

# Effect of anorthite and diopside on dielectric properties of Al<sub>2</sub>O<sub>3</sub>/glass composite based on high strength of LTCC substrate

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**Abstract** The green sheet of an alumina filler/glass matrix, which is a glass–ceramic based on an anorthite and diopside composite, is a low-fired substrate material for microelectronic packaging. In this study, alumina/glass sheets were prepared using a tape-casting process. The mechanical and dielectric properties of the sintered bodies were examined as a function of the sintering temperature. The volume of the crystalline phases was considered with the peak area of the XRD intensity for evaluating the alumina/glass composite. The flexural strength and dielectric properties of the sintered alumina/glass composites were  $167.2 \pm 13.1$  MPa for the four-point bending test, 5.51 for the dielectric constant and 2,078 MHz for the quality factor, respectively. The dielectric constant was dependent on the volume of crystalline phases present.

## Introduction

In the microelectronic packaging industry, low-temperature co-fired ceramic (LTCC) substrates have been developed to satisfy the requirements of high signal propagation speed, good reliability and low cost [1–4]. LTCC substrates can be fired with low melting conductors such as copper (1,083 °C) and silver (961 °C). To deal with the requirements of LTCC substrates, the dielectric constant ( $k$ ) needs to be lower than that of alumina ( $\approx 9$ ) for preventing signal propagation delay [5–7]. Furthermore, the LTCC substrate

should be matched with the thermal expansion coefficient (CTE:  $3\text{--}5 \times 10^{-6}/\text{K}$ ) of silicon semiconductor chips to avoid the damage caused by thermal stress and be tough enough to endure the many stresses to ensure the reliability of performance [7].

Glass–ceramics have been reported to be suitable LTCC substrates with optimal properties such as low  $k$  ( $\sim 5$ ), CTE ( $3\text{--}5 \times 10^{-6}/\text{K}$ ), sinterability at low temperatures ( $<950$  °C) and high strength [8–12]. The main candidates of the glass–ceramics for applications to the LTCC substrates are cordierite ( $2\text{MgO}\text{--}2\text{Al}_2\text{O}_3\text{--}5\text{SiO}_2$ ), anorthite ( $\text{CaO}\text{--}\text{Al}_2\text{O}_3\text{--}2\text{SiO}_2$ ) and diopside ( $\text{CaO}\text{--}\text{MgO}\text{--}2\text{SiO}_2$ ) based on glass–ceramic [8–12]. Considering the mechanical properties of the glass–ceramics, the glasses transformed into a glass–ceramic require high crystallinity and low porosity. Moreover, the crystallinity of the glass–ceramic should be related to the dielectric properties [4, 5].

To improve the high strength of substrate for multifunctional ceramic substrates, our approach of works is that a mixture of two glasses should have high densification and a complex microstructure after sintering at low temperature ( $<900$  °C). The reason for this is that the glasses have different thermal properties such as the glass transition temperature, Littleton softening point and onset point of crystallization [4, 10]. Furthermore, the addition of fillers to improve the functional properties of glass–ceramics during densification at the firing temperature should be possible.

In this study, the two glasses were chosen on account of the dependence of their thermal properties and crystal phase, which were transformed into anorthite ( $\text{CaO}\text{--}\text{Al}_2\text{O}_3\text{--}2\text{SiO}_2$ ) and diopside ( $\text{CaO}\text{--}\text{MgO}\text{--}2\text{SiO}_2$ ). In addition, alumina, as a filler, was added to the mixture of the frits as a reinforcing agent. The aim of this study was to improve the low dielectric and mechanical properties of a glass–ceramic by mixing two different glasses and alumina

Jinho Kim and Seongjin Hwang equally contributed to the article.

