Thermal conductivity of $Sb_{2-x}In_xTe_3$ single crystals

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Abstract

$Sb_{2-x}In_xTe_3$ single crystals (x = 0.0; 0.1; 0.2 and 0.4) were prepared from the elements Sb, In, and Te of 5N purity by a modified Bridgman method. The obtained crystals were characterized by measurements of the temperature dependence of the electrical conductivity, Seebeck coefficient and thermal conductivity in the temperature range of 5-300 K. Subtracting the electronic component of thermal conductivity κ_e from the total thermal conductivity κ we obtain the lattice thermal conductivity κ_L. At low temperatures, κ_L data up to 100 K can be fitted well using Debye model considering that phonons scatter on boundaries, point defects, charge carriers, and other phonons. κ_e was calculated from experimental values of resistivity ρ using Wiedemann-Franz relation $\kappa_e = LT/\rho$, where L is the Lorenz number and T is the absolute temperature. In order to evaluate the effect of the scattering mechanism on the magnitude of κ_e, the value of the Lorenz number was determined for various scattering mechanism (acoustic phonons, optical phonons, ionized impurities) and assuming that the studied crystals are degenerate semiconductors, thus $L = L_0 = (\pi^2/3)(k_B/e)^2$.

Introduction

Antimony telluride Sb_2Te_3 belongs to the layered-type semiconductors with tetradymite structure (space group D^5_{3d}). This compound is a component of materials which are used for the construction of thermogenerators and solid-state coolers. P-type $Bi_{0.5}Sb_{1.5}Te_3$ is used for these applications [1]. Therefore, an investigation of the ternary crystals of the tetradymite-type based on Sb_2Te_3 is interesting both for basic and applied research.

Samples of the Sb_2Te_3-In_2Te_3 system, i.e. $Sb_{2-x}In_xTe_3$ ternare solid solutions, have been studied in a number of papers. Considerable attention has been devoted to determine the phase diagram and mutual solubility of both components [2-5]. Ternary single crystals $Sb_{2-x}In_xTe_3$ have been characterized in papers [6-8] by measurements of the Hall coefficient, electrical conductivity, Seebeck coefficient, reflectivity in the range of the plasma resonance frequency and transmittance spectra in the infrared region. The values of the transport coefficients and optical properties indicate that the concentration of free charge carriers drops with increasing concentration of In atoms built into the Sb_2Te_3 crystal lattice; this fact has been explained in papers [6,8] by the idea of interaction of substitutional In_{Sb}^{x} defects with anti-site $Sb_{Te}^{/}$ defects in the Sb_2Te_3 crystal lattice. The model of the point defects in the $Sb_{2-x}In_xTe_3$ crystal lattice has also been presented [9]. The valence-band of the $Sb_{2-x}In_xTe_3$ single crystals has been characterized by measurements of the Shubnikov-de Haas effect and photoinduced "transient thermoelectric effect" [10] and, based on the analysis of the experimental data, a two-valence-band model for these crystals has been proposed. However, the temperature dependence of the thermal conductivity of $Sb_{2-x}In_xTe_3$ single crystals has not yet been studied.

In this paper, we present the results of measurements of the temperature dependence of electrical conductivity, Seebeck coefficient and thermal conductivity in the temperature range of 5-300 K. With the aim to elucidate how the thermal conductivity is affected by incorporation of indium atoms into the crystal lattice of Sb_2Te_3 we fit and analyze the temperature dependence of thermal conductivity of $Sb_{2-x}In_xTe_3$ single crystals.

Experimental

The starting polycrystalline materials for growing the single crystals were prepared from the elements Sb, Te, and In of 5N purity.

The polycrystalline materials were synthesized in conical quartz ampoules charged with quantities of Sb, Te and In in the ratio corresponding to the stoichiometry $Sb_{2-x}In_xTe_3$ (x = 0.0; 0.1; 0.2 and 0.4). The charged ampoules were then evacuated to a pressure of 10^{-4} Pa and sealed. The synthesis was carried out in a horizontal furnace at a temperature of 1073 K for 48 hours.

The single crystals were grown using the Bridgman method. A conical quartz ampoule, containing the synthesized polycrystalline material, was placed in the upper (warmer) part of the Bridgman furnace, where it was annealed at 1003 K for 24 hours. Then it was lowered into a temperature gradient of 400 K/5 cm at a rate of 1.3 mm/h.

