Journal of Chemistry and Technologies, 2026, *34*(2), 431-438

Journal of Chemistry and Technologies

pISSN 2663-2934 (Print), ISSN 2663-2942 (Online).

journal homepage: http://chemistry.dnu.dp.ua
editorial e-mail: chem.dnu@gmail.com

UDC 546:72.682.815.22

QUASIBINARY SECTIONS OF THE In_2S_3-FeS–PbS SYSTEM

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Received 1 December 2025; accepted 22 April 2026; available online 20 June 2026

Abstract

Phase equilibria in the In_2S_3–FeS–PbS ternary system were investigated based on experimental studies of quasi-binary sections. The samples were synthesized by the ampoule method and examined using differential thermal analysis (DTA), X-ray diffraction (XRD), and microstructural Analysis (MSA). Seven quasi-binary sections ($FeIn_2S_4$–$PbIn_2S_4$, FeS–$PbIn_2S_4$, FeS–$Pb_6In_{10}S_{21}$, $FePbIn_4S_8$–In_2S_3, FeS–$FePbIn_4S_8$, $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–$PbIn_2S_4$, $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–PbS) were experimentally studied, and their quasi-binary character was established. In addition, limited solid-solution regions were observed in several of these sections. It was established that two quaternary compounds, $FePbIn_4S_8$ and $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$, are formed in the In_2S_3–FeS–PbS system. These compounds were identified as congruently melting phases with melting temperatures of 1140 K and 1150 K, respectively. The $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ compound crystallizes in the monoclinic crystal system with lattice parameters a = 14.558 Å, b = 3.856 Å, c = 15.558 Å, β = 96.87°, V = 867 Å^3, Z = 1. The obtained experimental results allowed the phase equilibria to be established and provide a consistent description of phase relations in the In_2S_3–FeS–PbS system.

Keywords: quasi-binary sections; quaternary compound; lattice parameters; eutectic; $FeIn_2S_4$; monoclinic; physicochemical analysis; $Pb_6In_{10}S_{21}$.

КВАЗІБІНАРНІ ПЕРЕРІЗИ СИСТЕМИ In_2S_3–FeS–PbS

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Анотація

Фазові рівноваги в потрійній системі In_2S_3–FeS–PbS були досліджені на основі експериментального вивчення квазібінарних перерізів. Зразки синтезувалися ампульним методом і досліджувалися за допомогою диференційного термічного аналізу (DTA), рентгенівської дифракції (XRD) та мікроструктурного аналізу (MSA). Було експериментально досліджено сім квазібінарних перерізів ($FeIn_2S_4$–$PbIn_2S_4$, FeS–$PbIn_2S_4$, FeS–$Pb_6In_{10}S_{21}$, $FePbIn_4S_8$–In_2S_3, FeS–$FePbIn_4S_8$, $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ –$PbIn_2S_4$, $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–PbS), і встановлено їх квазібінарний характер. Крім того, в деяких із цих перерізів спостерігалися обмежені області твердих розчинів. Встановлено, що в системі In_2S_3–FeS–PbS утворюються дві почвірні сполуки: $FePbIn_4S_8$ та $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$. Ці сполуки ідентифіковано як конгруентно плавкі фази з температурами плавлення 1140 K і 1150 K відповідно. Сполука $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ кристалізується в моноклінній кристалічній системі з параметрами ґратки: a = 14.558 Å, b = 3.856 Å, c = 15.558 Å, β = 96.87°, V = 867 Å^3, Z = 1. Отримані експериментальні результати дозволили встановити фазові рівноваги та забезпечити узгоджений опис фазових співвідношень у системі In_2S_3–FeS–PbS.

Ключові слова: квазібінарні перерізи; почвірна сполука; параметри ґратки; евтектика; $FeIn_2S_4$; моноклінна сингонія; фізико-хімічний аналіз $Pb_6In_{10}S_{21}$.

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doi: 10.15421/jchemtech.v34i2.345003

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Introduction

Ternary chalcogenide compounds such as $FeGa_2S_4$, $FeIn_2S_4$, and $NiGa_2S_4$ are widely used in microelectronics due to their unique magnetic, optical, and electronic properties [1–13]. In this context, the In_2S_3–FeS–PbS ternary system is of particular interest, as it enables the formation of complex multicomponent phases with potentially valuable functional characteristics.

