

## Compositional Effect of SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-BaO Ternary Glass System for Reversible Oxide Cell Sealing Glass

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### ABSTRACT

Thermal properties of a SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-BaO ternary glass system depending on compositional change of BaO have been examined to find a proper sealing material for reversible oxide cells. Glass transition temperature and thermal expansion coefficients increased simultaneously up to 55 mol% of BaO content. The structural role of BaO with regard to the thermal properties has been discussed on the basis of Raman spectroscopy results. Flowability of the glass at sealing temperature has been examined with packed glass powders of 12 mm diameter along with a high temperature optical microscope. The practical sealing property of the glass was also examined with YSZ coated with NiO-yttria stabilized zirconia (NiO-YSZ) and it showed good adhesion without noticeable reaction with NiO-YSZ layer.

**Key words :** Glass, Silicates, Sealing, Fuel cell, Thermal properties

### 1. Introduction

Solid oxide fuel cells (SOFC) produce electricity by the reaction of oxygen and hydrogen at elevated temperature producing water as a byproduct and have been extensively studied as a clean alternative energy source.<sup>1)</sup> On the contrary, solid oxide electrolysis cells (SOEC) decompose water with electricity producing oxygen and hydrogen gases.<sup>2)</sup> Since a SOFC can be also used as a SOEC and vice versa when the device is operated reversely, a reversible solid oxide cell (RSOC) can be a good alternative power source for small and medium sized buildings and thus also has been widely investigated.<sup>3-5)</sup> As a RSOC operates under the same conditions as a SOFC, hermetic sealing of RSOC components to prevent any possible leakage of gases is crucial for the efficiency and long-term stability of the cell. Since it operates at elevated temperature normally above 700°C in SOFC mode, the sealing material should be stable at operating temperature and show a good flow tendency and adhesion property to the cell components during the sealing process, which normally is carried out above 850°C. Moreover, due to the high coefficient of thermal expansion (CTE) of the SOFC or RSOC components ( $> 110 \times 10^{-7}/^{\circ}\text{C}$ ), the sealing material should also have a high CTE to avoid possible thermal stress between cell components during operation.

Glass materials with a high glass transition temperature ( $T_g$ ) and proper flow behavior at sealing temperature as well as a high CTE are thus required for SOFCs and RSOCs. Since the  $T_g$  of a glass system increases with structural strengthening components, which normally decrease CTE, it is difficult to find a proper glass system simultaneously having a high  $T_g$  and a high CTE. SiO<sub>2</sub>-BaO based glass systems such as SiO<sub>2</sub>-BaO-CaO-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-BaO-Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>-BaO-B<sub>2</sub>O<sub>3</sub><sup>6-9)</sup> have been widely studied for SOFC sealing materials due to their high  $T_g$  and high CTE. Although their potential for sealing materials has been reported, there has been no systematic study on the effect of BaO content on the ternary system and its structural role to provide a high  $T_g$  with a high CTE at the same time has not been adequately discussed so far.

Thus, in this study, a SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-BaO ternary glass system has been studied to find proper RSOC sealing materials and to understand the compositional effect of BaO on the thermal properties. With fixed content of SiO<sub>2</sub>=20, 25, and 30 mol%,  $T_g$  and CTE were monitored with BaO content and their respective structural change was inspected and discussed with Raman spectroscopy. The feasibility of Seal as a RSOC sealing material also has been examined.

### 2. Experimental Procedure

The glass compositions used in this study were 20SiO<sub>2</sub>-(80-x)B<sub>2</sub>O<sub>3</sub>-xBaO (SBB20x), 25SiO<sub>2</sub>-(75-x)B<sub>2</sub>O<sub>3</sub>-xBaO (SBB25x), and 30SiO<sub>2</sub>-(70-x)B<sub>2</sub>O<sub>3</sub>-xBaO (SBB30x) (in mol%), where x was varied from 45 to 60 mol%, respectively. High purity raw materials (> 99.9%) were weighed and thoroughly mixed with ball milling. Glasses were melted at 1400–

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1450°C for 1 h in an alumina crucible and then quenched in a brass mold, followed by annealing at 350–650°C for 5 h. The obtained glasses were ground into powder under 45 μm in size.

