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PHASE EQUILIBRIA IN THE PbSe-$AgSbSe_2$ SYSTEM

Mansimova Shabnam Hamlet[1], Babanly Kamala Nagi[2], Mashadiyeva Leyla Farhad[2]

[1]Baku State University
23, Z.Khalilov str., AZ-1148, Baku, Azerbaijan
[2]Acad.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-$AgSbSe_2$ 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-$AgSbSe_2$ system is quasibinary and pertaining to the peritectic type. Note that at room temperature the $AgSbSe_2$-based solubility is 80 mol% and the PbSe-based solubility is ~2 mol%.

Keywords: *PbSe-$AgSbSe_2$ 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^VX_2 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-$AgSbSe_2$ system. Some similar systems such as PbSe-$AgBiSe_2$, PbTe-$AgBiTe_2$, SnTe-$AgSbTe_2$, and SnTe-$AgBiTe_2$ 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.*Fm*3*m*) with a unit-cell parameter *a*=6.1243Å [22].

The $AgSbSe_2$ compound also melts congruently at 908 K [23] and crystallizes in a cubic structure (Sp.Gr.*Fm*3*m*) with a lattice parameter a = 5.786 Å [24].

2. EXPERIMENTS

Synthesis

Owing to their congruent character of melting, the PbSe and $AgSbSe_2$ 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. $AgSbSe_2$ was synthesized by direct synthesis in a resistance furnace at 950 K followed by

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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). 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-$AgSbSe_2$ system were prepared by melting the starting compounds in quartz ampules under vacuum followed by homogenizing annealing at 800 K (700 h).

Methods

Phase equilibria in the PbSe-$AgSbSe_2$ 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 $K \cdot min^{-1}$ under the vacuum. Temperatures of thermal effects were taken mainly from the heating 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 $10° \leq 2\theta \leq 70°$; 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-$AgSbSe_2$ system is constructed (Fig. 1). This system is a quasibinary cross-section of the Ag_2Se-PbSe-Sb_2Se_3 system and is characterized by peritectic equilibrium. The peritectic coordinates correspond to 18 mol% $AgSbSe_2$ and 1220 K. At a peritectic temperature the solubility based on $AgSbSe_2$ 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-$AgSbSe_2$ 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% $AgSbSe_2$ 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-$AgSbSe_2$ alloys. The compositions of alloys for PXRD analyzes are expressed as 2PbSe-$AgSbSe_2$. 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% $AgSbSe_2$ are qualitatively similar to those of pure $AgSbSe_2$. Note that X-ray diffraction patterns of alloys with compositions of 10 and 30 mol% $AgSbSe_2$ consist of a set of diffraction lines of two cubic phases.

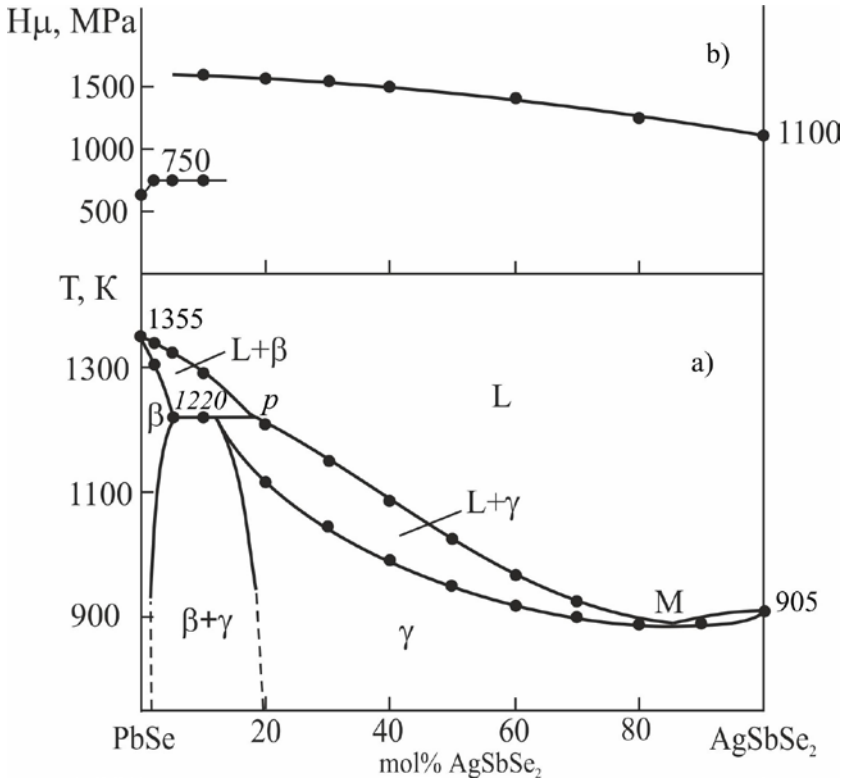

Fig.1. Phase diagram (a) and composition dependence graph of the micro-hardness of the alloys hardened from 800 K (b) for the PbSe-AgSbSe$_2$ system

