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PHASE EQUILIBRIA IN THE PbSe-AgSbSe₂ SYSTEMMansimova Shabnam Hamlet¹, Babanly Kamala Nagi², Mashadiyeva Leyla Farhad²¹Baku State University

23, Z.Khalilov str., AZ-1148, Baku, Azerbaijan

²Acad.M. Nagiyev Institute of Catalysis and Inorganic Chemistry

National Academy of Sciences of Azerbaijan;

113, H.Javid Ave., AZ-1143, Baku, Azerbaijan, e-mail: leylafm76@gmail.com

The phase equilibria in the PbSe-AgSbSe₂ system were studied by means of differential thermal analysis, powder X-ray diffraction technique and micro-hardness measurement. A T-x diagram and composition dependence graphs of the lattice period and micro-hardness were constructed. It found that the PbSe-AgSbSe₂ system is quasibinary and pertaining to the peritectic type. Note that at room temperature the AgSbSe₂-based solubility is 80 mol% and the PbSe-based solubility is ~2 mol%.

Keywords: PbSe-AgSbSe₂ system, phase diagram, solid solutions, crystal lattice, micro-hardness

1. INTRODUCTION

Heavy metals-based chalcogenides and their derivative complex phases have drawn tremendous attention in recent years because of their potential use in high-technologies due to their outstanding physical properties [1-5]. Various materials such as Ag-B^V-X and Ag-A^{IV}-B^V-X (where A^{IV}-Sn, Pb; B^V-Sb, Bi; X-S, Se, Te) alloys have high ZT values and are among the most promising thermoelectric materials [6-8]. In particular, ternary semiconducting compounds with general formula AgB^VX₂ excited interest due to their thermoelectric, optical and electronic properties. In addition, they are phase-changing materials and can be used as a switching medium in rewritable optical memories [9-11].

Optimization of functional properties of these materials can be achieved by changing their composition. It is based, in turn, on the

research into phase equilibria in the systems consisting of structural analogues, since they are expected to form wide range solid solutions [12-15].

In this paper, we present the results of the research into phase equilibria in the PbSe-AgSbSe₂ system. Some similar systems such as PbSe-AgBiSe₂, PbTe-AgBiTe₂, SnTe-AgSbTe₂, and SnTe-AgBiTe₂ were studied earlier and new phases of variable composition discovered therein [16-20].

Lead selenide melts congruently at 1354 K [21] and crystallizes in a cubic NaCl structure (Sp.Gr.Fm3m) with a unit-cell parameter $a=6.1243\text{\AA}$ [22].

The AgSbSe₂ compound also melts congruently at 908 K [23] and crystallizes in a cubic structure (Sp.Gr.Fm3m) with a lattice parameter $a = 5.786\text{\AA}$ [24].

2. EXPERIMENTS

Synthesis

Owing to their congruent character of melting, the PbSe and AgSbSe₂ compounds crystallize from a melt of stoichiometric composition upon cooling. For the synthesis, the elementary components with a purity of at

least 99.999% were used. Stoichiometric amounts of the starting components were put into silica tubes with a diameter of about 1.5 cm and sealed under a pressure of 10^{-2} Pa. AgSbSe₂ was synthesized by direct synthesis in a resistance furnace at 950 K followed by

cooling in a switched-off furnace. PbSe was synthesized in a two-zone inclined furnace. The lower hot zone was heated to 1400 K, and the cold one to 900 K, which is somewhat lower than the boiling point of selenium (958 K) [20]. The purity of the synthesized compounds was checked by the by differential-thermal analysis (DTA) and powder X-ray diffraction technique (PXRD).

Methods

Phase equilibria in the PbSe-AgSbSe₂ system were investigated by means of DTA and PXRD technique, as well as micro-hardness measurement.

