Physica B 405 (2010) 4240–4244

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Reverse Monte Carlo simulation of Ge_xSe_{100-x} glasses

A.H. Moharram [a,*], A.M. Abdel-Baset [b]

[a] Faculty of Science, King Abdul Aziz University, Rabigh Campus, P.O. Box 334, Saudia Arabia
[b] Physics Department, Faculty of Science, Assiut University, Assiut 71516, Egypt

ARTICLE INFO

Article history:
Received 7 April 2010
Received in revised form
8 July 2010
Accepted 9 July 2010

Keywords:
X-ray diffraction
Chalcogenide glasses
Reverse Monte Carlo
Short-range order
Medium-range order

ABSTRACT

Amorphous Ge_xSe_{100-x} (with x=10, 20 and 40 at%) alloys were prepared using the melt–quench technique. Two-dimensional Monte Carlo of the total pair distribution functions (MCGR) have been found and used to assemble the three-dimensional atomic configurations using the reverse Monte Carlo (RMC) method. The simulations are useful to compute the partial pair distribution functions $g^{rmc}_{Ge-Ge}(r)$, $g^{rmc}_{Ge-Se}(r)$, $g^{rmc}_{Se-Se}(r)$ and the partial structure factors $S^{rmc}_{Ge-Ge}(r)$, $S^{rmc}_{Ge-Se}(r)$, $S^{rmc}_{Se-Se}(r)$ of the studied glasses. The partial pair distribution functions indicate that the basic building units are $GeSe_4$ and Ge_2Se_6 tetrahedral units in the Se-rich and Ge-rich glasses, respectively. Some of these tetrahedral units are connected by the homopolar units as confirmed by the bond angle distribution functions. The partial structure factors have shown that not only the homopolar Ge–Ge bonds, but also Se–Se bonds are behind the appearance of the first sharp diffraction peak (FSDP) in the total structure factor.

1. Introduction

Chalcogenide glasses present a great potential for application in technological devices, such as optical fibers, memory materials and switching devices, but their use is limited due to several factors. One of them is the difficulty in obtaining information about atomic structures, which define the short-range order (SRO) of the alloy. Although, many kinds of structural studies for amorphous Ge–Se alloys [1–6] have been performed to investigate the short-range order of the system, the glass network structure of these alloys is not yet fully understood.

High-resolution diffraction technique with a wide range of the scattering vector (K) is required for structural studies of the amorphous materials. For example, high-energy X-ray diffraction measurements have some advantages [7]: highly structural information due to the wider range of K, smaller correction terms, and easy to compare with neutron diffraction data because of similar transmission method. Unfortunately, the X-ray source used in the present experiment, CuKα target emits radiation with wavelength λ=1.5418 Å, does not have wide range of the scattering vector. To overcome this problem, two-dimensional Monte Carlo of the total pair distribution function (MCGR) has been found, which is used to assemble three-dimensional atomic configuration using the reverse Monte Carlo (RMC) method.

Some of the structural intermediate-range order (IRO) information can be obtained from the experimental diffraction data. Reverse Monte Carlo (RMC) simulation [8,9] represents, when used carefully, a powerful tool to extract these information. It assembles three-dimensional atomic configurations using experimental diffraction data implicitly in the simulation. The intimate connection between computational and experimental processes means that the better quality, and higher resolution of the experimental data, the more reliable RMC model of a network structure for vitreous materials. The RMC method is considered as an inverse problem in which the experimental data are enforced to build atomic configurations that have the desired structural and electronic properties. The main point is to set up a generalized function containing as much information as possible, and then optimize the function for generating configurations toward exact agreement with the experimental data.

