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Sinterability, microstructure and properties of glass/ceramic composites

A.A. El-Kheshen[a,*], M.F. Zawrah[b]

[a]Glass Research Department, National Research Center, 12622 Dokki, Cairo, Egypt
[b]Refractory & Ceramics Department, National Research Center, 12622 Dokki, Cairo, Egypt

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Abstract

Two series of glass/ceramic composites, glass/mullite (MG) and glass/spinel (SG) were prepared from borosilicate glasses and mullite or magnesium aluminate spinel. Both composites contain 50, 60, 70, 80 wt.% borosilicate glass. The formation of cristobalite in the glass matrix of low firing glass/ceramic composite substrates limits the efficiency of the ceramic substrate when it is used in circuit boards. In the present study, addition of mullite or spinel to a borosilicate glass as a ceramic filler caused the diffusion of mullite or spinel constituents into the glass matrix and prevented the formation of a cristobalite. Spinel suppresses cristobalite formation more effectively than mullite, and results in lower dielectric constant and thermal expansion coefficients.

Keywords: B. Composite; C. Mechanical properties; D. Glass; Ceramic; Densification

1. Introduction

Great progress has been made during the last decade to increase the operational speed of large-scale integrated circuits (LSIs). The demand for microelectronic packaging technology to make use of LSIs has also been increased [1]. Co-fired multilayer ceramic circuit boards are considered one of the most promising technologies among all of the microelectronic packaging candidates [1–3].

Glass/ceramic composites which can be used in these ceramic circuits must possess such requisite properties as a low thermal expansion and low dielectric constant. These properties make possible the high density direct mounting of bare LSI chips as well as high-speed signal propagation [4,5]. Furthermore, the lowering of sintering temperature through the use of glass make it possible to co-fire with low resistance conductors such as gold and copper [6]. In some cases, however, devetrification in the glass phase makes it difficult to obtain the required properties. Also, cristobalite precipitation in the composite which takes place during firing, makes the composite more difficult to densify because the composite is more viscous than the single-phase glass [1].

Glass/mullite and glass/spinel composites which consist of borosilicate glass and mullite or spinel, respectively, are expected to suppress cristobalite precipitation as they contain aluminium ions which are responsible for the inhibition of cristobalite formation.

A typical glass component in the composites system is borosilicate glass. The reasons are (a) its low softening temperature (820°C), which is assumed to mainly decide the sintering temperature of the glass/mullite and glass/spinel composites, (b) its superior chemical resistance property, (c) its lower dielectric constant (4.8 at 1 MHz) and lower thermal expansion coefficient ($3.0–4.8\times10^{-6}$/°C) than that of ceramics, and (d) its ease for mass production [7, 8].

In the present work, we investigate the addition effect of ceramics containing-Al ions, like mullite ($3Al_2O_3{\cdot}2SiO_2$) and spinel ($MgO{\cdot}Al_2O_3$) to borosilicate glass on suppression of cristobalite precipitation which affects on thermal expansion, dielectric constant and hardness of borosilicate glass/ceramic composites to be applied in electronic devices.

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* Corresponding author. Fax: +20-2-337-0931.
E-mail address: aelkheshen1@hotmail.com (A.A. El-Kheshen).

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2. Experimental procedures

2.1. Preparation of glasses and ceramic materials

For the glass system, one kind of borosilicate glass system (SiO_2–B_2O_3–Na_2O) was adopted as given in Table 1. The raw materials used for glass preparation were SiO_2, H_3BO_3 and Na_2CO_3 as pure chemicals, and the respective batches prepared in the required composition were melted in a platinum crucible for 1 h at 1500–1550 °C in an electric furnace. The melt was rapidly quenched in water, crushed and ground into fine glass powders.

1:1 mole ratio of 99% pure α-alumina and magnesia were sintered at 1550 °C for 1 h to obtain magnesium aluminate spinel (MA). Mullite ceramic material was prepared by firing 3:2 mole ratio of pure alumina and fumed silica (which produced as a by-product from ferrosilicon alloy industries) at 1550 °C for 1 h. The mullite ceramic contains a small amount of cristobalite as unreacted silica. The chemical analysis of glass and ceramic starting materials are summarized in Table 1.