DTA of the equilibrated alloys was carried out using a NETZSCH 404 F1 Pegasus system. The measurement was performed between a room temperature and ~1400 K with heating and cooling rate of 5 K·min⁻¹ under the vacuum. Temperatures of thermal effects were taken mainly from the heating

Melting temperatures and crystallographic parameters of obtained compounds nearly coincide with the literature data [22, 24] (Tables 1 and 2).

The alloys of the 2PbSe-AgSbSe₂ system were prepared by melting the starting compounds in quartz ampules under vacuum followed by homogenizing annealing at 800 K (700 h).

curves. NETZSCH Proteus Software was used to measure and evaluate the data obtained.

The PXRD analysis was performed with the Bruker D8 diffractometer (CuK_α radiation), with a step size of 0.02° between 10° ≤ 2θ ≤ 70°; the data obtained were collected at room temperature. The unit cell parameters of examined alloys were calculated by indexing of powder patterns and the use of Topas V3.0 software.

The micro-hardness was measured on a PMT-3 microhardometer with a load of 20 g.

3. RESULTS

Based on the obtained experimental data (Table 1), a phase diagram and the dependence graph of the micro-hardness on the composition of the PbSe-AgSbSe₂ system is constructed (Fig. 1). This system is a quasibinary cross-section of the Ag₂Se-PbSe-Sb₂Se₃ system and is characterized by peritectic equilibrium. The peritectic coordinates correspond to 18 mol% AgSbSe₂ and 1220 K. At a peritectic temperature the solubility based on AgSbSe₂ is 87 (γ-phase) and based on PbSe is 5 mole% (β-phase), and at room temperature is 80 and ~2 mole%, respectively. The minimum point (M) is observed on liquidus and solidus curves of the γ-phase.

The results of micro-hardness measurements are in good agreement with the phase diagram. Fig.1b shows the graph of composition dependence of the micro-hardness for the PbSe-AgSbSe₂ alloys hardened from 800 K. The micro-hardness of the γ-phase

gradually increases from 1100 to 1550 MPa. Then the value of micro-hardness remains constant. As for alloys of 2, 5 and 10 mol%, the micro-hardness of the β-phase has a constant value (750 MPa) and is somewhat higher than for the pure PbSe. This shows that in the range of 2-20 mol% AgSbSe₂ composition the alloys of the system consist of a two-phase mixture β+γ.

In Fig.2 presents the powder X-ray diffraction patterns of some annealed PbSe-AgSbSe₂ alloys. The compositions of alloys for PXRD analyzes are expressed as 2PbSe-AgSbSe₂. This is necessary to determine the possible linear dependence of the lattice period on composition. As can be seen, the diffraction patterns of alloys containing ≥40 mol% AgSbSe₂ are qualitatively similar to those of pure AgSbSe₂. Note that X-ray diffraction patterns of alloys with compositions of 10 and 30 mol% AgSbSe₂ consist of a set of diffraction lines of two cubic phases.

Fig.1. Phase diagram (a) and composition dependence graph of the micro-hardness of the alloys hardened from 800 K (b) for the PbSe-AgSbSe₂ system

Fig.2. XRD powder patterns for starting compounds and some alloys of the 2PbSe-AgSbSe₂ system. 1-PbSe; 2-10mol% AgSbSe₂; 3-30mol% AgSbSe₂; 4-40mol% AgSbSe₂; 5-60mol% AgSbSe₂; 6-80 mol% AgSbSe₂; 7-AgSbSe₂.

