Enhanced thermoelectricity in composites by electronic structure modifications and nanostructuring

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The thermoelectric performance of nanocomposites with locally distorted density of states is investigated. The analytical expressions we have derived allow us to explore the effects of localized states modeled as Lorentzians on the materials transport properties in terms of their sharpness and locations relative to the Fermi level. Further optimization of the transport through nanostructuring design is also explored. We show that composites with both locally distorted density of states and nanostructure integration open the possibility for significant enhancement of the thermoelectric performance at room temperature. © 2010 American Institute of Physics. [doi:10.1063/1.3464288]

There has been extensive research in the area of thermoelectric (TE) materials devoted to exploring ways to enhance the figure of merit $ZT = S^2\sigma T/(\kappa_e + \kappa_L)$ governing their performance ($S$, $\sigma$, $T$, $\kappa_e$, and $\kappa_L$ are the Seebeck coefficient, electrical conductivity, absolute temperature, electronic, and lattice thermal conductivity, respectively). The advantages of incorporating nanoparticles or synthesizing granular composites are to reduce $\kappa_e$ and/or enhance $S$ due to carrier-interface scattering.1–7 These beneficial changes are usually accompanied by a reduction in $\sigma$. Proper design of the composite is then needed to ensure optimum $ZT$.

Localized distortion of the density of states (DOS) of narrow band gap semiconductors has also been identified as a powerful way to improve the TE efficiency.8 This effect is a result of a state localized over a narrow energy range in the gap or near the band edges arising from the strong hybridization of the impurity orbitals with the neighboring deep states of the host material. PbTe and PbTe-based alloys doped with group-III impurities and O-doped ZnSe have been shown to exhibit such resonant states.9–11 Recent experiments12 demonstrated that the figure of merit of Ti-doped PbTe can be doubled at $T=773\, ^{\circ}\mathrm{K}$ as a result of such DOS distortions.

Although the potential for enhanced TE properties due to DOS restructuring has been recognized, the effect of resonant levels in realistic electronic materials structure on all carrier properties entering $ZT$ has not been established yet. One proposed modified DOS consists of a $\delta$-peak at the Fermi level with a constant background.8 In real materials, however, $g(E)$ is a convolution of an energy dependent component due to the bulk and peaks due to the localized levels.9,10 Reference 8 showed that it is not beneficial to have a constant background component because it destroys the $\delta$-function enhancement on the TE properties. And yet recent experiments attributed the doubling of $ZT$ in PbTe due to such states in DOS.12

Thus the idea of localized features in realistic materials DOS needs further elucidation in terms of the collective influence of the relevant electronic structure features. We will consider n-type PbTe as the host material described by a nonparabolic two-bands energy model. By assuming a peaked form of the localized level in the DOS we will answer the following questions: What are the best characteristics of the resonant level in terms of its shape and location to achieve an optimum TE performance? Is a $\delta$-function in a particular location the best way to increase $ZT$ or not? We will also explore possibilities to see if nanocomposite PbTe with locally distorted DOS can result in further enhancement of $ZT$.13 The question of the benefits of nanostructuring design of a material with already improved TE characteristics by proper impurity doping will also be addressed.

To enhance the TE properties, one needs to either modify the energy dependent DOS $g(E)$ or the energy dependent mobility $\mu(E)$. Let’s consider first the enhancement route through DOS. The energy dispersion relation near the band edges for bulk PbTe is described by the two-band Kane model ($h^2k^2/2m^* = E + \alpha E^2$, where $\alpha = 1/E_g^0(T)$ accounts for the nonparabolicity with a temperature dependent energy gap at the $L$ point11 $E_g^0(T) = 0.19 + 0.0004 \times T$ eV. The effective mass $m^*$ is $m^*(T) = m^*(0) \times [(E_g^0(E)/E_g^0(0)]$. The parameters entering the energy dispersion (and later used in our calculations) are given in Ref. 5.

In order to take into account the specific bulk DOS and the contribution from a localized state, we propose the following form for the modified DOS:

$$g(E) = \frac{\sqrt{2}}{\pi^2(m^*/h^2)^{3/2}} \sqrt{E(1 + \alpha E)(1 + 2\alpha E)} + cw/[((E - E_0)^2 + w^2)],$$

where the first term corresponds to the regular bulk DOS,15 while the second one to the presence of a peaked feature of Lorentzian form located at $E_0$ with half width half maximum (HWHM) $w$. The scale parameter $c$ determines the height of the resonant state. $g(E)$ is schematically shown in Fig. 1(a) for a particular choice of $c$, $w$, and $E_0$. The electronic properties are found using the solution of the Boltzmann equation within the relaxation time approximation, found in Refs. 8 and 14. For the calculations here, the electron group velocity $v_g(E)$ and the carrier relaxation time $\tau_p(E)$ are needed. Using Eq. (1) and the two-band Kane model, we find
with \( \eta = c \tan^{-1}(E_0/w) \). If \( c = 0 \), one recovers \( v_\phi \) in pure bulk PbTe.\(^{15}\) If \( c \neq 0 \), \( v_\phi(E) \) also depends on the Lorentzian peak. For example, for a very sharp peak (large \( c \) and/or \( w \rightarrow 0 \)), \( v_\phi(E) \) will be highly reduced in the vicinity of the peak.

