Terahertz Time-Domain Spectroscopic Study of Oxide Glass with Entropic Elasticity

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***Abstract*—For disordered systems, a universal excitation called the boson peak appears in the terahertz range. In this study, we performed terahertz time-domain spectroscopy on an oxide glass with entropic elasticity—mixed alkali metal metaphosphate glass with the chemical composition $Li_{0.25}Na_{0.25}K_{0.25}Cs_{0.25}PO_3$ ($LiNaKCsPO_3$)—to detect the boson peak. The obtained spectra were compared with results of low-frequency Raman scattering and low-temperature specific heat measurements.**

I. INTRODUCTION

ENTROPIC elasticity, a property typical of rubbers and organic polymers with and effective restoring force, is not known to occur in oxide glasses. However, $LiNaKCsPO_3$ glass, a type of metaphosphate glass with entropy elasticity, was discovered by Inaba *et al.* [1]. Metaphosphate glasses RPO_3 (R: alkaline metal) mainly have straight chain structures in which the tetrahedral connected to each other by the two corner oxygen atoms [2].

Disordered materials exhibit universal dynamics in the terahertz (THz) region, that is, the so-called boson peak (BP). This is recognized as one of the unsolved problems in glass physics [3]. The BP appears universally in the THz region in the spectrum of the vibrational density of states (VDOS) divided by the squared frequency. The spectrum deviates from the Debye model predictions for a crystalline system and has been experimentally and theoretically investigated for several decades [3,4]. Recently, we found that the BP in the infrared (IR) spectrum appears in the representation of $\alpha(\nu)/\nu^2$ [4-6], where $\alpha(\nu)$ is the absorption coefficient, although this fact was known to past researchers.

In this study, we performed terahertz time-domain spectroscopy (THz-TDS) and low-frequency Raman scattering measurement of $LiNaKCsPO_3$ glass to investigate its BP behavior. Additionally, we extracted the VDOS spectrum $g(\nu)$ from the experimental data of the low-temperature specific heat. The IR and Raman light-vibration coupling coefficients ($C_{IR}(\nu)$ and $C_{Raman}(\nu)$) were determined, and $C_{IR}(\nu)$ was evaluated using Taraskin's universal model [7].

THz-TDS is a spectroscopic technique that uses a femtosecond laser for the emission and detection of a terahertz pulse wave to determine the optical constants of a sample. In our experiment, the THz spectra of the samples were measured in the frequency range 0.2–4.5 THz, using a terahertz spectrometer (RT-10000, Tochigi Nikon Co.) [8-12]. For the light source, a mode-locked titanium sapphire laser (Ti: Sapphire laser) was used with a central wavelength of 780 nm,

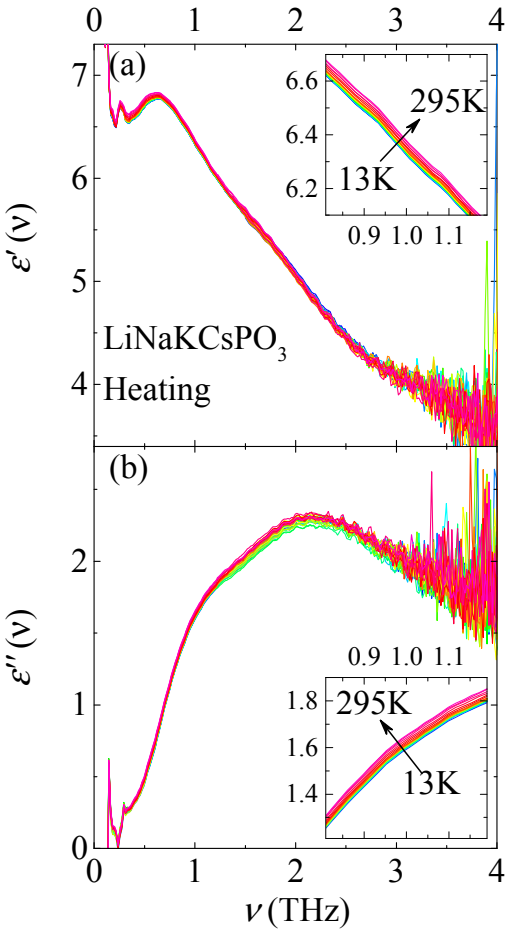

Fig. 1. Temperature dependence of the (a) real and (b) imaginary parts of the complex dielectric constants of $LiNaKCsPO_3$ glass, during the heating process, at 13 K to 295 K The data are plotted every 10 K above 20 K. For convenience, we have assumed 1 THz = 33.3 cm^{-1}

a time width of approximately 100 fs, and a repetition frequency of 80 MHz. To eliminate the influence of water vapor present in the air, parts of the off-axis ellipsoidal mirrors and sample stage were enclosed in a metal chamber with continuously flowing dry air.