To determine their physical properties, the samples of the dimensions of 10x3x3 mm^3 were cut out from the middle part of the single crystals.

Seebeck coefficient (thermopower) and thermal conductivity were determined using a longitudinal steady-state technique in a cryostat equipped with a radiation shield. Thermal gradients were measured with the aid of fine chromel-constantan differential thermocouples, and a miniature strain gauge served as a heater. For the Seebeck probes we used fine copper wires that have previously been calibrated and their thermopower contribution was subtracted from the measured thermopower. The electrical conductivity has been studied using a Linear Research ac bridge with 16 Hz excitation. Measurements of these parameters were made over the temperature range of 5-300K.

Results and discussion

The results of the measurement of temperature dependences of Seebeck coefficient $\alpha(\Delta T \perp c)$ and electrical conductivity $\sigma_{\perp c}$ are presented in Figures 1 and 2.

From the obtained results it can be seen that the incorporation of In atoms into the Sb_2Te_3 crystal structure results in an increase of the Seebeck coefficient; the values of the electrical conductivity with increasing content of indium

in the samples decrease. This implies that In-doping of Sb_2Te_3 crystal structure leads to a decrease in the concentration of holes. This result agrees well with the conclusions reported in previous papers [2,5-10].

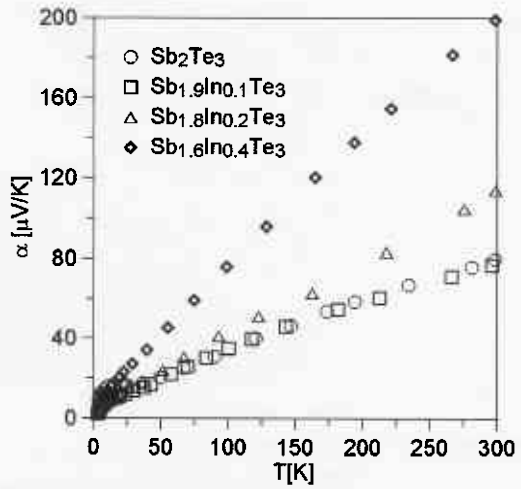

Figure 1. Temperature dependence of the Seebeck coefficient $\alpha(\Delta T \perp c)$ of $Sb_{2-x}In_xTe_3$ single crystals.

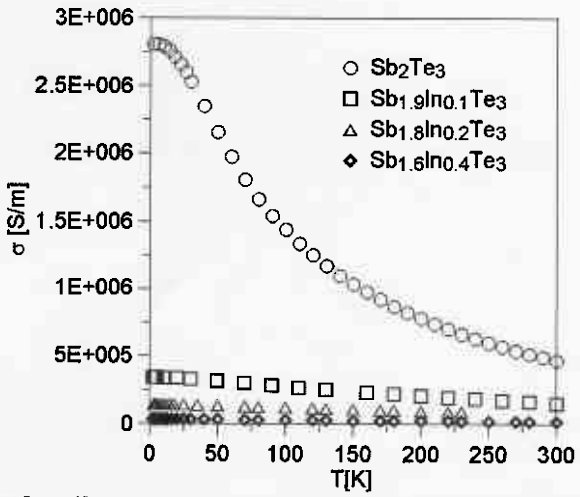

Figure2. Temperature dependence of the electrical conductivity $\sigma_{\perp c}$ of $Sb_{2-x}In_xTe_3$ single crystals.

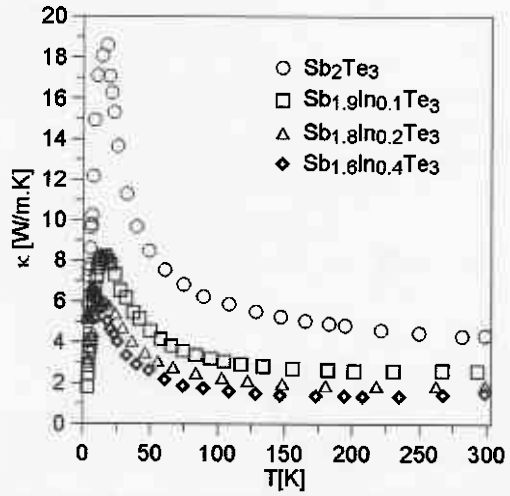

Figure 3. Temperature dependence of the total thermal conductivity κ of $Sb_{2-x}In_xTe_3$ single crystals.

