Structure, Structural Relaxation and Ion Diffusion in Sodium Disilicate Melts

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We have investigated Na$_2$Si$_2$O$_5$ melts with inelastic neutron scattering at temperatures up to 1600 K. The Si-O network relaxes on a time scale of ns, whereas the Na ion relaxation dynamics are found on a time scale of 10 ps. The elastic structure factor exhibits at $\simeq 0.9$ Å$^{-1}$ an emerging prepeak which becomes more pronounced with increasing temperature. The prepeak is caused by the formation of sodium rich regions in the partially disrupted Si-O tetrahedral network.

Silicate melts have great relevance both in earth science and technology: The physical properties of magma (molten silicate rock) dominate many geological processes and technological glasses are synthesized from the molten state. These silicate melts, natural and technological, are multicomponent systems. A considerable effort has been made to investigate a wide range of silicate melts with the general aim of linking structural with physical properties and to develop an atomic level understanding of their structure and dynamics. Nevertheless, experiments on the structure and microscopic dynamics in the viscous melt well above the conventional glass transition temperature $T_g$ are rare. Here, we present inelastic neutron scattering results on sodium disilicate melts and show that at temperatures well above $T_g$ significant changes in the elastic structure factor occur that are caused by sodium rich regions in the partially disrupted Si-O tetrahedral network. The existence of sodium rich regions has a strong influence on the sodium ion transport and may very well be the cause for the weak temperature dependence of the viscosity at higher temperatures. Our results on structure and dynamics can be rationalized using results of recent molecular dynamics simulations.

Alkali silicates are a simplified analog for most magmas and technological glasses. Compared with pure silica, with a caloric glass transition temperature $T_g$ at $\simeq 1500$ K, the addition of Na$_2$O partially disrupts the Si-O$_2$ network structure resulting in a halving of the $T_g$ at sodium disilicate. In addition, sodium disilicate has been the subject of extensive molecular dynamics simulations and thoroughly investigations. Inelastic neutron scattering covers a dynamic range that gives insight not only into dynamics on microscopic time scales but also into the medium range structure of silicate melts. In addition, the results can provide input for simulations used e.g. to model magma properties in volcanic activity and are an experimental test of molecular dynamics simulations.

Sodium disilicate Na$_2$Si$_2$O$_5$ was synthesized from ultrapure Na$_2$CO$_3$ and SiO$_2$ powders. The mixture was melted in a Pt crucible and stirred with a Pt$_{80}$Rh$_{20}$ spindle at superliquidus temperatures until it was homogeneous and bubble free. Differential scanning calorimetry yielded a glass transition temperature at $\simeq 741$ K in agreement with the literature value at $T_g \simeq 737$ K. For the neutron scattering experiment the sample was encapsulated in a Pt sample cell giving an annular sample geometry of 40 mm in height, 22.5 mm in diameter and a 1.25 mm wall thickness.

We performed inelastic neutron scattering measurements on the time-of-flight spectrometer IN6 at the Institut Laue-Langevin in Grenoble. An incident neutron wavelength of $\lambda = 5.1$ Å$^{-1}$ yielded an energy resolution of $\delta E = 93$ µeV (FWHM) and an accessible wave number range of zero energy transfer of $q = 0.3 - 2.0$ Å$^{-1}$. Spectra were measured in the glass at 400 K and in the viscous melt at 800 K and between 1200 K and 1600 K in steps of 100 K. During cooling measurements were repeated at each temperature. No change between spectra obtained during heating and cooling could be detected. Additional high-energy resolution spectra at 300 K, 1300 K, 1400 K, 1500 K, and 1600 K were obtained on the new backscattering spectrometer of the NIST Center for Neutron Research in Gaithersburg having a sub-µeV energy resolution and, in the set-up used, an accessible wave number range of $q = 0.6 - 1.6$ Å$^{-1}$.

The raw data reduction consists of normalization to a vanadium standard, correction for self absorption and container scattering, and interpolation to constant wave numbers $q$ in order to obtain the scattering law $S(q, \omega)$. Further, $S(q, \omega)$ was symmetrized with respect to the energy transfer $\hbar \omega$ by means of the detailed balance factor. Whereas scattering from the Si and O atoms is exclusively coherent, Na scatters coherently and incoherently. The incoherent scattering from Na reflects itself in a flat background in the elastic structure factor $S(q, \omega = 0)$.

