Electrical and thermal transport properties of $(TlBiS_2)_{1-x}(2PbS)_x$ alloys

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Abstract

A high efficiency of thermoelectric conversion can be achieved by using materials with a maximum figure of merit Z, i.e. materials with a high Seebeck coefficient S, high electrical conductivity σ and low thermal conductivity K. Investigations of transport phenomena in alloys of the $(TlBiS_2)_{1-x}(2PbS)_x$ system have shown that in solid solutions of type $(A^3B^5C^6_2)_{1-x}(2A^4B^6)_x$ cation substitution according to the scheme $2A^{4(+2)} \rightarrow A^{3(+1)} + B^{5(+3)}$ leads to a strong decrease in lattice thermal conductivity K_L. In an area ($X = 0.50$) of the $K_L = f(C)$ curve the lattice part of the thermal conductivity of $(TlBiS_2)_{1-x}(2PbS)_x$ alloys decreases to 0.26 W m^{-1} K^{-1}, which is approaching the theoretical minimum. As a result, the dependence of the thermoelectric figure of merit on composition $Z = f(C)$ of alloys of the $(TlBiS_2)_{1-x}(2PbS)_x$ system passes through a maximum in the area $X = 0.50$, exceeding by $\sim$25% the respective value of Z for lead sulfide at room temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Lead chalcogenides are some of the best thermoelectric materials for working temperatures in the range 500–900 K [1, 2]. The high value of the thermoelectric figure of merit in lead chalcogenides is conditioned by a favourable set of important parameters and characteristics [3, 4]:

- The multivalley nature of energetic spectrum of carrier charge.
- The low value of lattice thermal conductivity, caused by heavy atoms which form these phases.
- The high mobility of carriers in highly doped levels, caused by a low scattering efficiency on electrical centres because of high static electrical permittivity.

- The positive sign of the thermal coefficient of the band gap due to the contribution of intrinsic conductivity and sharply declining figure of merit Z on shifting to a higher temperature.

The need to extend the range of materials with properties similar to A^4B^6 semiconductors is obvious and connected with the increasing need in various areas of engineering for more effective thermoelectric devices working at average temperatures. Such materials are represented by a solid solution between A^4B^6 and $A^3B^5C_2^6$ compounds [5]. Deeper scattering of phonons compared with electrons was revealed in solid solutions in the 1950s [1], and over the past four decades efforts to increase thermoelectric efficiency have focused on improving the established thermoelectric materials by reducing their lattice thermal conductivity. This way of increasing the figure of merit is still being pursued.

2. General considerations

In fact, the efficiency of a thermoelectric conversion device is determined by the value of the figure of merit Z of a material from which the n- and d-type branches are made (see, for example [3, 4]):

$$Z = S^2\sigma/K \tag{1}$$

where S, σ and K are the Seebeck coefficient, electrical conductivity and total thermal conductivity respectively.

The general expression for the total thermal conductivity of a sample can be written as

$$K = K_L + K_e + K_b + K_f \tag{2}$$

where K_L is the lattice (phonon) part of the thermal conductivity, K_e is due to the charge carriers and K_b and K_f are the bipolar and photon parts respectively. As the optimal carrier concentration at which Z achieves its maximum value is, as a rule, rather high ($n \geqslant 10^{19}$ cm^{-3}) and this maximum is realized before the appearance of intrinsic electrical conductivity as in expression (2) the last two terms can be omitted. Therefore

$$K = K_L + K_e. \tag{3}$$

In this case value of the figure of merit may be evaluated from the expression

$$Z = \frac{S^2\sigma}{K_L + K_e}. \tag{4}$$

Using the expression for electrical conductivity

$$\sigma = en\mu, \tag{5}$$

where e is electron charge, n is carrier concentration and μ is the mobility of the carrier, and the Wiedemann–Franz law (linking thermal conductivity K_e due to the charge carriers with electrical conductivity σ of samples),

$$K_e = L\sigma T, \tag{6}$$

where L is Lorenz number and T is absolute temperature, the finite expression for the figure of merit coefficient Z can be written

$$Z = \frac{S^2 en\mu}{K_L + en\mu LT}. \tag{7}$$

As can be seen from expression (7) the values of S, σ and K_e determining the figure of merit Z are strongly interconnected with each other because all of them are a function

of temperature T and carrier concentration n. Besides, due to the different nature of the dependences $S = f(n, T)$ and $\sigma = f(n, T)$, to obtaining a larger power factor $S^2\sigma$ a compromise is necessary between values of the thermopower S and electrical conductivity σ, which is rather difficult. Besides, both S and σ (through chemical potential) are dependent on the width of the band-gap E_g, which also determines a suitable interval of working temperatures.

