

REPUBLIC OF AZERBAIJAN

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ABSTRACT

Of the dissertation for the degree of Doctor of Philosophy

**PHASE EQUILIBRIA AND PROPERTIES OF THE
INTERMEDIATE PHASES IN QUASI-TERNARY
SYSTEMS $\text{Ag}_2\text{X-PbX-Sb}_2\text{X}_3$ (X- Se, Te)**

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GENERAL DESCRIPTION OF WORK

The relevance of the theme and the degree of development.

Modern scientific-technical progress is directly related to the creation and application of unique functional materials. Metal chalcogenides occupy a special place among these materials. They have been widely studied as semiconductor materials since the middle of the last century. The development of nano-engineering in the last two decades, the discovery of graphene and topological insulators, has given a new impulse to the development of chemistry and material science of metal chalcogenides. Researches showed that the binary compounds Bi_2Se_3 , Bi_2Te_3 and Sb_2Te_3 have a tetradimity-like structure and ternary analogs formed in the $\text{A}^{\text{IV}}\text{-B}^{\text{V}}\text{-Te}$ ($\text{A}^{\text{IV}}\text{-Ge, Sn, Pb; B}^{\text{V}}\text{-Sb}$) systems have topological insulator properties are quite promising for the application and can be used in spintronics, quantum computers, medicine and et al.

Complex chalcogenides as well as valuable thermoelectric materials. Much of the recent research has focused on the multi-component chalcogenide phases that occur in the $\text{Ag-A}^{\text{IV}}\text{-B}^{\text{V}}\text{-Se (Te)}$ quaternary systems, especially LAST, TAGS, and others. (LAST, TAGS are the capital letters of the elements in these phases in English (Lead-Argentum-Stibium-Tellurium, Tellurium-Argentum-Germanium-Selenium)) is devoted to the fabrication of the composites based on them and the study of their thermoelectric properties. Analysis of the literature data shows that these materials are located in the $\text{Ag}_2\text{Te-A}^{\text{IV}}\text{Te-B}^{\text{V}}_2\text{Te}_3$ concentration area. Therefore, a purposeful search of these phases and composite materials requires a direct study of phase equilibria, intermediate phases, thermodynamic and crystallographic properties of these intermediate phases in order to optimize their compositions and functional properties.

Taking into account the above, in recent years, Azerbaijani scientists have carried out a comprehensive study of a number of $\text{Ag}_2\text{Te-A}^{\text{IV}}\text{Te-B}^{\text{V}}_2\text{Te}_3$ systems. Wide area of solid solutions, as well as two- and three-phase areas that are of interest as composite materials were determined and physical parameters that characterize the crystallization of

these alloys from the liquid phase have been identified. However, the $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ system and its selenium analog, where the LAST materials were formed, were not studied until our studies.

The purpose and objectives of the study: obtaining new results on the thermodynamic and crystallographic properties of the phase relations in the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ and $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ systems and intermediate phases formed in them which are of great interest in the search of thermoelectric materials.

To achieve this goal, the following **specific tasks** were set and solved:

✓ investigation of phase equilibria in the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ and $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ systems by the including of the EQ method to the traditional methods of phase equilibrium studies and phase diagrams construction;

✓ the refinement of phase diagrams of some boundary quasi-binary systems of these systems;

✓ determination of the primary crystallization phases and homogeneity areas of intermediate phases detected in the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ and $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ systems, obtaining individually and identification of various solids solutions;

✓ refinement the solid-state equilibrium diagram of the $\text{PbSe-Sb}_2\text{Se}_3\text{-Se}$ subsystem by using the EMF method and calculation the thermodynamic functions of the lead-stibium selenides;

✓ by using various modifications of the EQ method, the thermodynamic study of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ and $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ systems, calculation the partial and integral thermodynamic functions of solid solutions formed.

Research methods. The studies were conducted using DTA, PXRD, EQ, microstructure and SEM analysis methods, as well as microstructure measurements. The DTA was conducted using a Linseis STA PT 1600 and a "Termoskan-2" device, as well as on a multichannel DTA unit assembled based on the electronic TC-08 Thermocouple Data Logger. Powder X-ray diffraction patterns of the compounds and alloys were recorded on Bruker D2 Phaser and D8 ADVANCE diffractometers using CuK_α - radiation. Diffractograms were analyzed by computer software crystal lattice parameters were

calculated. Scanning electron microscopes "Field Emission Scanning Electron Microscope JEOLJSM-7600F", "Tescan Vega 3" and C-4EQMM 500T were used for microstructure analysis. The microhardness of the samples was measured using a ПИМТ-3 device.

Main provisions for the defense.

- 1. New information on phase equilibria in the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ and $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ quasi-ternary systems, different poly- and isothermal sections of their phase diagrams, the liquidus surface projections of both systems and non- and monovariant equilibria that were determined;

- 2. A new specified version of the phase diagram of the $\text{PbSe-Sb}_2\text{Se}_3$ system, the solid-phase equilibria diagram of the $\text{PbSe-Sb}_2\text{Se}_3\text{-Se}$ system;

- 3. New phases in the investigated systems, their primary crystallization and homogenization areas, crystallographic parameters;

- 4. Results of EMF measurements of circuits with solid electrolyte concerning PbSe electrode and liquid electrolyte concerning Ag electrode for $\text{PbSe-Sb}_2\text{Se}_3\text{-Se}$ system and 2PbX-AgSbX_2 sections of $\text{Ag}_2\text{X-PbX-Sb}_2\text{X}_3$ systems, partial molar functions of PbSe , Pb and Ag in alloys of investigated systems, the standard integral thermodynamic functions of the formations and solid solutions.

Scientific novelty.

The following **new results** were obtained and defended:

- a new version of the phase diagram of the $\text{PbSe-Sb}_2\text{Se}_3$ system which is different from the literature data is plotted and it was established that the system is characterized by ternary compounds $\text{Pb}_2\text{Sb}_2\text{Se}_5$, $\text{Pb}_4\text{Sb}_6\text{Se}_{13}$ and PbSb_2Se_4 formed with decomposition by peritectic reaction ;

- for the first time, the character of the physical and chemical interaction in the $\text{Ag}_2\text{X-PbX-Sb}_2\text{X}_3$ (X-Te, Se) systems was determined. It was shown that they are quasiternary sections of the corresponding quaternary systems and are characterized by the formation of wide areas of the solid solutions with cubic structures;

- the liquidus surface projections of both systems, a number of poly- and isothermal sections of phase diagrams were plotted, prima-

ry crystallization and homogenization areas of intermediate phases, types, and coordinates of non- and monovariant equilibria were determined;

– quaternary selenide and telluride phases of different compositions were obtained individually based on the phase diagrams, and their cubic lattice constants and microstructure dependencies on the composition were determined;

– the solid-phase equilibria diagram of the $\text{PbSe-Sb}_2\text{Se}_3\text{-Se}$ system was plotted based on EMF measurements concerning PbSe electrode; the partial and integral thermodynamic functions of the $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$, $\text{Pb}_2\text{Sb}_2\text{Se}_5$, $\text{Pb}_4\text{Sb}_6\text{Se}_{13}$ and PbSb_2Se_4 compounds were calculated;

– by using the EMF measurements concerning Ag and PbTe electrodes, the 2PbX-AgSbX_2 systems were investigated in the 300-450 K temperature interval; the partial molar functions of PbSe(Te) and Pb, as well as the integral thermodynamic functions of the formations and standard entropies of the solid solutions, were calculated.

The theoretical and practical significance of the work.

