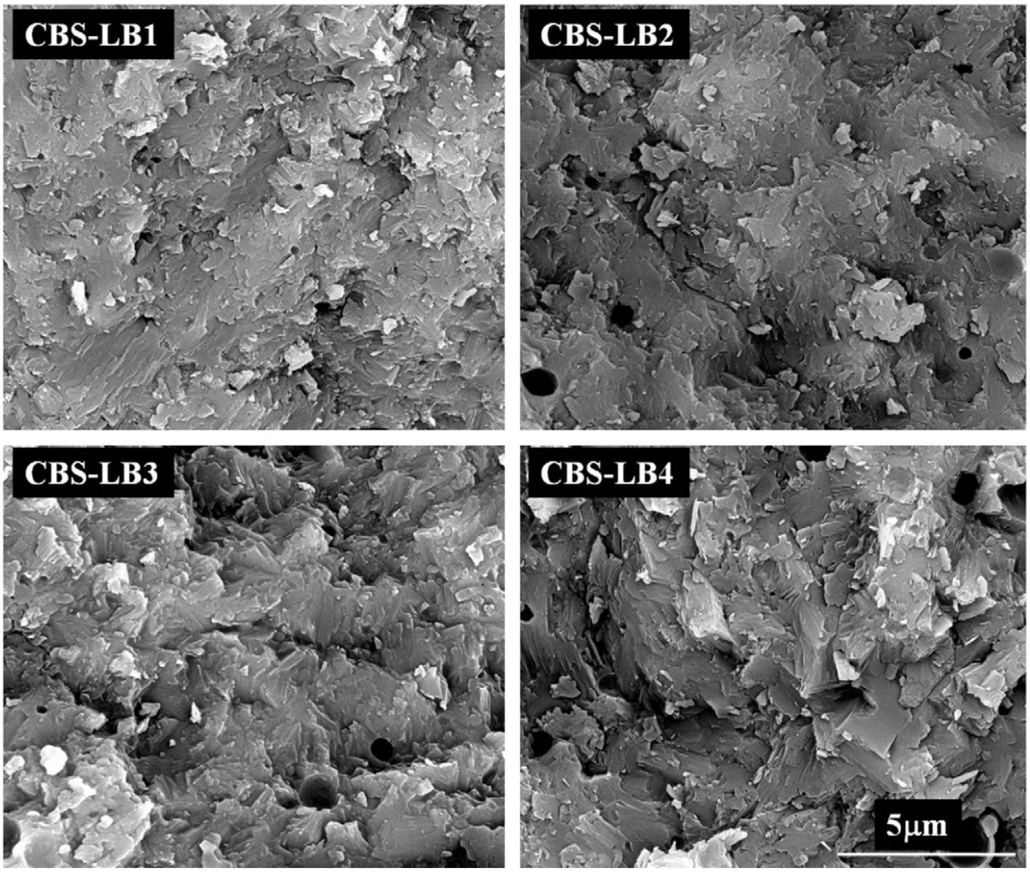

Fig. 4. The cross-section microstructures of the CBS samples with different amount of LB additions.

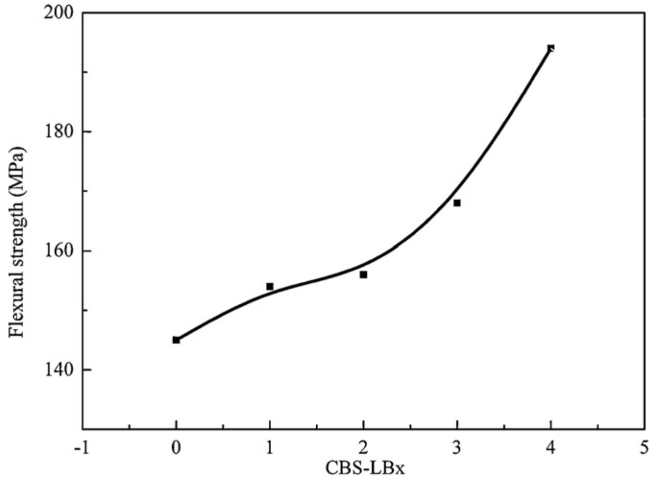

Fig. 5. The flexural strength properties of the CBS samples with different amount of LB additions.

