STRUCTURAL PECULIARITIES AND THERMOELECTRIC PROPERTIES OF LAYERED CHALCOGENIDES WITH COMPLEX CRYSTAL LATTICES AND A LOW THERMAL CONDUCTIVITY

Zemskov V.S.[1], *Shelimova L.E.*[1], *Konstantinov P.P.*[2], *Avilov E.S.*[1],
Kretova M.A.[1], *Nikhezina I.Yu.*[1]
([1]Institution of RAS Baikov Institute of Metallurgy and Materials Research, RAS,
49, Leninskiy Ave., Moscow, 119991, Russia;
[2]Institution of RAS, Ioffe Physics and Technical Institute, RAS, 26, Polytehpnicheskaya Str.,
Saint-Petersburg, 194021, Russia)

- *Crystalline structure and thermoelectric properties of layered compounds in $PbSe$-Bi_2Se_3 quasi-binary system have been investigated. Compositions of three compounds: $Pb_5Bi_6Se_{14}$, $Pb_5Bi_{12}Se_{23}$ and $Pb_5Bi_{18}Se_{32}$ belonging to $[(PbSe)_{5m}[(Bi_2Se_3)_3]_n$ homologous series have been identified. These compounds have the following m and n values: $Pb_5Bi_6Te_{14}$ (m = 1, n = 1); $Pb_5Bi_{12}Se_{23}$ (m = 1; n = 2) and $Pb_5Bi_{18}Se_{32}$ (m = 1, n = 3). The compounds are formed by superimposition along the (a) axis of two layer fragments: $[(PbSe)_5]$ and $[(Bi_2Se_3)_3]$. The compounds have monoclinic lattices of kanizzarite mineral type. The Hall effect and the electric resistivity have been investigated in the temperature range from 80 to 670 K, and the Seebeck coefficient and thermal conductivity – in the temperature range from 80 to 360 K. A correlation is noted between the character of change in the thermoelectric properties and crystalline structure of ternary compounds. Ternary compounds are characterized by a low lattice thermal conductivity related to effective phonon scattering on potential barriers between the layer fragments $[(PbSe)_5]$ and $[(Bi_2Se_3)_3]$. The thermoelectric properties of PbSe-based solid solution alloys have been studied.*

Introduction

Current interest in chalcogenide systems formed by compounds with cubic structure of *NaCl* type, on the one hand, and compounds with tetradymite-type structure, on the other hand, is related to a search for new ternary and quarternary chalcogenides with complex crystal lattices and a low lattice thermal conductivity. This search is based on the development of a concept of building a homologous series of layered compounds typical of a large number of chalcogenide systems, as well as the use of these concepts for the prediction of composition and structure of new compounds having good prospects for use in thermoelectric devices [1]. The $PbSe$-Bi_2Se_3 quasi-binary system alloys are of interest for the fabrication of new medium-temperature thermoelectric materials with a low lattice thermal conductivity.

The diagram of state of $PbSe$-Bi_2Se_3 system was first studied in [2] by thermal and microstructural analysis methods. In the system there were discovered three tetradymite-like compounds formed according to peritectic reactions. The microstructural analysis and differential thermal analysis (DTA) were used to establish the existence of a rather wide range of *PbSe*-based solid solutions: up to 20 mol.% Bi_2Se_3 at 993 K and nearly 10 mol. % Bi_2Se_3 at 770 K.

Conflicting data can be found in the literature concerning the crystalline structure and composition of compounds formed in $PbSe$-Bi_2Se_3 system.

Papers [3 – 5] present the results of electron diffraction study of thin film compounds $Pb_2Bi_2Se_5$ and $PbBi_2Se_4$ obtained by sputtering on heated *NaCl* cleavages with subsequent annealing at temperature 453 – 473 K for 1.5 – 7.0 hours. The $Pb_2Bi_2Se_5$ compound was obtained in [3] by sublimation of an alloy with the initial composition $PbBi_2Se_4$ and has a hexagonal lattice with parameters: $a = 0.422$ nm; $c = 1.642$ nm (space group $P3m1$). The $PbBi_2Se_4$ compound was obtained in thin films by sublimation of a sample with the initial composition $PbBi_4Te_7$. The $PbBi_2Se_4$ compound has, according to [4], a rhombohedral lattice with parameters $a = 0.416$ nm; $c = 3.920$ nm (in hexagonal packing). For $PbBi_4Te_7$ compound in paper [5] the lattice parameters ($a = 0.425$ nm; $c = 2.268$ nm) were calculated based on the general regularity of formation of tetradymite-like compounds with octahedral coordination.

Unlike the data in [3 – 5], in papers [1, 6, 7] on the basis of X-ray study of the bulk crystals it is supposed that compounds of $PbSe$-Bi_2Se_3 system refer to a lower symmetry. In paper [1], a homologous series of compounds in $PbSe$-Bi_2Se_3 system is described that has a corresponding generalized formula: $[(PbSe)_5]_m[(Bi_2Se_3)_3]_n$ ($m = 1$; $n = 1 - 3$). In this paper, the formulae of three compounds belonging to the above-referenced homologous series are given: $Pb_5Bi_6Se_{14}$ ($m = 1$, $n = 1$), $Pb_5Bi_{12}Se_{23}$ ($m = 1$, $n = 2$) and $Pb_5Bi_{18}Se_{32}$ ($m = 1$, $n = 3$). The compounds have a monoclinic lattice of kanizzarite mineral type and are formed by superposition of the two types of layer fragments: $[(PbSe)_5]$ and $[(Bi_2Se_3)_3]$ that are packed along the a axis of crystal lattice.

