The present invention discloses heavily doped PbSe with high thermoelectric performance. Thermoelectric property measurements disclosed herein indicated that PbSe is high zT material for mid-to-high temperature thermoelectric applications. At 850 K a peak zT>1.3 was observed when n>=1.0x10^20 cm^-3. The present invention also discloses that a number of strategies used to improve zT of PbTe, such as alloying with other elements, nanostructuring and band modification may also be used to further improve zT in PbSe.
Figure 1

(a) Graph showing the relationship between $S$ (in $\mu$V/K) and $n_H$ (in $10^9$ cm$^{-3}$) at different temperatures: 800K, 600K, 450K, and 300K. The data points are from Vinogradova et al.

(b) Graph showing the relationship between $S$ (in $\mu$V/K) and $T$ (in K) at different concentrations: $10^{18}$, $6 \times 10^{18}$, $10^{19}$, $3 \times 10^{19}$, $10^{20}$, $2 \times 10^{20}$, and $3 \times 10^{20}$. The data points are from Alekseeva et al.
Figure 2

(a) 

(b) 

$T^{-2.5}$
Figure 3
Figure 4
Figure 7

![Graph a](image)

![Graph b](image)
Figure 8
HEAVILY DOPED PbSe WITH HIGH THERMOELECTRIC PERFORMANCE

SUMMARY OF THE INVENTION

In certain embodiments, the invention teaches a method of manufacturing a compound, including: providing a quantity of Pb; providing a quantity of Se; providing a quantity of an element selected from the group consisting of: Na, Li, K, Rb, Cs, Tl, Au, Ag, and Cu; loading the elements into containers; and melting the elements, followed by quenching, annealing and hot pressing. In some embodiments, the composition is of a formula: \( A_x \cdot Pb_{1-x} \cdot Se \), wherein \( A \) is selected from the group consisting of: Na, Li, K, Rb, Cs, Tl, Au, Ag, and Cu. In some embodiments, \( A = Na \). In some embodiments, the composition has a maximum thermoelectric figure of merit (\( zT \)) of greater than 1.0 at 750K.

In certain embodiments, the invention teaches a method of manufacturing a compound, including: providing a quantity of Na; providing a quantity of Pb; providing a quantity of Te; loading the elements into containers; and melting the elements, followed by quenching, annealing and hot pressing. In some embodiments, the compound is of a formula: \( Na_x \cdot Pb_{1-x} \cdot Te \), and 0.005\( \leq x \leq 0.02 \). In some embodiments, the composition has a maximum thermoelectric figure of merit (\( zT \)) of greater than 1.0 at 750K.

Na\( _{1-x} \cdot Pb_x \cdot Te \), wherein 0.005\( \leq x \leq 0.02 \). In some embodiments, the composition has a maximum thermoelectric figure of merit (\( zT \)) of greater than 1.0 at 750K.

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All references cited herein are incorporated by reference in their entirety as though fully set forth. Unless defined otherwise, technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

As disclosed herein, polycrystalline PbSe doped with Na were prepared. Thermoelectric property measurements indicated that PbSe is high ZT material for mid-to-high temperature thermoelectric applications. At 850 K a peak ZT=1.3 was observed when n=1.0x10^20 cm^-3. The high ZT originates from the large effective band gap at high temperature and low lattice thermal conductivity comparable to PbTe. In addition, significant non single parabolic band behavior is observed which is likely to enhance the transport properties for thermoelectric applications. Results disclosed herein demonstrate that PbSe is a good thermoelectric material. As also disclosed herein, many strategies used to improve ZT of PbTe, such as alloying with other elements, nanostructuring and band modification are also very likely to be useful to further increase ZT in PbSe.

As further disclosed herein, p-type PbTe materials with high doping levels of Na were prepared, and the electrical properties were determined to be 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 high effective mass. These heavy mass carriers lead to a large Seebeck coefficient (compared to n-type PbTe) and high thermoelectric figure of merit of ZT=1.3. The high ZT is intrinsic to PbTe and is likely to contribute to the high ZT observed in related p-type PbTe-based systems such as PbTe: Tl and nanostructured materials.

