Phase equilibria in the Ag$_2$S–Ag$_8$GeS$_6$–Ag$_8$SiS$_6$ system and some properties of solid solutions

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Abstract
Phase equilibria in the Ag$_2$S–Ag$_8$GeS$_6$–Ag$_8$SiS$_6$ system were studied using differential thermal analysis and powder X-ray diffraction technique. Boundary section Ag$_8$SiS$_6$–Ag$_8$GeS$_6$ liquidus surface projection, an isothermal section of the phase diagram at 300 K, and some polythermal sections of the studied system were constructed. The formation of continuous series of solid solutions between both crystalline modifications of the starting compounds was determined in the Ag$_8$SiS$_6$–Ag$_8$GeS$_6$ system. The liquidus surface of the Ag$_2$S–Ag$_8$SiS$_6$–Ag$_8$GeS$_6$ system consists of two fields corresponding to the primary crystallization of the high-temperature modifications of the HT-Ag$_8$Si$_{1-x}$Ge$_x$S$_6$ and HT-Ag$_2$S phases. Lattice parameters for both modification of solid solutions were calculated based on powder X-ray diffraction data. The concentration dependence of lattice parameters obeys Vegard’s rule. The obtained new phases are of interest as environmentally safe materials with thermoelectric properties and mixed ion-electron conductivity.

Keywords: Argyrodite family compounds, Silver-germanium sulfide, Silver-silicon sulfide, Phase equilibria, Solid solutions, T-x diagram, Crystal structure

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1. Introduction

Binary and more complex chalcogenides of copper and silver are valuable functional materials [1-3]. Among these compounds, synthetic analogs of the argyrodite mineral with formula \( \text{Ag}_n\text{B}^m\text{X}_k \) (A – Cu, Ag; B\(^m\) – Si, Ge, Sn; X – S, Se, Te) have high thermoelectric performance at low temperatures and are of special interest because they are environmentally safe [4–12]. At the same time, these compounds have semiconductor, photovoltaic, and optical properties [13–18]. On the other hand, the presence of highly concentrated and highly mobile Ag\(^+/\)/Cu\(^+\) ions distributed in a rigid anionic framework is ensured in the crystal structure of this class of compounds. Due to this feature of the crystal structure, some of the argyrodite compounds have high ionic conductivity for Cu\(^+\) (Ag\(^+\)) cations, which makes them very promising for use in the preparation of photoelectrode materials, electrochemical solar energy converters, ion-selective sensors, etc. [19–22].

Study of new multicomponent materials is based on information about the phase equilibrium of the corresponding systems and the thermodynamic properties of the phases formed in them [23–26]. As the argyrodite family compounds are isostructural, there is a high probability of the formation of solid solutions in systems composed of these compounds. In [27–34], phase equilibria were studied in several systems consisting of argyrodite phases, and continuous series of solid solutions were found.

The present study aimed to obtain a complete picture of the phase equilibrium of the Ag\(_8\)GeS\(_6\) – Ag\(_2\)SiS\(_6\) ternary system and some properties of solid solutions.

2. Experimental

2.1. Synthesis

Ag\(_8\)S, Ag\(_2\)SiS\(_6\), and Ag\(_2\)GeS\(_6\) compounds were synthesized by melting stoichiometric mixtures of the corresponding elements with high purity (no less 99.9999 %) in quartz ampoules under vacuum conditions (10\(^{-6}\)Pa). As the saturated vapor pressure of sulfur (\(T_{\text{boiling}} = 717 \text{ K}\)) is high at the melting temperature of all three compounds, their synthesis was carried out in a two-zone furnace. The furnace was gradually heated to a temperature of 40–50 K above the melting point of the synthesized compound. The part of the ampoule outside the oven is constantly cooled. Due to the process of cooling with water for 2–3 hours, the sulfur accumulated in the form of vapor at the end of the ampoule was condensed and sent to the reaction zone, and after absorbing most of the sulfur, the ampoule was completely inserted into the furnace. After keeping the ampoule in the furnace for 4–5 hours, they were gradually in the off-furnace mode.

