

**E.M. Godzhayev, G.S. Dzhafarova, S.I. Safarova**

Azerbaijan Technical University, 25, Huseyn Javid Ave., Baku,  
AZ 1000, Republic Azerbaijan

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**BAND STRUCTURE OF  $TlInTe_2$  AND THERMOELECTRIC FIGURE OF MERIT OF SOLID SOLUTIONS ON ITS BASIS**

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*In this work, using pseudopotential methods, the band structure of ternary compound  $TlInTe_2$  is calculated, the origin of valence band and conduction band is identified, and, on the basis of temperature dependences of the electrical conductivity, Seebeck coefficient and thermal conductivity, the thermoelectric figure of merit of solid solution of the type  $TlIn_{1-x}Ln_xTe_2$ , where  $Ln$  is  $Ce, Nd, Pr, Sm, Eu$ , is calculated in the temperature range of 300 – 700 K.*

**Key words:**  $TlIn_{1-x}A_x^{III}Te_2$  solid solutions, band structure, thermoelectric figure of merit, group-theoretic analysis.

### **Introduction**

State-of-the-art technology widely employs thermoelectric materials with high thermoelectric figure of merit. It is known that thermoelectric figure of merit of semiconductor materials is proportional to the ratio between current carrier mobility and crystal lattice thermal conductivity.

The thermoelectric figure of merit reaches maximum under certain concentration of carriers. To increase the thermoelectric figure of merit, it is necessary to find materials with maximum ratio between current carrier mobility and thermal conductivity, to create in these materials the concentration of carriers assuring optimal thermoelectromotive force, to develop methods for further increase of the ratio between current carrier mobility and lattice thermal conductivity.

These problems are solved as follows. A different substance, crystallized in the same syngony, is introduced into material crystal lattice. In such systems solid substitution solutions are formed. In this case distortions prove to be rather efficient for the dissipation of thermal vibrations, the wavelength of which at ordinary temperatures is little more than lattice constant, and, as a result, lattice thermal conductivity is considerably reduced, and mobility is reduced only slightly. On the other hand, the most efficient thermoelectric materials are based on multi-component semiconductor compounds or solid solutions comprising heavy elements with a complex or defective crystalline and a complex electronic structure. These requirements are met by solid solutions of the type  $TlIn_{1-x}A_x^{III}Te_2$ , obtained with a partial substitution of indium atoms by third group atoms, including lanthanides in  $TlInTe_2$  lattice. The data can be found in the literature that  $TlIn_{1-x}Ga_xTe_2$  solid solutions possess high thermoelectric figures of merit [1]. However, information on the research of thermoelectric figure of merit of solid solutions of the type  $TlIn_{1-x}Ln_xTe_2$  is not available. In this connection, the purpose of this work is to study the thermoelectric properties of solid solutions of the type  $TlIn_{1-x}Ln_xTe_2$ , where  $Ln$  is  $Ce, Pr, Nd, Sm, Eu$ .

The electrical conductivity ( $\sigma$ ), Seebeck coefficient ( $\alpha$ ) and thermal conductivity ( $\chi$ ) were measured using a compensation method, the errors of measuring  $\sigma, \alpha, \chi$  were 5, 7 and 4 %, respectively.

The alloys were synthesized by alloying the initial components taken in stoichiometric ratio, in

evacuated to 0.0133 Pa and sealed quartz ampoules. For synthesis of  $TlIn_{1-x}Ln_xTe_2$  alloys as the initial substances there were used  $Tl - 99.99$  mas.%,  $In - 99.99$  mas.%,  $Pr$ -comprising rare-earth element – 0.5,  $Ca-0.01$ ,  $Cu-0.04$ ,  $Fe-0.03$ ,  $Ce$ -comprising rare-earth element – 0.6,  $Ca-0.01$ ,  $Cu-0.02$ ,  $Fe-0.01$ ,  $Nd$ -comprising rare-earth element – 0.31,  $Ca-0.01$ ,  $Cu-0.01$ ,  $Tl-0.017$ ,  $Sm$ -comprising rare-earth element – 0.05,  $Fe-0.01$ ,  $Cu-0.01$ ,  $Eu$ -comprising rare-earth element – 0.03,  $Cu-0.016$  and tellurium  $A-1$ . The temperature of the heater comprising quartz ampoules with the substance was raised to 750 to 900 K at the rate of 20 to 30 K/h depending on the composition. At these temperatures the samples were held for 2 – 3 hours and then heated to 1150 to 1250 K and held for another 4 – 5 hours. After that the samples were cooled to room temperature at the rate of 10 K/hour.

