Thermoelectric properties of $Sb_{2-x}Ag_xTe_3$ single crystals

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Abstract

$Sb_{2-x}Ag_xTe_3$ single crystals (x = 0.0; 0.014; 0.018 and 0.022) were prepared from the elements Sb, Ag, and Te of 5N purity by a modified Bridgman method. The obtained crystals were characterized by measurements of the temperature dependence of the electrical resistivity, Hall coefficient, Seebeck coefficient and thermal conductivity in the temperature range of 5-300 K. It was observed that with an increasing Ag content in the samples the electrical resistance, the Hall coefficient and the Seebeck coefficient decrease. This means that the incorporation of Ag atoms into the Sb_2Te_3 crystal structure results in an increase in the concentration of holes in the doped crystals. The observed effect is explained by a model of defects in the crystals. Subtracting the electronic component of thermal conductivity from the total thermal conductivity we obtain the lattice thermal conductivity κ_L. At low temperatures, κ_L has an approximate T^2 dependence and the data up to 100 K can be fitted well assuming that phonons scatter on boundaries, point defects, charge carriers, and other phonons.

1. Introduction

Antimony telluride Sb_2Te_3 belongs to the layered-type semiconductors with tetradymite structure (space group D_{3d}^5), which are used as materials for the construction of thermogenerators and solid-state coolers [1]. For the application of Sb_2Te_3 in these devices it is necessary to prepare single or polycrystalline materials with well defined physical parameters (electrical and thermal conductivity, mobility of free current carriers, thermoelectric power) which can be modified by doping with suitable foreign atoms. Therefore, an investigation of the effect of various dopants on the physical properties of Sb_2Te_3 is interesting both for basic and applied research.

The influence of silver impurity atoms on physical properties of Sb_2Te_3 single crystals has been studied in several papers [2-4]. The crystals $Sb_{2-x}Ag_xTe_3$ and $Sb_2Ag_xTe_3$ were characterized by the measurements of plasma resonance frequency, electrical conductivity and Hall coefficient in papers [2,3]. It was found that the hole concentration increases with Ag-concentration for both crystal series. This effect was ascribed to the formation of substitutional defects $Ag_{Sb}^{//}$. The Hall coefficient, electrical resistivity, and Shubnikov - de Hass effect were studied on $Sb_2Ag_xTe_3$ crystals in paper [4]. Ag in the Sb_2Te_3 lattice was shown to be an acceptor. Measurements of the Shubnikov-de Haas effect revealed that the incorporation of Ag atoms has no effect on the energy spectra.

Studies of the Seebeck coefficient and thermal conductivity of Ag-doped Sb_2Te_3 crystals have however not yet been done.

In the present paper, samples of $Sb_{2-x}Ag_xTe_3$ single crystals are characterized by measurements of the temperature dependence of electrical resistance, Hall coefficient, Seebeck coefficient and thermal conductivity in the temperature range of 5-300 K, with the aim to investigate how these quantities are affected by incorporation of silver atoms into the crystal lattice of Sb_2Te_3.

2. Experimental

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

The starting polycrystalline materials were prepared from a mixture of Sb, Te, and Ag, corresponding to the stoichiometry $Sb_{2-x}Ag_xTe_3$, in silica ampoules evacuated to a pressure of 10^{-4} Pa. The synthesis was carried out in a horizontal furnace at 1073 K for 48 h.

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.

The obtained single crystals, 50 mm in length and 10 mm in diameter, could be easily cleaved. Their trigonal axis (c-axis) was always perpendicular to the pulling direction so that the (0001) plane was parallel to the ampoule axis. The orientation of the cleavage faces was carried out using the Laue back-diffraction technique which confirmed that these faces were always (0001).

To determine their physical properties, samples with dimensions of 10x3x3 mm^3 were cut out from the middle part of the single crystals. The concentration of silver in these samples was determined by atomic emission spectrometry (AES).