As further disclosed herein, the presence of a sharp increase in 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, is likely to lead to further improvements in ZT.

Unless otherwise stated, carrier density and carrier concentration are used interchangeably in the instant disclosure.

In some embodiments, the numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth, used to describe and claim certain embodiments of the application are to be understood as being modified in some instances by the term “about.” Accordingly, in some embodiments, the numerical parameters set forth in the written description and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by a particular embodiment. In some embodiments, the numerical parameters should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of some embodiments of the application are approximations, the numerical values set forth in the specific examples are reported as precisely as practicable.

In some embodiments, the present invention teaches a compound of the formula A_x Pb_{1-x}Se, wherein “A” is selected from the group consisting of: Na, Li, K, Rb, Cs, Tl, Au, Ag, and Cu. Other substitutional defects producing p-type conductivity include PbSe_{1-x}X, where X is selected from the group consisting of: Sb, Bi, As, Sn, and Ge. One of skill in the art would readily appreciate that other elements with similar characteristics of heavily doping the material p-type, such as alloys with Sn or Ge that induce p-type defects, could be substituted for those disclosed herein. In some embodiments, “A” is Na. In certain embodiments, 0.005≤x≤0.02. In some embodiments, the composition has a maximum thermoelectric figure of merit (ZT) of greater than 1.3 at 850 K.

In certain embodiments, the present invention teaches a thermoelectric material including a compound of the formula A_x Pb_{1-x}Se, wherein “A” is selected from the group consisting of Na, Li, K, Rb, Cs, Tl, Au, Ag, and Cu. Other substitutional defects producing p-type conductivity include PbSe_{1-x}X, where X is selected from the group consisting of: Sb, Bi, As, Sn, and Ge. One of skill in the art would readily appreciate that other elements with similar characteristics of heavily doping the material p-type, such as alloys with Sn or Ge that induce p-type defects, could be substituted for those disclosed herein. In some embodiments, “A” is Na. In certain embodiments, 0.005≤x≤0.02. In some embodiments, the composition has a maximum thermoelectric figure of merit (ZT) of greater than 1.3 at 850 K.

In some embodiments, the invention discloses a thermoelectric material including a compound of the formula Pb_{1-x}Sn_xSe. In certain embodiments, 0≤x≤0.3. In some embodiments, the invention discloses a thermoelectric material including a compound of the formula Na_{1-x}Pb_xTe. In some embodiments, 0.005≤x≤0.02. In some embodiments, the composition has a maximum thermoelectric figure of merit (ZT) of greater than 1.0 at 750K. In some embodiments, nanostructuring is used to further increase ZT.

In certain embodiments, the invention discloses a method of manufacturing a compound, including: providing a quantity of Pb; providing a quantity of Se; providing a quantity of an element selected from the group consisting of: Na, Li, K, Rb, Cs, Tl, Au, Ag, and Cu; loading the elements into containers; and melting the elements, followed by quenching, annealing and hot pressing. In certain embodiments, the compound is of a formula including A_x Pb_{1-x}Se. In some embodiments, “A” is selected from the group consisting of: Na, Li, K, Rb, Cs, Tl, Au, Ag, and Cu. Other elements with similar characteristics could be substituted for those disclosed herein. In certain embodiments, 0.005≤x≤0.02.

In some embodiments, all of the elements of the compound are loaded into sealed quartz ampoules and melted at 1,400 K for 6 hours. Afterwards, the ampoules are quenched in water and annealed at 950 K for 60 hours. Ground powders are then loaded into graphite dies and hot pressed at 873 K (40 MPA) under argon for 30 minutes. In certain embodiments, the compound is of a formula comprising A_x Pb_{1-x}Se. In some embodiments, “A” is selected from the group consisting of: Na, Li, K, Rb, Cs, Tl, Au, Ag, and Cu. One of skill in the art would readily appreciate that other elements with similar characteristics could be substituted for those disclosed herein. In certain embodiments, 0.005≤x≤0.02.

