

Comparison of thermoelectric properties of polycrystalline and sintered PbTe doped with chromium and iodine

Aleksandra Królicka, Andrzej Hruban, Andrzej Materna, Mirosław Piersa, Stanisława Strzelecka, Wojciech Dalecki, Magdalena Romaniec, Krzysztof Orliński

Instytut Technologii Materiałów Elektronicznych
ul. Wólczyńska 133, 01 - 919 Warszawa;
e-mail: aleksandra.krolicka@itme.edu.pl

Abstract: In this paper we compare the electrical and thermoelectric properties of polycrystalline PbTe doped with chromium and iodine, obtained by the Bridgman method and the sintered material obtained following the powder processing procedure. The highest values of the Seebeck coefficient for the polycrystalline and sintered material are as follows: $-160 \mu\text{V/K}$ ($T = 675 \text{ K}$) and $-311 \mu\text{V/K}$ ($T = 573 \text{ K}$), respectively, thus indicating a significant improvement in the thermoelectric properties of the sintered material. The studies of the influence of the powder particle size on the properties of the sintered material were carried out.

Key words: thermoelectricity, PbTe, ball milling, pressing, sintering

Porównanie właściwości termoelektrycznych polikrystalicznego i spiekane go PbTe domieszkowanego chromem i jodem

Streszczenie: W artykule przedstawiono porównanie własności elektrycznych i termoelektrycznych polikrystalicznego telurku ołowiu domieszkowanego chromem i jodem, otrzymanego za pomocą metody Bridgmana z własnościami materiału spiekane go otrzymanego z proszków. Najwyższe wartości współczynnika Seebecka polikrystalicznego materiału i materiału po spiekaniu wynoszą odpowiednio: $-160 \mu\text{V/K}$ ($T = 675 \text{ K}$) oraz $-310 \mu\text{V/K}$ ($T = 573 \text{ K}$) i wskazują na znaczną poprawę parametrów termoelektrycznych materiału otrzymanego w wyniku spiekania. Przeprowadzono badania wpływu wielkości ziaren proszku na własności materiału spiekane go.

Słowa kluczowe: termoelektryczność, PbTe, mielenie kulowe, prasowanie, spiekanie

1. Introduction

Recently a significant development has been observed in the area of the nanoscale properties of thermoelectric (TE) materials and the control of their structure. Obtaining low dimensional structures, fine-grained materials with many grain boundaries and materials with nanometer precipitates makes it possible to improve the thermoelectric efficiency described by the figure of merit (Z). The modern synthesis and crystallization techniques enable reaching higher values of the Seebeck coefficient and thermal conductivity reduction at the same time. This makes them potential candidates for playing a crucial role in the world of renewable energy in the nearest future.

In order to capture the essence of the subject matter the most important details are given. The efficiency of TE materials depends on the following parameters: thermal conductivity, electrical conductivity and the Seebeck coefficient. These parameters are connected with each other by the following formula:

$$Z = \frac{\sigma S^2}{\kappa}, \quad (1)$$

where σ is the electrical conductivity, S is the Seebeck coefficient and κ is the thermal conductivity. The resulting figure of merit Z is more commonly used in its dimensionless form, ZT (where T is the absolute temperature)

in order to simplify the presented results. The S , κ and σ values are in fact closely interrelated, since they are determined by the same physical phenomena – defects and impurities that affect one of these properties usually also affect the other. Therefore, finding a compromise between them is the greatest and most difficult challenge in the production of these materials.

The free carrier concentration in semiconductors, which is influenced by doping, has a strong impact on the figure of merit. Fig. 1 illustrates the dependence of several thermoelectric parameters on the concentration of free carriers. While increasing the carrier concentration has generally harmful effect on the Seebeck coefficient, the electrical conductivity increases due to the increased number of carriers. On the other hand, the electric contribution to thermal conductivity (κ_e) becomes the dominant thermal conductivity mechanism at high values of carrier concentration. While values of all parameters are optimal for semiconductors, both insulators and metals have high values for single parameters but accordingly poor for others [1].

Typically, the appropriate values of carrier concentration in TE materials range between 10^{19} and 10^{21} cm^{-3} [2 - 3]. To ensure that the Seebeck coefficient is large, there should be a low carrier compensation degree. It means a few dopants of other type since mixed n -type/ p -type charge carriers lead to the opposite Seebeck effect and hence to low thermopower. It is also necessary to select

