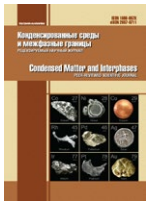

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Phase equilibria and some properties of solid solutions of $PbGa_2S_4$–$SmGa_2S_4$ and $PbGa_2Se_4$–$SmGa_2Se_4$ systems

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Abstract

Objectives: In connection with the transition to green energy, the search for, synthesis of, and investigation into alternative energy sources and the materials required for them are of great importance. One of the methods for obtaining such promising materials is the study of phase diagrams between isostructural compounds. In this regard, phase equilibria in the $PbGa_2S_4$–$SmGa_2S_4$ and $PbGa_2Se_4$–$SmGa_2Se_4$ systems were investigated using physicochemical analysis methods (DTA, XRD, measurements of microhardness and density), and their phase diagrams were constructed.

Conclusions: It has been established that the specified systems are quasi-binary and are characterized by the formation of continuous substitution-type solid-solution areas. The solid solutions $Pb_{1-x}Sm_xGa_2S_4$ and $Pb_{1-x}Sm_xGa_2Se_4$ crystallize in the orthorhombic crystal system and belong to the $EuGa_2S_4$ structural type. Their unit-cell parameters vary within the following ranges: $Pb_{1-x}Sm_xGa_2S_4$ a = 20.745–20.706 Å; b = 20.464–20.380 Å; c = 12.236–12.156 Å; $Pb_{1-x}Sm_xGa_2Se_4$ a = 21.722–21.782 Å; b = 21.202–21.350 Å; c = 12.3047–12.390 Å; Space group: *Fddd*, Z = 32. Several physicochemical properties of the $Pb_{1-x}Sm_xGa_2S_4$ and $Pb_{1-x}Sm_xGa_2Se_4$ solid solutions have been investigated.

Keywords: System, Solid solution, Unit cell, Lattice parameter, Phase diagram

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1. Introduction

Modern scientific and technological progress is largely driven by the use of functional materials possessing unique properties. This necessitates systematic research, synthesis, design, and comprehensive investigation of their fundamental characteristics. In this context, the study of phase diagrams between isostructural compounds forming continuous series of solid solutions provides an opportunity to control the functional properties of the resulting materials [1–7].

At present, the study of alternative energy sources is one of the highest-priority areas of scientific research worldwide. Solving this problem is closely associated with the development of new efficient energy converters, particularly thermoelectric and photovoltaic materials [8–15].

The primary compounds ($PbGa_2S_4$, $SmGa_2S_4$; $PbGa_2Se_4$, $SmGa_2Se_4$) have been studied in sufficient detail [16–25]. According to [17], the compound $PbGa_2S_4$ is formed by the peritectic reaction $L+PbS \leftrightarrow PbGa_2S_4$ and melts incongruently at 1203 K, it crystallizes in the orthorhombic system with the following unit-cell parameters: a = 20.44 Å; b = 20.64 Å; c = 12.09 Å, space group Fddd, Z = 32, d = 4.94 g/cm³, and belongs to the $EuGa_2S_4$ structural type. According to [13], $PbGa_2S_4$ melts congruently at 1163 K and has lattice parameters: a = 20.706 Å; b = 20.380 Å; c = 12.156 Å. An analysis of the literature data [13, 16–18] shows that, with the exception of one study [18], all other authors assert that $PbGa_2S_4$ melts congruently. Therefore, in the present study we relied on the results of the most recent works [13]. Our synthesized and investigated $PbGa_2S_4$ sample confirmed the congruent nature of its melting, which is consistent with [16, 17]. $PbGa_2S_4$ is a wide-bandgap semiconductor and exhibits multifunctional properties: laser [13], paramagnetic [26], and optically active characteristics [27–29]. $PbGa_2Se_4$ also melts congruently at 1050 K [19–21] and has a structural type of $EuGa_2S_4$ (a = 21.72 Å; b = 21.20 Å; c = 12.30 Å).

