

Elastic Properties of Potassium Borate Glass in a Wide Composition Range Studied by Brillouin Scattering

Mitsuru Kawashima, Yu Matsuda, Yasuteru Fukawa, Seiichi Mamiya, Masao Kodama¹, and Seiji Kojima*

Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

¹Department of Applied Chemistry, Sojo University, Kumamoto 860-0082, Japan

Received November 19, 2008; accepted April 5, 2009; published online July 21, 2009

The elastic properties of potassium borate glass, $x\text{K}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3$, where x is the molar composition of K_2O in mol%, have been investigated by Brillouin scattering spectroscopy over a wide composition range of $2 \leq x \leq 42$ mol%. From the observed values of longitudinal sound velocity, the elastic constant has been determined and compared with that of lithium borate glass. The sound velocity increases with increasing x below $x = 30$; however, for a further increase in x , it decreases owing to the softening caused by the formation and increase in the number of nonbridging oxygen atoms. The absorption coefficient also increases markedly above $x = 30$ owing to the scattering of acoustic waves by nonbridging oxygen atoms. The temperature dependences of both sound velocity and absorption coefficient of $14\text{K}_2\text{O}\cdot 86\text{B}_2\text{O}_3$ show a markedly change at approximately the glass transition temperature T_g of 395°C .

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DOI: 10.1143/JJAP.48.07GA03

1. Introduction

The structure and physical properties of alkali metal borate glass are dependent anomalously on glass composition. For example, the thermal expansion coefficient of potassium borate glass shows a minimum at a K_2O content of approximately $x = 20$. This property has been called the “borate anomaly” and discussed on the basis of the variation of intermediate structural units.¹⁾ Since elastic properties are sensitive and indicative of change in glass structure, it is very important to investigate the dependences of elastic properties on the composition of potassium borate glass systems over a wide glass-forming range to provide new insights into the borate anomaly.

The composition of potassium borate glass is denoted by $x\text{K}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3$, where x is the molar composition of K_2O in mol%. The structure of a boron oxide glass, B_2O_3 , consists of a random three-dimensional network of BO_3 triangles, where O denotes a bridging oxygen atom with a large proportion of almost planar B_3O_6 boroxol rings.²⁾ With an increase in alkali metal oxide content, the coordination numbers of boron atoms change from 3 to 4, resulting in the formation of BO_4 tetrahedra by the cross-linking of BO_3 group units that form a rigid glass network.^{3,4)}

Kodama, one of the present authors, already reported the dependences of elastic properties on the composition of potassium borate glass up to 34 mol% of K_2O , which is equivalent to the bulk glass-forming range, as determined by the ultrasonic pulse–echo overlap method.⁵⁾ Bulk samples are required to perform this method. Since the glass-forming ability of high K_2O composition samples is poor, they crystallize easily; therefore, the available glass samples become thin and fragile. Thus, it is impossible to perform the ultrasonic pulse–echo overlap method using a transducer for compositions with a high K_2O composition above 32 mol%. However, changes in elastic properties are expected for higher K_2O composition owing to the marked increase in the number of nonbridging oxygen atoms. Moreover, since it is difficult to evaluate the damping of ultrasonic sound velocity of alkali borate glass by the

ultrasonic pulse–echo overlap method, the sound absorption of potassium borate glass has not yet to be studied.

In the present study, Brillouin spectroscopy has been employed to investigate high K_2O glass compositions. The usefulness of Brillouin spectroscopy to explore elastic properties using a finely focused laser beam without any contact with a sample has been shown in our previous papers.^{6–8)} The elastic properties of compositions with a value of x up to 42 were successfully observed, and $x = 42$, which may be the upper limit for K_2O composition for glass-forming compositions obtainable by conventional plate quenching. The dependences of both elastic constant and absorption coefficient on K_2O composition have been investigated over a wide composition range of $2 \leq x \leq 42$ mol%. Recently, the temperature dependence of sound velocity and absorption of $14\text{M}_2\text{O}\cdot 86\text{B}_2\text{O}_3$, where $\text{M} = \text{Li}$ or K , has been studied by Brillouin scattering⁹⁾ to understand the mechanism of sound absorption from 15 to 300 K. In this study, the temperature dependence of elastic properties is also investigated from room temperature up to the high temperature of 500°C above T_g by Brillouin spectroscopy.