One of skill in the art would readily appreciate the elements could alternatively be melted at a variety of different temperatures for different amounts of time. Merely by way of example, melting could be performed at between 600 K and 1500 K for between 0.5 and 24 hours. One of skill in the art would similarly appreciate that annealing could be accom-
plished at a variety of different possible temperatures for different amounts of time. For example, at temperatures ranging from 600 K to 1200 K for between 1 and 120 hours. Hot pressing can also be accomplished at a range of temperatures and for different amounts of time. For example, the temperature could be between 700 K and 1000 K for between 10 and 120 minutes.

In some embodiments, the invention discloses a method of manufacturing a compound, including: providing a quantity of Na; providing a quantity of Pb; providing a quantity of Te; loading the elements into containers; and melting the elements, followed by quenching, annealing and hot pressing. In some embodiments, the compound is of a formula including Na$_x$Pb$_{1-x}$Te, wherein 0.005 < $x$ < 0.02. In some embodiments, the composition has a maximum thermoelectric figure of merit (zT) of greater than 1.0 at 750K. One of skill in the art would readily appreciate that other elements with similar characteristics could be substituted for those disclosed herein.

In some embodiments of the invention, compounds are manufactured by melting, annealing and hot-pressing. Stoichiometric mixtures of high purity Na (99%), Pb (99.999%) and Te (99.9999%) ingots are sealed in graphite coated ampoules under vacuum and heated to 1,273 K at ~500K/hour. After soaking at 1,273 K for about 6 hours, the ampoules are cold-water quenched and annealed at 973 K for 48 hours. The resulting ingots are pulverized and hot pressed at 700 K for 1 hour. In some embodiments, the compound is of a formula including Na$_x$Pb$_{1-x}$Te, wherein 0.005 < $x$ < 0.02. In some embodiments, the composition has a maximum thermoelectric figure of merit (zT) of greater than 1.0 at 750K. One of skill in the art would readily appreciate that other elements with similar characteristics could be substituted for those disclosed herein. One of skill in the art would likewise appreciate that alternative methods of making the compounds could be used. For example, the compounds could be heated at a temperature ranging from 600 to 1500 K for between 0.5 and 24 hours. Similarly, the annealing can be performed at a temperature ranging from 600 to 1200 K for between 1 and 120 hours. Finally, hot pressing can be alternatively performed at a temperature ranging from 700 to 1000 K for between 10 and 120 minutes.

In certain embodiments of the invention, one or more thermoelectric materials disclosed herein are used in a thermoelectric device. In some embodiments, a temperature gradient is applied to the thermoelectric device and electrical energy is collected. In some embodiments, electrical energy is applied to the thermoelectric material and heat is transferred from a first space at a first operation temperature to a second space at a second operation temperature, wherein the first operation temperature is lower than the second operation temperature.

Merely by way of example, thermoelectric modules including those made of materials disclosed herein are used to harness waste heat from automotive exhaust (500K-600K) to produce electricity and reduce CO2 emissions.

One skilled in the art will recognize many methods and materials similar or equivalent to those described herein, which could be used in the practice of the present invention. Indeed, the present invention is in no way limited to the methods and materials described.
Parabolic Band (SPB) model\textsuperscript{10} with $m^*=0.28 m_e$ and assuming acoustic phonon scattering dominates. Results here agree well with available data reported by Vinogradova et al. on Na–PbSe as shown in FIG. 1(a).\textsuperscript{19}

As the temperature increases from 300 K to 450 K, the disagreement with the SPB model begins to appear for high $n_p$ samples. By 800 K the SPB model provides a qualitatively poor fit to the data. This suggests that the valence band structure is nearly parabolic at 300 K but becomes considerably non-parabolic at higher temperatures. This not only results in the deviation of data from the SPB model at high temperatures, but also enables the rapid increase of $S$ with temperature\textsuperscript{20} in heavily doped samples, which benefits thermoelectric performance.

