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Characterization of the low temperature firing $BaO–B_2O_3–SiO_2$ glass: The effect of BaO content

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Abstract

In the low temperature sinterable glass system of $BaO–B_2O_3–SiO_2$, the structural changes of the glasses and the resultant changes in the properties of the glasses were examined as a function of BaO content. ^{11}B MAS-NMR analysis was conducted in order to examine the coordination number of borons in the glass. It showed that the amount of O_4 was greatest at 35 mol% of BaO. The glass transition temperature, hardness, thermal expansion coefficient and dielectric constant of the glasses were examined and the results were explained on the basis of the structural change.

Keywords: Glass; Borate anomaly; Thermal properties; Dielectric properties; NMR

1. Introduction

With great progress in flat panel display industries, there has been increasing interest in borosilicate glass and its application to barrier ribs, transparent dielectrics and sealing glasses.[1–3] Since B_2O_3 glasses have a low softening temperature, they have been used as sintering aids for the application to low temperature ceramic co-firing (LTCC). Among the borosilicate glass components, B_2O_3, which plays a role in the network former, is composed of a basic unit of two-dimensional BO_3 triangles. Although infinite chains are formed in the crystal, it is known that the aggregates of three such triangles form the B_3O_6 boroxol groups, which in turn form an irregular network.[4] When a network modifier is added, the incorporation of alkali oxides lead to a coordination shift from three-coordinated (BO_3) to four-coordinated borons (BO_4) with alkali ions adjoining the BO_4 tetrahedron and without formation of the places of separation. The structure has not been weakened. On the contrary, it has become strengthened since the number of points of polyhedron linkage has rise from three to four. The structure was weakened until the formation of BO_3 groups with nonbridging oxygen set in at a higher network modifier content. Changes in property with variations of the composition are denoted with the borate anomaly, and the phenomena has been examined in various glass systems.[5–11]

The structure of glass has been studied by nuclear magnetic resonance (NMR)[7–12] and Raman spectroscopy[12–17] for about 40 years. As an example, ^{11}B NMR was first used by Bray et al. in order to quantify the proportions of three- and four-coordinated borons in B_2O_3, borate and borosilicate glasses.[15,16] Their later studies led to a structural model,[17,18] which accurately accounted for the boron speciation in sodium borosilicate glasses and was successful enough in predicting many physical and chemical properties of alkaline borosilicate glasses.[19–21]

In this study, the amount of SiO_2 was fixed at 10 mol% and the amount of BaO was changed in the $BaO–B_2O_3–SiO_2$ ternary glass system. A quantitative analysis of the three- and four-coordinated borons in the glasses was conducted by using the ^{11}B MAS-NMR analysis as a function of BaO content. The sintering behavior of the glass specimens with various amounts of BaO content was examined. The thermal expansion coefficient, glass transition temperature, hardness and dielectric characteristics of the sintered samples were also analyzed.

2. Experimental

High purity chemicals $BaCO_3$ (Kojundo chemical lab co., Ltd, 99.6%, Japan), H_3BO_3 (as above, 99.9%, Japan) and SiO_2 (as above, 99.9%, Japan) were used as the raw materials. The amount of SiO_2 was fixed at 10 mol%, and the remaining 90 mol% was filled with BaO and B_2O_3. The content of BaO, which plays the role of glass modifier, was increased, and the employed batch compositions are presented in Table 1. Weighed

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raw powders were mixed in an alumina crucible for 15 min. and melted at 1200 °C for 30 min in a Pt crucible. The molten glass in the crucible was put into cold water for quenching. The glass frit was roughly crushed in an alumina mortar then Planetary-milled for 2 h at 400 rpm. Crystallization of the glasses was analyzed by using an X-ray diffractometer (MO3-XHF, MAC Science Co., Japan) in the 2θ theta angle between 20–60° with a scanning speed of 4°/min and a sampling interval of 0.02°. The glass transition temperature of the glasses was analyzed by using a DSC (Thermal Analyzer, DSC 2920, TA Instruments, U.S.A.) in the temperature range between room temperature and 630 °C at a heating rate of 10 °C/min in air. The structure of the glasses was examined by a 600 MHz Solid-State NMR Spectrometer (Unity INOVA600, Varian, USA) at room temperature in air on the basis of the ^{11}B NMR analysis.