The synthesized compounds were identified by differential thermal analysis (DTA) and X-ray diffraction (XRD) technique. Thus, the DTA results of Ag\(_8\)S, Ag\(_2\)SiS\(_6\), and Ag\(_2\)GeS\(_6\) compounds showed that their polymorphic transition and melting temperatures agree well with the literature data given above. X-ray diffraction analysis confirmed the homogeneity of the synthesized samples and the diffraction patterns of all three compounds agree with the literature data [19–28]. DTA and XRD results of the synthesized compounds are listed in the Table 1.

Alloys of the Ag\(_2\)S – Ag\(_8\)GeS\(_6\) – Ag\(_2\)SiS\(_6\) system were prepared by melting mixtures of the
obtained starting compounds in different proportions in vacuumed quartz ampoules. To bring the samples to the equilibrium state, they were thermally treated for a long time (500 h) at 900 K. Two samples were prepared for each composition in the Ag\textsubscript{8}GeS\textsubscript{6}–Ag\textsubscript{8}SiS\textsubscript{6} system, one of which was gradually cooled in a switched-off furnace after thermal treatment, and the other one was quenched by dropping the ampoule in cold water at 900 K.

2.2. Research methods

All the alloys were analyzed using powder XRD and DTA techniques. Powder XRD analysis was performed in a Bruker D2 PHASER diffractometer using CuKα radiation within the scanning range of 2θ = 5°–75°. DTA measurements were recorded with a “Netzsch 404 F1 Pegasus system” differential scanning calorimeter (under flowing argon atmosphere) and a multichannel device based on the electronic “TC-08 thermocouple data logger” (in sealed quartz tubes). The measurement results were processed using the NETZSCH Proteus Software. The temperature measurement accuracy was within ±2 K.

3. Results and discussion

From the present experimental data and published reports on the Ag\textsubscript{2}S–Ag\textsubscript{8}GeS\textsubscript{6} and Ag\textsubscript{2}S–Ag\textsubscript{8}SiS\textsubscript{6} constituent binaries, we obtained a detailed picture of phase equilibria in the Ag\textsubscript{2}S–Ag\textsubscript{8}GeS\textsubscript{6}–Ag\textsubscript{8}SiS\textsubscript{6} system.

3.1. The border section Ag\textsubscript{8}SiS\textsubscript{6}–Ag\textsubscript{8}GeS\textsubscript{6}

Based on the DTA and XRD results, the phase diagram of the Ag\textsubscript{8}SiS\textsubscript{6}–Ag\textsubscript{8}GeS\textsubscript{6} system was constructed. As can be seen from Fig. 1, continuous series of solid solutions are formed between both low (γ-phase) and high-temperature modifications (δ-phase) of the initial compounds. A special point of interest is that even though the melting temperatures (1231 and 1218 K) and polymorphic transformation temperatures (512 and 491 K) of the primary compounds are very close to each other, the extreme points on both the liquidus and solidus and δ ↔ γ phase transition curves not observed.

The lattice parameters of both ternary compounds and solid solutions were calculated using the TOPAS3.0 computer program and the results are listed in Table 1.

![Phase diagram of the Ag\textsubscript{8}SiS\textsubscript{6}–Ag\textsubscript{8}GeS\textsubscript{6} system](image)

