

Effects of various oxide fillers on physical and dielectric properties of calcium aluminoborosilicate-based dielectrics

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Abstract Physical and dielectric properties of LTCC (low temperature co-fired ceramics) materials based on a typical calcium aluminoborosilicate glass and various fillers such as Al_2O_3 , BaTiO_3 , CaTiO_3 , TiO_2 , ZrO_2 , MgO and SiO_2 were investigated. Densification, crystallization and thermal and dielectric properties were found to strongly depend on the type of filler. The XRD patterns of Al_2O_3 , BaTiO_3 , CaTiO_3 and MgO samples demonstrated crystalline phases, $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{BaAl}_2\text{Si}_2\text{O}_8$, CaTiSiO_5 and $\text{CaMgSi}_2\text{O}_6$, respectively, as a result of firing at 850 °C. For the sample containing CaTiO_3 filler, specifically, dielectric constant increased drastically to approximately 19.9. A high quality factor of >210 and a high TCE (temperature coefficient of expansion) of >8.5 ppm/°C were obtained for the composition containing MgO or SiO_2 . Near zero TCF (temperature coefficient of frequency) was obtained for the samples containing TiO_2 . The purpose of this work is to investigate the effects of various ceramic fillers on physical and dielectric properties and ultimately to provide the technical guidelines for the proper choice of filler in various LTCC systems.

Keywords LTCC · Dielectrics · Dielectric constant · Glass · Filler

1 Introduction

The low temperature co-fired ceramic (LTCC) technology has been extensively studied from its technical and

commercial significance in the field of highly-integrated electronic components and modules [1–4]. The LTCC system generally consists of glass and ceramic. Most of compositional studies have been focusing on the development of new glass formula as a critical factor in determining the final performance of LTCC components and devices. On the other hand, the choice of filler has not been extensively investigated while Al_2O_3 has been considered as a common choice. The refractive Al_2O_3 has been advantageous in most of commercial LTCC materials due to cost effectiveness, easy availability with diverse particle sizes and less reactivity with glass [5, 6]. Al_2O_3 with an optimal content, typically ranging from 30 to 50 wt%, is known to further maximize mechanical strength and inertness to the adverse chemical environments. There have been limited reports dealing with the effects of various oxide fillers other than Al_2O_3 , in which an identical glass is used as an LTCC constituent [7–11].

This preliminary work intends to demonstrate the effects of various oxide fillers, such as Al_2O_3 , CaTiO_3 , TiO_2 , ZrO_2 , MgO and SiO_2 , on physical and dielectric properties of the resultant LTCC materials. The property changes from the different fillers are expected from the unique characteristics of each filler. For example, a high dielectric constant of BaTiO_3 may lead to a higher k LTCC that is suitable for capacitive applications. The CaTiO_3 filler having $\text{TCF}=+800$ ppm/°C may be a desirable choice in improving TCF to near zero when combined with a negative TCF glass [12, 13].

A fixed amount of an identical glass based on the common calcium aluminoborosilicate will be used to directly compare the effects of each filler on densification, crystallization, thermal coefficient of expansion (TCE) and dielectric properties. Correlations of phase development and densification behavior to properties of each material system are the major purpose of this work.

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2 Experimental

A typical calcium aluminoborosilicate glass based on $\text{CaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ as a common constituent was used in this study. The glass was prepared by melting the mixed raw materials of the corresponding reagent grade oxides in a platinum crucible at 1500 °C for 2 h and by subsequent quenching into a water bath. The quenched glass was ball-milled with stabilized zirconia balls for 20 h to make frit. The glass itself was characterized to have a glass transition temperature of 682 °C, a softening temperature of 697 °C and dielectric properties of $k \sim 6.3$ and $\tan \delta \sim 0.0011$. No crystallization was observed up to 850 °C, which is our target sintering temperature.

