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Densification and microwave dielectric behaviors of $CaO–B_2O_3–SiO_2$ glass-ceramics prepared from a binary glass composite

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ABSTRACT

In this study, a binary $CaO–B_2O_3–SiO_2$ (CBS) glass composite CBS 950 comprising a high SiO_2 content (67.3 mol%) and a low SiO_2 content (23.3%) of $CaO–SiO_2–B_2O_3$ glasses was prepared. The sintering behavior, structural evolution, and dielectric properties of the binary glass composite were characterized and compared to those of a single CBS glass (CBS-11) with the exact same composition. CBS-11 glass densified rapidly within a narrower temperature range (≈800 °C) as compared to CBS-950 glass (from ≈700 °C to 875 °C). It was found that crystallization of CaB_2O_4 phase in CBS-950 glass was easier than that in CBS-11 glass during heat treatment. Activation energy of CaB_2O_4 phase in CBS-950 glass was determined to be 307 kJ/mol. The best glass-ceramic was resulted from CBS-950 glass sintered at 900 °C, which possesses a dielectric constant of 3.77 and a dielectric loss of 0.0012 at frequency of 4.3 GHz. CBS-950 glass is superior to CBS-11 glass for use as LTCC substrates in terms of overall performance.

1. Introduction

Multilayer ceramic substrate is widely used in commercial and military electronic devices due to its high capacity and low cost. Low-temperature co-fired ceramics (LTCC) technology uses glass-ceramic materials for substrate and boasts the advantages of low dielectric constant and high component density [1,2]. LTCC uses screen-printing technology to embed passive components like capacitors, resistors and inductors into multilayer ceramic substrate with low resistance precious metals as electrodes and interconnections. They form an integrated component after undergoing the cofiring process at 850–900 °C.

Ideal LTCC substrate materials should possess several characteristics such as low dielectric constant and low dielectric loss, high thermal conductivity, low thermal expansion coefficient (close to Si and GaAs), robustness against environmental stress, and low cost. Several approaches, including glass-ceramics (crystallizable glass) and glass + ceramics (multiphase ceramics) [3–7], have been adopted to fabricate ceramic substrates. The properties of LTCC substrate materials depend on the properties and the extent of each phase present and the morphology, continuity, and connectivity of each phase [6,8]. In fabricating desirable LTCC substrates, complete densification and well crystallization are necessary for achieving good mechanical properties and dielectric properties such as high Q value. Porosity and low degree of crystallinity would lead to relatively poor mechanical properties, and residual glass is detrimental to the Q value at microwave frequency. Binary glass composite including a high softening point glass and a low softening glass has been used to achieve the above requirements [9–12]. The low softening glass served as sintering flux to enhance the densification of the high softening point glass [6]. The binary glass composites have the advantages of avoiding the problems caused by the interaction between refractory filler and glass, improving densification, adjusting dielectric properties and tailoring mechanical properties [9,13].

Calcium borosilicate glass ($CaO–B_2O_3–SiO_2$; CBS) is one of the most important LTCC substrate materials suitable for mass production thanks to its low thermal expansion coefficient, low dielectric constant, and low material cost [3]. Substantial studies of CBS glasses can be found in literature [14–20]. A previous study [21] has revealed the densification behavior, crystallization mechanism, and electrical properties of several selected CBS glass compositions. In this study, a LTCC binary glass composite comprising a high SiO_2 content and a low SiO_2 content of CBS glasses was prepared. The densification behavior, structural evolution, and dielectric properties of the CBS binary glass composite were characterized and compared to those of a CBS glass with the exact same composition.

2. Experimental procedure

The design of the glass compositions in this study was based on the phase diagram of $CaO–B_2O_3–SiO_2$ system [22], and the formulations are marked in Fig. 1. To prepare CBS-4, CBS-9, and CBS-11 glasses, the starting raw materials including $CaCO_3$ (99.9% Wako), H_3BO_3 (99.9% Wako) and SiO_2 (99.5% Wako) were mixed and milled, based on the weight percentages shown in Table 1, in methyl alcohol solution using polyethylene jars and zirconia balls for 12 h and then oven-dried overnight at

