

Selenium Impurity in Bismuth and Lead Tellurides

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Abstract

Electrical and thermoelectric properties of a lightly doped $n\text{-Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution have been studied in the temperature range 77-300 K. The results are compared with data for the compound $\text{PbTe}_{0.9}\text{Se}_{0.1}$ with a similar magnitude of the Seebeck coefficient S at 84 K. Along with lower thermal conductivity κ , $n\text{-Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ has a higher electrical conductivity σ and a much weaker dependence of $\sigma(T)$. As a result, the power coefficient $S^2\sigma$ in optimal samples begins to decrease only when the density of minority carriers becomes significant. In this case, S considerably exceeds the standard value of $200 \mu\text{VK}^{-1}$. The reduction of the electron density reduces the thermoelectric figure of merit Z at its maximum and slightly lowers the temperature of the maximum; therefore, the expected effect on the average value of Z in the range 77-300 K is absent. Similar behavior is observed in $\text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12}$, although the effect is less pronounced. The experimental results are discussed taking into account possible changes in the dominant scattering mechanisms, carrier density, and electron energy spectrum.

Introduction

The elaboration of high-efficiency thermoelectric materials based on ternary solid solutions $(\text{BiSb})_2\text{Te}_3$ and $\text{Bi}_2(\text{TeSe})_3$ has led to the development and wide use of thermoelectric coolers for the room-temperature range. Further research has begun that aims to widen the operation range down to liquid-nitrogen temperature [1-3]. According to [1, 2], in n -type materials the highest figure of merit Z in the range below room temperature was obtained in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ at the electron densities $(3\text{-}8) \cdot 10^{18} \text{ cm}^{-3}$, which corresponds to Seebeck coefficient $|S| = 100\text{-}160 \mu\text{VK}^{-1}$ at $T \approx 84 \text{ K}^*$. The maximum value of Z in the dome-shaped $Z(T)$ curve for solid solutions with $x = 0.21\text{-}0.36$ exceeds $3 \cdot 10^{-3} \text{ K}^{-1}$ and corresponds to temperatures 220-270 K. Studies of thermoelectric properties of lower-doped samples with $x = 0.3$ and 0.36 (in which $|S|$ is as high as $\sim 200 \mu\text{V K}^{-1}$ at 84 K) [3] have demonstrated a more complex temperature dependence of the figure of merit. At temperatures below 150 K, the figure of merit increases as temperature decreases, reaching values of $(2.0\text{-}2.4) \cdot 10^{-3} \text{ K}^{-1}$ at 84 K; the maximum in the dome-shaped portion of the $Z(T)$ curve still lies at temperatures of about 250 K, but the value of Z is

significantly smaller than that for samples with higher electron density. In this study, we continued a research on the thermoelectric properties of n -type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ solid solutions. We aimed to reveal which specific features in the properties of the material appeared at decreased electron density and find out how these features affected the value and behavior of the thermoelectric figure of merit in the temperature range 77-300 K.

Experimental results

To study the Seebeck coefficient and electrical and thermal conductivities in the temperature range 85-340 K, we fabricated samples of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ solid solution with an Se content of 10 at % in the chalcogenide sublattice ($x = 0.3$). The technique of vertical zone melting was used, and the doping was carried out by introducing chlorine.

To reveal the specific features in the behavior of the material under study at low temperatures, we compared the thermoelectric properties of two lightly doped solid solutions, $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and $\text{PbTe}_{1-x}\text{Se}_x$, with an equal Se content (10 at %). $\text{PbTe}_{1-x}\text{Se}_x$ is chosen as a reference material, because its thermoelectric properties at low temperatures are well described in terms of a single-band model with a nonparabolic dispersion law and electron scattering on phonons and on the short-range potential of neutral impurity centers [4]. Figure 1 shows temperature dependences of the electrical and thermoelectric characteristics of these solid solutions with similar values of thermoelectric power at 84 K. The comparison of the temperature dependences of thermal conductivity (curves 3, 3') shows that the law of change of $\kappa(T)$ is virtually the same in both alloys, not counting the very small (less than 4% at the maximum) departure from this law in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ at temperatures of 110-225 K. This decrease in κ does not affect the amplitude and position of the maximum figure of merit Z_{max} , and only slightly raises Z in this temperature range. The decrease in thermal conductivity observed in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution has a noticeable effect on the figure of merit. For example, the increase in Z_{max} because of the decrease in total thermal conductivity is $\sim 20\%$.

