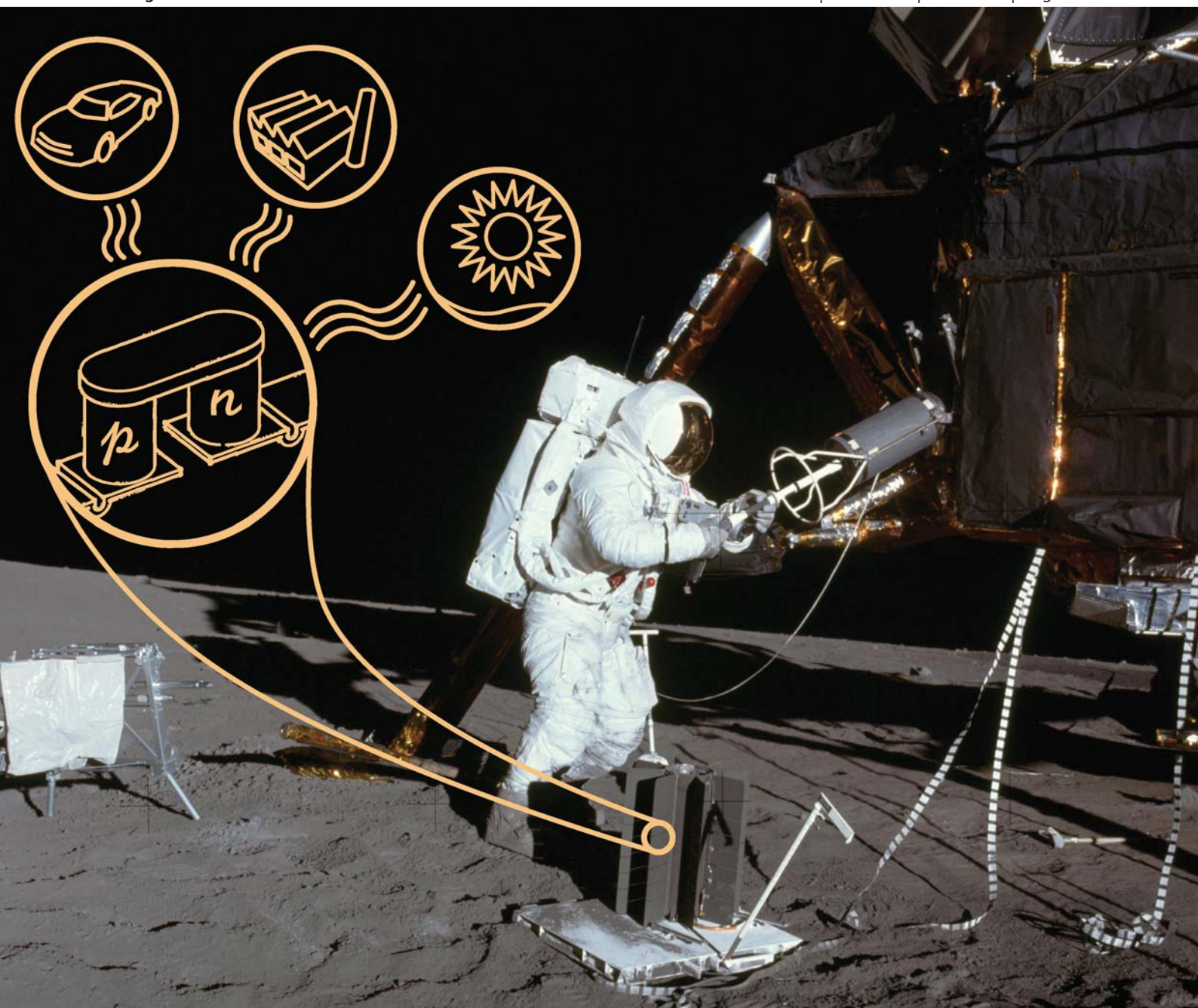


Energy & Environmental Science

www.rsc.org/ees

Volume 4 | Number 6 | June 2011 | Pages 1929–2324



ISSN 1754-5692

RSC Publishing

COVER ARTICLE

Snyder *et al.*
High thermoelectric figure of merit in heavy hole dominated PbTe

COMMUNICATION

Fennell *et al.*
Potential synergy between power generation, cement manufacture and CO₂ abatement

High thermoelectric figure of merit in heavy hole dominated PbTe

Yanzhong Pei, Aaron LaLonde, Shiho Iwanaga and G. Jeffrey Snyder*

Received 20th September 2010, Accepted 9th December 2010

DOI: 10.1039/c0ee00456a

Thermoelectric transport properties of p-type PbTe:Na, with high hole concentrations of approximately 10^{20} cm^{-3} , are reinvestigated from room temperature to 750 K. The greatly enhanced Seebeck coefficient at these doping levels can be understood by the presence of a sharp increase in the density of states around the Fermi level. As a result, the thermoelectric figure of merit, zT , reaches ~ 1.4 at 750 K. The influence of these heavy hole carriers may contribute to a similarly high zT observed in related p-type PbTe-based systems such as Tl-doped PbTe and nanostructured composite materials.

