Conductivity-limiting bipolar thermal conductivity in semiconductors

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Intriguing experimental results raised the question about the fundamental mechanisms governing the electron-hole coupling induced bipolar thermal conduction in semiconductors. Our combined theoretical analysis and experimental measurements show that in semiconductors bipolar thermal transport is in general a “conductivity-limiting” phenomenon, and it is thus controlled by the carrier mobility ratio and by the minority carrier partial electrical conductivity for the intrinsic and extrinsic cases, respectively. Our numerical method quantifies the role of electronic band structure and carrier scattering mechanisms. We have successfully demonstrated bipolar thermal conductivity reduction in doped semiconductors via electronic band structure modulation and/or preferential minority carrier scatterings. We expect this study to be beneficial to the current interests in optimizing thermoelectric properties of narrow gap semiconductors.

Thermal conduction in solids is one of the most fundamental physical processes. It reveals the nature of lattice dynamics as well as phonon scattering mechanisms. Thermal conductivity of solids also influences many technologically important topics including thermal insulation and management of energy storage and conversion systems, microelectronics, data storage devices; efficiency of thermoelectric materials; and stability of sensors and actuators. For semiconductors the low temperature thermal conductivity is not substantially distinct from those of insulators; at elevated temperatures, however, it becomes interesting and yet intriguing due to the vital roles of charge carriers and their interactions. A signature of electron-hole coupling in semiconductors is the bipolar thermal conduction at elevated temperatures, when the calculated lattice thermal conductivity ($\kappa_{LT}$, where $\kappa$ is the total thermal conductivity, $L$ the Lorenz number, $\sigma$ the electrical conductivity, and $T$ the absolute temperature) is significantly higher than the $T^{-1}$ temperature dependence expected for phonon-phonon interaction dominated thermal conductivity1-7. Similar effect has also been found in semimetals8-10. For intrinsic semiconductors, it is well recognized that the mobility ratio between electrons and holes ($b = \mu_e/\mu_p$) determines the bipolar thermal conductivity ($\kappa_b$), which maximizes when $b \approx 1^{11,12}$. Consequently, $\kappa_b$ is insignificant for InSb, primarily due to its very large mobility ratio ($b > 100$)$^{13}$. In the case of heavily doped semiconductors, the mobility ratio however is no longer a valid guide for understanding or predicting $\kappa_b$, due to the substantially different majority and minority carrier concentrations. For example, recent experiments showed significant $\kappa_b$ in p-type heavily-doped skutterdites despite of the mobility ratio between two carriers being greater than 10 (hole mobility $\sim 1-5$ cm$^2$/V-s with a concentration of $\sim 10^{22}$ cm$^{-3}$ and electron mobility $\sim 30-50$ cm$^2$/V-s with a concentration of $\sim 10^{18-19}$ cm$^{-3}$ at 800K, according to our numerical analyses which are presented below)$^{14-18}$, while the n-type skutterdites do not show appreciable $\kappa_b$, consistent with the rather small $b$ value ($\sim 1/50$)$^{19-20}$. Similar observations have been reported for many
other semiconductors. These intriguing results necessitate comprehensive understanding of $\kappa_b$ in semiconductors. A recent report attempted to model $\kappa_b$ in doped Bi$_2$(Te$_{0.85}$Se$_{0.15}$)$_3$ crystals but was unable to capture the specific roles of electronic band structure and carrier scattering mechanisms on $\kappa_b$.

In this study we report a combined experimental and computational effort that focused on unraveling the general behavior of $\kappa_b$ in semiconductors. A numerical method for modeling the temperature dependence of $\kappa_b$ for intrinsic as well as extrinsic (heavily doped) semiconductors encompassing a wide range of band gap and electronic band structure has been developed. We find that $\kappa_b$ in semiconductors is in general "conductivity-limiting". In analogous to the bipolar ionic conduction and multiple-step diffusion processes, in which the overall kinetics are determined (limited) by the lower rate species or processes, the bipolar thermal conduction is limited by the charge carrier with lower partial electrical conductivity. Therefore, it is determined by the minority carrier partial electrical conductivity and by the mobility ratio ("mobility-limiting") in extrinsic and intrinsic semiconductors, respectively. In order to validate these findings, we experimentally demonstrated $\kappa_b$ reduction based on electronic band structure modulation and preferential minority carrier carrier scattering. These results largely broaden our understanding of thermal conduction in semiconductors as well as offer insights for optimizing thermoelectric properties of narrow gap semiconductors.