The differences between the temperature dependences of electrical conductivity (Fig. 1, curves 1, 1') and Seebeck coefficient (Fig. 1, curves 2, 2') in the alloys under study are of fundamental importance. The temperature variation of both parameters is much stronger in the solid solution based on PbTe . The change in the electrical conductivity is especially strong: in $\text{PbTe}_{0.9}\text{Se}_{0.1}$ solid solution, σ decreases by more than an order of magnitude as temperature increases from 84 to 300 K, whereas in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ it decreases only by a factor of 4.2. Since the Seebeck coefficient in

* In comparing the properties of the materials, we will use the temperatures 84 and 250 K. The latter value is chosen taking into account that, in lightly doped samples of this material, the contribution of intrinsic carriers at room temperature is considerable.

$\text{PbTe}_{0.9}\text{Se}_{0.1}$ increases by a factor of 2.5 in this temperature range, the power coefficient $S^2\sigma$ naturally declines sharply as temperature increases. When the thermal conductivity decreases slowly, the thermoelectric figure of merit reaches its maximum at a temperature of about 100 K (Fig. 2). In this case, the magnitude of the Seebeck coefficient does not exceed its standard value of $\sim 200 \mu\text{V K}^{-1}$, which corresponds to scattering mechanisms with the exponent r in the dependence of the relaxation time on energy equal to -0.5 in cases of scattering on acoustic phonons and on the short-range impurity potential.

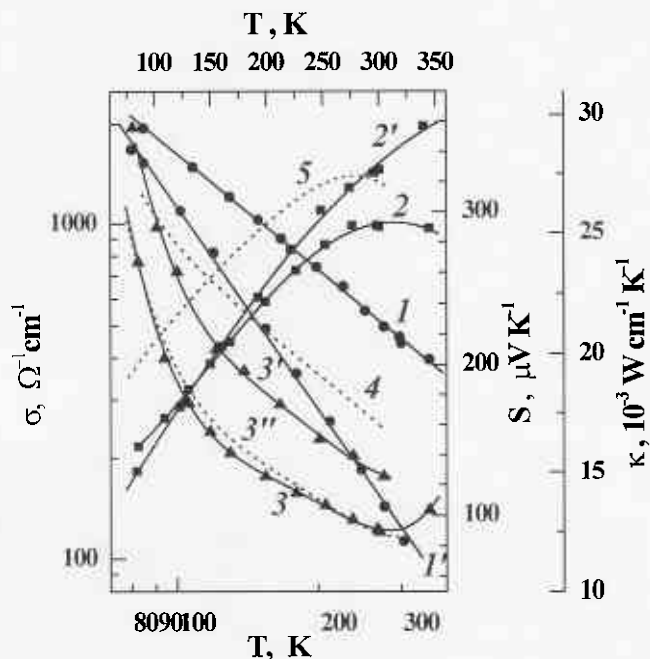


Fig. 1. Temperature dependences of (1, 1') electrical conductivity σ (log-log scale), (2, 2') Seebeck coefficient S (linear scale), and (3, 3') thermal conductivity κ (linear scale) for (1, 2, 3) $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and (1', 2', 3') $\text{PbTe}_{1-x}\text{Se}_x$ solid solutions with equal Se content (10 at %) and similar values of S at 84 K. (4, 5) σ and S , respectively, for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ with lower electron density [3]. (3'') Hypothetical thermal conductivity of solid solution based on Bi_2Te_3 calculated under the assumption that its temperature behavior is similar to that in the material based on PbTe .

A completely different situation is observed for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution. At 84 K, the power coefficient in this material is higher because of higher σ . As temperature increases, the difference becomes much greater, because, despite the weaker increase in the thermoelectric power, $S^2\sigma$ not only does not decrease until the onset of intrinsic conduction, but even increases slightly, as can be seen in Fig. 2. Only a noticeable contribution of holes to the transport phenomena radically changes the temperature dependence $S^2\sigma = f(T)$, so that this parameter steeply decreases. Since the appearance of minority carriers also changes the behavior of $\kappa(T)$, the thermoelectric figure of merit reaches its maximum and then starts to decrease steeply. Thus, the intrinsic

conduction is the factor that limits the rise of $Z(T)$ in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution. Clearly, in this material Z_{max} corresponds to higher temperatures and higher values of the Seebeck coefficient (in the case under study, $|S| \approx 290 \mu\text{V K}^{-1}$).

