The local structure of As−Se−S chalcogenide glasses studied by neutron diffraction and Raman scattering

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ABSTRACT

The local structures of amorphous $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$, $As_{33.3}Se_{33.3}S_{33.4}$ chalcogenide glass semiconductors have been studied by neutron diffraction and Raman scattering methods. The neutron diffraction data-sets were modeled by Reverse Monte Carlo (RMC) simulation technique. Several first and second neighbour distances, coordination numbers and bond-angle distributions have been calculated. It is established that the first neighbour atomic distances are overlapping at three characteristic distances, namely the S−S and Se−S are centered at 2.2(5) Å, while the As−S and Se−Se are centered at 2.35 Å, the As−As and As−Se are centered at 2.4(5) Å. The average coordination numbers in $As_{40}Se_{60}$ ($Z_{As} = 3.03$; $Z_{Se} = 2.02$) and $As_{40}Se_{30}S_{30}$ ($Z_{As} = 3$; $Z_{Se} = 2.07$; $Z_S = 2$) compositions were determined and found to be consistent with, "8-N" rule. The slight deviations from this rule is discovered in case of $As_{33.3}Se_{33.3}S_{33.4}$ ($Z_{As} = 3.07$; $Z_{Se} = 2.09$; $Z_S = 1.95$) composition. The main role in the formation of medium range order belongs to Se−Se bonds. It has been identified that the replacement of Se with S atoms causes a slight change in coordination numbers. The similarity of $\theta_{Se−As−Se}$ and $\theta_{As−Se−As}$ bond angle distributions suggest that S atoms have a similar role in the structure formation as Se atoms. The RMC models highlighted a glassy network built-up from $AsSe_3$ trigonal bipyramids, in all binary and ternary samples.

1. Introduction

The chalcogenide glassy semiconductors (CGS) are characterized by unique physical properties. Such materials are transparent in the visible and near IR region of the spectrum, have high photosensitivity and optical nonlinearity. Chemical composition, introduction of impurities, radiation and temperature change their optical refractive index and optical absorption edge. These features allow the chalcogenide glasses for successful applications in the different nano- and optoelectronics devices, i.e. in optical storage devices, planar waveguides, fiber amplifiers, optical switches, lasers etc. [1–3].

The structure of chalcogenide glasses is distinguished by the absence of long range order (strict periodicity in the arrangement of atoms) and the presence of short-range order - the coordination number, the type of atoms surrounding the atom, bond lengths (interatomic distances), bond angles and the medium-range order - the existence of the areas covered by several coordination spheres in which structural elements are located a certain order.

The nature of the short- and medium range order defines the basic physical properties of such materials. According to Gubanov [4] and Mott [5], semiconductors with covalent bonds between atoms, follow the so-called rules of "8-N". Under this rule, semiconductors have a structure in which an atom with N(N ≥ 4) valence electrons forms 8-N bonds, i.e. has 8-N nearest neighbours [6]. These rules are valid for all incoming atoms in the material and are better executed in disordered materials than in the crystals. Changing the chemical composition leads to the fact that every atom of the new structure is able to use all its valence electrons in the formation of bonds with the surrounding atoms or ions, which must be accompanied by a change in the local structure (short- and medium-range order). Thus, by changing the chemical composition, structure and physical properties can be modified.

The detailed study of the local structure, as a function of the chemical composition and the level of doping are necessary for understanding the mechanism of the electronic processes occurring in them and also for establishing methods for controlling parameters of the local structure and thereby influence the electronic processes. Such studies allow to expand the application of CGS materials and also to improve the parameters of the existing devices based on them.

The structure and physical properties of chalcogenide glasses is of great interest. Most of these studies have been devoted to amorphous

As_2Se_3, As_2S_3 and the other binary glassy semiconductors [7–12]. However, studies have shown that compound chalcogenide glasses are promising materials for practical purposes. It is due to the fact that, ternary chalcogenide glasses have more attractive electronic properties. They have a wide area of transparency and high non-linear properties [13].

The present work is devoted to the study of local structure at the level of short- and medium range order in $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{33.3}Se_{33.3}S_{33.4}$ glassy semiconductors. For this purpose the main structural units which form an amorphous matrix and covalent bonds, responsible for medium range order were studied using neutron diffraction and Raman scattering methods [14]. For modeling the structure, Reverse Monte Carlo (RMC) simulations were used, that provide significant information about the local structure of the amorphous matrix. Use of such models determines many of the atomic structural parameters, in particular the total and partial structure factors ($S(Q)$ and $S_{ij}(Q)$), total and partial pair correlation functions ($G(r)$ and $g(r)$), average coordination number and the angle distribution of the chemical bonds. The structure of $As_{40}Se_{60}$ is extensively researched [7,15–18]. S atoms are used for the substitution of the Se atoms in the glass network since the atomic parameters (mass and size) contribute significantly to the modification of the glass structure. In addition, the study of stoichiometric and non-stoichiometric CGS materials containing an excessive concentration of the chalcogen atoms allows us to understand the role of these atoms in the formation of the basic structure.

