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INTERACTION IN THE SYSTEM $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ ¹S.K.Jahangirova, ²Sh.H.Mammadov, ³G.R.Gurbanov, ²O.M.Aliyev¹Azerbaijan State Pedagogical University²Academician M.Nagiyev Institute of Catalysis and Inorganic Chemistry of NAS of Azerbaijan³Azerbaijan State Oil and Industry University

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The interaction in the system $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ which is the internal section of quasi ternary system $\text{Cu}_2\text{S--Ga}_2\text{S}_3\text{--PbS}$ has been studied for the first time using the methods of differential-thermal, X-ray phase and microstructural analyses and measurement of micro hardness and $T\text{--}x$ state diagram has been plotted. It was established that the section $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ belongs to a simple eutectic type with coordinates of eutectic point: 60 mol% PbGa_2S_4 and $T=1015$ K. The formation of narrow regions of solid solutions was established on the basis of components.

Keywords: interaction, system, eutectic, solid solution, X-ray analysis.

Introduction

It is known that ternary sulphides CuGaS_2 and PbGa_2S_4 exhibit unique physical properties (photosensitivity, induced approximate photoeffects, photoelectric memory, luminescence and other) [1–4], which also have an applied value in various fields of electronics and before first of all for photoelectronics.

In the system $\text{PbS--Ga}_2\text{S}_3$ [5, 6] compounds PbGa_2S_4 and $\text{Pb}_2\text{Ga}_2\text{S}_5$ are formed. According to [5] both compounds are formed by peritectic reaction and melt with decomposition at 1203 and 1173 K, correspondingly. Unlike [5], in the work [6] it was established that PbGa_2S_4 and $\text{Pb}_2\text{Ga}_2\text{S}_5$ melt congruently at 1163 and 1033 K, correspondingly, and the whole system $\text{PbS--Ga}_2\text{S}_3$ acts like the systems $\text{Cu}_2\text{S--Ga}_2\text{S}_3$ [7] and $\text{SrS--Ga}_2\text{S}_3$ [8]. According to [2], PbGa_2S_4 is a phase of a variable composition. Compound PbGa_2S_4 belongs to structural type of EuGa_2S_4 and is crystallized in rhombic syngony ($a=20.44$, $b=20.64$, $c=12.09$ Å. Space group – $Fddd$, $z=32$. $\rho=4.94\text{g/cm}^3$ [5].

According to [9] CuGaS_2 melts congruently at higher than 1548 K, belongs to structural type of chalcopyrite and is crystallized in tetragonal syngony with lattice parameters of $a=5.349$, $c=10.470$ Å. CuGaS_2 is a p -type semiconductor with band-gap energy of $\Delta E=2.38$ eV.

The present work is aimed at studying the interaction in the system $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ and plotting $T\text{--}x$ -state diagram.

Experimental part

We studied the system $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ to detect the character of chemical interaction between tiogallates of copper and lead, as well as to establish the existence of the regions of compounds and phases of variable composition. In the experimental part of the work we used the methods of differential-thermal (DTA), X-ray phase, microstructural analyses and measurement of microhardness. DTA was performed on thermoanalyzer NTR-70 in a temperature range of 298–1400 K. Heating rate is 10 grad/min. Aluminium oxide was used as standard. Diffractograms were taken on D2 Phaser (CuK_α -radiation, Ni-filter). Microstructure analysis was performed on microscope PMT–3 at loads selected from the measurement of each phase. Density was determined using picnometer method. 17 alloys of different composition were synthesized for this system (Table 1).

Results and discussion

Samples were synthesized from ternary sulphides by alloying in 10^{-3} MPa quartz ampoules sealed and preliminarily pumped of full residual pressure at 1200–1400 K for 8 hours with the rate of 10–15 grad/min. After the reaction we performed homogenizing annealing for 20 days at 900–950 K depending on the composition. According to thermal analysis we observed two thermal effects belonging to liquidus and solidus of the system.

Table 1. Results of thermal, microstructure analyses, measurements of microhardness and determination of density of alloys of the system $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$

Composition, mol%		Thermal heating effects, K		Phase composition
CuGaS_2	PbGa_2S_4	solidus	liquidus	
100	—		1548	single-phase
97	3.0	1475	1510	α (single-phase)
95	5.0	1420		α (single-phase)
90	10	1320	1430	$\alpha+\beta$
80	20	1130	1330	$\alpha+\beta$
70	30	1010	1240	$\alpha+\beta$
60	40	1015	1150	$\alpha+\beta$
50	50	1015	1070	$\alpha+\beta$
45	55	1015	1035	$\alpha+\beta$
40	60	1015	—	eutectic
35	65	1015	1030	$\alpha+\beta$
30	70	1015	1040	$\alpha+\beta$
25	75	1015	1060	$\alpha+\beta$
20	80	—	1080	$\alpha+\beta$
15	85	1030	1100	α (single-phase)
10	90	1070	1120	α
5.0	95	1110	1140	α
3.0	97	1130	1150	α
0.0	100		1163	single-phase

Fig. 1. Phase diagram of the section $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$.

State diagram of the system CuGaS_2 – PbGa_2S_4 plotted according to physico-chemical analyses is shown in Figure 1.

Microstructure analysis of annealed alloys (diluted solution of nitric acid was used as an etching agent) showed that alloys comprising 0–7 and 83–100 mol % PbGa_2S_4 are single-phase, but the rest alloys are double-phase.

Results of X-ray phase analysis are consistent with the data of microstructure analysis and confirm the formation of a narrow field of solid solutions in the system based on primary ternary sulphides (Figure 2).