Cylindrical samples (diameter of 12 mm) with 4 g of glass powder were formed by packing with a uniaxial press to examine the glass stability and flowability under heat treatment at 800°C and 900°C for 30 minutes. The  $T_g$  was determined by a differential scanning calorimeter (DSC-60, Shimadzu, Japan) and the CTE was determined in the range of room temperature to  $T_g$  by a thermo-mechanical analyzer (TMA-60H, Shimadzu, Japan). Raman spectroscopy (ARAMIS, Horiba Jobin Yvon, France) with an Ar-laser source (514 nm center wavelength) was used to investigate the glass structure. Crystalline phase after heat treatment of the glass was determined by X-ray diffraction (Mini Flex 600, Rigaku, Japan) and the flowability of the glass was determined by a heating microscope (Misura(R) 3 HSM, TA Instruments, United States). A scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (TESCAN, MIRALMN, Czech) was applied to examine the reaction between the glass and RSOC component.

### 3. Results and Discussion

Under the same melting conditions, all compositions formed clear glasses except SBB3060 ( $x=60$ ), which did not properly melt. The thermal properties of the obtained glasses were then examined. Fig. 1 exhibits the  $T_g$  change of SBB glasses with BaO content. As can be found in the figure,  $T_g$  increases with the addition of BaO up to 55 mol% for SBB20x and SBB25x and decreases thereafter at the fixed  $\text{SiO}_2$  content.  $T_g$  decreased from 50 mol% for SBB30x glasses. It is known that alkali- or alkaline earth-oxides (ROs) facilitate the formation of  $\text{BO}_4$  units and network connectivity within borosilicate glasses with increasing  $T_g$  and

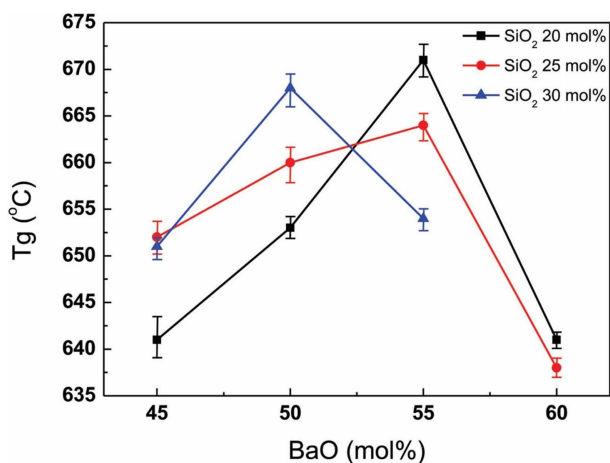


Fig. 1. Glass transition temperature ( $T_g$ ) of  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-BaO}$  ternary glasses with varying BaO content for each fixed  $\text{SiO}_2$  concentration.

viscosity up to a given concentration, but generate non-bridging oxygens (NBOs) with decreasing  $T_g$  at higher concentrations.<sup>10,11</sup> Holbrook *et al.*<sup>8</sup>) inspected the topology and glass structure change according to BaO content of  $(\text{BaO})_x(\text{B}_2\text{O}_3)_{32}(\text{SiO}_2)_{68}{}_{100-x}$  glasses and also observed an increase and decrease of  $T_g$  with an increase of BaO content. After Raman and volumetric analyses, as previously reported,<sup>8</sup>) they also suggested that the formation of  $\text{BO}_4$  tetrahedral units and charge compensation role of Ba-ions were responsible for the increase of  $T_g$  while the depolymerization role of BaO at a high concentration of BaO decreases the  $T_g$ . Thus, the change of  $T_g$  with BaO content can be elucidated in a similar way. The discrepancy of the  $T_g$  compared to the previous literatures<sup>12,13</sup>) is possibly due to the dissolution of  $\text{Al}_2\text{O}_3$  from alumina crucible during the melting process. The effect of  $\text{Al}_2\text{O}_3$  on  $T_g$  and viscosity on  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-BaO}$  system is currently under study.

