The Roles of Grain Boundaries in Thermoelectric Transports

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Fudong Zhang¹, Di Wu^{1*}, and Jiaging He^{2*}

² Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China

* Corresponding author, E-mail: wud@snnu.edu.cn; he.jq@sustech.edu.cn

Abstract

Grain boundary scattering was long recognized and widely utilized to regulate the transports of charge carriers and phonons in thermoelectric materials; nevertheless, the understanding of grain boundaries in lots of literatures seems somewhat lopsided and way too simplified, without distinguishing the exact microstructural characters for each individual case. In this perspective, we first review the well-known functions of grain boundaries on the electrical and thermal transport properties based on some representative thermoelectric series. Next, we try to deepen the understanding of the roles of grain boundaries in the following two aspects: (1) whether the grain boundaries are large-angle or small-angle ones, and what the difference between them in affecting electrical/thermal performance is; (2) whether the grain boundaries are clean and sharp as lattice discontinuity defects, if not, how can the grain boundaries as an individual phase affect the thermoelectric transports. At last, we suggest that further investigations engaging more detailed microstructural information of grain boundaries are urgently necessary in order to better realize a positive trade-off between lattice thermal conductivity and electrical power factor for an overall enhanced thermoelectric performance.

Key words: grain boundary angle; grain boundary phase.

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Main text

Thermoelectric effects, capable of directly and reversibly converting low-grade waste heat into electricity without moving parts, are exhibiting grain potential in the fields of power generation and heat pumping. The energy conversion efficiency of a thermoelectric device is generally determined by a dimensionless figure-of-merit ZT of consisting materials, $ZT = S^2 \sigma T / (\kappa_{lat} + \kappa_{ele})$, where S, σ , T, κ_{lat} , κ_{ele} denote the Seebeck coefficient, electrical conductivity, absolute temperature (in Kelvin), lattice thermal conductivity, and electronic thermal conductivity, respectivelyy^[1]. Effective approaches to obtain enhanced ZT values shall simultaneously maximize the power factor ($PF = S^2 \sigma$) and minimize the thermal conductivity ($\kappa = \kappa_{\text{lat}} + \kappa_{\text{ele}}$)^[2–3]. Unfortunately, these thermoelectric parameters are strongly coupled with each other, making it difficult to improve one individual parameter without degrading the others. Among these couplings, the most remarkable and tangled one is the tradeoff between lattice thermal conductivity and carrier mobility [4-9] via hierarchical microstructural defects.

Grain boundary (GB) is one of the most common and effective microstructural defects to realize a reduced lattice thermal conductivity, whose role on phonon scattering is usually modeled by a characteristic relaxation time $\tau^{-1} = v/d^{[10-12]}$, where v is the sound velocity and d the grain size. According

to this simplified model, a refined grain size necessarily leads to an enhanced phonon scattering rate and thus reduced lattice thermal conductivity. Although extremely impressively low lattice thermal conductivities and high thermoelectric properties were indeed achieved through nano-crystal preparation^[13-15] complying with this model, this simplified model encountered severe difficulty recently. Kim et al[16] took use of excess tellurium-assisted liquid phase sintering and fabricated a series of *p*-type Bi_{0.5}Sb_{1.5}Te₃ samples with record low lattice thermal conductivity, and ascribed it to the dense dislocation arrays embedded at micron-scale grain boundaries; subsequently, Meng et al^[17] reported in Yb-filled CoSb₃ that excess antimony-assisted liquid phase compaction could also produce micron-scale GBs with dense dislocations and significantly reduced lattice thermal conductivity. This obvious deviation prompts us to rethink the simplified phonon scattering model at grain boundaries.

Grain boundaries in principle refer to the interfaces between two grains with different crystal orientations. In the ideal case, a grain boundary has no thickness and only represents a plane of lattice discontinuity. At a high-angle grain boundary (HAGB) where the lattice discontinuity is large, the transport of low-frequency phonon (wavelength comparable with the dimension of grain boundaries) would be severely impeded and charge carriers encounter quite high an energy barrier across the boundary. In this point of view, the trans-

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¹ Key Laboratory for Macromolecular Science of Shaanxi Province, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, China

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ports of heat-carrying phonons and charge carriers are closely coupled; therefore, it seems difficult to realize a positive trade-off between them via regulating the GB angles. Nevertheless, researchers reported that grain refinement is an effective strategy to enhance phonon scattering for a reduced lattice thermal conductivity κ_{lat} without deteriorating electrical conductivity^[18-21]. For instance, Zheng et al systematically compared the thermoelectric performances of p-type Bi05Sb15Te3 zone-melted (ZM) ingots with samples synthesized with melt spinning plus a plasma-activated sintering (MS-PAS), as shown in Figure 1^[22]. As the back-scattered electron (BSE) images show in Figure 1a-b, the as-cast ZM ingots exhibit long strip shape micron-scale grains (> 100 µm) while the grains of MS-PAS samples are much smaller (< 30 μm in average). It is surprisingly found that the lattice thermal conductivity gets significantly reduced from ~ 1.0 Wm⁻¹ K⁻¹ to ~