**Results and Discussion**

Bipolar thermal conductivity in semiconductors can be expressed as:

$$\kappa_b = \frac{\sigma_n \sigma_p}{\sigma_n + \sigma_p} (\alpha_p - \alpha_n)^2 T,$$

where $\sigma_n$ and $\sigma_p$ (subscript $i=n, p$) are the partial electrical conductivity and Seebeck coefficient for electrons and holes, respectively. For a single parabolic band, the Seebeck coefficient of each carrier can be written as:

$$\alpha_i = \pm \frac{k_B}{e} \left[ \xi_i \left( \frac{\lambda_i + 5/2}{\lambda_i + 3/2} \right) \left( \xi_p + 2F_i(\xi_p) \right)^2 \right],$$

where $k_B$ is the Boltzmann constant, $e$ the free electron charge, $\xi$ the reduce Fermi energy, $\lambda$ the carrier scattering parameter, $F_i$ the Fermi integral of the order of $x$. Therefore $\xi_n + \xi_p = -E_g/k_BT$, where $E_g$ is the band gap. For acoustic phonon scattering ($\lambda = -1/2$), the term $(\alpha_n - \alpha_p)^2$ can be written as:

$$\left( \frac{k_B}{e} \right)^2 \frac{E_x}{k_BT} + \frac{2F_i(\xi_p)}{F_i(\xi_n)} + \frac{2F_i(\xi_p)}{F_i(\xi_n)}$$

which is associated with the total energy carried by electron-hole pairs (band gap energy and kinetic energies). The electrical conductivity of each carrier is:

$$\sigma_i = i e \mu_i,$$

where $i=n, p$ designates the carrier concentrations of electron and hole, respectively.

**“Conductivity-Limiting” Bipolar Thermal Conductivity.** To elucidate the bipolar thermal conduction behavior in semiconductors, we may rearrange Eq. (1) into (assuming acoustic phonon scattering $\lambda = -1/2$, which is valid for most thermoelectric materials)

$$\frac{\left( \frac{k_B}{e} \right)^2 \frac{E_x}{k_BT} + \frac{2F_i(\xi_p)}{F_i(\xi_n)} + \frac{2F_i(\xi_p)}{F_i(\xi_n)}}{\kappa_b} = \frac{1}{\sigma_n} + \frac{1}{\sigma_p}.$$

For a given material at a fixed $T$, the variation of $\left[ \frac{E_x}{k_BT} + \frac{2F_i(\xi_p)}{F_i(\xi_n)} + \frac{2F_i(\xi_p)}{F_i(\xi_n)} \right]^2$ as a function of $\xi_p$ or $\xi_n$ is rather negligible, while the carrier concentrations and the partial electrical conductivity $\sigma_i$ (right side of Eq. (4)) could change by several orders of magnitude because of the activation behavior of the charge carriers. Here $2F_i(\xi_p)/F_i(\xi_n)$ and $2F_i(\xi_n)/F_i(\xi_p)$ are the reduced kinetic energies of holes ($\xi_p/k_BT$) and electrons ($\xi_n/k_BT$), respectively, which only slightly change their numerical values when varying the Fermi level. To verify these analyses, numerical data for $p$-type skutterudites ($R$Fe$_3$NiSb$_{12}$) with $E_x=0.2$eV, $m_p^*=5$ $m_o$, $m_n^*=2$ $m_o$ at 800 K are plotted in fig. 1, where $m_p^*$, $m_o$, and $m_n$ are the effective mass of holes, effective mass of electrons, and free electron mass, respectively. The details of the calculations will be discussed below. As shown in fig. 1(a), with increasing $\xi_p$ from ~1 (weakly-degenerate) to 2 (degenerate), $2F_i(\xi_p)/F_i(\xi_n)$ only increases from 4.2 to 5.3, ~25% increases; whereas $p$ increases by a factor of ~10 and the minority carrier partial conductivity $\sigma_o$ decreases by a factor of ~20. These suggest that for semiconductors in general, Eq. (1) or (4) can be approximated as $1/\kappa_b(T) \propto 1/\sigma_p(T) + 1/\sigma_n(T)$, therefore $\kappa_b$ in semiconductors is actually "conductivity-limiting".
analogous to the rate-limiting phenomena in kinetic diffusion processes. For intrinsic semiconductors, since \( n = p \), Eq. (4) can be further approximated to be \( 1/\kappa_b(T) \propto \mu_p(T) + 1/\mu_n(T) \), consistent with the large body of literature already developed. In the case of extrinsic semiconductors \((n \gg p \text{ or } p \gg n)\), \( \kappa_b \) is primarily determined by the partial electrical conductivity of the minority carriers, not by the mobility ratio. A linear dependence of \( \kappa_b \) vs. \( \sigma_n \) at 800 K for \( p \)-type doped skutterudites, as shown in fig. 1(b), further substantiates our proposed "conductivity-limiting" concept for bipolar thermal conduction in semiconductors.