In January of 1959, the headlines of the newspapers in Washington, DC, USA, heralded the “world’s first atomic battery”, printing a picture of President Eisenhower examining a Radioisotope Thermoelectric Generator (RTG) on his desk in the nation’s capital.^{1,2} This 5 watt generator utilized the Seebeck effect of the semiconductor PbTe to convert radioisotope heat to electricity. The thermoelectric properties of PbTe were extensively studied in both the USA (led by the 3M corporation) and the Soviet Union for military and space applications in the 1950’s and early 1960’s.^{3–5} The fabrication of thermoelectric devices, such as the RTG, requires both n- and p-type semiconductor materials. PbTe can be made p-type by replacing some of the divalent Pb with monovalent Na.⁶ It was Na-doped PbTe, called “2P-PbTe”, that was used in the 1959 RTG and for several NASA missions in the 1960’s.⁷

The performance of a TE material is characterized by the TE figure of merit, $zT = S^2 T / \rho(\kappa_E + \kappa_L)$, where S , ρ , κ_E and κ_L are the Seebeck coefficient, resistivity, and the electronic and lattice components of the thermal conductivity, respectively. During the early research efforts in the 1950’s and 1960’s the Seebeck

coefficient and resistivity could be measured accurately, however, the thermal conductivity measurement at high temperature was a notoriously difficult task.⁸ As a result of this challenge, the 1960 report by Fritts (at 3M) uses the room temperature lattice thermal conductivity value at high temperature. Fritts’ assumption of a constant lattice thermal conductivity leads to an underestimated maximum zT value of ~ 0.7 . This relatively low value is similar to the “3P-PbTe” material later used by Teledyne for NASA.⁷ The data reported by Fritts, with the same maximum zT , were therefore assumed to be accurate for PbTe:Na.^{4,7,10–13}

Reliable high temperature thermal conductivity measurement of semiconductors remained a challenge until the advent of the flash diffusivity technique, developed in the USA in the early 1960’s.⁸ However, by then, the focus of thermoelectric research within the USA had switched from PbTe to Si–Ge alloys,¹⁴ due to Si–Ge being a more capable material for higher temperature use. While Soviet research was leading the effort to understand the physics of PbTe,⁵ they did not use the flash diffusivity method and few high temperature measurements of κ were reported.^{15–19} It is perhaps not surprising then, that until now, there has been no well documented report on the high temperature thermal conductivity of heavily doped PbTe:Na showing the maximum zT is closer to 1.4 rather than 0.7.

Materials Science, California Institute of Technology, Pasadena, CA, 91125, USA. E-mail: jsnyder@caltech.edu

Broader context

Thermoelectrics used to generate electricity from radioisotope heat for NASA can now be used for waste heat recovery on earth. The cover image shows Apollo-12 astronaut Gordon Bean preparing to load a Pu-238 radioisotope heat source into a PbTe-based thermoelectric generator. The generator produced 73 watts of power for the Apollo lunar surface experiments for nearly eight years. Pristine p-PbTe thermoelectric materials typified by Na-doping was successfully used for power generation on the earliest NASA missions about 60 years ago, yet the thermoelectric performance of this material was underestimated due to the difficulties on accurate estimation of the thermal conductivity and achieving optimum sodium doping at that time. Reinvestigation of this simple material reveals that with heavy doping the system actually shows a thermoelectric figure of merit, zT , as high as ~ 1.4 (twice that previously believed) because of the complex band structure. This zT is comparable with the recently discovered PbTe:Tl with resonant state enhancement of the Seebeck effect, and similar results with nanostructures, providing an additional explanation (and simple, less toxic solution) for high zT in PbTe-based thermoelectrics.

