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Thermoelectric properties of fine-grained sintered $(Bi_2Te_3)_{25}$–$(Sb_2Te_3)_{75}$ p-type solid solution

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P-type semiconductor alloy compacts of the composition $(Bi_2Te_3)_{25}$ – $(Sb_2Te_3)_{75}$ with grain size (L) in the range $30 > L > 20$ μm, $20 > L > 15$ μm, $15 > L > 10$ μm, $10 > L > 5$ and $L < 5$ μm were prepared by cold press at a pressure of 77×10^7 Nm^{-2}. The samples were sintered at 673 K. Measurements of the Seebeck coefficient, electrical resistivity and thermal conductivity were carried out. The experimental results show that the Seebeck coefficient increases, but not much from the single crystal. The electrical resistivity increases in particular for the size $L < 5$ μm with a reduction in grain size. The total thermal conductivity seriously decreases as grain size decreases. It is concluded that the figure of merit of the compacted alloy would be significantly improved through the use of fine-grained powders of size 30–10 μm.

1. Introduction

Alloys of the semiconductor Bi_2Te_3 and its compounds with Sb_2Te_3, Bi_2Se_3 and Sb_2Se_3 are candidates for good thermoelectric materials [1]. Bismuth telluride and its alloys are the only established thermoelectric materials that exhibit anisotropic properties. The electrical and mechanical properties are higher along the two equivalent principal directions parallel to the (1 1 1) cleavage planes than along the c-axis, which is perpendicular to these planes [2–5]. The conversion efficiency of a semiconductor's thermocouples depends on the temperature range over which the device operates, its average temperature, and the figure of merit, z, for the thermocouples material [6].

$$Z = \alpha^2/\rho\kappa \qquad (1)$$

where α is the Seebeck coefficient, ρ is the resistivity, and κ is the thermal conductivity.

Thermal conductivity is the sum of the contributions arising from the lattice thermal conductivity (phonon) κ_L, and the electronic thermal conductivity κ_e, i.e. $\kappa = \kappa_L + \kappa_e$ [6, 7]. In semiconductors, thermal conductivity is mainly caused by phonons [8]. Later this gives an interest in the use of the cold or hot pressing technique. This technique has offered a possibility of reducing the lattice thermal conductivity due to the scattering of phonons caused by grain boundaries, and hence improving the figure of merit [9]. For isotropic semiconductor alloys such as Si–Ge [8] and PbTe [10], it is always expected that the figure of merit, Z, will be improved on obtaining grains that are small enough for the onset of phonon scattering. Hypothetically, the same treatment cannot be applied to anisotropic BiTe based alloys, since there is a preferred direction parallel to the (1 1 1) plane.

The object of this work is to see the net effect on thermoelectric properties resulting from loss of preferred orientation and reduction of thermal conductivity caused by phonon scattering at grain boundaries.

2. Experimental procedure

The alloy selected for this study is a p-type semiconductor $(Bi_2Te_3)_{25}$ – $(Sb_2Te_3)_{75}$. This alloy has a high figure of merit at room temperature [3]. The energy gap is found to be increased by adding Se as a dopant. And the highest energy gap is expected to be between 0.25 and 0.6 wt % of Se [11]. The alloy under investigation was doped with 0.35 wt % of selenium.

The starting elemental materials were (Te and Se Johnson Mathy Specpure), (Bi and Sb annular grade reagent BDH). The elements with the desired dopant were melted inside an evacuated silica tube. A raise rate of 1 °C min^{-1} was employed. The molten charge was maintained molten for a period of 6 hours at 1073 K, then cooled at the same rate. The silica tube was turned upside down and the heating/cooling cycle repeated. The polycrystals rod was first broken down into small grains. Wet milling using a planetary mill was used to obtain fine-grain powders; ethanol was used. The powder was graded using wet sieving through oscillating sieves of sizes L in the ranges $30 > L > 20$ μm, $20 > L > 15$ μm, $15 > L > 10$ μm, $10 > L > 5$ μm and $L < 5$ μm. Disc-shaped samples 13 mm in diameter and approximately 2 mm thick were produced by cold pressing using an alloy steel die under a pressure of 77×10^7 Nm^{-2}. The samples were sintered at 673 K for a period of 6 hours under argon gas. The very fine powder of grain size $L < 5$ μm could not be compacted at room temperature. The die which contained the powder was heated to about 360 K and then pressed while it was hot, followed by sintering as previously mentioned.

