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Transport properties of undoped and Br-doped PbTe sintered at high-temperature and pressure $\geq$4.0 GPa

Yongkwan Dong [a], Michael A. McGuire [b,1], Abds-Sami Malik [c,*], Francis J. DiSalvo [a,*]

[a] Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, NY 14853-1301, USA
[b] Department of Physics, Clark Hall, Cornell University, Ithaca, NY 14853, USA
[c] Diamond Innovations, 6325 Huntley Road, Worthington, OH 43085, USA

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ABSTRACT

The thermoelectric properties of nominally undoped PbTe and Br doped PbTe materials sintered at high-pressure and high-temperature (HPHT) have been studied. All samples show n-type semiconducting behavior with negative thermopower. For undoped PbTe, four different HPHT treatments were performed at pressures between 4.0 and 6.5 GPa. PbTe doped with Br at 0.5, 1.0, 2.0, $3.0 \times 10^{19}\,\mathrm{cm}^{-3}$ was HPHT treated at 4.0 GPa and 1045 °C. As the dopant concentration increases, the absolute thermopower decreases, thermal conductivity increases, and electrical resistivity decreases. At a nominal dopant concentration of $1.0 \times 10^{19}\,\mathrm{cm}^{-3}$, carrier mobility of $1165\,\mathrm{cm}^2/\mathrm{V\,s}$ and dimensionless thermoelectric figure-of-merit, *ZT*, of around 0.27 at 300 K were obtained. These results demonstrate that HPHT post-processing is a viable and controllable way of tuning the thermoelectric properties of PbTe-based materials.

1. Introduction

Thermoelectric materials can be used for the direct conversion of thermal to electrical energy and *vice versa*. With these materials, electricity can be used to pump heat (thermoelectric coolers; Peltier effect) or heat can be used to generate electricity (thermoelectric generators; Seebeck effect) [1]. In general, the efficiency of thermoelectric materials is expressed by the figure-of-merit, $Z = S^2\sigma/\kappa$, where S is the thermopower (Seebeck coefficient), σ the electrical conductivity, and κ the thermal conductivity. In determining device efficiency, Z times temperature (ZT) is the relevant parameter and is dimensionless. A material needs a large absolute S (negative for n-type; positive for p-type) to maximize ZT, while electrical resistivity and thermal conductivity should be low. The three parameters in Z can be varied by changing the doping levels, but not in an independent manner [2].

Among many promising thermoelectric materials, lead telluride (PbTe), which adopts the NaCl structure type, has been intensively studied. Since conventional PbTe has a maximum ZT in the range of 300–400 °C, PbTe has potential applications in converting waste heat to electricity [3]. Improvements in the thermoelectric performance of PbTe have been achieved through various synthetic and materials processing techniques. These techniques have included alloying with elements such as Sn or Se to reduce thermal conductivity and tune the band gap, doping with elements such as Br or Na to increase carrier density and hence electrical conductivity, or reducing the grain size of hot pressed and sintered materials to reduce thermal conductivity through grain boundary scattering [4–6]. It has also been found that the Seebeck coefficient can be enhanced by grain boundaries or nanometer size inclusions [7,8], and manipulating the electronic structure through Tl doping [9]. Another fruitful line of investigation has involved alloying PbTe with $AgSbTe_2$ [10,11]. More recently, these materials have been found to possess a complex nanostructure, possibly accounting for their enhanced thermoelectric properties [12,13].

Studies of thermoelectric materials at high-pressures, in the range up to 4 GPa, have found large increases in the thermoelectric figure-of-merit while under pressure [14–16]. These studies were done primarily with diamond anvil cells, and the measurements were made while samples were under pressure. Studies of undoped and doped lead chalcogenides at high-pressures up to ~10 GPa have shown that, for p-type material, the Seebeck coefficient at room temperature, under increasing pressure, first decreases then becomes negative and reaches a maximum absolute value at around 3–4 GPa [17–19]. Interestingly, these materials undergo a phase transition from NaCl to GeS

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* Corresponding authors.
E-mail addresses: abds-sami.malik@diamondinnovations.com (A.-S. Malik), fjd3@cornell.edu (F.J. DiSalvo).

