Irreversibility of Pressure Induced Boron Speciation Change in Glass

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It is known that the coordination number (CN) of atoms or ions in many materials increases through application of sufficiently high pressure. This also applies to glassy materials. In boron-containing glasses, trigonal BO₃ units can be transformed into tetrahedral BO₄ under pressure. However, one of the key questions is whether the pressure-quenched CN change in glass is reversible upon annealing below the ambient glass transition temperature (Tg). Here we address this issue by performing ¹¹B NMR measurements on a soda lime borate glass that has been pressure-quenched at ~0.6 GPa near Tg. The results show a remarkable phenomenon, i.e., upon annealing at 0.9Tg the pressure-induced change in CN remains unchanged, while the pressurised values of macroscopic properties such as density, refractive index, and hardness are relaxing. This suggests that the pressure-induced changes in macroscopic properties of soda lime borate glasses compressed up to ~0.6 GPa are not attributed to changes in the short-range order in the glass, but rather to changes in overall atomic packing density and medium-range structures.

Any natural or man-made material will exhibit a significant change in microstructure and properties when subjected to high pressure⁴–⁵; particularly the coordination number (CN) of atoms or ions will generally increase with pressure⁶–⁹. It has long been known that when a glassy material or its liquid state is subjected to sufficiently high pressure, significant changes can take place in the local and medium-range structure, vibrational density of states, and physical properties⁴–⁸,¹⁰,¹¹. In recent years, theoretical modeling approaches have provided insights regarding the structural response of various non-crystalline materials to composition, temperature, and pressure¹¹–¹⁵. Nevertheless, the relationship between structure and dynamics in glass and glass-forming melts under high pressures remains a challenging problem in condensed matter science. The difficulties in addressing this problem are due to both experimental limitations at high pressures and the inadequacy of computer simulations under such conditions. It is crucial to determine the link between the microscopic structure and macroscopic properties of glasses under high pressure from both scientific and technological perspectives, since the glass structures frozen-in under elevated pressure may give rise to properties unattainable under ambient pressure. Borate glass is the quintessential example of glass capable of dramatic changes in short-range order as a function of composition, pressure, and thermal history, and hence we select a simple ternary borate system, namely, sodium-calcium-borate glass, for this study in order to address the above mentioned challenging problem. Boric oxide (B₂O₃) is also widely used as a network forming constituent in many high-tech glass materials owing to its contribution to high glass forming ability and low melting temperature, and for its favorable impact on thermal, mechanical, and optical properties.

One of the most striking structural features of borate glasses is the transformation of the coordination number (CN) of boron from three to four upon compression¹⁶–¹⁹, which is associated with anomalous pressure dependence of viscosity⁶,¹⁶ and topological disorder⁴,¹². Densification of borate glasses can be achieved by applying isostatic pressure to glass directly at room temperature¹⁶,¹⁷, or by pressure-quenching from the molten state¹⁶,²¹. However, the elastic part of the densification relaxes during pressure release, i.e., the density of a compressed glass at ambient pressure decreases to the value before compression upon reheating below the glass transition temperature (Tg).¹⁷ For vitreous B₂O₃, it has been shown that the fraction of boroxol rings decreases with increasing pressure¹⁶,²⁵, leading to densification of the glass¹⁶ and increase of elastic moduli²⁰. When the pressure applied at room temperature is released, such densification is irreversible since the local structures may be topologically/ stereochemically unfavorable for the reformation of boroxol rings¹⁶. However, it is not clear whether this irreversibility of densification is linked to the CN change of boron²⁵. More recently, it has been found that the BO₃
fraction suddenly drops at pressures just above 4 GPa and then approaches zero as the pressure is further increased. A structural response of vitreous \( \text{B}_2\text{O}_3 \) to pressure below 4 GPa was not detected. After decompression from high pressure the boron coordination reverts back from tetrahedral to trigonal, however, the densification is apparently permanent. It has been attempted to correlate these changes in microscopic structure with the macroscopic properties. For example, the viscosity of the \( \text{B}_2\text{O}_3 \) liquid along the melting curve has been shown to decrease by 4 orders of magnitude upon a pressure increase up to 5.5 GPa but then remains unchanged upon further increase of the pressure. However, a generally accepted viewpoint about the microscopic origin of the pressure-induced changes in the macroscopic properties is still lacking.

