

# MOLECULAR LIKE STRUCTURAL UNITS IN SULFUR ENRICHED AMORPHOUS As-S-Ge ALLOYS

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**INTRODUCTION:** The existence of an ordering of atoms in chalcogenide glasses, at distances that exceed the sphere of the first neighbors, initially named as medium – range order (MRO) [1], has been known for a long time. Its nature and features have been discussed along the years in a number of extensive reviews, which contributed to develop and adjust the viable models of the chalcogenide glass structure.

## EXPERIMENTAL PROCEDURES:

The glassy alloys were prepared by melt-quenching method of pure (99,999%) As, S and Ge in quartz ampoules, evacuated up to  $5 \cdot 10^{-5}$  Torr. Seven compositions, listed in Table I in the form of  $(\text{GeS}_4)_x(\text{AsS}_3)_{1-x}$  alongside with the atomic percentage of elemental components, have been synthesized along the examined compositional section. The density  $\rho$  of the synthesized glassy materials (Table I) was determined via hydrostatic weighing in toluene with accuracy  $\pm 0,2\%$ . Structural investigations were carried out by the X – ray analyses using the Bruker D8 Advance (Bruker, Germany) diffractometer with  $\text{CuK}\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$  (reflection geometry).

Nr.	Composition [x]	As, at. %	S, at. %	Ge, at. %	Density, $\rho$ (kg/m <sup>3</sup> )	D, [nm]	d, [Å]
1	0	25	75	0	2678	2,015	4,67
2	0.17	20	76	4	2687	1,868	4,64
3	0.33	15,3	77	7,7	2618	1,193	4,34
4	0.5	11,1	77.8	11	2574	1,248	4,38
5	0.67	7,1	78.6	14,3	2545	1,363	4,60
6	0.83	3,5	79.3	17,2	2486	1,913	5,30
7	1.00	0	80	20	2455	1,895	5,37
8	$\text{As}_2\text{S}_3$	40	60	0	3160	1,261	4,47

## RESULTS:

XRD patterns (Fig. 1a) exhibit broad halos, which are typical for the glassy state but the IR vibrational spectra (Fig. 2) exhibit two oscillatory modes at  $310 \text{ cm}^{-1}$  and  $374 \text{ cm}^{-1}$  that correspond to A - S bonds in pyramidal  $\text{AsS}_3/2$  structural units and to Ge-S bonds in tetrahedral  $\text{GeS}_4/2$  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  $\text{GeS}_4$  only the high-frequency mode at  $374 \text{ cm}^{-1}$  can be observed.

