CRYSTALLINE STRUCTURE AND THERMOELECTRIC PROPERTIES OF LAYERED TETRADIMITE-LIKE CHALCOGENIDES

V.S. Zemskov[1], L.E. Shelimova[1], P.P. Konstantinov[2], M.K. Zhitinskaya[3],
E.S. Avilov[1], M.A. Kretova[1], I.Yu. Nikhezina[1]

([1]Institution of RAS Baikov Institute of Metallurgy and Materials Research, RAS,
49, Leninsky Ave., Moscow, 119991, Russia;
[2]Institution of RAS, Ioffe Physics and Technical Institute, RAS, Saint-Petersburg,
26, Polytechnic Str., 194021, Russia;
[3]Saint-Petersburg State Polytechnic University
Saint-Petersburg, 29, Polytechnic Str., 195251, Russia)

- *Single crystals of $PbSb_2Te_4$ (p-type) and $PbBi_4Te_7$ (n-type) compounds doped with electrically active impurities (Cd, Ag, Cu) were grown by Czochralski method. The Seebeck coefficient, the electrical and thermal conductivities of these single crystals were measured in the temperature range of $80 – 350$ K in two crystallographic directions: parallel (across the layers) and perpendicular (along cleavage planes) to trigonal axis c. The Hall effect was measured in the same crystallographic directions in the temperature range of $77 – 450$ K. Essential anisotropy of the measured kinetic coefficients was revealed. Compounds are characterized by low lattice thermal conductivity which is essentially lower as compared to that for alloys based on Bi_2Te_3. Analysis of mechanism of introduction of electrically active impurities into crystal lattice of ternary compounds was made. The experimental data for p-type $PbSb_2Te_4$ was analyzed within the single-band and double-band valence band models.*

Introduction

A search for novel thermoelectric materials (TEM) for thermogenerators (TEG) is a relevant task of science and technology. Thermoelectric generators are used for conversion into electricity of heat generated by many sources, such as solar heat, vehicular exhaust gas heat, heat from garbage incineration, etc. Reduction of lattice thermal conductivity κ_{ph} is one of efficient ways of improving thermoelectric figure of merit of TEM for thermogenerators [1]. At the present time, a search is actively pursued for novel thermoelectric materials based on ternary or quarternary layered chalcogenides with complex crystal lattices and a low thermal conductivity [2]. Compounds with complex structures comprising heavy elements possess low values of lattice thermal conductivity due to efficient phonon scattering. Ternary layered tetradimite-like compounds in quasi-binary systems $A^{IV}B^{VI} – A^V_2B^{VI}_3$ ($A^{IV} –$ *Ge*, *Sn*, *Pb*: $A^V – Bi$, *Sb*; $B^{VI} – Se$, *Te*) are interesting in this context, since in these systems homologous series of layered compounds of $nA^{IV}B^{VI}·mA^V_2B^{VI}_3$ type are formed, and there is a great variety of mixed-layer compounds, structurally and compositionally more complex as compared to conventional solid solutions based on Bi_2Te_3 [3-5]. The unit cells of ternary compounds are formed by multi-layer packages of different type, orderly alternating along the trigonal axis *c*. Layered structure of ternary compounds is closest cubic packing of *Te* atoms, with *Ge*(*Sn*, *Pb*) and *Bi*(*Sb*) atoms located in the octahedral voids thereof. In so doing, cations occupy only part of octahedral voids.

The $PbSb_2Te_4$ (p-type) and $PbBi_4Te_7$ (n-type) compounds belong to homologous series $nPbTe·mSb_2Te_3$ and $nPbTe·mBi_2Te_3$ with the values ($n = 1$, $m = 1$) and ($n = 1$, $m = 2$), respectively, and are of interest for production of new TEM [6, 7]. The $PbSb_2Te_4$ compound is formed according to peritectic reaction and has a 21-layer lattice with the following parameters in hexagonal packing:

$a = 0.4350(1)$ nm, $c = 4.1712(2)$ nm (space group $R3m$) [5]. The unit cell of this compound comprises three seven-layer packages *TeSbTePbTeSbTe*, orderly alternating along the trigonal axis *c*. Compound $PbBi_4Te_7$ melts congruently at 858 K [8] and has a 12-layer lattice with the following parameters: $a = 0.4409$ nm, $c = 2.4000$ nm (space group *P3m1)* [4]. The unit cell of $PbBi_4Te_7$ comprises layered packages of two types: one seven-layer *TeBiTePbTeBiTe* and one five-layer *TeBiTeBiTe* [6]. In $PbSb_2Te_4$ and $PbBi_4Te_7$ structures the bonds inside multi-layer packages are ion-covalent, and the bond between packages is mainly due to weak Van der Waals forces. Efficient phonon scattering on potential barriers at the interface between layer packages can be an important factor of lattice thermal conductivity reduction in layered compounds [6].

The objective of this work included growth and *X*-ray study of crystals of ternary compounds, study of the anisotropy of thermoelectric properties and study of the effect of doping with electrically active impurities (*Cd, Ag, Cu*) on the anisotropy of thermoelectric parameters and microhardness of *n*-type single crystals based on compound $PbBi_4Te_7$, as well as *p*-type single crystals based on compound $PbSb_2Te_4$.

Experimental procedure

Single crystals of the above compounds were grown by Czochralski method with liquid phase replenishment from floating crucible. The charge for growth was synthesized in evacuated quartz ampoules from elements taken in appropriate proportions at 1070 K for 5 hours. Crystals of ternary compounds were grown onto single-crystal seeds of compositions $(Bi_2Te_3)_{0.90}(Sb_2Te_3)_{0.05}(Sb_2Se_3)_{0.05}$ and $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ for *n*- and *p*-type material, respectively. Czochralski grown crystals were from 20 to 30 mm in diameter, about 100 mm long and were oriented along cleavage planes in [1010] direction. Ternary compounds were identified by *X*-ray analysis of single-crystal cleavages through the use of automatic diffractometer DRON-UM (*CuK_α*-radiation) [9].