2.2. Preparation of glass/ceramic composites

Fine glass powders as above prepared were well mixed with spinel or mullite. Eight composite batches for both mullite and spinel were designed as MG5, MG6, MG7, MG8, and SG5, SG6, SG7, SG8, respectively their batch compositions are summarized in Table 1. The mixed batches were uniaxially pressed at 60 MPa in a disc shape of about $\frac{1}{2}$ inch diameter and height. The pressed batches were then fired for 1 h in air at 900–1100 °C.

2.3. Properties of glass/ceramic composites

Apparent porosity and bulk density for the sintered samples of glass/ceramic composites were measured by the Archimedes method. The bulk density was used to calculate the relative density, where the theoretical density of each batch composition was calculated by mixture rule. Identification of crystalline phases was carried out by X-ray diffraction (XRD) analysis using a Philips Powder Camera (Type CPM 9920/02) with CuK_α radiation and Ni filter. The microstructure of the sintered composites were observed by a scanning electron microscope (SEM: GEOL, XL30). Hardness was also measured.

The dielectric constant of the fired composites was measured at 1 MHz. The samples were prepared in the form of discs of 10mm in diameter and 1–2.4 mm thick by cutting of sintered bodies. Philips R.L.C bridge type PM 6304 programmable automatic RLC meter was used for measuring the dielectric constant (ε^-) at room temperature.

The thermal expansion coefficient (TEC) in the temperature range from room temperature to 700 °C was measured at heating rate 5 °C/min using a dilatometer system type Linseis model 76/1250.

Table 1
Chemical and batch compositions of glass and glass/ceramic composites

Chemical composition (wt.%)			Batch composition (wt.%)			
Oxides	Glass	Fumed silica (F.S)	Samples	Glass	Mullite	Spinel
SiO_2	80.5	96.85	MG5	50	50	–
B_2O_3	12.9	–	MG6	60	40	–
Na_2O	3.8	0.45	MG7	70	30	–
Al_2O_3	2.2	1.02	MG8	80	20	–
K_2O	0.4	0.54	SG5	50	–	50
CaO	0.2	0.69	SG6	60	–	40
Fe_2O_3	–	0.22	SG7	70	–	30
MgO	–	0.23	SG8	80	–	20

3. Results and discussion

3.1. Sintering process of the composites

In glass and glass-ceramic systems, sintering takes place by the viscous flow of a glass phase [9]. Liquid phase sintering mechanisms are classified by three stages: glass redistribution, solid-particle rearrangement and viscous flow of liquid-phase glass [10].

The desired characteristic of glass/ceramics are achieved by sintering to full densification. Viscous sintering of glass and glass/ceramic composite systems with rigid inclusion has been studied by several researchers [11–13] .

Rabinovich [10] has suggested also that only glasses with slow rates of surface crystallization can densify by sintering.

In contrast, Budd [14] has reported that, the completion of sintering prior to commencement of crystallization is not always a prerequisite for attaining high final density.

Fig. 1 (a,b) shows the relation between sintering temperature and the relative density as well as apparent porosity (open pores) of glass/ceramic composites fired at 900–1100 °C. It appears that the relative density of glass/mullite and glass/spinel composites increased gradually up to 97.2 and 94.3, respectively, with the increasing of the sintering temperature up to 1100 °C. The apparent porosity, however decreased near zero at 1000 °C for MG7, MG8, SG7 and SG8 and at 1100 °C for MG5, MG6, SG5 and SG6. These can be explained by considering that, the composites are densified increasingly with the increasing of sintering temperature so, the open pores disappear, as the closed pores increase with the increasing of firing temperature.