To measure the Seebeck coefficient, heat was applied to the sample which was placed between two small perfectly parallel brass cylinders. The temperature

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difference between these two cylinders was measured using k-type thermocouples and a sensitive Keithley digital thermometer. The potential difference was obtained at the position of the two thermocouples using a sensitive Fluke digital multimeter. It is possible to evacuate the atmosphere and introduce any desired gas. Helium gas was used at atmospheric pressure throughout the measurements in order to reduce evaporative loss at elevated temperature.

The resistivity measurements were made using a DC four-probe technique. The specimen is contained in a small cylindrical ceramic box. The four probes are placed over the specimen, and the probes' pressure is adjusted by using a pressing nut.

The thermal conductivity measurements were obtained by measuring the thermal diffusivity using the transient laser flash technique. The thermal conductivity of material κ is related to the thermal diffusivity α' by the simple relation $\kappa = \rho C_P \alpha'$ [7], where ρ is the density and C_P is the specific heat per unit of mass. It is an acceptable approximation to assume that C_P suffers a very small variation for temperatures above 100 K [12]. These two quantities can be easily measured. The specific heat is measured at room temperature. The heat pulse source is an IR neodymium glass laser, with a wavelength of 1.064 μm. The temperature sensor is a thermocouples or an IR detector [13]. Thermocouples type κ was used.

The measurements were obtained over the temperature range 120–750 K.

3. Results and discussion

BiTe and its related pseudo-binary and ternary alloys have been extensively studied in single crystal form below room temperature [2, 3, 14] and by Rosi *et al.* [14] at high temperature. This work is intended to examine the influence of fine grain on the figure of merit.

The alloy under investigation was found to be isotropic for samples annealed at 673 K. The samples change to an anisotropic state if the temperature exceeds 680 K. This is presumably due to an anisotropic alignment of the grain at high temperature [15]. This work deals with samples annealed at 673 K.

3.1. Seebeck coefficient

A maximum increase of the Seebeck coefficient α from about 154 μVK^{-1} before sintering to more than 250 μVK^{-1} after sintering at room temperature was observed. The variation of α with temperature is shown in Fig. 1. The rise in α and the occurrence of a maximum is to be expected [14]. The rapid decrease at about 330 K occurred due to the onset of intrinsic conductivity. The variation of the Seebeck coefficient with grain size is shown in Fig. 2 for different temperatures. As can be seen, α increases with increasing grain size. For temperatures of $T < 400$ K the Seebeck coefficient increases by about 20% as the grain size increases from $L < 5$ μm to $30 > L > 20$ μm. For high temperatures where $T > 600$ K, α decreases with increasing grain size and then increases to a value not much different from the $L < 5$ μm value.

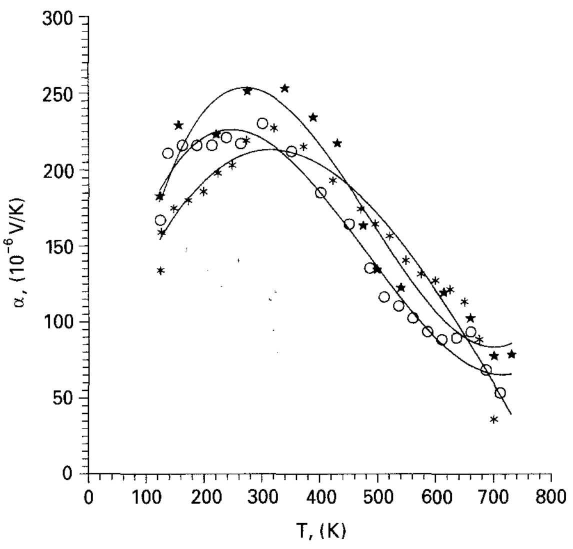

Figure 1 The variation of the Seebeck coefficient with temperature for the alloy with three different grain sizes. The solid lines indicate a best fit to a polynomial of order 4. ★ $30 > L > 20$ μm, ○ $10 > L > 5$ μm, * $L < 5$ μm.