[1] Now at: Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

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type structure in this pressure range and S maximizes just before the transition occurs. At greater pressures, S approaches zero and the electrical resistivity decreases by about 3 orders of magnitude, suggesting a metallic phase at high-pressures. These experiments were carried out under cold compression, with no heating, and all the measurements were done on the sample while it was under pressure. These enhanced properties did not persist upon release of pressure [17].

PbTe has also been synthesized under high-pressure and high-temperature (HPHT) conditions by reacting Pb and Te under pressures up to 5.3 GPa at 1100 K [20,21]. Property measurements were done at ambient pressure and a significant improvement of ZT at room temperature was reported, increasing from 0.04 for samples prepared at atmospheric pressure to 0.87 for samples synthesized at 5.3 GPa. However, a decrease in the thermopower from $\sim$350 to $\sim$125 μV/K was reported, as well as a decrease in resistivity by 2 orders of magnitude, with increasing synthesis pressure. This result deserves careful consideration and verification, since the maximum ZT possible for $S = 125\,\mu\text{V/K}$ is 0.64, assuming that the Wiedemann–Franz law [22] (Eq. (1)) is valid in this system. This report prompted us to look in detail at the effects of pressure on PbTe [23]. We found HPHT processing of conventionally synthesized PbTe resulted in materials with larger $|S|$, but also higher ρ and slightly higher lattice thermal conductivity, suggesting that the main effect of the processing was to eliminate lattice defects (vacancies) which act as electronic dopants. In fact, the conventionally synthesized PbTe used in that study was p-type, likely due to low levels of unintentionally introduced Pb vacancies, and HPHT processing resulted in a material which was n-type, as expected for stoichiometric PbTe.

The same investigators who originally reported enhanced thermoelectric performance in HPHT synthesized PbTe have also looked at iodine doped PbTe [24] and found the highest room temperature power factor at an iodine doping level of 0.03 mol% (equivalent to $1\times10^{19}\,\text{cm}^{-3}$). The doped PbTe was synthesized from Pb, Te, and PbI_2, at 3.5 GPa and 1200 K.

Here, we report on the thermoelectric properties of nominally undoped and also Br doped, HPHT sintered PbTe. Unlike the materials reported before [20,24], our samples were first synthesized using conventional techniques, and then subjected to the HPHT treatment. Our purpose here is to explore the effects of HPHT sintering on the transport properties at ambient pressure, not to optimize the high-temperature ZT. The results presented here extend our previous work, which was focused on undoped materials, to doped materials. Optimization would also require doping and alloying, in conjunction with, we believe, HPHT sintering. Thus, all electronic properties measurements were carried out, as in our previous contribution, in the temperature range from 80 to 300 K and at ambient pressure or in vacuum. For comparison, we also measured samples that were not HPHT treated, but sintered in evacuated silica tubes. We have found that HPHT sintering induces changes in the electronic properties that persist at ambient pressures.

2. Experimental

PbTe: high purity Te ingot (99.9999%, Alfa Aesar) and Pb shot (99.9999%, Alfa Aesar) were loaded into silica tubes in a 1:1 molar ratio (total sample mass of 15 g/tube) inside an Ar-filled glove box to minimize exposure of the reactants to air. A conservative estimate of the uncertainty in the loaded compositions, assuming an error of ±0.5 mg in weighing the starting materials, is about $\pm0.01\%$. Covered tubes were quickly moved to a vacuum line, evacuated (10^{-3} Torr), and sealed with flame under vacuum. The tubes were heated to 930 °C over 18 h, held at this temperature for 2 h, and cooled to 850 °C over 6 h. Thereafter, the furnace was turned off and the reaction tubes cooled to room temperature. The samples had clearly melted to form a solid slug on cooling to room temperature (PbTe congruently melts at 924 °C). Powder X-ray diffraction showed the product to be single phase PbTe with the NaCl structure type. At the measured diffraction signal to noise levels, if any second phase is present, it is limited to less than a few percent.