This brief analysis of the problem allows us to understand the reasons why the results achieved in this area for bulk materials are rather modest. It also helps us to understand why the thermoelectric materials in use have varied little over the years. Today, as was the case 40 years ago, the base materials are Bi–Sb alloys for a working temperature interval of 100–200 K, alloys based on Bi_2Te_3 compounds (for 200–400 K), alloys based on A^4B^6 compounds (for 500–900 K) and SiGe and their related alloys (for 800–1200 K). The optimal value of carrier concentration is strictly determined from expression (7). It is easily noticed that one of the few possible ways of improving the figure of merit for a specific material remains increasing its μ/K_L by reducing its lattice thermal conductivity K_L. The coefficient K_L is determined mainly by phonon scattering mechanisms, some of which have little influence on carrier mobility. Actually, in multiple quantum well (MQW) structures improvement of thermoelectric efficiency also occurs significantly due to reduction of lattice thermal conductivity K_L. By selecting the period of the MQW structure selective scattering of phonons is realized [6, 7].

3. Results and discussion

This work presents the results of an investigation into transport phenomena (primarily thermal conductivity) in solid solutions of the system $(TlBiS_2)_{1-x}(2PbS)_x$. The objective of the investigation consists in studying the possibility of obtaining new effective thermoelectric materials based on the A^4B^6 semiconductor group. The basic conceptual approach is traditional—to increase the thermoelectric effectiveness of alloys by decreasing their lattice thermal conductivity. To achieve our objectives, we need to determine the changes (with composition) of the lattice thermal conductivity K_L in alloys of the $(TlBiS_2)_{1-x}(2PbS)_x$ system for cases when substitution in the cation sublattice occurs according to the scheme $2A^{4(+2)} \rightarrow A^{3(+1)} + B^{5(+3)}$.

Ternary compounds of the type $TlB^5C_2^6(B^5$—Bi, Sb, As; C^6—Te, Se, S) are isoelectronic analogues of binary A^4B^6 semiconductors [5]. $TlBiS_2$ melts congruently at $740\,°C$, crystallizes into a rhombohedral lattice (with space group symmetry D_3^5d) and has a band gap width E_g at room temperature of 0.42 eV. Unlike most known semiconductors, the band gap width in $TlBiS_2$ semiconductors increases with increase in temperature [5, 8]. Taking into account the above mentioned data and the fact that in the periodic table Tl precedes Pb and Bi follows it, so $TlBiS_2$ compounds can be regarded as 'pseudo' PbS. With lead sulfide $TlBiS_2$ compounds form wide intervals (equilibrated at room temperature) of solid solution [5, 9]. At $T > 600\,°C$ in $(TlBiS_2)_{1-x}(2PbS)_x$ systems a continuous solid solution is formed, but at a moderate speed of cooling (in an unconnected furnace regime) in the range of composition $0.12 < x < 0.40$ alloys suffer phase disaggregation, and samples of this composition interval at $T < 600\,°C$ become two phases. For a comparatively higher speed of cooling (chilling samples from $T = 720\,°C$ in a basin with liquid nitrogen) alloys of the composition interval $0.12 < x < 0.40$ keep a cubic (single phase) structure for an unlimited time at room temperature. It is important to denote that as a result of disaggregation alloys of the concentration interval $0.12 < x < 0.40$ become two phases but they keep quite a good chemical homogeneity. The alloys have a shallow disperse structure reminiscent of a eutectic. Shallow disperse phases present saturated solid solutions of composition $x = 0.12$ and 0.40 with rhombohedral and cubic structures respectively.

Table 1. Carrier concentrations and their mobilities for $(TlBiS_2)_{1-x}(PbS)_x$ alloys at different temperatures.

n, μ	$x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1.0$
$n_{77\,K}(10^{19}\ cm^{-3})$	2.94	3.07	2.30	2.94	1.28
$n_{300\,K}(10^{19}\ cm^{-3})$	5.17	4.73	2.81	3.45	1.63
$\mu_{77\,K}\ (cm^2\ V^{-1}\ s^{-1})$	1200	158	96	122	632
$\mu_{300\,K}\ (cm^2\ V^{-1}\ s^{-1})$	229	76	41	76	381

The choice of the $TlBiS_2$–PbS section from $A^3B^5C_2^6$–A^4B^6 type systems is not by chance but is dictated by the focus of this work. The $TlBiS_2$–PbS system is more suitable for this task because the energetic spectrum of charge carriers in $TlBiS_2$ is almost parabolic [8] as in PbS [3, 4]. Moreover energy gaps in $TlBiS_2$ and in PbS are close in value ($E_g = 0.42$ and 0.40 eV respectively) and they have a similar temperature dependence ($dE_g/dT > 0$) [5, 8]. In this connection the energetic spectrum of intermediate alloys remains unchanged with respect to the energetic spectrum characteristic of their start phases. Such a simplified model is very appropriate for trustworthy determination of the Lorentz number and then the electronic part of the thermal conductivity for each alloy.

