

Physical and Dielectric Properties of Aluminoborosilicate-Based Dielectrics Containing Different Divalent Oxides

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ABSTRACT

The variations of physical and dielectric properties of low temperature dielectrics based on typical aluminoborosilicate glasses modified with several divalent oxides were investigated. The divalent oxides studied here included CaO, MgO, BaO, SrO and ZnO. All samples containing either 35 wt% or 45 wt% alumina filler were prepared at the same processing condition and then fired at 850°C for 30 min. The resultant characteristics of fired samples depended on the choice of the divalent ion and the content of the alumina filler. Except for the ZnO modification, all other samples containing 35 wt% filler demonstrated promising densification as they exhibited reasonably high densities of 3.07-3.31 g/cm³ and high shrinkages of 14.0-16.4%. Particularly, the sample containing ZnO was distinguished with large variations compared to the base sample, which can be highlighted with earlier densification and crystallization at unexpectedly low temperatures. The negative effects of the ZnO modification on densification and dielectric properties were thought to be associated with earlier crystallization potentially by influencing effective densification via viscous flow. As an optimum composition, the sample containing only CaO showed the most promising characteristics such as $k \sim 8.05$ and $\tan \delta \sim 0.0018$ when 35 wt% alumina filler was used.

Key words: Dielectric, LTCC, Aluminoborosilicate, Crystallization

1. Introduction

Low temperature co-fired ceramics (LTCC) have been actively investigated primarily focusing on the field of ceramic electronic packages requiring high density integration.¹⁻³⁾ The proper design of the LTCC materials is essential in producing successful ceramic-based packages utilizing inexpensive co-fireable Ag-based conductors. Several requirements for the LTCC materials, such as low temperature processing below 850°C and low dielectric constant, make the glass as an evitable choice in producing the LTCC materials. The low k LTCC usually consists of low temperature softening glass and ceramic filler. The ceramic filler is required mainly for providing dimensional stability and physical strength. Among a lot of known low temperature softening glasses, calcium aluminoborosilicate-based glasses have been known as one of the most promising in terms of resultant physical, thermal and dielectric properties.⁴⁻¹²⁾ However, there is no systematic report on the effects of detailed compositional changes of glass on the final LTCC performance although many competitive commercial LTCC materials are based on the calcium aluminoborosilicate glasses.

This work intends to provide an example of the effects of

divalent substitutions, such as Mg, Ba, Sr and Zn, in a typical calcium aluminoborosilicate glass on the physical and dielectric properties of the LTCC samples containing alumina (Al₂O₃) filler. Densification and crystallization behavior resulted from the different divalent oxides will be correlated to the observed performance of the samples.

2. Experimental

Calcium aluminoborosilicate glasses modified with various divalent oxides such as MgO, BaO, SrO and ZnO were prepared by melting corresponding raw materials in a platinum crucible at 1500°C for 2 h and by subsequent quenching into a water bath. The base glass composition contains 25 mol% CaO, as designated with the "CaO" glass. Only 10 mol% of 25 mol% CaO was substituted with each divalent oxide, i.e., MgO, BaO, SrO or ZnO, while the relative ratios among all other glass constituents such as Al, Si and B were kept in all glasses. For example, the "MgO" glass means that it contains 15 mol% CaO and 10 mol% MgO.

The quenched glass was ball-milled with stabilized zirconia balls for ~20 h to make frit. A fixed filler materials of Al₂O₃ (99.9%, ALM43, Sumitomo) was chosen to produce the final dielectrics. The glass frit and alumina filler were admixed at two fixed weight ratios of 65/35 and 55/45 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)