Doped PbTe: PbTe samples with nominal Br dopant concentrations of 0.5, 1, 2, and $3\times10^{19}\,\text{cm}^{-3}$ were prepared with Pb, Te, and $PbBr_2$ (99.999%, Alfa Aesar) which were weighed according to the nominal stoichiometry of $PbTe_{(1-x)}Br_x$ by using the same method described above. The tubes were heated to 950 °C over 18 h, held at this temperature for 3 h, and then the furnace was turned off and the reaction tubes cooled to room temperature.

For comparison to the HPHT sintered samples, a sample of undoped PbTe was ground into a powder, pressed (10 kpsi) into a pellet, and annealed at 400 °C over 12 h in an evacuated, sealed, silica tube. Similarly, one Br doped ($1\times10^{19}\,\text{cm}^{-3}$) sample was sintered under vacuum at 520 °C for 12 h to compare against HPHT sintered samples. Sample densities were measured using a He gas pycnometer (Micromeritics AccuPyc 1330).

HPHT sintering: HPHT sintering was performed at Diamond Innovations Inc. (DI). Materials synthesized at Cornell University were transported to DI in vacuum sealed fused silica tubes. Powders were obtained by crushing the material in an agate mortar and pestle, at DI, in an Ar filled glove box (LabMaster, M. Braun, Inc.) maintained at <1 ppm O_2 and H_2O, and sieving to be between 50 and 100 μm particle sizes. Pellets were pressed on a hydraulic press to $>90\%$ theoretical density, then encased in high purity graphite (NAC-500, NAC Carbon Products, Inc.). This was then assembled into a high pressure cell consisting of salt (NaCl) and graphite components, with an integrated heater circuit, and pressed on a belt type apparatus. All high pressure cell components were stored under vacuum at $\sim$150 °C prior to use and the assembled cells were stored in an Ar filled glove box until immediately prior to pressing. Pressure was estimated by monitoring the irreversible densification of silica [25] and temperature calibration was done by measuring *in situ* with a K-type thermocouple inserted in the cell. HPHT sintering was accomplished in $\sim$15 min, with total time at soak temperature and pressure of 10 min. After the HPHT treatment, samples were cut into several rectangular bars with approximate dimensions of $0.5\times0.3\times0.3\,\text{cm}^3$ by wire EDM (electrical discharge machining). For non-HPHT samples the dimensions were $0.9\times0.45\times0.3\,\text{cm}^3$.

Properties measurements: The surfaces of the bars were cleaned with SiC sandpaper and washed with hexane to remove any remaining dust on the surface prior to characterization. Measurements of TE properties were performed over the temperature range of 80–300 K using a home built apparatus described elsewhere [26]. A conservative estimate of errors for the measurement are within $\pm5\%$ for S, $\pm10\%$ for ρ, and $\pm10\%$ for κ [26]. TE properties were measured with two samples simultaneously. One was used for thermopower and thermal conductivity measurements and another one for electrical resistivity measurements. Copper was deposited onto the ends of the samples electrochemically using $CuSO_4$ dissolved in diluted H_2SO_4. Good thermal and electrical contacts could then be made by soldering onto the samples using indium metal for the measurement of thermal conductivity κ, thermopower S, and electrical resistivity ρ. The voltage contacts for the resistivity measurements were made using fine gauge copper wire and silver paste (Dupont Conductor Composition 4922N).

Hall measurement was carried out for Br-doped PbTe samples using a 1.5 T electromagnet [22,27], using the same samples that were used for electrical resistivity measurements. The samples were mounted in a plastic frame and had four Cu leads attached. Two leads were designated to provide the current with long sample direction, while the other two were used for measuring the voltage perpendicular to both the current and applied magnetic field. A Keithley 224 current source was used to control the current (100 mA) through the sample. The Hall voltage was monitored with a Keithley 181 nanovoltmeter. The zero-field voltage was used as a measure of the alignment of the voltage contacts. This voltage was confirmed to be much smaller than the Hall voltage, which was measured using a net field of 2.8 T (−1.4 and 1.4 T).