Thermoelectric properties were measured in two crystallographic directions: parallel (indexes 33) and perpendicular to trigonal axis *c* (indexes 11). The following independent components of tensors of kinetic coefficients were measured: thermoEMF α_{11}, α_{33}; electrical conductivity σ_{11}, σ_{33}; thermal conductivity κ_{11}, κ_{33} and the Hall coefficient R_{123}, R_{321}. Indexes at coefficients correspond in the order of their arrangement: the first – to direction of measured electrical field, the second – to direction of the electrical current or temperature gradient, the third – to direction of the magnetic field.

Microhardness was measured by means of "Reichert" microscope with "Polivar-met" adapter.

Experimental results and their discussion

Doping of $PbBi_4Te_7$ with cadmium. Polycrystalline samples of solid solution with heterovalence substitution $PbBi_{1-x}Cd_xTe_7$ ($0 < x < 0.06$) were studied in [6]. It was established that the alloy of composition $PbBi_{3.94}Cd_{0.06}Te_7$ has optimal thermoelectric properties. As a result, this composition was used in the present paper in the manufacture of *n*-type single crystals.

X-ray analysis of single-crystal chips made it possible to determine parameter *c* of crystal lattice $PbBi_4Te_7$ and $PbBi_{3.94}Cd_{0.06}Te_7$. Comparison of parameters *c* of crystals $PbBi_4Te_7$ ($c = 2.3934(2)$ nm) and $PbBi_{3.94}Cd_{0.06}Te_7$ ($c = 2.3928(2)$ nm) at equal distance from the seed shows that introduction of *Cd* leads to reduction of parameter *c*. It is related to smaller size of *Cd* atoms (octahedral covalent radius *Cd*: $R_{Cd} = 0.138$ nm [10]) as compared to dimensions of *Bi* atoms ($R_{Bi} = 0.165$ nm [10]) which are substituted by cadmium in cation sublattice.

Results of measuring the Seebeck coefficient and the electrical conductivity of $PbBi_4Te_7$ and the alloy of solid solution $PbBi_{3.94}Cd_{0.06}Te_7$ at 300 K along the trigonal axisв *c* and perpendicular to it are represented in Table 1. The anisotropy of thermoEMF, the electrical and thermal conductivity of

$PbBi_4Te_7$ is close to the anisotropy of properties in a binary compound Bi_2Te_3. The values of $\Delta\alpha$ for $PbBi_4Te_7$ and solid solution $PbBi_{3.94}Cd_{0.06}Te_7$ are approximately equal and close in value to thermoEMF anisotropy for Bi_2Te_3: $\Delta\alpha = 16$ µV/K [11].

Table 1

Results of measuring the Seebeck coefficient and the electrical conductivity at 300 K along the trigonal axis c (α_{33}, σ_{33}) and perpendicular to it (α_{11}, σ_{11}) for $PbBi_4Te_7$, $PbBi_{3.94}Cd_{0.06}Te_7$ solid solution and n-type $PbBi_4Te_7$ doped with silver

Compound	α_{11}, µV/K	α_{33}, µV/K	$\Delta\alpha$, µV/K	σ_{11}, S/cm	σ_{33}, S/cm	σ_{11}/σ_{33}
$PbBi_4Te_7$	− 18	− 40	22	3358	784	4.3
$PbBi_{3.94}Cd_{0.06}Te_7$	− 20	− 40	20	3694	654	5.6
$PbBi_4Te_7<Ag>$	− 28	− 36	8.0	3655	1584	2.3
Compound	$\kappa_{11(ph)}\cdot10^3$, W/cm·K	$\kappa_{33\,(ph)}\cdot10^3$, W/cm·K	$\kappa_{11(ph)}/\kappa_{33\,(ph)}$			
$PbBi_4Te_7$	17.1	5.2	3.3			
$PbBi_{3.94}Cd_{0.06}Te_7$	9.3	6.5	1.4			

The lattice thermal conductivity was calculated by subtraction from the total thermal conductivity of the electron component estimated by the law of Wiedemann-Franz: $\kappa_{el} = L\sigma T$, where L is Lorentz number. Standard Lorentz number was used that was calculated for single-band model for the case of strong degeneracy: $L = \pi^2/3(k_0/e)^2$. The data demonstrating a change in lattice thermal conductivity at 300 K at substitution Cd atoms for Bi is given below [9].

From the referred data it can be seen that introduction of Cd leads to essential reduction of $\kappa_{11(ph)}$ with a slight change of $\kappa_{33(ph)}$. Formation of substitutional defects of Cd'_{Bi} type in a layer contributes to efficient scattering of phonons on mass and voltage fluctuations, which results in decrease of $\kappa_{11(ph)}$. Weak change of $\kappa_{33(ph)}$ can be related to slight change in the character of interatomic interaction between layered packages on introduction of Cd.

Investigation of the temperature dependences of the kinetic coefficients of $PbBi_{3.94}Cd_{0.06}Te_7$ (Fig. 1 *a-d*) has shown that anisotropy of α increases with temperature growth (Fig. 1 *a*), whereas the electrical conductivity anisotropy in this case is reduced (Fig. 1 *c*). The value of σ_{11}/σ_3 in $PbBi_{3.94}Cd_{0.06}Te_7$ alloy varies from $\sigma_{11}/\sigma_{33} = 5.9$ at 85 K to $\sigma_{11}/\sigma_3 = 5.6$ at 300 K. The lattice thermal conductivity anisotropy varies from $\kappa_{11(ph)}/\kappa_{33(ph)} = 2.0$ at 85 K to $\kappa_{11(ph)}/\kappa_{33(ph)} = 1.4$ at 300 K. At temperatures above 150 K one can observe the anomalous dependences $\kappa_{11(ph)} = f(T)$ and $\kappa_{33(ph)} = f(T)$ (Fig. 1 *b*). The anomalous behaviour of lattice thermal conductivity becomes apparent in considerable deviation from the law $\kappa_{ph} \sim T^{-1}$.

