

Peculiarities of Raman scattering belong to As-Se, As-Se-Te chalcogenide glasses and pair-partial correlation function and their 3D-atomic configuration

R.I. Alekberov^{1*}, A.I. Isayev¹, S.I. Mekhtiyeva¹, Margit Fabián^{2,3}

¹*Institute of Physics of Azerbaijan National Academy of Sciences, 131 H. Javid ave., Baku AZ1143, Azerbaijan*

²*Wigner Research Centre for Physics, H-1525 Budapest P.O.B. 49, Hungary*

³*Centre for Energy Research, H-1525 Budapest P.O.B. 49, Hungary*
e-mail: rahim-14@mail.ru

Abstract

Maximum frequencies of $223 \pm 0.4 \text{ cm}^{-1}$ and $176 \pm 0.4 \text{ cm}^{-1}$ observed in the spectrum is related to the main structural element AsSe_3 and vibration modes of the structural elements As_2Te_3 . The second peaks observed in the radial distribution of pair partial correlation function is associated with the correlations between the pyramidal structural elements $\text{AsSe}_{3/2}$ and $\text{AsTe}_{3/2}$. As a result of the description of the local structure of the substances $\text{As}_{40}\text{Se}_{60}$, $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ was confirmed presence of the most various configurations in 3D-atomic or molecular configuration by modeling of RMC.

Keywords: chalcogenide glasses, correlation function, raman scattering, atomic configuration, local structure.

Received: 15 november 2021

Accepted: 10 december 2021

Published: 27 december 2021

1. Introduction

Studies show that As-S-Se and As-Se-Te glasses have low phonon interaction energy, high chemical resistance the higher transparency in the near-infrared region of the spectrum and the wide range of optical refractive index than binary As-S, As_2Se_3 , As_2S_3 , As_2Te_3 binary chalcogenides[1], which increase their application prospects for fiber optics [2]. That is, despite the development of fibers based on binary chalcogenide As_2S_3 , As_2Se_3 , GeS_2 , GeSe_2 glasses with minimal optical loss and relatively wide optical transparency, their tendency to crystallization, relatively superior phonon interaction (compared to chalcogenide glasses with three or more complex components), low glass transition temperature and chemical resistance, poor nonlinear optical properties limits the possibility of successful application. It is known that the electronic properties of binary and complex component chalcogenide glasses a lot depend on their local structural properties.

The main purpose of this article is to reveal the relationship between the properties of Raman scattering belong to As-Se, As-Se-Te chalcogenide glasses, the pair-partial correlation function and 3D-atomic configuration (molecular configuration).

2. Experiments

The glassy samples with compositions of $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ 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. The density of $\text{As}_{40}\text{Se}_{60}$ and $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ glass materials was measured by Archimedes' principle using liquid (water). The accuracy was better than ± 0.02 g/cm³. Amorphous films of all compositions and thicknesses ~ 10 μm were prepared by thermal evaporation with the deposition rate 0.4–0.5 $\mu\text{m}/\text{min}$ 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. Results and discussion

Figure 1 shows the Raman scattering spectrum of $\text{As}_{40}\text{Se}_{60}$, $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ chalcogenide glass compositions. As a result of changes in the chemical composition, the spectra of raman scattering of the studied substances undergo significant changes.

