Expression of interfacial Seebeck coefficient through grain boundary engineering with multi-layer graphene nanoplatelets†

Yue Lin,†‡a Maxwell Wood,†b Kazuki Imasato,†c Jimmy Jiahong Kuo,†d David Lam,†a Anna N. Mortazavi,†cd Tyler J. Slade,†e Stephen A. Hodge,†f Kai Xi,†g Mercouri G. Kanatzidis,†c David R. Clarke,†c Mark C. Hersam†ae and G. Jeffrey Snyder†a,b

Energy filtering has been a long-sought strategy to enhance a thermoelectric material’s figure of merit $zT$ through improving its power factor. Here we show a composite of multi-layer graphene nanoplatelets (GNP) and n-type Mg$_3$Sb$_2$ leads to the expression of an energy filtering like effect demonstrated by an increase in the material’s Seebeck coefficient and maximum power factor, without impact on the material’s carrier concentration. We analyse these findings from the perspective of a heterogeneous material consisting of grain and grain boundary phases, instead of a more traditional and common analysis that assumes a homogeneously transporting medium. An important implication of this treatment is that it leads to the development of an interfacial Seebeck coefficient term, which can explain the observed increase in the material’s Seebeck coefficient. The contribution of this interfacial Seebeck coefficient to the overall Seebeck coefficient is determined by the relative temperature drop across the grain boundary region compared to that of the bulk material. In Te doped Mg$_3$Sb$_2$ we show the introduction of GNP increases the interfacial thermal resistance of grain boundaries, enhancing the contribution of the interfacial Seebeck coefficient arising from grain boundaries to the overall Seebeck coefficient. Without significant detriment to the electrical conductivity this effect results in a net increase in maximum power factor. This increased interfacial thermal resistance also leads to the synergistic reduction of the total thermal conductivity. As a result, we enhance $zT$ of the Mg$_3$Sb$_2$ to a peak value of 1.7 near 750 K. Considering the two-dimensional nature of the grain boundary interface, this grain boundary engineering strategy could be applied to a few thermoelectric systems utilizing various two-dimensional nanomaterials.

1 Introduction

Electron filtering$^{1,2}$ was theoretically proposed$^{3,4}$ to enhance the thermoelectric power factor (PF = $z^2\sigma$) of materials. In an n-type semiconductor, low energy electrons have a smaller contribution to the material’s Seebeck coefficient ($\alpha$).$^{5,6}$ An energy

Broader context

Optimizing the thermoelectric properties in a material has always been a balancing act of inversely correlated material’s properties. This counterpoise has traditionally been mediated by tuning the carrier concentration in a semiconductor as to strike an optimal balance between the material’s Seebeck coefficient and conductivity. Energy filtering is a concept that thinks outside the box of this common paradigm and offers a mechanism to boost a material’s Seebeck coefficient without a change in the semiconductor’s carrier concentration. While a long-sought strategy to enhance thermoelectric performance, energy filtering has had few successful demonstrations to date. We revisit the concept from a heterogeneous perspective and reveal a missing key to be an interfacial Seebeck coefficient. Using Mg$_3$Sb$_2$ as an example material, we experimentally demonstrate a grain boundary engineering approach to realize the benefit of energy filtering, through the addition of graphene. We observe an over 40% increase in the material’s high temperature $zT$ (1.73 near 773 K), without changing the material’s carrier concentration. This work provides a framework to understand energy filtering using the interfacial Seebeck coefficient. We anticipate the interfacial Seebeck concept together with the experimental strategy utilizing graphene will catalyse the growth of interface and grain boundary engineering of thermoelectric materials.

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‡ These authors contributed equally to this work.
filtering approach surmises that these low energy electrons can be preferentially blocked by an energy barrier, resulting in an increase in thermopower (the magnitude of Seebeck coefficient). One way that has been postulated to introduce the energy barriers is through creation of grain boundaries (Fig. 1a).\textsuperscript{5,7} The existence of grain boundaries may also scatter phonons, resulting in a reduction in lattice thermal conductivity ($k_L$).\textsuperscript{6} In this case, the figure of merit $zT$ ($zT = PE/k_L$) would be enhanced through the synergistic effect of a rise in power factor (often used as a signature of energy filtering) and a reduction in thermal conductivity ($k = k_e + k_L$, where $k_e$ is electronic contribution of the thermal conductivity). However, the existence of boundaries can substantially reduce a material's mobility and therefore its electrical conductivity ($\sigma$).\textsuperscript{10} In order for these barriers to increase $x^2\sigma$, any reduction in $\sigma$ must be compensated by an increase in $x^2$ such that the overall $x^2\sigma$ is increased. In practice there are few successful demonstrations of an improvement of $x^2\sigma$ and no viable thermoelectric materials with improved $x^2\sigma$ via an energy filtering strategy.\textsuperscript{7,11,12} A possible reason why previous studies have struggled is due to a disconnect between theoretical and experimental approaches. While most experimental studies of energy filtering acknowledge inhomogeneity in their material is important to create an energy filtering effect,\textsuperscript{11,14} most if not all theoretical analysis is done using a homogenous transport theory\textsuperscript{1,15,16} (see S1 in ESI,\textsuperscript{†} for brief review of previous experimental work dealing with the energy filtering concept). In most cases, electron barriers at grain boundaries do more harm than good to the electronic properties of thermoelectric materials.