The development of new materials with enhanced optical and luminescent properties remains one of the important challenges in materials science. The incorporation of PbS into the In_2S_3–FeS system leads to the formation of more complex phase equilibria and significantly affects the physicochemical behavior of the system. In particular, the addition of PbS promotes the formation of new multicomponent phases, alters phase stability, and enables the tuning of semiconductor properties. This, in turn, highlights the relevance of studying such systems as promising materials for optoelectronic and photonic applications.

Previous studies have investigated the FeS–In_2S_3, FeS–PbS, and PbS–In_2S_3 systems [14–23]. These systems form the basis for understanding the phase relations in the In_2S_3–FeS–PbS ternary system.

According to [15; 16], the PbS–In_2S_3 system forms two ternary compounds, $PbIn_2S_4$ and $Pb_6In_{10}S_{21}$, melting at 1163 K and 1178 K, respectively. $PbIn_2S_4$ crystallizes in the orthorhombic system (a = 11.688 Å, b = 3.8528 Å, c = 13.763 Å, Z = 4), while $Pb_6In_{10}S_{21}$ belongs to the monoclinic crystal system (a = 27.629 Å, b = 3.863 Å, c = 15.705 Å, β = 95.90°, Z = 2).

The FeS–In_2S_3 system has been studied by physicochemical methods, and the formation of $FeIn_2S_4$ has been established [17–20]. This compound melts congruently at 1163 K and forms continuous solid solutions with In_2S_3. It crystallizes in the cubic system and belongs to the spinel structural type (a = 10.530 Å) [18].

The synthesis of complex functional materials and the study of their temperature–composition relationships are of particular importance [24–28].

The FeS–PbS system is of eutectic type and has been extensively studied [29–35]. Due to discrepancies in previously reported phase diagrams, this system was reexamined, and the eutectic composition was refined [36].

Analysis of the FeS–In_2S_3 and PbS–In_2S_3 systems shows that materials obtained from these systems are promising for magneto-optical, luminescent, and photoelectric applications.

Despite the available data on the boundary systems, the phase equilibria within the In_2S_3–FeS–PbS ternary system remain insufficiently investigated, especially in terms of quasi-binary sections and the formation of quaternary compounds.

In the present work, seven quasi-binary sections of the In_2S_3–FeS–PbS system were systematically studied using DTA, XRD, and MSA methods. Several of these sections were previously investigated by the authors; however, in this study, all sections are analyzed under consistent experimental conditions and integrated into a unified phase equilibrium scheme.

The aim of this work is to systematically investigate quasi-binary sections and establish phase equilibria in the In_2S_3–FeS–PbS ternary system based on experimental data, thereby providing a comprehensive and unified description of phase relationships and contributing to the development of new functional chalcogenide materials.

Experimental

Synthesis

The samples were synthesized by the ampoule method. The starting materials were sealed in evacuated quartz ampoules (residual pressure $\sim 10^{-3}$ Pa) and heated at 600–1200 K for 6–8 h. Depending on the composition, the synthesized samples were subjected to homogenizing annealing for 350–400 h at 850–1000 K.

Research methods

The obtained samples of the In_2S_3–FeS–PbS system were investigated by Differential Thermal Analysis (DTA), X-ray Diffraction (XRD), and Microstructural Analysis (MSA), as well as by density and microhardness measurements.

DTA was carried out using a NETZSCH 404 F1 Pegasus instrument in the temperature range from room temperature up to ~1450 K, depending on the sample composition, at a heating rate of 10 K/min. The temperature accuracy was ±2 K.

Powder X-ray diffraction (PXRD) was performed using $CuK\alpha_1$ radiation (λ = 1.54056 Å) on a Bruker D2 Phaser diffractometer.

Microhardness measurements were carried out using a PMT-3 tester, with loads selected individually for each phase.

Microstructural analysis was performed on polished and chemically etched samples using a

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MIM-7 microscope. A solution of $K_2Cr_2O_7$ and H_2SO_4 (1 : 1), diluted with water, was used as the etchant.

The density of the samples was determined by the pycnometric method using toluene as the working liquid.

Results and Discussion

The obtained samples were experimentally investigated by DTA, XRD and MSA methods, allowing the determination of phase equilibria, phase compositions and invariant reactions in the system.

The FeS–$Pb_6In_{10}S_{21}$ quasi-binary section was experimentally investigated [37]. The corresponding phase diagram is presented in Fig. 1.