Synthesis of $(TlBiS_2)_{1-x}(PbS)_x$ alloys was carried out using a method developed in [9]. Polycrystalline samples were prepared using a powder metallurgy approach (cold compacted with consequent sintering of chips). The investigated alloys had n-type conductivity. Ohmic contacts to the samples were made by electric welding. The total thermal conductivity of samples was measured by the stationary comparative method at room temperature. A measurement accuracy of about 5–7% was achieved at the expense of the use of standard thin plates of Bi_2Te_3 of both n- and p-type and also due by the use in the experimental installation of materials with well-known thermal conductivities such as NaCl, melted quartz, etc.

The temperature dependence of electrical conductivity $\sigma = f(T)$ and thermopower $S = f(T)$ for $(TlBiS_2)_{1-x}(PbS)_x$ alloys in the temperature interval 77–300 K has a metallic character [5]. The concentration of free carriers and their mobility were determined at 77 and 300 K (table 1) on the basis of data about electrical conductivity and Hall coefficient.

The data for the concentration interval $0.10 < x < 0.40$ are related to single-phase samples which were obtained by chilling these samples from temperatures higher than the cupola disaggregation temperature.

During all the intervals of changing alloy composition the carrier concentration changes within the limits of an order. For alloys in the interval $0.40 \leqslant x \leqslant 1.00$ with a cubic structure the concentration of charge carriers practically does not change with temperature in the interval 77–300 K. This permits us to suppose that alloys of the indicated composition interval have a high value of static dielectric permeability and as a result impurities are already ionized at low temperature (at least at 77 K). In such circumstances it can be concluded that alloys of the composition interval $0.40 \leqslant x \leqslant 1.00$ inherit properties of PbS.

The dependences of electrical conductivity on composition of alloys at 77 and 300 K for the $(TlBiS_2)_{1-x}(PbS)_x$ system are shown in figure 1. Change in the thermopower in dependence on their composition at 90 and 300 K is shown in figure 2.

As can be seen at about $x = 0.50$ the dependence $\sigma = f(C)$ passes through a minimum while the dependence $S = f(C)$ at this composition passes through a small maximum (141.3 μV K^{-1}). Further absolute value of thermopower S decreases, about $X = 0.80$ it passes through a minimum (102.5 μV K^{-1}), then it increases up to value corresponding to PbS (211.9 μV K^{-1}).
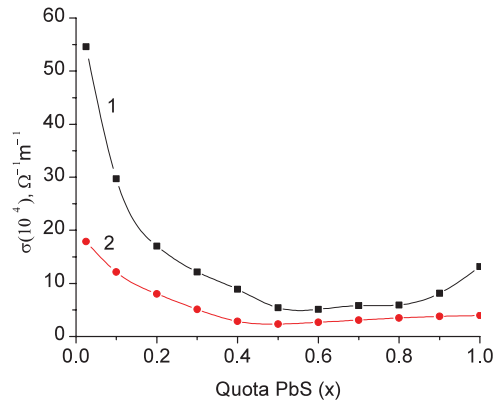
Figure 1. Electrical conductivity of the $(TlBiS_2)_{1-x}(PbS)_x$ alloys as a function of composition x at 77 (1) and 300 K (2).

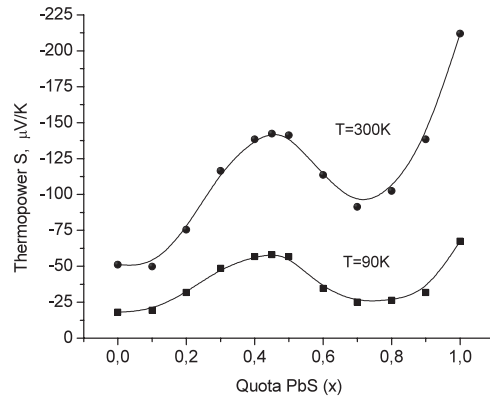**Figure 2.** Thermopower of the $(TlBiS_2)_{1-x}(PbS)_x$ alloys as a function of composition x at different temperatures.

