Thermoelectric properties of HPHT sintered In-doped $Pb_{0.5}Sn_{0.5}Te$

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ABSTRACT

The thermoelectric properties of $Pb_{0.5}Sn_{0.5}Te$ doped with In at 1.0, 2.0, and $3.0 \times 10^{19}/cm^3$ and sintered at a high pressure and high temperature (HPHT) of 4.0 GPa and 800 or 900 °C, respectively, have been studied. All samples show p-type semiconducting behavior with positive thermopower. We find that HPHT sintering of conventionally synthesized materials improves their thermoelectric properties. The highest power factor is obtained for In doping of $2.0 \times 10^{19}/cm^3$ with 13.5 μW/cm K^2 at 230 °C. The corresponding figure of merit is 1.43×10^{-3}/K. This represents a twofold improvement in thermoelectric figure of merit, compared to the conventionally sintered materials reported in the literature. When exposed to 400 °C for 10 days, samples sintered at 900 °C exhibit more stable thermoelectric properties, while the properties of those sintered at 800 °C deteriorated. These results demonstrate that HPHT sintering is a viable and controllable way of tuning the thermoelectric properties of PbTe-based materials.

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1. Introduction

The efficiency of thermoelectric materials is a function of 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 a useful figure of merit and is a dimensionless number. 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.

In previous contributions, we have demonstrated the beneficial effects of sintering thermoelectric materials under high pressure high temperature (HPHT) conditions [1,2]. We hypothesized that sintering under modest pressure, in the 4–6 GPa range, leads to a reduction in lattice defect density, resulting in increased thermopower in undoped PbTe [2] and an order of magnitude improvement in thermoelectric figure of merit in Br-doped PbTe [1], when measured at room temperature.

Our findings can be compared to the literature reports of large increases in the figure of merit when thermoelectric materials are placed under pressure up to 4 GPa [3–5]. Also, 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 [6–8]. These experiments, unlike ours, were carried out under cold compression, with no heating, and all the reported measurements were done on the sample while it was under pressure. The enhanced thermoelectric properties did not persist upon the release of pressure [6]. Iodine-doped PbTe has been synthesized from Pb, Te, and PbI_2 under HPHT conditions [9] and then characterized at ambient pressure. This material was found to have the highest room temperature power factor ($24.2 \ \mu W \ cm^{-1} \ K^{-2}$) at an iodine doping level of 0.03 mol% (equivalent to $1 \times 10^{19}/cm^3$) [9]. Similarly, $AgSbTe_2$ synthesized from the elements, under HPHT conditions, was found to yield decreasing thermopower and resistivity with increasing synthesis pressure [10,11].

For commercial applications, PbTe-based materials are attractive since these materials generally have ZT maximum in the range 300–400 °C, making them suitable for applications in converting waste heat to electricity [12]. Improvements in their thermoelectric performance have been achieved through various synthetic and materials processing techniques including alloying with elements such as Sn or Se to reduce thermal conductivity and tune the band gap, doping with elements such as Br or In to modify carrier concentration and hence electrical conductivity, and reducing the grain size of hot pressed and sintered materials to reduce thermal conductivity through grain boundary scattering [13–15]. It has also been found that the Seebeck coefficient can be enhanced by grain boundaries or nanometer size inclusions [16,17], and manipulating the electronic structure through Tl doping [18]. Another fruitful line of investigation has involved

alloying PbTe with $AgSbTe_2$ [19,20]. More recently, these materials have been found to possess a complex nanostructure, possibly accounting for their enhanced thermoelectric properties [21,22].

Solid solutions of PbTe and SnTe expressed as $Pb_{1-x}Sn_xTe$ with $0 \leq x \leq 1$ yield well known p-type thermoelectric materials [23]. For $x \geq 0.25$, these materials possess positive thermopower values over the entire temperature range 300–700 K [24,25]. By doping with In the carrier concentration can be tuned to optimize thermoelectric performance [26]. But, until now, there have been no reports of these materials being sintered at HPHT conditions.

Here we report on the thermoelectric properties of $Pb_{0.5}Sn_{0.5}Te$ doped with In at 1.0, 2.0, and $3.0 \times 10^{19}/cm^3$. We have compared our results to literature reports of materials conventionally synthesized and sintered using powder metallurgical methods [26]. We find that the appropriate choice of HPHT sintering conditions can double the figure of merit (Z), when measured at use temperatures circa 200–300 °C, over that of the same conventionally fabricated material. Additionally we find that these enhanced thermoelectric properties persist even when the samples are subjected to a temperature of 400 °C for 10 days, demonstrating their robustness to use conditions.