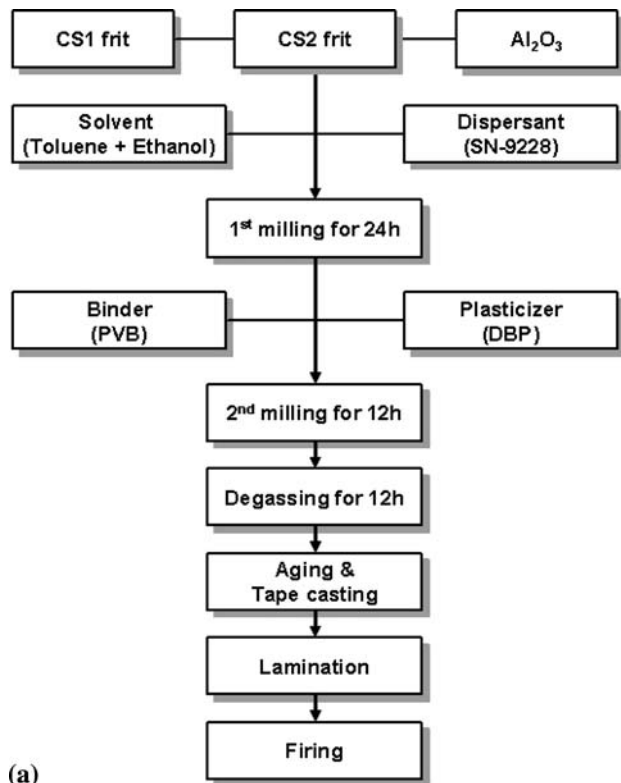
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at certain mixing proportions for applications of LTCC substrates. The mechanical and dielectric properties of the sintered bodies were investigated as a function of the sintering temperature and volume of crystalline phases.

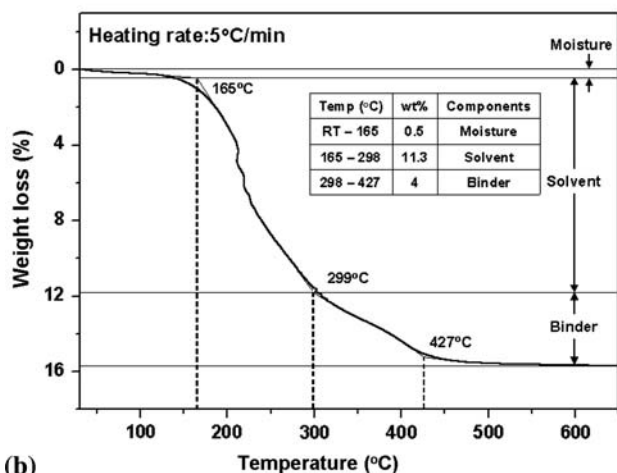
### Experimental procedure

The raw materials for the glass frits were  $55\text{SiO}_2\text{-}7\text{Al}_2\text{O}_3\text{-}23\text{CaO-}10\text{MgO-}3\text{Na}_2\text{O-}2\text{Fe}_2\text{O}_3$  (CS1, in mol%) and

$50\text{SiO}_2\text{-}22\text{Al}_2\text{O}_3\text{-}23\text{CaO-}5\text{B}_2\text{O}_3$  (CS2, in mol%), which have high purity (Aldrich, USA). The batches were melted in a platinum crucible at  $1,500\text{ }^\circ\text{C}$  for 3 h. The glass melts were quickly poured and quenched on a ribbon roller. The cullets were pulverized by using a planetary mono mill for 7 h (CS1:  $d_{50}$ — $1.4\text{ }\mu\text{m}$  and CS2:  $d_{50}$ — $1.7\text{ }\mu\text{m}$ ). The CS1 and CS2 glass frits were mixed in a ratio of 30:70 wt% using a ball mill for 24 h and then dried at  $130\text{ }^\circ\text{C}$  for 24 h. The resulting glass frits and  $\text{Al}_2\text{O}_3$  powder (99.8%, Sumitomo Co. Japan, AES-11( $d_{50} = 0.5\text{ }\mu\text{m}$ )) were mixed in a weight ratio of 90:10. The mixture of the frits and the  $\text{Al}_2\text{O}_3$  powder was first ball-milled with zirconia balls for 24 h in a toluene/ethanol solvent and dispersant (SN-9228). A binder (PVB) and plasticizers (DBP) were added to the slurries and milled for a further 24 h. The green sheet was made from the slurry using a tape-casting machine (TCA 400, Techgen Co., Korea). The green sheet (thickness:  $74\text{ }\mu\text{m}$ ) was laminated and then sintered at different temperatures for 1 h at a rate of  $5\text{ }^\circ\text{C}/\text{min}$ . Figures 1 and 2 show a flow chart of the experimental produce, weight loss of the sheet, image of the sintered bodies and a cross-sectional SEM image.

