UDC 546(57,81,68,22)

Sharafat H. Mammadov [a], Guseyn R. Gurbanov [b], Rana A. Ismailova [b]

PHASE DIAGRAM OF THE $AgGaS_2$–$PbGa_2S_4$ SYSTEM

[a] Institute of Catalysis and Inorganic Chemistry named after academician M. Naghiyev, Baku, Republic of Azerbaijan
[b] Azerbaijan State Oil and Industry University, Baku, Republic of Azerbaijan

Lead and silver thiogallates are notable for their practical applications in nonlinear optical devices, detectors, solar cells, photodiodes, and phosphors. This study aims to develop materials with multifunctional properties and investigate the $AgGaS_2$–$PbGa_2S_4$ system. The initial sulfides, $AgGaS_2$ and $PbGa_2S_4$, were synthesized from high-purity elements sealed in evacuated quartz ampoules (0.133 Pa). Complex alloys of the $AgGaS_2$–$PbGa_2S_4$ system were prepared at 1200–1350 K. Polycrystalline samples were annealed at 850 K for 270 hours. Phase equilibria in the $AgGaS_2$–$PbGa_2S_4$ system were analyzed using a combination of physicochemical methods, including differential thermal analysis, powder X-ray diffraction, microstructural analysis, microhardness, and density measurements, and the phase diagram was constructed. The system was identified as a quasi-binary section of the quasi-ternary Ag_2S–Ga_2S_3–PbS system, belonging to the eutectic type. The eutectic point was determined at 1100 K and 55 mol.% $PbGa_2S_4$. Solid solution regions were identified based on the primary components. At room temperature, the $AgGaS_2$ solid solution region extends to 10 mol.% $PbGa_2S_4$, while the $PbGa_2S_4$ solid solution region extends to 18 mol.% $AgGaS_2$. At the eutectic temperature, these solubilities increase to 20 and 25 mol.%, respectively. $AgGaS_2$-based solid solutions crystallize in chalcopyrite-type structures, while $PbGa_2S_4$-based solid solutions adopt orthorhombic structures.

Keywords: PbS–Ga_2S_3–Ag_2S, quasi-binary system, solid solutions, $AgGaS_2$, ternary system, eutectic.

DOI: 10.32434/0321-4095-2025-158-1-22-26

Introduction

Crystals of silver and lead thiogallates have recently aroused particular interest in the study of systems containing sulfides with the formulae $A^{I}B^{III}C_2^{VI}$ and AB_2C_4. First of all, this is due to the emerging possibilities of their practical use in the manufacture of nonlinear optical devices, detectors, solar cells, photodiodes and phosphors [1–9]. The study of the optical properties of $PbGa_2S_4$ lead thiogallate crystals revealed that it is a promising material for optoelectronics [10].

In the PbS–Ga_2S_3 system [11,12], compounds of $PbGa_2S_4$ and $Pb_2Ga_2S_5$ are formed. According to ref. [11], both compounds are formed by a peritectic reaction and melt with decomposition at temperatures of 1203 and 1173 K, respectively. In contrast to ref. [11], study [12] found that $PbGa_2S_4$ and $Pb_2Ga_2S_5$ melt congruently at 1163 and 1033 K, respectively; and in general, the PbS–Ga_2S_3 system behaves like the Cu_2S–Ga_2S_3 and SrS–Ga_2S_3 systems. According to ref. [13], $PbGa_2S_4$ is a phase of variable composition. The $PbGa_2S_4$ compound belongs to the $EuGa_2S_4$ structural type and crystallizes in the orthorhombic system (a=20.44 Å, b=20.64 Å, c=12.09 Å; space group Fddd, z=32, ρ=4.94 g/cm^3 [11]).

Study of the Ag_2S–Ga_2S_3 system showed that three compounds are formed in the system with the compositions $AgGaS_2$, Ag_9GaS_6 and $Ag_2Ga_{20}S_{31}$.

$Ag_2Ga_{20}S_{31}$ is formed by a peritectic reaction at a temperature of 1263 K, and the compounds $AgGaS_2$ and Ag_9GaS_6 are congruent at 1270 K and 1063 K, respectively. The compounds $AgGaS_2$ and Ag_9GaS_6 crystallize in the chalcopyrite structural type: a=5.7544 Å, c=10.299 Å; space group I42d. The Ag_9GaS_6 compound crystallizes into orthorhombic systems with parameters a=10.777 Å, b=7.706 Å, c=7.605 Å.

