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Preparation and properties of low temperature sintered CaO–B$_2$O$_3$–SiO$_2$ microwave dielectric ceramics using the solid-state reaction

XIAOHUA ZHOU, ENZHU LI*, SHILIN YANG, BO LI, BIN TANG, YING YUAN, SHUREN ZHANG

School of Microelectronics and Solid State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China

The LTCC CaO–B$_2$O$_3$–SiO$_2$ (CBS) ceramics were synthesized via solid-state reaction process without any sintering aid. The effects of different sintering temperatures and B$_2$O$_3$ content on the microwave and mechanical properties were investigated. The results show that the best sintering temperature is around 950 °C and increasing amount of B$_2$O$_3$ promotes the crystallization of CaB$_2$O$_4$ enhancing the flexure strength of the CBS ceramics. However, the dielectric and mechanical properties deteriorated rapidly while the amount of B$_2$O$_3$ exceeded 25 wt.%. The sample with 20.5 wt.% B$_2$O$_3$ sintered at 950 °C had the best properties with $\varepsilon_r = 6.06$; $\tan\delta = 0.0015$ (1 MHz) and a high flexure strength $\sigma_f > 180$ MPa.

Keywords: *solid state reaction; LTCC; CaO–B$_2$O$_3$–SiO$_2$; flexural strength; microwave properties*

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1. Introduction

Low-temperature co-fired ceramics (LTCC) has been widely investigated and has become increasingly attractive for high frequency applications. Due to the increasing demand for microwave and millimeter-wave applications, such as the front-end module for mobile phones, 3G cellulars, wireless local-area networks and radar for automobiles, a lot of attention has been paid to the development of LTCC technology [1–9]. Among several LTCC systems, CaO–B$_2$O$_3$–SiO$_2$ (CBS) is one of the most important LTCC materials because of its low loss dielectric properties and excellent compatibility with Au, Ag or Cu, as the best high frequency conductors [10–12].

There are three ways to synthesize the LTCC CBS ceramics: (1) glass-ceramics (crystallizable glass) [13, 14]: it is a devitrifying glass system which forms crystalline phases during processing. The controlled crystallization in the case of crystallizable glass based glass-ceramics LTCC shows improved mechanical behavior, lower dielectric

constant, loss, and thermal expansion coefficient (TEC) due to crystallization of suitable phase from the glass matrix. A typical commercially used CBS glass-ceramics system (A6, Ferro Co.) has been developed by Chia-Ruey Chang et al. [15]. However, because of the instability during the traditional glass melting, it is hard to guarantee the reliability of the products. Furthermore, the high cost of glass melting also restricts the commercial use of the CBS glass-ceramics. (2) sol-gel method [16]: the CBS glass powders are prepared by sol-gel process instead of glass preparation. Although the process of glass melting, pouring and quenching is avoided, the sol-gel process is also unstable and costly for the industrial use, therefore it is studied as the exploratory research. (3) solid-state reaction process [17]: the traditional method for ceramics production with simple technique, high stability and low cost. However, the CBS ceramics synthesized via solid-state reaction usually need to be sintered at a high temperature to achieve high enough density. The sintering temperatures of CBS in open reports are somewhat too high (usually higher than 1000 °C). However, the uses of sintering aids worsen the properties of the CBS ceramics

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*E-mail: lienzhu@uestc.edu.cn

dramatically. In this paper, the pure CBS ceramics synthesized via solid-state reaction process were investigated thoroughly. The compositional effects on the sintering temperatures, dielectric properties and especially the mechanical properties were studied for the actual use.

2.   Experimental procedure

The starting raw materials were $Ca(OH)_2$, H_3BO_3 and silica sol (29.5 wt. % SiO_2) with purity higher than 99 %. The mole ratio of Ca:Si was fixed to 1.2 according to the previous study [18], and the compositions of the S1 – S4 samples are shown in Table 1. The materials were milled for 7 h in deionized water. The mixtures were dried and calcined at 700 °C for 4 h. Then the mixtures were mixed with acrylic acid to make pellets (20 cm in diameter and 2 mm in height) and also the elongated samples (60 mm in length, 7 mm in width and 5 mm in height) by isostatic pressing. The samples were sintered at the temperatures of 900 °C, 950 °C, 975 °C and 1000 °C, for 2 h at 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 pellets were carried out by using a simultaneous thermal analyzer (NETZSCHSTA 449c, Germany, at a heating rate of 10 °C/min). The bulk densities of the sintered samples were determined by the Archimedes method. The shrinkage 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 with 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.

