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Thermoelectric and Mechanical Properties of Novel Hot-Extruded PbTe *n*-Type Material

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Lead telluride-based materials demonstrate the highest thermoelectric performance in the temperature range from 200°C to 400°C, and they are of interest for numerous waste heat recovery applications. Unfortunately, these conventionally grown materials are usually very brittle, which results in significant material loss during module manufacturing and a decrease in module reliability when subjected to continuous vibrations common for automotive applications. We present a hot extrusion process developed for the first time for PbTe which yields polycrystalline materials with strong mechanical properties combined with high thermoelectric performance. *n*-Type lead telluride was extruded from conventionally synthesized and powdered material at temperatures in the range of 450°C to 520°C depending on material stoichiometry. The extruded rods were of cylindrical shape with 2.54 cm diameter and lengths up to 40 cm. Young's modulus measured using mechanical spectroscopy varied from 59 GPa to 51 GPa for temperatures in the range of 20°C to 300°C. Slicing and dicing of extruded rods to obtain cubical samples with 2 mm side demonstrated no difficulties, illustrating the material homogeneity and its potential for manufacturing module legs. The microstructure of the material was studied by scanning electron microscopy. Doping with antimony iodide during the milling process controls the conduction electron concentration in the range from 1×10^{19} cm^{-3} to 6×10^{19} cm^{-3}. For optimized doping of 0.08 wt.% SbI_3, the maximum thermoelectric figure of merit (ZT) reaches a value of 0.99 at 380°C, as measured by the Harman method. The combination of high thermoelectric performance and improved fracture toughness makes this novel hot-extruded polycrystalline PbTe material highly competitive for many applications.

Key words: Thermoelectric, lead telluride, extrusion, waste heat recovery

INTRODUCTION

Lead telluride is one of the first materials with demonstrated high thermoelectric performance for converting heat into electricity.[1] Optimal working temperatures around 400°C are easily compatible with many heat sources such as engine exhaust gases, direct flame exposure, or radioisotope heating.[2–5] Important improvements in material performance can be achieved when lead telluride is alloyed with Sn or Se,[1] which reduces the thermal conductivity, or when alloyed with Cd or Tl, causing Seebeck coefficient enhancement due to modification of the electronic structure of the conduction band.[6,7] Unfortunately, conventionally grown lead telluride-based materials are very brittle,[8–11] in particular *p*-type PbTe, causing substantial problems during TE module manufacturing. Hot pressing of powdered PbTe results in improved mechanical properties but produces relatively small amounts of inhomogeneous material.[9] Similar problems, well known for bismuth telluride-based alloys, were solved by using hot extrusion of powdered material.[12–14] We suggest hot-extruded *n*-type and *p*-type lead telluride as potentially novel

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materials with improved properties and better perspectives for large-scale production. However, actual extrusion of lead telluride at reasonable temperatures and pressures remained questionable prior to this study because of the rock-salt-type crystal structure of PbTe, which does not present crystallographic planes with weak van der Waals bonding forces. Those easily sliding planes, well known in bismuth telluride-based alloys, are very favorable for plastic deformation during hot extrusion. Earlier[15] successful extrusions of a natural mineral (galena, 79.9% PbS) and of synthesized PbS from low- to middle-grade purity were performed at 650°C, but no practical application has been identified and no electric or thermal properties have been reported.[15] In this study we started with the practical realization of a hot extrusion process applied to n-type PbTe which resulted in mechanically strong n-type homogeneous material with high thermoelectric performance.

MATERIAL PREPARATION AND MECHANICAL PROPERTIES

Fragments (10 mm to 15 mm size) of undoped conventionally synthesized PbTe were mixed with antimony iodide (SbI_3) ranging from 0 wt.% to 0.2 wt.%. SbI_3 is incorporated as an n-type dopant to control the carrier concentration. After milling in an attritor under a protective argon atmosphere, the grain size distribution shows a large dispersion from 0.4 μm to about 100 μm. The maximum volume percentage of grains was at about 10 μm in size, as evaluated by laser diffraction particle size analyzer (Coulter LS200). Powders were sieved prior to extrusion to eliminate a small number of particles larger than 200 μm. Extrusion dies with diameters of 6 mm, 10 mm, and 25.4 mm were used to produce homogeneous rods with total mass up to 2 kg. The extrusion temperature was maintained in the range of 450°C to 520°C depending on material stoichiometry. These temperatures correspond to a fraction between 0.58 and 0.66 of the melting temperature (T_m) of PbTe, which is close to the values between 0.56 and 0.67 of T_m for PbS extrusion as reported in Ref. 15. Excessive amount of lead in the starting material requires a reduction of the extrusion temperature. Figure 1 shows photos of sections of one successfully extruded PbTe rod with 25.4 mm diameter.