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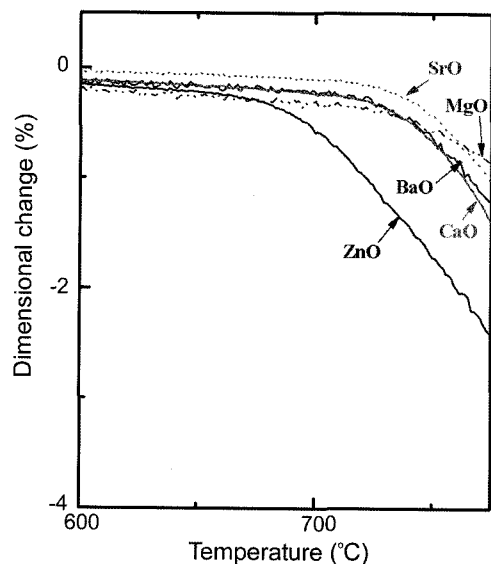


Fig. 1. TMA curves measured at a heating rate of 5°C/min for the samples containing 35 wt% alumina filler.

binder solution, and then pressed uniaxially at 80 MPa to form disk pellets with a diameter of 12 mm. The pellets were sintered at 850°C for 30 min at a constant heating rate of 5°C/min.

Crystallization behavior was examined by a differential thermal analyzer (DTA, TG/DTA-92, SETRAM Co., Calurie, France) at a heating rate of 5°C/min and by an x-ray diffractometer (Rigaku B/Maz-2500/PC, Tokyo, Japan) using Cu K α radiation with 2θ from 15 to 80°. Shrinkage behavior was obtained at a heating rate of 5°C/min by the thermo-mechanical analysis (TMA) using a dilatometer (Dilatonic Tokyo Industry, Japan). The microstructures of the sintered samples were examined by scanning electron microscopy (SEM, 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. Dielectric properties were measured using an impedance analyzer (HP4194A) at a fixed frequency of 1 MHz.

3. Results and Discussion

Fig. 1 shows the TMA curves of the samples containing different divalent oxides, such as CaO, SrO, BaO, MgO and ZnO, with 35 wt% alumina filler as an example. The abrupt dimensional change with increasing firing temperature means that densification of the sample starts with dimensional shrinkage. The samples modified with MgO, SrO and BaO did not show significant changes in the densification behavior. Only the "ZnO" glass sample demonstrated serious changes in the behavior of densification, which had the lowest densification onset temperature of ~670°C compared to ~730°C for the base "CaO" glass sample. The similar

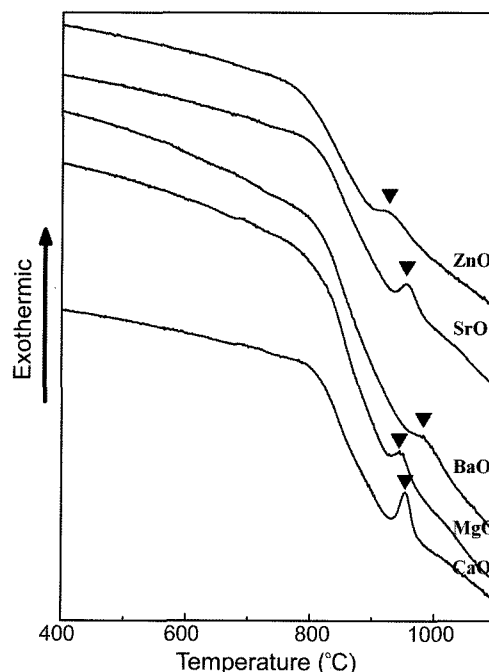


Fig. 2. DTA curves measured at a heating rate of 5°C/min for the samples containing 35 wt% alumina filler.

effect of ZnO in lowering densification temperature was reported in the La-Zn-B-O glass system where the substitution with Zn resulted in the reduction of densification temperature by 20°C.¹³⁾

Fig. 2 shows the DTA curves of the samples containing 35 wt% alumina filler. The DTA curves show the typical thermal behavior of glass with increasing temperature, which can be characterized by a sudden decrease of curve due to the softening of glass and a distinct exothermic peak (indicated by inverted triangles) due to the crystallization of glass. Particularly, the crystallization temperature corresponding to distinctive exothermic peaks in the DTA curves were considerably dependent on the type of divalent oxide. Compared to the peak crystallization temperature of 950°C for the base "CaO" glass sample, the effect of ZnO was significant by showing a reduced peak temperature of ~920°C. It is interesting to note that the "BaO" glass sample demonstrated the higher crystallization peak of ~980°C. From the observed comparable softening points of all modified samples, the crystallization changes, especially induced by ZnO or BaO, are not likely to be related to the change in softening of glass. The "SrO" sample showed mostly similar crystallization behavior with that of the base sample. It is proposed that the choice of the divalent oxides can play a role in controlling crystallization. The effect of BaO may be most recommendable in that regard wherever the late crystallization is required for full densification.