Various filler materials such as Al_2O_3 (99.9% purity, 3 μm in average, ALM43, Sumitomo), BaTiO_3 (99%, 0.63 μm , Aldrich), CaTiO_3 (99+%, 1.1 μm , Aldrich), TiO_2 (99+%, 1.0 μm , Aldrich), ZrO_2 (99%, 3 μm , Aldrich), MgO (98%, 60 μm , Aldrich) and SiO_2 (99.6%, 0.93 μm , Aldrich) were chosen to produce the final dielectrics. The glass frit and filler were admixed at a fixed weight ratio of 60/40 by ball-milling in ethanol for 18 h. The mixture was dried on a hot plate and mixed with a 1.5 wt% PVA (poly vinyl alcohol) binder solution, and then pressed uniaxially at 80 MPa to form disk pellets with a diameter of 12 mm. Particularly, Ag electrode (6142D, DuPont) was screen-printed on the pellet to investigate co-fireability and the degree of Ag diffusion during firing. The pellets were sintered at 850 °C for 30 min at a heating rate of 5 °C/min.

Crystallization behavior was examined by a differential thermal analyzer (TG/DTA-92, SETARAM Co., Caluire,

France) up to 1100 °C at a heating rate of 5 °C/min and confirmed by an X-ray diffractometer (Rigaku B/Maz-2500/PC, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation over the 2θ range of 20° to 70°. Thermal coefficient of expansion (TCE) of each sample was measured from room temperature to 300 °C in air using a dilatometer (Dilatonic Tokyo Industry, Tokyo) at the same heating rate of 5 °C/min. The microstructures of the sintered samples were examined by scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectroscope (Hitachi S-4200, Tokyo, Japan).

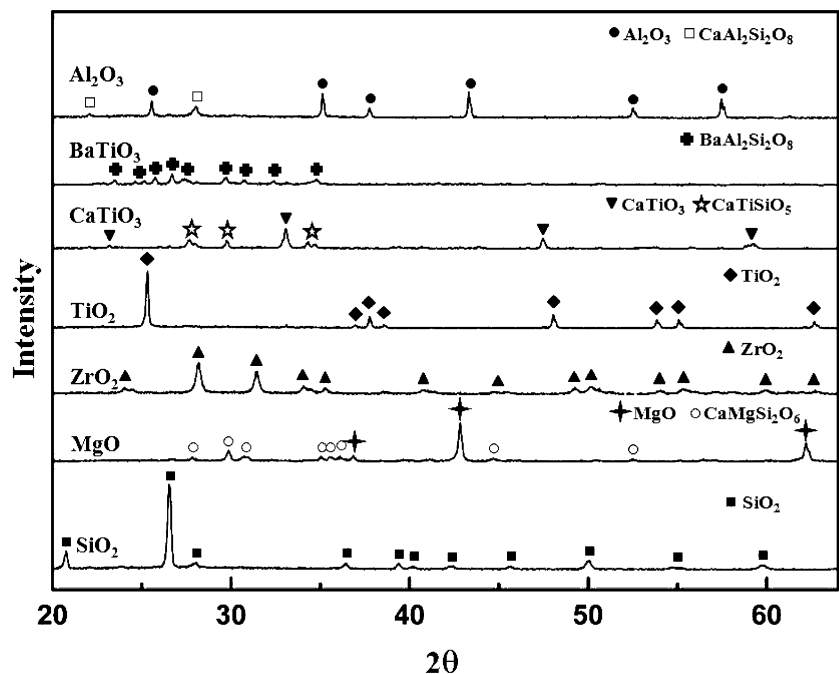
The bulk density was measured using the Archimedes principle. The x - y shrinkage of the samples was obtained by measuring the diameters of samples before and after sintering. In microwave frequency range, the dielectric properties were measured using a network analyzer (HP8720ES, Hewlett-Packard, USA) in the S_{21} transmission mode by the Hakki–Coleman dielectric resonator method. The dielectric quality factor (Q) was calculated from the data obtained at the frequency of the TE₀₁₁ mode. The temperature coefficient of resonance frequency (TCF) was measured in the temperature range of 25 to 70 °C.

3 Results and discussion

3.1 Crystallization and densification

Figure 1 shows the XRD patterns of samples containing 40 wt% of various fillers fired at 850 °C for 30 min. The XRD pattern for the sample containing Al_2O_3 filler suggests that

Fig. 1 XRD diffraction patterns of the samples containing various oxide fillers and fired at 850 °C



