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Densification and properties of glass/cordierite composites

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Abstract

Five borosilicate glass/cordierite composite samples were prepared from pure chemicals such as H_3BO_3, Al_2O_3, MgO, silica sand, Na_2CO_3 and K_2CO_3. The glass and cordierite were separately prepared at 1500–1550 °C before mixing the composite batches. These composite batches composed of 50/50, 40/60, 30/70, 20/80 and 10/90 wt.% of glass/cordierite, respectively. The composite samples were sintered at 1100 and 1300 °C. Densification parameters, XRD, microstructure, thermal expansion and dielectric constant were addressed. The results revealed that, for the composites with ≥ 60 wt.% cordierite, no crystallization of cristobalite from the glass took place. The presence of cristobalite results in an undesirable high coefficient of thermal expansion. The thermal expansion of all the composites was in a range of 4.2 $\times 10^{-6}$/K to 3.8 $\times 10^{-6}$/K. It was also found that the bulk density decreases with the increase of cordierite content at the used sintering temperature due to the lower amount of liquid phase produced from the glass. The dielectric constant of the obtained composites was between 4.7 and 5.8. The precipitation of cristobalite did not affect the dielectric constant of the resulting composites because the dielectric constant of cristobalite itself is 3.8 as compared with that of glass (4.6) and cordierite (5.3).
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1. Introduction

In view of the current focus of the electronic industry to fabricate high power and high-speed packages, extensive research in the development of materials for packaging application is being carried out worldwide. The aim is to achieve optimized systems exhibiting lower dielectric constant and lower processing temperatures than current materials, as well as good thermal expansion match to silica, optimal thermal conductivity, high mechanical strength and dimensional stability [1]. Several glasses, glass ceramics and ceramics are being increasingly considered as substrates in innovative package designs [1]. In particular, very low-dielectric constant substrate materials including glass/ceramic combinations of the type quartz + borosilicate glass, cordierite + borosilicate glass, silica + borosilicate glass and alumina + borosilicate glass have been developed, reaching to dielectric constants <5 [1].

Glass has been widely added to ceramics to fabricate microelectronics packaging substrates that can be cofirable with high electrical conductivity metallization [2,3]. Ceramic platelets are being considered as the reinforcing component in ceramic and glass matrices because they have improved environmental safety, production economics, and thermal stability compared with whiskers [4]. The product glass + ceramic is a composite consisting of a refractory ceramic filler in a low-softening glass matrix phase. This approach gives us the flexibilities in designing materials with a desired combination of dielectric, thermal and mechanical properties. Moreover, since the low-softening glass becomes a fluid liquid during sintering, it also promotes the densification of glass + ceramic at a temperature lower than that required for ceramics, thus improving the reliability of ceramic packages [5]. Borosilicate glasses, especially, have low-softening point (820 °C) and thus enable sintering. The ceramic phase in

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the glass + ceramic composite acts mainly as filler to inhibit curling when the glass is soft. The ceramic phases that have the potential to meet substrate goals are mullite ($3Al_2O_3 \cdot 2SiO_2$), celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$), quartz and α-cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) which were used in present investigation.

Cordierite and cordierite-based ceramics posses a number of attractive properties, such as low coefficient of thermal expansion and the resulting thermal shock resistance [6], low density, low thermal conductivity and low-dielectric constant, and they are widely used in various electronic and thermo-mechanical applications.

It has been previously shown that the densification of glass + ceramics [7–10] can be described by conventional three-stages liquid-phase sintering, i.e., particle rearrangement, dissolution and precipitation, and solid state sintering. Depending upon the reactivity between glass and ceramic filler, the densification of glass + ceramics systems can be classified as non-reactive [11–12], partially reactive [13], and completely reactive [14]. For non-reactive systems, no dissolution and precipitation of ceramic filler in glass are observed during densification, such as, our case, borosilicate glass + cordierite [15], and the densification is primarily achieved in the first stage. For systems with high-viscosity glass melt, a combination of melt formation, melt redistribution, and particle rearrangement is generally observed in the first stage of liquid-phase sintering. For partially reactive systems, the dissolution of ceramic filler in glass is localized and limited, and no particle growth and shape accommodation are observed, such as borosilicate glass + alumina [13]. For completely reactive systems, the dissolution of refractory filler in low-softening glass is extensive and shape accommodation is observed during sintering, such as alumina + glass [16].