3. Results and discussion

We begin by discussing the effects of HPHT processing on undoped PbTe. Table 1 lists the HPHT conditions used to sinter these materials, and the measured transport properties for these samples are shown in Figs. 1–3. Also given for comparison are the properties for PbTe that was sintered under vacuum, at 400 °C for 12 h. This undoped non-HPHT PbTe shows n-type semiconducting behavior with negative values of *S*. Stoichiometric PbTe has a narrow band gap and is expected to be n-type because the mobility of electrons in the Pb based conduction band is greater than that of holes in the Te based valence band [2,4].

In Fig. 1, it is clear that both sintering pressure and temperature influence the measured properties. The highest *ZT*, 0.1 at 300 K, is obtained for sample 2 whereas the lowest value is obtained for sample 1. Sample 4 is quite similar to the non-HPHT PbTe and sample 3 shows some improvement over the non-HPHT PbTe.

Table 1
The HPHT sintering conditions used for undoped PbTe. Conditions used to process sample 2 were used for all Br doped PbTe samples.

Sample labels	Pressure (GPa)	Temperature (°C)	Time (min)
1	6.5	1175	10
2	4.0	1045	10
3	5.5	1045	10
4	5.5	1175	10

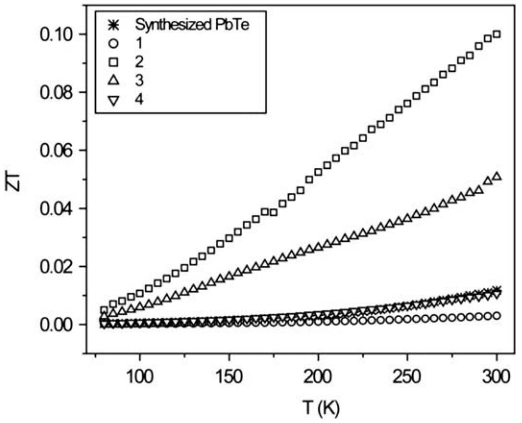

Fig. 1. The calculated *ZT* values for undoped PbTe sintered under the conditions listed in Table 1. For comparison, data for PbTe that were sintered under vacuum are also given. The data for sample 4 and synthesized PbTe overlap each other.

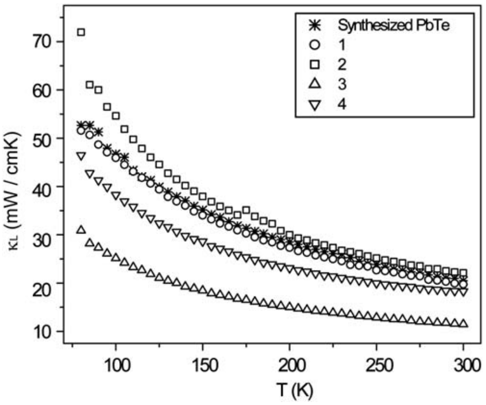

Fig. 2. The phonon contribution to the total measured thermal conductivity for undoped PbTe sintered under HPHT conditions.

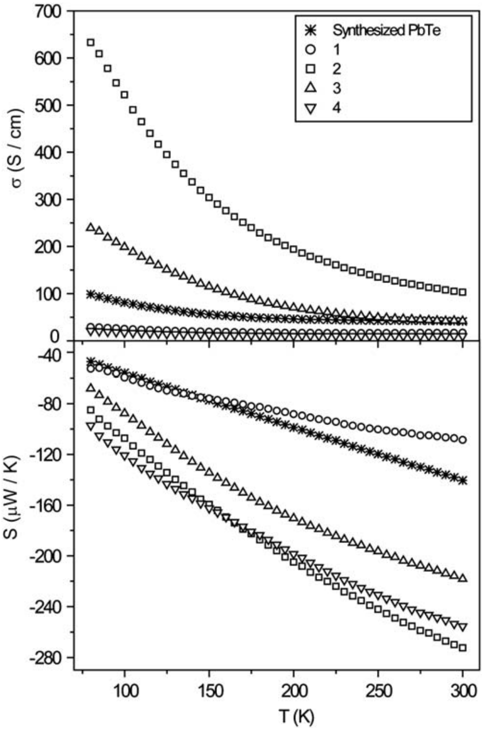

Fig. 3. The electrical conductivity (top) and the Seebeck coefficient (bottom) is given for undoped PbTe sintered under HPHT conditions.