The theoretical significance of the dissertation is that the new results set on the phase equilibrium and thermodynamic properties in the $\text{Ag}_2\text{X-PbX-Sb}_2\text{X}_3$ systems are a contribution to the chemistry and thermodynamics of multicomponent metal chalcogenides. These results are the scientific basis for the development and selection of technological conditions for the synthesis and growth of the monocrystals of the multi-component phases with variable composition found in these systems. The new non-stoichiometric phases obtained are potential thermoelectric materials and their application parameters, especially LAST materials, can be optimized as a result of appropriate physical studies.

The phase diagrams of the investigated systems, as well as the thermodynamic, crystallographic, and other properties of new intermediate phases, are fundamental physicochemical characteristics of materials and can be included in relevant handbooks and information databanks.

According to Google Scholar Citations, 16 references have be-

en made to author's articles published in international scientific journals on dissertation topics

Some results obtained in the dissertation work can also be used in the higher educational institutions of the republic when teaching special courses "Solid State Chemistry", "Inorganic Materials", "Physical and Chemical Analysis".

Testing and application. The results of the work were reported and discussed at the following scientific conferences: XVI Российская конференция по физической химии и электрохимии расплавленных и твердых электролитов (Екатеринбург, 2013); XII International conference on crystal chemistry of intermetallic compounds (Lviv, 2013); XV, XVII Всероссийские конференции "Высокочистые вещества и материалы. Получение, анализ, применение" (Нижний Новгород, 2015, 2018); Тезисы Докладов Республиканской научной конференции, посвященной 90-летию юбилею Академика Тогрула Шахтактинского (Баку, 2015); VII, VIII Всероссийская конференция "Физико-Химические процессы в конденсированных средах и на межфазных границах", ФАГРАН, (Воронеж, 2015; 2018); 2nd and 3th International Turkic World Conferences on Chemical Sciences and Technologies (Skopje, 2016; Baku, 2017); 13-е Совещание с международным участием "Фундаментальные проблемы ионики твердого тела" (Черноголовка, 2016); XI Международное Курнаковское Совещание по физико-химическому анализу (Воронеж, 2016); Ümummilli lider N. Əliyevin anadan olmasının 95-ci ildönümünə həsr olunmuş "Müasir təbiət elmlərinin aktual problemləri" (Gəncə, 2018); Всероссийская конференция "Химия твердого тела и функциональные материалы" и XII всероссийский симпозиум с международным участием "Термодинамика и материаловедение" (Санкт-Петербург, 2018); Akademik M.Nağıyevin 110 illiyinə həsr olunmuş "Nağıyev qıraətləri" beynəlxalq konfransı (Bakı, 2018); XXII International Conference on Chemical Thermodynamics In Russia (Saint Petersburg, 2019);

Published works. Based on the materials of the dissertation, 25 scientific works -10 articles (7 of them in international indexed journals) and 15 report thesis (7 of them in international conferences)

were published .

The name of the organization in which the dissertation work is carried out. The dissertation work was carried out in the laboratory of “ General and Inorganic Chemistry ” department of Baiku State University.

Personal contribution of the author. Statement of the dissertation problem, experimental research and processing of the results. The author's share in the co-authorship of scientific works was decisive.

Volume and structure of work. The dissertation consists of an introduction (10699 symbols), four chapters (I chapter – 28181 symbols, II-36092 symbols, III- 44685 symbols, IV-31919 symbols), main results, a list of used scientific literature in 205 titles and has a volume of 149 pages. The thesis includes 63 figures and 34 tables.

MAIN CONTENT OF WORK

In the introduction, the relevance of the dissertation topic is substantiated, the goal, tasks, scientific novelty, theoretical and practical significance are formulated.

The first chapter briefly describes and critically analyzes the literature data on the physico-chemical properties of the initial compounds of the $\text{Ag}_2\text{X-PbX-Sb}_2\text{X}_3$ (X-Se, Te) systems. The phase diagrams of the quasi-binary $\text{Ag}_2\text{X-PbX}$, $\text{Ag}_2\text{X-Sb}_2\text{X}_3$ and $\text{PbX-Sb}_2\text{X}_3$ sections, as well as crystallochemical, thermal, thermodynamic data for the intermediate phases, are given and analyzed.

This chapter also explores the modern physical and chemical studies of multi-component chalcogenide systems containing silver, p^2 - and p^3 -elements, the relevance of the topic and the choice of objects are justified.

The second chapter is devoted to syntheses and experimental research methods

For the syntheses, the elemental components (Ag, catalog number 7440-22-4; Pb-7439-92-1; Sb-7440-36-0; Se-7782-49-2; Te-13494-80-9) of a high degree of purity purchased from the German company Alfa Aesar were used.

Alloys of the studied systems were prepared from previously synthesized and identified binary and ternary compounds in vacuo-

med up to $\sim 10^{-2}$ Pa and sealed quartz ampoules. After synthesis, the samples for investigations by the DTA method were annealed at 500 K ($\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system) or 750K ($\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ system) during 500-600h and then cooled slightly.

Samples for PXR, MSA, and microhardness measurements were kept at temperatures for 300 s, corresponding to the isothermal sections of phase diagrams and then quenched into cold water. For the EMF measurements, the alloys-right electrodes were annealed at 400 K within 500h.

Studies have been conducted using DTA, PXR, EMF, microstructure and SEM analysis methods, as well as microhardness measurements (see research methods section).

The third chapter summarizes the results of the study of the phase relations in the quasi-ternary $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ and $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ systems.

At the beginning of the chapter, the refinement phase diagrams of the boundary systems $\text{PbSe-Sb}_2\text{Se}_3$ of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system were presented and compared with the literature data.

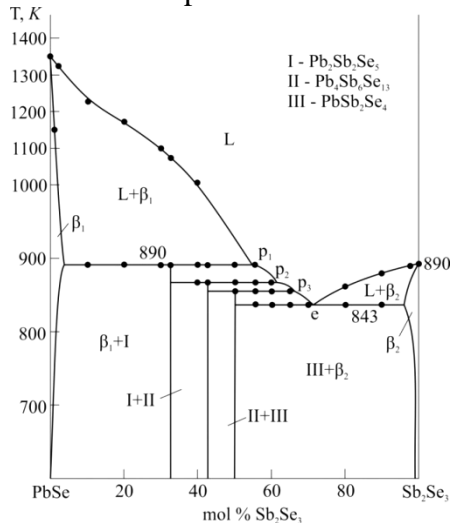
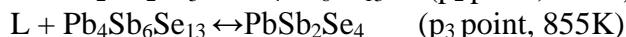
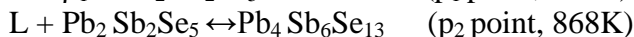


Figure 1. The phase diagram of the $\text{PbSe-Sb}_2\text{Se}_3$ system

As can be seen (Fig.1), the $\text{PbSe-Sb}_2\text{Se}_3$ system is quasi-ternary and is characterized by ternary compounds $\text{Pb}_2\text{Sb}_2\text{Se}_5$, $\text{Pb}_4\text{Sb}_6\text{Se}_{13}$ and PbSb_2Se_4 formed with decomposition by peritectic

reaction ;



The crystal lattice parameters calculated by using the Topas V3.0 computer software are the following:

$\text{Pb}_2\text{Sb}_2\text{Se}_5$: orthorombic Sp.gr. Pnam, $a=24.591(8)$; $b=19.757(8)$; $c=4.166(8)$ Å.

