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Lattice thermal conductivity of ultra high temperature ceramics ZrB$_2$ and HfB$_2$ from atomistic simulations

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Atomic Green-Kubo simulations are performed to evaluate the lattice thermal conductivity for single crystals of the ultra high temperature ceramics ZrB$_2$ and HfB$_2$. Recently developed interatomic potentials are used for these simulations. Heat current correlation functions show rapid oscillations, which can be identified with mixed metal-Boron optical phonon modes. Results for temperatures from 300K to 1000K are presented.

I. INTRODUCTION

The class of materials referred to as ultra high temperature ceramics (UHTC), including ZrB$_2$ and HfB$_2$, have high melting points, good chemical stability, and reasonable mechanical properties. They are candidate materials for applications involving high temperature environments, such as sharp leading edges for hypersonic vehicles, propulsion systems, and refractory crucibles. They have also been discussed as buffer materials for microelectronics. Unlike most ceramics, these materials are distinguished by their high thermal conductivity. High thermal conductivity offers a number of advantages for high temperature applications, including improved thermal shock resistance and enhanced thermal radiation by efficient distribution of thermal energy over available surfaces.

ZrB$_2$ and HfB$_2$ are broadly similar materials, but have nontrivial differences. Zr and Hf have comparable atomic radii and valence electronic structure, making their diboride analogues electronically almost indistinguishable. However, the large mass difference between Zr and Hf atoms leads to significant deviations, especially in the vibrational spectra of the diborides. These differences are expected to affect their lattice thermal conductivity as well. The crystal structure of ZrB$_2$ and HfB$_2$ is the AlB$_2$-type C32 with space group P6/mmm. These materials are layered with alternating planes of close packed hexagonal Zr/Hf and open hexagonal, graphic B. Metal atoms are situated directly above/below 6-membered rings in the adjacent Boron planes. A detailed ab initio study of the structure and properties of these materials was recently presented.

High thermal conductivity ceramics, such as ZrB$_2$ and HfB$_2$, have significant contributions from both electronic and phononic thermal carriers to the total thermal conductivity $\kappa_{tot}$. The electronic component $\kappa_e$ can be estimated from the electrical conductivity $\sigma$ using the Weidemann-Franz (WF) empirical relation, $\kappa_e = \kappa_0 \sigma T$, where $\kappa_0$ is the Lorentz constant $(2.45 \times 10^{-8} \text{W} \cdot \Omega \cdot \text{K}^{-2})$ and $T$ is the temperature. The phonon part $\kappa_{ph}$ cannot be measured directly and is usually inferred by subtracting $\kappa_e$ from $\kappa_{tot}$. The lattice thermal conductivity can be accessed directly, however, from molecular dynamics (MD) simulations.

Thermal conductivity measurements for single crystal ZrB$_2$ at room temperature have been reported as 140W/(m·K) in the basal direction and 100W/(m·K) along the c-axis. These single sample results included neither a characterization of defects that will reduce $\kappa_{tot}$ nor individual estimates for $\kappa_e$ and $\kappa_{ph}$. Thermal conductivity data has not been reported for single crystal HfB$_2$, although such samples have been fabricated.

Thermal conductivity of polycrystalline ZrB$_2$ and HfB$_2$ has been more thoroughly studied. Room temperature measurements give 60W/(m·K) for ZrB$_2$ and 104W/(m·K) for HfB$_2$. The reduction of $\kappa_{tot}$ relative to single crystals comes primarily from the thermal resistance of grain boundaries. Variations of $\kappa_{tot}$ with grain size can be substantial.

For ZrB$_2$ at 300K, $\kappa_e$ was estimated to be $32\text{W/(m·K)}$ using the WF relation, giving 28W/(m·K) for $\kappa_{ph}$. As a function of temperature, $\kappa_{tot}$ for polycrystalline ZrB$_2$ rises gradually up to at least 1800K, primarily due to a monotonically increasing $\kappa_e$. Conversely, $\kappa_{ph}$ decreases as $1/T$, saturating to a value of $18\text{W/(m·K)}$ above 1000K, which is well above the Debye temperature ($T_D = 750\text{K}$) for this material. For HfB$_2$, $\kappa_{tot}$ is generally higher than for ZrB$_2$, although a detailed comparison accounting for defect distributions and microstructure has not been done. Separate estimates for $\kappa_{ph}$ in HfB$_2$ have not been made, although behavior similar to ZrB$_2$ is expected. Based on these results, we estimate the lattice contribution to $\kappa_{tot}$ to be on the order of 40%. This suggests, for single crystals, that the lattice component will be at least $56\text{W/(m·K)}$ within the planes and $40\text{W/(m·K)}$ in the normal direction.

