SYSTEMATIC INVESTIGATION OF THE MISORIENTATION- AND TEMPERATURE-DEPENDENT KAPITZA RESISTANCE IN CeO_2

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Abstract The misorientation- and temperature-dependent grain boundary thermal (Kapitza) resistance in CeO_2 is investigated using molecular dynamics simulations. A few empirical potentials for molecular dynamics simulations are evaluated for their predicted properties such as the phonon dispersion curves, bulk thermal conductivity, and grain boundary structures. Through the comparison of these properties with experimental results, the most reasonable potential (Gotte2007) is selected. The Kapitza resistances of tilt and twist grain boundaries with misorientation angles ranging from 3° to 60° are calculated and a clear transition angle at about 16° is observed. The Kapitza resistance is found to increase almost linearly with misorientation angle in the low-angle regime but remain nearly constant at the high-angle regime, a behavior very similar to the grain boundary energy. A nearly linear correlation between Kapitza resistance and grain boundary energy is thus obtained. Similar to the grain boundary energy, the Read-Shockley model can well describe the misorientation-dependent Kapitza resistance at low-angle regime. The Kapitza conductance (the inverse of Kapitza resistance) is found to increase almost linearly with temperature in our simulations.

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1. Introduction

Mass, charge and energy transport properties of a material system are intimately connected to the presence of interfaces, either homogenous type such as grain boundaries (GBs) or heterogeneous type such as interfaces between different materials or phases. In the context of the heat transfer, the effect of increased thermal resistance due to an interface was discovered by Kapitza in 1941¹ in the liquid helium-metal system, but later has been demonstrated to be ever-present in any type of interfaces.² Therefore, an interface thermal resistance is termed as Kapitza resistance, and it plays an important role in many technological applications. For example, high density of heterogeneous interfaces in BiTe/SbTe superlattices and subsequent reduction of the thermal conductivity due to Kapitza resistance is the key in making these materials the most efficient thermoelectric to date.³ In contrast, in applications where thermal conductivity has to be maximized interfaces might be detrimental to the performance of materials or devices. For example, interfacial resistance prevents efficient cooling of the high-power GaN electronics and is currently a bottleneck for harvesting their full potential.⁴

In many ceramic materials, where phonons are the main thermal energy carriers, interfaces provide an additional phonon scattering mechanism which qualitatively explains the reduction of the thermal conductivity as the density of interfaces increases. The mechanism is applicable to not only the aforementioned heterogeneous interfaces, but also homogenous interfaces such as GBs. Yang et al. explicitly demonstrated the effect in the nanocrystalline ZrO_2 ,⁵ by finding that thermal conductivity depends strongly on the grain size and decreases rapidly with the increased interfacial density. Quantitative prediction of the thermal conductivity reduction due to GBs is essential in many applications, such as nuclear fuel performance, or thermal barrier coatings. Unfortunately, quantitative theories developed in the past, so-called acoustic mismatch model (AMM) and diffuse mismatch model (DMM)² are not applicable in the context of GBs. Namely, AMM predicts zero thermal conductivity for any homogenous interface, while DMM predicts that GBs of any orientation will have the same Kapitza resistance. Thus, important details of the Kapitza resistance of GBs such as the dependence on misorientation, remain largely unexplored. Experimental measurements either focused on the averaged Kapitza resistance over a GB population^{5, 6}, or studied the resistance in bicrystals that are laborious to fabricate and thus only a limited number of GB misorientations are sampled.⁷ Molecular dynamics simulations have been employed to study misorientation dependence in symmetric $\langle 001 \rangle$ twist GB in diamond⁸ and a limited sampling of the GBs in Si^{9, 10} and UO_2 .¹¹ While restricted to small number of GBs, these studies demonstrated that boundary conductance correlates strongly with the GB energy. In this work we address the thermal transport properties of a large number of twist and tilt GBs in ceria (CeO_2) of different misorientations via non-equilibrium molecular dynamics (NEMD) approach.

NEMD has been widely used for studying phonon-mediated thermal transport problems in semiconductors and oxides as outlined in a recent review.¹² Since MD can model much larger simulation systems than density functional theory (DFT) method can do, many microstructural features such as grain boundaries,^{8, 11} voids,^{13, 14} and dislocations¹⁵ can be included in the simulation. However, the main disadvantage of the NEMD for the thermal transport simulations is the reliance on the empirical potentials, which typically are not fitted to reproduce those. We therefore first evaluate the quality of the available ceria potentials^{16, 17} with respect to bulk thermal conductivity and GB structures, both of which can be compared with experiments. For bulk thermal conductivity, we employ a fast and accurate approach based on the solution of the Boltzmann Transport Equation (BTE) for phonons as implemented in the PhonTS package.¹⁸ For GB structures, we construct some special GBs in MD simulations and compare their minimum-energy structures with the published high-resolution transmission electron microscopy (TEM) images in literature. While accurate bulk thermal conductivity and GB structures do not guarantee an adequate representation of the interfacial resistance due to the integral nature of

thermal conductivity,¹⁹ it is nevertheless a reasonable way to select the most appropriate potential for the simulations.