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 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 subtracted from the measured sample thermopower. The Hall effect and electrical conductivity were studied using a Linear Research ac bridge with 16 Hz excitation in a magnet cryostat capable of fields up

to 5T. Measurements of these parameters were made over the temperature range of 5-300K.
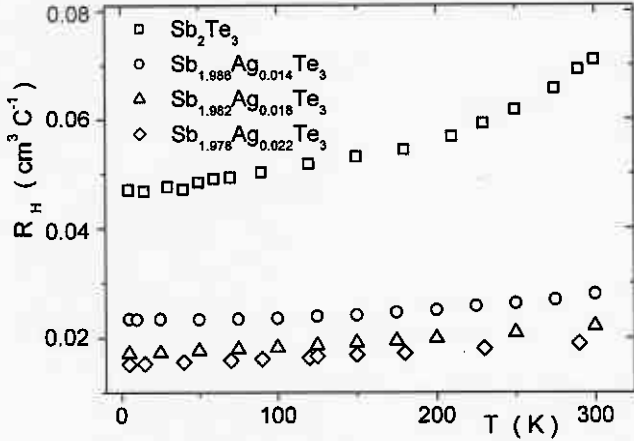

Figure 1. Temperature dependence of the Hall coefficient $R_H(B\|c)$ of $Sb_{2-x}Ag_xTe_3$ single crystals.

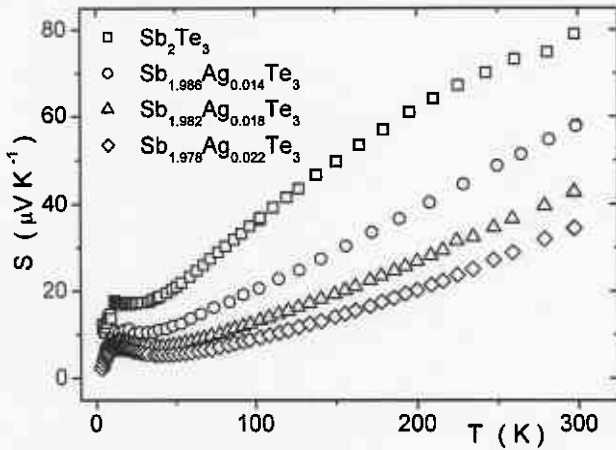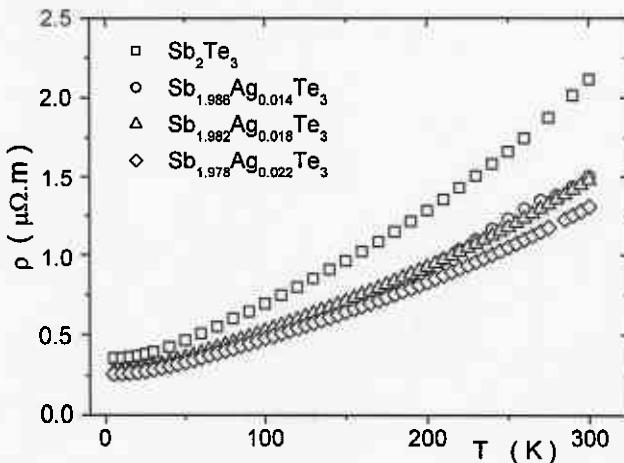**Figure 2.** Temperature dependence of the Seebeck coefficient $S(\Delta T \perp c)$ of $Sb_{2-x}Ag_xTe_3$ single crystals.

Figure 3. Temperature dependence of the electrical resistivity $\rho_{\perp c}$ of $Sb_{2-x}Ag_xTe_3$ single crystals.

**Table 1.** Values of the transport parameters at T = 300 K for $Sb_{2-x}Ag_xTe_3$ single crystals

No.	x	$\rho_\perp$ [$u\Omega$/m]	$R_H(B\|c)$, [cm^3/C]	$\alpha(\Delta T \perp c)$ [μV/K]
1	0	2.12	0.071	79
2	0.014	1.50	0.028	58
3	0.018	1.48	0.022	43
4	0.022	1.41	0.019	35

3. Results and discussion

The temperature dependences of Hall coefficient $R_H(B\|c)$, Seebeck coefficient $S(\Delta T \perp c)$ and electrical resistivity $\rho_{\perp c}$ are presented in Figures 1–3. The values of these parameters at T=300 K are summarized in Table 1.

