

Boson Peaks and Excess Heat Capacity of Lithium Borate GlassesSeiji Kojima,^{1,*} Yu Matsuda,¹ Masao Kodama,¹ Hitoshi Kawaji,² and Tooru Atake²¹*Graduate School of Pure and Applied Sciences,**University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan*²*Materials and Structure Laboratory, Tokyo Institute of Technology,**Yokohama, Kanagawa 226-8503, Japan*

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The heat capacity of rapidly quenched lithium borate glass was measured by a relaxation method between 2 K and 300 K to clarify the origin of a boson peak. The boson peak of lithium borate glass was also studied by Raman scattering measurements. Upon increasing the lithium composition, the peak value of C_p/T^3 shows remarkable decrease, while the peak temperature of C_p/T^3 increases markedly. Both the peak temperature of C_p/T^3 and Raman boson peak frequency linearly increase upon increasing the Li_2O content and show a strong correlation with the shear modulus. The universal nature of C_p/T^3 and Raman boson peak indicates that the distribution of the low-energy excess density of states (VDoS) remains the same with increasing Li_2O content.

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I. INTRODUCTION

The universality of topologically disordered system is one of the current topics in condensed matter physics [1, 2]. Low-energy inelastic scattering spectra show a broad response called as “boson peak” (BP). The reduced spectra of BP divided by the Bose-Einstein factor are temperature independent. Since BP is the peak of $g(E)/E^2$, where $g(E)$ is the vibrational density of states (VDoS), it originates from the low-energy excess of VDoS over the Debye prediction. As another feature of BP, namely, the heat capacity of glass at low temperatures shows the bump of C_p/T^3 vs. T plot, which is higher than the Debye level, and is also related to the excess VDoS [3]. Up to the present, the various physical models on BP were known, while there is still no reliable physical model. The correlation between BP and fragility has attracted much attention. A strong glass is more vibrational than a fragile glass and shows an intense BP and a weak fast relaxation process (FRP). In contrast, a fragile one is more relaxational than a strong glass and shows a weak BP and an intense FRP [4]. However, the understanding of such correlation has been not yet clarified.

Among structural glasses, borate glass is one of the typical strong glasses, and it consists of a random three-dimensional network of BO_3 triangles with a large fraction of almost planar B_3O_6 boroxol rings and the coordination number of boron is three [5]. The physical properties of alkali borate glasses drastically vary with the alkali composition resulting from the variation of the intermediate topological order, and these behaviors

are known as “borate anomaly.” The alkali metal modifier causes the increase of the coordination number of boron from three to four [6]. With increasing alkali composition, the fraction of boroxol rings decreases and they change into other structural units, i.e., pentaborate, triborate, diborate, and metaborate groups. These various structural groups have been studied extensively [7, 8]. As to the microscopic origin of BP of a pure borate glass ($x=0.0$), the libration of two adjacent boroxols was predicted by the Hyper Raman scattering study [9]. The high-resolution inelastic x-ray scattering (IXS) study of $x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ ($x=0.20, 0.33$) glasses reported that the strong scattering occurs at the Ioffe-Regal limit [10]. The formula of lithium borate glasses was denoted by $x\text{Li}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$, where x indicates the mole fraction of Li_2O . X-ray Brillouin scattering of $\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ ($x=0.33$) showed that the boson peak frequency about 70 cm^{-1} is equal to the Ioffe-Regal limit [11]. Recently, the universal link between BP and transverse phonons was discussed theoretically on the basis of transverse vibrational modes associated with the defective soft structure, and it has been proposed that the origin of BP relates to the Ioffe-Regal limit for transverse modes, above which these phonons no longer propagate [12].

In this study, for the clarification of the physical mechanism of boson peaks, quenched lithium borate binary glasses, $x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ (LiB) are studied in a large range of x by measuring heat capacity at low temperatures and Raman scattering at room temperature to clarify the universal nature of BP.

II. EXPERIMENTAL

The glass samples, $x\text{Li}_2\text{O}-(1-x)\text{B}_2\text{O}_3$, with the Li_2O content ranging from 0.02 to 0.26 were specially prepared for the investigation of the homogeneous binary glass system. All glasses with high homogeneity were prepared by the solution method [13] in order to investigate the inherent nature of binary mixtures of lithium borate glasses. The heat capacity measurement was performed using the calorimeter employing a relaxation method. Quantum Design PPMS was used for the measurement in the temperature range from 2 to 300 K [14]. The low-frequency Raman scattering was measured at the room temperature using an Ar ion laser with a power of 50 mW, an additive triple-grating spectrometer Jobin Yvon (T64000), and a conventional photon-counting system [15, 16].