Figure 2 shows the CTE variation depending on the BaO content. As demonstrated in the figure, CTE increased with BaO content when  $\text{SiO}_2$  was fixed. Based on the structural role of BaO within borosilicate glass for  $T_g$  behavior, CTE is expected to decrease due to the increased  $\text{BO}_4$  units and network connectivity. However, CTE increased for all SBB glasses with BaO addition. It should be noted that the CTE is directly related to the bond strength of a solid and the replacement of  $\text{B}_2\text{O}_3$  with BaO effectively reduces the average bond strength due to the weak bond strength of Ba-O (561.9 kJ/mol) compared to that of B-O (808.8 kJ/mol).<sup>12</sup>) Thus, it appears that the CTE of the present system has been more effectively determined by the average bond strength of components than the structural change of the glass. It should be also noted that, considering the high CTE of RSOC components, the CTE of the glass should be higher than  $100 \times 10^{-7}/^\circ\text{C}$  to reduce the possible thermal stress induced at the interface. According to the results obtained in Fig. 2, SBB2560 appears to be suitable for RSOC applications.

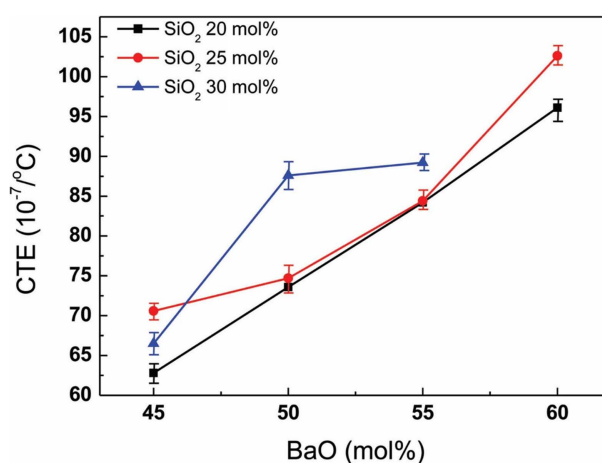


Fig. 2. Coefficient of thermal expansion (CTE) of  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-BaO}$  ternary glasses with varying BaO content for each fixed  $\text{SiO}_2$  concentration.

The structural change of the current glasses with BaO has been investigated with Raman spectroscopy. As shown in Fig. 3, all glasses show similar Raman peak evolution with the increase of BaO content for all the fixed SiO<sub>2</sub> content. Raman shifted peak assignments are summarized in Table 1. As found in the figure, Raman peaks gradually varied up to 55 mol% of BaO. As BaO increased in lieu of B<sub>2</sub>O<sub>3</sub>, the peak at ~ 1040 cm<sup>-1</sup> has been shifted to the lower energy side, implying the development of Q<sup>2</sup> among the existing Q<sup>3</sup> units, where Q<sup>n</sup> represents the [SiO<sub>4</sub>] tetrahedral unit with the number of bridging oxygens (n). The evolution of Raman peaks at 530 ~ 560 cm<sup>-1</sup> at the expense of the peak at ~ 490 cm<sup>-1</sup> indicates that the increase of [BO<sub>4</sub>] units replacing [SiO<sub>4</sub>] as BaO increases. These changes also have been observed with SiO<sub>2</sub> content variation<sup>8)</sup> and suggest that the formation of [BO<sub>4</sub>] structural units along with the structural variation of [SiO<sub>4</sub>] supporting the increase of T<sub>g</sub>. However, it should be noted that the peak at ~ 900 cm<sup>-1</sup> has been highly improved when BaO content was 60 mol%, indicating that the [SiO<sub>4</sub>] structural units exist mostly in Q<sup>1</sup> and Q<sup>2</sup> units.