Fig. 2 shows the phonon contribution to the total thermal conductivities. The total thermal conductivity is a sum of phonon (lattice) and electronic thermal conductivities ($\kappa_{\text{tot}} = \kappa_{\text{elec}}+\kappa_{\text{phon}}$). The electronic contribution to the thermal conductivity (mW/cm K) is related to the electrical resistivity by the Wiedemann–Franz law [22]:

$$\frac{\kappa_{\text{elec}}\rho}{T} = 2.45\times10^{-8}\,\frac{V^2}{K^2} \qquad (1)$$

Here, ρ is the electrical resistivity (Ω cm) and T the temperature (K).

In this case, the electronic contribution to the total thermal conductivity is small because the electrical conductivities (Fig. 3) are so low. It is apparent that samples 1 and 2 are quite similar to the non-HPHT PbTe sample in thermal conductivity whereas 4 is somewhat less and 3 is much less (Fig. 2). But, near 300 K, HPHT processing had only a small effect on the measured thermal conductivity except for sample 3.

Sample 3, and to a lesser extent sample 4, appear to be outliers, with lower thermal conductivity over the entire temperature range of measurement. This is a significant data point especially because both samples were sintered at 5.5 GPa. A plausible explanation, that is in agreement with previous reports [20,21], is that, under the specific sintering conditions for sample 3 (and 4), especially upon cooling, formation of grain boundaries is favored, and thus may lead to lower thermal conductivity due to grain boundary scattering. At the end of the HPHT sintering cycle, the sample is cooled to $<200\,^{\circ}$C in $\sim$30 s, while still under pressure.

Nevertheless, in agreement with previously reported results [15,23] HPHT sintering has a larger effect on the Seebeck coefficient and the electrical conductivity (Fig. 3), which are optimal for sample 2, resulting in the highest *ZT* overall. Sample 3 had relatively poorer electrical conductivity and thermopower as did sample 4.

Comparing samples 3 and 4, which were pressed at 5.5 GPa but at different temperatures (1045 and 1175 °C, respectively), the data suggest that sintering at a lower temperature yields higher electrical conductivity but that sintering at higher temperature yields a higher Seebeck coefficient. Similarly, comparing conditions 1 and 4, which were both sintered at the same nominal temperature of 1175 °C but at different pressures (6.5 and 5.5 GPa, respectively) and also looking at conditions 2 and 3, which were sintered at the same temperature (1045 °C) but at different pressures (4.0 and 5.5 GPa, respectively), the data suggest that sintering at lower pressure yields a higher Seebeck coefficient. Also, comparing condition 2 and 3, lower pressure sintering resulted in higher electrical conductivity, but comparing conditions 1 and 4, there was no difference in electrical conductivity. Taken together, the data suggest that thermopower and electrical conductivity depend on both sintering pressure and temperature. Although there is not enough data at the moment to determine the optimum sintering pressure and temperature, it seems clear that higher sintering pressures and temperatures than those attempted here would not lead to enhanced properties. Overall, sample 2 was sintered at the lowest pressure and temperature and gave the highest *ZT*. A search for optimal sintering conditions (for undoped materials) would have to commence at those conditions and encompass lower pressures and temperatures.

Our previously reported results [23] had presented data for p-type, undoped, PbTe, which upon HPHT processing, at 6.5 GPa, transformed into n-type material. Nevertheless, some common behavior is apparent between the earlier data and the results presented here: the thermal conductivity is, generally, not drastically changed by HPHT sintering, and the high processing pressure (6.5 GPa) ultimately proved detrimental to performance.

Although clear systematic relationships between transport properties and HPHT processing conditions are difficult to ascertain from the present study, the strong influence of sintering condition on thermoelectric performance is clearly demonstrated. We find that the transport properties are in fact remarkably sensitive to HPHT processing. For example, changing the pressure from 6.5 to 5.5 GPa (samples 1 and 4) results in an order of magnitude increase in *ZT*. Furthermore, the electrical conductivity and the Seebeck coefficient change in ways that are not easily attributed to simple unintentional changes in dopant or vacancy concentration. For instance, increasing pressure from 4.0 to 5.5 GPa (samples 2 and 3) decreases both the electrical conductivity and the Seebeck coefficient.

