

PACS 61.43.Fs

The structure of glassy HgS-GeS₂

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Abstract. The glass HgS_(x)-GeS_{2(100-x)} ($0 \leq x \leq 50$) was subjected to X-ray analysis. The radial distribution functions were calculated using the integral Fourier transformation based on X-ray scattering curves. The average interatomic distances within the first and second coordination spheres were determined. It is suggested that the transformational changes of scattering curves are related to the emergence of heterogeneity due to Hg₄GeS₆ inclusions.

Keywords: glassy alloy, radial distribution function, average interatomic distances, heterogeneity.

Manuscript received 12.07.05; accepted for publication 25.10.05.

1. Introduction

The main factor that determines the totality of physical properties of glasses is their structure. The most reliable in studying the glass structure are diffraction measurement methods, in particular, X-ray diffraction that enables the researcher to directly determine the location of diffraction centers. Since the structure and properties of material are closely related, it is worthwhile to trace possible changes in the structure and physical properties of glasses when introducing the modifying additions. Such changes can be observed in germanium disulphide, if GeS₂ forms a wide glass-forming area with the modifier. This is caused by the fact that GeS₂ glasses possess saturated covalent bonds, and any substantial changes in the structure and properties are unlikely with a low modifier concentration. Using a fast quenching technique [1], we introduced 50 mol. % of HgS into GeS₂ achieving a wide area of glass formation.

2. Experimental procedure

The amorphous alloys of HgS_(x)-GeS_{2(100-x)} system at $x = 0, 10, 20, 30, 35, 40, 42, 50$ (x denotes mol.% of HgS) were subjected to X-ray analysis using a diffractometer DRON-4.0. Focusing was carried out according to the Breg-Brentano geometry. Glassy alloys were exposed to X-rays $K_{\alpha} = 1.54178 \text{ \AA}$ (copper tube) for 10 s with the scanning step 0.1° .

3. Results and discussion

X-ray scattering intensity curves are represented in s -space (Fig. 1). They have three main peaks within the wavevector interval from 1 to 7 \AA^{-1} . The GeS₂ glass has the first sharp diffraction peak (FSDP) at the wavevector value $s = 1.042 \text{ \AA}^{-1}$. With introducing the HgS FSDP shifts towards greater values of the wavevector. FSDP is a most intensive in GeS₂ and decreases sharply with introducing HgS₍₁₀₎. This tendency preserves until the HgS content reaches 35 mol. %. This shows that the HgS modifier loosens the more homogeneous structure of germanium diselenide. X-ray scattering intensity curves undergo substantial transformational changes for the samples with 35 to 50 mol. % of HgS.

To determine which of the phases of the glassy alloy under study is responsible for changes in the shape of X-ray scattering intensity curves, we compared the diffraction patterns of the HgS₍₅₀₎-GeS₂₍₅₀₎ alloy (at $x = 50$), GeS₂ glass (at $x = 0$), and Hg₄GeS₆ crystalline compound (Fig. 2). The diffraction pattern for this compound was taken from [2]. The basis for such a comparison is provided by the phase diagram of the HgS-GeS₂ system in [3]. According to [3], in the alloys at $x = 0$ to 42, GeS₂ crystallizes first, the second is Hg₄GeS₆. In the phase diagram, the alloy containing 44 ± 2 mol. % of HgS corresponds to the double eutectic point. On further increasing the HgS content, a change in the crystallization order occurs.

