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

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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 \(^\circ\)C to 1100 \(^\circ\)C.

However, it is difficult to investigate at high temperature because alkali germanate glasses melt above 850 \(^\circ\)C. 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 \(^\circ\)C using a compact infrared image furnace, and Sandercock-type Fabry-Perot interferometer.

2. Experimental

Alkali germanate glasses, \( xR_2O \cdot (100-x)GeO_2 \), represented as a function of \( R_2O \) (alkali metal oxide, \( R = \text{Li, Na, K, Rb, Cs} \)) 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(·H\(_2\)O). The necessary mass of them were calculated by the chemical reaction formula (1),

\[
2xROH \cdot H_2O + (100-x)GeO_2 \rightarrow xR_2O \cdot (100-x)GeO_2 + 3xH_2O.
\]  

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 \(^\circ\)C 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\(_2\)O·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 \(^\circ\)C. The values of Brillouin shift \((\Delta V_{\text{L}})\) and FWHM \((\Gamma)\) were determined accurately from the observed Brillouin spectra fitting by a Voigt function. The longitudinal sound velocity \((V_L)\) and absorption coefficient \((\alpha_L)\) were calculated from the \(\Delta V_{\text{L}}\) and \(\Gamma\) using the equations (2) and (3),

\[
V_L = \frac{\Delta V_{\text{L}} \lambda}{2n \sin(\theta/2)},
\]  

\[
\alpha_L = \frac{\pi \Gamma}{V_L},
\]

where \(\lambda\) is the wavelength of the incident laser beam (532 nm), \(n\) is the refractive index and \(\theta\) is the scattering angle (180°). The \(n\) values of each sample are obtained from the study reported by Murthy and Ip [7].
Figure 2 shows the temperature dependences of the $V_L$ on $28R_2O\cdot72GeO_2$ 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 $\alpha_L$ on $28R_2O\cdot72GeO_2$ glasses. The values of $\alpha_L$ are very low below $T_g$, and the difference caused by alkali species isn’t seen. While, the $\alpha_L$ 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 $28Li_2O\cdot72GeO_2$ glass was determined from the $\Delta \nu_{180}$ and $\Gamma$. Moreover, the activation energy $\Delta E$ was determined by using the Arrhenius law to discuss the relaxation process in the GHz frequency range.

References