The scanning electron microscopy images of a fractured surface presented in Fig. 2 reveal dense homogeneous material with grain sizes in the range of several micrometers. At higher magnification (Fig. 2b) some porosity can be observed. Figure 2b shows no grains of submicron size, which is a sign of the dynamic recrystallization process of the initial powdered material during hot extrusion. In this process smaller grains disappear while favoring the growth of larger grains, which reduces the total surface energy.

Fig. 1. Two sections of a 25.4-mm-diameter rod extruded from powdered n-type PbTe (the scale is graduated in cm).

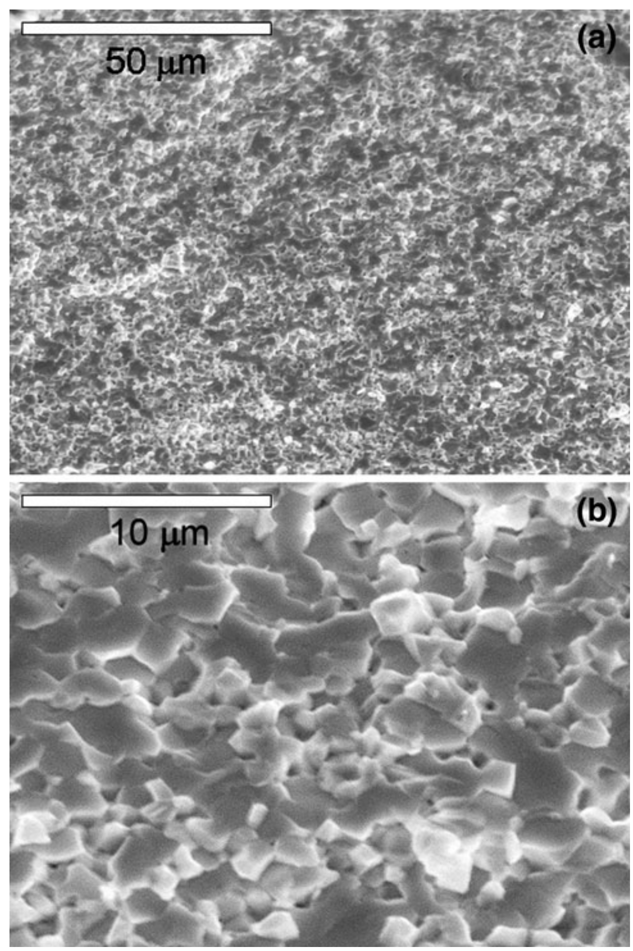

Fig. 2. Scanning electron microscopy images of two transverse sections of a 25.4-mm-diameter rod extruded from sieved n-type powder. Horizontal scale lines in figures (a) and (b) are equal to 50 μm and 10 μm, respectively.

Material densities were determined by Archimedes' method. Extrusion with smaller dies results in densities from 8.15 g/cm^3 to 8.2 g/cm^3, while extrusion with the 25.4-mm die produced material with density of about 8.18 g/cm^3, corresponding to porosity of less than 0.5% relative to the published density of 8.219 g/cm^3 for Czochralski-grown PbTe single crystals.[16]

Information about the elastic properties of thermoelectric materials is essential to simulate the mechanical stresses which are experienced by cooling or generator modules under working conditions.[17] A direct stress–strain study leads to physical destruction of the analyzed specimen and is usually applied to small portions of produced materials. Nondestructive evaluation of Young's modulus performed on the entire rod has obvious advantages. Therefore, we characterized 200-mm-long extruded rods by mechanical spectroscopy, a technique which has been described in detail previously.[18] Young's modulus (E) can be calculated by measuring the frequency of excited fundamental oscillations, specimen geometry, and material density.[18] Figure 3 shows a linear decrease of E when the temperature T at which the measurement is carried out increases from 20°C up to 300°C. Variation of Young's modulus for temperatures higher than 0.5Θ, where Θ = 175 K is the Debye temperature for PbTe,[19] can be described by the following empirical equation:[20]