In the recently discovered n-type thermoelectric material Mg$_3$Sb$_2$,\textsuperscript{17,18} this has become extremely apparent. Mg$_3$Sb$_2$ is an example of a material with charged grain boundaries that lead to an energy offset ($\Delta E$) between the conduction band minimum (CBM) in the grain and that of the grain boundary (Fig. 1a).\textsuperscript{19} This physical picture is essentially the same as what is predicted to increase a material's Seebeck coefficient through electron filtering.\textsuperscript{11,12} However, instead of benefitting from grain boundaries, previous reports on n-type Mg$_{3}$Sb$_{1.3}$Bi$_{0.3}$ have found significantly lower thermoelectric performance with smaller grains. This has been traced to the added electrical resistance at grain boundaries where the effect of grain boundaries\textsuperscript{20} on the lattice thermal conductivity and Seebeck coefficient was reported as largely negligible.\textsuperscript{19,20}

This reality suggests that any grain boundary engineering strategies that include energy filtering to improve $zT$ must carefully weigh the effects on all transport properties. Interfaces such as grain boundaries are frequently introduced into thermoelectric materials to reduce the phonon mediated or lattice thermal conductivity. Typically, the hope is that such interfaces effectively lower lattice thermal conductivity without significantly hindering the electron mobility. Strategies to improve the effectiveness of grain boundaries, by increasing the thermal interface resistance of each boundary have been successful in a few examples.\textsuperscript{21–23} Inserting nano-carbon additives (i.e. graphene\textsuperscript{24} and carbon nanotube) to grain boundaries of these materials has successfully reduced lattice thermal conductivity without significant detriment to the conductivity. Thus, carefully engineered grain boundaries with combined electronic and thermal effects could lead to improved $zT$.

Interfacial thermal resistance is typically described as a Kapitza resistance\textsuperscript{25,26} where the resistance occurs across a two-dimensional interface. Although the interfacial region could be several-nanometres in thickness,\textsuperscript{27} the thermal properties can be sufficiently described without defining a thickness. Considering polycrystalline materials as a heterogeneous material consisting of grain regions and interfacial grain boundary regions enables quantitative understanding of the interfacial effects of both thermal and electrical resistances as additional resisters in series with the grain resistance.

In this work, we demonstrate how using a self-consistent two-phase model for electronic (Fig. 1c) and thermal transport (Fig. 1d) can lead to effects that could be interpreted as energy filtering. The energy offset at grain boundaries in materials with charged grain boundaries like Mg$_3$Sb$_2$ leads the interfacial region to be more electrically resistive but also have a larger Seebeck coefficient compared to the bulk. We find that the key to observe an energy filtering effect is to maximize the temperature drop across the grain boundary region. We use this insight to explain energy filtering effects witnessed in magnesium antimonide (Mg$_{3.3}$Sb$_{1.99}$Te$_{0.01}$) composites with GNP.\textsuperscript{28} The addition of GNP increases interfacial thermal resistance at the grain boundaries (Fig. 1b) and thus increases the temperature drop across the grain boundary region (Fig. 1d). This in turn leads to an increased expression of the interfacial Seebeck coefficient arising from grain boundaries that adds to the total Seebeck coefficient, which enhances the material's maximum power factor and figure of merit $zT$ (Fig. 2).