The two components of the Hall coefficient tensor grow with increasing temperature at somewhat different rate (Fig. 1 *d*). The Hall coefficient anisotropy is reduced with increasing temperature from $R_{321}/R_{123} = 1.4$ at 77 K to $R_{321}/R_{123} = 1.1$ at 440 K for $PbBi_{3.94}Cd_{0.06}Te_7$ alloy. Thus, in the case when a dopant results in formation of substitutional defects in a layer of Cd'_{Bi} type, its introduction contributes to growth of σ_{11} and reduction of $\kappa_{11(ph)}$ without essential change in σ_{33} and $\kappa_{33(ph)}$. This makes cadmium a promising dopant for $PbBi_4Te_7$ leading to improvement of thermoelectric properties in the direction of cleavage planes.

Doping of $PbBi_4Te_7$ with silver. *X*-ray study of single-crystal cleavages of $PbBi_4Te_7<Ag>$

($N_{Ag} \sim 4.8 \cdot 10^{19}$ cm^{-3}) shows that introduction of *Ag* leads to growth of crystal lattice parameter *c*. Parameter *c* for undoped *PbBi$_4$Te$_7$* single crystal is equal to *c* = 2.3934(2) nm, and parameter *c* for doped compound is: *c* = 2.3964(2) nm, which is appreciably higher than the former value. Based on the small size of *Ag* atoms (octahedral covalent radius of silver is R_{Ag} = 0.136 nm [10]) one could expect a reduction in parameter *c* in case of substitution in the layer of larger size *Pb, Bi* atoms by silver atoms, however, it is not observed. The discovered increase of parameter *c* on introduction of *Ag* can be explained by entry of silver atoms into Van der Waals gaps between seven-layer and five-layer packages in the structure of *PbBi$_4$Te$_7$*.
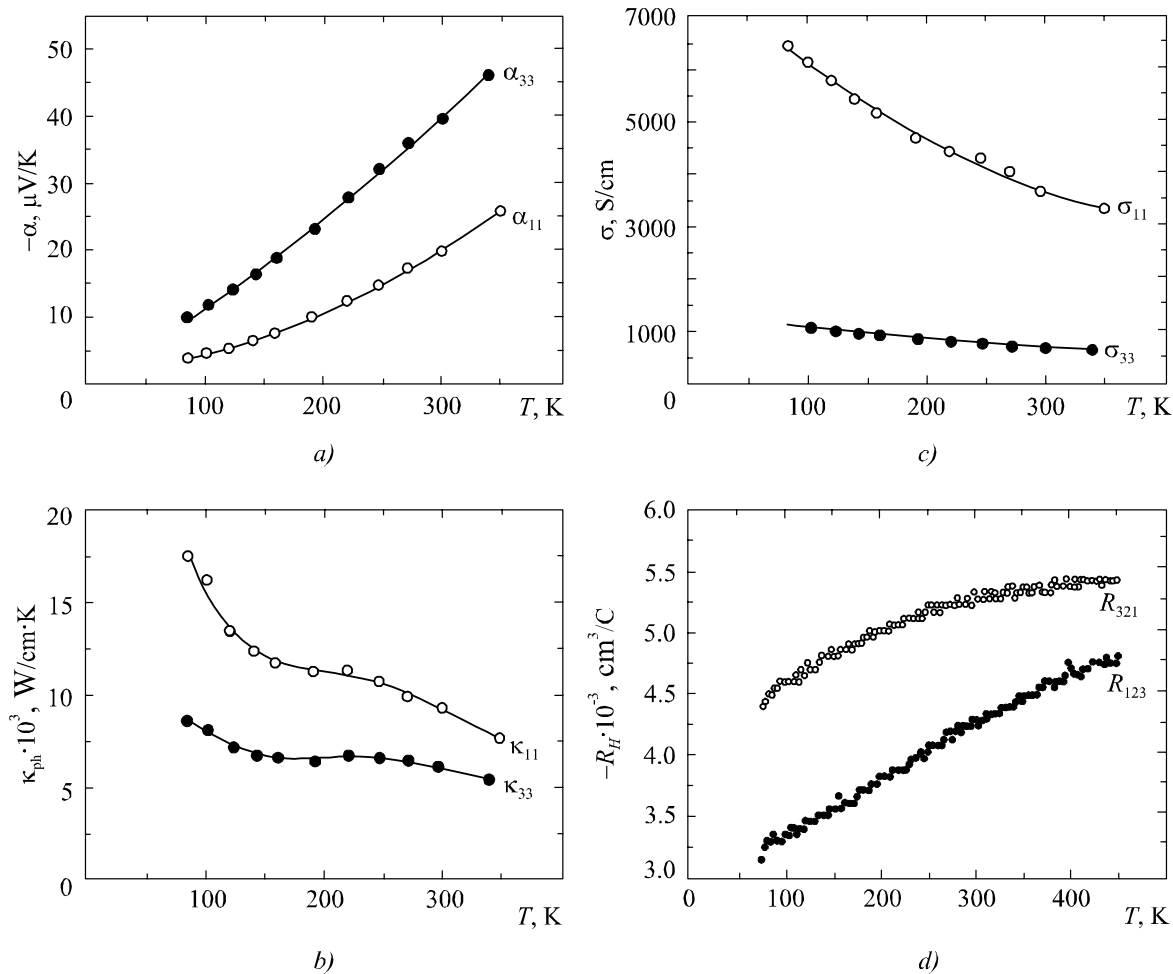

Fig. 1. Temperature dependences for two crystallographic directions
of the Seebeck coefficient (a), lattice thermal conductivity (b),
the electrical conductivity (c) and the Hall coefficient (d) of PbBi$_{3.94}$Cd$_{0.06}$Te$_7$ alloy.