X-ray diffraction study of the glassy Ge_xSe_{1-x} systems [10,11], in a wide concentration range $0 \leq x \leq 0.33$, has demonstrated that besides the well-established SRO information, a pre-peak appeared in the total structure factor $S(K)$ at a scattering vector K of about 1.1 Å^{-1}. The pre-peak, being clear evidence for existence of the intermediate-range order (IRO), showed a systematic decrease in intensity and shifts towards higher K-values with decrease in Ge concentration. A similar variation in the pre-peak of the structure factor with Ge content was also observed using the neutron diffraction measurement [12]. In the present work, the short- and intermediate-range orders (SRO and IRO) for three $Ge_{10}Se_{90}$, $Ge_{20}Se_{80}$ and $Ge_{40}Se_{60}$ glasses have been studied using Monte Carlo of pair distribution (MCGR) and the reverse Monte Carlo (RMC) simulations.

* Corresponding author.
E-mail addresses: mohar200@yahoo.com, amoharram@kau.edu.sa (A.H. Moharram).

0921-4526/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.07.018

2. Reverse Monte Carlo (RMC)

Three-dimensional arrangement of N atoms is placed into a cubic cell with periodic boundary conditions. The atomic number density (ρ) should be the same as the experimental value. The positions of the atoms are chosen randomly. The partial pair distribution function $g_{ij}^{cal}(r)$ can be calculated from the initial configuration [8] by

$$g_{ij}^{cal}(r) = \frac{n_{ij}(r)}{4\pi r^2 dr \rho c_i} \tag{1}$$

where c_i is the concentration of i-type atoms and $n_{ij}(r)$ the number of j-type atoms at a distance between r and $r+dr$ from a central i-type atom, averaged over all atoms as centers. The total pair distribution $g^{cal}(r)$ is calculated from

$$g^{cal}(r) = \frac{1}{\langle f \rangle^2} \sum_{i,j=1}^{m} c_i c_j f_i f_j \left[g_{ij}^{cal}(r) - 1 \right] \tag{2}$$

where m is the number of elements in the sample ($m=2$ for the present work), f_i the atomic scattering factor and $\langle f \rangle = \sum_i c_i f_i(K)$. The deviation χ^2 of the calculated $g^{cal}(r)$ from the experimental, $g^{exp}(r)$, obtained from the MCGR method, can be computed from the expression

$$\chi^2 = \sum_{i=1}^{n} \frac{[g^{cal}(r_i) - g^{\exp}(r_i)]^2}{\sigma^2(r_i)} \tag{3}$$

where n is the number of experimental points and $\sigma^2(r_i)$ the statistical error. Move one atom at random, and recalculate $g^{cal}(r)$ of the new configuration. If χ^2 decreases, the change is accepted, while if it increases, the move is accepted with probability of $\exp(-\Delta\chi^2/2)$ where $\Delta\chi^2$ is the change in χ^2. As the number of accepted atom moves increases, χ^2 will initially decrease until it reaches an equilibrium value. Thus, the atomic configuration corresponding to the equilibrium should be consistent with the experimental functions within the experimental errors. All the results shown in this article are based on the partial and total functions obtained at the equilibrium level. Fourier transformation of the partial pair distribution, $g_{ij}(r)$, gives the partial structure factor

$$S_{ij}(K) = \rho \int_0^\infty 4\pi r^2 (g_{ij}(r) - 1) \frac{\sin Kr}{Kr}\, dr \tag{4}$$

The above function is important for determination of the intermediate-range order parameters and also to specify the bond type responsible for the existence of the FSDP. On the other hand, the short-range order parameters such as the inter-atomic distances, the partial coordination number and the bond angle distribution can be obtained from the $g_{ij}(r)$ functions.

3. Experimental technique

Glassy chalcogenide of Ge_xSe_{100-x} (with $x=10$, 20 and 40 at%) alloys were prepared using the melt–quench method. The glassy nature of the quenched alloys was confirmed by X-ray diffraction technique. X-ray diffraction experiment was done using a Philips diffractometer (PW-1710). The XRD patterns were recorded at 40 kV and 30 mA, with a graphite monochromator, using the CuKα line ($\lambda=1.5418$ Å), with scanning speed of 0.04°/min. The experiment was done in the scattering angle range $4 \le 2\theta \le 115°$ in steps of 0.1°, which corresponds to K-vector range $0.284 \le K \le 6.874$ Å^{-1}. Copper source was chosen for two reasons. Firstly, its characteristic energy is lower than Ge K absorption edge energy. Therefore, the scattering comprises no fluorescence X-rays, and the anomalous terms in the atomic factors of Ge and Se are very small. Secondly, for obtaining the precise data of the pre-peak, the K-resolution is better than that with targets having higher characteristic energies.

