

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).^{5,7} The existence of grain boundaries may also scatter phonons, resulting in a reduction in lattice thermal conductivity (κ_L).⁸ In this case, the figure of merit⁹ zT ($zT = PF/\kappa$) 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 ($\kappa = \kappa_e + \kappa_L$, where κ_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 (σ).¹⁰ In order for these barriers to increase $\alpha^2\sigma$, any reduction in σ must be compensated by an increase in α^2 such that the overall $\alpha^2\sigma$ is increased. In practice there are few successful demonstrations of an improvement of $\alpha^2\sigma$ and no viable thermoelectric materials with improved zT via an energy filtering strategy.^{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,^{13,14} most if not all theoretical analysis is done using a homogenous transport theory^{1,15,16} (see S1 in ESI,† 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_3Sb_2 ^{17,18} this has become extremely apparent. Mg_3Sb_2 is an example of a material with charged grain boundaries that lead to an energy offset (ΔE) between the conduction band minimum (CBM) in the grain and that of the grain boundary (Fig. 1a).¹⁰ This physical picture is essentially the same as what is predicted to increase a material's Seebeck coefficient through electron filtering.^{11,12} However, instead of benefitting from grain boundaries, previous reports on n-type $\text{Mg}_3\text{Sb}_{1.5}\text{Bi}_{0.5}$ 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 boundaries¹⁰ on the lattice thermal conductivity and Seebeck coefficient was reported as largely negligible.^{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.^{21–23} Inserting nano-carbon additives (*i.e.* graphene²⁴ 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^{25,26} where the resistance occurs across a two-dimensional interface. Although the interfacial region could be several-nanometres in thickness,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 resistors 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_3Sb_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 ($\text{Mg}_{3.2}\text{Sb}_{1.99}\text{Te}_{0.01}$) composited with GNP.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).^{30–32} 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 $|\alpha|$ compared to the rest of the bulk.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.^{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.^{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



