Thermophysical properties of reaction processed zirconium diboride

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THERMOPHYSICAL PROPERTIES OF REACTION PROCESSED ZIRCONIUM DIBORIDE

by

JASON MICHAEL LONERGAN

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Approved by:

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Jeffrey Smith
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The introduction and literature review sections in this document provide pertinent information about the structure and thermophysical properties of zirconium diboride that are the focus of this work. The body of this dissertation has been compiled in the style for publication in peer reviewed journals. The first paper, pages 55 to 94, entitled “Sintering Mechanisms and Kinetics for Reaction Hot Pressed ZrB₂,” was submitted for publication to the *Journal of the American Ceramic Society* in August 2014. The second paper, pages 95 to 108, entitled “Zirconium Diboride with High Thermal Conductivity,” was published in the *Journal of the American Ceramic Society* in May 2014. The third paper, pages 109 to 145, entitled “Thermal properties of ZrB₂ Ceramics with Hf contents up to 0.33 at%,” will be submitted to the *Journal of the European Ceramic Society*, and the fourth paper, pages 146 to 185, “Thermal Properties of ZrB₂ with Varying Boron Isotope Ratios,” will be submitted to the *Journal of Applied Physics*, planned for November of 2014.

The appendix describes an additional study on the effects of porosity and grain size on the thermal properties of ZrB₂. This section contains experimental results on the thermal properties of specimens that contain 0.25 to 25 vol% porosity, as well as full dense specimens, that have grain sizes ranging from 6 to 12µm. This work is presented in the format of the *Journal of American Ceramic Society* and is entitled “The Effects of Porosity and Grain Size on Thermal Properties of ZrB₂.”
This dissertation focuses on the thermophysical properties of high purity zirconium diboride ceramics. These ceramics have shown promise for potential applications such as leading edge materials for next generation hypersonic vehicles. The overall goal of this work was to improve the understanding of the thermal properties and maximize the thermal conductivity of ZrB$_2$. Four main areas were investigated in this work. First, the sintering kinetics and the intrinsic thermal properties of reaction processed ZrB$_2$ were studied and compared to ZrB$_2$ produced by hot pressing commercial powders. The reaction process produced ceramics with higher thermal conductivity and enhanced densification. Next, Hf impurity concentrations were varied showing that decreasing Hf content increased thermal conductivity. Finally, isotope enrichments were performed showing that lighter isotopes increased lattice frequency and subsequently thermal conductivity. Fully enriched Zr$^{10}$B$_2$ had a thermal conductivity of 145 W/m·K which is the highest value for ZrB$_2$ reported to date. Scattering models based on quantum mechanics were used with density functional theory to analyze the effects of impurities and isotopes on the electron and phonon density of states. Overall, this work adds insight into the fundamental mechanisms behind the thermophysical properties of ZrB$_2$.

Tailoring compositions to reduce Hf content and adjusting boron isotope concentration has led to improved thermal properties at all temperatures. The processing conditions, reported properties, and insights gained from models will help the realization of ZrB$_2$ as a leading edge material for the next generation of hypersonic vehicles.
I would like to begin by thanking my advisor Dr. William Fahrenholtz for his assistance and guidance through my time in Rolla. He has taught me a great deal about staying focused with my research and how to analyze my data. I would also like to thank him for all his patience and guidance as I learning how to structure and present my findings (both in the form of a talk and a technical document). I would also like to thank Dr. Greg Hilmas, my co-advisor, for his valuable insight and guidance throughout my research.

I would like to thank the rest of my committee: Drs. Jeffrey Smith, Mohamed Rahaman, and George Waddill. They have taught me a great deal in the fundamentals of materials science as well as given guidance in crucial areas of my research.

To all my friends and colleagues who have been part of the UHTC research group; thanks for all your help and support, showing me around Rolla, and for sitting down to drink good beer and share stories.