2 A two-phase description for a heterogeneous material with grain boundaries

In a material with grain boundaries, both the charge and phonon transport behaviour are different in grains and at grain boundaries. A charge barrier at a grain boundary has the effect of adding an interfacial resistance at the grain boundaries (Fig. 1c).\textsuperscript{20–32} Meanwhile the potential barrier, or band offset at the grain boundary (Fig. 1a) should lead to the grain boundary region having a larger magnitude of the Seebeck coefficient $|z|$ compared to the rest of the bulk.\textsuperscript{33} On the other hand, phonon transport is influenced by the structural difference at the grain boundaries such as lattice mismatch, which induces additional interfacial thermal resistance (Kapitza resistance) at the grain boundaries.\textsuperscript{25,34} As a result, a material with charged grain boundaries can be better understood under a two-phase model consisting of grain phase and grain boundary phase. In this model, the grain phases and grain boundary phases are connected in a series circuit (Fig. 1c and d), which is one of the limiting cases of effective medium theory.\textsuperscript{35–37} We use this simplified model to simulate and explain the Seebeck coefficient, thermal conductivity, and electrical conductivity of the material made up of grain and grain boundary phases. We acknowledge that in reality the transport occurs over a three-dimensional network of grains/grain boundaries, where both
Fig. 1  Illustration of the energy filtering effect in polycrystalline Mg₃Sb₂ with electron filtering at the grain boundaries (GB). (a) The high energy electrons contribute more to the Seebeck coefficient than the low energy electrons. By changing the band structure at the grain boundaries, the low energy electrons can be preferentially "filtered out", therefore increasing the magnitude of the Seebeck coefficient. The band offset ($\Delta E$) between the conduction band minimum (CBM) of the grain and the grain boundary (GB) acts as the electron filter so that the grain boundary region has a larger magnitude of the Seebeck coefficient ($|\alpha_{gb}|$).

(b) to (e) Electron and Phonon transport in the samples without (left) and with (right) GNP (G) at the grain boundaries modelled as a series circuit. Grain boundaries in our model are more electrically and thermally resistive than the bulk material, which leads to an additional resistance voltage ($V_R$) drop and temperature ($T$) decrease. We find the addition of GNP does not introduce an additional barrier for electron transport but does increase the interfacial thermal resistance at the boundaries. Based on our two-phase model, an increased thermal resistance at grain boundaries will lead to an increased temperature drop in the grain boundary phase ($\Delta T_{gb}$) of the material (d), thus a larger grain boundary voltage ($\Delta V_{gb} = x_{gb} \Delta T_{gb}$) (e). Due to the grain boundary Seebeck coefficient being larger than the bulk Seebeck coefficient ($|\alpha_{gb}| > |\alpha_g|$), the enhanced temperature drop in the grain boundary phase increases the magnitude of the overall Seebeck coefficient ($|\alpha_t|$, see eqn (1)).
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3 Results and discussion

3.1 Physical characterisation

Based on SEM (Fig. S8, ESI†) and TEM (Fig. S10, ESI†) analysis, we confirm that GNP is generally well distributed in the Mg$_{3.2}$Sb$_{1.99}$Te$_{0.01}$ matrix without much localised aggregation (further shown by Raman spectroscopy (Fig. S12, ESI†)). The material at the grain boundaries is identified as GNP$^{24}$ with average thickness of $\sim 3$ nm (Fig. S10 and Section S5.10, ESI†). STEM-EDX (Fig. S11, ESI†) analysis shows the presence of MgO between grains. The existence of charged grain boundaries in Mg$_3$Sb$_2$ have been previously rationalized by the presence of Mg vacancies in the grain boundaries,$^{10}$ where MgO could be involved in the removal of Mg as de Boor$^{41}$ et al. has shown in Mg$_2$Si. (See session S5.4 for detailed discussion, ESI†). Both XRD (Fig. S13, ESI†) and XPS (Fig. S14, ESI†) analysis confirms that the introduction of GNP does not introduce detectable structural and compositional change at a bulk scale.

3.2 Transport implications of energy filtering in Mg$_3$Sb$_2$Mg$_3$Sb$_3$

An effect analogous to electron filtering is observed in Te doped Mg$_3$Sb$_3$ by increasing the ratio of the temperature drop across grain boundaries to the total temperature drop across the sample $\Delta T_{gb}/\Delta T$. We experimentally achieve this result in two different ways. The first was realized by decreasing the grain size (nano structuring) of our material via sintering at lower temperature (see S6.3, ESI†), resulting in a larger fractional amount of grain boundary “phase" in our sample. The second was realized by compositing of our material with GNP, which increased the interfacial thermal resistance at the grain boundaries. As a control we compare our samples with the energy filtering effect to a large grain sample in which the grain boundary contribution to electron and thermal transport is minimized.