2. Experimental Procedure

All glasses were prepared with high homogeneity to investigate the alkali metal borate glass system.⁵⁾ The starting materials were analytical-reagent-grade KOH and H_3BO_3 . To achieve the high homogeneity of the samples, they were first reacted in an aqueous solution. As an extension of a previous study,⁵⁾ the glass samples were prepared in the composition range of $34 \leq x \leq 42$ mol% using plate quenching by rapid cooling. The thermal glass transition temperature of each sample was determined from the temperature dependence of heat flow curve obtained by temperature-modulated differential scanning calorimetry (TMDSC; TA Instruments DSC2920). The TMDSC is described in detail elsewhere.¹⁰⁾ Then, the quenched samples were annealed at approximately the thermal glass transition temperature for 2 h and cooled at a rate of 1 K/min to room temperature. The actual compositions of all samples were analyzed with respect to both x and $(100-x)$ by potentiometric titration chemical analysis.¹¹⁾

The experimental setup of a Brillouin scattering apparatus is described elsewhere.^{6–8)} One of the special features of

*E-mail address: kojima@ims.tsukuba.ac.jp

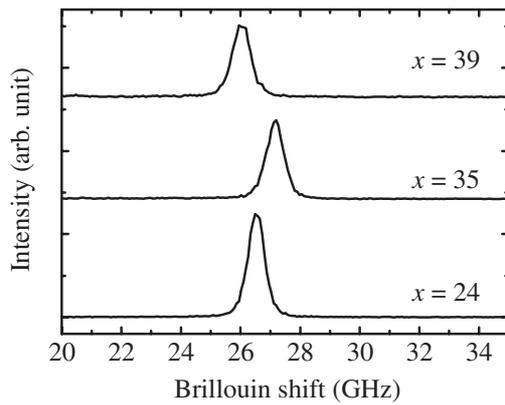


Fig. 1. Brillouin spectra at a backward scattering geometry.

this system is the combination of a microscope and a Sandercock-type 3 + 3 passes tandem multipass Fabry–Perot interferometer (FPI). The Brillouin scattering spectra at room temperature were measured at a backward scattering geometry for the composition range of $2 \leq x \leq 42$ mol %. This scattering geometry enables the measurement of the longitudinal acoustic (LA) mode. A free spectral range of 50 GHz was applied for measurements, and the scanning range was between -40 and 40 GHz to obtain the Brillouin spectra. A standard photon counting system and a multi-channel analyzer were used to accumulate the signals.

The temperature dependences of longitudinal sound velocity and absorption coefficient were measured up to 500°C at a backward scattering geometry using a HTMS 600 (Linkam) as a temperature controller. The free spectral range was 40 GHz, and the scanning range was between -30 and 30 GHz.

3. Results and Discussion

Figure 1 shows the Brillouin spectra of the potassium borate glass ($x = 24, 35, 39$) measured at a backward scattering geometry. There is a peak of the LA mode in the Stokes component. The longitudinal sound velocity (V_L) is calculated from the Brillouin shift ($\Delta\nu_{180}$) by the equation

$$V_L = \frac{\Delta\nu_{180}\lambda}{2n \sin(\theta/2)}, \quad (1)$$

where λ is the wavelength of the incident beam (532 nm), θ is the scattering angle, and n is the refractive index. The values of n for each sample are taken from the data of Bresker and Evstropiev.¹²⁾

The dependence of V_L on alkali metal composition is shown in Fig. 2. The open circles denote the reference values of potassium borate glass reported by Kodama.⁵⁾ The values of V_L obtained by Brillouin scattering are in good agreement with those obtained by the ultrasonic pulse–echo overlap method. The solid triangles indicate the values for lithium borate glass shown for comparison.^{8,13)} The results for potassium borate glass show that sound velocity increases up to 30 mol % with increasing K_2O composition and then decreases with a further increase in the K_2O composition.

The longitudinal modulus (L), one of the elastic constants, is calculated by the equation

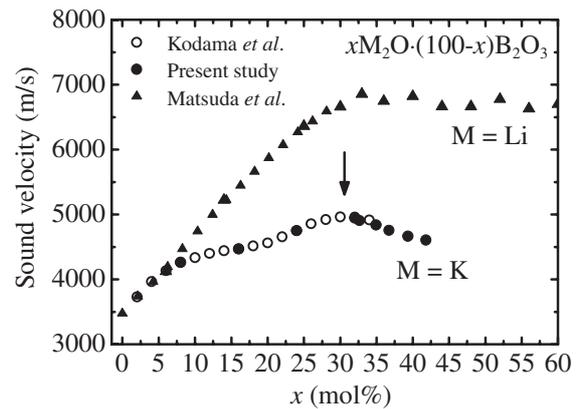


Fig. 2. Dependence of longitudinal sound velocity on the composition of $x\text{M}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3$ glass ($M = \text{Li}, \text{K}$). Open circles represent values reported by Kodama.⁵⁾ Solid triangles represent values reported by Matsuda *et al.*^{8,13)}