To investigate the effect of HPHT processing on doped samples, we chose to use the processing conditions which gave the best *ZT* for the undoped material (sample 2). The results of these studies on Br-doped PbTe are addressed next.

Four samples with Br doping levels of 0.5, 1, 2, and 3×10^{19} cm^{-3} were prepared and their *ZT* is plotted in Fig. 4. It is known that the best PbTe thermoelectric materials are doped to achieve a carrier concentration $n\approx10^{19}$ cm^{-3} [28]. In our case, the best *ZT* of around 0.27 at 300 K, is achieved at a nominal Br doping level of 1×10^{19} cm^{-3}. In order to test the reproducibility of this result, another sample was made, under the same nominal HPHT sintering conditions, from the same powder batch, and a *ZT* of 0.21 at 300 K was measured. The slight discrepancy in values can be attributed to measurement uncertainty and some variability in the HPHT sintering conditions, but the general trend of properties with Br doping remains unchanged.

Since the carrier concentrations of the Br doped samples are relatively high compared with the undoped samples discussed earlier, the electronic contribution to the total thermal conductivity is much greater. Still, it is more instructive to look at the phonon contribution to the thermal conductivity rather than the total thermal conductivity. Fig. 5 shows that the lattice thermal conductivity of the doped samples with Br at 0.5, 1.0, 2.0, and 3.0×10^{19} are nearly the same, especially at higher temperatures. Both undoped samples closely track each other as well. At a dopant concentration of 1.0×10^{19} cm^{-3}, the phonon thermal conductivity is lower, but still within experimental uncertainty of the other values.

Fig. 6 shows that, as expected, the electrical conductivity generally increases with increasing dopant concentration, but that the conductivity of 1.0 and 2.0×10^{19} Br doped samples are quite similar, with the higher doped sample exhibiting slightly more conductivity at higher temperatures. The Seebeck coefficient, also shown in Fig. 6, follows the expected trend, decreasing with increasing carrier concentration with the undoped sample being highest. The thermopower is expected to decrease as the carrier density increases due to a decreasing curvature in the electronic

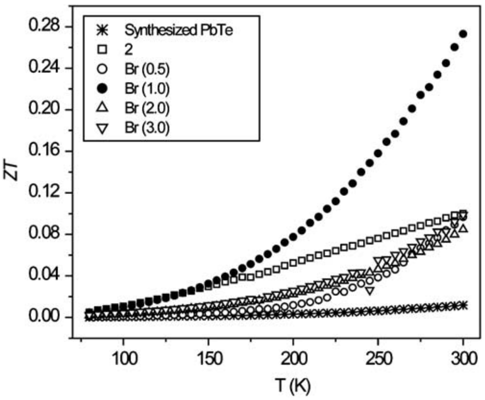

Fig. 4. The *ZT* for Br doped, HPHT processed PbTe. For comparison, data from Fig. 1, for undoped, non-HPHT processed (synthesized PbTe) and undoped, HPHT processed (2) PbTe is repeated again here.

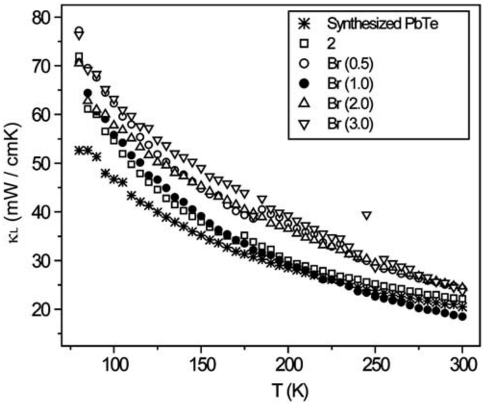

Fig. 5. The phonon thermal conductivity of undoped and Br doped PbTe samples.

density of states at the Fermi level and due to the increase of the carrier concentration, which reduces the mobility of the carriers. The optimal combination of thermopower and electrical conductivity is achieved at a nominal doping level of 1.0×10^{19}.

