The n- and p-type Mixed Layered Tetradymite-like Compounds with Low Lattice Thermal Conductivity: Growth, Structure and Thermoelectric Properties

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Abstract

The mixed layered (ML) tetradymite-like compounds in the PbTe-Bi_2Te_3 and PbTe-Sb_2Te_3 quasi-binary systems have been investigated by X-ray diffraction study (XRD) of single crystals and by measurement of their thermoelectric (TE) properties. The ingots with directional structure were grown by vertical version of Bridgman as well as by Czochralski technique with supply of the melt from a floating crucible. The atomic coordinates, the equivalent positions, site occupancy and interatomic distances in the $PbBi_4Te_7$ and $PbSb_2Te_4$ structures have been determined by an automatic four-circle XRD Syntex P1 diffractometer (MoKα-radiation). The PbTe-Sb_2Te_3 phase diagram was refined. Two compounds ($PbSb_2Te_4$, $PbSb_4Te_7$) have been discovered in this system. The existence of the $Pb_2Sb_6Te_{11}$ compound described earlier in Ref. [1] was not confirmed in the present work. The ML compounds are characterized by low lattice thermal conductivity which is significantly lower than that for Bi_2Te_3-based alloys. Further decreasing lattice thermal conductivity is reached by preparing the alloys of $PbBi_4(Te_{1-x}Se_x)_7$ ($0 \le x \le 0.20$) solid solutions with isovalent anion substitution.

Introduction

One of the modern approaches which is developed at present time consists of the creation of new ternary and quaternary chalcogenides with complex crystal structures and complicated electronic structures near the Fermi energy. These structures with large unit cells and heavy elements are expected to possess by low thermal conductivity due to effective scattering of phonons that are responsible for the transfer of heat in the materials [2]. Tetradymite-like ternary compounds in the systems $A^{IV}B^{VI}$-$A^V{}_2B^{VI}{}_3$ (A^{IV}-Ge,Sn,Pb; A^V-Bi; Sb; B^{VI}-Se,Te) are potentially attractive thermoelectric materials of n- and p-type conductivity [3,4]. It is found in Ref. [3, 4] that homologous series of nGeTe·$m$$Bi_2Te_3$ (n=1-5; m=1-4) and nPbTe·$m$$Bi_2Te_3$ (n=1,2; m=1-4) compounds are formed in the GeTe-Bi_2Te_3 and PbTe-Bi_2Te_3 systems. A variety of complex structures with large unit cells can be obtained by changing the n/m ratio.

The nPbTe·$m$$Bi_2Te_3$ compounds annealed during 1000 h at 770 K were identified by X-ray diffraction of single crystal cleaved planes and powders [5]. The following multi-layer nPbTe·$m$$Bi_2Te_3$ compounds were discovered in PbTe-Bi_2Te_3 system: $PbBi_2Te_4$ (N=21), $PbBi_4Te_7$ (N=12), $Pb_2Bi_6Te_{11}$ (N=57), $PbBi_6Te_{10}$ (N=51) and $PbBi_8Te_{13}$ (N=66), where N is a number of layers per unit cell. All the nPbTe·$m$$Bi_2Te_3$ compounds under study were n-type conductivity and had rather high electron concentration [4]. The compounds are characterized by low lattice conductivity: (κ_{ph}=6.0-7.3)·10^{-3} W/cm·K at 300 K. The $PbBi_4Te_7$ compound has a good potential for thermoelectric application as n-type material in intermediate temperature range (450-650 K). It is known that the lattice thermal conductivity can be decreased by introducing large mass and strain fluctuations in the crystal lattice by preparing solid solutions (i.e., alloy scattering). The n-type $PbBi_4(Te_{1-x}Se_x)_7$ solid solutions with anion substitution are especially of interest for achieving low lattice thermal conductivity without decreasing carrier mobility.

There are contradictory and limited data in literature concerning to PbTe-Sb_2Te_3 phase diagram. According to Ref. [1], the $Pb_2Sb_6Te_{11}$ ternary compound was suggested to exist in the PbTe-Sb_2Te_3 system. However, crystal structure of this compound was not determined. It was found in Ref. [6, 7] that the PbTe-Sb_2Te_3 quasi-binary system belongs to eutectic type without forming any ternary compounds.

