Thermoelectric enhancement in PbTe with K, Na co-doping from tuning the interaction of the light and heavy hole valence bands

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The effect of K and K-Na substitution for Pb atoms in the rock salt lattice of PbTe was investigated to test a hypothesis for development of resonant states in the valence band that may enhance the thermoelectric power. We combined high temperature Hall-effect, electrical conductivity and thermal conductivity measurements to show that K-Na co-doping do not form resonance states but can control the energy difference of the maxima of the two primary valence sub-bands in PbTe. This leads to an enhanced interband interaction with rising temperature and a significant rise in the thermoelectric figure of merit of p-type PbTe. The experimental data can be explained by a combination of a single and two-band model for the valence band of PbTe depending on hole density that varies in the range of $1 - 15 \times 10^{19} \text{cm}^{-3}$.

I. INTRODUCTION

The primary ellipsoidal valence and conduction bands in the ground state of PbTe consist of four valleys contributing to a substantially high Seebeck coefficient which makes it an outstanding thermoelectric material for fundamental investigations and for power generation in the temperature regime 600-800 K. Recently, compelling improvements of the thermoelectric figure of merit have been demonstrated through strong reduction of the lattice thermal conductivity achieved from nano-structuring of the PbTe matrix. The thermodynamically driven formation of nanostructure rich in Ag-Sb, Na-Sb, Ag-Sn-Sb, and S that are embedded endotaxially in the PbTe matrix have shown reduced lattice thermal conductivity while at the same time not substantially degrading the beneficial electrical properties of pure PbTe. The figure of merit is expressed through the dimensionless quantity $Z = S^2 \sigma T / \kappa_{lat}$, $S$ being the Seebeck coefficient, $\sigma$ the electrical conductivity and $\kappa_{lat}$ the total thermal conductivity comprising contributions of the lattice phonons and charge carriers. The transport parameters entering the figure of merit strongly depend on temperature and different materials are considered for different temperature regimes.

The maximum thermoelectric figure of merit, $Z_{max}$, that can be attained at a given temperature $T$, depends on a quite diverse set of materials parameters according to Eq. (1):

$$Z_{max} = \frac{\gamma e^{(r+1/2)} T^{3/2} \tau_z \sqrt{m_x m_y m_z}}{\kappa_{lat}}$$

In the above, $\kappa_{lat}$ is the thermal conductivity of the lattice, $m_i$ is the effective mass in the i-th direction in the crystal, $\tau_z$ is the relaxation time of the carriers moving in the direction of the current flow (assumed to be z) and $\gamma$ is the degeneracy of the band extrema near the Fermi energy. It follows that for an isotropic system, high $\gamma$ and low $\kappa_{lat}$ values contribute significantly to high figure of merit.

From a practical point of view the lattice thermal conductivity, $\kappa_{lat}$, of PbTe via nanostructuring and alloying is reaching its low limit. Therefore, further improvements in the ZT of PbTe can be sought through large enhancements of the efficiency of charge transport quantified by the product $S^2 \sigma$, also known as the power factor. One approach to enhancing the power factor in PbTe has been described by Martin et al. who have studied p-type PbTe nanocomposites and found that grain boundary scattering dominates charge transport acting as an energy filtering effect that enhances thermopower. Furthermore, Faleev and Léonard have suggested enhancements in the power factor in the presence of metal-
lic nanoinclusions. Again, an energy filtering effect is in-
voked due to band bending at the semiconductor-metal
interface that considerably modifies the electronic scatter-
ing time. Recently, Heremans et a\textsuperscript{12} have investigated
distortions in the density of states (DOS) of Tl-doped
PbTe that can enhance the Seebeck coefficient, and hence
the power factor, leading to increased figure of merit.\textsuperscript{13,14}
Such distortions in the DOS are known as resonant states
that induce Fermi level pinning and have been observed
in a number of narrow band gap chalcogenide semicon-
ductors such as GeTe and SnTe.\textsuperscript{15-17} The issue of the
distortions in DOS and the presence of resonance states
is still an open question and it has been recently discussed
in detail in the theoretical work of Singh.\textsuperscript{18}

In general, dopants in narrow band gap semiconductors
do not form mid-gap states.\textsuperscript{19} Rather, impurity states
outside the energy gap, also known as deep defect states,
are formed and interact strongly with the lattice in a
way that considerable distortions, not always resonant-
like, in the shape and energy distribution of the DOS
can develop.\textsuperscript{18} In order for resonant states to benefit the
thermoelectric properties they should have a sharp distribu-
tion in energy, $\varepsilon$, and preferably be located in energy
span within $0.5\text{eV}$ from the Fermi level in order to be
accessible by usual thermoelectric transport processes.\textsuperscript{20}
Since there is no experimental way to predict \textit{a priori} the
formation and behavior of resonating states in PbTe, it is
evident that the selection of appropriate chemical substi-
tutions for either Pb or Te could benefit from theoretical
calculations.