Table 1. DTA data and micro-hardness measurements for the PbSe-AgSbSe₂ system

Compositions, <i>mol% AgSbSe₂</i>	Thermal effect, <i>K</i>	Micro-hardness, <i>MPa</i>
0 (PbSe)	1355	650
2	1280; 1345	750
5	1220; 1325	750
10	1220; 1285	750; 1550
20	1110; 1210	1550
30	860; 1125	1520
40	995; 1080	1500
50	950; 1025	
60	920; 970	1420
70	900; 925	
80	890	1250
90	890	
100 (AgSbSe ₂)	905	1100

Table 2. Phase compositions and crystallographic parameters of phases for the 2PbSe-AgSbSe₂ system

Compositions, <i>mol% AgSbSe₂</i>	Phase compositions	Cubic lattice parameters, <i>Å</i>
0 (PbSe)	β	<i>a</i> =6.1246(5)
10	β+γ	<i>a</i> =6.1184(6); <i>a</i> =6.0091(7)
20	β+γ	<i>a</i> =6.1187(7); <i>a</i> =6.0101(7)
30	β+γ	<i>a</i> =6.1185(6); <i>a</i> =6.0094(7)
40	γ	<i>a</i> =5.9882(6)
60	γ	<i>a</i> =5.9244(5)
80	γ	<i>a</i> =5.8521(5)
100 (AgSbSe ₂)	γ	<i>a</i> =5.7882(5)

To determine the mutual solubility of the starting compounds in the analyzed system, we plotted the concentration dependences of the cubic lattices parameters (Fig. 3). The unit cell parameters of intermediate alloys were calculated (Table 2). An accuracy of the crystal lattice parameters is shown in parentheses. It revealed that the dependence has fracture points in the composition ~39 mol% AgSbSe₂ which correspond to the limiting composition of γ-solid solutions based on AgSbSe₂. The composition of 39 mol% AgSbSe₂ in the 2PbSe-AgSbSe₂ system corresponds to the alloy with ~24 mol% AgSbSe₂ on the phase diagram (Fig. 1). It

should be noted that in the β+γ two-phase region, the lattice periods of the two coexisting phases have constant values regardless of the overall composition of the alloys while within the limits of homogeneity region of the γ phase the lattice period is a linear function of the composition.

The difference between the examined PbSe-AgSbSe₂ system and above-mentioned PbSe-AgBiSe₂, PbTe-AgBiTe₂, SnTe-AgSbTe₂ and SnTe-AgBiTe₂ [16-20] is that the continuous series of high-temperature solid solutions were detected in them. The presence of a wide interval (3-39 mol% AgSbSe₂) of solubility gap in the system PbSe-AgSbSe₂

(Fig. 3) is apparently associated with the fact that the difference between the crystal lattice periods of the starting compounds is more than in other systems examined.

Fig.3. Concentration dependences of cubic lattices parameters

3. CONCLUSION

The PbSe-AgSbSe₂ system is a quasibinary cross-section of the Ag₂Se-PbSe-Sb₂Se₃ system and is characterized by peritectic equilibrium (18 mol% AgSbSe₂ and 1120 K). Formation of a wide area of solid solutions based on AgSbSe₂ (~80 mol%) has

been revealed. The solubility based on PbSe is much lower not to exceed 2 mol%. The crystal lattice parameters and micro-hardness values of the obtained solid solutions have been determined.

4. ACKNOWLEDGMENTS

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REFERENCES

1. Applications of Chalcogenides: S, Se, and Te, ed. by Gurinder Kaur Ahluwalia, Springer, 2016.
2. Kolobov A.V., Tominaga J. Two-Dimensional Transition-Metal Dichalcogenides. Springer International Publishing, 2016, 538 p.
3. Gao M-R., Xu Y-F., Jiang J. and Yu S-H. Nanostructured metal chalcogenides: synthesis, modification, and applications in energy conversion and storage devices. *Chemical Society Reviews*. 2013, vol. 42, pp. 2986-3017.
4. Babanly M.B., Yusibov Y.A., Abishev V.T. Ternary Chalcogenide Based on Copper and Silver., BSU Publisher, 1993, 341 p. (In Azerbaijan).
5. Babanly M.B., Chulkov E.V., Aliev Z. S., Shevel'kov A.V., and Amiraslanov I. R. Phase diagrams in the materials science of topological insulators based on metal chalcogenides. *Russ. J. Inorg. Chem.*, 2017, vol.62, no. 13, pp. 1703–1729.
6. Shevelkov A.V. Chemical aspects of the design of thermoelectric materials. *Russ. Chem. Rev.*, 2008, vol. 77, pp. 1-19.
7. Gayner C., Kar K.K. Recent advances in thermoelectric materials. *Progress in Materials Science*. 2016, vol. 83, pp. 330–382.