It was established that a single quaternary compound, $Fe_{1.5}Pb_{5.5}In_{10}S_{22}$ ($Fe_3Pb_{11}In_{20}S_{44}$), is formed in this system. This compound melts congruently at 1150 K and exhibits a homogeneity range extending from 35 to 46 mol.% $Pb_6In_{10}S_{21}$.

Due to the congruent melting behavior of $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$, the FeS–$Pb_6In_{10}S_{21}$ section is divided into two subsystems: FeS–$Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ and $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–$Pb_6In_{10}S_{21}$. Both subsystems are of eutectic type.

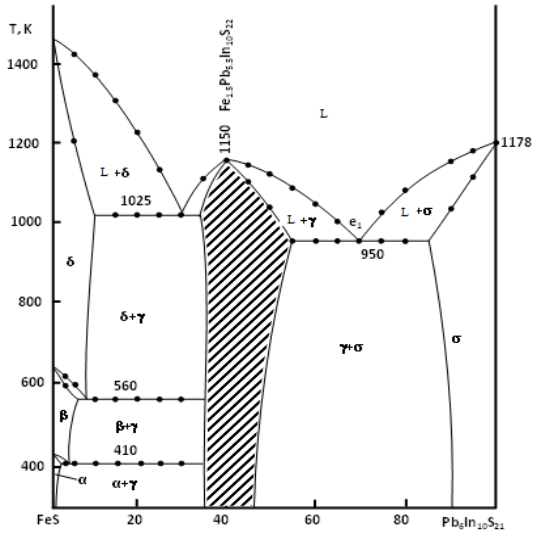

Fig. 1. Phase diagram of the FeS-$Pb_6In_{10}S_{21}$ system [37]

As shown in Fig. 1, the system is characterized by the formation of the congruently melting compound $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ and two eutectic equilibria. The eutectic reactions occur at 30 mol.% $Pb_6In_{10}S_{21}$ and T ≈ 1025 K, and at 70 mol.% $Pb_6In_{10}S_{21}$ and T ≈ 950 K.

Limited solid solubility was observed in the system: up to 1 mol.% $Pb_6In_{10}S_{21}$ in FeS and up to 10 mol.% FeS in $Pb_6In_{10}S_{21}$.

X-ray study showed that the $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ compound crystallizes in a monoclinic system with lattice parameters a = 14.558, b = 3.856, c=15.558 Å, β = 96.870, ν = 867 Å, z = 1. Calculation of X-ray diffraction patterns of $Fe_{1,5}Pb_{5,5}$ $In_{10}S_{22}$ and $FePbIn_4S_8$ compounds are given in Table 1.

The standard enthalpy ($\Delta_{f,298}$) and Gibbs energy of formation (Δ_fG_{298}) for the $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ compound were calculated to be 833 ± 34 kJ/mol and 757 ± 34 kJ/mol, respectively. In addition, the entropy (S_{298}) was found to be 33 kC/mol. [38].

Table 1

X-ray diffraction calculations for $FePbIn_4S_8$ and $Fe_{1.5}Pb_{5.5}$ $In_{10}S_{22}$ compounds

$FePbIn_4S_8$		$Fe_{1,5}Pb_{5,5}In_{10}S_{22}$		$Pb_6In_{10}S_{21}$	
d_{exp}	I/I_0	d_{exp}	I/I_0	d_{exp}	I/I_0
6.1607	5	4.9655	5	15.6423	5
4.5437	20	4.6638	8	13.7474	5
4.1955	15	4.5293	20	9.9469	5
3.7455	30	4.2721	5	7.8205	5
3.5664	25	3.9587	25	6.5447	10
3.4086	50	3.8767	30	5.4391	10
3.1973	100	3.8037	40	4.5862	10
2.8478	30	3.6812	10	4.5467	20
2.7198	20	3.63085	20	4.2813	55

2.6579	35	3.5800	30	3.9585	10
					Continued from Table 1
2.5753	20	3.4203	100	3.9050	50
2.4878	10	3.28197	25	3.8649	20
2.3685	10	3.1833	20	3.8255	60
2.2601	5	3.12978	10	3.7259	20
2.5689	10	3.05298	10	3.6999	5
2.1009	10	2.89909	40	3.6564	5
2.0443	60	2.83284	30	3.5599	20
1.9403	30	2.7443	80	3.4979	85
1.8796	80	2.70905	40	3.4291	5
1.8467	15	2.6663	20	3.2709	60
1.6864	10	3.6317	15	3.1906	65
1.6217	10	2.53436	15	3.1607	10
1.5456	8	2.4514	10	3.1335	10
1.4212	10	2.39155	70	3.1037	30
1.3834	10	2.33335	20		
1.3276	10	2.2348	20		
1.2537	6	2.05127	20		
1.2274	15	1.94936	25		
		1.92782	70		
		1.6792	20		

The FeS–$PbIn_2S_4$ quasi-binary section was experimentally investigated. The resulting phase diagram is shown in Fig. 2. The system is of eutectic type, with a eutectic point at 45 mol.% FeS and T = 985 K.