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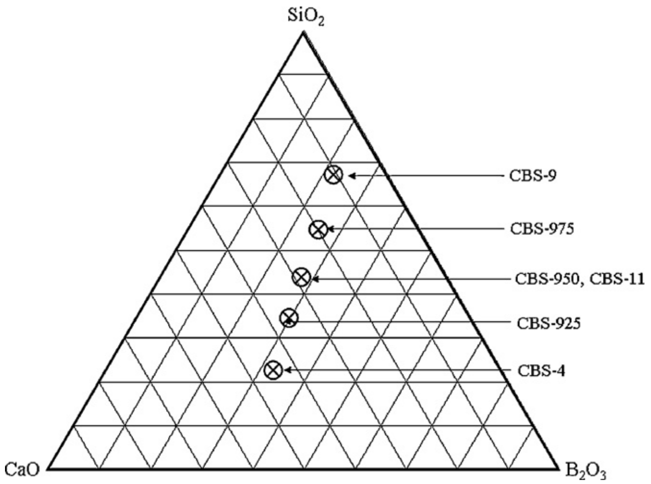

Fig. 1. Formulation design of this study.

80 °C. After drying, the powders were put into Pt/Rh (80/20) crucible, molten in the temperature range of 1500–1650 °C in air, and kept at the melting temperature for 1 h. The molten glasses were then quenched into de-ionized water. The ground glass powders were sieved through a 60-mesh screen. Subsequently, the glasses were re-milled in isopropyl alcohol for 10 h in a planetary ball mill. The pulverized glass powders were then subjected to phase analysis using X-ray diffraction (XRD, Rigaku DMX-2200) with Cu-Kα radiation to confirm their amorphous nature. Glasses of CBS-925, CBS-950, and CBS-975 were prepared by mixing CBS-4 and CBS-9 glasses with the proportions of CBS-9/CBS-4 equal to 25 wt%/75 wt%; 50 wt%/50 wt%; and 75 wt%/25 wt%, respectively. The glass mixtures were mixed in methyl alcohol solution using ball mill for 1 h and then oven-dried at 80 °C. In order to understand the sintering behavior of a binary–glass composite as compared to a single glass having the same composition, the formulations were intentionally designed in such a manner that the composition of CBS-11 glass was exactly identical to that of CBS-950 binary glass composite.

Differential thermal analysis (DTA) was performed on the glasses using PerkinElmer calorimeter (Series 1700 DTA) at different heating rates to evaluate the possible reactions during heating and the activation energies for the formation of crystallites. After being granulized with 2 wt% of 15% polyvinyl alcohol (PVA) solution, the glass powders were pressed into disc-shaped compacts with a diameter of 9.8 mm and a thickness of 5 mm under a uniaxial pressure of 140 MPa. The samples were then heat-treated at 450 °C for 3 h to eliminate the PVA, followed by sintering at the temperatures between 700 °C and 925 °C for 15 min with a heating rate of 5 °C/min. For understanding the effects of glass compositions on the sintering characteristic, dilatometric analyses were performed to characterize the longitudinal shrinkage of the glass with respect to temperature. Experiments were performed using a DIL 402C dilatometer in air and at a heating rate of 5 °C/min so as to trace the onset temperature of the densification during sintering.

Density measurements on the CaO–SiO$_2$–B$_2$O$_3$ glass-ceramics were conducted using a liquid displacement method with water as the medium. Phase identification on the sintered glass-ceramics was performed using XRD. Scanning electron microscopy (SEM, Hitachi S4700) and energy dispersive spectroscopy (EDS) studies were used to reveal the microstructures of the sintered samples. The normal (z) components of the dielectric constants (ε_r) and dielectric losses (tan δ) of the glass-ceramics at microwave frequencies were measured in the TM$_{0l0}$ mode using a Damaskos Model 400 [23] with a network analyzer (HP 8722ES). A cylindrical-shaped unmetallized sample with an aspect ratio (diameter/height) $\gg$1 was used to chock off many interfering modes. The sample was positioned inside the circular cavity with good contact to top and bottom plates. Dielectric constant and tan δ were calculated from the frequency of the TM$_{0l0}$ resonant mode.

Table 1
Compositions of various CaO–B$_2$O$_3$–SiO$_2$ glass-ceramics.

