PHYSICAL REVIEW B **78**, 214203 (2008)

Probing and modeling of pressure-induced coordination transformation in borate glasses: Inelastic x-ray scattering study at high pressure

Sung Keun Lee,[1,*] Peter J. Eng,[2,3] Ho-kwang Mao,[4,5] and Jinfu Shu[4]
[1]*School of Earth and Environmental Sciences, Seoul National University, Seoul 151-742, Korea*
[2]*Consortium for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637, USA*
[3]*James Franck Institute, University of Chicago, Chicago, Illinois 60637, USA*
[4]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, USA*
[5]*HPCAT, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA*
(Received 3 October 2008; published 9 December 2008)

Here, we report on the *in situ* synchrotron inelastic x-ray scattering spectra of Na-borate glasses at high pressure up to 25 GPa. The pressure-induced boron coordination transformation from $^{[3]}$B to $^{[4]}$B is *linear* with pressure characterized by a *single* value of $(\partial\, ^{[3]}\mathrm{B}/\partial P)_T$. Previous studies of Li-borate and pure-borate glasses show a *nonlinear* transformation with *multiple* $(\partial\, ^{[3]}\mathrm{B}/\partial P)_T$ values for different pressure ranges, revealing the important role cation field strength plays in densification and pressure-induced structural changes. Considering the distribution of the energy difference between low- and high-pressure states $(\Delta\varepsilon)$ in the energy landscape and the variance of the ratio $\Delta\varepsilon$ to its pressure gradient $(\partial\Delta\varepsilon/\partial P)_T$ as a measure of network flexibility with pressure, an amorphous system with a large variance in $\Delta\varepsilon$ at 1 atm and/or a small $(\partial\Delta\varepsilon/\partial P)_T$ may undergo a gradual coordination transformation (e.g., Na borates). In contrast, a system with the opposite behavior (e.g., Li borates) undergoes an abrupt coordination transformation. The results and concepts of this study thus can shed light on opportunities to study the effect of composition on the nature of densification in low-*z* oxide and other archetypal glasses and melts.

DOI: 10.1103/PhysRevB.78.214203 PACS number(s): 61.43.Fs, 62.50.−p, 61.05.cj

I. INTRODUCTION

The nature of pressure-induced structural changes in amorphous materials remains unsolved in modern physical chemistry, condensed-matter physics, glass sciences, and earth science. While the structural transition in crystalline solids with pressure is described mostly by the first-order phase transition, in amorphous oxides they are usually characterized by gradual or abrupt changes in atomic structures such as coordination number (e.g., Refs. 1–15). An atomistic prediction using a conceptual model to account for the extent of gradual transition (i.e., the degree of pressure rigidity—defined later) is unavailable for many important glass-forming systems. Experimental studies of pressure-induced structural changes in glasses with high atomic numbers (large x-ray scattering factors) have been available as a result of advances in high-pressure elastic hard x-ray and neutron-scattering techniques.[8,16,17] The situation for glasses comprising low-*z* elements is limited, until recently,[18] due to the lack of suitable experimental probes. Conventional probes of low-*z* glasses such as elastic x-ray scattering, x-ray spectroscopy with soft x-ray, and vibrational spectroscopy have limited usefulness and neutron scattering has only been successful at relatively low pressures (below 6–8 GPa). Solid-state NMR is useful for investigating element-specific local structures in glasses *quenched from melts* at high pressure;[1,5,19–23] however, *in situ* high-pressure NMR for solids with a sufficient resolution is currently unavailable. The inherent difficulties of current technology pose major challenges for probing structural changes in low-*z* glasses over wide pressure ranges.

High-pressure quenched glasses may potentially yield new classes of materials with enhanced chemical and mechanical properties. Na borates are important model low-*z* oxide glass-forming liquids, with applications such as technologically important glasses.[24–26] Borate glasses are in general one of the prototypical amorphous oxides, along with silica and germanates, and thus pressure-induced coordination transformation of the system can provide much needed insights into the fundamental knowledge behind the structural evolution of multicomponent covalent oxide glasses with pressure. Pressure-induced bonding transitions in borates can be a useful model for structural changes in oxide melts with pressure, giving insight into the nonlinear pressure dependence of their macroscopic transport properties in the earth's interior.[27,28] This sheds light on a previously unknown structure-property relation in oxide glasses at high pressure. Despite the importance of Na-borate glasses, no high-pressure experimental data have been available.