Following the theoretical work of Ahmad et a\textsuperscript{12} which predicts a resonant-like DOS distortion in p-type
Pb$_{1-x}$A$_x$Te, (where A=K, Rb, Cs, but not Na) we in-
vestigated doped PbTe giving particular emphasis on K,
since our data suggest that the larger Rb and Cs ions
appear to not substitute effectively for Pb. Further-
more, following the relevant theory on resonance scat-
tering we doped PbTe concurrently with K and Na, the
former intended as a possible resonance state and the
latter, being an electrically active dopant that yields no
impurity states, to tune the Fermi energy and to check for
Fermi level pinning.\textsuperscript{13,20} We have also studied control
samples without K and containing Na only as a dopant.
Although, our experimental results cannot support the
presence of resonant scattering in our samples, we did
observe enhancements in the power factor of the speci-
mens at high temperature. We discuss our findings with
respect to the high temperature electronic band structure
of PbTe that takes into account the coexistence of two
valence bands, a light- and a heavy-hole band, and the
interaction between them which can be tuned by the pres-
ence of K in the lattice. The interplay between the two
types of valence bands can be tuned with K-Na codop-
ing to create a sharply changing DOS near the Fermi
energy in a fashion similar to a resonant state. In this
paper we combine, X-ray diffraction with high tempera-
ture Hall-effect, electrical conductivity, thermopower,
and thermal conductivity measurements to show that
codoping of PbTe with K and Na is an efficient way to
control the energy separation between the maxima of the
valence bands in order to achieve an effective Fermi level
pinning, at a given temperature, with respect to the car-
rier concentration. We show that, in effect, this creates a
resonant-like modification in the DOS which can be
tuned by the K ions although these ions by themselves
do not form a resonant level. A maximum $ZT$ $\sim$1.3
at 700 K was observed as a result of increased power factor
rather than reduced thermal conductivity.

\section*{II. EXPERIMENTAL DETAILS}

Samples with the chemical formulas, Pb$_{1-x}$Na$_x$Te,
Pb$_{1-x}$K$_x$Te and Pb$_{0.9875-x}$K$_{0.0125}$Na$_x$Te were produced
by reacting high purity metals (American Elements Pb
99.99%, 5N Plus Te 99.999%, Aldrich K $>$99.95%,
Aldrich Na $>$99.95%) as starting materials. (For
simplicity, in the following we adopt the notation:
Pb$_{1-x}$Na$_x$Te $\rightarrow$ PbTe:Na x%, Pb$_{1-x}$K$_x$Te $\rightarrow$ PbTe:K
x%, Pb$_{0.9875-x}$K$_{0.0125}$Na$_x$Te $\rightarrow$ PbTe:K 1.25%:Na x%).

Approximately 15mg of K and 4.5-12 mg of Na (per 10g of
product) were first loaded in carbon coated silica tubes
inside a glove box under nitrogen atmosphere. The K
and Na mass was used as a reference to calculate ap-
propriate quantities of Pb ($\sim$6.5g per 10g of product)
and Te ($\sim$3.8g per 10g of product) that were added in the
respective tube. All tubes were subsequently evac-
uated and fused. The tubes were fired at 1050 $^\circ$C over 12
hours and soaked at that temperature for 4 h before
rapidly cooling them to room temperature over a period
of 3 h. All sample ingots produced are metallic silvery
gray in color and are strong enough to undergo cutting
and polishing. The bottom part of the ingot was used
to determine the thermal diffusivity of coin-shaped sam-
ple's with a typical diameter of 7.9 mm and thickkess of
$\sim$ 2mm. The thermal conductivity, $\kappa$, was then calcu-
lated by the relation $\kappa = DC_p\rho$, where D is the thermal
diffusivity, $C_p$ is the heat capacity under constant pres-
sure and $\rho$ is the mass density of the specimens. To
increase the accuracy of thermal conductivity data the
density of the samples was extracted by measuring their
volume in an Accupyc-1340 pycnometer. This method
yields a mass density 8.1-8.21 g/cm$^3$, that practically coincides with the theoretical one, and yields 5-10% better accuracy compared to the density calculated using the geometrical dimensions of the specimens. Furthermore, Cp was carefully adjusted to match $\sim$ 98% that of PbTe according to the data by Blachnik et al. 24.