Batch no.	CaO		B$_2$O$_3$		SiO$_2$		CaO/SiO$_2$
	(mol%)	(wt%)	(mol%)	(wt%)	(mol%)	(wt%)	
CBS-4	45.0	41.2	31.7	36.0	23.3	22.8	1.9
CBS-9	10.5	9.5	22.2	25	67.3	65.5	0.2
CBS-11	27.8	25.4	27.0	30.5	45.3	44.1	0.6
CBS-925	36.4	33.3	29.3	33.2	34.2	33.5	1.2
CBS-975	19.1	17.4	24.6	27.8	56.3	54.8	0.3
CBS-950	27.8	25.4	27.0	30.5	45.2	44.1	0.6

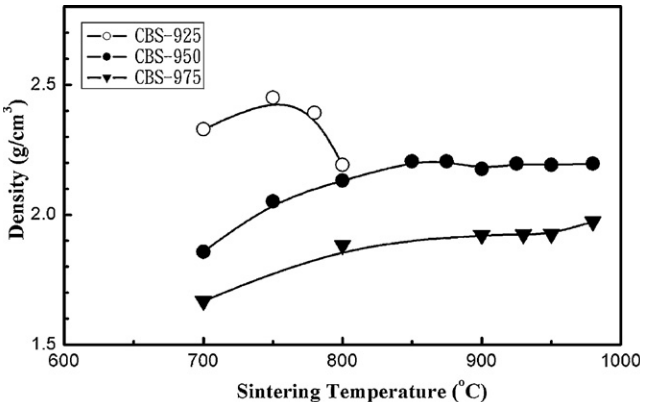

Fig. 2. Densities of CBS-925, CBS-975, and CBS-950 glasses sintered at various temperatures.

3. Results and discussion

Fig. 2 shows the densities of CBS-925, CBS-950, and CBS-975 glasses sintered at different temperatures for 30 min. The sintered density is strongly dependent on the ratio of CBS-4 and CBS-9 glasses in the composites. A previous study [21] examined a CBS-4 glass (containing 45.0 mol% of CaO, 31.7 mol% of B$_2$O$_3$, and 23.3 mol% of SiO$_2$, densified at 715 °C accompanied with a small amount of tridymite SiO$_2$ formation in an amorphous matrix) and a CBS-9 glass (with a small amount of tridymite SiO$_2$ present, containing 10.5 mol% of CaO, 22.2 mol% of B$_2$O$_3$, and 67.3 mol% of SiO$_2$, densified at 1035 °C with the concurrent crystallization of quartz and tridymite forms of SiO$_2$), and the softening points of the CBS-4 and CBS-9 glasses emerged to be 697 °C and 895 °C respectively. In this study, CBS-925 glass composed of 25 wt% CBS-9 glass and 75 wt% CBS-4 glass has the lowest sintering temperature (750 °C) for obtaining the maximum densification. It achieved the highest sintered density value (2.46 g/cm^3) among all systems. The low sintering temperature of CBS-925 glass is due to the low SiO$_2$ content, and its high density is caused by the rich content of high molecular weight BaO. Both CBS-950 and CBS-975 glasses densified at 855 °C and retained similar densities at higher sintering temperatures. The maximum density decreased with increasing CBS-9 ratio. Similarly, the sintered density was observed to decrease rapidly with increasing sintering soaking time.

Dilatometric results of CBS-925, CBS-950, and CBS-975 glasses, indicating the shrinkage profile versus temperature, are shown in Fig. 3. The shrinkage behaviors are in coincidence with the sintering temperatures required to achieve maximum bulk density as shown in Fig. 2. XRD analyses showed that densification of all systems proceeded simultaneously with devitrification, which resulted in

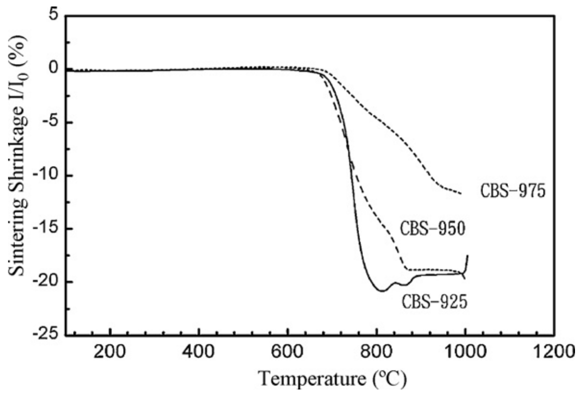

Fig. 3. Sintering shrinkage curves for CBS-925, CBS-950, and CBS-975 glasses.

