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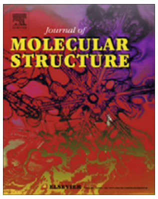

Temperature dependence of elastic properties in alkali borate binary glasses

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ABSTRACT

The elastic properties of alkali borate glasses, $xM_2O{\cdot}(100-x)B_2O_3$ (M = Li, Na, K, Rb, Cs, $x = 14, 28$), have been investigated by Brillouin scattering spectroscopy from room temperature up to 1100 °C. Above the glass transition temperature, T_g, the longitudinal sound velocity, V_L, decreases markedly on heating. Such significant changes of the elastic properties result from the breakdown of the glass network above T_g. Alkali borate family with the same x shows the similar behavior in the temperature variations of V_L up to around T_g. The absorption coefficient, α_L, increases gradually above T_g. With the increase of the size of an alkali ion, the slope of V_L just above T_g decreases. Since the fragility is related to the slope, the present results suggest that the fragility of alkali borate glasses increases as the size of alkali ion decreases. Such an alkali dependence of the fragility is discussed on the basis of the fluctuation of the boron coordination number.

1. Introduction

Pure B_2O_3 glass has a random three-dimensional network of BO_3 triangles with a large fraction of almost planar B_3O_6 boroxol rings. It is known that alkali borate glasses show the anomalous composition dependences of physical properties, such as density [1], sound velocity [2,3] and thermal expansion [4], by the addition of alkali oxide to pure B_2O_3 glass. Previous studies reported that the structural origins of such anomalies are strongly related to the change of the boron coordination number from three to four and the formation of non-bridging oxygen [5]. The fourfold coordinated boron atoms enhance the network rigidity by the cross-linking of borate framework. In contrast, the non-bridging oxygen destroys the borate network. The negative charge of the network sites is compensated by the positive charge of alkali ions, M^+. The alkali ions do not directly participate in the network formation and occupy interstitial voids. As a consequence, the structures of modified borate glasses are essentially built up from the covalently bonded structural units. While, the ionic bonds are formed between M^+ and the B–O anionic units, and their bond strength depends on the specific alkaline cation. The studies by nuclear magnetic resonance (NMR) [5] and Raman scattering measurement [6] show that the fraction of fourfold coordinated boron atoms of alkali borate glasses decreases as the size of an alkali ion increases at room temperature. This fact indicates that the preference large alkalis induce the creation of non-bridging oxygen. Therefore, for the same alkali composition, the sound velocity and elastic moduli increase as the size of an alkali ion decreases.

The elastic properties far below a glass transition temperature, T_g, are relatively stable in comparison with the temperature variation above T_g. In contrast, the breakdown of the network starts above T_g. The breakdown of the structural integrity is reflected in the rapid decrease of the rigidity. The network rigidity is directly connected to the structural (α) relaxation process characterized by the Angell's fragility. Therefore, to make clear the mechanism of a glass transition and the nature of supercooled liquid, it is necessary to clarify the elastic properties over a wide temperature range. Moreover, the understanding of elastic properties at high temperatures is very important for the glass manufacturing process.

In this study, we employ Brillouin scattering spectroscopy to measure elastic properties at high temperatures up to 1100 °C. Although the non-destructive and non-contact Brillouin scattering is a powerful tool to investigate the elastic properties at high temperatures, only a few investigations were reported until now on elastic properties of alkali borate glasses above T_g using Brillouin scattering. Masnik et al. showed the temperature dependences of longitudinal elastic modulus of sodium borate glasses and discussed a relaxation process above T_g in the GHz frequency region [7]. Ike et al. reported the temperature dependences of the elastic properties of lithium borate glasses [8]. Since their results focus on the effect of temperature and composition dependences, the influence of an alkali ion and alkali dependence of fragility were not sufficiently discussed. In this study, the temperature dependence of elastic properties in alkali borate glasses $xM_2O{\cdot}(100-x)B_2O_3$ (M = Li, Na, K, Rb, Cs, $x = 14, 28$), where x denotes the molar composition (mol%), are investigated by Brillouin scattering up to

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1100 °C. The influence of alkali cations to the temperature dependence of the elastic properties and the variation of fragility are discussed.

2. Experimental

xM$_2$O·(100 − x)B$_2$O$_3$ (M = Li, Na, K, Rb, Cs, x = 14, 28) glasses were prepared by the solution method [9]. This method is useful to obtain the high homogeneity of glasses. Analytical-reagent-grade MOH and H$_3$BO$_3$, starting materials, were reacted in an aqueous solution to achieve the high homogeneity. Then the mixed solution was transferred to a dry box and after the complete evaporation of water a chemically synthesized powder was obtained. The powder was melted in a furnace at 1000 °C, and then the melt was quenched by pressing between two aluminum plates. The actual compositions of all samples were analyzed with respect to both x and (100 − x) by the potentiometric titration chemical analysis [10].

The experimental setup of a Brillouin scattering apparatus is described elsewhere [8]. The features of this system are the combination of an optical microscope (Olympus BH-2) and a Sandercock-type 3 + 3 passes tandem multipass Fabry–Perot interferometer. The Brillouin scattering spectra were measured at a backward scattering geometry. A standard photon counting system and a multichannel analyzer were used to accumulate the signals. To measure the spectra at high temperatures up to 1100 °C, we prepared the compact IR image furnace (Yonekura, IR-TP) specially customized for the present experiments. The combination of Brillouin apparatus and the compact IR image furnace enable us to prove elastic properties over a wide temperature range.