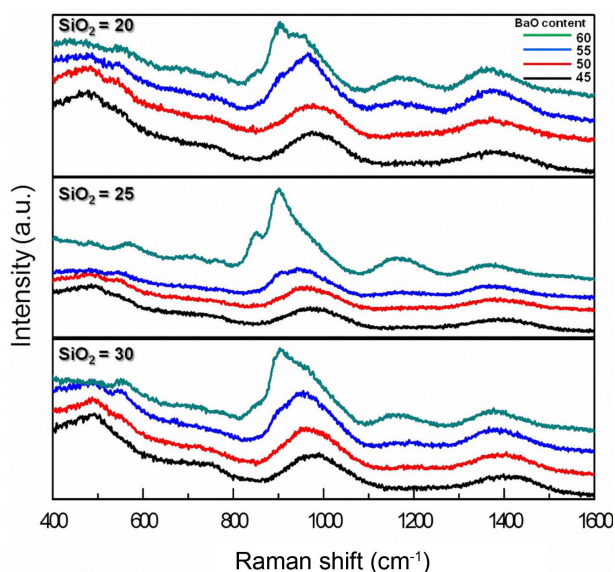


Fig. 3. Raman peak shifts for SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-BaO ternary glasses with varying BaO content for each fixed SiO<sub>2</sub> concentration.

Table 1. Raman Peak Assignments of SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-BaO Ternary Glass System

Raman Peaks (cm <sup>-1</sup> )	Assignments	Ref.
497	Oxygen symmetric stretch of 4-membered rings of SiO <sub>4</sub> units in SiO <sub>2</sub>	[8]
530	Oxygen symmetric stretch of 4-membered mixed rings of one BO <sub>4</sub> and three SiO <sub>4</sub> units as in Reedmergnerite	[8]
843	Si-O <sup>-</sup> stretching in Q <sup>0</sup> units	[13]
877	Si-O <sup>-</sup> stretching in Q <sup>1</sup> units	[13]
934 ~ 1000	Si-O <sup>-</sup> stretching in Q <sup>2</sup> units	[13], [14]
1040	Si-O <sup>-</sup> stretching in Q <sup>3</sup> units	[15]
1140	Asymmetric stretch of BO <sub>3</sub> <sup>3-</sup>	[16]
1300 ~ 1450	B-O <sup>-</sup> attached to large borate group	[17]

The peaks at ~ 840 and 1140 cm<sup>-1</sup> represent the formation of orthoborates [BO<sub>3</sub><sup>3-</sup>] units and have been developed above 55 mol% of BaO. Along with the development of Q<sup>1</sup> and Q<sup>2</sup> units, this clearly supported the increased number of NBOs within the glass structure and the role of BaO as an efficient structure modifier above 55 mol%. Thus, it appears that BaO acts as a charge compensator, forming [BO<sub>4</sub>] units with modification of the SiO<sub>4</sub> network below 55 mol%, and efficiently depolymerizes the glass network, forming NBOs above 55 mol% within the present glass system. These structural changes, as discussed earlier, elucidate the variation of T<sub>g</sub> with BaO content.

In order to be used as a hermetic sealing material for RSOC operating up to 750°C, it is desirable for the glass to show minimized viscous flow up to 800°C while it should guarantee a good flow at sealing temperature, for example,

