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Intermediate-range Order in Lead Metasilicate Glass

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Abstract

The complementarity of anomalous X-ray scattering (AXS) and neutron diffraction (ND) techniques is used here to investigate the nature and origin of intermediate-range order in lead metasilicate glass. Both X-ray and neutron structure factors reveal small peaks at low wave vector which are shown to be associated with intermediate-range order of the Pb-O network. The combination of AXS and ND is shown to be a powerful tool to correlate contributions from the different atom pairs to such a peak. The information thus derived is compared with results from alkali germanate glasses and with structural data on corresponding crystalline compounds.

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1. Introduction

The PbO-SiO_2 system forms glasses over a wide range compositions up to 90 mol% PbO. The glass-forming ability at high concentrations of PbO is explained by assuming that the Pb ions act as a network former. Numerous X-ray [1,2] and neutron diffraction [3] and spectroscopic [4] studies have been reported on this system, leading to controversial description of the short-range order. These studies revealed the presence of PbO_4 or PbO_3 pyramids in PbO-rich glasses. Morikawa *et al.* [1] pointed out that most of Pb atoms in $2PbO{\cdot}SiO_2$ glass formed covalent PbO_4 pyramids and two or three connected PbO_4 pyramids form zigzag chains acting as network formers. On the other hand, Imaoka *et al.* [2] concluded that, for $PbO{\cdot}SiO_2$ and $2PbO{\cdot}SiO_2$ glasses, models containing separate chains of PbO_3 pyramids and SiO_4 tetrahedra showed best agreement with the X-ray diffraction data. However, a recent molecular dynamics simulation study of $PbO{\cdot}SiO_2$ glass [5] indicated that models of PbO_4 or PbO_3 pyramids defined by peak fitting to the first Pb-O coordination shell in the real space correlation function imposes certain constraints on the Pb atom environment in the glass.

The nature of intermediate-range order in glasses remains one of the outstanding problems in condensed matter physics [6]. The most general and persistent evidence of intermediate-range order is the first sharp diffraction peak (FSDP), the feature observed at low wave vector in the structure factor $S(Q)$ of many systems, including oxide and chalcogenide glasses and complex liquids [7,8]. The wave vector Q_1 of the FSDP corresponds to a length scale $L_1 = 2\pi/Q_1$ on the order of 2.5 r_1 (r_1 is the nearest-neighbor distance in the glass), greater than the dimensions of the nominal building blocks of the glasses [8,9]. Recently, the nature and origin of extended-range order, corresponding to a correlation length L_0 that is greater than that of the intermediate-range order and characterized by a diffraction peak in $S(Q)$ at lower wave vector than the FSDP, was probed in alkali germanate glasses using a combination of anomalous X-ray scattering (AXS) and neutron diffraction (ND) [10,11].

Spectroscopic tools such as EXAFS and NMR have proved successful for investigating the cation surroundings and network structure, respectively. However, these methods cannot give a quantitative description of the structure beyond the first coordination shell. Considerable information can be obtained by combining X-ray diffraction and ND, and using AXS at the

absorption edges of the elements. Differential analysis of AXS makes it possible to determine the environment of a specific cation [10,11].

In this paper X-ray and neutron results for the structure of lead metasilicate glass ($PbSiO_3$) and pure silica glass (SiO_2) are presented. The information obtained is compared with results on alkali germanate glasses in which an extended cation ordering exists [10,11] in order to discuss the relationship between the intermediate-range order and the specific nature of the glass-forming ability of the PbO-SiO_2 system. ND results for the orthorhombic lead monoxide crystal (β-PbO), which is made up of infinite Pb-O zigzag chains [12], are also presented to compare the environment of Pb in the lead silicate glass and lead oxide crystal.

2. Experimental procedure

2.1. Sample preparation

$PbSiO_3$ glass was prepared by quenching from the melt in a platinum crucible for 2 h at 1100 ℃. For X-ray measurements the $PbSiO_3$ and SiO_2 glasses were prepared in solid form and polished give smooth (~ 50 μm roughness) flat surfaces toward the X-ray beam. For the neutron measurements the glasses were crushed and loaded into thin-walled vanadium cans. The atom number density ρ and glass transition temperature T_g of the $PbSiO_3$ glass sample were 0.0626 $Å^{-3}$ and 695 K, respectively. The β-PbO powder sample used for ND was obtained commercially from CERAC (99.999% pure).

