Structural heterogeneity and pressure-relaxation in compressed borosilicate glasses by in situ small angle X-ray scattering

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Structural heterogeneity and pressure-relaxation in compressed borosilicate glasses by in situ small angle X-ray scattering


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We report on Brillouin and in situ small angle X-ray scattering (SAXS) analyses of topological heterogeneity in compressed sodium borosilicate glasses. SAXS intensity extrapolated to very low angular regimes, $I(q = 0)$, is related to compressibility. From Brillouin scattering and analyses of the elastic properties of the glass, the Landau-Placzek ratio is determined and taken as a direct reflection of the amplitude of frozen-in density fluctuations. It is demonstrated that with increasing fictive pressure, topological (mid- and long-range) homogeneity of the glass increases significantly. Heating and cooling as well as isothermal scans were performed to follow the evolution of density fluctuations upon pressure recovery. For a sample with a fictive pressure $p_f$ of 470 MPa, complete recovery to $p_f = 0.1$ MPa was observed to occur close to the glass transition temperature. The values of fictive and apparent fictive temperature, respectively, as obtained via the intersection method from plots of $I(q = 0)$ vs. temperature were found in good agreement with previous calorimetric analyses. Isothermal scans suggest that mid- and long-range recovery govern macroscopic density relaxation.

I. INTRODUCTION

A complete description of the glass transition requires consideration of both the time-temperature ($t,T$) and temperature-pressure ($t,p$) planes.1 A glass which is obtained from a super-cooled liquid by varying $p$ and/or $T$ may then be described according to its fictive pressure $p_f$ (Ref. 1) and fictive temperature $T_f$. $P_f$ and $T_f$ represent the configurational state, which was imposed on the glass during freezing. Their values stand for the last point on the real $p,T$-plane at which, for a given observation time, the system was in a fully relaxed (equilibrium) state. Together, they describe the “distance from equilibrium”4 of the considered glass and, hence, its potential energy at real $p$ and $T$. In a pragmatic consideration, they can be used to assess the system’s thermomechanical history and resulting physical properties (e.g., molar volume, homogeneity, network topology, and coordination), respectively, which were generated during freezing. Depending on the observation time, endothermal relaxation, and exothermal recovery, respectively, occur towards real $T$ and $p$. Thereby, $p_f$ and $T_f$ appear to relax simultaneously. The relaxation timescale appears to equal the timescale of shear relaxation12 and, thus, is primarily governed by viscosity $\eta$. Since viscosity depends on network topology, it must be considered as a non-equilibrium property, too.13 While on the $t$, $T$-plane, viscosity always relaxes antiparallel to $T_t$, the problem is more complex on the $t$, $p$-plane, where $d\eta/dp$ can be either positive or negative.14, 15 Depending on the examined glass, non-equilibrium viscosity (pertinent to the frozen-in structural configuration) can be observed either at $p < p_f$ or at $p > p_f$.12, 16 The thermodynamic implications are not restricted to the entropy term but will also affect the compressibility. Hence, also the compressibility comprises a configurational part. The state which is frozen-in during the glass transition can then be observed by enthalpy measurements as well as by compressibility measurements to assess residual and dynamic density and concentration fluctuations. In the present work, to investigate the compressibility variation with fictive pressure for a representative sodium borosilicate glass, we are employing two experimental methods: Synchrotron small angle X-ray scattering (SAXS) and evaluation of the Landau-Placzek ratio (LPR). SAXS intensity extrapolated to very low angular regimes ($q = 0$) is directly related to compressibility.17, 18 LPR, the ratio between Rayleigh scattering, originating from elastic fluctuations and Brillouin scattering, based on acoustic interactions, reflects directly the amplitude of frozen-in density fluctuations.19 Beyond previous calorimetric and structural analyses of pressure effects on short-range order, this approach will enable to assess and correlate heterogeneity as a function of $p_f$ and $T_f$ on the mid- to long-range scale.
II. EXPERIMENTAL