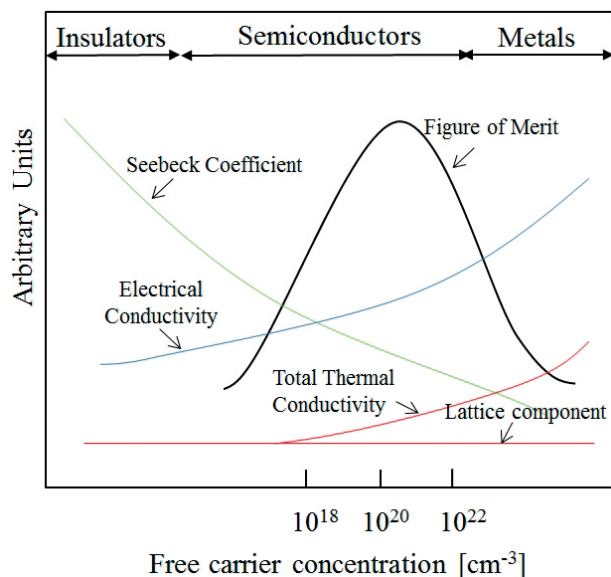


Fig. 1. Relation between thermoelectric parameters: Seebeck coefficient, electrical conductivity, thermal conductivity, figure of merit and free carrier concentration [1].

Rys. 1. Zależność parametrów termoelektrycznych współczynnika Seebecka, przewodności elektrycznej, przewodności cieplnej, dobroci termoelektrycznej od koncentracji nośników [1].

appropriate dopants and materials with suitable energy bandgaps to have both a single carrier type and sufficiently high carrier mobility. High efficiency TE materials are the materials with energy bandgaps lower than 1 eV, which is typical for heavily doped semiconductors. It is very important to make thermal and electronic conditions that determine the ZT value independent from each other. This has lately been the key strategy to improve ZT .

Group IV - VI semiconductor compounds, including PbTe, are most commonly used in TE applications in appliances called thermoelectric generators (TEGs). These are the materials operating in the temperature range of about 400 - 600 °C. By introducing various types of dopants like La or Cr and adding for example I dopant, high thermopower values can be obtained, thus improving ZT [4]. Chromium is a donor dopant in PbTe and it substitutes for Pb in the lattice. Iodine is also an n -type dopant producing donor centers in PbTe [1]. It has recently been suggested [5 - 12] that n -type PbTe double-doped with both chromium and iodine displays a strong increase in thermopower at temperatures starting from 400 K and reaching 600 K, leading to a strong power factor enhancement at these temperatures. It is due to forming a resonant level 100 meV above the conduction band minimum of PbTe:Cr. The distortion in the conduction band, taking place as a result of this effect, leads to a local enhancement of density of states (DOS). On the other hand, by controlling electron concentration due to the iodine doping, the Fermi level position is tuned and the Fermi level pinning can be obtained. Paul *et al.* [5] reported obtaining the coincidence of the Fermi level position with the distorted band, at temperatures above 375 K,

which enabled a significant thermopower improvement. In this investigation, achieving results comparable to these of Paul was attempted by fabricating double-doped PbTe : (Cr + I) [13]. However, we obtained lower values of TE parameters comparing to that of Paul and the explanation for this is given in this paper. Still, it is worth noting that other authors also made attempts to reproduce the results arrived at by Paul [13]. In the end, they did not observe the enhancement of thermopower and high power factor reported by Paul *et al.*

2. Experimental details

PbTe ingots with the 0.01 and 0.03 mol. % of PbI₂ were fabricated using the following procedure. Stoichiometric amounts of Pb, Te, PbI₂, having the purity of at least 99.99 %, were placed in quartz ampoules. This was followed by sealing the ampoules at the pressure of 10⁻⁶ - 10⁻⁷ Torr. The amount of 0.01 mol. % PbI₂ turned out to be insufficient to change the type of the material from p to n . As a result, the ingot of partly n -type conductivity was obtained following electrical parameters: $n = 4.04 \times 10^{18} \text{ cm}^{-3}$, $\rho = 1.17 \times 10^{-3} \text{ } \Omega\text{cm}$ and $\mu = 1322 \text{ cm}^2/\text{Vs}$. The remaining part of the crystal was p -type, however, the carrier concentration was reduced to $n = 4.94 \times 10^{17} \text{ cm}^{-3}$ at $\rho = 7.06 \times 10^{-2} \text{ } \Omega\text{cm}$ and $\mu = 119 \text{ cm}^2/\text{Vs}$. The amount of 0.03 mol. % PbI₂ added to PbTe crystal resulted in achieving mostly n -type conductivity and the electron concentration was $4 \times 10^{18} \text{ cm}^{-3}$. Subsequently, the ingot of Pb_{1-x}Cr_xTe:I ($x = 0.009$) was fabricated following the same procedure. Increasing the amount of the iodine dopant combined with adding 0.56 mol. % of Cr enabled changing the type of conductivity in the whole ingot. As a result, the level of carrier concentration ranged from 10¹⁹ to 10²⁰ cm⁻³, which is a desirable value.