Thermoelectrics are attracting renewed interest because of their ability to harvest electricity from waste heat.²⁰ Increasing zT by optimizing S , ρ and κ_E is challenging as these parameters are interrelated through the carrier concentration (n),^{10,21} however, the lattice thermal conductivity remains an independent parameter and can be reduced to increase zT . One approach to minimize κ_L and enhance zT in PbTe materials has been the incorporation of nano-inclusions that act as phonon scattering centers resulting in zT values up to 1.4–1.7 at ~ 700 K.^{22–24}

An alternative approach using a different mechanism has resulted in zT as high as ~ 1.5 (using Dulong–Petit heat capacity), being achieved in p-type Tl-doped PbTe with hole concentrations close to $5 \times 10^{19} \text{ cm}^{-3}$. The high zT is attributed to the Tl-doping introducing a strong enhancement of the density of states (DOS) due to a resonant state near the Fermi level that results in a significant enhancement of the Seebeck coefficient.²⁵ The most direct evidence for the presence of the resonant state is the room temperature Seebeck coefficient of PbTe:Tl being significantly larger than that of normal PbTe materials with the same doping level (Fig. 1a).

Conversely, a similar behavior of enhanced DOS around the Fermi level in a heavily doped p-type PbTe without resonant states has been found or proposed in both theoretical and

experimental studies, described either by an additional band^{5,26,27} or a complex Fermi surface²⁸ slightly below (~ 0.2 eV) the valence band edge. Therefore, the transport properties of PbTe at high doping levels (without resonant states) will be dominated by heavy mass holes, particularly at high temperatures due to the broadening of Fermi distribution. In the recently reported calculation by Singh,²⁸ this DOS enhancement adequately explains the high Seebeck coefficient of PbTe:Tl without including resonant states.

Experimentally, Na will dope PbTe with hole concentrations ranging from $\sim 10^{18}$ to $\sim 10^{20} \text{ cm}^{-3}$ (ref. 5 and 29–32) and does not introduce resonant states.^{26,33} The S of PbTe:Na decreases with hole concentration according to the Pisarenko relation expected for a single parabolic band at low hole concentrations.³² The dependence of S on n at high carrier concentrations shows a deviation^{5,29–32} from the trend expected from the Pisarenko relationship, leading to an increased Seebeck coefficient (Fig. 1a).

Here we confirm the previous results on S , ρ and n for heavily doped PbTe:Na and measure the high temperature thermal conductivity, resulting in a zT reaching ~ 1.4 in heavily doped samples at ~ 750 K, rather than the long-held assumption of the maximum zT of ~ 0.7 . We confirm both the heavy hole character in PbTe:Na as well as the enhanced S in PbTe:Tl due to resonant states.

Polycrystalline $\text{Na}_x\text{Pb}_{1-x}\text{Te}$ ($0.5\% < x < 2\%$) samples were synthesized by melting, annealing and hot-pressing. Stoichiometric mixtures of high purity Na (99%), Pb (99.999%) and Te (99.9999%) ingots were sealed in graphite coated ampoules under vacuum and heated to 1273 K at $\sim 500 \text{ K h}^{-1}$. After soaking at 1273 K for about 6 hours, the ampoules were cold-water quenched and annealed at 973 K for 48 hours. The resulting ingots were ground into powder and hot pressed at 700 K for 1 hour. Pellets with a relative density of 98% or higher were used for measurements of the transport properties. The Seebeck coefficient was obtained from the slope of the thermopower vs. temperature gradients using Chromel–Nb thermocouples. The resistivity and Hall coefficient (R_H) were simultaneously measured using the van der Pauw technique under a reversible magnetic field of 2 T. Thermal diffusivity was measured by the laser flash method (Netzsch LFA 457). All of the measurements were carried out under vacuum in the temperature range of 300–750 K. Consistent measurements, within $\sim 10\%$ for Seebeck and resistivity, were confirmed at NASA's Jet Propulsion Laboratory (JPL) (using W–Nb thermocouples) and at ZTPlus Inc. using the ULVAC-ZEM3 system on a sample with $zT \sim 1.4$ at 700 K. Scanning Seebeck coefficient measurements (at 300 K) on the sample with Hall carrier density of $9 \times 10^{19} \text{ cm}^{-3}$ showed a Seebeck coefficient variation of only $5 \mu\text{V K}^{-1}$ (full width for 90% of the data). Heat capacity (C_p) is estimated by $C_p (k_B \text{ per atom}) = 3.07 + 4.7 \times 10^{-4} \times (T/\text{K} - 300)$, which is obtained by fitting the experimental data reported by Blachnik and Igel³⁴ within an uncertainty of 2% for all the lead chalcogenides at $T > 300$ K. It should be emphasized that this simple equation agrees well with the theoretical prediction³⁵ taking the lattice vibration (Debye temperature⁵ of 130 K), dilation (bulk modulus³⁶ of 39.8 GPa, the linear coefficient⁵ of thermal expansion of $20 \times 10^{-6} \text{ K}^{-1}$) and charge carriers contributions into account. At 700 K or above this equation gives $C_p \sim 10\%$ higher than the Dulong–Petit value. The combined uncertainty for the determination of zT is $\sim 20\%$.