The paper is organized as follows: In the section 2 we describe the computational methods employed in this work. Section 3 presents BTE calculations of the thermal conductivity in a bulk ceria predicted by various interatomic potentials available from the literature and motivates the potential choice for the GB studies. In Section 4 we present structural analysis of the GBs predicted by the selected potential and compare the GB structures with available experimental data, thus further validating the choice of potential. These results are discussed and related to other GB properties. In the next two sections we present our results of the Kapitza resistance for a large number of tilt and twist GBs of different orientations and at different temperatures. Finally, we discuss our results and present conclusions of this work.

2. Computational details

The quality of classical potentials of CeO₂ employed in this work has been surveyed previously with respect to their predicted surface properties by Galea et al.¹⁶ and mechanical properties by Xu et al.¹⁷ with some overlap in potentials tested. We maintain the designation of the potentials used in these two works and use the designation by Xu et al.¹⁷ for overlapping potentials. Since these works a few additional potentials appeared in the literature.^{20, 21} Unfortunately, the parameters for the ceria potential developed by Walsh et al.²¹ were not reported, while the potential developed by Burbano et al.²⁰ has not been implemented in PhonTS software. Therefore, we exclude these potentials from our discussion. All the potentials considered here employ the same functional form which includes a Coloumbic term that describes the electrostatic interaction between ionic charges q_i and q_j , and a Buckingham term that has both short-range repulsion and long range attraction

$$V(r_{ij}) = \frac{q_i q_j}{r} + A e^{-\rho r_{ij}} - \frac{C}{r_{ij}^6}, \quad (1)$$

where r_{ij} is the distance between two ions i and j , A , ρ and C are Buckingham potential parameters. Nearly all potentials also include a core-shell model²² which accounts for atomic polarizability. The essence of the core-shell model is to represent the negatively charged electron cloud around an ion (core) as a massless spherical shell. In the model, the shell is connected to the core by a harmonic potential so that it can move a distance relative to the ion core position to capture the polarization effect.

Thermal conductivity of bulk ceria is computed by BTE for phonon formalism, as described in details elsewhere.²³ In short, this approach calculates lattice thermal conductivity by considering lattice vibrations, or phonons, as heat carriers. In a harmonic picture, thermal conductivity by phonons is infinite, thus the leading anharmonic cubic term is considered using the perturbation theory. This leads to phonon-phonon scattering via 3-phonons processes. We further assume weak non-equilibrium and linearize BTE in terms of the function $\Phi_{\vec{k},n}$ which describes the deviation from the equilibrium Bose-

Einstein distribution $f_{\vec{k},n}^0$ of the phonons in state with wave-vector $\vec{k}$ and branch n . BTE thus takes the form

$$-\vec{v}_{\vec{k},n} \cdot \frac{\partial f_{\vec{k},n}^0}{\partial T} \nabla T = \frac{1}{k_B T} \left\{ \sum_{\vec{k}',n',\vec{k}'',n''} \left[(\Phi_{\vec{k},n} + \Phi_{\vec{k}',n'} - \Phi_{\vec{k}'',n''}) \Lambda_{\vec{k},n,\vec{k}',n',\vec{k}'',n''}^{\vec{k},n} + \frac{1}{2} (\Phi_{\vec{k},n} - \Phi_{\vec{k}',n'} - \Phi_{\vec{k}'',n''}) \right] \Lambda_{\vec{k},n,\vec{k}',n',\vec{k}'',n''}^{\vec{k}',n'} + \dots \right\} \quad (2)$$

In this equation, $\vec{v}_{\vec{k},n}$ is the group velocity of the phonon; T is the temperature; k_b is a Boltzmann constant; Λ is the equilibrium transition rates for a specific process, computed on the basis of the

perturbation theory. The first term on the right hand side describes the recombination process, where two phonons in the states k, n and k', n' combine to form a phonon in the state k'', n'' , while the second term describes dissociation process for a phonon k, n into two phonons k', n' and k'', n'' . Transition rates for these processes can be computed from the following expressions

