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Effect of cristobalite formation on sinterability, microstructure and properties of glass/ceramic composites

M.F. Zawrah[a,*], E.M.A. Hamzawy[b]

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

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Abstract

Six glass/ceramic composite materials were prepared from pure alumina and borosilicate glass (BSG) with chemical composition of 99.0 Al_2O_3 and 80.5 SiO_2, 12.9 B_2O_3, 3.8 Na_2O, 2.2 Al_2O_3, 0.4 K_2O and 0.2 CaO wt.%, respectively. These batches were sintered at different firing temperatures up to 1300 °C. XRD, microstructure and properties, namely thermal expansion, dielectric constant and hardness of prepared composites were examined, respectively. The results reveal that the crystallization of borosilicate glass in glass/alumina composite can be prevented by varying the alumina content in the glass matrix, by which the diffused aluminum ion change the structure of glass. When approximately $\geqslant 30$ wt.% of alumina filler is added, the structure of glass changes enough to decrease the formation of cristobalite crystals and consequently decrease the thermal expansion coefficient and dielectric constant. In glass/alumina system, phase formation is influenced by firing temperature and alumina content as follows: (a) when alumina content and firing temperature are low, the precipitated phase is cristobalite, (b) at high temperature and high alumina content, mullite is formed in the glass phase. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Cristobalite; Sinterability; Microstructure properties; Glass/ceramic composites

1. Introduction

Many engineering materials contain multiple phases among these, there are composites in high degree of technological development during the last decade [1]. The properties of multiphase systems depend on the properties and amount of each phase present. In glass/ceramic composites, for example, the composition and percentage of the crystalline phase present can determined not only the microstructure of the material, but the composition of the residual glass [2,3].

Glass/alumina composites which consist of borosilicate glass and alumina are expected as useful substrate materials for integrated circuits (IC), because they can be densified at low temperature and can get the properties of low dielectric constant and thermal expansion coefficient close to that of silicon [4,5]. In addition, the properties of the dielectric constant and thermal expansion coefficient can be controlled easily by changing the components and composition because they are not precipitated with secondary crystalline phases. At the beginning of the 1980s, glass/ceramics composites were noted as substrate materials for electronic devices because of the properties described above, and a lot of reports were presented on dielectric constant, thermal expansion property, and mechanical strength of various kinds of composites [6].

A typical glass component in the composites system is borosilicate glass. The reasons for this are (a) its low softening temperature (820 °C), which is assumed to mainly decide the sintering temperature of the glass/alumina composites, (b) its superior chemical resistance property, (c) its lower dielectric constant and lower thermal expansion coefficient than of alumina, and (d) its ease for mass production. In any kinds of glasses adopted, however, the constituents and composition have not been clarified, the characterization of glass/alumina composites or the glass themselves have not been sufficiently clarified [7].

The objective of the present work is to study sinterability, microstructure as well as thermal expansion, dielectric constant and hardness of borosilicate glass/alumina composites used in electronic devices.

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* Corresponding author. Fax: +20-2-3370931.
E-mail address: mzawrah@hotmail.com (M.F. Zawrah).

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2. Experimental procedure

2.1. Preparation of glasses

For the glass system of the studied composites, 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 those glasses were SiO_2, H_3BO_3 and Na_2CO_3 as pure chemicals, and the respective batches prepared in the required composition were placed in a platinum crucible and fused for 1 h at 1300–1550 °C in an electric furnace. The melt was rapidly quenched in water and crushed into fine glass powder by a ball mill.

2.2. Preparation of glass/alumina composites

99% Pure α-alumina with mean particle size >100 μm and the fine glass powders as above prepared were well mixed and semi-dry pressed uniaxially at 60 MPa in a disc shape of about $\frac{1}{2}$ inch diameter and height. The pressed batches were then fired for 5 h in air at temperatures in the range 600–1300 °C. Table 1 shows chemical composition of the prepared borosilicate glass as well as the batch compositions of the prepared composite, which designed as C1, C2, C3, 54, C5 and C6 batches.