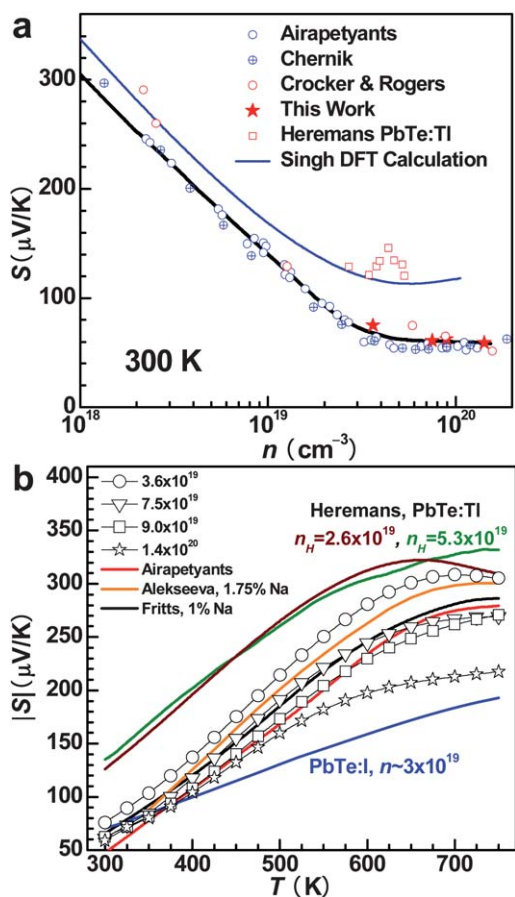


Fig. 1 (a) Room temperature Seebeck coefficient *versus* carrier concentration for p-type PbTe doped with Na^{19,30–32} and Tl.²⁵ The solid black line is the relationship shown by Airapetyants *et al.*³² (b) Temperature dependent Seebeck coefficient for both p-^{3,19,25,32} and n-type³ materials with high carrier concentrations.

X-Ray diffraction and scanning electron microscope analysis was used to confirm that the materials for this study are single phase. The samples have room temperature Hall carrier densities (n_H) of 3.5, 7.5, 9.0 and $14 \times 10^{19} \text{ cm}^{-3}$, estimated by $n_H = 1/eR_H$. Fig. 1a shows the Hall carrier density dependent Seebeck coefficient at room temperature.

The samples made for this study are consistent with the previous studies on PbTe:Na single crystals^{30,32} showing the same in S vs. n behavior at room temperature (Fig. 1a), including the deviation which results in a flattening of the curve at $S \sim 60 \mu\text{V K}^{-1}$.

It has been asserted that this deviation in Seebeck coefficient, as well as other electronic transport property behavior, could be explained by a two-band model (light and heavy bands),^{5,29–32,37–39} similar to that found in the $\text{La}_{3-x}\text{Te}_4$ system.⁴⁰ At low hole concentrations the light mass band dominates the Seebeck coefficient and other transport properties, while at high hole concentrations the heavy band contribution enhances the Seebeck coefficient beyond the value predicted by the Pisarenko relationship for the light hole band.^{5,32} The band offset (difference in energy between the band maxima of light and heavy bands) has been reported to be temperature dependent, such that the light band goes below the heavy band at approximately 450 K.^{5,41} A modeling study, based on multi-parabolic bands and the above described band structure features, predicted an optimized zT as high as ~ 1.7 in heavily doped ($\sim 10^{20} \text{ cm}^{-3}$) p -PbTe at $\sim 750 \text{ K}$, which is about twice that of n -PbTe,³⁷ due to the heavy mass carriers behavior.

Fig. 1a also shows the Seebeck coefficient predicted from DFT calculations²⁸ of p -PbTe (blue solid line). The calculation shows a similar flattening, where the Seebeck coefficient becomes approximately constant at $S \sim 120 \mu\text{V K}^{-1}$ when the carrier density is greater than $\sim 4 \times 10^{19} \text{ cm}^{-3}$. The difference between the calculated and experimental Seebeck coefficient may originate from the uncertainties of the band structure and/or the associated temperature dependence. It should also be noted that the experimental carrier density is a Hall density (n_H), while the DFT carrier density is a doping density, n . It is believed that n_H is much smaller than n when the mobility ratio of heavy holes to light holes is small.^{5,42} In one sample, spectroscopic analysis suggested an actual hole density (n) of $\sim 15 \times 10^{19} \text{ cm}^{-3}$ while Hall measurement³² showed a hole density (n_H) of only $\sim 9 \times 10^{19} \text{ cm}^{-3}$.

