



Effect of SiO₂ Addition to BaO-ZnO-B₂O₃ Glass on Dielectric and Thermal Properties for Application to Barrier Ribs of Plasma Display Panels

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Abstract. The effect of SiO₂ addition to barium zinc borate (BaO-ZnO-B₂O₃, BZB) glass on dielectric and thermal expansion properties was investigated. When SiO₂ was added to the glass batch to form a SiO₂-BaO-ZnO-B₂O₃ (SBZB) glass, the dielectric constant decreased significantly from 15.5 to 9.9. When SiO₂ (quartz) was further added to the SBZB in the form of filler particles to yield ceramic filler-reinforced SBZB microcomposites, the dielectric constant was further decreased. The coefficient of thermal expansion (CTE) of SBZB was slightly lower than the allowable range, while the filler addition to SBZB correspondingly increased CTE to the allowable range. Thus, the addition of SiO₂ to BZB glass to form SBZB glass and further addition to SBZB in the form of ceramic filler were shown to be amenable ways to tailor the dielectric constant as well as CTE of the barrier rib glass for the PDP application.

Keywords: SiO₂, barium zinc borate glass, filler, barrier rib

1. Introduction

Lead borosilicate glasses have been mostly used as barrier ribs in plasma display panel (PDP) systems [1–3] due to desirable application properties such as low softening temperature, comparable coefficient of thermal expansion to aluminium borosilicate glass panels such as PD200 ($8.3 \times 10^{-6}/\text{K}$; Asahi Glass, Tokyo, Japan), low dielectric constant, and high reflectivity. In addition to the basic components such as PbO-B₂O₃-ZnO-SiO₂, several minor components such as Al₂O₃, TiO₂, and MgO were added to modify the properties of the glass itself. Also, crystalline ceramic fillers were further added to form a ceramic particulate-glass microcomposite to tailor reflectivity, dielectric constant, coefficient of thermal expansion, and fracture toughness.

Recently, interest in lead-free glasses [4–6] has greatly increased due to the deleterious effect of Pb on

health and environment [7]. A notable alternative glass system to the Pb-based system is the recently reported BaO-ZnO-B₂O₃ (BZB) system [8–9], which has been shown to have dielectric constants of 14–18 and a coefficient of thermal expansion (CTE) of $8-9 \times 10^{-6}/\text{K}$ [9]. Since a high dielectric constant can result in a delay of the signal response of the pixel in PDP, the desirable dielectric constant of the glass is less than about 12 [10–11]. Although the CTE of the BZB glass is comparable to the aluminium borosilicate glass panel (about $8-9 \times 10^{-6}/\text{K}$), it is necessary to adjust its dielectric constant to less than about 12. Therefore, the present study aims to reduce the dielectric constant of the BZB glass. In light of Appen and Breska [12], addition of SiO₂ to a glass composition is one of the most efficient ways to decrease the dielectric constant of the glass as compared to the addition of other readily available oxides. Thus, in the current work, the dielectric constant reduction resulting from SiO₂ addition to the BZB glass system was investigated.

The first issue related to the SiO₂ addition into the BZB glass is whether the new batch composition forms

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a stable glass (SBZB) composition with a sufficiently low softening point. The second issue is whether the SiO₂, a low-dielectric-constant material, can be used as ceramic filler in the SBZB system to form a stable SiO₂ (quartz) particle-reinforced glass matrix microcomposite via densification at a sufficiently low temperature. Finally, it is necessary to investigate the resultant change in CTE with the addition of the low-dielectric-constant filler.

2. Experimental Procedure

The compositions of glass batches are shown in Table 1. Appropriate amounts of BaCO₃ (−325 mesh, B1012, Cerac Inc., Milwaukee, WI, USA), ZnO (High Purity, Chemicals, Saitama, Japan), B₂O₃ (−850 μm, High Purity, Chemicals, Saitama, Japan) and SiO₂ (Quartz, avg. particle size of 0.8 μm, High Purity, Chemicals, Saitama, Japan) powders were mixed to form a 100g batch and ball milled using zirconia balls in ethanol medium for 12 h.¹ The batch was then melted in a platinum crucible at 1300°C for 1 hr in air, followed by quenching to room temperature. The quenched glass was pulverised to an average particle size of 1.0 μm using a planetary mill (Model PM400, Retsch, Germany) with zirconia balls and a container. The powder was then granulated after immersion into a 10 wt% polyvinyl alcohol (PVA)–water solution and subsequent drying. The granulised glass frits were then uniaxially pressed in a disk shape at about 1.3 × 10³ kgf/cm², followed by densification at 575°C or 2 h in air. As shown in Table 1, the densified specimens are denoted as BZB and SBZB depending on their compositions.