Paper [6] presents the results of determination of crystalline structure of the first term of $Pb_5Bi_6Se_{14}$ homologous series by powder diffraction method with the use of synchrotron radiation. According to this paper, the lattice belongs to a monoclinic system and is characterized by the following parameters: $a = 1.60096(2)$ nm, $b = 0.420148(4)$ nm, $c = 2.15689(3)$ nm, $\beta = 97.537(1)^\circ$ (space group $P21/m$). Determination of the occupancy of sites in $Pb_5Bi_6Se_{14}$ structure shows the presence of vacancies in cation sublattice and demonstrates formation of substitutional defects of $Bi^{\bullet}_{Pb}$ and Pb'_{Bi} type.

Apart from the above listed compounds, the existence of a series of compounds close to $PbSe$ is reported, namely $Pb_9Bi_4Se_{15}$ (U-phase), $Pb_8Bi_6Se_{17}$ (V-phase) and $PbBi_2Se_4$ (W-phase) with the orthorhombic structures of the cheirovskite, lillianite and weibullite mineral types, respectively [8]. In so doing, the composition was ascribed to these compounds by analogy to PbS-Bi_2S_3 system compounds [9 – 11].

Our purpose in this work was to specify phase equilibriums in $PbSe$-Bi_2Se_3 system and to study the thermoelectric properties of ternary compounds formed in this system, as well as of $PbSe$-based sold solutions alloys.

Experimental procedure

For the investigation of $PbSe$-Bi_2Se_3 system two series of samples were synthesized: alloys obtained by directional crystallization of melts (oriented crystals) [12], and annealed polycrystalline samples. As the initial materials, high-purity Pb, Bi and Se were used with the content of basic substance at least 99.99 %. To specify phase equilibriums in $PbSe$-Bi_2Se_3 system, polycrystalline samples of $PbSe$-Bi_2Se_3 alloys were synthesized in evacuated quartz ampoules from elements taken in proper ratios. Synthesis was made at temperature of 1020 – 1190 K depending on the composition of alloys with their subsequent cooling to 770 K at a rate of 4 degrees/min. From this temperature the alloys were cooled in the air. The resulting samples were annealed for 200 – 400 hours at 770 K, following which they were quenched in water with ice. The choice of alloys fore study was based on $PbSe$-Bi_2Se_3 phase diagram constructed in paper [2], as well as on the new data on the composition of compounds obtained in papers [1, 6, 7].

To specify the solubility limit of Bi_2Se_3 in $PbSe$, as well as the existence of compounds close to $PbSe$ [8], oriented crystals of layered compounds in $PbSe$-Bi_2Se_3 system were grown by vertical

Bridgman method in quartz ampoules with a cone-shaped bottom. Crystallization rate was 0.25 mm/min, and gradient at the crystallization front was ~ 60 K/cm. Ingots of length about 6 cm and diameter 0.7 – 0.8 cm were obtained. The *X*-ray analysis of $PbSe\text{-}Bi_2Se_3$ alloys was conducted by means of automatic diffractometer DRON-UM (graphite monochromator, CuK_α-radiation). Monocrystalline chips for *X*-ray analysis were cut out of polycrystalline ingots and “oriented” crystals along cleavage planes (100) of crystal lattice. The alloys were also investigated by metallography and microhardness measurement methods. The thermoelctrical and electrophysical properties of polycrystalline samples of *PbSe*-based solid solutions and “directional” crystals were measured at room temperature over a wide temperature range.

The experimental results and their discussion

Results of *X*-ray analysis and microhardness measurement for samples of $PbSe\text{-}Bi_2Se_3$ system

In this paper, the existence of three afore-referenced ternary compounds was proved. In the region of compositions 85.7 – 62.5 mol.% *PbSe* at 770 K one can observe two phases: *PbSe*-based solid solution and a ternary compound *k*I. In the region of compositions 62.5 – 45.45 mol.% *PbSe* there is a two-phase region (*k*I + *k*II), and in the range of compositions 45.45 – 35.71 mol.% *PbSe* – a two-phase region (*k*II + *k*III). In the alloy containing 20 mol.% *PbSe*, apart from compound *k*III, there was observed the presence of *X*-ray reflections of Bi_2Se_3 compound, Fig. 1.