Table 2
Phases present in various glasses before and after sintering.

Batch No.	Before Sintering	After Sintering
CBS-4	Amorphous	Amorphous SiO_2 (Tridymite)
CBS-9	Amorphous SiO_2 (Tridymite)^t	Amorphous SiO_2 (Quartz) SiO_2 (Tridymite)
CBS-925	Amorphous SiO_2 (Tridymite)^t	SiO_2 (Cristobalite) $Ca_2B_2O_5$ CaB_2O_4
CBS-950	Amorphous SiO_2 (Tridymite)^t	SiO_2 (Tridymite) CaB_2O_4
CBS-975	Amorphous SiO_2 (Tridymite)^t	SiO_2 (Tridymite) CaB_2O_4

t: trace quantity.

the formation of glass-ceramics. Phases present in the samples before and after sintering are listed in Table 2. CBS-925 produced a rapid densification associated with greater than 20.6% shrinkage. Crystallization of SiO_2 (cristobalite), $Ca_2B_2O_5$, and CaB_2O_4, apparently, does not retard the densification process due to the existence of a large portion of CBS-4 glass. CBS-950 glass experienced fast shrinkage occurring in the temperature range from 680 °C to 780 °C. Afterward, the shrinkage slowed down due to the crystallization of SiO_2 (tridymite) and CaB_2O_4. The total shrinkage ended up being 18.8%. The shrinkage route of CBS-975 glass was quite different from those of CBS-925 and CBS-950 glasses. Reflection points and a shoulder appeared due to the concurrent crystallization. Crystallites in huge amount curbed particle rearrangement during the densification process, either slowing down or ceasing the shrinkage. A higher sintering temperature is required to cause more shrinkage and to accelerate the densification rate. Based on the densification behavior, CBS-950 glass reveals a potential for use in LTCC substrate material requiring a wide processing window such as a sintering temperature between 850 °C and 950 °C.

To understand the densification, structural evolution and dielectric properties of the binary glass composite as compared to a single glass with the same composition, CBS-950, consisting of 50 wt% CBS-4 glass and 50 wt% CBS-9 glass, was further characterized and compared with CBS-11 glass. Both systems have the exact same formulation, i.e. 27.8 mol% of CaO, 27.0 mol% of B_2O_3, and 45.2 mol% of SiO_2. Fig. 4 shows the densities of CBS-950 and CBS-11 glasses sintered at various temperatures. The density of CBS-950 glass started to increase at ≈700 °C and reached the maximum at 875 °C, whereas, that of CBS-11 glass changed rapidly at ≈800 °C and was saturated at about 850 °C. The latter apparently densified rapidly within a narrower temperature range as compared to the former. Dimensional changes of CBS-950 and CBS-11 glasses with respect to temperature during continuous heating at a rate of 5 °C/min are shown in Fig. 5. Significant shrinkage of the binary glass CBS-950 started at 680 °C and ended at 875 °C with total shrinkage of 18.8%. Constituent of CBS-4 glass in CBS-950 glass served as sintering flux to enhance the densification of the high SiO_2 content of CBS-9 glass. In spite of the same composition, CBS-11 and CBS-950 glasses displayed different shrinkage paths. CBS-11 glass began to shrink at ≈688 °C and had a shoulder appeared at 850 °C due to concurrent crystallization. It was finalized with a total shrinkage similar to that of CBS-950 glass at 900 °C. The differences in the shrinkage curves of CBS-950 and CBS-11 imply that each has its own distinct densification mechanism.

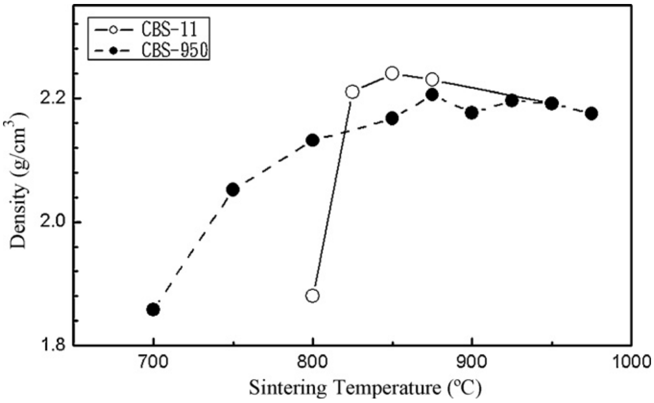

Fig. 4. Densities of CBS-950 and CBS-11 glasses sintered at various temperatures.