The compositions of the SiO₂ filler-added specimens (SBZB + 5S, SBZB + 10S, and SBZB + 14S) are shown in Table 2. The pulverised SBZB glass frits were mixed with an appropriate amount of SiO₂ (Quartz, avg. particle size of 0.8 μm, High Purity, Chemicals, Saitama, Japan) using a magnetic stirrer in an ethanol medium, followed by drying and further pulverization using alumina mortar and pestle. Then,

Table 1. Compositions of glass specimens (mol%).

Specimens	BaO	SiO ₂	ZnO	B ₂ O ₃
BZB	25	–	25	50
SBZB	10	10	40	40

Table 2. Compositions of SiO₂ filler-added microcomposites (wt%).

Specimens	SBZB glass frits	SiO ₂ filler
SBZB + 5S	95	5
SBZB + 10S	90	10
SBZB + 14S	86	14

the dried powder mixture was granulised, uniaxially pressed, and densified under the same conditions as the BZB and SBZB glass specimens.

In order to quantify the residual amount of crystalline SiO₂ ceramic filler (quartz) in SBZB + 5S, SBZB + 10S, and SBZB + 14S specimens, a quantitative X-ray diffraction (CuKα, radiation, 2°/min, MacScience Co., Model M18XHF-SRA, Japan) was performed using 20 wt% silicon powder (−325 mesh, Morton Thiokol Inc., Danvers, MA, USA) as the internal standard. The calibration chart shown in Fig. 1 was established based on maximum peak intensities from the (101) plane in SiO₂ (JCPDS No. 46-1045) and the (111) plane in Si (JCPDS No. 27-1402). After establishing the calibration chart, the microcomposite specimens with unknown amounts of residual SiO₂ crystal phase were pulverized and mixed with a 20 wt% silicon standard, followed by XRD measurement to determine the intensity ratio of the SiO₂ to the silicon standard. The amount of the residual crystalline SiO₂ phase was quantified from the determined intensity ratios using the calibration chart shown in Fig. 1.

For the measurement of dielectric constant of the specimens, an In-Ga paste was used as the electrode material. The dielectric constant was determined

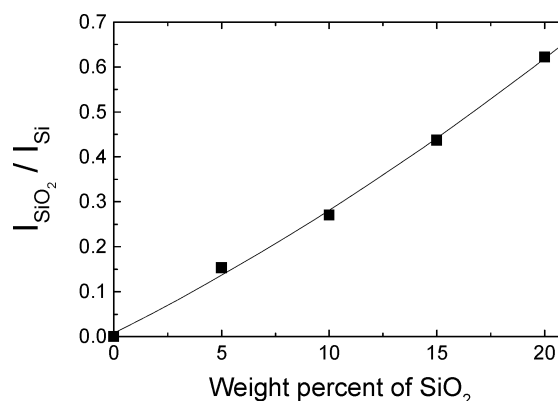


Fig. 1. XRD calibration chart for the quantification of crystalline SiO₂ in the SBZB glass matrix.

in the frequency range of 10 to 10 MHz using an impedance analyser (Hewlett-Packard, Model 4194A, USA). Thermal expansion coefficient of the specimens was measured using a horizontal-loading dilatometer (Netzch Instruments, Model DIL 402PC, Germany).

3. Results and Discussion

3.1. Thermochemical Stability of SiO₂-Added Specimens

The as quenched SBZB glass frits showed a softening temperature of about 575°C in the thermal expansion experiment with no evidence of crystallization when heated up to 600°C in differential thermal analysis and XRD (not shown), which is in agreement with other BZB compositions elsewhere [9]. This result confirms that the newly studied composition, SBZB, also forms a stable glass with a low softening point. The next issue regarding the thermochemical stability is whether the additionally added SiO₂ filler to the SBZB glass forms a stable microcomposite. If the SiO₂ filler inhibits the densification of the glass frits, all the added SiO₂ will be present in crystalline form; thereby the quantitative analysis of the specimen would yield no appreciable change in the amount of crystalline SiO₂ phase. On the other hand, if the SiO₂ filler is dissolved into the glass during the densification, there would be a decrease in SiO₂ amount after the densification, and thus it is necessary to investigate how much of the added SiO₂ filler has survived or been dissolved. The residual amount of crystalline SiO₂ filler phase in the SBZB glass matrix composites based on the quantitative XRD is shown in Fig. 2. Although quantification of less than 5 wt% in XRD is generally difficult, the samples studied in the current work showed a negligible background near the peaks of interest, and thus quantification as low as 2 wt% was possible. In Fig. 2, the addition of 5, 10 and 14 wt% SiO₂ ceramic filler yielded only 2.5, 6.4 and 10.5 wt% of the residual crystalline SiO₂ phase, respectively, indicating that the dissolution of SiO₂ ceramic filler into the SBZB glass was significant. However, a considerable amount of residual SiO₂ ceramic filler was still observed.

