Thermoelectric Properties of Quaternary $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ Single Crystals

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Abstract

Crystals of a quaternary system based on $(Sb_{0.75}Bi_{0.25})_2Te_3$ doped with In were prepared using the Bridgman technique. Samples with varying content of In were characterized by the measurements of electrical conductivity $\sigma_{\perp c}$, Hall coefficient $R_H(B||c)$, Seebeck coefficient $\alpha(\Delta T\perp c)$ and thermal conductivity κ $(\Delta T\perp c)$. The measurements indicate that by incorporating In in $(Sb_{0.75}Bi_{0.25})_2Te_3$ one lowers the concentration of free holes. This effect is explained in terms of a point defect model in the crystal lattice. We discuss further the temperature dependence of the thermoelectric figure of merit $Z=\sigma\alpha^2/\kappa$ of the samples. It is observed that low concentrations of In atoms in the $(Sb_{0.75}Bi_{0.25})_2Te_3$ crystal lattice result in a substantial increase in the parameter Z in the temperature region 100 - 300K.

1. Introduction

It is well known that properly doped $(Sb_{0.75}Bi_{0.25})_2Te_3$ is used as p-type leg of thermoelectric modules working in the vicinity of room temperature, having $ZT=\sigma\alpha^2T/\kappa$ value close to 1. The formation of ternary or even quaternary systems can be beneficial due to an appreciable decrease in the thermal conductivity in these systems. One should, however, also examine the influence of the ternary or quaternary component on the electrical conductivity σ and the Seebeck coefficient α.

This contribution aims to investigate the influence of In as a fourth component of the system on the thermoelectric performance of $(Sb_{0.75}Bi_{0.25})_2Te_3$ single crystals.

2. Experimental

The starting polycrystalline materials of nominal composition $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ (x = 0.0, 0.05, and 0.15) for pulling of the single crystals were synthesized from the elements of 5N purity in conical quartz ampoules evacuated to 10^{-4} Pa. The synthesis was carried out by heating the reaction mixture at 1073 K for 48 hours. The growth of the crystals was carried out in the same ampoule using a modified Bridgman technique. The details of the method applied, together with the conditions leading to the growth of perfect single crystals, are described in our earlier paper [1]. The samples of single crystals are characterized by measurements of the temperature dependence of electrical conductivity, Hall coefficient, Seebeck coefficient and thermal conductivity in the temperature range of 5-300 K. The experimental techniques are described elsewhere [2].

3. Results and discussion

The results of the measurements of temperature dependence of electrical conductivity $\sigma_{\perp c}$, Seebeck coefficient $\alpha(\Delta T\perp c)$ and thermal conductivity κ $(\Delta T\perp c)$ are presented in Figs. 1-3. In the Table 1 we summarize the room temperature values of the transport properties and the unit cell volume of the crystal lattice. It is evident that the unit cell volume decreases with the increasing content of In. This corroborates the formation of a solid solution. Regarding the atomic radius of In one would expect the decrease of the unit cell volume. We note that this result – incorporation of In atoms in cation sublattice - is in accord with Ref.[3].

Table1 Volume of unit cell V, Hall coefficient $R_H(B||c)$, electrical conductivity $\sigma_{\perp c}$, and Seebeck coefficient $\alpha(\Delta T\perp c)$ of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ single crystals at T = 300K.

x	V [nm^3]	$R_H(B\|\|c)$ [cm^{3}C^{-1}]	$\sigma_{\perp c}$ [Ω^{-1}cm^{-1}]	$\alpha(\Delta T\perp c)$ [μVK^{-1}]
0	0.48686	0.105	2440	144.8
0.05	0.48659	0.120	1230	159.1
0.15	0.48598	0.330	804	107.4

From the changes of the Hall coefficient, it is evident that with the increasing content of In in the sample the concentration of holes decreases. In accordance with Refs. [3,4], indium atoms enter the cation sublattice and form uncharged point defects $In_{Me}^{\times}$ (Me is Bi or Sb). Thus indium produces neither free electrons nor holes in accord with the following equation

$$(2V_{Me} + 3V_{Te}) + (2In + 3Te) = 2\ In_{Me}^{\times} + 3Te_{Te}, \qquad (1)$$

where V_{Sb} is a vacancy in the cation sublattice, V_{Te} is a vacancy in the Te-sublattice, and Te_{Te} is a Te atom in the Te-sublattice. In this scenario the change in the concentration of free carriers must be linked to an interaction of In with native defects of the host structure. Now we will attempt to explain qualitatively the observed decrease in the concentration of holes. The principal point defects in the structure of $(Sb_{0.75}Bi_{0.25})_2Te_3$ are antisite defects Bi_{Te}^{-1} or Sb_{Te}^{-1} producing holes and tellurium vacancies V_{Te}^{+2} producing electrons. The antisite defects are dominant and thus $(Sb_{0.75}Bi_{0.25})_2Te_3$ is a p-type semiconductor. The equilibrium of the native defects in this case is described by the following equation

$$Me_{Sb} + V_{Te}^{+2} + 2e^{-} \Leftrightarrow Me_{Te}^{-1} + V_{Sb}^{-3} + 4\ h^{+}. \qquad (2)$$