The glass frits were cold isostatically pressed (CIP) under a pressure of 100 MPa for 3 min so as to form green pellets. The pellets were sintered in the temperature range between 540–630 °C for 2 h at a heating rate of 5 °C/min then furnace cooled. The density of the sintered pellets was measured by the Archimedes method. The hardness and the thermal expansion coefficient of the sintered specimens were measured using a Vickers indenter (MXT-CX7E, Japan) and a dilatometer (DIL 402 C, Netzsch, Germany), respectively. The dielectric characteristics of the sintered specimens were analyzed by using an impedance gain phase analyzer (HP-4194A, USA) at 1 MHz.

3. Results and discussion

Fig. 1 represents the X-ray diffraction patterns of the $BaO–B_2O_3–SiO_2$ glasses as a function of BaO content. As seen in the figure, two big broad peaks around $2\theta = 25°$ and 43° which are typical features of borate glasses, were observed regardless of the BaO content.[22]

Fig. 2 shows the ^{11}B MAS-NMR analysis of the glasses as a function of BaO content. Two peaks at −2.5 to −12.5 ppm and −17.5 to −25 ppm can be clearly observed in every glass. It is known that the peaks at −2.5 to −12.5 ppm and 17.5 to −25 ppm originated from the trigonal three coordinated borons (BO_3) and the tetrahedral four coordinated borons (BO_4), respectively.[12] Among the two peaks, the BO_3 peak is broader than the BO_4 peak since two different types of BO_3 structures coexist; one type consisted of only bridging oxygen in the structure and the other type consisted of one or two non-bridging oxygen in the structure.[10,11,23]

Table 1
Compositions employed in the $BaO–B_2O_3–SiO_2$ glass system

Designation	BaO (mol%)	B_2O_3 (mol%)	SiO_2 (mol%)
Ba20	20	70	10
Ba25	25	65	10
Ba30	30	60	10
Ba35	35	55	10
Ba40	40	50	10
Ba45	45	45	10

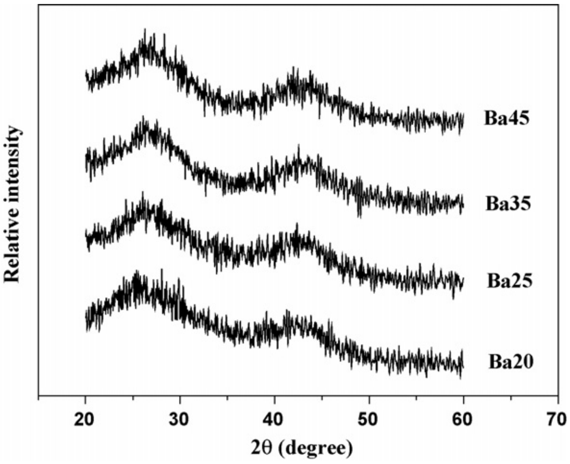

Fig. 1. X-ray diffraction patterns of glass powder as a function of BaO content.

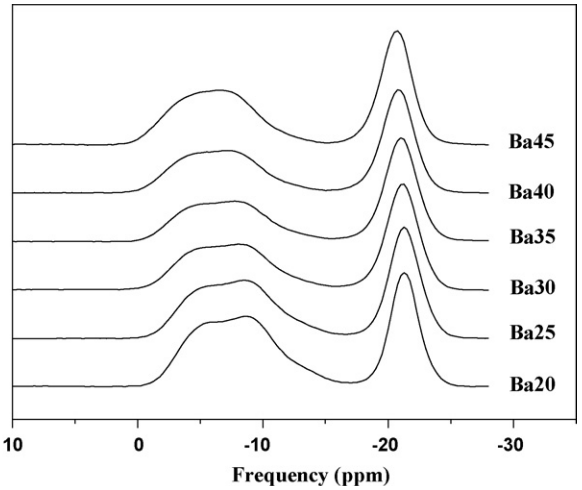

Fig. 2. Typical ^{11}B MAS-NMR spectra of barium borosilicate glasses as a function of BaO content.