2.3. Evaluation of properties of glass/alumina composites

Using the fired samples of glass/alumina composites, apparent porosity and bulk density were measured by the Archimedes method. The measured bulk density were used to calculate the relative density after calculating the theoretical density of each composition 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 and microanalysis of the sintered composites were observed by a scanning electron microscope (SEM: GEOL, XL30) attached with EDS unit. As a respective electrical property of the fired composites, the dielectric constant at 1 MHz was measured by BK precision 878 LCR meter. The sintered pellets were painted with silver paste on two surfaces and fired to form an electrode [8]. The mean thermal expansion coefficient (TEC) in the temperature range from room temperature to 800 °C at heating rate 10 °C/min was measured using a dilatometer system type Linseis model 76/1250. The mechanical property by means of hardness was also measured.

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

Chemical compositon (wt.%)			Batch composition (wt.%)		
Oxides	Glass	Alumina	Samples	Glass	Alumina
SiO_2	80.5	–	C1	95	5
B_2O_3	12.9	–	C2	90	10
Na_2O	3.8	–	C3	80	20
Al_2O_3	2.2	99.8	C4	70	30
K_2O	0.4	–	C5	60	40
CaO	0.2	–	C6	50	50

3. Results and discussion

3.1. Sintering of the composites

It has been previously shown that the densification of glass/ceramic composites can be described by conventional three-stage liquid phase sintering [9–15] i.e. particle rearrangement, dissolution and precipitation, and solid state sintering. Depending upon the reactivity between glass and ceramic, the densification of glass + ceramic can be further classified as nonreactive, partially reactive, and completely reactive systems. Little dissolution of ceramic filler in glass during firing is observed for nonreactive systems, such as borosilicate glass (BSG) + cordierite [14] in which the densification is mainly achieved by particle rearrangement. The required amount of glass content to achieve densification decreases with increasing the particle size ratio between the ceramic filler and glass [16]. For partially reactive systems such as BSG + alumina [9], the dissolution of the ceramic filler in glass is localized and limited, and no particle growth and shape accommodation are observed. The required BSG content to achieve densification is close to that of nonreactive systems such as BSG + cordierite [14,15]. A global dissolution of ceramic filler in low softing glass is found for completely reactive systems including BSG + high silica glass [16], in which the required BSG content i.e. 20–40 vol.%, to obtain high densification is much lower than that needed for nonreactive and partially reactive systems i.e. 40–60 vol.% [14,15]. A lower and slower densification results when larger BSG or ceramic filler particle is used for a completely reactive system [9].

Fig. 1a and b shows the relationship between firing temperature and the relative density and apparent porosity of glass/ceramic composites fired at various temperatures in the range from 700 to 1300 °C. It appears that the relative density increases gradually in samples C1, C2, C3 and C4 with the increasing of firing temperature in the range below 1100 °C, but decreases in the range above 1100 °C. At the same time the samples C5 and C6 still need a higher temperature to complete their densification, this is due to their higher content of Al_2O_3 than the former samples.

Apparent porosity, however, decreases with the increase of firing temperature until becoming near zero at 1100 °C in C1, C2, C3 and C4, and staying zero at temperatures beyond that temperature. These results suggest that the composites are densified increasingly