The synthesis was carried out using a resistance furnace at temperatures up to 1000 °C. The duration of the process was 5.5 hours until all material elements were homogenized. The material was mixed every 15 minutes for even better homogenization of the elements. After 3 h the furnace was moved to the vertical position and it was held in this position for the next 2.5 hours at temperatures up to 954 °C (PbI₂ boiling point). Subsequently, direct, vertical crystallization was conducted. The velocity of this process was 12 mm/h in order to obtain fine-grained polycrystalline material (Fig. 2a). After ingot fabrication, it was cut into specimens and the electrical and thermoelectric measurements of polycrystalline PbTe were carried out.

Additionally, we fabricated sintered cylindrical discs of PbTe:Cr,I following the procedure of dry ball milling, cold pressing and sintering the obtained powders. The milling process was performed in a planetary ball mill in the air under the following conditions: $v = 600 \text{ rpm}$ for $t = 5 \text{ min}$, and $v = 250 \text{ rpm}$ for $t = 15 \text{ min}$. Milling jar and balls were made out of tungsten carbide. For cold pressing the powders were loaded into a graphite die and pressed using

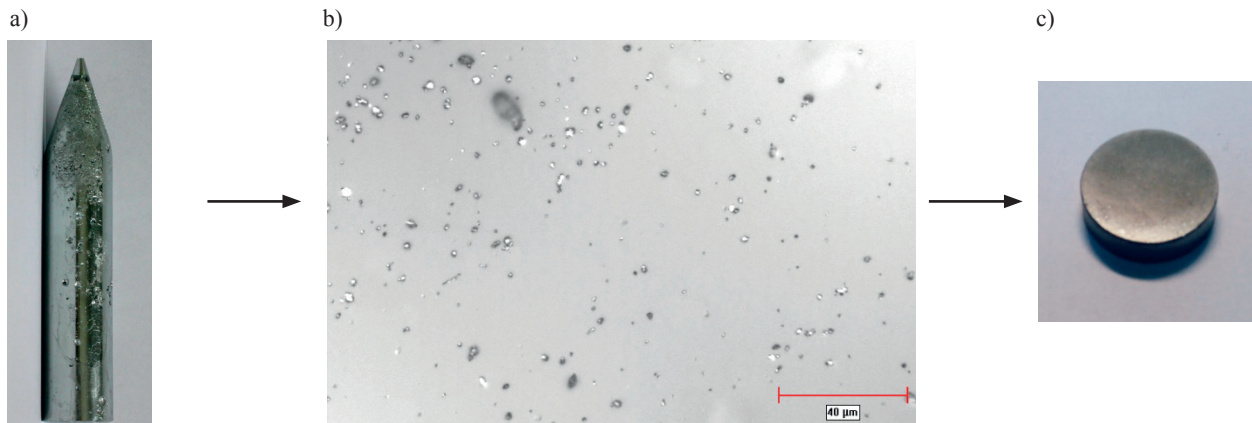


Fig. 2. a) PbTe polycrystal obtained by the Bridgman method, b) powder particles of the material (larger dark objects are the clumps of smaller particles), c) pellet obtained by cold pressing and sintering.

Rys. 2. a) Polikryształ otrzymany metodą Bridgmana, b) cząstki proszku PbTe (widoczne większe ciemne obiekty, to aglomeraty mniejszych ziaren), c) pastylka otrzymana w wyniku sprasowania na zimno i spiekania.

the pressure of 30 atm. The material was annealed for 3 h, at 600 °C in an iodine atmosphere. The obtained cylindrical discs were 19 mm in diameter and ranged in height from 2 mm to 5 mm (Fig. 2c).

The investigation of the structural properties of the powdered material was carried out. The powder particle size analysis indicated that ~ 80 % of particles have diameters ranging from 300 nm to 1 μm. Maximum measured diameter values were of ~ 12 μm but it is supposed that these are not single particles but clumps of particles (Fig. 2b). However, it has already been noted that when nanoscale powders are mixed (and densified) with micron-scale powders, conglomeration occurs [14]. By comparison, the measured grain size of the polycrystalline material obtained by the Bridgman method ranged from ~ 200 to ~ 900 μm. The powder particle size measurements were also performed using the laser diffraction method and confirmed these results.

The polycrystalline and sintered materials were characterized using the following methods:

- electrical measurements (including carrier concentration, mobility and resistivity) - by measuring the Hall voltage as a function of temperature up to 725 K,
- the Seebeck coefficient – using set of two heaters - one acting as a heat source and the other, as a heat sink - by measuring temperature gradients and the Seebeck voltage with two chromel-alumel thermocouples of 0.5 mm diameter. The Seebeck coefficient was determined from the ratio of the measured thermoelectric power and the temperature difference,
- the thermal conductivity – by measuring density (ρ), the specific heat (C_p), using the Simultaneous Thermal Analysis (NETZSCH STA 449F1 apparatus) and the thermal diffusivity (α) using the laser flash method (LFA 457 laser flash apparatus) - both as a function of temperature. The eventual thermal conductivity was determined using the following formula:

$$\kappa(T) = \rho(T) \cdot C_p(T) \cdot \alpha(T). \quad (2)$$

3. Results and discussion

The electrical and thermoelectric measurements were performed after each stage of the technological process (after obtaining the polycrystalline material and after preparing sintered discs).