The total carrier relaxation time is taken to obey the Matthiessen’s rule \( \tau^{-1}_{\text{total}}(E) = \sum \tau^{-1}_{\text{mech}}(E) \), where each scattering mechanism has an independent contribution \( \tau_{\text{mech}}(E) \). For bulk PbTe, the most relevant mechanisms are due to electron-acoustic phonon, electron-optical phonon, and electron-charged impurity scatterings.\(^5\) They can be described as \( \tau_{\text{mech}}(E) = a(T)E^j \) where \( r_j = -1/2, 1/2, \) and \( 3/2 \) for scattering by acoustic phonons, nonpolar optical phonons, and ionized impurities, respectively. The \( a_j \) are temperature dependent and we use the expressions given in Ref. 5.

The lattice contribution \( \kappa_L \) is calculated using the Holland–Callaway model given in Refs. 16 and 17 with numerical values from Ref. 18. Here we take only the Umklapp phonon scattering with relaxation time \( \tau_{\text{ph}, \text{Umklapp}} = \alpha T n_o^2 \), since this is the dominant mechanism for the considered range of temperatures \( T \in [50, 300] \) K. The constant \( \alpha \) is determined by requiring that \( \kappa_L = 2 \text{ Wm}^{-1}\text{K}^{-1} \) for bulk PbTe at \( T = 300 \) K.\(^6\)

Our strategy now is to explore the localized level characteristics in the host bulk PbTe in order to maximize the TE performance. In all subsequent calculations the carrier concentration corresponding to the undistorted DOS is taken to be \( n = 5.67 \times 10^{18} \) cm\(^{-3} \). The scale parameter \( c = 10^{-20} \text{ eV/cm}^3 \) is set to fit ab initio reported values for the DOS of PbTe doped with cationic impurities.\(^10\) Changing the aspect ratio through \( w \) will describe a localized level with sharper or wider features. From Fig. 2, one notices that \( \delta^2 \sigma \) and \( ZT \) increase as the peak becomes closer to the Fermi level. Despite the large thermal conductivity \( \kappa \) due to the electronic contribution \( \kappa_e \), \( \kappa \) approaches \( \kappa_F \) and slowing down of the electrons, the overall \( ZT \) is about 3.5 times larger than \( ZT \) for regular PbTe at \( T = 300 \) K.

The TE characteristics can further be optimized by changing the HWHM [Figs. 2(c) and 2(d)]. However, \( ZT \) experiences a maximum at certain \( w \) [insets of Fig. 2(d)]. This indicates that having a very sharp, \( \delta \)-function-like feature in DOS is not always beneficial for TE enhancement. For very small HWHM (\( w < 2 \) meV), the background from the host PbTe is dominant resulting in reduced values of \( ZT \) approaching those for bulk.

Another route for TE enhancement is to change the mobility \( \mu(E) \) by introducing additional energy dependent scattering mechanisms. Interface scattering of low energy carriers from grain boundaries or nanostructured inclusions can result in an increased \( ZT \) due to the increased mean energy per carrier. Here, we propose that bulk PbTe with locally distorted \( g(E) \) and with integrated nanoinclusions is a system in which such changes can be beneficial for a much improved \( ZT \) at room temperature. The nanoinclusions are assumed to be randomly distributed as shown in Fig. 1(b) and they are modeled as spherical potential barriers with average radius \( R_0 \) and finite height \( V_0 \). Low energy electrons will be filtered out, while the high energy ones will determine the transport. The electron-nanoinclusion scattering relaxation time is calculated using the Born approximation through the Fermi golden rule.\(^6\)

\[
\tau_{\text{e,incl}}^{-1}(E) = n_i \int \frac{2 \pi}{\hbar} \left[ \int d^3 r [V_0 e^{2ikr \sin(\theta/2)}]^2 \right] g(E),
\]