The abovementioned studies were carried out on vitreous \( \text{B}_2\text{O}_3 \) at room temperature and rather high pressure up to 22.5 GPa. It should be noted that the structure of glasses compressed at room temperature (in diamond anvil cell) is different from that obtained by pressure-quenching liquids from above \( T_g \), even though the main structural changes upon compression (i.e., decreased fraction of boroxol rings and increased fraction of tetrahedral boron) are identical. It should also be noted that modified borate and pure \( \text{B}_2\text{O}_3 \) glasses have different initial concentration of boroxol rings and may exhibit different densification mechanisms. However, Lee et al. have shown that the pressure dependent structural changes of a lithium borate glass are similar to those of vitreous \( \text{B}_2\text{O}_3 \). In particular, they showed that the pressure-induced CN change in \( \text{Li}_3\text{B}_4\text{O}_7 \) glass from three-coordinated to four-coordinated boron at room temperature begins around 5 GPa and the \( \text{BO}_3 \) fraction increases with pressure from about 50% at 1 atm to more than 95% at 30 GPa.

In this work we investigate the microscopic and macroscopic responses of the soda-lime borate glass to comparatively low pressure at an elevated temperature around the \( T_g \). Since numerous high pressure studies at room temperature have already been reported in literature and it is also our aim to detect the sensitivity of glass structure and properties to the low pressure. Moreover, these conditions are chosen to be able to prepare compressed samples, which are large enough to allow for subsequent characterization of macroscopic properties. The as-produced glass has a nonzero equilibrium concentration of \( \text{BO}_3 \) due to the presence of network modifiers (\( \text{Na}_2\text{O} \) and \( \text{CaO} \)) that act to charge balance the tetrahedral boron species. Only recently has it been found that boron speciation (i.e. the ambient \( T_g \) annealed under ambient pressure at 688 K, i.e., 0.9 times its macroscopic properties is still lacking.

The structural changes upon compression are also reversible upon annealing at room temperature. This is also evident from the relaxation of refractive index manifested as an enhancement of the overshoot during the first DSC upscan. This is also evident from the relaxation of refractive index manifested as an enhancement of the overshoot during the first DSC upscan. This is also evident from the relaxation of refractive index manifested as an enhancement of the overshoot during the first DSC upscan. This is also evident from the relaxation of refractive index manifested as an enhancement of the overshoot during the first DSC upscan. This is also evident from the relaxation of refractive index manifested as an enhancement of the overshoot during the first DSC upscan. This is also evident from the relaxation of refractive index manifested as an enhancement of the overshoot during the first DSC upscan. This is also evident from the relaxation of refractive index manifested as an enhancement of the overshoot during the first DSC upscan.

With increasing isostatic pressure, the overshoot in the isobaric heat capacity (\( C_p \)) above \( T_g \) increases as illustrated in Fig. 2a, where the evolution of \( C_p \) with temperature during the first DSC upscan is shown. This overshoot is considered to be a direct consequence of the nonexponentiality of the relaxation process, i.e., due to broadening of the relaxation time distribution. This also implies that subjecting the glass to high pressure forces the glass into a lower region of the enthalpy landscape compared to the glass under ambient pressure, even though it should be noted that the enthalpy landscape itself is changing as a function of pressure. In agreement with previous studies, we find that an increase in isostatic pressure enhances the nonexponentiality of the enthalpy relaxation as measured \textit{ex situ}. With increasing pressure on the glass, the density of the glass increases, and at the same time the topological degree of atomic freedom decreases as well due to the \( \text{BO}_3 \rightarrow \text{BO}_4 \) conversion, i.e., the increase of network connectivity. Upon heating through the glass transition region, the glass compressed at higher pressures should exhibit a larger jump in configurational entropy in order to approach the liquid state. This is also shown in Fig. 2b, in which the pressure dependence of the fictive temperature (\( T_f \)) is plotted. The procedure for determining \( T_f \) based on DSC data is described elsewhere.