Non parabolic behavior in PbSe can be described with different models. The non parabolic Kane model\textsuperscript{21} has been used for PbSe\textsuperscript{22} and other IV-VI compounds. However, for the Kane model to deviate from SPB more at high temperatures requires an effective mass change with both temperature as well as carrier density.\textsuperscript{16,23} Alternatively; non SPB features in PbSe can be modeled using multiple offset valence bands. A heavy hole band 0.35 eV below (at 0 K) the first light hole band edge has been proposed.\textsuperscript{12,23,24} with the offset value decreasing with increasing temperature in some models. In this way, the heavy band will gradually contribute more to the carrier transport and increase Seebeck coefficients as the temperature is increased. This qualitatively explains the observed $S$ at different temperatures.

The resistivities of all samples increase with temperature (FIG. 2(a)), due to the mobilities ($\mu$) decreasing with temperature. Resistivity for the sample reported by Alekseeva et al. roughly matches with heavily doped samples.

The exponent $r$ in $\mu(T)$ changes with doping levels from $\sim 2.5$ ("1E19") to $\sim 1$ ("2E20"), as can be seen in FIG. 2. Such behavior is common for heavily doped lead chalcogenides when acoustic phonon scattering dominates the carrier transport.\textsuperscript{23} As the temperature further increases, a $r=2.5$ is necessary to describe the $\mu(T)$ curve for all samples. While not wishing to be bound by any one particular theory, the temperature dependent mass and non SPB band structure may explain the $\mu(T)$ behavior in heavily doped samples\textsuperscript{26}, while for samples with lower doping levels, the impact of excitation of minority carriers must be taken into account. The samples '1E19' and '1E20' show unusually low mobility at 300 K that may be due to grain boundary effects or extrinsic impurities that only affect resistivity and mobility at low temperature. At high temperatures, the mobility and resistivity have a consistent trend as the other samples. Importantly, in their calculation Parker and Singh\textsuperscript{12} assumed $\mu(T)$ for heavily doped samples, which is verified here only for $T=600$ K; while, as admitted by the authors, $zT$ at higher temperature would be overestimated, since the influence of the heavy band feature on mobility was not accounted for, but, as disclosed herein, it will take place at high temperatures.

The thermal conductivities $K$ measured up to 850 K are shown in FIG. 3. For most samples, $K$ decreases monotonically with temperature, except for lightly doped samples in which the bipolar effect leads to a noticeable increase at high temperature. The $K$ at 850 K increases with doping levels as expected from the increased electronic contribution. For samples with $n_p\rightarrow1\times10^{20}$ cm$^{-3}$ (300 K), this value is about 1 W m$^{-1}$ K$^{-1}$, which is very impressive given their high electric conductivity.

The sample from Alekseeva's work shows higher thermal conductivity throughout the temperature range. Compared with the inventors' heavily doped samples at 850 K its $K$ is 50% higher, which is the primary reason for the low $zT=0.6$ found in this sample.

The lattice thermal conductivity is calculated by subtracting the electronic contribution using $\kappa_e=\frac{3\pi^2 k_B^2 n_p}{2\mu_e}$ with the Lorenz number $L$. Calculating assuming acoustic phonon scattering and SPB model.

The calculated $\kappa_e$ of Na doped PbSe is $1.8\pm0.2$ W m$^{-1}$ K$^{-1}$ at 300 K, consistent with available data.\textsuperscript{12,13} For the sample '1E18' (without Na doping) the measured $K$ is $1.7$ W m$^{-1}$ K$^{-1}$ at 300 K, which represents mostly the lattice contribution, since $\kappa_e$ is negligible ($0.05$ W m$^{-1}$ K$^{-1}$). '6E19' and '1E20' show unreasonably high $\kappa_e$ at room temperature, which can be explained by the abnormality in $\mu(T)$ near room temperature that voids the acoustic phonon scattering assumption and thus underestimates $\kappa_e$.