A limited solid-solution region based on $PbIn_2S_4$ (γ-phase) was observed, extending up to 10 mol.% FeS. These solid solutions crystallize in the orthorhombic crystal system.

According to X-ray diffraction data, the lattice parameters decrease with increasing FeS content: for pure $PbIn_2S_4$, a = 11.686 Å, b = 3.853 Å, c = 13.764 Å, whereas for the solid solution containing 10 mol.% FeS, a = 11.65 Å, b = 3.82 Å, c = 13.70 Å.

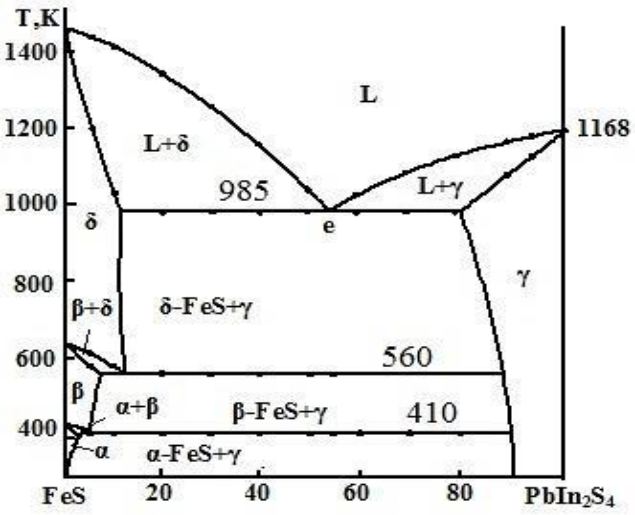

Fig. 2. Phase diagram of the FeS-$PbIn_2S_4$ system

The phase transformations α-FeS ⇄ β-FeS and β-FeS ⇄ δ-FeS are eutectoid in nature and occur at 410 K and 560 K, respectively.

An experimental study of the $FeIn_2S_4$–$PbIn_2S_4$ quasi-binary section was carried out. The corresponding phase diagram is shown in Fig. 3. It was established that a quaternary compound, $FePbIn_4S_8$, is formed in this system.

The liquidus surface of the section consists of three primary crystallization fields corresponding to α (solid solution based on $FeIn_2S_4$), $FePbIn_4S_8$, and β (solid solution based on $PbIn_2S_4$).

As seen from Fig. 3, the compound $FePbIn_4S_8$ (γ-phase) melts congruently at 1140 K and divides the system into two eutectic subsystems.

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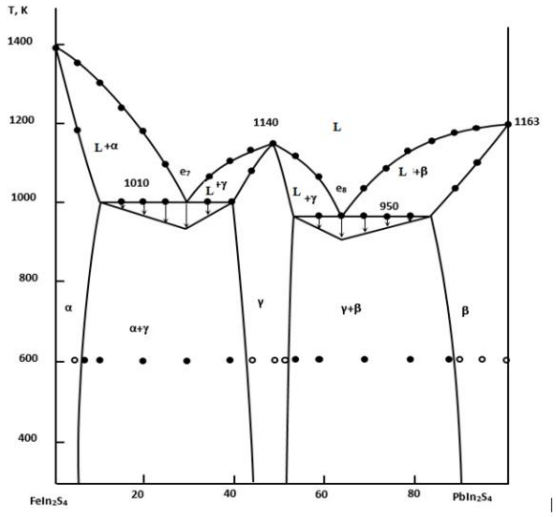

Fig. 3. Phase diagram of the $FeIn_2S_4$-$PbIn_2S_4$ [38]

Limited solid solubility was observed in the system: up to 5 mol.% $PbIn_2S_4$ in $FeIn_2S_4$ and up to 10 mol.% $FeIn_2S_4$ in $PbIn_2S_4$.