The compressed glass relaxes in the glass transition region during the first upscan and recovers back to its original state with respect to enthalpy, i.e., that of the uncompressed glass. In other words, the enthalpy level of the glass reaches that of the glass cooled under standard conditions, e.g., at 10 K/min and ambient pressure. This is seen from the second DSC upscans as shown in the inset of Fig. 2a and in Supplementary Figure S1. Enthalpy recovery of the compressed glass during the DSC upscan is a “structural depression” process, induced by thermal excitation under ambient pressure. The structural depression leads to an increase in enthalpy, which is manifested as an enhancement of the overshoot during the first DSC upscan. This is also evident from the relaxation of refractive index before and after the first DSC upscan (Fig. 3). With increasing isostatic pressure, the refractive index at 633 nm increases due to densification, but the measured value on the sample following the first

**Results**

**Physical properties and heat capacity.** The glass composition under study is 25Na_2O – 10CaO – 65B_2O_3 (mol%). As reported previously, the density and Vickers hardness of this glass increase approximately linearly with increasing isostatic pressure (inset of Fig. 1). The glass isostastically compressed at 570 MPa is then annealed under ambient pressure at 688 K, i.e., 0.9 times its ambient \( T_g \) for various durations (\( t_a \)). This results in a decrease of both density and Vickers hardness with increasing annealing duration (Fig. 1). In other words, these macroscopic properties of the compressed glass are relaxing during annealing towards those of the glass prior to compression. While Vickers hardness has essentially decreased to its original value prior to compression (5.0 GPa) after annealing for 6 h, density has only decreased to \(~2.47 \text{ g/cm}^3\) after annealing for 24 h, which is significantly higher than the value prior to compression (2.438 g/cm^3), i.e., density has relaxed by only 43% of the total possible relaxation.

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![Figure 1](Image)

**Figure 1 | Relaxation of macroscopic properties.** Evolution of density (\( \rho \)) and Vickers hardness (\( H_v \)) with annealing duration (\( t_a \)) at 0.9 \( T_g \) = 688 K of the borate glass compressed at 570 MPa. The dashed lines indicate the values of \( \rho \) and \( H_v \) prior to compression. Inset: impact of isostatic pressure (\( p \)) on \( \rho \) and \( H_v \). The errors of \( \rho \) and \( H_v \) are around \pm 0.005 g/cm^3 and \pm 0.2 GPa, respectively.
Structural response. $^{11}$B magic-angle spinning (MAS) NMR spectra obtained at 16.4 T (700 MHz) for the 0.57 GPa compressed glass annealed for different durations are shown in Fig. 4a. These spectra are characterised by a broad peak centered at +15 ppm, corresponding to $^{11}$BIII sites, and a relatively narrow peak centered around +2 ppm, corresponding to $^{11}$BIV sites. The spectra vary slightly with annealing time, which reflects minor changes in either the relative proportions of $^{11}$BIII and $^{11}$BIV, or changes in bond angles and distances involving boron and oxygen. We quantify these differences by accurate simulation of the spectral lineshapes and subsequent determination of the fraction of tetrahedral to total boron ($N_t$) through integration. The simulation parameters are given in Supplementary Table S1, and two examples of the deconvolution through integration. The simulation parameters are given in Supplementary Table S1, and two examples of the deconvolution through integration.

DSC upscan is independent of the initially applied pressure during compression.

Discussion

Our work has shown that upon annealing at $0.9T_g$ of a soda lime borate glass compressed up to ~0.6 GPa, the pressure-induced change in CN remains unchanged while the pressurised values of macroscopic properties such as density, refractive index, and hardness are relaxing. This suggests that the pressure-induced changes in macroscopic properties of such glasses are not attributed to changes in the short-range order, in agreement with previous studies at relatively low pressure$^{25}$. In sodium boroaluminosilicate glasses it has been shown that while pressure-induced density changes are related to changes in boron coordination, the relatively small difference in partial molar volume of the $BO_3$ and $BO_4$ structural units cannot account for the dominant part of the density change$^{25}$. Instead it was suggested that the shortening of the Na–O bond upon compression is a more likely factor governing the density change$^{25,54}$. Such changes were observed at considerably higher pressures than the current study and thus may not in fact account for the findings reported.
isostatic pressure on integration of peaks in Fig. 4a, with annealing duration. Inset: impact of variable pressure series (inset) and annealed for various durations at 0.9N. NMR spectra at 16.4 T of the samples compressed at 570 MPa and then annealed for various durations (see Fig. 2a). Once the compressed glass is subjected to annealing around $T_g$, the "tightened state" of glass will relax, leading to the decrease of density and hardness. However, the thermal energy at 0.9$T_g$ could be insufficient for breaking the B-O bonds in favor of formation of BO$_3$ units, despite the fact that structural relaxation generally occurs even at temperatures below 0.9$T_g$. It should be noted that changes in boron speciation due to annealing at 0.92$T_g$ have previously been reported for non-compressed borosilicate glasses" and the thermomechanically trapped state of the glass studied herein thus appears to be different from that of the thermally trapped glass.

