THERMAL CONDUCTIVITY OF PRESSED $Sb_2Te_3 + Bi_2Te_3$ POWDERS

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INTRODUCTION

The semiconductor material Sb—Bi—Te is used mainly for thermoelectrical refrigeration of small performance and climatization, for constructing small thermogenerators and for special purposes. It always presents the p-type branch of the thermoelement, and its thermoelectric figure of merit is the biggest among all known materials at low temperatures.

This paper deals with the influence of the grain size, of the amount of impurities and of processing upon the thermal conductivity of the optimum pressed solid solution consisting of 75 mol % Sb_2Te_3 + 25 mol % Bi_2Te_3 with a surplus of 3 weight % of Te.

PREPARATION OF SAMPLES AND MEASUREMENT METHOD

Initial raw materials were of the following purity: Sb 99.995 %, Bi 99.999 %, Te 99.999 %. As active impurity Pb powder g. r. was used.

Various grain sizes were gained by crushing and sieving. Powdered material was pressed into samples of the size $5 \times 5 \times 20$ mm, either by cold pressing followed by sintering (designation PS) or by hot pressing (PT), or by hot pressing followed by annealing (PTŽ). Exact specification of the material and sample processing is to be found in [1].

Thermal conductivity was measured in the Laboratory of E. K. Iordanišvili in Leningrad. The heat flow proceeded from a heated Cu-block through a primary standard of thermal conductivity (ternar solid solution), a Cu-plate, the measured sample, a second Cu-plate and a second standard to a cold Cu-block. Sufficiently old ternar solid solutions have been used as standards to maintain an exactly given value of thermal conductivity. The standards were contacted with the Cu by BiSn; between the sample and the Cu-plates InGa eutecticum was used to improve contacts. Temperatures were measured by chromel-kopel thermo-couples.

Measurements were made in the air at the steady state at an average temperature of the sample of approximately 300 °K. For computing the thermal conductivity λ [$Wcm^{-1}deg^{-1}$] we used the formula derived from the equality of thermal flows through standards and the measured sample with regard to thermal losses to surroundings. The accuracy of measurements of λ was approximately ± 7 %, reproducibility ± 3 %.

The lattice thermal conductivity λ_m was computed from the formula

$$\lambda_m = \lambda - \lambda_e$$

where the electron component of the thermal conductivity is expressed by the formula

$$\lambda_e = L\sigma T.$$

The Lorenz number L [V^2deg^{-2}] was taken from the graphic dependence $L = f(\alpha)$ obtained by means of theoretical relations for α and L as the functions of the chemical potential [2], at a coefficient of scattering $r = 0$; the electrical conductivity σ [$\Omega^{-1}\,cm^{-1}$] was determined by measurements at an average temperature of 300 °K. It is necessary to remark that the bipolar diffusion thermal conductivity contribution, which could be of influence in materials of the least electrical conductivity, was not considered in the calculation. The accuracy of determining L and T was approximately ± 1 %, the accuracy of measurements of σ was ± 4 %.

In the following chapters we are dealing with the electron component of thermal conductivity, its lattice component and the thermal conductivity from the point of view of dependences on the amount of impurity (paragraph **a**), on the grain size (**b**) and on the processing (**c**).

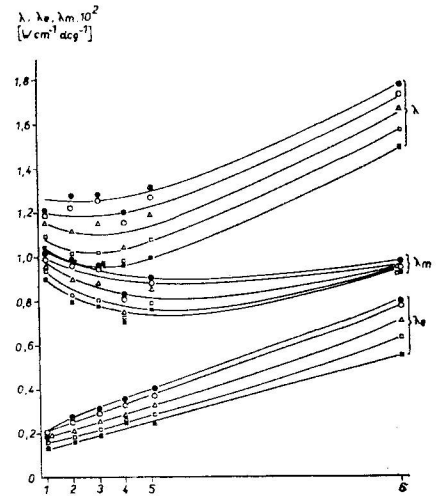
THE ELECTRON COMPONENT OF THERMAL CONDUCTIVITY

On the basis of measured dependences and their mutual comparisons it is possible to express the following conclusions:

a. The electron component of thermal conductivity with an increasing amount of the admixture of Pb (Fig. 1—3) is increasing, because the density of mobile holes increases [1] (variations in the values of the holes' mobility and of the Lorenz number are considerably smaller).

b. The decrease of the electron component with decreasing grain size (Fig. 4—6) is also due mainly to the decreasing concentration [1]. The relatively big decrease of λ_e in fine-grained PT-materials is aided by oxidation of the powdered material in hot press-form just before pressing. The increase of the electron component with decreasing grain size of big grains doped by a small

Fig. 1. PS-material: dependence of thermal conductivity and its components on the amount of impurities. Parameter is the grain size. 1 — without Pb, 2 — .015 weight % of Pb, 3 — .030 %, 4 — .045 %, 5 — .060 %, 6 — .200 %. ● = 2 — 1 mm, ○ = 1 — .5 mm, △ = .5 — .2 mm, □ = = .2 — .06 mm, ■ < .06 mm.