The morphology of the residual SiO₂ filler after densification was characterized by scanning electron microscopy (SEM) as shown in Fig. 3(a). Two distinctive regions appeared: a grey major region (marked as

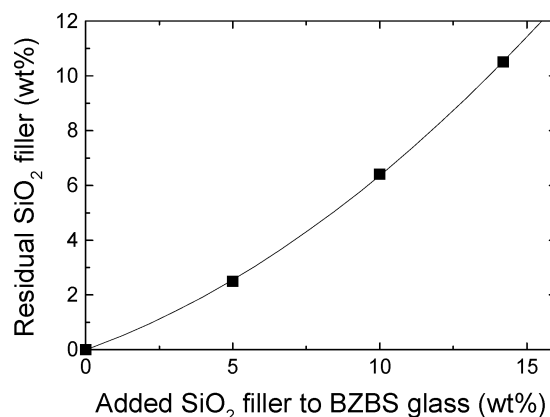
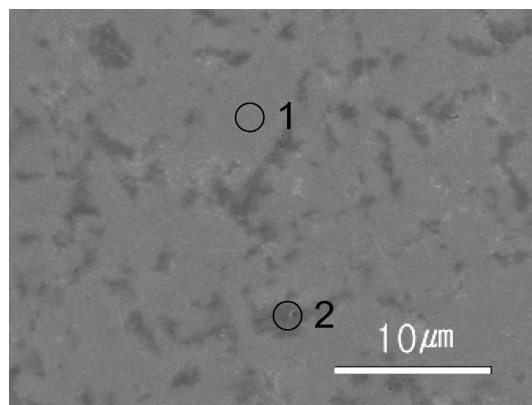
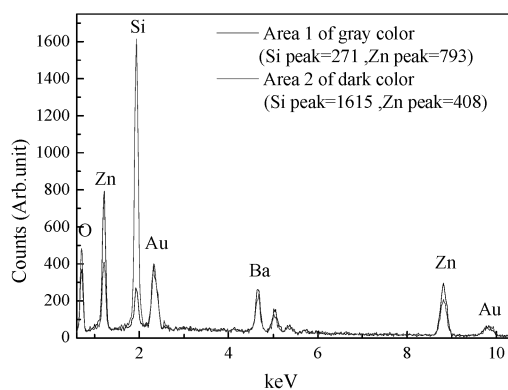


Fig. 2. Change in weight percentage of residual crystalline SiO₂ phase in the SBZB glass matrix as a function of SiO₂ filler addition.



(a)



(b)

Fig. 3. (a) SEM image of SBZB glass + 14 wt% SiO₂ and (b) EDS in the ceramic filler (dark area) and the glass matrix (gray area).

“1”) and a relatively darker region (marked as “2”) in the secondary electron mode. As confirmed by the energy dispersive spectroscopy (EDS) result (Fig. 3(b)), the darker areas were relatively rich in silicon, implying that these regions are the residual SiO₂ filler. The shape of the residual filler was rather irregular, differing from its original roughly spherical shape (not shown). These regions existed along the boundaries of the former glass frits. This microstructural feature and quantitative XRD result indicate that a SiO₂ filler addition to SBZB glass results in an appreciable dissolution into the glass matrix to achieve a chemical bonding with matrix. Thus, the specimen successfully forms a ceramic filler-reinforced glass matrix microcomposite with a strong filler/matrix interface bonding. The relative density of all the microcomposite specimens was 98.5, 97.5, 97.1, and 96.0%, for SBZB, SBZB + 5S, SBZB + 10S, and SBZB + 14S, respectively, indicating a successful densification with the fillers.