The electrical conductivity, $\sigma$, and Seebeck coefficient, S, were measured simultaneously under a helium atmosphere ($\sim$ 0.1 atm) from room temperature to $\sim$ 700 K using a ULVAC-RIKO ZEM-3 system. The Hall coefficient was measured in a home-made high temperature apparatus, which provides a working range from 300 K to 873 K. The samples were working-mounted and protected with argon gas to avoid possible oxidization at high temperature. The Hall resistance was monitored with a Linear Research AC Resistance Bridge (LR-700), and the data were taken in a field of $\pm$ 1 T provided by an air-bore Oxford Superconducting Magnet. The hole densities, $p$, at room temperature were extracted on the assumption of a single band which gives for the Hall coefficient, $R = 1/pe$, where $e$ is the electron charge.

III. RESULTS AND DISCUSSION

Resonance scattering is a form of selective scattering where carriers exhibiting relaxation times and mean free paths within certain limits are scattered preferentially compared to carriers whose energies lie outside these limits. 25 This selectivity, in effect, has a strong impact on the electronic properties which can lead to an enhancement of S as a function of carrier concentration at a given temperature when compared to the same property in the absence of resonating scattering. Usually, the reference temperature is 300K where S of PbTe follows the so-called Pisarenko formula (non-degenerate):

$$S = \frac{k_B}{e} \left[ \frac{5}{2} + \frac{2}{p} \left( \frac{m^*_d k_B T}{2\pi \hbar} \right)^{3/2} \right]$$

where $r$ is the scattering parameter that takes the value -1/2 for acoustic phonon scattering, $m^*_d$ is the effective mass, $k_B$ the Boltzmann constant, $\hbar$ the reduced Planck’s constant, $e$ the electronic charge and $T$ the temperature. We note that the high symmetry of the valence and conduction bands in PbTe makes Eq. (2) equivalent for both n- and p-type samples with the same non-degenerate carrier densities where electron-acoustic phonon scattering is dominant. 24

A distortion in the DOS would result in a deviation from the Pisarenko line expressed as an enhancement in the S values at T=300K for a particular hole density. 24

Considerable deviations from Eq. (2) can also occur in highly degenerate p-type PbTe as a result of the special nature of the valence band structure of PbTe. Allgaier 24 has shown that Hall data in this region can be explained by assuming a more complex valence band structure. In this model a principal highly non-parabolic band, hitherto called band 1 (light hole), with energy extrema located at the (111) directions in k-space coexists with a parabolic band, hitherto called band 2 (heavy hole). These bands have substantially different properties; band 1 is characterized by high energy dispersion, a light effective mass ($\sim$ 0.2$m_0$), and a lower density of electronic states (DOS) compared to band 2 that exhibits a heavy effective mass (1.2-2$m_0$) has a high DOS and weaker dispersion. 25 At T=0 K, the top of band 2 is located 0.14-0.17 eV below that of band 1.25 Therefore, increasing carrier doping moves the Fermi level deeper in energy and closer to band 2.

FIG. 1: a) Seebeck coefficient as a function of carrier concentration (Pisarenko plot) at T=300K for PbTe samples doped with Na (open squares), K (open triangles) and co-doped with K-Na (filled circles). The co-doped samples correspond to 1.25% K and varying Na concentration. The black solid line is the theoretical Pisarenko line that takes into account the valence band structure of PbTe. Notice the change in curvature around 2 x 10$^{19}$ cm$^{-3}$. The dashed line corresponds to a single non-parabolic band line with the assumption of electron-phonon scattering and holds well for non-degenerate doping. The inset to Fig. 1a shows the hole density as a function of increasing Na concentration for co-doped samples of PbTe:K 1.24%:Na $\pm$%. b) Schematic of the DOS, $g(\varepsilon)$, versus energy, $\varepsilon$, that shows the band overlap at an arbitrary band maxima energy separation, $\Delta \varepsilon$. When the chemical potential, $\xi$, is sufficiently high there is a sudden increase in the DOS which acts to effectively pin the Fermi energy with any further increase of the hole density.