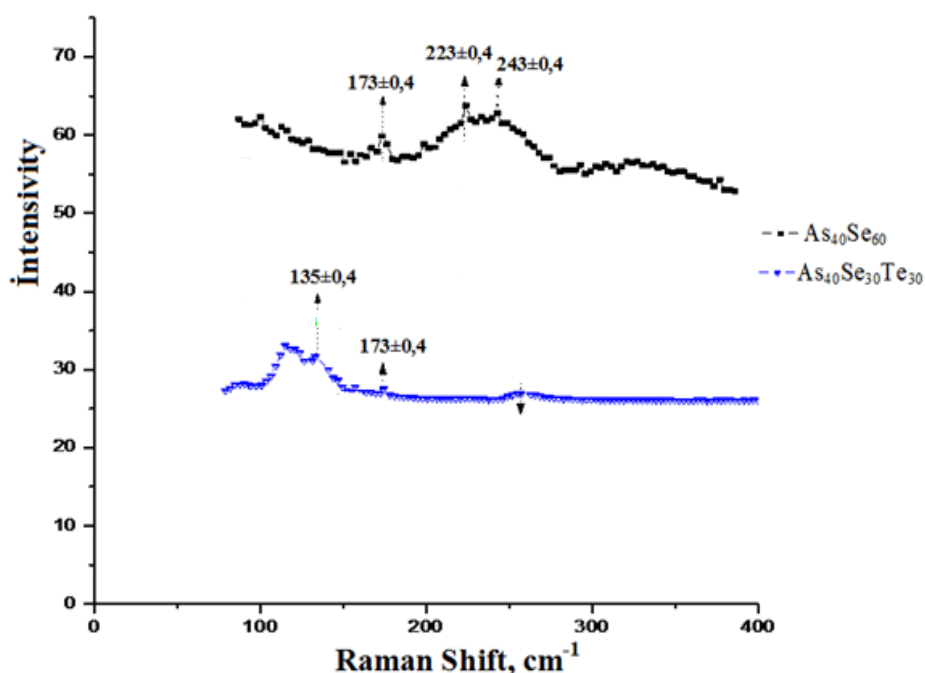


Figure 1. Raman scattering spectrum of $\text{As}_{40}\text{Se}_{60}$, $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ chalcogenide glass compositions.

The Raman spectrum belonging to $\text{As}_{40}\text{Se}_{60}$ has a scattering band covering the frequency range $195 \pm 0.4 \div 295 \pm 0.4$ cm^{-1} and peak frequency of 223 ± 0.4 cm^{-1} belonging to the main structural element AsSe_3 is observed, which forms an amorphous matrix of the substance. Relatively weak peaks in the frequency range $238 \pm 0.4 \div 258 \pm 0.4$ cm^{-1} of the scattering band in the spectrum are associated with annular and chain selenium molecules [3]. The

raman spectrum of $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ have scattering bands with frequencies ranging from $100 \pm 0.4 \div 160 \pm 0.4 \text{ cm}^{-1}$ and have maximum with frequencies 110 ± 0.4 ; 136 ± 0.4 ; 159 ± 0.4 ; 176 ± 0.4 ; $258 \pm 0.4 \text{ cm}^{-1}$. The maximum frequency of $176 \pm 0.4 \text{ cm}^{-1}$ observed in the spectrum is related to vibration modes of the structural elements As_2Te_3 [4].

In Figure 2 second peaks observed in the radial distribution of pair partial correlation function is associated with the correlations between the pyramidal structural elements $\text{AsSe}_{3/2}$ and $\text{AsTe}_{3/2}$. This result shows that the intensity of FSDP in all compounds depends on the atomic mass of chalcogen and more dependent on cation-cation bonds.