The analysis using two-band model and both DFT calculations^{27,28} discussed above indicates the presence of an enhanced DOS close to the valence band edge, at nearly the same location in the Brillouin zone⁴³ which predicts the flattening of S (Fig. 1a).

In contrast, n -type PbTe^{26,28} lacks a DOS enhancement around the Fermi level and shows a more typical Seebeck coefficient proportional to absolute temperature. With increasing temperature, the pronounced enhancement of the Seebeck coefficient in p -type materials indicates an increasing number of heavy mass holes contribute to the transport properties, due to a broader Fermi distribution at high temperatures. Below 400 K, p - and n -type PbTe have similar S due to similar effective masses⁵ ($0.36m_e$ for light hole and $0.3m_e$ for electron). However, a significant discrepancy starts at $\sim 400 \text{ K}$ with the p -type material showing an atypical increase in slope of S vs. T resulting in a larger Seebeck coefficient at temperatures higher than 400 K. This observation is consistent with the two-band model in which

the band offset between light and heavy hole bands becomes smaller with temperature and vanishing at $\sim 400 \text{ K}$.^{5,41,44}

The PbTe:TI²⁵ system shows an even higher S than the various PbTe:Na samples, indicating that there is an enhancement effect present due to the resonant states. Although it is concluded that the resonant states by TI-doping are responsible for the enhancement of the Seebeck coefficient²⁵ at room temperature, the heavy mass behavior is likely to be additionally contributing to the Seebeck coefficient in PbTe:TI at higher temperatures.

Additionally, the carrier mobility in PbTe:TI has been found to be decreased by a significant factor of 3–5.²⁵ Both PbTe:TI and PbTe:Na have a similar temperature dependence of Hall mobility as shown in Fig. 2, however, the mobility of PbTe:Na is approximately twice that of PbTe:TI over the whole temperature range. The resonant impurity states in the TI-doped material should lead to a reduced group velocity and therefore reduced carrier mobility.

The total thermal conductivity (κ) of the PbTe:Na samples is shown in Fig. 3b as open symbols. Since Na acts as an effective acceptor, the increased hole concentration (Fig. 1a) results in a decreased resistivity as shown in Fig. 3a. As a result of the decreased resistivity, the electronic contribution to the thermal conductivity, as determined by Wiedemann–Franz law ($\kappa_E = LT/\rho$), is increased resulting in a larger total thermal conductivity as shown in Fig. 3b.

Due to the complexity and the non-parabolicity of the valence band structure around the Fermi level, accurate determination of the Lorenz number (L) is difficult. An estimation of L can be made using a single parabolic band (SPB) model with acoustic scattering⁴⁵ resulting in an L with a deviation of less than 10% as compared with a more rigorous single non-parabolic band and multiple band models calculation.^{46,47} The estimation of the lattice thermal conductivity (Fig. 3b, solid symbols) is made by subtracting the electronic component (κ_E) from the total thermal conductivity, $\kappa_L = \kappa - \kappa_E$. The estimated lattice thermal conductivity for both PbTe:Na and PbTe:TI is approximately $2 \text{ W m}^{-1} \text{ K}$ at room temperature and $\sim 0.8 \text{ W m}^{-1} \text{ K}$ at $\sim 750 \text{ K}$, and these values are also consistent with n -type PbTe materials, within the uncertainty range of L -estimation.^{5,48} The slightly higher κ_L for the lowest carrier density sample at $T > \sim 550 \text{ K}$ is

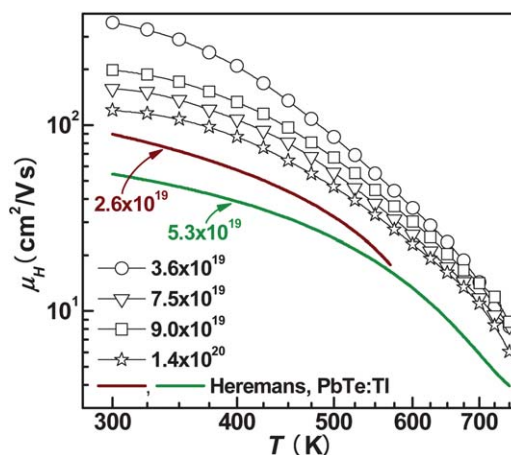


Fig. 2 Hall mobility versus temperature for PbTe:Na and the comparison with that of PbTe:TI.²⁵