The dependence of total thermal conductivity K of $(TlBiS_2)_{1-x}(PbS)_x$ alloys on their composition at room temperature is shown in figure 3.

As can be seen in intermediate alloys the coefficient of total thermal conductivity decreases greatly with changing composition: at about $x = 0.50$ the dependence $K = f(C)$ passes through a minimum. It is important to note that the value of K in the area of the minimum in the $K = f(C)$ curve is almost six times less than the total thermal conductivity of PbS. The Wiedemann–Franz law (6) was used for determination of the electronic part of the thermal conductivity. We used the following as an approximation of the dispersion parabolic law, applied to both PbS [3, 4] and $TlBiS_2$ [5, 8] and also appropriate for intermediate alloys and the elastic mechanism of carrier scattering [10]:

$$L = \left(\frac{k_o}{e}\right)^2 \left\{ \frac{(r + 7/2) F_{r+5/2}(\zeta^*)}{(r + 3/2) F_{r+1/2}(\zeta^*)} - \frac{(r + 5/2)^2 F_{r+3/2}^2(\zeta^*)}{(r + 3/2)^2 F_{r+1/2}^2(\zeta^*)} \right\}. \tag{8}$$

The value of the Lorentz number for each alloy composition has been determined. In expression (8) F_n is the Fermi integral, r is a parameter determined by carrier scattering mechanisms and ζ is the normalized level of the chemical potential. This was determined
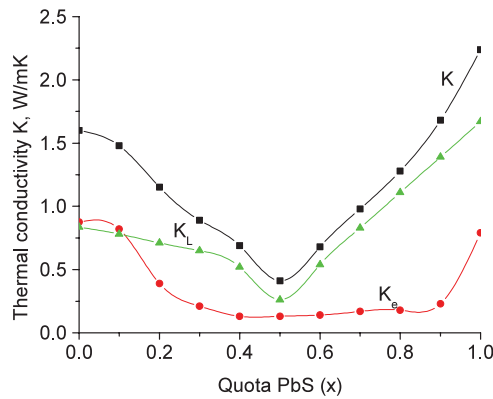
Figure 3. Thermal conductivity of $(TlBiS_2)_{1-x}(PbS)_x$ alloys as a function of composition x at 300 K; K_L is the lattice part, K_e is due to the charge carriers, K is total thermal conductivity.

from thermopower by the expression [11]

$$S = \frac{k_o}{e} \left\{ \frac{(r + 5/2) F_{r+3/2}(\zeta^*)}{(r + 3/2) F_{r+1/2}(\zeta^*)} - \zeta^* \right\} \tag{9}$$

for an area of extrinsic conductivity at an arbitrary degree of degeneration. According to data for the transverse Nernst–Ettingshausen effect [12], for the parameter r we took a value of $-1/2$, which corresponds to scattering mainly on acoustic phonons.

Thus values of the electronic part of the thermal conductivity K_e and lattice K_L are determined for each composition and are represented in figure 3. For an alloy with $x = 0.50$ the lattice thermal conductivity decreases down to 0.26 W m^{-1} K^{-1}, only 17% of the value of lattice thermal conductivity of PbS (1.67 W m^{-1} K^{-1}). It should be noted that in alloys of PbTe–PbSe solid solutions the lattice part of thermal conductivity for composition in a vicinity of a minimum of curve $k = f(C)$ is 53% of the lattice thermal conductivity of PbTe [13]. In the Bi_2Te_3–Sb_2Te_3 system in the area of the minimum of the curve $k = f(C)$ the lattice thermal-conductivity of appropriate alloys is 66% of the lattice thermal conductivity of Bi_2Te_3 [14]. So in the $(TlBiS_2)_{1-x}(2PbS)_x$ system a stronger decrease in lattice thermal conductivity K_L is realized than usually takes place in so-called, established thermoelectric systems of types Bi–Sb, Bi_2Te_3–Sb_2Te_3 and PbTe–PbSe. Such a low value of thermal conductivity ($K = 0.7$ W m^{-1} K^{-1}) for crystalline semiconductors was shown earlier in Tl_9BiTe_6 chips [15]. In our case the thermal conductivity of alloys in the area $x = 0.50$ gives $K = 0.41$ W m^{-1} K^{-1}, comparable (at $T > 100$ K) with the thermal conductivity of clathrates of the type $Sr_4Eu_4Ga_{16}Ge_{30}$ ($K \geqslant 0.82$ W m^{-1} K^{-1}) [7] and skutterudites ($K \geqslant 1$ W m^{-1} K^{-1}) [16], some of which exhibit nearly glass-like behaviour.