According to data in [3], the decrease in the electron density in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution depresses the temperature increase in the Seebeck coefficient to an even greater extent. However, the behavior of the electrical conductivity with temperature is not modified; it is still described by the standard power law $\sigma \sim T^\beta$, where $\beta \approx -1.2$. This is illustrated by the data of [3] obtained for a sample with $S = -200 \mu\text{V K}^{-1}$ at 84 K (Figs. 1, 2). The steeper run of the $\sigma(T)$ dependence at $T < 125$ K [3], which is responsible for the anomalous behavior of Z at these temperatures, will be discussed below. Regarding the data on the figure of merit in the range 125-300 K, note the following: in this case, the power coefficient decreases as temperature increases, but this dependence is weaker than in $\text{PbTe}_{0.9}\text{Se}_{0.1}$ solid solution, and, therefore, the occurrence of a maximum in the $Z(T)$ dependence is still related to the onset of the intrinsic conduction, as discussed earlier. In this case, the Seebeck coefficient $|S|$ even exceeds $300 \mu\text{V K}^{-1}$.

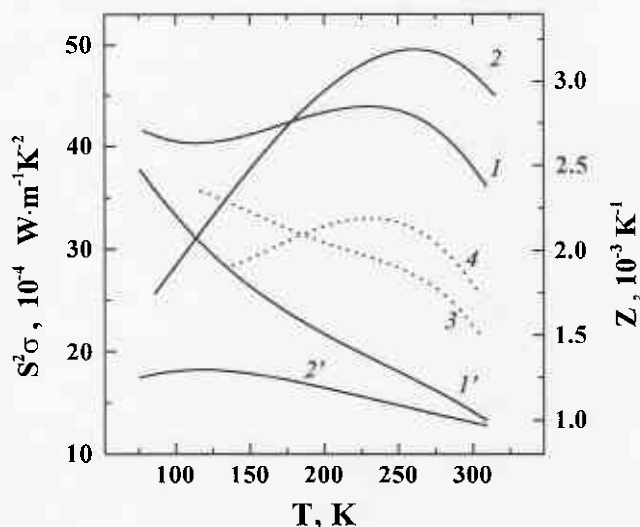


Fig. 2. Temperature dependences of (1, 1') the power coefficient $S^2\sigma$ and (2, 2') thermoelectric figure of merit Z for solid solutions based on (1, 2) Bi_2Te_3 and (1', 2') PbTe with 10 at % Se. Dashed lines: (3) $S^2\sigma$ and (4) Z for $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ with lower electron density [3].

Based on the data presented, we may conclude that the reduction of the doping level in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution, which is commonly used as a method to raise the average value of Z by lowering the temperature of the maximum in the $Z(T)$ dependence, has its limit for this material. Beyond this limit, the figure of merit decreases in virtually the whole temperature range; in this case the temperature of Z_{max} does not decrease. Evidently, as temperature increases, the increase in the Seebeck coefficient becomes too weak to noticeably compensate the decrease in electrical conductivity. The electrical conductivity is further depressed by the decrease in mobility, which is especially sensitive to the

degree of material perfection in lightly doped samples. For the range below room temperature, samples with a Seebeck coefficient of about 285-295 $\mu\text{V K}^{-1}$ and Z_{max} no lower than $3.2 \cdot 10^{-3} \text{K}^{-1}$ at $T=250 \text{K}$ are optimal.

The specific features discussed above are directly related to the introduction of Se into Bi_2Te_3 . When a small amount of Se is added, the related variations in properties are also small, although they are observable and have a similar behavior. To confirm this assertion, we use the data in [2] for $\text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12}$ solid solution and find that they are similar to those presented above: the maxima of $Z(T)$ dependences lie in the same temperature range, and their relationship with the intrinsic conduction is similar; there is no gain in Z at temperatures $T < 300 \text{K}$ in the samples with an electron density below a certain level; and the optimal value of $|S|$ noticeably exceeds $200 \mu\text{V K}^{-1}$.