From the obtained results it can be seen that the incorporation of Ag atoms into the Sb_2Te_3 crystal structure leads to a decrease of all investigated parameters. This implies that Ag-doping of the Sb_2Te_3 crystal structure produces an increase in the concentration of holes. This result agrees well with the conclusions reported in papers [2-4].

In agreement with papers [2,3], an increase in the hole concentration due to Ag doping can be explained by the incorporation of Ag atoms into the Sb-sublattice, i.e. by the substitution of Ag atoms for Sb atoms. The formation of these substitutional defects can be described by the following equation

$$2V_{Sb}^{///} + 3V_{Te}^{\cdot\cdot} + 2Ag + 3Te = 2Ag_{Sb}^{//} + 3Te_{Te} + 4h^\cdot \quad (1)$$
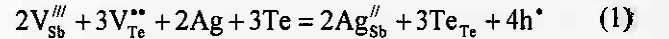
where $V_{Sb}^{///}$ and $V_{Te}^{\cdot\cdot}$ are vacancies in the antimony and tellurium sublattice, respectively, Te_{Te} are Te atoms in the Te-sublattice, and $h^\cdot$ are holes. In Eq.1 we suppose that every 2 incorporated Ag atoms are accompanied by 3 incorporated Te atoms. This assumption was based upon the fact that during the synthesis of the doped crystals, the starting composition corresponded to the formula $Sb_{2-x}Ag_xTe_3$.

To quantify the enhancement of the free carrier density with the density of the incorporated Ag atoms in the crystal structure of Sb_2Te_3, it is first necessary to determine the concentration of free current carriers P. As the experimental data presented in this paper do not allow us to obtain an exact value of P, we have determined an approximate value of P from the measured Hall coefficient $R_H(B\|c)$ in the following way: We used the expression $R_H(B\|c) = \gamma \dfrac{r_H}{Pe}$, where e is the electron charge, γ the structure factor, and r_H the scattering factor in the Hall constant. For γ we have used the value of 0.74 given in the paper [5] and we assumed that the value of γ does not change with the incorporation of Ag into the crystal lattice of Sb_2Te_3. Moreover, we took the value of the scattering factor r_H to be close to unity, i.e. $r_H = 1$. The approximate values of P, obtained in this way, are given in Table 2.

Changes in the hole concentration were calculated as $\Delta P = P - P_0$ (where P_0 is the concentration of holes in the undoped Sb_2Te_3 crystal). The ratio of the change in hole concentration

Table 2. Free carrier concentration in $Sb_{2-x}Ag_xTe_3$ single crystals.

No.	c_{Ag} $[10^{19} cm^{-3}]$	P $[10^{19} cm^{-3}]$	ΔP $[10^{19} cm^{-3}]$	$\Delta P/c_{Ag}$
1	0	6.60	-	-
2	9.15	16.5	9.9	1.08
3	11.50	21.0	14.4	1.25
4	13.95	24.3	17.7	1.27

ΔP to the density of the incorporated Ag atoms, $\Delta P/c_{Ag}$, gives rise to an increase of hole concentration per one Ag atom as shown in the last column of Table 2. According to Eq.1, $\Delta P/c_{Ag}$ values should be close to 2. From Table 2 it is evident that one incorporated Ag atom produces approximately 1 hole only. This means that Ag displays a doping efficiency of roughly 50%. A possible explanation of this fact is that Ag
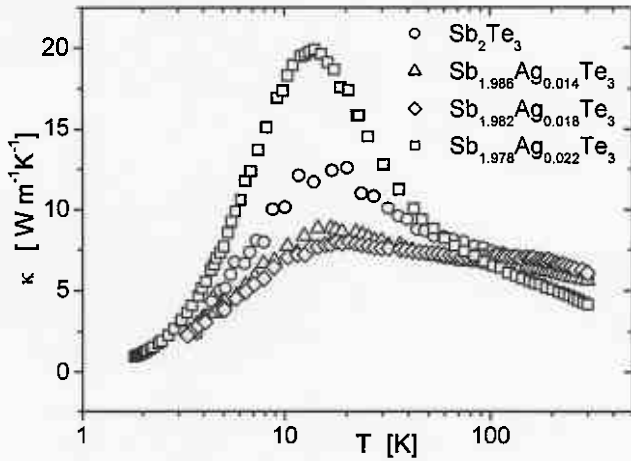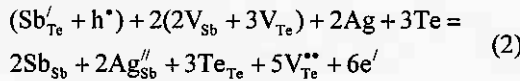