As was demonstrated by the previous study of *GeBi$_4$Te$_7$* compound doped with copper [12], the thermoelectric properties of layered compounds are rather sensitive to the appearance in Van der Waals gaps of 1B subgroup of periodic system. Table 1 and Fig. 2 – 4 represent the results of measuring thermoelectric properties of undoped and silver-doped *PbBi$_4$Te$_7$*. From this data it is obvious that the anisotropy of all kinetic coefficients is reduced on introduction of silver atoms to *PbBi$_4$Te$_7$* lattice. Component of the Seebeck coefficient tensor α_{11} is increased (electron concentration is reduced) on doping, and component α_{33} in this case is slightly reduced. Component of the electrical conductivity tensor σ_{33} is appreciably increased on introduction of silver, and component σ_{11} is practically unchanged on doping.
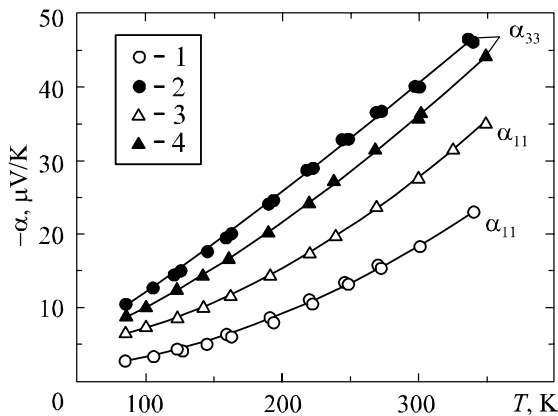
Fig. 2. Temperature dependences of the Seebeck coefficient for n-type PbBi$_4$Te$_7$, undoped (1, 2) and doped with silver (3, 4) 1, 3 − α$_{11}$; 2, 4 − α$_{33}$;.
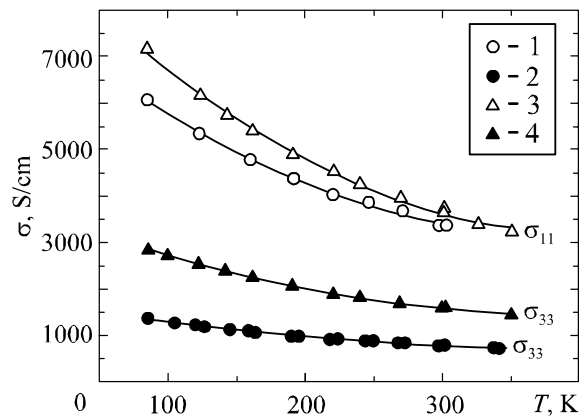
Fig. 3. Temperature dependences of the electrical conductivity for PbBi$_4$Te$_7$, undoped (1, 2) and doped with silver (3, 4) 1, 3 − σ$_{11}$; 2, 4 − σ$_{33}$.

From the reported data it is seen that at 350 K the lattice thermal conductivity has very low values in *PbBi$_4$Te$_7$<Ag>* crystal, especially in the direction of trigonal axis *c*.

The Seebeck coefficient anisotropy in a doped compound increases slightly with temperature growth (Fig. 2), and the electrical conductivity and thermal conductivity anisotropy is reduced (Fig. 3, 4). A change in the electrical and thermal conductivity on doping of *PbBi$_4$Te$_7$* with silver can be explained on the basis of *X*-ray analysis results, according to which silver atoms are embedded into Van der Waals gaps. The increase in tensor component σ$_{33}$ on introduction of *Ag* can be related to increased interaction between layered packages and reduced contribution of potential barriers at the interface of these packages to charge carrier scattering. At the same time, component σ$_{11}$ is little changed on introduction of *Ag*. This shows that substitutional defects of the type *Ag$_{Bi}$* or *Ag$_{Pb}$* cannot be prevalent defects in the cation sublattice. Weak change in σ$_{11}$ and strong change in σ$_{33}$ on doping testify in favour of mechanism of embedding *Ag* atoms into Van der Waals gaps.
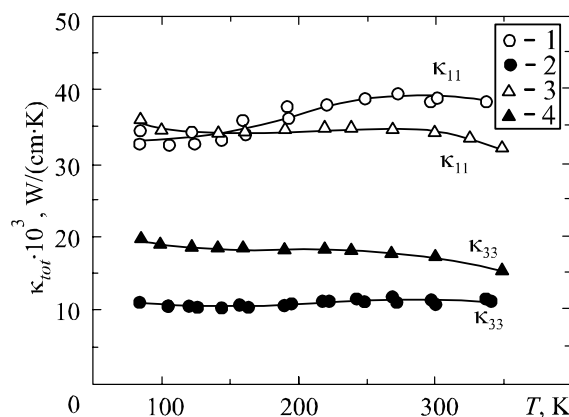

Fig. 4. Temperature dependences of thermal conductivity for n-type PbBi$_4$Te$_7$, undoped (1, 2) and doped with silver (3, 4) 1, 3 − κ$_{11(tot)}$; 2, 4 − κ$_{33(tot)}$.

Microhardness is known to be an important structure-sensitive parameter enabling certain conclusions to be made on the character of interaction between layered packages on doping of layered compounds with electrically active impurities. In Table 2 are represented the results of measuring microhardness along cleavage planes and perpendicular to them for *PbBi$_4$Te$_7$* single crystals undoped and doped with silver as compared to data reported in the literature for *Bi$_2$Te$_3$* [13]. Below is given data illustrating a change in lattice thermal conductivity κ$_{11(ph)}$ and κ$_{33(ph)}$ on doping with silver at 350 K.