4. Results and discussion

The experimental X-ray data of the present three $Ge_{10}Se_{90}$, $Ge_{20}Se_{80}$ and $Ge_{40}Se_{60}$ compositions were analyzed using some computer programs. The first step was to correct the observed X-ray intensities through background subtraction followed by absorption and polarization corrections. From the corrected X-ray intensities, the variations in the total structure factor, $S(K)$, with the scattering vector ($K=4\pi\sin\theta/\lambda$, where θ is half the scattering) can be obtained [13]. Fig. 1 shows the experimental total structure factors, $S(K)$, of the investigated glasses up to $K=6.874$ Å^{-1}. The existence of the first sharp diffraction peak (FSDP) is clear especially for the $Ge_{40}Se_{60}$ glass, which is located at $K=1.0$ Å^{-1}. FSDP is commonly observed in covalently bonded amorphous materials, which implies the presence of intermediate-range order. Its intensity decreases with decrease in Ge content to the point it appears as a shoulder in the $Ge_{10}Se_{90}$ composition. Indeed, not only its height changes with Ge content, but also it is shifted to a higher K-values with decrease in Ge content. The pre-peak is known to be much dependent on Ge–Ge correlations and, to a lesser extent, on Ge–Se correlations [14–16].

In the structural analysis using Fourier transformations [17,18], a modification factor was suggested to reduce the effect of termination data at a finite K_{max}. This factor in turn, while reduces the spurious oscillations, leads to a broadening of the genuine peaks in $g(r)$. To overcome this problem, an inverse method was applied to determine the pair distribution function from the total structure factor, measured by neutron or X-ray diffraction, using a MCGR program [19]. One of its advantages is that a direct estimation of errors in $g(r)$ is possible by repeating the process until getting a minimum deviation of the simulated values from the experimental S(K) ones, as shown in Fig. 1. The $g(r)$ function obtained from the MCGR method does not require integration process or integration limits, which means that considering K_{max} instead of infinity has no effect on the obtained functions [12]. For the present work, the starting value of $g(r)$ is zero below $r < 1.9$ Å and equals one for $r \ge 1.9$ Å. Fig. 2 shows the conventional (solid circles) of the pair distribution functions, $g(r)$, of the investigated Ge_xSe_{100-x} glasses together with the simulated

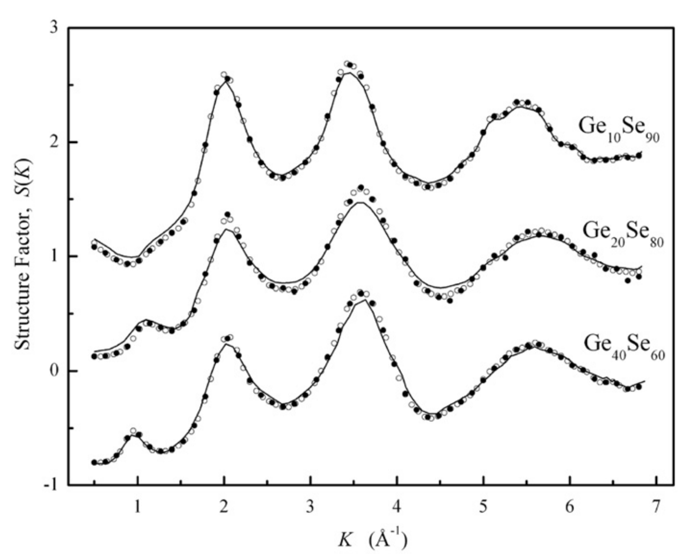

Fig. 1. Experimental X-ray structure factors (●) together with the results of MCGR (○) and RMC (–) simulations of the investigated Ge_xSe_{100-x} glasses.