III. RESULTS AND DISCUSSION

A. Heat capacity at low temperatures

Since the boson peak is closely related to the non-Debye excess heat capacity, the measurement of low-temperature heat capacity is very important. The heat capacity of pure borate glass was already well studied [17–19]. The heat capacity of lithium borate glasses was measured in the temperature between 2 and 300 K by a relaxation method using the Physical Property Measurement System (PPMS), Quantum Design. Figure 1 shows the temperature dependence of C_p/T^3 of lithium borate glasses $x\text{Li}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ with $x=0.08$,

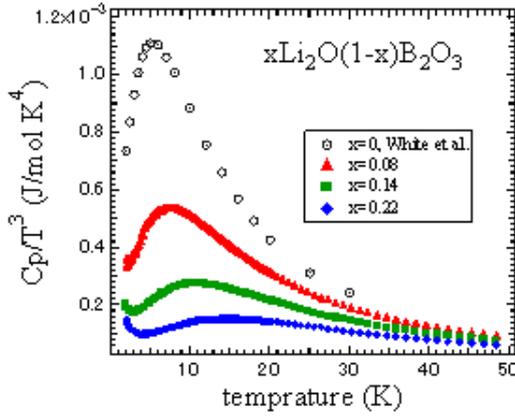


FIG. 1: Temperature dependences of heat capacity of lithium borate glasses $x\text{Li}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$ with $x=0.08, 0.14,$ and 0.22 . The numerical data corresponding to $x=0$ in ref. 17 are also plotted for comparison.

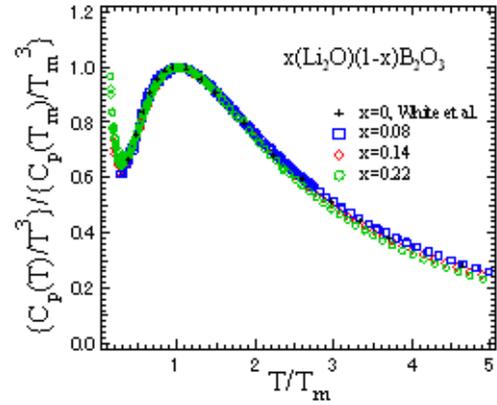


FIG. 2: Scaling of temperature dependences of heat capacity of lithium borate glasses $x\text{Li}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$ with $x=0.08, 0.14,$ and 0.22 . The numerical data corresponding to $x=0$ reported in ref. 17 are also plotted for comparison.

0.14, and 0.22. The numerical data corresponding to $x=0$ in ref. 17 are also plotted for comparison. With increasing x , the peak value of C_p/T^3 shows remarkable decrease. It indicates that the excess VDoS decreases as the fragility increases. In contrast, the peak temperature increases markedly. This behavior is consistent with the fact that BP energy increases with increasing x [15, 16].

The boson peak spectra observed by the neutron inelastic scattering shows the independence of scaled spectra in polyisobutylene (PIB) on pressure [21]. In LiB glasses, the glass network structure is densified and the density increases by about 20% from $x=0$ to 0.26 [13]. However, such densification is not the simple chemical pressure without any change of bonding. With increasing of the Li_2O content, the coordination number of boron increases gradually from three to four. Recently, it was found that the scaled curve is essentially the same for not only inelastic neutron scattering but also Raman scattering, except the very low-frequency part of neutron scattering below the BP frequency where strong elastic scattering is dominant [22, 24]. Therefore, the present result of the heat capacity is also scaled, as shown in Fig. 2. The normalized curves of C_p/T^3 divided the maximum value vs. T divided by the maximum temperature are independent on the Li_2O content.

Such a universal scaling indicates that the way of the distribution of VDoS basically remains the same, even though the structures drastically change with the composition. These results indicate that the remarkable increase of the BP frequency does not mean the declination of the low-frequency excess modes.