$\text{Pb}_4\text{Sb}_6\text{Se}_{13}$: monoclinic, Sp.gr. I2/m, $a=24.591(3)$; $b=4.0910$; $c=25.212(1)$ Å, $\beta=93.95^\circ$.

PbSb_2Se_4 : orthorombic, Sp.gr. Pnm, $a=21.206(9)$; $b=26.660(9)$; $c=4.068(1)$ Å.

It should be noted that the results of the $\text{PbSe-Sb}_2\text{Se}_3$ system reflecting the equilibrium state were only possible after long thermal treatment. This is primarily due to the fact that the peritectic equilibria of the ternary compounds presented in the system are very close (890, 868, and 855K), resulting in a very small initial crystallization field (Fig. 1).

Another point should be noted. Both literary versions of the phase diagram show that the PbSb_2Se_4 compound melts congruently. If this were the case, it would crystallize directly from the alloy and no further thermal processing would be required for complete homogenization. Our experiments have shown that this compound is completely homogenized only after the three-step thermal treatment, while the X-ray diffraction pattern consists of a mixture of several phases.

Thermograms of the PbSb_2Se_4 compound both before and after the thermal treatment also show its incongruent melt (Fig.2). It can be seen from the thermogram there is the thermal effect at 842 K (the eutectic point melting) which disappears after thermal treatment. The 3 thermal effects in the DTA curve after annealing are fully consistent with the phase diagram (Fig.1) and indicate the incongruent melting of this compound.

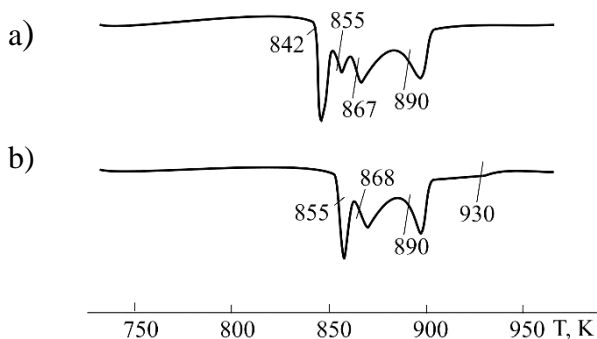


Figure 2. The thermograms of the alloys with composition 50 mol% Sb_2Se_3 : before (a) and after (b) thermal annealing

$\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system. Researches showed that only one quasi-binary section (PbSe-AgSbSe_2) of this system divides it into two independent subsystems.

The PbSe-AgSbSe_2 system belongs to the peritectic type (Fig3). Peritectic point (p) has coordinates $\sim 18\text{mol}\%$ AgSbSe_2 and 1230 K. At the peritectic point, the homogeneity fields of the β - and γ - phases are maximal and are ~ 5 and 88 mol%. Liquidus and solidus curves of the γ -phase cross the total minimum point (M-895K) at ~ 85 mol% AgSbSe_2 .

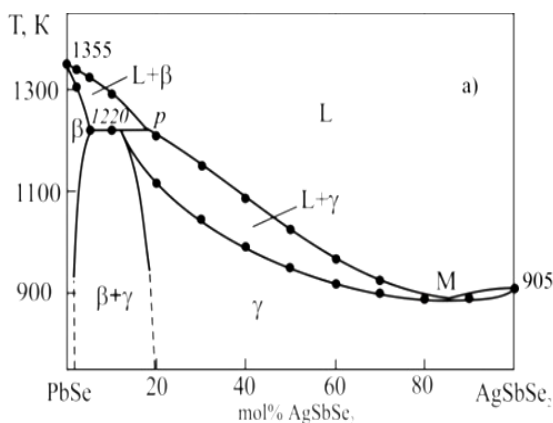


Figure 3. The phase diagram of the PbSe-AgSbSe_2 system
 PXRD, microhardness and EMF measurements confirm the

phase diagram. As can be seen from Fig. 4, the samples of the γ -phase is one-phase, and their XRD patterns are qualitatively similar to that of AgSbSe_2 . In the diffractograms of the samples in the $\beta+\gamma$ field, the XRD patterns consist of the set of reflections of both phases. The crystal lattice parameter of solid solutions calculated based on PXRD are given in Table 1.

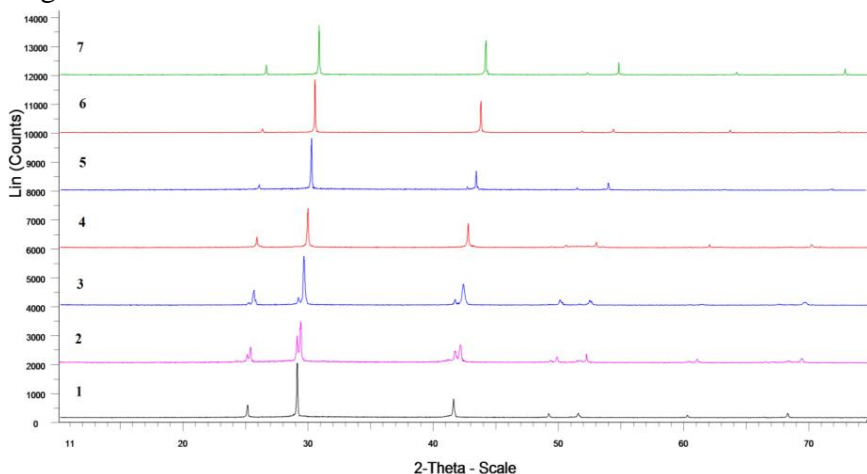


Figure 4. PXRD of the sme samples of the 2PbSe-AgSbSe_2 system, mol% AgSbSe_2 : 1-PbSe; 2-10; 3-30; 4-40; 5-60; 6-80; 7-100.

Table 1
Phase compositions and cubic lattice constants for the alloys of the 2PbSe-AgSbSe_2 system

Composition, mol% AgSbSe_2	Phase composition	cubic lattice constants, Å	
0 (PbSe)	β	6.1246(5)	
10	$\beta_1+\gamma$	6.1184(6);	6.0091(7)
20	$\beta_1+\gamma$	6.1187(7);	6.0101(7)
30	$\beta_1+\gamma$	6.1185(6);	6.0094(7)
40	γ		5.9882(6)
60	γ		5.9244(5)
80	γ		5.8521(5)
100 (AgSbSe_2)	γ		5.7882(5)

The graph constructed based on these quantities (Fig. 5) allows

us to determine the maximal concentration of the γ -phase at room temperature. It can be seen, in the 0-60 mol% 2PbSe composition interval the lattice parameter is linear function of the composition. With a higher value of the PbSe contents the lattice parameter is constant. The breakpoint in the "a-x" curve (39 mol% AgSbSe₂) shows the saturated composition of the γ -phase.