A. Sample preparation and compression experiments

Conventionally melted glasses of composition 16 Na2O-10 B2O3-74 SiO2 (mol %, denoted NBS) were provided by S. Reinsch of the Federal Institute of Materials Testing, BAM, Berlin, Germany. Samples from the identical melting campaign have been used by us in previous studies.5,6,9,10,12 Further details on synthesis and basic properties (including water content and homogeneity) are provided in the mentioned publications. In analogy to the procedures described in Refs. 5, 10, 12, glasses with frozen-in pressure of 0.1 MPa, 250, MPa and 470 MPa were produced using a cold seal pressure vessel. For that, individual samples (~4×4×40 mm3) were exposed to the target pressure for 10 min at a temperature of 10 K above the glass transition temperature \( T_g \), using Argon gas as compression medium. Subsequently, they were cooled under pressure by switching-off the furnace (corresponding to a cooling rate of \( \sim 3.6 \) to \( 4.6 \pm 0.2 \) K/min12), hence freezing-in the compressed state. Following compression, samples were cut with a diamond wire saw to \( 4\times4\times0.5 \) mm2 and polished (SiC, isopropanol) on both sides for SAXS. For Brillouin scattering experiments, sample bars of \( \sim 4\times4\times30 \) mm2 were cut from the remaining glass bars and polished (SiC, diamond, water) on all faces.

B. Small angle x-ray scattering

Synchrotron SAXS measurements were performed on the BM02 beamline of the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Two different experimental set-ups were employed: For measurements at ambient temperature, a sample-detector distance of 237 mm was used, yielding the observed reciprocal angular scattering interval of 0.06 Å\(^{-1} \) < \( q < 2.15 \) Å\(^{-1} \), where \( q = \frac{4\pi}{\lambda} \sin(\theta)/2 \) is the modulus of the scattering vector and \( \theta \) half of the scattering angle. A high-temperature molybdenum furnace provided by BM02 was used for in situ measurements in the interval of 0.07 Å\(^{-1} \) < \( q < 1.10 \) Å\(^{-1} \) with a sample-detector distance of 345 mm. For all samples, an incident energy of 19.8 keV was used, what lies far from the K-absorption edge of Mo. Data were collected with a charge coupled device camera. Accumulation times were 100 s for ambient-temperature measurements and 20 s for temperature scanning experiments. Heating and cooling rates were 3 K min\(^{-1} \) in order to approximately match the rates under which the original samples were produced and 50 K min\(^{-1} \) for isothermal experiments, respectively. Radial integration, background subtraction, and corrections for cosmic rays have been performed on the data. For \( q \)-space calibration octadecanol20 and silver behenate21 spectra were collected. Changes in thickness and orientation of the sample, variation in incident flux and normalization to the absorption of the sample were considered using scintillation counters to monitor the x-ray intensity in the front and behind the sample. In addition, the SAXS background signal, which originated mainly from the employed Kapton windows and air scattering was recorded systematically.

C. Brillouin scattering

Brillouin scattering experiments were carried out to further correlate SAXS experiments and structural heterogeneity and to determine the Landau-Placzek ratio for this specific case. A triple-pass tandem Fabry–Perot interferometer (Sandercock) was used as a spectrometer in the Brillouin scattering system. A frequency doubled Nd:YAG laser at \( \lambda = 532 \) nm was employed as light source. The average incident light power was 100 mW. Brillouin scattering spectra were recorded with 512 channels and accumulated 300 times. Spectra were taken in 180° back scattering and 90° right angle scattering geometry as well as for 90R scattering geometry. The Brillouin shift \( \nu \) was calculated from

\[
\nu = \frac{2nc \sin \theta}{\lambda},
\]

where \( n \) is the refractive index at wavelength \( \lambda \) of the incident light, \( \theta \) is the angle between the wavevectors \( \mathbf{k}_0 \) and \( \mathbf{k} \), and \( c \) is the velocity of sound in the material. For the employed geometries, this reduces to

\[
v_{180} = \frac{2nc}{\lambda} \tag{2}
\]

for a scattering angle of 180°,

\[
v_{90} = \frac{\sqrt{2}cn}{\lambda} \tag{3}
\]

for a scattering angle of 90°, and

\[
v_{90R} = \frac{c\sqrt{4n^2 - 2}}{\lambda} \tag{4}
\]

for 90R geometry. To calculate the velocity of sound, the refractive index for \( \lambda = 543.5 \) nm was measured using the m-line technique. Values are given in Table I.