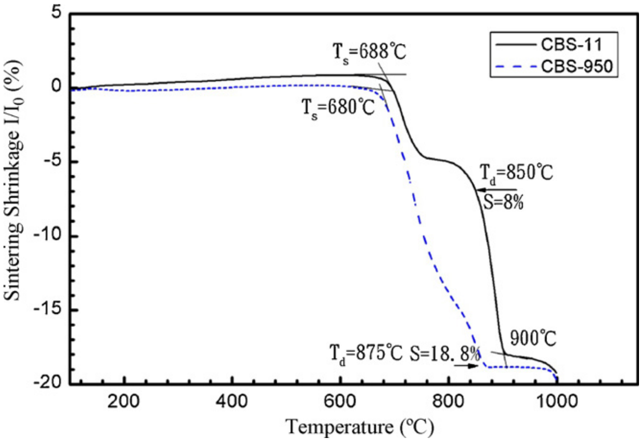

Fig. 5. Dimensional changes of CBS-950 and CBS-11 glasses with respect to temperature during continuous heating at a rate of 5 °C/min.

Fig. 6 shows the DTA results of CBS-950 and CBS-11 glasses at a heating rate of 10 °C/min. For CBS-950 glass, an exothermic reaction peaked at 888 °C corresponds to the crystallization of CaB_2O_4

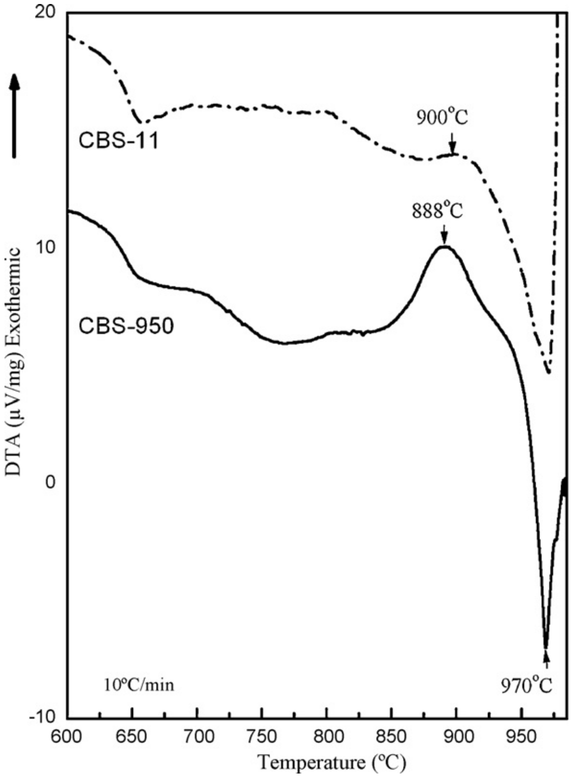

Fig. 6. DTA results of CBS-950 and CBS-11 glasses.

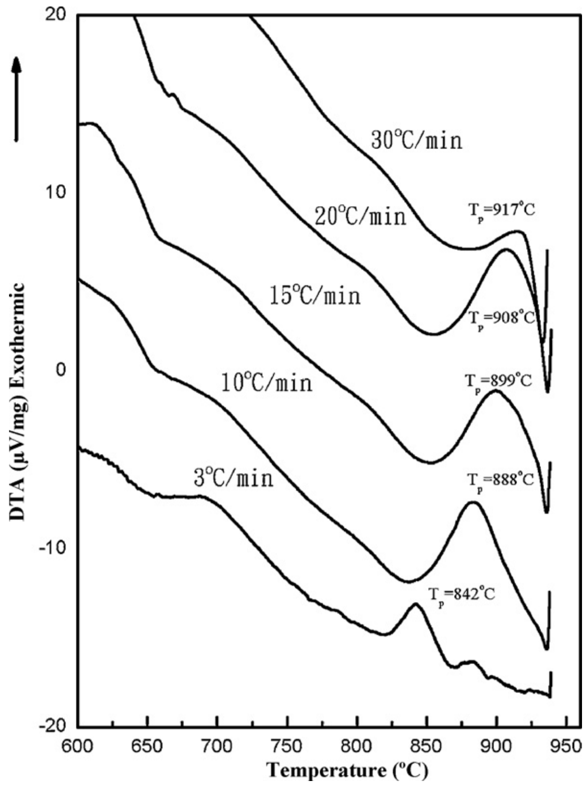

Fig. 7. DTA results of CBS-950 glass measured at different heating rates.

