The study of the quasi-triple system FeS–Ga$_2$S$_3$–Ag$_2$S by a FeGa$_2$S$_4$–AgGaS$_2$ section

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Abstract

The interest in the study of systems containing sulphides with the formula AIB$^{III}$C$^{VI}$, is generated in particular by emerging opportunities for their practical use in the production of non-linear optical devices, detectors, solar cells, photodiodes, luminophors, etc. Therefore, taking into account the search for new promising materials based on silver and iron thiogallates, the goal of this work is to study the quasi-binary section FeGa$_2$S$_4$–AgGaS$_2$ of the quaternary system Fe–Ag–Ga–S.

The alloys of the AgGaS$_2$-FeGa$_2$S$_4$ system were synthesised from high-purity base metals: iron – 99.995 %, gallium – 99.999 %, silver – 99.99 %, and sulphur – 99.99 %. The alloys were studied using differential thermal analysis, X-ray phase analysis, and microstructural analysis as well as microhardness measurement and density determination.

Using the methods of physicochemical analysis, a T-x phase diagram of the AgGaS$_2$-FeGa$_2$S$_4$ section, which is the internal section of the quasi-triple FeS–Ga$_2$S$_3$–Ag$_2$S system, was studied and constructed for the first time. It was established that this system is of the simple eutectic type. The composition of the eutectic point is 56 mol% FeGa$_2$S$_4$ and $T = 1100$ K. The solid solution ranges were determined on the basis of the source components. Based on FeGa$_2$S$_4$ and AgGaS$_2$, the solubility stretches to 10 and 16 mol% respectively. With decreasing temperature, the solid solutions narrow and, at room temperature, comprise 4 mol% AgGaS$_2$ based on iron thiogallate (FeGa$_2$S$_4$) and 11 mol% FeGa$_2$S$_4$ based on silver thiogallate (AgGaS$_2$).

Keywords: phase diagram, solid solution, FeGa$_2$S$_4$, AgGaS$_2$, quasi-triple system, eutectic, X-ray analysis, FeS–Ga$_2$S$_3$–Ag$_2$S.

1. Introduction

The interest in the study of systems containing sulphides with the formula AIB$^{III}$C$^{VI}$ is generated in particular by emerging opportunities for their practical use in the production of non-linear optical devices, detectors, solar cells, photodiodes, luminophors, etc. [1–17].

The reported data shows that multicomponent sulphide compounds, especially those containing magnetic (FeGa$_2$S$_4$, Fe$_2$Ga$_2$S$_5$, FeIn$_2$S$_5$, etc.) ions, are functional materials and are used in the production of magneto-optical devices, photodetectors, lasers, light modulators, etc. [18–25].

The source components comprising the quaternary system Ag–Fe–Ga–S were thoroughly studied in [26–42]. Compositions AgGaS$_2$, Ag$_2$GaS$_4$, and Ag$_2$Ga$_2$S$_5$ were established during the study of the Ag$_2$S–Ga$_2$S$_3$ binary system [26, 30, 31]. Ag$_2$Ga$_2$S$_5$ is formed from them by a peritectic reaction at 1268 K while AgGaS$_2$ and Ag$_2$Ga$_2$S$_5$ melt congruently at 1270 and 1063 K respectively. AgGaS$_2$ crystallises within the chalcopyrite-type structure ($a = 5.7544$, $c = 10.299$ Å space group I42d) [27] and is a $p$-type semiconductor with a band gap of $\Delta E = 2.75$ eV [32].

The phase diagram of the section Ga$_2$S$_3$–FeS was studied in [33–42]. The authors established...
that triple compounds FeGa$_2$S$_4$ and Fe$_2$Ga$_2$S$_5$ are formed in the system Ga$_2$S$_3$–FeS \cite{38,42}.

The microhardness of the FeGa$_2$S$_4$ and Fe$_2$Ga$_2$S$_5$ compounds are $4000\pm5$ and $3500\pm5$ MPa respectively \cite{42}.

The FeGa$_2$S$_4$ compound melts congruently at $1418\,\text{K}$ \cite{38}, although, according to \cite{39}, FeGa$_2$S$_4$ is formed by a peritectic reaction at $1343\,\text{K}$ and undergoes polymorphous transformation at $1283\,\text{K}$. FeGa$_2$S$_4$ crystallises in a rhombic crystal system of the ZnAl$_2$S$_4$ type with the following parameters: $a = 1.289\,\text{nm}$, $b = 0.751$, $c = 0.609\,\text{nm}$ \cite{40}. According to \cite{41}, this compound has two crystalline modifications: low-temperature trigonal P3ml: $a = 0.3654\,\text{nm}$, $c = 1.2056\,\text{nm}$; and high-temperature rhombic: $a = 1.289$, $b = 0.751$, $c = 0.609\,\text{nm}$.