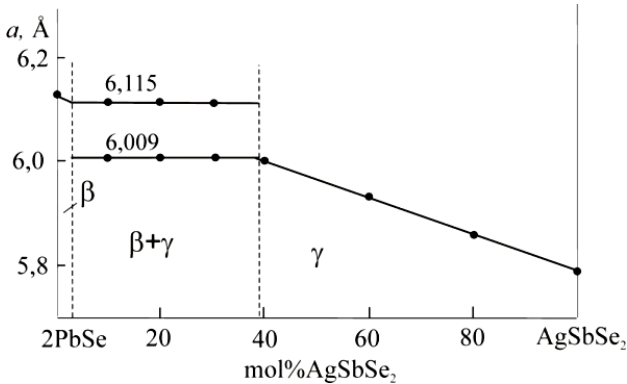


Figure 5. The dependence of the crystal lattice parameters on the composition for the alloys of the 2PbSe-AgSbSe₂ system

Solid-phase equilibria diagram of the Ag₂Se-PbSe-Sb₂Se₃ system. Figure 6 shows the isothermal sections at 300 and 800 K of the phase diagram of the Ag₂Se-PbSe-Sb₂Se₃ system. Apparently, they are qualitatively similar, and the specificity of the system is that there is a wide solution area (γ) based on AgSbSe₂. At 800 K, this area is 80 mol% in length along the quasi-binary PbSe-AgSbSe₂ section, and width expanding along the AgSbSe₂ reach 12-13mol%-. The solubility of PbSe is approximately 2-3mol%. The γ -phase plays a crucial role in the formation of phase areas in the system. It forms connod lines with all other phases. As a result, a number of two- and three-phase areas are formed in the system (Fig.6). At 300 K, instead α -phase the low-temperature modification of the Ag₂Se takes part and the homogeneity region of the γ -phase is narrows somewhat.

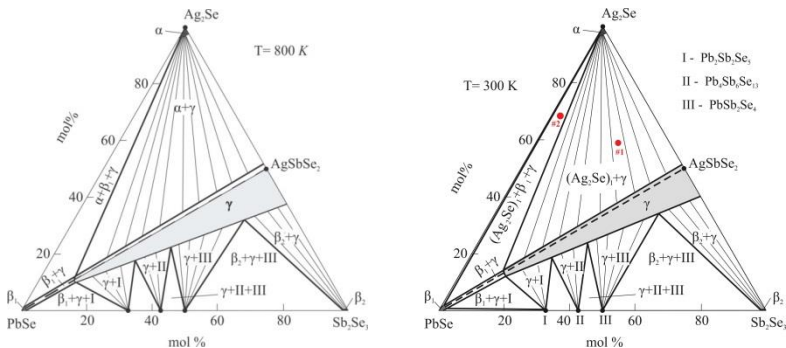


Figure 6. The isothermal sections at 300 and 800 K of the phase diagram of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system

The phase fields on the solid-phase equilibrium diagram were confirmed using PXR and SEM methods. Fig. 7 shows the diffractogram of 2 samples. Apparently, they contain $(\text{Ag}_2\text{Se})_{\text{I}}+\gamma$ and $(\text{Ag}_2\text{Se})_{\text{I}}+\beta+\gamma$ phases, which is fully consistent with the phase diagram.

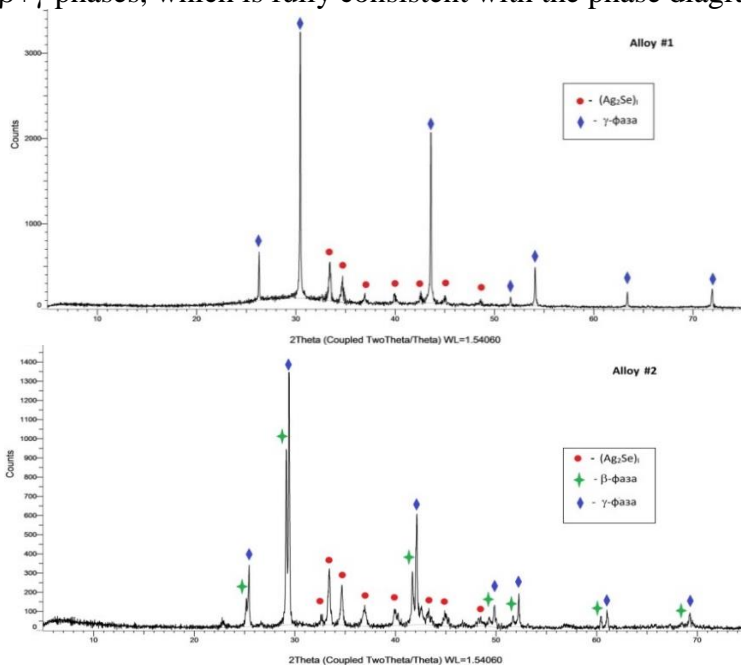


Figure 7. The PXR and compositions of the samples # 1 v# 2 showed on Fig.4 of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system

Liquid surface projection of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system. The liquidus surface consists of 7 primary crystallization fields (Fig. 8). The largest crystallization area is occupied by γ -phase. The primary crystallization areas are limited by 12 monovariant equilibrium curves and 13 nonvariant equilibrium points (including boundary quasi-binary systems).

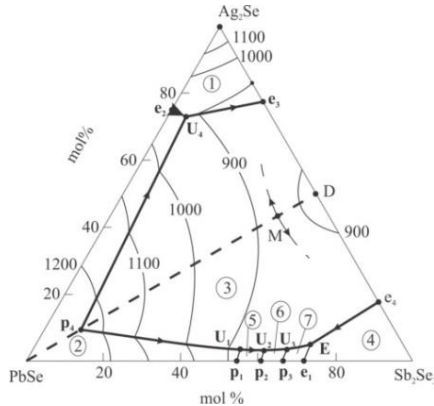


Figure 8. Liquid surface projection of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system. Primary crystallization fields: 1 - α ; 2 - β_1 ; 3 - γ ; 4 - β_2 ; 5 - $\text{Pb}_2\text{Sb}_2\text{Se}_5$; 6 - $\text{Pb}_4\text{Sb}_6\text{Se}_{13}$; 7 - PbSb_2Se_4

**Table 2
Nonvariant equilibria in the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system**

Point on fig.8	Equilibria	Composition, mol%		T, K
		Ag_2Se	Sb_2Se_3	
D	$\text{L} \leftrightarrow \text{AgSbSe}_2 (\gamma)$	50.0	50.0	908
P_1	$\text{L} + \beta_1 \leftrightarrow \text{Pb}_2\text{Sb}_2\text{Se}_5$	-	54.0	890
P_2	$\text{L} + \text{Pb}_2\text{Sb}_2\text{Se}_5 \leftrightarrow \text{Pb}_4\text{Sb}_6\text{Se}_{13}$	-	62.0	868
P_3	$\text{L} + \text{Pb}_4\text{Sb}_6\text{Se}_{13} \leftrightarrow \text{PbSb}_2\text{Se}_4$	-	66.0	855
P_4	$\text{L} + \beta_1 \leftrightarrow \gamma$	9.0	9.0	1230
e_1	$\text{L} \leftrightarrow \text{PbSb}_2\text{Se}_4 + \beta_2$	-	72.0	843
e_2	$\text{L} \leftrightarrow \alpha + \beta_1$	75.0	-	930
e_3	$\text{L} \leftrightarrow \alpha + \gamma$	77.0	23.0	793
e_4	$\text{L} \leftrightarrow \beta_2 + \gamma$	18.0	82.0	845
U_1	$\text{L} + \beta_1 \leftrightarrow \gamma + \text{Pb}_2\text{Sb}_2\text{Se}_5$	4.0	53.0	878
U_2	$\text{L} + \text{Pb}_2\text{Sb}_2\text{Se}_5 \leftrightarrow \gamma + \text{Pb}_4\text{Sb}_6\text{Se}_{13}$	3.5	60.5	860
U_3	$\text{L} + \text{Pb}_4\text{Sb}_6\text{Se}_{13} \leftrightarrow \gamma + \text{PbSb}_2\text{Se}_4$	4.0	65.5	850
U_4	$\text{L} + \beta_1 \leftrightarrow \alpha + \gamma$	73.0	5.0	910
E	$\text{L} \leftrightarrow \beta_2 + \gamma + \text{PbSb}_2\text{Se}_4$	5.5	69.5	843
M	$\text{L} \leftrightarrow \gamma$	43.0	43.0	895

Note: α , β_1 , β_2 , γ - are a high-temperature modification of the Ag_2Se compound, solid solutions based on PbSe , Sb_2Se_3 and AgSbSe_2 accordingly.

