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Elastic Properties of Alkali Germanate Glasses at High Temperatures Studied by Broadband Brillouin Scattering

広帯域ブリルアン散乱法によるアルカリゲルマン酸塩ガラスの高温での弾性的性質

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1. Introduction

Elastic properties of glassy materials are the current topics in material sciences. The microscopic structure of alkali germanate glasses, which are utilized as the optical fiber and infrared transmitting glass, changes dramatically with their compositions [1,2]. Some physical properties also show the marked temperature dependence above a glass transition temperature (T_g) [3]. Therefore, it is important to measure the elastic properties such as sound velocity and absorption coefficient over the wide temperature range from 25 ^oC to 1100 ^oC.

However, it is difficult to investigate at high temperature because alkali germanate glasses melt above 850 ^oC. Brillouin spectroscopy enables us to investigate the elastic properties at high temperature by using a finely focused laser beam without any contact with a sample [4].

In the previous study, we investigated the elastic properties of lithium germanate glasses at room temperature, and elucidated the relationship between the structural changes and the elastic properties [5]. In this study, temperature dependences of elastic properties of the selected compositional glasses are investigated up to 1100 ^oC using a compact infrared image furnace, and Sandercock-type Fabry-Perot interferometer.

2. Experimental

Alkali germanate glasses, $xR_2O \cdot (100\text{-}x)GeO_2$ represented as a function of R_2O (alkali metal oxide, R = Li, Na, K, Rb, Cs) mole fraction, were prepared by the aqueous solution method [6]. We selected x = 14 and 28 as x values. The starting materials were powdered GeO_2 and $ROH(\cdot H_2O)$. The necessary mass of them were calculated by the chemical reaction formula (1),

$$2xROH \cdot H_2O + (100 - x)GeO_2 \rightarrow xR_2O \cdot (100 - x)GeO_2 + 3xH_2O \cdot \quad (1)$$

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They were first made to react in an aqueous solution and dry in dryer for a week. After thermal dehydration completely, the chemically synthesized powder heated at approximately 1150 ^oC in the electric furnace. Alkali germanate glasses have a strong tendency to crystallize. Therefore, the glass samples were made by using the plate quenching technique with rapid cooling. All the samples were annealed for 10 minutes around T_g determined by the differential scanning calorimeter (DSC) to remove internal stresses.

The Brillouin spectra were measured at backward scattering geometry by a Sandercock-type 3+3 pass tandem multipass Fabry-Perot interferometer (FPI) combined with an optical microscope [4]. The compact IR image furnace (IR-TP) was used for temperature control.

3. Results and Discussion

Figure 1 shows the temperature dependence of Brillouin spectra on $28Li_2O \cdot 72GeO_2$ glass including longitudinal acoustic mode. On heating, the observed peaks shift to lower frequency and the full width at half maximum (FWHM) increases. The central peaks were observed above 850 ^oC. The values of Brillouin shift ($\Delta\nu_{180}$) and FWHM (Γ) were determined accurately from the observed Brillouin spectra fitting by a Voigt function. The longitudinal sound velocity (V_L) and absorption coefficient (α_L) were calculated from the $\Delta\nu_{180}$ and Γ using the equations (2) and (3),

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

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

where λ is the wavelength of the incident laser beam (532 nm), n is the refractive index and θ is the scattering angle (180^o). The n values of each sample are obtained from the study reported by Murthy and Ip [7].

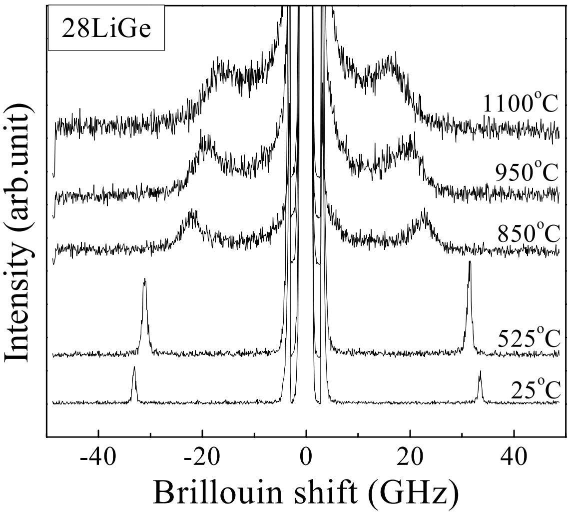

Fig.1 Temperature dependence of Brillouin spectra on $28Li_2O \cdot 72GeO_2$ glass.