The goal of this work is to study the quasi-binary section FeGa$_2$S$_4$–AgGaS$_2$ of the quaternary system Fe–Ag–Ga–S.

2. Experimental

Synthesis of the alloys of the AgGaS$_2$–FeGa$_2$S$_4$ system were conducted from base metals. The base metals (AgGaS$_2$ and FeGa$_2$S$_4$) were synthesised using high-purity: iron – 99.995 %, gallium – 99.999 %, silver – 99.99 %, and sulphur – 99.99 %. Stoichiometric mixtures of the elements were placed in vacuum quartz ampoules (17 cm long and 1.5 cm in diameter) with residual pressure $\sim 0.133\,\text{Pa}$ \cite{43}. Then the ampoule was placed in a two-zone furnace. The furnace was slowly heated from room temperature to the fusion temperature of the compound FeGa$_2$S$_4$. Sulphur becomes condensed in the cold region and returns to the interaction zone. The alloys in a liquid state were stirred at regular intervals. The outer part of the ampoule was cooled with water. After 1.5–2 hours in the cold region, the mass of the sulphur decreased. After that, the whole ampoule was placed in the furnace and held at a temperature of $1450\,\text{K}$ for 2.5 hours. The process of synthesis lasted for at least 4 hours. Then the obtained samples were homogenised at a temperature of $800\,\text{K}$ for 150 h. The alloys were studied using differential thermal analysis (DTA), X-ray phase analysis (XRD), and microstructural analysis (MSA) as well as microhardness measurement and density determination. XRD was performed on a D2 PHASER using Ni-filtered CuK$_\alpha$ radiation.

DTA of the alloys of the system was conducted on an HTP-73 device with a heating rate of 10 degrees per minute. Calibrating chromel-alumel thermocouples were used with Al$_2$O$_3$ as a reference standard. An etchant of the composition NH$_4$NO$_3$(5–8 wt%) + K$_2$Cr$_2$O$_7$(0.02–0.5 wt%) + conc. H$_2$SO$_4$ was used during the study of the microstructure of the alloys with the etching time of 20 sec. The microhardness of the alloys was measured on a microhardness tester PMT-3 at the loads 0.01 and 0.02 N. MSA of the system alloys was performed on a MIM-8 metallographic microscope on preliminarily etched sections polished with the paste.

3. Results and discussion

Based on the results of physicochemical analysis (DTA, XRD, MSA, and density determination), a phase diagram of the system AgGaS$_2$–FeGa$_2$S$_4$ was developed. The DTA results showed that all thermograms of the system alloys (90–10 mol% AgGaS$_2$) have three endoeffects each, except for the alloy containing 56 mol% FeGa$_2$S$_4$ while the alloys containing 90 and 10 mol% AgGaS$_2$ demonstrate two and four endoeffects each respectively (Table 1). The effects at $905\,\text{K}$ correspond to the phase transition $\alpha$-FeGa$_2$S$_4 \leftrightarrow \beta$-FeGa$_2$S$_4$.

As Fig. 1 shows, the phase diagram of the system AgGaS$_2$–FeGa$_2$S$_4$ belongs to the eutectic type with limited component solubility in solid state. The solubility at 500 K based on AgGaS$_2$ is...
11 mol% FeGa$_2$S$_4$ and 4 mol% AgGaS$_2$ based on FeGa$_2$S$_4$. The solubility at the eutectic temperature stretches to 16 and 10 mol% respectively. The eutectic has a composition of 56 mol% FeGa$_2$S$_4$ and crystallises at 1100 K.

The liquidus of the system AgGaS$_2$–FeGa$_2$S$_4$ consists of the primary crystallisation branches $\alpha$ and $\beta$ solid solutions crossing at 56 mol% FeGa$_2$S$_4$ and $T = 1100$ K. The temperature of the phase transition $\beta$(FeGa$_2$S$_4$)$\leftrightarrow$$\beta$‘(FeGa$_2$S$_4$) is reduced to 905 K under the influence of the second component. MSA of the annealed alloys showed that the alloys of the system AgGa$_2$S$_4$–FeGa$_2$S$_4$ are single-phase except for the alloys containing 11–96 mol% FeGa$_2$S$_4$.

Below solidus, $\alpha$ and $\beta$ solid solutions co-crystallise. The solubility regions based on source components are narrow: 11 mol% FeGa$_2$S$_4$ based on AgGaS$_2$ and 4 mol% AgGaS$_2$ based on the second component. Solubility limits were determined using the XRD and MSA of the alloys annealed and quenched at the temperature 700 K.