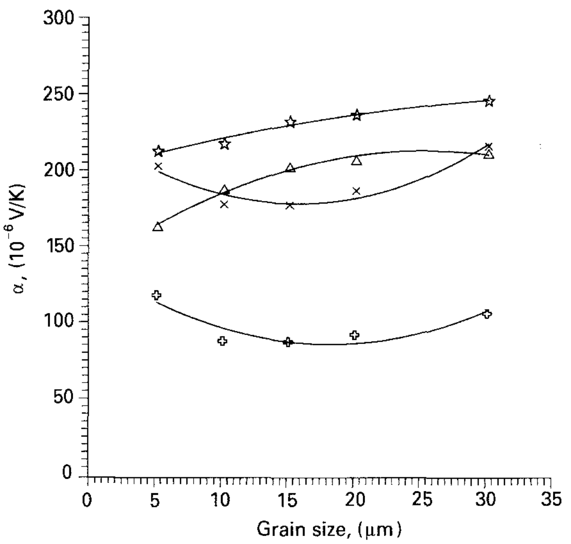

Figure 2 The variation of the Seebeck coefficient with grain size at four different temperatures. The solid lines indicate a best fit to a polynomial of order 2. △ $T = 140$ K, ☆ $T = 320$ K, × $T = 400$ K, ✥ $T = 600$ K.

The Seebeck coefficient for the sample where $L = 100$ μm is found to give approximately the same value as those where $30 > L > 20$ μm.

3.2. Electrical resistivity

The results of measuring electrical resistivity ρ at various temperatures up to 700 K are summarized in Fig. 3. In all cases ρ initially increases with increasing temperature, which is due to a decrease in carrier mobility as temperature goes up [12]. The sharp drop in ρ at about 380 K reflects the onset of intrinsic conduction. The temperature for transformation from an extrinsic to an intrinsic semiconductor is about 100 K lower for α than for ρ. This occurs because the Seebeck coefficient is more sensitive to a change in the transport mechanism in the degenerate or near-degenerate semiconductor than in resistivity [14, 16]. This is found for all samples with the exception of the sample where L < 5 μm, where the observed maximum value of electrical resistivity is shifted to a lower temperature (200 K).

The influence of grain size on electrical resistivity is shown in Fig. 4. The resistivity should be somewhere between that parallel to the (1 1 1) plane (i.e. 1.1×10^{-5} Ωm) at room temperature [16] and about four times this value for the direction perpendicular to the (1 1 1) plane, as the powder is composed of a random mix of crystallites of different orientation. The studies of Bi-Te compounds [17] and Si-Ge [18, 19] confirm that alloys prepared from compacted powders show a reduction in the carriers; this is because electrons are effectively scattered by imperfections such as grain boundaries. This will raise electrical resistivity. Fig. 4 supports this assumption, as it can be seen that resistivity increases with decreasing grain size (i.e. the finer the grain the higher the resistivity). The results indicate that this effect is a matter of great importance at low temperature. At a temperature of 120 K, $\rho = 1 \times 10^{-5}$ Ωm for L < 30 μm, while ρ becomes 90 times this value for L < 5 μm. For a high temperature of 700 K, $\rho = 3 \times 10^{-5}$ Ωm for L < 30 m, and it becomes 5 times this value for 1 < 5 m.