Table 3

Monovariant equilibria in the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system

Curve on fig.8	Equilibria	T, K
P ₄ U ₁	L+β ₁ ↔γ	1230-878
P ₁ U ₁	L+β ₁ ↔Pb ₂ Sb ₂ Se ₅	890-878
U ₁ U ₂	L↔γ+ Pb ₂ Sb ₂ Se ₅	878-860
P ₂ U ₂	L+Pb ₂ Sb ₂ Se ₅ ↔ Pb ₄ Sb ₆ Se ₁₃	868-860
U ₂ U ₃	L↔γ+ Pb ₄ Sb ₆ Se ₁₃	860-850
P ₃ U ₃	L+Pb ₄ Sb ₆ Se ₁₃ ↔ PbSb ₂ Se ₄	855-850
U ₃ E	L↔γ+ PbSb ₂ Se ₄	850-835
e ₁ E	L↔ β ₂ + PbSb ₂ Se ₄	843-835
e ₄ E	L↔ β ₂ + γ	845-835
P ₄ U ₄	L+β ₁ ↔γ	1230-910
e ₂ U ₄	L↔ α+β ₁	930-910
U ₄ e ₃	L↔ α+γ	910-793

The types and coordinates of the nonvariant equilibrium are given in Table 2, while monovariant equilibria and temperature ranges are present in Table 3.

The dissertation presents a number of poly- and isothermal sections of the phase diagram of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system which are discussed in the context of the general T-x-y diagram.

Ag₂Te-PbTe-Sb₂Te₃. This system does not have quasi-binary sections.

At 750 K, the system has a continuous β-solid solutions along the 2PbTe-"Ag_{0.84}Sb_{1.16}Te_{2.16}" section (Fig.9). In the Ag₂Te-Sb₂Te₃ system, the width of this section is 3-4 mol%, and when the content varies with the PbTe direction the width reaches 7-8 mol%. The PbTe-AgSbTe₂ section is in the region of β-phase homogeneity in the concentration range of 25-100 mol% PbTe; at low PbTe concentrations, this section crosses the two-phase field α+β. The β phase forms connods with the α- phase and the γ- phase based on Sb₂Te₃.

Solid-phase equilibria diagram at 300 K (Fig. 9). From the literature data, it is known that the Ag₁₉Sb₂₇Te₅₂ phase decomposes at 635 K and turns into an α+γ two-phase. This also leads to the decomposition of β-solid solutions in the Ag and Sb rich (<25mol% PbTe)

area. As a result, the homogeneity of the β -phase decreases and new $(\text{Ag}_2\text{Te})_1+\beta+\gamma$ and $\text{Ag}_2\text{Te}+\gamma$ heterogeneous phase areas are formed in the system.

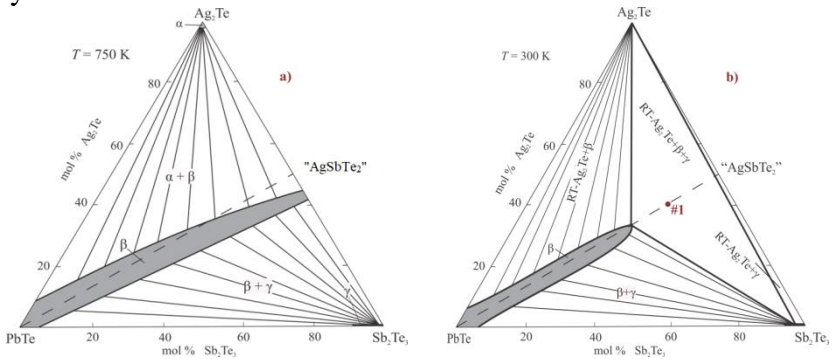


Figure 9. Isothermal sections at 750 and 300 K of the phase diagram of the Ag_2Te - PbTe - Sb_2Te_3 system

The presence of a large $(\text{Ag}_2\text{Te})_1+\beta+\gamma$ heterogeneous area in the system was confirmed by the RFA method. The diffractogram clearly shows the reflexes of all three phases (Fig.10).

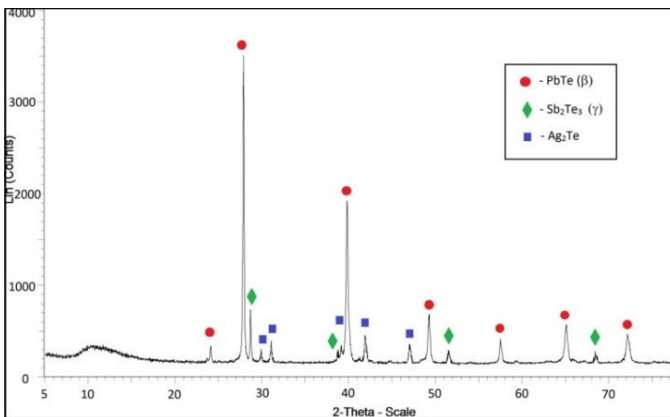


Figure 10. The PXRD and phase composition of the sample # 1 Ag_2Te - PbTe - Sb_2Te_3 system showed at Fig.9

The liquid surface projection of the Ag_2Te - PbTe - Sb_2Te_3 system (Fig.11) consists of 4 primary crystallization areas. The liquid surface of the β -phase is divided into two parts by the curve M_1M_2

connected to the minimum points M_1 and M_2 . These parts can also be described as β -phase liquid liquids based on $PbTe$ and $Ag_{19}Sb_{27}Te_{52}$.

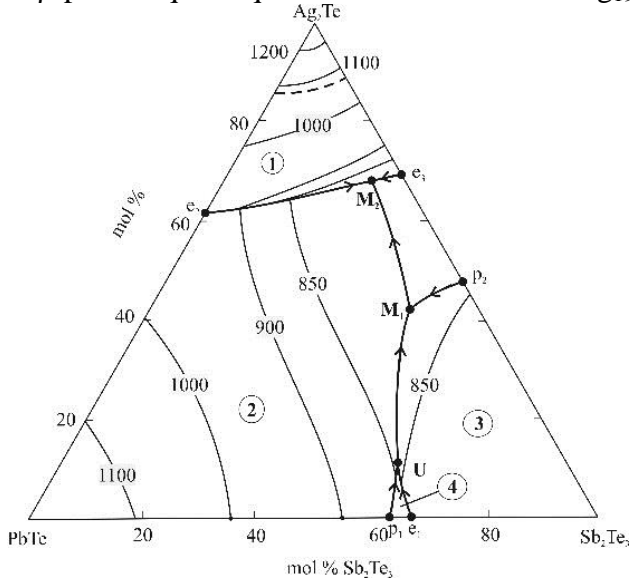


Figure 11. The liquid surface projection of the Ag_2Te - $PbTe$ - Sb_2Te_3 system. Primary crystallization areas: 1 – α (α'); 2 - β ; 3 - γ ; 4- $Pb_6Sb_2Te_{11}$.

In the $PbTe$ - Sb_2Te_3 system, the crystallization area of the $Pb_6Sb_2Te_{11}$ ternary compound (area 4), formed at a peritectic reaction at 860 K (Fig. 11, point P_1) and stable at a small temperature range (635-847 K) is found. By connecting the monovariant curves coming from P_1 and e_1 points at 847 K the $L+Pb_6Sb_2Te_{11} \leftrightarrow \beta+\gamma$ nonvariant transient reaction occurs. As a result, both the liquid phase and the ternary compound are fully utilized and the system becomes $\beta+\gamma$ bi-phase.