The objective of the present work was to grow single crystals of the most important representatives of the nPbTe·$m$$Bi_2Te_3$($Sb_2Te_3$) homologous series compounds, to study their structure and to investigate the thermal and electrical transport properties as well as TE properties of the $PbBi_4(Te_{1-x}Se_x)_7$ solid solutions with isovalent anion substitution.

Experimental

The $PbBi_4(Te_{1-x}Se_x)_7$ ($0 \le x \le 0.20$) alloys and the charges for crystal growing by Bridgman and Czochralski technique were prepared by melting elements in evacuated quartz tubes at 1070 K during 5 h and subsequently air-quenched. The $PbBi_4(Te_{1-x}Se_x)_7$ polycrystalline alloys were annealed at 770 K during 1000 h.

A rate of crystallization was 0.20-0.23 mm/min and a temperature gradient was 40-60 K/cm at the growth by Bridgman technique. The crystals obtained were 0.7-0.8 cm in diameter and 7-9 cm long. Single crystal of the $PbSb_2Te_4$ compound was grown by Czochralski technique with supply of the melt from floating crucible.

The X-ray diffraction (XRD) study was carried out using a DRON-UM automatic diffractometer (CuK_α--radiation, graphite monochromator, 2θ-θ step-scan mode). For refining the $PbBi_4Te_7$ and $PbSb_2Te_4$ structures, an automatic four-circle diffractometer Syntex P1, graphite-monochromated Mo K_α-radiation was used. The AREN crystallographic software package [8] was used in full-matrix least-squares approximation. Single crystal platelets were obtained by cleavage along the *(00l)* planes. The technique of measurements of transport properties is presented elsewhere [3].

Results and discussion

The $PbBi_4Te_7$ crystal structure

The $PbBi_4Te_7$ single crystals obtained by Bridgman method and cleaved from first solidified part of the ingots have been investigated by XRD. The $PbBi_4Te_7$ compound has 12-layer lattice with the following parameters in hexagonal configuration: a=0.4426 nm, c=2.3892 nm (space group $P\bar{3}m1$). The atomic coordinates, the equivalent positions (q) and the temperature factors (B) are presented in Table 1.

Table1. The atomic coordinates, the equivalent positions (q) and temperature factors (B) for the $PbBi_4Te_7$ structure (occupation factor μ=1,0) (R=4,24 %)

atom	x	y	z	q	B
Pb1	0	0	0	1 (a)	2.1
Bi2	1/3	2/3	0.8329	2 (d)	2.3
Bi3	1/3	2/3	0.5840	2 (d)	1.9
Te4	1/3	2/3	0.0781	2 (d)	1.7
Te5	0	0	0.2369	2 (c)	1.9
Te6	1/3	2/3	0.3439	2(d)	2.0
Te7	0	0	½	1(b)	1.7

R-factor is equal to 4.24 % for 141 X-ray diffraction reflections. The $PbBi_4Te_7$ unit cell contains layer packets of two types - one seven-layer packet: ❘Te(5)Bi(2)Te(4)Pb(1)Te(4)Bi(2)Te(5)❘ and one five-layer slab: ❘Te(6)Bi(3)Te(7)Bi(3)Te(6)❘. These packets are alternated orderly in the direction of hexagonal c axis. The structure can be represented by stacking of close-packed Te layers. The Pb and Bi atoms are distributed in octahedral interstices filling only a fraction of the cation positions. The atomic layers are arranged according to cubic close-packing law. The bonding inside the multi-layer packets has ionic-covalent character while bonds between the packets are preferentially achieved by weak van der Waals forces.

The $PbBi_4(Te_{1-x}Se_x)_7$ solid solutions ($0\leq x\leq 0.20$)

According to XRD of the powders, the lattice parameters of the solid solutions are decreased at increasing a degree of substitution of Te atoms by Se atoms as the Se atoms have the dimensions smaller than those of Te atoms (covalent octahedral radii of Te and Se atoms are equal to 0.156 nm and 0.140 nm, respectively). The dependencies a=f(x) and c=f(x) can be presented by the following linear equations: a=0.4426-0.0305x and c=2.3892-0.051x.