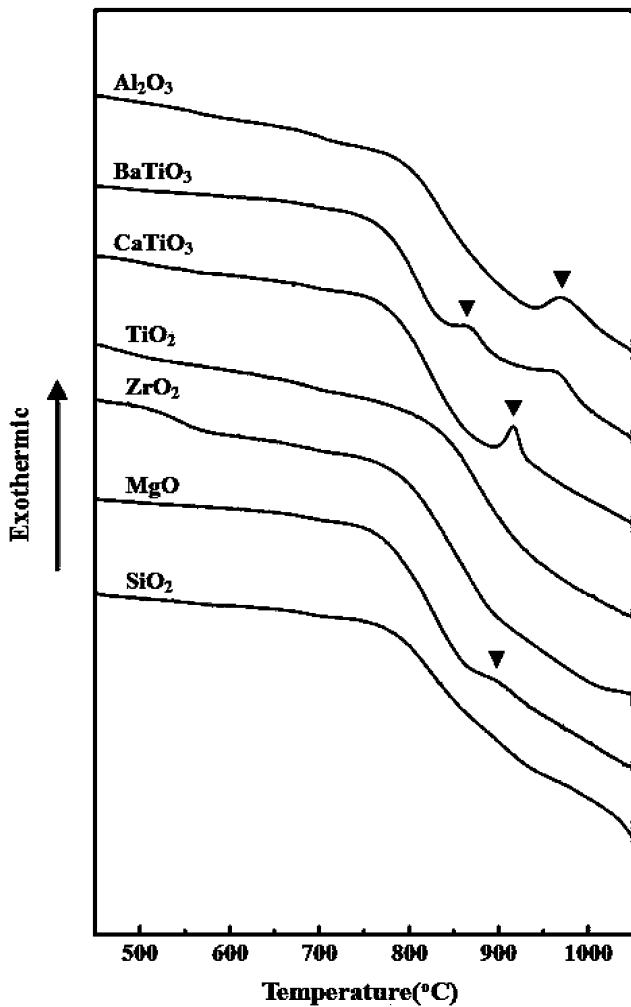


Fig. 2 DTA curves of the samples containing various oxide fillers

the crystalline phase corresponds to anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The anorthite phase has been found to be a major phase as reported in the LTCC compositions composed of typical calcium aluminoborosilicate and Al_2O_3 filler [14]. For the LTCC composition containing BaTiO_3 , the BaTiO_3 phase completely disappeared and the new $\text{BaAl}_2\text{Si}_2\text{O}_8$ phase was found to be predominant as a result of firing. It seemed that the BaTiO_3 filler reacted rigorously with glass during firing and Ti was not involved in the crystallization process since

only the $\text{BaAl}_2\text{Si}_2\text{O}_8$ phase was observed. Additional unexpected crystalline phases identified in other filler cases were CaTiSiO_5 for the CaTiO_3 filler and $\text{CaMgSi}_2\text{O}_6$ for the MgO filler. In cases of TiO_2 , ZrO_2 and SiO_2 , the peaks of the fillers were found as major peaks even after firing. Therefore, it can be assumed that the fillers of TiO_2 , ZrO_2 and SiO_2 do not actively participate in chemical reactions with glass and in the crystallization process during firing.

Figure 2 shows the DTA curves obtained at the heating rate of $5\text{ }^\circ\text{C}/\text{min}$ for samples containing 40 wt% of various oxide fillers. Table 1 represents the physical properties of the samples, including glass transition temperature (T_g), softening temperature (T_s), fired relative density and x - y shrinkage. The glass transition temperature ranged between 663 and $690\text{ }^\circ\text{C}$ and the softening temperature between 696 and $\sim 713\text{ }^\circ\text{C}$. It is noticeable that the Al_2O_3 sample had the higher temperatures of T_g (approximately $\sim 690\text{ }^\circ\text{C}$) and T_s (approximately $713\text{ }^\circ\text{C}$) while the SiO_2 sample possessed the lowest T_g of approximately $\sim 663\text{ }^\circ\text{C}$.