$$\begin{aligned}\Lambda_{\vec{k}, n, \vec{k}', n'}^{\vec{k}'', n''} &= \frac{2\pi}{\hbar} \Gamma_{nn', \vec{k}\vec{k}'}^2 f_{\vec{k}, n}^0 f_{\vec{k}', n'}^0 (f_{-\vec{k}'', n''}^0 + 1) \delta(\hbar\omega_{\vec{k}, n} + \hbar\omega_{\vec{k}', n'} - \hbar\omega_{\vec{k}'', n''}) \\ \Lambda_{\vec{k}, n}^{\vec{k}', n', \vec{k}'', n''} &= \frac{2\pi}{\hbar} \Gamma_{nn', \vec{k}\vec{k}'}^2 f_{\vec{k}, n}^0 (f_{-\vec{k}', n'}^0 + 1) (f_{-\vec{k}'', n''}^0 + 1) \delta(\hbar\omega_{\vec{k}, n} - \hbar\omega_{\vec{k}', n'} - \hbar\omega_{\vec{k}'', n''}), \\ \Gamma_{nn', \vec{k}\vec{k}'} &= i \frac{(\hbar/2)^{3/2}}{V^{1/2}} (\omega_{\vec{k}, n} \omega_{\vec{k}', n'} \omega_{\vec{k}'', n''})^{-1/2} \sum_{IJK} \frac{\bar{B}_{IJK; \vec{k}\vec{k}'}^{\vec{k}''}}{m_I^{1/2} m_J^{1/2} m_K^{1/2}} \vec{e}_{I; \vec{k}; n}^* \vec{e}_{J; \vec{k}'; n'}^* \vec{e}_{K; \vec{k}''; n''}^*\end{aligned}\quad (3)$$

here, $\hbar$ is the Planck's constant, I, J and K are indexes that count atoms of corresponding masses m in the primitive cell, V is the volume of the cell, while $\vec{e}_{I; \vec{k}; n}$ is the eigenvector of the phonon with frequency $\omega_{\vec{k}, n}$. $\bar{B}_{IJK; \vec{k}\vec{k}'}^{\vec{k}''}$ is a Fourier-transform component of the cubic anharmonic term and δ -functions enforce conservation of energy in the corresponding 3-phonon process. Once transition rates are calculated, BTE in Eq. (2) can be solved for unknown deviation from equilibrium $\Phi_{\vec{k}, n}$ thus allowing one to compute phonon heat current. Due to the assumption of weak non-equilibrium, or small temperature gradient, Fourier law is applicable and permits extraction of the thermal conductivity. All calculations in the Section 3 are performed using a six-atom orthorhombic primitive cell of CeO₂ with the k-mesh resolution for phonons calculations of 11×11×9. Thermal expansion is taken into account within the quasiharmonic approximation^{24, 25} and all calculations are performed at 300K. The relaxation time approximation (RTA) is found to be sufficiently accurate in ceria for the solution of the BTE, as compared with the full iterative solution; this result was also established in isostructural UO₂.²⁶

Kapitza resistance is calculated using NEMD. This method mimics a basic experimental setup for thermal conductivity measurements by introducing and removing a fixed amount of heat from the specific locations in the simulation cell thus establishing a thermal gradient between these two points. Knowledge of the amount of heat added/removed at those locations permits calculations of the heat current $\vec{j}$, while temperature measurements between them enable calculation of the thermal gradient. Thus Fourier law may be applied to calculate thermal conductivity of the material. If any interface, such as a GB, is placed in between the heater and cooler then there is a temperature jump ΔT at the interface. By measuring this jump Kapitza resistance R might be extracted using the equation

$$\Delta T = R \cdot \vec{j}_{\perp}. \quad (4)$$

The geometry that implements this approach is an elongated rectangular parallelepiped periodically repeated in each dimension, as illustrated in the Figure 1(a). Periodicity requires two identical regions to be present in the system, thus two measurements of the thermal jump is performed simultaneously. For the purpose of the temperature measurements, the simulation cell is partitioned into many slices along the long axis and the temperature of each slice is computed by averaging the atomic kinetic energy of atoms belonging to this slice. A representative of the temperature profile across a GB is shown in Figure 1(b). Initially, we equilibrate the entire simulation cell is using an Isothermal–isobaric (NPT) ensemble at 300K and zero pressure for 40 ps without adding/removing any energy into the heater/cooler. Equilibration is followed by imposing a microcanonical (NVE) ensemble and turning on heat addition/removal. Temperature distribution in the sample is typically stabilized within 10-15 ps, depending on the particular system size, after which temperature jump at the interfaces is averaged over the 1ns. Since different GBs have different cross sections, as well as different lengths of the simulation cells, we carefully verified that our results for Kapitza resistance are not sensitive to these parameters by considering different sized systems for one of the GBs. System sizes in this work range from ~30000 atoms for the high-angle GBs and up to ~500000 atoms for the low-angle ones. The typical

length of the simulation cell along the direction of the thermal gradient is about 400 Å, while the cross-section varies from 22.6Åx26.1Å for the high-angle $\Sigma 11$ twist GB to 126Åx126Å for low-angle $\Sigma 129$ twist GB. All the MD simulations are conducted using the LAMMPS software package²⁷.