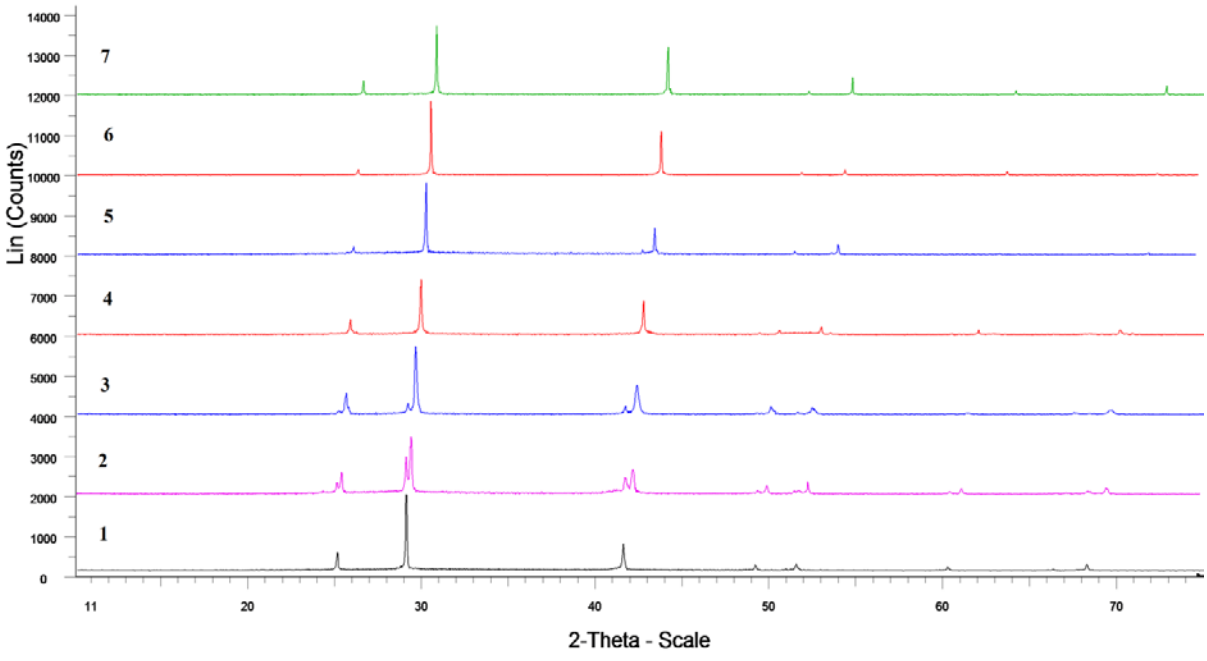

Fig.2. XRD powder patterns for starting compounds and some alloys of the 2PbSe-AgSbSe$_2$ system. **1**-PbSe; **2**-10mol% AgSbSe$_2$; **3**-30mol% AgSbSe$_2$; **4**-40mol% AgSbSe$_2$; **5**-60mol% AgSbSe$_2$; **6**-80 mol% AgSbSe$_2$; 7-AgSbSe$_2$.

Table 1. DTA data and micro-hardness measurements for the PbSe-$AgSbSe_2$ system

Compositions, *mol% $AgSbSe_2$*	**Thermal effect, *K***	**Micro-hardness, *MPa***
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-$AgSbSe_2$ system

Compositions, *mol% $AgSbSe_2$*	**Phase compositions**	**Cubic lattice parameters, *Å***
0 (PbSe)	β	*a*=6.1246(5)
10	β+γ	*a*=6.1184(6); *a*=6.0091(7)
20	β+γ	*a*=6.1187(7); *a*=6.0101(7)
30	β+γ	*a*=6.1185(6); *a*=6.0094(7)
40	γ	*a*=5.9882(6)
60	γ	*a*=5.9244(5)
80	γ	*a*=5.8521(5)
100 ($AgSbSe_2$)	γ	*a*=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% $AgSbSe_2$ which correspond to the limiting composition of γ-solid solutions based on $AgSbSe_2$. The composition of 39 mol% $AgSbSe_2$ in the 2PbSe-$AgSbSe_2$ system corresponds to the alloy with ~24 mol% $AgSbSe_2$ 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-$AgSbSe_2$ system and above-mentioned PbSe-$AgBiSe_2$, PbTe-$AgBiTe_2$, SnTe-$AgSbTe_2$ and SnTe-$AgBiTe_2$ [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% $AgSbSe_2$) of solubility gap in the system PbSe-$AgSbSe_2$

(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.