To determine the limits of the regions of solid solutions of the source components (AgGa$_2$S$_4$ and FeGa$_2$S$_4$), 98, 96, 95, 93, 91, 90, 89, 88 mol% were additionally synthesised from both sides. These alloys were annealed at 650 and 800 K with the annealing duration of 1 month (Table 2).

After the annealing, a microstructural analysis of the alloys was conducted that showed that there are limited solubility regions near AgGaS$_2$ and FeGaS$_4$. Solid solutions based on AgGaS$_2$ belong to the Ag$_2$GeS$_3$ structural type and crystallise in the monoclinic syngony. Within the solubility limits, the parameters of the crystal lattice increase: $a = 0.627\div0.748$, $b = 0.580\div0.664$, $c = 1.318\div1.386$ nm, $\beta = 93.27\div93.61$.

The results of the X-ray phase analysis are in good agreement with the data of the microstructural analysis and confirm the formation of solid solutions based on the source components in the system AgGa$_2$S$_4$–FeGa$_2$S$_4$.

The data of the X-ray powder patterns of the alloys of the system AgGa$_2$S$_4$–FeGa$_2$S$_4$ showed that the samples of the compositions 0–11 and 95–100 mol% FeGa$_2$S$_4$ are single-phase. Their diffraction lines are identical to the diffraction patterns of the source components (silver thiogallate and iron thiogallate). The diffraction pattern of the alloys containing 11–96 mol% FeGa$_2$S$_4$ is two-phase (Fig. 2).

4. Conclusions

1. Using the methods of physicochemical analysis (XRD, DTA, MSA), a phase diagram of the system AgGa$_2$S$_4$–FeGa$_2$S$_4$ was studied and constructed for the first time. It was established that the system is a quasi-binary cross-section of the FeS–Ga$_2$S$_3$–Ag$_2$S quasi-triple system and belongs to the simple eutectic type.

### Table 1. Composition, results of the DTA of alloys of the AgGa$_2$S$_4$–FeGa$_2$S$_4$ system

<table>
<thead>
<tr>
<th>Composition, mol%</th>
<th>Thermal effects, K</th>
</tr>
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<tbody>
<tr>
<td>100</td>
<td>1420</td>
</tr>
<tr>
<td>90</td>
<td>905, 980, 1235, 1405</td>
</tr>
<tr>
<td>80</td>
<td>905, 1100, 1375</td>
</tr>
<tr>
<td>70</td>
<td>905, 1100, 1510</td>
</tr>
<tr>
<td>60</td>
<td>905, 1100, 1175</td>
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<tr>
<td>56</td>
<td>1100 (eutectic)</td>
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<tr>
<td>50</td>
<td>905, 1100, 1145</td>
</tr>
<tr>
<td>40</td>
<td>905, 1100, 1195</td>
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<tr>
<td>30</td>
<td>905, 1100, 1230</td>
</tr>
<tr>
<td>20</td>
<td>905, 1100, 1250</td>
</tr>
<tr>
<td>10</td>
<td>1175, 1260</td>
</tr>
<tr>
<td>0.0</td>
<td>1270</td>
</tr>
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</table>

### Table 2. Annealing of the alloys of the AgGa$_2$S$_4$–FeGa$_2$S$_4$ system at temperatures of 650 and 800 K

<table>
<thead>
<tr>
<th>Composition, mol%</th>
<th>650 K phase count</th>
<th>800 K, phase count</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgGa$_2$S$_4$</td>
<td>FeGa$_2$S$_4$</td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>100 $\alpha$</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>98 $\alpha$</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>96 $\alpha+\beta$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>5.0</td>
<td>95 $\alpha+\beta$</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>7.0</td>
<td>95 $\alpha+\beta$</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>9.0</td>
<td>91 $\alpha+\beta$</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>10</td>
<td>90 $\alpha+\beta$</td>
<td>$\alpha+\beta$</td>
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<tr>
<td></td>
<td>89 $\alpha+\beta$</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td></td>
<td>88 $\alpha+\beta$</td>
<td>$\alpha+\beta$</td>
</tr>
<tr>
<td>100</td>
<td>0.0 $\beta$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>98</td>
<td>2.0 $\beta$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>96</td>
<td>4.0 $\beta$</td>
<td>$\beta$</td>
</tr>
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<td>95</td>
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<td>91</td>
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<td>90</td>
<td>10 $\alpha+\beta$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>89</td>
<td>11 $\alpha+\beta$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>88</td>
<td>12 $\alpha+\beta$</td>
<td>$\alpha+\beta$</td>
</tr>
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</table>
2. The formation of solid solutions based on their source components was found in the AgGaS$_2$–FeGa$_2$S$_4$ system. The solubility based on iron thiogallate at room temperature is 4 mol% AgGaS$_2$ and the solubility based on silver thiogallate is 11 mol% FeGa$_2$S$_4$.

**Conflict of interests**

The author declares that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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