The thermal and electrical transport properties at 300 K of polycrystalline samples of the $PbBi_4(Te_{1-x}Se_x)_7$ solid solutions are represented in Table 2.

Table 2. Thermoelectric properties of the $PbBi_4(Te_{1-x}Se_x)_7$ solid solutions alloys at room temperature

X	$N\cdot 10^{-20}$, cm^{-3}	- S, μV/K	σ, S/cm	μ_H, $cm^2/V\cdot s$	$\kappa_{ph}\ 10^3$, W/cm·K
0	2.40	58	1120	30	8.4
0.05	2.36	55	1587	42	6.5
0.10	1.77	59	1205	43	5.1
0.20	1.60	62	910	35	6.3

All the samples have n-type conductivity. The high carrier concentration is apparently related to a high concentration of native point lattice defects through the deviation from stoichiometry. Hall carrier concentration is decreased and Hall electron mobility is increased in the $0\leq x\leq 0.1$ composition range at the enhancement of x values what can be related to decreasing deviation from stoichiometry. The alloy with x=0.10 has low, near glass-like lattice thermal conductivity. Apparent enhancement of carrier mobility at the composition x=0.10 at simultaneous decreasing lattice thermal conductivity leads to increasing the μ_H/κ_{ph} ratio. The $PbBi_4(Te_{0.9}Se_{0.1})_7$ alloy is promising material for further optimization of its TE properties by doping with foreign impurities.

The thermal and electrical transport properties were measured in a wide temperature range for the $PbBi_4(Te_{1-x}Se_x)_7$ polycrystalline samples. The temperature dependencies of Seebeck coefficient in the range from 90 to 750 K are presented in Fig. 1.

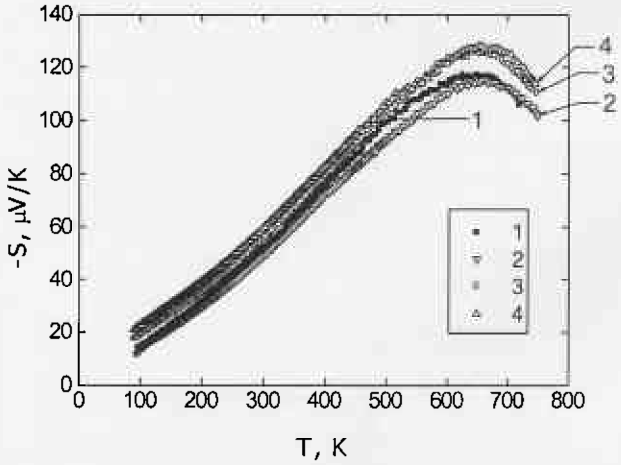

Fig. 1. Temperature dependencies of Seebeck coefficient for the $PbBi_4(Te_{1-x}Se_x)_7$ alloys, 1- x=0; 2 – x=0.05; 3 – x= 0.10; 4 – x=0.20.

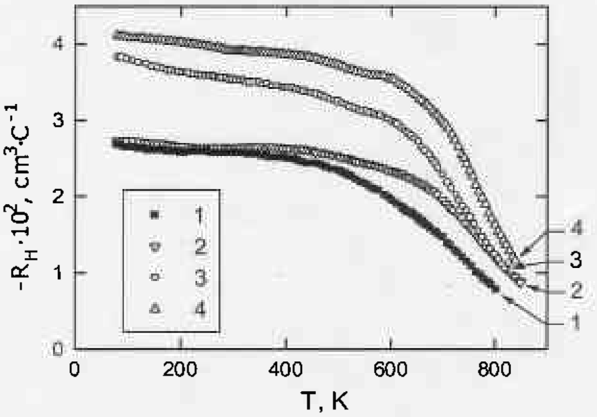

Fig. 2. Temperature dependencies of Hall coefficient for the $PbBi_4(Te_{1-x}Se_x)$ solid solutions. The compositions are marked as in Fig.1.

The alloys preserve n-type conductivity in all temperature range under study. A maximum of Seebeck coefficient is located near 620-650 K. Seebeck coefficient value (S=-130 μV/K) is characteristic for the x=0.10 composition at 650 K. The temperature dependencies of Hall coefficient in the range from 77 to 800 K are presented in Fig. 2. The R_H=f(T) dependencies are typical for heavily doped semiconductors.