Fig. 3 shows the relative amount of BO_4 as a function of BaO content by taking the total amount of BO_3 and BO_4 as 100%. The glass transition temperature (T_g) is simultaneously described in Fig. 3. The relative respective amounts of BO_3 and BO_4 in the

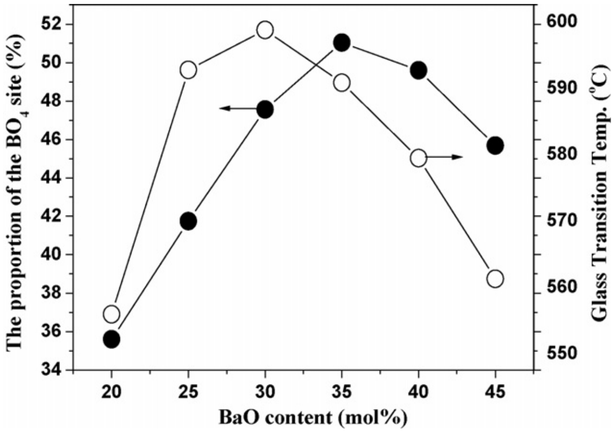

Fig. 3. The relative amount of BO_4 and T_g as a function of BaO content.

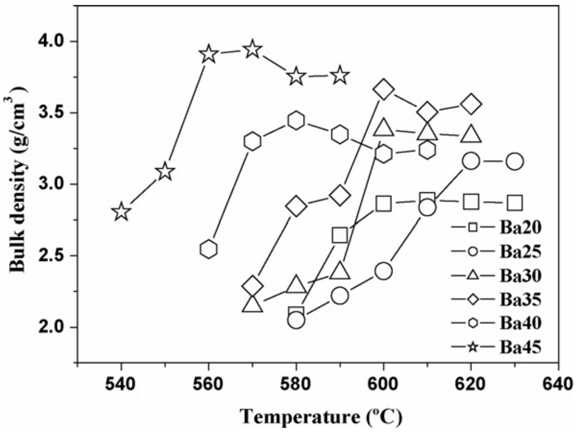

Fig. 4. The bulk density (g/cm^3) of sintered specimens as functions of sintering temperature and BaO content.

glass can be obtained by comparing the integrated area of the corresponding NMR peaks.[24] The amount of BO_4 increased as the content of BaO increased. The maximum amount of BO_4 was observed at Ba35. A further addition of BaO over 35 mol% led to a decrease in the amount of BO_4. This is due to the structural changes from BO_3 to BO_4 as the content of the glass modifier BaO increased, i.e., the BO_3 groups in the borosilicate glasses prefer a coordination change to BO_4 rather than producing non-bridging oxygen. This structural change in BO_4 will increase the stability of the glasses. The reverse structural change from the BO_4 groups to the non-bridging oxygen containing BO_3 groups occurred when more than 35 mol% of BaO is added, which reduced the stability of the glasses accordingly.[5,11]

On the other hand, T_g showed a close correlation with the amount of BO_4. The T_g increased with an increase in BaO content and it reached a maximum value at Ba30. Then, it decreased when more than 30 mol% of BaO was added. However, the BaO content where the maximum values appeared for the amount of BO_4 and T_g did not exactly coincide. The 5 mol% mismatch in the BaO content shown in Fig. 3 seemed to be caused by the partial contribution of BaO to the formation of BO_3 with non-bridging oxygens since the entire BaO did not contribute to BO_4 formation. Even though precise quantification of the two different types of BO_3 structures was not conducted by using ^{17}O, a peak broadening at −2.5 to −12.5 ppm is observed in Fig. 2 as the BaO content increased which signifies that BaO probably affected the formation of BO_3 with non-bridging oxygen structure.[10,11,23] The decreased T_g over 35 mol% of BaO can be attributed to the increase in the amount of the BO_3 structure with non-bridging oxygen by breaking the BO_4 structure.