The power factor $S^2\sigma$ (figure 4) and the figure of merit Z (figure 5) for alloys of the $(TlBiS_2)_{1-x}$–$(2PbS)_x$ system was determined on the basis of data obtained for electrical conductivity σ, thermopower S and total thermal conductivity K. As can be seen, the dependence $Z = f(C)$ in the area of composition $x = 0.50$ passes through a maximum. For alloys of composition $x = 0.50$ the value of Z exceeds by $\sim$25% the respective value for PbS.

It is important to note that the alloys of the investigated system (including an $x = 0.5$ alloy) were not specially annealed in order to optimize the power factor $S^2\sigma$. Such a behaviour of the $Z = f(C)$ curve is mainly due to the nature of the change of lattice thermal conductivity in the studied alloys. The obtained value of lattice thermal conductivity $K_L = 0.26$ W m^{-1} K^{-1}

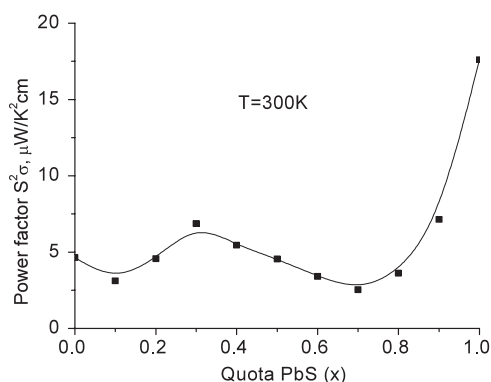**Figure 4.** Power factor of the $(TlBiS_2)_{1-x}(2PbS)_x$ alloys as function of composition x.

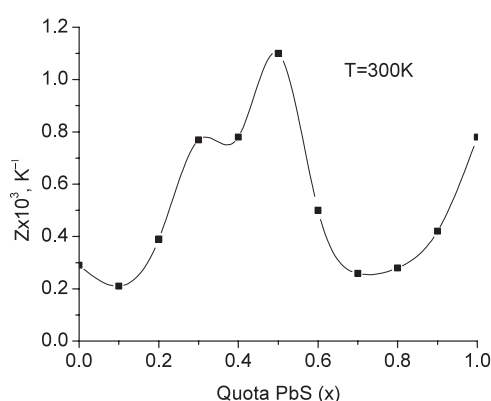**Figure 5.** Plot of the figure of merit Z of $(TlBiS_2)_{1-x}-(2PbS)_x$ alloys as a function of composition at 300 K.

for $(TlBiS_2)_{1-x}(2PbS)_x$ alloys in the area $x = 0.50$ is actually close to the theoretical estimate for the minimum that can be achieved in bulk crystalline semiconductors. According to [17] the minimum value of lattice thermal conductivity K_L for most semiconductors is estimated to be around $0.25 \text{ W m}^{-1} \text{ K}^{-1}$.

Such a behaviour of lattice thermal conductivity in alloys of the $(TlBiS_2)_{1-x}(2PbS)_x$ system can be explained by some additional contributions from scattering phonons.

One of the reasons for additional scattering is connected with the amplification of oscillation anharmonicity due to the presence of up to three types of heavy atoms of Tl, Pb and Bi in the cation sublattice. It is well known [1] that the random fluctuations of mass in solid solutions act as centres which scatter more effective high-frequency phonons. Apart from scattering due to alloying, the presence of grain boundaries can also contribute to the scattering of phonons. Grain boundaries mainly scatter [6] low-frequency phonons.

4. Conclusions

The investigation into transport properties of $(TlBiS_2)_{1-x}(2PbS)_x$ alloys has shown new possibilities for obtaining thermoelectrics with properties similar to A^4B^6 semiconductors and opened new paths to increase the thermoelectric effectiveness of the established thermoelectric

materials, lead chalcogenides. Using the example of the $(TlBiS_2)_{1-x}(2PbS)_x$ system it is shown that in solid solutions of the type $(A^3B^5C_2^6)_{1-x}$–$(2A^4B^6)_x$ upon substitution of one type of cation in the respective sublattice by two types according to the scheme $2A^{4(+2)} \rightarrow A^{3(+1)} + B^{5(+3)}$ a stronger decrease in lattice thermal conductivity than in a solid solution system A^4B^6–A^4B^6 with one type of cation (or anion) substitution is realized. Further progress may be achieved by investigating the thermoelectric properties of $(TlBiS_2)_{1-x}(2PbS)_x$ alloys at significantly higher temperature and by studying the possibility of adjustment of electrical parameters (power factor) of these alloys by variation of their composition and charge carrier concentration.

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