$$E(T) = E_{\mathrm{R}}[1 - b_{\mathrm{E}}(T - T_{\mathrm{R}})],$$

where E_{R} is the room-temperature Young's modulus, b_{E} is a fitting parameter related to the Grüneisen constant, and T_{R} is room temperature in Kelvin. The room-temperature value E_{R} of 58.86 GPa for low-frequency measurement of Young's modulus of extruded samples is close to 58.05 GPa, obtained for single-crystal undoped PbTe grown by the Czochralski technique[11] and clearly higher than the value of 54 GPa measured on hot-pressed polycrystalline specimens.[11] The coefficient b_{E} giving the linear variation of Young's modulus with temperature for our extruded material is 5.5×10^{-4} K^{-1}. This value is comparable to the values of 4.5×10^{-4} K^{-1} and 6.2×10^{-4} K^{-1} obtained for undoped and PbI_2-doped Bridgman-grown PbTe polycrystalline material[20] with E_{R} of 57.52 GPa and 57.70 GPa, respectively.

For successful thermoelectric applications a semiconductor material should demonstrate not only high ZT values in the desired temperature interval but also mechanical properties which are compatible with high-yield slicing and dicing operations. Unfortunately, conventionally grown lead telluride is very brittle, leading to elevated material loss during the cutting procedure. Hot-extruded small-grain polycrystalline PbTe, due to its high homogeneity, shows no difficulties in slicing and dicing operations, as demonstrated in Fig. 4. The rod was sliced with a low-speed diamond blade saw and then diced with 100% yield using an RFK 775 high-speed dicing saw from Diamond Touch Technology Inc., resulting in cubical 2 mm × 2 mm × 2 mm pieces as commonly used for thermoelectric generator module legs.

THERMOELECTRIC AND TRANSPORT PROPERTIES

Extruded lead telluride with no intentional doping has high electrical resistivity and presents no interest for thermoelectric applications. Usually PbI_2 is used to control the free electron concentration (n). However, we used antimony iodide because of the higher atomic proportion of iodine in the SbI_3 compound. Figure 5a shows a linear variation of n with SbI_3 doping ranging from 0 wt.% to 0.2 wt.%. The room-temperature electron Hall mobility gradually decreases with n due to increased scattering by ionized iodine donor centers and carrier–carrier scattering (Fig. 5b).

Figure 6 shows that the room-temperature figure of merit Z (K^{-1}) varies as is regularly expected with the electrical resistivity ρ, showing an extrapolated maximum value of 1.08×10^{-1} K^{-1} at about 7.0 $\mu\Omega$ m. The figure of merit and the electrical resistivity were measured simultaneously in

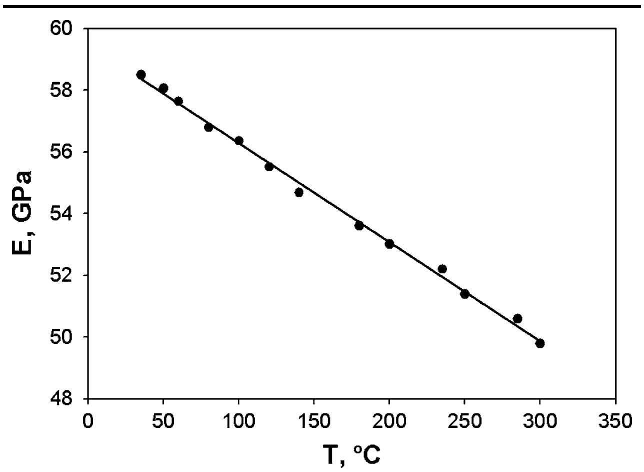

Fig. 3. Variation of Young's modulus as a function of temperature measured on an n-type PbTe extruded rod with 25.4 mm diameter and 200 mm length.

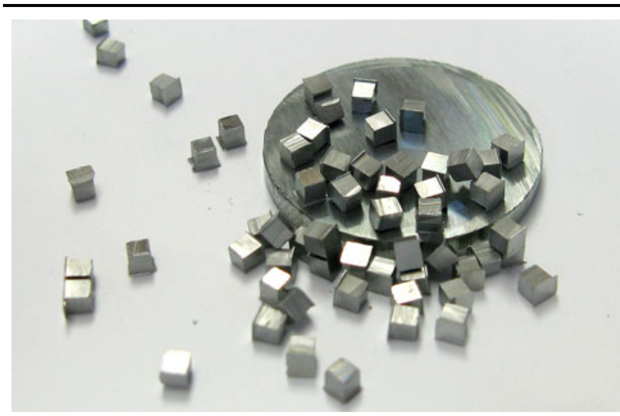

Fig. 4. Example of 25.4-mm-diameter extruded n-type rods sliced and diced to yield cubic pieces (2 mm side) as commonly used for module manufacturing.