phase. The area under the peak is proportional to the quantity of the crystallization. It seems that the exothermic peak for CBS-11 glass is not evident. The massive CaB_2O_4 crystallization in CBS-950 glass that occurred during heat treatment might be due to the seeding effect of the SiO_2 (tridymite) crystallite in the original CBS-9 glass, which served as nucleus for further crystallization. To further study the crystallization behavior of CaB_2O_4 phase in CBS-950 glass, the activation energy needs to be determined. The peak shift method, originally proposed by Kissinger [24], was used to calculate the activation energy of crystallization based on the following equation.

$$\ln\left(\frac{\alpha}{T_{\mathrm{p}}^2}\right) = \frac{C-Q}{RT_{\mathrm{p}}} \qquad (1)$$

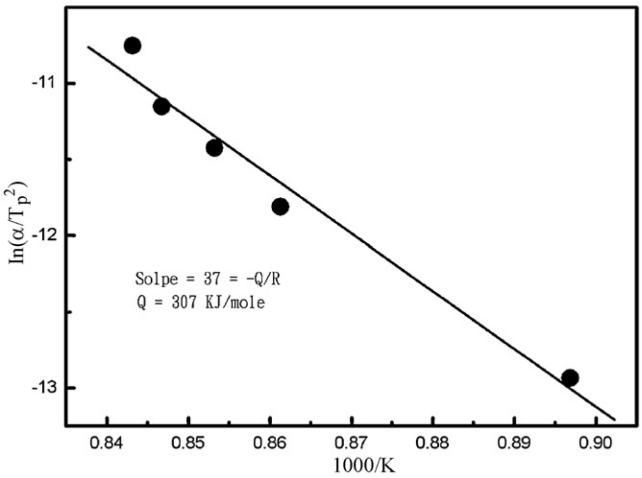

Fig. 8. $\ln(\alpha/T_{\mathrm{p}}{}^2)$ versus $1/T$p curve from the DTA results of CBS-950 glass shown in Fig. 7.

α is the heating rate, Tp the crystallization peak temperature, C a constant, Q the activation energy and R the ideal gas constant. According to the DTA thermographs obtained at different heating rates for the CBS-950 glass, it is expected that the rising heating rate would result in the increase in crystallization peak temperature, as shown in Fig. 7. Based on the result shown in Fig. 7, the slope of $\ln(\alpha/T_{\mathrm{p}}{}^2)$ versus $1/T$p curve plotted in Fig. 8 gives the activation energy. The activation energy of CaB_2O_4 phase was thus determined to be 307 kJ/mol, which is higher than that reported by Jean and Gupta [25] in their study of a commercial A-6 tape. Fig. 9 shows the SEM microstructures for the fracture surfaces of CBS-950 and CBS-11 sintered at 875 °C and 850 °C, respectively. CBS-950 glass seemed to contain more and larger CaB_2O_4 crystallites with a minor SiO_2 (tridymite) phase in the glass matrix than CBS-11 glass. These observations are in agreement with the XRD patterns shown in Fig. 10. CBS-11 contains trivial crystallites, represented by a set of low-intensity XRD peaks distributed in a glass matrix. Apparently the crystallization rate of CaB_2O_4 in CBS-11 glass is much slower than that in CBS-950 glass.

The physical properties of various $CaO–B_2O_3–SiO_2$ glass-ceramics are shown in Table 3. Dielectric constant and dielectric loss versus frequency for CBS-950 and CBS-11 glasses sintered at various temperatures are shown in Fig. 11. The dielectric constant and the dielectric loss change very slightly as frequency increases from 4.3 GHz to 18.6 GHz. Dielectric constants and dielectric losses of CBS-950 glass range respectively from 3.58 to 4.18 and 0.0009 to 0.0059 at the sintering temperatures ranging from 850 °C to 900 °C. Those of CBS-11 glass vary respectively from 4.12 to 4.53 and 0.0008 to 0.0104 at sintering temperatures from 825 °C to 875 °C. The low dielectric constants of the CBS-950 and CBS-11 glass-ceramics provide an attractive feature for minimizing cross talk and increasing signal transmission speeds. Among these results, CBS-950 glass sintered at 900 °C possesses the best microwave dielectric properties, including the lowest dielectric constant ranging from 3.77 to 3.85