Among the many composition controls on the structure of glasses, the cation field strength (i.e., charge/ionic radii) of network-modifying cations (e.g., Li^+, Na^+, and K^+) drastically affects their configurational thermodynamic and transport properties of silicates at constant ratio of network-modifying cations/network formers.[29] While the cation field strength is likely to play an important role in the pressure-induced densification in oxide glasses, its effect on the densification in borates and other prototypical oxides has not yet been explored. Inelastic x-ray scattering (IXS) (or x-ray Raman-scattering) technique using third-generation synchrotron light sources has been successfully applied to probe the details of electronic bonding structures around low-*z* elements in diverse molecules and crystals.[2,30–35] It has been recently demonstrated that IXS technique combined with advanced x-ray optics and the diamond-anvil cell (DAC) technique[32,34,35] can yield a new opportunity to study the bonding changes in low-z amorphous systems at high pressure.[2,31,36] Here, we explore the pressure-induced bonding changes in Na-borate glasses using IXS. With the aid of our previous studies on other borate glasses,[2,31] we elucidate the marked difference in densification behavior with varying cation field strength. We account for these differences with a conceptual model that utilizes pressure flexibility (the resistance to structural changes with increased pressurization) defined by the variance of the ratio of energy difference between high- and low-pressure states to its pressure gradient. We also briefly discuss the atomistic origins of the pressure rigidity in amorphous systems in general.

II. EXPERIMENTS

Sample preparation and synchrotron inelastic x-ray scattering

Na-diborate glass ($Na_2O:B_2O_3=1:2$, NB2) was synthesized by fusing B_2O_3 glass and Na_2CO_3 mixtures at 1100 K for 20 min and subsequent quenching. The glass was loaded into the sample chamber of a Be gasket in a DAC with a few ruby spheres (near the center and edge) as a pressure calibrant without a pressure medium. Diamonds with flat culets of 250 μm were used. The thickness of the sample in the gasket ranged between approximately 80 and 30 μm (decreasing with increasing pressure). This sample cell allowed us to achieve pressures of 25 GPa with a pressure difference at this highest pressure of approximately 3–4 GPa between the center and the edge of the cell. The boron K-edge IXS spectra were collected at 13ID-C of the GSECARS beamline at the Advanced Photon Source. The spectra are collected by scanning the incident-beam energy relative to the analyzer at a scattering angle of 17° with a linear array of six spherical Si(660) analyzers.[35] The elastic energy (E_0) is 9.6845 keV and the x-ray beam size was approximately 80 μm horizontally and 20 μm vertically. The spectrum at 1 atm was obtained by directly mounting a glass chip at the center of the goniometer. The raw IXS spectra were background subtracted and normalized to the continuum energy tail above approximately 210 eV, which apparently leads to form plateaus in the spectra above approximately 205 eV. The continuum tail with plateau is thus not likely due to unknown scattering contribution of boron atom that can complicate the quantification of boron fraction (see below).

III. RESULTS AND DISCUSSION

Figure 1 shows the IXS spectra of NB2 with varying pressure. As reported previously, a π^* feature at approximately 194 eV and broad σ^* at 203 eV are due to an electron transition from 1s to an unoccupied antibonding 2p_z and a transition from a 1s to an unoccupied B-O σ^* antibonding orbital, respectively, in tricoordinated boron $^{[3]}$B. A feature due to the presence of $^{[4]}$B appears between 198 and 200 eV, which corresponds to a transition from 1s to a 2p/2s σ^* antibonding orbital.[37,38] With increasing pressure, the π^* peak intensity ($^{[3]}$B) decreases while the σ^* feature associated with $^{[4]}$B increases, which is consistent with the general trend reported for pure-borate and Li-borate glasses.[2,31]