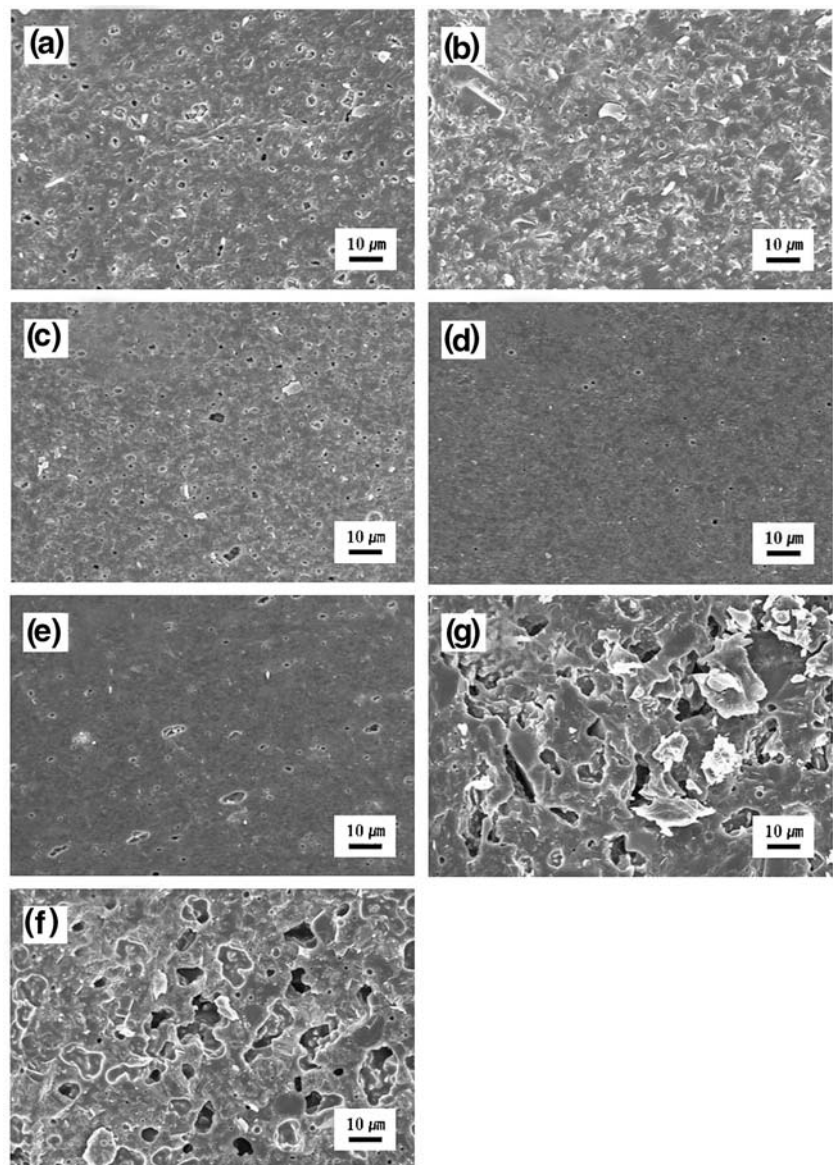
Exothermic peaks corresponding to crystallization (as indicated by arrows in Fig. 2) strongly depended on the type of filler, which matches well with the tendency of showing crystalline phases in the XRD patterns of Fig. 1. The LTCC compositions containing Al_2O_3 , BaTiO_3 , CaTiO_3 and MgO fillers had the exothermic peaks at 969 , 859 , 916 and $908\text{ }^\circ\text{C}$, respectively. The crystallization peaks are believed as correlated to the crystallization of $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{BaAl}_2\text{Si}_2\text{O}_8$, CaTiSiO_5 and $\text{CaMgSi}_2\text{O}_6$ as identified in the results of the XRD patterns in Fig. 1. In case of the LTCC compositions containing TiO_2 , ZrO_2 and SiO_2 fillers, there were no distinct crystallization peaks below $1100\text{ }^\circ\text{C}$. This is consistent with corresponding XRD patterns of Fig. 1, showing no crystalline phases after firing.

The microstructures of the samples containing 40 wt% of various fillers are shown in Fig. 3. The microstructures of Al_2O_3 , BaTiO_3 , CaTiO_3 , TiO_2 and ZrO_2 samples showed good densification with micro-pores of $<10\text{ }\mu\text{m}$. By contrast, the samples containing MgO and SiO_2 , as shown in Fig. 3(f) and (g), exhibited large pores developed on surface, indicating poor densification at the firing temperature. This observation is well matched with the low density

Table 1 Physical properties of the samples containing various oxide fillers.