At high temperatures the $\kappa_e(T)$ for heavily doped samples saturate (inset of FIG. 3) at a reasonably low 0.6 W m$^{-1}$ K$^{-1}$. While not wishing to be bound by any one particular theory, values lower than this in FIG. 3 could be due, in part, to the over-estimated Lorenz number from the single parabolic band assumption, and the $C_p$ is likely underestimated.

It is very striking that PbSe has such low thermal conductivity (for PbTe $\kappa_e=2$ W m$^{-1}$ K$^{-1}$ at 300K), even though intuitively substituting heavy Te with the lighter element Se would give the opposite result. Nevertheless, the similar thermal conductivities of PbSe and PbTe can be explained from the following expression of lattice thermal conductivity above Debye temperature and governed by Umklapp phonon scattering:\textsuperscript{37}

$$\kappa_l = \frac{8\pi k_B^3 \theta_D^4}{h^2 T^3}$$

where $\mu_e$, $h$, $\alpha$, $\rho$, $\theta_D$, and $\gamma$ are the Boltzmann constant, Planck's constant, the lattice parameter, density, Debye temperature and the acoustic phonon Gruneisen parameter which is a measure of anharmonic nature of lattice vibration, respectively. Using published $\gamma$ (Table II) and $\theta_D$ based on the inventors' speed of sound measurement on polycrystalline samples, the ratio of lattice thermal conductivity in PbSe and PbTe, $\kappa_{l_{PbSe}}/\kappa_{l_{PbTe}}$ at 300 K is calculated to be 1.0, consistent with the experimental result. The reason $\kappa_e$ in PbSe is not higher than in PbTe is because the lattice parameter $a$ of PbSe is smaller, and, more importantly, PbSe has a higher $\gamma$, i.e., a higher degree of anharmonicity in lattice vibration.

<table>
<thead>
<tr>
<th>Table II</th>
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<tbody>
<tr>
<td>Materials parameters of PbSe and PbTe that influence lattice thermal conductivity</td>
</tr>
<tr>
<td>PbSe</td>
</tr>
<tr>
<td>$\rho$ (g cm$^{-3}$)</td>
</tr>
<tr>
<td>$\theta_D$(K)</td>
</tr>
<tr>
<td>$a$ (Å)</td>
</tr>
<tr>
<td>$\gamma$</td>
</tr>
<tr>
<td>$\nu_f$(m/s)</td>
</tr>
<tr>
<td>$\nu_i$(m/s)</td>
</tr>
<tr>
<td>$\nu_{ac}$(m/s)</td>
</tr>
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The low thermal conductivities, together with the rapid increase of $S$ in heavily doped samples, lead to promising thermoelectric performance. In a wide range of doping levels, from $3\times10^{19}$ cm$^{-3}$ to $3\times10^{20}$ cm$^{-3}$, $zT$ greater than 1 were obtained when $T>700$ K (FIG. 4). A conservative estimation indicates peak $zT=1.3$ at 850 K with corresponding $n_p=1.5\times10^{20}$ cm$^{-3}$ (300K).
High Thermoelectric Figure of Merit in Heavy-Hole Dominated PbTe

On 16-17 Jan. 1959 the headlines in Washington D.C. USA newspapers heralded the “world’s first atomic battery” with a picture of President Eisenhower examining a Radioisotope Thermoelectric Generator (RTG) as it sat on his desk in the Oval Office of the White House. This 5 watt generator converted radioisotope heat to electricity using the Seebeck effect of Thermoelectric (TE) semiconductors made from n- and p-type PbTe. PbTe can be made p-type by replacing some divalent Pb with monovalent Na. Doping of Na made the “2P-PbTe” used in this 1959 generator and for several NASA missions in the 1960’s.