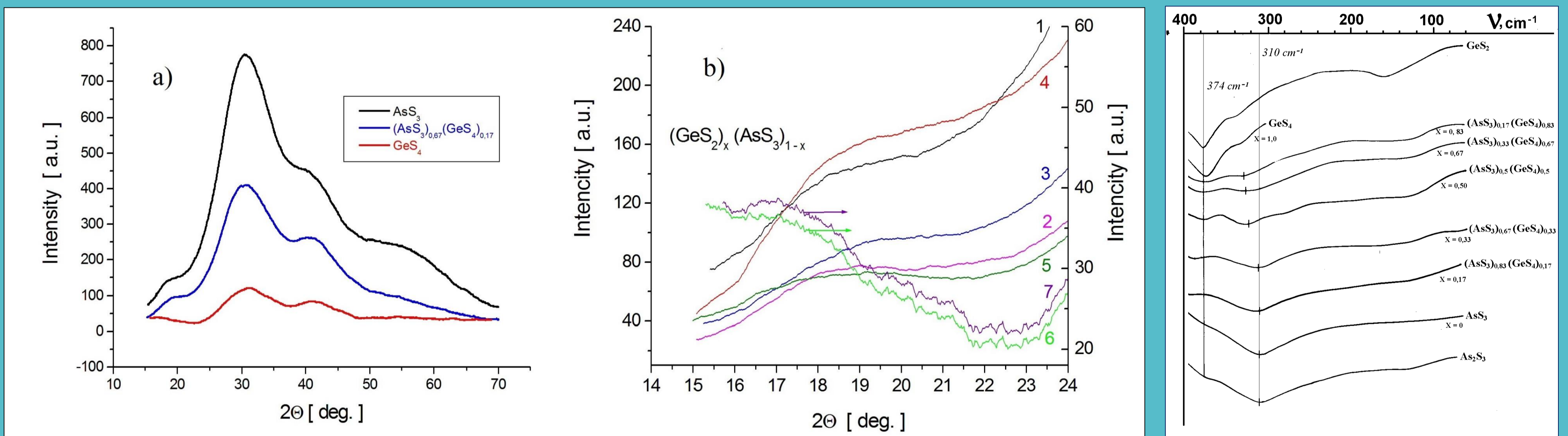


Figure 1. (a) X-ray diffraction patterns of bulk glasses of the pseudo-binary system  $\text{As}_2\text{S}_3 - \text{GeS}_4$ , (b) first sharp diffraction peak (FSDP), the numbers of the curves correspond to compositions indicated in Table I.

Fig 2. Far infrared transmission spectra of  $\text{As}_2\text{S}_3$ ,  $\text{GeS}_4$  and ternary  $(\text{GeS}_4)_x(\text{AsS}_3)_{1-x}$

On the other hand, the X-ray diffraction curves comprise so called first sharp diffraction peak (FSDP), the position and intensity of which evidently depend on the glass composition (Fig. 1b). As FSDP in amorphous materials is usually ascribed to the existence of some correlated domains with size of 2–3 nm we have carefully recorded and analyzed the position of the FSDP and its dependence on composition of examined amorphous materials (Fig. 3). From this figures can be clearly derived a maximum of the diffraction angle is clearly derived for glasses comprising about 7-8 at.% Ge that is composition  $(\text{GeS}_4)_{0,33}(\text{AsS}_3)_{0,67}$ . At the same time, the glass density (Fig. 4), by substitution of As atoms with Ge ones at first increases, but after reaching a weak maximum around  $x = 0,17$  (more similar to a shoulder) nearly linearly decreases, indicating the lack of an evident correlation to any evaluated above FSDP parameters. Providing the Bragg equation to the peak position, it can be obtained the structural period, i.e. inner distance between domains (d) but using Scherrer equation the correlated domain size has been assessed. The relevant computed results are given in Table I. It is seen that the domain's size changes not monotonically at substitution of As atoms with Ge ones.