2. Experimental

High purity Te ingot (99.9999%, Alfa Aesar), Pb shot (99.9999%, Alfa Aesar), Sn shot (99.9999%, Alfa Aesar), and In powder (−325 mesh, 99.999%, Alfa Aesar) were used without further purification. $Pb_{0.5}Sn_{0.5}Te$ samples with nominal In dopant concentrations of 1.0, 2.0, and 3.0 ($\times 10^{19}/cm^3$) were prepared with Pb, Sn, Te, and In which were weighed according to the nominal stoichiometry of $Pb_{1-x-y}Sn_xIn_yTe$. The elements were loaded into silica tubes (total sample mass of 15 g per 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 ± 0.01%. Covered tubes were quickly moved to a vacuum line, evacuated (10^{-3} Torr), and sealed with flame under vacuum. The tubes were heated to 950 °C over 15 h, held at this temperature for 3 h, and then 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 ($Pb_{0.5}Sn_{0.5}Te$ melts at ~850 °C) [27]. Powder X-ray diffraction showed the product to be single phase 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.

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, with an integrated heater circuit, and pressed on a belt type apparatus. All high pressure cell components were stored under vacuum at ~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 [28] and temperature calibration was done by measuring in situ with a K-type thermocouple inserted in the cell. HPHT sintering was accomplished in ~15 min with total time of 10 min at the soak temperature and a pressure of 4.0 GPa. Samples were pressurized prior to heating and then quenched at > 10 °C/s to < 200 °C, while still under pressure, before pressure

release. After HPHT treatment, samples were cut into rectangular bars with approximate dimensions of $0.5 \times 0.3 \times 0.2$ cm^3 by wire electrical discharge machining (EDM) and transported to Cornell University for property 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 80–300 K using an apparatus designed and built in-house, described elsewhere [29]. Conservative estimates of errors for the measurement are within ± 5% for S, ± 10% for ρ, and ± 10% for κ [29]. 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 epoxy (Epotek H20E, Ted Pella).

TE property measurements for temperatures greater than 300 K were done using an apparatus designed and built in-house described elsewhere [30]. Contacts to the ends of the bar shaped sample were made using silver epoxy (Epotek H20E), and used for current contact for ρ measurements, and heater/heat sink contacts for S measurements. The voltage contacts for the ρ measurements were made using fine gauge copper wire and silver epoxy (Epotek H20E). Thermocouple wires for S measurements were attached using silver epoxy (Epotek H20E).

High temperature thermal conductivity ($\kappa = DC_pd$) was calculated from the measured thermal diffusivity (D), heat capacity (C_p), and density (d). Thermal diffusivity and heat capacity were measured at the Jet Propulsion Laboratory in Pasadena, CA (for In-doped $Pb_{0.5}Sn_{0.5}Te$) or at the Thermophysical Properties Research Laboratory in West Lafayette, IN (for Br-doped PbTe). Errors in such measurements could arise from the sample geometry for high temperature thermal diffusivity. Thermal diffusivity is expressed by the equation, $D = (Kl^2/t)$, where K is a constant, l the thickness of the sample, and t the elapsed time. Errors in any one of these measurements would be compounded. Conservatively, we estimate that the error is ~20%.

3. Results and discussion

Our previous investigations on the PbTe system had suggested that significant improvements in thermoelectric properties could be obtained after HPHT sintering [1,2]. But sintering pressures greater than ~4.0 GPa were not effective. We presume that this is because PbTe undergoes a phase transformation from cubic to orthorhombic at 4.2 GPa [31]. We therefore kept the sintering pressure here at 4.0 GPa. As part of this study, we revisited the undoped n-type PbTe [1], but extended our measurement range to temperatures ≥ 300 K. For this sample, we have measured a thermopower of -272 μV/K at 300 K. However, as shown in Fig. 1, this very promising thermopower value was not stable when the material was exposed to higher temperature, up to 750 K. In fact, even during the measurement cycle to higher temperatures, we observed the thermopower diminish. By the third measurement cycle, the thermopower had diminished to that of a conventional, non-HPHT sintered PbTe. Similar experiments with non-HPHT sintered PbTe did not show such dramatic changes in thermopower. This observation supports our previous argument [1,2] that HPHT sintering reduces the concentration of lattice defects, thus leading to an improvement

of thermoelectric properties. Exposure to higher temperatures then re-introduces these defects, and, in this example, causes thermopower to degrade.