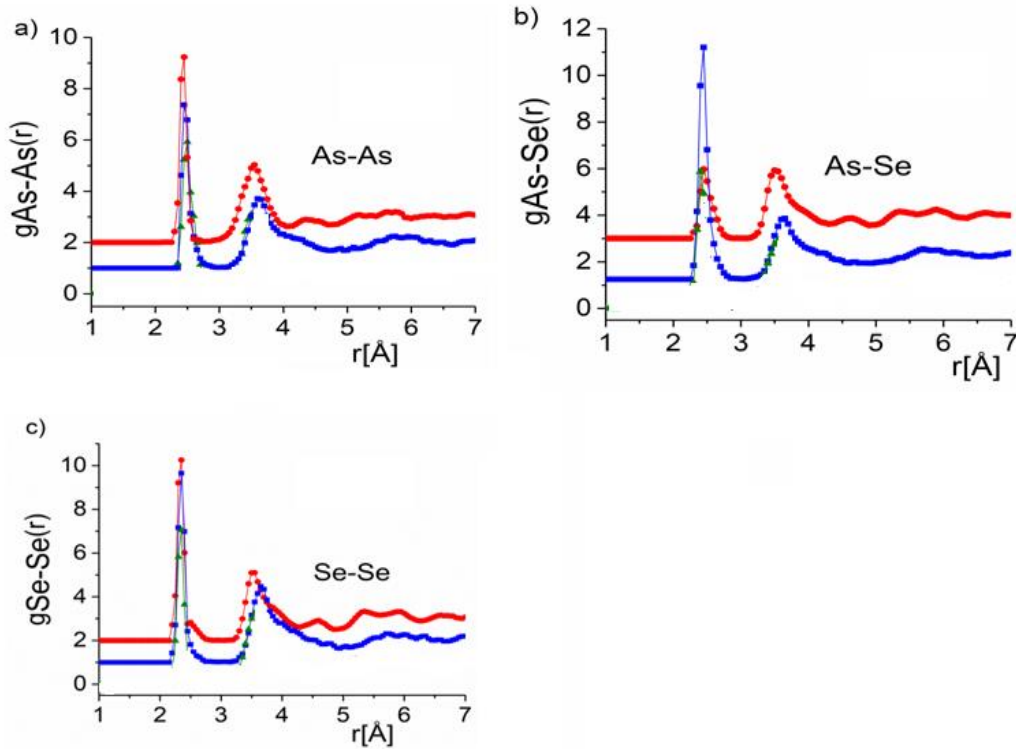


Figure 2. Pair-partial correlation functions: $g_{\text{As-As}}(r)$ (a), $g_{\text{As-Se}}(r)$ (b) and $g_{\text{Se-Se}}(r)$ (c): red line are belong to $\text{As}_{40}\text{Se}_{60}$ and blue line to $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$.

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 [5]. As an RMC starting model, for each composition a disordered atomic configuration was built up with a simulation box containing 5000 atoms [6]. Initially, a maximum step of random motion of 0.2 \AA was selected in the modeling box to obtain the best distribution view in the cubic configuration.

Figure 3 shows 3D atomic or molecular configuration descriptions of $\text{As}_{40}\text{Se}_{60}$, $\text{As}_{40}\text{Te}_{60}$ and $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ chalcogenide glass compositions. Comparison of the results of Raman scattering (Figure 1) and partial pair-correlation functions (Figure 2) and image of their inter-atomic correlations in 3D-atomic or molecular configuration with Reverse Monte-Carlo modeling is allowed to get a broad about near range order (NRO) and medium range order (MRO) of studied $\text{As}_{40}\text{Se}_{60}$, $\text{As}_{40}\text{Te}_{60}$ and $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$.

