HIGH-ENERGY X-RAY STUDY OF THE STRUCTURE OF VITREOUS B_2O_3

High-energy X-ray ($E \geq 30$ keV) diffraction (HEXRD) using a synchrotron radiation source affords several advantages in studies of the structures of encapsulated liquids and glasses in transmission geometry, including: (i) higher resolution in real space due to a wide range of momentum transfer ($\hbar Q$), (ii) smaller correction terms (especially for absorption), (iii) the use of extreme sample environments (high-temperature, high-pressure), and (iv) the ability of direct comparison between X-ray and neutron diffraction data. The HEXRD technique, in conjunction with model calculations and neutron diffraction experiments, comprises one of the best methods available for investigating the structure of liquids and glasses.

This study was undertaken in order to investigate the short- and intermediate-range structure of vitreous B_2O_3. High-energy (40.9 keV [1] and 61.7 keV) synchrotron X-ray diffraction experiments were performed to obtain an accurate structure factor, $S(Q)$, for vitreous B_2O_3 up to high Q (~ 35 Å^{-1}), with small systematic corrections. The X-ray diffraction measurements were carried out at **BL04B2** and **BL14B1** bending magnet beamlines. The reverse Monte Carlo (RMC) modelling technique [2] was then applied to both the HEXRD and the published neutron diffraction data [3]. RMC simulations were carried out on a system containing 4000 atoms using the X-ray-weighted and neutron-weighted [3] total structure factors $S(Q)$, simultaneously. On the basis of the RMC model, we discuss the validity of the boroxol ring model for vitreous B_2O_3.

The experimental X-ray-weighted and neutron-weighted structure factors, $S^X(Q)$ and $S^N(Q)$, are shown as red lines in Fig. 1. $S^X(Q)$ exhibits significant oscillations up to the maximum Q value

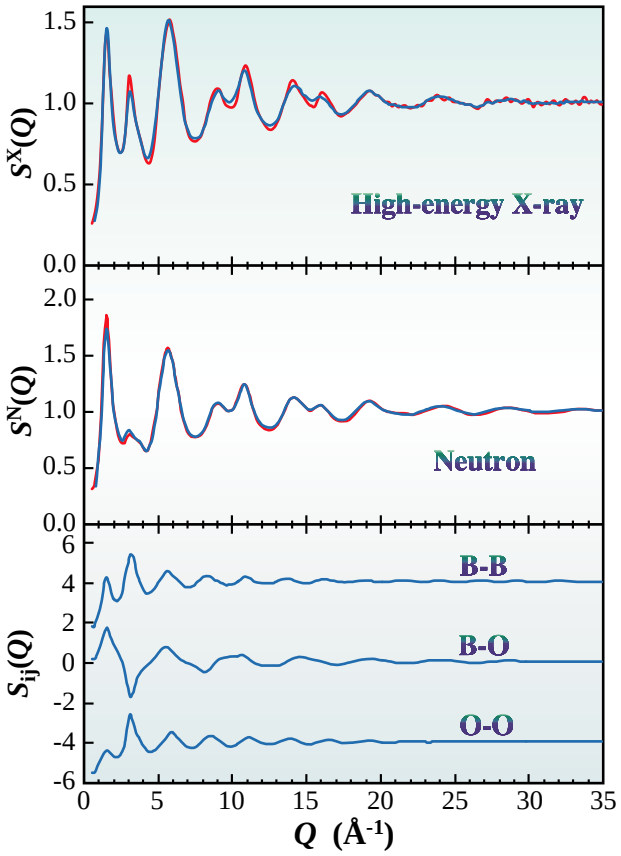

Fig. 1. Total and partial structure factors, $S^{X,N}(Q)$ and $S_{ij}(Q)$, respectively, from the RMC model (blue lines) for vitreous B_2O_3, in comparison with the experimental total structure factors (red lines).

of 35 Å^{-1}, although the oscillations in $S^N(Q)$ are at a considerably higher Q (> 40 Å^{-1}). There is a large discrepancy around 3 - 4 Å^{-1}, because of the difference in the intrinsic coherent scattering cross sections. The results of the RMC simulation are plotted as blue lines in Fig. 1 for comparison. Excellent agreement is obtained for both the structure factors, apart from minor deviation in $S^X(Q)$. The RMC model should be able to provide relatively detailed structural information, because of the contrast between the $S^N(Q)$ and $S^X(Q)$. The partial structure factors, $S_{ij}(Q)$, are also shown in Fig. 1. The first sharp diffraction peak (FSDP) observed at Q ~ 1.6 Å^{-1} implies the presence of intermediate-range order due to the cages formed by the topological connection of BO_3 units in the network [4]. This interpretation is supported by the RMC results, as the FSDP is found to be a positive feature in all three partial structure factors at Q ~ 1.6 Å^{-1} in Fig. 1.