Figure 4. Temperature dependence of the thermal conductivity κ of $Sb_{2-x}Ag_xTe_3$ single crystals.

atoms interact with native defects of Sb_2Te_3. It is well known [6] that dominant defects in Sb_2Te_3 are antisite defects Sb_{Te}'. This interaction can be described by the following equation

$$(Sb_{Te}' + h^{\bullet}) + 2(2V_{Sb} + 3V_{Te}) + 2Ag + 3Te = 2Sb_{Sb} + 2Ag_{Sb}'' + 3Te_{Te} + 5V_{Te}^{\bullet\bullet} + 6e' \quad (2)$$

According to [3] the lower doping efficiency relates to the fact that some Ag atoms form four-layer lamellae $[Ag_{0.5}Sb_{0.5}]$-Te-$[Ag_{0.5}Sb_{0.5}]$-Te, which corresponds to the $AgSbTe_2$ structure. In this structure the crystal planes of the cation sublattice are occupied randomly with Sb and Ag atoms. Even the presence of Ag atoms at interstitial positions can not be excluded. We note that $Ag_i^{\bullet}$ are supposed to be present in isostructural Bi_2Te_3 [3].

Temperature dependence of the total thermal conductivity κ is given in Fig. 4.

The values of κ for Sb_2Te_3 increase as the temperature decreases and a peak develops at a temperature near 13 K. Below the peak, κ decreases with an approximate T^2 dependence. It is evident that the incorporation of Ag atoms into the Sb_2Te_3 crystal structure results in the suppression of

the values of thermal conductivity in the entire temperature region.

Total thermal conductivity κ, in general, is the sum of two components, $\kappa = \kappa_L + \kappa_e$ 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 the parameters of which are not well established [4]. Therefore as an approximation for the following discussion we will consider only one type of hole. The electronic component of the thermal conductivity κ_e was calculated from the experimental values of resistivity ρ using
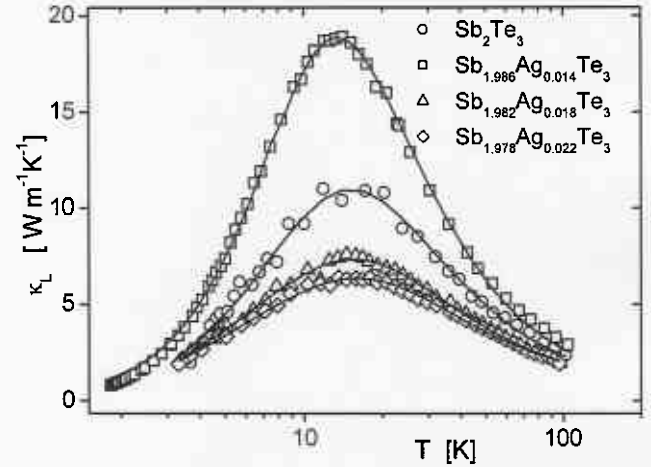

Figure 5. Temperature dependence of the lattice thermal conductivity κ_L of $Sb_{2-x}Ag_xTe_3$ single crystals (open symbols). The solid lines are fits to Eqs. 3 and 4, see text below.

the Wiedemann-Franz relation $\kappa_e = LT/\rho$, where L is the Lorenz number and T is the absolute temperature.