Figure 1 (a). Simulation setup for calculating the thermal properties using the non-equilibrium molecular dynamics. **(b)** A representative temperature profile across a GB (the other GB is induced by the periodic condition). The symbols are from MD simulation and the lines are least-square linear fits of the data in the linear regimes.

We note, that NEMD, as any MD simulations, does not include quantum effects in its description of atomic motion and thus strictly speaking is applicable for calculating the thermal conductivity at temperatures comparable and above the Debye temperature of the material of interest. In CeO_2 , the Debye temperature as defined from elastic constants is about 500 K. Since some MD simulations reported in this work were performed at somewhat lower temperature of 300K, we expect that our results will overestimate the boundary conductance. However, our main interest in this work is in the variability of boundary conductance with regard to misorientation angle, and we do not expect the trend to be affected by our choice of method.

3. Thermal transport in the bulk CeO_2 by classical potentials

We present results of our calculations of thermal conductivity as predicted by classical potentials using the BTE method in Figure 2. Both shell model and rigid-ion variants are presented for comparison with the experimental data.²⁸ One can see a significant variation in the predicted thermal conductivity at 300K ranging from 13.2 to 46.5 W/mK. Such variation is typical of different classical potentials developed for the same system, as observed in Si ²⁹, MgSiO_3 ³⁰, UO_2 ²⁵ and C ³¹. The variability stems from the fact that anharmonic properties of the materials, i.e. the properties that can be described as phonon-phonon interactions, are rarely targeted during potential fitting. Interestingly, although the phonons' structure is poorly reproduced by a potential, sometimes it may predict a reasonable thermal conductivity due to the cancellation of errors.¹⁹ As an example, we present in Figure 3 the phonon dispersion curves of the potentials considered in this work that predict thermal conductivities close to the experimental value in comparison with the phonon dispersion curves obtained from our ab initio density functional theory (DFT) calculations. The latter are in excellent agreement with previously published ab initio and inelastic neutron scattering data.³² Potentials presented in Figure 3 are IP4,³³ Inaba³⁴ and Gotte2007,³⁵ all of which (either with or without the core-shell model) predict thermal conductivity within 5% variation of the experimental value. IP4 shell model potential reproduces the transverse acoustic (TA) and first transverse optical (TO_1) modes very well, but the longitudinal acoustic (LA) mode has consistently greater energy than the reference DFT data. More importantly, the energies of the first longitudinal optic (LO_1) and second transverse optic (TO_2) modes are also significantly overestimated, with the difference at Γ point being $\sim 3\text{THz}$. Importance of these optical modes is two–

fold. Firstly, the LO_1 mode is expected to contribute substantially to the overall thermal conductivity based on the comparison with isostructural UO_2 ³⁶. Secondly, positioning of the optical modes dictates available 3-phonon scattering channels for the acoustic modes, and thus indirectly controls their contribution to the thermal transport. Inaba potential, which does not include the shell model, suffers even more from this deficiency of the optical modes, including the TO_1 mode, while the LA mode is quite accurate. In contrast, although Gotte2007 rigid-ion potential overestimates the energies of both TA and LA modes, the TO_1 , LO_1 and TO_2 modes are aligned much closer with the DFT data than other potentials. All the potentials significantly overestimate the most energetic second longitudinal (LO_2) mode. However, its energy is large enough so that it has a small influence on the overall thermal transport. Gotte2007 rigid-ion potential, on balance, has the best representation of the phonon structure among the surveyed potentials. It is extremely satisfactory to observe that Gotte2007 rigid-ion potential is also one of the better potentials for the prediction of the bulk thermal conductivity, with value of 18.3 W/mK at 300K, very close to the experimental value of 17.5 W/mK.

Figure 2. Thermal conductivity of CeO_2 as predicted by available interatomic potentials using Boltzmann Transport Equation method. The experimental value is taken from Khafizov et al.²⁸

For each potential that includes the shell model, we note that the thermal conductivity of the shell model variant is lower than that of the corresponding rigid-ion model, as shown in Figure 2. As discussed in details elsewhere²⁵, the shell model significantly softens the optical phonon modes in comparisons with rigid-ion-only models. This trend can also be observed in Figure 3, where red squares represent potentials with the shell model. This softening has two-fold effects on thermal conductivity: it reduces the phonon group velocity and increases the phase space for the possible three-phonon interactions. As a result the potentials with the shell model predict a lower thermal conductivity as compared with their rigid-ion counterparts, sometimes dramatically, as seen in the example of the Butler and IP4 potentials in Figure 2.