Figs. 3(a-c) show the temperature dependence of carrier concentration, carrier mobility and resistivity, respectively.

A decrease in current carrier concentration when compared with the values obtained for the polycrystalline material was observed. This was probably due to the evaporation of some part of the iodine dopant during milling and sintering because of local high temperatures in the material occurring during these processes. This is consistent with the literature data [15] reporting on the same effect when sintering PbTe with the Na dopant. On the other hand, it has already been demonstrated that ball milling the powders to nanograins causes strain within the material and this affects transport properties, including carrier concentration [16]. However this was found to have a beneficial effect on the Seebeck coefficient because in nanostructured semiconductors scattering of carriers due to strain is obtained and this results in S enhancement. S follows the Pisarenko formula [3]:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}, \quad (3)$$

$$\frac{1}{\rho} = \sigma = ne\mu, \quad (4)$$

where k_B is the Boltzmann constant, m^* is the carrier effective mass, e is the electron charge, h is the Planck constant, n is the carrier concentration, ρ is the electrical resistivity and μ is the carrier mobility.

Oxidation can be another reason for a decrease in the carrier concentration of the sintered material. Due to the

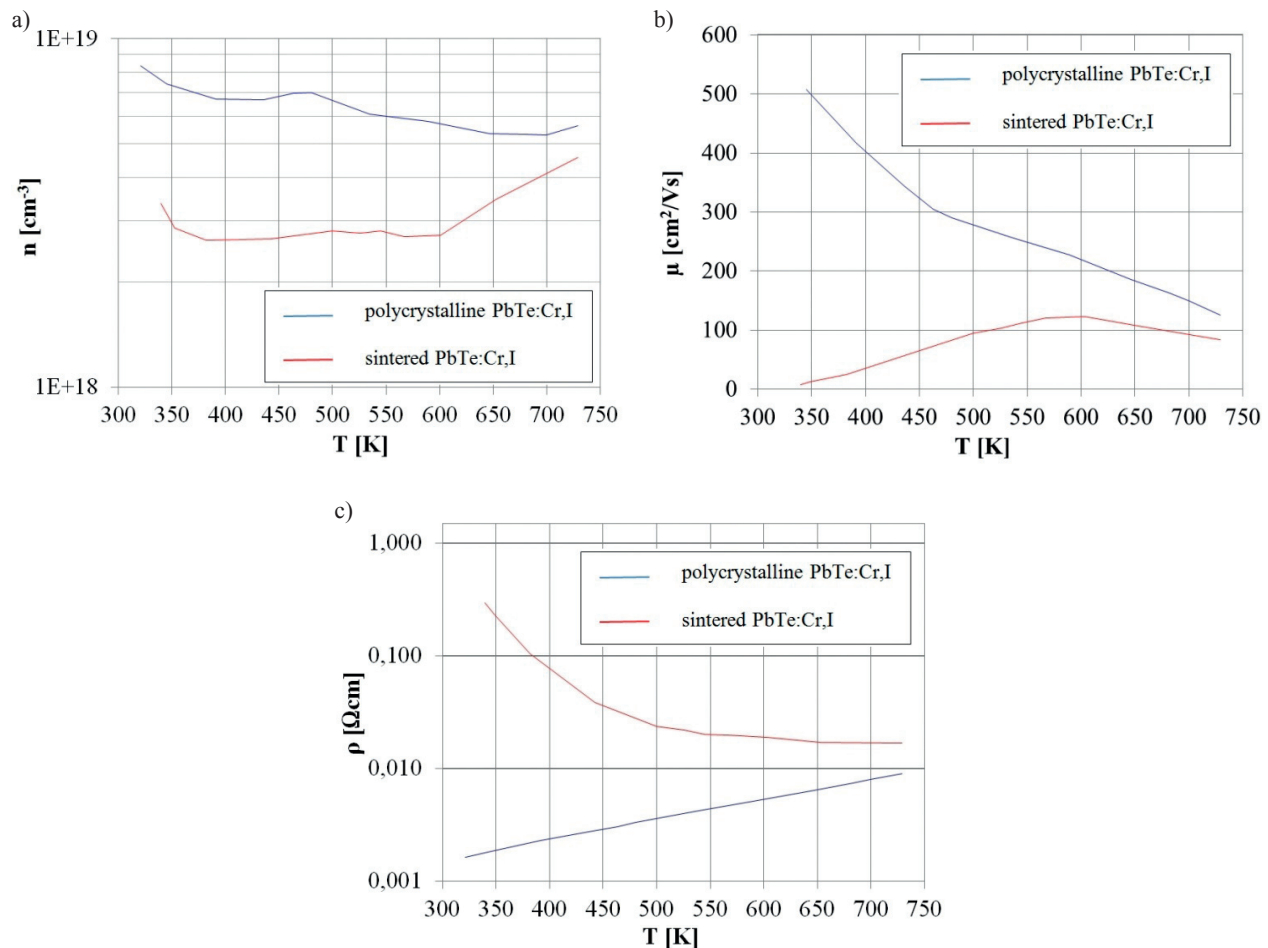


Fig. 3. Plot of electrical parameters versus temperature for PbTe:Cr,I; comparison of parameters for polycrystalline (blue line) and sintered specimens (red line): a) carrier concentration, b) carrier mobility, c) resistivity.

Rys. 3. Zależność parametrów elektrycznych od temperatury dla PbTe:Cr,I, porównanie parametrów próbek polikrystalicznych (niebieska linia) i po spiekaniu (czerwona linia): a) koncentracja nośników, b) ruchliwość, c) rezystywność.