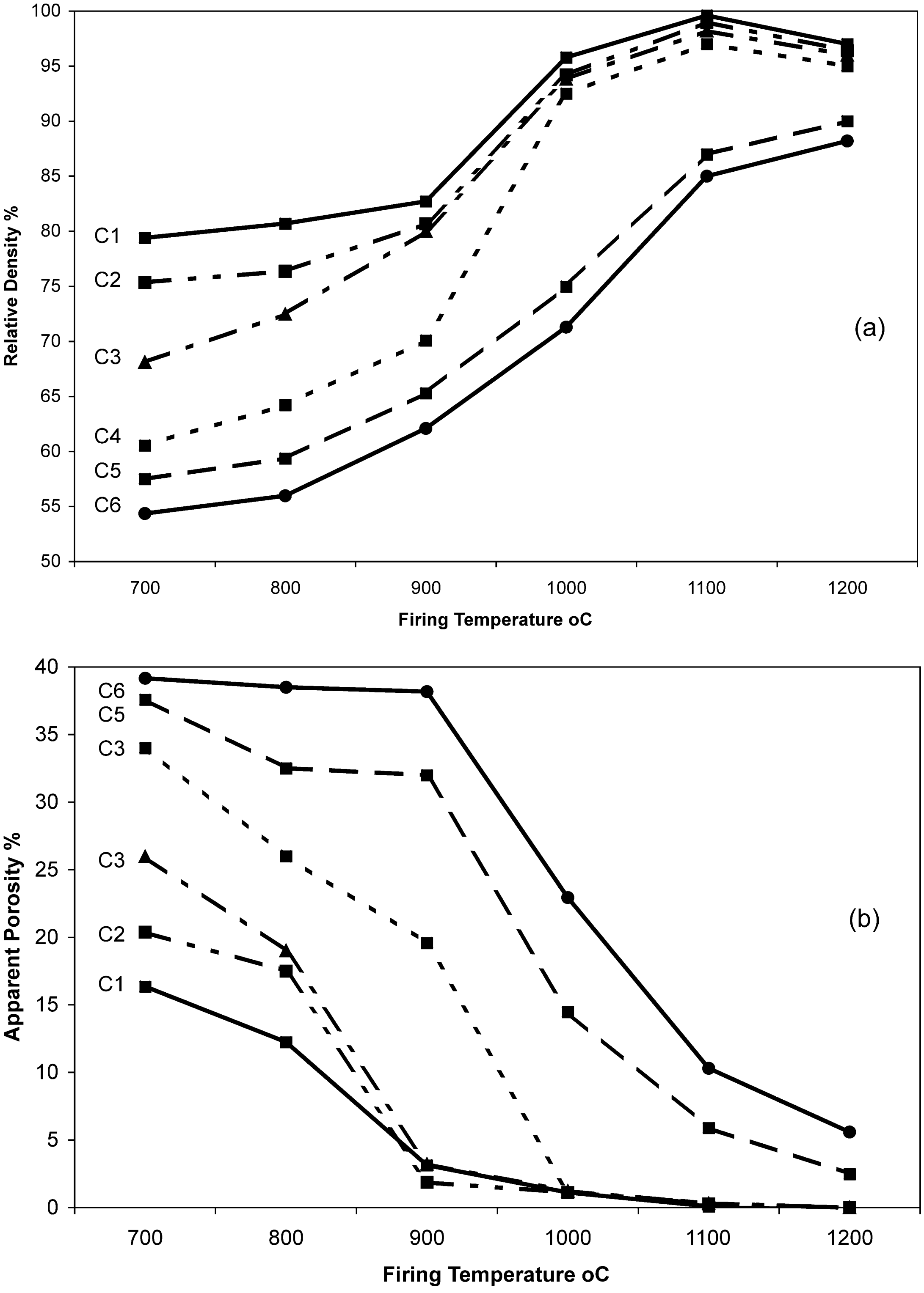

Fig. 1. Relative density and apparent porosity of sintered glass/ceramic composites after firing at different temperatures.

with the increased firing temperature in the range below 1000 °C, and open pores in the composites disappear, whereas closed pores increase with the increase of firing temperature in the range above 1000 °C.

The densification mechanism of glass/alumina composites can be explained as liquid phase sintering, the alumina powder is uniformaly dispersed in the glass matrix and the wettability between the glass and ceramic powder is essential to densification. A suitable amount of glass gives high density and strength. An optimum firing point for maximum densification may also exist for each glass/ceramic ratio [17]. Also from

Fig. 1, the amount of alumina content varied between 5 and 50 wt.% as going from C1 to C6. With an alumina content ⩾40 wt.% i.e. in C5 and C6, the optimum firing point is more than 1300 °C. Density increases quickly above 900 °C, with alumina content between 5 and 30 wt.%. The specimen with highest alumina content, however, shows little change in density. The samples C1, C2, C3 and C4 which contain 5–30 wt.% alumina have a relative density ⩾98% when fired at 1000–1100 °C, but C5 and C6 show 70–85% at that temperature.

3.2. Phase compositions

According to the glass phase formation diagram (Fig. 2) in glass/alumina composites determined by Yoshihiko et al. [18], cristobalite is precipitated when alumina content is low in the composites and the firing temperature is also low. Mullite formation appears in the composite at high alumina content and high firing temperature. For the broad remainder of the condition, only the amorphous glass phase appears for the firing condition of 5 h. The critical composition limit for preventing cristobalite is between 4.7 and 5.9 vol.% of alumina content. Mullite, alumina and the remaining glass phase are, therefore, all present in this composite.