Table 2

Microhardness of PbBi₄Te₇ single crystals measured parallel to cleavage planes
(H∥) and perpendicular to cleavage planes (H⊥)

Compound	$H_\parallel$, MPa	$H_\perp$, MPa	$H_\parallel/H_\perp$
Bi₂Te₃ [13]	340	259	1.31
PbBi₄Te₇	840(12)	730(14)	1.15
PbBi₄Te₇<Ag>	820(10)	730(15)	1.12
Compound	$\kappa_{11(ph)} \times 10^3$ W/cm·K	$\kappa_{33(ph)} \times 10^3$ W/cm·K	$\kappa_{11(ph)}/\kappa_{33(ph)}$
PbBi₄Te₇	17.1	5.2	3.3
PbBi₄Te₇<Ag>	4.4	2.9	1.5

From Table 2 it is seen that there exists marked microhardness anisotropy in the investigated single crystals due to the difference in chemical bonds in directions parallel and perpendicular to cleavage planes. The structure of Bi_2Te_3 is formed by 5-layer packages divided by Van der Waals gaps. Weak Van der Waals forces acting between 5-layer packages account for low $H_\perp$ values in Bi_2Te_3 single crystals [13]. Inside the quintets the bond is stronger – prevalently ion-covalent, causing higher values of microhardness ($H_\parallel$). In so doing, the ratio $H_\perp < H_\parallel$ is met. The same ratio is typical of $PbBi_4Te_7$, however, both $H_\perp$ and $H_\parallel$ microhardness values for this compound are considerably lower as compared to Bi_2Te_3. As was shown above, the structure of $PbBi_4Te_7$ is formed by one 5-layer and one 7-layer package divided by Van der Waals gaps. However, the role of Van der Waals interactions is reduced in $PbBi_4Te_7$, since the number of Van der Waals gaps in the structure of $PbBi_4Te_7$ compound is smaller than in the structure of Bi_2Te_3. Introduction of Ag into the lattice of $PbBi_4Te_7$ practically does not change the value of $H_\perp$. It can be due to competition of both factors. On the one hand, judging by the properties, Ag intercalation can intensify chemical interaction between packages, which should result in growth of $H_\perp$. On the other hand, crystal lattice distortions at embedding of Ag atoms to $PbBi_4Te_7$ lattice should lead to reduction of $H_\perp$. As a result of combined effect of these two factors, the value of $H_\perp$ on introduction of Ag is not changed.

On the whole, it should be noted that introduction of silver improves the thermoelectric properties of $PbBi_4Te_7$ in the direction of trigonal axis c, since in this direction the electrical conductivity σ_{33} is increased with a minor change of the Seebeck coefficient. Besides, the lattice thermal conductivity measured along the axis c (κ_{33}) (across the barriers) is appreciably reduced on doping with silver.

Thermoelectric properties of *p*-type alloys based on *PbSb₂Te₄*

Doping of *PbSb₂Te₄* with copper. *X*-ray study of single-crystal cleavage of $PbSb_2Te_4$ compound doped with copper ($N_{Cu} \sim 3 \cdot 10^{19}$ cm^{-3}) has shown that introduction of copper results in small growth of lattice parameter c. The obtained value $c = 4.1736(3)$ nm for doped compound exceeds a little the value $c = 4.1712(2)$ nm for undoped $PbSb_2Te_4$ determined in [5]. Taking into account small size of в Cu atoms ($R_{Cu} = 0.116$ nm [10]), it can be supposed that, at least partially, copper atoms are embedded into Van der Waals gaps between seven-layer packages.

Table 3 and Fig. 5 – 7 show the results of measuring in two crystallographic directions (parallel and perpendicular to trigonal axis c) the thermoelectric properties of $PbSb_2Te_4$ undoped and doped with copper. As can be seen from Table 3, the anisotropy of kinetic coefficients is essentially reduced

at introduction of *Cu* atoms. Due to doping the anisotropy of the Seebeck coefficient is reduced almost 6 fold. On the introduction of *Cu*, component of the electrical conductivity tensor σ_{33} increases 5-fold and component σ_{11} changes slightly.

The data presented in the table below demonstrate changes in lattice thermal conductivity at doping with copper at room temperature:

Table 3

Results of measuring the Seebeck coefficient and the electrical conductivity at 300 K along trigonal axis c (α_{33}, σ_{33}) and in direction perpendicular to it (α_{11}, σ_{11}) for undoped and copper-doped PbSb$_2$Te$_4$ of p-type

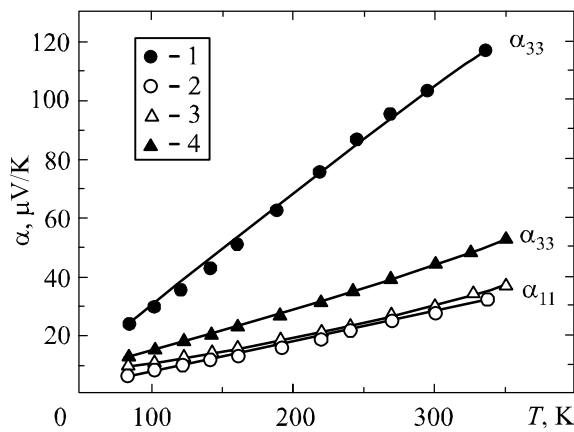| Compound	α_{11}, μV/K	α_{33}, μV/K	$\Delta\alpha$, μV/K	σ_{11}, Ω^{-1}cm^{-1}	σ_{33}, Ω^{-1}cm^{-1}	σ_{11}/σ_{33}
PbSb$_2$Te$_4$	26	107	81	2354	232	10.1
PbSb$_2$Te$_4$<Cu>	30	44	14	2971	1705	1.7
Compound	$\kappa_{11(ph)}\cdot10^3$ W/cm·K	$\kappa_{33(ph)}\cdot10^3$ W/cm·K	$\kappa_{11(ph)}/\kappa_{33(ph)}$			
PbSb$_2$Te$_4$	11.9	4.8	2.5			
PbSb$_2$Te$_4$<Cu>	2.7	8.4	<1			

