JOURNAL OF MATERIALS SCIENCE 27 (1992) 6062–6066

The change of the electric conductivity type in crystals of $Bi_{2-x}In_xTe_3$ solid solutions

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Room-temperature values of the Hall constant R_H ($B \parallel c$), Seebeck coefficient α ($\Delta T \perp c$), and the temperature dependence of the electric conductivity $\sigma_{\perp c}$ in the 120–360 K temperature interval have been investigated on samples of $Bi_{2-x}In_xTe_3$ crystals prepared by the Bridgman technique. It has been established on the basis of the changes of these transport coefficients with increasing content of indium that for values close to $x = 0.1$ the conductivity type changes from p-type to n-type. Suppression of the concentration of holes due to the incorporation of In atoms into the crystal lattice of p-Bi_2Te_3 is accounted for by a model of point defects in the $Bi_{2-x}In_xTe_3$ crystal lattice. It is assumed that the arising uncharged substitutional In_{Bi}^{x} defects polarize the Bi_2Te_3 lattice and thus lower the concentration of anti-site defects Bi'_{Te}, whose charges are compensated by holes. The dominant defects in the crystal lattice of n-$Bi_{2-x}In_xTe_3$ are the tellurium vacancies $V^{\bullet}_{Te}$.

1. Introduction

Solid solutions based on bismuth telluride Bi_2Te_3 represent an important group of semiconducting materials which find applications in thermoelectric devices. For example, in view of their pronounced Peltier effect and high value of the Seebeck coefficient, $Bi_{2-x}Sb_xTe_3$ and $Bi_2Te_{3-x}Se_x$ solid solutions are used for the construction of cooling elements and generators operating in the temperature range close to 300 K [1].

One of the pseudobinary systems, which receives attention in connection with potential thermoelectric applications, is the Bi_2Te_3–In_2Te_3 system. Its phase diagram and the study of mutual solubility of both components have been reported by others [2–6], and the growth of perfect $Bi_{2-x}In_xTe_3$ single crystals and their basic physical properties were described in our earlier papers [7–9]. The variations of the Hall constant and Seebeck coefficient with increasing indium content in the $Bi_{2-x}In_xTe_3$ samples showed that on exceeding a certain limiting concentration of indium the conductivity changes from p-type to n-type [1, 7]; however, this limiting concentration has not yet been determined.

In view of the fact that practical applications of these solid solutions call for a reproducible method of growing n-type or p-type materials with the desired concentration of free carriers, we present in this communication the results of measurements of the Hall constant, Seebeck coefficient and electrical conductivity of a series of single-crystalline samples $Bi_{2-x}In_xTe_3$ ($x = 0$–0.32) with the objective of determining the limiting indium concentration, i.e. the value of x where the change of electric conductivity type takes place. The variations of the above-mentioned transport coefficients with increasing indium content in the samples are further qualitatively explained using a model of point defects in the $Bi_{2-x}In_xTe_3$ crystals.

2. Experimental procedure

2.1. Preparation of single crystals

$Bi_{2-x}In_xTe_3$ single crystals were prepared from elements of 99.999% purity. The compounds were synthetised in conical quartz ampoules evacuated to 10^{-4} Pa. Homogenization of the batches and synthesis of the compounds was carried out in a horizontal furnace at 973 K for 48 h. The crystals were grown using a vertical Bridgman method. Prior to pulling, the ampoules containing the melt were heat-treated at 973 K for 24 h and, after the melt filled the tip of the ampoule, the ampoule was lowered through a temperature gradient of 400 K per 5 cm at a rate of 1.2 mm h^{-1}.

The single crystals obtained, 50–60 mm long and 9 mm in diameter, could be easily cleaved. Their trigonal axis c was always perpendicular to the pulling direction so that the (0 0 0 1) crystal plane was parallel to the ampoule axis. The orientation of the cleavage faces was checked using the Laue back-reflection method, which confirmed that these faces were always (0 0 0 1).