All non- and monovariant equilibria found in the Ag_2Te - $PbTe$ - Sb_2Te_3 system are given in Table 4.

The dissertation presents a number of poly- and isothermal sections of the Ag_2Te - $PbTe$ - Sb_2Te_3 system and describes them in detail. Let's look at the nature of interaction in the $PbTe$ -" $AgSbTe_2$ " section in the context with the liquidus surface (Fig.11) and the solid-phase diagram (Fig. 10).

Table 4

Nonvariant equilibria in the $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ system

The point on the Fig.9	Equilibria	Composition, mol%		T, K
		Ag_2Te	Sb_2Te_3	
P ₁	$\text{L}+\beta\leftrightarrow\text{Pb}_6\text{Sb}_2\text{Te}_{11}$	-	62	860
P ₂	$\text{L}+\gamma\leftrightarrow\text{Pb}_6\text{Sb}_2\text{Te}_{11}$	48	52	847
e ₁	$\text{L}\leftrightarrow\text{Pb}_6\text{Sb}_2\text{Te}_{11}+\gamma$	-	66	855
e ₂	$\text{L}\leftrightarrow\alpha+\beta$	62	-	967
e ₃	$\text{L}\leftrightarrow\alpha+\text{Ag}_{19}\text{Sb}_{27}\text{Te}_{52}$	70	30	813
U	$\text{L}+\text{Pb}_6\text{Sb}_2\text{Te}_{11}\leftrightarrow\beta+\gamma$	11	59	847
M ₁	$\text{L}\leftrightarrow\beta+\gamma$	42	46	825
M ₂	$\text{L}\leftrightarrow\alpha+\beta$	68	27	805
P ₁ U	$\text{L}+\beta\leftrightarrow\text{Pb}_6\text{Sb}_2\text{Te}_{11}$			860-847
e ₁ U	$\text{L}\leftrightarrow\text{Pb}_6\text{Sb}_2\text{Te}_{11}+\gamma$			855-847
UM ₁	$\text{L}\leftrightarrow\beta+\gamma$			847-825
P ₂ M ₁	$\text{L}+\gamma\leftrightarrow\text{Ag}_{19}\text{Sb}_{27}\text{Te}_{52}$			847-825
M ₁ M ₂	$\text{L}\leftrightarrow\gamma$			825-805
e ₂ M ₂	$\text{L}\leftrightarrow\alpha+\beta$			967-805
e ₃ M ₂	$\text{L}\rightarrow\alpha+\beta$			813-805

Although for a long time, the "AgSbTe₂" component was considered a chemical compound now it is now known that it is Ag₁₉Sb₂₇Te₅₂ and Ag₂Te two-phase mixture. As can be seen from the T-x diagram (Fig. 12), the PbTe-AgSbTe₂ section is located in the liquid surface of the β -phase. Therefore, this phase first crystallizes from the liquid. The presence on the liquidus curve of a minimum point in the ~10-12mol% PbTe region is associated with the intersection with the M₁M₂ monovariant curve. Below liquidus, the crystallization of the $\alpha + \beta$ eutectic mixture from liquid occurs. As a result, a three-phase area L+ α + β is formed. When the crystallization of eutectic is completed, a two-phase α + β (~0–25 mol% PbTe) area is formed. The crystallization of β -phase occurs within 30-100 mol% PbTe. It is noteworthy that β -phase melting (crystallization) occurs at large temperature intervals (up to 150 °). Because crystallization in real conditions is an equilibrium process, the slow cooling process inhomogeneity of the solid solution is observed.

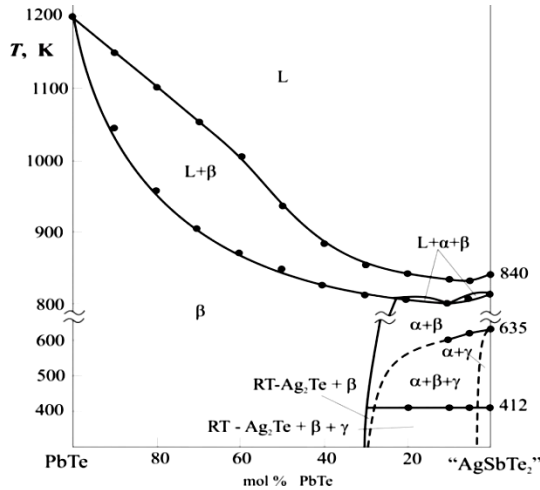
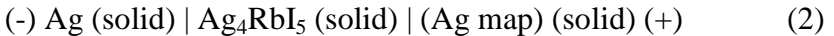
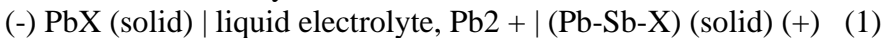


Figure 12. The polythermal section $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ of the phase diagram of the $\text{PbTe-“AgSbTe}_2\text{”}$ system

Chapter 4 is devoted to the thermodynamic investigation of three- and quaternary intermediate phases in the $\text{Ag}_2\text{X-PbX-Sb}_2\text{X}_3$ systems.

At the beginning of the chapter, the characteristics of the application of the EMF method to three-component and more complex heterogeneous systems are explored and experimental studies are planned.

For the thermodynamic studies



concentration cells were assembled and their EMF were determined by using high-voltage B7-34A digital voltmeter at a temperature range of 300-450 K.

The obtained experimental data were processed by the least-squares method and presented in the form

$$E = a + bT \pm t \left[\left(\frac{S_E^2}{n} \right) + S_b^2 \cdot (T - \bar{T})^2 \right]^{1/2} \quad (3)$$

In (3), n is the number of pairs of E and T values, S_E and S_b are the dispersions of the individual EMF measurements and coefficient b , \bar{T} is the average temperature, and t is the Student criterion. At a confidence level of 95% and the number of experimental points $n \geq 20$,

the Student criterion is $t \leq 2$.

Solid-phase equilibrium diagram and thermodynamic properties of ternary compounds in the PbSe-Sb₂Se₃-Se system. The results obtained by the EMF method as well as the PXRD results of the selective compounds which were synthesized in the PbSe-Sb₂Se₃-Se concentration area allowed us to obtain a scheme of the solid-phase equilibrium in this subsystem (Fig. 13).

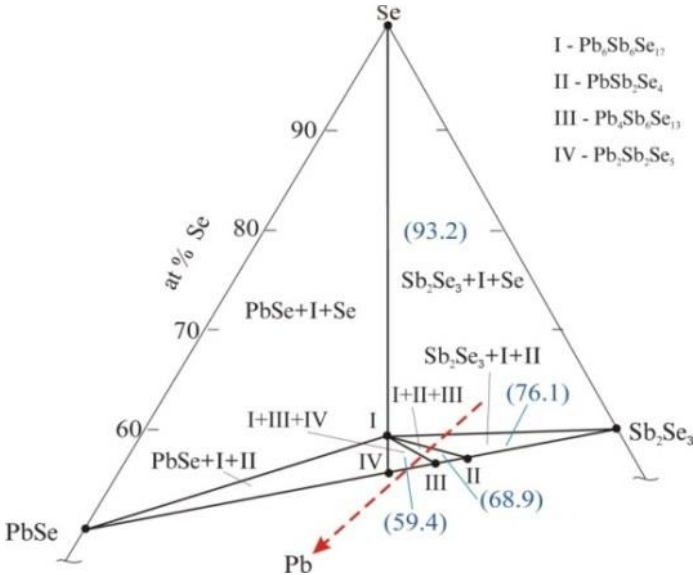


Figure 13. Solid-phase equilibria diagram of the PbSe-Sb₂Se₃-Se system at room temperature. Numbers in brackets are EMF values (mV) of the (1) type concentration cells

The EMF measurements of the (1) type concentration cell in the (3) type linear equation form are presented in Table 5.