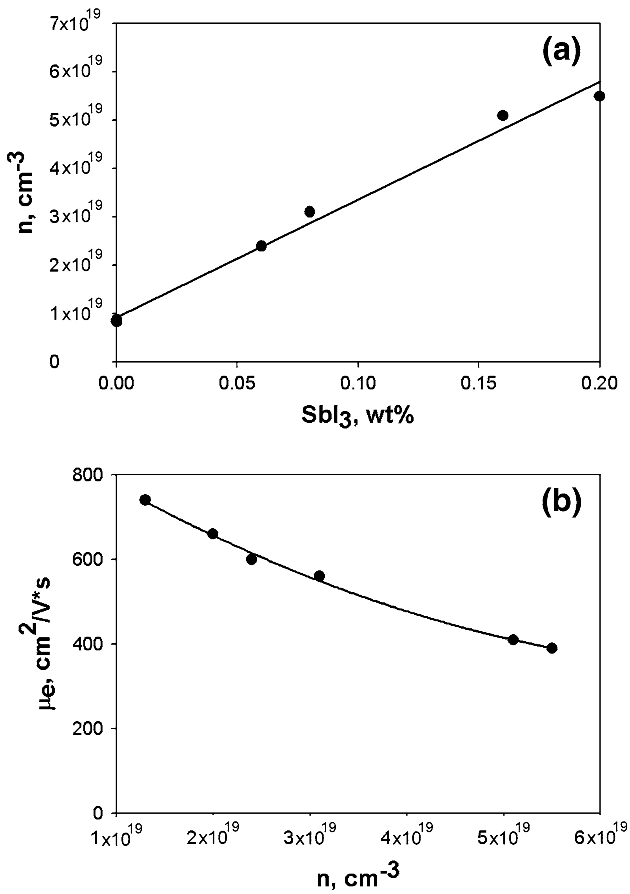

Fig. 5. Room-temperature electron concentration in extruded PbTe material as a function of SbI_3 doping (a), and mobility as a function of electron concentration (b).

vacuum using a custom-made calibrated Harman system. Cubic specimens (5 mm × 5 mm × 5 mm) were Ni-plated on opposite sides and wired using Pb-Sn solder.

The electrical conductivity decreases with absolute temperature following a power law $\sigma = \sigma_0 T^{\delta}$ with the power factor δ decreasing slightly in absolute value from -2.09 to -1.98 as the doping level was increased from 0.06 wt.% to 0.2 wt.% SbI_3, as shown in Fig. 7. A similar value of $\delta = -2.3$ was reported in Ref. 7 for the PbTe + 0.055% PbI_2 + 1% CdTe composition. Although we do not have high-temperature data for $n(T)$, if we make the reasonable assumption that it remains approximately constant for our nearly degenerate material, then we can equate the exponent δ to the exponent r of the electron mobility (μ_e) variation $\mu_e = \mu_0 T^r$ and compare it with the value of $r = -2.14$ reported for $\mu_e(T)$ in Ref. 21 for n-type lead telluride doped with PbI_2 to a comparable charge carrier concentration. The observed variation of electrical conductivity at elevated temperature in extruded PbTe is commonly attributed to electron scattering dominated by acoustic phonons.

Figures 5 and 6 show that it is possible to control the room-temperature properties of extruded mate-

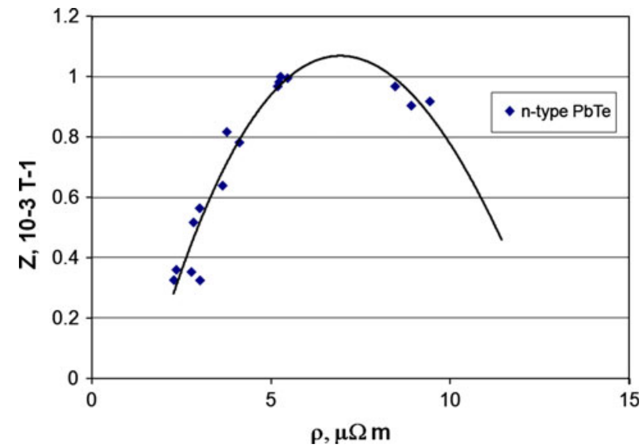

Fig. 6. Room-temperature figure of merit of extruded PbTe material as a function of electrical resistivity.