Fig. 5. Temperature dependences of the Seebeck coefficient for p-type PbSb$_2$Te$_4$, undoped (1, 2) and doped with copper (3, 4) 1, 3 – α_{11}; 2, 4 – α_{33}.
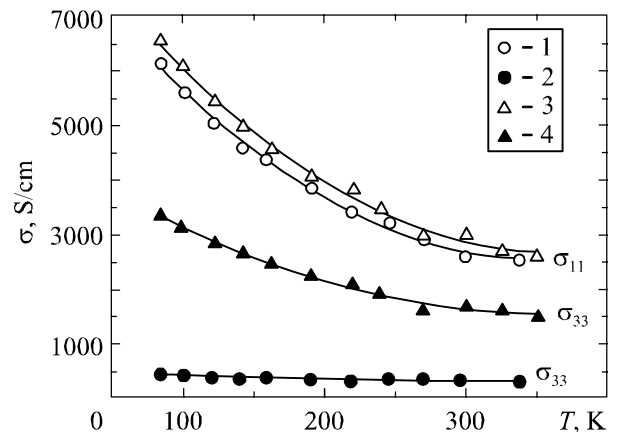
Fig. 6. Temperature dependences of the electrical conductivity for p-type PbSb$_2$Te$_4$, undoped (1, 2) and doped with copper (3, 4) 1, 3 – σ_{11}; 2, 4 – σ_{33}.

Component of thermal conductivity tensor $\kappa_{33(ph)}$ is increased, and component of thermal conductivity tensor $\kappa_{11(ph)}$ is decreased on doping with copper. As a result, the ratio $\kappa_{11(ph)}/\kappa_{33(ph)}$ becomes less than unity on introduction of *Cu* atoms. Such behaviour of lattice thermal conductivity in *PbSb$_2$Te$_4$<Cu>* shows that *PbSb$_2$Te$_4$<Cu>* realizes a complicated mechanism of copper entry into compound lattice. Alongside with its entry into Van der Waals gaps, defects of the type *Cu'$_{Pb}$* and *Cu''$_{Sb}$* can form that contribute to reduction of $\kappa_{11(ph)}$. Research on temperature dependences of thermoelectric properties has shown that, like in the case of *PbBi$_4$Te$_7$*, the Seebeck coefficient anisotropy of *PbSb$_2$Te$_4$* slightly increases (Fig. 5), and the electrical conductivity anisotropy (Fig. 6) decreases with temperature growth. The thermal conductivity anisotropy varies only slightly with temperature increase (Fig. 7).
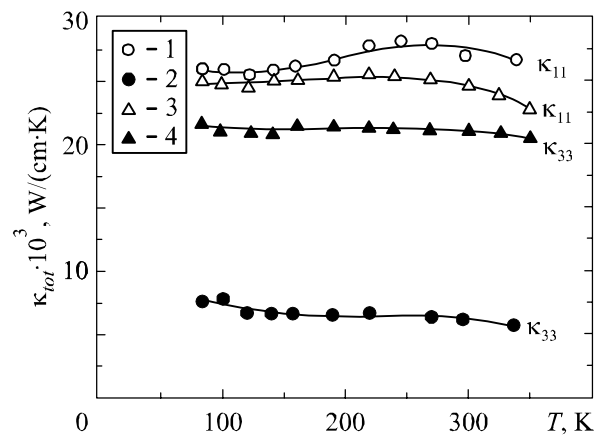
Fig. 7. Temperature dependences of total thermal conductivity for p-type PbSb$_2$Te$_4$, undoped (1, 2)
and doped with copper (3, 4) 1, 3 – κ$_{11(tot)}$; 2, 4 – κ$_{33(tot)}$.

Results of measuring microhardness of undoped and copper-doped *PbSb$_2$Te$_4$* compound are represented in Table 4.

Table 4

Microhardness of PbSb$_2$Te$_4$,single crystals measured parallel to cleavage planes (H$_\parallel$) and perpendicular to cleavage planes (H$_\perp$)

Compound	$H_\parallel$, MPa	$H_\perp$, Mpa	$H_\parallel / H_\perp$
PbSb$_2$Te$_4$	833(9)	680(14)	1.23
PbSb$_2$Te$_4$<Cu>	895(12)	826(14)	1.08

From Table 4 it is seen that introduction of copper into the lattice of *PbSb$_2$Te$_4$* compound leads to a marked growth of microhardness in both crystallographic directions. The behaviour of $H_\perp$ conforms to the assumption of *Cu* entry into Van der Waals gaps between seven-layer packages *TeSbTePbTeSbTe* of which crystal lattice of *PbSb$_2$Te$_4$* compound is built. Apparently, the introduction of copper leads to strengthening of chemical bond the layer packages which is accompanied by growth of $H_\perp$.

Analysis of experimental findings of investigation of *p*-type *PbSb$_2$Te$_4$* compound within the single-band and double-band models of valence band

The paper analyzes possible reasons for origination of Seebeck coefficient and electric conductivity anisotropy, as well as the anomalous behaviour of lattice thermal conductivity and Hall coefficient versus temperature for the undoped *PbSb$_2$Te$_4$* compound.

Single-band model. High concentration of holes in *PbSb$_2$Te$_4$* ($p = 3.0 \cdot 10^{20}$ cm^{-3}) enables using for the analysis of experimental results formulae for kinetic coefficients valid for strong degeneration of free carrier gas. The Seebeck coefficient in this case is equal to:

$$\alpha = \{k_0/e \cdot \pi^2/3\} \{k_0 T/\mu\}(r+1), \tag{1}$$

where μ is chemical potential, T is temperature, k_0 is Boltzmann constant, e is the value of electron charge, r is scattering parameter which is power exponent in the energy dependence of relaxation time $\tau(\varepsilon) \sim \varepsilon^{r-1/2}$.