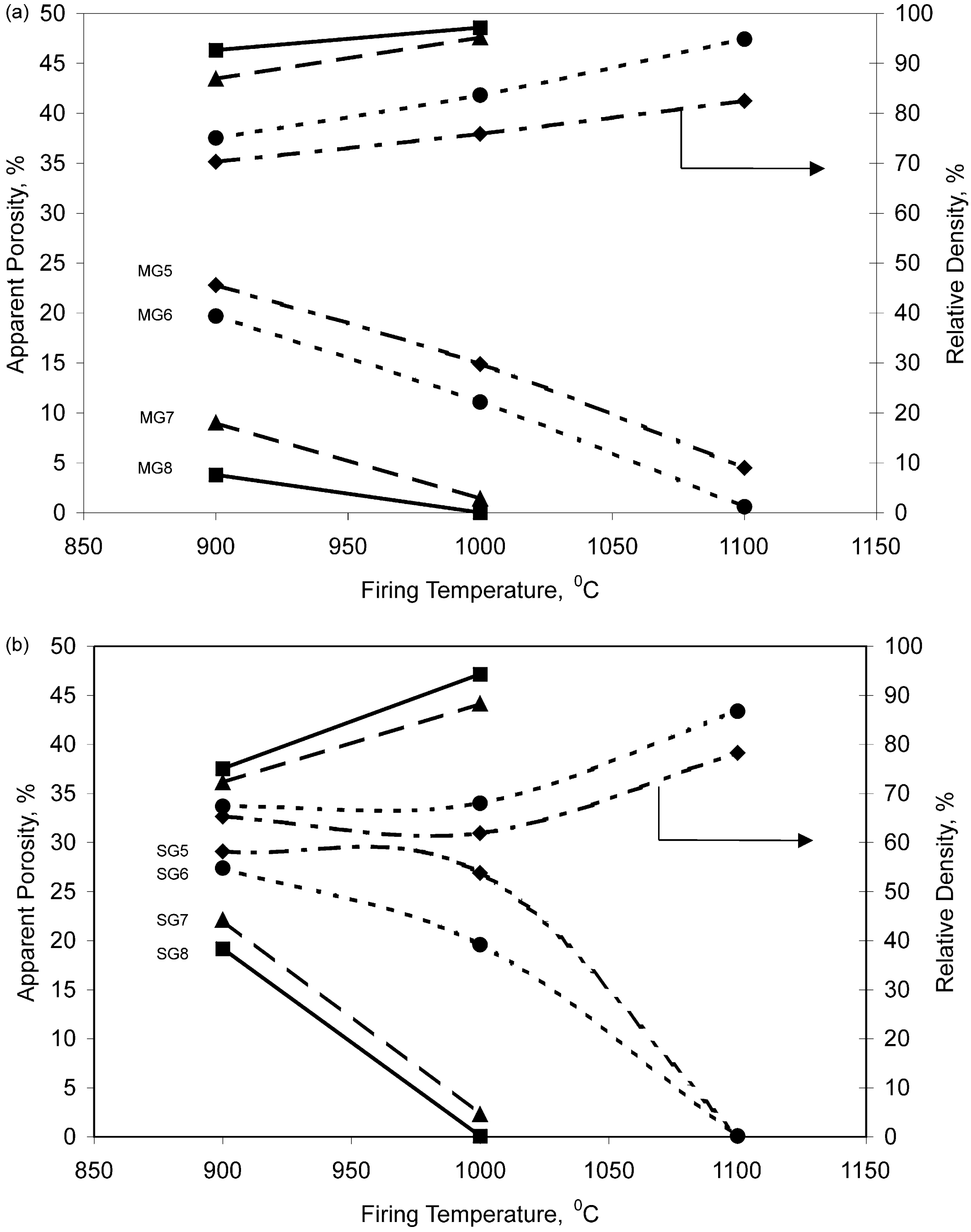

Fig. 1. (a) Relative density and apparent porosity of sintered glass/mullite composites after firing at different temperatures; (b) relative density and apparent porosity of sintered glass/spinel composites after firing at different temperatures.

The densification mechanism of both MG and SG can be explained as liquid-phase sintering by considering that mullite or spinel powders are uniformly dispersed in the glass phase matrix as the wettability between the glass and ceramic powder is good [15]. From Fig. 1 we can deduce that the specimen with highest mullite or spinel content (i.e. 40 and 50 wt.% for each) showed their highest density at firing temperature 1100 °C but composites containing 20 or 30 wt.% ceramics densified at 1000 °C, and showed the highest density in four samples due to the higher content of liquid phase.