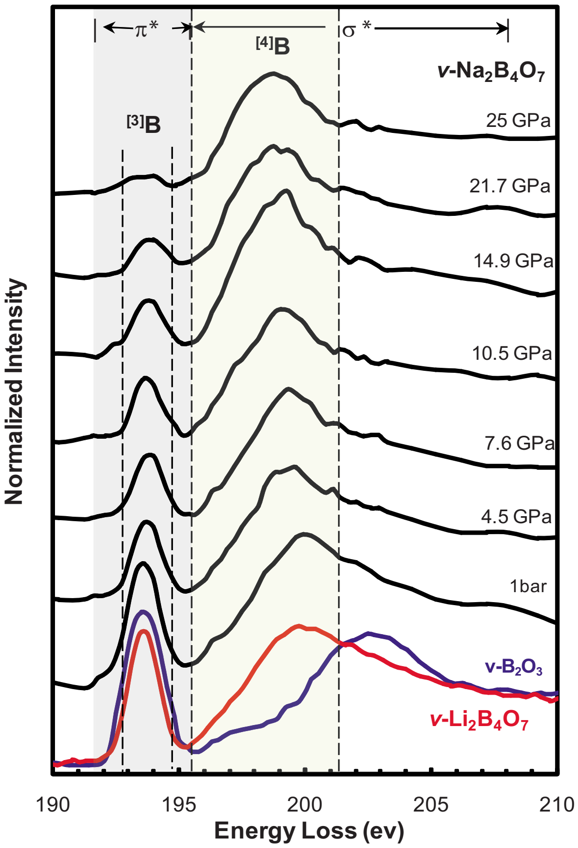

FIG. 1. (Color online) Boron K-edge inelastic IXS spectra of Na-diborate ($Na_2B_4O_7$) glasses with varying pressure, as labeled. The IXS spectra of Li-borate (red) and pure-borate glasses (blue) at 1 bar have been reported previously and are shown here for comparison purposes (Refs. 2 and 31). The spectra are plotted as the normalized scattered intensity vs the energy loss (incident energy-elastic energy).

Figure 2 shows the variation in the $^{[3]}$B fraction in alkali-borate glasses with pressure. The fractions of $^{[4]}$B and $^{[3]}$B are obtained by calculating the ratio of the area under the π^* peak to the total area from 192 to 210 eV and setting the fraction to 100% at 1 bar. This method has been used successfully for model glass and crystalline compounds.[37] Linear backgrounds extending from a π^* peak (around 193–194 eV) to 210 eV were subtracted from the spectra shown in Fig. 1 as suggested by previous B K-edge studies[37] to obtain quantitative fraction of boron coordination environments (see below for further discussion). The total intensity of the spectra $[J(\text{total})]$ from 192 to 210 eV was subsequently obtained. The spectral intensity for π^* feature $[J(\pi^*)]$ was obtained by fitting it with a single Gaussian function. The $[J(\pi^*)]/[J(\text{total})]$ ratio of the sample was further normalized to the ratio of spectral intensity in the B K-edge of reference material with 100% $^{[3]}$B (pure B_2O_3 glass at 1 atm). The $[J(\pi^*)/J(\text{total})]$ value for pure B_2O_3 glass is 0.354, which is consistent with the average value (0.354) predicted from the borate crystals with only $^{[3]}$B,[39] suggesting the robustness of the methods used here. The mole fraction of $^{[3]}$B in sample borate glass $[X(^{[3]}B_{\text{sample}})]$ is thus expressed as $[J(\pi^*)/J(\text{total})]_{\text{sample}}/[J(\pi^*)/J(\text{total})]_{\text{pure } B_2O_3 \text{ glass}}$.[39] About