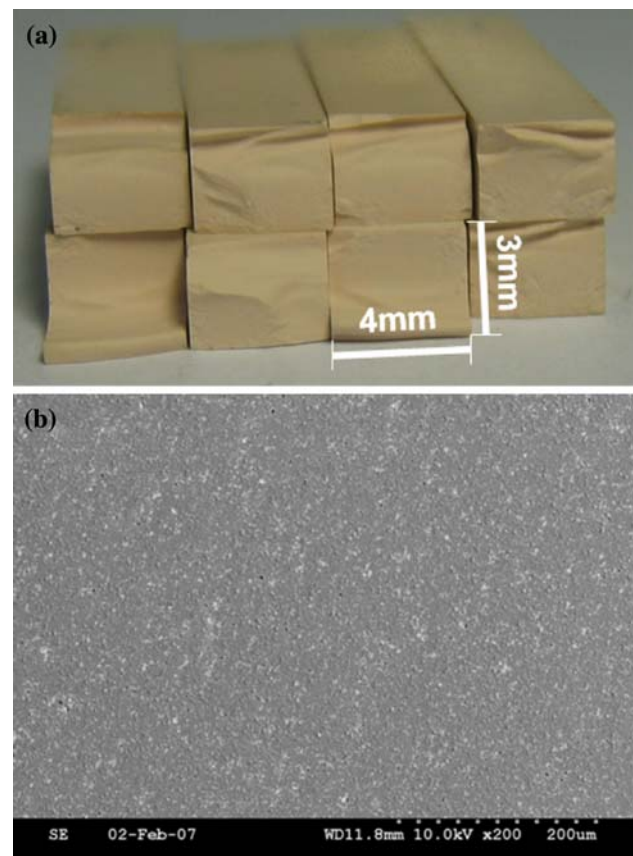


(a)



(b)

**Fig. 1** Schematic diagram of the experimental procedure (a) and weight loss of the sheet (b)



**Fig. 2** Photographic images of the sintered bodies with 50 sheets after the flexural strength test (a) and a cross-sectional SEM image of the sintered body (b) which does not show any voids/pores at the interface of sheets

The bulk density of the sintered samples was determined using the Archimedes method (standard deviation:  $\pm 0.2 \text{ g/cm}^3$ ). The glass transition temperature ( $T_g$ ), the onset point of crystallization ( $T_c$ ), and the crystallization peak ( $T_p$ ) were determined using a differential thermalgravimetric analyser (TG-DTA 8120, Rigaku Co., Japan) at a heating rate of  $10 \text{ }^\circ\text{C/min}$ . The shrinkage of the samples (diameter: 5 mm, height: 5 mm) prepared by metal mould (pressured at 2 ton) was measured using a dilatometer (L75HS, Linseis, Selb, Germany). The microstructures of the sintered sample were characterized by scanning electron microscopy (SEM, HITACHI, Japan). The porosity was observed by counting the pores with 10 images of SEM (standard deviation:  $\pm 0.39\%$ ). The crystalline phase of the sintered samples was identified by X-ray powder diffraction (XRD, Rigaku DMAX 2500, Japan). The flexural strength of the sintered samples (width: 3 mm, height: 4 mm, length: 36 mm) was determined using a four-point bending test (standard deviation:  $\pm 13 \text{ MPa}$ ). The dielectric constant and quality factor of the sintered samples were measured at room temperature using an LCR meter (4284A, Agilent, USA) at a frequency of 1 MHz.