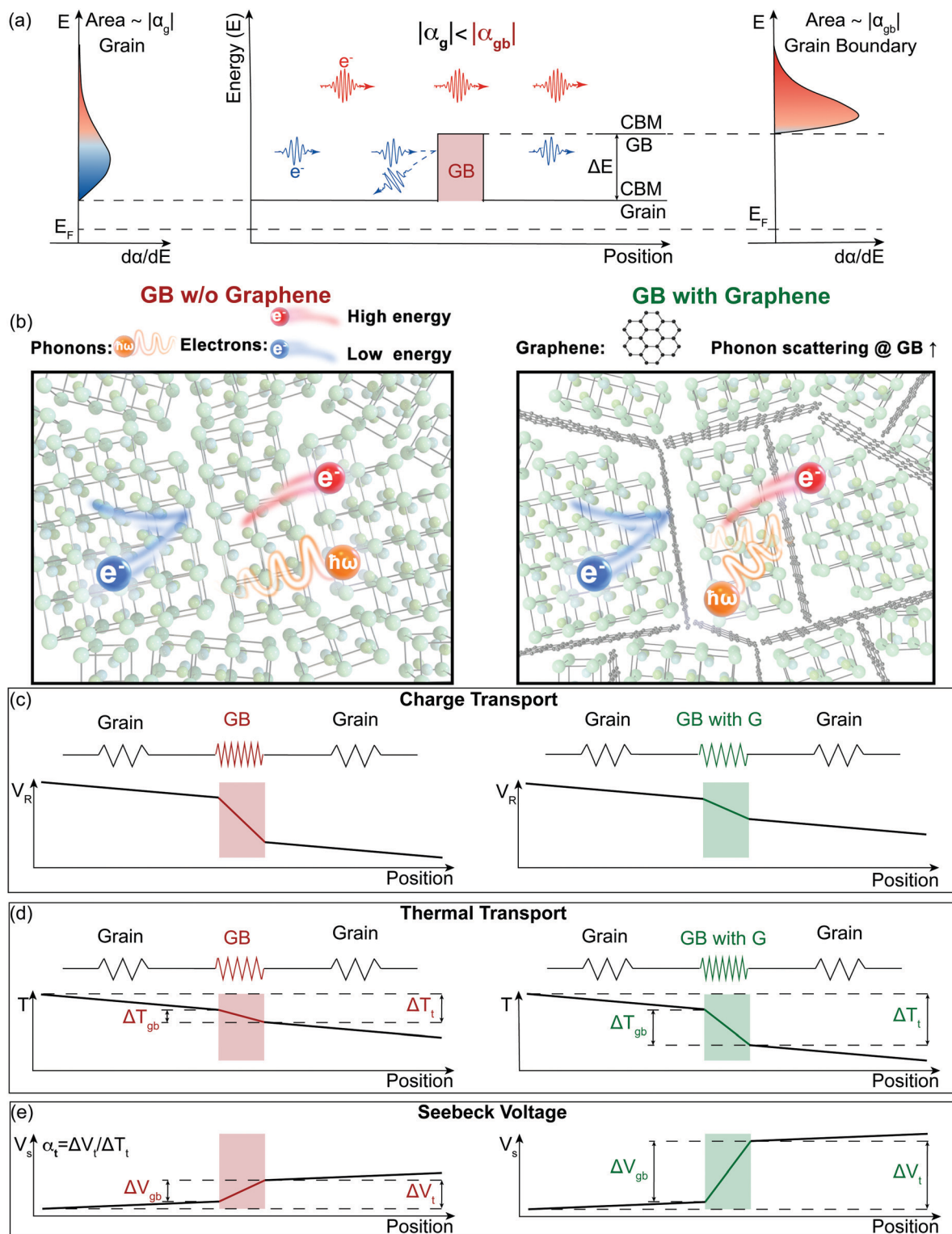


Fig. 1 Illustration of the energy filtering effect in polycrystalline Mg_3Sb_2 with electron filtering at the grain boundaries (GB). (a) The high energy electrons contribute more to the Seebeck coefficient than the low energy electrons. By changing the band structure at the grain boundaries, the low energy electrons can be preferentially “filtered out”, therefore increasing the magnitude of the Seebeck coefficient. The band offset (ΔE) 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 ($|\alpha_{gb}| > |\alpha_g|$). (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) drop. 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 (ΔT_{gb}) of the material (d), thus a larger grain boundary voltage ($\Delta V_{gb} = \alpha_{gb} \Delta T_{gb}$) (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)).