XRD results of glass/alumina composites fired at 1000 °C are shown in Fig. 3. The cristobalite and alumina peaks are detected in all glass/alumina composites. The cristobalite peaks disappeared gradually as a result of increasing of alumina-filler content. The lowest amounts of cristobalite are obtained after addition of 30, 40 and 50 wt.% of alumina i.e. C4, C5 and C6. Whereas Fig. 4 shows XRD of glass/alumina composites C3 and C4 fired at 1100 °C as well as C5 and C6 fired at 1300 °C. The crystallization of cristobalite phase in C3 and C4 increases by firing up to 1100 °C. Mullite phase appears as new phase in C5 and C6 with disappearance of cristobalite phase in C5. Although cristobalite is not expected to form in C6 at equilibrium state, several experimental results obtained during diffusion experiments indicate that SiO_2 present in a SiO_2-mullite coexistence region transforms into cristobalite [18–23].

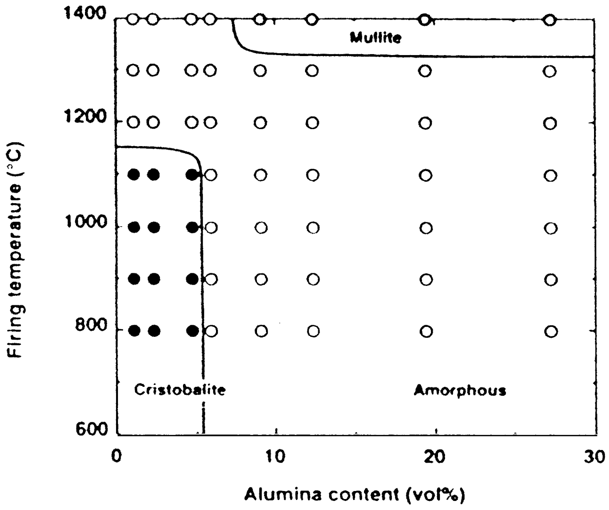

Fig. 2. Glass phase formation in glass/ceramic composites.

3.3. Microstructure

Microstructural change during sintering is also studied. As previously mentioned, the sintering mechanism of this system is liquid-phase sintering. Various microstructures

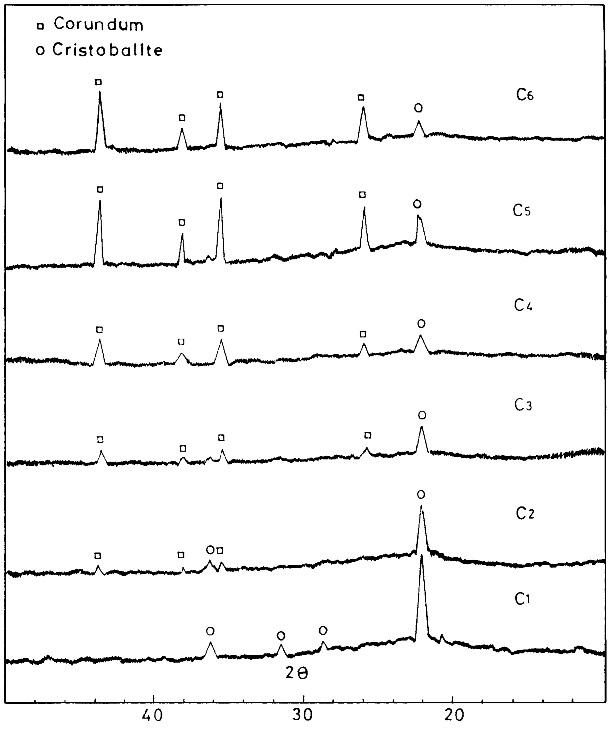

Fig. 3. XRD of sintered glass/ceramic composites at 1000 °C.

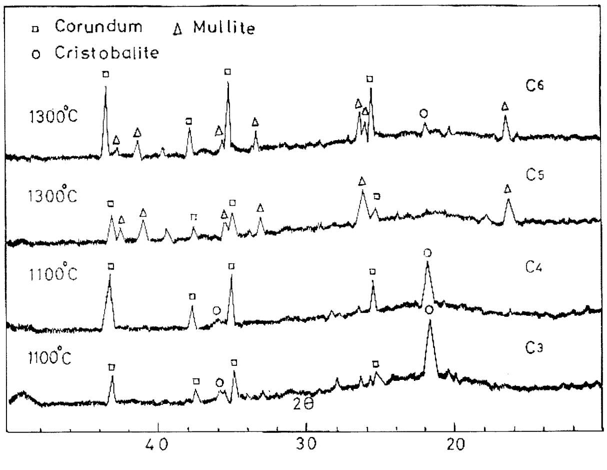

Fig. 4. XRD of sintered C3 and C4 at 1100 °C as well as of C5 and C6 sintered at 1300 °C.