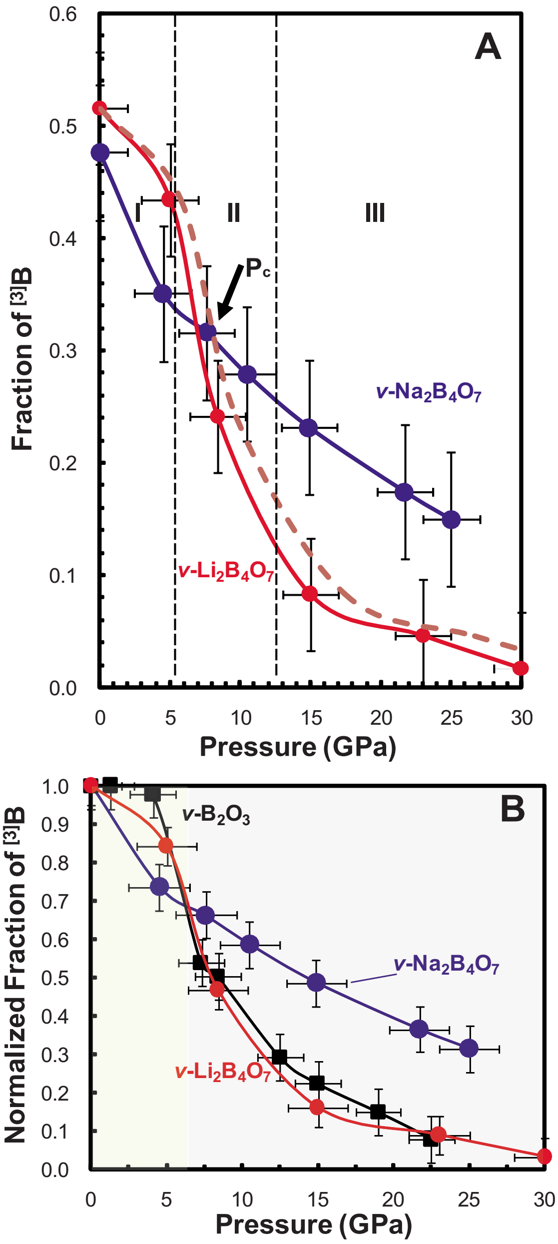

FIG. 2. (Color online) (a) Pressure dependence of the $^{[3]}$B fraction for $Na_2B_4O_7$ glass (red) and $Li_2B_4O_7$ glass (blue). The red dashed curve shows the Li-borate data that are shifted to correct for pressure gradients of 4 GPa at 25 GPa. Here we assume that the pressure difference between edge and center increases linearly with pressure. The black dashed lines for I, II, and III represent distinct pressure ranges with varying $(\partial\,^{[4]}B/\partial P)_T$ values. There are two distinct pressure ranges of densification: above and below the crossover pressure. (b) Normalized $^{[3]}$B fraction in borate glasses. The $^{[3]}$B fraction in pure-borate glasses is 100% and that in alkali-diborate glasses is approximately 50%; however, these fractions are normalized to the total fraction of $^{[3]}$B at 1 atm.

50% fraction of $^{[4]}$B in NB2 at 1 atm is in agreement with the value predicted by B-11 NMR.[2,26,37] Whereas the slightly better agreement [(3–4)% deviation from NMR] can be reached by extending the spectral range above 210 eV as suggested by the earlier quantification of $^{[3]}$B fraction in borosilicate glasses for larger Na_2O/B_2O_3 ratio (>1),[2,37,40] $[J(\pi^*)/J(\text{total})]_{\text{pure } B_2O_3 \text{ glass}}$ decreases with extension of spectral range and it further deviates from 0.354. This strongly suggests that the spectral intensity up to 210 eV is a reasonable approximation for the quantification of $^{[3]}$B fraction.

The $^{[4]}$B proportion increases with pressure up to 84% ± 4% at 25 GPa almost linearly characterized by a single value of $(\partial\,^{[3]}B/\partial P)_T$. An abrupt coordination transformation is not observed [Fig. 2(a)]. This trend is significantly different from those reported for pure-borate and Li-borate glasses where there are three distinct regions of $(\partial\,^{[3]}B/\partial P)_T$ values: (1) $(\partial\,^{[4]}B/\partial P)_T$ $[=-(\partial\,^{[3]}B/\partial P)_T]$ is the smallest in low-pressure ranges (I), (2) a dramatic coordination changes [largest $(\partial\,^{[4]}B/\partial P)_T$] are observed in the intermediate-pressure range (II), and (3) a considerably smaller $(\partial\,^{[4]}B/\partial P)_T$ in pressure range (III).[31] The varying behavior of the pressure-induced coordination transformation in Na-borate glass and other borate glasses demonstrates a previously unknown effect of cation field strength (in particular, ionic radii) on the densification behavior of borates.

The difference in densification between Na borates and Li borates with a crossover pressure (P_c) at approximately 6–8 GPa is also shown [Fig. 2(a), arrow]. As Li-borate data are shifted to estimate the possible uncertainty associated with the pressure gradient in the DAC (red dashed curve, see figure caption), the results are not significantly affected by this change. Below P_c the pressure-induced B coordination transformation is more effective in Na-borate glasses than in Li-borate glasses, with the situation reversed above P_c. The $^{[3]}$B fraction for Na borate at approximately 20 GPa is approximately 18%, while that for Li borate is approximately 6%.[31] We note that the onset of the pressure-induced boron coordination transformation from $^{[3]}$B to $^{[4]}$B in Na borate occurs under a pressure considerably lower than 6 GPa. More data points below 6 GPa are necessary to determine the onset pressure accurately. Figure 2(b) shows the normalized $^{[3]}$B fraction in borate glasses, where the $^{[3]}$B fractions for all glasses are scaled to be 100% at 1 atm. Again, the densification behaviors of pure- and Li-borate glasses are nearly identical showing a dramatic change around a P_c value of 6–8 GPa, while Na borates show a single densification pathway.

