Molecular like structural units in sulfur enriched amorphous As-S-Ge alloys

D. Tsiulyanu[1], M. Ciobanu[1*], S.A. Kozyukhin[2], E. Krivogina[2]

[1]Department of Physics, Technical University, Chisinau 2060, Moldova [2]Kurnakov Insitute of General and Inorganic Chemistry RAS, 31119991, Moscow, Russia

[*]*Corresponding author: ciobmarina@gmail.com*

The X- ray diffraction (XRD) and far infrared (IR) transmission spectra of sulfur enriched amorphous As-S-Ge alloys along the tie – line $(GeS_4)_x(AsS_3)_{1-x}$ have been studied with respect to material composition. It is shown that XRD patterns exhibit broad halos, which are typical for the glassy state but the IR vibrational spectra exhibit two oscillatory modes at 310 cm^{-1} and 374 cm^{-1} that correspond to A - S bonds in pyramidal $AsS_{3/2}$ structural units and to Ge-S bonds in tetrahedral $GeS_{4/2}$ structural units respectively. Increasing of the Ge content, results in increasing of the high - frequency mode intensity, but the low-frequency mode intensity decreases, so that in GeS_4 only the high-frequency mode at 374 cm^{-1} can be observed. On the other hand, the X-ray diffraction curves comprise so called first sharp diffraction peak (FSDP) [1], the position and intensity of which evidently depend on the glass composition. As FSDP in amorphous materials is usually ascribed to the existence of some correlated domains with size of 2−3 nm [2] we have carefully recorded and analyzed the position and parameters of the FSDP and their dependence on composition of examined amorphous materials. Although the FSDP peaks for some examined materials merge into shoulders, it was clearly observed that as a whole their parameters i.e., position, width and intensity strongly depend on glass composition. Therefore additionally, the density of the synthesized materials has been determined via method of hydrostatic weighing in toluene. The measured values of density were used to computer some basic physical parameters, such as molar volume, average atomic volume and compactness of the amorphous structure and their dependence on material composition. Comparison of these basic parameters with parameters of FSDP made us conclude that the correlated domains in sulfur enriched amorphous As-S-Ge alloys are nothing more than molecular- like $AsS_{5/2}$ structural units bonded in chains via bridges from elemental sulfur. Increasing of germanium concentration leads to reduction of sulfur chains of bridge to only two atoms that transforms the glass structure into three - dimensional one, consisting of S:$AsS_{3/2}$ and S: $GeS_{4/2}$ molecular – like structural units.

[1]. A.A. Vaipolin, E.A.Porai-Koshits. Structural models of glasses and the structures of crystalline chalcogenides // Sov. Phys.- Solid State – 1963. – 5. – p. 497 – 500.

[2]. K.Tanaka, K.Shimakawa. Amorphous Chalcogenide Semiconductors and Related Materials// Springer – 2011. – p. 29 – 48.