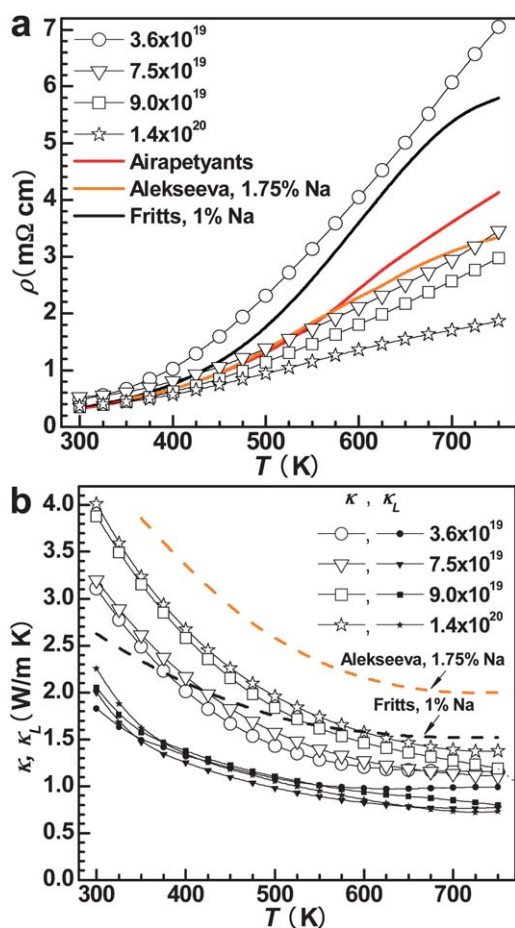


Fig. 3 Temperature dependent electrical resistivity (a), thermal conductivity and the lattice component of thermal conductivity (b) for PbTe:Na. Data plotted as lines are from the literature.^{3,19,32}

likely due to the bipolar contribution. In the previously reported study of Fritts,³ the temperature independent lattice thermal conductivity of $\sim 1.5 \text{ W m}^{-1} \text{ K}$ and non-degenerate L was used and resulted in an overestimation of the total thermal conductivity for 1% Na-doped PbTe at high temperatures, shown in Fig. 3b as a dashed black line.

The figure of merit for 1% Na-doped PbTe reported by Fritts was recalculated (Fig. 4) using the estimated lattice thermal conductivity for PbTe:Na. The resulting maximum zT of ~ 1.2 is nearly twice that originally reported because of the room temperature lattice thermal conductivity used for high temperatures.^{3,4,10} Using the same estimate for the temperature dependent lattice thermal conductivity in combination with other previously reported^{19,32} S and ρ for heavily doped PbTe:Na reveals an even higher zT .

The zT of 2P-PbTe reported by Skrabec and Trimmer⁴⁹ and also that of the 0.7% Na-doped PbTe reported by Kudman⁵⁰ are in excellent agreement with the sample herewith with n_H of $3.6 \times 10^{19} \text{ cm}^{-3}$ (0.5% Na-doping), suggesting the 2P-PbTe and 0.7% Na-doped samples⁵⁰ are slightly under-doped. An increase in hole density by increasing doping content of Na to 1–2% results in a further enhancement of zT to ~ 1.4 , primarily due to the suppression of minority carrier activation at high temperature.

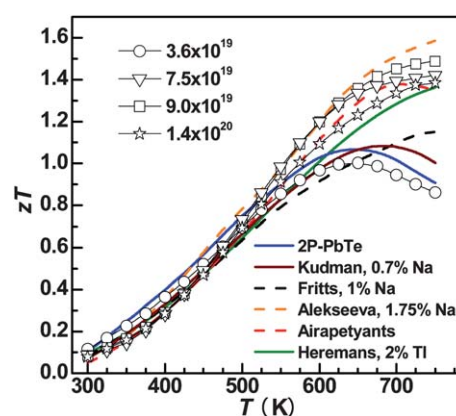


Fig. 4 Temperature dependent thermoelectric figure of merit for PbTe:Na, measured in this work (symbols), reported in the literature^{49,50} (solid lines) and that estimated from electronic transport data in the literature (dashed lines),^{3,19,32} as well as PbTe:Tl²⁵ (recalculated using the same heat capacity). The reported 2P-PbTe is consistent with the under-doped PbTe:Na.

As a result of the heavy hole dominated transport properties at high doping levels and high temperatures, these PbTe:Na materials with high Na content show comparable zT with the resonant PbTe:Tl²⁵ system—despite the further enhancement of S due to the Tl-resonant states (Fig. 1). The increased Seebeck coefficient by resonant states at the expense of carrier mobility appears to be responsible for the similar zT . Samples with $n_H > \sim 7.5 \times 10^{19} \text{ cm}^{-3}$ have been made reproducibly in our experiments showing $zT \sim 1.4$ at $\sim 750 \text{ K}$.