3.2. Phase composition and microstructure

3.2.1. Glass/mullite composites

Fig. 2 shows the X-ray diffraction pattern (XRD) of a glass/mullite system. As previously mentioned, we used a fumed silica, for mullite preparation. A small amount

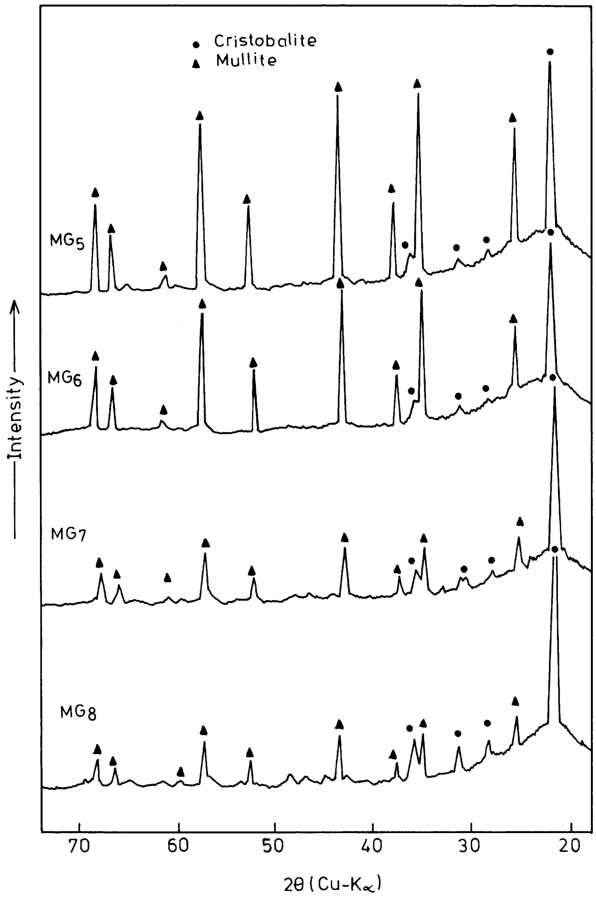

Fig. 2. XRD of glass/mullite composites sintered at (MG5 and MG6) 1100 °C and (MG7 and MG8) 1000 °C.

of this silica in the form of cristobalite is still unreacted during the formation of mullite, so the effect of mullite on suppression of cristobalite phase (produced from crystallization of glass) in the glass/mullite system, is very low. As show in Fig. 2, cristobalite phase has been slightly decreased with the increase of mullite contents up to 40 wt.% i.e. from MG8 to MG6 due the suppression effect of mullite on cristobalie formation. On the other hand, in the sample which contains 50 wt.% (MG5) of mullite, high intensity cristobalite peaks is appeared due to the presence of excess crystobalite in mullite-forming material (i.e. unreacted silica). The intensity of mullite peaks increases as the mullite content increase i.e. from MG8 to MG5.

Microstructural change during sintering was also studied. The sintering mechanism of the system is liquid-phase sintering. Various microstructures were examined, to study sintering phenomena. Fig. 3 shows the photomicrographs of the composites MG5 and MG6 sintered at 1100 °C, as well as MG7 and MG8 sintered at 1000 °C. It appears that the cristobalite (round shaped) was observed in all the photos, their amounts begin to decrease by increasing the mullite content, and increases again as the mullite content reaches 50%. At low firing temperature and low ceramic content, shaped pores were observed in the glass matrix (dark). For higher firing temperature, the pores in the glass matrix formed almost an ideal sphere as shown in Fig. 3. These results suggest that some sort of gases are generated from the inside of composite during firing, and that spherical pores are formed by these gases [16].

3.2.2. *Glass/spinel composites*

Fig. 4 shows the XRD results in the spinel/glass system, i.e. SG7 and SG8 samples which contain 30 and 20 wt.% spinel ceramic and fired at 1000 °C as well as SG5 and SG6 samples contain 50 and 40 wt.% spinel ceramic, fired at 1100C°. Both spinel and cristobalite phases are detected in all composite batches. By increasing the spinel content in composite, cristobalite peaks at around 22° decrease dramatically. This means that, the addition of spinel suppresses cristobalite precipitation. Past studies [17,18] have shown that alumina, aluminum nitride and cordierite inhibit cristobalite precipitation. The present results show also strong support for the belief that the Al ion is responsible for cristobalite suppression.