The properties of the Br doped samples, at 300 K, are summarized in Table 2. Comparing samples Br (1.0) and Br (2.0), it is immediately obvious that the two samples have similar electrical conductivity but that the former, as expected, has a greater Seebeck coefficient. Since electrical conductivity is a function of both carrier concentration and carrier mobility, it is necessary to look at the Hall measurements.

These are also presented in Table 2 for most of the HPHT sintered samples. As the carrier concentration increases, the Seebeck coefficient decreases, as explained earlier. However, the carrier mobility does not follow a simple trend, and in fact, peaks at a value of $1165\,\text{cm}^2/\text{V s}$, at a carrier concentration slightly greater than $0.5\times10^{19}\,\text{cm}^{-3}$. This sample, Br (1.0), has a nominal doping level of $1.0\times10^{19}\,\text{cm}^{-3}$. In other words, about half of the added dopant is active in producing carriers in this sample.

It is worth noting here that the optimal nominal doping level for iodine doped PbTe synthesized under HPHT conditions [24] was also found to be $1.0\times10^{19}\,\text{cm}^{-3}$ with a reported power factor of $24.2\,\mu\text{W/cm K}^2$. At higher and lower dopant concentrations, the power factor drops rapidly to $\sim20\,\mu\text{W/cm K}^2$. The thermopower in that sample is approximately $-130\,\mu\text{V/K}$ and resistivity is approximately $0.7\times10^{-3}\,\Omega\,\text{cm}$, although the thermal conductivity is not reported. The power factor for Br (1.0) is $23.4\,\mu\text{W/cm K}^2$. Although the exact synthesis conditions are different from those reported here, it does suggest that high-pressure plays a crucial role in affecting the material properties.

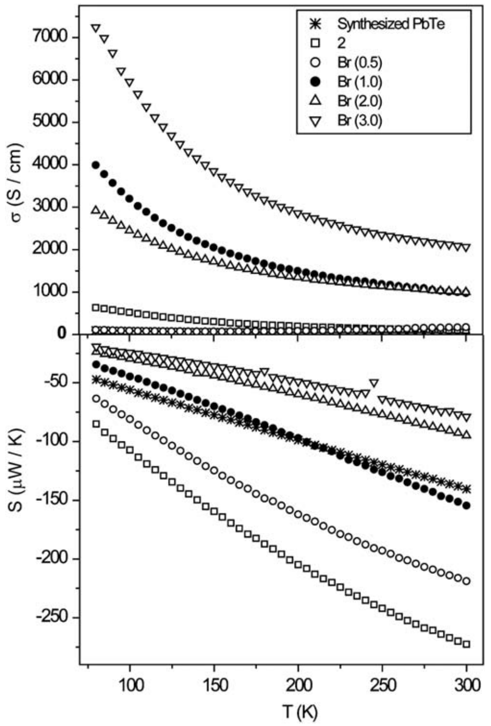

Fig. 6. The conductivity (top) and the Seebeck coefficient (bottom) is given for Br doped as well as undoped PbTe sintered under HPHT conditions.

Comparing to conventionally fabricated materials, typical values of Z for n-type PbTe at room temperature are near 0.4×10^{-3}/K [29]. Z for Br (1.0) is 0.9×10^{-3}/K at 300 K. A conventionally prepared, Br doped PbTe was reported to have thermopower of $-80\,\mu\text{V/K}$ and a conductivity of 3000 S/cm; which computes to a power factor $\sim19\,\mu\text{W/cm K}^2$ [30]. The thermal conductivity was not reported in that study.

We have prepared a sample (Br (1.0) non-HPHT) from the same powder batch as Br (1.0) but sintered under vacuum at 520 °C for 12 h and found thermopower of $-213\,\mu\text{V/K}$ and a conductivity of 133 S/cm (Table 2). In this sample, $Z=0.2\times10^{-3}$/K at 300 K. The bulk density of this sample was measured to be $7.97\,\text{g/cm}^3$ as compared with a density of $8.03\,\text{g/cm}^3$ for the corresponding HPHT sintered sample (Br (1.0)) suggesting that density differences are not contributing to differences in the transport properties. The properties of this sample are similar to that of (HPHT sintered) Br (0.5) even though the nominal dopant concentration is double. This suggests that HPHT sintering may increase the 'effectiveness' of dopants by removing lattice defects.