2.2. Experimental details

The AXS measurements were made on the X-7A beamline at NSLS, Brookheaven National Laboratory, using a solid state Ge detector (Ortec) to distinguish between fluorescence and elastically scattered photons. The spectra were recorded at two energies, about 300 and 25 eV below the Pb L_{III} absorption edge (measured value: 13055 eV), up to $Q\,(=4\pi\sin\theta/\lambda) = 12$ $Å^{-1}$. The ND measurements were done at IPNS, Argonne National Laboratory, on the GLAD [13]

spectrometer using a large range of wave vector Q (up to 40 Å^{-1}) to give high resolution in the real-space correlation function.

3. Data reduction

A single diffraction measurement of an n-component system gives an average structure factor $S(Q)$, which is a sum of a weighted average of the $n(n + 1)/2$ separate partial structure factors $S_{ij}(Q)$:

$$S(Q) = \sum_{ij} W_i(Q) W_j(Q) S_{ij}(Q), \qquad (1)$$

where the $W_i(Q)$ are the weighting factors for the radiation used and the concentrations of the components. The purpose of using the AXS is to neglect the partial structure factors that do not involve the element of interest (here Pb) by using data in which only the scattering factor of Pb has changed. This yields differential structure factor, $S^{X}_{Pb}(Q)$, which is a sum of the partial structure factors centered on Pb.

In X-ray and neutron experiments, standard procedures were made to correct for background, absorption, multiple scattering and inelastic scattering and to the normalize the results. For the AXS case, the values of the anomalous scattering factors, f' and f'', for $PbSiO_3$ glass were computed by Cromer and Liberman's method [14] in the vicinity of the Pb L_{III} absorption edge. The regular scattering factors $f_0(Q)$ were calculated from the values tabulated in the International Tables for Crystallography. The Pb $L\beta$ fluorescence contribution was subtracted from the total intensity by using the $L\alpha$ intensity multiplied by an experimentally determined ratio $L\beta/L\alpha = 0.29$.

4. Results and Discussion

Fig.1 shows the X-ray average structure factors $S^{X}(Q)$ for SiO_2 and $PbSiO_3$ glasses and the differential structure factor at the Pb L_{III} absorption edge, $S^{X}_{Pb}(Q)$ in $PbSiO_3$ glass. Neutron average structure factors $S^{N}(Q)$ for SiO_2 and $PbSiO_3$ glasses and β-PbO crystal are shown in

Fig. 2. They are plotted out to only $Q = 9.0$ Å^{-1} to emphasize the structural features which appear at low Q. These three kinds of structure factors represents the following different combinations of the partial structure factors:

$$S^{N} = 0.09S_{PbPb} + 0.08S_{PbSi} + 0.02S_{SiSi} + 0.34S_{PbO} + 0.15S_{SiO} + 0.32S_{OO}, \quad (2a)$$

$$S^{X} = 0.39S_{PbPb} + 0.17S_{PbSi} + 0.02S_{SiSi} + 0.30S_{PbO} + 0.07S_{SiO} + 0.06S_{OO}, \quad (2b)$$

$$S^{X}_{Pb} = 0.64S_{PbPb} + 0.13S_{PbSi} + \quad 0.23S_{PbO}, \quad (2c)$$

where the X-ray scattering factors are calculated at $Q = 0$. It is interesting to note that some partial structure factors (e.g. these related to Si-O and O-O) contribute more to the neutron average structure factor than the X-ray one. In the differential structure factor, the three Pb partial structure factors are the sole contributions.

The first feature in the X-ray and neutron structure factors of SiO_2 is the FSDP at $Q_1 = 1.52$ Å^{-1}, a characteristic signature of intermediate-range order [7,8]. In the case of SiO_2 it corresponds to a correlation length $L_1 = 2\pi/Q_1 = 4.1$ Å and is mostly due to cation-cation (e.g. Si-Si) correlations [15], as is generally the case in glassy materials [16,17].