Thanks Mom and Dad for everything. I never once failed for the lack of confidence or belief in myself and I must thank you for that. In addition, it was a great source of comfort to know I always had a good home and warm bed to return to.

To Charmayne Smith, the love of my life, I’m so happy I found you. You have been my best friend and my inspiration. I Love you more than words can describe.
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1. INTRODUCTION

The recent interest in the next generation hypersonic vehicle includes reusable atmospheric reentry vehicles for easier access to space, quicker transport of people and goods, as well as aircraft and missile systems for military applications such as fast response strike weapons.\textsuperscript{1,2,3,4,5} The hypersonic regime is generally considered to be Mach 5 or higher.\textsuperscript{4} Proposed designs for future hypersonic vehicles have sharp leading and trailing edges to enhance maneuverability. However, the temperatures that are generated at sharp leading edges increase as the radius decreases and can be in excess of 2000°C.\textsuperscript{5} In addition to high temperatures, sharp leading edges encounter high heat fluxes generated by convective flow at the stagnation point. Figure 1.1 is a depiction of the heat fluxes generated on a leading edge. A first order approximation of the heat flux given by Anderson\textsuperscript{6} was used by Kasen et al. to show the peak heat flux.\textsuperscript{2} At Mach 7, a leading edge with a 3 mm radius had a heat flux of 460 W/cm\textsuperscript{2} which dropped to 6 W/cm\textsuperscript{2} within 3 mm from the tip. The rapid drop in heat flux will result in high temperature gradients and consequently high thermal stresses. Increasing the thermal conductivity could lead to better heat transport away from the sharp edge, where heat is generated, to cooler areas, where heat is dissipated. In turn, increasing thermal conductivity will reduce thermal stresses and improve thermal shock resistance, leading to increased efficiency and operational speeds in hypersonic vehicles. Therefore, leading edge materials for next generation hypersonic vehicles should have melting temperatures in excess of 2000°C with high fracture strengths and thermal conductivities.
Figure 1.1. Depiction of a leading edge with heat fluxes related to conduction, convection, and radiation.  

\[ \dot{q}_{\text{conv}} = \dot{q}_{\text{rad}} + \dot{q}_{\text{cond}} \]

The materials currently available for use in aerospace applications include metal alloys and carbon-carbon ceramic composites. Figure 1.2 shows some characteristics of these materials.  

It is apparent that the metal alloys such as aluminum, titanium, or nickel have melting temperatures below intended operating conditions for hypersonic vehicles. Outside of traditional aerospace metals, rhenium possesses a melting temperature in excess of 3000°C which makes it a promising candidate material; however, it has a high density (22 g/cm³) and low oxidation resistance at elevated temperature. Among candidate ceramic materials, refractory carbides possess higher melting temperatures and lower densities than metals. Unfortunately, SiC undergoes a transition from passive to active oxidation around 1600°C, depending on atmospheric conditions, making it unsuitable for a hypersonic vehicle leading edge. Although they possess very high melting temperatures, C-C composites have very low thermal conductivities (~2 W/m·K), and poor oxidation resistance at elevated temperatures. The low thermal conductivity
will impede dissipation of the heat generated at the leading edge. In addition, refractory carbides undergo severe strength degradation at temperatures much lower than 2000°C. Therefore, the realization of reusable sharp leading edge components for the next generation hypersonic vehicle requires the design of a material system that has enhanced properties compared to materials currently available for aerospace applications.

ZrB$_2$ is a transition metal diboride that belongs to the ultra high temperature ceramic (UHTC) family of materials. Due to strong covalent bonding, ZrB$_2$ has gained interest for its high melting temperature (3250°C), hardness (23 GPa), and elastic modulus (489 GPa). In addition to mechanical properties, ZrB$_2$ has been investigated

Figure 1.2. Metal alloy and ceramic composites characteristics.\textsuperscript{5}
due to its promising thermal conductivity (60 W/m·K or higher from 25 to 2000°C), electrical conductivity ($10^7$ S/m), and oxidation resistance. Proposed applications that take advantage of these properties include hypersonic vehicle thermal protection systems, cutting tools, molten metal crucibles, microelectronic substrates, and high temperature electrodes.