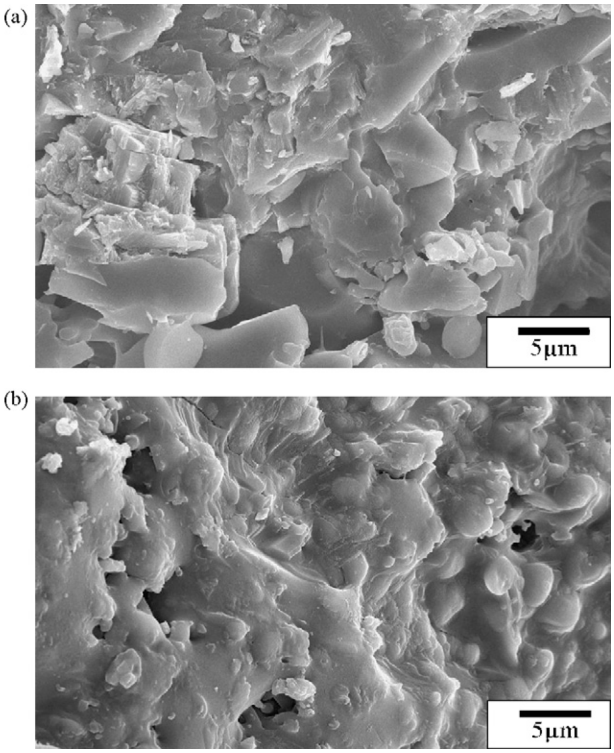

Fig. 9. SEM for fracture surfaces of (a) CBS-950 and (b) CBS-11 glasses sintered at 875 °C and 850 °C, respectively.

Table 3
Structure and physical properties of various CaO–B_2O_3–SiO_2 glass-ceramics.

Characters	CBS-4	CBS-9	CBS-950	CBS-11
Phase before sintering	Amorphous	Amorphous SiO_2 (Tridymite)	Amorphous SiO_2	Amorphous
Densification temperature (°C)	715	1035	875	850
Phase after sintering	Amorphous SiO_2 (Tridymite)	Amorphous SiO_2 (Quartz) SiO_2 (Tridymite)	CaB_2O_4 SiO_2 (t)	CaB_2O_4 SiO_2 (t)
Shrinkage (%)	–	–	18.8 (@875 °C)	8 (@850 °C)
Dielectric constant (ε_r)	7.8 (@12.5 GHz)	3.8 (@12.9 GHz)	4 (@12.8 GHz)	4.2 (@12.8 GHz)
Dissipation factor (tan δ)	0.011 (@12.5 GHz)	0.003 (@12.9 GHz)	0.004 (@12.8 GHz)	0.004 (@12.8 GHz)
$Q \times f_0$	1136	4300	3200	3200

t: trace quantity.

and the lowest dielectric loss (tan δ) varying from 0.0012 to 0.0043, as frequency varies from 4.3 GHz to 18.6 GHz.

Glass-ceramics prepared from a binary glass composite (CBS-950 glass) and a single glass (CBS-11 glass) with exactly the same composition were compared based on their sintering characteristics and physical properties. CBS-950 glass appears to be superior to CBS-11 glass for use as LTCC substrates in terms of overall performance. CBS-950 can be densified at the temperature range from 850 °C to 950 °C. The wide processing window provides a better processing compatibility with other materials. Glass-ceramic prepared from CBS-950 glass involves a larger amount of crystallites which enhances the mechanical strength of the glass-ceramics. It also possesses a low dielectric constant and a low dielectric loss, which are beneficial for use in microwave applications.