In this investigation, unlike most single glass systems discussed in the literature, we study the devitrification during sintering of a binary borosilicate glass mixture, containing low-softening borosilicate glass (BSG) and cordierite ceramic.

By changing the glass/ceramic volume ratio of the mixture, properties such as the dielectric constant and thermal expansion can be controlled, usually following the mixture rule [17]. In some cases, devitrification in the 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 microcracks formation during cooling. Also, cristobalite precipitation in the composite takes place during firing, makes the composite more difficult to densify because the composite is more viscous than the single-phase glass.

Because of many different authors have studied the glass/cordierite system with higher glass content reaching 90%, we will try to study the sintering, microstructure, thermal expansion and dielectric constant of glass/cordierite composites with higher cordierite content reaching to 90% to adopt it for using in large-scale integrated circuits (LSIS) and other applications.

2. Experimental procedure

2.1. Preparation of glasses and ceramic materials

For the glass system of the studied composites, one kind of borosilicate glass system BSG (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.

The cordierite ceramic ($2MgO$–$2Al_2O_3$–$5SiO_2$) was prepared from $MgCO_3$, Al_2O_3 and silica sand as pure chemicals. The stoichiometric amounts of these chemicals were mixed and semi dry pressed at 200 MPa in a mould of 0.5 in. diameter then sintered at 1500 °C for 2 h.

2.2. Preparation of glass/ceramic composites

Fine glass powders as above prepared were well mixed with the powder of cordierite. Five composite batches were

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

Sample number	Composite batches constituents		Oxide (wt.%)							
	BSG[a] (wt.%)	Cordierite[b] (wt.%)	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	B$_2$O$_3$	Na$_2$O	K$_2$O	CaO
CG5	50	50	64.69	18.87	0.03	6.74	6.32	1.86	0.20	1.88
CG6	40	60	61.61	21.42	0.04	8.07	5.03	1.47	0.16	2.20
CG7	30	70	58.52	24.51	0.05	9.41	3.76	1.11	0.12	2.52
CG8	20	80	55.51	27.61	0.06	10.67	2.50	0.73	0.08	2.85
CG9	10	90	52.50	30.68	0.06	11.95	1.24	0.37	0.04	3.17

[a] BSG: borosilicate glass powder.
[b] Powder.

designed as CG5, CG6, CG7, CG8 and CG9; as summarized in Table 1. The mixed batches were uniaxially pressed at 60 MPa in a disc shape of about 0.5 in. diameter and 0.5 in. height, then fired for 2 h in air at temperatures in the range of 1100–1300 °C.

2.3. Properties of glass/ceramic composites

Identification of the crystalline phases was carried out by X-ray diffraction (XRD) using a Philips Powder Camera (Type CPM 9920/02) with Cu Kα radiation and Ni filter. The microstructure of the sintered composites were observed by a scanning electron microscope (SEM: JEOL, JSM-T20). Apparent porosity (AP) and bulk density (BD) for the sintered samples of glass/ceramic composites were measured by water displacement method. The densities of 2.20 g/cm³ for BSG and 2.50 g/cm³ for cordierite ceramic were used to calculate the relative densities (RD) of glass/ceramic composites by using the mixture rule. Values of average linear thermal expansion coefficient (TEC) at 500 °C were measured in air at a heating rate of about 5 °C/min by using a dilatometer system type Linseis model 76/1250. A HP4191A LCR meters were used to measure the dielectric constant (ε^-) of the composites at room temperature and 1 MHz after painting the sintered pellets with silver paste on the two surfaces.

3. Results and discussion

3.1. Sintering

Fig. 1 shows the effect of cordierite ceramic contents (wt.%) on the bulk density of the composite samples at two different firing temperatures, i.e., 1100 and 1300 °C. From this figure we can deduce that, at low temperature, as the cordierite content increase the bulk density decrease in spite of its higher theoretical density (2.50 g/cm³) than that of borosilicate glass (2.34 g/cm³). This is due to the higher content of liquid phase in the samples containing low-cordierite content. This can be discussed by knowing that

[7], the borosilicate glass/cordierite ceramic composite is non-reactive systems, i.e., little dissolution and precipitation of ceramic filler in glass are occurring during densification, and the components are practically insoluble in each other and the densification is mainly achieved in the liquid-phase sintering, i.e., particle rearrangement. The rate-controlling step [18] during a non-reactive liquid-phase sintering (NLPS) can be obtained by comparing the calculated activation energy of densification with the activation energy of melt flow. If these values are comparable, the densification is considered to be controlled by viscous flow of melt, either melt formation or melt redistribution. Otherwise, the particles rearrangement process is the rate limiting step during NLPS [7]. In spite of the sample CG5 contains cristobalite which makes the composite difficult to densify, it shows the highest density value, because it contains the higher liquid-phase value.

