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Influences of alkali oxides on crystallization and dielectric properties of anorthite-based low temperature dielectrics

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The influences of alkali oxides as glass constituents for producing LTCC (Low Temperature Co-fired Ceramics) materials were investigated in terms of variations in physical and dielectric parameters. The LTCC materials were based on typical calcium zinc aluminoborosilicate glasses containing 1–3.5 mol% alkali oxides such as K_2O, Na_2O and Li_2O. All samples were prepared in the same experimental condition, i.e., the ratio of glass/filler and the final firing temperature of 850°C. Densification and crystallization behavior strongly depended on the type and amount of alkali oxides used. For example, crystallization peaks in the DTA curves tended to shift towards the lower temperature region by increasing the content of Na_2O and K_2O. Specifically, the effect of Li_2O was distinct in determining the crystallization behavior and subsequent dielectric properties of the LTCC system. Dielectric constant was measured as values of 7.18–7.78 but dielectric loss was significantly degraded specifically with the addition of 3 mol% Li_2O.

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1. Introduction

Promising low temperature co-fired ceramic (LTCC) materials have been developed for high density ceramic-based packages for various electronic and telecommunication applications. The LTCC system generally consists of glass and ceramic.[1)–3)] Successful LTCC designs have depended on the choice of glass formula that determines the final performance of the LTCC modules or devices. Calcium aluminoborosilicate glass has been a common choice in producing low dielectric constant (k) LTCC materials which meet a lot of performance requirements including physical, electrical and thermal properties.[4),5)] There has been no systematic report on the effects of glass constituents in the calcium aluminoborosilicate glass while several commercial low k LTCC materials based on the glass have been available.[6),7)] The typical glass is known to be susceptible to crystallization during firing, resulting in the formation of anorthite crystals around the LTCC target temperature of 850°C. Particularly, the addition of alkali oxides is known to be beneficial in producing homogeneous melts at relatively low temperatures.[8),9)] But the limited use of the alkali oxides is recommended due to unwanted reactions with co-fired Ag conductors.

This work intends to demonstrate for the first time the effects of changing alkali oxides in the typical calcium zinc aluminoborosilicate glass on physical and electrical properties. A fixed amount of identical Al_2O_3 ceramic filler will be used for this study. Correlations of phase development and densification behavior to properties of each glass-driven dielectric are the major focus of this work.

2. Experimental

Calcium zinc aluminoborosilicate glasses containing various combinations of alkali oxides such as Na_2O, K_2O and Li_2O were prepared by melting the corresponding raw materials in a platinum crucible at 1500°C for 2 h and by subsequent quenching into a water bath. The specified glass compositions are represented in **Table 1**. The base glass contains 0.5 mol% Na_2O and 0.5 mol% K_2O while other samples contain an extra amount of each alkali oxide. For example, the sample ID of K3.5 means the glass sample that contains the additional 3.0 mol% K_2O beyond the base content of 0.5 mol% K_2O. The alkali contents were limited as less than 3 mol% from the expected sensitivities of Ag diffusion and crystallization, which can influence the final performance of the dielectrics negatively. Note that the relative

Table 1. Compositions and Characteristics of the Samples Containing Different Alkali Contents

Sample ID	Specific Content (mol%)			T_s (°C)	$T_{c,\ onset}$ (°C)	$T_{c,\ peak.}$ (°C)	$I_{Ca(Al_2Si_2O_8)(004)}/I_{Al_2O_3(113)}$	$I_{ZnAl_2O_4(311)}/I_{Al_2O_3(113)}$
	Na_2O	K_2O	Li_2O					
Base	0.5	0.5	–	700	913	933	0.50	0
K3.5	0.5	3.5	–	698	896	922	0.83	0.75
Na3.5	3.5	0.5	–	669	873	895	1.00	0.95
Li1.0	0.5	0.5	1.0	648	862	892	1.00	0.97
Li3.0	0.5	0.5	3.0	575	820	849	1.01	1.02

ratios among the other glass components of Zn, Ca, Al, Si and B were not changed.

The quenched glass was ball-milled with stabilized zirconia balls for ~20 h to make frit. A fixed filler materials of Al_2O_3 (99.9%, ALM43, Sumitomo) was chosen to produce the final dielectrics. The glass frit and alumina filler were admixed at a fixed weight ratio of 65/35 by ball-milling in ethanol for 18 h. The mixture was dried on a hot plate and mixed with a 1.5 mass% PVA (poly vinyl alcohol) 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 (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 Kα radiation with 2θ from 15 to 80°. 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. Dielectric properties were measured using an impedance analyzer (HP4194A) at a fixed frequency of 1 MHz.