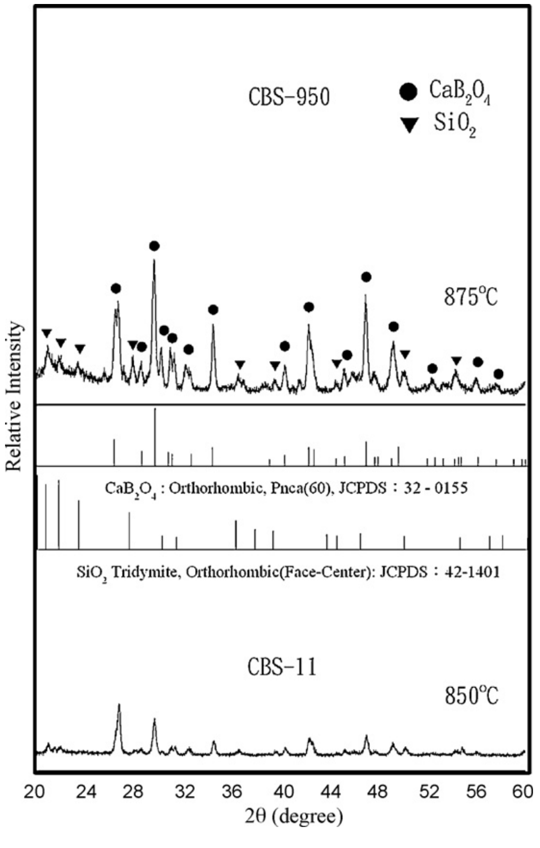

Fig. 10. XRD patterns of CBS-950 and CBS-11 glasses sintered at 875 °C and 850 °C, respectively.

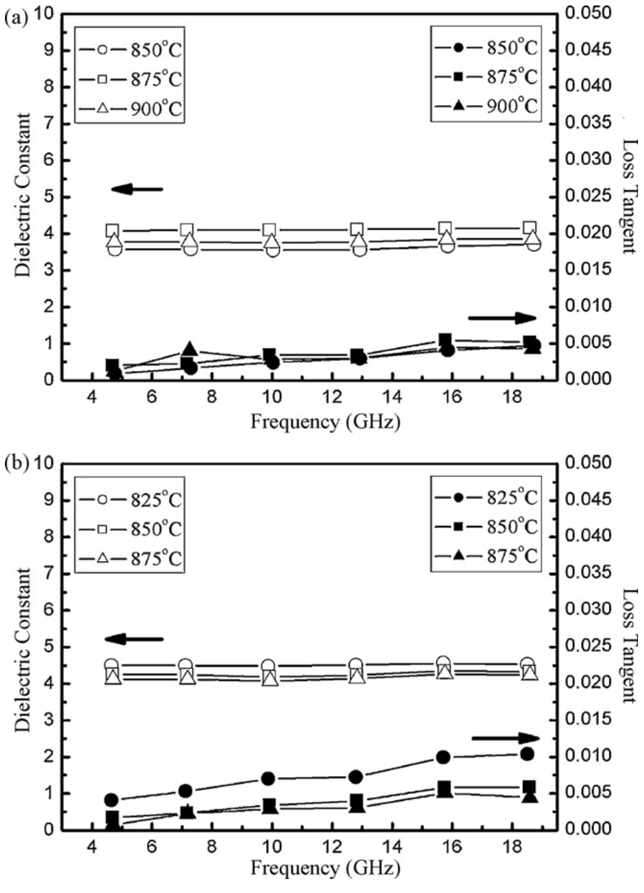

Fig. 11. Dielectric constant and dissipation factor versus frequency for (a) CBS-950 and (b) CBS-11 glasses sintered at different temperatures.

4. Conclusions

In this study, a binary glass composite CBS 950 in the CaO–B_2O_3–SiO_2 system was prepared. The sintering behavior, structural evolution, and dielectric properties of the binary glass composite were characterized and compared to those of a single glass (CBS-11) with the exact same composition. CBS-950 glass is observed to be superior to CBS-11 glass for use as LTCC substrates based on their overall performance. Dilatometric results revealed that a significant shrinkage of the binary glass CBS-950 started at 680 °C and ended at 875 °C. CBS-11 glass, displaying a different shrinkage path, began to shrink at ≈688 °C and had a shoulder appeared at 850 °C due to concurrent crystallization. Both glass finalized with a similar total shrinkage (≈18.8%) at 900 °C. DTA, XRD, and SEM results indicated a massive CaB_2O_4 formation in CBS-950 glass during heat treatment at ≈888 °C due to the seeding effect of the original SiO_2 (tridymite) crystallite in the high SiO_2 content glass (CBS-9). Moreover, the glass-ceramics prepared from CBS-950 glass possesses promising microwave dielectric properties which are beneficial for use in LTCC application.

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