Figure 1 displays the elastic structure factor of glassy and viscous sodium disilicate. Toward small $q$ the signal is dominated by incoherent contributions of the sodium...
atoms. The maximum around \( \sim 1.7 \, \text{Å}^{-1} \) reflects the coherent scattering mainly of the disrupted tetrahedral Si-O network. The intensity at \( q \) values larger than \( \sim 1.1 \, \text{Å}^{-1} \) is decreasing with increasing temperature and \( q \) which is well accounted for by the Debye–Waller factor. In contrast, at \( q \sim 0.9 \, \text{Å}^{-1} \) a pronounced prepeak is emerging with increasing temperature. We note that the signal is independent on thermal history indicating a process in thermoequilibrium as a cause for this change.

Our \( S(q, \omega = 0) \) at 400 K and 800 K are consistent with neutron diffraction results on sodium tetrasilicate \( Na_2Si_4O_9 \) where at temperatures up to some 180 K above \( T_g \) spectra display only a little change in the structure factor. \( ^{29}\text{Si} \) nuclear magnetic resonance (NMR) measurements on sodium disilicate \( ^{1}\text{O} \) in the metastable melt up to 876 K report a continuous but small change in the number of O atoms surrounding a Si atom with increasing temperature. At higher temperatures motion of the atoms becomes too fast for conventional NMR techniques. From wide angle X-ray diffraction on various sodium and potassium silicates and sodium disilicate at 295 K and 1273 K in particular, previous workers came to the conclusion that the structure of silicate melts is insensitive to temperature change. However, data quality especially in the \( q \) range below \( \sim 1.2 \, \text{Å}^{-1} \) is rather poor. The molecular dynamics simulations on sodium disilicate melts \( ^{2} \) do indeed exhibit a shoulder in the static structure factor at \( q = 0.94 \, \text{Å}^{-1} \). The molecular dynamics simulations \( ^{2} \) link this prepeak to a characteristic length scale of regions where the network is disrupted and where the sodium concentration is enhanced.

Figure 2 shows high–energy resolution backscattering spectra of sodium disilicate melts at \( q=1.6 \, \text{Å}^{-1} \). A measurement of the glassy sample at 300 K represents the instrumental resolution profile \( R(q, \omega) \). Above 1400 K a small broadening of the signal can be resolved. Around \( q \sim 1.6 \, \text{Å}^{-1} \) the signal is dominated by the scattering of Si and O. Structural relaxation of the partially disrupted tetrahedral Si-O network leads to a quasielastic broadening in the spectra. A common feature of structural relaxation in glass forming liquids is a stretching of correlation functions over a wider time range than expected for exponential relaxation \( ^{12,13} \). The line is a fit with the Fourier transform of the Kohlrausch stretched exponential function convoluted with the instrumental resolution function:

\[
R(q, \omega) \propto \{ A \left( \int dt \, e^{-i\omega t} \exp\left[-(t/\tau)^{\beta}\right] \right) + B \, \delta(\omega) \}. \quad (1)
\]

A best fit of expression (1) with \( B=0 \) gives a relaxation time of 4 ns and a stretching exponent \( \beta = 0.75 \pm 0.1 \). \( B=0 \) demonstrates that the dynamics of all atoms contributing to the quasielastic signal are on the same time scale. Scattering on considerably faster relaxation or vibration (ps time scale) results in a flat background. At 1600 K sodium disilicate has a viscosity of 4.5 Pa s. The relaxation time is consistent with the relaxation time estimated from viscosity showing that the data in Fig. 2 indeed display the network dynamics. A fit with a stretched exponential function to the coherent intermediate scattering function of Si and O correlations at 1.6 Å⁻¹ as obtained by the molecular dynamics simulations \( ^{14} \) gives \( \beta = 0.83 \) in accordance with our result.

At temperatures up to \( \sim 2 \times T_g \) the diffuse dynamics of the alkali atoms in silicate melts is appreciably faster than the structural relaxation \( ^{13} \). Figure 3 displays the scattering law \( S(q, \omega) \) of sodium disilicate as obtained on the neutron time-of-flight spectrometer IN 6. Well below \( q = 0.5 \, \text{Å}^{-1} \) the signal is dominated by the incoherent scattering on sodium. Diffusive motion of sodium causes a broad quasielastic signal. The lines in Fig. 3 are fits with expression (1), where the \( \delta \) function represents the elastic scattering contribution to the signal and \( B \) its amplitude. Best fits have been obtained with a stretching exponent \( \beta \) within \([0.7,0.8]\) in accordance with the MD simulations result of \( \beta = 0.77 \) for the incoherent intermediate Na scattering function \( ^{2,7} \). \( \beta < 1 \) indicates that Na diffusion is not a simple activated process. Resulting relaxation times (Fig. 3) show a small change with temperature with \( \tau \sim 29 \, \text{ps} \) at 1200 K and \( \tau \sim 13 \, \text{ps} \) at 1600 K.