The $FePbIn_4S_8$ compound forms eutectic equilibria with the initial components and exhibits a homogeneity range extending from 43 to 53 mol.% $PbIn_2S_4$ [39].

Phase relations in the $FePbIn_4S_8$–In_2S_3 quasi-binary section were analyzed experimentally. The phase diagram corresponding to this section is depicted in Fig. 4. The system is of eutectic type, with a eutectic point at 45 mol.% In_2S_3 and T = 1000 K.

As seen from Fig. 4, limited solid solubility is observed in the system: up to 10 mol.% $FePbIn_4S_8$ in γ-In_2S_3 and up to 10 mol.% In_2S_3 in $FePbIn_4S_8$.

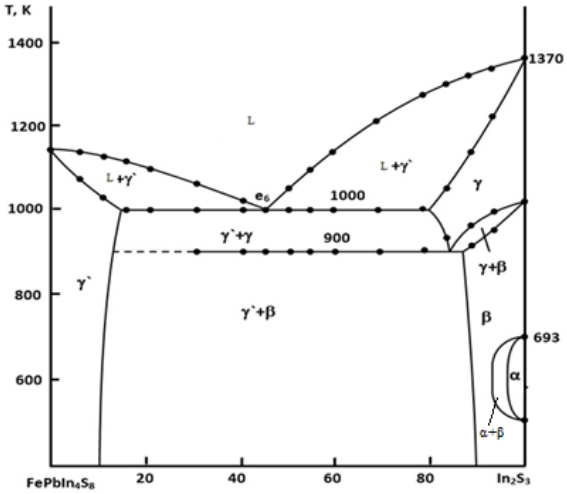

Fig. 4. Phase diagram of the $FePbIn_4S_8$-In_2S_3 system.

X-ray diffraction analysis showed that in solid solutions based on In_2S_3, the cubic crystal structure of γ-In_2S_3 is preserved.

The lattice parameters follow Vegard's law with increasing $FePbIn_4S_8$ content: a = 10.740 Å for pure γ-In_2S_3, a = 10.746 Å at 2 mol.% $FePbIn_4S_8$, a = 10.782 Å at 5 mol.% $FePbIn_4S_8$, and a = 10.824 Å at 10 mol.% $FePbIn_4S_8$.

The FeS–$FePbIn_4S_8$ quasi-binary section was characterized by experimental methods. A phase diagram of the investigated section is given in Fig. 5. The system is of eutectic type, with a eutectic point at 40 mol.% FeS and T = 975 K.

As seen from Fig. 5, the phase transformations α-FeS ⇄ β-FeS and β-FeS ⇄ δ-FeS are eutectoid in nature and occur at 411 K and 560 K, respectively.

Limited solid solubility was observed in the system: approximately 1 mol.% $FePbIn_4S_8$ in α-FeS and up to 10 mol.% FeS in $FePbIn_4S_8$.

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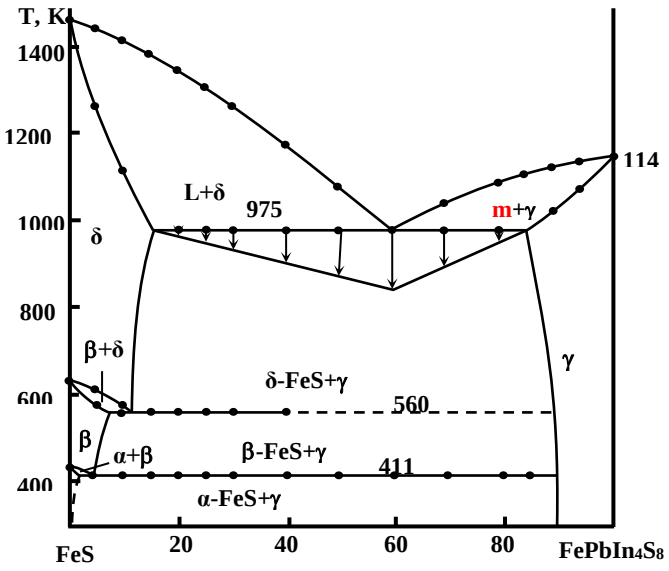

Fig. 5. Phase diagram of the FeS-$FePbIn_4S_8$ system

The $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–$PbIn_2S_4$ section exhibits quasi-binary behavior and is characterized by a eutectic-type phase diagram. The eutectic point is located at 50 mol.% $PbIn_2S_4$ and T = 980 K.