The temperature where onset of intrinsic conductivity develops, is dependent on the composition of the alloys. At increasing x value, the onset of intrinsic conductivity is displaced towards higher temperatures..

Temperature dependencies of electrical conductivity are presented in Fig.3. On the basis of ln(σ)=f(1/T) dependence, an energy gap of 0.31 eV was determined for x=0.20 alloy. This value is greater than the ordinary E_g value for other ML compounds (E_g=0.19-0.22 eV) [10,11]. The E_g enhancement at x increasing favours to displacement of maximum of thermoelectric figure of merit towards higher temperatures as compared to that for the $PbBi_4Te_7$ compound.

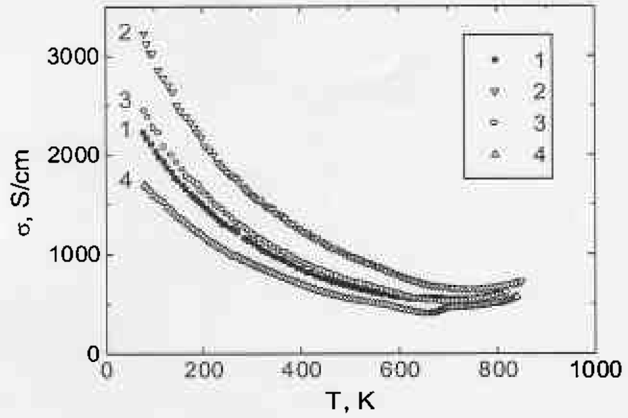

Fig. 3. Temperature dependencies of electrical conductivity for the $PbBi_4(Te_{1-x}Se_x)$ solid solutions. The compositions are marked as in Fig.1.

Temperature dependencies of electrical conductivity are characterized by the anomalies σ in the 600-650 temperature range. These anomalies can be related to phase transitions in solid state. The assumption about possibility of the phase transitions in the ML compounds was made at first in Ref. [9] where these compounds were investigated by thermal expansion and specific heat measurements.

Temperature dependencies of Hall carrier mobility in double logarithmic coordinates are presented in Fig. 4. The most high values of Hall carrier mobility (μ_H=$R_H\sigma$) are characteristic for the x=0.05 and x=0.10 compositions. The μ_H=f(T) dependencies follow to power law: $\mu_H \sim T^{-n}$ with n being markedly dependent on temperature. In the 77-250 K temperature range, the μ_H=f(T) dependencies are relatively weak and are expressed by $\mu_H \sim T^{-1/2}$ law for $PbBi_4Te_7$ and x=0.05 and x=0.10 alloys. A mixed carrier scattering mechanism by acoustic phonons and point lattice defects can be proposed in this temperature range [4]. Above 250 K, the contribution of carrier scattering by acoustic phonons increases at the enhancement of temperature.

Total thermal conductivity is weakly dependent on temperature as a result of alloy-disorder scattering of phonons. The solid solutions have values of lattice thermal conductivity considerably lower than those for the $PbBi_4Te_7$ compound. It is related to distortions of crystal lattice through the difference in atomic mass and dimensions of Te and Se atoms. As seen, κ_{ph} is decreased and κ_{el} (evaluated by using Wiedemann-Franz law) is increased at the enhancement of temperature.

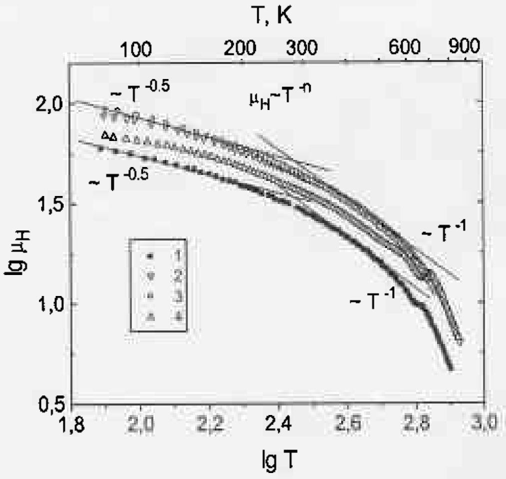

Fig.4. Temperature dependencies of Hall carrier mobility in double logarithmic coordinates. The compositions are marked as in Fig. 1.