3.   Results and discussion

The S1 – S4 samples were sintered at different temperatures. The results, as shown in Table 2,
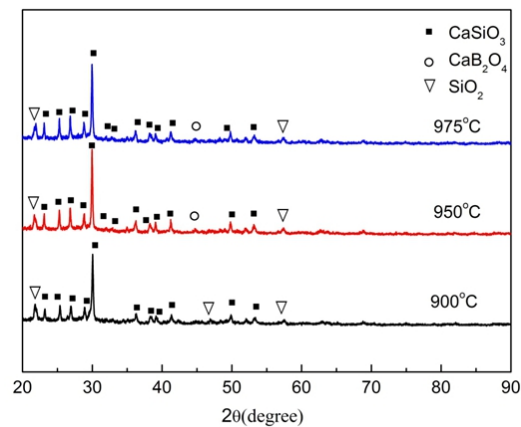

Fig. 1.   X-ray diffraction patterns of the S1 samples sintered at different temperatures.

show that 900 °C is not high enough for the optimum sintering. The samples with high amount of H_3BO_3 sintered at 975 °C and 1000 °C became deformed or meltdown. Therefore, the properties of S1 samples sintered at different sintering temperatures and S1 – S4 samples sintered at 950 °C were investigated in detail.

3.1.   S1 samples sintered at different temperatures

Fig. 1 shows the X-ray diffraction patterns of the S1 samples sintered at 900 °C, 950 °C and 975 °C. As the β-$CaSiO_3$ has excellent dielectric properties and good thermal stability [19], it is supposed to be the desired phase in CBS glass ceramics, widely applied to LTCC technology. It can be seen that the main phases are wollastonite (β-$CaSiO_3$, PDF#42-0550), calcium borate (CaB_2O_4, PDF#32-0155) and SiO_2 (PDF#83-1832). This result is consistent with the phase diagram of CaO–B_2O_3–SiO_2. CaB_2O_4 was only observed at 950 °C and 975 °C, indicating that higher sintering temperature enhances the crystallization of CaB_2O_4 [15].

The DSC curve of the S1 sample is shown in Fig. 2. The peaks may be slightly different with changing the heating rate. There is only one exothermic peak at around 780 °C. According to the XRD results, this peak is considered as the crystallization of the main phase (β-$CaSiO_3$). The endothermic peak at around 960 °C corresponds to

Table 1. The composition of CaO–B$_2$O$_3$–SiO$_2$ LTCC materials.

	S1	S2	S3	S4
Ca(OH)$_2$	27.9 wt%	26.1 wt%	24.2 wt%	22.8 wt%
Silica sol (29.5wt% SiO$_2$)	63.7 wt%	59.8 wt%	55.3 wt%	52.3 wt%
H$_3$BO$_3$	8.4 wt%	14.1 wt%	20.5 wt%	24.9 wt%

Table 2. Appearance of S1 – S4 samples with different sintering temperatures.

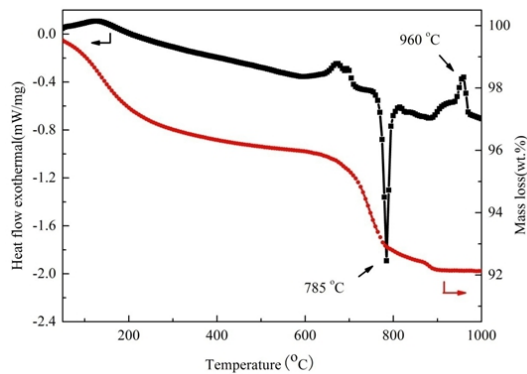| Temperature	S1	S2	S3	S4
900 °C	Not dense	Not dense	Not dense	Not dense
950 °C	Dense and no deform/melt	Dense and no deform/melt	Dense and no deform/melt	Dense and no deform/melt
975 °C	Deform slightly	Deform and Molten slag existed	Deform and Molten slag existed	Deform and Melt
1000 °C	Deform slightly	Molten slag existed	Melt	Melt

Fig. 2. The DSC and TG curves of the S1 sample.

Fig. 3. The bulk density and shrinkage of the S1 samples sintered at different temperatures.

the deformation and meltdown of the samples at 975 °C and 1000 °C.