The crystallization of the sample was confirmed by the XRD patterns of Fig. 3, which were obtained for the samples fired at the same temperature of 850°C for 30 min containing either 30 wt% or 45 wt% alumina filler. Distinct peaks

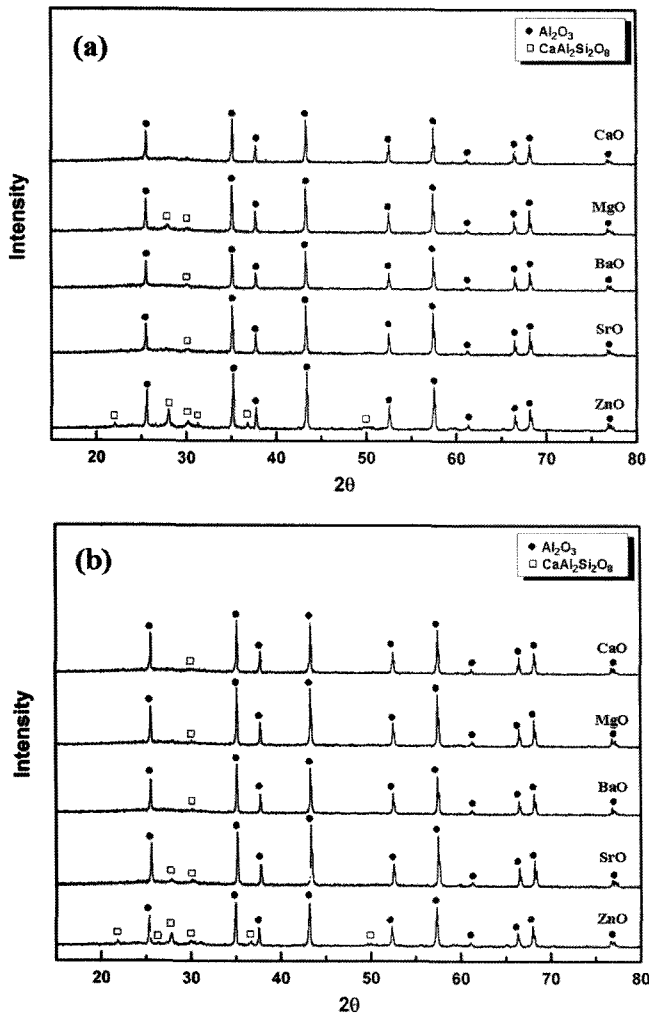


Fig. 3. XRD patterns of samples containing (a) 35 wt% and (b) 45 wt% alumina filler, sintered at the same temperature of 850°C for 30 min.

observed for all samples corresponded to the phase of Al_2O_3 used as filler. As a crystalline phase after firing, only anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) phase was found with minor traces in most of the samples except for the case of the “ZnO” glass sample. The “ZnO” glass sample showed distinct anorthite peaks because of its lower crystallization temperature than the others in DTA. The tendency of developing crystalline phase was identical in both cases of 35 wt% and 45 wt% filler-containing samples. These least crystallizations with MgO , BaO and SrO seemed to be correlated well with the observed changes of the crystallization peak in the DTA curves of Fig. 2.