3.3. Thermal conductivity

The temperature variations of the total thermal conductivity are displayed in Fig. 5 for three grain sizes. The increase in thermal conductivity at T > 300 K could be attributed to the onset of intrinsic conductivity, and thus the ambipolar contribution takes part in thermal conductivity (i.e $\kappa = \kappa_e + \kappa_L + \kappa_{amb}$) [3, 10]. Fig. 6 shows the variation of the total thermal

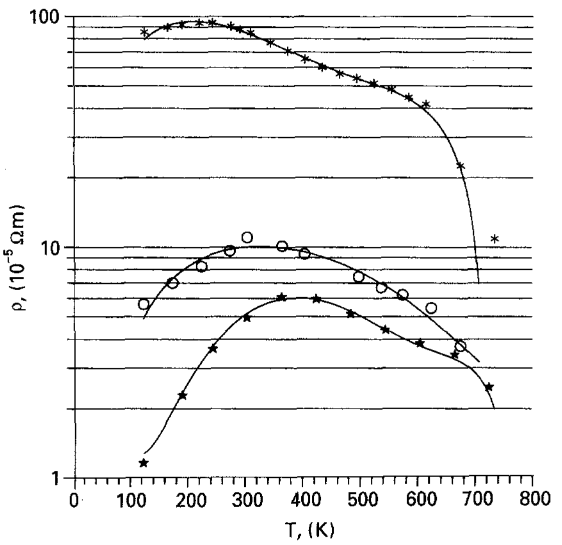

Figure 3 The variation of the resistivity with temperature for the samples of Fig. 1. The solid lines indicate a best fit to a polynomial of order 4. ★ 30 > L > 20 μm, ○ 10 > L > 5 μm, * L < 5μm.

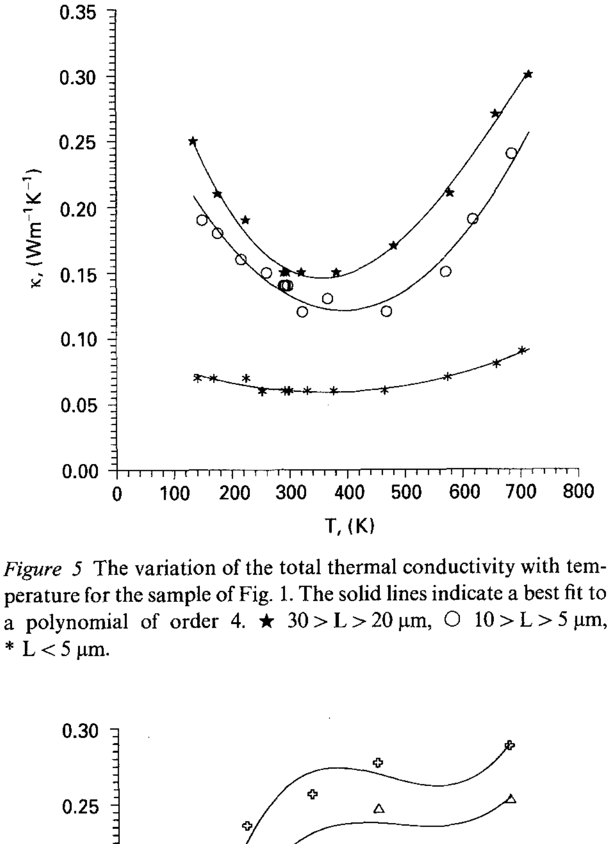

Figure 5 The variation of the total thermal conductivity with temperature for the sample of Fig. 1. The solid lines indicate a best fit to a polynomial of order 4. ★ 30 > L > 20 μm, ○ 10 > L > 5 μm, * L < 5 μm.