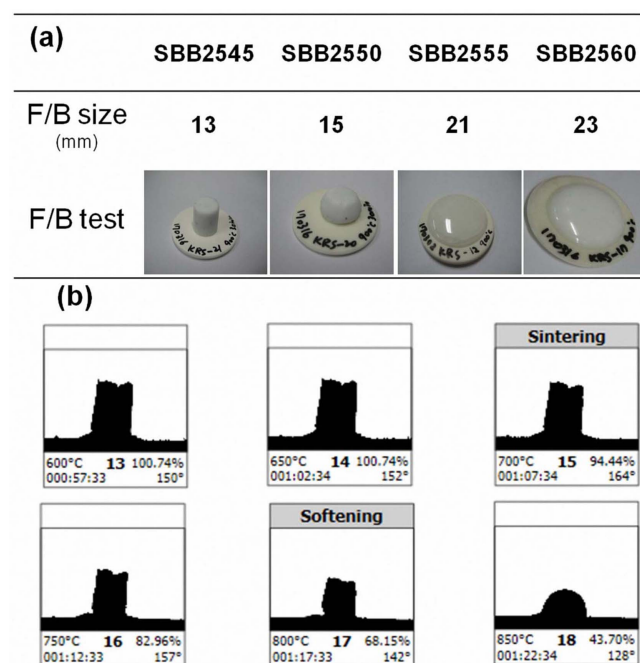
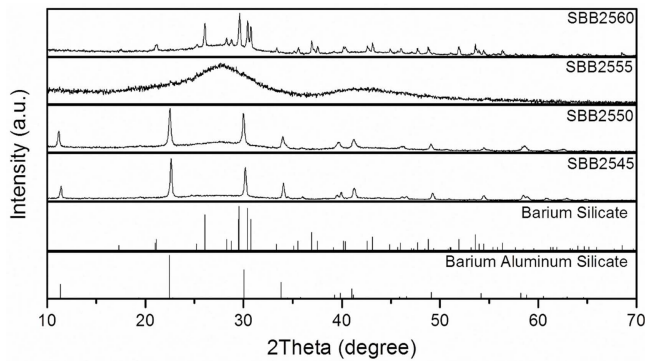


Fig. 4. (a) Flow button test results for SBB25x glasses sintered at 900 °C for 30 min. and (b) high temperature microscope images of SBB2560 glass powders with increasing temperature.



**Fig. 5.** XRD results of SBB25x glasses sintered at 900 °C for 30 min.

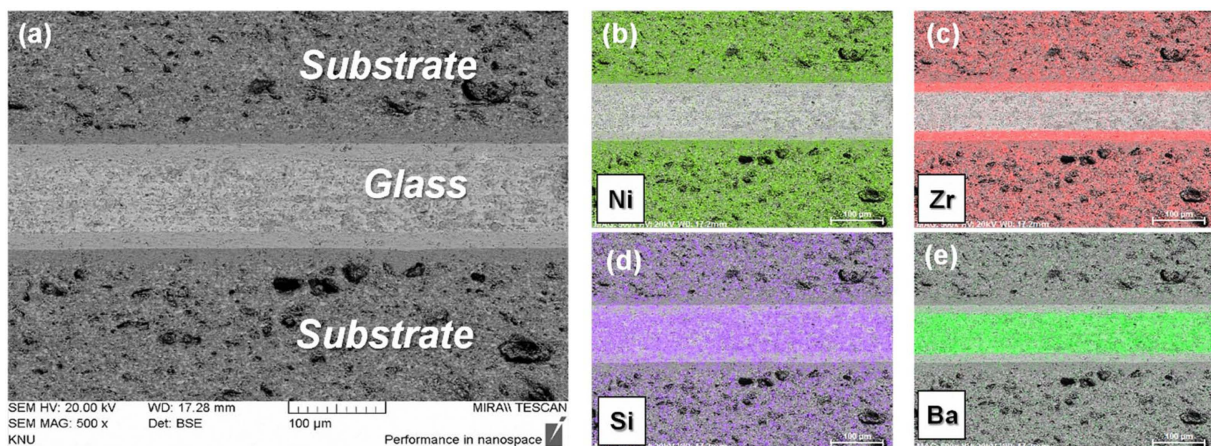
at 900°C. Fig. 4(a) shows the flow button test conducted at 900°C for SBB25x glasses with varying BaO content. As summarized in the figure, glasses with BaO content of 45 and 50 mol% showed no or limited flow while glasses with 55 and 60 mol% exhibited good viscous flow at the sealing temperature. Possible crystallization has been inspected with an X-ray diffractometer (XRD) and the results are depicted in Fig. 5. SBB2545 and SBB2550 glasses showed noticeable crystallization peaks corresponding to barium aluminum silicate ( $\text{BaAl}_2\text{Si}_2\text{O}_8$ ), which is expected to hinder the viscous flow at 900°C. Possible contamination of  $\text{Al}_2\text{O}_3$  from the alumina crucible may facilitate the crystallization. Crystallization can help to control the viscous flow of the glass during the long term operation of the cell increasing mechanical strength, but the glass-crystal interface also can be a crack source. Further study is required for the effect of the crystallization. SBB2555 showed characteristic diffuse XRD patterns demonstrating its glass stability at the sealing temperature while SBB2560 presented crystallization peaks due to barium silicate ( $\text{Ba}_2\text{SiO}_4$ ). Despite the crystallization, SBB2560 showed good viscous flow at the sealing temperature along with a high CTE for RSOC application. Thus, the viscous flow of SBB2560 glass with temperature variation has been examined using a high temperature