The top of band 2 moves up in energy with rising temperature and at $\sim$ 450-500 K can reach the top of band 1. At room temperature band 2 can be accessed by a high level of acceptor doping. When both bands are populated
with carriers the thermopower reflects the contribution of both bands according to the formula:

\[ S = \frac{S_1 b_p p_1 + S_2 p_2}{b_p p_1 + p_2} \]  

(3)

where \( S_1, S_2 \) denote individual thermopower contributions from the bands 1 and 2, \( p_1 \) and \( p_2 \) are the hole densities of bands 1 and 2, and \( b_p \) is defined as the mobility ratio of band 2 with respect to band 1. The results of such analysis at 300 K yield a constant \( S \) of \( \sim 56 \mu V/K \) for hole densities \( > 3 \times 10^{19} cm^{-3} \). 

Figure 1a displays the Pisarenko plot, \( S \) measured as a function of hole density, for PbTe:Na \( x \% \) \((0.1 \leq x \leq 2.5)\) specimens (squares), PbTe:K \( x \% \) \((0 \leq x \leq 2.5)\) specimens (triangles) and PbTe:K 1.25%:Na \( x \% \) \((0.4 \leq x \leq 2.5)\) specimens (filled circles) at \( T=300 \) K. The dotted black line is calculated from Eq. 2 and the solid line is the calculated line at the degenerate limit. Evidently, at room temperature there is no enhancement in \( S \) in contrast to the case of TI doped PbTe and therefore resonance scattering most probably does not take place in the K doped samples. The inset of Fig. 1 shows the monotonic increase of hole density with increasing Na doping in PbTe:K 1.25%:Na \( x \% \). Therefore, there is an apparent independence of \( S \) with increasing carrier concentration that is consistent with Fermi level pinning and can be qualitatively explained by the schematic shown in Fig 1b. 

The non-parabolic DOS (black line), \( g(\varepsilon) \), is overlapped at an energy \( \varepsilon' \) by the states emanating from band 2 (red line). The narrower dispersion of band 2 results in a considerable enhancement of \( g(\varepsilon) \) for \( \varepsilon > \varepsilon' \) and therefore the reduced Fermi energy, \( \xi \), is only weakly affected (‘effective pinning’) by changes in doping in this region at a given temperature. Increasing temperature brings about large changes in the DOS since it reduces the energy difference, \( \Delta \varepsilon \), of the two band extrema with respect to the Fermi energy. With rising temperature there is lattice thermal expansion which causes the heavy hole band 2 to rise in energy whereas the light hole band 1 falls in energy. Therefore, \( \Delta \varepsilon \) can be controlled not only with temperature but also with engineered lattice expansion of the materials. In the PbTe:K, and PbTe:K:Na samples we find that there is lattice expansion compared to pure PbTe and PbTe:Na, Fig. 2, consistent with the ionic radii of six-coordinate K\(^+\) (133 pm), Na\(^+\) (102 pm), and Pb\(^{2+}\) (119 pm). 

Next we present results and discuss the effect of temperature on the band structure and the thermoelectric properties of the co-doped samples in comparison to the control samples, i.e. PbTe doped with Na only. 

Figure 3(a) depicts \( \sigma \) as a function of temperature for selected specimens of the PbTe:K 1.25%:Na \( x \% \) series of samples. The nominal compositions (exact values of \( x \)) are shown in the figure. All samples exhibit high electrical conductivity at room temperature that decreases with increasing temperature.