From these equations by using relations

$$\Delta \bar{G}_i = -zFE$$

$$\Delta \bar{S}_i = zF \left(\frac{\partial E}{\partial T} \right)_p = zFb$$

$$\Delta \bar{H}_i = -zF \left[E - T \left(\frac{\partial E}{\partial T} \right)_p \right] = -zFa$$

the partial molar functions of PbTe were calculated. Then by their combination with standart thermodynamic formation functions of PbSe, the partial molyar functions of Pb were calculated (Table 6).

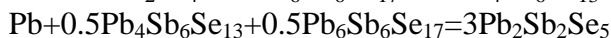
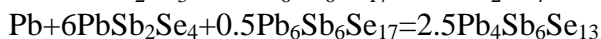
Table 5
Temperature dependences of the EMF measurements of the (1) type cells in the temperature range 300–450 K for the samples of the Pb-Sb-Se system

Phase area on the Fig.13	$E, mV=a+bT\pm t\cdot S_E(T)$
I-Sb ₂ Se ₃ -Se	$83.60+0.032T\pm 2\left[\frac{0.48}{24}+1.1\cdot 10^{-5}(T-374.3)^2\right]^{1/2}$
I-II- Sb ₂ Se ₃	$68.04+0.0269T\pm 2\left[\frac{0.25}{30}+4.35\cdot 10^{-6}(T-372.5)^2\right]^{1/2}$
I-II-III	$58.91+0.0333T\pm 2\left[\frac{0.27}{30}+4.72\cdot 10^{-6}(T-372.5)^2\right]^{1/2}$
I-III-IV	$43.63+0.0525T\pm 2\left[\frac{0.28}{30}+4.77\cdot 10^{-6}(T-376.0)^2\right]^{1/2}$

Table 6
Partial thermodynamic functions of the Pb in the Pb-Sb-Se system at 298 K

Phase area	$-\overline{\Delta G}_{Pb}$	$-\overline{\Delta H}_{Pb}$	$\overline{\Delta S}_{Pb},$ $J\cdot K^{-1}\cdot mol^{-1}$
	$kJ\cdot mol^{-1}$		
I-Sb ₂ Se ₃ -Se	114.45±3.11	116.13±2.58	-5.6±3.4
I-II- Sb ₂ Se ₃	111,18±3,07	113,13±2,41	-6,5±3,0
I-II-III	109,78±3,07	111,37±2,41	-5,3±3,0
I-III-IV	107,94±3,08	108,42±2,42	-1,6±3,0

From Fig.13 is can be seen, that the partial thermodynamic functions of lead refer to the potential-determining reaction



According to these reactions, the standard thermodynamic functions of formation and the standard entropies were calculated. For example, for $\text{Pb}_6\text{Sb}_6\text{Se}_{17}$ the calculations were based on the following relations:

$$\Delta_f G^0(\text{Pb}_6\text{Sb}_6\text{Se}_{17}) = 6\overline{\Delta Z}_{\text{Pb}} + 3\Delta_f Z^0(\text{Sb}_2\text{Se}_3)$$

$$\Delta_f H^0(\text{Pb}_6\text{Sb}_6\text{Se}_{17}) = 6\overline{\Delta Z}_{\text{Pb}} + 3\Delta_f Z^0(\text{Sb}_2\text{Se}_3)$$

$$S^0(\text{Pb}_6\text{Sb}_6\text{Se}_{17}) = 6\overline{\Delta S}_{\text{Pb}} + 6S^0(\text{Pb}) + 3S^0(\text{Sb}_2\text{Se}_3) + 2S^0(\text{Se})$$

For the calculations, we used the standard integral thermodynamic data given in handbooks. The obtained values are summarized in table 7. In all cases, the estimated standard deviations were calculated by accumulating the errors.

Table 7

Standard integral thermodynamic functions of formation and standard entropies for the samples of the $\text{PbSe-Sb}_2\text{Se}_3\text{-Se}$ system

Compound	$-\Delta_f G^0(298\text{K})$	$-\Delta_f H^0(298\text{K})$	$S^0(298\text{K})$,
	kJ·mol ⁻¹		J·K ⁻¹ ·mol ⁻¹
$\text{Pb}_6\text{Sb}_6\text{Se}_{17}$	1064±28	1080±20	1387±35
PbSb_2Se_4	239,5±6,2	243,0±3,9	320,5±7,2
$\text{Pb}_4\text{Sb}_6\text{Se}_{13}$	831,5±21,7	843,8±14,3	1070,4±21,9
$\text{Pb}_2\text{Sb}_2\text{Se}_5$	351,9±9,3	356,8±6,5	430,6±10,6

Thermodynamic properties of solids solutions in the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ and $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ systems. The partial molar thermodynamic functions of the Ag, PbSe, PbTe and Pb in the alloys of the 2PbX-AgSbX_2 systems were calculated based on EMF measurements of the (1) and (2) type concentration cells. Table 8 presents the partial molar functions of Pb in alloys of the 2PbX-AgSbX_2 systems at 298 K

The standard thermodynamic functions of formation of the solid solutions of the 2PbX-AgSbX_2 systems were calculated by integration of the Gibbs-Duhem equations along this section:

Table 8

The partial molar functions of Pb in alloys of the 2PbX-AgSbX₂ (X-Se, Te) systems at 298 K

Composition	$-\overline{\Delta G}_{\text{Pb}}$	$-\overline{\Delta H}_{\text{Pb}}$	$\overline{\Delta S}_{\text{Pb}},$
	$\text{kJ}\cdot\text{mol}^{-1}$		$\text{C}\cdot\text{J}^{-1}\cdot\text{mol}^{-1}$
(2PbSe) _{0.1} (AgSbSe ₂) _{0.9}	120.2±3.1	118.7±2.4	5.0±2.9
(2PbSe) _{0.2} (AgSbSe ₂) _{0.8}	112.7±3.1	112.0±2.4	2.3±2.8
(2PbSe) _{0.4} (AgSbSe ₂) _{0.6}	106.4±3.1	106.2±2.5	0.7±3.1
(2PbSe) _{0.6} (AgSbSe ₂) _{0.4}	100.9±3.1	101.7±2.4	-2.7±2.9
(2PbTe) _{0.2} (AgSbTe ₂) _{0.8}	77,43±1,70	75,97±1,57	4,90±4,77
(2PbTe) _{0.4} (AgSbTe ₂) _{0.6}	73,41±1,71	73,16±1,63	0,84±4,94
(2PbTe) _{0.6} (AgSbTe ₂) _{0.4}	70,57±1,67	70,95±1,43	-1,74±4,38
(2PbTe) _{0.8} (AgSbTe ₂) _{0.2}	68,94±1,68	69,72±1,45	-2,62±4,44

Table 9

The standard integral thermodynamic functions of solid solutions of the PbX-AgSbX₂ systems