Recently, we developed Tersoff style interatomic potentials for ZrB$_2$ and HfB$_2$. In this paper, we report results of atomistic Green-Kubo simulations of the lattice thermal conductivity $\kappa_{ph}$ for single crystal ZrB$_2$ and HfB$_2$. Direct

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measurement of $\kappa_{ph}$ is difficult in materials with high $\kappa_c$; therefore, simulations of the lattice component can be useful to isolate that particular thermal conduction mechanism. These computations represent the first atomistic simulations for ZrB$_2$ and HfB$_2$ and also the first nontrivial test of these new potentials.

II. METHOD

The Green-Kubo (GK) theorem relates the lattice thermal conductivity tensor $\kappa_{ij}$ to the integral of the ensemble average of the time correlation function of the heat current $J_i(t)$,

$$\kappa_{ij} = \frac{V}{k_B T^2} \int_0^\infty \langle J_i(0)J_j(t) \rangle dt,$$

where $i,j = x,y,z$, $V$ is the volume, $k_B$ is the Boltzmann’s constant, and $T$ is the temperature. The instantaneous heat current can be evaluated from the phase space configuration of the system at time $t$ as

$$\mathbf{J}(t) = \frac{1}{V} \left[ \sum_i e_i \mathbf{v}_i + \sum_{i<j} \left( \mathbf{f}_{ij} \cdot \mathbf{v}_j \right) \mathbf{x}_i \right],$$

where $e_i$ is the per atom energy of atom $i$, $\mathbf{f}_{ij}$ is the force on atom $i$ due to neighbor $j$, $\mathbf{v}_i$ is the velocity of atom $i$, and $\mathbf{x}_i = \mathbf{r}_i - \mathbf{r}_j$, where $\mathbf{r}_i$ is the position vector of atom $i$. The GK method implemented in the context of MD is essentially an exact method with the principal error dependent on the fidelity of the interatomic potentials. Solid argon, for example, which is well-described by a Lennard-Jones potential, gives thermal conductivity in very good agreement with experiment.\textsuperscript{14} The exact method with the principal error dependent on the fidelity of the interatomic potentials. Solid argon, for example, which is well-described by a Lennard-Jones potential, gives thermal conductivity in very good agreement with experiment.\textsuperscript{14}

MD simulations were performed using the LAMMPS package.\textsuperscript{15} Systems were prepared first with a NPT run to allow the volume to expand, followed by a NVE run to equilibrate the system at the desired $T$. Timesteps ranging from 0.1 fs to 1 fs were used as required to maintain energy conservation. Larger timesteps were generally used at low $T$ and smaller timesteps at higher $T$. After equilibration, time series data for the heat current was collected under NVE. To reduce statistical noise for $\kappa$, long NVE runs were required. For lower temperatures, $T = 300K$ for example, runs of 10ns with a 1fs time step were performed. For higher temperatures with smaller timesteps, runs with a comparable or larger number of steps were used. The largest number of steps considered was $4 \times 10^7$ steps. Eight independent simulations were performed for each system and at each temperature to control for the randomized initial velocities.

Correlation functions were evaluated from the heat current time series. To increase the statistics, correlations were considered in a sliding window through the data set. This approach gives errors that increase with the correlation time. The integral of the heat current correlation function (HCCF) $C_{ij}(t) = \langle J_i(0)J_j(t) \rangle$ was evaluated using the trapezoid rule. Time correlations up to 200ps gave well-convolved values for the thermal conductivity. A good discussion of the details of GK simulations can be found, for example, in Ref.\textsuperscript{18}.

Recently derived Tersoff style interatomic potentials\textsuperscript{13} were used for both ZrB$_2$ and HfB$_2$. For ZrB$_2$, two potentials were developed that were denoted “Pot 1” and “Pot 2.” “Pot 2,” however, gives lattice thermal conductivity values for $\kappa_z$ that are higher than the in-plane component, which is not consistent with experiment. “Pot 1” does give the correct ordering, and therefore, we focus our investigations using it.

We consider defect-free, single crystals. Thus, the only scattering mechanism will be phonon-phonon scattering. Real materials, including single crystals, however, contain a non-trivial distribution of defects. Previous simulations have shown significant reductions in thermal conductivity, due to defect scattering.\textsuperscript{16} Unit cells contained 12 atoms with 4 Zr/Hf atoms and 8 Boron atoms. Simulation cells of size $8 \times 8 \times 16$ were utilized, giving 12 288 atoms. Thermal conductivity values are well converged with respect to system size at this level.