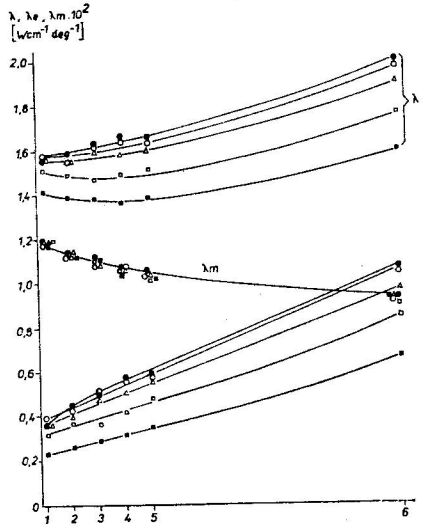


Fig. 2. PT-material: dependence of thermal conductivity and its components on the amount of impurities. Parameter is the grain size. Denotation as in Fig. 1.

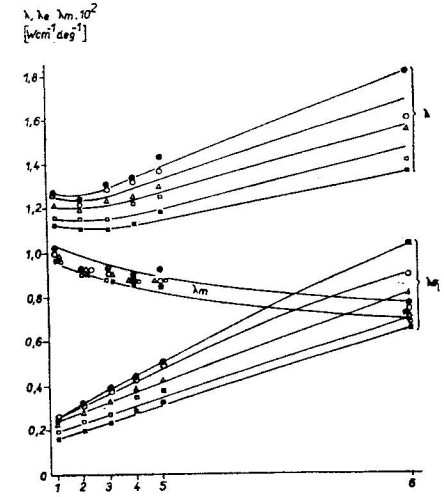


Fig. 3. PTŽ-material: dependence of thermal conductivity and its components on the amount of impurities. Parameter is the grain size. Denotation as in Fig. 1.

amount of impurities is due partly to the weak dependence of the hole density (on the latter factors) and also to the small influence of oxidation. But the decisi-

ve influence must be elsewhere. It is quite possible that microsplits result at hot pressing of the biggest grains, which fact contributes to the decrease of

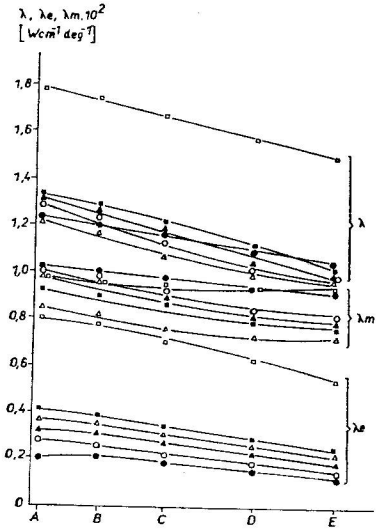


Fig. 4. PS-material: dependence of thermal conductivity and its components on the grain size. Parameter is the impurity content A = 2 — 1 mm, B = 1 — .5 mm, C = .5 — .2 mm, D = .2 — .06 mm, E < < .06 mm. ● — without Pb, ○ — .015 weight % of Pb, ▲ — .030 %, △ — .045 %, ■ — .060 %, □ — .200 %.

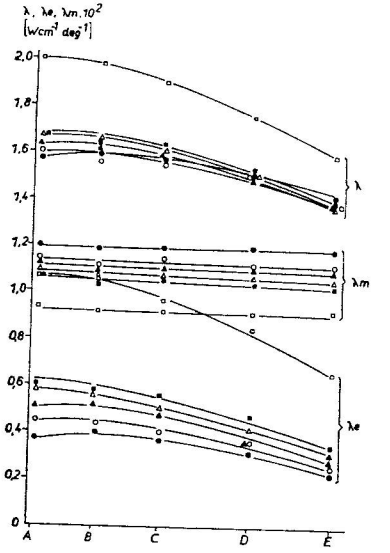


Fig. 5. PT-materal: dependence of thermal conductivity and its components on the grain size. Parameter is the impurity content. Denotation as in Fig. 4.

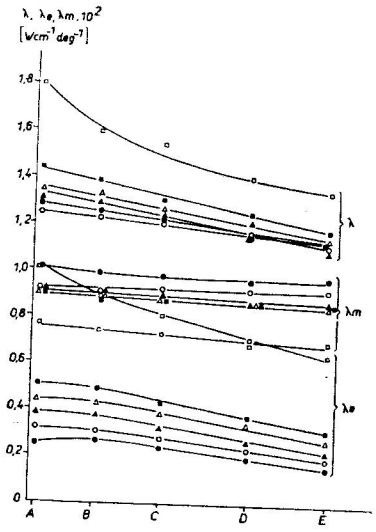


Fig. 6. PTŽ-material: dependence of thermal conductivity and its components on the grain size. Parameter is the impurity content. Denotation as in Fig. 4.

electrical conductivity and, thus, of λ_e as well. However, this phenomenon was not observed in PS-materials.