While further studies are necessary to confirm the atomic and nanometer-scale origins of the difference in pressure-induced coordination transformation in alkali borates, it is clear that the ionic radii and thus the cation field strength and associated changes in atomic arrangements (e.g., bond length and angle distribution) play a significant role in the densification behavior in alkali borates. There the small ionic radii of Li^+ (0.76 A) may not perturb the densification mechanism observed for pure-borate glasses. The larger ionic radii of Na^+ (1.02 A) in borates significantly alter the structural transition with pressure. Whereas Li- and Na-borate glasses have identical $^{[4]}B/^{[3]}B$ ratios and similar topological structures (boroxol ring content) at 1 atm, the relative stabilities of $^{[3]}$B and $^{[4]}$B in Li and Na borates diverge significantly at higher pressure. As discussed earlier,[31] $(\partial\,^{[4]}B/\partial P)_T$ may be regarded as the measure of an energy barrier for the boron coordination transformation. As the basis of this premise, pure- and Li-borate glasses have at least three distinct energy barriers for coordination transformation and thus multiple densification mechanisms. For Na-borate glasses, the change is more gradual with a single structural mechanism for coordination transformation suggesting a single transformation energy barrier.

To understand the pressure-induced coordination transformation in amorphous systems, an alternate conceptual model is needed to account for the difference in the densification behaviors of Na and Li borates. It is necessary for such model to describe structural transitions from abrupt to gradual in terms of the distribution of cluster energy difference between low- and high-energy cluster states upon compression. For this model it is *assumed* that the structure of glasses can be represented by an energy landscape with distribution of local minima for high-pressure (β) and low-pressure (α) stable coordination states where the energy of the $^{[3]}$B cluster is not constant but rather described by a distribution that depends on local and medium-range structures. The energy difference $\varepsilon_\beta - \varepsilon_\alpha$ between the two coordination states with pressure would then be described by a distribution such as a Gaussian with variance $[\sigma(\Delta\varepsilon)]^2$. Such distribution would result in a variation in the transition pressure (P_{tr}) where the energy difference between the two states is 0. P_{tr} can thus be expressed as the ratio of energy difference ($\varepsilon_\beta^0 - \varepsilon_\alpha^0$) at a reference pressure (e.g., 1 atm) to the isothermal pressure dependence of the difference in the energy states such that $P_{\mathrm{tr}} = -(\varepsilon_\beta^0 - \varepsilon_\alpha^0)/[\partial(\varepsilon_\beta - \varepsilon_\alpha)/\partial P]_T$. It is assumed that the cluster energy of each coordination states increases linearly with pressure and the transition is similar to the first-order transition in the cold-compressed DAC experiment (see below for further discussion). With a distribution of $\Delta\varepsilon$, the standard deviation $\sigma_p = \sigma(P_{\mathrm{tr}})$ and the P_{tr} distribution is thus identical to $\sigma(\Delta\varepsilon^0/(\partial\Delta\varepsilon/\partial P)_T)$. With a further assumption that $(\partial\Delta\varepsilon/\partial P)_T$ is monotonic, σ_p increases with increasing variance of $\Delta\varepsilon_p$ and decreasing $(\partial\Delta\varepsilon/\partial P)_T$. Based on these assumptions, the mole fraction $X_\alpha(P)$ of the coordination state α (stable at low pressure) can now be expressed as

$$X_\alpha(P) = 1 - \frac{1}{\sigma_p\sqrt{2\pi}}\int_0^P \exp\left[\frac{-(P' - P_{\mathrm{tr}})^2}{2\sigma_P^2}\right] dP' . \qquad (1)$$

Figure 3 shows the variation in $X_\alpha(P)$ as a function of pressure and σ_p. As σ_p decreases the coordination transformation in the glass is more abrupt approaching a first-order phase as σ_p goes to zero. For large σ_p the coordination transformation is more gradual with the coordination transformation appearing more linear as seen in Na-borate glass. A small value of σ_p sharpens the transition about the inflection point enhancing appearance of three distinct pressure ranges for $(\partial\,^{[4]}\mathrm{B}/\partial P)_T$, as seen in Li-borate and pure-borate glasses.[31] Here, inverse of σ_p can be regarded as the measure of an amorphous systems coordination state rigidity with pressure (defined here as pressure flexibility) that is capable of accounting for the abrupt or gradual changes in $X_\alpha(P)$. A glassy system with a large value of σ_p is thus *pressure flexible*, implying a more gradual change in the pressure-induced coordination states. A system with smaller σ_p may thus be described as *pressure rigid*, which would be suitable for describing an abrupt or polyamorphic transition in a narrow pressure range. For crystalline materials $\sigma_p = 0$ and thus without a variance in $\Delta\varepsilon^0$ and $[\partial(\varepsilon_\beta - \varepsilon_\alpha)/\partial P]_T$, $X_\alpha(P)$ shows an abrupt change in the coordination state at P_{tr} [i.e., $\lim_{\sigma_p=0} X_\alpha(P) = 1$ and 0 if $P < P_{\mathrm{tr}}$ and $P > P_t$, respectively].