**Fig. 1.** Phase diagram of the Ag\textsubscript{8}SiS\textsubscript{6}–Ag\textsubscript{8}GeS\textsubscript{6} system

<table>
<thead>
<tr>
<th>Composition, Mol % Ag\textsubscript{8}GeS\textsubscript{6}</th>
<th>Effect temperatures according to DTA data, K</th>
<th>Lattice parameters, Å; low-temperature phase obtained by slow cooling to 298 K, (Sp. gr. Pna\textsubscript{2}1)</th>
<th>Lattice parameters, Å; high-temperature phase obtained by quenching from 900 K (Sp. gr. F-43m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Ag\textsubscript{8}SiS\textsubscript{6})</td>
<td>512 ; 1231</td>
<td>15.0264 ; 7.4584 ; 10.5311</td>
<td>10.6225</td>
</tr>
<tr>
<td>10</td>
<td>510 ; 1229</td>
<td>15.0524 ; 7.4459 ; 10.5411</td>
<td>10.6348</td>
</tr>
<tr>
<td>20</td>
<td>506 ; 1227</td>
<td>15.0751 ; 7.4412 ; 10.5429</td>
<td>10.6436</td>
</tr>
<tr>
<td>40</td>
<td>503 ; 1225-1228</td>
<td>15.0926 ; 7.4523 ; 10.5562</td>
<td>10.6552</td>
</tr>
<tr>
<td>60</td>
<td>499 ; 1223</td>
<td>15.0962 ; 7.4601 ; 10.5626</td>
<td>10.6785</td>
</tr>
<tr>
<td>80</td>
<td>497 ; 1211</td>
<td>15.1265 ; 7.4694 ; 10.5774</td>
<td>10.6935</td>
</tr>
<tr>
<td>100</td>
<td>494 ; 1219</td>
<td>15.1545 ; 7.4705 ; 10.5823</td>
<td>10.7026</td>
</tr>
<tr>
<td>100</td>
<td>491 ; 1218</td>
<td>15.1442 ; 7.4713 ; 10.5912</td>
<td>10.7124</td>
</tr>
</tbody>
</table>
Ag₈GeS₆ and Ag₈SiS₆ compounds both have orthorhombic structure under room conditions (space group - Pna₂₁). The high-temperature modifications of both compounds are cubic (phase group F-43m). Table 1 lists the thermal effects and crystal lattice parameters of the starting compounds and solid solutions.

Graphs of the dependence of crystal lattice parameters on concentration were constructed (Fig. 2). As can be seen, the lattice parameters of both modifications of solid solutions increase linearly with Ge substitution, i.e., they follow Vegard’s rule.

Fig. 3 shows powder diffraction patterns of thermally treated and slowly cooled alloys. As can be seen, all intermediate alloys have the same diffraction pattern as the starting compounds. This indicates the formation of continuous series of solid solutions in the Ag₈SiS₆–Ag₈GeS₆ system between room temperature modifications of the starting compounds over the entire concentration range. A slight shift of the diffraction lines towards small angles is observed because of Si → Ge substitution. This is because the ionic radius of germanium is larger than silicon.

Fig. 4 shows powder XRD patterns of Ag₈SiS₆ – Ag₈GeS₆ alloys quenched at 900 K. Analysis of the XRD patterns of the quenched alloys shows the formation of continuous series of solid solutions between high-temperature modifications in the entire range. As can be seen, the diffraction patterns of high-temperature alloys have a
diffraction pattern characteristic of a cubic structure.

3.2. Solid phase equilibria in the Ag₂S–Ag₈GeS₆–Ag₈SiS₆ system at 300 K

Based on the XRD results of a number of equilibrium alloys within the Ag₂S–Ag₈GeS₆–Ag₈SiS₆ concentration triangle and the phase diagrams of boundary quasi-binary systems, a solid phase equilibria diagram of this system at 300 K was constructed (Fig. 5). The formation of the γ-phase in the Ag₈GeS₆–Ag₈SiS₆ boundary system, and the absence of other phases in the concentration triangle lead to the formation of a two-phase α’+γ field (where α’ is a solid solution formed on the basis of low-temperature Ag₂S). Connod lines are formed between α’ and γ-phases. The phase composition of room temperature alloys of the Ag₂S–Ag₈GeS₆–Ag₈SiS₆ system was determined by XRD. Fig. 5 shows the studied vertical sections and the composition of the alloys. For example, the diffraction patterns and phase compositions of alloys 1 and 2 from Fig. 5 are shown in Fig. 6. As can be seen, the diffraction patterns of both alloys consist of the sum of the diffraction lines of the low-temperature modification of Ag₂S and the γ-phase.