Temperature dependencs of the total thermal conductivity κ are given in Fig. 3. The values of κ for Sb_2Te_3 increase as temperature decreases and the dependence $\kappa = f(T)$ develops a peak at a temperature near 13 K. Below the peak, κ decreases with an appropriate T^2 dependence. It is evident, that the incorporation of In atoms into the Sb_2Te_3 crystal structure results in the suppression of this low-temperature peak.

Total thermal conductivity κ, in general, is the sum of two components; i.e., $\kappa = \kappa_L + \kappa_e$ where κ_e and κ_L are the electronic and lattice thermal conductivity contributions, respectively.

The exact calculation of κ_e is complicated by the likely presence of two valence bands [10] the parameters of which are not well established. Therefore as an approximation for the following discussion we will consider only one type of holes. The electronic component of the thermal conductivity κ_e was calculated from experimental values of resistivity ρ using the Wiedemann-Franz relation $\kappa_e = LT/\rho$, where L is the Lorenz number and T is the absolute temperature. In order to evaluate the effect of the scattering mechanism on the magnitude of κ_e, the value of the Lorenz number was determined from the general expression [11]

$$L = \left(\frac{k_B}{e}\right)^2 \left\{ \frac{(s+7/2)F_{s+5/2}(\eta)}{(s+3/2)F_{s+1/2}(\eta)} - \left[\frac{(s+5/2)F_{s+3/2}(\eta)}{(s+3/2)F_{s+1/2}(\eta)}\right]^2 \right\} \qquad (1)$$

where the value of s=-1/2 corresponds to the scattering on acoustic phonons, s=1/2 to the scattering on optical phonons and s=3/2 to the scattering on ionized impurities. The necessary Fermi level values η were calculated from the experimental values of the Seebeck coefficient using the expression [12]

$$\alpha = \pm\frac{k_B}{e}\left(\frac{(s+5/2)F_{s+3/2}(\eta)}{(s+3/2)F_{s+1/2}(\eta)} - \eta\right). \qquad (2)$$

As the temperature dependences of the Seebeck coefficient in the temperature region below 50 K are influenced by the phonon drag, the calculations were carried out only for temperatures above 50 K.

The values of the electronic component of thermal conductivity κ_e were also calculated under the assumption that Sb_2Te_3 can be considered as a degenerate semiconductor. For the calculation of κ_e from the experimental data of electrical resistivity we have used a constant value of the Lorenz number $L = L_o = (\pi^2/3)(k_B/e)^2$, the so-called Sommerfeld value. The results of the calculations are summarized in Figure 4.

It is evident that the differences in the values of κ_e calculated for different scattering mechanism for a degenerate semiconductor are negligible at temperatures below 100 K. Therefore for calculations of the lattice component of thermal conductivity $\kappa_L = \kappa - \kappa_e$, in the temperature region 5-100 K, we have used the value of κ_e obtained using the constant value of the Lorenz number L_o. We note that this simplification is in accordance with discussion presented in [13]. The calculated temperature dependences of κ_L are presented in Figure 5.