It is well-known that pores decrease the value of several material properties, including the electrical, thermal and mechanical properties [19]. Not only the porosity content but also the distribution of pores and their shape and orientation, i.e., the porosity structure, will affect the properties of the porous bodies [20]. In order to tailor the properties of the porous material it is necessary to be able to control the amount of porosity in sintered composites by increasing their densities. So, to obtain full density by NLPS, a sufficient quantity of liquid phase is required. Several values have been suggested by different research groups, e.g., 25% by Cannon and Lenel [21], 35 vol.% for spherical powders by Kingery [22], and 50 vol.% for irregular powders by Eremenko et al. [23]. However, no experimental results confirmed any of the above suggested liquid-phase contents. This is probably because the critical glass content is determined by too many variables, such as particle morphology, particle size ratio, particle size distribution, mixing uniformity, viscosity of the liquid-phase, packing density and the contact angle of melt on refractory powder, which are very difficult to control all together.

Fig. 1 strongly suggests that the densification is very sensitive to the amount of glass present and the sintering temperature used. It is further noted from Fig. 1 that, the
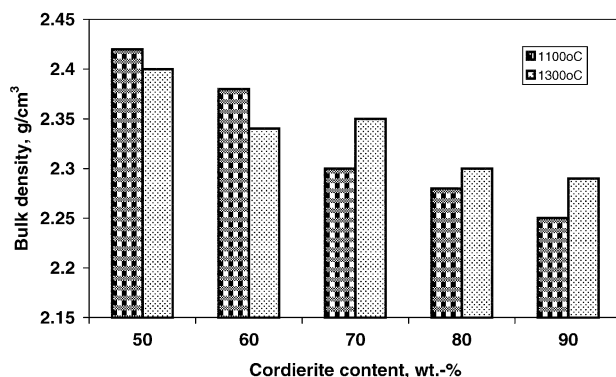

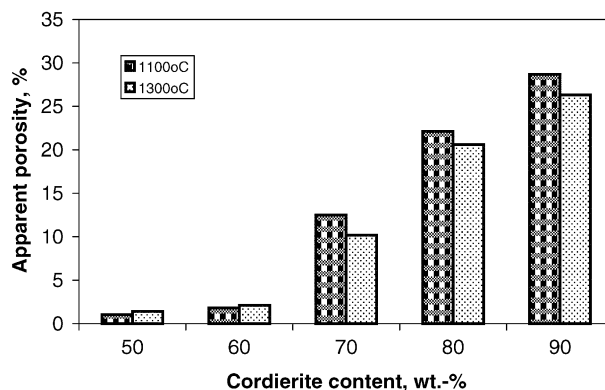Fig. 1. Bulk density of glass/cordierite composites.

Fig. 2. Apparent porosity of glass/cordierite composites.

values of the bulk density decreases with increasing sintering temperature specially with the higher glass content, i.e., in CG5 and CG6 samples, indicating that the densification is more sensitive to glass content at lower sintering temperature. Based on the results presented in Fig. 1, i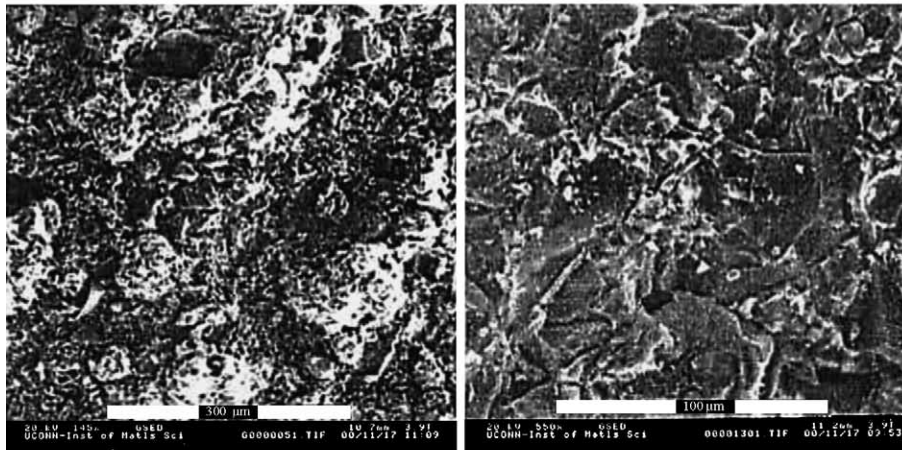t can be concluded that the densification is primarily controlled by the amount of glass present in the system. A high sintered density, can always be ensured with a large enough glass content, i.e., 50 wt.% in the present investigation at suitable sintering temperature.