3.2. Dielectric Property

Having shown the thermochemical stability of the newly studied specimens in the present work, i.e., SBZB, SBZB + 5S, SBZB + 10S, and SBZB + 14S, their dielectric and thermal expansion properties were investigated. Figure 4 shows the dielectric constant as a function of frequency for the investigated samples. As seen in Fig. 4, the dielectric constant of SBZB glass (9.9) was significantly lowered from BZB glass (15.5), indicating the efficiency of the SiO₂ addition to the

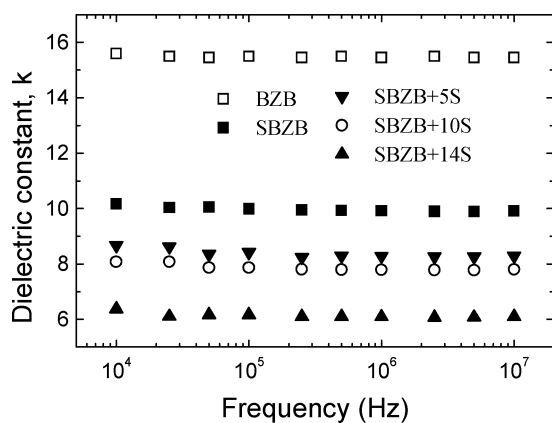


Fig. 4. Dielectric constants at various frequencies of the BZB, SBZB, SBZB + 5S, SBZB + 10S, and SBZB + 14S specimens.

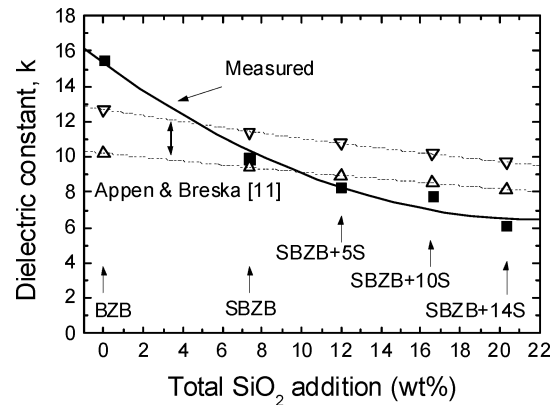


Fig. 5. Change in Dielectric constant at 1 MHz frequency as a function of total SiO₂ added to BZN composition and predicted values.

glass composition in reducing the dielectric constant. For these fired glass specimens (BZB and SBZB) from respective glass frits, there was no appreciable difference of dielectric constant from the as-quenched glass due to the successful densification.² As noted in Fig. 4, the dielectric constant of the specimens with quartz filler is even lower than the SBZB glass, indicating that the addition of quartz filler can further reduce the dielectric constant.

Figure 5 shows the dielectric constant measured at 1 MHz as a function of total SiO₂ addition together with the predicted values based on the model of Appen and Breska [12]. This empirical model provided factors from which the dielectric constants were calculated through the equation:

$$k = \frac{1}{100} \sum \kappa_i p_i$$

where p_i is the portion of the oxide ingredient in glass in mole percent and κ_i is the characteristic factor for each oxide. κ_i of BaO is 20.5, ZnO 14.4, B₂O₃ 3–8, and SiO₂ 3.8. In the case where the ceramic fillers were added (SBZB+5S, SBZB + 10S, and SBZB + 14S), the dielectric constants were calculated using the rule of mixture [13] based on SBZB glass and residual SiO₂ ceramic (dielectric constant is 3.9). The experimentally observed change in the dielectric constant from BZB to SBZB was more pronounced than the predicted trend by Appen and Breska [12]. However, the decrease in dielectric constant, with the filler addition to SBZB to form SBZBS + 5S, SBZBS + 10S, and SBZBS + 14S, was more or less similar to the trend predicted by the

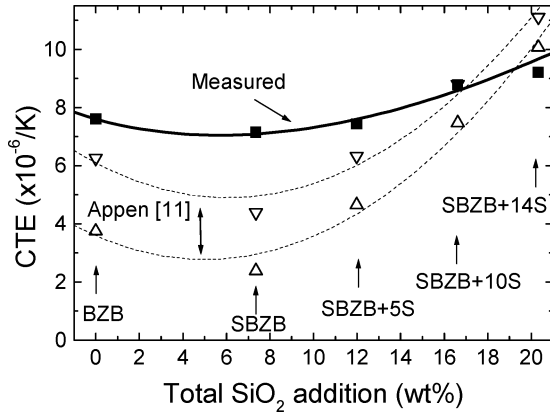


Fig. 6. Change in coefficient of thermal expansion as a function of total SiO₂ added to BZN composition and predicted values.

rule of mixture. The discrepancy between the model and experimental result may have arisen from the rough estimate of the provided dielectric constant factor κ_i of the model. This estimate varied notably depending on the type of the glass system and the number of constituents in the system, i.e., binary, ternary, or quarternary system, etc. [11]