Compared to other multicomponent glass forming liquids investigated so far the changes in the elastic structure factor of sodium disilicate melts are unexpected. Viscous metallic ZrTiNiCuBe melts show a similar temperature dependence of viscosity \( ^{13} \) as sodium disilicate when plotted versus \( T_g/T \) at temperatures well below the liquidus. In addition, diffusive dynamics of various atoms, that are smaller than the large structural Zr atoms, are appreciably faster than structural relaxation and also decoupled from viscous flow \( ^{16} \). Toward higher temperatures the temperature dependence of the viscosities of ZrTiNiCuBe and sodium disilicate deviate \( ^{6} \) which may very well be the result of the sodium rich regions in sodium disilicate: The formation of sodium rich regions leaves regions with a lower sodium concentration and hence with a less disrupted Si-O network leading to a higher viscosity of the entire system.

Besides a non-exponential structural relaxation viscous metallic melts exhibit a fast relaxation process \( ^{7} \) which can be visualized as a rattling of the atoms in the transient cages formed by their neighbors. This – so called – fast \( \beta \) relaxation, that prepares structural relaxation responsible for viscous flow, has been predicted by the mode coupling theory (MCT) of the liquid to glass transition \( ^{12} \) and has been found in many experiments and simulations on a variety of other glass forming systems \( ^{18} \). Molecular dynamics simulations on sodium disilicate show that the predicted factorization property for Si and O correlations holds in the fast \( \beta \) relaxation regime \( ^{7} \). The signal in the fast \( \beta \) relaxation regime, typically around 1 meV, is in sodium disilicate governed by the
incoherent contributions of the diffusing sodium atoms. However, since the sodium disilicate spectra do not show an indication for an additional fast process, its amplitude has to be small compared to the quasielastic line originating from the sodium diffusion. This compares well to results of a neutron scattering experiment on another network forming melt: In liquid GeO$_2$ a fast MCT $\beta$ relaxation process could not be detected up to $T = 2 \times T_g$ [19].

A recent molecular dynamics simulations study on sodium tetrasilicate [20] suggests the existence of sodium rich channels having a distance of about 6-8 Å. The prepeak at 0.9 Å$^{-1}$ corresponds to the distance between these channels. A similar behavior has been found in the MD simulations on sodium disilicate [7]. The microscopic picture given by the molecular dynamics simulations of regions that exhibit a higher sodium concentration is in agreement with our results.

In conclusion, we have investigated structure and dynamics in sodium disilicate melts with inelastic neutron scattering. The viscous melt well above $T_g$ exhibits changes in the elastic structure factor: With increasing temperature a pronounced prepeak emerges at $\simeq 0.9$ Å$^{-1}$ caused by sodium rich regions in the disrupted Si-O network. High resolution quasielastic neutron scattering shows structural relaxation of the partially disrupted Si-O tetrahedral network to be on a nanosecond time scale at 1600 K. The structural relaxation is non-exponential with a stretching exponent $\beta \approx 0.75$. Inelastic neutron scattering reveals diffusive dynamics of the sodium ions on a 10 ps time scale. Even in the equilibrium melt the Sodium ions diffuse in a relative immobile Si-O matrix.

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FIG. 1. Elastic structure factor $S(q, \omega = 0)$ of sodium disilicate: Toward small $q$ the signal is dominated by the incoherent contributions of the sodium atoms. The maximum around $\approx 1.7 \, \text{Å}^{-1}$ reflects the scattering of the partially disrupted tetrahedral SiO$_4$ network. With increasing temperature a pronounced shoulder is emerging at $q \approx 0.9 \, \text{Å}^{-1}$. The decrease in intensity at $q$ values larger than $\approx 1.1 \, \text{Å}^{-1}$ in turn mainly reflects the Debye–Waller factor.

FIG. 2. High-energy resolution backscattering spectra of a sodium disilicate melt. Around $q \approx 1.6 \, \text{Å}^{-1}$ the signal is dominated by the coherent scattering of Si and O. At 1600 K structural relaxation of the Si-O network is on a ns–time scale causing a broadening of the quasielastic line. The line represents a fit (1) giving a relaxation time of $\approx 4 \, \text{ns}$ and a stretching exponent $\beta = 0.75 \pm 0.1$.

FIG. 3. Scattering law $S(q, \omega)$ at $q = 0.5 \, \text{Å}^{-1}$ measured on the neutron time-of-flight spectrometer IN6. Diffusion of sodium ions results in a broad quasielastic signal that is described by (1) with a stretching exponent $\beta$ within $[0.7,0.8]$ and relaxation times $\tau$ at some 29 ps at 1200 K and some 13 ps at 1600 K.