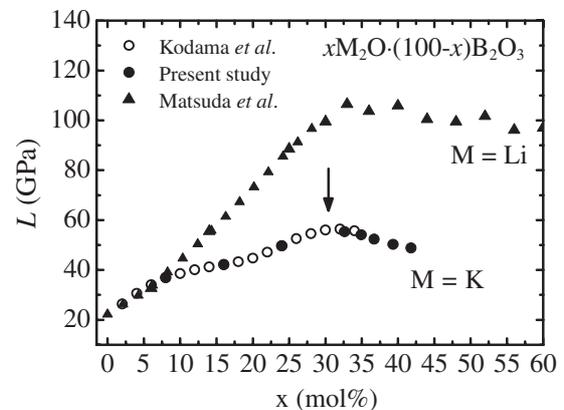


Fig. 3. Dependence of longitudinal modulus (L) on the composition of $x\text{M}_2\text{O}\cdot(100-x)\text{B}_2\text{O}_3$ glass ($M = \text{Li}, \text{K}$). Open circles represent values reported by Kodama.⁵⁾ The solid triangles represent values reported by Matsuda *et al.*¹³⁾

$$L = \rho \cdot V_L^2, \quad (2)$$

where ρ is the density of the sample. The values of ρ for potassium borate glass are taken from the data of Kodama *et al.*¹⁴⁾ and Lim *et al.*¹⁵⁾ Figure 3 shows the dependence of L on alkali metal composition. The triangles and circles denote the values for lithium borate and potassium borate glasses, respectively. The elastic constant increases up to 30 mol % with increasing K_2O composition and then decreases with a further increase in K_2O composition. There is a marked dependence of V_L on K_2O composition.

The dependence of L on the composition of the lithium borate glass has been explained by the presence of intermediate structural units in the borate network.^{8,10)} The value of L for lithium borate glass increases with increasing Li_2O composition up to 30 mol %. This behavior is strongly correlated with the formation of 4-coordinated boron atoms. The network structures of B_2O_3 glass are constructed by planar 3-coordinated boron atoms. The addition of Li_2O causes the formation of 4-coordinated boron atoms, resulting in the creation of three-dimensional rigid structural units. Therefore, the sound velocity and elastic constant increase up to a Li_2O composition of 30 mol %.

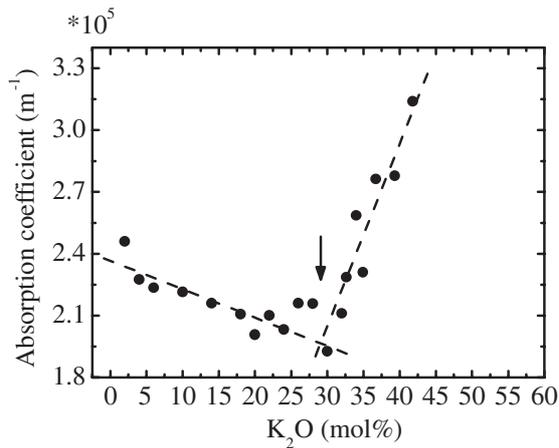


Fig. 4. Dependence of absorption coefficient (Γ) on K_2O composition of potassium borate glass. Dotted lines serve as visual guides.

It is found that the dependence of L on the composition of the lithium and potassium borate glasses is very similar in the Li_2O and K_2O composition ranges from 0 to 8 mol%. However, for alkali metal oxide compositions above 8 mol%, the dependence of L on the K_2O composition of potassium borate glass is much smaller than that on the Li_2O composition of lithium borate glass. The value of L for lithium borate glass increases linearly with increasing Li_2O composition up to 30 mol%. However, the value of L for potassium borate glass does not increase monotonically. This difference can be understood, as discussed in ref. 5, by the creation of nonbridging oxygen atoms in potassium borate glass, which destroys the glass network. The threshold creation of nonbridging oxygen atoms in the potassium borate glasses is a K_2O composition of 8 mol%, and the coordination number of boron atoms begins to change from 3 to 4.

In the range of Li_2O composition above 30 mol%, the value of L for lithium borate glass becomes nearly constant within the experimental uncertainty. In contrast, that for potassium borate glass decreases with a further increase in K_2O composition. These changes indicate the formation and increase in the number of intermediate structural units, include nonbridging oxygen atoms, such as $B\emptyset_2O$ and $B\emptyset O_2$. These results suggest that the effects of the creation of nonbridging oxygen atoms on the elastic properties are lower than those of $B\emptyset_4$ units composed of 4-coordinated boron atoms with four bridging oxygen atoms. The difference in the effects of the addition of alkali metals also suggests that the intermediate structural units of the alkali borate glasses are more sensitive to K_2O than Li_2O .