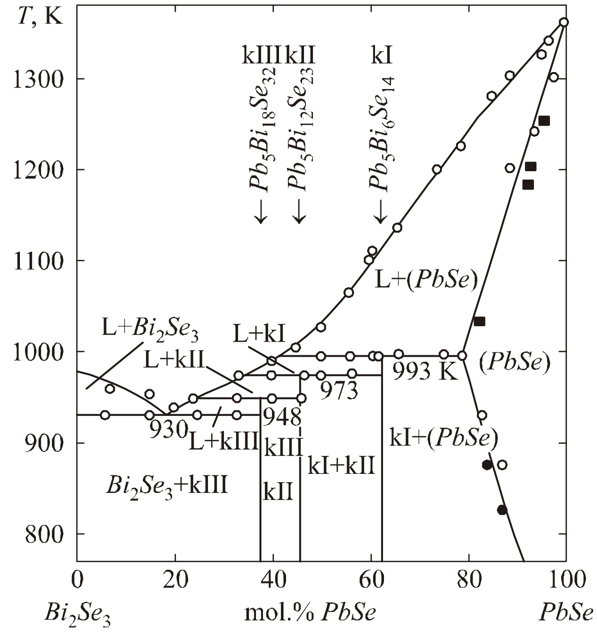


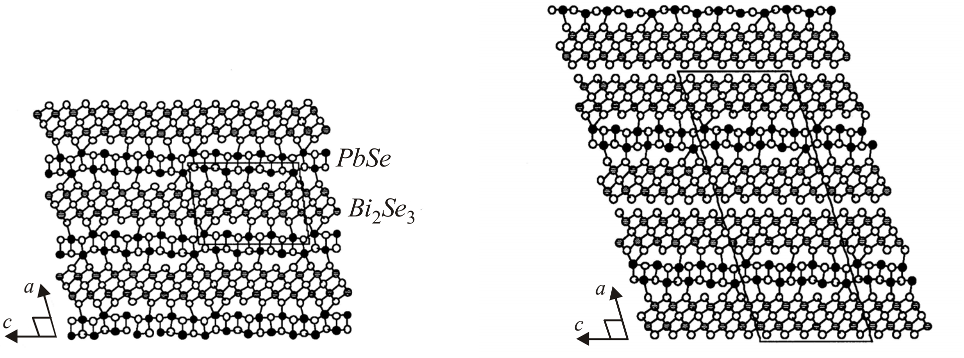
Fig. 1. Diagram of state of the quasi-binary system $PbSe\text{-}Bi_2Se_3$:
1 – DTA data [2]; 2 – two-phase alloys according to microstructural analysis data [2]
3 – results of crystallochemical calculation of Bi_2Se_3 solubility in PbSe [12]. Designations kI, kII and kIII correspond to $Pb_5Bi_6Se_{14}$, $Pb_5Bi_{12}Se_{23}$ and $Pb_5Bi_{18}Se_{32}$ compounds, respectively.

Compounds of this series have a low-symmetry monoclinic structure of the kanizzarite mineral type, Fig. 2. The *X*-ray powder analysis was used to determine parameters of monoclinic lattices of $Pb_5Bi_6Se_{14}$ and $Pb_5Bi_{12}Se_{23}$ compounds:

$Pb_5Bi_6Se_{14}$ $a = 1.5999(2)$ nm; $b = 0.4200(3)$ nm; $c = 2.1570(3)$ nm; $\beta = 97.54^\circ$;

$Pb_5Bi_{12}Se_{23}$ $a = 2.6415(9)$ nm; $b = 0.4199(5)$ nm; $c = 2.1542(5)$ nm; $\beta = 106.35(4)^\circ$.

The lattice parameters of $Pb_5Bi_{18}Se_{32}$ compound were not determined due to imposition of X-ray reflections of this phase on the respective reflections of $Pb_5Bi_{12}Se_{23}$ compound.



a) b)

Fig. 2. Structure of compounds (a) $Pb_5Bi_6Se_{14}$, (b) $Pb_5Bi_{12}Se_{23}$; white circles – Se atoms, black and gray – metal atoms [1].

The microstructural analysis of ternary compounds $Pb_5Bi_6Se_{14}$, $Pb_5Bi_{12}Se_{23}$ and $Pb_5Bi_{18}Se_{32}$ after annealing for 400 hours at 770 K has shown that compounds have irregular lamillar structure typical of heavily laminated compounds. For these compounds, microhardness measurement was carried out. The compounds have the following microhardness values: 700, 558 and 556 MPa for $Pb_5Bi_6Se_{14}$, $Pb_5Bi_{12}Se_{23}$ and $Pb_5Bi_{18}Se_{32}$, respectively. Microhardness is reduced, as the content of Bi_2Se_3 is increased. Low microhardness values of binary compounds Bi_2Te_3, Bi_2Se_3 are generally related to the presence of weak van der Waals bonds between the layer packages in the structures of these compounds. Reduction of microhardness in ternary compounds with increasing content of Bi_2Se_3 can be due to the increasing contribution of van der Waals bonds in going from $Pb_5Bi_6Se_{14}$ to $Pb_5Bi_{18}Se_{32}$ compound.

It should be noted that X-ray diffraction patterns lack X-ray reflections corresponding to U, V and W phases [8] with the orthorhombic structure of cheirovskite, linnianite and weibullite mineral type, respectively. Thus, in contrast to PbS-Bi_2S_3 system [8], these phases have not been found in the alloys of $PbSe$-Bi_2Se_3 system.