The purpose of this research work was to obtain materials with multifunctional properties and study the $AgGaS_2$–$PbGa_2S_4$ system.

Experimental

The alloys for studying the $AgGaS_2$–$PbGa_2S_4$ system were prepared from master alloys in evacuated quartz ampoules at a temperature of 1200–1350 K. Pure elements were used as starting materials (Ag, highly pure grade; Ga, Gl-000 grade; sulfur highly pure grade; and Pb containing main substance no less than 99.999%).

Polycrystalline samples were annealed at 850 K for 270 hours. The pressed alloys of the $AgGaS_2$–$PbGa_2S_4$ system were studied by differential thermal analysis (DTA), powder X-ray diffraction (XRD), microstructural analysis (MSA microscope MIM-7), measuring the density and microhardness (PMT-3 device). DTA was performed using NETZSCH 404 F1 Pegasus at room temperature to approximately 1400 K, depending on the alloy composition, at a heating rate of 10 K/min. Temperature accuracy was ±2 K. Powder X-ray diffraction data were examined on a Bruker D2 Phaser diffractometer using CuKα1 radiation (λ=1.54056 Å).

Results and discussions

In order to study the nature of the interaction in the $AgGaS_2$–$PbGa_2S_4$ system, 12 alloys were synthesized (Table).

The DTA results revealed two endothermic effects in the thermograms of alloys containing 0–100% $PbGa_2S_4$. Microstructural analysis data showed that alloys similar in composition to the ternary compounds $AgGaS_2$ and $PbGa_2S_4$ (100–90 and 100–82 mol.%, respectively) consist of one phase; with an increase in the content of the second component, two-phase regions are noted. In the subsolidus of the system, in the concentration range of 10–82 mol.% $PbGa_2S_4$, two phases (α+β) co-crystallize. The XRD results of alloys of the $AgGaS_2$–$PbGa_2S_4$ system are consistent with the MSA and DTA data and confirm the existence of solid solutions based on $AgGaS_2$ and $PbGa_2S_4$. Considering the results of DTA, MSA, XRF and microhardness measurements, a state diagram of the $AgGaS_2$–$PbGa_2S_4$ system was constructed (Fig. 1).

Results of thermal and microstructural analysis of alloys in the $AgGaS_2$–$PbGa_2S_4$ system

Composition, mol.%		Thermal effects, K	Phase composition
$AgGaS_2$	$PbGa_2S_4$		
100	0	1270	α
90	10	1180, 1245	α
80	20	1115, 1205	α+β
70	30	1100, 1175	α+β
60	40	1100, 1145	α+β
50	50	1100, 1125	α+β
45	55	1100 (eutectic)	α+β
40	60	110, 1130	α+β
30	70	1105, 1145	α+β
18	82	1110, 1155	β
10	90	1145, 1160	β
0	100	1165	β

As can be seen from Fig. 1, the system is a quasi-binary section of the quasi-ternary system Ag_2S–Ga_2S_3–PbS and belongs to the eutectic type. The liquidus system consists of two branches of the primary crystallization phase $AgGaS_2$ and $PbGa_2S_4$ intersecting the eutectic point, characterizing non-variant equilibrium

$$L \rightarrow \alpha(AgGaS_2)+\beta(PbGa_2S_4).$$

The coordinates of the eutectic point are as follows: 55 mol.% $PbGa_2S_4$ and T=1100 K. Based