Despite its promising thermal properties, much is still not understood about how fundamental electron and phonon transport mechanisms are affected by the composition and microstructure of ZrB$_2$ ceramics. Room temperature thermal conductivities for ZrB$_2$ ceramics range from 45 W/m·K to 130 W/m·K. As temperatures approach the intended application temperature (2000°C), thermal conductivities converge to values in the range of 60 to 80 W/m·K. Several researchers have studied the effects of additives and impurities in commercial ZrB$_2$ powders. Additives have been shown to improve densification, strength, fracture toughness, and oxidation properties, but generally lead to a reduction in thermal conductivity. In addition, most of the reported studies have been done using commercial powders that contain Hf and other transition metal impurities. Studies by Thompson and Zimmermann have shown that solid solution additions of W reduce room temperature thermal conductivity. In addition, McClane et al. have shown that transition metal solid solution additions such as Hf, Nb, Ti, and Y also lead to reductions in thermal conductivity. In order for the realization of ZrB$_2$ in many of its proposed applications, the intrinsic properties and mechanisms responsible for them must be understood.
Reaction processing methods have been identified as a fabrication route for refractory diborides to enhance densification and purity, as well as thermal properties. Guo et al. produced ZrB$_2$ with >95% relative density, without sintering additives, at 1750°C using a reaction spark plasma sintering process. In addition, reaction processing (RP) has yielded the highest thermal conductivities of ZrB$_2$ with values as high as 130 W/m·K at 25°C. High purity commercial powders, densified using traditional hot pressing (HP) have thermal conductivities reported around 90 W/m·K at 25°C. The reasons for the enhanced thermal properties are not fully understood, but higher purity of reaction processed ceramics could be one reason.

The focus of this work was to investigate the thermophysical properties of nominally phase pure ZrB$_2$ ceramics. Reaction hot pressing was chosen in order to produce high purity ceramics and tailor final compositions. Isothermal sintering was performed to study densification mechanisms and grain growth kinetics. High purity ZrH$_2$ and B powder sources were used to fabricate ZrB$_2$ ceramics with impurity contents as low as possible. Intrinsic thermal properties including thermal diffusivity, heat capacity, and electrical resistivity were studied on the resulting ceramics. The ability to tailor composition was utilized to study the effects of solid solution Hf impurities as well as ZrB$_2$ enriched with $^{10}$B and $^{11}$B isotopes. The important technical questions this work answered include:
1. What are the sintering mechanisms, grain growth kinetics, and resulting microstructures of reaction hot pressed ZrB₂ ceramics?

2. What are the intrinsic thermal properties of reaction processed ZrB₂ with high purity and relative density from 25 to 2000°C?

3. What are the effects of Hf on the thermal properties of ZrB₂?

4. What are the effects of boron isotope enrichment on the thermal properties of RHP ZrB₂?
2. LITERATURE REVIEW

2.1. CRYSTALLOGRAPHY AND BONDING

Zirconium diboride has the hexagonal AlB$_2$ type crystal structure with alternating layers of B atoms in graphite like rings and Zr atoms in a hexagonally closed packed arrangement (Figure 2.1).$^{10,32}$ Each zirconium atom is located in a close packed plane and has six other zirconium atoms as its nearest neighbors as well as twelve boron nearest neighbor atoms, six above and six below. Each boron atom has three other boron atoms within its plane as nearest neighbors and has six zirconium nearest neighbor atoms in adjacent planes. One of the unusual attributes of ZrB$_2$ is the multiple types of bonding. The boron sub-lattice exhibits graphite like sp$^2$ covalent bonding. The high strength of the B-B bonds increases the stiffness of the ZrB$_2$ unit cell and leads to high melting temperature and strength.$^{10}$ The M-B bonding is of mixed ionic and covalent nature and adds to the characteristic ceramic-like properties of ZrB$_2$. The M-M bonds in the zirconium sub-lattice are metallic in nature and give rise to high electrical and thermal conductivities.$^{33,34}$
2.2. DENSIFICATION

