Void distributions in liquid BiBr₃

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Abstract. The X-ray diffraction experiments and the reverse Monte Carlo analysis for liquid BiBr₃ have been performed to clarify the distribution of Bi and Br ions around voids, comparing with previous results derived in the neutron diffraction experiments. The hexagonal cages involving voids are formed by the corner-sharing of the trigonal pyramidal BiBr₃ blocks. The neighboring cages are linked together in highly correlated fashion. The observed pre-peak in $S(Q)$ at 1.3Å⁻¹ is related to the pre-peak of the void-based $S'_CC(Q)$ due to an intermediate chemical order in the structure. The pre-peak intensity increases with increasing temperature. This characteristic change for the pre-peak intensity is discussed by considering the modifications of the topology and stacking in the hexagonal cages.

1. Introduction

Many investigations [1-5] have been made to clarify how the void distribution and the network structure around voids correlate with the intermediate-range order in network-forming liquids. Recently we have discussed the network structure involving voids in the liquid (l-) Rb-Se mixture [3,5] and l-BiBr₃ mixture [4,5] through the neutron diffraction (ND) experiments. In the present paper we report the results of X-ray diffraction (XD) experiments and the reverse Monte Carlo (RMC) simulation for l-BiBr₃. The structural analysis by XD is complementally to ND. The large difference in relative scattering factors of Bi ions for X-rays and neutrons is helpful for extracting a reliable information on the partial pair correlation $S_i(Q)$. We describe the void structure obtained by Voronoi-Delaunay analysis and discuss the correlation between the spatial distribution of voids and connectivity of Bi and Br ions in l-BiBr₃.

2. Experiment

The energy-dispersive XD measurements for l-BiBr₃ were performed using synchrotron radiation at BL04B2 and BL08W in SPring-8. Monochromatized X-rays were incident on the sample and the scattered X-rays are detected with a Ge solid-state detector. The standard RMC technique developed by McGreevy [6] is used here to derive $S_i(Q)$ and the partial pair distribution function $g_{ij}(r)$. The total number of ions is 8000 and the size of a cell was about 60×60×60Å³. The details are described elsewhere [3-5]. We applied Voronoi-Delaunay method [7] to define the distribution of void sizes. We also study the relative position of voids and atoms around the void in space by treating the circumsphere as the center of spherical voids with relative positions and calculating a partial pair distribution function for them as if they were particles with scattered radiation.

3. Results and Discussion
Figure 1. Experimental $S(Q)$ (open circles) for l-BiBr$_3$ at 300, 400, 500 and 600°C together with the corresponding $S(Q)$ fit (solid line) obtained from RMC model at 300°C.

Figure 2. (a) Experimental $g(r)$ (open circles) for l-BiBr$_3$ at 600°C and the corresponding $g(r)$ fit (solid line) together with the concentration-weighted $g_{\text{Bi-Br}}(r)$, $g_{\text{Bi-Bi}}(r)$ and $g_{\text{Br-Br}}(r)$ obtained by RMC model. (b) Comparison between XD (solid line) and ND (dotted line) results for the RMC $g_{ij}(r)$.

Figure 1 shows the temperature variation of the structure factor $S(Q)$ for l-BiBr$_3$ and the corresponding RMC fit of $S(Q)$ at 300°C. A good agreement is found between the experimentally derived $S(Q)$ and the produced RMC structure. It is noticed that there exists a pre-peak located at 1.3Å$^{-1}$, which is well-known signature of intermediate-range order. The pre-peak exhibits an increase in intensity with increasing temperature.

Figure 2(a) illustrates the pair distribution function $g(r)$ for l-BiBr$_3$ at 600°C together with the corresponding RMC fit, and the partial pair distribution functions $g_{\text{Bi-Br}}(r)$, $g_{\text{Bi-Bi}}(r)$ and $g_{\text{Br-Br}}(r)$ computed from the RMC model. Excellent agreements are found between the produced RMC structure and the experimental XD results for $g(r)$. The intense first peak of $g(r)$ for l-BiBr$_3$ occurs at 2.7Å, which is attributable to the first peak of $g_{\text{Bi-Br}}(r)$. The second peak of $g(r)$ around 3.8Å is composed of the second peak of $g_{\text{Bi-Br}}(r)$ and the first peaks of $g_{\text{Bi-Bi}}(r)$ and $g_{\text{Br-Br}}(r)$. The comparison between XD and ND results for the RMC $g_{ij}(r)$ is shown in figure 2(b). The agreement between the RMC $g_{ij}(r)$ derived with XD and ND is fairly good, but small differences are noticed. The RMC results derived with XD data for $g_{\text{Bi-Br}}(r)$ indicate that an additional small bump appears at 3.4Å near the second peak (3.8 Å) of $g_{\text{Bi-Br}}(r)$ in contrast to that derived with ND. The peak position of $g_{\text{Bi-Br}}(r)$ lies at slightly lower $r$ for XD than for ND. It seems clear from the consideration of the large scattering factor of Bi ion for X-ray that the RMC results derived with XD data provide more detailed description of the Bi-Br correlation in l-BiBr$_3$.