Thermoelectric properties of ternary compounds

Table 1 represents charge carrier concentration, the Seebeck coefficient, the electric conductivity, the Hall mobility of charge carriers and the lattice thermal conductivity of ternary compounds at 300 K. The compounds have n-type conductivity and rather high electron concentration which is increased with growing Bi_2Se_3 content. Such a high electron concentration and relatively low against the binary components Hall mobility of electrons are apparently related to high concentration of crystal lattice point defects due to a deviation from stoichiometry. Paper [6] represents the results of determination of crystal lattice of $Pb_5Bi_6Se_{14}$ compound by powder diffraction method using synchrotron radiation. Determination of the occupancy of sites in $Pb_5Bi_6Se_{14}$ structure, according to [6], shows the presence of vacancies in cation sublattice, as well as demonstrates formation of substitutional defects of $Bi^{\cdot}_{Pb}$ and Pb'_{Bi} types. With regard to n-type conductivity of ternary compounds, it can be concluded that $Bi^{\cdot}_{Pb}$ substitutional defects are most probably donor defects responsible for n-type conductivity.

As can be seen from Table 1, ternary compounds are characterized by low lattice thermal conductivity values, considerably lower compared to κ_{ph}, of binary components ($\kappa_{ph} = 15.5 \cdot 10^{-3}$ W/cm·K for Bi_2Se_3 and $\kappa_{ph} = 13.6 \cdot 10^{-3}$ W/cm·K for *PbSe*). Low κ_{ph} values can be related to effective phonon scattering on the potential barriers between layer fragments $[(PbSe)_5]$ and $[(Bi_2Se_3)_3]$. It should be noted that coupling of these layer fragments is accompanied by a strong deformation leading to lattice distortions close to fragments and reducing κ_{ph}.

Table 1

Thermoelectric properties of $[(PbSe)_5]_m[(Bi_2Se_3)_3]_n$ homologous series compounds at 300 K

Compound	$n \cdot 10^{-20}$, cm^{-3}	$-\alpha$, μV/K	σ, S/cm	μ_x, cm^2/(V·s)	$\kappa_{ph} \cdot 10^3$, W/cm·K
$Pb_5Bi_6Se_{14}$	0.86	28	454	33	7.2
$Pb_5Bi_{12}Se_{23}$	1.15	27	375	20	5.9
$Pb_5Bi_{18}Se_{32}$	1.19	52	256	14	4.9

Structure and properties of "oriented" crystals

Results of *X*-ray study of "oriented" crystals obtained by the Bridgman method

Table 2 represents the batch compositions from which crystals were grown by the Bridgman method, periods of *PbSe* cubic lattice in the first solidified ingot portion and the results of crystallochemical calculation of Bi_2Se_3 solubility in *PbSe*. As a batch for growing oriented crystals, four compositions were used corresponding to possible *U*, *V*, *W* compounds from papers [8, 9]. The *X*-ray phase analysis of powders was made by sampling from the cone-shaped portion of ingots (the first solidified portion), from the middle and end portion. In all four cases the first crystallized phase is *PbSe*-based solid solution with a cubic lattice of *NaCl* type. Parameter *a* of cubic lattice was determined as a function of batch composition. The solubility of Bi_2Se_3 in *PbSe* was determined from this data by crystallographic calculation based on summation of corresponding volumes of *PbSe* and Bi_2Se_3 unit cells with the equal number of selenium ions.

The results of calculation of Bi_2Se_3 solubility in *PbSe* are in good agreement with the results [2] of solidus determination close to *PbSe* by DTA method and prove the availability of a wide range of *PbSe*-based solid solutions (at least 20 mol. % Bi_2Se_3). The *X*-ray analysis along the length of ingots has shown that with a further crystallization one can observe formation of ternary compounds $Pb_5Bi_6Se_{14}$ and $Pb_5Bi_{12}Se_{23}$. Phases with the structures of cheirovskite, lillianite and weibullite mineral types, found in PbS-Bi_2S_3 system [8 – 11] were not discovered in $PbSe$-Bi_2Se_3 system.

Table 2

The results of determination of PbSe lattice period in the first solidified ingot portion and the results of crystallochemical calculation of Bi_2Se_3 solubility in PbSe

№	Batch composition	*a*, nm of the first solidified ingot portion	Limit of Bi_2Se_3 solubility in *PbSe*, mol.%	*T*, K Liquidus [2]
34	$Pb_9Bi_4Se_{15}$ (*U*) [8]	0.61046	4.0	1250
30	$Pb_3Bi_2Se_6$ [9]	0.6077	6.8	1200
35	$Pb_8Bi_6Se_{17}$ (*V*) [8]	0.6072	7.25	1180
10	$PbBi_2Se_4$ (*W*) [8]	0.5990	17.9	1030