On the addition of 50 mol% of the PbO modifier to the silica network, two significant changes to the structure factors occur. First, the FSDP is shifted to higher wave vector, $Q_1 =$ 1.95 Å^{-1}, corresponding to a shorter correlation length $L_1 = 3.2$ Å. Its intensity is stronger with X-rays than with neutrons: according to the weighting factors given in Eq.(2), it is related to cation-cation, notably Pb-Pb, correlations, as is different from the case in pure SiO_2 glass. Second, a new broad peak or shoulder arises at $Q_0 \sim 1.2$ Å^{-1}, implying order on an extended range scale $L_0 \sim 5.2$ Å. Its intensity is weaker with X-rays than with neutrons: according to the weighting factors, it must involve oxygen correlations (O-O, Si-O and Pb-O); furthermore, it is positively correlated with Pb, appearing as a positive peak in $S^{X}_{Pb}(Q)$ which not involve O-O and Si-O correlations. It suggests that the new peak reflects predominantly the intermediate-range order of Pb-O correlations, corresponding to $L_0 \sim 2.3\, r_1$, using $r_1 = 2.3$ Å, the minimum Pb-O distance from Ref. 3, compared with $2.5\, r_1$ typical of FSDP's in oxide and chalcogenide glasses [7,8]. Alternatively, the nature of the new peak can also be explained as extended-range order of the Si-O network modified by Pb^{2+} ions, corresponding to $L_0 \sim 3.3\, r_1$, using $r_1 = 1.6$ Å: the

nearest-neighbor distance of Si-O, compared with values of L_0 ranging from 3.3 r_1 to 5.1 r_1 observed in various oxide glasses [10].

Results from AXS studies of heavy alkali (Rb, Cs) germanate glasses [10,11] suggest that such a new peak at lower Q reflects the extended range order in Ge-O network cage modified with heavy alkali ions, which support the picture of Wright *et al.* [18]; furthermore the peak appears as a negative peak in the differential structure factor around Rb K absorption edge and as a positive peak in that around Ge K absorption edge. In the case of $PbSiO_3$ glass, the presence of a secondary network made up of Pb-O correlations associated with the intermediate-range order reported here is expected. Thus, the nature of the intermediate-range or extended-range order in the lead silicate glass is different from that of the extended-range order in the heavy alkali germanate glasses. It may reflects the difference between the intermediate-range ordering of network modifiers (e.g. alkali and alkali-earth metal ions) with ionic bonding and that of intermediates (e.g. Pb^{2+}, Bi^{3+} etc.) [19,20] with covalent bonding to oxygen in the oxide glasses.

For the completeness, it should be mentioned that strong Bragg peaks found at low wave vectors, Q = 1.07 - 1.25 $Å^{-1}$, in orthorhombic β-PbO (yellow, massicot) [12] (Fig. 2) and tetragonal α-PbO (red, litharge) [21] correspond to L = 5.0 - 5.9 Å = 2.2 r_1 - 2.6 r_1, the same length scale as the intermediate-range order of Pb-O correlations in $PbSiO_3$ glass reported here. They appear to be caused by the Pb-O network (chains and layers). The implication that PbO in the glass network preserves a significant amount its crystal-like structure in reasonably large units associated with the intermediate-range order would explain the specific nature of the glass-forming ability of the $PbO-SiO_2$ system.

5. Conclusions

The differential X-ray and neutron structure factors in $PbSiO_3$ glass reveal a new peak or shoulder at low wave vector, implying a range of order extending beyond the intermediate-range order associated with the FSDP. The new peak reflects the periodicity of Pb-O network similar to that in lead oxide crystals. This result demonstrates that the combination AXS and ND offers

a powerful tool for extracting partial structure factor information from disordered systems.

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Figure Captions

Figure 1. X-ray average structure factors $S^{X}(Q)$ of SiO_2 and $PbSiO_3$ glasses obtained 25 eV below the Pb L_{III} edge, and the differential structure factor at the Pb L_{III} edge, $S^{X}_{Pb}(Q)$ in the $PbSiO_3$ glass. For definitions, refer to Eq. (2).