2.2.1. Driving Forces. The fundamental driving force for sintering is the reduction of the total Gibbs’ free energy of the system ($\Delta G_T$), which can be expressed as

$$\Delta G_T = \Delta G_v + \Delta G_b + \Delta G_s$$

(1)

where $\Delta G_v$, $\Delta G_b$, and $\Delta G_s$ represent the change in Gibbs’ free energy associated with the grain volume, boundary area, and surface area, respectively. The largest driving force for sintering in polycrystalline ceramics is the reduction in surface energy ($\Delta G_s$). This is accomplished through the reduction in surface curvature and the area of solid-vapor interfaces.\textsuperscript{35}
The surface energy of the system can be expressed as a combination of the surface area and surface energy, which can be represented as

$$\Delta G_s = \frac{3\gamma_{sv}V_m}{a}$$  \hspace{1cm} (2)

where $V_m$ is the molar volume, $\gamma_{sv}$ is the specific surface energy, and $a$ is the radius of the particles. The surface energy is equivalent to the decrease in Gibbs’ free energy that would take place for the formation of a fully dense body (i.e. a single crystal).\textsuperscript{36}

2.2.2. Fick’s First Law. For sintering to progress, atoms must move.\textsuperscript{36, 37, 38} This movement proceeds by diffusion, which can occur through many mechanisms. The rate at which the atoms diffuse depends on the mobility of atoms and vacancies. The phenomenological laws that are typically used to describe the motion of materials are independent of the medium in which diffusion is taking place. The movement of the diffusing species described by these laws is driven by concentration gradients. When the concentration is independent of time, the mathematics for this continuum approach is commonly referred to as Fick’s first law (Equation 3)\textsuperscript{36}

$$J_x = -D \frac{dC}{dx}$$  \hspace{1cm} (3)

where $C$ is concentration, $x$ is distance in the direction of diffusion, $J$ is the flux, in units of mass per unit area per unit time, and $D$ is the diffusion coefficient, in units of length squared divided by time. The temperature dependence of $D$ is typically expressed with an Arrhenius equation of the following form
where $D_o$ is the pre-exponential factor, $Q$ is the activation energy, $R$ is the gas constant and $T$ is the temperature. The diffusion coefficient underlines the importance of vacancies, defects, and temperature for the diffusion process. An atom must both acquire the energy to jump and have free space into which it can jump. Figure 2.2 is a graphical representation of Fick’s first law.

\[
D = D_o e^{-Q/RT}
\]

Figure 2.2. Depiction of Fick’s first law showing the concentration gradient. Adapted from “Fick’s First Law.” University of Cambridge, 7 July 2013.
2.2.3. Mechanisms of Sintering. Matter transport occurs from regions of higher chemical potential to regions of lower chemical potential. Six different mechanisms are typically considered for mass transport during sintering. All of these mechanisms lead to bonding and neck growth between particles; however, only some of these mechanisms lead to shrinkage and densification. The difference in Gibbs’ free energy between the neck and the surface of the particle provides the driving force required for diffusion. Figure 2.3 shows the six different mechanisms for mass transport that lead to sintering.36, 38

Mechanisms 1, 2, and 3 lead to neck growth without densification. These mechanisms reduce the curvature of the neck surface and reduce the driving force for sintering.

Figure 2.3. The six diffusion mechanisms that can occur during sintering.39
However, the source of material is the surface of one of the particles. As a result, grains coarsen and necks grow, but the centers of adjacent grains remain the same distance apart, so relative density does not change for these mechanisms. Grain boundary diffusion and lattice diffusion from the grain boundary to the pore, mechanisms 4 and 5, are the predominant densifying mechanisms in polycrystalline ceramics. These mechanisms remove material from between the centers of particles, allowing the particles to move closer together and causing macroscopic shrinkage of the powder compact. Hence, these are mechanisms that lead to densification during sintering.