The thermoelectric properties of PbTe were extensively studied in both the USA (lead by the 3M corporation) and the Soviet Union for military and space applications in the 1950’s and early 1960’s. As previously disclosed herein, the performance of a TE material is characterized by the TE figure of merit, $zT = S^2T / [ρ(κ_p + κ_e)]$, where $S$, $ρ$, $κ_p$, and $κ_e$ are the Seebeck coefficient, resistivity, and the electronic and lattice components of the thermal conductivity, respectively. At that time the Seebeck coefficient and resistivity could be...
measured accurately but thermal conductivity at high temperature was notoriously difficult to measure[5].

Not surprisingly then the 1960 report of Fritts, from 3M, does not use actual thermal conductivity data when showing a maximum zT of ~0.7. Instead, the room temperature lattice thermal conductivity was assumed at high temperatures[15–19], which underestimates zT. This relatively low maximum zT is similar with that for the “3P-PbTe”[10] used later by Teledyne for NASA[4]. The data of Fritts with the same maximum zT was therefore assumed to be accurate for PbTe:Na[5, 9, 11–13].

Not until the advent of the flash diffusivity technique, developed in the USA in the early 1960’s, were high temperature thermal conductivity measurements of semiconductors reliable[9,6]. However, by then, The USA had switched from studying PbTe to Si—Ge alloys[19] due to the capability for higher temperature use. The Soviet groups leading efforts to understand the physics of PbTe[1] were not using the flash diffusivity method and report few high temperature measurements of k[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 to show the maximum zT is actually ~1.5.

As previously disclosed herein, thermoelectrics are attracting renewed interest because of their ability to harvest electricity from waste heat[29]. Because the parameters S, p and κp are interdependent by the carrier concentration (n)[9, 21], the independent parameter, lattice thermal conductivity, can be reduced to increase zT. One proven route to minimize κp and enhance zT to 1.4–1.7 at ~700 K in PbTe materials[22–24] has been the incorporation of nano-inclusions that act as phonon scattering centers.

Using a different mechanism, zT as high as ~1.5 has been achieved in p-type Tl-doped PbTe with hole concentrations close to 5x10^{19} 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. 5a).

However, a similar behavior of enhanced DOS around the Fermi level in heavily doped p-type PbTe without resonant states, has been found or proposed in both theoretical and experimental studies, due to either an additional band[17, 26, 27] or a complex Fermi surface[28] 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 recent calculation by Singh[28], this DOS enhancement is enough to explain the high Seebeck coefficient of PbTe:Tl without including resonant states.

Experimentally, Na will dope PbTe with hole concentrations ranging from ~1x10^{19} to ~10^{20} cm^{-3}[29, 30] and does not introduce resonant states[26, 31]. The S of PbTe:Na decreases with hole concentration according to the Pisarenko relation expected for a single parabolic band at low hole concentrations[29]. The dependence of S on n at high carrier concentrations shows a deviation[8, 29, 32] from the trend expected from the Pisarenko relationship, leading to an increased Seebeck coefficient (FIG. 5a).

Here the inventors confirm the previous results on S, p, n for heavily doped PbTe:Na and measure the high temperature thermoelectric behavior, resulting in a zT reaching ~1.5 in heavily doped samples at ~750 K. The inventors demonstrate herein, both the heavy hole character in PbTe:Tl as well as the enhanced S in PbTe:Tl due to resonant states.

Polycrystalline Na0.5Pb0.5Te (0.005±0.0005) samples were synthesized by melting, annealing and hot-pressing. Stoichiometric mixtures of high purity Na (99.9%), Pb (99.999%) and Te (99.999%) ingots were sealed in graphite coated ampoules under vacuum and heated to 1273 K (~1000 °C) for 48 hours. The resulting ingots were pulverized and hot pressed at 700 K for 1 hour. Pellets with a relative density of 98% or higher were used for measurements of 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 2T. 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 ~10% for Seebeck and Resistivity were confirmed at JPL (using W-Nb thermocouples) and ULVAC-ZEM3 at ZTPlus on a sample with zT ~1.5 at 700K. Scanning Seebeck coefficient measurements (at 300K) on the sample with Hall carrier density of ~9x10^{19} cm^{-3} showed a Seebeck coefficient variation of only 5 µV/K (full width for 90% of the data). The Dulong-Petit heat capacity (C_p ~0.15 J/g-K, close to the experimental results from 150 to 270 K[15]) was used for the estimation of thermal conductivity. The combined uncertainty for the determination of zT is ~20%.