The most common mechanism of electron scattering in semiconductors in the temperature range of 77 – 400 K is scattering on crystal lattice acoustic vibrations, for which scattering parameter $r = 0$. From the lower value of Seebeck coefficient $\alpha_{11} = 10$ µV/K at 100 K for $r = 0$ we obtain parameter characterizing the degeneracy degree of hole gas $\mu^* = \mu/k_0 T \approx 28 >> 1$ and the Fermi level of holes

$\mu \approx 0.24$ eV. The obtained value μ^* confirms the validity of using formula (1) which in agreement with the experiment gives a linear temperature dependence of thermoEMF.

In the temperature range of 77 – 450 K in heavily doped semiconductors, apart from scattering on acoustic phonons, as a rule, an essential contribution is from scattering on Coulomb potential of ionized impurities and defects. Apparently, mixed mechanism of holes scattering is possible in $PbSb_2Te_4$. It can be one of the reasons for origination of thermoEMF anisotropy, assuming that different dominant scattering mechanisms act in different directions: in cleavage plane it is acoustic scattering, and in the direction of trigonal axis c – scattering on impurity ions.

In this case, for a larger component of Seebeck coefficient tensor α_{33}, assuming scattering parameter $r = 2$ and using the value of reduced chemical potential μ^* found earlier from component α_{11}, from formula (1) at temperature 100 K we obtain the value $\alpha_{33} = 30$ µV/K, close to experimental. Moreover, temperature derivatives $d\alpha_{33}/dT$ and $d\alpha_{11}/dT$ in the model under study should differ 3 times, which is observed in the experiment.

The data for temperature dependences of electrical conductivity also confirm the assumption made on scattering mechanisms. The electrical conductivity in cleavage plane σ_{11} decays approximately like $T^{-0.8}$, which is close to theoretical T^{-1} for the acoustic scattering mechanism in the case of strong degeneracy. At the same time, the electrical conductivity along the trigonal axis σ_{33} varies with temperature appreciably weaker ($\sigma_{33}, \sim T^{-0.3}$), as it should be with a dominant scattering of holes on impurity ions.

Analysis shows that the experimental data can be basically explained within a single-band spectrum model and mixed mechanism of holes scattering on the assumption that scattering on acoustic phonons is dominant in cleavage plane, and scattering on impurity ions – along the trigonal axis.

Double-band model for $PbSb_2Te_4$

To explain strong temperature dependence of both components of the Hall tensor and the unusual temperature dependence of thermal conductivity, a double-band model of valence band was employed in the paper. The consideration was based on the variant when transport phenomena involve current carriers (holes) of two types – light and heavy with different mobility anisotropy in different directions. For the calculation use was made of a phenomenological theory developed in [14] for a binary compound Sb_2Te_3. On assumption that partial Seebeck coefficients for light and heavy holes are isotropic, for conduction with participation of two hole types the thermoEMF anisotropy is described by the formula:

$$\Delta\alpha = \alpha_{33} - \alpha_{11} = \left(\alpha^{(1)} - \alpha^{(2)}\right)\nu\left(b_c - b_a\right)/b_c b_a, \qquad (2)$$

where $\nu = p_2/p_0$ is the ratio between light holes concentration and full concentration $p_0 = p_1 + p_2$, $b_a = u_1^a/u_2^a$, $b_c = u_1^c/u_2^c$ are their mobility ratios: b_a – in the direction of cleavage plane; b_c – in the direction perpendicular to cleavage plane, respectively.

From formula (2) it follows that at $\Delta\alpha > 0$ (which agrees with the experiment), $b_a / b_c > 1$. This condition is satisfied in the case when holes belonging to a band with higher mobility possess larger anisotropy. In particular, if hole mobilities in additional band (2) are higher than in the basic (1), ($b_a / b_c > 1$), then the anisotropy of hole mobility in the basic band (1) is smaller than the anisotropy of holes in the additional band (2), since

$$b_a / b_c = \left(u_1^a / u_1^c\right)/\left(u_2^a / u_2^c\right). \qquad (3)$$

The fact that Seebeck coefficient anisotropy is related to the emergence of second types of carriers (holes) enables using its temperature dependence (Fig. 8) [15] for evaluation of energy gap between

the basic and additional extremums. In the temperature range, when the contribution of second zone holes to conductivity is only beginning, i.e. when $v = p_2/p_0 \ll 1$, formula (2) takes on the form:

$$\Delta\alpha \sim v \sim \exp(-\Delta\varepsilon_v /k_0 T). \tag{4}$$
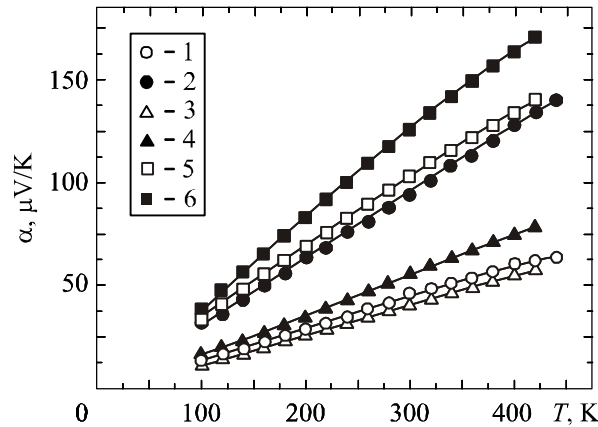

Fig. 8. Temperature dependences of the Seebeck coefficient of PbSb$_2$Te$_4$ compound:
1, 2 – experiment; 3 – 6 – rated values; 3, 4 – at r = 0; 5, 6 – r = 2;
1, 3, 5 – along cleavage planes; 2, 4, 6 – along the trigonal axis c.