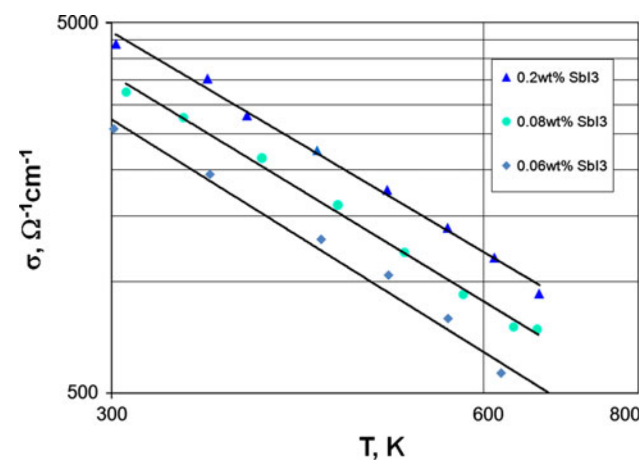

Fig. 7. Variation with temperature of the electrical conductivity of extruded PbTe material for several doping levels.

rials; however, lead telluride-based alloys are useful for thermoelectric energy conversion in the temperature range from 200°C to 400°C. Therefore, Harman ZT measurements were performed up to 400°C. For measurements at temperatures exceeding the melting point of the Pb-Sn solder, thermocouples and wires were attached to the samples with silver conducting epoxy paste stable up to 400°C.

Figure 8 shows the dimensionless figure of merit ZT as a function of temperature for several doping conditions. This figure also shows ZT values measured from room temperature up to 160°C for one of the samples with wiring attached by Pb-Sn solder. The consistency of these results with the measurements made using silver conductive paste on the same specimen proves the low resistance of the conductive paste and validates the high-temperature data. A maximum ZT value of 0.99 was reached at 390°C for optimized doping of 0.08 wt.% SbI_3. For this material the free carrier density is 3.1×10^{19} cm^{-3} and the room-temperature electron mobility is 560 cm^2/V s.

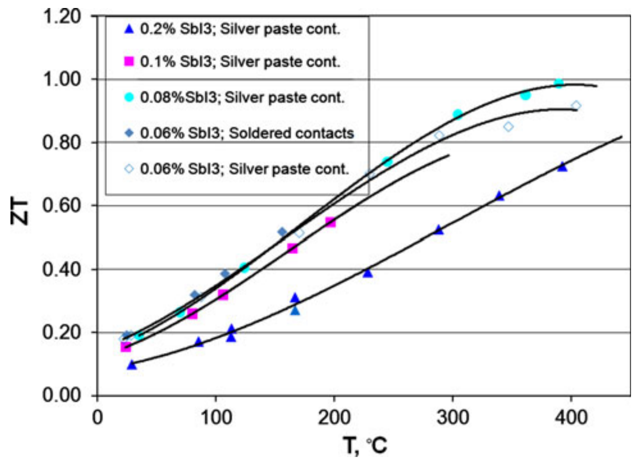

Fig. 8. Dimensionless figure of merit *ZT* as a function of temperature for samples with different SbI_3 doping levels and different contact options.

CONCLUSIONS

The novelty of this research consists of the practical realization of the hot extrusion process for lead telluride-based materials. From the very first runs this process was able to produce *n*-type PbTe rods with mass up to 2 kg, showing significant potential for scale-up to industrial material production. This is particularly important because all waste heat recovery applications require large-scale material production and device manufacturing. It is well known that the mechanical properties of *p*-type PbTe are much weaker than for *n*-type or undoped material. Therefore, the same validation is still needed for hot extrusion of *p*-type lead telluride.

The PbTe rods produced in this study demonstrate elastic properties similar to those of Bridgman-grown material, which is a sign of effective powder consolidation during hot extrusion. High material homogeneity and low risk of fracturing were confirmed by successful slicing and dicing tests.

For optimized doping of 0.08 wt.% SbI_3 the maximum *ZT* reaches a value of 0.99 at 380°C. However, it has to be noted that so far the material composition was not yet been optimized except for the doping level. Introducing Tl or Cd into PbTe to enhance the Seebeck coefficient by modifying the electronic structure, and alloying with Sn or Se to decrease the thermal conductivity, are some of the options to further increase the *ZT* value of this extruded material.

The combination of high thermoelectric performance and improved fracture toughness makes this novel hot-extruded polycrystalline PbTe material highly competitive for many large-scale industrial applications.

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