Figure 3. Phonon structure along the [001] direction as predicted by (a) DFT calculation, (b) IP4 potential, (c) Inaba potential and (d) Gotte2007 potential in CeO_2 . Black open symbols represent rigid ion potentials, while red open ones are shell model variants.

4. Grain boundary structures in CeO_2

In the previous section, the Gotte2007 rigid-ion potential was found to predict a reasonable bulk thermal conductivity with respect to the experimental value. Since the main focus of this work is to study the GB thermal resistance, it is necessary to investigate whether this potential also predicts reasonable GB structures. Previously, the structures of the two special coincidence lattice site (CSL) GBs in some fluorite oxides have been determined experimentally: $\langle 001 \rangle \Sigma 5(310)$ tilt with a misorientation angle of 36.9° and $\langle 001 \rangle \Sigma 5(210)$ tilt with a misorientation angle of 53.1° . Therefore, these two GBs are selected for comparison. The initially unrelaxed structures of the two GBs are created using the online software GBstudio³⁷. The gamma surface of each GB at 0 K, which is the GB energy landscape with respect to the relative in-plane translations between two grains³⁸, is mapped out using molecular statics calculations with the Gotte2007 potential. From the gamma surface, the minimum-energy GB structure for each GB is obtained.

Figure 4(a) shows the minimum-energy GB structure of the $\langle 001 \rangle \Sigma 5(310)$ tilt GB predicted by the Gotte2007 potential. The GB energy is about 2.51 J/m^2 . To the best of the authors' knowledge, the detailed experimental determination of this GB structure in CeO_2 is not available. However, previously Dickey et al.³⁹ used scanning transmission electron microscopy to determine the atomic structure of the $\langle 001 \rangle \Sigma 5(310)$ tilt GB in Yttria-Stabilized Cubic-Zirconia (ZrO_2) and the image is shown in Figure 4(b). The reconstructed GB structure based on the experimental investigation is schematically illustrated in Figure 4(c). Since both cubic ZrO_2 and CeO_2 have the same fluorite crystal structure with the space group of $Fm\bar{3}m$ (No. 225), we expect that in CeO_2 it has a similar $\langle 001 \rangle \Sigma 5(310)$ GB structure as in cubic ZrO_2 . Similar assumption has also been made for UO_2 by Nerikar et al.⁴⁰ previously. To compare with experiments, the two adjacent cation (Ce) layers in the Z direction are represented by larger spheres in different colors in Figure 4(a). The Ce sublattice forms a special structural unit at the GB, which is very similar to the experimentally determined structure (Figure 4(b-c)). The oxygen sublattice (smaller spheres in Figure 4(a)) is also similar to the reconstructed structure in experiment (Figure 4(c)), except for some small local distortions around each structural unit.

Figure 4. Comparison of the $\langle 001 \rangle \Sigma 5(310)$ tilt GB structure between this modeling work and experiment. (a) The GB structure in CeO_2 predicted by the Gotte2007 potential. Larger spheres in red and green colors represent Ce atoms at two adjacent layers in the Z direction, respectively. Small black spheres represent oxygen atoms. (b) The scanning transmission electron microscopy image of the cation positions at the GB in cubic ZrO_2 (image reproduced with permission),³⁹ which has the same crystal structure as CeO_2 . (c) The reconstructed GB structure based on experimental measurement in cubic ZrO_2 (image reproduced with permission).³⁹

Figure 5(a) shows the minimum-energy GB structure of the $\langle 001 \rangle \Sigma 5(210)$ tilt GB predicted by the Gotte2007 potential. The GB energy is about 2.53 J/m^2 . The Ce sublattice forms another type of structural unit at the GB, which is different from the structural unit of $\langle 001 \rangle \Sigma 5(310)$ tilt GB. Hojo et al.⁴¹ used scanning transmission electron microscopy to study the GB structure of the $\langle 001 \rangle \Sigma 5(210)$ tilt GB in CeO_2 and the image is shown in Figure 5(b). Clearly, the GB structural unit predicted by the Gotte2007 potential is very similar to that found in experiment. The positions of oxygen ions at the GB were not provided in Figure 5(b), but their positions in the grain interior are identical between our modeling and Hojo et al.'s experiment.