$SmGa_2S_4$ melts congruently at 1750 K [23–25] and crystallizes in the orthorhombic system with lattice parameters: a = 20.745 Å; b = 20.464 Å; c = 12.236 Å, space group Fddd, Z = 32, microhardness Hμ = 2800, density d = 4.28 g/cm³. $SmGa_2S_4$ is a semiconductor with a bandgap ΔE = 2.20 eV [23, 24]. Unlike $SmGa_2S_4$, the compound $SmGa_2Se_4$ melts incongruently at 1200 K and has a structural type of $EuGa_2S_4$ (a = 21.700 Å; b = 21.23 Å; c = 12.39 Å), with Hμ = 2700, d = 6.02 g/cm³, and ΔE = 1.40 eV [1, 25].

Since the thio- and selenogallates of lead and samarium exhibit laser, optical, and luminescent properties, the study of their chemical interactions holds promise for obtaining materials with multifunctional characteristics.

The aim of the present work is to investigate the phase equilibria in the $PbGa_2S_4$-$SmGa_2S_4$ and $PbGa_2Se_4$–$SmGa_2Se_4$ systems and to study the physicochemical properties of the $Pb_{1-x}Sm_xS_4$ (Se_4) solid solutions.

2. Experimental

The alloys were obtained by melting ternary sulfides or selenides of lead and samarium ($PbGa_2S_4$, $PbGa_2Se_4$, $SmGa_2S_4$, $SmGa_2Se_4$) in evacuated quartz ampoules at temperatures of 1300–1400 K. The initial ternary sulfides and selenides of lead and samarium were synthesized by melting high-purity elemental components. The molten alloys were held at the maximum temperature (1300–1400 K) for 30–40 minutes, then cooled to 1000 K and kept at this temperature for 1200 hours for homogenization. As a result, yellow-colored alloys suitable for physicochemical analysis were obtained.

The alloys (samples weighing 0.1–0.3 g) were examined using differential thermal analysis (DTA) on a Netzsch STA 449 F3 instrument (platinum–platinum/rhodium thermocouples, in the temperature range from room temperature to ~1450 K, heating rate 10 K·min^{-1}), X-ray phase analysis (XRD, Bruker D2 PHASER, CuKα radiation), microhardness measurements (on an PMT-3 microhardness tester), and density determination (using the pycnometric method with toluene as the filling medium). The measurement errors for DTA, XRD, microhardness, and density were ±3 K, ±0.001 Å, ±3 MPa, and ±0.3 g/cm³, respectively.

3. Results and discussion

The phase diagram of the $PbGa_2S_4$–$SmGa_2S_4$ system, constructed on the basis of physicochemical analysis, is shown in Fig. 1a.

As seen from Fig. 1a, the $PbGa_2S_4$–$SmGa_2S_4$ system is characterized by the complete mutual

