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**QUASI-BINARY SECTIONS AND TRIANGULATION OF FeS–Ga₂S₃–PbS
QUASI-TERNARY SYSTEM****U.A.Hasanova, Sh.H.Mammadov, O.M.Aliyev, I.B.Bakhtiyarly***M.Nagiyev Institute of Catalysis and Inorganic Chemistry, NAS of Azerbaijan**azxim@mail.ru*

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According to the results of differential thermal, X-ray phase and microstructural analyses the character of interaction in Fe–Ga₂S₃–PbS quasi-ternary system was studied and triangulated. It was determined that FeS–Ga₂S₃–PbS quasi-ternary system triangulates with eutectic type FeS–PbGa₂S₄, FeS–Pb₂Ga₂S₅ and FeGa₂S₄–PbGa₂S₄ quasi-binary sections to pseudo-ternary systems. In this systems a new quasi-ternary phase has not been found.

Keywords: quasi-ternary system, antiferromagnets, quasi-binary sections, eutectics, triangulates.

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Production and study of perspective photosensitive luminescent and laser materials containing magnetic ions are of special importance. At present particularly, FeGa₂S₄ and Fe₂Ga₂S₅ compounds obtained with the participation of iron monosulphide as Heisenberg's antiferromagnets attracts attention of scientists [1–4]. In these compounds the reason of antiferromagnetism is related to their crystal structure [1]. All iron ions in crystal structure are located in octahedral and have +2 oxidation degree. But in similar compounds iron ions exhibit variable oxidation degree. From this point study of FeS–Ga₂S₃–PbS quasi-ternary system is very relevant for searching a perspective material.

Side FeS–Ga₂S₃, FeS–PbS, PbS–Ga₂S₃ systems of FeS–Ga₂S₃–PbS quasi-ternary system as well as primary components found in binary systems (Fe–S, Pb–S, Ga–S) have been sufficiently studied in literature [5–18].

FeS–PbS system was studied by many authors [5, 6, 8–12] and its state diagram was plotted. State diagram of the system is quasi-binary, of an eutectic type, but in state diagrams the system differs for the composition and temperature of eutectics, as well as absence or presence of FeS phase transitions. Therefore, the system was reviewed and its state diagrams by us were constructed [18]. In our work we used troilite modification of FeS [18]. Coordinates of eutectic point: 45 mol % PbS and $T=1123$ K. Limited solubility regions are formed on the

basis of components. α -FeS $\leftrightarrow\beta$ -FeS $\leftrightarrow\delta$ FeS phase transition is of eutectoid type, occurs at 410 and 560 K, correspondingly.

FeS–Ga₂S₃ system is a quasi-binary section of Fe–Ga–S ternary system and characterized by the formation of FeGa₂S₄ and Fe₂Ga₂S₅ compounds. It should be noted that according to the authors [17] both compounds melt incongruently [16] and according to our researches FeGa₂S₄ melts congruently at 1418 K, Fe₂Ga₂S₅ melts at 1043 K by decomposing. FeGa₂S₄ compound has α and β modifications: α -FeGa₂S₄ crystallizes in hexagonal syngony ($a=3.654$, $c=12.056$ Å, Space group $P3m_1$), β -FeGa₂S₄ crystallizes in rhombic syngony ($a=12.89$, $b=7.51$, $c=6.09$ Å) [17]. Fe₂Ga₂S₅ compound forms 2H (hexagonal, $a=3.67$, $c=30.0$ Å, Space group $P6_3/mmc$) and 3R (rhombohedral, $a=3.67$, $c=45.0$ Å, Space group $R3m$) polytypes.

PbS–Ga₂S₃ system is quasi-binary and characterized by the formation of PbGa₂S₄ and Pb₂Ga₂S₅ compounds melting congruently at 1163 and 1063 K correspondingly [14, 15]. PbGa₂S₄ and Pb₂Ga₂S₅ are in an eutectic equilibrium between each other and primary components; Ga₂S₃–PbGa₂S₄ eutectics melts at 1133, PbGa₂S₄–Pb₂Ga₂S₅ eutectics melts at 1043, Pb₂Ga₂S₅–PbS eutectics melts at 1033 K.

Experimental part

Using pure elements (GL-000 gallium, "hp" 99.9999% pure sulphur, 99.9% pure iron obtained from decomposition of carbonyl and

99.99% pure lead) alloys were synthesized from FeS, Ga₂S₃ and PbS. Samples were melted for 8–10 hours in a vacuumed quartz ampoule. Depending on the composition of alloy maximum temperature of the synthesis was 1250–1400 K. During the process mechanical vibration was made for full mixing of an alloy. After keeping alloys at maximum temperatures for 30–45 minutes ampoule was cooled to 800–900 K with electrical furnace and was homogenized for a month in this mode. As a result of the interaction compact samples suitable for physical and chemical researches were obtained. FeS–Ga₂S₃–PbS quasi-ternary system was studied according to the complex results of physico-chemical analyses (DTA, X-ray phase, MSA). Thermal analysis was carried out on "Jupiter" STA440 F3 of "NET2SCH" (thermopair chromel-chromel alumel, heating rate 10⁰/min sample Al₂O₃), X-ray phase analysis was carried out on D2 Pilsener X-ray diffractometer of Bruker (CuK_α-radiation, Ni-filter), microstructural analysis was carried out on MIM-7 microscope, microhardness of alloys was measured on PMT-3.

