Semiconductor Physics, Quantum Electronics & Optoelectronics, 2016. V. 19, N 2. P. 205-207.
doi: 10.15407/spqeo19.02.205

PACS 61.05.cp, 78.30.Am, 78.30.Ly

Structural properties of chalcogenide glasses As_2Se_3 doped with manganese

O.P. Paiuk[1*], L.O. Revutska[2], A.V. Stronski[1], A.Yo. Gudymenko[1], H.V. Stanchu[1], A.A. Gubanova[3], Ts.A. Kryskov[3]
[1]*V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 41, Prospect Nauky, 03680 Kyiv, Ukraine*
[2]*National Technical University of Ukraine "KPI", Kyiv, Ukraine*
[3]*Kamianets-Podilsky National University, Kamianets-Podilsky, Ukraine*
**E-mail: paiuk@ua.fm*

Abstract. The paper presents the results of studying structural properties inherent to chalcogenide glasses doped with manganese. Investigations of the structure were carried out using Raman spectroscopy and X-ray diffraction. The function of radial distribution of atomic density and Raman spectra have been obtained and analyzed.

Keywords: chalcogenide glass, function of radial distribution of atomic density, short-range order.

Manuscript received 12.01.16; revised version received 05.04.16; accepted for publication 08.06.16; published online 06.07.16.

1. Introduction

Chalcogenide glasses (ChGs) are typical representatives of non-oxide glasses. These glassy alloys consist of elements belonging to the fifth (As, Sb) or fourth (Si, Ge) groups in Periodic Table and chalcogens (S, Se, Te). Distinctive features of these glasses are as follows: a wide range of transparency in the infrared region of the spectrum and high values of linear and nonlinear refractive indexes. ChGs have great potential for many applications including security screening, pharmaceutical, biological or medical science analysis, fabrication of optical elements, sensor and information technology and environmental monitoring, *etc*.

Special interest for their applications is related with chalcogenide glasses doped with optically active rare-earth and transition metal ions, because they alter electrical, thermophysical, mechanical, magnetic and optical properties of the host material due to structural and electronic changes of the glass network [1-4].

In this work, the influence of transition element (Mn) doping on structural properties of As_2Se_3 chalcogenide glass was studied.

2. Experiments and methods

As_2Se_3 glasses with the manganese concentrations 2 and 5 wt.% were prepared by the melt-quenching technique. The amorphous nature of the samples was verified at room temperature by X-ray diffraction (XRD) technique using ARL X'tra (Thermo scientific) diffractometer equipped with a copper tube. The voltage on the tube amounted to 45 kV, current – 30 mA. The scattering intensities were measured over an angular range of $2° \leq \theta \leq 140°$ with a step-size of $\Delta(\theta) = 0.2°$ and a count time of 5 s per step.

Room temperature Raman spectra were recorded using Fourier spectrophotometer Bruker IFS-55 Equinox with FRA-106 attachment (with measurement step 1 cm^{-1}). Nd:YAG laser light at 1.06 µm wavelength was used for excitation.

3. Results and discussion

3.1. XRD experiments

The experimental XRD profiles (Fig. 1) confirm the amorphous nature of the chalcogenide glass, which is a disordered system without long-range order and three-dimensional periodicity. The short-range order of the disordered system can be described with a radial distribution function of the atomic density (RDF) [5-9]. RDF is a spherically symmetric function with several peaks corresponding to the nearest neighbors, and allows to find the interatomic distance *r*.

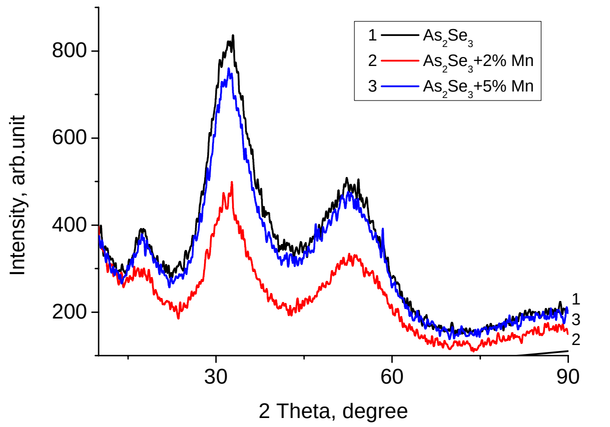


Fig. 1. The angular dependence of the X-rays scattered intensity for Mn doped As_2Se_3.

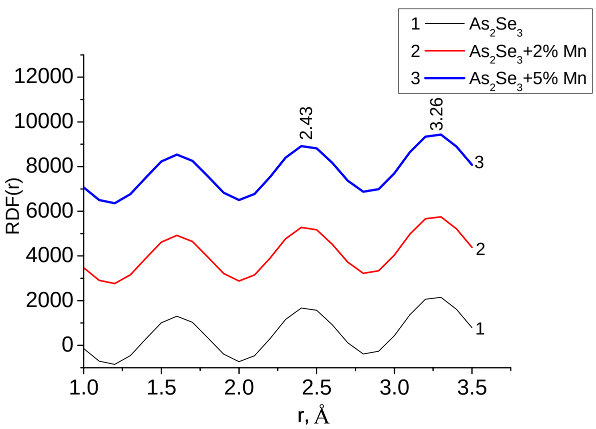


Fig. 2. The RDF profiles for Mn doped As_2Se_3 with Mn concentration (0, 2 and 5%) (the plots are shifted along the y-axis for clarity).

