EXAFS study of the local order in Ge-As-Se glasses

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Abstract

The nearest-neighbour environment of the Ge, As and Se atoms in ternary Ge$_x$As$_y$Se$_{1-x-y}$ systems with same mean coordination number (MCN = 2.5) have been investigated by the Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS). For all the glass compositions, Ge, As and Se are always 4, 3 and 2 coordinated, respectively. Ge atoms are bonded to Se atoms exclusively in the compositional range studied. Homopolar bonds are formed between some As or Se atoms in non-stoichiometric glasses. The results suggest a combined effect of chemical ordering and topological in this system.

1. Introduction

Chalcogenide glasses have received considerable attention over past few years due to their unique electrical and optical properties.\textsuperscript{1,2} They exhibit semiconductor behaviour with band gap energies from 1 to 3\textit{eV} and good transmissive performance in both 3-5\textmu m and 8-12\textmu m infrared spectral regions. While some commercial binary or ternary glass systems have been used very successfully for waveguide fabrication and in device demonstrations,\textsuperscript{3} it is still challenging to gain clear position of constituent atoms due to structure disorder.

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Basically, two major approaches have been employed to investigate the structure evolution of glassy materials: computer simulation and experimental observation. On the one hand, computer simulations such as Molecular Dynamics (MD) and Monte Carlo (MC) algorithms are successfully and widely used to quantitatively explore the geometric characteristics of the chalcogenide systems. Even though these theoretical methods could provide vivid structure images, the calculation processes are tedious and complicated. Besides, the credibility of the results rely heavily upon the chosen parameters and computer capacities. On the other hand, the rapid developments of experimental techniques, such as Nuclear Magnetic Resonance (NMR), High-resolution X-ray Photoelectron Spectroscopy (XPS) and Mössbauer Spectroscopy, enable scientists to further probe into the topological features of chalcogenide glasses. Particularly, the notable improvements of synchrotron radiation sources for x-ray absorption spectroscopic measurements has made Extended X-ray Absorption Fine Structure (EXAFS) become a powerful tool to obtain valuable structure information. This technique is direct, straightforward and sensitive to the atomic length scale. From EXAFS spectra, short-range, even intermediate-range structure around the specified atom could be determined, which could give reliable structure information about the number of nearest neighbors ($N$), the nearest neighbor bond length ($R$), and the bond angle ($\theta$) defining the spatial arrangement of the nearest neighbor atoms around each type of central atom.

With constant and prominent investigations, some representative structure models: covalent random network (CRN), chemically ordered network (CON), topological model, have been put forward to depict the possible spacial structure in covalent chalcogenides. The CON and the CRN models both satisfy the 8-$N$ rule and represent the distribution of bond types in a covalent network with multi-elements. In the CRN, the bonds are distributed between homopolar and heteropolar atomic pairs following a statistical probability based on the ratio of each type of atom in the composition. In contrast, the CON model favors the lowest energy system, in other words, the stable chemical compound systems are formed first and then, excess of the elements disperse among these units. Based on the constraints theory, the topological model argues that the glass structure is predominately controlled by the Mean Coordination Number ($MCN=\Sigma x_iMCN_i$, $x_i$ is the abundance of the $i$th component of a glass and $MCN_i$ is the valency of the $i$th constituent atoms), irrespective of their valence bonds. A floppy to rigid structural transition taking place at $MCN=2.4$, where was known as mechanical threshold and the glasses have the highest stability. Take into consideration of medium-range structures, another topological change from two-dimensional phase to three-dimensional networks is predicted when $MCN=2.67$.

In the present paper, we report the results about the local coordination environment of ternary $Ge_xAs_ySe_{1-x-y}$ glass family with same $MCN (=2.50)$, based on their respective Ge, As and Se $K$-edge EXAFS spectroscopy. An attempt is made to estimate the possible bond arrangement and the compositional effect.

2. Experimental

Chalcogenide glasses were typically synthesized from high purity (5N) Germanium, Arsenic and Selenium metals. These raw materials were weighed inside a dry nitrogen glove box and loaded into a pre-cleaned quartz ampoule. The loaded ampoule was dried under vacuum ($10^{-6}$ Torr) at 110°C for 4 hours to remove surface moisture from the raw materials. The ampoule was then sealed under vacuum using an oxygen hydrogen torch, and introduced into a rocking furnace for melting of the contents at 900°C. The melt was homogenized for a period not less than 30 hours, then the ampoule was removed from the rocking furnace at a predetermined temperature and air quenched. The resulting glass boule was subsequently annealed at a temperature 30°C below the glass transition temperature $T_g$, then slowly cooled to room temperature. After
that the glass boule was sectioned and the bulk glass was ground into powder with a size of 30 \( \mu m \). Finally, the powdered samples were stuck on adhesive tapes.