By the example of ingot grown from $Pb_3Bi_2Se_6$ batch, one can follow a change in the diffraction pattern according to directional crystallization of the melt. Fig. 3 represents four *X*-ray diffraction patterns of powders obtained at the distance of 1.5, 2.5, 3.5 and 5.0 cm from the beginning of ingot and corresponding to Figures *a*, *b*, *c*, *d* (Table 3). The *X*-ray pattern in Fig. 3 (*a*) corresponds to cubic structure of *NaCl* type typical of *PbSe*-based solid solution. The *X*-ray pattern in Fig 3 (*b*) demonstrates the presence, apart from *PbSe*, of additional reflections. Indexing of *X*-ray diffraction patterns in Fig. 3 (*c*, *d*) shows the presence of *X*-ray reflections of $Pb_5Bi_6Se_{14}$ and $Pb_5Bi_{12}Se_{23}$ compounds with monoclinic lattices. Presented in Table 3 are parameters of monoclinic lattices that are in good agreement with the results of *X*-ray phase analysis of monocrystalline cleavages. The presence of *X*-ray reflections of $Pb_5Bi_6Se_{14}$, $Pb_5Bi_{12}Se_{23}$ compounds in the middle and final ingot portions indicates the following peritectic reactions proceeding in the course of directional crystallization: $L + (PbSe) \leftrightarrow Pb_5Bi_6Se_{14}$ and $L + Pb_5Bi_6Se_{14} \leftrightarrow Pb_5Bi_{12}Se_{23}$ in conformity with the specified diagram of state represented in Fig. 1.

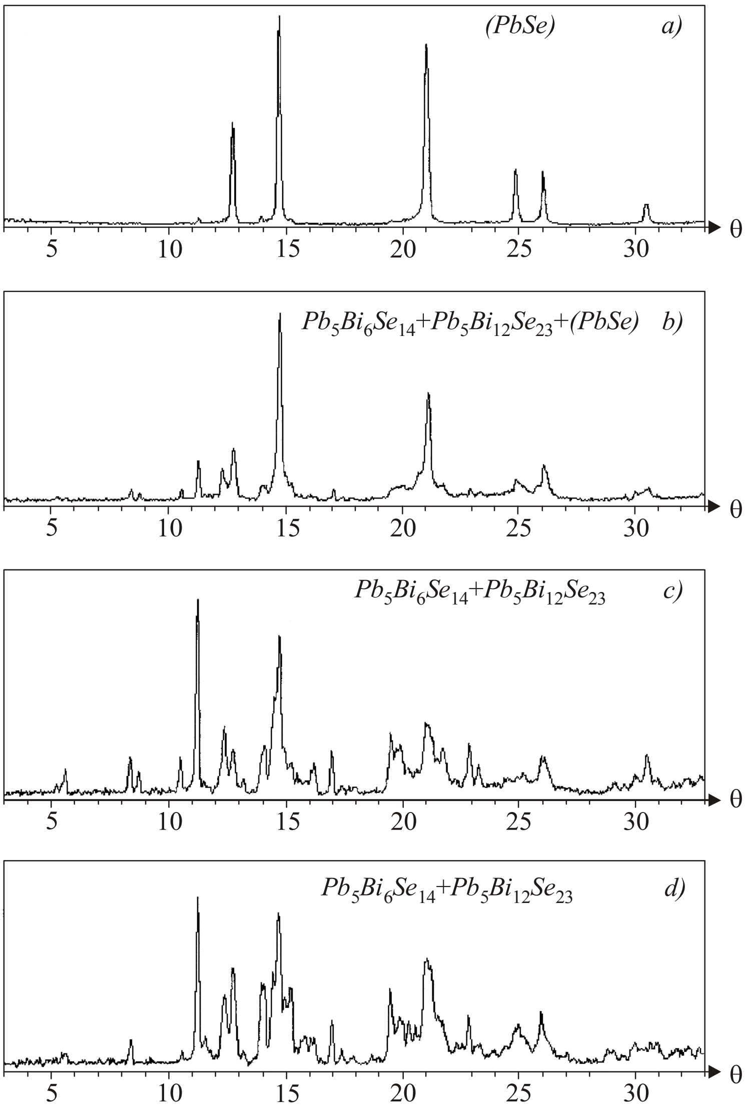


Fig. 3. X-ray diffraction patterns of powders obtained at the distance of 1.5, 2.5, 3.5 and 5.0 cm from the beginning of ingot grown by the Bridgman method from the batch of $Pb_3Bi_2Se_6$*, composition and corresponding to Figures a, b, c, d .*

Table 3

Results of using X-ray phase analysis for the determination of phase composition along the ingot grown by the Bridgman method from the batch of composition $Pb_3Bi_2Se_6$

№	Distance from the beginning of ingot (cm)	Phase composition	*a*, nm	*b*, nm	*c*, nm	β, degrees
30n2	1.5	*PbSe*-based solid solution	0.6077			
30k4	2.5	$Pb_5Bi_6Se_{14}$ + $Pb_5Bi_{12}Se_{23}$ + (*PbSe*)	1.5996(4) 2.637(2) 0.6070(3)	0.4200(7) 0.4202(11)	2.1576(7) 2.1522(11)	97.36(2) 106.40(5)
30k3	3.5	$Pb_5Bi_6Se_{14}$ + $Pb_5Bi_{12}Se_{23}$	1.600(8) 2.6371(10)	0.4200(8) 0.4199(5)	2.1557(8) 2.1525(5)	97.45(5) 106.39(5)
30k6	5.0	$Pb_5Bi_6Se_{14}$ + $Pb_5Bi_{12}Se_{23}$	1.5998(4) 2.6426(4)	0.4201(4) 0.4198(2)	2.1564(6) 2.1542(2)	97.61(3) 106.37(2)

Properties of *PbSe*-based solid solution alloys in *PbSe-Bi₂Se₃* system fabricated by the Bridgman method

Temperature dependences of the thermoelectric properties of *PbSe*-based solid solution alloys

Fig. 4 – 7 represent the temperature dependences of the Seebeck coefficient, the electric conductivity, total thermal conductivity and the lattice component of thermal conductivity for single-phase alloys of *PbSe*-based solid solution cut of the first solidified portion of ingots whose composition was determined by crystallochemical calculation (Table 2). The explored alloys fall in the category of heavily doped semiconductors [13] and are characterized by a high degree of disorder. As is evident from Figures 4, 5, the Seebeck coefficient grows, and the electric conductivity drops with temperature for the alloys of all four of compositions with different content of Bi_2Se_3.