surface adsorption of oxygen, the acceptor states in *n*-type PbTe are created. This draws electrons from within the grain and leads to hole concentration increase. Surface oxidation could occur during the milling process. An increase in both the local and the average temperature in the mill due to the dissipation of energy during collisions between the particles of powders is very important and difficult to estimate. As the particle diameter is reduced, the surface area/particle size ratio increases which results in an inversion from *n*- to *p*-type conduction [14]. One parameter which influences the temperature during the milling process is the thermal conductivity of the powdered material. It determines the intensity of heat removal from the place of collision. PbTe has low thermal conductivity, hence it does not remove the heat very quickly. On the other hand, all powder processing was undertaken in air atmosphere, without liquid and the material was milled at 600 rpm for some time. Taking all this into consideration, we suppose that oxidation can have a significant influence on the carrier concentration.

A decrease in carrier mobility, due to reduction of the grain size to nanometers was also observed (Fig. 3b).

Scattering of carriers on the grain boundaries and precipitates can be treated as an explanation of this phenomenon. This is an intentional effect, resulting in an increase in *ZT*.

The main purpose of this work was to investigate the TE properties of PbTe:Cr,I polycrystals and material prepared following the procedure of powdering, cold pressing and sintering. The TE properties were investigated at the temperatures ranging from 300 to 750 K.

The Seebeck coefficient of the material is negative, thus indicating the donor nature of the dopants (Fig. 4a). An increase in the absolute value of *S* as a function of temperature is observed. This can be related with increased resistivity resulting from a decrease in carrier mobility. At room temperature the absolute values of the Seebeck coefficient are lower as a result of higher carrier concentration at this temperature [17 - 19]. By obtaining the fine-grained material due to iodine incorporation the effective scattering of long mean free path phonons is realized [20 - 21]. This is likely to result in κ_L (lattice contribution to thermal conductivity) reduction thereby leaving holes/electrons unaffected (due to the so called energy filtering effect).