The indium content in the samples was determined using an extraction photometric method [10].

2.2. Measurement of transport coefficients

The room-temperature values of the Hall constant were determined on samples prepared from the central parts of the crystals, rectangular slabs of dimensions 15 mm × 3 mm × 0.1 to 0.3 mm. The experimental geometry corresponded to $R_H(B\|c)$. The samples were connected to an a.c. current supply of 170 Hz frequency, and the constant magnetic field induction B was equal to 1.1 T.

Values of the electric conductivity, $\sigma_{\perp c}$, were calculated from the voltage drop measured across the Hall contacts in the temperature range of 100 to 360 K.

The Seebeck coefficient was determined for the direction $\Delta T \perp c$, that is $\alpha(\Delta T \perp c)$. The temperature difference between the hot and cold junction was not higher than 10 K.

3. Results

The temperature dependence of the electrical conductivity σ of the p-type and n-type samples is shown in Figs 1 and 2, respectively. Fig. 3 shows the values of $R_H(B\|c)$, $\sigma_{\perp c}$ and $\alpha(\Delta T \perp c)$ at temperature 300 K plotted as functions of indium content in the samples. Numerical values of all investigated transport coefficients at $T = 300$ K, including the results of analysis of In content in the samples, are further summarized in Table I.

4. Discussion

4.1. Transport coefficients of $Bi_{2-x}In_xTe_3$ crystals

It is evident from Fig. 1, showing the temperature dependences of the electric conductivity $\sigma_{\perp c}$ of the p-$Bi_{2-x}In_xTe_3$ samples, that the incorporation of In atoms into the Bi_2Te_3 crystal lattice results in a marked decrease of the absolute value of $\sigma_{\perp c}$ and in a change of the character of the log $\sigma_{\perp c} = f(T)$ plot in the investigated temperature range. Whereas in "pure"

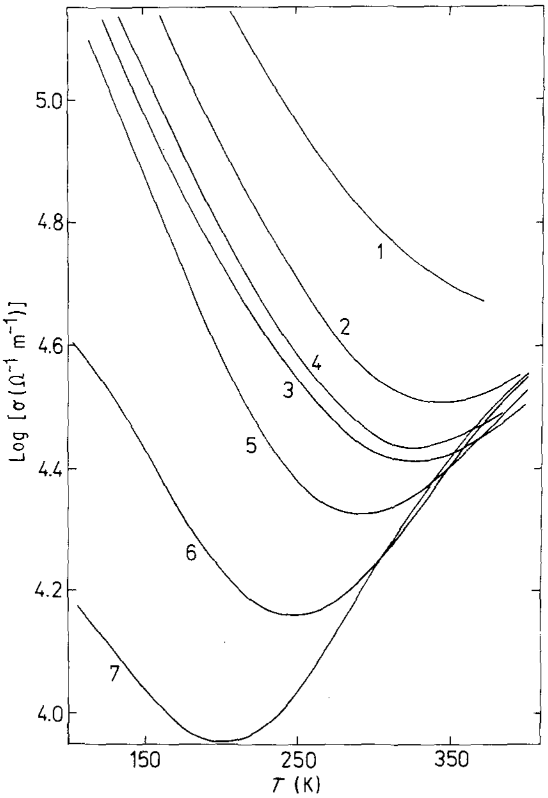

Figure 1 Temperature dependence of the electric conductivity $\sigma_{\perp c}$ in p-$Bi_{2-x}In_xTe_3$ samples. The samples are labelled according to Table I.