By increasing $\Delta T_{gb}/\Delta T,$ via these methods we see the Seebeck coefficient of the Mg$_{3.1}$Sb$_{1.99}$Te$_{0.01}$ is enhanced to varying degrees compared to that of large grain sample (Fig. 3d). In a typical thermoelectric material, an increase in a sample’s Seebeck coefficient is coupled with a decrease in the material’s carrier concentration. However, from Hall measurements (insert of Fig. 3b and Fig. S4d, ESI†) we do not observe a decrease in carrier concentration suggesting the increased Seebeck coefficient comes from an energy filtering-like effect. Furthermore, the electrical conductivity (Fig. 3c) of all samples begins to converge to a similar value at higher temperatures, where grain boundary scattering of electrons is less strong.$^{10}$ Therefore, we ascribe the observed changes of transport properties to microstructural changes rather than difference in carrier concentration of the bulk material. Note, the hall coefficient of poly-crystalline semiconductors is unaffected by the presence of grain boundaries in the limits where grain boundaries are highly resistive or much thinner than the grain.$^{12,43}$

Further evidence that an energy filtering effect is present is this system is given by the correlated behaviour of the sample’s
overall Seebeck coefficient ($\alpha_t$) and thermal conductivity ($\kappa_t$) shown in Fig. 3b according eqn (3).

$$\alpha_t = \frac{(\alpha_g - \alpha_{gb})\kappa_t}{\kappa_g} + \alpha_{gb}$$

All of the samples are well described by a single slope (Fig. 3b and Fig. S6, ESI†) as predicted from eqn (3) if $\alpha_g$, $\alpha_{gb}$ and $\kappa_g$ remain constant under the same temperature, suggesting the presence of an energy filtering effect. While the concept of interfacial thermal or electrical resistances are common the idea of an interfacial Seebeck coefficient $\alpha_{gb}$ is not. The Seebeck coefficient is an electronic transport property like conductivity and so it should not be surprising that an interfacial Seebeck coefficient resulting from the energy filtering should exist along with interfacial resistance.

3.3 Grain boundary engineering with GNP to amplify energy filtering effect in Mg$_{3.2}$Sb$_2$

Based on the temperature dependence of conductivity (Fig. 3c), the large grain Mg$_{3.2}$Sb$_2$ sample shows little grain boundary effect. Therefore we can assume the large grained sample’s other transport properties are close to those expected of a single crystal with no grain boundaries. By assuming the Seebeck coefficient and thermal conductivity of the large grain sample from Fig. 3d and e represents $\alpha_g$ and $\kappa_g$, we extract the $\alpha_g$ (shown as hollow points in Fig. 4a) and $\kappa_g$ from smooth fitted curves in $d$. The Dashed line is a guide to the eye, which can also be applied to give the value of the interfacial Seebeck coefficient (the intercept at $\kappa_t = 0$) by applying eqn (3). See Fig. S6 (ESI†) for other temperatures.

The insert is measured Hall carrier concentration versus measured Seebeck coefficient of Mg$_{3.2}$Sb$_{1.99}$Te$_{0.01}$ samples at 600 K. The samples have the same carrier concentration ($2.6 \times 10^{19}$ cm$^{-3}$) indicated as the dashed line) without dependency on the Seebeck coefficient. In the high temperature range where the influence of grain boundaries is significantly reduced, the electrical conductivity of all samples begins to converge, further supporting the assertion that the samples all have the same carrier concentration. Please see session S4 in ESI† for repeatability of the measurements.
curve of the large grain sample between 300 K to 650 K with a step of 50 K. For calculation of $zT_{gb}$ we also extract $\sigma_g$ and $k_g$ from smooth fitted curves of the other samples in Fig. 3d and e. By applying this procedure we can estimate the $zT_{gb}$ in the Mg$_{3.2}$Sb$_{1.99}$Te$_{0.01}$ samples with and without our addition of GNP and found the grain boundary Seebeck coefficient to be the same within experimental error in every sample (Fig. 4a). This observation suggests that the addition of GNP does not influence the energy offset of the electron filtering barrier, but may primarily acts to increase phonon scattering at the grain boundary. Structural characterization (see S5.3–S5.7, ESL†) further proved that the presence of GNP did not introduce any detectable elemental or compositional change.

Although the nano-grained sample (without GNP) exhibited an electron filtering effect, its overall power factor is significantly lower than that of the large grain sample (Fig. 3a). This observation indicates that the increase in Seebeck coefficient (Fig. 3d) by adding the electron barriers does not compensate the decrease in electrical conductivity (Fig. 3c). In contrast, the power factor of GNP/Mg$_{3.2}$Sb$_{1.99}$Te$_{0.01}$ samples is enhanced above 500 K when compared to the large grain sample. This is a result of greater enhancement in the overall Seebeck coefficient of the bulk material (Fig. 3d) with less impact in electrical conductivity (Fig. 3c).