If we make the simplifying assumption that these are all vacancy defects, then at equilibrium, the number of defects is $n = Ne^{-(\varepsilon + Pv_o)/k_B T}$ [32], where N is on the order of Avogadro's number of atoms, P the pressure, v_o the volume of each atom, k_B Boltzmann's constant, and T the temperature. The implicit assumption is that $n \ll N$. We can see from the equation, that as pressure is increased, the equilibrium concentration of vacancies will decrease. Assuming an activation energy for re-introducing defects, then upon pressure release, we have a system not at equilibrium with respect to vacancy defects. Subsequently, exposure to high temperatures, at atmospheric pressure, re-establishes the equilibrium defect concentration. The question then becomes, is it possible to stabilize the low defect concentration obtained under HPHT sintering when the material is exposed to use temperatures at atmospheric pressure? Or, expressed alternatively, is it possible to increase the activation energy for defect formation such that the material can be stable at use temperatures?

One clue was provided by the fact that we could repeatedly measure HPHT sintered PbTe at low temperatures (< 300 K) with no apparent degradation of thermoelectric properties, suggesting that the activation energy for vacancy formation was considerably above 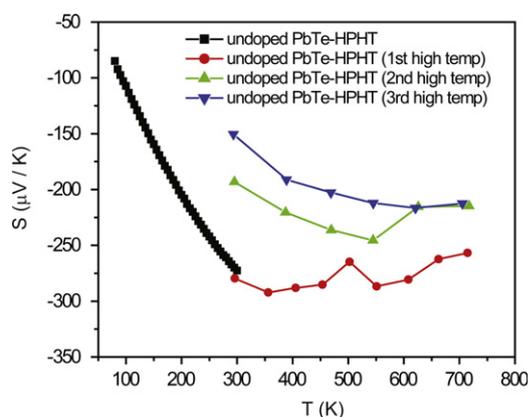room temperature. Reasoning that systems which are intentionally doped and alloyed may be more stable to defect formation, we focused our efforts on such systems. The PbSnTe system has been extensively reported in the literature [25–27,33] and has been used commercially for decades [23]. In particular, the composition $Pb_{0.5}Sn_{0.5}Te$ with In doping has been well characterized [25,26]. Although undoped $Pb_{0.5}Sn_{0.5}Te$ is intrinsically p-type [24], it is suggested that In dopant serves to pin the Fermi level [25].

Our results, at 300 K, for HPHT sintered $Pb_{0.5}Sn_{0.5}Te$ with In doping of 1.0, 2.0, and $3.0 \times 10^{19}/cm^3$ are summarized in Table 1. To facilitate comparison with literature data [26], the In concentrations are 0.03, 0.07, and 0.1 atom%. In an initial set of experiments, samples with each In doping level were sintered at 800–900 °C (A through E). In order to simulate use conditions, one set of samples (A1 through E1) was kept at 400 °C for 10 days in vacuum (sealed silica tube) prior to measurement while the remaining samples were not exposed to this high temperature.

Looking first at the samples that were sintered at 900 °C, there are no significant changes in thermopower and thermal conductivity of sample C1 and E1 compared to samples C and E, but electrical conductivity increases after heat exposure. This leads to a higher figure of merit for C1 and E1. However, comparing samples D–D1, electrical conductivity increases threefold and this leads to increasing total thermal conductivity by $\sim 25\%$ and reducing Seebeck coefficient by $\sim 50\%$. Overall, the ZT decreases by $\sim 50\%$.

For the two samples sintered at 800 °C, thermopower decreases by $\sim 50\%$ in both cases and thermal conductivity increases. However, electrical conductivity does not follow a clear trend, decreasing from A to A1 but increasing by threefold from B to B1. Overall, the ZT is decreased for both.

We have repeated the experiments with In doping of $2 \times 10^{19}/cm^3$ and for sintering temperatures of 900, 925, and 950 °C to determine if our observations are repeatable and to determine the role of sintering temperature at high pressures. Sample F1 is a duplicate of D1 and exhibits similar properties. (Note there is no corresponding sample F.) Comparing samples G–G1 and H–H1, we see that the overall behavior is similar to samples D and D1. The thermopower is still diminished by $\sim 50\%$, and the electrical conductivity almost doubles. There is also a substantial increase in total thermal conductivity. This suggests that variations in sintering temperature, in this range, do not have an appreciable effect on overall properties.

