Structure of Alkali Borate Glasses at High Pressure: B and Li *K*-Edge Inelastic X-Ray Scattering Study

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We report the first *in situ* boron *K*-edge inelastic x-ray scattering (IXS) spectra for alkali borate glasses ($Li_2B_4O_7$) at high pressure up to 30 GPa where pressure-induced coordination transformation from three-coordinated to four-coordinated boron was directly probed. Coordination transformation (reversible upon decompression) begins around 5 GPa and the fraction of four-coordinated boron increases with pressure from about 50% (at 1 atm) to more than 95% (at 30 GPa) with multiple densification mechanisms, evidenced by three distinct pressure ranges for $(d^{[4]}\mathrm{B}/dP)_T$. The lithium *K*-edge IXS spectrum for Li-borate glasses at 5 GPa shows IXS features similar to that at 1 atm, suggesting that the Li environment does not change much with pressure up to 5 GPa. These results provide improved understanding of the structure of low-z glass at high pressure.

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Alkali borate glasses have been used in diverse technologically important glasses and are one of the essential components of amorphous optical materials [1]. Geophysically, a minor fraction of borate component in silicate magma affects its dynamics in Earth's interior where the pressure-induced structural changes play a key role in controlling the thermodynamic and transport properties of melts [2–4]. Particularly, the pressure-induced coordination transformation is associated with the anomalous pressure dependence of viscosity [2,4,5] and changes in solubility of the elements [6], and topological disorder [7,8]. Despite their importance, pressure-induced changes in coordination for low-z glass including borates have been among the most difficult and illusive problems in physics, glass sciences, and geophysics.

Whereas $Li_2B_4O_7$ glasses have been studied at 1 atm mainly by B-11 NMR[2] and show that boron is both three- ($^{[3]}$B) and four- coordinated ($^{[4]}$B), with a $^{[4]}\mathrm{B}/^{[3]}\mathrm{B}$ ratio of about 1, their structure at high-pressure and pressure-induced coordination changes have been unknown. As discussed elsewhere [9], applications of synchrotron x-ray scattering to low z glass including borates at high pressure (combined with diamond anvil cell, DAC) has been limited due to the highly attenuating sample environment and small atomic scattering factors of low-z elements. Neutron scattering experiments can overcome this problem but require large sample volume, which limits the pressure range of study below 10 GPa. Vibrational spectroscopy or Brillouin (BR) scattering can be performed *in situ*, but have a small cross section often yielding ambiguous results. For low-z elements direct XANES and EXAFS studies require soft x ray and thus cannot penetrate the DAC environment. Solid-state NMR studies require 10–20 mg samples, limiting the maximum quench pressure for oxide glasses to 12 GPa [4,10].

Because of above-mentioned difficulties, there has been no *in situ* experimental evidence for the pressure-induced coordination changes in alkali borate glasses. Recent advances in synchrotron x-ray optics, multielement IXS analyzers, and improved DAC's have revealed details of the atomic configurations of crystalline materials at high pressure [11–15]. We previously utilized IXS to explore the structural details of amorphous oxides and provided the first experimental evidence for the coordination transformation of the archetypal B_2O_3 glasses from $^{[3]}$B to $^{[4]}$B [9]. We have extended this technique to more complex alkali borates to provide direct and quantitative measurements of coordination change vs pressure.

The atomic environment of network modifying cations (NMC, e.g. Li^+, Ca^{2+}) in oxide glasses is important for understanding transport properties including electric conductivity [16]. Unfortunately, they are difficult to study at high pressure due to the large topological disorder associated with the NMCs. A recent NMR study shows that the Na-O distance decreases with increasing pressure for Na-aluminosilicate glasses but increases with pressure for binary silicates [17], suggesting pressure-induced structural changes in the alkali environment are a complex function of composition and pressure. While several Li-*K* edge studies have been reported for oxides at 1 atm [18–20], the coordination environment for Li-borate glasses at high pressure is not well understood. We note that recent accurate isotopic substitution neutron diffraction yielded improved understanding of the Li environment in borate glasses at 1 atm [21,22]. We report the first Li-K edge IXS spectra for Li-borate glasses at high pressure. We also compare the pressure-induced structural changes in both borate and alkali borate glasses and discuss the general densification mechanisms in both.

$Li_2B_4O_7$ glasses were synthesized by melting Li_2CO_3 and B_2O_3 glasses at 773 K for about 30 min. The glass was loaded in a piston-cylinder type DAC with a Be gasket inside the glove box under an Ar environment. No pressure medium was used. The diamond culet size and gasket hole diameter are about 700 and 300 mm, respectively, with a sample thickness of about 120 mm. While previous studies of B_2O_3 glasses at high pressure reported a slow pressure response to cold compression, necessitating several hours of equilibration time [9,23], this slow pressure equilibration was not observed for Li-borate glasses.