3. Results and discussion

Figure 1 shows the DTA curves of each sample containing different contents of alkali oxides. Several noticeable data, such as the softening temperature of glass (T_s), the onset temperature of crystallization ($T_{c,\ onset.}$) and the peak temperature of crystallization ($T_{c,\ peak.}$), obtained from the curves of Fig. 1 are represented in Table 1. The DTA curves show the typical thermal behavior of glass with increasing temperature, which can be highlighted with a sudden decrease of curve due to the softening of glass above ~550°C and a distinct exothermic peak above ~850°C due the crystallization of glass. The crystallization of glass occurred regardless of glass composition while the strong dependence of the peak position on the type of alkali oxide was found. All extra additions of alkali oxides apparently played a role of reducing the softening temperature. As a most dominant example, the softening temperature was reduced from 700°C to 575°C for the Li3.0 sample compared to the base sample.

The crystallization behavior demonstrated the similar tendency of decreasing the temperature of crystallization with additional alkali oxides. The addition of 3 mol% Li_2O seemed to mostly affect $T_{c,\ peak}$ by reducing from 933°C to 849°C compared to $T_{c,\ peak.}$ of the base composition. The early crystallization of Li-based phases is well known as reported in various other Li silicate glass systems where the degree of crystallization is strongly dependent on the composition of glass and interactions of Li with other glass constituents.[10)–12)] On the other hand, the identical result of reducing $T_{c,\ peak}$ by the additions of Na and K has rarely been reported. This Na and K effect on crystallization is believed to be associated with the reduction of softening temperature in the glass system although it is unclear for the exact mechanism for promoting the crystallization.

Figure 2 shows the XRD patterns of each sample fired at 850°C for 30 min. The base sample showed crystalline anorthite ($CaAl_2Si_2O_8$) phase along with the phase of Al_2O_3 used as ceramic filler. All other samples modified with extra alkali oxides had an extra crystal corresponding to $ZnAl_2O_4$ phase. The relative contents of the crystalline phases depended on the alkali composition in glass as represented in Table 1 by the relative peak intensities ($I_{CaAl_2Si_2O_8(004)}/I_{Al_2O_3(113)}$ or $I_{ZnAl_2O_4(311)}/I_{Al_2O_3(113)}$) of either $CaAl_2Si_2O_8$ or $ZnAl_2O_4$ to Al_2O_3. The comparison of the ratios demonstrates quantitatively the relative effect of crystallization for each crystalline phase. For instance, the increase of the $I_{ZnAl_2O_4(311)}/I_{Al_2O_3(113)}$ ratio with alkali oxides indicates that the incorporated alkali oxides helped the crystallization of $ZnAl_2O_4$ when the degree of Al_2O_3 filler reactivity with glass is assumed identical for all glasses. The correlation of the intensity ratios to the crystallization peak temperature suggests that the early crystallization induced by additional alkali resulted in the strong

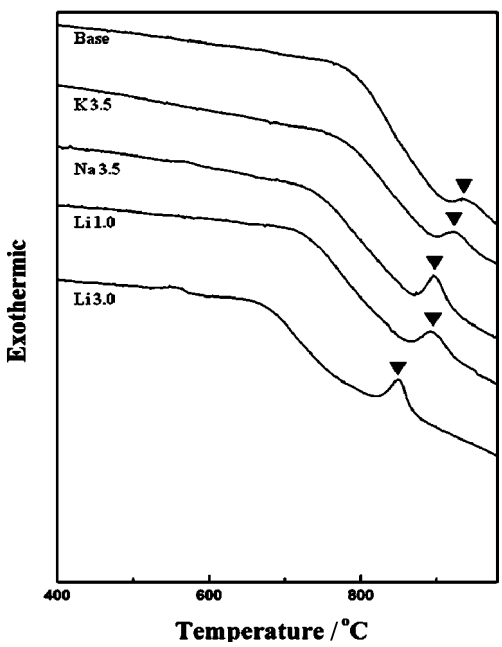

Fig. 1. DTA curves measured at a heating rate of 5°C/min for the samples containing different alkali contents.

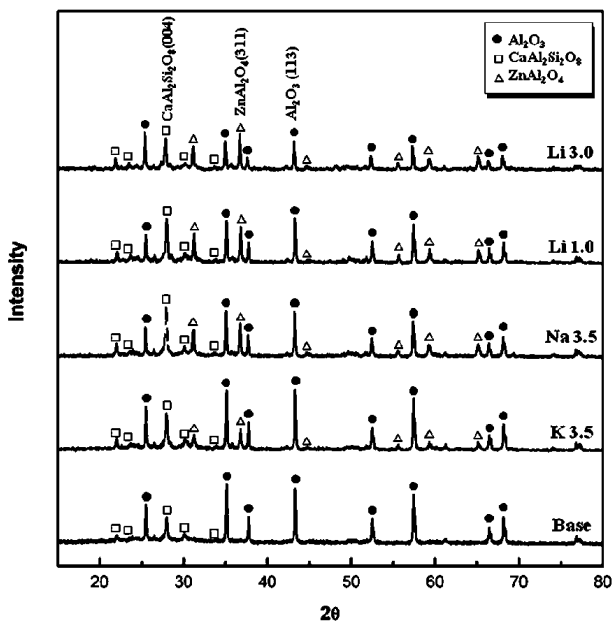

Fig. 2. XRD patterns of samples fired at 850°C for 30 min.