Table 2 shows crystal lattice parameters and some physico-chemical properties of solid solutions based on the compound PbGa_2S_4 .

As figure shows the system CuGaS_2 – PbGa_2S_4 is quasi-binary section of quasi-ternary system Cu_2S – Ga_2S_3 – PbS and belongs to eutectic type. Eutectic point has a composition of 60

mol% PbGa_2S_4 and melts at 1015 K. According to the data of microstructure and X-ray phase analyses solid solution range based on tiogallate of copper CuGaS_2 reaches 29 mol% of PbGa_2S_4 at eutectic temperature, but at 500 K – 7 mol% of PbGa_2S_4 . Crystal lattice parameters of these solutions vary in the range of: $a=5.349$ – 5.362 , $c=10.470$ – $10.49\text{\AA}$. Solid solution range based on PbGa_2S_4 reaches 20 mol% of CuGaS_2 at eutectic temperature, but at 500 K – 17 mol% of CuGaS_2 .

As Table 2 shows, at a higher content of copper tiogallate the parameters of rhombic lattice of solid solution range based on PbGa_2S_4 increases.

It was established that mutual cation substitution Cu^+ ($r_{\text{Cu}^+} = 0.98\text{\AA}$, $r_{\text{Pb}^{2+}} = 1.06\text{\AA}$) in solid solutions $(\text{PbGa}_2\text{S}_4)_{1-x}(\text{CuGaS}_2)_x$ is regulated by proximity of ionic radii, coordination number of cations and character of a chemical bond.

Table 2. Results of X-ray phase analysis of the system $(\text{PbGa}_2\text{S}_4)_{1-x}(\text{CuGaS}_2)_x$

Composition	Lattice parameters, $\text{\AA}$			$V, \text{\AA}^3$	Z	$d, \text{g/cm}^3$	$H_\mu, \text{kg/mm}^2$
	a	b	c				
$x=0.0$	20.44	20.64	12.09	5100.5	32	4.94	275
$x=0.02$	20.44	20.65	12.10	5107.2	32	4.90	284
$x=0.04$	20.448	20.66	12.14	5128.6	32	4.87	296
$x=0.08$	20.460	20.665	12.158	5140.4	32	4.80	312
$x=0.10$	20.466	20.674	12.164	5146.7	32	4.76	317
$x=0.12$	20.470	20.680	12.166	5150.1	32	4.75	320
$x=0.15$	20.479	20.685	12.174	5154.7	32	4.50	325
$x=0.17$	20.484	20.700	12.180	5164.5	32	4.46	330
$x=1$	5.349		10.470	299.5	4	4.29	440

Fig. 2. Diffractogram of CuGaS_2 – PbGa_2S_4 system alloys: 1 – CuGaS_2 , 2 – 17 mol % CuGaS_2 , 3 – 10 mol % CuGaS_2 , 4 – PbGa_2S_4 .

Thus, we have plotted T - x state diagram of the system $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ for the first time. It was established that section $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ is quasi-binary and belongs to eutectic type.

Conclusion

1. State diagram of section $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ in a wide range of concentrations was plotted for the first time and it was detected that it is quasi-binary section of quasi-ternary system $\text{Cu}_2\text{S--Ga}_2\text{S}_3\text{--PbS}$.

2. It was found that section $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ is eutectic type; coordinates of eutectic point correspond to 60 mol% of PbGa_2S_4 and 1015 K.

3. Solid solution ranges in the system $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ were determined. Solid solutions based on CuGaS_2 are formed at room temperature (300 K) up to 7 mol%, but on the basis of PbGa_2S_4 up to 17 mol%.

4. Solid solutions based on CuGaS_2 are crystallized in tetragonal syngony, solid solutions based on PbGa_2S_4 are crystallized in rhombic syngony.

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$\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ SİSTEMİNDƏ QARŞILIQLI TƏSİR

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Differensial termiki, rentgen faza, mikroquruluş analizləri və mikrobərkliyin ölçülməsi ilə ilk dəfə $\text{Cu}_2\text{S--Ga}_2\text{S}_3\text{--PbS}$ kvaziüçlü sisteminin daxili kəsiyi olan $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ sistemi tədqiq olunmuş və sistemin T - x hal diaqramı qurulmuşdur. Müəyyən olunmuşdur ki, $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ sistemi evtektik tipli olub, evtektika nöqtəsinin koordinatları 60 mol% PbGa_2S_4 və $T=1050$ K-dir. İlkin komponentlərin əsasında məhdud həllolma sahəsi olduğu müəyyən edilmişdir.

Acar sözləri: qarşılıqlı təsir, sistem, evtektika, bərk məhlul, rentgenfaza analizi.

ВЗАИМОДЕЙСТВИЕ В СИСТЕМЕ $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$

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Методами дифференциально-термического, рентгенофазового и микроструктурного анализов, а также измерением микротвердости впервые изучено взаимодействие в системе $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$, являющейся внутренним разрезом квазитройной системы $\text{Cu}_2\text{S--Ga}_2\text{S}_3\text{--PbS}$, и построена T - x -диаграмма состояния. Установлено, что разрез $\text{CuGaS}_2\text{--PbGa}_2\text{S}_4$ относится к простому эвтектическому типу с координатами эвтектической точки: 60 мол.% PbGa_2S_4 и $T=1015$ К. На основе компонентов установлено образование узких областей твердых растворов.

Ключевые слова: взаимодействие, система, эвтектика, твердый раствор, рентгенофазовый анализ.