High temperature elastic properties of lithium and caesium borate glasses, crystal and their melts.
リチウムセシウムホウ酸塩ガラス、結晶およびその融液の高温における弾性的性質

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1. Introduction

Nowadays, borates play an important role in advanced materials, for exsample, borate glasses used for glassfiber and textile, or nonlinear optic crystals, such as $CsLiB_6O_{10}$ (CLBO) [1]. Recentry, borate glass nanofibers are expected for wound healing. Alkali borate glass is used for structure materials, and it is investigated for a long time because of their interesting properties so-called borate anomaly. The composition dependences of various physical properties have extensively been studied. In contrast, the temperature dependence of physical properties has been not yet studied well. Since the elastic properties of glass are technologically important, in previous study we investigated the temperature dependence of elastic properties in alkali silicate and borate glasses over the wide temperature range [2, 3].

Brillouin scattering spectroscopy is a powerful tool to determine the elastic properties of materials at a GHz frequency range. In addition, glassy materials melt at high temperatures, Brillouin scattering that enabled to determine the elastic properties without any contact with sample is very effective in comparison with the standard ultrasonic technique. In this study, we investigate the elastic properties of alkali borate in liquid, supercooled liquid, glass, and crystalline states by the Brillouin scattering spectroscopy.

2. Experiments

The Brillouin scattering apparatus is a combination of a microscope and a sandercock-type 3 + 3 passes tandem multipass Fabry-Perot interferometer. The Brillouin scattering spectra were measured at a backward scattering geometry with a free spectral range of 60 GHz. The sample was placed inside the compact IR image furnace (Yonekura, IR-TP). The measurements were carried out by heating, and the temperature range was from room temperature to 1100 °C.

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All glass samples were prepared by the aqueous solution method and melt quenching technique. The quenched glasses were annealed for 2 hours at the glass transition temperature (T_g) determined by differential scanning calorimetry. CLBO crystals of optical grade are the products of the KOGAKUGIKEN Corporation.

3. Results and Discussion

Fig. 1 shows the Brillouin spectra of CLBO glass and crystal for various temperatures. The Brillouin doublets are fitted by the Lorentzian
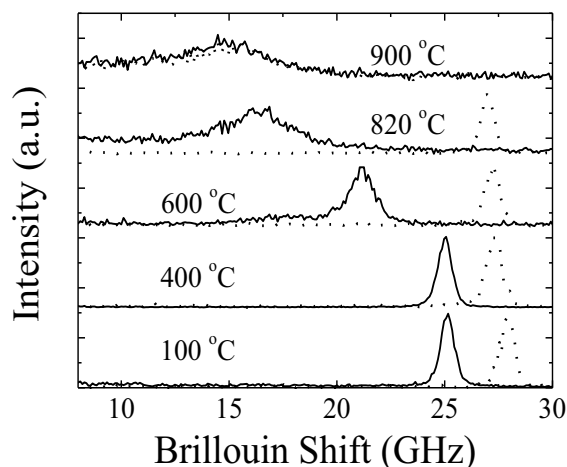

Fig. 1. The Brillouin spectrum of CLBO glass (solid line) and crystal (broken line) measured at various temperature.

function by the instrumental function of the interferometer. The longitudinal sound velocity (V_L) and absorption coefficient (α_L) are calculated from Brillouin shift and FWHM.

Fig. 2 is the temperature dependence of the longitudinal sound velocity V_L of CLBO glasses and crystal. Below T_g, with increasing temperature, V_L of both glasses and crystal are nearly constant. Above T_g, V_L of glasses decreases rapidly. In contrast, V_L of crystal remains constant. At the melting temperature (T_m), V_L of crystal drops and decreases dramatically. Above T_m, V_L of both glass and crystal are nearly the same.
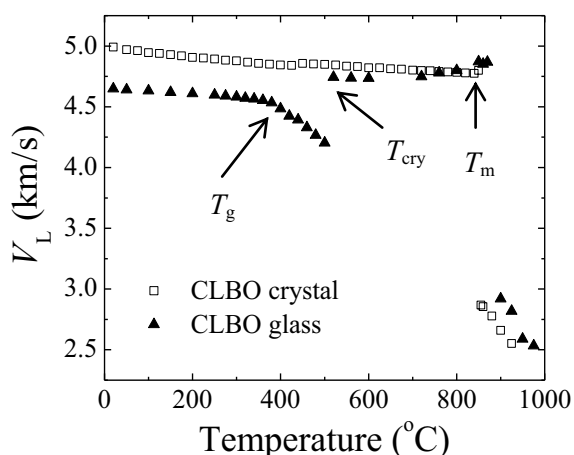
Fig. 2. Temperature dependence of longitudinal sound velocity (V_L) of samples. T_g, T_{cry} and T_m denote the glass transition temperature, crystallization temperature of glass and melting temperature of crystal, respectively.