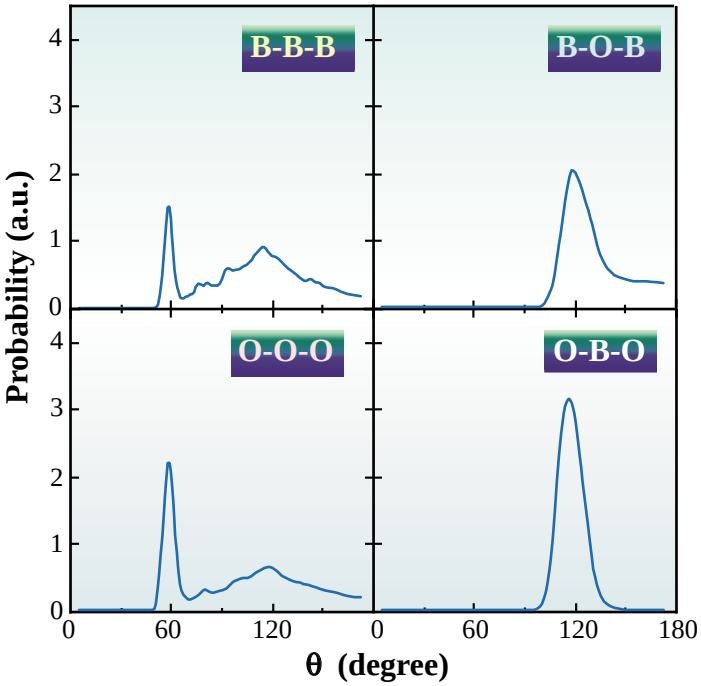

Fig. 2. Bond angle distributions for vitreous B_2O_3.

The bond angle distributions for B-B-B, O-O-O, B-O-B, and O-B-O are given in Fig. 2. The O-B-O and O-O-O distributions show a maximum close to the expected values for a regular BO_3 triangle of 120˚ and 60˚, respectively. The B-O-B angles are also narrowly distributed around a maximum near 120˚. The presence of a large number of planar boroxol rings (B_3O_6) is indicated by the small sharp peak at 60˚ in the B-B-B bond angle distribution. Recent neutron scattering studies of vitreous B_2O_3 indicate a model in which the majority of the boron atoms are in boroxol groups [3].

Figure 3 represents a 5 Å thick section of the RMC configuration, in which the presence of the boroxol rings is clearly visible. To estimate the fraction of the boroxol rings in vitreous B_2O_3 from the RMC configuration, the probability of finding a boron atom, which forms the B-B-B angle of 60˚ in the first coordination shell for B-B correlation, is calculated in Fig. 3. The value of the probability was found to be about 0.2, implying that the fraction of boroxol rings in vitreous B_2O_3 is not so large.

In order to obtain a more detailed understanding of the fraction of boroxol rings in the structure of vitreous B_2O_3, structural models of preserve-compacted B_2O_3 glasses are being generated from RMC fits to high-energy X-ray and neutron diffraction data.

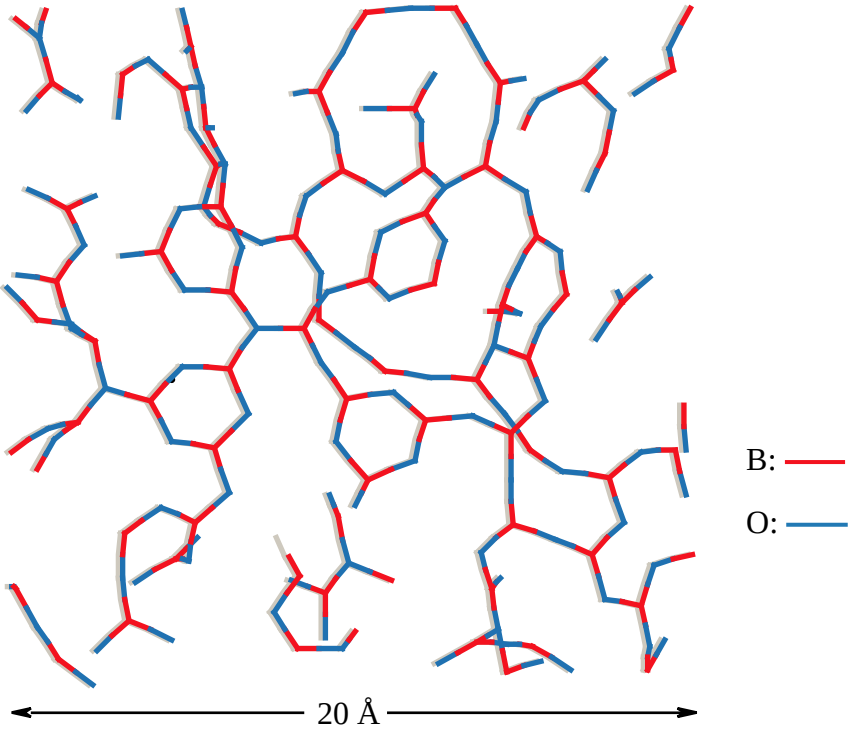

Fig. 3. A 5 Å thick slice of part of the largest RMC configuration for the borate (B-O) networks.

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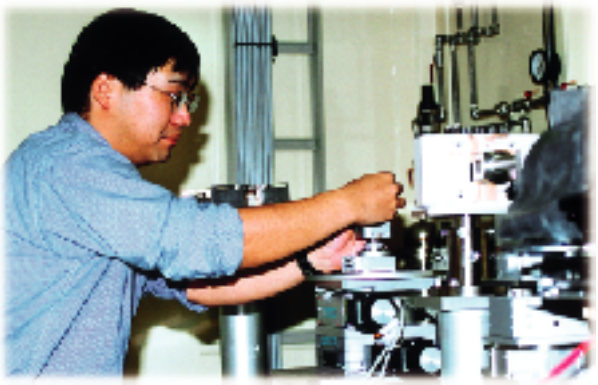

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