The apparent porosity goes in opposite trend to the bulk density as shown in Fig. 2.
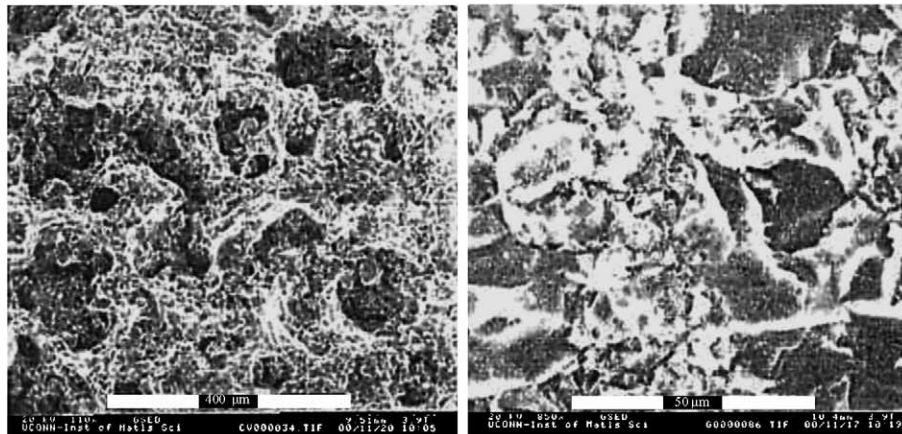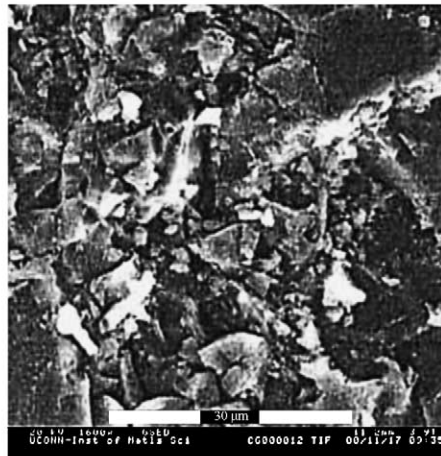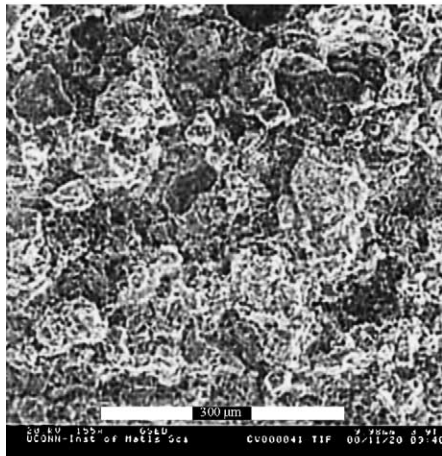
CG5
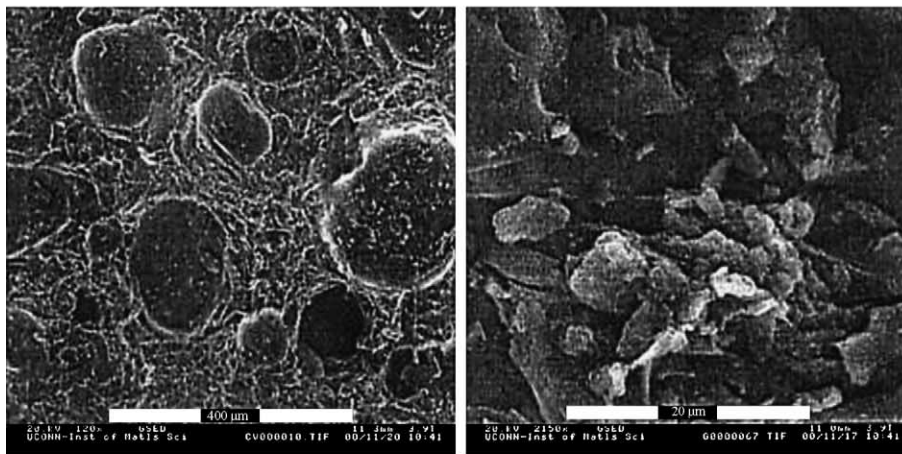
CG6