2.2.4. Continuum Hot Pressing Models. Thermal energy alone is often insufficient to fully densify many ceramics. A common solution to this problem is the addition of an external stress or pressure to the powders while sintering. Some of the original models for hot pressing were formulated by Coble who approached the intermediate and final stage hot pressing models through the modification of creep equations. Creep of polycrystalline can occur by lattice diffusion or grain boundary diffusion. Nabarro and Herring defined creep rates for both lattice (Equation 5) and grain boundary (Equation 6) diffusion creep

\[ \dot{\varepsilon} = \frac{40 D_p \Omega p_a}{3 G^2 kT} \]  

\[ \dot{\varepsilon} = \frac{47.5 D_{gb} \delta_{gb} \Omega p_a}{G^3 kT} \]

where \( \Omega \) is the atomic volume, \( p \) is the applied pressure, \( \delta \) is the grain boundary width, \( G \) is the grain size and \( k \) is the Boltzmann’s constant. The diffusion coefficient has an
Arrhenius dependence on temperature. The following modification of the creep equations attempts to incorporate two factors.\textsuperscript{36} The first is the relation of the creep rate to the densification rate and the second is the compensation for the presence of porosity. In hot pressing, two constants are the mass of the powder $M$ and the cross sectional area $A$ of the die. These constants are related to the density and thickness of the sample through

$$\frac{M}{A} = LD = L_0D_0 = L_fD_f$$ \hspace{1cm} (7)

where $L$ is the length of the ceramic compact and subscripts 0 and f indicate the initial and final values, respectively. Differentiating the equation with respect to time gives the rate of densification as described by:

$$-\frac{1}{L} \frac{dL}{dt} = \frac{1}{D} \frac{dD}{dt} = \frac{1}{\rho} \frac{d\rho}{dt}$$ \hspace{1cm} (8)

where $\rho$ is the relative density. To compensate for the presence of porosity, the effective stress on the grain boundaries is related to the externally applied stress and the surface curvature. By substitution of these relations into the applied stress term produces modified creep equations for hot pressing, which are summarized in Table 2.1.\textsuperscript{36}
Table 2.1. Modified Creep Equations to Describe Densification by Hot Pressing

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Intermediate stage</th>
<th>Final stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice diffusion</td>
<td>[ \frac{1}{\rho} \frac{dp}{dt} = \frac{40}{3} \left( \frac{D_1 \Omega}{G^2 kT} \left( p_\phi + \frac{\gamma_v}{r} \right) \right) ]</td>
<td>[ \frac{1}{\rho} \frac{dp}{dt} = \frac{40}{3} \left( \frac{D_1 \Omega}{G^2 kT} \left( p_\phi + \frac{2\gamma_v}{r} \right) \right) ]</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>[ \frac{1}{\rho} \frac{dp}{dt} = \frac{95}{2} \left( \frac{D_\mu \delta_e \delta_j \Omega}{G^2 kT} \left( p_\phi + \frac{\gamma_v}{r} \right) \right) ]</td>
<td>[ \frac{1}{\rho} \frac{dp}{dt} = \frac{15}{2} \left( \frac{D_\mu \delta_e \delta_j \Omega}{G^2 kT} \left( p_\phi + \frac{2\gamma_v}{r} \right) \right) ]</td>
</tr>
<tr>
<td>Dislocation motion(a)</td>
<td>[ \frac{1}{\rho} \frac{dp}{dt} = A \left( \frac{D_{\mu b}}{kT} \left( \frac{p_\phi}{\mu} \right) \right) ]</td>
<td>[ \frac{1}{\rho} \frac{dp}{dt} = B \left( \frac{D_{\mu b}}{kT} \left( \frac{p_\phi}{\mu} \right) \right) ]</td>
</tr>
</tbody>
</table>