These large changes in thermoelectric properties between samples sintered at high pressures and at different temperatures cannot be easily explained by the changes in stoichiometry. In each case, the samples were made from the same powder batch, the only difference being their sintering temperature at HPHT.

Fig. 1. The low temperature and high temperature thermopower of HPHT sintered n-type PbTe is plotted. When the material is exposed to temperatures > 300 K, the thermopower starts to deteriorate. By the third high temperature measurement cycle, thermopower is similar to that of a conventionally sintered sample.

Table 1
The HPHT sintering conditions and room temperature data for In-doped $Pb_{0.5}Sn_{0.5}Te$. The samples numbered A1, B1, etc. have been subjected to 400 °C for 10 days. Note that there is no sample F since sample F1 is a repeat of D1.

Sample	In ($\times 10^{19}/cm^3$)	Sintering temperature (°C)	400 °C, 10 d	S (μV/K)	κ (mW/cm K)	σ (S/cm)	ZT
A	1.0	800	N	111	17.11	763	0.165
B	2.0	800	N	129	12.69	662	0.259
C	1.0	900	N	117	17.23	610	0.146
D	2.0	900	N	132	15.25	671	0.231
E	3.0	900	N	144	12.91	365	0.175
G	2.0	925	N	122	15.11	826	0.245
H	2.0	950	N	136	13.76	685	0.280
A1	1.0	800	Y	51	21.66	559	0.020
B1	2.0	800	Y	55	21.80	1727	0.073
C1	1.0	900	Y	118	16.22	758	0.195
D1	2.0	900	Y	64	20.15	1812	0.109
E1	3.0	900	Y	121	14.75	735	0.218
F1	2.0	900	Y	53	20.57	1928	0.08
G1	2.0	925	Y	74	19.00	1761	0.153
H1	2.0	950	Y	64	18.67	1422	0.092

Furthermore, the samples exhibited very different behavior upon exposure to high temperature. These observations may be explained by the energy required for lattice defects to be 'annealed' out of the system. As explained above, higher pressure would favor lower defect concentrations at equilibrium. But the kinetics for reducing lattice defects would be faster at a higher sintering temperature.

It is somewhat difficult to discern a clear trend from the data presented, but, it is apparent that the concentration of charge carriers, both holes and electrons, is changing upon exposure to 400 °C and that the HPHT sintering temperature has some effect on the behavior after high temperature exposure. For samples that are HPHT sintered at 800 °C, the ZT diminishes by more than 70% after exposure to 400 °C. HPHT sintering at 900 °C appears to yield samples that are somewhat more stable to heat exposure. The ZT of these samples, for the most part, remain stable. In the one case where ZT does deteriorate, it is no more than 50%. Going to still higher sintering temperature of 925 or 950 °C does not seem to yield any further stability. We therefore limited further investigations into the high temperature transport properties to samples sintered at 900 °C. And in order to test their long-term stability and potential for applications, the transport properties were only measured after exposure to 400 °C for 10 days.

Fig. 2 shows the measured electrical resistivity and Seebeck coefficient in the temperature range from room temperature to 450 °C, for $Pb_{0.5}Sn_{0.5}Te$ at the three In doping levels. Each sample, C1, E1, and F1, was HPHT sintered at 900 °C and then exposed to 400 °C for 10 d before measurements were made. The electrical resistivity of all samples increases with temperature, indicating degenerate semiconducting behavior. Up to about 300 °C, higher electrical resistivity is accompanied by higher thermopower as expected. But beyond 300 °C, the thermopowers of samples with
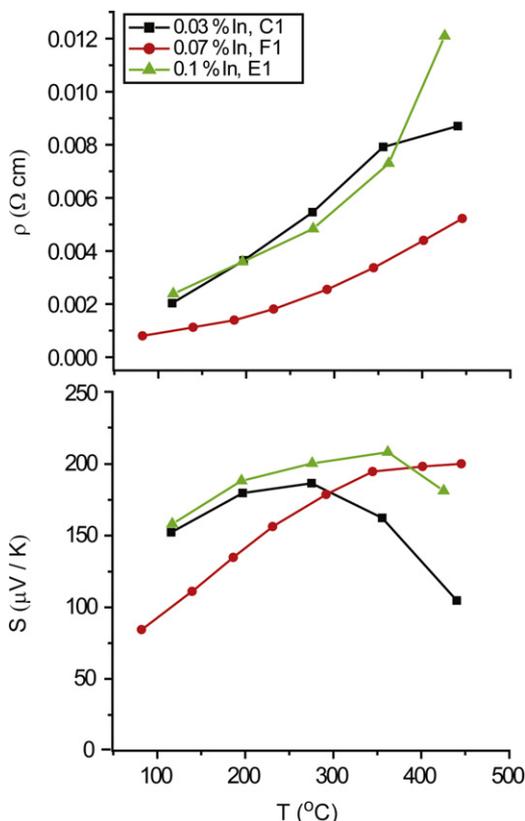
In doping at 1.0 and $3.0 \times 10^{19}/cm^3$ level off and then decline while that of the sample (F1) with In doping at $2.0 \times 10^{19}/cm^3$ continue to rise. The corresponding power factor for these samples, given in Fig. 3, shows that In at a nominal doping of $2.0 \times 10^{19}/cm^3$ yields high values in the temperature range 200–350 °C. The peak value, at ~250 °C, is 13.5 µW/cm-K^2.