To assess the scattering rate we assumed a single power law dependence of \( \sigma \sim 1/T^\delta \). Subsequently all data sets were scaled in \( 1/T^\delta \) and fitted to a straight line. The extracted \( \delta \) values as a function of Na concentration are given in Fig. 3(b). The values deviate from the normal \( 5/2 \) law\(^{27}\) with increasing \( x \) up to 1% and then the trend is reversed with a further increase in the Na content. This weaker power law dependence effectively maintains high electrical conductivity at high temperatures. It is worth pointing that \( \sigma \) of the 0% Na sample decreases faster compared to all other samples reaching a value of 168 S/cm at 720K with a \( \delta \) exponent of \( \sim 2.7 \). By comparison PbTe:K \( x \% \) samples also exhibit \( \delta \) values as high as 3 depending on \( x \). Samples co-doped with K and Na, however, exhibit \( \sigma \) values around 700K that range from 260 to 360 S/cm depending on the Na content with considerably lower \( \delta \) exponents of 2.6-1.3, see Fig. 3b. We note that a \( \delta \) value as low as 1.4 has been observed by Kolo- moets et al\(^{28}\) in two highly degenerate Na only doped PbTe samples \((8 \times 10^{19} and 1.4 \times 10^{20} cm^{-3} \) respectively) and this was explained in terms of interband scattering, i.e., the transfer of holes from band 1 to band 2. Since charge scattering in PbTe is dominated by phonons\(^{29}\) the reduction in the power law dependence of \( \sigma \) in the presence of K (expanded lattice compared to Na doping) may suggest significant phonon softening.

The Seebeck coefficient of the co-doped specimens PbTe:K 1.25%:Na \( x \% \) as a function of temperature is shown in Fig 4. At 300K a similar magnitude \( \sim 60 \mu V/K \) for all \( x \) values is observed as a result of degeneracy that pushes the Fermi energy within band 2. For \( T>300 \) K, \( S \) increases monotonically up to 700 K for all \( x \) values and the S-T curves remain below that of the purely K doped PbTe.
specimen. The values measured at 700 K range from 240 to 300 $\mu$V/K depending on $x$. It is noteworthy that for $x \geq 0.8\%$, the S curves coincide in temperature suggesting that the physical picture of Fig. 1(b) may also be in effect at high temperatures. In such a case the determining quantity for a high power factor is $\sigma$, which depends on factors affecting the carrier mobility e.g. defects, grain boundaries etc.

Figure 5 presents the Hall coefficient, $R_H$, as a function of $T$ for selected specimens of the PbTe:K 1.25%:Na $x\%$ series. $R_H$ increases with increasing $T$ up to a maximum value and then falls with a further increase in temperature. This maximum can be qualitatively explained on a two-band Hall coefficient model as a function of temperature. In such a model Allgaier assumed that the ratio of the Hall factors of the two bands is almost unity and that $b_p << 1$ expressed the Hall coefficient as:

$$\frac{R-R_0}{R_0} = \frac{(1-b_p)^2t}{(1+b_p)t^2}$$  \hspace{1cm} (4)

Here, $t = p_2/p_1$ is related to the DOS and the $F_{1/2}(\xi)$ Fermi integral and $R_0 = \sigma_1/e(p_2 + p_1)$, i.e., the Hall coefficient at sufficiently low $T$ where all holes are transferred to band 1. Furthermore $\Delta \varepsilon$ is related to the ratio of DOS of the two bands, $P$, and the Fermi energy at $T=0$ K through the formula:

$$\frac{2E_F}{3} \frac{\xi^{3/2}}{\Delta \varepsilon^{3/2}} = F_{1/2}(\xi) + PF_{1/2}(\xi - \frac{\Delta \varepsilon}{kB_T})$$  \hspace{1cm} (5)

Allgaier’s analysis emphasizes the importance of $P$, $b_p$, and $\Delta \varepsilon$. It is clear that $\Delta \varepsilon$ does not determine whether a maximum occurs, however it does specify where it occurs. The maximum in $R_H(T)$ shifts from 415K for $x=0.8\%$ to 430 K for $x=1.2\%$ before moving back to 410K for $x=1.6\%$. We relate the shift to lower temperatures in the $R_H$ maximum for the $x=1.6\%$ sample with its decreased lattice parameter compared to pure PbTe (see Fig. 2) that forces the lattice to restore PbTe:Na-like behavior. Such an effect would also explain the slight increase in $\delta$ observed for $x >1\%$.

The changing position of the $R_H$ maximum is a clear indication of energy shift in the band positions and therefore in $\Delta \varepsilon$. Further within this framework and for degenerate carrier densities Allgaier argued that $R_H$ should scale as $T^{3/2}$ as the result of classical statistics dominating in band 2. The slope of the $R_H$ vs $T^{3/2}$ is related to $\Delta \varepsilon$ and an estimate of the temperature dependence can be extracted. Indeed, our data above the peak scale linearly in $T^{3/2}$. Similar dependence was also observed for PbTe:Na samples. However the K-Na co-doped samples of similar carrier density to Na-only samples exhibit slopes that are an order of magnitude lower. Therefore,

FIG. 3: a) Electrical conductivity, $\sigma$, as a function of temperature for selected samples co-doped with K and Na. The nominal compositions are given. It is noteworthy that $\sigma$ remains high at elevated temperatures. Notice that the curve for 0% Na drops much faster. b) Power law exponents, $\delta$, of the electrical conductivity as a function of Na content for all co-doped samples. A minimum is reached at $x \sim 1\%$. The solid lines are guides to the eye.