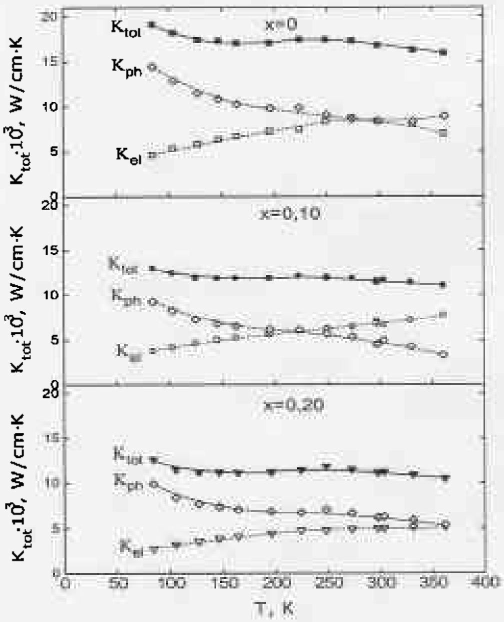

Fig. 5. Temperature dependencies of total (κ_{tot}), lattice (κ_{ph}) and electronic (κ_{el}) thermal conductivity for $PbBi_4(Te_{1-x}Se_x)_7$: x=0; x=0.10 and x=0.20.

The κ_{ph} and κ_{el} values become comparable at ~270 K, ~ 230 K and ~360 K temperatures in the $PbBi_4Te_7$ compound, x=0.10 and x=0.20 alloys, respectively. Near these temperatures, phonons and electrons carry equal contribution in heat transfer in the materials.

Thus, anion substitution in the $PbBi_4(Te_{1-x}Se_x)_7$ solid solutions favours to decreasing lattice thermal conductivity at simultaneous increasing electron mobility. The optimal combination of lattice thermal conductivity and electron mobility is reached in the $PbBi_4(Te_{0.9}Se_{0.1})_7$ alloy. For unoptimized $PbBi_4(Te_{0.9}Se_{0.1})_7$ alloy, ZT value is equal to 0.6 near 650 K.

The ML compounds in $PbTe$-Sb_2Te_3 system

Two compounds ($PbSb_2Te_4$, $PbSb_4Te_7$) were discovered in the $PbTe$-Sb_2Te_3 quasi-binary system by X-ray diffraction study. These compounds belong to the $nPbTe \cdot mSb_2Te_3$ homologous series. The $PbSb_2Te_4$ compound is formed by peritectic reaction: $L + PbTe \leftrightarrow PbSb_2Te_4$ at 860 K. The $PbSb_4Te_7$ compound is suggested to be formed according to a peritectoid reaction: $Sb_2Te_3 + PbSb_2Te_4 \leftrightarrow PbSb_4Te_7$. The existence of the $Pb_2Sb_6Te_{11}$ compound described earlier in Ref. [1] was not confirmed by XRD in the present work.

The $PbSb_2Te_4$ crystal structure was determined by XRD of single crystals using an automatic diffractometer Syntex P1. The $PbSb_2Te_4$ compound is isostructural to the $PbBi_2Te_4$. It has 21-layer lattice with the following parameters: a = 0.4350(1) nm, c = 4.1712(2) nm. Space group is $R\bar{3}m$ The XRD results are presented in Table 3 and Fig 6.