Filler materials	Average particle size (μm)	Filler content		T_g ($^\circ\text{C}$)	T_s ($^\circ\text{C}$)	Relative density (%)	x - y shrinkage (%)	TCE (ppm/ $^\circ\text{C}$)
		Wt%	vol%					
Al_2O_3	3.0	40	34	690	713	97.2	19.0	4.7
BaTiO_3	0.63	40	25	686	698	96.9	19.4	6.5
CaTiO_3	1.0	40	33	682	700	93.8	20.4	6.8
TiO_2	1.0	40	34	682	696	95.9	17.8	5.6
ZrO_2	3.0	40	25	682	703	97.5	17.2	5.3
MgO	60.0	40	36	680	700	85.3	15.3	8.6
SiO_2	0.93	40	48	663	705	87.1	15.7	9.1

Fig. 3 SEM images of samples containing 40 wt% (a) Al_2O_3 , (b) BaTiO_3 , (c) CaTiO_3 , (d) TiO_2 , (e) ZrO_2 , (f) MgO and (g) SiO_2 filler



and shrinkage values of the MgO and SiO_2 samples as represented in Table 1.

Basically, the densification behavior of LTCC is explained by viscous flow of glass during firing. The wetting between glass and ceramic filler leads to good densification in the glass and ceramic mixture as the glass covers initially the specific surface area of ceramic particles. The required content of glass should vary depending on the particle size of ceramic filler, i.e., the smaller particle size needs a higher content of glass to cover the higher specific surface area. Our previous work [5] on the effect of particle size of alumina filler reported that the optimal size of filler in the case of alumina ranged between 0.5 and 3.0 μm and two extreme sizes of 13 nm and 39 μm alumina could not produce good densification. All fillers used here pertain to this optimal range of particle size,

except for the case of MgO having a larger particle size of 60 μm . The larger particle size of MgO is believed to be associated with the poor densification.

At the same time, the volume fraction of each filler must be considered for the proper wetting. Densification can be retarded due to the insufficient amount of glass during liquid phase sintering. As indicated in calculated volume % in Table 1, an optimal amount of glass for full densification must vary depending on the density of each filler. The MgO and SiO_2 fillers having low densities had a relatively high volume fraction, which must require a higher content of glass for desirable wetting.

As an additional factor influencing the ultimate microstructure, the reactivity of filler with glass needs to be considered. The reaction with glass can result in crystallization or changed densification behavior. Probably, the

Table 2 Microwave dielectric properties of the samples containing various oxide fillers.

Filler materials	Resonance frequency (GHz)	Dielectric constant (k)	Quality factor (Q)	$Q \times f$ (GHz)	TCF (ppm/°C)
Al ₂ O ₃	15.1	8.3	143	2,159	-69
BaTiO ₃	13.3	12.2	152	2,022	-22
CaTiO ₃	9.6	19.9	118	1,459	12
TiO ₂	12.0	13.2	180	2,160	-4
ZrO ₂	15.5	9.3	172	2,666	-39
MgO	15.8	7.3	232	3,666	-53
SiO ₂	16.6	5.8	213	3,536	-39

strongest reaction happened in the case of BaTiO₃ filler as the peaks of BaTiO₃ disappeared after firing. As another example, the involvement of Al₂O₃ and SiO₂ in certain reactions during firing must be responsible for crystallization of CaAl₂Si₂O₈ and a lowered glass transition of approximately ~663 °C.

3.2 Property dependence of fillers

The TCE values were markedly changed depending on the type of fillers as represented in Table 1. As expected, the high thermal expansion fillers produce high TCE values of the dielectric samples. For example, the TCE of the sample containing Al₂O₃ with approximately ~6.7 ppm/°C showed 4.7 ppm/°C whereas the sample containing SiO₂ with approximately ~10 ppm/°C showed a higher value of 9.1 ppm/°C.

Table 2 shows microwave dielectric properties of the samples containing various fillers. The overall dielectric constant is determined by the intrinsic dielectric constant of filler materials. As expected, the use of high k BaTiO₃,

CaTiO₃ and TiO₂ must increase the dielectric constant of the resultant samples. It is interesting that BaTiO₃ was not much effective in enhancing dielectric constant due to the disappearance of high k BaTiO₃ phase after firing (Fig. 1). The crystalline phase of BaAl₂Si₂O₈, which was produced by reactions between BaTiO₃ and glass, is known to have $k \sim 12$ [15]. The CaTiO₃ sample exhibited the highest dielectric constant of 19.9, resulting from the presence of CaTiO₃ phase after firing (Fig. 1). It is interesting that the MgO and SiO₂ samples had the highest quality factor of >210 even with high porosity observed in Fig. 3. In the case of TCF, the fillers such as CaTiO₃ and TiO₂, which have positive TCF of 800 ppm/°C and 450 ppm/°C, respectively, were effective in obtaining near zero TCF values. The CaTiO₃ sample showed a positive value of 12 ppm/°C.