The RDF method is based on the dependence between the radial distribution function of atomic density $\rho(r)$ and the intensity of coherent X-ray scattering. In the case of monoatomic system, this relationship is described as follows (1):

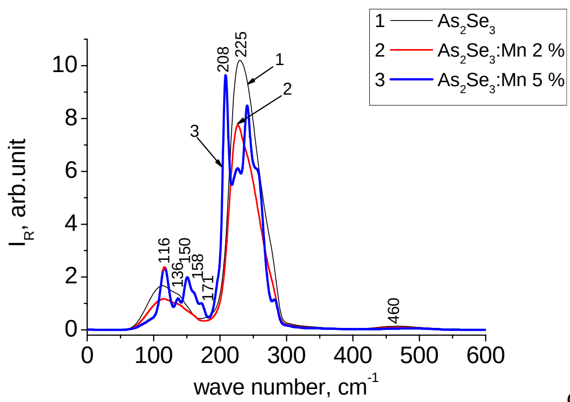
$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^\infty s\cdot i(s)\cdot \sin(sr)ds \quad (1)$$

where r is the interatomic distance, ρ_0 is the average atomic density, s is the magnitude of scattering vector and $i(s)$ is the intensity of coherent X-ray scattering.

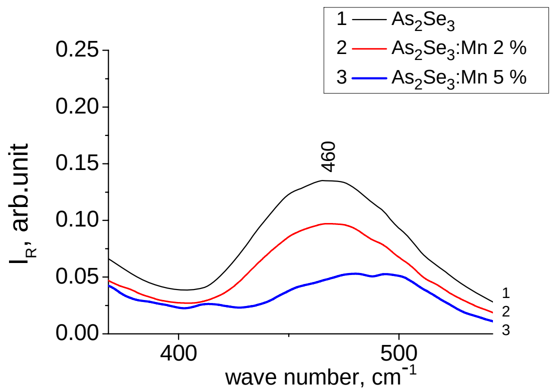
In Fig. 2, we demonstrate the calculated RDF profiles for Mn doped As_2Se_3 samples with the Mn concentration 0, 2 and 5%. As can be seen, addition of manganese does not significantly affect the structure of RDF profile. Also, the peaks positions of the RDF were not changed after the Mn introduction.

3.2. Fourier Raman spectra

From Fourier Raman spectra, information (Fig. 3a) on the structural changes in As–Se glasses doped with transition metals was obtained. Introduction of these dopants leads to the concentration increase of non-stoichiometric molecular fragments.



a)



b)

Fig. 3. *a* – Raman spectrum of As_2Se_3 manganese doped in different concentrations; *b* – enlarged fragment of the Raman spectrum at 460 cm^{-1}.

Introduction of manganese leads to the intensity increase 112, 138, 148, 158, 171, 180 cm^{-1} bands corresponding of non-stoichiometric molecular fragments containing homopolar As-As bonds and decreasing intensity of 460 cm^{-1} band (Fig. 3b) corresponding of Se-Se bonds [10]. The most intense bands at 208, 225 cm^{-1} Raman spectra of As_2Se_3 glasses within the molecular approach may be assigned to symmetric and antisymmetric vibrations of $AsSe_3$ structural units.

The main feature of Raman spectra after introduction of manganese into As_2Se_3 glass matrix is in the change of relative concentration of the main and non-stoichiometric structural elements typical for As_2Se_3 glasses.

4. Conclusions

Thus, the performed studies have shown that the introduction of transition metals (*e.g.*, manganese) doesn't substantially affect the positions of the first coordination sphere radii. Introduction of manganese leads to increase of the relative intensity of the bands corresponding to non-stoichiometric molecular fragments with homopolar As-As bonds and decreasing intensity of 460 cm^{-1} corresponding to Se-Se bonds.

Acknowledgements

The research was supported by the FP-7 SECURE-R21 project.

References

1. M.S. Iovu, S.D. Shutov, A.M. Andriesh et al., Spectroscopic studies of bulk As_2S_3 glasses and amorphous films doped with Dy, Sm and Mn // *J. Optoelectron. Adv. Mater.* **3**(2), p. 443-454 (2001).
2. V. Trnovcova, I. Frumar, D. Lezal, Influence of doping on physical properties of vitreous As_2Se_3 // *J. Non-Cryst. Solids*, **353**, p. 1311-1314 (2007).
3. A. Stronski, O. Paiuk, A. Gudymenko et al., Effect of doping by transitional elements on properties of chalcogenide glasses // *Ceram. Intern.* **41**, p. 7543-7548 (2015).
4. A.V. Stronski, M. Vlcek, A.I. Stetsun, A. Sklenar, P.E. Shepeliavyi, Raman spectra of Ag- and Cu-photo-doped $As_{40}S_{60-x}Se_x$ films // *J. Non-Cryst. Solids*, **270**, p. 129-136 (2000).
5. A.F. Skryshevsky, *Structural Analysis of Liquids and Amorphous Solids*. Moscow, Vysshaya shkola, 1980 (in Russian).
6. B.K. Weinstein, The theory of the method of radial distribution // *Crystallography*, **1**, p. 29-37 (1957).
7. A. Feltz, *Amorphous Inorganic Materials and Glasses*. VCH, Weinheim, Germany, 1993.
8. Y.G. Poltavtsev, V.M. Pozdnyakov, V.P. Rubtsov, X-ray diffraction studies of the structure and glassy As_2Se_3 and As_2S_3, X-ray studies of the structure and glassy As_2Se_3 and As_2S_3 // *Ukr. J. Phys.* **18**, p. 915-918 (1973).
9. E.M. Moroz, X-ray diffraction structure diagnostics of nanomaterial // *Russ. Chem. Rev.* **80**(4), p. 315-334 (2011).
10. E. Venger, A. Melnichuk, A. Stronski, *Photo-stimulated Processes in Vitreous Chalcogenide Semiconductors and Their Applications.* Kiev, Akademperiodika, 2007 (in Russian).