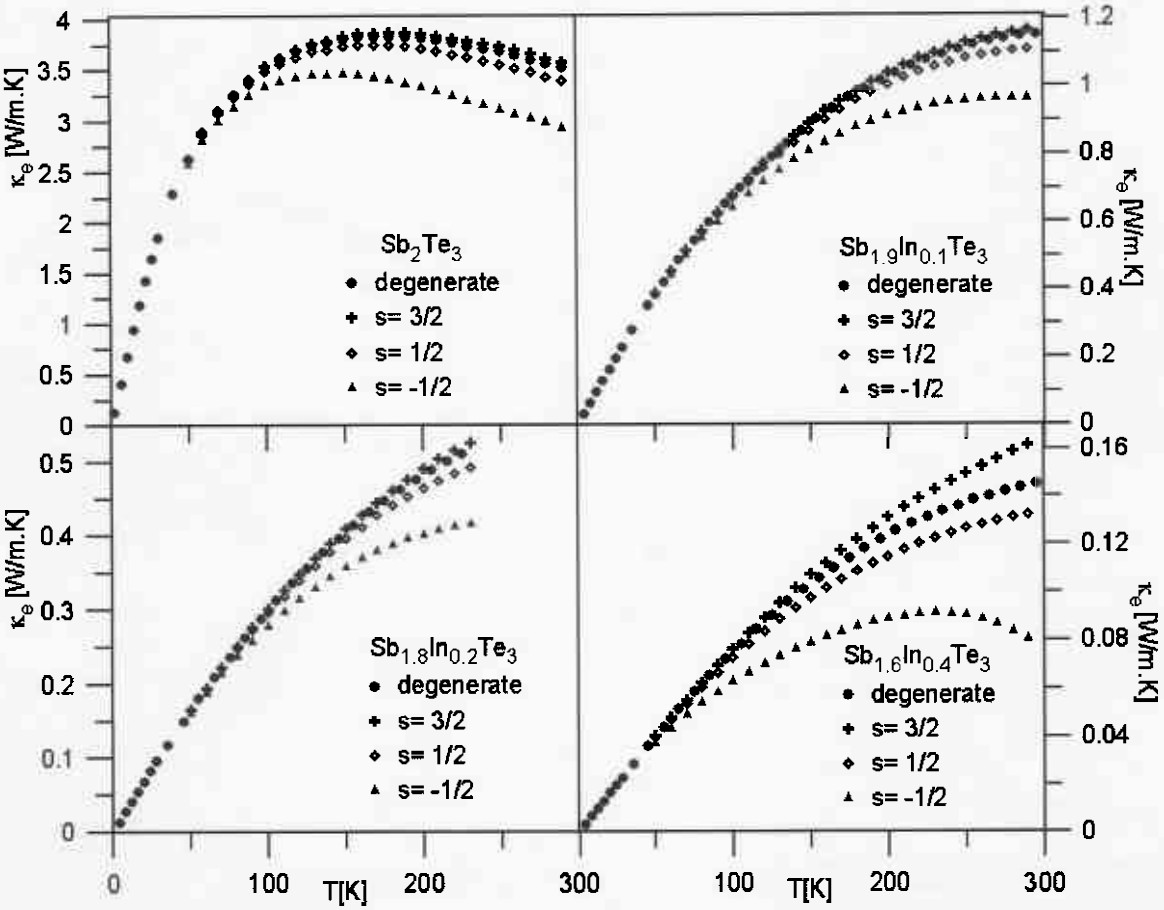

Figure 4. Temperature dependences of the electronic component of thermal conductivity κ_e of $Sb_{2-x}In_xTe_3$ single crystals assuming different scattering mechanisms.

From this figure we can see that In-doping of Sb_2Te_3 crystal structure results in a decrease in the lattice component of the thermal conductivity. Temperature dependences of the lattice thermal conductivity $\kappa_L = f(T)$ have been fitted within the Debye approximation using the following expression [15]:

$$\kappa_L(T) = \frac{k_B}{2\pi^2 v}\left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_C \frac{y^4 e^y}{\left(e^y - 1\right)^2} dy \qquad (3)$$

where k_B is the Boltzmann constant , $\hbar$ is the reduced Planck constant, y stands for dimensionless parameter $y = \hbar\omega/k_BT$, ω is the phonon frequency, θ_D is Debye temperature, v is the velocity of sound, and τ_C is phonon relaxation time. This relaxation time can be written in terms of individual scattering times accounting for various scattering processes as

$$\tau_C^{-1} = \frac{v}{d} + A\omega^4 + B\omega^2 T \exp\left(-\frac{\theta_D}{3T}\right) + C\omega \cdot \qquad (4)$$

Here d is the crystal dimension (d = 2mm here for the smallest one) and the coefficients A, B, and C are temperature independent fitting parameters. The terms in Eq. (4) stand for boundary, point-defect, three-phonon umklapp, and carrier-phonon scattering, respectively. The first three terms account for phonon scattering in dielectric crystals. The fourth term represents relaxation time for scattering of phonons by free carriers in a parabolic band.

