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Structural analysis of amorphous Ge-Se alloys prepared by Mechanical Milling

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Introduction

A recent interest focuses upon the structural feature on amorphous Ge_xSe_{1-x} alloys around x = 1/2. At present, there are limited structural information in this x range, because bulky amorphous alloys cannot be obtainable by rapid quenching the melts (RQ). There have so far been reported different structural information from the sputtered $Ge_{0.5}Se_{0.5}$ film. For example, Fuoss *et al*. have reported by the X-ray differential anomalous scattering study that the amorphous structure of $Ge_{0.5}Se_{0.5}$ has three-coordinated Ge and Se, similar to crystalline GeSe [1], while, according to the recent EXAFS study by Gurman *et al*. the alloy is made of four-coordinated Ge and two-coordinated Se [2]. Consequently, structural information from bulky samples with $x > 3/7$ are highly desired.

The present report describes results of the structural analysis on amorphous $GeSe_2$, Ge_3Se_4 and Ge_4Se_5 prepared by the Mechanical Milling (MM). The report presents also results of the structural analysis on amorphous $GeSe_2$ and Ge_3Se_4 prepared by RQ for comparison.

Experimental procedure

Purities of Ge and Se used were both 99.999%. The two elements were melted together in the required amounts in an evacuated quartz ampoule and reacted thoroughly with frequent agitation. The crystalline alloy prepared thus was annealed in advance to ensure its homogeneity. The powder sample was put into an YSZ vial together with YSZ balls. The mechanical milling was made employing a shaker ball mill (SPEX-8000) under Ar atmosphere. EXAFS studies for amorphous samples were carried out 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.

Results

Figure 1 describes the Fourier transform, $|F(R)|$, of the EXAFS oscillation function, $k^3\chi(k)$, at Ge and Se K-edges in amorphous $GeSe_2$ from the MM and RQ, respectively. The comparison of the $|F(R)|$ functional form at each K-edge from MM and RQ samples reveals that there is no difference about the atomic configuration in the first coordination shell in both samples. Any difference in the local order was also not found out between amorphous samples from the MM and RQ for Ge_3Se_4. Bond-lengths of Ge-Se and Ge-Ge in the first coordination shell in Ge_3Se_4 and Ge_4Se_5 obtained by the least squares fit to the observed EXAFS function were 2.36 and 2.48 Å, respectively, which are equal well to the corresponding covalent distances. Therefore, it has been suggested that covalent structural units containing the Ge-Ge bond such as $Se_{3/2}Ge\text{-}(GeSe_{2/2})_n\text{-}GeSe_{3/2}$ or $Ge(Ge_{(4-m)/4}Se_{m/2})$, are present in amorphous Ge-enriched alloys of Ge_3Se_4 and Ge_4Se_5, in addition to the $GeSe_{4/2}$ tetrahedron. Crystalline GeSe is well-known to possess the three-coordinated structure of a distorted NaCl-type. However, even amorphous Ge_4Se_5, the composition of which is considerably close to GeSe, takes the covalent 4(Ge)-2(Se) folded structure similar to that in crystalline $GeSe_2$.

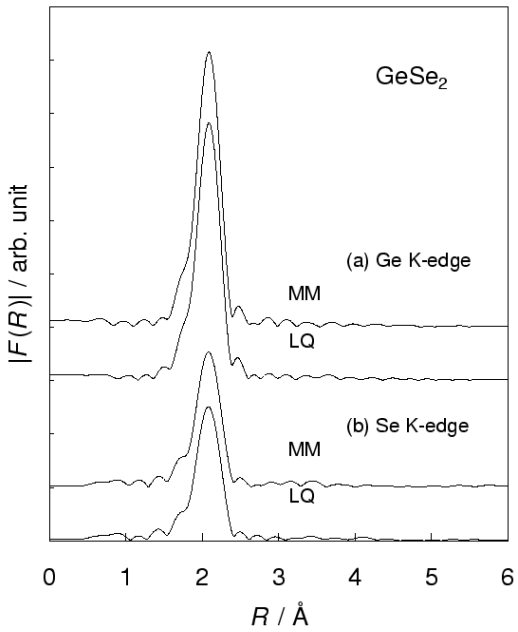

Fig. 1: Fourier transforms, $|F(R)|$, at the Ge K-edge(a) and Se K-edge(b) for amorphous $GeSe_2$.

References

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