### 2.2.5. Hot Pressing. 
A series of papers published during the 1960s established the fundamental understanding of ZrB\(_2\) and HfB\(_2\) densification and sintering kinetics.\(^{40,41,42,43}\) Full densification without sintering additives was only achieved with non-stoichiometric ZrB\(_{1.89}\). The authors concluded that the main densification mechanism for the temperature range 2000-2300°C was grain boundary diffusion through a liquid film.\(^{40}\) Accepted phase diagrams show that ZrB\(_2\) is a line compound and therefore ZrB\(_{1.89}\) should have been a mixture of ZrB\(_2\) and liquid Zr at the densification temperatures.\(^{10,44}\) Kinetic studies on stoichiometric HfB\(_2\) were conducted and are often used as a comparison due to the similarity in behavior of ZrB\(_2\) and HfB\(_2\).\(^{43}\) Kalish concluded that the initial stage of sintering was particle rearrangement and fragmentation. The final state of sintering was controlled by stress directed vacancy diffusion where the rate controlling mechanism was either lattice diffusion of boron or stress directed grain boundary diffusion of hafnium.\(^{43}\) Figure 2.4 shows the fit of the densification data to the diffusion model for densification.
Most densification studies since the 1960s have been on the effects of sintering additives for pressureless sintering (PS) or the effects of current assisted sintering in spark plasma sintering (SPS). It is evident that multiple sintering techniques have been widely for ZrB$_2$, but limited knowledge is available for intrinsic sintering mechanisms of stoichiometric high purity ZrB$_2$.

Figure 2.4. Relative density as a function of time over grain size data fit to a model for densification by grain boundary diffusion in HP experiments conducted by Kaufman and Clougherty.
2.2.6. Reaction Hot Pressing. Reaction hot pressing (RHP) has been identified as fabrication route to produce high purity ZrB₂ ceramics with high density at lower temperatures.\textsuperscript{32, 45, 51, 52, 53, 54} Studies by Chamberlain and Zhang\textsuperscript{32, 51} have shown that the reaction process can produce dense ceramics with lower grain sizes in both phase pure ZrB₂ and ZrB₂-SiC. The smaller size is thought to be responsible for the enhanced densification seen at lower temperatures with this technique. Although capable of densification at temperatures as low as 1650°C with SiC additions, grain coarsening in stoichiometric, phase pure systems increased the temperature required for full densification of ZrB₂ to 2100°C.\textsuperscript{32, 51} Enhanced densification has been observed in reaction methods, but the investigation of sintering mechanisms has been limited to measured densities and densification rates.

2.2.7. Sintering Studies. Figure 2.5 is a sintering map for reported relative densities as a function of temperature for recent studies on nominally phase pure ZrB₂ ceramics. Specimens that were reaction processed at temperatures ranging from 1650 to 2100°C had densities higher than 90%. In contrast, pressureless sintering did not produce relative densities higher than 80% without sintering aids. Similarly, hot pressing of commercial powders did not produce densities higher than 90% for temperatures below 2100°C. A combination of reduced grain sizes and increased defect concentrations cause by the reaction of the constituent powders is thought to be the reason for enhanced densification at lower temperatures.\textsuperscript{32, 51}
2.3. THERMAL PROPERTIES

ZrB$_2$ is a candidate material for many ultra-high temperature (UHT) applications in which high thermal conductivity will enhance performance. Thermal energy is typically transported by three mechanisms: conduction, convection, and radiation. All three are dependent on the thermal properties of the material. A comprehensive understanding of heat transfer is important for optimal performance. Diboride based ceramics have a combination of metallic and covalent bonding resulting in both electron and phonon heat transport. This leads to unusual combinations of properties that are not typically found in ionic or covalently bonded ceramics. In this section, phonon conductivity, electron conductivity, heat capacity, and thermal conductivity of ZrB$_2$ will be discussed along with phonon and electron scattering mechanisms.
2.3.1. Phonon Thermal Conduction. In a solid, atoms vibrate about equilibrium positions within the crystal lattice. These vibrations are strongly coupled with neighboring atoms through chemical bonds. Quantization of the standing waves that are generated are known as phonons. A phonon is generally labeled as $\omega(q,s)$ or $\omega_q$ where $q$ is the wave vector in the first Brillouin zone and $s$ is an index which refers to acoustic and optical branches.