Figure 2 shows the temperature dependences of the V_L on $28R_2O \cdot 72GeO_2$ glasses. The values of V_L decrease with increasing ionic radius, and decrease gradually up to about 500 °C. Above 500 °C, the V_L values decrease drastically and show the marked temperature dependences. These inflection points around 500 °C can be identified as T_g. This major change at T_g is considered by the structural reorganization [3]. The disruption of chemical bonds is highly correlated with this change. The T_g values decrease with increasing ionic radius as well as the results obtained by DSC in the same alkali compositions. No signal can be observed because of crystallization in the blank temperature range. The gradient at T_g reflects degree of glass network. The greater the gradient, the weaker the glass network become. Angell defined the fragility index as a way of classification of glasses. In our study, the gradients become greater with increasing alkali metal oxide. It is confirmed to change from strong to fragile.

Figure 3 shows the temperature dependences of the α_L on $28R_2O \cdot 72GeO_2$ glasses. The values of α_L are very low below T_g, and the difference caused by alkali species isn't seen. While, the α_L values increase drastically with temperature above T_g. The degree of increase is greater with decreasing ionic radius.

The temperature dependence of relaxation time of $28Li_2O \cdot 72GeO_2$ glass was determined from the $\Delta\nu_{180}$ and Γ. Moreover, the activation energy ΔE was determined by using the Arrhenius law to discuss the relaxation process in the GHz frequency range.

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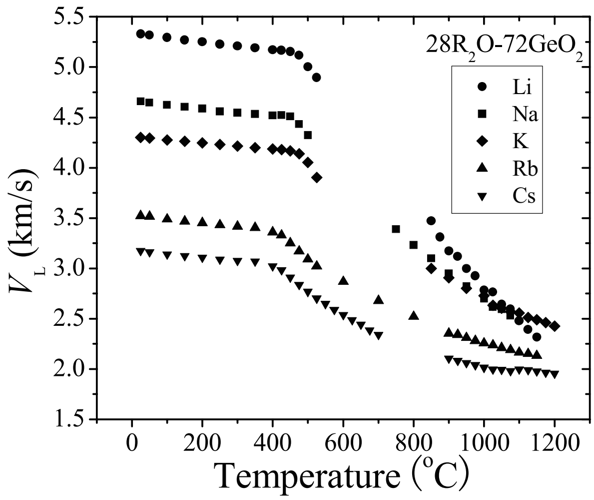

Fig.2 Temperature dependences of longitudinal sound velocity V_L on $28R_2O \cdot 72GeO_2$ glasses (R = Li, Na, K, Rb, Cs).

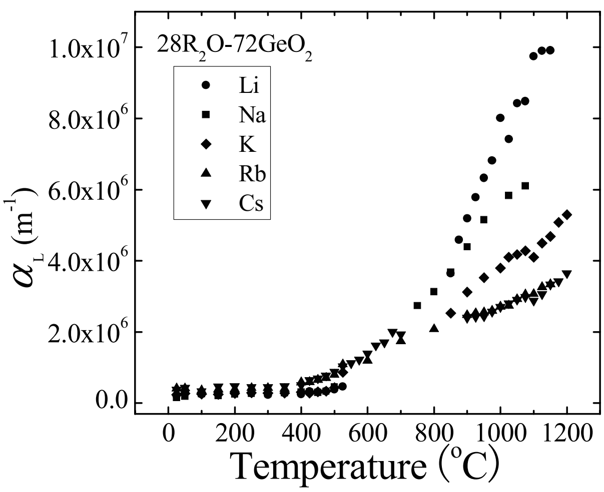

Fig.3 Temperature dependences of sound absorption coefficient α_L on $28R_2O \cdot 72GeO_2$ glasses (R = Li, Na, K, Rb, Cs).