EXAFS data at Ge, As and Se (11103, 111867 and 12658eV, respectively) were recorded at 1W1B-XAFS beam line of Beijing Synchrotron Radiation Facility in transmission mode. The beam line was equipped with a Si (111) monochromator. The EXAFS data were collected at room temperature using ionization chambers filled with mixtures of nitrogen and argon gases. The processing and analysis of EXAFS data were carried out by a standard technique using IFEFFIT software package. After background removal and normalization, the EXAFS oscillations are \( k^2 \)-weighted. Subsequently, the spectra were Fourier transformed by applying a Hanning window within the \( k \) range between 3.1 and 12 Å\(^{-1}\). The first shell peak of the Fourier transform was backward transformed through a Hanning window function with the width of 2 Å from 1 Å to 3 Å. Eventually, the fitting programs were processed and the results, e.g. the coordination number \( N \), the average interatomic distance \( R \) and the Debye-Waller factor \( \sigma^2 \) were presented.

3. Results

The uncorrected phase shift Fourier transform of \( k^2 \)-weighted EXAFS spectra for Ge, As and Se \( K \)-edges are shown in Fig. 1. Compared to the figures for As and Se \( K \)-edges, the second shell information is clearly observed at the Ge \( K \)-edge. Apparently, all the compositions preserve short-range order primarily to the first shell. The decreased amplitude in the higher \( R \) reflect distinct structure disorder in higher shell. The \( k^2 \)-weighted experimental Ge, As and Se \( K \)-edges first shell EXAFS spectra and their corresponding fitted curves are shown in Figs. 2. The experimental and fitted spectra are generally in good agreement. Compared to the Ge and Se \( K \)-edges, the amplitude of the curves for the As \( K \)-edge are lower. The structural parameters for the first coordination spheres of the Ge, As and Se obtained from the fitting procedure are given in Table 1. The results show that the nearest coordination number of Ge atoms are fixed at 4. The overwhelming majority of Se atoms are bound to Ge atoms with neglectable Ge-As bonds in the compositional range studied. The nearest neighbor bond lengths of Ge remained approximately constant, within the error, no matter whether they are deduced from Ge-edge data or from the neighboring Se atom data. The present results are consistent with those reported for \( \text{Ge}_{x}\text{As}_{y}\text{Se}_{1-x-y} \) \((x:y=1:1 \) and \( 1:2) \) glasses by Sen et al. On the other hand, from the As \( K \)-edge EXAFS spectra, two types of bonds (As-Se and As-As) are deduced as well and the role of As-As bonds become important with increasing As content. All the As atoms are found to be bonded to 3 atoms forming trigonal pyramidal configuration. The average nearest neighbor bond length for As atoms decreases slightly from 2.42(6)Å to 2.41(4)Å with decreasing As content, resulting from the formation of homopolar bonds in As-rich glasses. A similar variation trend is detected from the local structure information of Se atoms. The nearest coordination number for Se atoms in all glasses are kept around constant at 2. The average nearest neighbor distance for Se-atoms decrease significantly from 2.40(8)Å for \( \text{Ge}_{7.5}\text{As}_{35}\text{Se}_{57.5} \) to 2.39(2)Å for \( \text{Ge}_{20}\text{As}_{10}\text{Se}_{70} \), due to a certain amount of Se-Se bonds are obtained for the Se-rich samples.

4. Discussions

The analytic results obtained from present work suggest that, for all glasses with same MCN (=2.50) but different chemical compositions, the Ge, As and Se atoms have coordination number of 4, 3 and 2, respectively. This means that all the constituent atoms in this covalent system possess ideal coordinate environment with which they satisfy general valence law and obey the 8-\( N \) rule. It is worth noting that, the first shell coordination environment of Ge atoms does not modify significantly as a function of glass compositions in that the values of coordination number and bond length are hardly change. The reason
for this is related to different bond energies of different bond types. According to the Pauling relation, the Ge-Se heteropolar bonds have highest bond energy. Bonds are formed in the sequence of decreasing bond energy, showing the priority of formation of Ge-Se bonds over other bonds. The Ge and As atoms in the stoichiometric and Se-rich glasses are barely bonded to Se atoms forming main structural backbones of GeSe$_{4/2}$ and AsSe$_{3/2}$ polyhedral units, which naturally implies the presence of Se-Se homopolar bonds in Se-rich compositions. The result suggests that the GeSe$_{4/2}$ and AsSe$_{3/2}$ structural units are connected by additional
Se-Se bonds and is consistent with our earlier reported results. In terms of Se-poor glasses, the chemical ordering in the As nearest environment is lower than in the corresponding surroundings of Ge atoms, which indicated by large proportion of As-As homopolar bonds. Moreover, the mixed first-shell coordination environment around Ge and As Atoms imply the violation of CON model to some extent. Compared to their stoichiometric counterpart, the longer average bond lengths and the larger Debye-Waller factors imply increased network deformation, meaning that those small As molecular clusters embedded in a continuous random network. In principle, the appearance of some small homoatomic structure in Se-poor glasses could be broadly explained based on the values of bond enthalpies and promotional energies.