The simplest model involves a linear chain of identical atoms. The equation of motion, or wave, for any atom in this chain is of the form seen in Equation 10,

$$u_n = Ae^{i(qa-\omega t)}$$

where $a$ is the atomic spacing, $n$ denotes the atom, $A$ is the amplitude of the wave, $q$ is a propagation number, and $\omega$ is the angular frequency. The relation between the frequency and the wave number is obtained by Equation 11,

$$\omega(q) = \sqrt{\frac{4k}{m}} \sin \left( \frac{qa}{2} \right)$$

where $k$ is the force constant or the bond strength, and $m$ the mass of the atom. Both $q$ and $\omega$ must be real. The allowed values for the propagation number $q$ depend on the boundary conditions, which are imposed based on approximations to the infinite chain of atoms by creating a large circle containing $N$ discrete masses. Therefore, the $(N+n)^{th}$ mass must be identical to the $n^{th}$ mass and consequently, only the following states are allowed (Equation 12).
\[ q = \frac{2\pi n}{Na} \quad (12) \]

A slightly more complex model, but one better at approximating the phonon waves in a compound, involves a linear chain of alternating masses. This results in two separate equations for motion based on the two atomic masses as seen in Equations 13 and 14. \(^6\)

\[ u_{2n} = A_e e^{i(2na-\omega t)} \quad (13) \]

\[ u_{2n+1} = A_0 e^{i[(2n+1)a-\omega t]} \quad (14) \]

Solving the two simultaneous linear equations is done through a nontrivial secular equation (not shown) whose solution is \(^6\)

\[ \omega^2 = \frac{k}{m} \left\{ 1 \pm \left[ 1 - \frac{4m\sin^2(qa)}{M + m} \right]^{1/2} \right\} \quad (15) \]

As was the case in the monoatomic chain of atoms, the atomic vibrations, \(\omega\), and wave vectors, \(q\), must have real solutions. To set boundary conditions, the infinite chain is approximated by a large circle containing \(N\) masses and imposing the condition that the \((N+n)^{th}\) mass must be identical to the \(n^{th}\) mass which gives the following allowed states \(^6\)

\[ q = \frac{\pi n}{Na} \quad (16) \]

Figure 2.6 shows a typical phonon dispersion curve for a monoatomic and diatomic crystalline solids in which \(a_o\) is the lattice spacing. \(^5\)
The phonon distribution function can be derived as

\[ N^0_{\tilde{q}} = \frac{1}{\exp(\frac{\hbar \omega_{\tilde{q}}}{k_B T}) - 1} \]  

where \( \omega_{\tilde{q}} \) is the phonon frequency, \( \hbar \) is Dirac’s constant, \( k_B \) is Boltzmann’s constant, and \( T \) is the absolute temperature. By summing the total phonon distribution over all phonon modes, an expression for the total heat flux can be derived (Equation 18) where \( \bar{u}_g \) is the phonon group velocity.

\[ \bar{Q} = \sum_{\tilde{q}} N_{\tilde{q}} \hbar \omega_{\tilde{q}} \bar{u}_g \]  

The phonon thermal conductivity can then be expressed as shown in Equation 19.
Often, the phonon dispersion curve and eigenvectors are unknown. In 1912, Debye introduced a theory in which material properties could be approximated by using the maximum vibrational frequency of atoms in the lattice. He assumed that the range of frequencies for the oscillating atoms was the same as the acoustic vibrations in a continuous solid.\textsuperscript{61,62} Figure 2.7 shows the continuous Debye approximation for the phonon density of states for TiC.