Two terminal solid solutions are formed in the system: α, based on $Fe_{1.5}Pb_{5.5}In_{10}S_{22}$, and β, based on $PbIn_2S_4$.

The α-solid solution crystallizes in the monoclinic crystal system, whereas the β-solid solution belongs to the orthorhombic crystal system.

At room temperature, limited solid solubility is observed: up to 15 mol.% $PbIn_2S_4$ in $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ and up to 8 mol.% $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ in $PbIn_2S_4$.

The liquidus surface consists of two primary crystallization fields corresponding to the α- and β-solid solutions [40].

The $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–PbS section is characterized by quasi-binary behavior. The eutectic reaction occurs at 35 mol.% PbS and T = 1015 K.

Limited solid solubility is observed in the system: up to 2 mol.% $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ in PbS and up to 12 mol.% PbS in $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ [40].

As evident from the obtained data, all investigated systems represent quasi-binary sections of the In_2S_3–FeS–PbS ternary system. Table 2 summarizes the compositions and invariant points of these sections.

Table 2

Invariant points in quasi-binary sections of the In_2S_3–FeS–PbS ternary system

Section	Invariant point	T (K)	FeS (mol%)	In_2S_3 (mol%)	PbS (mol%)	Reaction
$FeIn_2S_4$–$PbIn_2S_4$	eutectic	950	17.5	50	32.5	L ⇆ β + γ
$FeIn_2S_4$–$PbIn_2S_4$	eutectic	1010	35	50	15	L ⇆ α + γ
FeS–$PbIn_2S_4$	eutectic	985	48	26	26	L ⇆ δ-FeS + γ
FeS–$Pb_6In_{10}S_{21}$	eutectic	1025	70	16	14	L ⇆ δ-FeS + $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$
FeS–$Pb_6In_{10}S_{21}$	eutectic	950	30	38	32	L ⇆ $Pb_6In_{10}S_{21}$ + $Fe_{1.5}Pb_{5.5}In_{10}S_{22}$
$Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–$PbIn_2S_4$	eutectic	980	6	46	48	L ⇆ α + β
$Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–PbS	eutectic	1015	8	65	27	L ⇆ $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ + PbS
$FePbIn_4S_8$–In_2S_3	eutectic	1000	14	72	14	L ⇆ $FePbIn_4S_8$ + In_2S_3
FeS–$FePbIn_4S_8$	eutectic	975	55	30	15	L ⇆ α-FeS + $FePbIn_4S_8$

Phase equilibria in the In_2S_3–FeS–PbS ternary system were comprehensively investigated using physicochemical analysis methods (DTA, XRD, and MSA). Seven quasi-binary sections were experimentally studied, and their quasi-binary nature was confirmed.

Based on the obtained results, a consistent and unified description of phase relationships in the system has been established. It was shown that two quaternary compounds, $FePbIn_4S_8$ and $Fe_{1.5}Pb_{5.5}In_{10}S_{22}$, are formed and melt congruently at 1140 K and 1150 K, respectively.

The obtained results significantly expand the understanding of phase equilibria in the In_2S_3–FeS–PbS system and provide a reliable basis for further investigation and design of new

multicomponent chalcogenide materials with potential functional applications.

Conclusions

Phase equilibria in the In_2S_3–FeS–PbS ternary system were comprehensively investigated using physicochemical analysis methods (DTA, XRD, MSA).

Seven quasi-binary sections ($FeIn_2S_4$–$PbIn_2S_4$, FeS–$PbIn_2S_4$, FeS–$Pb_6In_{10}S_{21}$, $FePbIn_4S_8$–In_2S_3, FeS–$FePbIn_4S_8$, $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–$PbIn_2S_4$, $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$–PbS) were experimentally studied, and their quasi-binary character was established.

Based on the obtained experimental results, phase relationships in the system were determined.

It was established that two quaternary compounds, $FePbIn_4S_8$ and $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$, are formed in the system and melt congruently at 1140 K and 1150 K, respectively.

The $Fe_{1,5}Pb_{5,5}In_{10}S_{22}$ compound crystallizes in the monoclinic crystal system with the following lattice parameters: a = 14.558 Å, b = 3.856 Å, c = 15.558 Å, β = 96.87°, V = 867 $Å^3$, Z = 1.

Conflicts of Interest

The authors declare no conflict of interest.

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