The absorption coefficient α for the LA mode is determined from the full width at half maximum (FWHM) of the Brillouin component by the equation

$$\alpha = \frac{\pi\Gamma}{V_L}, \quad (3)$$

where Γ is the FWHM. The dependence of the absorption coefficient on the K_2O composition of potassium borate glass is shown in Fig. 4. The absorption coefficient decreases with increasing K_2O composition from $x = 2$ to 30. Since the coordination number of boron atoms changes

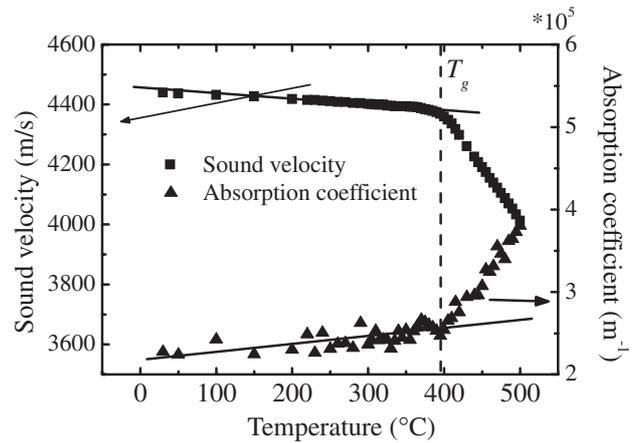


Fig. 5. Temperature dependences of longitudinal sound velocity (V_L) and absorption coefficient (Γ) of $14K_2O \cdot 86B_2O_3$ glasses. T_g denotes the glass transition temperature determined by Brillouin scattering. Solid lines serve as visual guides.

from 3 to 4 within this range,¹⁶⁾ the decrease in absorption coefficient is considered to be caused by the increased number of cross-linking borate units at higher K_2O composition. However, above $x = 30$, the absorption coefficient markedly increases with increasing K_2O composition. As was mentioned above for the elastic constant, the number of nonbridging oxygen atoms, which destroy the borate network, markedly increases above a K_2O composition $x = 30$ in potassium borate glass. The increase in absorption coefficient with increasing K_2O composition is considered to be caused by the increase in the number of nonbridging oxygen atoms. Specifically, the nonbridging oxygen atoms loosely connected to the network induce the energy dissipation of elastic wave propagation, thereby causing the damping of the sound wave to increase. It is found that the dependence of the absorption coefficient on K_2O composition is correlated with that of the elastic constant.

The temperature dependences of the Brillouin spectra were measured at the backward scattering geometry at temperature up to 500 °C. Figure 5 shows the temperature dependences of longitudinal sound velocity and absorption coefficient of $14K_2O \cdot 86B_2O_3$. Below 395 °C, the sound velocity very slightly decreases with increasing temperature, and the absorption coefficient gradually increases. In contrast, above 395 °C, the sound velocity decreases markedly with increasing temperature, while the absorption coefficient shows a rapid increase. This inflection point at 395 °C can be identified as the glass transition temperature, T_g . This result indicates that the structures of the glass network become weaker or softer above 395 °C. Very recently, the absorption coefficient in the low-temperature region from 15 to 300 K was studied by Carini *et al.*⁹⁾ from the viewpoint of thermally activated relaxation and vibrational anharmonicity; they predicted a linear increase in sound absorption coefficient and a linear decrease in sound velocity with increasing temperature. The present results are consistent with their predictions below T_g and provide new insights into the behavior of the elastic properties of potassium borate glass related to liquid-glass transition over a wide temperature range.

4. Conclusions

The elastic properties of potassium borate glasses have been investigated over a wide K₂O composition range of $2 \leq x \leq 42$ mol % by Brillouin scattering spectroscopy. The dependences of sound velocity (V_L), longitudinal modulus (L), and absorption coefficient (Γ) on K₂O composition have been clarified. The value of L increases up to 30 mol % K₂O, then decreases with a further increase in K₂O composition. The absorption coefficient decreases up to approximately 30 mol % with increasing K₂O, whereas above 30 mol % it markedly increases with increasing K₂O composition. Both the dependences of L and absorption coefficient on K₂O composition are discussed in terms of the changes of coordination number of boron atoms in low K₂O composition and the presence of nonbridging oxygen atoms in high K₂O. The temperature dependences of the sound velocity and absorption coefficient clearly change around the glass transition temperature 395 °C.

Acknowledgement

The author (Y.M.) is thankful for the JSPS Research Fellowship 19-574.

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