Fig. 2. $k^3$-weighted first shell EXAFS spectra at (a) Ge, (b) As and (c) Se K-edge. Solid lines represent experimental data and dot lines correspond to fitted results.
Table 1 Ge, As and Se K-edge EXAFS structural parameters (the coordination number N, the bond length R and Debye-Waller factor $\sigma^2$) for Ge$_{x}$As$_{y}$Se$_{1-x-y}$ glasses

|                | Ge-Se           | Ge-As           | As-Se           | As-As           | Se-Ge           | Se-As           | Se-Se           |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|
| Ge$_7$As$_{35}$Se$_{57.5}$(-10) | N     | 3.84            | 0.16            | 0.45            | 0.51            | 1.49            | -              |
|                | $R$(Å)          | 2.37(7)         | 2.42(8)         | 2.42(6)         | 2.38(2)         | 2.41(6)         | -              |
|                | $\sigma^2$(Å)   | 0.005           | 0.009           | 0.007           | 0.006           | 0.004           | -              |
| Ge$_{10}$As$_{30}$Se$_{60}$(-5) | N     | 3.73            | 0.27            | 0.36            | 0.65            | 1.36            | -              |
|                | $R$(Å)          | 2.37(8)         | 2.42(9)         | 2.37(2)         | 2.41(8)         | 2.41(8)         | -              |
|                | $\sigma^2$(Å)   | 0.005           | 0.004           | 0.005           | 0.004           | 0.007           | -              |
| Ge$_{12.5}$As$_{25}$Se$_{62.5}$(0) | N     | 3.91            | 0.08            | 0.21            | 0.81            | 1.19            | -              |
|                | $R$(Å)          | 2.37(5)         | 2.42(7)         | 2.42(5)         | 2.37(4)         | 2.41(9)         | -              |
|                | $\sigma^2$(Å)   | 0.004           | 0.006           | 0.006           | 0.003           | 0.007           | -              |
| Ge$_{15}$As$_{20}$Se$_{65}$(5)  | N     | 3.94            | 0.06            | 0.21            | 0.85            | 0.75            | 0.42           |
|                | $R$(Å)          | 2.37(3)         | 2.42(5)         | 2.42(8)         | 2.36(5)         | 2.42(0)         | 2.37(5)        |
|                | $\sigma^2$(Å)   | 0.007           | 0.004           | 0.004           | 0.002           | 0.007           | 0.002          |
| Ge$_{20}$As$_{10}$Se$_{70}$(+5) | N     | 3.96            | 0.05            | 0.21            | 0.85            | 0.75            | 0.55           |
|                | $R$(Å)          | 2.37(5)         | 2.42(5)         | 2.42(1)         | 2.36(5)         | 2.42(0)         | 2.36(9)        |
|                | $\sigma^2$(Å)   | 0.007           | 0.005           | 0.004           | 0.004           | 0.007           | 0.004          |

An interesting feature should be mentioned here for Ge K-edge transform in the range of 3-4Å, corresponding to the intermediate range information around Ge atoms. As can be seen from the Fig. 1(a), a wide weak peak is shown over this region related to the Ge-Ge distance arising from the edge-sharing GeSe$_{4/2}$ tetrahedra. At first, the position of this peak shifts slightly towards lower R from Se-poor composition to stoichiometric one. Based on the law of Cosines, this change can cause the increase of Ge-Se-Ge bond angle within Ge$_2$Se$_2$ four-fold ring into 102.4(8)°, which approximating the ideal value of 109.4(8)° for regular tetrahedron. As for Se-rich ones, the peaks move back to higher R, suggesting some distortion between layer structure. Due to the presence of Se chains in the structural backbone, an amount of Van der Waals bonds might be expected to spread among the connectivity, exerting an significant influence on the inter-atomic distance and behaving an decrease in density values. 22 In addition, the higher valence ions of like charges in edge-sharing polyhedra will repel each other to minimize the electrostatic potential, which further affects the arrangement of atomic structure.

5. Conclusions

The nearest-neighbor bonding structure of five pieces of ternary Ge-As-Se glasses with same mean coordination number of 2.50 but different chemical compositions have been investigated by their individual K-edges EXAFS spectra. The main conclusions from the present study are as follows.

(i) All Ge-As-Se ternary glasses are 4-3-2 coordinated irrespective of glass chemical compositions.

(ii) The main structure of glasses are supposed to be make up of tetrahedral GeSe$_{4/2}$ and pyramidal AsSe$_{3/2}$ units, accompanied with the additional As or Se molecular clusters dispread among them.

(iii) The coexistent effects of chemical ordering and topological have been proved in this system.

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