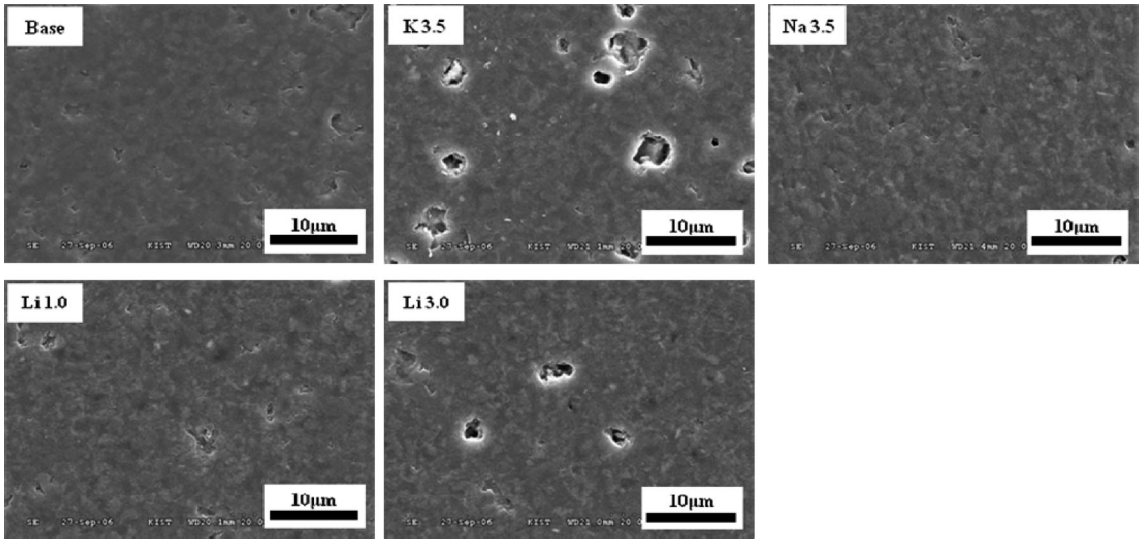

Fig. 3. Surface microstructures of samples fired at 850°C for 30 min.

Table 2. Physical and Dielectric Properties of the Samples with Different Alkali Contents

Sample ID	Fired Density (g/cm^3)	x–y Shrinkage (%)	Dielectric Constant at 1 MHz	Dielectric Loss at 1 MHz
Base	3.16	16.28	7.28	0.0014
K3.5	3.07	14.19	7.18	0.0015
Na3.5	3.22	15.94	7.75	0.0020
Li1.0	3.22	16.61	7.78	0.0015
Li3.0	3.05	15.53	7.57	0.0125

development of $ZnAl_2O_4$ although it was difficult to find the separate exothermic peak corresponding to the $ZnAl_2O_4$ crystallization in DTA due to te overlapped crystallization peaks and/or the less sensitivity of the instrument.[13] The Li3.0 sample was found most influential in such regard.

Surface microstructures of samples fired at the same temperature of 850°C for 30 min are seen in **Fig. 3**. Well-densified surfaces have been found in the base, Na3.5, and Li1.0 samples. The K3.5 and Li3.0 samples showed macro pores developed on the surface. These poor microstructures are well correlated to the measured density values in **Table 2** where the linear shrinkage values are also represented. Usually, early crystallization is known to hinder densification of glass by reducing the effects of viscous flow driven by glass during sintering.[14)–16)] This effect of the densification hindrance may be applicable to the Li3.0 sample which showed the earliest crystallization starting at 820°C.

Table 2 summarizes the dielectric properties of the samples measured at 1 MHz. All samples showed low dielectric constants below 8.0 and acceptable dielectric losses for the LTCC applications. It is noticeable that dielectric loss of the Li3.0 sample showed the highest value of 0.0125. Dielectric constant tends to increase with the addition of alkali oxides except the K3.5 samples that resulted poorly dense. This observed increase in dielectric constant is likely associated with a higher dielectric constant (k~8.5)[17] of $ZnAl_2O_4$ (compared to k~7.14 for anorthite[18]) that was observed in the XRD pattern of Fig. 2 when the additional alkali oxides were added.

4. Conclusions

The effects of alkali oxides, K_2O, Na_2O and Li_2O, on the physical and dielectric properties of a calcium zinc aluminoborosilicate glass-based dielectrics suitable for the LTCC applications were investigated. Some unexpected results including early crystallization and involvement of the second $ZnAl_2O_4$ phase were found by the alkali additions when an identical firing condition was applied. The influence of Li was found most influential in determining the final physical and dielectric properties of the resulting dielectrics.

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