Physical and chemical interaction at the Ag_8GeS_6–Hg_4GeS_6 section

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Vertical section Ag_8GeS_6–Hg_4GeS_6 of the Ag_2S–HgS–GeS_2 system is of interest due to the formation of quaternary phase with semiconducting properties [1].

The two end compounds of this section belong to the argyrodite family of the general formula $A^{m+}_{(12-n)/m}B^{n+}X^{2-}_6$ ($A = Cu^+, Ag^+, Cd^{2+}, Hg^{2+}$; $B = Ga^{2+}, Si^{4+}, Ge^{4+}, Sn^{4+}, P^{5+}, As^{5+}$; $X = S^{2-}, Se^{2-}, Te^{2-}$) which got its name from the argyrodite mineral Ag_8GeS_6 [2]. The compounds of argyrodite structure are solid-state semiconductor materials with mixed ionic and electrical conductivity and can be used as optical, superionic and thermoelectric materials.

A significant number of representatives of the $Ag^{I}_8M^{IV}X^{VI}_6$ type (M = Si, Ge, Sn; X = S, Se, Te) is known. Their properties and method of formation were described first in [3, 4].

Synthetic argyrodite (Ag_8GeS_6) is formed in the Ag_2S–GeS_2 system which has been researched repeatedly [5-13]. The results are unambiguous regarding the formation of the Ag_8GeS_6 compound and are very different in number and composition of compounds in the Ag_8GeS_6–GeS_2 part. Ag_8GeS_6 melts congruently within 1213–1228 K range and has a polymorphous transformation within 473–493 K [5-13]. The structure of HT-modification is face-centered cubic (a=1.070 nm) [4, 7], that of low-temperature modification is orthorhombic (space group $Pna2_1$, a=1.5149, b=0.7476, c=1.0589 nm [6], space group $Pna2_1$, a=1.5137, b=0.7483, c=1.0590 nm) [12].

According to [114], Hg_4GeS_6 forms in the HgS–GeS_2 system that has another ternary compound $HgGe_2S_5$. Hg_4GeS_6 forms in the peritectic reaction $L + HgS \Leftrightarrow Hg_4GeS_6$ at 993 K. Compound Hg_4GeS_6 undergoes polymorphous transformation at 668 K. LTM-Hg_4GeS_6 crystallizes in space group Cc with lattice parameters: a=0.1234, b=0.7127, c=1.2360 nm, β=108°34′ [14].

The existence of the $Ag_6Hg_{0.82}GeS_{5.82}$ compound and another compound was found according to the results of X-ray phase and microstructural analyses at the Ag_8GeS_6–Hg_4GeS_6 section in the investigation of the isothermal section of the quasi-ternary system Ag_2S–HgS–GeS_2 at 670 K (Fig. 1) [1]. The existence of the quaternary compound $Ag_6Hg_{0.82}GeS_{5.82}$ which crystallizes in its own structural type, space group $P2_13$ with cell parameter a=1.05547 nm, was reported in [15]. This phase has a significant homogeneity region that is localized along the Ag_8GeS_6–Hg_4GeS_6 section in the range of 22–31 mol.% Hg_4GeS_6. Tetragonal structure with a relatively large unit cell (a=1.4619, c=2,0796 nm) was established for another compound $Ag_2Hg_3GeS_6$ [1].

According to DTA (weak effects of solid-phase transformations) and additional studies involving high-temperature X-ray diffraction (DORIS III synchrotron, Hasylab, Hamburg), it was established that two intermediate phases, γ and δ, are stable above room temperature

between the end compounds of the Ag_8GeS_6–Hg_4GeS_6 section (rather, their solid solution ranges α and β, respectively). They exist to ~500 K (γ) and ~400 K (δ). Monoclinic structure of the Hg_4GeS_6 compound is stable to ~680 K. Unlimited solid solubility (ε-solid solution) between HT-modifications of the original argydrodites Ag_8GeS_6 and Hg_4GeS_6 is established. Equilibria in the subsolidus area are shown in Fig. 2.

1 – single-phase – continuous ε-solid solution series of HT-Ag_8GeS_6 and Hg_4GeS_6, cubic space group F-43*m*;

2 – single-phase ternary phases: orthorhombic α-phase (LT-Ag_8GeS_6), space group $Pna2_1$, and monoclinic β-phase (LT-Hg_4GeS_6), space group *Cc*;

3 – single-phase quaternary phases: cubic γ-phase ($Ag_6Hg_{0.82}GeS_{5.82}$), space group $P2_13$, and tetragonal δ-phase ($Ag_2Hg_3GeS_6$);

4 – two-phase samples.

Two-phase regions are situated between single-phase areas within these temperatures. Solid-phase interaction between α- and γ-, γ- and δ-, δ- and β-phases has eutectoid nature. ε-solid solution decomposes at the following temperatures and compositions: $\varepsilon_1 \leftrightarrow \alpha + \gamma$ (first process: 405 K, 12 mol.% Hg_4GeS_6), $\varepsilon_2 \leftrightarrow \gamma + \delta$ (second process: 325 K, 67 mol.% Hg_4GeS_6), $\varepsilon_3 \leftrightarrow \alpha + \gamma$ (third process: 360 K, 85 mol.% Hg_4GeS_6).

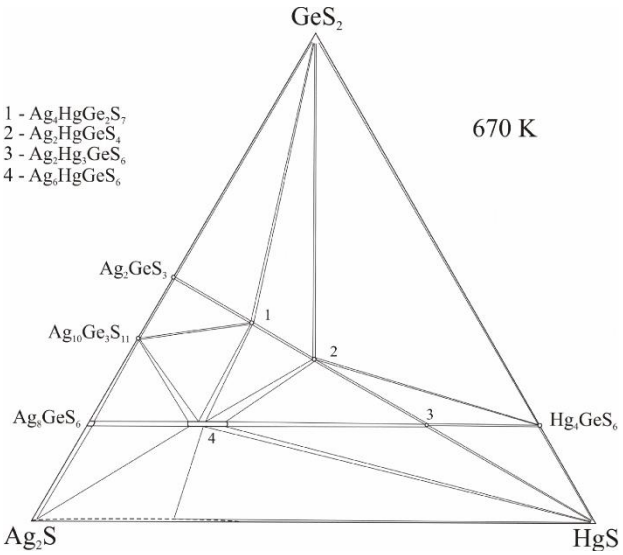

Fig. 1. Phase diagram of the Ag_2S–HgS–GeS_2 system at 670 K [1]

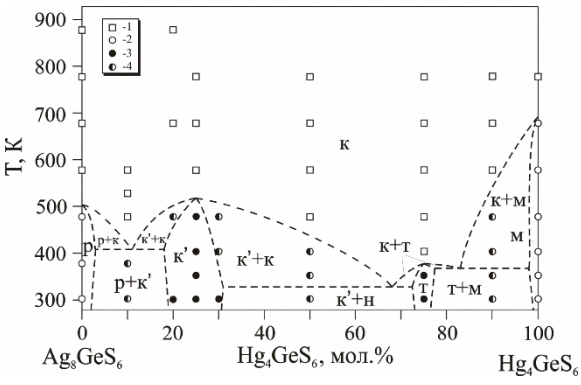

Fig. 2. Phase diagram of the subsolidus area of the Ag_8GeS_6–Hg_4GeS_6 system

Since HT-modifications of Ag_8GeS_6 and Hg_4GeS_6 form a continuous solid solution series by substitution ($2\ Ag^+ \leftrightarrow Hg^{2+}$), they crystallize in the same cubic symmertry in the space group *F*–43*m*.

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