Figure 5. Comparison of the $\langle 100 \rangle \Sigma 5(210)$ tilt GB structure between modeling and experiment. (a) The GB structure in CeO_2 predicted by the Gotte2007 potential. Large blue spheres represent Ce atoms and small black spheres represent oxygen atoms. (b) The scanning transmission electron microscopy image of the GB structure in CeO_2 (image reproduced with permission).⁴¹

Overall, the Gotte2007 rigid-ion potential predicts very reasonable $\langle 001 \rangle \Sigma 5(310)$ tilt and $\langle 001 \rangle \Sigma 5(210)$ tilt GB structures with respect to experimental results. Given the fact the this potential predicts excellent bulk elastic properties¹⁷, good bulk thermal conductivity as discussed in Section 3, and very reasonable GB structures, the rigid-ion version of this potential is selected for studying the GB thermal resistance in this work.

5. Misorientation-dependence of Kapitza boundary resistance in CeO_2

With the best potential for thermal transport in CeO_2 bulk and GB structures identified we now turn our attention to Kapitza resistance of GBs in CeO_2 . Similar to the method described in Section 4, GBs used in this work are all obtained using GBStudio software.³⁷ Both twist and tilt GBs are studied. For twist boundaries, rotation axis is oriented along the $\langle 001 \rangle$ direction with misorientation angle in the range of 3.47° - 43.6° , along the $\langle 011 \rangle$ direction with angles in between 13.4° - 86.6° , and along the $\langle 111 \rangle$ direction with angles of 13.2° - 60.0° . For tilt GBs, the rotation axis is oriented along $\langle 001 \rangle$ and the misorientation angles in the range of 3.27° - 53.13° . Total number of GBs considered is 33, making it significantly larger than previous similar investigations in other materials^{7,8,11}.

Figure 6. Kapitza resistance (a,c) and GB energy (b,d) in CeO_2 as a function of the misorientation angle for twist (a,b) and tilt (c,d) GBs. Lines are the results of the Read-Shockley-like model fit to the entire dataset.

Using the method described in the Section 2, the Kapitza resistance of each GB predicted by the Gotte2007 potential is calculated with molecular dynamics simulations at 300 K. Figure 6(a,c) show the results of the Kapitza resistance as a function of the misorientation angle for twist and tilt GBs,

respectively. One main observation from the calculation results is that Kapitza resistance has two distinct regimes around 16° : low-angle regime ($< 16^\circ$) and high-angle regime ($\geq 16^\circ$).

In the low-angle regime, the Kapitza resistance increases almost linearly with the misorientation angle. In previous experimental measurement of low-angle twist GBs in Al_2O_3 ,⁷ the GB Kapitza resistance also increases almost linearly with misorientation-angle. Therefore, the trend of our results is in excellent agreement with the experimental trend. In the high-angle regime, the Kapitza resistance seems to reach a saturated value. The saturated value depends on the GB families. For $\langle 001 \rangle$ tilt GBs, the saturated value is around $0.45 \text{ m}^2\text{K/GW}$. For the three families of twist GBs, the value fluctuates around $0.35 - 0.65 \text{ m}^2\text{K/GW}$. By average, the $\langle 011 \rangle$ twist family has the highest resistance while the $\langle 001 \rangle$ twist family has the lowest one.

The transition angle of 16° between two distinct regimes in GB thermal resistance coincides with the conventional definition of low- and high- angle GBs in metallic systems, in which GB energy is used as a criterion. In low-angle GBs, each GB consists of an array of isolated dislocations and the spacing between dislocations decreases with increasing misorientation angle. In high-angle GBs, the dislocation cores overlap. As a result, the GB energy increases with increasing misorientation angle and saturates at a certain value when the misorientation angle is larger than 16° (except for some special CSL GBs such as $\Sigma 3$ twin GB). To investigate whether this definition also applies to oxide systems, we calculate the GB energies of the twist and $\langle 001 \rangle$ tilt GBs using molecular statics simulations, as shown in Figure 6(b,d). Clearly, in CeO_2 the GB energy also has two distinct regimes and the transition angle is around 16° . Therefore, the conventional definition of low- and high-angle GBs for metals is also applicable for oxides.

The similarity between GB thermal resistance and GB energy with respect to misorientation angle indicates that there may be a strong correlation between them. Previous theoretical investigations identified a strong correlation between the GB energy and its Kapitza resistance^{8, 11} for diamond and UO_2 . Note that in these studies only a limited number of GBs (most of them are high-angle ones) were studied and the smallest angle was about 10° . To investigate whether such a correlation exists for both low- and high-angle GBs, we therefore present Kapitza resistance versus GB energy in CeO_2 for a wide range of misorientation angles and with a large number of GBs (33 in total) in Figure 7. As one can see there is indeed a very strong correlation between these two quantities. Note that the linear dash-dot line shown in Figure 7 is only a guide for the eye. The exact correlation may not be a simple linear function because the extrapolation of such a linear correlation at the vanishing GB energy will result in a unphysically negative value.