Evaluation of energy gap between bands 1 and 2 yielded the value $\Delta\varepsilon_v \sim 0.24$ eV. Thus, experimental data for the Seebeck effect do not contradict the assumption on the effect of additional band on transport phenomena in *PbSb$_2$Te$_4$*. Fig. 9 represents a schematic of supposed band spectrum of *PbSb$_2$Te$_4$* compound. Using the value of the above energy gap, as well as the values of effective masses, mobilities of light and heavy holes, their ratios, the Hall factor values and their ratios, for bands 1 and 2 as trimming parameters there were calculated temperature dependences of components R_{ijk} with a double-band model developed in [14] for *Sb$_2$Te$_3$*. Fig. 10 represents experimental and rated values of R_{ijk}. It is obvious that the rated and experimental data are in good agreement with each other. Moreover, in agreement with the experiment R_{123} is larger than R_{321} over the entire investigated temperature range.
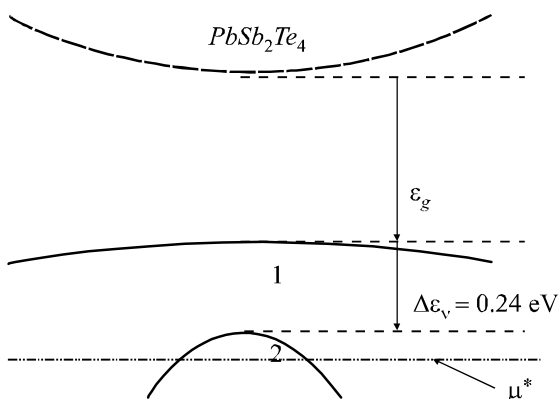

Fig. 9.Schematic of possible band spectrum of
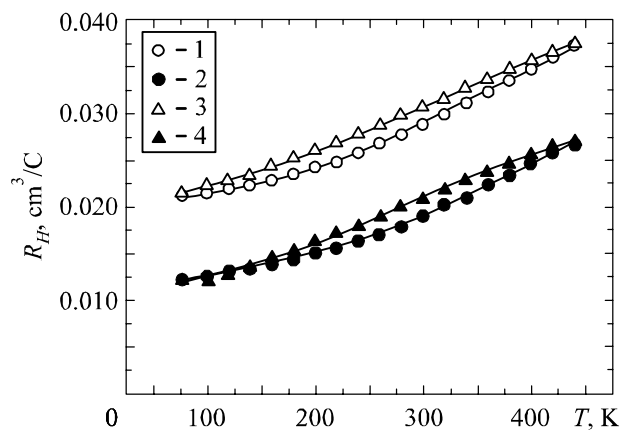*p-type PbSb$_2$Te$_4$ compound.*

Fig. 10. Temperature dependences of the Hall
coefficient components R$_{ijk}$: 1, 2 –experiment; 3, 4 –
two-band model calculation; 1, 3 – R$_{123}$ – magnetic field
parallel to axis c; 2, 4 – R$_{321}$ – magnetic field
perpendicular to axis c.

Conclusion

- The investigated ternary compounds are heavily anisotropic semiconductors due to the difference in the character of chemical bond inside layered packages and between them. The bonds inside the packages are ion-covalent, and the bond between the packages is mostly realized by weak Van der Waals forces causing the presence of Van der Waals gaps, as well as the presence of pronounced cleavage planes.

- Based on the *X*-ray analysis of single-crystalline cleavages $PbBi_{3.94}Cd_{0.06}Te_7$, a conclusion was made that *Cd* substitutes *Bi* atoms in the layer. Formation of substitution defects of Cd'_{Bi} type in the layer contributes to efficient scattering of phonons on the mass and voltage fluctuations leading to reduction of $\kappa_{11(ph)}$.

- X-ray study has shown that on doping of $PbBi_4Te_7$ with silver the most probable doping mechanism is entry of silver into Van der Waals gaps between five-layer and seven-layer packages in $PbBi_4Te_7$ structure.

- When $PbSb_2Te_4$ is doped with copper, one can suppose partial entry of *Cu* atoms into Van der Waals gaps between seven-layer packages in $PbSb_2Te_4$ structure.

- Such mechanism of integration of 1B-subgroup elements of periodic system into the lattice of compounds $PbBi_4Te_7$ and $PbSb_2Te_4$ produces a considerable effect on thermoelectric properties of these compounds. Anisotropy of all investigated kinetic coefficients is reduced, namely the Seebeck coefficient, electric and thermal conductivity.

- Study of the anisotropy of thermoelectric properties of single crystals has shown that doping with cadmium improves thermoelectric properties of $PbBi_4Te_7$ towards cleavage planes, and doping with silver – towards the trigonal axis *c*.

- Marked microhardness anisotropy is shown to exist in the investigated single crystals $PbBi_4Te_7$ and $PbSb_2Te_4$ due to the difference in the character of chemical bonds in parallel and perpendicular directions to cleavage planes.

- Kinetic coefficients in the direction of the trigonal axis *c* are strongly affected by potential barriers at the interface between layered packages. In layered compounds, component of tensor κ_{33} (across the barriers) is considerably less than component κ_{11} (in the direction of cleavage planes). It is apparently related to efficient phonon scattering on potential barriers at the interface between seven-layered and five-layered packages divided by Van der Waals gaps.

- The role of barriers on doping with silver is reduced due to increased interaction between layer packages. This results in a marked growth of electric conductivity tensor component σ_{33}.

- Investigation performed on high-quality single crystals has shown that the above ternary compounds are promising for production of medium-temperature TEM with a low lattice thermal conductivity. The choice of optimal orientation of single-crystalline samples contributes to improvement of thermoelectric material properties.

- The anisotropy data of the Seebeck coefficient and thermal conductivity of $PbSb_2Te_4$ are well explained within a single-band model with different mechanisms of charge carrier scattering along the axis *c* and perpendicular to it. The anomalous behaviour of tensor components of the Hall coefficient is explained within the double-band model of valence band. Evaluation of the energy gap between subbands 1 and 2 of valence band yielded the value $\Delta\varepsilon_v \sim 0.24$ eV.

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