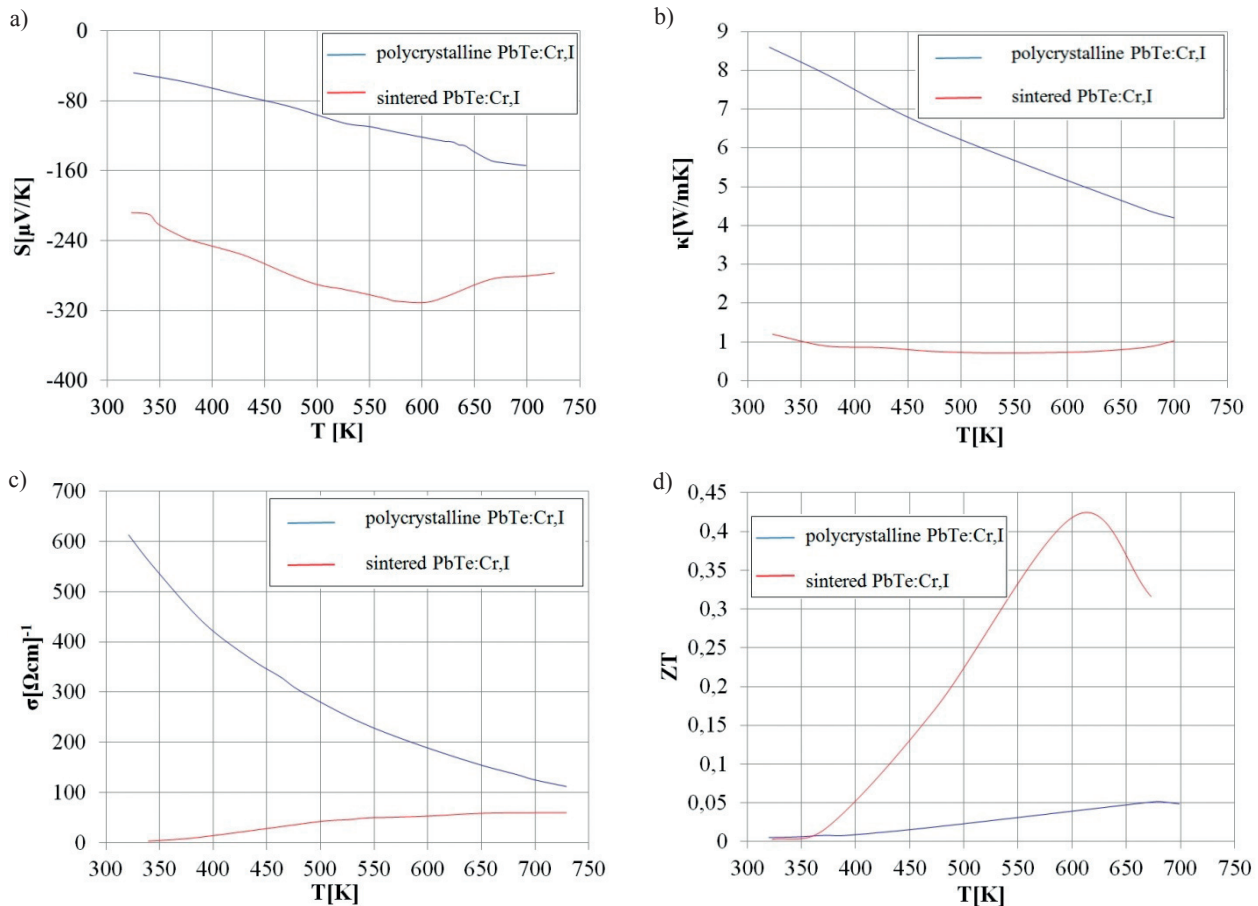


Fig. 4. a) Seebeck coefficient, b) thermal conductivity, c) electrical conductivity and d) figure of merit of PbTe:Cr,I versus temperature; comparison of polycrystalline material (blue line) and sintered specimens (red line).

Rys. 4. Zależność: a) współczynnika Seebecka, b) przewodności cieplnej, c) przewodności elektrycznej, d) parametru ZT od temperatury; porównanie własności materiału polikrystalicznego (niebieska linia) i spiekane (czerwona linia).

To calculate the thermal conductivity of the material, specific heat and diffusivity measurements were carried out. A substantial decrease in thermal conductivity for the sintered material was also observed (Fig. 4b). This could result from the coherent scattering of the mid-to-long mean-free-path phonons on grain boundaries as well as on chromium and tellurium precipitates.

The electrical conductivity of the polycrystalline material decreases when increasing temperature as PbTe is a degenerated semiconductor, in which the carrier mobility decreases with temperature, due to a high carrier concentration (Fig. 4c). It is also consistent with the literature data [5]. The electrical conductivity of the sintered material is lower comparing with that of the polycrystalline material. The reason for this is probably the lower value of carrier concentration. The electrical conductivity of the sintered material gets slightly increased when the temperature is raised, which is related with a slight increase in carrier concentration. In general the obtained values of σ are too low to reach satisfactory ZT values and greater efforts have to be made in order to achieve higher performances.

The ZT enhancement of the sintered material is observed in Fig. 4d when compared with the polycrystalline material and this is probably due to the increase of the

Seebeck coefficient and thermal conductivity decreases as a result of phonon scattering on grain boundaries at high temperatures.

Fig. 5 shows scanning electron microscopy (SEM) micrographs for polycrystalline PbTe:Cr,I, obtained using the Bridgman method. In micrographs for Te and Cr, the spots with more intensive green and blue colour can be observed. In the same places in the Pb micrograph there is a blank. This suggests that Pb atoms are displaced by Cr atoms and phases, containing Te and Cr, are formed. This procedure was intentional and resulted in the phonon scattering enhancement. Therefore, exceeding the solubility limit of Cr results in the reduction of thermal conductivity. Probably Te and Cr do not form one single phase but are placed next to each other within grain boundaries. This can be learned from the analysis of the sintered material, demonstrating large Te precipitates in the absence of Pb (Fig. 6). On the other hand, chromium is uniformly distributed throughout the specimen and the iodine content is below detection limit in both cases. However, its presence was detected in fluorescence.