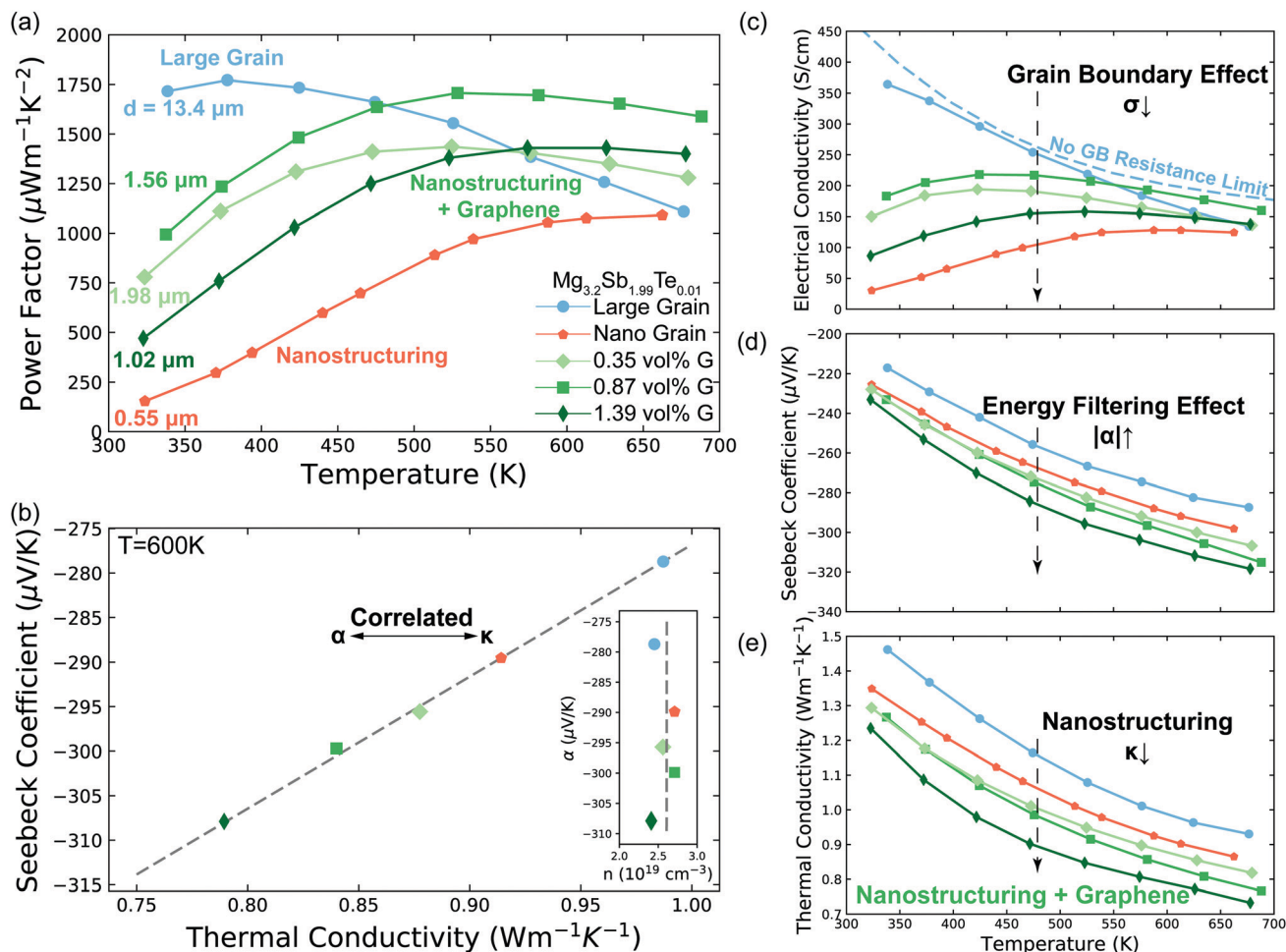


Fig. 3 Transport properties of $\text{Mg}_{3.2}\text{Sb}_{1.99}\text{Te}_{0.01}$ with varying grain size and GNP concentration (G) concentration. (a) Temperature dependent power factor of the samples. The average grain size d of each sample was measured by EBSD (S5.2, ESI†). (b) Linear correlation between Seebeck coefficient and thermal conductivity. The samples with lower thermal conductivity show larger Seebeck coefficient, signalling the importance of grain boundary Kapitza resistance on the energy filtering effect. The data points are extracted from the 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 $\text{Mg}_{3.2}\text{Sb}_{1.99}\text{Te}_{0.01}$ samples at 600 K. The samples have the same carrier concentration ($2.6 \pm 0.2 \times 10^{19} \text{cm}^{-3}$, indicated as the dashed line) without dependency on the Seebeck coefficient. (c) to (e) Seebeck coefficient, electrical conductivity and thermal conductivity of the samples. The no grain boundary (GB) resistance limit (c) is estimated by assuming acoustic-phonon scattering ($T^{-3/2}$) is the sole scattering mechanism.¹⁰ Note here the enhancement in Seebeck coefficient (d) is not as a result of a reduction in carrier concentration as measured by Hall effect (see Fig. 3b and Fig. S4d, ESI†). 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.

overall Seebeck coefficient (α_t) and thermal conductivity (κ_t) shown in Fig. 3b according eqn (3).

$$\alpha_t = \frac{(\alpha_g - \alpha_{gb})\kappa_t}{\kappa_g} + \alpha_{gb} \quad (3)$$

All of the samples are well described by a single slope (Fig. 3b and Fig. S6, ESI†) as predicted from eqn (3) if α_g , α_{gb} and κ_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 α_{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 $\text{Mg}_{3.2}\text{Sb}_2$

Based on the temperature dependence of conductivity (Fig. 3c), the large grain $\text{Mg}_{3.2}\text{Sb}_2$ 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.¹⁰ By assuming the Seebeck coefficient and thermal conductivity of the large grain sample from Fig. 3d and e represents α_g and κ_g , we extract the α_g (shown as hollow points in Fig. 4a) and κ_g from smooth fitted



curve of the large grain sample between 300 K to 650 K with a step of 50 K. For calculation of α_{gb} , we also extract α_t and κ_t from smooth fitted curves of the other samples in Fig. 3d and e. By applying this procedure we can estimate the α_{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, ESI†) 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, ESI.†):

$$\frac{d}{\kappa_t} = \frac{d}{\kappa_g} + \rho_{\text{Kapitza}} \quad (4)$$

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

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

$$\frac{d}{\sigma_t} = \frac{d}{\sigma_g} + \rho_{\text{el-gb}} \quad (5)$$

By applying the no grain boundary (GB) resistance limit (Fig. 3c) as the electrical conductivity of the grain (σ_g), this equation enables estimation of interfacial electrical resistivity ($\rho_{\text{el-gb}}$) (Fig. 4c). Compared to the nano-grained sample, the average $\rho_{\text{el-gb}}$ 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 ρ_{Kapitza} , interfacial electrical resistance $\rho_{\text{el-gb}}$ and interfacial Seebeck coefficient α_{gb} , the thermoelectric efficiency across the same temperature drop can be defined in the same manner, giving an interfacial zT_{gb} as

$$zT_{gb} = \frac{\alpha_{gb}^2}{\rho_{\text{el-gb}}/\rho_{\text{Kapitza}}} T \quad (6)$$