Fig. 3 shows the densities and shrinkage of the S1 samples at different sintering temperatures. Both the density and the shrinkage at first increase and then decrease, and they achieve the maximum value of 2.588 g/cm^3 and 26.7 % at 950 °C, respectively. The low density at 900 °C may be due to the incomplete crystallization of CaSiO$_3$ and CaB$_2$O$_4$ and the remains of SiO$_2$ (ρ(CaSiO$_3$) = 2.78 – 2.91 g/cm^3, ρ(CaB$_2$O$_4$) = 2.47 g/cm^3, ρ(SiO$_2$) = 2.20 – 2.66 g/cm^3). On the other hand, it also ma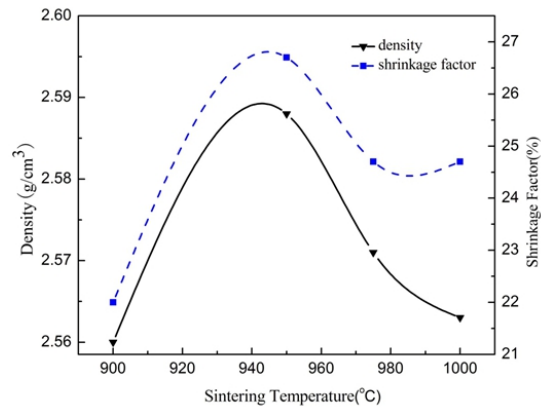y due to the low shrinkage as it corresponds to the compact-ness of the sample. The higher the shrinkage is the fewer pores are formed. Therefore, the low shrinkage indicates more pores formed at 900 °C, which is also associated with the low density. With the temperature increase, the shrinkage and the density increase because of crystallization of the CaSiO$_3$ and the number of pores decreases. However, the density decreases when the temperature is higher than 950 °C, which may due to the formation of CaB$_2$O$_4$ and glass phase.

The dielectric constants (ε_r) and loss (tanδ) of S1 samples sintered at different temperatures are
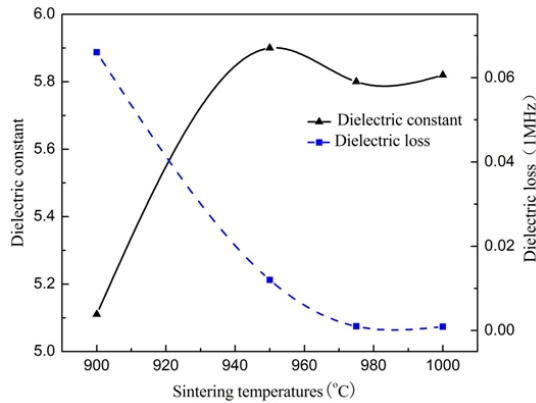
Fig. 4. The dielectric properties (1 MHz) of the S1 samples sintered at different temperatures.

shown in Fig. 4. The sample sintered at 900 °C shows a low ε_r and high $\tan\delta$ due to the remaining SiO_2 and pores. The ε_r achieves the maximum value at 950 °C and then decreases, which is caused by the crystallization of CaB_2O_4. As the polarizability of B^{3+} (0.003) is less than that of Si^{4+} (0.026) and Ca^{2+} (0.100), the formation of CaB_2O_4 results in some decrease in the polarizability of the sample, leading to a lower dielectric constant [20]. The value of $\tan\delta$ decreases with the increase in sintering temperatures also indicating the crystallization of $CaSiO_3$ and CaB_2O_4, and the decrease in the number of pores. All the results are consistent with the previous results of XRD, density and shrinkage.

3.2. S1 – S4 samples sintered at 950 °C

In the previous experiments, it was found that the best properties of the ceramics were achieved at 950 °C. The properties of the samples with different amounts of H_3BO_3 sintered at 950 °C were investigated as follows.

Besides the dielectric, electrical and thermal properties, a high flexural strength is also required for high reliability packaging applications, but the reported values (around 100 MPa) are not high enough. Table 3 lists the dielectric properties and bending strength of some commercial LTCC materials and the S1 – S4 samples sintered at 950 °C [21]. The dielectric constants ε_r of the S1 – S3 samples are almost the same around 6.06, and

the loss tangent δ decreases with increasing the amount of H_3BO_3. However, all the properties of S4 sample have worsened rapidly due to the excess of glass phase. Furthermore, with the increase of H_3BO_3, the flexural strength σ_f firstly increases and then decreases. S3 sample shows the maximum σ_f value of about 190 MPa. This result indicates that the best amount of the H_3BO_3 is about 20 wt. %, corresponding to the 25 % B_2O_3, which is consistent with the report [14]. S3 sample shows the best properties of $\varepsilon_r = 6.06$, $\tan\delta = 0.0015$ (1 MHz) and $\sigma_f = 190$ MPa, which are the same as for the samples prepared using the traditional glass melting method and sol-gel method.

Ferro A6 series LTCC material is CBS glass-ceramics sintered at 850 °C. It is supposed that the CaB_2O_4 could effectively improve the flexural strength and the increased amount of H_3BO_3 could enhance the crystallization of CaB_2O_4. Fig. 5 shows the DSC curve of S3 sample. Compared with Fig. 2, it can be seen that the exothermic peak at around 790 °C, corresponding to the crystallization of $CaSiO_3$ of S3 sample, is less than that of S1 sample, and the peak at around 820 °C, corresponding to the crystallization of CaB_2O_4 of S3 sample, is obviously sharper and larger. Fig. 6 shows the X-ray diffraction patterns of S1 – S4 samples. It can be seen that the main phase for all the samples is $CaSiO_3$. However, the S3 and S4 samples show obviously peaks of CaB_2O_4. The results clarify that the increase of H_3BO_3 enhances the crystallization of CaB_2O_4, resulting in the high flexural strength.