3. Results and discussion

3.1. Temperature dependence of elastic property of alkali borate glasses

The temperature dependence of Brillouin spectra of 28Rb$_2$O·72B$_2$O$_3$ glass is shown in Fig. 1. The observed spectrum contains a longitudinal acoustic (LA) mode and a central peak. The Brillouin shift of a LA mode decreases on heating. The central peak appears above 700 °C, and its intensity increases on further heating. The central peak was observed in all samples at high temperatures, and its intensity increases as the size of an alkali ion decreases.

These Brillouin spectra were analyzed by convoluting a Lorentzian spectral function with a Gaussian broadening function. The longitudinal sound velocity, V_L, and absorption coefficient, α_L, of the samples were determined from Brillouin shift, $\Delta\nu_{180}$, and FWHM, Γ, using the following equations:

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

$$\alpha_L = \frac{\pi\Gamma}{V_L}, \tag{2}$$

where n is the refractive index, λ is the wavelength of the incident beam (532 nm) and θ is the scattering angle (180°). The values of n for each sample are taken from the data of Refs. [11,12]. Since the values are available only at room temperature, it is assumed that the change of n is much smaller than that of Brillouin shifts.

Fig. 2a and b shows temperature dependences of V_L and α_L in 14M$_2$O·86B$_2$O$_3$ glass. Fig. 3a and b shows those of 28M$_2$O·72B$_2$O$_3$ glass. Such temperature dependences are commonly observed for glass-forming liquids [13,14]. Each V_L decreases very rapidly above an inflection point between 300 °C and 400 °C. This characteristic inflection point can be identified as T_g. In the case of "strong" pure SiO$_2$ glass, the elastic properties exhibit a monotonous increase on heating even above T_g [15]. The anomaly near T_g is remarkable in "fragile" alkali borate glasses of which anharmonicity are much stronger than that of pure SiO$_2$ glass. At room temperature, V_L increases as the size of an alkali ion decreases. The fraction of fourfold coordinated boron atoms at the same alkali composition becomes large as the size of an alkali ion decreases [5]. The fourfold boron atoms increase the network rigidity by the cross-linking of borate framework with the covalent B–O bonds, and subsequently yields higher T_g. Therefore, the inflection point (T_g) shifts become higher temperature as the size of an alkali ion decreases. While,

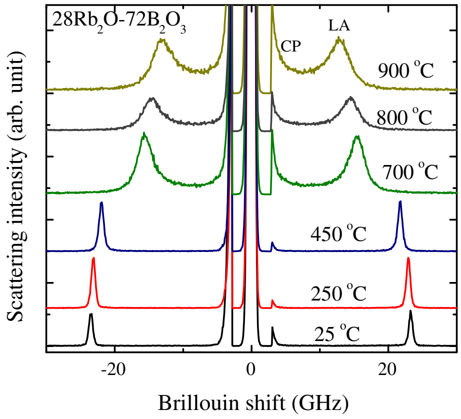

Fig. 1. Temperature dependence of Brillouin spectra of 28Cs$_2$O·72B$_2$O$_3$ glass, measured at backward scattering geometry. LA and CP denote the longitudinal acoustic phonon and central peak, respectively.

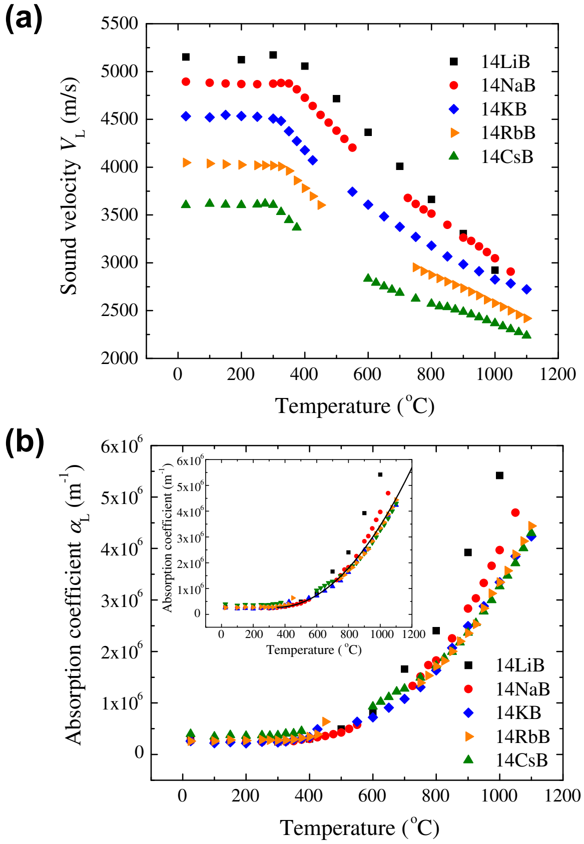

Fig. 2. Temperature dependences of (a) longitudinal sound velocities and (b) absorption coefficients of 14M$_2$O·86B$_2$O$_3$ glasses. Inset of (b): fitting curve of the quadratic form.