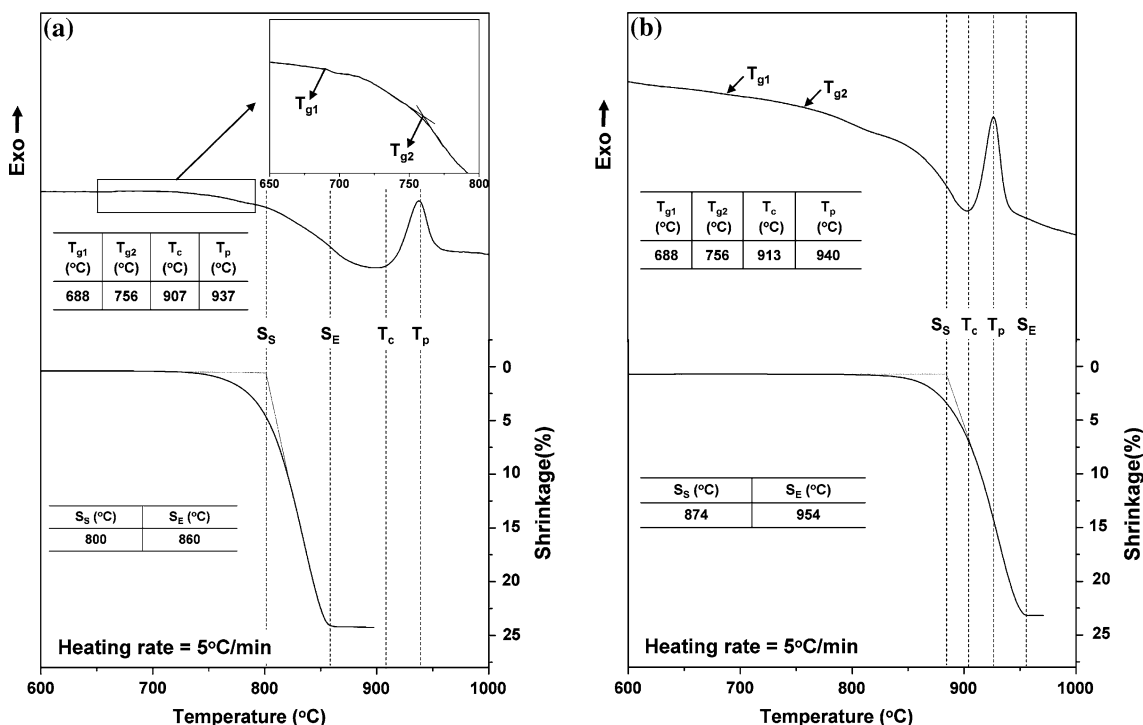
**Results and discussion**

As shown in Fig. 1, the organic materials were fully burned at temperatures  $>600 \text{ }^\circ\text{C}$ , and the laminated sheets had a

uniform microstructure after firing. The  $T_g$  of the CS1 and CS2 frits was reported to be 688 and  $756 \text{ }^\circ\text{C}$ , respectively [13]. Furthermore, crystallization of the CS1 and CS2 frits was the result of bulk crystallization rather than surface crystallization in each of the glass systems. The CS1 and CS2 frits were crystallized as diopside and anorthite, respectively.