X-ray diffraction and scanning electron microscope analysis was used to confirm that the materials for this study were single phased. The obtained samples have room temperature Hall carrier densities (n_H) of 3.5, 7.5, 9.0 and 14x10^{19} cm^{-3} estimated by n_H=1/eR_H. FIG. 5a 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[29, 30] showing the same in S vs. n behavior at room temperature (FIG. 5a), including the deviation which results in a flattening of the curve at S ~60 µV/K.

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)[17, 29–32, 35–37] much like that found the La_xTe_y system[31]. At low hole concentrations the light 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 band[17, 29]. 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 400 K[17, 39]. 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 (~10^{20} cm^{-3}) p-PbTe at ~750K, which is about twice of that in n-PbTe[35], due to the heavy mass carriers behavior.

FIG. 5a also shows the Seebeck coefficient predicted from DFT calculations[29] of p-PbTe (blue solid line). The calculation shows a similar flattening due to a complex Fermi surface, where the Seebeck coefficient becomes approximately constant at S ~120 µV/K when the carrier density is greater than ~4x10^{19} cm^{-3}. The difference between the calculated and experimental Seebeck coefficient may originate from the uncertainties of band structure and/or the associated temperature dependence. It should also be noted that the
The analysis using two-band model and both DFT calculations discussed above, indicate the presence of enhancement of DOS close to valence band edge, which predicts the flattening of S (FIG. 5a). Thus the observed flattening of the Seebeck coefficient can be explained by either the complex Fermi surface found by Singh, or an offset heavy band model. In contrast, n-type PbTe 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 contributing 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 masses for light hole and 0.3m<sub>e</sub> for electron). However, a significant discrepancy starts at ~400 K with p-type material showing an atypical increase in slope of S vs. T resulting in a larger Seebeck coefficient at temperatures higher than 400K. This observation is consistent with the two band model in which the band offset between light and heavy bands becomes smaller with temperature and vanishing at ~400 K<sup>7</sup>,<sup>39</sup>,<sup>41</sup>. The PbTe:Tl 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 coefficient at room temperature, the heavy mass behavior is likely to be additionally contributing to the Seebeck coefficient in PbTe:Tl at higher temperatures. Additionally, the carrier mobility in PbTe:Tl has been found to be decreased by a significant factor<sup>25</sup>. Both PbTe:Tl and PbTe:Na have a similar temperature dependence of Hall mobility as shown in FIG. 6, however the mobility of PbTe:Na are approximately twice that of PbTe:Tl over the whole temperature range. The resonant impurity states in the Ti-doped material should lead to a reduced group velocity and therefore reduce carrier mobility.