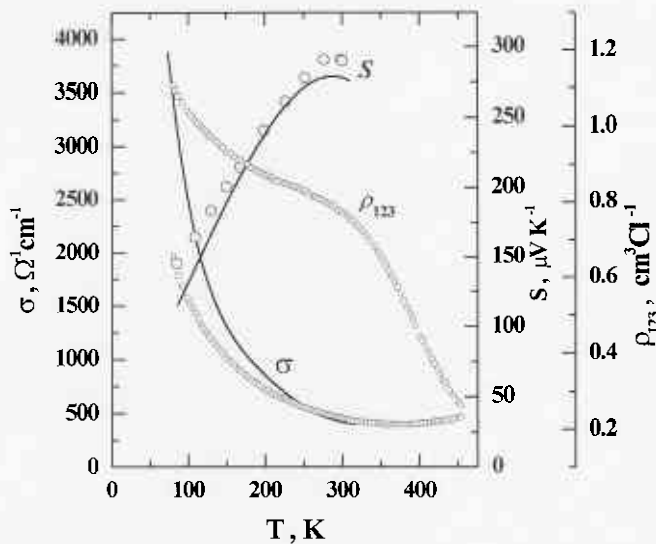


Fig. 3. Temperature dependences of electrical conductivity σ , Seebeck coefficient S , and Hall coefficient ρ_{123} . Solid lines: $\text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12}$ [2]; circles: $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ (this study). The samples are characterized by similar values of S at 250 K.

Discussion

It is of interest to make a quantitative comparison of the experimental data for solid solutions $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ and $\text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12}$, which have the same value of Seebeck coefficient at 250 K. As can be seen from Fig. 3, the temperature dependence of S in $\text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12}$ is not weakened as much as that in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$, and, therefore, the samples of these two compositions, which have equal values of S and σ at 250 K, show a significant difference in these parameters at 84 K. Linear extrapolation of the Seebeck coefficient to 0 K does not yield zero S in either of these alloys.

If we assume that two alloys with different compositions and equal values of S have the same electron density at 250 K (at room temperature, this result was obtained for the doping range $(1 \cdot 10^{18} - 5 \cdot 10^{19}) \text{cm}^{-3}$ in [1]) and this density is

temperature-independent, then the low-temperature electron mobility strongly depends on the material composition; its value considerably decreases as the Se content increases. As S also noticeably changes (increases) in this case, it is obvious that the observed facts cannot be explained only by taking into account the scattering on the short-range potential of impurities ($r=-0.5$, the same as for scattering on acoustic phonons). The estimates of scattering on the Coulomb potential of ionized defects, which is effective for low-energy carriers and thus yields higher values of S , have shown that the contribution of this mechanism in the materials under study is small [5]. In this situation, it seems natural to suppose that the specific features observed in the transport phenomena in lightly doped $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ solid solutions are related to the modification of the energy spectrum of electrons. Thus, it seemed useful to estimate how the effective mass varies with temperature at different alloy compositions, as was done for more heavily doped $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ solid solutions with $x = 0.12$ and 0.45 [5].

In determining the temperature dependence of the effective mass, $m^* \sim T^s$, we assumed, as in [5], that the electron density N does not change in the range 84-250 K and mechanisms with the parameter $r = -0.5$ dominate in scattering. Figure 4 shows $\log m^* \sim \log(T^{-1} F_{3/2}^{-2/3}) = f(\log T)$ (here F are the Fermi integrals) for solid solutions with 4 and 10 at % Se; their properties are shown in Fig. 3. For a lightly doped solid solution with 4 at % Se ($x = 0.12$), all the points in the range of impurity conduction are well fitted to the straight line 1 with the slope $s = 0.36$. This means that the density-of-states effective mass increases with temperature as $m^* \sim T^{0.36}$, which is indicative of the nonparabolicity of the electronic spectrum. The smaller value $s = 0.04$ for a more heavily doped sample [5] is in agreement with the result obtained, because the nonparabolicity in strongly degenerate samples does not lead to a significant increase in the averaged effective mass with increasing temperature. The behavior of the effective mass in $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ solid solution with temperature in the range 240-120 K is qualitatively the same, only the slope of the corresponding plot, $m^* \sim T^{0.21}$ (curve 2), is smaller. However, at $T < 120 \text{K}$ the character of the dependence is reversed: the effective mass increases as temperature decreases. This may indicate that either the description of scattering by the relation $\tau \sim \epsilon^{-0.5}$ becomes incorrect at low temperatures or the assumption of a constant carrier density in the conduction band is not well justified.

In the first case, it is evident that, for a linear decrease in the effective mass to continue as T decreases to below 120 K, the negative exponent in the energy dependence of the relaxation time (see above) must decrease in magnitude, which would indicate an enhancement in the scattering of low-energy electrons. This can occur, for example, in solid solutions with an inhomogeneous distribution of components within the sample, which gives rise to a random profile of the bottom of the conduction band. In this case, localization at low temperatures is also possible. In lightly doped samples, this mechanism of carrier scattering can be dominant at low temperatures.