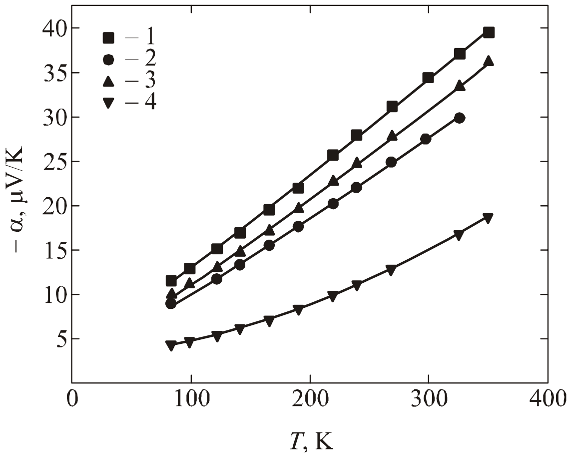


Fig. 4. Temperature dependences of the Seebeck coefficient for PbSe-based solid solution alloys 1 – 4.0 mol.% Bi_2Se_3; 2 – 6.8 mol.% Bi_2Se_3; 3 – 7.25 mol.% Bi_2Se_3; 4 – 17.9 mol.% Bi_2Se_3

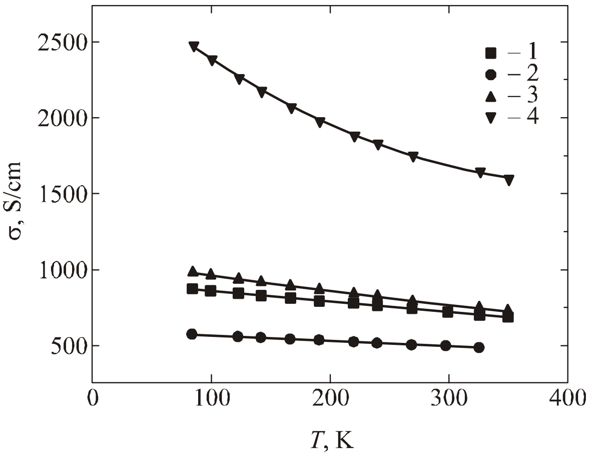


Fig. 5. Temperature dependences of the electric conductivity for PbSe-based solid solution alloys, composition designations correspond to Fig. 4.

The temperature dependences of total thermal conductivity shown in Fig. 6 demonstrate little thermal conductivity increase with a rise in temperature typical of amorphous bodies. The lattice thermal conductivity has only a weak dependence on temperature (Fig. 7), as is commonly observed for heavily doped semiconductors. It should be noted that the alloy with the content of 17.9 mol.% Bi_2Se_3 differs markedly in its properties from the alloys lying in the range of compositions 4 – 7 mol.% Bi_2Se_3. This alloy is characterized by low Seebeck coefficient values and, hence, high electron concentration, as well as high electric and thermal conductivity over the entire investigated temperature range.

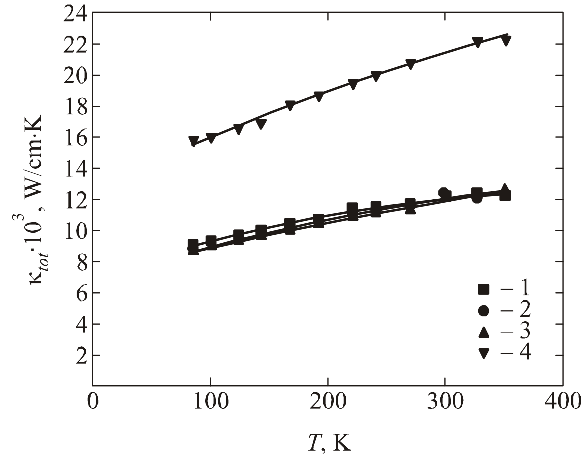


Fig. 6. Temperature dependences of total thermal conductivity for PbSe-based solid solution alloys, composition designations correspond to Fig. 4.