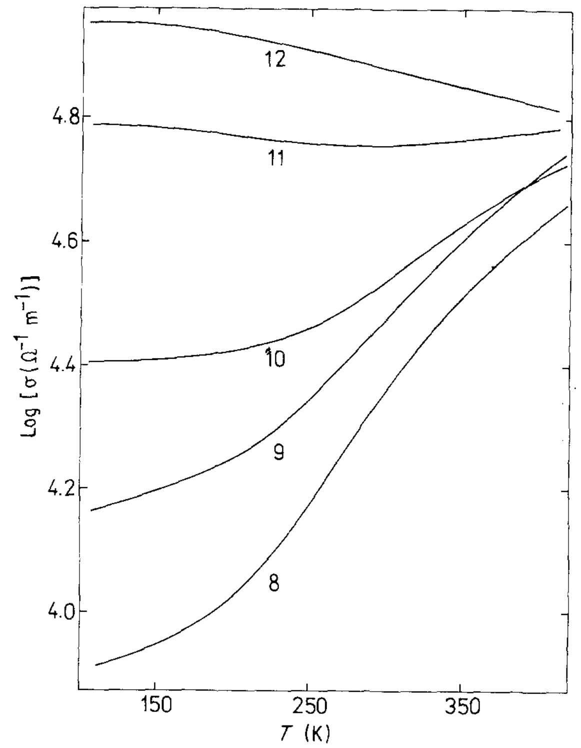

Figure 2 Temperature dependence of the electric conductivity $\sigma_{\perp c}$ in n-$Bi_{2-x}In_xTe_3$ samples. The samples are labelled according to Table I.

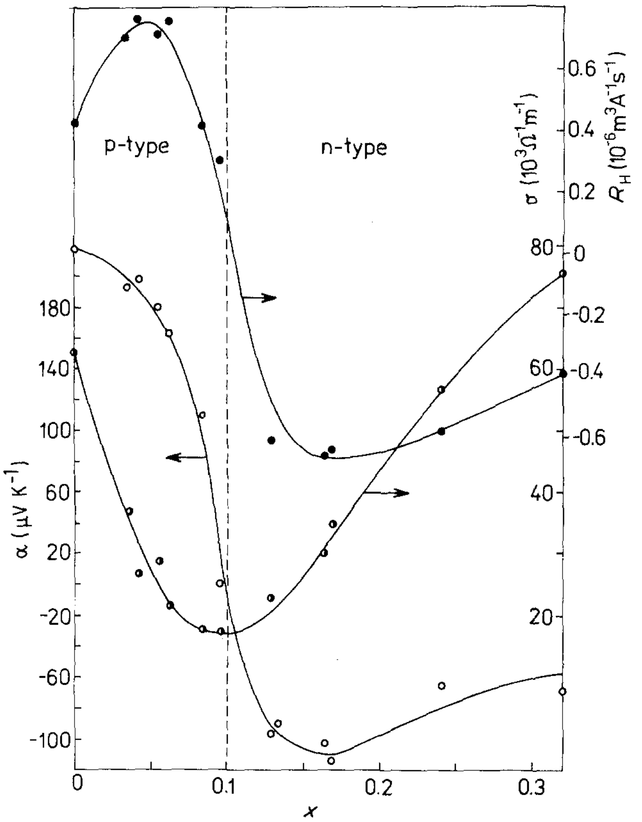

Figure 3 Plots of (●) Hall constant $R_H(B\|c)$, (◑) electric conductivity $\sigma_{\perp c}$ and (○) Seebeck coefficient $\alpha(\Delta T \perp c)$ at 300 K of $Bi_{2-x}In_xTe_3$ crystals against indium content x.