**Numerical Modeling.** Data presented in fig. 1 were calculated by our numerical method for modeling the temperature dependence of \( \kappa_b \) in semiconductors. Our numerical method aimed at discerning the underlying physics that controls \( \kappa_b \), including the electronic band structure features and carrier scattering mechanisms. We use the experimental carrier concentration values as those of the majority carriers. Based on the majority carrier concentration and Seebeck coefficient at room temperature, and the maximum Seebeck coefficient value at elevated temperatures, we can determine the Fermi level, the majority carrier effective mass and \( E_g \)). The minority carrier effective mass is used as an adjustable parameter. The majority and minority carrier concentrations and their temperature dependences are calculated based on semiconductor statistics. In order to obtain the \( T \) dependence of mobility, we first modeled its carrier concentration dependence at room temperature. We then assumed that the carriers are predominantly scattered by the acoustic phonons, therefore \( \mu_p(T) = \mu_p(300 \text{ K}) (T/300 \text{ K})^{-3/2} \) and \( \lambda_n = \lambda_p = -1/2 \). For example, the room temperature carrier mobility of \( n \)-type and \( p \)-type 3d transition metal-based skutterudite antimonides \( R_x(\text{Fe},\text{Co},\text{Ni})_3\text{Sb}_12 \) as a function of carrier concentration is shown in fig. 2, where \( R \) represents fillers and \( x \) the filling fraction. The data were taken from the literature and were well represented by an empirical expression (the solid lines in fig. 2).

![Figure 1](image-url)
$\mu_i(300\text{K}) = \mu_i^0 + \frac{\mu_i^{\text{max}} - \mu_i^0}{1 + \left(\frac{i}{i_{\text{ref}}}\right)^a}$

where $i_{\text{Ref}}$ is the reference carrier concentration, approximately where degeneracy sets in, $a$ is a fitting parameter, and $\mu_i^0$ and $\mu_i^{\text{max}}$ are the minimum and maximum possible mobility, respectively. In general, the carrier concentration dependence of mobility for all semiconductors studied in this work can be well accounted by this phenomenological formula and the fitting parameters are summarized in the Table S1 (Supporting Information, SI).

Bipolar Thermal Conductivity Reduction. In order to examine the validity of the minority carrier dominated bipolar thermal conduction in heavily doped semiconductors, and to utilize the concept of modifying $\kappa_b$ presented, we investigated ways of $\kappa_b$ reduction motivated by the recent quest for high efficiency thermoelectric materials that necessitate low thermal conductivity. It is well known that in filled skutterudites, the triple degenerate conduction band minimum (CBM) is primarily composed of...
$d$-orbitals from the transition metals (TMs), with some contribution from Sb $p$-states ($p$-$d$ hybridization). Thus the density of states (DOS) at the CBM can be effectively adjusted by varying the TMs. Our first principles calculations reveal that in the $p$-type Ba-filled skutterudites, DOS at the CBM decreases significantly with decreasing Fe/Co ratio on the TM sites from 2:2 to 1:3, as shown in fig. 4(a), mainly due to the higher energy and thus more contribution of 3$d$ orbitals of Fe as compared with those of Co. The distinct DOS of minority carrier band further suggests that $\kappa_b$ for $p$-type Ba$_{0.5}$Co$_3$Fe$_2$Sb$_{12}$ should be smaller than BaCo$_2$Fe$_2$Sb$_{12}$ due to the minority carrier partial conductivity reduction. Data for 800 K $\kappa_b$ vs. the majority carrier (hole) concentration for a series of Ba$_x$Co$_3$Fe$_2$Sb$_{12}$ and BayCo$_2$Fe$_2$Sb$_{12}$ samples are plotted in fig. 4(b), and the lines represent fitting to the data using the minority carrier effective masses $m^*_n=1.3m_0$ and $m^*_p = 2.2m_0$, respectively. This electronic band modulation induced $\kappa_b$ reduction substantiates the dominant role of the minority carriers. Because of the commonly triple-degenerate and 3$d$-orbital-dominated nature of the CBM, the minority carrier effective masses of the $p$-type skutterudites are usually much higher than those of the $n$-type, in which the minority carrier band is mainly composed of single-degenerate Sb $p$-orbital-featured light bands. Therefore, the predominant underlying reason for large differences in $\kappa_b$ between the $n$- and $p$-type skutterudites is actually due to the effective mass differences between the corresponding conduction and valence (minority) bands.