are examined, to study sintering phenomena. At low temperature, i.e. 900 °C, the photomicrographs (Fig. 5) of the composites C1, C2 and C3 show softening and fluidizing of borosilicate glass particles while beginning to bond to each other. Also different shaped and unshaped pores are observed in the glass matrix with the appearance of rounded grains of cristobalite phase which started to crystallize, and their amounts increase from C1 to C3. By increasing the firing temperture up to 1000 °C, as shown in Fig. 6, the amount of rounded cristobalite crystals are generally higher than that fired at 900 °C. At the same time their amounts decrease from C1 to C6, and almost disappear in C6 with the formation of rounded open pores. The cristobalite crystals are distributed throughout the entire glass matrix. Decreasing the crystallization in these composites is prevented by the diffusion of aluminum ions into the glass matrix because it acts as a network former in the glass. These results are supported by Imanaka et al. [18] who investigated the effect of preventing borosilicate glass crystallization by the addition of various typs of ceramic fillers. Those researchers concluded that aluminum-ion-containing ceramic fillers such as alumina, aluminum nitride and mullite can prevente cristobalite formation in the glass matrix. Generally, the homogeneity and diffusion between glass and alumina in the composites fired at 1000 °C are more significant than that fired at 900 °C which lead to a pore decrease and consequently a relative density increase. We assume that the decrease of relative density of C5 and C6 is due to their higher content of alumina and may be related to the evolution of the spherical closed pores inside the composite. The rounded cristobalite crystals in the composite microstructure (Fig. 6) are provided by EDS analysis (Fig. 7) and by XRD as shown previously in Fig. 3. A ceramic composition that will densify at such low firing temperature as 1000 °C is possible with glass/ceramic materials. Crystallization during firing changes the TEC dramatically, thus resulting in a material far from suitable for the high-density packaging of large-scale integrators (LSIs).