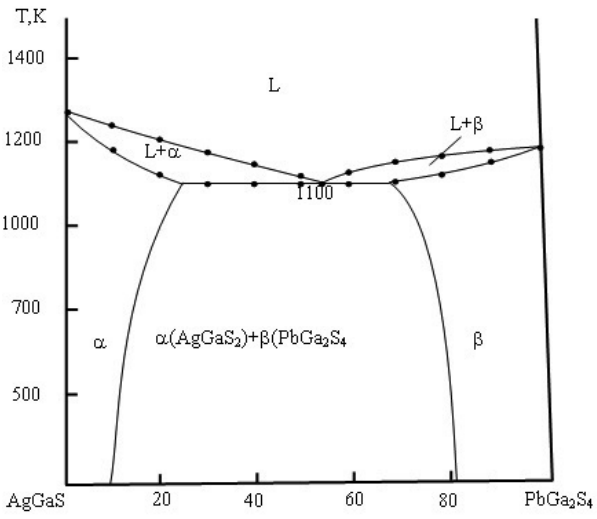

Fig. 1. Phase diagram of the $AgGaS_2$–$PbGa_2S_4$ system

on the initial components, limited areas of solid solutions are formed. The results of X-ray phase analysis showed that the diffraction patterns of alloys containing 0–10 mol.% $PbGa_2S_4$ and 0–18 mol.% $AgGaS_2$ are identical to the diffraction patterns of the parent ternary compounds $AgGaS_2$ and $PbGa_2S_4$, respectively. They are substitutional solid solutions. Based on the data obtained, the microhardness of the alloys of the $AgGaS_2$–$PbGa_2S_4$ system was measured and a microhardness (Hμ) *vs.* composition diagram was constructed (Fig. 2).

The graph shows that the microhardness values of samples rich in $AgGaS_2$ and $PbGa_2S_4$ increase significantly from 3860 to 3990 MPa and from 2250 to 2400 MPa with the formation of solid solutions.

The densities of samples belonging to the $AgGaS_2$–$PbGa_2S_4$ system were measured and a density *vs.* composition diagram was constructed (Fig. 3). It showed that the density of the samples varies within the density of the original sulfides ($AgGaS_2$ and $PbGa_2S_4$).

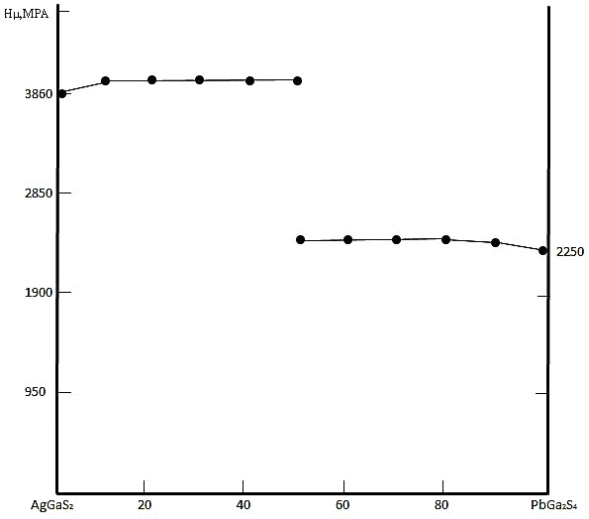

Fig. 2. Hμ *vs.* x diagrams of the $AgGaS_2$–$PbGa_2S_4$ system

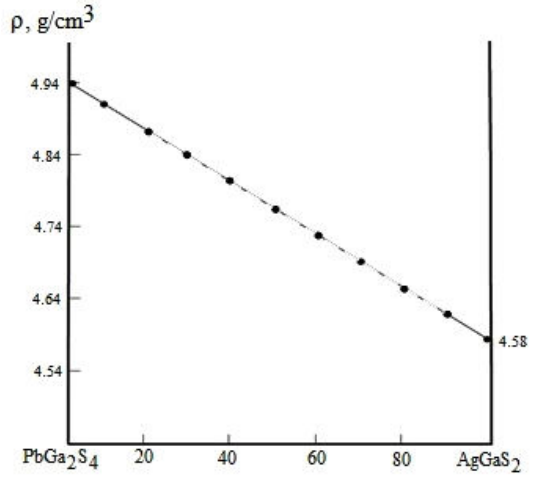

Fig. 3. ρ *vs.* x Diagram of the $PbGa_2S_4$–$AgGaS_2$ system

Conclusions

1. Using physical and chemical analysis methods (DTA, XRF, and MSA), the T *vs.* x phase diagram of the $AgGaS_2$–$PbGa_2S_4$ system was constructed. It was determined that the $AgGaS_2$–$PbGa_2S_4$ system is a quasi-binary cross-section of the quasi-ternary system Ag_2S–Ga_2S_3–PbS and belongs to the eutectic type.