where \( n_i = 3 \xi/(4 \pi R_0^3) \) is the concentration of inclusions with volume fraction \( \xi \), \( d \Omega \) is the solid angle element, and the integration over \( d^3 r \) is carried out over the volume of the spherical nanoinclusion. This approach is valid for scattering potentials satisfying the condition \( V_0 \ll h^2/(m^* R_0) \). From Eq. (3) one obtains

\[
\tau_{\text{e,incl}}^{-1}(E) = 3 \pi^3 V_0 \xi g(E)(4R_0 \sin 4R_0 k + \cos 4R_0 k + 32R_0^8 k^4 - 8R_0^2 k^2 - 1)/(8h \hbar R_0^8 k^8),
\]

with the energy dependent wave vector

\[
k(E) = (3 \pi^2)^{1/3} \frac{1}{2} \left( 2m^* \right)^{1/3} (3 \pi^2 h^3) [E(1 + aE)]^{3/2} - c \tan^{-1}(E_0 - E/w) + \eta^{1/3}.
\]

![FIG. 1. (Color online) (a) Schematics of the locally distorted DOS. The red dashed line corresponds to DOS of pure bulk PbTe; \( E_F \) and \( E_0 \) denote the Fermi level and the peak position, respectively. (b) Schematics of spherical nanoinclusions embedded in a bulk host; \( V_0 \) and \( R_0 \) represent the nanoinclusion average potential height and radius, respectively.](Image 1)

![FIG. 2. (Color online) \( S^* \sigma \) and \( ZT \) for different \( \Delta E = E_F - E_0 \) [(a) and (b)] vs \( T \) with \( w = 0.075 \) eV. \( S^* \sigma \) and \( ZT \) vs \( T \) are also given for regular bulk PbTe (dashed lines), which correspond to data in Ref. 17. [(c) and (d)] vs peak aspect ratio (varied through its HWHM parameter \( w \)) at \( T = 300 \) K.](Image 2)
The phonon-nanoinclusion scattering relaxation time is calculated following the procedure outlined in Ref. 20 within the near-geometrical scattering approximation $\tau_{\text{phon,incl}}^{-1} = 3v_i/2R_0$, where $v_i$ is the speed of sound outside the inclusion with its value is given in Ref. 15.

Figures 3(a) and 3(d) show that the optimum transport is obtained again for rather localized states at $E_F$. It is also interesting to note that for peaks further away from $E_F$ ($\Delta E > 0.1$ eV), $ZT$ (and $S^2\sigma$) exhibits a minimum for certain $w$ [inset of Fig. 3(d)]. Thus it seems that in such cases it is more desirable to have a broad level rather than a sharp one. This is an indication that for large $\Delta E$ it may be better to have an extra energy band rather than a localized distortion in DOS.

The TE properties can further be improved by changing the nanoinclusions characteristics. Our results from Figs. 3(b) and 3(e) show that there is an optimum barrier height seen as a maximum in $S^2\sigma$ and $ZT$. The $R_0$ dependence is less pronounced—Figs. 3(c) and 3(f). After a certain size, $S^2\sigma$ practically does not change, while $ZT$ exhibits a rather shallow maximum found to be in the $R_0 \approx (2, 10)$ nm region. It is also found that regardless of the peak position $E_0$, the maximum $ZT$ is always around twice as compared to $ZT$ when there are no inclusions (horizontal dashed lines).

Comparing the power factor of PbTe with and without nanoinclusions shows that there is rather a small interval over $V_0$ (for example, for $\Delta E=0$, $V_0$ must be less than 3 meV), where an enhancement is observed. However, $ZT$ shows a much larger interval over $V_0$ for which its values are above the horizontal lines (for $\Delta E=0$, $V_0$ must be less than 0.17 eV)—Figs. 3(b) and 3(e). Interestingly, $S^2\sigma$ shows enhancement for larger nanoinclusions, while $ZT$ is always higher regardless of the values of $R_0$ [Figs. 3(c) and 3(d)], indicating the beneficial changes in $\kappa_L$ due to the presence of the nanoinclusions.

In conclusion, we have shown that PbTe nanocomposites for which the electronic structure is modified by a localized state in the DOS, is a potential candidate for TE applications at room temperature. Our investigation allows us to propose different ways for TE properties enhancement by utilizing not only nanostructuring but also modifications of the bulk host DOS. The optimum design can easily be determined by the analytical formulas we have derived, which take into account the simultaneous effects of the bulk host DOS and the characteristics of the nanostructure integration. We show that significant enhancement is possible for strongly localized DOS modifications at the Fermi level. However, even if the existing resonant impurity doping cannot provide exactly these features, one can further utilize proper nanostructure engineering to obtain systems with significant TE enhancement.

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