8. Kusz B., Miruszewski T., Bochentyn B., Łapin'ski M., and Karczewski J. Structure and Thermoelectric Properties of Te-Ag-Ge-Sb (TAGS) Materials Obtained by Reduction of Melted Oxide Substrates. *J. Electron. Mater.*, 2016, vol. 45, no. 2, pp.1085-1093.
9. Morelli D.T., Jovovic V., Heremans J.P. Intrinsically minimal thermal conductivity in cubic I-V-VI₂ semiconductors. *Phys. Rev. Lett.*, 2008, vol. 101, no. 3, pp. 035901.
10. Hoang K., Mahanti S.D., Atomic and electronic structures of I-V-VI₂ ternary chalcogenides *Journal of Science: Advanced Materials and Devices*. 2016, vol.1, pp. 51-56.
11. Guin S.N., Chatterjee A., Biswas K., Enhanced thermoelectric performance in p-type AgSbSe₂ by Cd-doping. *RSC Adv.*, 2014, vol. 4, no. 23, pp. 11811.
12. Villars P., Prince A., Okamoto H. Handbook of Ternary Alloy Phase Diagrams (10 volume set). American Technical Publishers, 1995, 15000p.
13. Zlomanov V.P., Khoviv A.M. and Zavrazhnov A.Yu. Physicochemical Analysis and Synthesis of Nonstoichiometric Solids. In: InTech. Materials Science - Advanced Topics, 2013, pp.103-128
14. Imamaliyeva S.Z., Gasanly T.M., Gasymov V.A., Babanly M.B. Phase relations in the Tl₉SbTe₆-Tl₉GdTe₆ and Tl₉SbTe₆-Tl₉TbTe₆ systems. *Kimya Problemleri - Chemical Problems*, 2017, no. 3, pp. 241-247. (In Azerbaijan).
15. Alakbarova T.M., Jafarov Y.I., Mustafayeva A.L., Babanly M.B. Tl₂Te-Tl₉BiTe₆-Tl₈GeTe₅ system. *Kimya Problemleri - Chemical Problems*, 2017, no.4, pp. 355-363. (In Azerbaijan).
16. Aliev I.I., Babanly K.N., and Babanly N.B. Solid Solutions in the Ag₂Se-PbSe-Bi₂Se₃ System. *Inorg. Mater.*, 2008, vol. 44, no.11, pp.1179-1182.
17. Babanly N.B., Aliev I.I., Babanly K.N. and Yusibov Yu.A. Phase Equilibria in the Ag₂Te-PbTe-Bi₂Te₃ System. *Russ. J. Inorg. Chem.*, 2011, vol. 56, no. 9, pp. 1472-1477.
18. Mashadiyeva L.F., Kevser J.O., Aliev I.I., Yusibov Y.A., Taghiyev D.B., Aliev Z.S., Babanlı M.B. Phase Equilibria in the Ag₂Te-SnTe-Sb₂Te₃ system and thermodynamic properties of the (2SnTe)_{1-x}(AgSbTe₂)_x solid solution. *Phase equilibria and diffusion*. 2017, vol. 38, no.5, pp. 603-614.
19. Mashadiyeva L.F., Kevser J.O., Aliev I.I., Yusibov Y.A., Taghiyev D.B., Aliev Z.S., Babanlı M.B. The Ag₂Te-SnTe-Bi₂Te₃ system and thermodynamic properties of the (2SnTe)_{1-x}(AgBiTe₂)_x solid solutions series. *J.Alloys.Comp.*, 2017, vol. 724, pp. 641-648.
20. Mashadiyeva L.F., Mansimova Sh.G., Yusibov Yu.A., Babanlı M.B. Thermodynamic Study of the 2PbTe-AgSbTe₂ System Using EMF Technique with the Ag₄RbI₅ Solid Electrolyte *Russian Journal of Electrochemistry*. 2018, vol. 54, no. 1, pp. 106–111.
21. Shelimova L.E., Tomashik V.N., Grytsiv V.I., Diagrammy sostoyaniya v poluprovodnikovom materialovedenii (sistemy na osnove khal'kogenidov Si, Ge, Sn, Pb) (Phase Diagrams in Semiconductor Materials Research: Systems of Si, Ge, Sn, and Pb Chalcogenides), Moscow: Nauka Publ., 1991.
22. Dalven R. A review of the semiconductor properties of PbTe, PbSe, PbS, and PbO. *Infrared Phys.*, 1969, vol. 9, pp. 141-184.
23. Boutserrit A., Ollitrault-Fichet R., Rivet J., Dugué J. Description du système ternaire Ag-Sb-Se. *Journal of Alloys and Compounds*. 1993, vol. 191, no. 2, pp. 223-232.
24. Geller S., Wernick J. H. Ternary semiconducting compounds with sodium chloride-like structure: AgSbSe₂, AgSbTe₂, AgBiS₂, AgBiSe₂. *Acta Cryst.*, 1959, vol. 12, pp. 46-52.