2. In the $AgGaS_2$–$PbGa_2S_4$ system, the formation of solid solutions of the initial components was revealed. The solubility based on $AgGaS_2$ at room temperature (300 K) is 10 mol.% $PbGa_2S_4$, and that on the basis of $PbGa_2S_4$ is 18 mol.% $AgGaS_2$.

REFERENCES

1. *Lattice* dynamical properties and elastic constants of the ternary chalcopyrite compounds $CuAlS_2$, $CuGaS_2$, $CuInS_2$, and $AgGaS_2$ / Kushwaha A.K., Khenata R., Bouhemadou A., Bin-Omran S., Haddadi K. // J. Electron. Mater. – 2017. – Vol.46. – P.4109-4118.

2. *Dislocations* that decrease size mismatch within the lattice leading to ultrawide band gap, large second-order susceptibility, and high nonlinear optical performance of $AgGaS_2$ / Zhou H., Xiong L., Chen L., Wu L. // Angew. Chem. Int. Ed. – 2019. – Vol.58. – No. 29. – P.9979-9983.

3. *Li G., Chu Y., Zhou Z.* From $AgGaS_2$ to Li_2ZnSiS_4: realizing impressive high laser damage threshold together with large second-harmonic generation response // Chem. Mater. – 2018. – Vol.30. – No. 3. – P.602-606.

4. *Pressure* effect of the vibrational and thermodynamic properties of chalcopyrite-type compound $AgGaS_2$: a first-principles investigation / Yang J., Fan Q., Yu Y., Zhang W. // Materials. – 2018. – Vol.11. – No. 12. – Art. No. 2370.

5. *Synthesis* and characterization of $AgGaS_2$ nanoparticles: a study of growth and fluorescence / Paderick S., Kessler M., Hurlburt T.J., Hughes S.M. // Chem. Commun. – 2018. – Vol.54. – P.62-65.

6. *New* sellmeier and thermo-optic dispersion formulas for $AgGaS_2$ / Kato K., Okamoto T., Grechin S., Umemura N. // Crystals. – 2019. – Vol.9. – Art. No. 129.

7. *Mammadov S.* The study of the quasi-triple system FeS–Ga_2S_3–Ag_2S by a $FeGa_2S_4$–$AgGaS_2$ section // Kondensirovannye Sredy i Mezhfaznye Granitsy. – 2020. – Vol.22. – No. 2. – P.232-237.

8. *Asadov S.M., Mustafaeva S.N., Guseinov D.T.* X-ray dosimetric characteristics of $AgGaS_2$ single crystals grown by chemical vapor transport // Inorg. Mater. – 2017. – Vol.53. – P.457-461.

9. *Anisotropy* of acousto-optic figure of merit for the collinear diffraction of circularly polarized optical waves at the wavelength of isotropic point in $AgGaS_2$ crystals / Mys O., Adamenko D., Skab I., Vlokh R. // Ukr. J. Phys. Opt. – 2019. – Vol.20. – P.73-80.

10. *Optical* phonons in $PbGa_2S_4$ crystals / Kamenshchikov V.N., Stefanovich V.A., Gad'mashi Z.P., Sidei V.I., Suslikov L.M. // Phys. Solid State. – 2007. – Vol.49. – P.351-355.

11. *Chilouet A., Mazurier A., Guittard M.* Systeme Ga_2S_3–PbS diagramme de phase, etude crystallographique // Mater. Res. Bull. – 1979. – Vol.14. – P.1119-1124.

12. *A new* low-phonon lead thiogallate crystal as a matrix for mid-IR lasers / Badikoya D., Badikov V., Doroshenko M., Fintisova A., Shavyrdyaeva G. // Photonics. – 2008. – No. 4. – P.24-27.

13. *Electron* paramagnetic resonance of Dy^{3+} ions in lead thiogallate single crystals / Asatryan G.R., Badikov V.V., Kramushchenko D.D., Khramtsov V.A. // Phys. Solid State. – 2012. – Vol.54. – P.1245-1248.