The values of the electronic component of thermal conductivity κ_e were calculated under the assumption that Sb_2Te_3 can be considered a degenerate semiconductor. To calculate 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. Substracting κ_e from the total thermal conductivity we obtain the lattice component κ_L. The calculated temperature dependences of κ_L are presented in Figure 5.

According to the discussion presented in [7], the approximation used in the calculation of κ_e of Sb_2Te_3 crystals is plausible for temperatures under 100K. Therefore, in Fig.5 κ_L is given for the temperature range of 5–100 K.

From this figure we can see that Ag-doping of the Sb_2Te_3 crystal structure results in a decrease in the lattice component of the thermal conductivity. Temperature dependences of κ_L have been fitted within the Debye approximation using the following expression [8]:

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

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

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

Here d is the crystal dimension ($d = 2$mm 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.

To make use of Eqs.3 and 4, one needs the Debye temperature θ_D. In fact, this temperature is strictly not a constant but is temperature dependent. While $\theta_D(T)$ is known for Bi_2Te_3 [9,10], the corresponding temperature dependence for Sb_2Te_3 is not available. We make an assumption that, while different in magnitude, the $\theta_D(T)$ of both Bi_2Te_3 and Sb_2Te_3 are similar. Accordingly, the temperature dependence of $\theta_D(Bi_2Te_3)$ was shifted to fit the value of $\theta_D(Sb_2Te_3) = 160$K at T=80K. This dependence was fitted and expressed by means of two polynomials

$$\theta_D \text{ (T=2-8K)} = 107.617 + 1.291T - 0.008T^2$$
$$\theta_D \text{ (T=8-100K)} = 91.258 + 3.188 - 0.064T^2 + 5.895e\text{-}4T^3 - 2.008e\text{-}6T^4$$

which, in turn, were used in fitting Eqs.3 and 4. The sound velocity was estimated in Ref. 7 to be $v = 2900$ m.s^{-1}. The results of the fit are summarized in Table 3 and in Fig. 5.

Upon inspecting fitting parameters in Table 3, it is evident that the primary influence of silver on the lattice thermal conductivity arises via the large increase in the point defect scattering parameter A. It can be written as [11]

$$A = \frac{\Omega\Gamma}{4\pi v^3} , \quad (6)$$

where Ω is the unit cell volume (for Sb_2Te_3 $\Omega = 0.161$ nm^3), Γ is the scattering parameter which for a compound A_aB_b can be written as [12]

$$\Gamma(A_aB_b) = \frac{a}{a+b}\left(\frac{M_A}{M_m}\right)^2 \Gamma(A) + \frac{b}{a+b}\left(\frac{M_B}{M_m}\right)^2 \Gamma(B), \quad (7)$$

where M_m is the mean atomic mass of atoms forming the compound, $M_m = (aM_a + bM_b)/(a+b)$. $\Gamma(A,B)$ is the scattering parameter of the substitutional impurity at the respective site ,

$$\Gamma(A,B) = \alpha(1-\alpha)[(\Delta M/M_{ave})^2 + \epsilon(\Delta\delta/\delta_{ave})^2] \quad (8)$$

where α is the relative concentration of impurity at the respective site ($\alpha = x/2$ in this case), $\Delta M = M_i - M(A,B)$ is the atomic mass difference between the impurity and an atom normally associated with that lattice site, $\Delta\delta = \delta_i - \delta$ is the difference in radii between the impurity and the atom normally associated with that lattice site, M_{ave} and δ_{ave} are the

Table 3. Fitting parameters for theoretical analysis of lattice thermal conductivity of $Sb_{2-x}Ag_xTe_3$ single crystals as they refer to Eqs.4 and 5.

No.	x (actual)	A (10^{-43}s^3)	B (10^{-18}s.K^{-1})	C (10^{-4})
1	0	9.6	27	0.82
2	0.014	31	27	1.2
3	0.018	97	23	1.1
4	0.022	140	20	1.0

Table 4. Values of the parameter ϵ and the ratio R of $Sb_{2-x}Ag_xTe_3$ single crystals resulting from the analysis of parameter A, see text for details.