Fig. 5 exhibits the scanning electron micrographs of spinel/glass composites, from which we can deduce that, as the spinel content increase the cristobalite formation (round shaped) decreases. At 1000 °C and low ceramic content i.e. 20 and 30 wt.%, the photomicrographs of the composites SG7 and SG8 show softening and fluidizing of borosilicate glass particles bonding each other. Also some pores are observed in the glass matrix (SG7 > SG8) with the appearance of rounded grains of cristobalite phase started to crystallize. Their amounts increase from SG7 to SG8. By increasing the amount of added spinel and firing temperature up to 1100 °C as in SG5 and SG6, the rounded cristobalite crystals are generally lower than that fired at 1000 °C with the increasing of pores in SG5 than SG6. At the same time their amounts decrease from SG6 to SG5. The cristobalite crystals are distributed throughout the entire glass matrix. These results are confirmed by the X-ray patterns discussed previously.

However, the cristobalite suppression also depends on the specific nature of the ceramic additive material. In our work, mullite ceramic is less effective on suppression of cristobalite formation than pure spinel. This is due to the presence of some unreacted silica in the form of cristobalite phase in the mullite raw material which increase the total amount of cristobalite present in mullite or produced from the crystallization of glass. These results can be explained in Fig. 6 which shows the relation between the ceramic content and cristobalite peak intensity as detected from XRD.

3.3. *Properties of glass/ceramic composites*

3.3.1. *Thermal expansion*

Table 2 summarizes the measured properties of MG and SG composites after sintering at 1000 and 1100 °C.