Such correlation makes it possible to apply an extended Read-Shockley model for describing the dependence of the Kapitza resistance on the GB angle.⁸ Such a model describes the GB resistance R on GB misorientation angle θ as (the same expression is applied to GB energy E , but with the replacement of parameters R with E)

$$R(\theta) = \begin{cases} 0 < \theta < 45^\circ: \sin(2\theta) (R_c^< - R_s^< \ln(\sin(2\theta))) \\ 45^\circ < \theta < 90^\circ: (R_c^< - R_c^>) + \sin(180^\circ - 2\theta) (R_c^> - R_s^> \ln(\sin(180^\circ - 2\theta))) \end{cases} \quad (5)$$

Figure 7. Correlation between GB energy and Kapitza resistance in CeO₂. Dash-dot line is a guide to the eye.

Where R_c and R_s are adjustable parameters. Fitting to our MD data, the values of these parameters are $R_c^< = 0.483$, $R_s^< = 0.276$, $R_c^> = 0.011$ and $R_s^> = -0.024$, in the unit of $\text{m}^2 \cdot \text{K} / \text{GW}$. Note that the same set of parameters are used for both twist and tilt GBs. Solid lines in Figure 6 represent the results of the fit, and as expected, at low angle boundaries it represents the data exceptionally well, while for larger angles the agreement is slightly less satisfactory. Such an expression for the GB Kapitza resistance permits us to estimate the average Kapitza resistance of GBs in CeO₂, if the GB distribution is known. Unfortunately, no such data is previously available for CeO₂.

6. Temperature-dependence of Kapitza Resistance

Kapitza resistance depends on not only GB misorientation, but also temperature.^{5, 42} To investigate the temperature dependence, molecular dynamics simulations were conducted to calculate the GB Kapitza resistance from 300 K to 2000 K, using the $\langle 001 \rangle \Sigma 5(310)$ tilt GB as a representative GB. Note that the melting temperature of CeO₂ in air is about 2753 K.⁴³ Even though the potential may predict a slightly different melting temperature, it is believed that the temperature range considered in this work is well below the melting temperature. The GB structure at the highest temperature (2000 K) was also checked after the simulation. Although the anion sublattice had some local distortions, the GB structural unit formed by the cations still had a very similar geometry as that in Figure 4. At each temperature, the system volume was relaxed in a NPT ensemble for about 40 ps before a thermal gradient was applied in a NVE ensemble. Using the same method described in Section 2 the GB Kapitza resistance was calculated. The result is shown in Figure 8(a). Clearly, the Kapitza resistance decreases with the increasing temperature. This temperature-dependent behavior of the Kapitza resistance is opposite to the thermal resistivity but similar as the thermal conductivity of the single crystal. Approximately, the GB Kapitza resistance can be fitted with a $1/(A+B \times T)$ function, where $A = 1.95914 \text{ GW/m}^2 \cdot \text{K}$ and $B = 9.7686 \times 10^{-4} \text{ GW/m}^2 \cdot \text{K}^2$. To compare with literature results, the temperature-dependent GB thermal

conductance, which is the inverse of the Kapitza resistance, is shown in Figure 8(b). The GB thermal conductance increases almost linearly with temperature, consistent with previous molecular dynamics simulations of UO_2 ⁴⁴ and a Lennard-Jones system.⁴⁵ Experimentally, the interface Kapitza conductance also increases approximately linearly with temperature in many materials,^{5, 42} such as GBs in yttria-stabilized-zirconia (YSZ), interfaces of $\text{Al}/\text{Al}_2\text{O}_3$, GeSbTe/ZnS , and metal/ SiO_2 /silicon (MOS), etc. However, the reported experimental data are at the low temperature range, typically below 400 K.

Note that all these simulations only examine the classical regime due to the inherent limitations of the classical molecular dynamics on describing the quantum effects and therefore comparison with experiments should be made with care. As mentioned above, experimental data is typically reported in the low temperature regime, where quantum effects are important and introduce more complicated temperature dependence. In the frameworks of AMM or DMM,² which accounts only for elastic scattering at the interfaces, temperature dependence enters through the phonon occupation numbers, and exhibits a behavior similar to that of the heat capacity: increasing as T^3 from absolute zero, leveling off around the Debye temperature, and remaining nearly constant at higher temperatures. In contrast, NEMD also accounts for the anharmonic or inelastic scattering effects, which were argued to be responsible for the linear increase of the Kapitza conductance.^{44, 45} However, to date there is no complete theoretical understanding of why that dependence should be linear. Moreover, the experimental data for GB thermal conductance in yttria-stabilized-zirconia (YSZ)⁵ does not show a clear linear increase in the high temperature regime, albeit the maximum temperature (480K) might not be sufficiently high. We thus conclude that while the linear increase in boundary conductance is well established in the NEMD simulations, experimental evidence of the effect so far is still lacking.