Li and B K-edge IXS spectra were collected at the GSECARS beam line 13ID-C at Advanced Photon Source. The DAC was mounted on a multiaxis goniometer where IXS spectra were collected by scanning the incident beam energy relative to the fixed analyzer energy of 9.687 keV with a resolution of 1.16 eV FWHM. The monochromatic x-rays produced by a cryogenically cooled double crystal Si(111) monochromator were focused to 20×20 μm ($H \times V$) with a large KB mirror pair. The inelastic x rays were collected at a scattering angle of 18° using a linear array of six spherical Si(660) analyzers [12]. Boron K-edge spectra were collected with varying pressures from 1 atm to 30 GPa. A ruby fluorescence pressure scale was used. Li K-edge IXS spectra of Li-borate glasses at 1 atm were collected for the sample mounted directly on the goniometer without DAC. The 5 GPa spectrum was collected for the sample in the DAC, using the same geometry as B K edge.

Figure 1 presents the boron K-edge IXS spectra for $Li_2B_4O_7$ glasses with varying pressures up to 30 GPa—IXS spectrum for v-v-B_2O_3 at 1 atm reported previously [9] is shown here for comparison. As confirmed in the earlier boron K-edge IXS and XANES studies at 1 atm, the features near 194 eV and 203 eV are characteristic of $^{[3]}$B. This is due to the transition of a boron 1 s electron to an unoccupied boron antibonding $2p_z$ orbital (labeled π^*) and the transition of a boron 1 s electron to an unoccupied B-O σ^* antibonding orbital [9,24–26]. The spectrum for $Li_2B_4O_7$ at 1 atm shows another σ^* feature at 198–200 eV that corresponds to a transition from 1 s core electron to $2p/2s$ σ^* antibonding orbital in $^{[4]}$B [24]. The formation $^{[4]}$B with addition of alkali cation (i.e., $^{[4]}$B+ alkali cation = $^{[4]}$B) is consistent with previous B-11 NMR study at 1 atm [1].

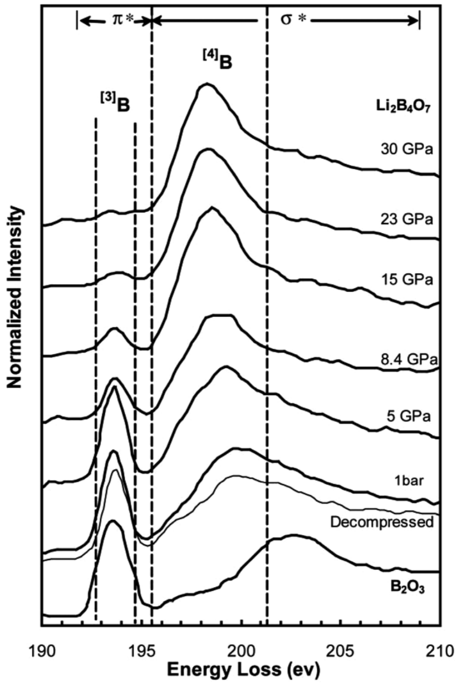

FIG. 1. Boron K-edge inelastic x-ray scattering spectra for $Li_2B_4O_7$ glass and B_2O_3 glass (bottom) at pressures ranging from 1 bar to 30 GPa as labeled. Thin line refers to IXS spectra for $Li_2B_4O_7$ glass decompressed to 1 atm from 30 GPa. Boron K-edge IXS spectra for pure B_2O_3 glasses at 1 bar is previously reported [9]. The spectra are plotted as normalized scattered intensity vs energy loss (incident energy—elastic energy).

As seen in Fig. 1, increasing pressure results in an increase of the σ^* ($^{[4]}$B) feature near 198–200 eV and gradually decreases π^* intensity ($^{[3]}$B), providing unambiguous evidence for the coordination transformation from $^{[3]}$B to $^{[4]}$B. Figure 2 presents the variation of the $^{[3]}$B fraction with pressure. The $^{[3]}$B fraction was determined by calculating the ratio of the area under the π^* features to total spectral area from 190 eV to 210 eV and then renormalizing the fractions to 100% at 1 bar of B_2O_3 glasses [9]. Each spectrum was fit with four Gaussians (one for π^* and the others for σ^* region) and from this fit the π^* fraction over total area is determined.