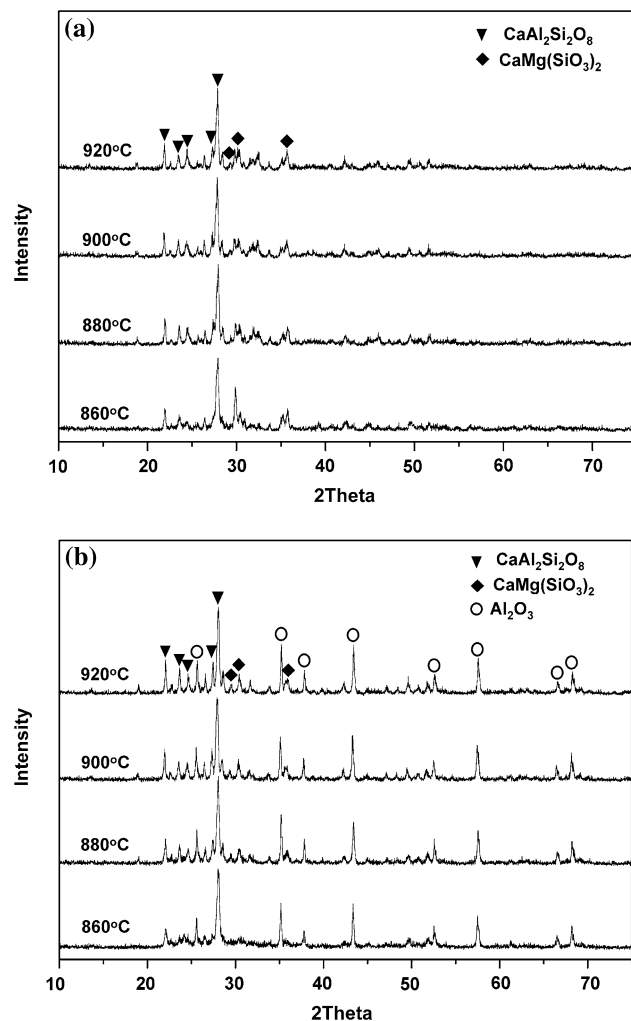
As shown in Fig. 3a, the  $T_{g1}$  and  $T_{g2}$  of the mixed frits were 688 and  $756 \text{ }^\circ\text{C}$ , respectively. However, there was only one  $T_c$  detected at  $913 \text{ }^\circ\text{C}$ , and the  $T_p$  of the mixed frits was observed at  $937 \text{ }^\circ\text{C}$ . This means that the mixed frits crystallize into a phase despite the presence of the CS1 and CS2 frits. The shrinkage of the mixed frits was correlated to the CS1 frit. The starting point of shrinkage ( $S_s$ ) is  $800 \text{ }^\circ\text{C}$ , which indicates that the CS1 frit contributed to the sintering of the CS2 frit at low temperature. The ending point of shrinkage ( $S_E$ ) is  $860 \text{ }^\circ\text{C}$ . Therefore, it is found that the crystallization occurs in the dense glass.

A comparison of Fig. 3a and b reveals the addition of alumina in the mixed frits affects the DTA results and the shrinkage. The  $T_c$  and  $S_s$  of the composite increased significantly to  $913$  and  $874 \text{ }^\circ\text{C}$ , respectively. However, the  $T_p$  of composite ( $940 \text{ }^\circ\text{C}$ ) is similar to the mixed frits. This is attributed to the formation of the crystalline phase. However, the shrinkage of the composite increased linearly until  $954 \text{ }^\circ\text{C}$  despite the formation of the crystalline phase. Therefore, the addition of a filler should affect the formation of the crystalline phase and the shrinkage.



**Fig. 3** The DTA and shrinkage curves for the frits (a) and sheets (b) (frits with alumina filler)

In Fig. 4, the crystalline phases of the mixed frits and sheets sintered as a function of temperature were identified by the XRD patterns. Both crystallized into diopside and anorthite phases. However, the intensity of the XRD patterns of two crystalline phases in the frits and sheets differed significantly at different temperatures (Table 1). The area of the main XRD peak for the ratio of diopside and anorthite in the frits decreased with increasing sintering temperature. The formation of diopside in the frits should decrease with increasing sintering temperature. However, in case of the sheet, the ratio of the area of the main XRD peaks for diopside and anorthite was maximized at 880 °C. This suggests that the addition of alumina in the mixed frits is related to the formation of the crystalline phases. The addition of alumina to the mixed frits affected the formation of anorthite. Furthermore, the volume of the crystalline phases in the LTCC substrate can be