The general decrease of λ_e with the reducing of grain size is connected with decreasing material non-homogeneity [3]. With regard to its layer structure, the single crystal material is of a considerable non-homogeneity with respect to electrical conductivity. The σ-value of the perpendicular direction to the press-direction is bigger than that of the parallel direction. It is due to an oriented arrangement of grains having a single crystal character. The smaller the grains are, the smaller is the ratio of σ-values measured in different directions and our measured σ-value (perpendicular to press-direction) decreases. It is necessary to observe that according to patent [4], anisotropy of electrical conductivity can be practically annihilated by grinding the material instead of crushing it.

c. The biggest λ_e is found in the PT-material, this fact being due to the biggest density of holes [1]. The annealing of PT-materials melts down the excessive Te, which is the cause of a decrease of the hole density, hence also of λ_e. Distinctly lower value of λ_e in PS-materials is substantiated by lower hole concentration (in comparison with PTŽ), which is caused probably by the disappearing of the surplus Te during the hot pressing. Cold-pressed samples contain more Te dissolved during the annealing and causing a decrease of the hole density.

LATTICE COMPONENT OF THERMAL CONDUCTIVITY

On the basis of measured dependences and their mutual comparison it is possible to arrive at the following conclusion:

a. An increasing amount of Pb admixture causes generally the decrease of the lattice component, which may be explained by an increasing phonon scattering on the impurity atoms. The behaviour of λ_m in PS-materials doped by .06 % and especially .20 weight % of Pb is, however, anomalous. It is possible to express the hypothesis that at these concentrations the Pb-atoms create a certain system in the material, so that they do not appear like defects but they increase the bond strength and decrease the coefficient of anharmonicity H in the equation

$$\frac{1}{\lambda_m} = 3H \frac{T - \Theta/3}{v}$$

which is applicable at temperatures above the Debye-temperature Θ (v is the sound velocity) [5].

However, another explanation is possible, namely the hypothesis that the

lattice component of thermal conductivity was computed wrongly. Supposing the scattering-coefficient in case of the biggest doping being e. g. $r = 1$, the Lorenz number increases up to about 30—40 %, which is the cause of a decreasing lattice component. At present it is not possible to decide which of these explanations is better.

The fact that in PT and PTŽ-materials such anomaly was not observed is due evidently to some phenomenon acting during the hot pressing, namely either to the oxidation of the powdered material in the hot press-form just before pressing or to the disappearing of the surplus Te during the hot pressing.

b. With the decreasing of grain size, λ_m slightly decreases (Fig. 4—6), which is evidently due to an additional scattering of phonons on the grain boundaries. In PT and PTŽ-materials this decrease is practically negligible, which may be explained by the fusion of grains during the hot pressing (no scattering on the grain boundaries), and also by the occuring of microsplits in the gross-grained samples (low value of σ in gross-grained samples with a small Pb-doping).

c. The biggest values of λ_m are generally to be found in PT-materials. It is interesting that by annealing these materials, λ_m drops on the average to 20 % of the original value, whence it is possible to conclude that the introducing of Te-atoms into the lattice causes an increase of H. This hypothesis holds also as an explanation of the lowest value of λ_m in fine-grained PS-materials with a small impurity content (containing a greater surplus of Te). In gross-grained materials with a small impurity content the values of λ_m in PTŽ and PS-materials are similar (the escaping of Te during hot pressing is evidently smaller in this case), while the biggest value of λ_m in case of the biggest doping of PS-samples may be explained in the same way as in paragraph a.

THERMAL CONDUCTIVITY

The dependences of thermal conductivity are estimated only as a superposition of the dependences of λ_e and λ_m.

a. The dependence of λ upon the impurity concentration diminishes at the beginning (Fig. 1—3), because the decrease of the lattice component is bigger than the increase of the electron component. With further adding of Pb, however, λ_e keeps increasing uniformly, whereas λ_m decreases now less (in PT and PTŽ-materials) or it even increases (PS), so that in diagrams there are minima (approximately at .015—.030 weight % of Pb), which are more pronounced and shifted to the range of bigger concentrations of impurities in small grains.

b. Decreasing λ with the reduction of grains (Fig. 4—6), which is relatively the smallest in the samples without impurities, is caused almost exclusively

by the electron component. It is only in PS-materials that the dependence of λ_m also takes part in the decrease of λ.

c. The biggest λ in PT-materials is due to values of both components (λ_e on the average decreases by 25 %, λ_m by 20 %). The most important results arrived at are that the lowest values of thermal conductivity have been obtained in cold-pressed samples (with the exception of the case of the biggest impurity content, in which the electron component is the major factor).

CONCLUSIONS

According to the results of our measurements, the amount of impurities, the grain size and also the processing of samples influence the value of thermal conductivity and its components. The reasons or at least the probable reasons of all measured dependences are given in this paper.*

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