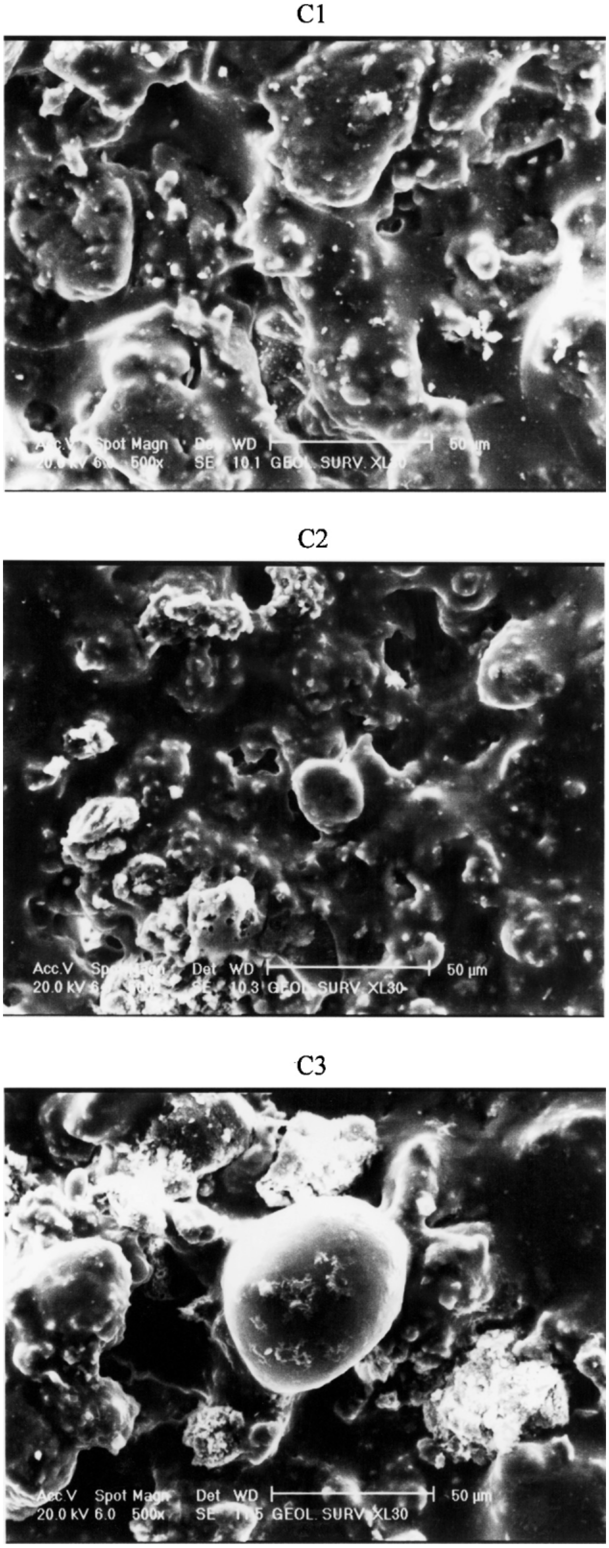

Fig. 5. Photomicrographs of C1, C2 and C3 composites sintered at 900 °C.

3.4. Properties of glass/alumina composites

Table 2 summarizes measured properties of G/A composites after sintering at 1000 °C. The decrease of the thermal expansion coefficient is directly related to the cristobalite suppression. As previously mentioned, cristobalite formation decreases from C1 up to C6 as the glass content decreases; therefore, at low ceramic additive levels, the TEC of the composites is dominated by the volume fraction of cristobalite formation. Because the TEC of cristobalite is high, the TEC of the composites with the presence of cristobalite exhibits much higher values than that expected by a mixture rule using the original raw materials volume fractions and properties. In the region where cristobalie formation is suppressed (more than 5.9 vol.%) the variation in TEC of the composites follows a linear curve determined by the mixture rule. In some cases, devitrification in the