Figure 2. Neutron average structure factors $S^{N}(Q)$ of SiO_2 and $PbSiO_3$ glasses and the β-PbO crystal.

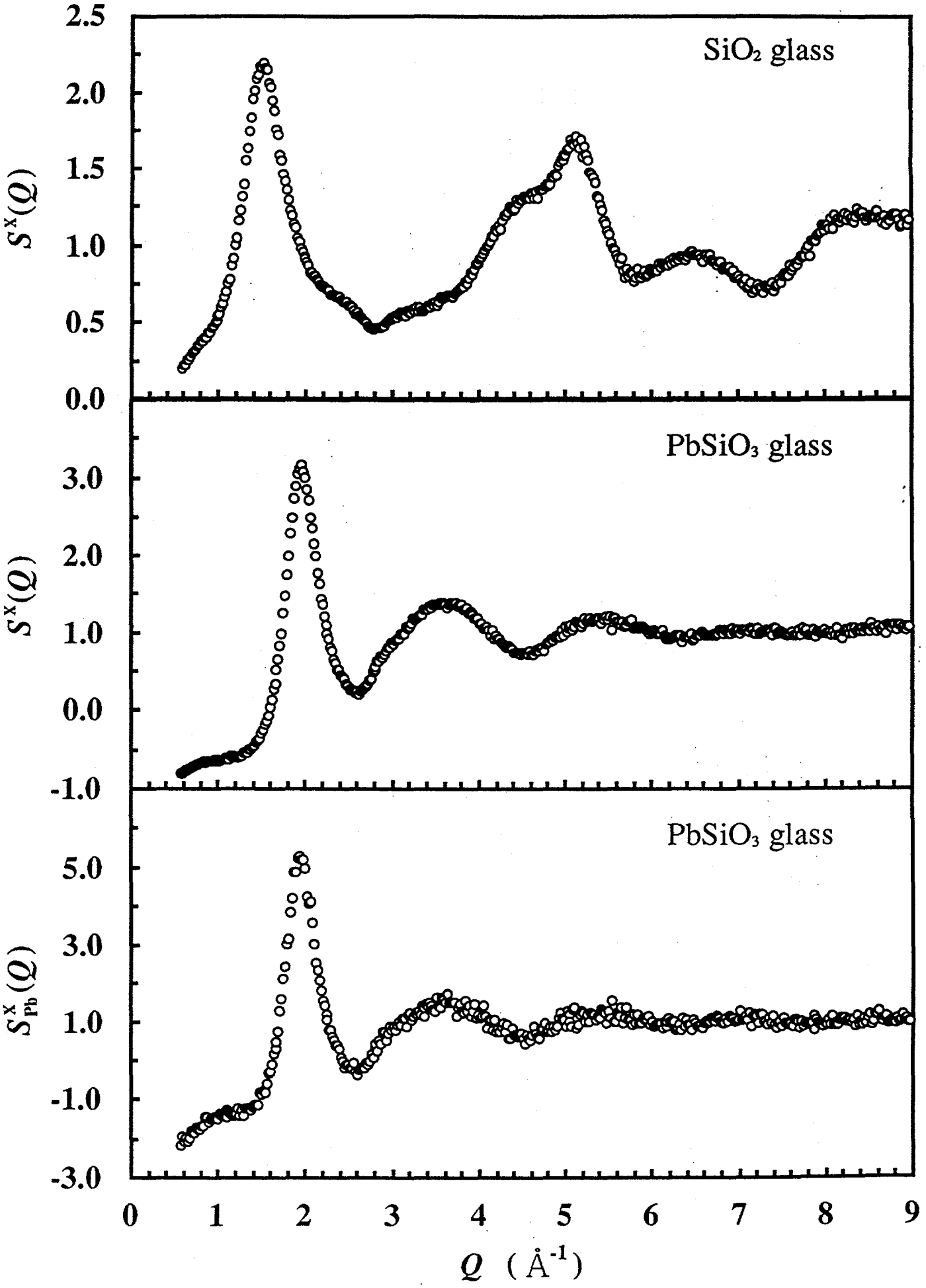

Fig. 1 Suzuki et al.