We suppose that the decrease in the concentration of holes is caused by a fraction of In incorporated in the host structure which shifts the equilibrium specified by Eq. 2 to the left. This process can be described by the following equation

$$2\,(Me_{Te}^{-1} + V_{Me}^{-3}) + 8h^{+} + (2V_{Me} + 3V_{Te}) + (2In + 3Te) =$$

$$= 2Me_{Me} + 3Te_{Te} + 2\,In_{Me}^{\times} + 2\,V_{Te}^{+2} + 4e^{-}\ . \qquad (3)$$

We note that the idea of interaction of impurity atoms with native defects of the host lattice was also used previously to describe free carrier changes in other tetradymite type crystals [5,6]

In accordance with the above discussed decrease in the concentration of holes, the incorporation of In in the structure of $(Sb_{0.75}Bi_{0.25})_2Te_3$ results in a decrease of the electrical conductivity σ (see Fig. 1).

From Fig. 2 it is evident that the magnitude of the Seebeck coefficient of the sample with x = 0.05 is higher compared to the magnitude of the undoped sample (x = 0). This effect is consistent with the observed decrease in hole concentration. The different character of temperature dependence $\alpha = f(T)$ for sample with x = 0.15 is probably linked to a change in the carrier scattering mechanism which, in turn, is connected with the change in the concentration of charged point defects as follows from Eq. 3.

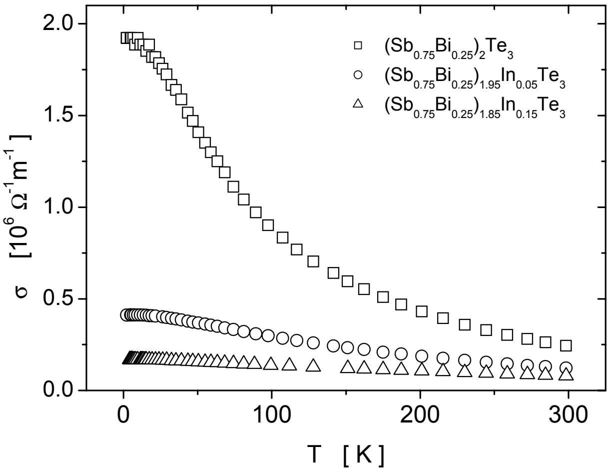

Fig. 1 The electrical conductivity $\sigma_{\perp c}$ as a function of temperature of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ single crystals.

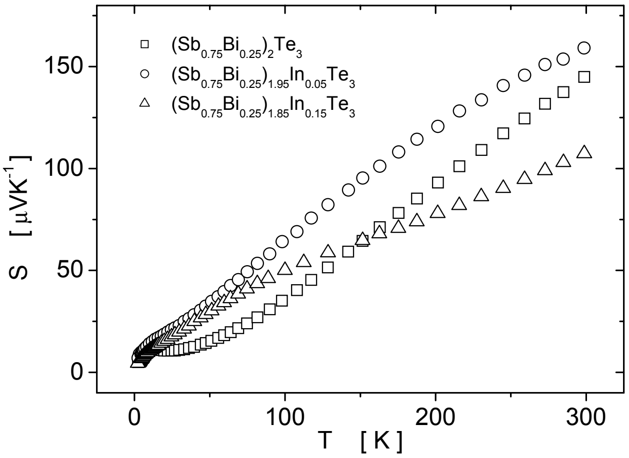

Fig. 2 The Seebeck coefficient $\alpha(\Delta T \perp c)$ as a function of temperature of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ single crystals.

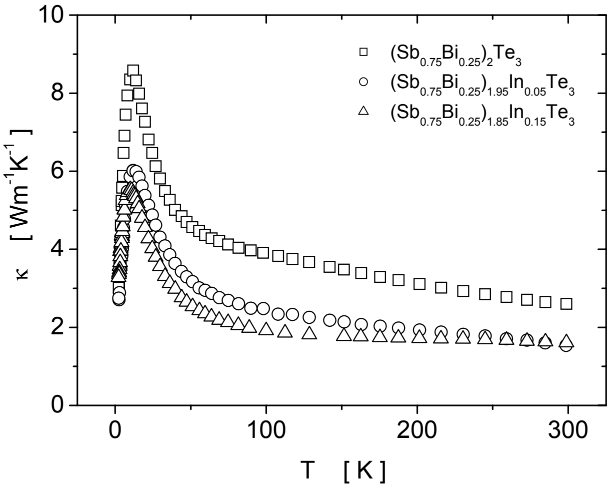

Fig. 3 The thermal conductivity κ $(\Delta T \perp c)$ as a function of temperature of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ single crystals.

