EXTENDED-RANGE ORDER IN GLASSES

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EXTENDED RANGE ORDER IN GLASSES

The origin of intermediate-range order (IRO)\(^1\) in glasses remains one of the outstanding problems in condensed matter physics since indirect early evidence for its manifestation was seen in the Raman spectra of some glasses.\(^2-4\) The most general and persistent evidence of IRO, however, is the first sharp diffraction peak (FSDP), the feature observed at low wave-vector in the average structure factor \(S(Q)\) of many systems, including oxide, silicate and chalcogenide glasses and complex liquids.\(^5-7\) The FSDP is characterized by the fact that product of its wave vector \(Q_1\) and the nearest-neighbor distance \(r_1\) lies in the range 2.2-2.8, implying correlation lengths of the order of 2.5 \(r_1.\)\(^6\) The origin of the FSDP is controversial: it has been variously attributed to the presence of layer-like structures in the glass,\(^8\) to random packing of appropriate structural motifs,\(^5\) and to chemical ordering of voids and cations.\(^9\) Regardless of its origins, the FSDP clearly represents correlation lengths greater than those associated with the nominal building blocks of oxide and chalcogenide glasses.

In this Letter, we report unambiguous evidence of structure extending well beyond the correlation length typical of the FSDP, based on recent neutron and anomalous x-ray scattering experiments on rubidium germanate glasses. We show that this structure is related to chemical ordering of the metal atoms and associated topological ordering of the oxygens.

The glasses were prepared with special care to avoid water contamination of bulk and surface. Neutron diffraction measurements were made at ambient temperature with the SANDALS instrument at ISIS, Rutherford Appleton Laboratory, and the new GLAD instrument at IPNS, Argonne National Laboratory. The data were corrected and normalized with the use of standard techniques. Anomalous x-ray scattering experiments were done at the X-7A beam line at NSLS, Brookhaven National Laboratory. Data presented here are corrected for dead-time and incident flux but not multiple or Compton scattering or absorption.
The neutron and x-ray weighted structure factors are:

\[ S^N(Q) = \sum_{q} c_i \bar{b}_i \bar{b}_j S_{ij}(Q) / \left| \sum_{k} c_k \bar{b}_k \right|^2 \]  

(1a)

\[ S^X(Q) = \sum_{q} c_i c_j Z_i Z_j f_i(Q) f_j^*(Q) S_{ij}(Q) / \left| \sum_{k} c_k Z_k \right|^2 \]  

(1b)

where \( c_i, \bar{b}_i, Z_i \), and \( f_i(Q) \) denote the concentration, neutron scattering length, atomic number and x-ray form factor for element \( k \) and \( S_{ij} \) are the Faber-Ziman partial structure factors. The weighting factors, \( W^N_i = c_i \bar{b}_i / \left| \sum_{k} c_k \bar{b}_k \right| \) and \( W^X_i = c_i Z_i / \sum_{k} c_k Z_k \) determine the extent to which element \( i \) contributes to the neutron and x-ray structure factors, respectively.

The average neutron structure factors \( S^N(Q) \) for \( \nu\)-GeO\(_2\) and \( \nu\)-(Rb\(_2\)O)\(_x\)(GeO\(_2\))\(_{1-x}\) with \( x = 0.1, 0.2 \) and 0.33 are shown in Fig. 1. The first feature in the structure factor of \( \nu\)-GeO\(_2\) is a peak at \( Q \sim 1.54 \) Å\(^{-1}\): using \( r_1 = 1.74 \) Å from Ref. 10, we obtain \( Q r_1 = 2.68 \) for \( \nu\)-GeO\(_2\), clearly identifying this feature as the FSDP. The correlation length associated with IRO in \( \nu\)-GeO\(_2\) is thus \( \sim 4 \) Å, considerably larger than the Ge(O\(_{1/2}\))\(_4\) tetrahedra or the distances between them (\( r_{\text{GeGe}} = 3.17 \) Å).