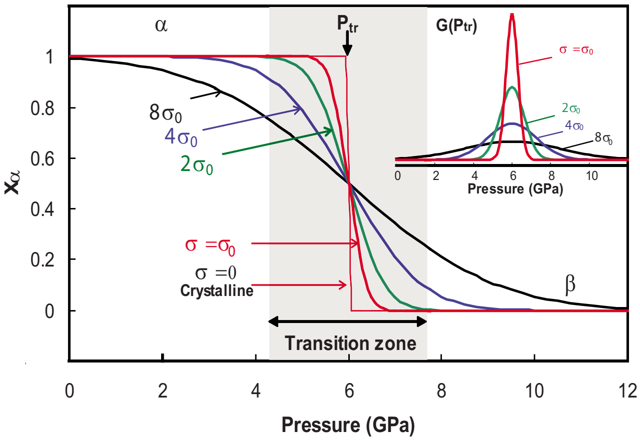

FIG. 3. (Color online) Variation in mole fraction $X_\alpha(P)$ of low-pressure coordination state (α) as a function of pressure and the variation σ_p with $P_{\mathrm{tr}} = 6$ GPa and $\sigma_p^0 = 0.3$ GPa. The transition zone is the pressure range for a rapid coordination transformation. The distribution $G(P_{\mathrm{tr}})$ of P_{tr} as a function of pressure is shown in the inset.

The above formalism can be used to describe the differences in the densification behavior between Na-borate and other borate glasses. Each system can be characterized with a unique σ_p where for example the value of σ_p for Li-borate glasses is smaller than the value for Na-borate glasses. A smaller σ_p value is due to a smaller variance in $\Delta\varepsilon^0$ and/or a larger pressure gradient of $\Delta\varepsilon$. Since the topological disorder (and thus the distribution in the energy landscape) in oxide glasses often increases with increasing cation field strength at 1 atm,[41] the smaller σ_p value for Li-borate and pure-borate glasses is, therefore, likely due to a larger pressure gradient of $\Delta\varepsilon$. The remarkable difference in densification behaviors in alkali borates also suggests that borate glasses with larger ionic radii (e.g., Na^+) are more pressure flexible due to a smaller pressure gradient of $\Delta\varepsilon$. Microscopically, the pressure-induced topological variations in the boroxol rings (trimember planar ring) and nonrings can play an important role in their coordination transformation.[31] The type of charge-balancing cations in borate glasses can thus significantly affect the stability of the borate topology at high pressure. Therefore, the lower-pressure rigidity in Na borate compared to Li borate may result from the fact that a larger ionic radius (Na^+) likely reduces the relative stability difference between the $^{[4]}$B and $^{[3]}$B clusters at high pressure. This leads to a decrease in the pressure gradient of $\Delta\varepsilon$ and thus larger σ_p. Further studies involving varying radii and cation charge (e.g., K^+, Mg^{2+}, and Ca^{2+}) in borate glasses would be necessary to confirm the systematic effect of composition on the pressure-induced structural changes. The above conceptual model may be used to describe the densification behavior in other *cold-compressed* noncrystalline systems.

Whereas the model was derived to explain the pressure dependence for borate glasses, the mathematical model utilizing pressure rigidity is rather general and can thus be applicable to the other systems. It should be noted that the experimentally observed $X_\alpha(P)$ are not symmetric about P_{tr}, suggesting that the Gaussian distribution is an over simplification and that more complicating distribution is needed that considers asymmetrical variations in $\Delta\varepsilon$ and its pressure gradient. We note that the model is possible mostly because of the unexpected experimental observation that the trends in pressure-induced coordination transformation in two alkali-borate glasses are completely different. This manifests an experimental verification of the effect of cation field strength on pressure-induced coordination changes in simple archetypal oxide glasses. We finally note that cold compression of a glass at high pressure could lead to a situation where structural transition may also be kinetically broadened in addition to thermodynamic distribution in energy landscape. Kinetic study of structural relaxation at a single pressure remains to be explored.[42]

IV. CONCLUSIONS

In situ high-pressure IXS with advanced x-ray optics and DAC technology has enabled us to reveal anomalous pressure-induced structural changes in Na-borate glasses, which are characterized by a single densification pathway in stark contrast to the multiple pathways shown in Li- and pure-borate glasses. The different densification behaviors among the archetypal-borate glasses are mostly due to the previously unknown dependence of network flexibility—defined as the variance of the ratio of $\Delta\varepsilon$ to its pressure gradient $(\partial\Delta\varepsilon/\partial P)_T$—on cation field strength. The methods and results of this study provide another insight and opportunities to study the effect of composition on the nature of densification in oxide glasses.