Ag metallization has been the most popular choice as an external or internal electrode due to its superior conductivity and cost effectiveness. The diffusion of Ag into dielectric ceramics during co-firing has often been the issue that needs to be resolved [16, 17]. In this study, all samples were investigated in terms of the Ag reactivity by co-firing

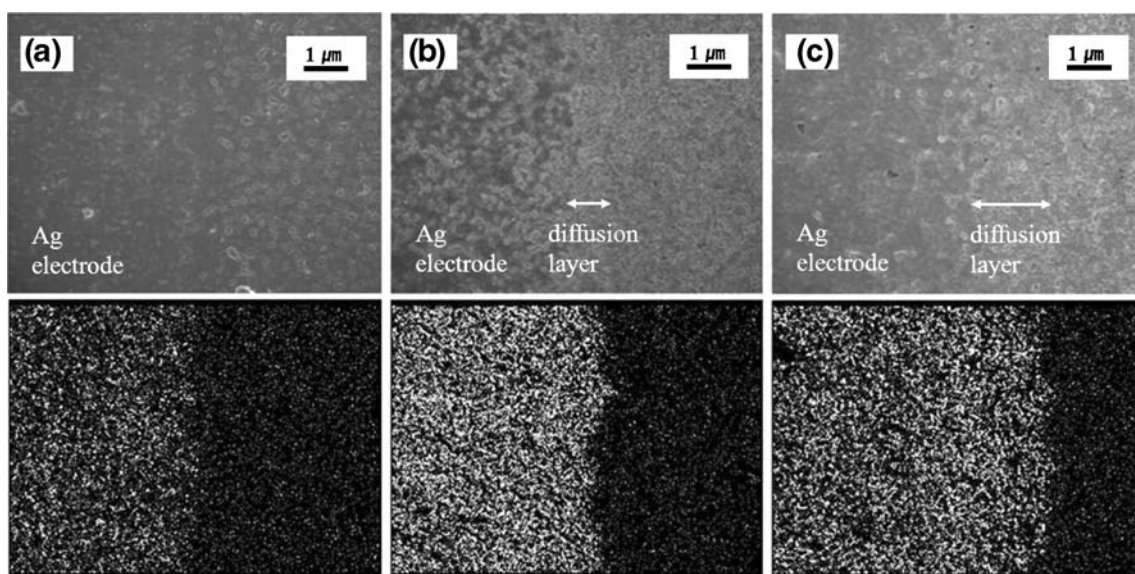


Fig. 4 SEM and energy dispersive X-ray spectroscopy (EDS) images of the Al₂O₃, MgO and SiO₂ filler samples, showing the interface between the dielectric and Ag conductor after firing at 850 °C for 30 min

the dielectric sample with a screen-printed Ag pattern. Figure 4 shows the interface regions between the dielectric and Ag conductor with elemental mappings of Ag for the selected samples containing Al_2O_3 , MgO and SiO_2 fillers co-fired with Ag at 850 °C for 30 min. The Ag diffusion was dependent on the choice of filler. The samples containing Al_2O_3 , BaTiO_3 , CaTiO_3 , TiO_2 and ZrO_2 fillers did not show any Ag diffusion while only two fillers of MgO and SiO_2 had a significant diffusion across the interface as shown the elemental mapping of Ag in Fig. 4.

4 Conclusions

The choice of a filler among various candidates, such as Al_2O_3 , BaTiO_3 , CaTiO_3 , TiO_2 and ZrO_2 , MgO and SiO_2 , in the LTCC applications were concluded to be the critical factor in determining the final physical, thermal and dielectric properties. Specific performance targets should be considered when adopting an appropriate filler. For high dielectric constants, CaTiO_3 was effective in producing $k \sim 19.9$ as a result of the presence of CaTiO_3 phase due to the less reactivity with glass during firing. The use of MgO and SiO_2 led to high TCE >8.6 , high Q factor >210 and low density $<2.76 \text{ g/cm}^3$. These examples on the performance dependence of filler are believed to be related to the crystallization and densification behavior, which are predominantly influenced by chemical reactivity with glass and physical interactions between glass and ceramic during firing.

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