In summary, p -type PbTe materials with high doping levels of Na were prepared and the electrical properties are consistent with previously reported results. Both the experimental results and the theoretical calculations suggest that the electronic transport properties of these samples are heavily influenced by a high DOS near the Fermi level leading to holes with heavy effective mass. These heavy mass carriers lead to a large Seebeck coefficient (compared to n -type PbTe) and high thermoelectric figure of merit of ~ 1.4 at $\sim 750 \text{ K}$. These results make Na-doped PbTe a superior material for practical applications as it is less toxic than the Tl containing counterpart. The high zT observed is intrinsic to PbTe and may contribute to the high zT observed in related p -type PbTe-based systems such as PbTe:Tl²⁵ and nanostructured materials.²³

The presence of a sharp increase in the density of states near the Fermi level is a beneficial characteristic in some high zT materials. As this is a purely electronic effect, reductions in the lattice thermal conductivity, through nanostructuring, for example, should lead to further improvements in zT .

This work is supported by NASA-JPL and DARPA Nano Materials Program. The authors thank Alex Z. Williams and Fred Harris for careful measurements of transport properties at JPL and ZTPlus Inc.; and Norb Elsner for useful discussions and Michael Boettger for the design of the cover image.

References

- U. S. DoE, Atomic Power in Space, a History, <http://www.fas.org/nuke/space/index.html>.