ACKNOWLEDGMENTS

We thank Byungdal So for help with experiments and S. Sen for helpful discussion. Use of the APS was supported by DOE Basic Energy Sciences (BES) under Contract No. W-31-109-Eng-38. GSECARS was supported by DOE-BES-Geosciences, NSF-Earth Sciences, and the State of Illinois. HPCAT was supported by DOE-BES-Materials Science, DOE-NNSA, CDAC, NSF, DOD-TACOM, and the W. M. Keck Foundation. S.K.L. was supported by funds from Korea Science and Engineering Foundation through National Research Laboratory (Grant No. 2007-000-20120).

---

*Author to whom correspondence should be addressed. sungklee@snu.ac.kr

[1] J. R. Allwardt, J. F. Stebbins, B. C. Schmidt, D. J. Frost, A. C. Withers, and M. M. Hirschmann, Am. Mineral. **90**, 1218 (2005).

[2] S. K. Lee, P. J. Eng, H. K. Mao, Y. Meng, M. Newville, M. Y. Hu, and J. F. Shu, Nat. Mater. **4**, 851 (2005).

[3] P. F. McMillan, J. Mater. Chem. **14**, 1506 (2004).

[4] S. Sen, S. Gaudio, B. G. Aitken, and C. E. Lesher, Phys. Rev. Lett. **97**, 025504 (2006).

[5] J. L. Yarger, K. H. Smith, R. A. Nieman, J. Diefenbacher, G. H. Wolf, B. T. Poe, and P. F. McMillan, Science **270**, 1964 (1995).

[6] J. Nicholas, S. Sinogeikin, J. Kieffer, and J. Bass, Phys. Rev. Lett. **92**, 215701 (2004).

[7] C. Meade, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **69**, 1387 (1992).

[8] G. H. Wolf and P. F. McMillan, in *Structure, Dynamics, and Properties of Silicate Melts*, edited by J. F. Stebbins, P. F. McMillan, and D. B. Dingwell (Mineralogical Society of America, Washington, D.C., 1995), Vol. 32, p. 505.

[9] C. T. Prewitt and R. T. Downs, in *Ultrahigh-Pressure Mineralogy—Physics and Chemistry of the Earth's Deep Interior*, edited by R. J. Hemley, Reviews in Mineralogy Vol. 37 (Mineralogical Society of America, Washington, D.C., 1998), pp. 283–317.

[10] F. X. Zhang, J. W. Wang, U. Becker, J. Lian, J. Z. Hu, S. Saxena, and R. C. Ewing, J. Am. Chem. Soc. **129**, 13923 (2007).

[11] V. Iota, C. S. Yoo, J. H. Klepeis, Z. Jenei, W. Evans, and H. Cynn, Nat. Mater. **6**, 34 (2007).

[12] C.-S. Yoo, High Pressure Materials Research: Novel Extended Phases of Molecular Triatomics, in *Chemistry at Extreme Conditions*, edited by M. R. Manaa (Elsevier, Amsterdam, 2005), p. 165.

[13] C. S. Yoo, B. Maddox, J.-H. P. Klepeis, V. Iota, W. Evans, A. McMahan, M. Y. Hu, P. Chow, M. Somayazulu, D. Hausermann, R. T. Scalettar, and W. E. Pickett, Phys. Rev. Lett. **94**, 115502 (2005).

[14] W. J. Evans, M. J. Lipp, C. S. Yoo, H. Cynn, J. L. Herberg, R. S. Maxwell, and M. F. Nicol, Chem. Mater. **18**, 2520 (2006).

[15] E. Soignard, P. F. McMillan, and K. Leinenweber, Chem. Mater. **16**, 5344 (2004).

[16] M. Guthrie, C. A. Tulk, C. J. Benmore, J. Xu, J. L. Yarger, D. D. Klug, J. S. Tse, H-k. Mao, and R. J. Hemley, Phys. Rev. Lett. **93**, 115502 (2004).

[17] L. Cormier, G. Ferlat, J.-P. Itie, L. Galoisy, G. Calas, and G. Aquilanti, Phys. Rev. B **76**, 134204 (2007).

[18] S. K. Lee, Geochim. Cosmochim. Acta **69**, 3695 (2005).

[19] S. K. Lee, J. Phys. Chem. B **108**, 5889 (2004).