The Landau-Placzek \( R_{LP} \) ratio was determined by dividing the integrated intensity of the Rayleigh contribution \( I_C \) of the scattering spectra with the integrated intensity of the Brillouin doublet \( I_B \),

\[
R_{LP} = \frac{I_C}{2I_B}. \tag{5}
\]

During the measurements, great care was taken to avoid the occurrence of uncontrolled reflexions, which could increase the apparent Rayleigh intensity. Ten individual measurements were carried out and only the smallest value was kept. Obtained data are given in Table I. Calculation of the elastic properties was done via the following equations:

Shear modulus \( G \):

\[
G = \rho \cdot c_t^2 \tag{6}
\]

Bulk modulus \( K_S \):

\[
K_S = \rho \cdot c_l^2 - \frac{4}{3}G \tag{7}
\]

Youngs modulus \( E \):

\[
E = \frac{c_l^2}{c_l^2 - c_t^2} \tag{8}
\]

References:

1. ...
TABLE I. Measured and calculated elastic properties.

<table>
<thead>
<tr>
<th>p₁ (MPa)</th>
<th>n</th>
<th>ρ (g/cm³)</th>
<th>c (km/s)</th>
<th>p_f (MPa)</th>
<th>n</th>
<th>ρ (g/cm³)</th>
<th>c (km/s)</th>
<th>M (GPa)</th>
<th>G (GPa)</th>
<th>K (GPa)</th>
<th>S (GPa)</th>
<th>E (GPa)</th>
<th>R_LF</th>
<th>σ</th>
<th>I_q = 0.1</th>
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<td>46.2</td>
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<td>0.204</td>
<td>82</td>
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<td>1.5229</td>
<td>2.548</td>
<td>6.13</td>
<td>3.74</td>
<td>95.8</td>
<td>35.6</td>
<td>48.3</td>
<td>85.8</td>
<td>39</td>
<td>0.204</td>
<td>63</td>
<td></td>
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</tr>
</tbody>
</table>

Poisson Ratio σ:

\[ \sigma = \frac{c_l^2 - 2c_t^2}{2(c_l^2 - c_t^2)} \]  

High frequency longitudinal modulus M:

\[ M = \rho \cdot c_l^2 \]  

The density ρ was determined separately using helium pycnometry. Values are given in Table I.

III. RESULTS AND DISCUSSION

A. Ambient temperature experiments and structural heterogeneity of compressed NBS glasses

The short-range structure of alkali borosilicate glasses and, specifically NBS is relatively well-studied. It is known that boron may be present in two coordination states, i.e., trigonal [BO₃] groups and tetrahedral [BO₄] groups. Partitioning into these states depends strongly on composition, thermal history, and pressure. From combined ¹¹B, ²³Na, ²⁷Al, and ²⁹Si NMR spectroscopy, calorimetry and molar volume analyses of compressed and stretched samples, we have recently concluded that following compression, the change in Boron coordination number and, hence, short-range structure does not suffice to explain the resulting difference in density. Rather, it was noted that mid- and long-range order (LRO) variation, which could not be assessed by NMR must be considered.

SAXS patterns of NBS for three different degrees of compression are shown in Fig. 1. As already noted, we assume that the pressure under which the glasses were produced corresponds to the fictive pressure p_f of this respective sample. Then, the degree of compression is about 0.0 %, 1.0 %, and 2.2 %, respectively, for p_f of 0.1, 250, and 470 MPa. SAXS patterns show the first sharp diffraction peak (FSDP) at \( \sim q = 1.8 \) Å⁻¹, and a flat signal at lower q. With increasing pressure, the maximum of the FSDP is shifted to higher q-values (inset of Fig. 1). Position and shape of the FSDP are related to mid- and short-range order (MRO/SRO). Therefore, the shift in FSDP caused by increasing p_f is related to changes in MRO and SRO. A clearer view at this can be obtained by considering the reduced radial distribution function G(r) (Fig. 2). G(r) was formally calculated from SAXS data using the RAD software package. In a first consideration, the obtained functions of G(r) clearly reflect a decrease in short-range spacing.

In contrast to the FSDP, the flat signal in the low q-region is related to the amplitude of density fluctuations, which reflect LRO (note that in the explored domain of T_f we assume that concentration fluctuations may be neglected). Considering the low-q region of Fig. 1, a gradual decrease occurs in intensity with increasing fictive pressure. Hence, the amplitude of density fluctuations decreases and the glass becomes more homogeneous with increasing p_f (viz., values of I(q = 0.1), Table I). This observation is consistent with our previous assessment of the excess vibrational density of states.