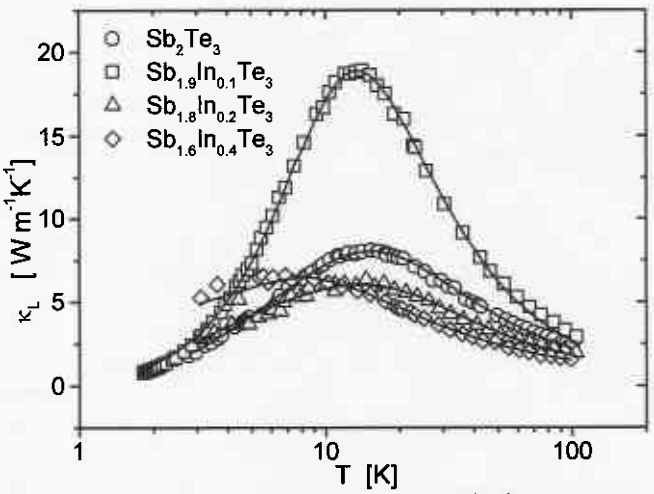

Figure 5. Temperature dependences of the lattice component of thermal conductivity κ_L of $Sb_{2-x}In_xTe_3$ single crystals. The solid lines through the data are theoretical fits to Eqs. (3) and (4).

Experimental dependences $\kappa_L = f(T)$ (points in Fig. 5) were fitted in accordance with discussion presented in [13] and parameters given in [14]. The obtained results -- the values of the coefficients A, B and C are summarized in Table 1.

Samples	$A(10^{-43}s^3)$	$B(10^{-18}s.K^{-1})$	$C(10^{-3})$
Sb_2Te_3	9.65	27	8.2
$Sb_{1.9}In_{0.1}Te_3$	95	20	9.0
$Sb_{1.8}In_{0.2}Te_3$	290	15.4	4.5
$Sb_{1.6}In_{0.4}Te_3$	2312	3.1	0.025

Table 1 Fitting parameters for the theoretical analysis of the lattice thermal conductivity κ_L of $Sb_{2-x}In_xTe_3$ single crystals.

Upon inspecting the fitting parameters in Table 1, it is clear that the primary influence of indium on the lattice thermal conductivity of Sb_2Te_3 is reflected in the rapidly rising coefficient *A*, i.e., in the substantial increase in point defect scattering. We also note that the pre-factors *B* and *C* tend to decrease with the increasing concentration of In which implies the decrease in umklapp and free carrier scattering, respectively. The decrease of parameter *C* agrees well with the decrease in hole concentration.

For the evaluation of the suitability of materials for thermoelectric applications one usually makes use of the figure of merit $Z = \sigma\alpha^2/\kappa$ (where σ is the electrical conductivity, α is the Seebeck coefficient and κ is the total thermal conductivity). Temperature dependence of Z for $Sb_{2-x}In_xTe_3$ crystals is presented in Fig. 6. Based on the transport measurements we can state that In doping in the Sb_2Te_3 crystals does not improve the parameters decisive for thermoelectric applications. This is likely due to a significant decrease of free carrier mobility [6].

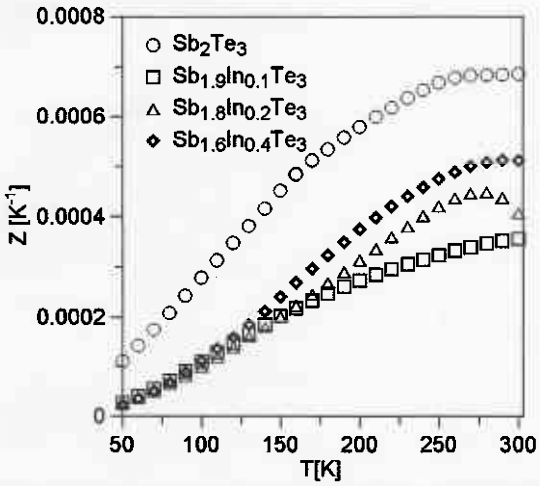

Figure 6. Temperature dependence of the figure of merit Z.

Conclusions

From the results of the characterization of $Sb_{2-x}In_xTe_3$ single crystals we have come to the following conclusions:

1. Doping of Sb_2Te_3 crystals by In-atoms results in a decrease in the hole concentration.

2. Lattice thermal conductivity can be fitted well assuming that phonons scatter on boundaries, point defects, charge carriers, and other phonons within the Debye approximation. Incorporation of In-atoms into Sb_2Te_3 crystal lattice affects primarily point defect scattering.

3. Doping Sb_2Te_3 crystals by In-atoms decreases the value of the figure of merit Z and, therefore, indium is not an effective dopant for thermoelectric materials of the tetradymite type used for thermoelectric applications.

Acknowledgement

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