It is known that the $\alpha$ relaxation is decoupled from the $\beta$ and $\gamma$ relaxations below $T_g$. Generally, for network glass systems, the $\alpha$ relaxation is dominated by the change of the network connectivity (e.g., the boron speciation), and the $\beta$ relaxation is controlled by the local motion of structural units (e.g., the change of bond angles). In this context, it is understandable that the density relaxes upon annealing slightly below $T_g$, whereas the CN remains unchanged since the former is of the $\beta$ relaxation feature requiring low temperature and the latter is of the $\alpha$ relaxation feature demanding the temperature to exceed $T_g$. According to literature the $\beta_{III}$-to-$\beta_{IV}$ ratio increases with increasing temperature above $T_g$. It is expected that the thermomechanically induced $\beta_{IV}$ units would be converted to $\beta_{III}$ units when the temperature is well above $T_g$. In contrast to the density decay, the hardness is fully recovered by annealing at 0.9$T_g$ to the original value more quickly, as shown in Fig. 1. This could be related to the dominant contribution of the $\gamma$ relaxation process, or to contributions of hydrated structure relaxations of a near surface volume (OH-groups and molecular water) to the relaxation of hardness. The latter has been found recently to proceed more rapidly than both $\alpha$ and $\beta$ relaxations. This implies that the hardness relaxation be governed by the fast local network relaxation of the surface layer.

The irreversibility of the thermomechanically induced change in boron speciation upon annealing at 0.9$T_g$ implies that the free energy barrier for forming a given structural state (i.e., boron speciation) can be overcome not only chemically, but also thermomechanically. This allows for tailoring of both microscopic and macroscopic properties, since the increased network connectivity that remains after annealing should increase, e.g., chemical durability and thermal shock resistance. To further understand this effect, we consider the

Figure 4 | Structural response to annealing. (a) Solid state $^{11}$B MAS NMR spectra at 16.4 T of the samples compressed at 570 MPa (solid line) and then annealed for various durations ($t_a$) at 0.9$T_g$ = 688 K. (b) Evolution of fraction of tetrahedral to total boron ($N_4$), which is obtained through integration of peaks in Fig. 4a, with annealing duration. Inset: impact of isostatic pressure on $N_4$ in absence of annealing (corresponding $^{11}$B spectra are shown in Supplementary Figure 2a). The error of $N_4$ is ±0.5 at% for the variable pressure series (inset) and ±1 at% for the variable annealing time study. The latter has higher error due to changes in lineshape and thus more difficulty in fitting the $^{11}$B MAS NMR data. (c) Solid state $^{23}$Na MAS NMR spectra at 16.4 T of the samples compressed at 570 MPa and then annealed for various durations at 0.9$T_g$ = 688 K.
enough thermal energy available for the system to sample the phase space. However, since there is no decrease of $N_t$ during annealing, the boron coordination number from decreasing. Another possibility is the lack of a thermodynamic driving force for the coordination change. According to the random pair model of Gupta, the equilibrium $N_t$ value of the studied composition is 49.2 at%\(^{42,43}\). Hence, the $N_t$ of the compressed glass is closer to the ambient equilibrium value than that of the as-prepared glass (see inset of Fig. 4b), i.e., there is no thermodynamic driving force to convert B\(^{IV}\) into B\(^{III}\) units.

**Methods**

**Sample preparation.** Glass with composition (in mol%) of 25Na\(_2\)O – 10CaO – 65B\(_2\)O\(_3\) was prepared using melt-quenching technique in an inductively heated crucible and to reach a mass comparable to that of the sapphire standard (40.76 mg). The formation of sp(3) bonding in compressed BN. *Phys. Rev. Lett.* 115, 014202 (2015).


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**Author contributions**
Y.Z.Y. conceived the study. M.M.S., R.E.Y., S.S., M.P. and U.B. prepared the samples, performed the measurements, and contributed to analysis of the data. M.M.S. and Y.Z.Y. wrote the manuscript with inputs from R.E.Y., J.D., H.B. and J.C.M. All authors were involved in the discussions.

**Additional information**
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

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