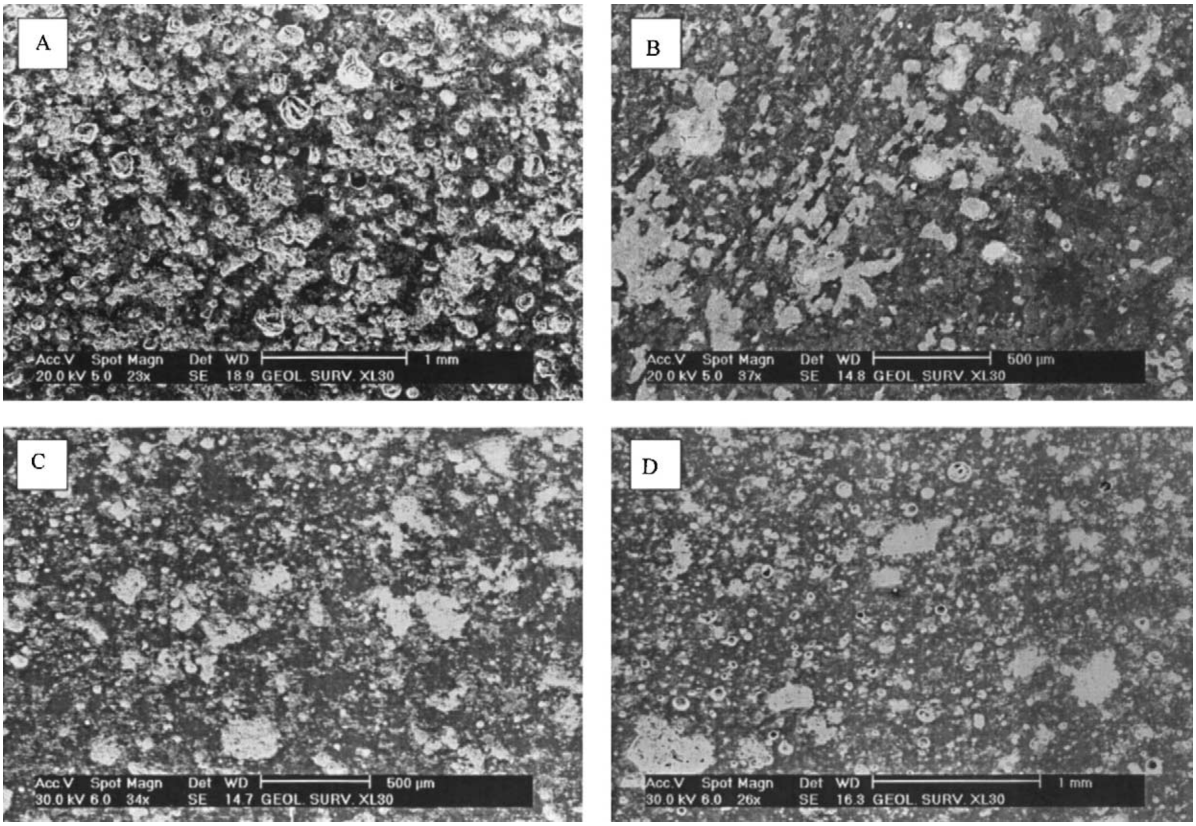

Fig. 3. Photomicrographs of glass/mullite composites: (A) MG5, (B) MG6, (C) MG7, (D) MG8.

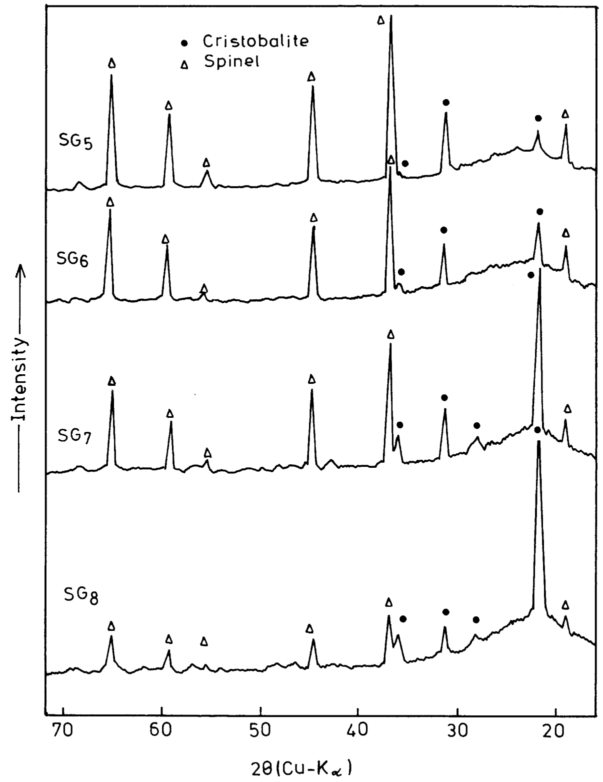

Fig. 4. XRD of glass/spinel composites sintered at (MS5 and MS6) 1100 °C and (MS7 and MS8) 1000 °C.

At low ceramic additive levels, the thermal expansion coefficient (TEC) of the composite is dominated by the volume fraction of cristobalite precipitation. Because the thermal expansion coefficient of cristobalite is high, the TEC of the composites with the presence of cristobalite exhibits much higher values than the value expected by a mixture rule using the original raw material volume fractions and properties [1]. From Table 2, it appears that the thermal expansion behavior of both glass/mullite and glass/spinel composites at 700 °C decreases with increase of mullite or spinel content due to the suppression of cristobalite formation. Except for the MG5, its TEC is relatively higher than that of MG6 and MG7 due to the presence of the high percent of cristobalite phase (Fig. 6). In some cases, devetrification in glass phase makes it difficult to obtain the required properties. In particular, it is thought that cristobalite is an unfavorable transformation product in terms of thermal expansion behavior. Cristobalite transforms from α- to β-cristobalite structure around 200 °C. This transformation causes a large volume change and provides much higher thermal expansion than expected from the mixture rule, and moreover, sometimes causes microcrak formation during cooling. Also, cristobalite precipitation in the composites makes more difficult to densify. Thus, it is desirable that borosilicate glass remains in the amorphous state during and after firing i.e. not crystallize to cristobalite.