FIG. 4: Seebeck coefficient, $S$, as a function of temperature for PbTeK 1.25%:Na $x\%$ samples, with $x$ noted on the figure. Notice that at room temperature all S values for the co-doped samples coincide. At higher temperatures the curves scale with Na concentration (lower S for higher Na content) reflecting the corresponding increase in hole density up to $x \sim 0.8\%$. For $x \geq 1\%$ all S-T curves coincide pointing to an effective pinning mechanism as explained in Fig 1b.
we conclude that co-doping affects not only $\Delta \varepsilon$ but also its temperature dependence making band 2 rise in energy at a much slower rate with increasing temperature.

We note that lattice expansion in PbTe causes band 1 to decrease and band 2 to increase in energy which effectively diminishes $\Delta \varepsilon$ between the valence bands 1 and 2. At $T > 400K$ as the lattice continues to expand it places band 2 higher in energy than band 1 and band 2 completely dominates transport. The K-Na co-doping where Na is varied while K is kept constant allows the precise control of the Fermi level and opens a wider temperature range where bands 1 and 2 are forced to interact. Since both the total $S$ and total $\sigma$ in the two valence band picture are weighted quantities (see Eq. 3), the interaction of the two bands for a wider temperature range implies higher power factors. This is because $S$ is almost constant and independent of doping while the interband scattering mechanism lowers the exponent $\delta$ in the temperature dependence of the electrical conductivity.

Figures 6(a) and (b) compare power factors between co-doped samples and Na-only or K-only samples with similar carrier densities at room temperature. Figure 6(a) refers to samples exhibiting carrier densities in the range $4 - 5 \times 10^{19} cm^{-3}$ and Fig. 6(b) refers to samples with carrier densities of $9 - 10 \times 10^{20} cm^{-3}$. Increasing K concentration in PbTe does not affect the carrier density beyond $5 - 6 \times 10^{19} cm^{-3}$, an effect attributed to the solubility limit of K. Therefore Fig. 6(b) compares co-doped samples with Na-only doped samples. Evidently, the co-doped samples exhibit enhanced power factors in both cases. We note that for the heavily doped samples (Fig. 6(b)) at 300K the PbTe:Na sample has the highest power factor. However the power factor of the co-doped specimen exhibits a steeper slope in temperature and at $T \sim 400K$ it has already exceeded that of PbTe:Na. For $T > 400K$ the power factor of the co-doped samples is consistently 15-25% higher (depending on temperature). The maximum power factor achieved at 700K is $S^2\sigma(700K) \sim 23.5 \mu W/cmK^2$. It should also be noted that the power factor of the PbTe:Na ($\sim 10^{20} cm^{-3}$) sample benefits primarily from a high electrical conductivity and not from a high Seebeck coefficient which at 700 K is $\sim 210 \mu V/K$.

![FIG. 5: Hall coefficient, $R_H$, as a function of temperature for three selected co-doped samples with nominal compositions indicated on the graph. The arrows show that the position of the peak shifts to higher temperatures for the sample with doping in the vicinity of 1.2% Na, i.e. where the minimum power law exponent in electrical conductivity is observed.](image)