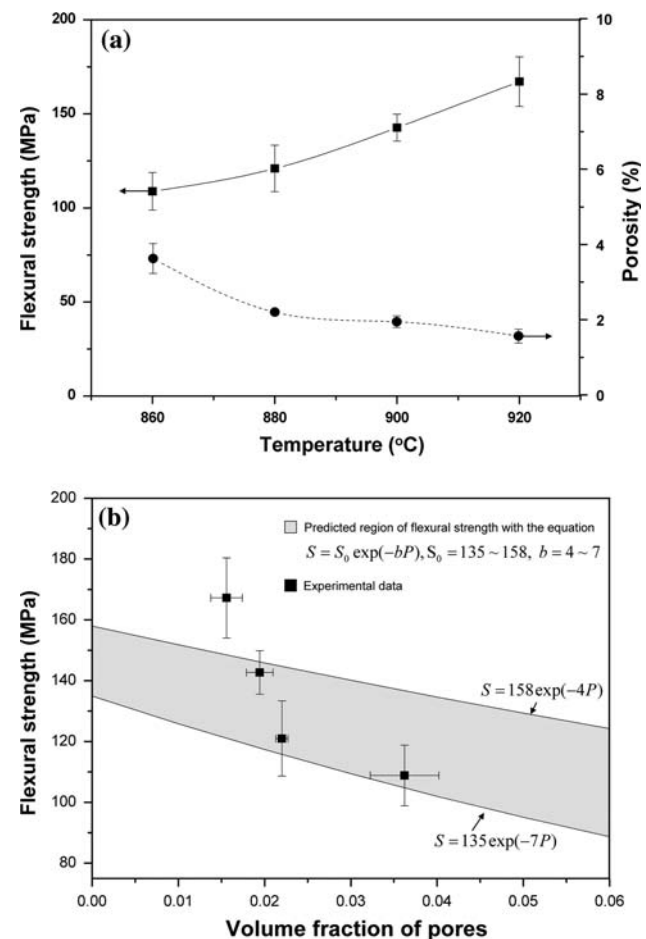
**Fig. 4** X-ray diffraction patterns of the mixed frits (a) and sheets (frits with alumina filler) (b) sintered at different temperatures for 1 h

**Table 1** Main peak area of the XRD peaks for the crystalline phases as a function of the sintering temperature

Sintering temperature (°C)	Main peaks area of XRD intensity for diopside ( $I_d$ ), anorthite ( $I_a$ ) and alumina ( $I_A$ )			
	Frits (Fig. 4a)		Sheet (Fig. 4b)	
	$I_d/I_a$	$I_d/I_A$	$I_d/I_A$	$I_a/I_A$
860	31.4/65.4	1.2/77.4	1.2/21.6	77.4/21.6
880	10.2/71.8	8.6/73.7	8.6/23.0	73.7/23.0
900	7.4/72.2	7.5/74.0	7.5/22.8	74.0/22.8
920	6.4/73.2	6.4/75.3	6.4/22.3	75.3/22.3

predicted, assuming that the area of the main XRD peak for the crystalline phases indicates the crystallinity.

The flexural strength of the composites increased with increasing the sintering temperature (Fig. 5a). The porosity



**Fig. 5** Flexural strength and porosity of the composites sintered as a function of temperature (a) and the prediction and the experimental data for the relationship between the flexural strength and the volume fraction of pores (b).  $S$ : Flexural strength of composite,  $S_0$ : Flexural strength of composite without pores [14],  $b$ : constants [15].  $P$ : volume fraction of pores

of the composites sintered from 860 to 920 °C for 1 h was observed to be <5%, and the highest porosity of the composite was found at the sample sintered at the 860 °C. The change in strength and porosity is related to the microstructure, crystalline phases and pores. During sintering, the rate of the crystal growth of anorthite affects the formation of pores [16]. Moreover, the pores are related to the flexural strength of the composites: a decrease in porosity contributes to an increase in flexural strength of composites. In Fig. 5b, the experimental equation, which was related between the flexural strength and the volume fraction of pores, was plotted based on the previous researches [14, 15]. However, our results were not correlated to the equation. Therefore, we suggest that the increase in the flexural strength should be related to the crystalline phases and the crystallinity, rather than only the porosity. The intensity of the XRD peaks for the crystalline phases changed slightly at sintering temperatures >860 °C. A comparison of the XRD intensity of anorthite and the alumina filler showed that the filler was associated with the anorthite. Therefore, when the porosity of the composite is constant, the flexural strength is related to the degree of the reaction between the anorthite and the alumina.