The partial coordination number $(N_{ij})$ can be estimated from the RMC configurations by counting the number of ions $(j)$ inside a sphere of radius $R_C$ centered at a given ion $(i)$. The estimated values of $N_{ij}$ at 300°C are listed in table 1.

These results define the spatial arrangements of Bi and Br ions in l-BiBr$_3$. The basic building unit of the network can be considered as the trigonal pyramidal BiBr$_3$ blocks with Bi-Br distance of 2.7Å wherein three Br ions reside in the corner separated by 3.8Å. The pyramidal BiBr$_3$ blocks are linked together through a Br bridge (corner sharing). The interconnected pyramidal BiBr$_3$ blocks (Bi-Bi distance ~3.8Å) form a honeycomb-like network composed of the hexagonal cages in a highly correlated fashion supporting voids (See figure 4).
A substantial modification of $g_{\text{sc}}$ scattering factor of Bi ion for X-ray. This interesting behavior derived in the X-ray data, while it is not visible in the results pre-peak increases in height and becomes narrower in width with increasing temperature (See Figure 1). It can be seen that there is a chemical order pre-peak of $S_{\text{c}c}(Q)$/$C_{\text{c}}C_{\text{bi}}$ at $Q=1.3\AA^{-1}$ which is at the same position as in the observed pre-peak of $S_{i}(Q)$. $S_{\text{v}v}(Q)$ has the corresponding minimum, and $S_{\text{v}v}(Q)$ and $S_{\text{v}v}(Q)$ have the corresponding maxima. It should be stressed that the pre-peak increases in height and becomes narrower in width with increasing temperature (See figure 1). This interesting behavior derived in the X-ray data, while it is not visible in the results derived in ND experiments, is immediately understandable from consideration of a large scattering factor of Bi ion for X-ray.

The changes in the topology and stacking of the cages are reflected on the pre-peak of $S(Q)$. A substantial modification of $g_{\text{sc}}(r)$ peak around 5Å by raising temperature as seen in figure 3.
is associated with the change in the spatial orientation of cages. The hexagonal cages formed by BiBr$_3$ blocks may bend at high temperature along a common edge which links cages together and the pairs of Bi ions on the neighboring cage come closer together than they would have preferred under simple Coulomb repulsion as a consequence of covalency of bonds [9]. The tridimensionally connected cages construct a stable network. Consequently, the network is modified to a denser stacked configuration. The ordering of voids is simply related to a strong correlation between cages. The coordination number of voids around a void $N_{VV}$ indicates that it increases from 3–4 to 5–6 by raising temperature. The intensity of the pre-peak is coupled to the modification of the network structure. The covalently bonded network in l-BiBr$_3$ is built on the trivalency of Bi plus one lone-pair electron and the monovalency of Br plus one bonding electron or hole. The relationship between the network and electronic structure awaits future work.

4. Conclusion
The distributions of Bi and Br ions around voids for l-BiBr$_3$ have been determined from the XD measurements and RMC analysis. The hexagonal cages involving voids are formed by the corner-sharing of the trigonal pyramidal BiBr$_3$ blocks. The strong preference of Bi ion for threefold coordination helps to bind the neighboring cages in highly correlated fashion. The pre-peak of $S(Q)$ at 1.3Å$^{-1}$ is related to the pre-peak of the void-based $S'_{CC}(Q)$ due to an intermediate chemical order in the structure. The increase in the height of pre-peak with temperature arises from a modification of the network to a denser stacked configuration owing to a strong correlation between cages involving voids.

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Figure 5. (a) Concentration-concentration structure factor $S_{CC}(Q)/C_vC_{Bi}$ together with experimental $S(Q)$. (b) Partial structure factors $S'_{V-Bi}(Q)$, $S'_{Bi-Bi}(Q)$ and $S'_{V-V}(Q)$ in l-BiBr$_3$ at 600°C produced from RMC configurations.