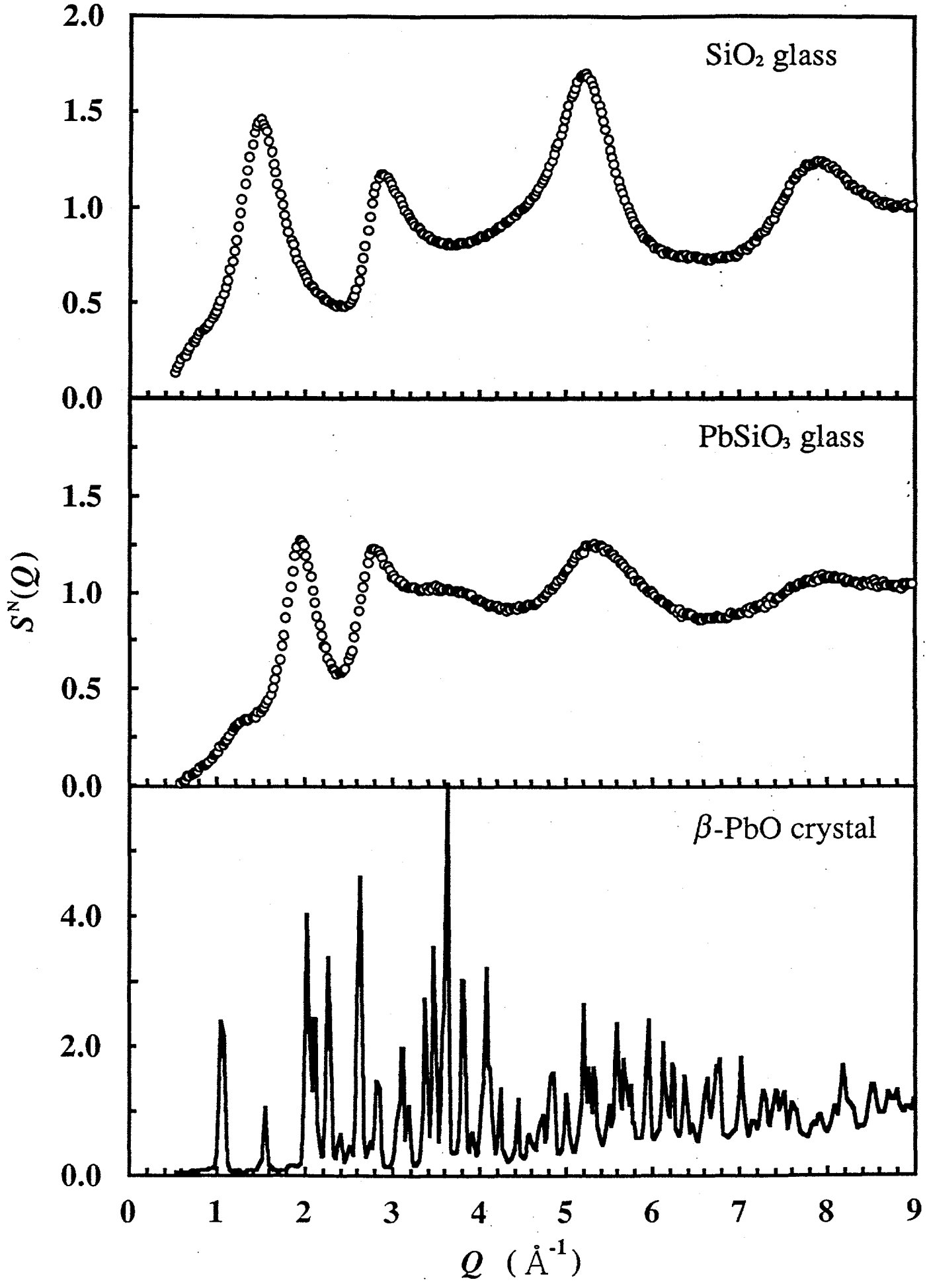

Fig 2, Susman et al