![FIG. 6: (a) Power factors as a function of temperature for PbTe:K, PbTe:Na and PbTe:K:Na samples corresponding to a room temperature hole density of $\sim 4.5 \times 10^{19} cm^{-3}$. The co-doped sample outperforms the PbTe:Na and PbTe:K samples for $T > 400K$. (b) Power factors for PbTe:Na and PbTe:K:Na samples corresponding to a room temperature hole density of $\sim 9 - 10 \times 10^{19} cm^{-3}$. Clearly, the co-doped sample exhibits a higher power factor for $T > 400K$ reaching $24 \mu W/cmK^2$ at 700K.](image)
pure PbTe is also plotted (dotted line). At high temperatures, i.e. T>500K the extracted $\kappa_{lat}$ of the co-doped samples are not particularly low and follow reasonably well that of PbTe despite heavy doping with K and Na. The picture is quite different for T<500K, where it is evident that the extracted $\kappa_{lat}$ for PbTe:K 1.25%:Na 1% and PbTe:K 1.25%:Na 1.4% is higher than that for pure PbTe. The same holds true for other co-doped samples with Na content above 0.8%. This indicates that the Lorenz number used in the calculation of $\kappa_{el}$ cannot correctly account for the electronic contribution to the thermal conductivity in this region. Instead, an $L$ value of 20-50% higher than $L_0$ should be used at room temperature. This is another manifestation of interband scattering which evidently provides a rare mechanism of increasing considerably the Lorenz number above the fully degenerate value of $L_0$. The higher $L$ number than $L_0$ implies the carriers transfer larger amounts of heat in the material than what is predicted by $L_0$. This involves the release of excess energy as heat by the carriers when they move from one band to the other. In fact, Kolomoets has shown that such an effect should be present whenever two bands coexist at the Fermi energy, like in semimetals, not necessarily restricted to bands of the same carrier type.

\[ \kappa_{1-2} = \frac{T\sigma_1\sigma_2}{\sigma_1 + \sigma_2}(S_2 - S_1)^2 \]  

Therefore, data in Fig. 7 include (a) the lattice contribution, (b) the band interaction contribution of Eq. 6, (c) the carrier contribution from band 2, which is parabolic and should exhibit a Lorenz number $L_0$ and (d) the carrier contribution from band 1 which is non parabolic and the Lorenz number is a complex function of generalized Fermi integrals of the band gap and the reduced chemical potential. Clearly, the above considerations complicate the analysis for the extraction of a Lorenz number as a function of T, which is beyond the scope of this paper. The data in Fig 7(a) and 7(b) further support the argument that the interband scattering mechanism is at play for a wider temperature range in the co-doped samples as a result of both lattice expansion and doping in band 2. In contrast, crossing below the baseline in Fig. 7(b) around 425 K for the PbTe:Na ($\sim 10 \times 10^{19} cm^{-3}$) specimen supports previous suggestions that band 2 dominates transport in PbTe above $\sim 425K$.

The resulting figures of merit for several of the codoped samples in this study are shown in Fig. 8. The maximum value measured reaches 1.3 at 700 K and this enhancement over conventional Na doped PbTe (ZT~0.9) is primarily associated with the enhanced power factors discussed above.

![FIG. 7: Thermal conductivity, $\kappa$, as function of temperature for three co-doped samples: PbTe:K 1.25%:Na 0.6%, PbTe:K 1.25%:Na 1%, PbTe:K 1.25%:Na 1.4%. The filled symbols correspond to the total $\kappa$ and the corresponding open symbols to the extracted lattice part of $\kappa$. The black solid line corresponds to the lattice part of $\kappa$ of pure PbTe. The star symbols represent the extracted lattice thermal conductivity of a PbTe:Na sample with a hole density of $10 \times 10^{19} cm^{-3}$ at room temperature. Notice that for co-doped samples with increased Na content, in the range $300 \leq T \leq 500$ K, the lattice thermal conductivity deviates considerably from that of pure PbTe.](image1)

![FIG. 8: Thermoelectric figure of merit, ZT, for selected K-Na co-doped samples, in comparison to the best PbTe sample doped with Na only.](image2)
IV. CONCLUSIONS

The Seebeck and Hall effect data of K, Na and K-Na doped PbTe do not support the development of resonant levels in the electronic band structure of PbTe but, rather, point to the importance of the heavy-hole valence band. Nevertheless, an enhancement in the thermoelectric properties similar in nature to what might be expected from resonance levels is observed and is attributed to the behavior of the heavy-hole valence band which responds to the lattice expansion with K doping and can be controlled to a significant degree by adjusting the Fermi energy with Na doping. Effectively, this causes the heavy-hole valence band to rise in energy and and adjust the Fermi energy and create a significant enhancement in the DOS that gives rise to interband scattering. This mimics the influence of a resonance level and has positive effects on the thermoelectric power factor.

As a result, $ZT \sim 1.3$ is reached around 700K purely on account of the enhancement in the electronic properties and without a marked reduction in thermal conductivity.

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