Density fluctuations in liquids are generally related to the instantaneous isothermal compressibility χ¹ due to...
thermodynamic predictions,
\[
I(q = 0) \propto T \cdot \chi_T^0(T).
\]
(11)

It is noteworthy that, in an equilibrated system, \( I(q = 0) \) should be zero at 0 K, which is not the case for glasses where density fluctuations are frozen-in when the liquid passes the glass transition. To take account of these residual density fluctuations, Eq. (11) transforms to\(^\text{17}\)
\[
I(q = 0) \propto T_1 \left[ \chi_T^0(T_1) - \chi_S^0(T_1) \right] + T_1 \left[ \chi_S^0(T_1) - M_\infty^{-1}(T_1) \right] + T M_\infty^{-1}(T). \tag{12}
\]
Here, \( T_1 \) is the fictive temperature, \( \chi_T^0 \) and \( \chi_S^0 \) are the isothermal and adiabatic compressibilities, respectively, and \( M_\infty \) is the high frequency longitudinal modulus. This expression comprises three different terms. The last one is a function of temperature and related to phononic vibrations, whereas the first two are related to entropic fluctuations and local variations in structure, respectively. When light is interacting with density fluctuations in materials, the vibrational term will contribute to Brillouin scattering, whereas the entropic and local variation in structure will contribute to Rayleigh scattering. Therefore, the Landau-Placzek ratio defined as the ratio between Rayleigh and Brillouin scattering can be described by
\[
R_{LP} (298 \, \text{K}) = M (298 \, \text{K}) \left[ \chi_{298}^0 (T_1) - M_\infty^{-1} (T_1) \right] \frac{T_1}{298 \, \text{K}}.
\tag{13}
\]

This expression is the ratio of the first two terms of Eq. (12) over the third term. The investigated compressed NBS glasses exhibit a decrease in LPR with increasing \( p_f \) (Table I). This reflects an increase in homogeneity due to pressure-treatment. Even for an increase of the vibrational contribution (increase in \( M_\infty \) by 9.5%), the frozen-in terms of the density fluctuations are strongly decreasing with compression, resulting in an overall decrease of 17% in LPR. As a result, we estimate the total decrease in frozen-in density fluctuations to about 27% when comparing the uncompressed glass and the glass with \( p_f \) of 470 MPa. We relate this large decrease to the evolution of the isothermal compressibility.

All elastic constants were observed to increase with increasing degree of compression (increasing densification). The Poisson ratio remains practically unaffected by compression, at least in the considered pressure regime. This indicates equivalent evolution of shear and bulk elastic properties and also that compression did not affect mechanical domains in the sample (at least within the considered pressure regime). The value of the Poisson ratio is relatively low, which implies that the densification process is not finished and further densification could be achieved by applying higher pressure.

**B. In situ SAXS and relaxation phenomena**

As mentioned above, the amplitude of density fluctuations is related to the intensity of the small angle scattering curve in the low \( q \)-region.\(^{27,28}\) This can be approximated via\(^\text{17–19}\)
\[
I(q) = I(q = 0) e^{bq^2}, \tag{14}
\]
where \( b \) is a coefficient depending on temperature.