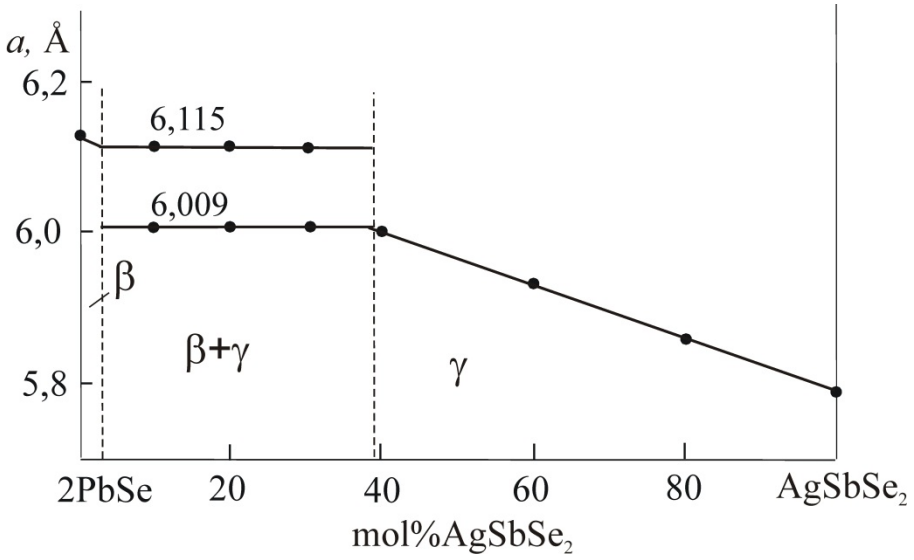

Fig.3. Concentration dependences of cubic lattices parameters

3. CONCLUSION

The PbSe-AgSbSe$_2$ system is a quasibinary cross-section of the Ag$_2$Se-PbSe-Sb$_2$Se$_3$ system and is characterized by peritectic equilibrium (18 mol% AgSbSe$_2$ and 1120 K). Formation of a wide area of solid solutions based on AgSbSe$_2$ (~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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$PbSe\text{-}AgSbSe_2$ SİSTEMİNDƏ FAZA TARAZLIQLARI

[1]Ş.H. Mənsimova, [2]K.N. Babanlı, [2]L.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 $PbSe\text{-}AgSbSe_2$ sistemində faza tarazlıqları öyrənilmişdir. Sistemin T-x diaqramı, həmçinin qəfəs parametrlərinin və mikrobərkliyin tərkibdən asılılıq qrafikləri qurulmuşdur. Müəyyən edilmişdir ki, $PbSe\text{-}AgSbSe_2$ sistemi kvazibinardır və peritektik tipli hal diaqramı əmələ gətirir. Otaq temperaturunda $AgSbSe_2$ əsasında həllolma 80 mol%, PbSe əsasında isə ≤2 mol% təşkil edir.
Açar sözlər: *$PbSe\text{-}AgSbSe_2$ sistemi, faza diaqramı, bərk məhlullar, kristal qəfəs, mikrobərklik.*

ФАЗОВЫЕ РАВНОВЕСИЯ В СИСТЕМЕ $PbSe\text{-}AgSbSe_2$

[1]Ш.Г. Мансимова, [2]К.Н. Бабанлы, [2]Л.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 $PbSe\text{-}AgSbSe_2$ изучены методами дифференциального термического и рентгенофазового анализов и измерением микротвердости. Построены Т-х диаграмма и графики зависимости периода решетки и микротвердости от состава. Установлено, что система $PbSe\text{-}AgSbSe_2$ является квазибинарной и относится к перитектическому типу. При комнатной температуре растворимость на основе $AgSbSe_2$ составляет 80 мол.%, а на основе PbSe ≤2 мол.%.
***Ключевые слова**: система $PbSe\text{-}AgSbSe_2$, фазовая диаграмма, твердые растворы, кристаллическая решетка, микротвердость*