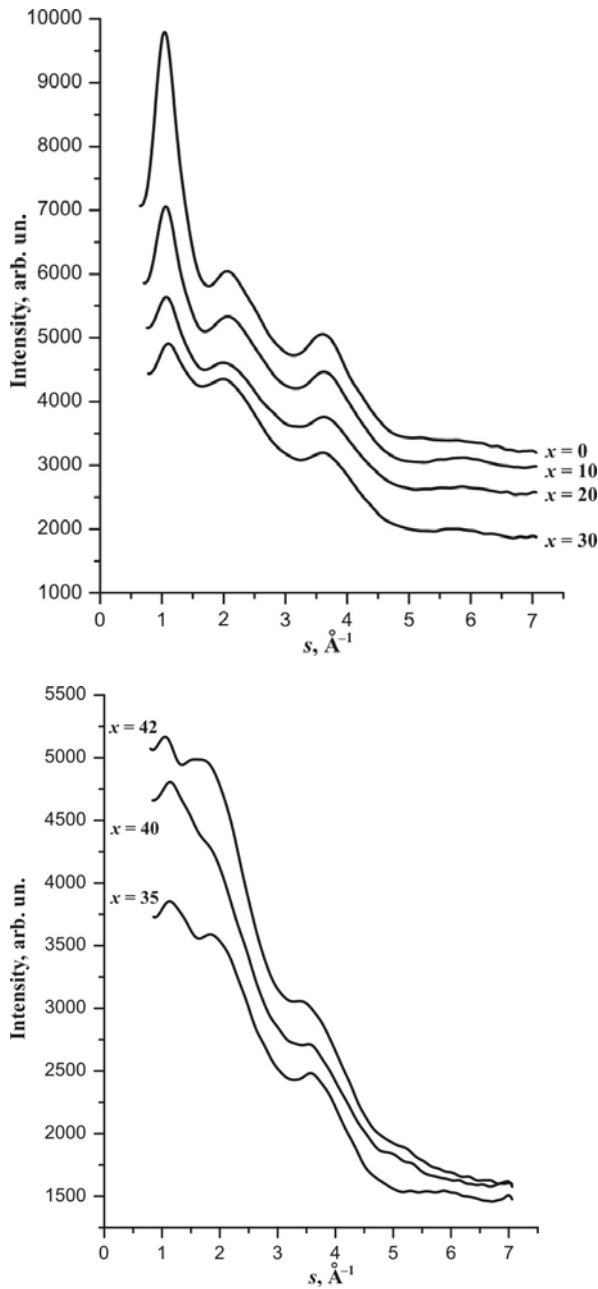


Fig. 1. X-ray scattering intensity in glassy $\text{HgS}_{(x)}\text{-GeS}_{2(100-x)}$ alloys.

Fig. 2 shows that the most intensive reflexes of the Hg_4GeS_6 crystalline compound correlate well with the position of the alloy peaks at $x = 50$. In general, the curve for $x = 50$ can be represented as the additive sum of two other diffraction patterns ($x = 0$ and the Hg_4GeS_6 curve). Therefore, the data obtained suggests that the structural elements of the $\text{HgS}_{(50)}\text{-GeS}_{2(50)}$ alloy are microregions of Hg_4GeS_6 .

On the basis of X-ray scattering intensity curves and using the integral Fourier transformation, we calculated the binary functions of atomic distribution

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty s[a(s) - 1] \sin(sr) ds$$

and radial distribution functions $G(r) = 4\pi^2 \rho_0 g(r)$ [4, 5], where ρ_0 is the mean atomic density; $s = \frac{4\pi}{\lambda} \sin \Theta$ is the

wavevector, and $a(s)$ is the structural factor. For calculation of the structural factor, we took into account the following: atomic distribution function f^2 with a partial contribution of each sort of atoms, incoherent scattering, and correction for polarization using the technique described in [4, 5].

The radial distribution functions $G(r)$ obtained by us are shown in Fig. 3. We estimated the main structural parameters – distances to the nearest neighbours r_1, r_2 as positions of the first two peaks of the functions $g(r)$. Calculation of the area under the first peak of the functions $G(r)$ yielded mean coordinate numbers A_1 . These parameters are listed in Table.

Table. Structural parameters of glassy alloys of $\text{HgS}_{(x)}\text{-GeS}_{2(100-x)}$ system.

x	0	10	20	30	35	40	42
r_1 [Å]	2.22	2.22	2.22	2.22	2.22	2.21	2.21
r_2 [Å]	3.24	3.24	3.22	3.23	3.22	3.17	3.19
A_1	3.38	3.27	3.12	3.04	2.98	2.73	2.69

As can be observed, the interatomic distance within the first coordination sphere $r_1 = 2.22 (\pm 0.01)$ Å doesn't change with the change in the composition. The value r_1 well accords with the results in [6, 7] obtained using X-

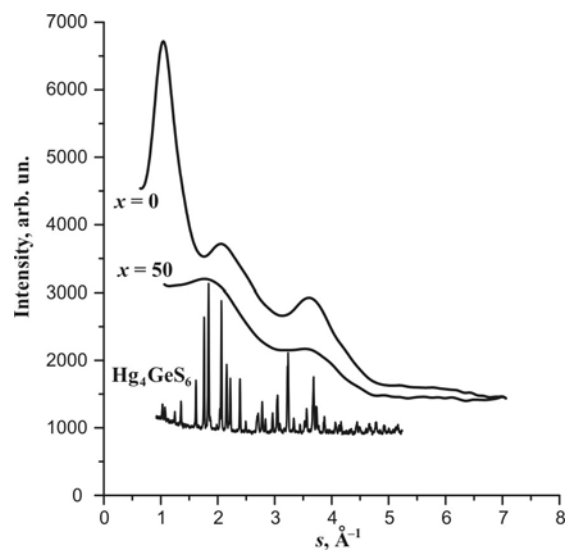


Fig. 2. Comparison of diffraction patterns of glassy $\text{HgS}_{(x)}\text{-GeS}_{2(100-x)}$ alloys and the Hg_4GeS_6 crystalline compound.