Surface microstructures of samples containing 35 wt% and 45 wt% alumina filler and fired at the same temperature of 850°C for 30 min are seen in Figs 4 and 5, respectively. The overall well-densified surfaces were found in all samples except for the “ZnO” glass sample even having the lowest onset temperature of densification. The “ZnO” glass sample demonstrated significantly larger pores developed randomly on the surface. The poor characteristics of micro-

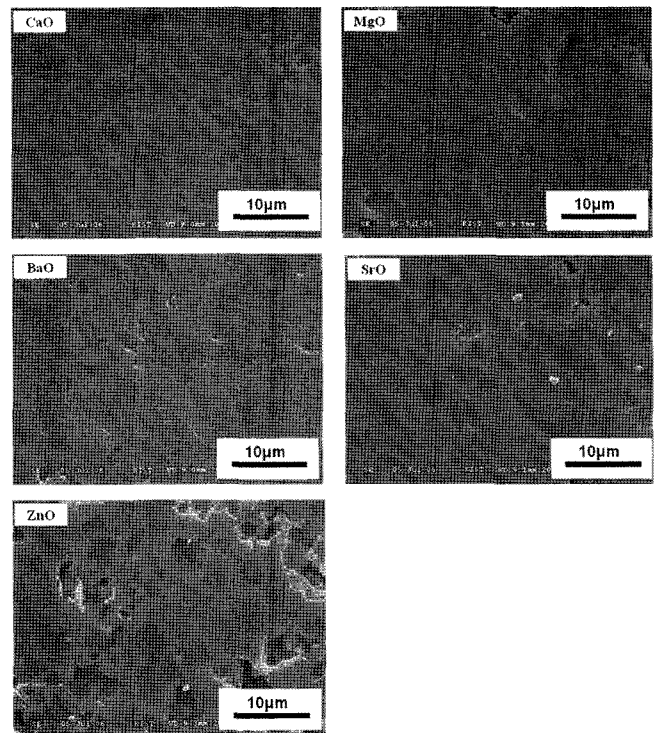


Fig. 4. SEM photographs of the samples containing 35 wt% alumina filler, fired at 850°C for 30 min.

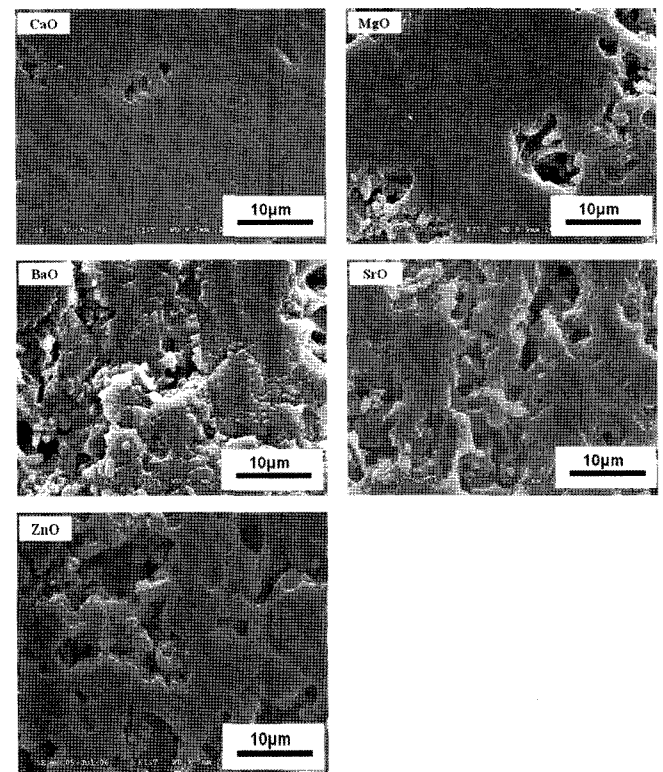


Fig. 5. SEM photographs of the samples containing 45 wt% alumina filler, fired at 850°C for 30 min.

structure driven by ZnO are understood as associated with the hindrance effect of sintering by early crystallization.