TABLE I Transport coefficients of $Bi_{2-x}In_xTe_3$ crystals at 300 K

Sample No.	x	$\sigma_{\perp c}$ ($10^3\Omega^{-1}m^{-1}$)	$R_H(B\parallel c)$ ($10^{-6}m^3A^{-1}s^{-1}$)	$\alpha(\Delta T\perp c)$ ($\mu V K^{-1}$)
1	0	62.4	0.42	218
2	0.034	35.9	0.70	193
3	0.042	27.0	0.76	198
4	0.055	28.8	0.71	180
5	0.062	21.6	0.75	163
6	0.083	17.8	0.41	110
7	0.095	17.3	0.30	1
8	0.128	22.9	− 0.61	− 97
9	0.163	30.1	− 0.66	− 103
10	0.168	34.7	− 0.64	− 114
11	0.240	56.8	− 0.58	− 65
12	0.320	75.9	− 0.39	− 68

Bi_2Te_3 the conductivity $\sigma_{\perp c}$ monotonously decreases with increasing temperature, $\log \sigma_{\perp c} = f(T)$ curves of $Bi_{2-x}In_xTe_3$ crystals exhibit a minimum, which becomes more pronounced with increasing indium content and shifts to lower temperatures. These variations can be qualitatively accounted for in the following way.

The decrease of the absolute value of the electric conductivity is probably connected with the fact that the incorporation of In atoms into the Bi_2Te_3 crystal lattice leads to a suppression of the hole concentration; in other words, it gives rise to a decrease in the concentration of acceptor levels. Therefore, if the concentration of acceptor levels decreases with increasing indium content, it is evident that in samples of higher In content these levels are occupied at lower temperatures than in the samples of lower In content. Then, at higher temperatures, the conductivity is connected with the transition of electrons from the valence band into the conduction band–i.e. the intrinsic conductivity. Hence it follows that the decreasing part of the $\log \sigma_{\perp c} = f(T)$ curve describes the conductivity connected predominantly with the occupation of acceptor levels, whereas the increasing part characterizes the intrinsic conductivity. In the region of the minimum on the $\log \sigma_{\perp c} = f(T)$ plot the electric conductivity is connected with the concentration of both acceptors and electrons, and the minimum shifts towards lower temperatures with decreasing concentration of acceptor levels.

On the basis of this qualitative analysis of the temperature dependence of the conductivity of p-$Bi_{2-x}In_xTe_3$ samples we can adopt the following conclusion: in $Bi_{2-x}In_xTe_3$ crystals with a low concentration of holes the electric conductivity is determined not only by the concentration of holes and their mobility, but also by the concentration and mobility of electrons excited from the valence to the conduction band. The exact description of the transport coefficients of such samples calls for using a two-band model. In these crystals, i.e. crystals based on Bi_2Te_3, the description is further complicated by the splitting of the conduction and/or the valence band into two sub-bands, i.e. by the existence of light and heavy electrons and holes [11, 12]. In view of the fact that the band structure parameters of $Bi_{2-x}In_xTe_3$ mixed crystals are not known, and cannot be determined on the basis of the results presented by us, we shall restrict our analysis to a qualitative evaluation of the variations of the transport coefficients with increasing indium content in the $Bi_{2-x}In_xTe_3$ samples.

Our qualitative conclusion on the connection of the transport coefficients of $Bi_{2-x}In_xTe_3$ crystals both with the concentration of holes and with the concentration of free electrons, in the range of low hole concentration, is in good agreement with the conclusion of Fleurial *et al.* [13], who describe the relations between the electric conductivity, Hall constant, Seebeck coefficient and thermal conductivity of Bi_2Te_3 samples of both p- and n-type on the basis of a two-band model, whereby they accept the idea of the excitation of electrons from the valence to the conduction band.

It is evident (see Fig. 2) that in n-$Bi_{2-x}In_xTe_3$ crystals the electrical conductivity $\sigma_{\perp c}$ of the sample with lower In content increases with increasing temperature, which is in agreement with the idea of electrons being excited from the valence to the conduction band. The decrease of the $\log \sigma_{\perp c} = f(T)$ curves with increasing temperature in samples with the highest In content (sample Nos 11 and 12) is connected, in our opinion, with the fact that these highly doped materials are most probably already degenerate semiconductors.