- 2 E. Gamarekian, in *Washington Post*, 17 Jan. 1959, p. A1.
- 3 R. W. Fritts, in *Thermoelectric Materials and Devices*, ed. I. B. Cadoff and E. Miller, Reinhold Pub. Corp., New York, 1960, pp. 143–162.
- 4 R. R. Heikes, R. C. Miller and R. W. Ure, in *Thermoelectricity: Science and Engineering*, ed. R. R. Heikes and R. W. Ure, Interscience Publishers, New York, 1961, pp. 405–442.
- 5 Y. I. Ravich, B. A. Efimova and I. A. Smirnov, *Semiconducting Lead Chalcogenides*, Plenum Press, New York, 1970.
- 6 E. S. Toberer, A. F. May and G. J. Snyder, *Chem. Mater.*, 2010, **22**, 624–634.
- 7 R. D. Abelson, in *Thermoelectrics Handbook: Macro to Nano*, ed. D. M. Rowe, CRC/Taylor & Francis, Boca Raton, 2006, ch. 56, pp. 1–7.
- 8 W. J. Parker, R. J. Jenkins, G. L. Abbott and C. P. Butler, *J. Appl. Phys.*, 1961, **32**, 1679–1684.
- 9 It was known but not well publicized that 3P-PbTe, which also contained Sn and Mn, had lower zT than 2P-PbTe. The high zT p-type PbTe:Na materials were abandoned because of the challenges making good electrical contacts, weak mechanical properties and enhanced reactivities of Na-doped PbTe over 3P-PbTe. Resolving these issues still remains to be addressed.
- 10 G. J. Snyder and E. S. Toberer, *Nat. Mater.*, 2008, **7**, 105–114.
- 11 V. Fano, in *CRC Handbook of Thermoelectrics*, ed. D. M. Rowe, CRC Press, Boca Raton, Florida, 1995, p. 261.
- 12 G. J. Snyder, in *Thermoelectrics Handbook: Macro to Nano*, ed. D. M. Rowe, CRC/Taylor & Francis, Boca Raton, 2006, ch. 9, pp. 1–26.
- 13 C. Wood, *Rep. Prog. Phys.*, 1988, **51**, 459–539.
- 14 C. B. Vining, in *CRC Handbook of Thermoelectrics*, ed. D. M. Rowe, CRC Press, Boca Raton, Florida, 1995, pp. 329–337.
- 15 A. V. Petrov, in *Thermoelectric Properties of Semiconductors*, ed. V. A. Kutasov, Consultants Bureau, New York, 1964, p. 17.
- 16 E. D. Devyatkova and V. A. Saakyan, *Izvestiia Akademii nauk SSSR. Serii fizicheskaiia*, 1967, **2**, 14.
- 17 B. A. Efimova, L. A. Kolomoets, Y. I. Ravich and T. S. Stavitskaya, *Sov. Phys. Semiconduct.*, 1971, **4**, 1653–1658.
- 18 G. T. Alekseeva, V. K. Zaitsev, A. V. Petrov, V. I. Tarasov and M. I. Fedorov, *Fiz. Tverd. Tela*, 1981, **23**, 2888–2893.
- 19 G. T. Alekseeva, E. A. Gurieva, P. P. Konstantinov, L. V. Prokofeva and M. I. Fedorov, *Sov. Phys. Semiconduct.*, 1996, **30**, 1125–1127.
- 20 L. E. Bell, *Science*, 2008, **321**, 1457–1461.
- 21 A. F. Ioffe, *Semiconductor Thermoelements, and Thermoelectric Cooling*, Infosearch, London, 1957.
- 22 Y. Pei, J. Lensch-Falk, E. S. Toberer, D. L. Medlin and G. J. Snyder, *Adv. Funct. Mater.*, 2011, **21**, 241–249.
- 23 M. G. Kanatzidis, *Chem. Mater.*, 2010, **22**, 648–659.
- 24 K. F. Hsu, S. Loo, F. Guo, W. Chen, J. S. Dyck, C. Uher, T. Hogan, E. K. Polychroniadis and M. G. Kanatzidis, *Science*, 2004, **303**, 818–821.
- 25 J. Heremans, V. Jovovic, E. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee and G. J. Snyder, *Science*, 2008, **321**, 554–557.
- 26 K. Hoang, S. D. Mahanti and M. G. Kanatzidis, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 115106.
- 27 D. Bilec, S. Mahanti, E. Quarez, K.-F. Hsu, R. Pcionek and M. Kanatzidis, *Phys. Rev. Lett.*, 2004, **93**, 146403.
- 28 D. J. Singh, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 195217.
- 29 A. J. Crocker and L. M. Rogers, *J. Phys. Colloq.*, 1968, **29**, C4-129–C124-132.
- 30 I. A. Chernik, V. I. Kaidanov, M. I. Vinogradova and N. V. Kolomoets, *Sov. Phys. Semiconduct.*, 1968, **2**, 645–651.
- 31 A. J. Crocker and L. M. Rogers, *Br. J. Appl. Phys.*, 1967, **18**, 563–573.
- 32 S. V. Airapetyants, M. N. Vinograd, I. N. Dubrovsk, N. V. Kolomoet and I. M. Rudnik, *Sov. Phys. Solid State USSR*, 1966, **8**, 1069–1072.
- 33 S. Ahmad, S. D. Mahanti, K. Hoang and M. G. Kanatzidis, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 155205.
- 34 R. Blachnik and R. Igel, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1974, **29**, 625–629.
- 35 O. Delaire, A. F. May, M. A. McGuire, W. D. Porter, M. S. Lucas, M. B. Stone, D. L. Abernathy, V. A. Ravi, S. A. Firdosy and G. J. Snyder, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **80**, 184302.
- 36 M. Lach-hab, D. A. Papaconstantopoulos and M. J. Mehl, *J. Phys. Chem. Solids*, 2002, **63**, 833–841.
- 37 L. M. Sysoeva, M. N. Vinograd, N. V. Kolomoet and Y. I. Ravich, *Sov. Phys. Semiconduct.*, 1970, **3**, 975–977.
- 38 R. S. Allgaier and B. B. Houston, *J. Appl. Phys.*, 1966, **37**, 302–309.
- 39 R. S. Allgaier, *J. Appl. Phys.*, 1961, **32**, 2185–2189.
- 40 A. May, D. Singh and G. Snyder, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **79**, 153101.
- 41 Y. W. Tsang and M. L. Cohen, *Phys. Rev. B: Solid State*, 1971, **3**, 1254.
- 42 E. H. Putley, *The Hall Effect and Related Phenomena*, Butterworths, London, 1960.
- 43 H. Sitter, K. Lischka and H. Heinrich, *Phys. Rev. B: Solid State*, 1977, **16**, 680–687.
- 44 A. A. Andreev and V. N. Radionov, *Sov. Phys. Semiconduct.*, 1967, **1**, 145–148.
- 45 C. M. Bhandari and D. M. Rowe, in *CRC Handbook of Thermoelectrics*, ed. D. M. Rowe, CRC Press, Boca Raton, Florida, 1995, p. 45.
- 46 I. A. Smirnov, M. N. Vinograd, N. V. Kolomoet and L. M. Sysoeva, *Sov. Phys. Solid State USSR*, 1968, **9**, 2074–2079.
- 47 S. Ahmad and S. D. Mahanti, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 165203.
- 48 K. Ahn, C. P. Li, C. Uher and M. G. Kanatzidis, *Chem. Mater.*, 2009, **21**, 1361–1367.
- 49 E. A. Skrabek and D. S. Trimmer, in *CRC Handbook of Thermoelectrics*, ed. D. M. Rowe, CRC Press, Boca Raton, Florida, 1995, p. 272.
- 50 I. Kudman, *Metall. Trans.*, 1971, **2**, 163–168.