Table2 The thermal conductivity κ $(\Delta T \perp c)$, its electronic and lattice components κ_e, κ_L of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ single crystals at T = 300 K.

x	$\kappa\,(\Delta T \perp c)$ $[Wm^{-1}K^{-1}]$	$\kappa_e\,(\Delta T \perp c)$ $[Wm^{-1}K^{-1}]$	$\kappa_L\,(\Delta T \perp c)$ $[Wm^{-1}K^{-1}]$
0	2.57	1.74	0.83
0.05	1.56	0.91	0.65
0.15	1.61	0.60	1.01

From Fig. 3 we can see that upon doping with In the thermal conductivity κ decreases in the entire temperature region measured. Generally $\kappa = \kappa_e + \kappa_L$ where κ_e and κ_L are, respectively, the electronic and lattice parts of the thermal conductivity. The observed decrease can be ascribed primarily to a decrease in κ_e, which is connected with the decrease in the concentration of free carriers, (see Table 2). On the other hand, the lattice part of thermal conductivity does not change markedly. The electronic component of thermal conductivity κ_e in Table 2 was computed using the relation $\kappa_e = L\sigma T$, where we used the Lorenz number L in the elastic limit approximation, i.e., $L = L_0 = \pi^2(k_B/e)^2/3$. This rough approximation is close enough to reveal the trend.

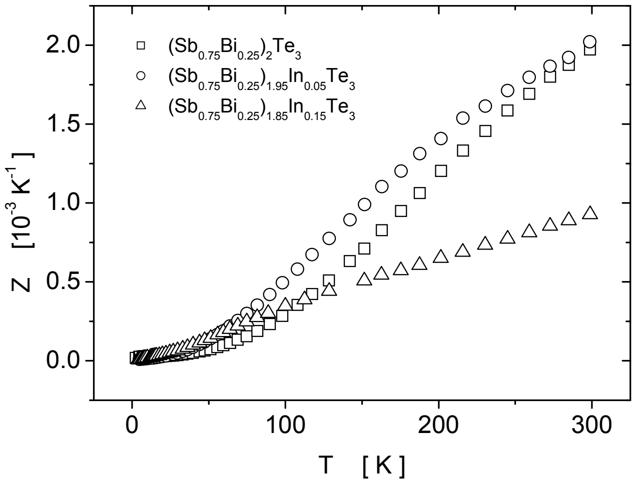

Fig. 4 The figure of merit Z as a function of temperature of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ single crystals.

The thermoelectric figure of merit Z as a function of temperature is shown in Fig. 4. While higher concentrations of In suppress the magnitude of the parameter Z, lower concentrations of In cause an increase (up to 30%) of the parameter Z compared to $(Sb_{0.75}Bi_{0.25})_2Te_3$ in the temperature region 100 – 200K. Interestingly, a closer examination reveals that the character of the temperature dependence of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ is very close to that of $(Sb_{0.75}Bi_{0.25})_2Te_3$ despite a pronounced difference in the electrical conductivity. Figure 4 suggests that indium shifts the maximum of the parameter Z towards lower temperatures, which is consistent with the decrease in free carrier concentration upon doping with indium.

Conclusions

Crystals of quaternary system based on $(Sb_{0.75}Bi_{0.25})_2Te_3$ doped with In were prepared using the Bridgman technique. Indium incorporated in the host structure enters the cation sublattice and forms uncharged point defects $\mathrm{In}_{\mathrm{Me}}^{\times}$ (Me is Bi or Sb). Although nominally electrically inactive, In induces a change in free hole concentration the origin of which is most likely due to interaction of indium with the native point defects. Samples with varying content of In were characterized by the measurements of electrical resistivity, Hall coefficient, Seebeck coefficient and thermal conductivity. The measurements indicate that by incorporating indium in $(Sb_{0.75}Bi_{0.25})_2Te_3$ one lowers the concentration of free holes. This effect is explained in terms of a point defect model.

While high In concentrations decrease the dimensionless figure of merit $ZT = \sigma\alpha^2T/\kappa$ of the samples, very low concentrations of In (up to x = 0.05) may be beneficial for thermoelectric properties since the figure of merit of $(Sb_{0.75}Bi_{0.25})_{2-x}In_xTe_3$ exceeds that of $(Sb_{0.75}Bi_{0.25})_2Te_3$ in the entire range of temperatures up to 300K. In the regime of temperatures between 100K and 200K the enhancement is as much as 30%.

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