Our second example of $\kappa_b$ reduction takes the advantage of preferential scattering of the minority carriers. Normally in heavily doped semiconductors, the minority carriers are non-degenerate. Given the electronic band structure of a material and the Fermi level (determined by the majority carrier concentration), one can calculate the range of minority carrier wavelength. For example, the electron wavelength in a heavily-doped $p$-type Bi$_2$Te$_3$ ($p=3.5\times10^{19}$ cm$^{-3}$) is approximately between 10 nm and 50 nm, as shown in fig. 5(a). We compare $\kappa_b$ of $p$-type zone melted (ZM) and nanostructured (Nano) Bi$_{0.5}$Sb$_{1.5}$Te$_3$ prepared by the melt spinning combined with subsequent spark plasma sintering (MS-SPS) technique. Figure 5(b) shows, at comparable majority carrier concentrations between the ZM and Nano samples, a significant $\kappa_b$ reduction is achieved when nanoprecipitates are introduced into the sample. The minority carrier partial electrical conductivity is determined by $E_g$, minority effective mass and mobility. The estimated small $E_g$ variation between ZM and Nano is only responsible for 20% of the $\kappa_b$ reduction. For a large system like nanostructured Bi$_{0.5}$Sb$_{1.5}$Te$_3$, a full electronic band structure calculation.

Figure 3. (a) Experimental (symbols) and fitted (solid lines) bipolar thermal conductivity of intrinsic Si single crystal and degenerate Yb$_{5}$Fe$_{3}$NiSb$_{12}$ vs. $T$. (b) Experimental ($\kappa_b^{Exp}$) and calculated ($\kappa_b^{Cal}$) bipolar thermal conductivity for intrinsic Si and Ge single crystals, and degenerate Bi$_2$Te$_3$-based zone melted (ZM) compounds and $p$-type skutterudites at various temperatures. The dashed line represents $\kappa_b^{Cal}=\kappa_b^{Exp}$. 
is computationally unfeasible. It is difficult to directly determine $m_n^*$ (minority carrier) at the CBM. The estimated $m_n^*$ values of n-type doped ZM and Nano Bi$_{2}$Te$_{2.7}$Se$_{0.3}$ are 1.0 $m_0$ and 1.1 $m_0$, respectively$^{38,68}$. If we assume comparable $m_n^*$ at CBM between the ZM and Nano samples, the major part of $\kappa_b$ reduction between the p-type ZM and Nano Bi$_{0.5}$Sb$_{1.5}$Te$_3$ with comparable majority hole concentrations could be attributed to the reduction of minority carrier mobility ($\mu_n$) corroborated by our $\kappa_b$ fittings, where $\mu_n = 4095$ cm$^2$/V-s for the ZM and 1115 cm$^2$/V-s for the Nano. The TEM image (inset of fig. 5(b)) shows that the sizes of nanoprecipitates closely match those of the minority electron wavelengths. Given the majority hole wavelength is estimated to be ~2 nm, we postulate a strong preferential minority carrier scattering by the nanoprecipitates in the Nano Bi$_{0.5}$Sb$_{1.5}$Te$_3$. Similar $\kappa_b$ reduction can also be observed in nanostructured n-type Bi$_2$(Te,Se)$_3$ compounds$^{38,69,70}$. Extensive recent studies have established the role of nanostructure on lattice thermal conductivity reduction$^{63,65}$, we propose an “preferential minority carrier scatterings” for $\kappa_b$ reduction, which is partially responsible for the thermoelectric performance gains reported, especially at elevated temperatures$^{61,71}$. Recent theoretical work has also demonstrated that similar $\kappa_b$ reduction via heterostructure barriers scattering is possible$^{72}$. Finally we caution that nanostructure induced band structure modulation reported in AgPb$_{m}$SbTe$_{2-m}$ might be possible for Bi$_{0.5}$Sb$_{1.5}$Te$_3$, which could be responsible for part of the $\kappa_b$ reduction.

