ANL/MSD/PP--77977

EXTENDED-RANGE ORDER IN GLASSES

Adam G. J. Ellison, David Long Price, Marie-Louise Saboungi
Argonne National Laboratory
Argonne, IL 60439

Rui-Zhong Hu*, Takeshi Egami
University of Pennsylvania
Philadelphia, PA 19104

W. Spencer Howells
Rutherford-Appleton Laboratory
Chilton OX11 0QX
United Kingdom

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

November, 1992

Submitted to Nature

RECEIVED

OCT 14 1994

/sm

DISCLAIMER

OSTI

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This work is supported by the Division of Materials Sciences, Office of Basic Energy Sciences of DOE, under contract No. W-31-109-ENG-38.

*Present Address: W. R. Grace and Co., Columbia, MD 21044

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

875

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Extended-Range Order in Glasses

Adam G. J. Ellison, David Long Price
Marie-Louise Saboungi

Argonne National Laboratory
Argonne, Illinois 60439

Rui-Zhong Hu* , Takeshi Egami
University of Pennsylvania
Philadelphia, Pennsylvania 19104

W. Spencer Howells
ISIS, Rutherford-Appleton Laboratory, U. K.

To Be Submitted to Nature

November 06,1992

* Present Address: W. R. Grace and Co., Columbia, MD 21044

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 glass⁸, to random packing of appropriate structural motifs⁵, and to chemical ordering of voids and cations⁹. 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:

$$S^N(Q) = \sum_{ij} c_i c_j \bar{b}_i \bar{b}_j^* S_{ij}(Q) / \left| \sum_k c_k \bar{b}_k \right|^2 \quad (1a)$$

$$S^X(Q) = \sum_{ij} c_i c_j Z_i Z_j f_i(Q) f_j^*(Q) S_{ij}(Q) / \left| \sum_k c_k Z_k f_k(Q) \right|^2 \quad (1b)$$

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, $W_i^N = c_i \bar{b}_i / \left| \sum_k c_k \bar{b}_k \right|$ and $W_i^X = c_i Z_i / \sum_k c_k Z_k$ 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 ν -GeO₂ and ν -(Rb₂O)_x(GeO₂)_{1-x} with $x = 0.1, 0.2$ and 0.33 are shown in Fig. 1. The first feature in the structure factor of ν -GeO₂ is a peak at $Q \sim 1.54 \text{ \AA}^{-1}$: using $r_1 = 1.74 \text{ \AA}$ from Ref. 10, we obtain $Q_1 r_1 = 2.68$ for ν -GeO₂, clearly identifying this feature as the FSDP. The correlation length associated with IRO in ν -GeO₂ is thus $\sim 4 \text{ \AA}$, considerably larger than the Ge(O_{1/2})₄ tetrahedra or the distances between them ($r_{\text{GeGe}} = 3.17 \text{ \AA}$).

On the addition of the modifier Rb₂O to the GeO₂ network, however, the FSDP is no longer the first feature in $S(Q)$. Instead, a new peak arises at $Q_0 = 0.9 \text{ \AA}^{-1}$ implying a correlation length $\sim 7 \text{ \AA}$, 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 Rb₂O 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 Rb₂O 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 Rb₂O produces extended-range order, but this order starts to break down as the Rb₂O concentration is further increased.

The EROP also appears in the x-ray diffraction patterns of these glasses. Fig. 2 compares raw diffraction data for ν -GeO₂ and ν -(Rb₂O)_{0.2}(GeO₂)_{0.8}. As in the neutron data, an FSDP is present for both glasses, and a pronounced EROP appears at $Q_0 = 0.9 \text{ \AA}^{-1}$ 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 ν -GeO₂, 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.^{11,12} In ν -(Rb₂O)_{0.2}(GeO₂)_{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 ν -(Rb₂O)_{0.2}(GeO₂)_{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 :