Received 23.05.2024

ФАЗОВА ДІАГРАМА СИСТЕМИ $AgGaS_2$–$PbGa_2S_4$

Ш.Г. Маммадов, Г.Р. Гурбанов, Р.А. Ісмаїлова

Тіогаллати свинцю та срібла вирізняються широкими можливостями практичного застосування в нелінійних оптичних пристроях, детекторах, сонячних батареях, фотодіодах та люмінофорах. Метою цього дослідження є розробка матеріалів із багатофункціональними властивостями та вивчення системи $AgGaS_2$–$PbGa_2S_4$. Вихідні сульфіди $AgGaS_2$ і $PbGa_2S_4$ були синтезовані з високочистих елементів у кварцових ампулах, евакуйованих до тиску 0,133 Па. Комплексні сплави системи $AgGaS_2$–$PbGa_2S_4$ були одержані за температури 1200–1350 K. Полікристалічні зразки відпалювали за температури 850 K протягом 270 годин. Фазові рівноваги в системі $AgGaS_2$–$PbGa_2S_4$ були досліджені за допомогою комплексу фізико-хімічних методів, включаючи диференціальний термічний аналіз, рентгенівську порошкову дифракцію, мікроструктурний аналіз, вимірювання мікротвердості та густини, що дозволило побудувати фазову діаграму. Було встановлено, що система $AgGaS_2$–$PbGa_2S_4$ є квазібінарним перерізом квазі-потрійної системи Ag_2S–Ga_2S_3–PbS і належить до евтектичного типу. Евтектична точка має координати: температура 1100 K і вміст 55 мол.% $PbGa_2S_4$. Ділянки твердих розчинів ідентифіковано на основі початкових компонентів. За кімнатної температури ділянка твердих розчинів на основі $AgGaS_2$ розширюється до 10 мол.% $PbGa_2S_4$, а на основі $PbGa_2S_4$ – до 18 мол.% $AgGaS_2$. За евтектичної температури ці розчинності зростають до 20 і 25 мол.%, відповідно. Тверді розчини на основі $AgGaS_2$ кристалізуються в структурах типу халькопіриту, тоді як тверді розчини на основі $PbGa_2S_4$ мають орторомбічну структуру.

Ключові слова: PbS–Ga_2S_3–Ag_2S; квазібінарна система; тверді розчини; $AgGaS_2$; потрійна система; евтектика.

PHASE DIAGRAM OF THE $AGGAS_2$–$PBGA_2S_4$ SYSTEM

Sharafat H. Mammadov [a], Guseyn R. Gurbanov [b, *], Rana A. Ismailova [b]

[a] Institute of Catalysis and Inorganic Chemistry named after academician M. Naghiyev, Baku, Republic of Azerbaijan

[b] Azerbaijan State Oil and Industry University, Baku, Republic of Azerbaijan

[*] e-mail: ebikib@mail.ru

Lead and silver thiogallates are notable for their practical applications in nonlinear optical devices, detectors, solar cells, photodiodes, and phosphors. This study aims to develop materials with multifunctional properties and investigate the $AgGaS_2$–$PbGa_2S_4$ system. The initial sulfides, $AgGaS_2$ and $PbGa_2S_4$, were synthesized from high-purity elements sealed in evacuated quartz ampoules (0.133 Pa). Complex alloys of the $AgGaS_2$–$PbGa_2S_4$ system were prepared at 1200–1350 K. Polycrystalline samples were annealed at 850 K for 270 hours. Phase equilibria in the $AgGaS_2$–$PbGa_2S_4$ system were analyzed using a combination of physicochemical methods, including differential thermal analysis, powder X-ray diffraction, microstructural analysis, microhardness, and density measurements, and the phase diagram was constructed. The system was identified as a quasi-binary section of the quasi-ternary Ag_2S–Ga_2S_3–PbS system, belonging to the eutectic type. The eutectic point was determined at 1100 K and 55 mol.% $PbGa_2S_4$. Solid solution regions were identified based on the primary components. At room temperature, the $AgGaS_2$ solid solution region extends to 10 mol.% $PbGa_2S_4$, while the $PbGa_2S_4$ solid solution region extends to 18 mol.% $AgGaS_2$. At the eutectic temperature, these solubilities increase to 20 and 25 mol.%, respectively. $AgGaS_2$-based solid solutions crystallize in chalcopyrite-type structures, while $PbGa_2S_4$-based solid solutions adopt orthorhombic structures.