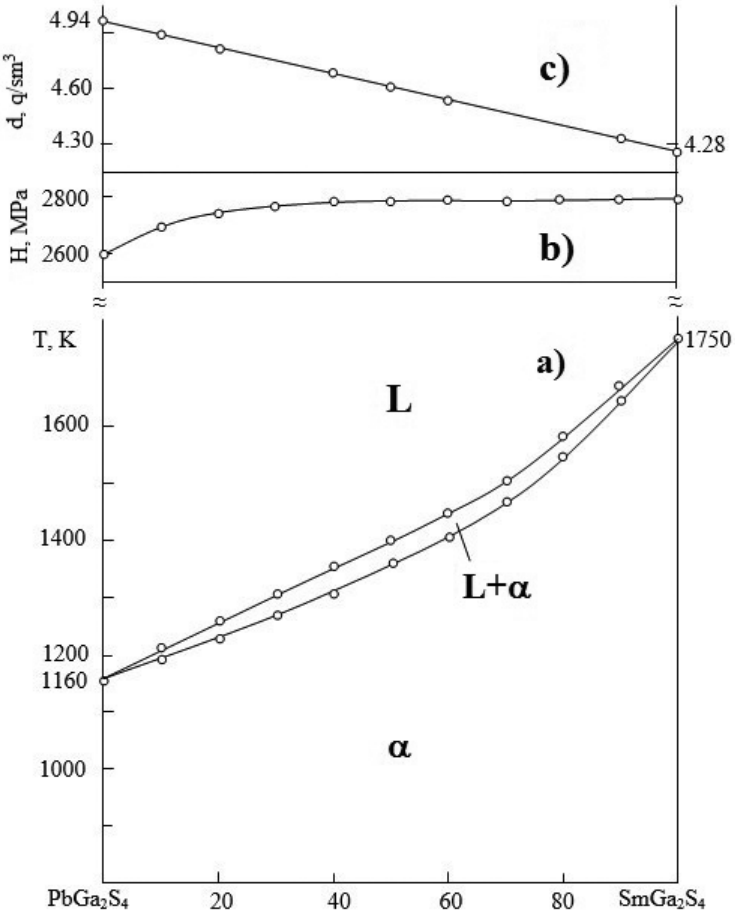

Fig. 1. *T-x* phase diagram of the $PbGa_2S_4$–$SmGa_2S_4$ system (a), dependence of microhardness (b) and density (c) on the composition

solubility of the components in both the liquid and solid states and corresponds to a first-type phase diagram according to Rosenbaum [30]. No extremum point is observed on the liquidus and solidus curves; their temperatures vary monotonically between the melting points of the initial ternary sulfides ($PbGa_2S_4$ and $SmGa_2S_4$).

The maximum temperature difference between corresponding points on the liquidus and solidus lines is 25 K (see Fig. 1a). Therefore, one could expect a common extremum point (minimum or maximum) on these curves. On the other hand, it should be noted that Rosenbaum first-type phase diagrams usually occur in systems where the thermodynamic functions of mixing in both the liquid and solid states are very low or very similar. The composition dependences of microhardness and density for the $PbGa_2S_4$–$SmGa_2S_4$ system are presented in Figs. 1b and 1c.

X-ray phase analysis of the samples annealed at 1000 K after thermal treatment shows that all samples of the $PbGa_2S_4$ - $SmGa_2S_4$ system, including the starting sulfides, exhibit diffraction patterns characteristic of the orthorhombic crystal system (Fig. 2). This indicates that at 1000 K continuous series of solid solutions with orthorhombic structure are formed between the initial compounds. The compositional dependence of lattice parameters, shown in Fig. 3, has a linear character, which indeed confirms the formation of a continuous solid-solution series. Using the TOPAS-3 software, the structural type and the unit-cell parameters of the $Pb_{1-x}Sm_xGa_2S_4$ solid solutions were determined; the results are presented in Table 1.

Table 1 also contains the DTA results obtained after thermal treatment at 1000 K. Based on these data, along with the XRD results, the *T*–*x* phase diagram of the $PbGa_2S_4$–$SmGa_2S_4$ system was constructed (Fig. 1a).