[20] S. K. Lee, K. Mibe, Y. Fei, G. D. Cody, and B. O. Mysen, Phys. Rev. Lett. **94**, 165507 (2005).

[21] X. Xue, J. F. Stebbins, M. Kanzaki, and R. G. Tronnes, Science **245**, 962 (1989).

[22] S. E. Ashbrook, A. J. Berry, D. J. Frost, A. Gregorovic, C. J. Pickard, J. E. Readman, and S. Wimperis, J. Am. Chem. Soc. **129**, 13213 (2007).

[23] S. E. Ashbrook, A. J. Berry, W. O. Hibberson, S. Steuernagel, and S. Wimperis, J. Am. Chem. Soc. **125**, 11824 (2003).

[24] A. C. Wright, S. A. Feller, and A. C. Hannon, in *Borate Glasses, Crystals, and Melts*, Vol. 2, Proceedings of the Second International Conference, Abingdon, 1996 (Society of Glass Technology, Sheffield, UK, 1997).

[25] C. K. Jayasankar, K. Ramanjaneya Setty, P. Babu, Th. Troster, and W. B. Holzapfel, Phys. Rev. B **69**, 214108 (2004).

[26] Y. H. Yun and P. J. Bray, J. Non-Cryst. Solids **27**, 363 (1978).

[27] R. J. Hemley, H. K. Mao, P. M. Bell, and B. O. Mysen, Phys. Rev. Lett. **57**, 747 (1986).

[28] B. T. Poe, P. F. McMillan, D. C. Rubie, S. Chakraborty, J. L. Yarger, and J. Diefenbacher, Science **276**, 1245 (1997).

[29] A. Navrotsky, in *Structure, Dynamics, and Properties of Silicate Melts*, edited by J. F. Stebbins, P. F. McMillan, and D. B. Dingwell (Mineralogical Society of America, Washington, D.C., 1995), p. 121.

[30] T. T. Fister, F. D. Vila, G. T. Seidler, L. Svec, J. C. Linehan, and J. O. Cross, J. Am. Chem. Soc. **130**, 925 (2008).

[31] S. K. Lee, P. J. Eng, H. K. Mao, Y. Meng, and J. F. Shu, Phys. Rev. Lett. **98**, 105502 (2007).

[32] Y. Q. Cai, H. K. Mao, P. C. Chow, J. S. Tse, Y. Ma, S. Patchkovskii, J. F. Shu, V. Struzhkin, R. J. Hemley, H. Ishii, C. C. Chen, I. Jarrige, C. T. Chen, S. R. Shieh, E. P. Huang, and C. C. Kao, Phys. Rev. Lett. **94**, 025502 (2005).

[33] P. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, M. Odelius, H. Ogasawara, L. A. Naslund, T. K. Hirsch, L. Ojamae, P. Glatzel, L. G. M. Pettersson, and A. Nilsson, Science **304**, 995 (2004).

[34] Y. Meng, H. K. Mao, P. J. Eng, T. P. Trainor, M. Newville, M. Y. Hu, C. C. Kao, J. F. Shu, D. Hausermann, and R. J. Hemley, Nat. Mater. **3**, 111 (2004).

[35] W. L. Mao, H. K. Mao, P. J. Eng, T. P. Trainor, M. Newville, C. C. Kao, D. L. Heinz, J. F. Shu, Y. Meng, and R. J. Hemley, Science **302**, 425 (2003).

[36] J. F. Lin, H. Fukui, D. Prendergast, T. Okuchi, Y. Q. Cai, N. Hiraoka, C. S. Yoo, A. Trave, P. Eng, M. Y. Hu, and P. Chow, Phys. Rev. B **75**, 012201 (2007).

[37] M. E. Fleet and S. Muthupari, Am. Mineral. **85**, 1009 (2000).

[38] W. H. E. Schwarz, L. Mensching, K. H. Hallmeier, and R. Szargan, Chem. Phys. **82**, 57 (1983).

[39] I. A. J. Garvie, A. J. Craven, and R. Brydson, Am. Mineral. **80**, 1132 (1995).

[40] M. E. Fleet and S. Muthupari, J. Non-Cryst. Solids **255**, 233 (1999).

[41] B. O. Mysen and P. Richet, *Silicate Glasses and Melts: Properties and Structure (Developments in Geochemistry)* (Elsevier, Amsterdam, 2005).

[42] O. B. Tsiok, V. V. Brazhkin, A. G. Lyapin, and L. G. Khvostantsev, Phys. Rev. Lett. **80**, 999 (1998).