While the change in the $^{[3]}$B fraction is small at pressures below 5 GPa, a dramatic coordination transformation with a larger $-(d^{[3]}B/dP)_T[= (d^{[4]}B/dP)_T]$ is observed between 5–10 GPa. Above 15 GPa, $-(d^{[3]}B/dP)_T$ is significantly reduced. A negligible fraction of $^{[3]}$B was observed above 25 GPa indicating that, most of boron is four-coordinated around 30 GPa. The current data, together with previous data for the v-B_2O_3 glasses, show dramatic changes in pressure dependence up to 30 GPa. The pressure ranges labeled I, II, and III in the Fig. 2 mark regions of distinct $(d^{[3]}B/dP)_T$, suggesting the existence of multiple densification mechanisms. Region I is characterized by the smallest $(d^{[4]}B/dP)_T$ indicating that the densification is mainly due to topological variation (e.g., bond angle and length) without coordination transformation [8]. Region II has the largest $(d^{[4]}B/dP)_T$ characteristic of significant coordination transformation within relatively narrow pressure range. In region III, the $(d^{[4]}B/dP)_T$ is much smaller than the region II indicating a larger energy penalty for the coordination transformation. We note that the coordination transformation in v borates and alkali

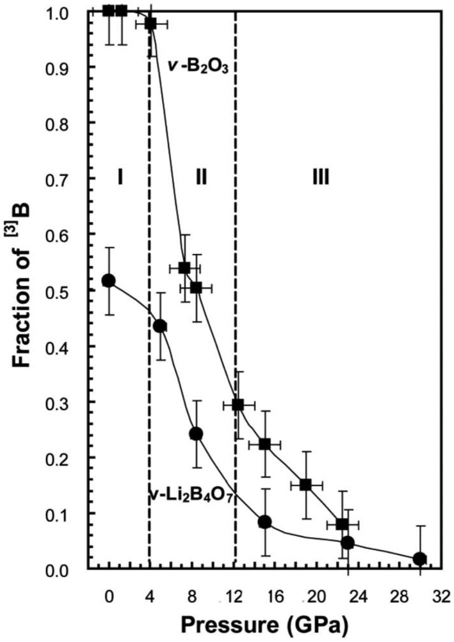

FIG. 2. Pressure dependence of the $^{[3]}$B percentage for $Li_2B_4O_7$ glass (circle) and B_2O_3 glass (squares). Dashed lines are guides to the eye only. I, II, and III refer to distinct pressure ranges with potentially varying densification mechanisms.

borate is *gradual* regardless of $(d^{[4]}\mathrm{B}/dP)$ value and thus may not be regard as a manifestation of abrupt first-order-like structural transition in borates [9,27].

Whereas we arbitrarily draw similar pressure ranges for both pure and alkali borates, they have different densification mechanisms. In our previous pure v-B_2O_3 study a shift of π^* peak position (to increasing energy) was observed, attributed to a decrease in the B-O bond length [9,25]; interestingly, in this present study the π^* peak shift is not observed, suggesting that B-O bond length change with pressure is greater for pure B_2O_3 glasses than Li-borate glasses. Whereas the origin of this difference is not very clear, it may arise from the structural differences between these two glasses at 1 atm, such as the variation of ring-topology caused by alkali cations: the fractions of boroxol ring consisting of three corner shared BO_3 triangle and nonring components vary with alkali contents in a complex manner [28]. An additional possibility is the presence of NBO for the alkali borate glasses at 1 atm. While there are no NBO's in the pure B_2O_3 glass and it is generally accepted that there are no NBO in alkali diborate glasses, our preliminary O-17 2D NMR data for Na-diborate glasses show the presence of about 11% of Na-NBO (Lee *et al.*, to be published).

After decompression from high pressure the fraction of $^{[3]}$B in Li-borate glasses is fully recovered indicating that the coordination transformation is reversible—an effect observed in B_2O_3 glasses as well. The B_2O_3 also showed evidence for permanent densification arising from the permanent π^* energy shift after decompression. The evidence of permanent densification in Li-B_2O_3 glass is, however, not observed, which may stem from varying densification mechanisms for both glasses. If there are no NBO's at 1 atm (as is the case for B_2O_3 glass), triply-coordinated oxygen (coordinated by three $^{[4]}$B, tricluster) associates with the formation of a highly coordinated cation, i.e., $^{[3]}\mathrm{B} + \mathrm{BO} \Rightarrow {}^{[4]}\mathrm{B}$ + triply coordinated oxygen [9]. This would lead to following pressure dependence $(d^{[4]}\mathrm{B}/dP)_T = (d\chi_{\mathrm{tricluster}}/dP)_T$. The NBO fraction in the oxide glasses plays an important role in the pressure-induced densification where highly coordinated framework units form at the expense of NBO [7,10,29,30]. The formation of $^{[4]}$B at high pressure in alkali borate glasses may be accompanied by a decrease in NBO content, i.e., $^{[3]}\mathrm{B} + \mathrm{NBO} \Rightarrow {}^{[4]}\mathrm{B}$ as well as the formation of triply coordinated oxygen. Note, however, that the fraction of NBO in alkali borate is not significant (about 11%) and thus pressure-induced topological variations (i.e. ring⟨=⟩non-ring, $^{[3]}$B in boroxol ring⟨=⟩$^{[4]}$B, $^{[3]}$B in nonring⟨=⟩$^{[4]}$B) may play an important role in the permanent densification.