The density of the composites decreased with increasing sintering temperature (Table 2). The group of crystalline phases and the porosity affects the density of the composites. A decrease in porosity contributes to an increase in the quality factor and a decrease in the dielectric constant [19–21]. However, the 5% porosity did significantly affect the dielectric properties [20]. The group crystalline phases and grain sizes are strongly related to the dielectric properties [21]. The composites were composed of diopside, anorthite, alumina and residual glass.

The increase in quality factor with increasing temperature, as shown in Table 2, is the result of an increase in crystal size [20, 21]. It means that the number of grain boundaries per unit volume should decrease with crystal growth. Therefore, the grain size of the composite can increase with increasing sintering temperature. Furthermore, the CTE of the composites is related to the group crystalline phases, the crystallinity and the porosity, as

shown in Table 2. Therefore, the CTE of the sintered composites was dominated by anorthite and the residual glass.

To confirm the effect of the crystalline phases on the dielectric constants, the volume fraction of the crystalline phases was predicted based on the area of the main XRD peak (Fig. 6). The diopside, anorthite and alumina from (27.3)CS1, (65.6)CS2 and (7.1)alumina in vol% from the area of the main XRD peak of the mixed frit sintered at 860 °C, the sheet sintered at 860 °C and the sheet sintered at 880 °C were considered to have 100% crystallinity. Furthermore, the area of the main XRD peak for the alumina was added to the volume of the anorthite. The volume of the crystalline phases was calculated using the following Eq. 1;

$$V_{\text{sheet(diopside)}} = \frac{I_{100\% \text{crystallinity(diopside)}}}{V_{\text{CS1}}} \times I_{\text{sheet(diopside)}} \quad (1)$$

where  $V_{\text{sheet(diopside)}}$  is the volume fraction of the diopside in the sheet sintered as a function of temperature,  $I_{100\% \text{crystallinity(diopside)}}$  is the main peak area of XRD intensity for the mixed frit sintered at 860 °C,  $V_{\text{CS1}}$  is 27.3

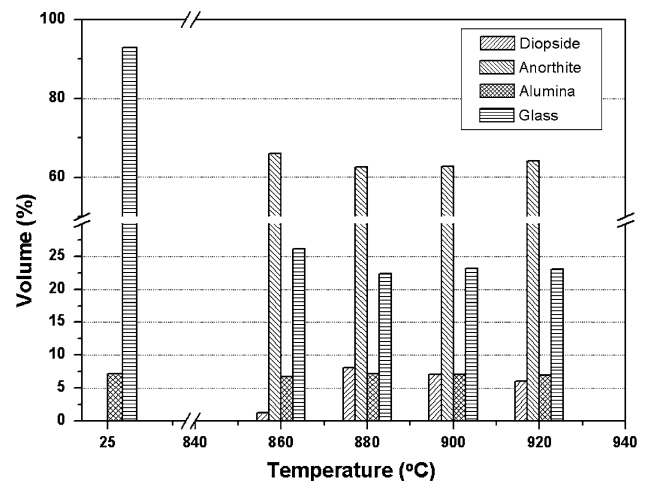


Fig. 6 Predicted volume of the crystalline phases based on the area of the main XRD peak in Fig. 4

Table 2 Physical, thermal and electric properties of the glass–ceramic composites (Green sheets (CS1:CS2:Al<sub>2</sub>O<sub>3</sub> = 27:64:9 in wt%))

Properties	Glasses		Sintering temperature (°C) for 1 h				Crystalline phases		
	CS1	CS2	860	880	900	920	<sup>a</sup> diopside	<sup>b</sup> anorthite	<sup>c</sup> alumina
Density (g/cm <sup>3</sup> )	2.8	2.7	2.87	2.83	2.64	2.66	2.8	2.71	3.92
CTE (10 <sup>-6</sup> /K)	6.7	5.1	5.2	5.0	5.2	4.8	10	4.82	8.2
Dielectric constant at 1 MHz (at room temperature)	8.26	8.57	5.51	6.20	6.23	6.92	7.1	6.2	9.8
Quality factor (MHz)	338	579	28	220	755	2,078	5,000	2,000	1,000
Porosity (%)	0	0	3.6	2.2	1.9	1.6	<5	<5	–

