Applied Chemical Engineering (2019) Volume 2 Issue 2
doi: 10.63019/ace.v1i2.586

Roentgenographic investigation of solid-phase equilibria in the PbSe-$AgSbSe_2$ system

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ABSTRACT

The solid-phase equilibria in the 2PbSe-$AgSbSe_2$system were studied by using the powder X-ray diffraction method. It is established that the system is characterized by the formation of ~60 mol% solid solutions basedon $AgSbSe_2$.Solubility based on PbSe is about 3mol%. The cubic lattice parameters of solid solutions are defined.

Keywords: *silver-antimony selenide; lead selenide; solid solutions; powder X-ray diffraction; crystal lattice*

1. Introduction

Chalcogenides of heavy metals and their derivative phases are very attractive to the high-technologies thanks to their outstanding physical properties[1-3]. In particular, various materials such as Ag-B^V-Teand Ag-A^{IV}-B^V-Te(A^{IV}-Sn, Pb; B^V-Sb, Bi) alloys have high ZT valuesand are among the most promising thermoelectric materials[4-6]. Recent studies showed that some complex chalcogenidesof heavy p-metalsexhibit also topological surface states and can be used inspintronics and quantum computing[7,8]. In addition,silver chalcogenides and complex phases on their basis have mixed superion-electron conductivity and may beapplied in thermoelectric energy converters and differention-optical devices[9,10].

Optimization of functional properties of these materials can be achieved by changing their composition. This is based in turn on the study of systems consisted of structural analogs, since they can be expected to form wide regions of solid solutions[11, 12].

In this paper, we present the results of X-ray diffraction studies of solid-phase equilibria in the 2PbSe-$AgSbSe_2$ system.

Earlier we have studied some similar systems, in which new phases of variable composition were revealed:PbSe-$AgBiSe_2$[13], PbTe-$AgBiTe_2$ [14], SnTe-$AgSbTe_2$ [15], andSnTe-$AgBiTe_2$[16].

PbSeand$AgSbSe_2$ compounds crystallize in cubicNaClstructure(Sp.Gr.Fm3m) with lattice parameter: a=6.1243Å[17],a=5.786 Å[18], accordingly.

2. Experiments and results

The PbSe and $AgSbSe_2$compounds melt congruently at 1354 K[19] and 908 K[2]. Therefore, they crystallize from amelt 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 tubesof about 20 cm in length and diameter of about 1.5 cm and sealed under a pressure of 10^{-2} Pa. $AgSbSe_2$wassynthesized by direct synthesis in a resistance furnace at 950 K followed by cooling in the 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[20]. The purity of the synthesized compounds was controlled by the XRD method by using the Bruker D8 diffractometer(CuK_α radiation), with a step size of 0.02°between 10°≤ 2θ ≤ 70°; data were collected at room temperature.The unit cell parameters of intermediate alloys were calculated by indexing of powder patterns using Topas V3.0 software. An accuracy of the crystal lattice parameters is shown in parentheses (Table).Crystallographic

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parameters of obtained compounds, practically almost coincide with the literature data[17, 18].

Compositions %$AgSbSe_2$	Phase compositions	Cubic lattice parameters, Å
0 (PbSe)	α	a=6.1246(5)
10	α+β	a=6.1184(6); a=6.0091(7)
20	α+β	a=6.1187(7); a=6.0101(7)
30	α+β	a=6.1185(6); a=6.0094(7)
40	β	a=5.9882(6)
60	β	a=5.9244(5)
80	β	a=5.8521(5)
100	β	a=5.7882(5)

Table 1. Phase compositions and crystallographic parameters of phases of the 2PbSe-$AgSbSe_2$ system

The alloys of the 2PbSe-$AgSbSe_2$ system were prepared by melting of the starting compounds in quartz ampules under vacuum followed by homogenizing annealing at 800 K (700 h).

In Fig.1, the powder X-ray diffraction patterns of some annealed alloys are presented. As can be seen, the diffraction patterns of alloys containing ≥40 mol% $AgSbSe_2$ are qualitatively similar to those for pure $AgSbSe_2$. X-ray diffraction patterns of alloys with compositions of 10, 20 and 30 mol% $AgSbSe_2$ consist of a set of diffraction lines of two cubic phases.