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

$$\frac{\partial S^X(Q)}{\partial f_{\text{Rb}}} \sim 0.269 S_{\text{RbRb}} + 0.468 S_{\text{RbGe}} + 0.263 S_{\text{RbO}} \quad (2b)$$

Raw diffraction data for $\nu\text{-(Rb}_2\text{O)}_{0.2}\text{(GeO}_2\text{)}_{0.8}$ 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 $Q = 5 \text{ \AA}^{-1}$ 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 $\nu\text{-(Rb}_2\text{O)}_{0.2}\text{(GeO}_2\text{)}_{0.8}$. 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_{RbGe} is negative and S_{RbRb} and S_{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 $Q_2 = 2.8 \text{ \AA}^{-1}$. In $\nu\text{-GeO}_2$, and presumably $\nu\text{-(Rb}_2\text{O)}_{0.2}\text{(GeO}_2\text{)}_{0.8}$ 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_{SiO} makes a negative contribution to this peak while S_{SiSi} and S_{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 $2\pi/Q_2 \sim 2.2 \text{ \AA}$, in phase with $\sin(Q_2 r)$ for g_{SiSi} and g_{OO} but out of phase for g_{SiO} . We propose a similar origin for the EROP: chemical ordering of Rb and Ge with a period $2\pi/Q_0 \sim 7 \text{ \AA}$, 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 $\text{M}_2\text{O-SiO}_2$ glasses ($M = \text{K}$ and Li) show an EROP at $Q_0 \sim 1 \text{ \AA}^{-1}$ only for $M = \text{K}$.¹³ Likewise, we have found an EROP for $\nu\text{-(M}_2\text{O)}_{0.2}\text{(SiO}_2\text{)}_{0.8}$ with $M = \text{K, Rb}$ 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 $\text{\AA}$. MD simulations of $\nu\text{-(Rb}_2\text{O)}_{0.33}\text{(SiO}_2\text{)}_{0.67}$ indicate that Rb-Rb correlations peak at approximately 7-8

Å, a value comparable with the length scale of correlations deduced from the EROP.¹⁵

The Q values characteristic of different types of order in a glass or liquid can be understood by scaling with appropriate length parameters.⁶ 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 $Q_i d_s$ vs. $Q_i r_1$ 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.

ACKNOWLEDGMENTS. This work was supported by the U.S. Department of Energy (DOE), Division of Materials Sciences, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38, and by the National Science Foundation under Grant DMR-90-01704. We gratefully acknowledge the assistance of the Operations Staffs at IPNS, ISIS, and NSLS.

References

1. S. R. Elliott, *Nature* **354**, 445-452 (1991).
2. W. L. Konijnendijk and J. M. Stevels, *J. Non-Cryst. Solids* **18**, 307-331 (1975).
3. P. M. Bridenbaugh, G. P. Espinosa, J. E. Griffiths, J. C. Phillips and J. P. Remeika, *Phys. Rev.* **B20**, 4140-4144 (1979).
4. F. L. Galeener, *Solid State Commun.* **44**, 1037-1040 (1982)
5. S. C. Moss and D. L. Price, in *Physics of Disordered Materials*, ed: D. Adler, H. Fritzsche, S. R. Ovshinsky (Plenum, New York, 1985), pp. 77-95.
6. D. L. Price, S. C. Moss, R. Reijers, M.-L. Saboungi and S. Susman, *J. Phys.: Condens. Matter* **1**, 1005-1008 (1989); M. L. Saboungi, W. Geertsma and D.L. Price, *Ann. Rev. Phys. Chem.* **41**, 207 (1990).
7. P. H. Gaskell, M. C. Eckersley, A. C. Barnes and P. Chieux, *Nature* **350**, 675-677 (1991).
8. J. C. Phillips, *J. Non-Cryst. Solids* **43**, 37-77 (1981).
9. S. R. Elliott, *Phys. Rev. Lett.* **76**, 711-714 (1991).
10. J. A. E. Desa, A. C. Wright and R. Sinclair, *J. Non-Cryst. Solids* **99**, 276-288 (1988).
11. P. Vashishta, R. K. Kalia, J. P. Rino, and I. Ebbsjo, *Phys. Rev.* **B41**, 12197-12208 (1990).
12. I. T. Penfold and P. S. Salmon, *Phys. Rev. Lett.* **67**, 97 (1991);
P. Vashishta, R.K. Kalia, G.A. Antonio and I. Ebbsjo, *Phys. Rev. Lett.* **62**, 1651 (1989).
13. A. Hannon, B. Vessal and J. M. Parker, *J. Non-Cryst. Solids*, in press (1992).
14. A. J. G. Ellison, J. E. Dickinson, Jr., and A. Navrotsky, to be published
15. B. Vessal, G. N. Greaves, P. T. Marten, A. V. Chadwick, R. Mole and S. Houde-Walter, *Nature* **356**, 504-506 (1992).