CG7

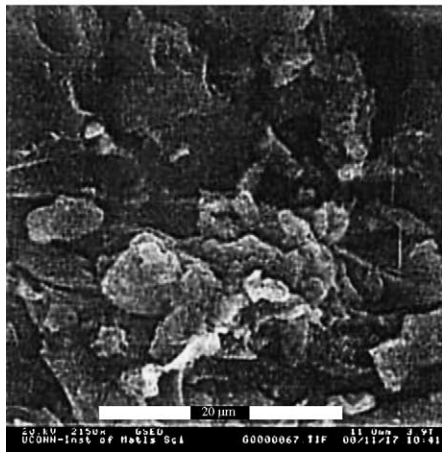Fig. 3. Microstructure of glass/cordierite composites.

CG8

CG9

Fig. 3. (*Continued*).

3.2. Microstructure

Fig. 3 shows the microstructure of the sintered borosilicate glass/cordierite composites at two firing temperatures, i.e., at (1100–1300 °C). It is interesting to note that, the initial cordierite grain does not change its size and the corners remain sharp, indicating that little dissolution and precipitation take place during densification. The densification of borosilicate glass-filled cordierite ceramics in this study is concluded to be achieved in the first stage of liquid-phase sintering, i.e., melt redistribution and particle rearrangement. Similar results were also observed in the alumina-glass system by Kingery et al. [11]. It is also interesting to note that round shaped cristobalite particles observed in the samples with low-cordierite content (CG5 sample) begins to disappear by increasing the cordierite added to the glass. This inhibition occurs as a result of forming a reaction layer around each alumina particle in cordierite, caused by strong coupling between Al^{3+} from cordierite and alkali ions from boro-silicate glass.

By examination of the microstructure of the sintered composites, it revealed that the sintering proceeds by initial transformation of the melted glass into spheres, followed by the spreading of the melt into the pores yielding shrinkage and densification [7].

3.3. Phase composition

Fig. 4 shows the XRD of three glass/ceramic composites CG5, CG6 and CG7 sintered at 1300 °C for 2 h in addition to the XRD of the well-crystallized glass sample. From this figure, it appears that only crystallized glass and the sample CG5 shows cristobalite peaks. By increasing the cordierite content, peaks characterizing cristobalite could not be detected, but only the peaks of cordierite appeared. In particular, it is thought that cristobalite is an unfavorable transformation products in terms of thermal expansion behavior. 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. Thus, it is desirable that the
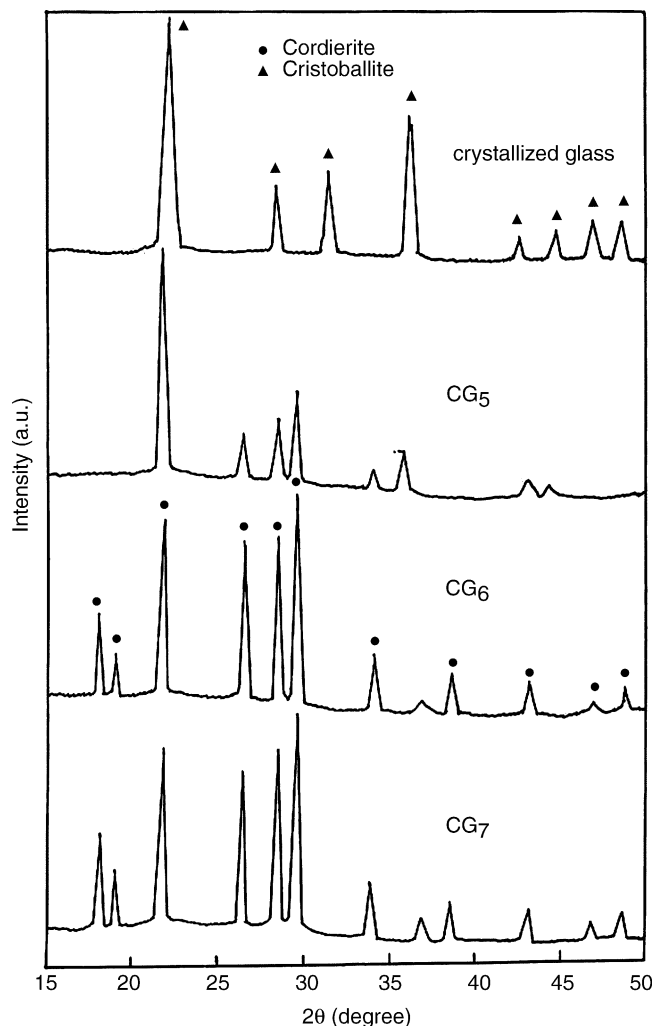
Fig. 4. XRD of glass/cordierite composites: (●) cordierite, (▲) cristobalite.