Equation (14) provides the opportunity to extrapolate \( I(q = 0) \) from a linear regression of \( \ln(I) \) as a function of \( q^2 \) as shown in Fig. 3 (note that for the linear fit, only a rather small \( q \)-range was used to exclude the influence of Kapton and other background scattering at low \( q \) and overlap with the FSDP at high \( q \)). Resulting extrapolated values of \( I(q = 0) \) are plotted as a function of temperature in Fig. 4(a). Figure 4(a), therefore presents the variation of the amplitude of density fluctuations during heating and subsequent cooling of NBS with \( p_f \) of 0.1 and 470 MPa, respectively. For the uncompressed glass (\( p_f = 0.1 \) MPa), the intensity of the scattering curve at \( q = 0 \) slightly increases with temperature until it reaches the region of glass transition. Above \( T_\gamma \), that is, in the liquid state, the slope of \( I(q = 0) \) vs. \( T \) increases notably, reflecting increasing dynamic heterogeneity in the liquid state. Cooling scans where recorded in order to confirm this observation: within the experimental accuracy, they overlap fully with heating scans; heterogeneity follows the same path upon heating and cooling. It is noteworthy that, since the SAXS measurement was performed at approximately the same heating/cooling rates as were applied during original sample synthesis, collected data are free of additional thermal relaxation effects. \( T_\gamma \) may be approximated from the intersection of two tangents applied on the low and high temperature regimes, resulting in a value of 561 °C for the uncompressed sample. This value is in good agreement with a previous calorimetric study.\(^{10}\) For the sample with higher \( p_f \) (470 MPa), in accordance with \textit{ex situ} analyses, lower \( I(q = 0) \) is generally observed at \( T < T_\gamma \) (reflecting higher topological homogeneity of the sample). Upon heating, \( I(q = 0) \) increases with a slope similar to the uncompressed sample until the region of glass transition is reached. Subsequently, \( I(q = 0) \) sharply increases until at high temperature, the value of the uncompressed glass is attained. Upon subsequent cooling, the sample follows the path of the uncompressed glass. The sharp increase in the proximity of \( T_\gamma \) is a clear reflection of structural recovery of long-range order as a result of...
recovers \( p_f \) to ambient pressure and expansion of the network. The intersection of the tangents for the low and high temperature regime yields a temperature of 539 °C (470 MPa). In accordance with previous arguments, this temperature is denoted apparent fictive temperature \( T_{\text{fA}} \), since it comprises contributions of both pressure and temperature relaxation.\(^\text{12,29}\) Again, the obtained value is in good agreement with previous calorimetric analyses \((T_f \sim 570 \degree C)\) for uncompressed NBS and \( \sim 548 \degree C \) for NBS after compression at 500 MPa and cooling at \( \sim 4.5 \text{ K/min} \).\(^\text{10}\)

According to Eqs. (11) and (12), outside the relaxation regime between about 470 and 590 °C, the slope of \( I(q = 0) \) over \( T \) is governed by \( M_{\infty}^{-1}(T_f) \) and \( \chi^g(T) \) in glass and liquid, respectively. It is, therefore, noted that in the present experiment, no significant modification of \( M_{\infty}^{-1}(T_f) \) could be found for variations of \( p_f \). This is in good agreement with the already discussed analyses of elastic properties. On the contrary, for the transition from glass to supercooled liquid, the slope of \( I(q = 0) \) over \( T \) increase by about one order of magnitude, which confirms the previous Brillouin scattering analyses. From the LPR, it was concluded that the biggest part of the decrease in density fluctuation with increasing \( p_f \) is related to the decrease in isothermal compressibility at \( T_{\text{fA}} \).

Time–temperature transformation kinetics of compressed NBS glass have been studied on the basis of macroscopic density relaxation during isothermal heat treatment.\(^\text{12}\) Accordingly, isothermal in situ SAXS experiments were conducted here on the sample with \( p_f = 470 \text{ MPa} \) at 515 °C, 530 °C and 540 °C (Fig. 4(b)). In comparison to in situ heating experiments, pressure recovery results in a gradual increase in scattering intensity \( I(q = 0) \). As expected, relaxation occurs faster at higher temperature. While the data appear to confirm previous macroscopically obtained relaxation kinetics, a complete evaluation is presently not possible because of experimental reasons, the observation time could not be extended so far as to obtain complete recovery at the lower treatment temperatures. Tentatively, we conclude here that LRO recovery governs macroscopic density recovery.

**IV. SUMMARY**

Within this study, high \( p_f \) sodium borosilicate glasses were investigated by Synchrotron SAXS and Brillouin scattering experiments to assess their structural and topological homogeneity. From Brillouin scattering and analyses of the elastic properties of the glass, the Landau-Placzek ratio was determined and taken as a direct reflection of the amplitude of frozen-in density fluctuations. SAXS patterns were collected in situ during heating and cooling as well as under isothermal conditions to follow the evolution of density fluctuations with pressure recovery. For a sample with \( p_f = 470 \text{ MPa} \), complete recovery to \( p_f = 0.1 \text{ MPa} \) was observed to occur close to the glass transition temperature. The values of fictive and apparent fictive temperature, respectively, as obtained via the intersection method from plots of \( I(q = 0) \) vs. temperature, were found in good agreement with previous calorimetric analyses. Isothermal scans suggest that mid- and long-range recovery govern macroscopic density relaxation. It was demonstrated that with increasing fictive pressure, mid-, and long-range homogeneity of the glass increases significantly.

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