III. RESULTS

Lattice thermal conductivity was obtained for both ZrB$_2$ and HfB$_2$ at temperatures of 300K, 600K, 800K, and 1000K. In Fig. 1, the normalized HCCF $C_{xx}(t)$ is presented for three different systems: ZrB$_2$ at $T = 300K$; HfB$_2$ at $T = 300K$; and HfB$_2$ at $T = 1000K$. Analogous results can be obtained for $C_{yy}$ and $C_{zz}$. A distinctive feature of these curves is their rapid and regular oscillation. The oscillation frequency and decay for ZrB$_2$ and HfB$_2$ at 300K are similar, reflecting the broad commonalities of these materials. However, for HfB$_2$ at 1000K, there is significantly stronger damping. These features will be directly reflected in the values for $\kappa$. This oscillatory behavior is different from many HCCFs reported in the literature and is often seen in complex systems with a number of optical modes of similar frequency, for example, in silica.\textsuperscript{17} The HCCF for monoatomic systems, such as silicon, may decay monotonically for long times, but can show oscillatory features for short times.\textsuperscript{18} Oscillatory HCCFs have also been observed in systems with nontrivial mass differences.\textsuperscript{19}

The HCCF oscillations can be analyzed in more detail by examining the Fourier transform. In Fig. 2, the power spectra for six different HCCFs are displayed: the $C_{xx}$ and

![FIG. 1. (Color online) Normalized heat current correlation function (HCCF) $C_{xx}(t)$ as a function of time. Unlike monoatomic systems, the HCCF for ZrB$_2$ and HfB$_2$ have rapid, regular oscillations.](image-url)
The values are 74 W/m K for ZrB₂, and the same components for HfB₂. As expected, there is a rapid decrease as a function of T. In this temperature regime, anharmonic phonon scattering dominates with the phonon mean free path decreasing as 1/T. Fits of the different data sets to 1/T are shown in the graph. All four curves converge to similar values for HfB₂ at high T, which at T = 1000 K, is about 5 W/(m·K). Compared to experiment, however, the high T values obtained from our simulations for HfB₂ are probably too low. Lattice thermal conductivity for polycrystalline ZrB₂, for example, saturates around 18 W/(m·K), which can be considered a lower bound for our single crystal results. The low T values at high T most likely reflect a limitation in the description of the anharmonic part of the interatomic potentials, which results in increased phonon-phonon scattering.

IV. DISCUSSION

Further insight can be obtained by considering the approximate relation \( \kappa_{ph} = \frac{1}{3} \rho C V_s \lambda_{ph} \), where \( \rho \) is the density, \( C \) is the specific heat, \( V_s \) is the velocity of sound, \( \lambda_{ph} \) is the phonon mean free path, and \( \kappa_{ph} \) is the isotropic lattice thermal conductivity.

Next, we consider the temperature dependence of the lattice thermal conductivity. In Fig. 4, we plot both the in-plane \( \kappa_{||} \) and the normal \( \kappa_{zz} \) conductivities at four different temperatures: 300 K, 600 K, 800 K, and 1000 K for ZrB₂ and HfB₂.
conductivity. Both experimental and computed values for these quantities are given in Table I. The specific heat of these materials is comparable with a value of $\sim 48J/(mol \cdot K)$. The velocity of sound can be evaluated using $v_s = 0.87\sqrt{E/\rho}$, where $E$ is the bulk modulus, giving $5.16km/s$ for $ZrB_2$ and $3.78km/s$ for $HfB_2$ based on the experimental values, while giving $5.45km/s$ for $ZrB_2$ and $5.29km/s$ for $HfB_2$ based on values from the interatomic potentials. Since $v_s \sim \sqrt{1/M}$, $ZrB_2$ is expected to have a higher $v_s$ than $HfB_2$, which is reflected in the $v_i$ derived from experimental numbers. However, the $HfB_2$ interatomic potential gives a modulus too high by a factor of 2X, thus the theoretical values of $v_i$ for the two materials are comparable. Estimates for the phonon mean free path can be obtained using experimental and simulation results for $\bar{k}_{ph}$. For $ZrB_2$ at 300K, an experimental estimate of $51W/(m \cdot K)$ for $\bar{k}_{ph}$ gives $\lambda_{ph} = 11.3nm$, while the simulation value of $54W/(m \cdot K)$ for $\bar{k}_{ph}$ gives $\lambda_{ph} = 11.4nm$. These results are in very good agreement, although an accurate experimental estimate for $\bar{k}_{ph}$ requires further study. For $HfB_2$ at 300K, experimental data is not available. The simulation value of $70W/(m \cdot K)$ for $\bar{k}_{ph}$ gives $\lambda_{ph} = 14.3nm$ for that material.

### V. CONCLUSIONS

In this paper, atomistic Green-Kubo simulations for the lattice thermal conductivity of $ZrB_2$ and $HfB_2$ were performed for a range of temperatures. Interatomic potentials for these materials were recently developed, and this paper represents the first non-trivial test of those potentials. Oscillations in the heat current correlation functions can be identified with mixed $Zr/Hf - B$ optical phonon modes arising from the large metal/Boron mass difference. Agreement with available experimental results is very good at room temperature, but is probably too low at higher temperatures, e.g., $T = 1000K$.

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