The ternary compound  $TlInTe_2$  belongs to chain semiconductors of the type  $TlSe$ , is crystallized in the structure with bulk-centered tetragonal lattice with  $D_{4h}^{18}(I4/mcm)$  symmetry group.

From considerations of a chemical bond, the formula of  $TlInTe_2$  compound is written as  $Tl^+(In^+Te_2)^-$ . In this compound the ions  $In^{3+}$  and their nearest tetrahedral environment of four  $Tl_2^+$  ions form negatively charged chains  $-Tl_2^{2-} - In^{3+} - Te_2^{2-}$  – along the tetragonal  $\bar{c}$  axis. Univalent ions  $Tl^+$  are localized between the four chains, having in this case an octahedral environment of eight ions  $Te^{2-}$ .  $TlInTe_2$  is crystallized in tetrahedral syngony with the lattice parameters  $a = 8.482 \text{ \AA}$ ,  $c = 7.792 \text{ \AA}$ . The band structure of  $TlInTe_2$  was calculated by pseudopotential methods [2-4]. Maximum kinetic energy of plane waves was 20 rydbergs. The lattice parameters were  $a = 8.494 \text{ \AA}$ ,  $c = 7.181 \text{ \AA}$ , the chalcogen parameter  $x = 0.181$ .

About 2700 plane waves were used in the expansion of wave function. The results of calculation of  $TlInTe_2$  band structure are given in the Figure 1. The obtained data suggests the following conclusions.

1. The top of valence band is at high-symmetry point  $T(0, 2\pi/a, 0)$  on the surface of Brillouin zone and corresponds to irreducible representation of  $T_3$ , and the bottom of conduction band is on the line  $D(\pi/a, \pi/a, k)$ , also located on the surface of Brillouin zone between the points  $P(\pi/a, \pi/a, \pi/c)$  and  $N(\pi/a, \pi/a, 0)$ , corresponds to irreducible representation of  $D$ . The energy gap width 0.66 eV, obtained from calculations, fits the experimental data well [5-9].
2. The lowest-energy direct transition is done approximately at point  $T$  between the states  $T_3$  and  $T_4$ . According to selection rules,  $T_3 - T_4$  transition is forbidden in a dipole approximation. The bottom of conduction band at point  $T$  is a saddle point. The minimum lies a short distance from point  $T'(0, 0, 2\pi/c)$ , which is an equivalent of  $T$  beyond the Brillouin zone, namely at point  $A(0, 0, \pi/c)$   $[1+(c/a)]^2$  at the boundary of Brillouin zone along  $A_1$  line and corresponds to irreducible representation of  $A_2$ .
3. The third largest minimum of conduction band is also located on line  $A$  at point  $A(0, 0, \pi/c)$  and corresponds to irreducible representation of  $A_4$ .
4. According to composition and nature the valence bands can be divided into three groups. According to group-theoretic analysis, the lowest group consisting of four zones nearly  $-11$  eV owes its origin to  $5s$  states of  $Te$ . The middle group of four zones in the area of  $-3.5$  to  $-6$  eV mainly comes from  $6s$  states of  $Tl$  atoms and  $5s$  states of  $In$  atoms. The upper group, structurally most complicated, consisting of 10 overlapping zones in the area from 0 to  $-3.5$  eV, is mainly formed by  $5p$  states of  $Te$  atoms,  $5p$  states of  $In$  atoms. It should be noted that in the vicinity of valence band top the states of univalent ion  $Tl^+$  begin to appear, whose main contribution is observed at point  $T$ . The main contribution to formation of the two lower conduction bands is made by a trivalent  $In^{3+}$  ion taking part in the formation of ion-covalent bond with  $Te^{2-}$  ions.