Fig. 3 shows the variations of the investigated transport coefficients of $Bi_{2-x}In_xTe_3$ crystals with increasing value of x. It is clear that the increasing content of indium in the Bi_2–Te_3 crystal lattice gives rise in the range of p-type conduction to a pronounced decrease of the absolute value of $\sigma_{\perp c}$, which is probably connected with suppression of the concentration of holes. On further increase of the x value, the $\sigma_{\perp c} = f(x)$ dependence passes through a minimum; here the conductivity type changes from p to n and in the n-type range the values of $\sigma_{\perp c}$ increase with increasing x, which testifies that the concentration of free electrons increases.

The decrease of the $\alpha = f(x)$ dependence with increasing x is connected with the idea discussed above, namely that the transport coefficients of $Bi_{2-x}In_xTe_3$ crystals in the temperature range close to 300 K are determined by the concentration and mobility of both electrons and holes. Likewise, the minimum on the

$\alpha = f(x)$ dependence – seen in the range of n-type conductivity – is probably due to the same effect.

The complex band structure of $Bi_{2-x}In_xTe_3$ crystals is obviously responsible also for the extrema in the $R_H = f(x)$ dependence, visible both in the region of p-type and in the region of n-type conductivity.

The values of the electric conductivity, Seebeck coefficient and Hall constant, shown in Fig. 3, justify us in accepting an important conclusion – namely the conclusion of a change of the electric conductivity type of $Bi_{2-x}In_xTe_3$ crystals with increasing indium content, which is the goal of the present communication. It is clear from this figure that the change of the conductivity type from p-type to n-type occurs in the range of x values close to $x = 0.1$.

4.2. Point defects in $Bi_{2-x}In_xTe_3$ crystals

In this section we shall attempt to make use of ideas on possible pathways of incorporation of indium atoms into the Bi_2Te_3 crystal lattice, in order to account for the decrease in the concentration of holes and for the change of the conductivity type from p to n with increasing value of x in $Bi_{2-x}In_xTe_3$ samples.

The incorporation of indium atoms into the crystal lattice of Bi_2Te_3 can be realized by the formation of point defects (interstitial atoms, substitutional defects in the bismuth sublattice, substitutional defects in the tellurium sublattice) or, as the case may be, by so-called intercalation, i.e. by the building-in of indium atoms into the van der Waals gap.

The incorporation of In atoms into interstitial sites does not seem to be probable. The fact that interstitials, as a rule, are easily ionized should manifest itself by a rapid decrease of the concentration of holes with increasing x in $Bi_{2-x}In_xTe_3$ samples. However, the variation of the concentration of holes with increasing indium content is, compared for example with that due to the incorporation of gallium atoms into the Bi_2Te_3 lattice, relatively small. That is to say, it follows from the results reported [14] that a very low concentration of gallium atoms (much lower than that of indium) results in the change from p-type to n-type conductivity. Moreover, it is difficult to accept the idea that indium entering the Bi_2Te_3 lattice would first, i.e. up to a certain concentration, occupy interstitial sites and only at higher concentration would substitutional defects arise; in other words, it is highly improbable that the formation energy of interstitials would be lower than the formation energy of substitutional defects. Such effect should be seen, for example, in the dependence of the electric conductivity on indium content in the samples; in the range of p-type electric conductivity the In atoms entering the lattice would first bring about an abrupt decrease of electric conductivity values in consequence of the formation of ionized interstitials, then the hole conductivity would either increase or remain constant as a consequence of the charged or uncharged substitutional defects that would arise on further increase of indium content in the samples. The experimentally determined variation of the electric conductivity in p-type samples is, however, in contradiction with this idea (see Fig. 3).

The substitution of Te atoms with indium, as considered by Rosenberg and Strauss [2], does not come into account either, since the incorporation of indium atoms into tellurium sites would lead to the formation of negatively charged substitutional defects and hence to an increase in the concentration of holes.