Table 2
Properties of sintered glass/ceramic composites

Samples	Composites properties	
	TEC at 500 °C $\times 10^{-6}$/K	Dielectric constant at 1 MHz
CG5	4.2	4.7
CG6	4.6	4.9
CG7	4.4	5.2
CG8	4.0	5.5
CG9	3.8	5.8

at 20–500 °C. This table indicates that the TEC decreases as the cordierite weight percent increases which can be explained by recognizing that the thermal expansion coefficient of borosilicate glass is $3.2 \times 10^{-6}\,K^{-1}$, for cordierite is $2.2 \times 10^{-6}\,K^{-1}$ [25] and $50 \times 10^{-6}\,K^{-1}$ for cristobalite [26]. Because the thermal expansion coefficient of cristobalite is high, the TEC of the composite with high cristobalite content exhibits much higher values than that expected by a mixture rule using the original raw material volume fractions. So by increasing the cordierite percent, cristobalite disappeared and the thermal expansion decreases.

3.5. Dielectric constant

As far as the dielectric constant is concerned, one of the most useful way to obtain a lower dielectric constant 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. But in this work the used percent of ceramic (50–90% cordierite) was ≥ the amount of glass to be used not only in packaging technology but also in different applications. Also, cordierite was chosen for this examination because it has lowest dielectric constant and low thermal expansion, close to that of silicon as compared with many types of ceramics.

Table 2 shows also dielectric constant of glass/cordierite composites measured at 1 MHz and room temperature. Assuming the dielectric constant of glass and cordierite are 4.6 and 5.3, respectively [25] while for cristobalite it is 3.8. The above results indicate that the precipitation of cristobalite does not affect the dielectric constant of the resulting composites. The dielectric constant of the obtained composites was in the range of 4.7–5.8.

4. Conclusion

For the composites with ≥60 wt.% cordierite, no crystallization of cristobalite from the glass have been observed. The thermal expansion of all the composites was in the range of 4.2–3.8×10^{-6}/K. It was also found that the bulk density decrease with the increase of cordierite content

borosilicate glass remain in the amorphous state during and after firing [24]. This inhibition of cristobalite formation is a result of the formation of a reaction layer around the alumina particles, owing to the strong coupling between Al^{3+} from cordierite and alkali ions from the borosilicate glass, as mentioned before, thus preventing transport of alkali ions in the glass which is necessary for formation of cristobalite. It is obvious that, Al^{3+} ions present in cordierite is the key element for suppressing the devitrification of borosilicate glass.

3.4. Properties of glass/ceramic composites

3.4.1. Thermal expansion

The glass/cordierite system specimens showed a relatively high thermal expansion coefficient. The calculated TEC of the system is 2–$3 \times 10^{-6}\,K^{-1}$, slightly lower than that of silicon [11].

Table 2 shows the effect of cordierite ceramic content on the thermal expansion coefficient of the composite samples

at the used sintering temperature due to the lower amount of liquid-phase produced from the glass. The dielectric constant of the obtained composites was between 4.7 and 5.8. The precipitation of cristobalite did not affect the dielectric constant of the resulting composites because the dielectric constant of cristobalite itself is 3.8 as compared with that of glass (4.6) and cordierite (5.3).

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