High temperature thermal conductivity (obtained by the flash diffusivity–specific heat method) was calculated from the equation $\kappa = DC_p d$ where the sample density (7.13 g/cm^3, F1) was determined by He pycnometry. Fig. 4 shows the total thermal conductivity in the temperature range up to 450 °C for the In doped sample F1. Also shown for comparison is the thermal conductivity for HPHT sintered PbTe doped with Br ($1 \times 10^{19}/cm^3$). We have previously reported on HPHT sintered Br doped, PbTe [1]. We would expect the thermal conductivity for un-alloyed PbTe to be higher and this is borne out by the results. The thermal conductivity for the In-doped $Pb_{0.5}Sn_{0.5}Te$ samples, in the temperature range 200–350 °C, is < 1.0 W/m-K. The value for conventionally synthesized materials is 1.5 W/mK [26].

Also in Fig. 4 we plot the lattice thermal conductivity, calculated from the Wiedemann–Franz law ($\kappa_{elec} \times \rho = L_0 \times T$) where the Lorenz constant $L_0 = 2.45 \times 10^{-8}$ WΩ/K^2 [32]. This value for L_0 is valid assuming scattering of the carriers is elastic. This is generally a valid assumption for thermoelectric materials
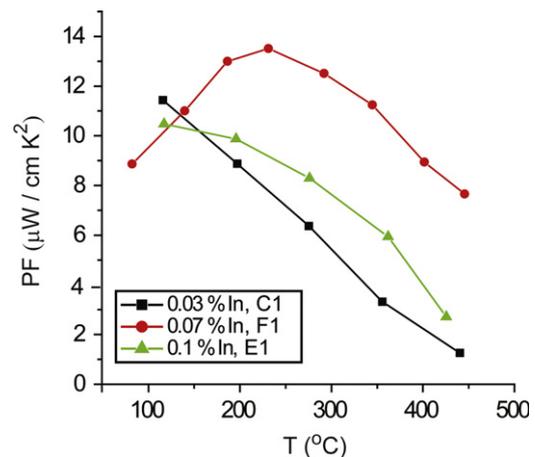
Fig. 3. Calculated power factor for In-doped $Pb_{0.5}Sn_{0.5}Te$ is plotted.

Fig. 2. Measured electrical resistivity (top) and Seebeck coefficient (bottom) for In-doped $Pb_{0.5}Sn_{0.5}Te$. All samples were sintered at 900 °C and then exposed to 400 °C for 10 days.
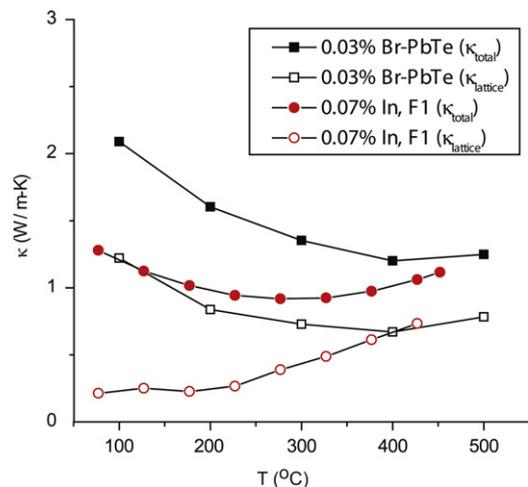
Fig. 4. Total thermal conductivity of sample F1 as calculated from the measured thermal diffusivity, heat capacity, and density. The lattice thermal conductivity is also plotted, and for comparison, the thermal conductivity for Br-doped PbTe is given.
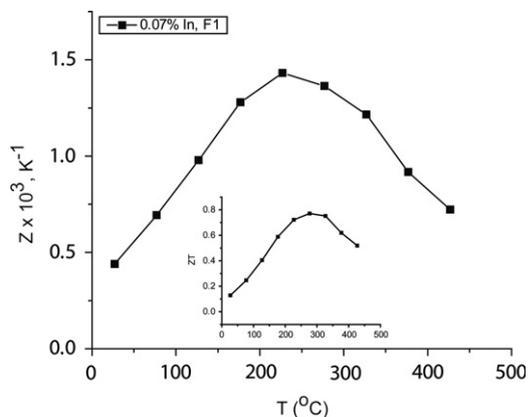
Fig. 5. Calculated thermoelectric figure of merit for sample F1. The inset plots the ZT for the sample.