Table 3. The atomic coordinates, the occupation factors (in atomic parts) (μ), the equivalent positions (q), temperature factors (B) for the $PbSb_2Te_4$ structure (R=3.15 %)

Atom	x	y	z	μ	q	B
Me1	0	0	0	0.52Pb,0.27Sb, 0.21Te	3(a)	2.0
Me2	0	0	0.4272	0.86 Sb, 0.14 Pb	6(c)	1.7
Te3	0	0	0.1337	0.96 Te, 0.04 Pb	6(c)	1.1
Te4	0	0	0.2882	0.93 Te, 0.07 Pb	6(c)	1.2

Reliability index is R=3.15 % for the 60 XRD reflections. There are three seven-layer packets per unit cell. The distance between the adjacent seven-layer packets is much greater than interatomic distances within the packets (Fig. 6). The bonds between seven-layer packets are preferentially achieved by weak van der Waals forces. Based on XRD results, some conceptions concerning to the nature of point lattice defects in the $PbSb_2Te_4$ structure can be developed. As follows from the Table 3, the $PbSb_2Te_4$ compound is characterized by a high degree of lattice disorder. Tthe Pb'_{Sb} substitution defects as well as the Pb''_{Te} and Sb'_{Te} anti-site defects are expected to be the most reasonable nonstoichiometric defects of acceptor type.

The $PbSb_4Te_7$ compound is isostructural to the $PbBi_4Te_7$ and has 12-layer structure with the following parameters: a=0.4306 nm, c=2.4017 nm.

Thermoelectric properties

Thermoelectric properties have been investigated for p-type $PbSb_2Te_4$ perfect single crystal which was grown by Czochralski technique. Seebeck coefficient, electrical and thermal conductivity have been measured at room temperature in two crystallographic directions: parallel and perpendicular to the cleavage plane, i.e. $\perp c$ and $\| c$, respectively. The results of measurement of Seebeck coefficient and electrical conductivity of p-type $PbSb_2Te_4$ single crystal in comparison with those for the binary Sb_2Te_3 compound [12] with tetradymite-type structure (space group is *R3m*) are presented in Table 4.

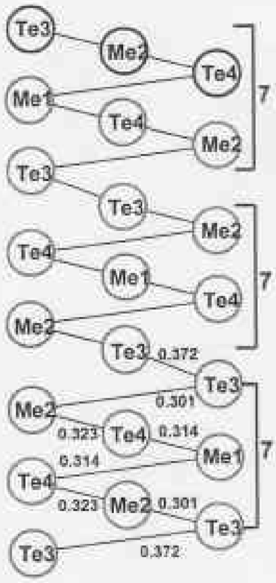

Fig. 6. Schematic projection of the $PbSb_2Te_4$ structure on the (11$\bar{2}$0) plane.

Table 4. The results of measurement in two crystallographic directions of TE properties at room temperature for p-type $PbSb_2Te_4$ and p-type Sb_2Te_3 [12] single crystals

Compound	$S_{\|}$, µV/K	$S_{\perp}$, µV/K	ΔS, µV/K	$\sigma_{\|}$, S/cm	$\sigma_{\perp}$, S/cm	$\sigma_{\|}/\sigma_{\perp}$
$PbSb_2Te_4$	37	86	49	1774	226	7.8
Sb_2Te_3	73	90	17	4150	2340	1.8

*$\|$ and $\perp$ - thermoelectric properties were measured parallel and perpendicular to the cleavage plane, respectively.

The results of measurement of thermal conductivity in two crystallographic directions at room temperature are presented below:

$\kappa \cdot 10^3$, W/cm·K	$\kappa_{\|}$·	$\kappa_{\perp}$·	$\kappa_{\|}/\kappa_{\perp}$
$PbSb_2Te_4$	26.2	6.2	4.2
Sb_2Te_3	47.0	26.2	1.8

As seen, the $PbSb_2Te_4$ crystal is highly anisotropic in Seebeck coefficient, electrical conductivity and thermal conductivity. As follows from $PbSb_2Te_4$ crystallographic constitution, anisotropy of electrical and thermal transport properties is determined by the weakness of inter-packet bonding between seven-layer packets which is realized by weak van der Waals forces. It is noteworthy, that the anisotropy in TE properties in the Sb_2Te_3 crystal is much lower than that in the $PbSb_2Te_4$ crystal. It can be related to the difference in crystallographic constitution of the $PbSb_2Te_4$ and Sb_2Te_3. In tetradymite-type Sb_2Te_3 structure, the ($Te^{(1)}$ Sb $Te^{(2)}$Sb $Te^{(1)}$) five-layer packs are stacked according to cubic close-packing law [13]. It is believed that the five-layer slabs are preferentially bonded by van der Waals forces [13]. The distance between the adjacent five-layer packets: $Te^{(1)}$-$Te^{(1)}$ (0.364 nm) is much greater than the distances Sb-$Te^{(1)}$ (0.306 nm) and Sb-$Te^{(2)}$ (0.316 nm) within the five-layer packets. But this distance is lower than corresponding distance in the $PbSb_2Te_4$ structure (0.372 nm).