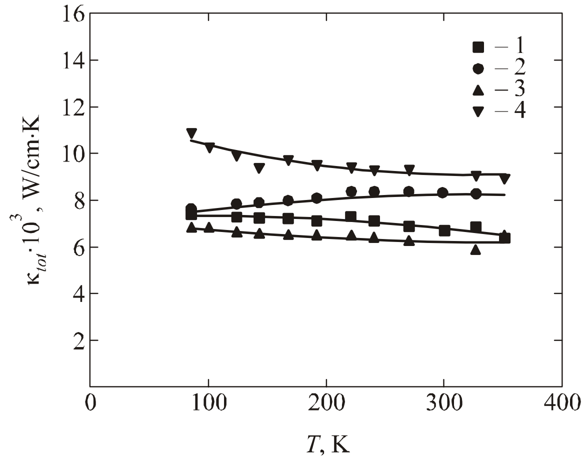


Fig. 7. Temperature dependences of the lattice thermal conductivity for PbSe-based solid solution alloys, composition designations correspond to Fig. 4.

Concentration dependences of the thermoelectric properties and microhardness of *PbSe*-based solid solution alloys

The results of measuring the thermoelectric properties and microhardness at 300 K are represented in Table 4. Fig. 8 – 10 show the concentration dependences of the thermoelectric properties of *PbSe*-based solid solution alloys at temperature 300 K. For the construction of these dependences we used the data from handbook [14] for pure *PbSe* at 300 K, as well as the data represented in Fig. 4 – 7 of the present work. As can be seen from Fig. 8 – 10, on the concentration dependences in the region of 5 – 7 mol.% Bi_2Se_3 there are anomalies in the variation of thermoelectric properties. Close to this composition there is a kink on the composition dependence of the Seebeck coefficient (Fig. 8), as well as a minimum on the curves of electric conductivity (Fig. 9) versus Bi_2Se_3 composition. On the concentration dependences of thermal conductivity (Fig. 10), the curves of $\kappa_{tot} = f$(composition) and $\kappa_{ph} = f$(composition), respectively, there are also strongly pronounced anomalies.

A nonmonotonic change of microhardness with increasing content of Bi_2Se_3 was observed in *PbSe*-based solid solution alloys (Table 4). High microhardness values were observed in the composition range of 4.0 – 6.8 mol.% Bi_2Se_3. With a content equal to or higher than 7 mol.% Bi_2Se_3, the microhardness decreases markedly. The resulting data shows that the character of crystal lattice disorder of *PbSe*-based solid solution depends on the content of Bi_2Se_3.

There seem to be two mechanisms of Bi_2Se_3 entry into *PbSe* lattice. With a low content of Bi_2Se_3 (to 5.0 – 7.0 mol.%), cation vacancies are formed according to the afore-referenced substitution scheme: $3Pb^{2+} \leftrightarrow 2Bi^{3+}$+ vacancy. These alloys are characterized by a low lattice thermal conductivity, which is related to fluctuations of atomic masses and voltages at substitution of bismuth atoms for lead atoms, as well as to formation of cation vacancies due to different valences of *Pb* and *Bi* atoms. Formation of these vacancies contributes to creation of local elastic deformation fields leading to microhardness growth.

Table 4

Thermoelectric properties and microhardness at 300 K of PbSe-based solid solution alloys with cubic lattice of NaCl type

Mol.% Bi_2Se_3	-α, μV/K	σ, S/cm	$\kappa_{tot}10^3$, W/cm·K	κ_{ph} 10^3, W/cm·K	*H*, MPa
0 [13]	160	370	16.3	13.8	585(25)
4.0	34	720	12.0	6.8	1680(30)
6.8	28	500	12.0	8.4	1730(20)
7.25	31	765	10.9	5.3	960(30)
17.9	15	1587	21.7	10.2	960(12)

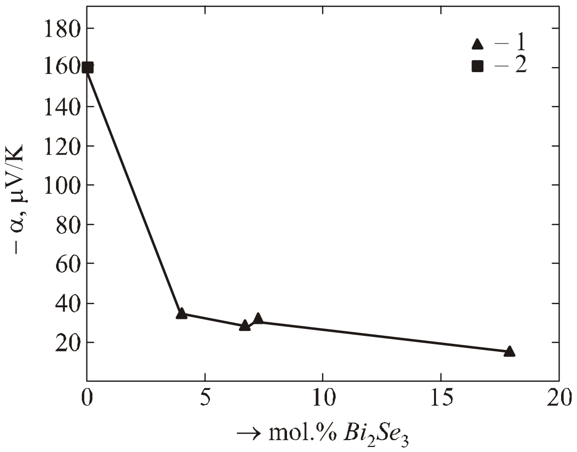


Fig. 8. Concentration dependences of the Seebeck coefficient for PbSe-based solid-solution range at 300 K. 1 – data reported here; 2 – data reported in work [14] for pure PbSe.

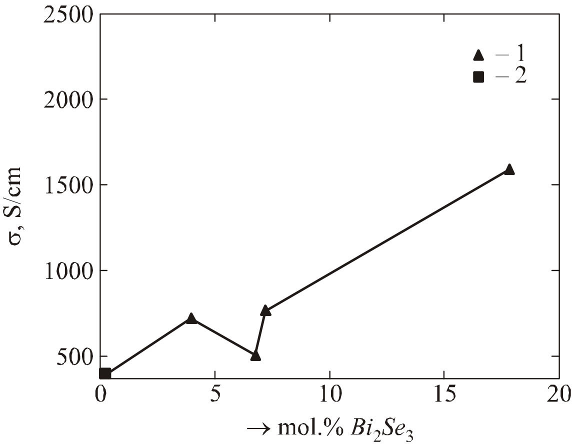


Fig. 9. Concentration dependences of the electric conductivity for PbSe-based solid-solution range at 300 K. The designations are the same as in Fig. 7.