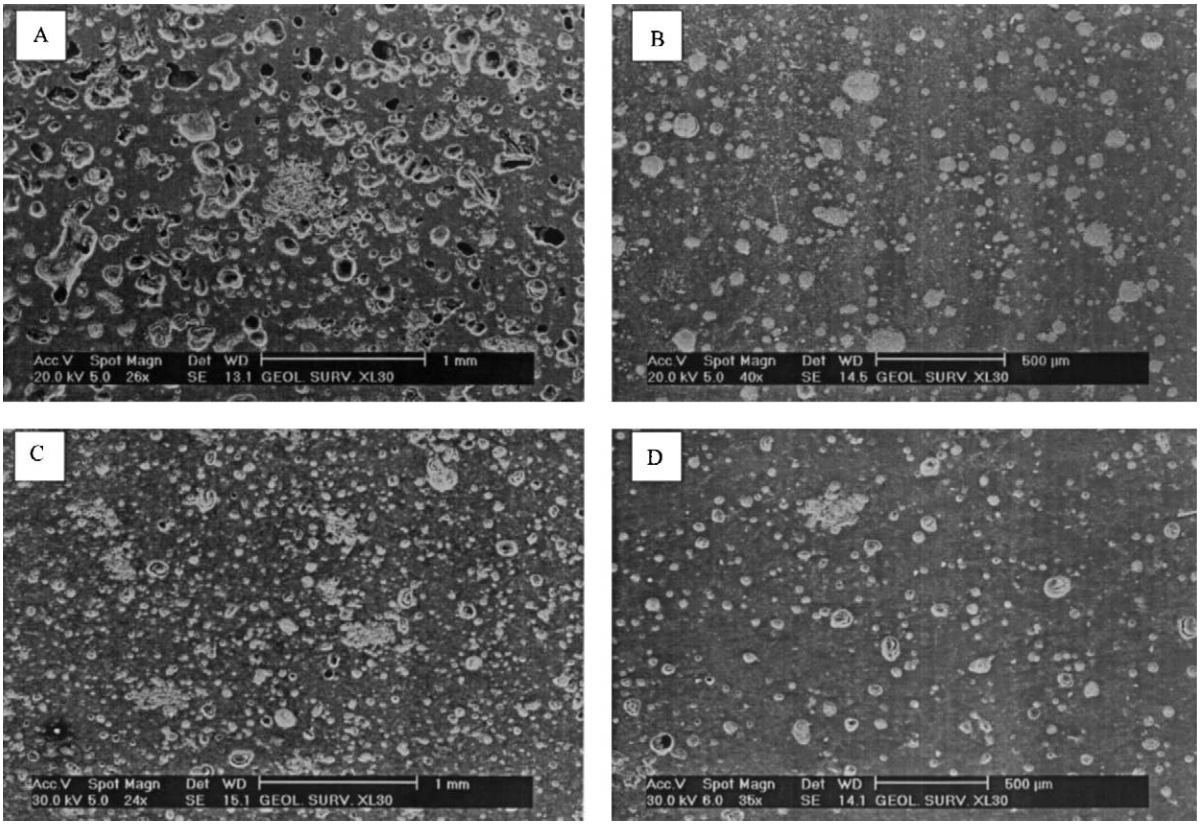

Fig. 5. Photomicrographs of glass/spinel composites: (A) SG5, (B) SG6, (C) SG7, (D) SG8.