3.3. Liquidus surface projection of the Ag₂S–Ag₈GeS₆–Ag₈SiS₆ system

The liquidus surface projection of this system consists of two fields, which correspond to the primary crystallization of the δ-phase and α solid solutions based on the high-temperature modification of the Ag₂S compound (Fig. 7). These fields are bounded by the e1e2 monovariant eutectic curve:

L ↔ α + δ.

(1)

3.4. Some polythermal sections of the phase diagram

The Ag₂S-[A] section ([A] – Ag₂Si₁₋₀.₅Ge₀.₅Se₀.₅ solid solution). The liquidus of this section (Figure 8) consists of two curves of primary crystallization fields of α and δ solid solutions.
Fig. 5. Isothermal section of the Ag$_2$S–Ag$_8$SiS$_6$–Ag$_8$GeS$_6$ system at 300 K

Fig. 6. Powder XRD patterns (300 K) of Ag$_2$S–Ag$_8$SiS$_6$–Ag$_8$GeS$_6$ alloys: (a) alloy – #1 and (b) alloy – #2 in Fig. 5
The crystallization process ends with the formation of the two-phase field \( \alpha + \delta \). Below the liquidus, crystallization proceeds according to the eutectic reaction (1). Since the temperatures of e1 and e2 eutectic equilibria on \( \text{Ag}_2\text{S}–\text{Ag}_8\text{GeS}_6 \) and \( \text{Ag}_2\text{S}–\text{Ag}_8\text{GeS}_6 \) boundary systems differ little (Fig. 7), the temperature interval of this monovariant eutectic equilibrium is very small (2–3°). Therefore, in Figure 8, the \( L + \alpha + \delta \) three-phase field is delimited by a dotted line. Thermal effects at the 503–510 K range correspond to monovariant equilibrium \( \delta \leftrightarrow \alpha + \gamma \). There is no more than 5% solubility area based on the high-temperature modification of \( \text{Ag}_2\text{S} \). The horizontal line at 443K corresponds to the polymorph transformation \( \alpha \leftrightarrow \alpha' \).

The \( \text{Ag}_8\text{SiS}_6–[\text{B}] \text{Ag}_2\text{S–}[\text{A}] \) section ([B] is alloy of the 5\( \text{Ag}_2\text{S}–\text{Ag}_8\text{GeS}_6 \) system containing 50 mol % \( \text{Ag}_8\text{GeS}_6 \)). This section is entirely located in the primary crystallization field of the \( \delta \)-phase (Fig. 9)
and firstly δ-solid solutions crystallize from the liquid phase. Crystallization continues according to the monovariant eutectic reaction (1) and ends with the formation of two-phase mixtures α + δ. Then δ ↔ α + γ monovariant eutectoid reaction (512–491) and polymorphic transformation of Ag$_2$S (443 K) take place.

3. Conclusion

The phase equilibria of the Ag$_2$S–Ag$_8$GeS$_6$–Ag$_8$SiS$_6$ plane of the Ag–Si–Ge–S system were studied. The liquidus surface projection of the mentioned subsystem, solid phase equilibria diagram at 300 K, as well as two polythermal sections of the phase diagram were constructed. It was determined that continuous series of solid solutions are formed between both crystallographic modifications of the starting compounds in the boundary Ag$_8$SiS$_6$–Ag$_8$GeS$_6$ system. Based on powder diffractograms, the homogeneity of both solid solutions was confirmed, and their crystal lattice types and parameters were determined. It is shown that the dependence of the lattice parameters on the composition obeys Vegard’s rule. The obtained new non-stoichiometric phases are of particular interest as environmentally safe, thermoelectric, and mixed ion-electron conducting materials.

Author contributions


Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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