PbSe-AgSbSe₂ SİSTEMİNDƏ FAZA TARAZLIQLARI¹Ş.H. Mənsimova, ²K.N. Babanlı, ²L.F. Məşədiyeva*Bakı Dövlət Universiteti**AZ 1148 Bakı, Z.Xəlilov küç., 23**AMEA-nın akad. M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu**AZ 1143, Bakı, H.Cavid pr., 113; e-mail: eylafm76@gmail.com*

Differensial termiki və rentgenfaza analizi üsulları ilə, həmçinin mikrobərkliyin ölçülməsilə PbSe-AgSbSe₂ sistemində faza tarazlıqları öyrənilmişdir. Sistemin T-x diaqramı, həmçinin qəfəs parametrlərinin və mikrobərkliyin tərkibdən asılılıq qrafikləri qurulmuşdur. Müəyyən edilmişdir ki, PbSe-AgSbSe₂ sistemi kvazibinardır və peritektik tipli hal diaqramı əmələ gətirir. Otaq temperaturunda AgSbSe₂ əsasında həllolma 80 mol%, PbSe əsasında isə ≤2 mol% təşkil edir.

Açar sözlər: *PbSe-AgSbSe₂ sistemi, faza diaqramı, bərk məhlullar, kristal qəfəs, mikrobərklik.*

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ PbSe-AgSbSe₂¹Ш.Г. Мансимова, ²К.Н. Бабанлы, ²Л.Ф. Машадиева*Бакинский государственный университет**AZ 1148 Баку, ул. З.Халилова, 23**Институт катализа и неорганической химии им. акад. М.Нагиева**Национальной АН Азербайджана**AZ 1143 Баку, пр.Г.Джавида, 113; e-mail: eylafm76@gmail.com*

Фазовые равновесия в системе PbSe-AgSbSe₂ изучены методами дифференциального термического и рентгенофазового анализов и измерением микротвердости. Построены T-x диаграмма и графики зависимости периода решетки и микротвердости от состава. Установлено, что система PbSe-AgSbSe₂ является квазибинарной и относится к перитектическому типу. При комнатной температуре растворимость на основе AgSbSe₂ составляет 80 мол.%, а на основе PbSe ≤2 мол.%.

Ключевые слова: *система PbSe-AgSbSe₂, фазовая диаграмма, твердые растворы, кристаллическая решетка, микротвердость*