Phase	$-\Delta_f G^0(298\text{K})$	$-\Delta_f H^0(298\text{K})$	$S^0(298\text{K}),$
	$\text{kJ}\cdot\text{mol}^{-1}$		$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
(2PbSe) _{0.1} (AgSbSe ₂) _{0.9}	103.3±4.8	102.2±5.1	183.0±6.0
(2PbSe) _{0.2} (AgSbSe ₂) _{0.8}	114.3±5.0	113.6±5.0	185.2±5.5
(2PbSe) _{0.4} (AgSbSe ₂) _{0.6}	136.8±5.3	136.6±4.8	189.0±4.8
(2PbSe) _{0.6} (AgSbSe ₂) _{0.4}	158.2±5.6	159.1±4.6	190.9±4.0
(2PbTe) _{0.2} (AgSbTe ₂) _{0.8}	69.8±1.2	67.0±0.9	204.9±3.7
	<i>67.3±1.1</i>	<i>66.0±0.7</i>	<i>202.2±3.0</i>
(2PbTe) _{0.4} (AgSbTe ₂) _{0.6}	89.1±1.8	86.8±1.5	211.5±3.8
	<i>86.3±1.6</i>	<i>85.4±0.9</i>	<i>208.2±3.5</i>
(2PbTe) _{0.6} (AgSbTe ₂) _{0.4}	106.4±2.3	105.2±2.0	216.1±3.5
	<i>104.3±2.0</i>	<i>104.2±0.9</i>	<i>213.7±3.4</i>
(2PbTe) _{0.8} (AgSbTe ₂) _{0.2}	122.2±2.9	122.3±2.5	220.0±3.5
	<i>119.0±2.5</i>	<i>121.9±1.1</i>	<i>218.4±3.9</i>

Note: the values in italics are calculated based on measurements of EMF circuits of type (2).

$$\begin{aligned} \Delta_f Z^0[(2\text{PbX})_x(\text{AgSbX}_2)_{1-x}] = \\ = (1-x) \int_0^x \frac{\Delta \bar{Z}_{\text{PbX}}}{(1-x)^2} dx + 2x \Delta_f Z^0(\text{PbX}) + (1-x) \Delta_f Z^0(\text{AgSbX}_2) \end{aligned} \quad (9)$$

The obtained results are presented in Table 9. Table 9 also contains integral thermodynamic data obtained from EMF measurements of the (2) type concentration cells. As can be seen, the data obtained by two modifications of the EMF method are practically identical.

RESULTS

1. The systems $\text{Ag}_2\text{X-PbX-Sb}_2\text{X}_3$ (X-Se, Te) have been studied by DTA, XRD, microstructure analyses, as well as microhardness and EMF measurements of concentration chains of type

(-) PbX (bærk) | maye elektrolit, Pb^{2+} | (Pb-Sb-X) (bærk) (+)

(-) Ag (bærk) | Ag_4RbI_5 (bærk) | (Ag xælitədə) (bærk) (+)

Some poly- and isothermal sections, as well as the projection of the liquidus surfaces of both systems are constructed, the primary crystallization fields of phases and types of non- and monovariant equilibria, coordinates of points and curves on the T-x-y diagrams are defined. It has been established that these systems are quasi-ternary planes of the Ag-Pb-Sb-X quaternary system and are characterized by the formation of solid solutions with cubic structures.

2. A new version of the phase diagram of the $\text{PbSe-Sb}_2\text{Se}_3$ system is different from the literature is constructed. According to plotted diagram, the system is characterized by formation of the $\text{Pb}_2\text{Sb}_2\text{Se}_5$, $\text{Pb}_4\text{Sb}_6\text{Se}_{13}$ vø PbSb_2Se_4 melted with decomposition by peritectic reactions at 890, 868, 855 K, respectively.
3. It has been established that the liquid surface of the $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ quasi-ternary system consists of 7 primary crystallization areas. The only PbSe-AgSbSe_2 quasi-binary section of the system belongs to the peritectic type and divides it into two independent subsystems. The sub-system $\text{Ag}_2\text{Se-PbSe-AgSbSe}_2$ belongs to the nonvariant eutectic type, while the $\text{PbSe-AgSbSe}_2\text{-Sb}_2\text{Se}_3$ subsystem has a more complex phase equilibria, accompanied by a number of non- and monovariant, transitional, and eutectic equilibria.
4. The T-x-diagram of the $\text{Ag}_2\text{Te-PbTe-Sb}_2\text{Te}_3$ system has 4 primary

crystallization surfaces, and continuous high-temperature ($635 < T < 830$ K) substitutional solid solutions are formed along the PbTe-Ag₁₉Sb₂₇Te₅₂ section. However, this system is not triangulated, since cooling, starting with 635 K, the Ag₁₉Sb₂₇Te₅₂ and its rich β -solid solutions are partially decompose and various heterogeneous areas are formed in the triangle.

5. By studying the samples of the Ag₂X-PbX-Sb₂X₃ systems after annealing at different temperatures, a number of "composition-properties" diagrams have been established and the homogeneity areas of the solid solutions have been refined. It has been found that the lattice parameters of solid solutions on the PbSe-AgSbSe₂ and PbTe-Ag₁₉Sb₂₇Te₅₂ sections are a linear function of the composition.
6. Based on EMF measurements concerning PbSe electrode, the solid-phase equilibria diagram of the PbSe-Sb₂Se₃-Se system was plotted including Pb₆Sb₆Se₁₇, Pb₂Sb₂Se₅, Pb₄Sb₆Se₁₃ and PbSb₂Se₄ compounds; the partial molar functions of the PbSe and integral thermodynamic functions of the compounds were calculated.
7. By using two modifications of the EMF method, the 2PbX-AgSbX₂ sections of the 2PbX-AgSbX₂ systems were investigated; the partial molar functions of PbSe(Te), Pb, and Ag were calculated; the standard integral thermodynamic functions for saturated compositions of solid solutions were calculated by potential-forming reactions method, while for intermediate compositions, the integration of the Gibbs-Duhem equation by two ways was used. The results obtained are in good agreement with each other.

The main results of the dissertation were published in the following scientific works:

1. Машадиева Л.Ф., Мансимова Ш.Г., Бабанлы М.Б., Байрамов В.Э., Юсибов Ю.А., Исследование растворимости и термодинамических свойств твердых растворов в системах Sn(Pb)Te-AgSbTe₂ методом ЭДС с твердым электролитом Ag₄RbI₅ / XVI Российская конференция "Физическая химия и электрохимия расплавленных электролитов", - Екатеринбург: – 2013,– с.135.
2. Mashadiyeva L.F., Mansimova Sh.H., Babanly M.B. Phase equi-

- libria in $\text{Ag}_2\text{Se-PbSe-Sb}_2\text{Se}_3$ system and some properties of intermediate phases / XII International conference on crystal chemistry of intermetallic compounds, – Lviv: – 2013, – p.79
3. Мансимова Ш.Г., Машадиева Л.Ф., Ильяслы Т.М., Бабанлы М.Б. Фазовые диаграммы систем $\text{PbX-AgSbX}_2\text{-X}$ (X-S, Se) и некоторые свойства твердых растворов / XV Всероссийская конференция "Высокочистые вещества и материалы. Получение, анализ, применение", – Нижний Новгород: – 2016, – с.118.
 4. Мансимова Ш.Г., Бабанлы К. Н., Машадиева Л.Ф., Бабанлы Н.Б. Фазовая диаграмма системы $\text{Ag}_2\text{Se-PbSe-AgSbSe}_2$ / Тезисы Докладов Республиканской научной конференции, посвященной 90-летию юбилею Академика Тогрула Шахтагинского, – Баку: –2015, – с.131.
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