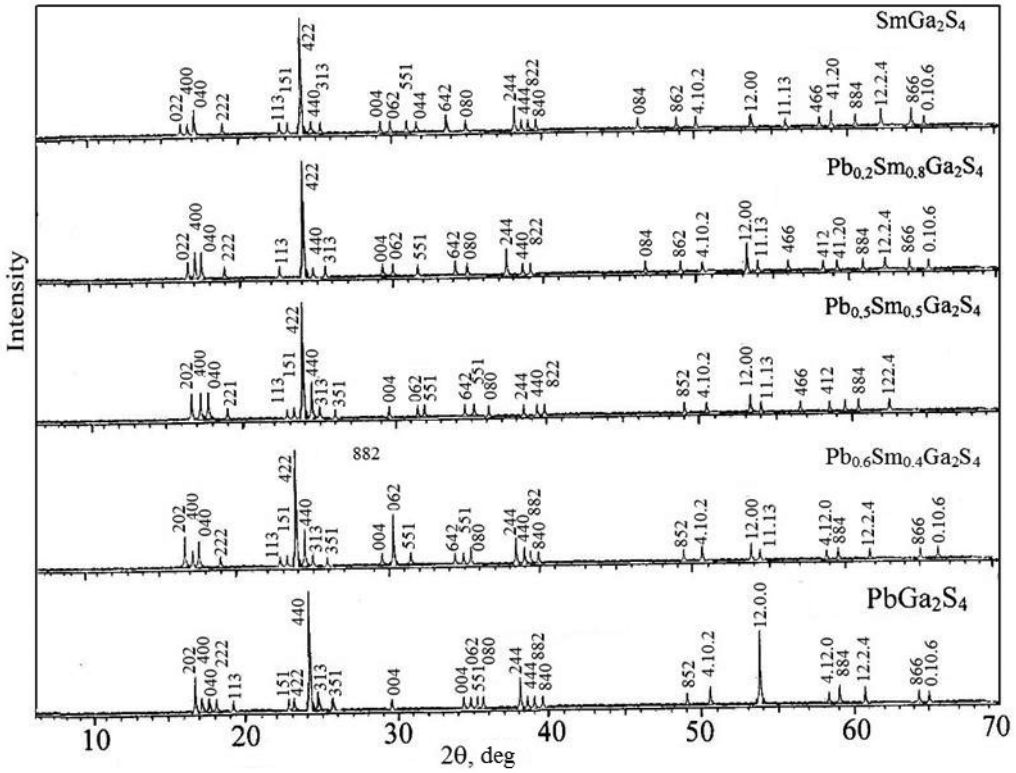

Fig. 2. The XRD patterns of the $PbGa_2S_4$–$SmGa_2S_4$ system

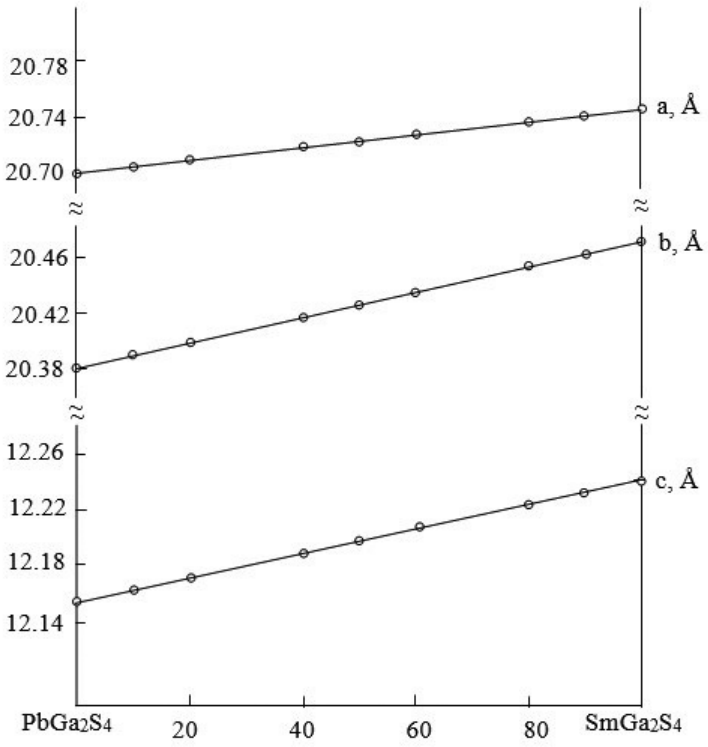

Fig. 3. Dependence of lattice parameters on the composition of solid solutions of the $PbGa_2S_4$–$SmGa_2S_4$ system

Table. 1. Results of DTA, XRD, microhardness, and density of alloys of the $PbGa_2S_4$–$SmGa_2S_4$ system

Composition, mol % $SmGa_2S_4$	Thermal effects, K	Lattice parameters, Å			Space group	*Z*	$H_μ$, MPa	d_{pik}, g/sm^3
		a	*b*	*c*				
$PbGa_2S_4$	1163	20.706	20.380	12.156	*Fddd*	32	2650	4.94
10	1205, 1225	20.708	20.378	12.164	*Fddd*	32	2700	4.85
20	1230, 1260	20.712	20.384	12.180	*Fddd*	32	2750	4.70
40	1320, 1350	20.716	20.420	12.198	*Fddd*	32	2760	4.56
50	1390, 1410	20.728	20.425	12.218	*Fddd*	32	2780	4.48
60	1455, 1480	20.732	20.440	12.220	*Fddd*	32	2790	4.36
80	1575, 1610	20.736	20.460	12.226	*Fddd*	32	2800	–
90	1666, 1680	20.740	20.462	12.234	*Fddd*	32	2800	4.30
$SmGa_2S_4$	1750	20.745	20.464	12.236	*Fddd*	32	2800	4.28

Thus, in both the liquid and solid solutions, the deviation from ideality in the substitution of lead by samarium is very small.