B. Raman boson peak

In first-order Raman scattering spectra, BP appears between 25 and 100 cm^{-1} in alkali borate glasses [15]. The variation of Raman scattering spectra in the range between

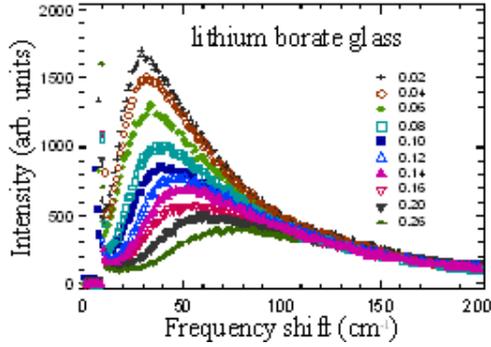


FIG. 3: Raman scattering spectra of lithium borate glasses $x\text{Li}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$ with $x=0.02$ – 0.26 .

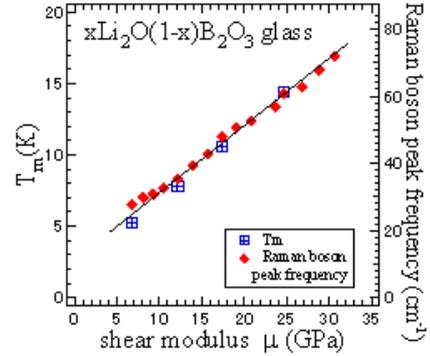


FIG. 4: Correlation between the peak temperature of C_p/T^3 , the Raman boson peak frequency and the shear modulus in lithium borate glasses $x\text{Li}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$ with $x=0.02$ – 0.26 .

$x=0.02$ and 0.26 is shown in Fig. 3. With increasing the Li_2O content x , BP frequency ω_{bp} shows remarkable hardening, whereas the peak intensity $I(\omega_{bp})$ at the BP frequency decreases markedly. Such a decrease of intensity is consistent with the Sokolov's prediction [4] because the fragility of lithium borate glasses increases with increasing x .

C. Correlation between boson peak and shear modulus

The origin of BP was extensively studied, whereas the unified picture has been not yet confirmed. Recently, the correlation between the BP frequency and the Ioffe-Regal limit at the wave vector Q_{IR} was examined in the inelastic x-ray measurements of LiB glasses [10, 11]. In the Rayleigh scattering regime below Q_{IR} , plane acoustic modes propagate [23] and the elastic scattering by defects causes the damping of acoustic phonon proportional to ω^4 . While above Q_{IR} the acoustic modes are nonpropagating, and the damping is proportional to ω . It is suggested that such an Ioffe-Regal crossover is related to ω_{bp} . The recent numerical simulation study predicted the difference of the Ioffe-Regal crossover between the longitudinal acoustic (LA) mode and the transverse acoustic (TA) mode [12]. The result indicates that BP is related to transverse vibrational modes associated with defective soft structures in the disordered state. In fact, the contribution of transverse modes is dominant in VDoS; however, the transverse mode cannot be observed by inelastic x-ray scattering [12], and no experimental examination related to transverse mode is reported.

According to the prediction in ref. 12, ω_{bp} is given by

$$\omega_{bp} = \omega_{IR}^T \propto \mu, \quad (1)$$

where ω_{IR}^T is the Ioffe-Regal limit for a TA mode and μ is the shear modulus. The close relation between Raman boson peaks and neutron boson peak is also found very recently [24]. The maximum temperature T_m of C_p/T^3 and BP frequency ω_{bp} determined by Raman scattering were plotted against the shear modulus as shown in Fig. 4. It is found that the

maximum temperature of C_p/T^3 and the BP frequency show clear correlation with the shear modulus. It holds that

$$\omega_{bp} \propto T_m \propto \mu. \quad (2)$$

This fact is in agreement with the theoretical prediction that the boson peak frequency is equal to the Ioffe-Regal crossover for transverse mode [12].

IV. CONCLUSION

The heat capacity of rapidly quenched lithium borate glass was measured by a relaxation method between 2 K and 300 K. The temperature dependence of C_p/T^3 shows clear peak between 5 K and 20 K. The boson peak of lithium borate glass was also studied by Raman scattering measurements. Both the peak temperature of C_p/T^3 and Raman boson peak frequency linearly increase with increasing Li_2O content, and show the clear correlation with the shear modulus. It is found that the temperature dependence of C_p/T^3 and the boson peak spectra are well scaled by the master curve. It indicates that with increasing the Li_2O content the function of the distribution of VDoS remains the same even if the density and network structure show drastic changes. Further extensive study is required to clarify the mechanism on this universal nature of scaled boson peak spectra when both density and network structure change markedly [25].

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