The bulk density of the sintered specimens as functions of temperature and BaO content are presented in Fig. 4. The optimum sintering temperature where the maximum bulk density was obtained increased from 610 °C in Ba20 to 620 °C in Ba25. The optimum sintering temperature then decreased with the increase in BaO content and it reached 570 °C in the case of Ba45. This behavior is similar to that of the T_g (but not exactly the same) and the structural change with respect to the BaO content.

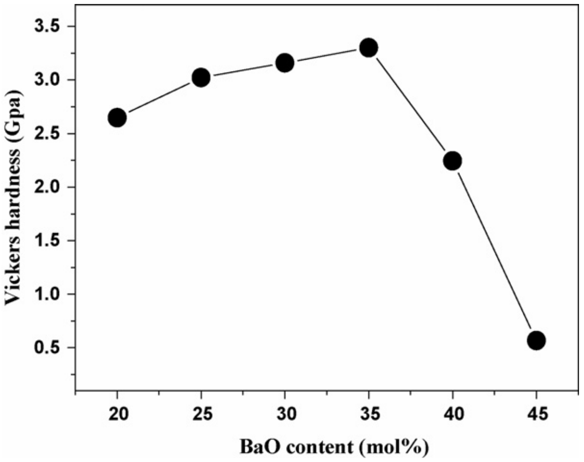

Fig. 5. Vickers hardness (Gpa) of the specimens. A 2N lord was applied during indentation.

Fig. 5 shows the Vickers hardness of the sintered specimens each of which has the highest bulk density. The hardness increased with the BaO content until the BaO content reached 35 mol%. Then, the hardness decreased with the further addition of BaO. The composition of Ba35 where the maximum hardness was revealed coincides with the composition where the largest amount of BO_4 was obtained. This result supports the fact that the hardness of the glasses is in proportion to the amount of the BO_4 structure.

Fig. 6 shows the thermal expansion coefficient (α) of the specimens sintered at their optimum temperatures. In the case of Ba20, α was 9.14×10^{-6}/°C. The α decreased with the BaO content until the α reached the minimum value of 7.78×10^{-6}/°C at Ba35. Then it increased to 9.65×10^{-6}/°C with the further addition of BaO up to 45 mol%. A theoretical calculation of α was carried out on the basis of the following equation suggested by Winkelmann and Schott (1).[25] The results are presented with a solid line in Fig. 6.

$$\alpha = \frac{1}{100}(\alpha_1 p_1 + \alpha_2 p_2 + \cdots + \alpha_n p_n) = \frac{1}{100}\sum \alpha_i p_i \qquad (1)$$

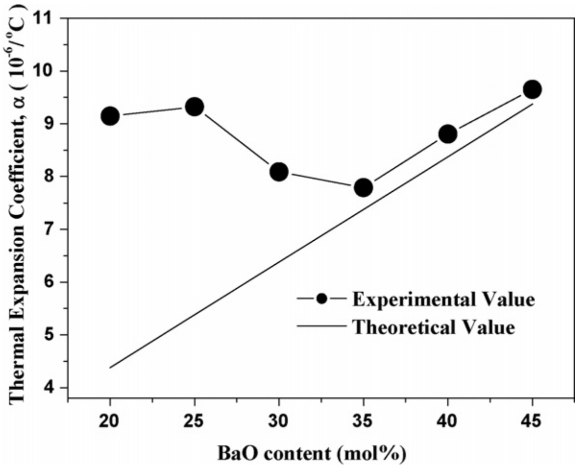

Fig. 6. Thermal expansion coefficient (α) as a function of BaO content.

