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Short-range order of As-S-Br chalcohalide glasses

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Introduction

Optical and structural properties of amorphous As- and Ge-chalcohalide systems have been studied extensively from the view point of the exploitation of new materials capable of transmitting light in the mid-infrared region [1]. Following results of recent structural studies, these amorphous systems can be classified into three groups: glasses containing (1) mixed-anion units ($GeSe_{(4-n)/2}I_n$ tetrahedra in the Ge-Se-I system), (2) metal-halide molecular units (AsI_3 molecular units in the As-(Se, S)-I system) and (3) direct halogen-chalcogen bonding (As-Se-Br and As-Te-I systems). It is very interesting to explore what factors decisively influence the formation of structural units in these amorphous systems. For this purpose, it is necessary to obtain further structural information on chalcohalide systems containing S, Br and Cl atoms, structural studies of which have been considerably limited. The present report describes results of EXAFS studies on amorphous $(As_2S_3)_{1-x}Br_x$ and $As_{0.4-x}S_{0.6}Br_x$ alloys.

Experimental procedure

Amorphous alloys were prepared by heating required amounts of As, S and $AsBr_3$ (purities of all 99.99%) in an evacuated quartz ampoule up to 600 ºC for 48 h and quenching the ampoule containing the melt into an ice-water bath. EXAFS studies for amorphous $(As_2S_3)_{1-x}Br_x$ alloys with x = 0~0.682 and $As_{0.4-x}S_{0.6}Br_x$ alloys with x = 0.1 and 0.2 were carried out using a silicon (111) channel-cut monochromator at the BL-12C station of KEK-PF. The intensity of the incident beam, I_0, and that of the transmitted beam, I, were measured using ionization chambers filled with a N_2(85)-Ar(15) mixture for I_0 and with a N_2(50)-Ar(50) mixture for I, respectively. Energy ranges covered were from 11365 to 13245 eV for the As K-edge and from 12970 to 13245 eV for the Br K-edge, respectively.

Results

Fourier transforms, $|F(R)|$, of the EXAFS oscillation functions, $k^3\chi(k)$, at the As K- and Br K-edges are given in Fig. 1. The main peak in $|F(R)|$ at the As K-edge (1(a)) in both alloys, which contains only the contribution of As-S pairs at x=0, obviously shifts to larger R with increasing x, presumably due to the introduction of As-Br pairs arising from the formation of $AsBr_3$ molecular units. On the other hand, $|F(R)|$ at the Br K-edge (1(b)) exhibits a symmetrical peak and the peak position is roughly constant at any x. This implies that Br-As pairs alone are formed around Br atoms, and that other pairs, such as Br-S, are negligible. It is therefore apparent also in the result of the EXAFS study that Br atoms in the amorphous As-S-Br system are preferentially bonded to As atoms to form $ArBr_3$ molecular units.

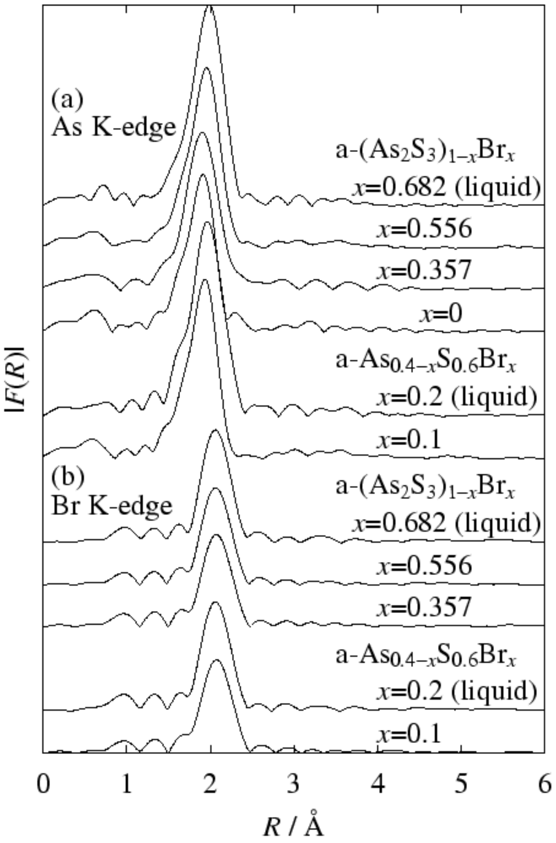

Fig. 1: Fourier transforms, $|F(R)|$, at the As K-edge(a) and Br K-edge(b) in amorphous $(As_2S_3)_{1-x}Br_x$ and $As_{0.4-x}S_{0.6}Br_x$ alloys, respectively.

The fitting analysis for the observed $k^3\chi(k)$ indicates that values of r_{As-S} and r_{As-Br} (or r_{Br-As}) are obtained to be 2.26 and 2.36 Å, respectively, which are unchanged at any x. A complete agreement between r_{As-Br} from the As K-edge data and r_{Br-As} from the Br K-edge ones ensures the validity of the present fitting analysis.

References

[1] J.S.Sanghera et al., J.Non-Cryst. Solids 103, 155 (1988).

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