As shown in Fig. 4a, the $PbGa_2Se_4$–$SmGa_2Se_4$ system is partially quasi-binary. Due to the incongruent melting of $SmGa_2Se_4$, the quasi-binary nature of the system is disrupted in alloys near this compound. Therefore, in the concentration range of 60–100 mol % $SmGa_2Se_4$, a three-phase area appears at high temperatures; however, at low temperatures, continuous solid solutions of the $EuGa_2S_4$ type are formed. In the composition interval 0–40 mol % $PbGa_2Se_4$, α-solid-solution crystals precipitate primarily from the melt. In compositions richer in $SmGa_2Se_4$, the SmSe compound crystallizes. As

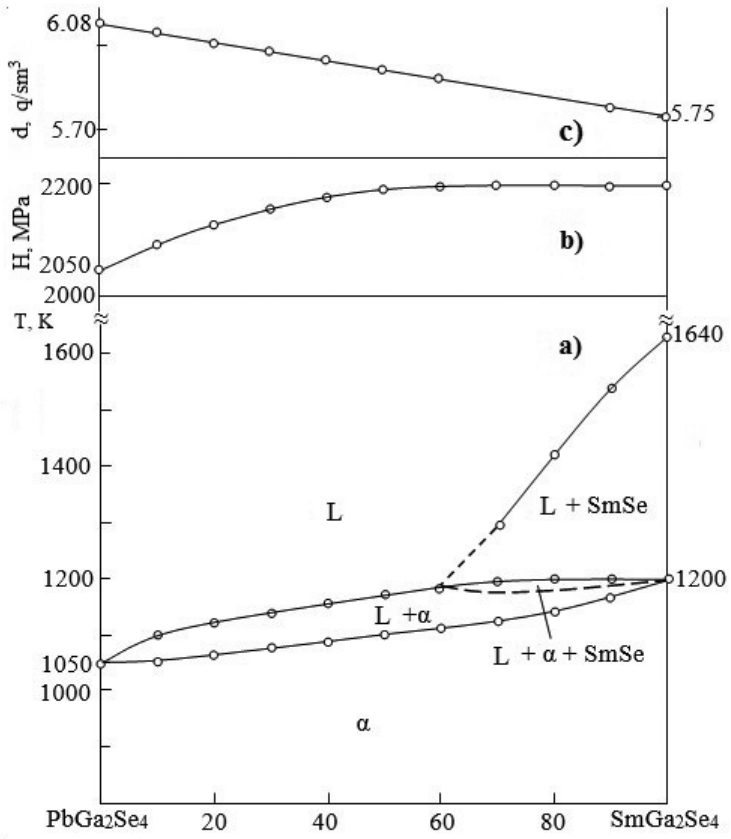

Fig. 4. *T-x* phase diagram of the $PbGa_2Se_4$–$SmGa_2Se_4$ system (a) and the dependence of microhardness (b) and density (c) on the composition

a result of the univariant peritectic reaction L + SmSe ↔ α, a three-phase area L + SmSe + α should form below 1200 K. However, this field was not experimentally detected due to its narrow temperature interval and is shown schematically by a dashed line.

The liquidus of the $PbGa_2Se_4$ – $SmGa_2Se_4$ system contains two areas corresponding to the primary crystallization of SmSe and of the α-phase.

The XRD results, the composition dependences of lattice parameters (Fig. 5), as well as the microhardness and density measurements (Figs. 4b, 4c) are consistent with the phase diagram of the $PbGa_2Se_4$ – $SmGa_2Se_4$ system.

In the $PbGa_2Se_4$ – $SmGa_2Se_4$ system, the initial compounds and all alloys exhibit similar diffraction patterns, with slight shifts of the reflections. The variation in orthorhombic lattice parameters of the $Pb_{1-x}Sm_xGa_2Se_4$ solid solutions as a function of composition, along with the DTA results, are given in Table 2.