Results and discussion

FeS–PbGa₂S₄ system is quasi-binary, there is an eutectic equilibrium between components (Figure 1). Liquidus of the system consists of primary crystallization curves of β'-solid solutions based on δ-FeS and PbGa₂S₄ and

cross at eutectic point relevant to 35 mol% of FeS at 875 K. α-FeS ↔ β-FeS ↔ δ-FeS phase transitions occur at 405 and 550 K correspondingly. The first phase transition is practically observed in all alloys, but β-FeS ↔ δ-FeS phase transition occurs only in 0–20 mol% of PbGa₂S₄ concentration range.

On the basis of PbGa₂S₄ at room temperature solubility limit is restricted in the range of 85–100 mol% PbGa₂S₄. β'-solid solutions crystallize in rhombic syngony in the type of EuGa₂S₄ (*a*=20.44–20.32, *b*=20.64–20.55, *c*=12.09–12.02 Å, *Z*=32, Space group Fddd, *d*=4.94–5.15 g/sm³, *H_μ*=2250–2500 MPa).

FeS–Pb₂Ga₂S₅ system is a quasi-binary section of quasi-ternary system and is of eutectic type (Figure 2).

Coordinates of an eutectic point: 40 mol % FeS and *T*=850 K. On the basis of FeS solubility was not practically determined, but on the basis of Pb₂Ga₂S₅ 20 mol % of solid solution with rhombic structure is formed.

FeGa₂S₄–PbGa₂S₄ system is quasi-binary section of quasi-ternary system, its state diagram is of simple eutectic type. It should be noted that according to the results of X-ray analysis in primary researches the formation of FePbGa₄S₈ quaternary compound at 1:1 ratio of components was given in [19], but this did not prove its value in further studies.

Fig.1. Phase diagram of the system FeS–PbGa₂S₄.

Fig.2. Phase diagram of the system FeS–Pb₂Ga₂S₅.

Fig.3. The triangulation of the FeS–Ga₂S₃–PbS quasi-triple system: 1 – FeGa₂S₄–Ga₂S₃–PbGa₂S₄, 2 – FeS–FeGa₂S₄–PbGa₂S₄, 3 – FeS–PbGa₂S₄–Pb₂Ga₂S₅, 4 – FeS–Pb₂Ga₂S₅–PbS.

It was determined that in the system eutectic equilibrium occurs. Coordinates of an eutectic point are 45 mol % FeGa₂S₄, $T=950$ K. α -FeGa₂S₄ $\leftrightarrow$ β -FeGa₂S₄ phase transition is of eutectoid type and occurs at 920 K. On the basis of α -FeGa₂S₄ 5 mol % of solid solution is formed, but on the basis of PbGa₂S₄ 10 mol % of solid solution with rhombic structure is formed.

As it is seen all 3 sections are quasi-binary, triangulates FeS–Ga₂S₃–PbS quasi-ternary system to 4 subsystems (Figure 3).

Triangulation of quasi-ternary system can be used in future in projection of liquidus surface of FeS–Ga₂S₃–PbS quasi-ternary system and for determination of the composition of alloys to grow monocrystals of the compounds FeS, FeGa₂S₄ and Ga₂S₃ which melt at high temperatures.

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$\text{FeS-Ga}_2\text{S}_3\text{-PbS}$ KVAZIÜÇLÜ SİSTEMİNİN KVAZİBİNAR KƏSİKLƏRİ VƏ TRIANQULYASIYASI

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Differensial-termiki, rentgenfaza, mikroquruluş analizlərin nəticələrinə əsasən $\text{FeS-Ga}_2\text{S}_3\text{-PbS}$ kvaziüçlü sistemində qarşılıqlı təsirin xarakteri araşdırılmış və trianqulyasiya edilmişdir. Müəyyən edilmişdir ki, $\text{FeS-Ga}_2\text{S}_3\text{-PbS}$ kvaziüçlü sistemi evtektik tipli $\text{FeS-PbGa}_2\text{S}_4$, $\text{FeS-Pb}_2\text{Ga}_2\text{S}_5$ və $\text{FeGa}_2\text{S}_4\text{-PbGa}_2\text{S}_4$ kvazibinar kəsikləri ilə dörd psevdouçlü sistemə trianqulyasiya edir. Sistemdə yeni dördlü faza aşkar edilməmişdir

Açar sözlər: kvaziüçlü sistem, antiferromaqnitlər, kvazibinar kəsiklər, evtektika, trianqulyasiya.

КВАЗИБИНАРНЫЕ СЕЧЕНИЯ И ТРИАНГУЛЯЦИЯ КВАЗИТРОЙНОЙ СИСТЕМЫ $\text{FeS-Ga}_2\text{S}_3\text{-PbS}$

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По результатам дифференциально-термического, рентгенофазового и микроструктурного анализов изучен характер взаимодействия в квазитройной системе $\text{FeS-Ga}_2\text{S}_3\text{-PbS}$ и осуществлена триангуляция. Установлено, что квазитройная система $\text{FeS-Ga}_2\text{S}_3\text{-PbS}$ триангулируется по квазибинарным сечениям $\text{FeS-PbGa}_2\text{S}_4$, $\text{FeS-Pb}_2\text{Ga}_2\text{S}_5$ и $\text{FeGa}_2\text{S}_4\text{-PbGa}_2\text{S}_4$ на четыре псевдотройные системы. В системе не наблюдается образование новой четверной фазы.

Ключевые слова: квазитройная система, антиферромагнетики, квазибинарные сечения, эвтектика, триангуляция.