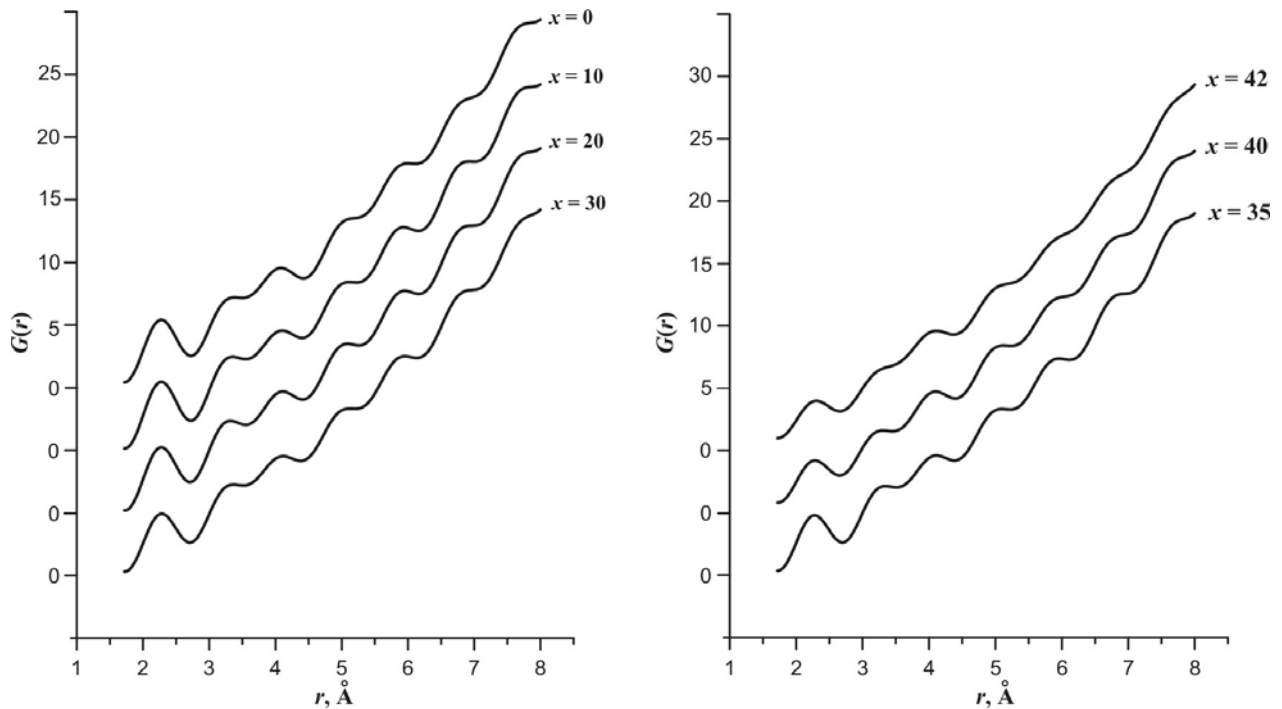


Fig. 3. Radial distribution curves of the atomic density of glassy $\text{HgS}_{(x)}\text{-GeS}_{2(100-x)}$ alloys.

ray and neutron diffraction measurements. Such interatomic distances are characteristic for a glass that is composed of $\text{GeS}_{4/2}$ tetrahedra between Ge-S atoms [6, 7]. This indicates structural proximity of modified HgS glasses and “pure” germanium disulphide. The value of interatomic distances in the second coordination sphere is 3.24 \AA for GeS_2 , which corresponds to the distance between S-S atoms [6, 7]. With introducing HgS, r_2 slightly decreases. The decrease of the coordination number A_1 (Table) as well as the decrease in the intensity of X-ray scattering evidences the loosening effect of HgS modifier.

4. Conclusions

Studies on the structure of glasses using the X-ray diffraction measurements showed that the introduction of the HgS modifier leads to loosening the glass-forming network of the HgS- GeS_2 system. Transformational changes in the shape of X-ray scattering intensity curves with high content of HgS (over 30 mol. %) are most likely related to the increase of heterogeneity due to Hg_4GeS_6 inclusions.

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