4. Conclusions

The results presented here show that both HPHT sintering conditions and the dopant concentration are critically important to thermoelectric performance in PbTe.

The drastic changes in the electrical properties induced by HPHT processing are particularly interesting. Order of magnitude changes in ZT and σ, and factor of two changes in S are observed. The changes are not easily attributed to changes in dopant concentrations, and suggest that other more complex mechanisms (perhaps involving grain boundaries) are at work in determining the resulting thermoelectric performance.

In the case of undoped PbTe, higher pressure and temperature are likely detrimental to ZT, but a sintering pressure of 4.0 GPa and temperature of 1045 °C seemed better over that of ambient pressure as well as higher pressure sintering. Although in the case of Br doped materials different HPHT sintering conditions were not explored, it seems reasonable to expect that higher sintering pressures and temperatures would be detrimental to performance. However, it is likely that the HPHT sintering conditions chosen are not the optimal ones.

In the doped samples, as expected, the thermopower decreases as the dopant concentration increases. Lattice thermal conductivity essentially remains unchanged, and electrical conductivity generally increases. However, around a calculated carrier concen-

Table 2
A summary of the properties of various Br doped, and undoped PbTe samples. Carrier mobility (μ) is calculated by $\mu=1/(ne\rho)$ where n is the calculated carrier concentration, e the electric charge, and ρ the measured electrical resistivity. σ, S, and κ data were taken at 300 K.

Sample	Carrier conc. (cm^{-3})	Calc. carrier conc. (cm^{-3})	Calc. carrier mobility ($\text{cm}^2/\text{V s}$)	σ (S/cm)	S (μV/K)	κ (mW/cm K)	Calc. ZT
PbTe (HPHT)	No doping	–	–	103.1	−272.6	22.87	0.100
Br (0.5)	0.5×10^{19}	0.308×10^{19}	347.8	171.4	−218.9	25.52	0.097
Br (1.0)	1.0×10^{19}	0.525×10^{19}	1164.9	979.3	−154.6	25.74	0.273
Br (1.0) non HPHT	1.0×10^{19}	–	–	133.0	−213.0	25.4	0.071
Br (2.0)	2.0×10^{19}	–	–	997.1	−94.8	31.71	0.085
Br (3.0)	3.0×10^{19}	2.027×10^{19}	637.9	2068.8	−78.8	38.95	0.099

tration of $0.5\times10^{19}\,\mathrm{cm}^{-3}$ (nominal doping of $1.0\times10^{19}\,\mathrm{cm}^{-3}$) the optimal carrier mobility of $1165\,\mathrm{cm}^2/\mathrm{V\,s}$ (generally carrier mobilities greater than $1000\,\mathrm{cm}^2/\mathrm{V\,s}$ is one of the requirements of a good thermoelectric) [2] and a *ZT* of 0.27, at 300 K, is achieved.

It is surprising to obtain such a high figure-of-merit in a relatively simple system. Generally, good thermoelectric materials must also be alloyed in order to reduce thermal conductivity. But thermal conductivity is minimally affected by HPHT sintering conditions and is not especially low in these materials.

Density can have a significant effect on thermoelectric properties and the HPHT sintered materials are dense. The density of Br (1.0) is $8.03\,\mathrm{g/cm^3}$, but its density is not appreciably higher than that of the corresponding non-HPHT sintered material ($7.97\,\mathrm{g/cm^3}$). So the increased performance of HPHT sintered material cannot be attributed to densification. High carrier mobilities may arise however because HPHT sintering may reduce the concentration of lattice defects leading to the unimpeded flow of charge carriers through the crystal. In this view, HPHT sintering not only consolidates the material, but also removes lattice defects, an idea we have put forward in a previous contribution [23]. We expect that HPHT sintering may also be applicable to other thermoelectric materials systems and we will report on higher temperature measurements in the future.

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