On the addition of the modifier Rb\(_2\)O to the GeO\(_2\) network, however, the FSDP is no longer the first feature in \( S(Q) \). Instead, a new peak arises at \( Q_0 = 0.9 \) Å\(^{-1}\) implying a correlation length \( \sim 7 \) Å, larger than any previously reported in a glass. We refer to this new aspect of the structure as extended-range order. The behavior of the extended-range order peak (EROP) with increasing Rb\(_2\)O content contrasts with the behavior seen for the FSDP. The FSDP moves to higher \( Q \) but still remains within the range of its typical values in oxide and chalcogenide glasses. The EROP, in contrast, remains at essentially the same position. The FSDP becomes less intense with increasing Rb\(_2\)O concentration \( x \), whereas the intensity of the EROP increases up to \( x = 0.2 \) and then decreases for larger \( x \). Thus the addition of a small amount of Rb\(_2\)O produces extended-range order, but this order starts to break down as the Rb\(_2\)O concentration is further increased.
The EROP also appears in the x-ray diffraction patterns of these glasses. Fig. 2 compares raw diffraction data for $\nu$-GeO$_2$ and $\nu$-(Rb$_2$O)$_{0.2}$(GeO$_2$)$_{0.8}$. As in the neutron data, an FSDP is present for both glasses, and a pronounced EROP appears at $Q_0=0.9$ Å$^{-1}$ for the rubidium germanate glass.

Comparison of the x-ray and neutron intensities of the different peaks provides additional information about the origin of the diffraction peaks. In $\nu$-GeO$_2$, the neutron weighting factors $W_i^N$ (Eq. 1a) are 0.414 and 0.586 for $i=\text{Ge}$ and O, respectively, while the x-ray factors $W_i^X$ (Eq. 1b) are 0.667 and 0.333, respectively. The exaggerated intensity of the FSDP in the x-ray patterns therefore indicates that it is due primarily to cation-cation correlations; as is generally the case in oxide and chalcogenide glasses. In $\nu$-(Rb$_2$O)$_{0.2}$(GeO$_2$)$_{0.8}$, the $W_i^N$ are 0.527 (O), 0.331 (Ge), and 0.142 (Rb), whereas the $W_i^X$ are 0.263 (O), 0.468 (Ge) and 0.269 (Rb). From the definitions given in Eq. (1), it follows that correlations involving two metal atoms (Ge or Rb) are emphasized in $S^X$ relative to $S^N$, while all correlations involving O are de-emphasized; thus, the predominance of the FSDP in the x-ray pattern of $\nu$-(Rb$_2$O)$_{0.2}$(GeO$_2$)$_{0.8}$ confirms that also in this glass it is mostly due to Ge-Ge correlations. The relative weakness of the EROP in the x-ray pattern compared with $S^N(Q)$ suggests that it reflects correlations involving oxygen atoms but may also involve metal-metal correlations that make a negative contribution to this peak.

To probe the origin of the FSDP and EROP in greater detail, anomalous x-ray scattering measurements were made near the Ge and Rb K-shell absorption edges. Since the scattering amplitude of an element below an absorption edge increases with decreasing photon energy, a change in the intensity of a diffraction peak with the photon energy implies that pair correlations involving that element contribute to the peak. More precisely, it follows from Eq. (1b) that:

$$\frac{\partial S^X(Q)}{\partial f_{\text{Ge}}} \sim 0.269 S_{\text{GeRb}} + 0.468 S_{\text{GeGe}} + 0.263 S_{\text{GeO}}$$ (2a)

$$\frac{\partial S^X(Q)}{\partial f_{\text{Rb}}} \sim 0.269 S_{\text{RbRb}} + 0.468 S_{\text{RbGe}} + 0.263 S_{\text{RbO}}$$ (2b)
Raw diffraction data for \( \nu-(\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8} \) are shown in Fig. 3, collected at (a) 13.3 and 200 eV below the Ge absorption edge (11.1036 keV), and (b) 19.3 and 300 eV below the Rb absorption edge (15.2023 keV). The near-edge data have been re-normalized so that at \( Q = 5 \text{ Å}^{-1} \) they have the same absolute intensities as the data collected far from the edge. The FSDP has a positive derivative with changes in the scattering amplitudes of both Rb and Ge, so that it follows from Eq. (2) that Rb-Rb and/or Rb-Ge correlations as well as Ge-Ge correlations contribute to the IRO in \( \nu-(\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8} \). The intensity of the EROP is positively correlated with the scattering amplitude of Ge, but negatively correlated with that of Rb. This behavior can be explained in terms of chemical ordering involving metal atoms if \( S_{\text{RbGe}} \) is negative and \( S_{\text{RbRb}} \) and \( S_{\text{GeGe}} \) are positive at the wave-vector corresponding to the EROP. In addition, the large size of the Rb ions causes a deficiency of oxygen nearby, leading to oxygen-oxygen correlations and enhancing the magnitude of the EROP in the neutron diffraction patterns.