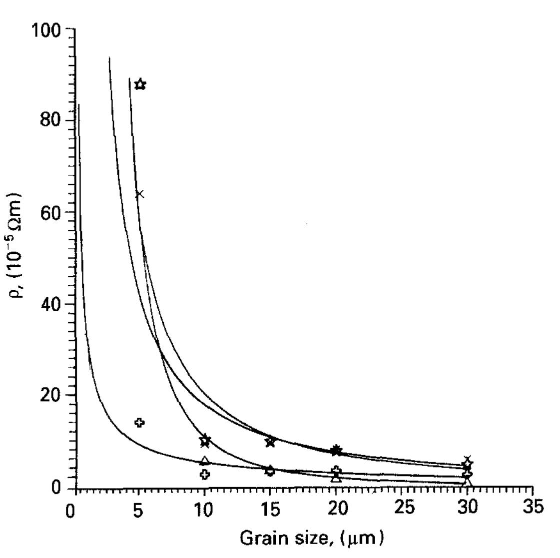

Figure 4 The variation of the resistivity with grain size at four different temperatures. The solid lines indicate a best fit to a power function. △ T = 140 K, ☆ T = 320 K, × T = 400 K, ✥ T = 700 K.

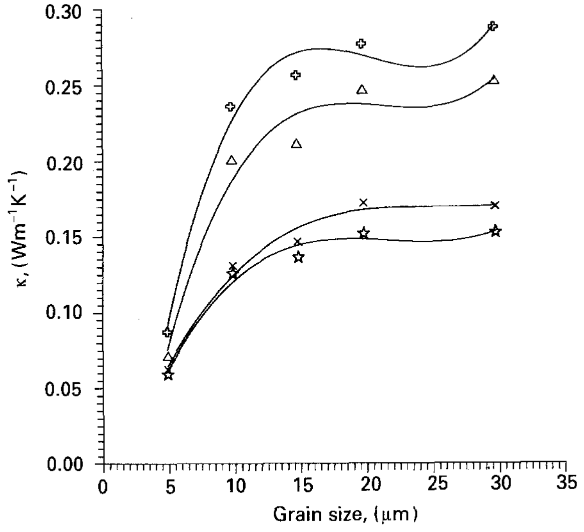

Figure 6 The variation of the total thermal conductivity with grain size at four different temperatures. The solid lines indicate a best fit to a polynomial of order 4. △ T = 140 K, ☆ T = 320 K, × T = 500 K, ✥ T = 700 K.

conductivity with grain size, at four different temperatures. The decreases with a reduction in grain size are expected. The ratio $\kappa_{\text{pressed}}/\kappa_{\text{single crystal}}$ as a function of grain size at room temperature is shown in Fig. 7.

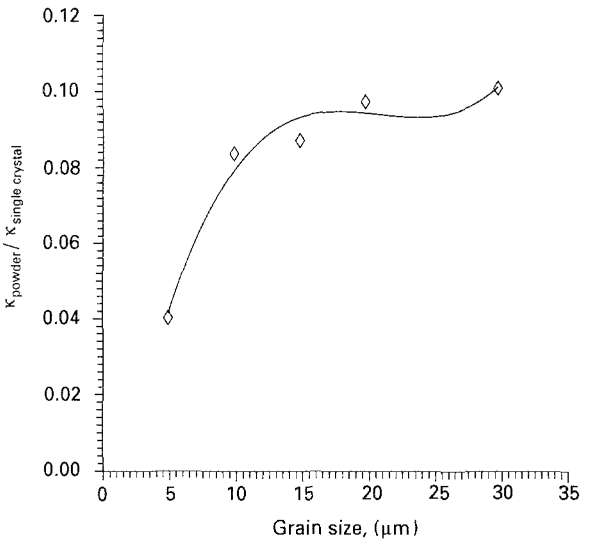

Figure 7 The variation of $\kappa_{\text{powder}}/\kappa_{\text{single crystal}}$ with grain size at room temperature. The solid line indicates a best fit to a polynomial of order 4.