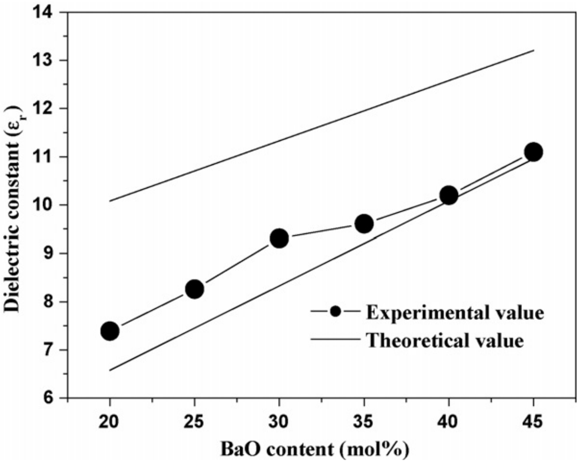

Fig. 7. Dielectric constant (ε_r) of specimens as a function of BaO content.

where p_i represents the portion of the individual oxides in mol% and α_i is the characteristic factor for each oxide; BaO is 20, B_2O_3 is −5.0 to 0.0 and SiO_2 is 0.5–3.8. A remarkable difference between the theoretical expectation and the experimental results can be observed in the compositional range for all content between Ba20 and Ba35. This is thought to be due to the ignorance of the structural change of the borons and it takes into account the compositional changes only in evaluating the characteristic factor (α_i) in the equation.[25] Since the structural change from BO_3 to BO_4 tightens the structure and the BO_4 structure improves the hardness of the specimen, the minimum α was obtained at Ba35. The α increased over Ba35 due to the weakened glass as the BO_4 network structure broke into the BO_3 structure with non-bridging oxygen.

Fig. 7 shows the dielectric constant (ε_r) of the sintered specimens. The dielectric constant gradually increased from $\varepsilon_r = 7.39$ at Ba20 to $\varepsilon_r = 11.10$ at Ba45 as more BaO was added. The calculated theoretical dielectric constant of the specimens is presented by solid lines in the figure. The calculation was carried out on the basis of Appen and Bresker's Eq. (2).[26]

$$\varepsilon = \frac{1}{100}(\varepsilon_1 p_1 + \varepsilon_2 p_2 + \cdots + \varepsilon_n p_n) = \frac{1}{100}\sum \varepsilon_i p_i \qquad (2)$$

where p_i represents the portion of the individual oxides in mol% and ε_i is the characteristic factor for each oxide: BaO is 20.5, B_2O_3 is 3–8, and SiO_2 is 3.8. Since the factor of B_2O_3 is dependent upon the glass composition, the characteristic factor for B_2O_3 changed from 3–8, and the two solid lines in Fig. 7 show the range of the calculated dielectric constant. The experimental results of the dielectric constant stayed within the theoretical range, and the structural changes did not seem to affect the dielectric constant of the specimens. The increase in the dielectric constant with BaO is attributed to the increase in the fraction of non-bridging oxygen in the specimens. Since Ba^{2+} ion has high polarizability, it is believed that an increase in BaO mainly contributed to the increase in the dielectric constant.

4. Conclusion

In the $BaO–B_2O_3–SiO_2$ glass system, according to the ^{11}B NMR analysis, structural changes from BO_3 to BO_4 and vice versa were observed when the BaO content increased. Since the structural changes from BO_3 to BO_4 resulted in the structure strengthening of the glasses, these changes had an influence on viscosity, glass transition temperatures, thermal expansion coefficients, optimum temperatures of densification and hardness of the specimens. Therefore, the maximum hardness and the minimum thermal expansion coefficients were observed at Ba35 in accordance with the amount of BO_4. The dielectric constant of the glasses, however, was dependent upon the BaO content.

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