The total thermal conductivity (κ) of the PbTe:Na samples are shown in FIG. 7a as open symbols. Since Na acts as an effective acceptor, the increased hole concentration (FIG. 5a) results in a decreased resistivity as shown in FIG. 7a. As a result of the decreased resistivity, the electronic contribution to the thermal conductivity, as determined by Wiedemann-Franz law (κ<sub>e</sub> = LT/p), is increased resulting in larger total thermal conductivity as shown in FIG. 7b. 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 scattering<sup>43</sup> resulting in an L with a deviation of less than 10%<sup>25</sup> as compared with a more rigorous non-parabolic band model calculation<sup>44</sup>. The estimation of the lattice thermal conductivity (FIG. 7b, solid symbols) is made by subtracting the electronic component from the total thermal conductivity, κ<sub>tot</sub> = κ<sub>e</sub> - κ<sub>L</sub>. The estimated lattice thermal conductivity for both PbTe:Na and PbTe:Tl is approximately 2 W/m·K at room temperature and ~0.7 W/m·K at ~750 K, these values are also consistent with n-type PbTe materials, within the uncertainty range of L-estimation<sup>7</sup>,<sup>45</sup>.
parameter to the optimized values to truly reveal the resonant scattering effect. Experimentally, this can be done in four different TI compositions: 0.5% TI, x % Na—PbSe (x = 0, 0.25, 0.5, 0.75); 1% TI, x % Na—PbSe (x = 0, 0.5, 1, 1.5, 2); 1.5% TI, x % Na—PbSe (x = 0, 0.75, 1.5, 2, 2.5); 2% TI, x % Na—PbSe (x = 0, 1, 1.5, 2, 2.5). There is no explicit data on how the resonant scattering influences TE properties when T is above, about 450K. So, together with Na—PbSe this work will further advance the understanding of both PbSe and the influence of resonant scattering on TE properties.

While not wishing to be bound by any one particular theory, it appears PbSe resembles PbTe in the sense of the light band/heavy band structure in their valence band. The difference is 1) the effective mass of the light band is smaller in the PbSe case (0.28 vs 0.35) the effective mass of the heavy band should also be different but there is no conclusion as to whether it is smaller or larger; 2) the gap between the light band and the heavy band is larger. This feature determines PbSe shows peak $zT$ at a higher temperature than PbTe (and also that at low temperature $zT$ would be lower). While not wishing to be bound by any one particular theory, because PbTe and PbSe form a complete solid solution, there is a good possibility that by changing the composition $\text{PbTe}_x\text{Se}_{1-x}$, the $zT$ curve can be tuned, so that peak $zT$ can be achieved at different temperatures. This would be particularly useful when making graded TE devices.

Another candidate likely to be useful is Sn. Because alloying with Sn greatly changes the band structure of PbTe (the energy level crossover), it seems likely that Sn will have a similar effect on PbSe. This is likely to be useful, because: 1) the peak $zT$ temperature would likely be controllable; 2) the position of impurity states (TI) might be controlled by the composition of $\text{Pb}_x\text{Sn}_{1-x}\text{Se}$; this then might affect the temperature at which the resonant scattering is most effective; 3) there is evidence Sn defect centers have similar features as TI; and 4) it is likely Sn can increase mechanical behavior and decrease thermal conductivity.

Furthermore, the skilled artisan will recognize the applicability of various features from different embodiments. Similarly, the various elements, features and steps discussed above, as well as other known equivalents for each such element, feature or step, can be employed in various combinations by one of ordinary skill in this art to perform methods in accordance with the principles described herein. Among the various elements, features, and steps some will be specifically included and others specifically excluded in diverse embodiments.


REMARKS

Accordingly, embodiments of the present application are not limited to that precisely as shown and described.
What is claimed is:
1. A compound of the formula Na$_x$Pb$_{1-x}$Se, wherein 0.005 < $x$ < 0.025, and wherein density of the compound is 98% or greater of the theoretical value, and 3x$10^{19}$ cm$^{-3}$ < $n$ < 5x$10^{20}$ cm$^{-3}$.
2. The compound of claim 1, wherein the composition has a maximum thermoelectric figure of merit (zT) of greater than 1.3 at 850 K.
3. A thermoelectric material comprising a compound of the formula Na$_x$Pb$_{1-x}$Se, wherein 0.005 < $x$ < 0.025, and wherein density of the compound is 98% or greater of the theoretical value, and 3x$10^{19}$ cm$^{-3}$ < $n$ < 5x$10^{20}$ cm$^{-3}$.
4. The thermoelectric material of claim 3, wherein the composition has a maximum thermoelectric figure of merit (zT) of greater than 1.3 at 850 K.