FIGURE CAPTIONS

Figure 1. Neutron structure factor $S^N(Q)$ for ν - GeO_2 and ν -(Rb_2O) $_x$ (GeO_2) $_{1-x}$.

Figure 2. X-ray diffraction data for ν - GeO_2 (closed symbols) and ν -(Rb_2O) $_{0.2}$ (GeO_2) $_{0.8}$ (open symbols).

Figure 3. X-ray diffraction data for ν -(Rb_2O) $_{0.2}$ (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 $Q_i d_s$ vs. $Q_i r_1$, 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 $S(Q)$: $\bullet$ Q_0 (EROP); $\circ$ Q_1 (FSDP); $\square$ Q_2 (Coulomb peak); Δ Q_3 (hard-sphere peak).

Table 1. Structural data for selected oxide glasses. (Symbols are explained in the text)

Glass	r_1	d_s	Q_0	Q_1	Q_2	Q_3
$(\text{Rb}_2\text{O})_{0.1}(\text{GeO}_2)_{0.9}$	1.74	3.06	0.95	1.84	2.72	4.75
$(\text{Rb}_2\text{O})_{0.2}(\text{GeO}_2)_{0.8}$	1.77	2.95	0.92	1.95	2.75	4.82
$(\text{Rb}_2\text{O})_{0.33}(\text{GeO}_2)_{0.67}$	1.74	3.12	0.96	2.01	2.70	4.88
$(\text{K}_2\text{O})_{0.26}(\text{SiO}_2)_{0.74}^{\text{a}}$	1.63	3.11	1.00	2.14	2.92	5.26
$(\text{K}_2\text{O})_{0.15}(\text{Li}_2\text{O})_{0.17}\text{SiO}_2^{\text{a}}_{0.68}$	1.63	2.98	1.10	2.03	2.81	5.26
$(\text{K}_2\text{O})_{0.2}(\text{SiO}_2)_{0.8}^{\text{b}}$	1.62	3.15	0.80	1.95	2.97	5.32
$(\text{K}_2\text{O})_{0.14}(\text{Rb}_2\text{O})_{0.06}(\text{SiO}_2)_{0.8}^{\text{b}}$	1.62	3.15	0.79	1.94	2.94	5.30
$(\text{K}_2\text{O})_{0.08}(\text{Rb}_2\text{O})_{0.12}(\text{SiO}_2)_{0.8}^{\text{b}}$	1.62	3.15	0.76	1.92	2.90	5.27
$(\text{K}_2\text{O})_{0.2}(\text{ZrO}_2)_{0.2}(\text{SiO}_2)_{0.6}^{\text{c}}$	1.63	3.70	1.14	1.96	3.00	5.00
$(\text{K}_2\text{O})_{0.2}(\text{TiO}_2)_{0.2}(\text{SiO}_2)_{0.6}^{\text{c}}$	1.63	3.70	1.17	2.01	2.81	5.27

^a Data from ref. 13

^b Data from ref. 14

^c Data from ref. 15

Figure 1

Ellison et al

Figure 2. Ellison et al

Fig 4 Euison et al.