0.5 Wm⁻¹ K⁻¹ after grain refinement, Figure 1d, and that the charge carrier mobility μ_{H} and power factor *PF* of MS-PAS samples can still compete with those of as-cast ZM ingots at the same composition/carrier concentration, Figure 1c. It can thus be concluded that grain refinement alone in the case of HAGB can indeed induce strengthened phonon scattering but tends to make little changes to energy barrier height which determines the charge carrier transport across GBs. In another word, as long as the lattice discontinuity (GB angles) of HAGB retains, one can take use of grain refinement to realize a partial de-coupling between electrical and thermal conductivity; once the GB angles change, the height of energy barrier at GBs would change accordingly, resulting in unfore-seeable variation of electrical transport behavior in lots of literatures^[23–26].



Fig. 1 (a)(b) Comparison of BSE images between rough grains in an as-cast ingot and refined grain in a MS sample of the same $Bi_{0.5}Sb_{1.5}Te_3$ composition. Reproduced with permission.^[22] Copyright 2014 Wiley-VCH. (c) carrier mobility and *PF*, (d) *T* dependence κ_{lat} of $Bi_{0.5}Sb_{1.5}Te_3$ ingot and mechanically robust polycrystal by grain refinement ^[22].

Grain boundaries also have profound effects on charge carrier transport, *i.e.*, charge carrier mobility and Seebeck coefficient. The degrading of carrier mobility across grain boundaries is counted as grain boundary scattering, while the mechanism explaining how Seebeck coefficient gets enhanced at grain boundaries is usually defined as the energy filtering effect^[27]. Martin *et al*^[28] found a unique temperature dependence of carrier mobility in PbTe-based nano-composites, and proposed that charge carriers that are trapped at grain boundaries would form energy barriers that impede further electrical conduction of those low-energy charge carriers which contribute negatively to the overall Seebeck coefficient across the boundaries. A subsequent work^[29] obtained a fitted value of barrier height at grain boundaries and explained the enhanced power factor in ZnSb-based thermoelectric material in a more theoretical aspect. However, the physical meaning of fitted energy barrier heights at GBs in most works were not provided, whether and how they shall



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be related to the localized crystalline orientation/mismatching at GBs were rarely discussed.

Heat-carrying phonons and charge carriers get indiscriminately scattered across a high-angle grain boundary; however, when they travel across a low-angle grain boundary (LAGB) where the lattice orientations of neighboring grains are close, things are quite different. At a typical LAGB, lattice discontinuity concentrates at localized dislocations whose density is determined by the GB angle ϕ ; high- and mid- frequency phonons would be scattered by the dislocation arrays but charge carriers (except for low-energy ones) could always pass through the boundary along the (relatively) continuous lattice in between neighboring dislocation arrays where local strain is minimal. In the past decades, several processing technologies have been developed to introduce a high fraction of LAGB in state-of-the-art TE materials^[16,18,30–33]. LAGB can be obtained usually *via* a liquid phase sintering method and featured by the dense dislocation arrays as shown in Figure 2^[16–17]. Geometric phase analysis (GPA) indicates that elastic strain is mainly localized near dislocation cores, and the splitting of fast Fourier transform (FFT) patterns near GBs can be used to determine how large the lattice mismatching angle is



Fig. 2 Low-angle grain boundaries. (a)-(e) Periodic Moiré patterns at LAGBs and FFT images of adjacent grains crossing a tilt-type GB. Reproduced with permission.^[16] Copyright 2015 American Association for the Advancement of Science. (f)(g) Selected electrical and thermal transport properties of S-MS sample with HAGBs and Te-MS sample with LAGBs^[16]. (h) A high-resolution LAGB in Bi_{0.5}Sb_{1.5}Te₃ alloy, (i)-(j) GPA mappings, and (k) corresponding FFT images. Reproduced with permission.^[32] Copyright 2017 Elsevier.



between two adjacent grains^[32]. When dense dislocation arrays are meticulously designed at LAGBs, a synergy of reduced lattice thermal conductivity and improved charge carrier mobility than that of control samples with HAGBs can eventually be achieved^[16]. As the lattice discontinuity (GB angle) decreases, two effects will be induced: (1) dislocation density at GBs reduces, and (2) energy barrier height goes down. The first effect goes against the enhancement of phonon scattering while the second effect is in favor of higher charge carrier mobility; a balance has to exist at an optimal LAGB angle. It is also worth noting that grain refinement could ruin the LAGB character since the crystalline orientation physically tends to be very random when refined grains are being compacted during a typical heat/pressure-assisted sintering process, turning into the HAGB case as mentioned above. One also needs to be noticed that there are no universal rules suggesting LAGBs are preferred than HAGBs or vice versa. Whether HAGBs or LAGBs are preferred depends on the actual thermal transport character in a specific material. Specifically, if the thermal conduction in a specific material is dominated by low-frequency phonons, then it is suggested using HAGBs to realize reduction of lattice thermal conductivity; by this way, one might (but not necessarily) achieve a positive trade-off between reduced lattice thermal conductivity and simultaneously reduced electrical conductivity. If the conduction transport is dominated by mid- and high- frequency phonons in a certain material where HAGBs are not capable of reducing lattice thermal conductivity effectively,

one then needs LAGBs to regulate phonon transport without obviously affect charge carrier transport, eventually realizing an overall positive trade-off between them.