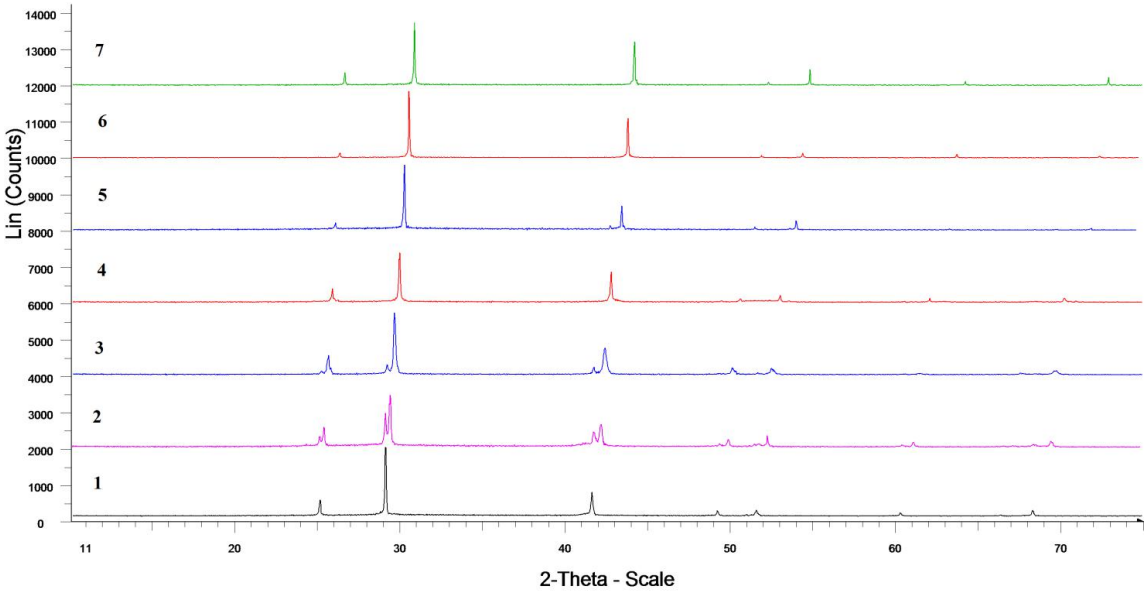

Рис.1. XRD powder patterns for starting compounds and some alloys of the 2PbSe-$AgSbSe_2$.
1-PbSe;2-10mol%; 3-30mol%; 4-40mol%; 5-60mol%; 6-80 mol%$AgSbSe_2$; 7-$AgSbSe_2$.

To determine the mutual solubility of the starting compounds in the studied system, we plotted the concentration dependences of the cubic lattices parameters (Table, Fig. 2). It is established that the dependencies have fracture points at compositions of ~3 and ~39 mol% $AgSbSe_2$, which correspond to the limiting compositions of α- and β-solid solutions based on PbSe and $AgSbSe_2$, respectively. It should be noted that in the α + βtwo-phase region, the lattice periods of the two coexisting phases have constant values regardless of the overall composition of the alloys, while

within the homogeneity region of the β phase the lattice period is a linear function of the composition, i.e. obey the Vegard's law.

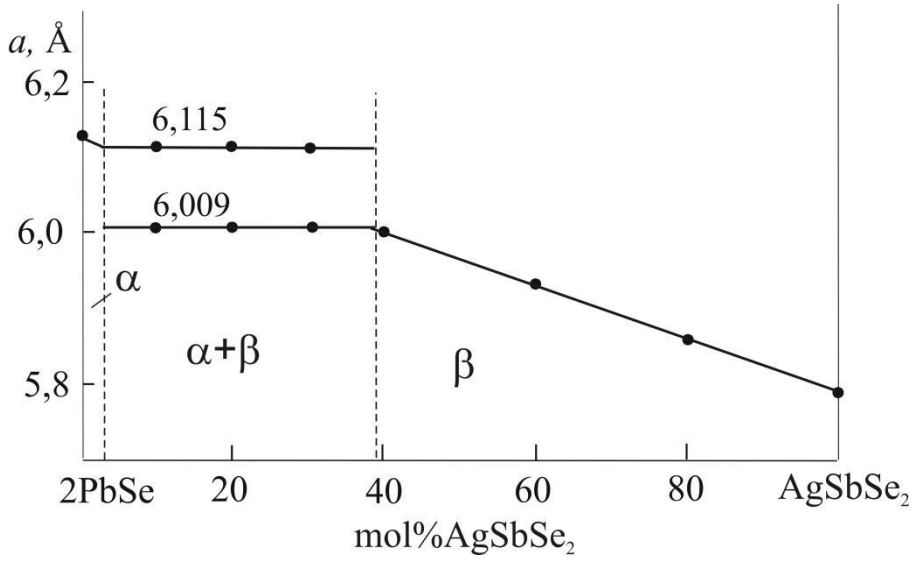

Fig.2: Concentration dependences of cubic lattices parameters.

The difference between studied system and above-mentioned [13-16] is that continuous series of high-temperature solid solutions were detected in them. The presence of a wide interval (3-39 mol% $AgSbSe_2$) of dissolution in the system 2PbSe-$AgSbSe_2$ (Fig. 2), is apparently associated with a large difference between the crystal lattices periods of the starting compounds.

3. Conclusion

Formation of a wide area of solid solutions based on $AgSbSe_2$ (40 mol%) is established in the 2PbSe-$AgSbSe_2$system based on the XRD results. The solubility based on PbSe is much lower and does not exceed 3 mol%. The crystal lattices parameters of the obtained solid solutions are determined.

Acknowledgment

The work has been carried out within the framework of the international joint research laboratory "Advanced Materials for Spintronics and Quantum Computing" (AMSQC) established between Institute of Catalysis and Inorganic Chemistry of ANAS (Azerbaijan) and Donostia International Physics Center (Basque Country, Spain).

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