No.	x (actual)	ϵ	R
2	0.014	183	170
3	0.018	192	440
4	0.022	211	500

weighted averages of mass and radius at that lattice site, respectively, and ϵ is the phenomenological parameter. The first term of Eq.8 accounts for mass fluctuation and the second term accounts for atomic radius fluctuations, i.e., elastic strain.

The exact radii of Sb and Ag in Sb_2Te_3 are unknown. The average distance between Sb and Te in the compound (0.311 nm) would rather support an ionic crystal picture ($r(Sb^{+3}) + r(Te^{-2}) = 0.90 + 2.07$ nm), than a covalent one ($r(Sb) + r(Te) = 1.37 + 1.36$ nm). To keep the things consistent we use for all elements the ionic crystal values and $r(Ag^{+1}) = 1.29$ nm [13].

The calculated values of the ϵ parameter and the ratio $R = \epsilon(\Delta\delta/\delta_{ave})^2/(\Delta M/M_{ave})^2$ are summarized in Table 4. The actual concentration (AES-value) was used for an evaluation. Increasing values of both ϵ and R may suggest the presence of more than one type (Ag''_{Sb}) of defect which dominate at different temperatures. Another possible explanation is the interaction of Ag''_{Sb} with native defects. As there is no direct evidence which one of the Ag-defects is dominant, (also the above discussion of transport data is ambiguous) the situation becomes very complex and any further discussion is likely pointless. We observe little change in both parameters B and C, which means that umklapp and electron-phonon interactions are not influenced by the incorporation of Ag in the Sb_2Te_3 matrix.

Suitability of materials for thermoelectric applications is usually judged by the thermoelectric figure of merit $Z = \sigma\alpha^2/\kappa$, where $\sigma = 1/\rho$ is the electric conductivity, α is the Seebeck coefficient and κ is the total thermal conductivity. Temperature dependence of Z for the $Sb_{2-x}Ag_xTe_3$ crystals is given in Fig. 6.

It is evident that Ag-doping of Sb_2Te_3 crystals leads to a decrease in the value of their figure of merit. In spite of the fact that the free carrier concentration of the samples is not optimized we can conclude that Ag-doping in Sb_2Te_3 crystals is unlikely to improve the parameters decisive for thermoelectric applications. Inspecting the transport data it is clear that upon Ag-doping the free carrier mobility decreases.
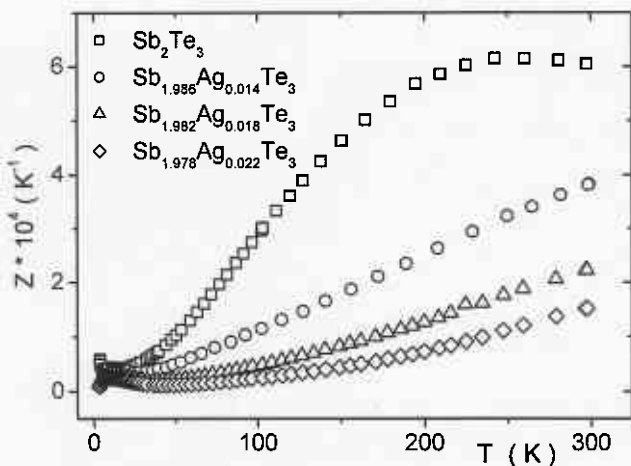
Figure 6. Temperature dependence of the figure of merit Z of $Sb_{2-x}Ag_xTe_3$ single crystals.

On the other hand, we note that doping of tetradymite-type crystals like Sb_2Te_3 and Bi_2Te_3 with transition metals can result in the preparation of novel materials with interesting magnetic properties. For example, $Sb_{2-x}V_xTe_3$ crystals have recently been shown to display properties characteristic of the diluted magnetic semiconductors [14].