microscope, as displayed in Fig. 4(b). Shrinkage of the glass powders started at 700°C but the visual viscous flow started from 800°C. The results clearly suggest that the glass can be a good candidate for SOFC or RSOC operating at 700 ~ 750°C along with a good viscous flow property at the sealing temperature and high CTE.

The binding property of the SBB2560 glass has been inspected with YSZ coated with NiO-YSZ substrates with sintering temperature at 900°C for 30 min. The glass was thoroughly mixed with ethyl cellulose-based organic vehicle to make a paste with a mixing ratio of 7:3 in wt.%. The organic vehicle was removed at 450°C for 1 h during the heat treatment process for sealing. As can be found in Fig. 6, the intermediate layer between the glass and substrate is the YSZ coating layer of the NiO-YSZ substrate. And the glass bonded well to the NiO-YSZ layer with minimized pores trapped. No crystallization or a noticeable reaction layer was observed. Elemental analysis via SEM-EDS revealed that the elements for sealing glass and NiO-YSZ layer were well confined within each material, clearly supporting the restricted reaction between them as well as the practical feasibility of the present glass as a RSOC sealing material.

#### 4. Conclusions

$\text{SiO}_2\text{-B}_2\text{O}_3\text{-BaO}$  ternary glasses were synthesized with varying BaO and  $\text{B}_2\text{O}_3$  content at fixed  $\text{SiO}_2$  concentrations. When BaO content was increased at the expense of  $\text{B}_2\text{O}_3$ , CTE increased while  $T_g$  showed a maximum at around 55 mol% of BaO. The formation of  $[\text{BO}_4]$  tetrahedral units strengthening the glass network was considered to be responsible for the increase of  $T_g$  and the effective network breakage generating NBOs,  $Q^1$  and  $Q^2$  units of  $[\text{SiO}_4]$  and  $[\text{BO}_3^-]$  units were responsible for the decrease of  $T_g$  at high BaO content. The increase of CTE in spite of network strengthening with BaO is attributed to the decrease of bond strength due to B-O replacement with Ba-O. SBB2560 showed a high CTE with reasonable flow characteristics at



**Fig. 6.** (a) SEM image of the cross-section after binding the SBB2560 glass with NiO-YSZ substrates. Elemental mapping of (b) Ni, (c) Zr, (d) Si, and (e) Ba obtained via SEM-EDS is also shown in the figure.

the operating and sealing temperatures. It also showed a good adhesion property without crystallization and reactions with YSZ coated with NiO-YSZ, demonstrating its feasibility for RSOC applications. However, further study is required to improve the glass stability and further examinations such as studying the binding properties with other RSOC components and long-term leak tests also should be carried out for practical application of the glass materials.

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