The total thermal resistance is a sum of thermal resistance in the grain phase and Kapitza resistance at the grain boundary. For a material with average grain size $d$, we have (see S3.2 for detailed derivation, ESL†):

$$\frac{d}{k_t} = \frac{d}{k_g} + r_\text{Kapitza}$$

Here, the average grain size $d$ can be determined by electron backscatter diffraction (EBSD, see S5.2, ESL†), enabling the estimation of $r_\text{Kapitza}$ (Fig. 4b). Compared to the nano-grained sample, the $r_\text{Kapitza}$ increased by a factor of ~6 with the addition of GNP.

The electron transport is under the same configuration as the thermal transport:

$$\frac{d}{\sigma_t} = \frac{d}{\sigma_g} + r_\text{el-gb}$$

By applying the no grain boundary (GB) resistance limit (Fig. 3c) as the electrical conductivity of the grain ($\sigma_g$), this equation enables estimation of interfacial electrical resistivity ($r_\text{el-gb}$) (Fig. 4c). Compared to the nano-grained sample, the average $r_\text{el-gb}$ remains the same with the addition of GNP in the temperature range above 500 K where the energy filtering showing benefit.

Within the experimentally derived formulations of interfacial thermal resistance $r_\text{Kapitza}$, interfacial electrical resistance $r_\text{el-gb}$ and interfacial Seebeck coefficient $z_{gb}$, the thermoelectric efficiency across the same temperature drop can be defined in the same manner, giving an interfacial $zT_{gb}$ as

$$zT_{gb} = \frac{z_{gb}^2}{r_\text{el-gb}/r_\text{Kapitza}}T$$

The improvement of the total $zT$ (Fig. 2) is presumably a result of $zT_{gb}$ being greater than the bulk $zT$ consistent with prior analysis of electron filtering. While the minimum thermal conductivity provides an important limit to bulk $zT$, Kapitza resistances are known to be able to be considerably large. In this way, the benefit of energy filtering effect was realized. Similar correlation between measured Seebeck and thermal conductivity, and significant improvement in $zT$ were also observed in Si$_{0.80}$Ge$_{0.20}$B$_{0.016}$ (see S5.8, ESL†).
5.2 Preparation of GNP/Mg₃.2Sb₁.99Te₀.01 compound

For production of GNP/Mg₃.2Sb₁.99Te₀.01 compound, the calculated amount of GNP was dispersed in anhydrous and deoxygenated Dimethylformamide (DMF) with assistance of sonication for 30 minutes. The resultant mixture was then filtered and dried in a vacuum oven for 12 hours under ambient temperature. Before sintering, the compound was mechanically mixed for 5 minutes by using the high-energy mill to ensure homogeneous dispersion of GNP. The weight ratio of raw materials to balls is 1:10 in this case. For control purpose, the powders for Mg₃.2Sb₁.99Te₀.01 samples without GNP were treated with the same process.

5.3 Sintering and annealing of Mg₃.2Sb₁.99Te₀.01 and GNP/Mg₃.2Sb₁.99Te₀.01 composite

The processed powders were loaded into a graphite die and sintered by using an induction rapid hot press (RHP). For the large grain sample and the samples with GNP, the sintering condition was 1073 K with 45 MPa pressure for 20 minutes. For the nano-grain samples, the sintering condition was 873 K with 45 MPa pressure for 60 minutes. Afterwards, the hot-pressed pellets were annealed at 873 K under a magnesium rich environment for 48 hours.

All the above-described processes were carried out under protection of argon atmosphere. More detailed description is available in the ESI.†

4 Conclusion and perspective

Electron filtering has been predicted to be an effective approach in enhancing thermoelectric performance. By applying a two-phase model and introducing an interfacial Seebeck coefficient term, we shed new light onto the design principles and applications of the energy filtering concept. Examining Mg₃.2Sb₁.99Te₀.01 as an example, we increased Kapitza thermal resistance of the grain boundary phase, by utilizing GNP as a grain boundary engineering additive. This in turn promoted temperature drop across the grain boundary region, which increased the expression of the interfacial Seebeck coefficient in Mg₃.2Sb₁.99Te₀.01. This approach, in contrast to simply reducing grain size, minimizes the impact to electron charge transport, thus enhancing thermoelectric performance. We encourage the community to investigate the materials showing correlation of reduced thermal conductivity and rising Seebeck coefficient with nanostructuring.

Conflicts of interest

There are no conflicts to declare.

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