Table 1. Physical and Dielectric Properties of the Samples Containing Different Divalent Oxides in Glass

Divalent oxide	Tape composition (wt%)		Density (g/cm ³)	x-y shrinkage (%)	Dielectric constant	Dielectric loss
	Glass	Alumina				
CaO	65	35	3.14	16.4	8.05	0.0018
MgO	65	35	3.07	16.1	7.56	0.0037
BaO	65	35	3.31	15.1	6.94	0.0023
SrO	65	35	3.24	14.0	6.80	0.0033
ZnO	65	35	2.88	9.1	5.79	0.0032
CaO	55	45	3.00	12.5	7.80	0.0025
MgO	55	45	2.75	10.4	5.86	0.0037
BaO	55	45	2.76	7.9	5.83	0.0055
SrO	55	45	2.69	8.0	5.78	0.0072
ZnO	55	45	2.75	5.5	5.20	0.0048

Generally, full densification in the case of LTCC, consisting of low softening glass and ceramic filler, is achieved when crystallization occurs after sufficient densification via viscous flow of glass at low temperatures.^{13,14} Accordingly, early crystallization of anorthite in case of the “ZnO” glass sample is believed to affect densification negatively in some extent.

On the other hand, the overall coverage of glass phase to alumina filler seemed to be not enough in samples containing 45 wt% alumina filler as shown in Fig. 5 where significantly porous structures were observed. Particularly the samples with MgO, BaO and SrO became apparently porous with the increase of filler to 45 wt%. The values of fired density and x-y shrinkage for both 35 wt% and 45 wt% alumina-containing samples are represented in Table 1. The density and shrinkage values tend to match well each other, which generally means that a high density comes from a high shrinkage with less porosity. The values are also consistent with the observed characteristics of microstructures. For example, the “ZnO” glass samples with high porosities showed the lowest density and shrinkage values at both 35 wt% and 45 wt% alumina cases.

Modifications with other divalent Mg, Ba and Sr oxides are thought to be desirable in terms of densification specifically in the case of 35 wt% Al₂O₃ samples as represented in Table 1. The higher densities of >3.07 g/cm³ with reasonably good characteristics of microstructures of the “MgO”, “BaO” and “SrO” glass samples in Fig. 4 should be acceptable for the LTCC applications. Higher densities of BaO (5.7 g/cm³) and SrO (4.7 g/cm³) compared to that of CaO itself (3.3 g/cm³) very likely contributed to the obtained higher absolute values of density, 3.31 g/cm³ for the “BaO” sample and 3.24 g/cm³ for the “SrO” sample. The density of the “CaO” glass sample was 3.14 g/cm³ (Table 1). On the other hand, all the “MgO”, “BaO” and “SrO” glass samples containing 45 wt% Al₂O₃ filler exhibited inferior density and shrinkage values.

Table 1 also represents the dielectric constant and loss for each sample, measured at 1 MHz. The values were averaged from at least 5 samples through multiple trials over the multiple samples. Overall dielectric constant ranged

between 5.20 and 8.05, depending on the type of modification and the content of alumina filler. All dielectric loss values must be acceptable for the LTCC applications as they are low enough as <0.0072. It is worth to mention that relatively lower dielectric constant and higher dielectric loss were found at the sample containing 45 wt% alumina filler than the samples containing 35 wt% alumina filler. This can surely be attributed to poorer densification found in the 45 wt% filler samples. Large pores must result in low dielectric constant and high dielectric loss.

As expected from the poor densification, the “ZnO” glass sample can be distinguished with lower dielectric constants and poorer dielectric losses as the corresponding example. It was not believed that the distinct anorthite phase observed in case of the “ZnO” glass sample affected seriously the dielectric properties as poor densification was thought to be dominantly responsible for impaired dielectric properties. The base “CaO” glass sample is considered as best in that promising microstructure is developed with appropriate dielectric constant and loss at the temperature of 850°C which is the target temperature for LTCC applications.

4. Conclusions

The physical and dielectric properties of an LTCC system containing calcium aluminoborosilicate but modified with different divalent oxides such as MgO, BaO, SrO and ZnO were investigated. The modifications with MgO, BaO and SrO did not show significant degradation in the case of 35 wt% alumina filler-containing samples by possessing proper dielectric properties as a result of good densification. The sample containing ZnO in glass demonstrated apparent negative effects on densification and dielectric properties presumably due to the unexpected earlier crystallization of anorthite phase. The samples containing only CaO was believed to be most promising because they showed the lowest dielectric losses regardless of filler content with least porosity as a result of 850°C firing.

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