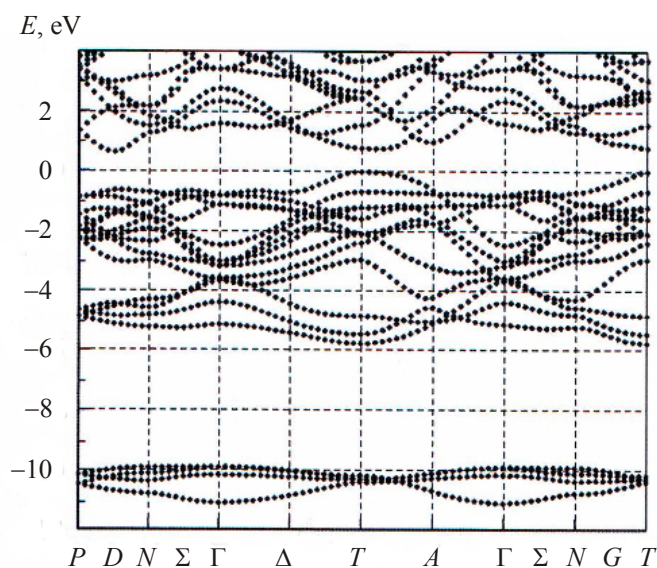


Fig. 1. Band structure of  $TlInTe_2$  compound.

These results show that the band structure of  $TlInTe_2$  is complex. In works [10-12] based on differential-thermal, microstructural, X-ray phase analyses it was established that in  $TlInTe_2$ - $TlLnTe_2$  systems there is a solubility region based on  $TlInTe_2$ . In works [5-7] the electrophysical and thermal properties of solid solutions of the type  $TlIn_{1-x}Ln_xTe_2$  were studied. These crystals satisfy the requirements of efficient thermoelectric materials, i.e. they are multi-component, comprise heavy elements and possess complex crystalline and band structures.

Investigations of the temperature dependences of the electrical conductivity, Seebeck coefficient and thermal conductivity of  $TlIn_{1-x}Ln_xTe_2$  alloys were conducted in the temperature range of 300 to 700 K.

Experimental data shows that in solid solutions based on  $TlInTe_2$  with increasing content of lanthanides in the alloys, the electrical conductivity grows by two orders of magnitude and then thermal conductivity is reduced. Therefore, it could be expected that in  $TlInTe_2$ - $TlLnTe_2$  systems in certain compositions and in certain temperature range the thermoelectric figure of merit reaches the value which is of practical significance.

We have analyzed the thermoelectric peculiarities of  $TlInTe_2$ - $TlLnTe_2$  solid solutions in the temperature range of 300 to 700 K. The results of calculation of the thermoelectric figure of merit of  $TlInTe_2$ - $TlLnTe_2$ ,  $Ln$ -Ce, Pr, Nd, Sm, Eu alloys are given in the Table. As it follows from the Table, for all investigated alloys it is typical that as the content of lanthanides increases, the thermoelectric figure of merit grows. Increase in  $Z$  is also observed with temperature growth, and at 700 K the value of  $Z$  proves to be especially high. For  $TlIn_{1-x}Eu_xTe_2$  solid solutions at 700 K  $Z$  is on the order of  $2 - 2.5 \cdot 10^{-3} K^{-1}$ . Probably, the increase in  $Z$  is due to the fact that with a constant ratio between mobility and crystal lattice thermal conductivity in compounds with a complex structure the effective mass of charge carriers increases, and with a rise in carrier concentration or temperature, the Fermi level gets into a subband of heavy carriers. Then the important role is played not only by the energy gap width, but also by the energy gap between the subbands. This fact can be satisfied in  $TlIn_{1-x}Ln_xTe_2$  crystals, since in  $TlInTe_2$  the upper part of valence band is mainly formed of  $5p$  states of tellurium and indium atoms. With a partial substitution of indium atoms by lanthanide atoms, both  $6s^2$  and  $5d^1$  lanthanide electrons take part in the formation of the upper part of valence band. Accordingly, there is a reduction of the energy gap and increase in free carrier concentration thermoelectric figure of merit of  $TlIn_{1-x}Ln_xTe_2$  crystals.