2. Experimental details

2.1. Sample preparation

The glassy samples with compositions of $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{33.3}Se_{33.3}S_{33.4}$ were synthesized from 5N purity elements by the conventional melt-quenching method. The components of a proper composition were placed in a quartz ampoule, which was evacuated to a residual pressure of 10^{-3} Pa. The synthesis were performed in a rotary furnace as the ampoules were heated up to 950 °C and kept at this temperature for 12 h, the furnace was rotated for homogeneous melting. After finishing the synthesis, the ampoules were pulled out and were quenched in air, part of the samples was powdered for the neutron diffraction studies. Densities of chalcogenide glasses, ρ were calculated using the formula:

$$\rho = \left[\frac{w_0}{(w_0 - w_L)}\right]\rho_L \qquad (1)$$

where w_0 and w_L the weight of the sample in air and in liquid (water) and density of liquid (water) is equal to 1 g/cm^3 at room temperature. The density of $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{33.3}Se_{33.3}S_{33.4}$ glass materials was measured by Archimedes' principle using liquid (water). The accuracy was better than ± 0.02 g/cm^3.

2.2. Neutron diffraction measurements

Neutron diffraction (ND) data have been obtained on the 2-axis 'PSD' monochromatic neutron diffractometer (wavelength was $\lambda_0 = 1.068$ Å; $Q = 0.45$–9.8 Å^{-1}) at the 10 MW Budapest Research Reactor [19], with thermal neutrons. The powder specimen of about 3–4 g/each was placed in cylindrical vanadium container of 8 mm diameter, 50 mm height and 0.07 mm wall thickness. Neutron diffraction has been measured at room temperature, each acquisition lasted ~24 h to get a good signal to noise ratio. The raw data was corrected and normalized for detector dead time, background, absorption and variations in the detector solid angle. The structure factors, $S(Q)$'s were evaluated from the raw experimental data, using the program package available at the facility.

2.3. Raman scattering experiments

Amorphous films of all compositions and thicknesses ~10 μm were prepared by thermal evaporation with the deposition rate 0.4–0.5 μm/min on glass substrates in vacuum under the pressure 10^{-4} Torr. Raman studies were carried out on three-dimensional Confocal Laser Microspectrograph (Tubitak, Turkey). The excitation source was He-Ne laser (25 mW) operating at a wavelength of 632.8 nm. Cross-section radius of laser beam incident on the film sample was ~1 μm. Exposure time was 1–90 s.

3. Reverse Monte Carlo simulations

The experimental diffraction data was treated by the RMC simulations in order to get structural information about the possible atomic configurations. The software package RMC^{++} was used to simulate the experimental $S(Q)$ data [20]. The squared difference between experimental and calculated $S(Q)$ data from a 3-dimensional atomic configuration is minimized. The RMC algorithm calculates the one-dimensional partial atomic pair correlation functions $g_{ij}(r)$, which were inverse Fourier transformed to calculate the partial structure factors, $S_{ij}(Q)$:

$$S_{ij}(Q) = 1 + \frac{4\pi\rho_0}{Q}\int_0^{r_{max}} r[g_{ij}(r) - 1]\sin Qr dr \qquad (2)$$

where r_{max} is the half edge-length of the simulation box of the RMC calculations. The actual computer configuration was modified by moving the atoms randomly until the calculated $S(Q)$ agrees with the experimental data within the experimental error. Moves were only accepted if they were in accordance with certain constraints (see below those ones which were applied in this work). In multicomponent samples, the total pair function, $G(r)$ is given by the sum of the partial pair correlation functions ($g_{ij}(r)$) - these functions give the probability density for an atom of the i species to have a neighbour of the j species at a given distance r, $g_{ij}(r)$ (denoted as $g(r)$ in rest of the article):

$$G(r) = \sum_i \sum_j w_{ij} g_{ij(r)} \qquad (3)$$

with w_{ij} the weighting factors,

$$w_{ij}^{ND} = \frac{c_i c_j b_i b_j}{\left[\sum_{i,j}^k c_i b_j\right]^2} \qquad (4)$$

where c_i, c_j are the molar fractions of the components, b_i, b_j the coherent neutron scattering amplitudes. As an RMC starting model, for each composition a disordered atomic configuration was built up with a simulation box containing 10,000 atoms. In the RMC simulation procedure the atomic densities of 0.0355, 0.035 and 0.034 atoms/Å^3 and half-box lengths of 34.668, 32.931 and 32.931 Å were taken for the $As_{40}Se_{60}$, $As_{40}Se_{30}S_{30}$ and $As_{33.3}Se_{33.3}S_{33.4}$ glasses, respectively. Two types of constraints were used; namely the minimum interatomic distances between atomic pairs (cut-off distances) and connectivity constraints. Several RMC runs were carried out by modifying the cut-off distances and the results of each run were carefully checked to obtain reliable data for each $g(r)$ and coordination number distributions, $Z(n)$. The partial atomic pair correlations, $g(r)$ were determined from RMC simulations with a good reproducibility and acceptable statistics.

4. Results

4.1. Neutron diffraction and RMC results

The good agreement between the experimental and calculated structure factors ($S(Q)$) indicate that the modeling is able to reproduce the differences between the compositions. Fig. 1 shows the total