There is also a second possible source of the anomaly in the $m^*(T)$ dependence obtained: the increase in the electron

density with temperature. In this case, the structure of the electronic spectrum in the given materials must be discussed. Valuable information can be obtained from temperature measurements of the Hall effect. Unfortunately, the determination of the temperature dependence of the electron density encounters problems related to the lack of data on how the anisotropy coefficient and Hall factor change when the mechanism of scattering becomes operative. Nevertheless, general trends can be revealed by comparing the Hall data for samples that differ in composition and doping level. In this study, we present only the first result of projected systematic studies of this kind, and this result refers to the $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ sample under study (Fig. 3). In the measurements of the Hall coefficient, the directions of current and Hall field were in the cleavage plane, and the magnetic field was normal to it. Assuming that the observed decrease in ρ_{123} with increasing temperature is related to the increase in electron density, we took this effect into account in our calculations and obtained curve 2' in Fig. 4 for the dependence $m^*(T)$. In this case, all the calculated points fall with satisfactory precision on the straight line $m^* \sim T^{0.22}$. Taking into account that an even stronger decrease in ρ_{123} with increasing temperature was observed for a sample of the same composition and similar properties in [3], we may conclude that an increase in electron density with increasing temperature is quite probable in these materials. Thus, a qualitative explanation for the specific features observed is obtained.

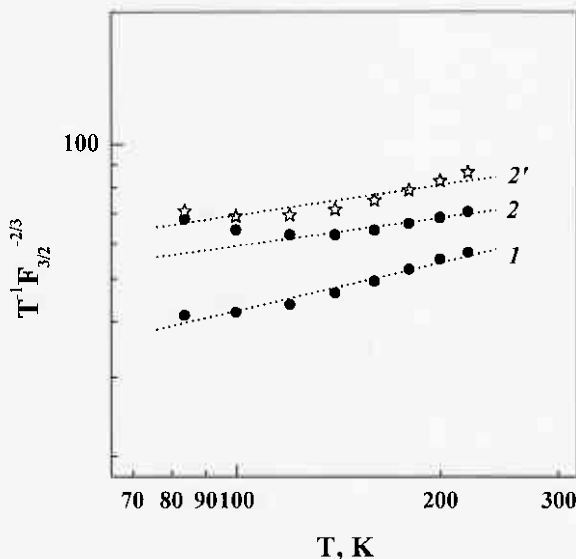


Fig. 4. Temperature dependences of the effective mass for lightly doped solid solutions, (1) $\text{Bi}_2\text{Te}_{2.88}\text{Se}_{0.12}$ and (2, 2') $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$. (2) $N = \text{const}(T)$ and (2') $N = f(T)$.

It remains to be understood what is the reservoir from which electrons pass to the conduction band as temperature increases. Several alternatives are possible. One is related to the inhomogeneity of the material, as discussed above.

Another possibility is that a level related to structural or impurity defects is formed near the bottom of the conduction band. In terms of this model, it is possible to account for the steeper temperature dependence of the electrical conductivity at $T < 125$ K in $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ solid solutions with $x = 0.3$ and 0.36 and $S \approx 200 \mu\text{V K}^{-1}$ at 84 K, as mentioned above. Finally, the reservoir of electrons might be the heavy conduction band, whose existence in the materials in question has been discussed earlier [6]. The small separation between the heavy and light bands at 0 K and its positive temperature coefficient could stimulate the transfer of carriers to the light band with the rise of temperature; in this case, the effective density would increase.

Conclusion

We may conclude that the rather high electrical conductivity and its slight decrease as the temperature increases in the range 85-300 K, along with low thermal conductivity, are specific features of the thermoelectric properties of the n- $\text{Bi}_2(\text{TeSe})_3$ solid solutions. They discriminate between the given materials and the similar materials based on PbTe. These peculiarities are responsible for the increase in the figure of merit and for the shift of its maximum to higher temperatures, where the transport properties fundamentally change under the effect of intrinsic carriers. It is most likely that the anomalies in the temperature behavior of σ and Z_{max} are the result of an increase in electron density with increasing temperature, which, in one's turn, may be a consequence of complex energy spectrum.

Acknowledgments

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