*Table*

*Thermoelectric parameters of  $TlIn_{1-x}Ln_xTe_2$  system alloys*

Compositions	300 K				500 K				700 K			
	$\alpha \cdot 10^6$ , V/K	$\sigma$ , S/m	$\chi$ , W/m·K	$Z \cdot 10^{-3}$ , K <sup>-1</sup>	$\alpha \cdot 10^6$ , V/K	$\sigma$ , S/m	$\chi$ , W/m·K	$Z \cdot 10^{-3}$ , K <sup>-1</sup>	$\alpha \cdot 10^6$ , V/K	$\sigma$ , S/m	$\chi$ , W/m·K	$Z \cdot 10^{-3}$ , K <sup>-1</sup>
$TlIn_{0.97}Ce_{0.03}Te_2$	800	1214	0.973	0.80	766	1116	0.96	0.65	750	1220	0.807	0.85
$TlIn_{0.95}Ce_{0.05}Te_2$	780	1360	0.87	0.95	684	1360	0.85	0.75	670	1403	0.70	0.90
$TlIn_{0.93}Ce_{0.07}Te_2$	720	1480	0.74	1.04	592	1782	0.79	0.79	583	1516	0.69	1.75
$TlIn_{0.97}Pr_{0.03}Te_2$	790	1290	0.77	1.05	760	1230	0.91	0.78	732	1310	0.78	0.89
$TlIn_{0.95}Pr_{0.05}Te_2$	770	1360	0.84	1.25	780	1600	0.82	1.04	708	1510	0.76	1.0
$TlIn_{0.93}Pr_{0.07}Te_2$	760	1580	0.82	1.11	682	1860	0.76	1.14	650	1920	0.71	1.14
$TlIn_{0.97}Nd_{0.03}Te_2$	700	1390	0.86	0.79	700	1590	0.90	0.87	680	1800	0.71	1.712
$TlIn_{0.95}Nd_{0.05}Te_2$	710	1580	0.84	0.95	690	1790	0.80	1.06	660	2600	0.65	1.74
$TlIn_{0.93}Nd_{0.07}Te_2$	680	1774	0.82	1.01	670	1980	0.74	1.2	590	2930	0.60	1.69
$TlIn_{0.97}Sm_{0.03}Te_2$	740	1400	0.92	0.84	720	1520	0.87	0.90	700	2200	0.68	1.58
$TlIn_{0.95}Sm_{0.05}Te_2$	710	1620	0.80	1.02	680	1760	0.86	0.95	640	2700	0.64	1.73
$TlIn_{0.93}Sm_{0.07}Te_2$	680	1910	0.76	1.19	640	1890	0.82	0.95	610	3000	0.62	1.8
$TlIn_{0.97}Eu_{0.03}Te_2$	743	1490	0.91	1.63	716	1610	0.85	0.97	790	2460	0.66	1.89
$TlIn_{0.95}Eu_{0.05}Te_2$	710	1689	0.76	1.14	684	2092	0.8	1.22	690	2900	0.63	2.19
$TlIn_{0.93}Eu_{0.07}Te_2$	680	2100	0.65	1.50	666	2864	0.7	1.81	660	3300	0.59	2.44

The obtained results testify that thermoelectric figure of merit of  $TlIn_{1-x}Ln_xTe_2$  solid solutions can be increased and controlled with a variation of their composition. Research works in this direction should be continued.

## Conclusion

In this work, the band structure of ternary compound  $TlInTe_2$  was calculated using pseudopotential methods, the origin of valence band and conduction band of this phase was identified, and the results of research on thermoelectric properties of  $TlIn_{1-x}Ln_xTe_2$  alloys obtained by substitution of trivalent indium atoms by *Pr*, *Nd*, *Ce*, *Sm* and *Eu* atoms in  $TlInTe_2$  lattice in the temperature range of 300 to 700 K were stated. It was established that in certain temperature range these alloys possess high values of thermoelectric figure of merit and can be used in thermoelectric converters.

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Submitted 05.04.2012.