operating at or above room temperature. The lattice thermal conductivity of the Br-doped PbTe decreases from ~1.2 to about 0.7 W/mK at 400 °C before rising to 0.8 W/mK at 500 °C. This is comparable to what has been reported before [34] for PbTe. By contrast, sample F1 shows a remarkably low lattice thermal conductivity, ~0.2 W/mK, in the range 100–200 °C, increasing to ~0.8 W/mK at 450 °C. This low value of lattice thermal conductivity is comparable to that of thallium-based thermoelectric materials [34], and n-type PbTe sintered from very fine ($<1\,\mu m$ particle size) powder [35].

In Fig. 5 we show the figure of merit ($Z=S^2\sigma/\kappa$) for sample F1. The HPHT sintered material has approximately 2 times the figure of merit of conventionally sintered materials [26] at its highest value and is consistently higher over the entire temperature range. These results show that enhanced figure of merit is achieved by improved Seebeck coefficient and lower thermal conductivity over conventionally sintered materials.

4. Conclusions

The results presented here demonstrate that HPHT sintering of thermoelectric materials can lead to a permanent increase in thermoelectric figure of merit. The methods used here can be easily adapted to manufacturing. However, the beneficial effects of HPHT sintering can only be realized if the material and sintering conditions are appropriately chosen. For unalloyed PbTe, for instance, the enhancement of thermoelectric properties was fleeting and quickly diminished when the material was exposed to high temperatures. It appears that alloying, at least in the case of In-doped $Pb_{0.5}Sn_{0.5}Te$, is a necessary pre-requisite. We believe that alloying helps to stabilize low defect concentrations obtained from HPHT sintering and we suggest that other alloy systems could similarly benefit. The sintering condition also is important; too low a sintering temperature is not effective. The changes we have observed cannot be simply attributed to unintentional changes in dopant concentration during HPHT sintering. The sintering cycle is brief, the sample is quenched prior to pressure release, and the pressures employed preclude any loss of volatile material. Our sample density as measured by He pycnometer was 7.13 g/cm^3 close to the theoretical density of 7.30 g/cm^3 [31]. Further optimization of the sintering condition is also possible.

The high figure of merit ($Z=1.43\times10^{-3}$/K; 0.07% In–$Pb_{0.5}Sn_{0.5}Te$), which is a twofold improvement compared to conventionally synthesized [26] In-doped $Pb_{0.5}Sn_{0.5}Te$ ($0.6–0.7\times10^{-3}$/K) arises from slightly higher thermopower and lower thermal conductivity, while the electrical resistivity is

comparable. It is reasonable to suggest that, starting from conventionally synthesized materials with optimized properties, HPHT sintering may yield significant further improvements. The very low, although not unprecedented, lattice thermal conductivity cannot be attributed only to the effect of alloying. Particle size must also have a contribution in lowering thermal conductivity [14,15] although we have not yet quantified this effect. Starting with even smaller particle size powder may be an avenue for further optimization, though this may require still higher sintering pressures in order to consolidate such powders.

The ability of these HPHT sintered samples to maintain high thermoelectric performance after heat exposure is only a preliminary result. But it is an important finding in contrast to the result of Fig. 1 and gives some indication of their usefulness. Indeed, thermoelectric systems have operated continuously for decades with minimal degradation in performance. At present, we do not have any indication whether HPHT sintered materials would show similar stability in the long term.

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