Pressure-induced coordination transformation of NMCs has been extremely difficult to explore and thus the atomic environments around light elements such as Na and Li at high pressure are previously unstudied. Figure 3 shows the first IXS Li K-edge spectra for $Li_2B_4O_7$ glasses at 1 atm and 5 GPa where several Li K-edge features were shown. While the broad Be plasmon feature (inset), due to Be gasket used in the DAC, complicates the Li- K-edge measurement, background subtraction of Be plasmon was successful, allowing us to observe two weak features around 60 and 63 eV. Similar features were reported for crystalline Li-halides and Li-silicates and are due to a transition from 1 s core electron to valence band free orbitals [20]. Not surprising, the Li-IXS 1 atm and 5 GPa spectra show little difference (Fig. 3), a result similar to the boron K-edge IXS spectra measured at the same pressures (Fig. 1). The Li K-edge results are given here as a preliminary benchmark and more extensive theoretical and experimental Li K-edge studies of model compounds are required to obtain the systematic effect of composition and pressure on their local structures and IXS features.

The pressure-induced coordination changes in the oxide glasses results in the complex pressure dependence of macroscopic properties, such as viscosity (η), diffusivity crystal-melt partitioning coefficient ($D^{\text{crystal-melt}}$), and the solubility (K) of elements in the melts [31]. The following relations may be applicable to borate glasses and their precursor melts at high pressure:

$$\begin{aligned}(d^{[4]}\mathrm{B}/dP)_T &= (d\eta/dP)_T = -(dK/dP)_T \\ &= (dD^{\text{crystal melt}}/dP)_T. \qquad (1)\end{aligned}$$

The detailed $(d^{[4]}\mathrm{B}/dP)_T$ trend (either associated with changes in NBO and triply-coordinated oxygen) in borate glasses enable us to infer the changes in these important macroscopic properties. We also note that pressure-induced changes in medium-range order could contribute to the changes in the macroscopic properties.

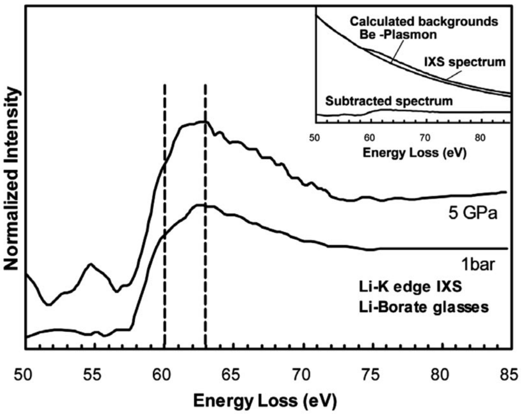

FIG. 3. Li *K*-edge inelastic x-ray scattering spectra for Li-B_2O_3 glasses at 1 atm and 5 GPa. The inset shows the background subtraction methods for IXS spectra at 5 GPa where a significant contribution from Be plasmon was subtracted. Here, a contribution from Be plasmon was fitted using complex linear function and then is subtracted from the IXS spectra, yielding IXS spectra free from the Be plasmon effect.

In conclusion, we reported the first direct experimental evidence for the pressure-induced coordination transformation in the alkali-borate glasses using synchrotron IXS. The densification mechanisms of alkali-borate and pure borate glasses are different yet their pressure dependence showed similar characteristics: region I (low pressure regime) was marked with topological variation without coordination transformation and region II (about 5–10 GPa) was characterized by the largest $(d^{[4]}\mathrm{B}/dP)_T$ value. Finally, in region III (above 10 GPa) with a smaller $(d^{[4]}\mathrm{B}/dP)_T$ a larger energy penalty for coordination transformation than in region II is observed. While Li *K*-edge spectra for borate glasses shows a negligible difference between 1 atm and 5 GPa, further experiments at high pressure could reveal pressure-induced coordination changes of the NMCs as well as the framework cation. The current results for alkali borates provide essential information about pressure dependence of their macroscopic properties and thus magmatic processes in the Earth's interior.

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