Fig. 7 shows the SEM results of etched surfaces of the S1 – S4 samples sintered at 950 °C after polishing. It can be seen that with H_3BO_3 added, the S2 and S3 samples become more dense and compact. Elongated grains can be observed obviously in the S2 and S3 samples. However, with more H_3BO_3 added, the excess glass phase has been formed in the S4 sample, which explains the decrease in the flexural strength and worsening the dielectric properties.

4. Conclusions

The LTCC CBS ceramics were synthesized via solid-state reaction process without any sinter-

Table 3. Properties of Lab samples and some commercial LTCC materials.

LTCC sample	S1	S2	S3	S4	Dupont 951	Ferro A6	Heraeus CT700	NEC GCS60
ε_r	6.04	6	6.06	4.69	7.8	5.9	7.5 – 7.9	6.0
$\tan\delta$	0.014	0.0028	0.0015	0.067	0.003	0.002	0.002	0.002
	(1 MHz)	(1 MHz)	(1 MHz)	(1 MHz)	(3 GHz)	(5 GHz)	(1 MHz)	(1 MHz)
σf(MPa)	108.2	118.4	183.1	94	316	245	290	250

Fig. 5. The DSC and TG curves of the S3 sample sintered at 950 °C.

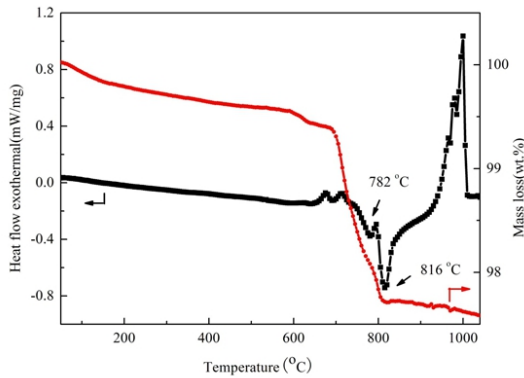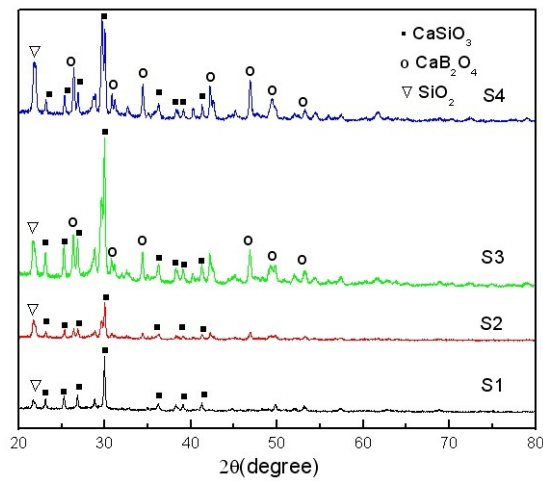Fig. 7. The SEM pictures of the surface of S1 – S4 samples sintered at 950 °C.

Fig. 6. X-ray diffraction patterns of the S1 – S4 samples sintered at 950 °C.

ing aid. The best sintering temperature is around 950 °C with the main phases of β-CaSiO$_3$, CaB$_2$O$_4$ and few SiO$_2$. The increased amount of B$_2$O$_3$ makes the microstructure more compact 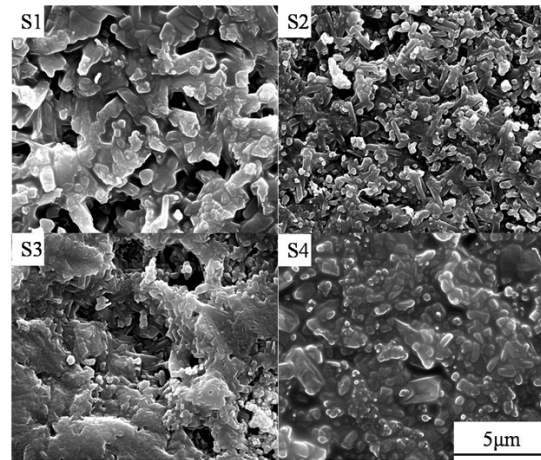and promotes the crystallization of CaB$_2$O$_4$, enhancing the flexure strength of the CBS ceramics. However, when the amount of B$_2$O$_3$ exceeds 25 wt. %, the dielectric and the mechanical properties worsen rapidly due to the excess of glass phase. The sample with 20.5 wt. % B$_2$O$_3$ sintered at 950 °C shows good properties of $\varepsilon_r = 6.06$, $\tan\delta = 0.0015$ (1 MHz) and a high flexure strength $\sigma_f > 180$ MPa.

Acknowledgements

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