The quantitative analysis also confirmed the presence of the secondary phase revealing the stoichiometric deviations of the material. The reason for such difficulties in

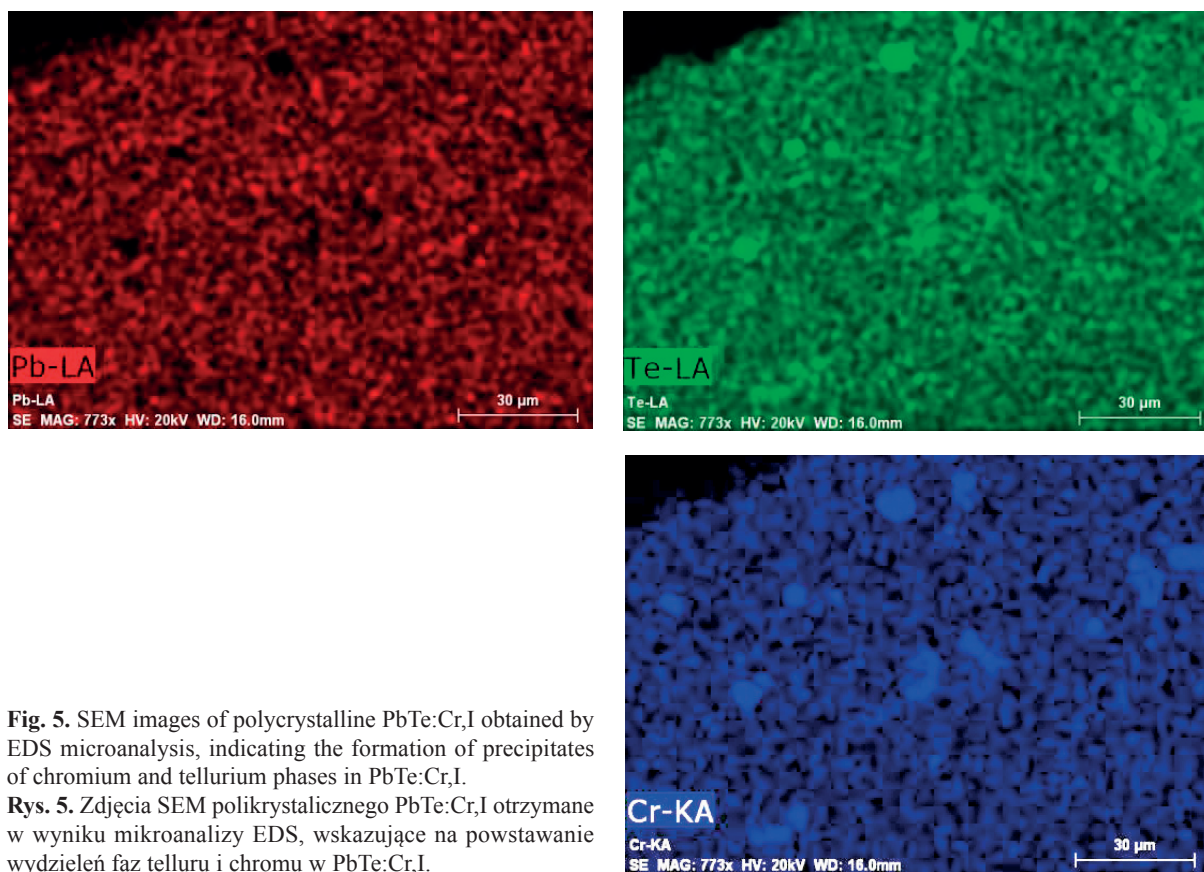


Fig. 5. SEM images of polycrystalline PbTe:Cr,I obtained by EDS microanalysis, indicating the formation of precipitates of chromium and tellurium phases in PbTe:Cr,I.

Rys. 5. Zdjęcia SEM polikrystalicznego PbTe:Cr,I otrzymane w wyniku mikroanalizy EDS, wskazujące na powstawanie wydzieleni faz telluru i chromu w PbTe:Cr,I.