It is interesting to compare the behavior of the EROP with that of the peak at \( Q_2 = 2.8 \text{ Å}^{-1} \). In \( \nu-\text{GeO}_2 \), and presumably \( \nu-(\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8} \) as well, it is attributed to chemical ordering of Ge and O. In Molecular Dynamics (MD) simulations of \( \nu-\text{SiO}_2 \) (we are not aware of equivalent work for \( \nu-\text{GeO}_2 \)), \( S_{\text{SiO}} \) makes a negative contribution to this peak while \( S_{\text{SiSi}} \) and \( S_{\text{OO}} \) make positive contributions.\(^{11}\) The peak arises in all three partials from Coulomb oscillations in the partial pair correlation function \( g_{ij}(r) \) with period \( 2\pi/Q_2 \sim 2.2 \text{ Å} \), in phase with \( \sin(Q_2t) \) for \( g_{\text{SiSi}} \) and \( g_{\text{OO}} \) but out of phase for \( g_{\text{SiO}} \). We propose a similar origin for the EROP: chemical ordering of Rb and Ge with a period \( 2\pi/Q_0 \sim 7 \text{ Å} \), accompanied by topological ordering of the oxygen atoms.

Diffraction patterns of alkali silicate glasses show anomalies at low Q that may reflect extended-range order. Recent measurements of \( \text{M}_2\text{O}-\text{SiO}_2 \) glasses (\( \text{M} = \text{K} \) and \( \text{Li} \)) show an EROP at \( Q_0 \sim 1 \text{ Å}^{-1} \) only for \( \text{M} = \text{K} \).\(^{13}\) Likewise, we have found an EROP for \( \nu-(\text{M}_2\text{O})_{0.2}(\text{SiO}_2)_{0.8} \) with \( \text{M} = \text{K}, \text{Rb} \) and in the vitreous analog of wadeite, \( \text{K}_2\text{ZrSi}_3\text{O}_9 \).\(^{14}\) It is interesting that K-K and Zr-Zr distances in crystalline \( \text{K}_2\text{ZrSi}_3\text{O}_9 \) are on the order of 6-7 Å. MD simulations of \( \nu-(\text{Rb}_2\text{O})_{0.33}(\text{SiO}_2)_{0.67} \) indicate that Rb-Rb correlations peak at approximately 7-8
Å, a value comparable with the length scale of correlations deduced from the EROP.  

The Q values characteristic of different types of order in a glass or liquid can be understood by scaling with appropriate length parameters. Values of the nearest neighbor distance $r_1$, the mean interatomic spacing $d_s$ [$\rho^{-1} = (\pi/6)d_s^3$] and the wave vectors $Q_0 - Q_3$ of the first four diffraction peaks corresponding to the EROP, FSDP, Coulomb peak, and hard-sphere peak, respectively, are given in Table I for some selected glasses. The variations of $Q_id_s$ vs. $Q_ir_1$ for these peaks in several glasses are shown in Fig. 4. Over the range of glasses chosen, the EROP and FSDP clearly have characteristic Q values when scaled in this way.

In summary, we have identified a new type of order in glasses that we term extended-range order, characterized by diffraction peaks at Q values below those typical of the FSDP associated with intermediate-range order. A comparison of neutron and x-ray diffraction data and a careful study of anomalous x-ray scattering from rubidium germanate glasses shows that, at least in this system, the EROP is the result of chemical ordering of the two cations with respect to one another and an associated topological ordering of the oxygen atoms.

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References
FIGURE CAPTIONS

Figure 1. Neutron structure factor $S^N(Q)$ for $\nu$-GeO$_2$ and $\nu$-$(\text{Rb}_2\text{O})_x(\text{GeO}_2)_{1-x}$.

Figure 2. X-ray diffraction data for $\nu$-GeO$_2$ (closed symbols) and $\nu$-$(\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8}$ (open symbols).

Figure 3. X-ray diffraction data for $\nu$-$(\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8}$ taken at:
   (a) 200 eV (closed symbols) and 13.3 eV (open symbols) below the Ge K absorption edge.
   (b) 300 eV (closed symbols) and 19.3 eV (open symbols) below the Rb K absorption edge.