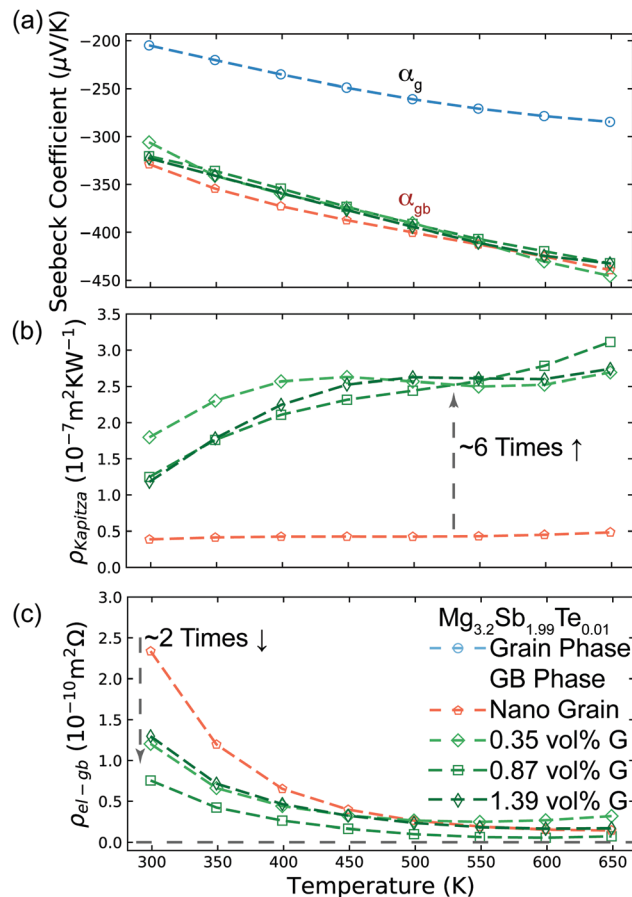


Fig. 4 Analysis of $Mg_{3.2}Sb_{1.99}Te_{0.01}$ samples with and without GNP using the two-phase model. (a) Seebeck coefficient of the grain phase (α_g) and grain boundary phase (α_{gb}) in the various $Mg_{3.2}Sb_{1.99}Te_{0.01}$ samples with and without the presence of GNP. $|\alpha_{gb}|$ is significantly higher than that of the grain phase, due to the presence of an energy barrier at grain boundaries. The inferred α_{gb} of all samples are the same, reflecting the same band offset at the grain boundaries with and without GNP. α_{gb} was inferred by applying eqn (3), while α_g was extracted from the smooth fitting curve of the large grain sample in Fig. 3d between 300 K to 650 K with a step of 50 K. (b) Interfacial thermal resistance (ρ_{Kapitza}) of the grain boundary phase in various $Mg_{3.2}Sb_{1.99}Te_{0.01}$ samples. The inclusion of GNP in the grain boundary results in an increase of ρ_{Kapitza} . ρ_{Kapitza} was inferred by applying eqn (4) and the measured grain size (see S5.2, ESI†). (c) Interfacial electrical resistance ($\rho_{\text{el-gb}}$) of the grain boundary phase in various $Mg_{3.2}Sb_{1.99}Te_{0.01}$ samples. $\rho_{\text{el-gb}}$ was inferred by applying eqn (5). The incorporation of GNP in the grain boundary results in a decrease of $\rho_{\text{el-gb}}$ in the temperature range below 500 K. For the range above 500 K where the energy filtering effect showing benefit, the GNP incorporation does not promote reduction of $\rho_{\text{el-gb}}$.

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.⁹ While the minimum thermal conductivity provides an important limit to bulk zT , Kapitza resistances are known to be able to be considerably large.^{44,45} 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, ESI†).⁴⁶



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