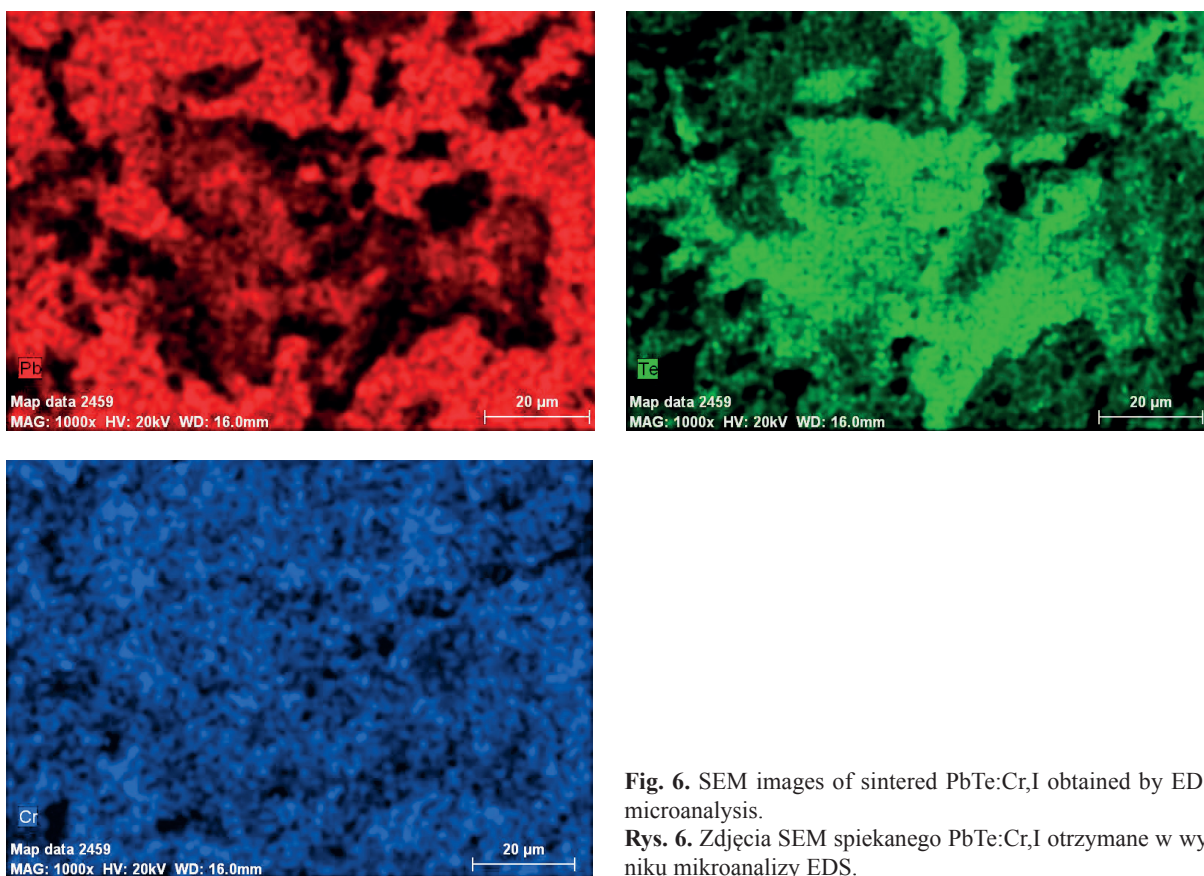


Fig. 6. SEM images of sintered PbTe:Cr,I obtained by EDS microanalysis.

Rys. 6. Zdjęcia SEM spiekane PbTe:Cr,I otrzymane w wyniku mikroanalizy EDS.

obtaining a uniform distribution of the chromium dopant can be explained by taking into account the very high melting point of Cr (1907 °C) and the very low boiling point of tellurium (988 °C). Therefore, the chromium dopant incorporation occurs only by diffusion. However, this procedure turned out to be beneficial – in our previous investigation we obtained crystal doped with 12.3 mol. % of Cr and the electron concentration in this material was $6 \times 10^{18} \text{ cm}^{-3}$. Such a procedure of doping PbTe crystals with Cr and hence, increasing their carrier concentration can be also found elsewhere [13].

4. Conclusions

In summary, *n*-type polycrystalline PbTe doped with iodine and chromium was prepared by the Bridgman method. The sintered material obtained by ball milling, cold-pressing and alloying polycrystalline PbTe was also fabricated. The SEM analysis of both polycrystalline and sintered materials was carried out. The electrical and thermoelectric properties of these materials were determined. For polycrystalline PbTe, the following results were achieved:

- the Seebeck coefficient: - 160 $\mu\text{V/K}$ ($T = 675 \text{ K}$),
- thermal conductivity: 5 - 3.4 W/mK (600 - 850 K),
- electrical conductivity: 200 - 125 $[\Omega\text{cm}]^{-1}$ (600 - 700 K),
- the figure of merit (ZT): 0.06 ($T = 675 \text{ K}$).

For sintered PbTe we have achieved the following results:

- the Seebeck coefficient: - 311 $\mu\text{V/K}$ ($T = 573 \text{ K}$),
- thermal conductivity: 0.75 - 1.025 W/mK (600 - 700 K),
- electrical conductivity: 53 - 59 $[\Omega\text{cm}]^{-1}$ (600 - 730 K),
- figure of merit (ZT): 0.42 ($T = 603 \text{ K}$).

The thermal conductivity of the latter material is strongly reduced due to the much lower grain size when compared to that of the former material. This, in connection with better Seebeck coefficient values allowed obtaining a significant increase in ZT for the sintered material. This fact and the knowledge gained during the present study are promising and provide us with clues on how to obtain sintered *n*-type PbTe with much better properties in the future.

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