4. Conclusion

Phase equilibria in the $PbGa_2S_4$-$SmGa_2S_4$ and $PbGa_2Se_4$–$SmGa_2Se_4$ systems were investigated for the first time using physicochemical analysis methods, and their phase diagrams were constructed. It has been established that the $PbGa_2S_4$-$SmGa_2S_4$ system is quasi-binary and is characterized by the formation of a continuous series of solid solutions. The $PbGa_2Se_4$–$SmGa_2Se_4$ system is partially quasi-binary; at low temperatures (in the subsolidus area), the initial components dissolve completely in one another. It was determined that the solid solutions crystallize in the orthorhombic system and have a structural type of $EuGa_2S_4$.

Contribution of the authors

O. M. Aliyev – scientific supervision, text editing. D. S. Ajdarova – research concept, discussion of results, participation in data processing, manuscript preparation. R. M. Agaeva – data processing and participation in manuscript preparation. V. M. Rahimova – literature search and participation in experimental work.

Conflict of interests

The authors declare that they have no known competing financial interests or personal

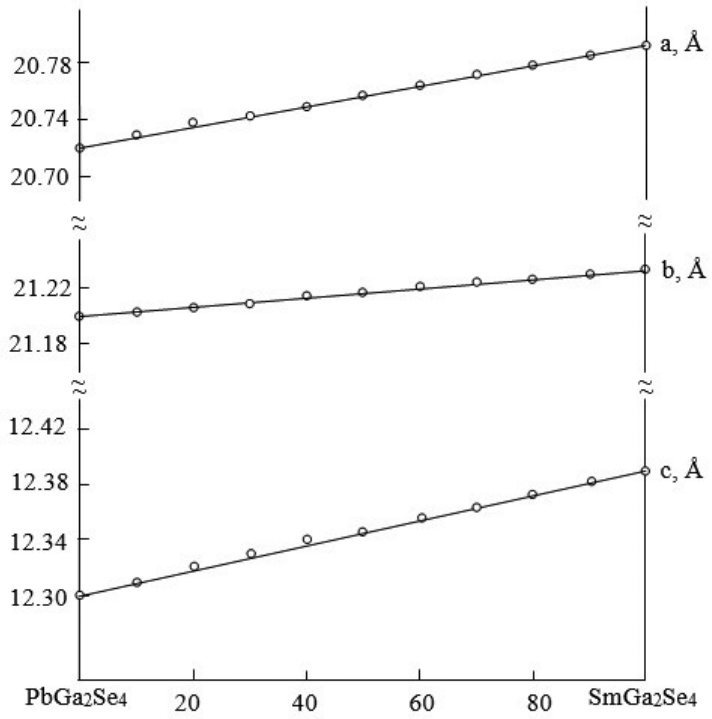

Fig. 5. Dependence of lattice parameters on the composition of solid solutions of the $PbGa_2Se_4$ – $SmGa_2Se_4$ system

Table. 2. Results of DTA, XRD, microhardness, and density of alloys of the $PbGa_2Se_4$ – $SmGa_2Se_4$ system

Composition, mol % $SmGa_2Se_4$	Thermal effects, K	Lattice parameters, Å			$H_μ$, MPa	d_{pik}, g/sm³
		a	*b*	*c*		
$PbGa_2Se_4$	1150	21.722	21.202	12.304	2050	6.08
10	1060, 1090	21.724	21.204	12.310	2100	5.90
20	1065, 1120	21.735	21.205	12.320	2140	5.85
30	1070, 1140	21.740	21.207	12.330	2180	5.84
40	1080, 1160	21.748	21.208	12.338	2180	5.82
50	1100, 1180	21.752	21.210	12.344	2190	5.80
60	1110, 1190	21.758	21.218	12.358	–	5.78
70	1120, 1200, 1390	21.760	21.220	12.364	–	–
80	1140, 1210, 1470	21.775	21.224	12.378	2200	–
90	1170, 1210, 1570	21.780	21.225	12.384	2200	5.77
$SmGa_2Se_4$	1200, 1640	21.782	21.235	12.390	2220	5.75

relationships that could have influenced the work reported in this paper.

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