In a supercooled liquid state, V_L of annealed glass is interesting feature. First it decreases, and then it jumps to the higher values at about 500 $^{\circ}$C. Finally, it becomes to the nearly same value with that of crystal. In comparison with the previous studies of crystallization of amorphous materials by heating, cooling and annealing [4, 5], it is concluded that the supercooled liquid changed to crystalline state at about 500 $^{\circ}$C (T_{cry}).

In order make clear the effect of annealing on the elastic property, experimental data of quenched and annealed samples are compared. **Fig. 3** shows the temperature dependence of V_L of CLBO glasses below the glass transition region. The values of V_L for annealed and quenched glasses show remarkable difference at room temperature. Near T_g, V_L of a quenched sample increases slightly and have a cusp, whereas V_L of an annealed sample shows no increase. Similar behavior was reported in SiO_2, GeO_2, and B_2O_3 glasses [6].
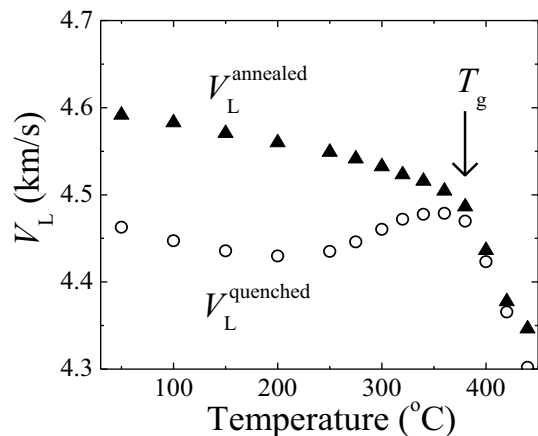

Fig. 3. Temperature dependence of V_L of CLBO glasses below the glass transition region. The solid triangles and open circles represent data for an annealed and a quenched sample, respectively.

Fig. 4 shows the scaled temperature dependence of V_L of glass samples. Temperature and V_L is scaled by T_g and V_L at T_g, respectively. T_m of glass is shown by the empirical equation ($T_g / T_m = 2/3$). Below T_g, all scaled V_L can fall into the master curve. While above , the composition dependence appears. This fact means that the glass network is essentially constructed by boron and oxide atoms below T_g. Whereas above T_m, the glass network is broken and the influence of alkali ions may appear.
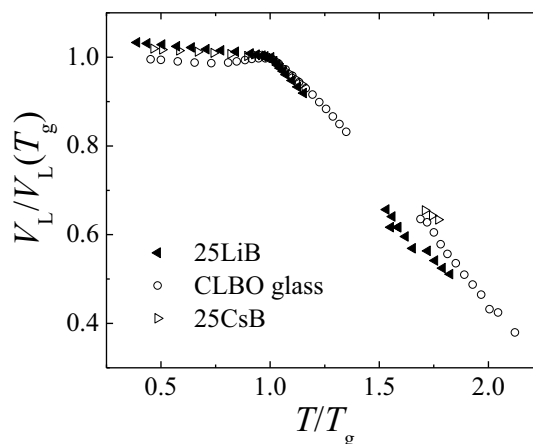

Fig. 4. Scaled V_L of glass samples as a function of T/T_g.

4. Conclusion

The high temperature elastic properties of alkali borate in liquid, supercooled liquid, glass, and crystalline states were investigated by the Brillouin scattering. The annealing effect on acoustic property is clearly observed below T_g as the differenc of sound velocity between annealed and quenched glasses. Above T_g, the remarkable decrease of sound velocity is observed in supercooled and eqilibirium liquid states.

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