<sup>a</sup> diopside [10], <sup>b</sup>anorthite [17] and <sup>c</sup>alumina [18]



**Table 3** Dielectric constant of the empirical mixing rule [3, 21] and predicted the crystalline phases with the composites (Green sheets (CS1:CS2:Al<sub>2</sub>O<sub>3</sub> = 27:64:9 in wt%))

Sintering temperature (°C)	Dielectric constants × Volume fraction from Eq. 2					Dielectric constants		
	Diopside (7.1) [10]	Anorthite (6.2) [17]	Alumina (9.8)[18]	Residual glass		<sup>1</sup> ε	<sup>2</sup> ε	<sup>3</sup> ε
				<sup>1</sup> ε	<sup>3</sup> ε			
RT	–	–	0.69	7.88	7.88	8.57	–	8.57
860	0.08	4.09	0.65	0.77	2.22	5.68	5.51	7.04
880	0.57	3.87	0.7	1.16	1.90	6.32	6.20	7.04
900	0.5	3.89	0.69	1.23	1.96	6.33	6.23	7.04
920	0.43	3.97	0.07	2.44	1.95	7.02	6.92	6.42

<sup>1</sup> ε: dielectric constants of a sheet excluding porosity:  ${}^2\varepsilon = {}^1\varepsilon(1 - P) + P$  [17]

<sup>2</sup> ε: experimental dielectric constants

<sup>3</sup> ε: dielectric constant of residual glass: 8.47 for mother glass

and  $I_{\text{sheet(diopside)}}$  is the main peak area of XRD intensity for the sheet sintered as a function of temperature. The volume fraction of the crystalline phases can be predicted using that method.

The predicted volume fraction of the crystalline phases was used to calculate the dielectric constant with the widest empirical mixture rule [3, 21]. The dielectric constant of the residual glass was changed by the formation of the crystalline phase. In Table 3, the dielectric constant for the volume fraction of crystalline phases was calculated using the following Eq. 2:

$${}^1\varepsilon = \varepsilon_{\text{diopside}}V_{\text{diopside}} + \varepsilon_{\text{anorthite}}V_{\text{anorthite}} + \varepsilon_{\text{Al}_2\text{O}_3}V_{\text{Al}_2\text{O}_3} + \varepsilon_{\text{residualglass}}V_{\text{residualglass}} \quad (2)$$

where  ${}^1\varepsilon$  and  $\varepsilon$  are the total dielectric constants of the composite and the crystalline phase, respectively, and  $V$  is the volume fraction of the crystalline phase. If the crystalline phases have a fixed dielectric constant with previous results [8, 18], the dielectric constant of the residual glass for the sheet sintered at each temperature is in the range of approximately 2.94–10.57. However, the mother glasses (CS1 and CS2) have a dielectric constant of 8.26 and 8.57, respectively. Therefore, the dielectric constant of the mother glass is 8.47 using the empirical mixture rule. If the dielectric constant of the mother glass is unchangeable, the sheet sintered should be approximately 6.89, which is related to the crystalline phases. During crystallization, metal ions, which are highly polarized, should remain in the residual glass. Assuming that the dielectric constant of the residual glass maintained its mother glasses, the dielectric constant of the crystalline phases in the composites ranges from 3.29 to 4.97. Therefore, the dielectric constant depends on the amount of diopside and anorthite. The volume of the crystalline phases is correlated with the sheet properties such as mechanical, dielectric and thermal properties. For an LTCC substrate, the volume fraction of

the crystalline phase in the glass-ceramic material should be considered.

## Conclusion

The mechanical and dielectric properties of sheet composites of CS1, CS2 frits and alumina filler for potential applications as an LTCC substrate were investigated as a function of temperature. The mechanical and dielectric properties were found to be dependent on the porosity and volume of the crystalline phases. In the glass matrix, an increase in the volume of the diopside and anorthite resulted in an increase and decrease in the dielectric constant, respectively. For a low dielectric constant, the volume of the crystalline phase for anorthite in the glass matrix should be increased. These results suggest that the sheet is a good candidate as an LTCC substrate. However, the volume of the crystalline phases affects the dielectric constant of the composites.

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