Figure 4. Plot of $Q_id_s$ vs. $Q_ir_1$, where $d_s$ is the mean interatomic spacing, $r_1$ is the nearest-neighbor distance, and $Q_i$ is the wave vector of the $i^{th}$ peak in $S(Q)$: • $Q_0$ (EROP); ○ $Q_1$ (FSDP); $Q_2$ (Coulomb peak); △ $Q_3$ (hard-sphere peak).
Table 1. Structural data for selected oxide glasses. (Symbols are explained in the text)

<table>
<thead>
<tr>
<th>Glass</th>
<th>$r_1$</th>
<th>$d_s$</th>
<th>$Q_0$</th>
<th>$Q_1$</th>
<th>$Q_2$</th>
<th>$Q_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Rb}<em>2\text{O})</em>{0.1}(\text{GeO}<em>2)</em>{0.9}$</td>
<td>1.74</td>
<td>3.06</td>
<td>0.95</td>
<td>1.84</td>
<td>2.72</td>
<td>4.75</td>
</tr>
<tr>
<td>$(\text{Rb}<em>2\text{O})</em>{0.2}(\text{GeO}<em>2)</em>{0.8}$</td>
<td>1.77</td>
<td>2.95</td>
<td>0.92</td>
<td>1.95</td>
<td>2.75</td>
<td>4.82</td>
</tr>
<tr>
<td>$(\text{Rb}<em>2\text{O})</em>{0.33}(\text{GeO}<em>2)</em>{0.67}$</td>
<td>1.74</td>
<td>3.12</td>
<td>0.96</td>
<td>2.01</td>
<td>2.70</td>
<td>4.88</td>
</tr>
<tr>
<td>$(\text{K}<em>2\text{O})</em>{0.26}(\text{SiO}<em>2)</em>{0.74}$</td>
<td>1.63</td>
<td>3.11</td>
<td>1.00</td>
<td>2.14</td>
<td>2.92</td>
<td>5.26</td>
</tr>
<tr>
<td>$(\text{K}<em>2\text{O})</em>{0.15}(\text{Li}<em>2\text{O})</em>{0.17}\text{SiO}_2$</td>
<td>1.63</td>
<td>2.98</td>
<td>1.10</td>
<td>2.03</td>
<td>2.81</td>
<td>5.26</td>
</tr>
<tr>
<td>$(\text{K}<em>2\text{O})</em>{0.2}(\text{SiO}<em>2)</em>{0.8}$</td>
<td>1.62</td>
<td>3.15</td>
<td>0.80</td>
<td>1.95</td>
<td>2.97</td>
<td>5.32</td>
</tr>
<tr>
<td>$(\text{K}<em>2\text{O})</em>{0.14}(\text{Rb}<em>2\text{O})</em>{0.06}\text{SiO}_2$</td>
<td>1.62</td>
<td>3.15</td>
<td>0.79</td>
<td>1.94</td>
<td>2.94</td>
<td>5.30</td>
</tr>
<tr>
<td>$(\text{K}<em>2\text{O})</em>{0.08}(\text{Rb}<em>2\text{O})</em>{0.12}\text{SiO}_2$</td>
<td>1.62</td>
<td>3.15</td>
<td>0.76</td>
<td>1.92</td>
<td>2.90</td>
<td>5.27</td>
</tr>
<tr>
<td>$(\text{K}<em>2\text{O})</em>{0.2}(\text{ZrO}<em>2)</em>{0.2}\text{SiO}_2$</td>
<td>1.63</td>
<td>3.70</td>
<td>1.14</td>
<td>1.96</td>
<td>3.00</td>
<td>5.00</td>
</tr>
<tr>
<td>$(\text{K}<em>2\text{O})</em>{0.2}(\text{TiO}<em>2)</em>{0.2}\text{SiO}_2$</td>
<td>1.63</td>
<td>3.70</td>
<td>1.17</td>
<td>2.01</td>
<td>2.81</td>
<td>5.27</td>
</tr>
</tbody>
</table>

- a Data from ref. 13
- b Data from ref. 14
- c Data from ref. 15
Figure 1

Ellison et al
Fig 3: Ellison et al.
Fig 4. Wilson et al.