Keywords: PbS–Ga_2S_3–Ag_2S; quasi-binary system; solid solutions; $AgGaS_2$; ternary system; eutectic.

REFERENCES

1. Kushwaha AK, Khenata R, Bouhemadou A, Bin-Omran S, Haddadi K. Lattice dynamical properties and elastic constants of the ternary chalcopyrite compounds $CuAlS_2$, $CuGaS_2$, $CuInS_2$, and $AgGaS_2$. *J Electron Mater.* 2017; 46: 4109-4118. doi: 10.1007/s11664-017-5290-6.

2. Zhou H, Xiong L, Chen L, Wu L. Dislocations that decrease size mismatch within the lattice leading to ultrawide band gap, large second-order susceptibility, and high nonlinear optical performance of $AgGaS_2$. *Angew Chem Int Ed.* 2019; 58(29): 9979-9983. doi: 10.1002/anie.201903976.

3. Li G, Chu Y, Zhou Z. From $AgGaS_2$ to Li_2ZnSiS_4: realizing impressive high laser damage threshold together with large second-harmonic generation response. *Chem Mater.* 2018; 30(3): 602-606. doi: 10.1021/acs.chemmater.7b05350.

4. Yang J, Fan Q, Yu Y, Zhang W. Pressure effect of the vibrational and thermodynamic properties of chalcopyrite-type compound $AgGaS_2$: a first-principles investigation. *Materials.* 2018; 11(12): 2370. doi: 10.3390/ma11122370.

5. Paderick S, Kessler M, Hurlburt TJ, Hughes SM. Synthesis and characterization of $AgGaS_2$ nanoparticles: a study of growth and fluorescence. *Chem Commun.* 2018; 54: 62-65. doi: 10.1039/C7CC08070K.

6. Kato K, Okamoto T, Grechin S, Umemura N. New sellmeier and thermo-optic dispersion formulas for $AgGaS_2$. *Crystals*. 2019; 9: 129. doi: 10.3390/cryst9030129.

7. Mammadov S. The study of the quasi-triple system $FeS-Ga_2S_3-Ag_2S$ by a $FeGa_2S_4-AgGaS_2$ section. *Kondensirovannye Sredy i Mezhfaznye Granitsy*. 2020; 22(2): 232-237. doi: 10.17308/kcmf.2020.22/2835.

8. Asadov SM, Mustafaeva SN, Guseinov DT. X-ray dosimetric characteristics of $AgGaS_2$ single crystals grown by chemical vapor transport. *Inorg Mater*. 2017; 53: 457-461. doi: 10.1134/S0020168517050028.

9. Mys O, Adamenko D, Skab I, Vlokh R. Anisotropy of acousto-optic figure of merit for the collinear diffraction of circularly polarized optical waves at the wavelength of isotropic point in $AgGaS_2$ crystals. *Ukr J Phys Opt*. 2019; 20: 73-80. doi: 10.3116/16091833/20/2/73/2019.

10. Kamenshchikov VN, Stefanovich VA, Gad'mashi ZP, Sidei VI, Suslikov LM. Optical phonons in $PbGa_2S_4$ crystals. *Phys Solid State*. 2007; 49: 351-355. doi: 10.1134/S1063783407020278.

11. Chilouet A, Mazurier A, Guittard M. Systeme Ga_2S_3–PbS diagramme de phase, etude crystallographique. *Mater Res Bull*. 1979; 14: 1119-1124. doi: 10.1016/0025-5408(79)90205-8.

12. Badikoya D, Badikov V, Doroshenko M, Fintisova A, Shavyrdyaeva G. A new low-phonon lead thiogallate crystal as a matrix for mid-IR lasers. *Photonics*. 2008; (4): 24-27.

13. Asatryan GR, Badikov VV, Kramushchenko DD, Khramtsov VA. Electron paramagnetic resonance of Dy^{3+} ions in lead thiogallate single crystals. *Phys Solid State*. 2012; 54: 1245-1248. doi: 10.1134/S1063783412060042.