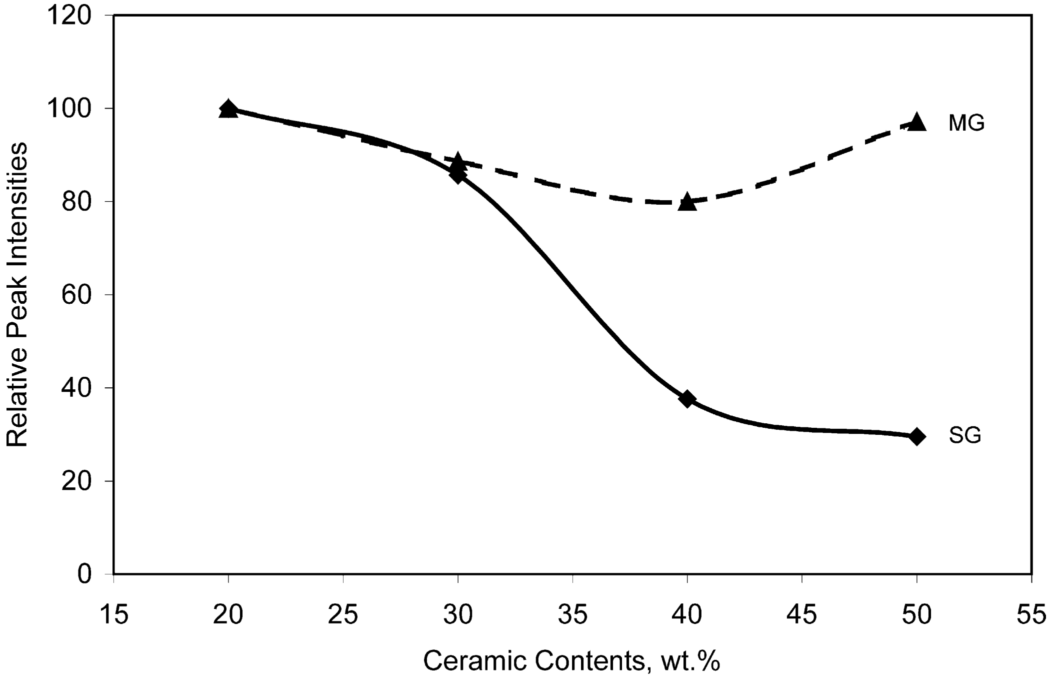

Fig. 6. Cristobalite peak intensity (at $2\theta = 22°$) as related to ceramic content.

3.3.2. Dielectric constant

A demand for high-speed signal propagation in computer and communications systems has resulted in major progress in the fields of LSIs and circuit boards. To enable high-speed switching of large-scale integrators (LSIs) in a system, the circuit boards should have a low dielectric constant, thus allowing the high-speed signal to propagate with a shorter delay [19,20]. As far as the dielectric constant is concerned, one of the most useful way to obtain a lower dielectric constant is by increas-

Table 2
Properties of sintered glass/ceramic composites

Samples	Composites properties		
	Hardness (kg/mm^2)	Dielectric constant at 1 kHz	T. E. C. at 700 °C $\times 10^{-6}$
MG5	606	6.6	7.0
MG6	606	6.0	6.0
MG7	464	5.5	6.8
MG8	432	5.0	7.5
SG5	642	6.0	4.8
SG6	620	5.4	5.1
SG7	603	5.0	6.2
SG8	583	4.6	7.3

ing the glass content i.e. decreasing the ceramic content in the glass/ceramic composites. Therefore, preventing cristobalite precipitation and decreasing the ceramic content in the composite are regarded as the prime requirement for glass/ceramic composites used for packaging application. Table 2 shows also dielectric constant of both glass/mullite and glass/spinel composites. The dielectric constant increases as the ceramic content increases. Because glass and cristobalite have nearly equal dielectric constants, the formation of cristobalite has little effect on the values of the dielectric constant of the composites [8].

3.3.3. Hardness

Some crystal phases, even when present in only a small volume fraction seem to result in marked enhancement of hardness. Table 2 shows the hardness of the borosilicate glass/spinel and mullite composites. As the ceramic content increase, the hardness is linearly increase due to the higher hardness of both ceramics than that of glass used, since the hardness of low expansion borosilicate glass is 442 kg/mm^2 [21]. It also appears that the hardness of glass/spinel composites is higher than that for glass/mullite composites, because the spinel ceramic has higher hardness than that of mullite ceramic.

4. Conclusion

Materials with low dielectric constant, and low sintering temperatures, were studied for application to future high-speed circuit boards. A glass/ceramic composites is one of the most effective materials for producing low dielectric constant and low sintering temperatures. We examined the effect of ceramic-containing Al ions addition, such as mullite and spinel, into the borosilicate glass on suppression of cristobalite precipitation, which would increase the thermal expansion coefficient (TEC).

In glass/mullite composites, as the mullite content increases the cristobalite phase decreases and begins to increase again in the sample contains 50 wt.% of mullite. In glass/spinel system, as the spinel content increases the intensity of the cristobalite peaks decreases. Both systems have low dielectric constant and thermal expansion, but the spinel is much effective than mullite.

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