The second mechanism of Bi_2Se_3 entry into *PbSe* lattice is realized with a high content of Bi_2Se_3 and is accompanied by the electric and thermal conductivity growth, as well as by the reduced microhardness of alloys. Such a change in the thermoelectric properties can be due to formation of complexes and filling of the earlier formed cation vacancies. Analyzing the nature of possible complexes in a heavily doped *PbSe*-based solid solution, one should mention a close relation that exists between the formation of complexes and the specific features of structure and properties of semiconductor crystals [14]. In paper [14], the nature of complexes in crystals doped with *Ge* and *Si* was studied with the application of mass-spectral analysis. It was shown that complexes in vapour-gas phase to a large extent reflect the real structure of complexes in crystal under study. Mass spectrometric study showed that emerging of complexes depends on the concentration of doping impurity in a crystal. In the light of [14] it was interesting to consider the mass spectrometric data for Bi_2Se_3 with a view to reveal possible molecular forms in which this compound can be found in *PbSe*-

based solid solution [15]. Below are given the forms of gaseous molecules obtained in [15] by means of mass spectrometric analysis at temperatures 633 – 778 K. In the gas-vapour phase above the solid Bi_2Se_3 the molecule forms were found as follows: *Bi*; Bi_2; *BiSe* and Se_2. Supposing such molecular-type complexes exist in the solid phase, then the microhardness and Seebeck coefficient decrease, the electric and thermal conductivity growth with a high content of Bi_2Se_3 can be related to filling of cation vacancies with *Bi* atoms with formation of Bi'''_V type defects. Formation of *BiSe* complexes leads to a shift from a quasi-binary $PbSe$-Bi_2Se_3 cut towards the *PbSe-BiSe* cut. In so doing, the substitutional defects of donor type $Bi^{\bullet}_{Pb}$ are formed. Complexes of Se_2 type are little probable, since the introduction of *Se* must have changed the conductivity type from *n*- to *p*-, however, conductivity type did not change over the entire investigated concentration range. Thus, concentration dependences of the thermoelectric properties depend on different character of crystal lattice disorder of *PbSe*-based solid solution with a low concentration of Bi_2Se_3 and a considerable concentration thereof which, however, lies within the solid-solution range.

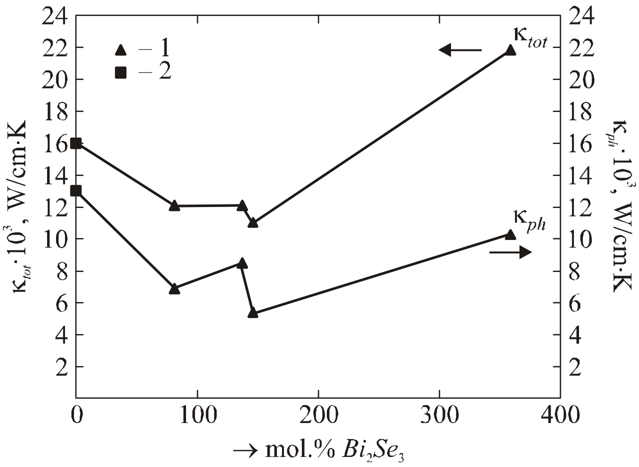


Fig. 10. Concentration dependences of total and lattice thermal conductivity for PbSe-based solid-solution range at 300 K. The designations are the same as in Fig. 7.

Conclusions

The *X*-ray phase analysis, the thermoelectric properties and microhardness measurement techniques have been used to study ternary compounds with monoclinic lattices belonging to $[(PbSe)_5]_m[(Bi_2Se_3)_3]_n$ homologous series, as well as *PbSe*-based solid solution alloys with cubic lattice of *NaCl* type.

It has been shown that of paramount importance in reducing lattice thermal conductivity in $[(PbSe)_5]_m[(Bi_2Se_3)_3]_n$ compounds is the effective phonon scattering on potential barriers between $[(PbSe)_5]$ and $[(Bi_2Se_3)_3]$ layer fragments, as well as on point defects of donor type. Crystal lattice stresses generated on mating of $[(PbSe)_5]$ and $[(Bi_2Se_3)_3]$ layer fragments in the structure of $[(PbSe)_5]_m[(Bi_2Se_3)_3]_n$ compounds result in lattice distortions close to the boundaries of these fragments and also contribute to κ_{ph} reduction.

It has been shown that the thermoelectric properties of *PbSe*-based solid solution alloys with a cubic lattice depend heavily on the content of Bi_2Se_3. Anomalies close to 7 mol% Bi_2Se_3 have been found on the concentration dependences of thermoelectric properties. Apparently, there are two mechanisms of Bi_2Se_3 entry into solid solution lattice and its influence on such structure-sensitive properties as microhardness and lattice thermal conductivity. The former mechanism works with a low content of Bi_2Se_3 and leads to formation of cation vacancies, and the latter mechanism is apparent on approximation to the boundary of $PbSe$-based solid solution region and is related to formation of complexes.

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