3.3. Thermal Expansion Property

Finally, we present the change in coefficient of thermal expansion resulting from the addition of SiO₂. Figure 6 shows the change in coefficient of thermal expansion as a function of SiO₂ addition. Also shown in Fig. 6 are the predicted values based on Appen [11],

$$\alpha = \sum \alpha_i p_i$$

where α_i indicates the mole percent of the individual oxides and p_i is the characteristic factor for each oxide. In Appen's model, p_i for BaO is 20, ZnO 5.0, SiO₂ 3.8, and B₂O₃ is -5.0 to 0.0. For the case of SiO₂ filler-added microcomposites, the model originally proposed by Turner [12] was used:

$$\alpha_c = \frac{\alpha_m V_m K_m + \alpha_f V_f K_f}{V_m K_m + V_f K_f}$$

where α is the coefficient of thermal expansion, V the volume fraction, K the bulk modulus ($=E/3(1-2\nu)$), where E is the elastic modulus and ν the Poisson's ratio. The subscripts m , f , and c denote the glass matrix,

quartz filler, and the microcomposite. For the calculation, the predicted value of SBZB glass by Appen was used for α_m and α_f was $19.35 \times 10^{-6}/K$ [13]. E_m and E_f values were 18.5 and 87 GPa [14], respectively.

In Fig. 6, the prediction using the model of Appen [12] underestimated the measured CTEs of BZB and SBZB glasses, although there is some similarity in the trend of change on a qualitative base. Such underestimation was also found for a number of BZB glass compositions [9]. This discrepancy between the model and experimental result may have arisen from the rough estimate of the provided CTE factor p_i of the model. Similar to the case of the dielectric constant, the results also varied depending on the type of the glass system and number of constituents in the system [11].

For the case of filler-added specimens, the addition of SiO₂ in the form of ceramic filler (quartz) to the SBZB glass was predicted to yield a pronounced increase in the coefficient of thermal expansion based on the model of Turner [12]. The increase in measured CTE with the addition of quartz filler was, however, less pronounced than the prediction. The CTE values for BZB and SBZB glasses were slightly lower than the value of the aluminium borosilicate glass panels such as PD200 ($8.3 \times 10^{-6}/K$). However, the addition of SiO₂ filler to SBZB glass gradually increased the CTE to the allowable range. Therefore, the quartz filler addition can be used as a way to tailor the CTE of the microcomposite to be compatible with the PDP glass substrates, in addition to the control of the dielectric constant.

4. Conclusions

The effect of SiO₂ addition to BaO-ZnO-B₂O₃ (BZB) glass on dielectric and thermal properties was investigated from the viewpoint of its application to barrier ribs of plasma display panels. SiO₂ (quartz) was first added as a constituent to form SiO₂-BaO-ZnO-B₂O₃ (SBZB) glass. Then, SiO₂ was further added to the SBZB glass frits as crystalline ceramic filler. From the XRD data and SEM, it was found that the SiO₂ filler partially dissolved into the SBZB glass matrix to form a chemical bond with the SBZB glass.

The SiO₂ addition as a glass constituent decreased the dielectric constant of the glass significantly from 15.5 to 9.9. The further addition of SiO₂ to the SBZB glass as a form of crystalline filler further decreased the dielectric constant from 9.9 to 6.0. As for the coefficient

of thermal expansion (CTE), the SiO₂ addition as a glass constituent decreased the CTE slightly from 7.7 to $7.2 \times 10^{-6}/\text{K}$, but further SiO₂ addition to SBZB glass as a form of ceramic filler up to 14 wt% increased the CTE of glass from 7.2 to $9.3 \times 10^{-6}/\text{K}$. Thus, the CTE of glass could be adjusted to the CTE of PD200 ($8.3 \times 10^{-6}/\text{K}$) through the addition of SiO₂ into BZB glass. The addition of SiO₂ to BZB glass to form SBZB glass and the further addition of SiO₂ to SBZB in the form of ceramic filler (quartz) were shown to be effective means for tailoring the dielectric constant as well as the CTE of the barrier rib glass for the PDP application.

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Notes

1. The processing conditions for SBZB composition is shown herein. The conditions for BZB reference composition is described elsewhere [9].
2. For the measurement of the dielectric constant of the as-quenched glass specimens, the specimens were post-annealed to inhibit ther-

mal stress-induced cracking during cutting for dielectric sample preparation.

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