Confocal micro-Raman measurements were performed with a depolarized backscattering geometry [13]. A frequency-doubled diode-pumped solid-state neodymium doped yttrium aluminum garnet laser oscillation in a single longitudinal mode at 532 nm (Oxxius LMX-532S-300) was employed as the excitation source. An inhouse-built microscope with ultra-narrowband notch filters (OptiGrate)

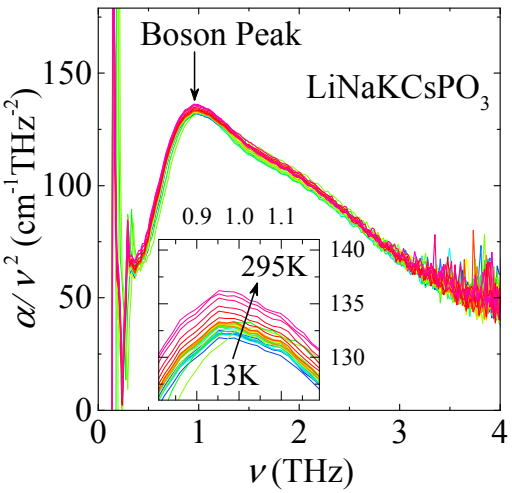

Fig. 2. Temperature dependence of the BP plot of $\alpha(\nu)/\nu^2$ of $LiNaKCsPO_3$ glass, during the heating process, at 13 K to 295 K The data are plotted every 10 K above 20 K. For convenience, we have assumed 1 THz = 33.3 cm^{-1}

was used to focus the excitation laser and collect the Raman-scattered light. The scattered light was analyzed using a single monochromator (Jovin-Yvon, HR320, 1200 grooves/mm) equipped with a charge-coupled device (CCD) camera (Andor, DU420).

II. Results

Fig. 1 shows the temperature dependence of the complex dielectric constant $\varepsilon(\nu)$ of the $LiNaKCsPO_3$ glass during the heating process, as measured via THz-TDS. As the temperature increases, the values of both the real and imaginary parts of $\varepsilon(\nu)$ increase slightly, as shown in the inset of Fig. 1. At the lowest temperature, a peak is observed at approximately 0.7 THz in the real part $\varepsilon'(\nu)$. However, the imaginary part $\varepsilon''(\nu)$ exhibits an inflection point at 1.0 THz and a peak located around 2.0 THz. This resonance-like behavior is a universal feature of glassy materials around the BP frequency, as reported in previously [6,11].

Next, to observe the BP in the IR spectrum, the variation in $\alpha(\nu)/\nu^2$ with the frequency (ν) was examined, as shown in Fig. 2. At the lowest temperature of 13 K, a peak is clearly observed at 0.95 THz, which is the BP in the IR spectrum. The BP frequency shows almost no change from low to high temperatures.

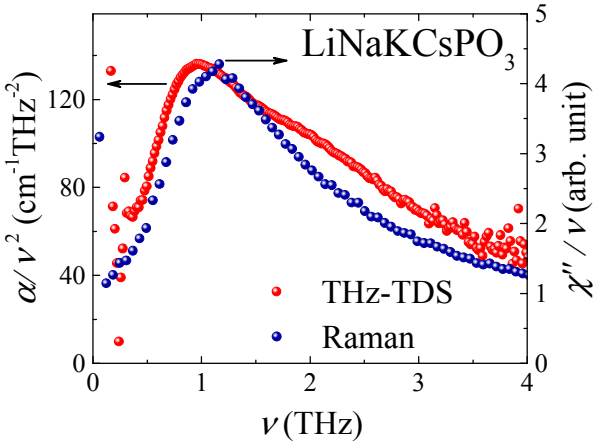

Fig. 3. Comparison of the BP spectra of the $LiNaKCsPO_3$ glass detected by the THz-TDS and the low-frequency Raman scattering.

Fig. 3 shows the BP in the plot of $\alpha(\nu)/\nu^2$ vs. ν for the LiNaKCsPO3 glass at low temperature. For comparison, the BP of the Raman scattering spectrum is plotted in the spectrum of $\chi''(\nu)/\nu$, where $\chi''(\nu)$ is the imaginary part of the Raman susceptibility. In the spectrum of $\chi''(\nu)/\nu$, the BP frequency is approximately 1.13 THz, which is 1.2 times greater than that of the IR spectrum.

The discrepancy between $\nu_{BP\text{-}IR}$ and $\nu_{BP\text{-}Raman}$ is attributed to the different frequency dependences of $C_{IR}(\nu)$ and $C_{Raman}(\nu)$. IR spectroscopy has the advantage of being able to determine the absolute value of the absorption coefficient. As a result, we can quantitatively determine and evaluate not only the line-shape but also the absolute value of $C_{IR}(\nu)$. Taraskin *et al.* proposed a universal functional form for the $C_{IR}(\nu)$ of glass-forming materials and analyzed our results using the proposed model [7].

III. Summary

We successfully determined the BP of $LiNaKCsPO_3$ glass using THz-TDS and low-frequency Raman scattering. In a presentation, we will show results of the quantitative analysis $C_{IR}(\nu)$ using Taraskin's model. Additionally, we will discuss the effects of the BP frequency of alkali metal metaphosphate glasses on the cation mass.

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