Figure 8. Temperature dependence of (a) GB Kapitza resistance, and (b) GB Kapitza conductance (inverse of Kapitza resistance) for the $\langle 100 \rangle \Sigma 5(310)$ tilt GB. The symbols are from molecular dynamics simulations and the lines are fitted curves.

7. Discussion

In this work, we have conducted non-equilibrium molecular dynamics simulations to calculate GB Kapitza resistance for a large number of GBs and found that the GB Kapitza resistance has a nearly linear relation with the misorientation angle below 16° and above this angle the resistance is insensitive to the misorientation angle. This result suggests that we may use a very simple relation to estimate the Kapitza resistance of many GBs if we know the misorientation angle and the saturated value of the resistance. For example, if the Kapitza resistances of a few high-angle GBs are determined experimentally, the misorientation-dependent Kapitza resistance in the entire misorientation spectrum may be extrapolated

using the relation obtained in this work without doing laborious experiments. We may also use the GB energy to estimate the Kapitza resistance because they have a strong correlation.

In the grain-size-dependent thermal conductivity model developed by Yang et al.,⁵ the effective thermal conductivity (k_{eff}) of a polycrystal can be estimated as,

$$\frac{1}{k_{eff}} = \frac{1}{k_0} + \frac{R}{D} \quad (6)$$

where k_0 is the thermal conductivity in the single crystal, R is GB Kapitza resistance, and D is grain size. In this analytical model, the Kapitza resistance is assumed to be isotropic. According to our work, this assumption seems to be valid as long as the majority of GBs are high-angle ones. If there are a large population of low-angle GBs, this relation should be modified to account for the misorientation-dependent Kapitza resistance of low-angle GBs.

Although there is some good agreement between our modeling results and experiments, (for example, the linear trend of the misorientation-dependent Kapitza resistance in the low-angle regime agrees well with experimental result of Al_2O_3 for low-angle GBs⁷, the magnitude of the Kapitza resistance obtained from our simulations is much lower than those obtained from experiments in many oxides, typically one order of magnitude lower, as shown in Table 1. Even though there are some uncertainties in the experimental samples and measurement techniques, the discrepancy cannot be ignored. One possible reason is that the GB structures studied here are ideal CSL GBs without any defects and impurities, while in experiments GBs are not as ideal as in modeling. Another possible reason is that the empirical potential may still need further improvement.

Table 1. Comparison of GB Kapitza resistance in oxides between experiments and molecular dynamics simulation.

Materials	GB Kapitza Resistance at 300 K (m ² K/GW)	Method
Al_2O_3 (13° twist)	15.4	Experiment ⁷
Al_2O_3 (96% density)	15.0	Experiment ⁴⁶
YSZ (ZrO_2 with 10% Y_2O_3)	4.5	Experiment ⁵
CeO_{2-x} ($x=0.27$)	27.8	Experiment ²⁸
CeO_2	0.45	MD (this work)

8. Conclusions

In this work we systematically investigated Kapitza resistance of twist and tilt GBs as a function of the misorientation angle and temperature in CeO_2 using molecular dynamics simulations. We clearly demonstrated that the correlation between the GB energy and Kapitza resistance for both low- and high-angle GBs using a large number of GBs. We also found that the critical transition angle for Kapitza resistance is around 16°, consistent with the conventional definition of low- and high-angle GBs based on GB energy. The Kapitza conductance (inverse of Kapitza resistance) is found to increase with temperature even at high temperatures. To this end, we first carefully surveyed available interatomic potentials for CeO_2 with respect to their bulk thermal transport properties as well as detailed atomistic structures of the GBs. Through the comparison with experiments, the potential of Gotte2007 was found

to be the most adequate potential with respect to other potentials. Using results from our molecular dynamics simulations, we applied an extended Read–Shockley model and developed a simple expression for the GB Kapitza resistance (and energy) that can be used to predict GB thermal resistance given the misorientation angle in either twist or tilt grain boundaries.

Acknowledgements

AC and XB equally contributed to the calculations performed, analysis of the data, and preparation of the manuscript. Work supported through the Laboratory Directed Research & Development (LDRD) Program at Idaho National Laboratory under the project tracking number 13-105. This manuscript was coauthored by a contractor (Battelle Energy Alliance, LLC) of the US Government under the Department of Energy Contract No DE-AC07-05ID14517. Accordingly, the US Government retains and the publisher, by accepting the paper for publication, acknowledges that the US Government retains a nonexclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for US Government purposes.

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