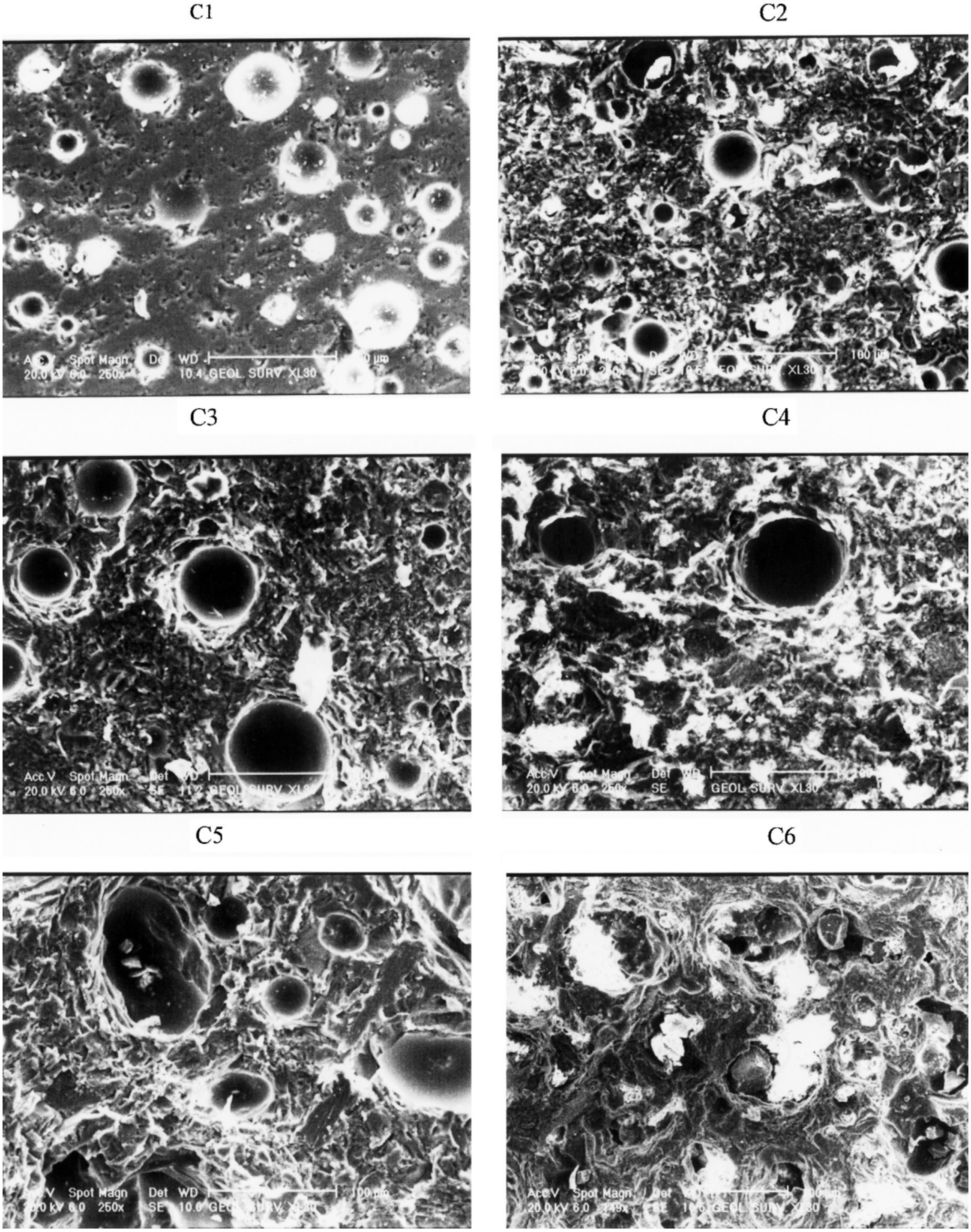

Fig. 6. Photomicrographs of glass/ceramic composites sintered at 1000 °C.

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 leads to a more difficult densification because the composite is more viscous than the single-phase. Thus, it is desirable that borosilicate glass remains in the amorphous state during and after firing.

As far as the dielectric constant is concerned, one of the most useful ways to obtain a lower dielectric constant

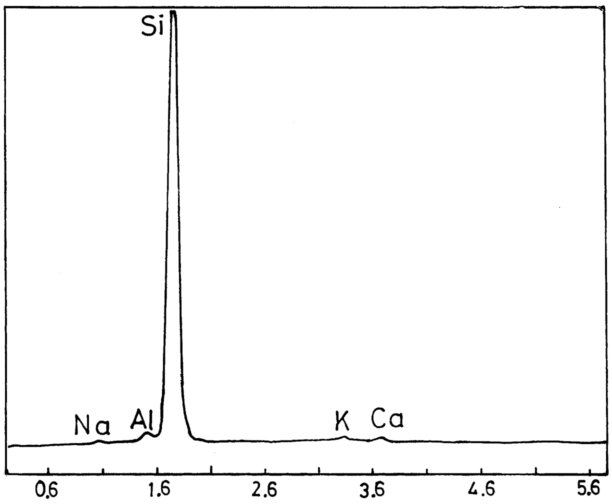

Fig. 7. EDS analysis of rounded crystals in the glass/ceramic composites.

Table 2
Properties of sintered glass/ceramic composites

Samples	Composites properties		
	T.E.C. at 300 °C $\times 10^{-6}$	Dielectric constant at 1 kHz	Hardness kg/mm^2
C1	9.2	6.8	595
C2	7.0	6.3	642
C3	7.0	5.8	772
C4	4.9	5.2	681
C5	4.5	6.4	–
C6	4.6	7.2	–

is by increasing 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 glass/alumina composites. The data sets closely follow the simple mixture rule. That is to say as the alumina content increases, the dielectric constant increases linearly. Assuming the dielectric of alumina and glass used in this study are 10 and 4.1, respectively, the dielectric constant dependence on the ceramic content can be expressed as $\varepsilon = 5.9V + 4.1$ for alumina/glass system, where ε is the dielectric constant of the composite and V is the ceramic content in vol.% in the composites [18]. The dielectric constant of C1 and C2 is due to their higher content of cristobalite, whereas, the higher value of C5 and C6 is due to the higher content of alumina.

The hardness of these composites is also shown in Table 2. It appears that the hardness increases also linearly by increasing the alumina content. This is due to the higher hardness of alumina than that of glass used in this study.

4. Conclusion

The results show that the crystallization of borosilicate glass in glass/alumina composite can be prevented by varying the alumina content in the glass matrix, by which the diffused aluminum ion change the structure of glass. When approximately $\geqslant 30$ wt.% of alumina filler is added, the structure of glass changes enough to decrease the formation of cristobalite crystals and consequently decrease the thermal expansion coefficient and dielectric constant

In glass/alumina system, phase formation is influenced by firing temperature and alumina content as follows: (a) when alumina content and firing temperature are low, the precipitated phase is cristobalite, (b) at high temperature and high alumina content, mullite is formed in the glass phase.

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