It indicates that the bond between five-layer slabs is stronger than that between seven-layer packets, possibly because of contribution of covalent bonding. Apparently, such difference in character of chemical bonds can be a reason of difference in the anisotropy of TE properties in the $PbSb_2Te_4$ and Sb_2Te_3 crystals.

The results of measurement of in-plane thermoelectric properties for the unoptimized $PbSb_2Te_4$ single crystal in temperature interval 320-720 K are presented in Fig. 7.

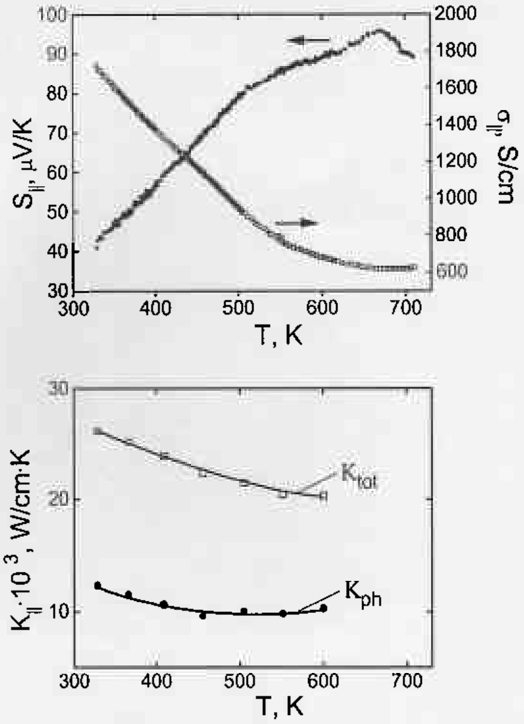

Fig. 7. Temperature dependencies (a) of Seebeck coefficient and electrical conductivity; (b) of total thermal conductivity and lattice thermal conductivity measured in the direction parallel to the cleavage plane.

Seebeck coefficient increases with temperature reaching a maximum near 675 K. Electrical conductivity decreases with temperature in the 320-550 K temperature range. Total thermal conductivity changes from $26\cdot10^{-3}$ W/cm·K at 320 K to $20\cdot10^{-3}$ W/cm·K at 600 K. In all temperature range under study, electronic component of thermal conductivity is higher than its lattice constituent Lattice thermal conductivity is rather low (κ_{ph}=$9.6\cdot10^{-3}$ W/cm·K) in a wide temperature range. The present work demonstrates that the $PbSb_2Te_4$ compound is promising TE material of p-type conductivity for thermoelectric power generation. Optimization of the carrier concentration by doping with foreign impurities or by controlling the deviation from stoichiometry should considerably improve thermoelectric properties of this compound.

Conclusions

The ML compounds in the $PbTe\text{-}Bi_2Te_3$ and $PbTe\text{-}Sb_2Te_3$ quasi-binary systems are concluded to be promising thermoelectric materials both n- and p-type conductivity, respectively. The formation of n-type $PbBi_4(Te_{1-x}Se_x)_7$ solid solutions with isovalent anion substitution favours to decreasing lattice thermal conductivity through large mass and strain fluctuations at simultaneous increasing Hall carrier mobility.

Two new ML compounds ($PbSb_2Te_4$, $PbSb_4Te_7$) of p-type conductivity have been discovered in the $PbTe\text{-}Sb_2Te_3$ quasi-binary system by X-ray diffraction study. The $PbSb_2Te_4$ single crystal was grown by Czochralski technique. Thermoelectric properties of the $PbSb_2Te_4$ single crystals were measured in two crystallographic directions: parallel ($\perp c$) and perpendicular ($\| c$) to the cleavage planes. High anisotropy in Seebeck coefficient, electrical and thermal conductivity was discovered for the $PbSb_2Te_4$ single crystal.

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