**Summary**

To conclude, our combined theoretical analysis and experimental measurements have established that in semiconductors bipolar thermal transport is in general a “conductivity-limiting” phenomenon, which is controlled by the carrier mobility ratio and the minority carrier partial electrical conductivity for the intrinsic and extrinsic cases, respectively. The numerical method we developed quantifies the role of electronic band structure and carrier scattering mechanisms. We have also demonstrated feasible strategies for manipulating the bipolar thermal conductivity in doped semiconductors via electronic band structure modulation and/or preferential minority carrier scatterings. We expect our study to be beneficial to the current interests in optimizing thermoelectric properties of narrow gap semiconductors.

**Methods**

Samples in this study were synthesized by a combination of induction melting and long-term high-temperature annealing, by zone melting, or by MS-SPS, and the details of which were documented...
High-resolution transmission electron microscopy (TEM) images were collected using a JEM-2100F TEM. Electrical conductivity ($\sigma$) and Seebeck coefficient ($\alpha$) were simultaneously measured by an Ulvac ZEM-3 under a low-pressure helium atmosphere. Thermal conductivity was calculated from the measured thermal diffusivity ($D$), specific heat ($C_p$), and density ($d$) using the relationship $\kappa = D C_p d$.

Thermal diffusivity $D$ was tested by laser flash diffusivity method using a Netzsch LFA-457 system, and $C_p$ was measured by a Netzsch DSC 404F1 using sapphire as the reference. The accuracy of the $\kappa$ measurements is estimated to be ~10% and the precision <5%.

$\kappa_b$ were extrapolated from $\kappa_b + \kappa_L = \kappa_L - \sigma T$ by assuming lattice thermal conductivity $\kappa_L$ is inversely proportional to $T$. Hall measurements were performed on a Janis cryostat equipped with a 9 Tesla superconducting magnet. The carrier concentration of electron ($n$) or hole ($p$) and the corresponding Hall mobility $\mu_n$ or $\mu_p$ (subscript $n$ represents the electron and $p$ the hole) were estimated from the measured Hall coefficient ($R_H$) and electrical conductivity by the relation $\frac{1}{\rho} = n e R_H$ and $\mu = \frac{1}{\sigma R_H}$, respectively.

The first-principles electronic band structure calculations were performed with the generalized gradient approximation functional of Perdew, Burke, and Ernzerhof, with projected augmented wave method, as implemented in Vienna $ab$ initio simulation package (VASP). The computational techniques are similar to those published previously. The de Broglie wavelengths ($\lambda$) is defined as, $\lambda = h/m^*v$, where $h$, $m^*$, and $v$ are the Planck constant, carrier effective mass, and drift velocity, respectively. $m^*$, $v$ and $\lambda$ of degenerate majority carriers are almost energy independent ($k_BT$ within the Fermi level), while for non-degenerate minority carriers these values are energy dependent, which are derived from band structure. The detailed calculation method is shown in Supporting Information, and the calculated density of state, $m^*_n$ and $v_n$ of electrons for $p$-type Bi$_2$Te$_3$ ($\xi_p = 0.25$, $m^*_p = 1.3 m_0$) are shown in figure S2 (SI).

Figure 5. (a) The calculated electron wavelength, and the product of the Fermi-Dirac distribution function and electronic density of states $f(E) g(E)$ vs. energy with the zero point corresponding to the conduction band minimum ($E_c$). (b) The experimental and modeled bipolar thermal conductivity vs. temperature, for $p$-type zone melted (ZM) and nanostructured (MS-SPS) Bi$_{0.5}$Sb$_{1.5}$Te$_3$. The inset is a TEM picture of the MS-SPS bulk sample which shows 10–50 nm nanoprecipitates. (The room temperature minority carrier mobilities of ZM and Nano samples are $\mu_n = 4095$ and 1115 cm$^2$/V·s, respectively).

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Author Contributions
Jihui Yang designed research; S.W., Jiong Yang, and T.T. performed research; Jihui Yang, W.Z. and X.T. analyzed data; and Jihui Yang, S.W., and Jiong Yang wrote the paper. All authors reviewed the manuscript.

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