Grain boundaries are usually hypothesized to be mere planar defects where lattice discontinues; however, this hypothesis encounters difficulties in explaining the abnormal dependence of electrical conductivity on temperature and the overestimation of lattice thermal conductivity, for instance in degenerate semiconductor Mg₃Sb₂^[34] and others^[25,35]. Kuo et al^[34,36-37] proposed a two-phase model which counts for the role of grain boundaries in electrical and thermal conduction as an individual phase in Mg₃Sb₂-based materials, and experimentally observed the composition deviation of GBs from that of main matrix using atom probe tomography (APT), Figure 3a-d. With properly selected parameters, this two-phase model addresses the discordance of electrical can thermal contribution to heat-conduction, and induces that lattice thermal conductivity derived with traditional method (GB as planar defect) is actually overestimated. Moreover, once introducing a temperature dependent resistivity for the GB phase, this two-phase model can also resolve the thermally-activated electrical conduction behavior as shown in Figure 3e. The GB-resistances of both charge carriers and phonon are detrimental to the overall thermoelectric performance. One possible way to eliminate the GB-resistance is to reduce the grain boundary density as shown in Figure 3f; however, one needs to reconsider how to compensate the simultaneously weakened phonon scattering. Constructing



Fig. 3 (a) Equivalent circuits for treating thermal and electrical resistance of grain boundaries. (b) Electrical and thermal transports in conventional use of the Wiedemann-Franz law (Fig. 3(b)-left) and when considering thermal and electrical resistance of grain boundaries in a two-phase model (Fig. 3(b)-right). Reproduced with permission.^[34] Copyright 2020 Royal Society of Chemistry. (c)(d) 3D reconstruction of the atom distribution and projected atom density map in *n*-type Mg_3Sb_2 by Atom Probe Tomography (APT), the upper-right inset is a scanning electron microscope image. Reproduced with permission.^[36] Copyright 2019 Wiley-VCH. (e) Scheme of thermally activated conduction behavior diminishing with increased grain size in $Mg_{3,2}Sb_{1,5}B_{0,49}Te_{0,01}$. (f) Upper limit of the figure-of-merit *ZT* with different grain size. Reproduced with permission.^[37] Copyright 2018 Royal Society of Chemistry.



LAGBs with proper GB angle and dislocation density could be a good choice. Another possible way to eliminate the GB-resistance is to optimize synthesis technique to avoid element segregation at grain boundaries; as thus, the GB regulation of HAGBs and LAGBs is then applicable. Furthermore, one also needs to pay attention to the thermodynamic stability of the grain interfaces as studied by Xiong *et al*^[38] when they explored the sintering details for Bi₂Te_{2.7}Se_{0.3} nanoplatelet-composites for TE applications. Regulable thermodynamic behavior of grain boundary phases might provide additional benefits to thermoelectric optimization.

In this perspective, we addressed the importance of lattice discontinuity degree at GBs for phonon and charge carrier transports in the view point of high-angle grain boundary and low-angle grain boundary, and also distinguished grain boundaries as mere planar defects from the case that GBs stand as an individual secondary phase engaging electrical and thermal conduction. The specific microstructure at grain boundaries is much more complicated than what we usually treated in traditional electrical/thermal transport models, and also varies from case to case. Detailed investigations of local microstructural characters at grain boundaries are thus necessary and may help us better understand the various electrical/thermal transport behaviors due to grain boundary scattering in each specific case, so as to guide the grain boundary regulation for an overall beneficial trade-off between electrical and thermal conduction in thermoelectrics.

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Conflict of interest

The authors declare no conflict of interest.

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Biographies



Fudong Zhang is currently a Ph.D. candidate in School of Materials Science and Engineering, Shaanxi Normal University. His primary research interest is focused on Bi_2Te_3 -based thermoelectric compounds, specifically, the sample synthesis, characterization and mechanism of thermoelectric transport.



Di Wu joined School of Materials Science and Engineering of Shaanxi Normal University in 2017, after spending four years in Southern University of Science and Technology as a research assistance professor. His researches currently focus on interrelation between physical properties and microstructures in functional materials, such as ther-

moelectric materials and dielectric/ferroelectric ceramics.



Jiaqing He is a Chair professor at Southern University of Science and Technology (SUSTech). He received his joint Ph.D. degree in physics from both Juelich Research Center and Wuhan University in 2004. He was a post-doctor at Brookhaven National Laboratory (2004–2008), research associate (2008– 2010) and research assistant professor

(2010–2012) at Northwestern University, and a professor at Xi'an Jiaotong University (2012–2013) and SUSTech (2013-2019). His research interests include transmission electron microscopy, thermoelectric materials, and structure and property relationship.