Conclusions

From the results of the measurements of transport coefficients of $Sb_{2-x}Ag_xTe_3$ crystals we have come to the following conclusions:

1. Doping of Sb_2Te_3 crystals by Ag-atoms results in an increase in the hole concentration. We assume that this effect is due to the incorporation of Ag atoms into the Sb-sublattice and the formation of negatively charged substitutional defects of Ag_{Sb}''.

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 Ag-atoms into Sb_2Te_3 crystal lattice affects primarily point defect scattering.

3. Doping Sb_2Te_3 crystals by Ag-atoms decreases the value of the figure of merit Z, primarily because their carrier mobility is much depressed. Thus, silver is not an effective dopant of thermoelectric materials based on the tetradymite type structure.

References

1. Nolas, G. S., Sharp, J., Goldsmid, H. J., hermoelectric Basic Principles and New Materials Developments, Springer (Berlin, Heidelberg, 2001), pp. 111-131
2. Horák, J., Lošťák, P., Šiška, L., Stordeur, M., "The Nature of Silver Impurity Atoms in Antimony Telluride", *Phys. Status Solidi (b)*, Vol. 114 (1982), pp. 39-45
3. Navrátil, J., Klichová, I., Karamazov, S., Šrámková, J., Horák, J., "Behavior of Ag Admixtures in Sb_2Te_3 and Bi_2Te_3 Single Crystals", *J. Solid State Chem.*, Vol. 140 (1998), pp. 29-37
4. Kulbachinskii, V. A., Kaminskii, Yu., Kytin, V. G., Lošťák, P., Drašar, Č., de Visser, A., "Vliyanie serebra na galvanomagnitnye svoistva i energeticheskii spektr smeshannykh kristallov $(Bi_{1-x}Sb_x)_2Te_3$", *Zhur. Exper. Teor. Fiziki*, Vol. 117 (2000), pp. 1242-1250
5. Stordeur, M., Simon, G., "Investigation of the Weak-Field Charge Transport in Semiconducting V_2-VI_3 Compounds with Trigonal Symmetry", *Phys. Status Solidi (b)*, Vol. 124 (1984), pp. 799-806
6. Horák, J., Drašar, Č., Novotný, R., Karamazov, S., Lošťák, P., "Non-Stoichiometry of the Crystal Lattice of Antimony Telluride", *Phys. Status Solidi (a)*, Vol. 149 (1995), pp. 549-556
7. Dyck, J. S., Chen, W., Uher, C., Drašar, Č., Lošťák, P., "Heat Transport in $Sb_{2-x}V_xTe_3$ Single Crystals", *Phys. Rev. B*, Vol. 66, (2002), pp. 125206-1 – 125206-6.
8. Callaway, J., "Model for Lattice Thermal Conductivity at Low Temperatures", *Phys. Rev.*, Vol. 113 (1959), pp. 1046 -1051
9. Gultyaev P.V., Petrov A. V., "The Specific Heats of a Number of Semiconductors", Sov. Phys. Solid State. Vol. 1 (1959) pp.330-34
10. Shoemake G. E., Rayne J. A., Ure R. W., "Specific Heat of n-and p-Type Bi_2Te_3 from 1.4 to 90°K", *Phys. Rev.*, Vol. **185** (1969) pp.1046-1056
11. Klemens P. G., "The Scattering of Low-Frequency Lattice Waves by Static Imperfections", *Proc. Phys. Soc. London*, Vol. **A68** (1955) 1113-1128
12. Abeles B., "Lattice Thermal Conductivity of Disordered Semiconductor Alloys at High Temperatures", *Phys. Rev.*, Vol. **131** (1963) pp.1906-1911
13. Shannon R. D., "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides", *Acta Crystallographica*, Vol. **A32** (1976) pp.751-767
14. Dyck, J. S., Hájek, P., Lošťák, P., Uher, C., "Diluted Magnetic Semiconductors Based on $Sb_{2-x}V_xTe_3$ $(0.01 \leq x \leq 0.03)$", *Phys. Rev. B*, Vol. 65 (2002), pp. 115212-115217.