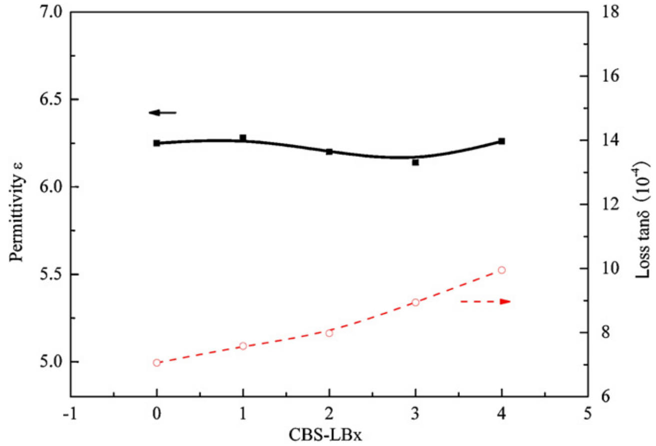

Fig. 6. The dielectric properties (10 GHz) of the CBS samples with different amount of LB additions.

of the flexural strength with the LB additions might result from the promotion of crystallization of $CaSiO_3$ as mentioned above, as the $CaSiO_3$, as mentioned above, because the $CaSiO_3$ is the acicular crystal which can promote the mechanical property of the glass–ceramic.

The dielectric properties measured at 10 GHz of the CBS samples with different amount of LB additions are shown in Fig. 6. The relative permittivities are all around 6.25. The loss is below 10×10^{-4} for all the samples and slightly increase with LB addition due to the pore formation. Compare with the data of the commercial products as shown in Table 1 [25], the CBS-LB samples show a relatively low permittivity and low loss with a high flexural strength. The excellent microwave properties of the CBS-LB samples indicate that these materials may be promising candidates for LTCC technology. The enhancement of the dielectric properties is probably because of the crystallization of $CaSiO_3$ caused by the LB addition, as mentioned above. And the enhancement may also be attributed to the modification of the initial stoichiometry of CBS with the B_2O_3 addition. Further study is undergoing for accurate understanding of the improvement mechanisms for CBS glass–ceramics.

Table 1
Properties of relative commercial LTCC materials [25].

Company	Composition	Permittivity	Loss/10^{-4}	Flexural strength/Mpa
This work	CBS-LB	6.26	9.96 (10 GHz)	193
Ferro	A6M	5.9	20 (3 GHz)	–
Dupont	951	7.8	33 (3 GHz)	–
Heraeus	CT700	7.5	22 (1 MHz)	240
Kyocera	G55	5.7	12.5 (10 GHz)	200
NEC	GCS78	7.8	33 (1 MHz)	250

4. Conclusion

The La_2O_3–B_2O_3 (LB) addition formed by the traditional solid-state process was chosen as the novel sintering aid of the CaO–B_2O_3–SiO_2 (CBS) glass–ceramic (sintering temperature: 850 °C). The results showed that the LB addition promotes the crystallization of the $CaSiO_3$ but high amount of the LB addition leads to the formation of more pores, which is due to the liquid phase formed during the sintering process. The flexural strength is enhanced because of the promotion of $CaSiO_3$ crystallization with the LB additions, and the CBS-LB samples show excellent microwave dielectric properties. The CBS-LB4 sample shows a high flexural strength of 193 MPa, ε_r of 6.26 and loss of 9.96×10^{-4} (10 GHz), indicating that this material is a promising candidate of LTCC technology.

Acknowledgement

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