4. Conclusions

The aim of this study was to see the effect of the grain size on the electrical properties of the $(Bi_2Te_3)_{25}$–$(Sb_2Te_3)_{75}$ alloy. The results indicate that the Seebeck coefficient of the compacted material remains nearly the same as its single crystal, with the exception of the sample $30 > L > 20$ μm, where it increases by about 19 %. For other sizes, the enhancements are not more than 4 %. The electrical resistivity increases with decreases in grain size. And the total thermal conductivity shows a substantial decrease with grain size. Figs. 8 and 9 show the variation of the figure of merit with temperature and with grain size, respectively. The decrease in the total thermal conductivity improved the figure of merit compared to the single crystal. At room temperature the improvements for the sizes $30 > L > 20$ μm, $20 > L > 15$ μm, $15 > L > 10$ μm and $10 > L > 5$ μm are about 114 %, 38 %, 16 %, and 5 %, respectively. The very fine-grained powder of $L < 5$ μm shows a remarkable reduction of about 75 % in the figure of merit. This could be attributed to the sample's high resistivity.

The room temperature experimental results are displayed in Table I. The implication of these results is that the performance of the figure of merit would be significantly improved by the use of fine-grain powder with grain sizes in the range 30–10 μm.

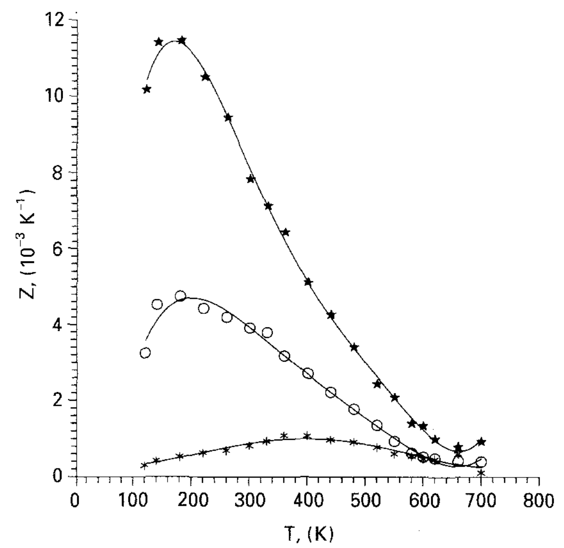

Figure 8 The variation of the figure of merit with temperature for the samples of Fig. 1. The solid lines indicate a best fit to a polynomial of order 4. ★ $30 > L > 20$ μm, ○ $10 > L > 5$ μm, * $L < 5$ μm.

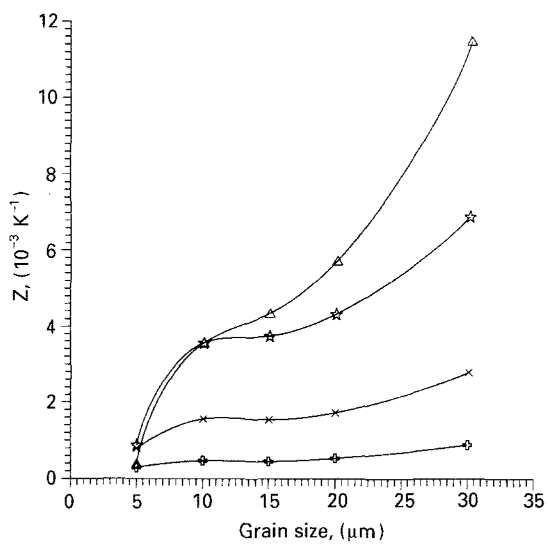

Figure 9 The variation of the figure of merit with grain size at four different temperatures. △ T = 140 K, ☆ T = 320 K, × T = 500 K, ✧ T = 700 K.

TABLE I Room temperature properties of investigated compounds

Specimen	α (10^{-6} VK^{-1})	ρ (10^{-5} Ωm)	κ (Wm^{-1}K^{-1})	Z (10^{-3}K^{-1})	Improvement %
Single crystal[a]	210	0.98	1.27	3.54	
Single crystal[b]	155	2.1	0.61	1.87	
$30 > L > 20$ μm	250	5.5	0.15	7.6	114
$20 > L > 15$ μm	235	8	0.14	4.9	38
$15 > L > 10$ μm	230	10	0.13	4.1	16
$10 > L > 5$ μm	220	10.4	0.125	3.7	5
$L < 5$ μm	215	88	0.06	0.88	disimp. 75

[a] adapted from [14]
[b] adapted from [20]

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