The idea that the In atoms would enter the van der Waals gap also seems improbable. Intercalated indium atoms would in this case be obviously ionized in consequence of the high permittivity of Bi_2Te_3 crystals and would therefore provoke a much faster decrease of the concentration of holes with increasing indium content. Also, contrary to the experimental results, the change of the conductivity type would be observed at a lower value of x.

On the basis of this qualitative analysis we conclude that the most probable pathway would be the incorporation of indium atoms into the bismuth sublattice – i.e. the formation of substitutional defects of In on Bi sites. According to the ideas that were presented in our earlier papers [15, 16, 17] the decrease in the concentration of holes due to the incorporation of In atoms into the Bi_2Te_3 crystal lattice can be explained in the following way.

If we accept the ideas put forward by Krebs [18] about the nature of the chemical bond, which are based on the concept that the bond between Bi and Te in the crystal lattice of Bi_2Te_3 is realized by electrons from p-orbitals of both elements, the substitutional defect of indium atoms on bismuth sites will be formally uncharged, i.e. In_{Bi}^{x}, so that we assume the excitation of two 5s electrons into p-orbitals. However, if we take into account that the electronegativity of In atoms is lower than that of bismuth, we can argue that the substitutional defect will carry a partial positive charge, $In_{Bi}^{(+\delta)}$. As a consequence of this charge the polarity of the bonds in the Bi_2Te_3 crystal lattice increases. Increasing bond polarity results in a suppression of the concentration of anti-site defects of bismuth atoms on tellurium sites, Bi'_{Te}, which were shown to exist in the Bi_2Te_3 crystal lattice [19] and whose existence is due to the minimal bond polarity. The decrease in the concentration of anti-site defects will manifest itself by a decrease in the concentration of acceptor levels and hence also in the concentration of holes.

This idea concerns the crystals with hole conductivity. With increasing indium content in $Bi_{2-x}In_xTe_3$ crystals, however, we observed a change in the conductivity type and the samples with $x > 0.1$ exhibited electron conductivity. The appearance of electron conductivity is not easy to explain. None the less, the following picture seems acceptable.

If we adopt the idea that the crystal lattice of p-Bi_2Te_3 contains beside anti-site Bi'_{Te} defects also negatively charged bismuth vacancies V'_{Bi} and positively charged tellurium vacancies $V^{\bullet}_{Te}$, then, in view of the electroneutrality of the crystal, the sum of the negative charges (corresponding to Bi'_{Te} and V'_{Bi}) must be equal to the sum of the positive charges (corresponding to $V^{\bullet}_{Te}$ and holes $h^{\bullet}$). In the process of incorporation of indium atoms into the crystal lattice the vacancies V'_{Bi} become occupied and, at the same time, the increasing bond polarity leads to a lowering of the concentration of anti-site defects $\mathrm{Bi}_{\mathrm{Te}}'$, which is connected with suppression of the concentration of holes. Taking this mechanism of incorporation of indium atoms into the $\mathrm{Bi_2Te_3}$ lattice as probable, one cannot exclude that the increase in the concentration of indium will eventually lead to the situation where the dominant charged defects in the crystal lattice will be the tellurium vacancies $\mathrm{V}_{\mathrm{Te}}^{\bullet}$, which will result in a change of the conductivity type from p to n in view of the compensation of their charges by free electrons. Further increase of the concentration of free electrons, observed to take place on increasing the concentration of indium in n-type samples, could then be easily explained by realizing that the increasing content of In atoms in the bismuth sublattice, i.e. $\mathrm{In}_{\mathrm{Bi}}^{x}$, is responsible for a further decrease of the concentration of bismuth vacancies $\mathrm{V}_{\mathrm{Bi}}'$, which results in a strengthening of the inequality $[\mathrm{V}_{\mathrm{Bi}}'] \ll [\mathrm{V}_{\mathrm{Te}}^{\bullet}]$.

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Received 5 July 1991
and accepted 17 February 1992