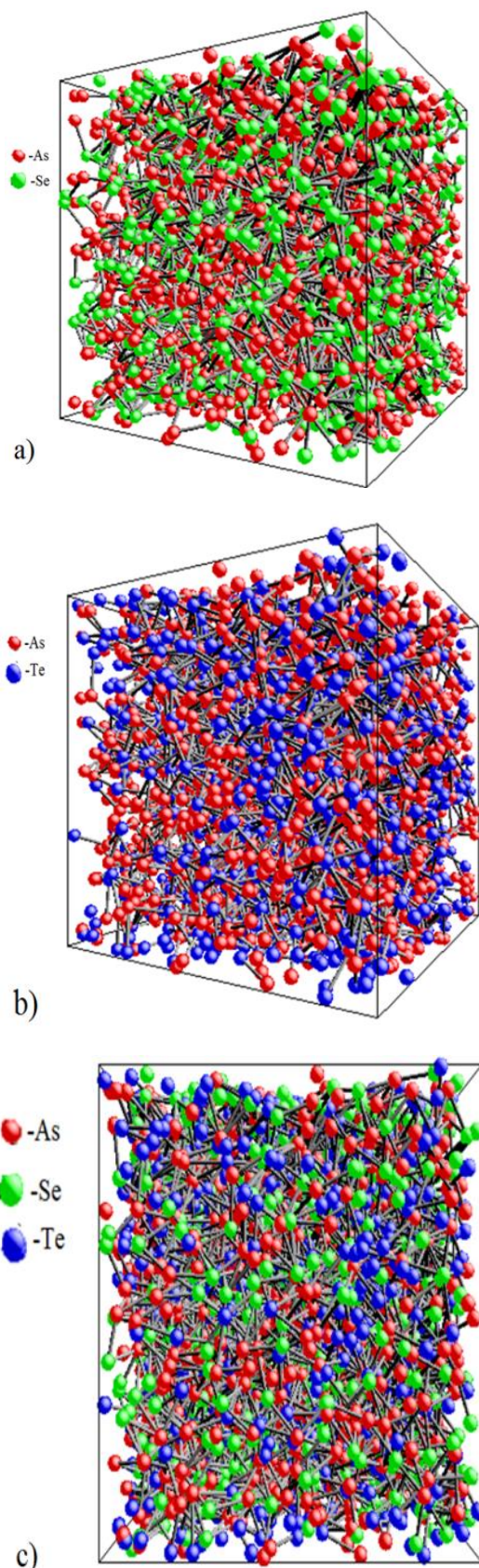


Figure 3. 3D-atomic or molecular configuration images of substances $\text{As}_{40}\text{Se}_{60}$ (a), $\text{As}_{40}\text{Te}_{60}$ (b), $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ (c) built with reverse Monte Carlo modeling.

As shown from Figure 1 the maximum frequency of $176 \pm 0.4 \text{ cm}^{-1}$ observed in the Raman scattering spectrum of tellurium-containing samples was associated with vibration

modes of the structural elements As_2Te_3 [4]. Many authors [7] shows that maximum observed at frequency values of about $195 \pm 0.4 \text{ cm}^{-1}$ mainly corresponds to $\text{AsTe}_{3/2}$ -structural elements. The scattering band corresponding to a maximum of 238 ± 0.4 – $239 \pm 0.4 \text{ cm}^{-1}$ and $241 \pm 0.4 \text{ cm}^{-1}$ is considered to belong to vibration modes of the chaotically located –Se – Se – Se– bonds [4, 3, 8]. On the other hand, the observed features of the partial correlation functions unequivocally prove that the correlations Se-Se and As-Se and As-Te play a decisive role in the formation of MRO, which is reflected in 3D-atomic or molecular configuration images of substances $\text{As}_{40}\text{Se}_{60}$ (a), $\text{As}_{40}\text{Te}_{60}$ (b). Also the observation maximum of 110 and 136 cm^{-1} frequencies in the Raman spectrum belong to $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ (Figure 1) is associated with asymmetric valence modes of the Se–As–Te chain included in the amorphous matrix [4]. As a result of the description of the local structure of the substance $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ is confirmed by the presence of the most various configurations of these modes in 3D-atomic or molecular configuration by modeling of RMC (Figure 3(c)).

4. Conclusion

The observed features of the partial correlation functions unequivocally prove that the correlations Se-Se and As-Se and As-Te play a decisive role in the formation of medium range order (MRO) The second peaks observed in the radial distribution of pair partial correlation function is associated with the correlations between the pyramidal structural elements $\text{AsSe}_{3/2}$ and $\text{AsTe}_{3/2}$. As a result of the description of the local structure of the substances $\text{As}_{40}\text{Se}_{60}$, $\text{As}_{40}\text{Se}_{30}\text{Te}_{30}$ was confirmed presence of the most various configurations in 3D-atomic or molecular configuration by modeling of RMC.

References

1. A.I. Isayev, S.I. Mekhtiyeva, R.I. Alekperov, N.Z. Jalilov, Ya.G. Gasanov, *Journal of Non-Oxide Glasses* **1**(2) (2009) 113-120.
2. R.I. Alekberov, A.I. Isayev, S.I. Mekhtiyeva, M. Fábíán, *Physica B: Condensed Matter* **550**(1) (2018) 367-375.
3. G. Lucovsky, R.M. Martin, *J. Non-Cryst.Solids* **8**(10) (1972) 190.
4. R.I. Alekberov, S.I. Mekhtiyeva, G.A. Isayeva, A.I. Isayev, *PTS* **48**(6) (2014) 823-826.
5. R.L. McGreevy, L. Pusztai, *Mol. Simul.* **1** (1988) 359–367.
6. R.I. Alekberov, S.I. Mekhtiyeva, A.I. Isayev, M. Fabian, *J. Non - Crystalline Solids* **470**(15) (2017) 152-159.
7. D. Brandová, R. Svoboda, M. Liška, J. Málek, D. Brandová, *Journal of Non-Crystalline Solids* **475** (2017) 121-128.
8. W.Y. Li, S. Seal, C. Rivero, *Journal of Applied Physics* **98** (2005) 053503-053514.