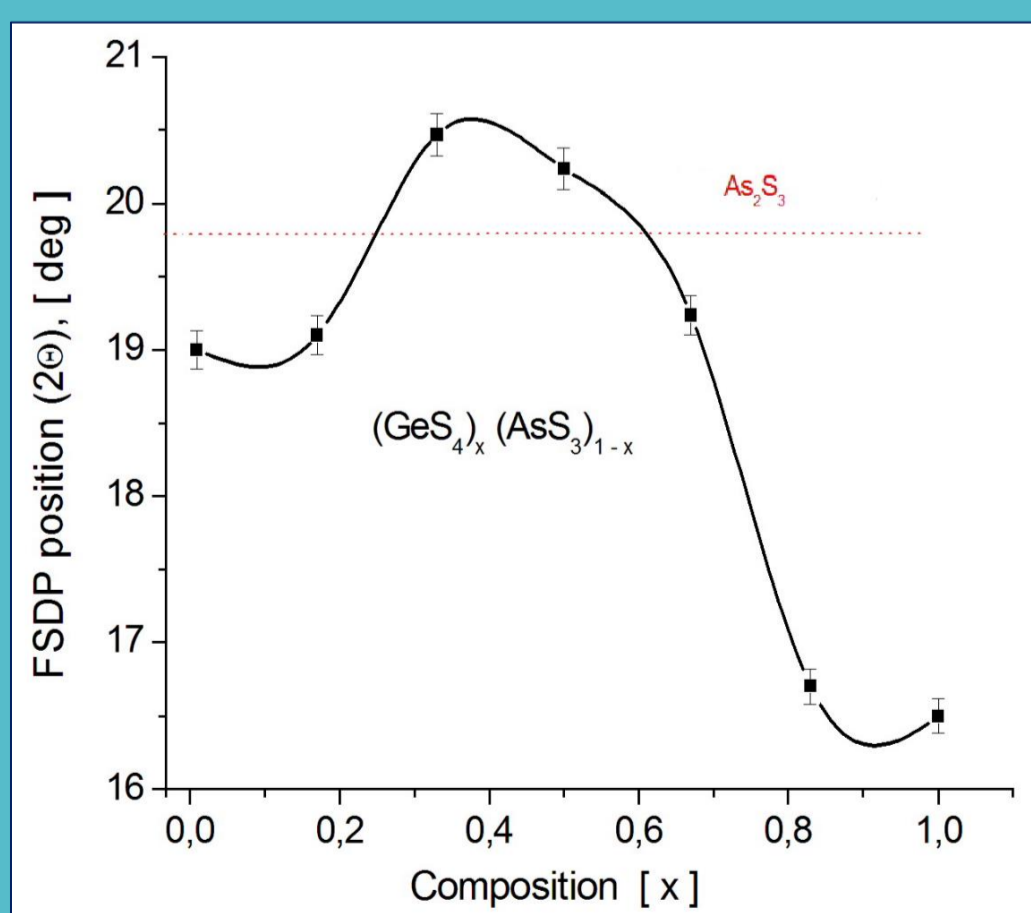


Fig.3. FSDP position versus glass composition

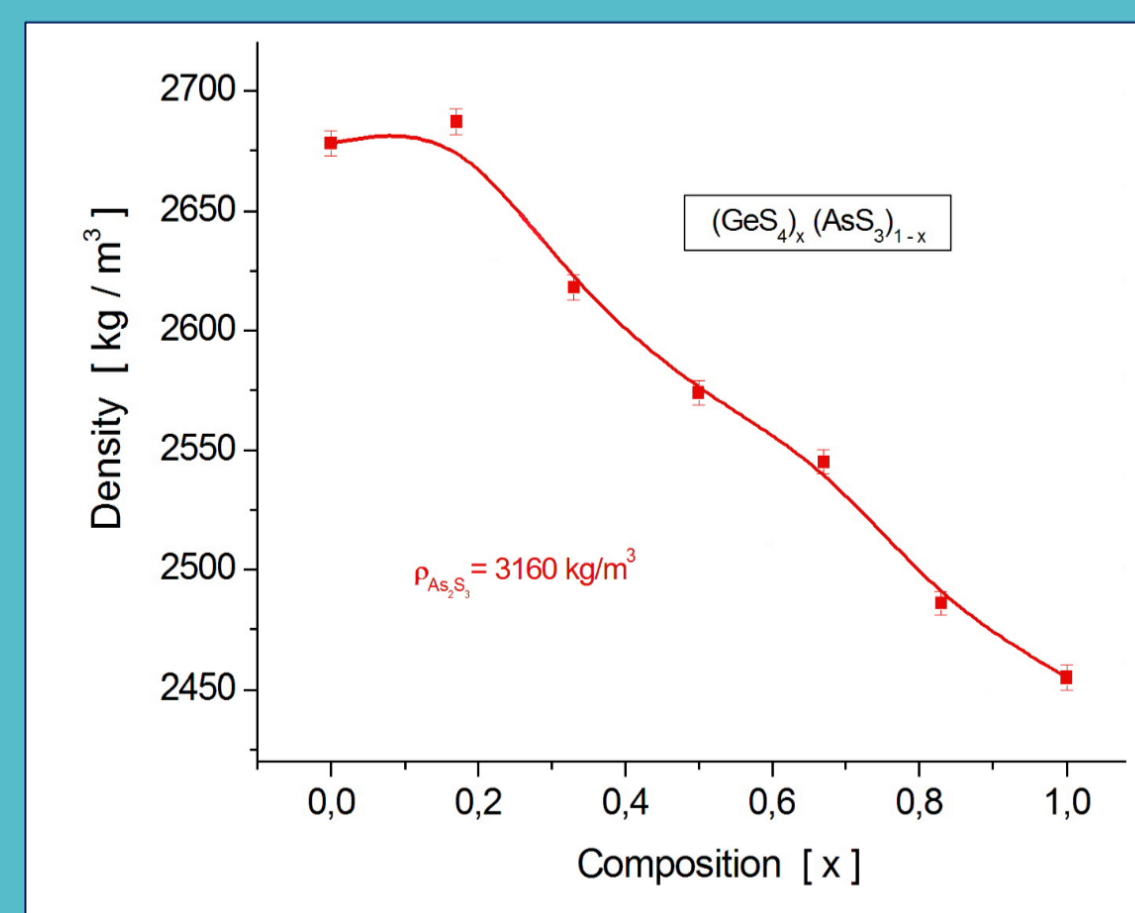


Fig.4. Dependence of density on the glass composition

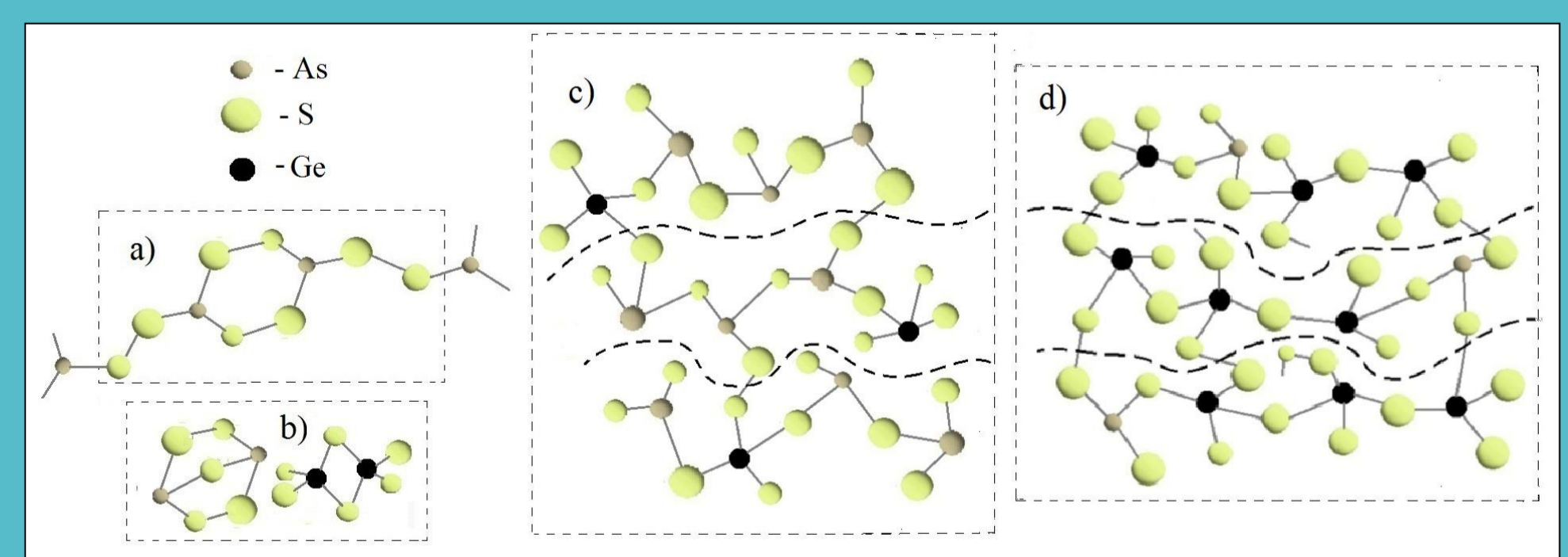


Fig.5. Schematic drawings of glass atomic network structural units

## CONCLUSIONS:

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 structural units. The substitution of trifold coordinated As atoms by fourfold coordinated Ge ones in non-stoichiometric  $\text{AsS}_3 - \text{GeS}_4$  glasses leads to a non-monotonic modification of medium range ordering structure (Fig.5), i.e. transition of pyramidal s.u. bridged in chains via dual S atoms to clusters  $\text{AsS}_3/2$  and  $\text{GeS}_4/2$  tetrahedral structural units followed by transition to 2D trigonal layer-like units  $\text{AsS}_3/2$ , where layers of As are sandwiched between layers of sulfur, sometimes linked either by twofold coordinated sulfur or fourfold coordinated Ge atoms and further to tetragonal layer-like units  $\text{GeS}_4/2$ , where layers of Ge are sandwiched between layers of sulfur, linked also by both twofold coordinated sulfur and fourfold coordinated Ge atoms.

## REFERENCES:

[1] J.C. Phillips, Topology of covalent non-crystalline solids II: Medium – range order in chalcogenide alloys and a-Si(Ge), J. Non-Cryst. Solids 43 (1981) 37-77.