\begin{equation}
k_p = -\frac{\bar{Q}}{VT} = \frac{1}{3} \sum_q \hbar \omega_q \nu_q^2 \tau_q \frac{\partial N^0_q}{\partial T}
\end{equation}

\textbf{Figure 2.7. Phonon density of states }F(v)\textbf{ for TiC and the Debye model representation.}\textsuperscript{62}

Using the Debye theory assumption of an average phonon velocity ($\nu$) gives a continuous density of states for increasing vibrational frequencies which allows replacement of the
summation in Equation 19 by an integral such that $v_{q'}, q' = v \cdot g$ for all phonon branches.\textsuperscript{57} This leads to Equation 20, where $\omega_D$ is the Debye frequency.

$$k_L = \frac{1}{2\pi^2 v} \int_0^{\omega_D} \hbar \omega \tau_q(\omega) \left( \frac{\hbar \omega/k_B T^2}{\exp(\hbar \omega/k_B T) - 1} \right) d\omega \quad (20)$$

Making the substitutions $x = (\hbar \omega/k_B T)$ and $\theta_D = \hbar \omega/k_D$ results in the Debye approximation for lattice thermal conductivity (Equation 21) where $\tau_i(x)$ represent the time between scattering events for all phonon scattering processes.\textsuperscript{57}

$$k_L = \frac{k_B}{2\pi^2 v} \left( \frac{k_B}{\hbar} \right)^3 T^3 \int_0^{\theta_D} \tau_i(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (21)$$

This expression describes lattice thermal conductivity in terms of the vibrational frequencies of atoms in the lattice. When applied to real materials, it can help provide insight into the effect of scattering mechanisms on the lattice thermal conductivity of solids. One of the strengths of the Debye theory is its ability to accurately predict the lattice thermal conductivity for insulating materials with minimal knowledge of the complex lattice vibrations of a material.
2.3.2. Electron Thermal Conduction. Free electron theory considers each electron as a periodic potential or wave moving without disturbance.\textsuperscript{57, 60} This model assumes that the sum of all potentials across the system must add to zero.\textsuperscript{59} The wave equation for a free electron in this case can be described by the time independent Schrödinger equation for a free electron (Equation 22)\textsuperscript{59, 60}

\begin{equation}
-\frac{\hbar^2}{2m} \nabla^2 \psi_k + V_x \psi_k = \varepsilon_k \psi_k \tag{22}
\end{equation}

where \( m \) is the mass of the electron, \( \hbar \) is the Dirac function, and \( V_x \) is the potential energy at the point defined by wave vector \( \vec{k} \). This equation has a solution of the form (Equation 23) where \( V \) is the volume within which the electron is confined.\textsuperscript{59, 60}

\begin{equation}
\psi_k = \frac{1}{V^{1/2}} e^{i \vec{k} \cdot \vec{r}} \tag{23}
\end{equation}

Substitution of Equation 23 into Equation 22 gives the relationship between the energy \( \varepsilon_k \) and the wave vector \( \vec{k} \) (Equation 24).

\begin{equation}
\varepsilon_k = \frac{\hbar^2 k^2}{2m} \tag{24}
\end{equation}

The importance of this result is that without any further constraints all values of \( k \) are allowed solutions. This means that all electron states within the same energy form a sphere in \( k \)-space extending to a maximum energy. The next step in constraining the model is to determine how many electrons can fit into a given state. The Pauli exclusion principle states that a given quantum state can accommodate only one electron of a given
half-integral spin. Therefore, only two electrons are allowed in the k=0 level and additional electrons must occupy higher energy levels. This filling of energy levels will continue until all electrons below a certain energy \( \eta_f \) are filled. Applying the Pauli exclusion principle at T=0 K, the boundary between the filled and empty states (Fermi energy) is given as Equation 25,

\[
\eta_f = \frac{\pi^2 \hbar^2}{2m} \left( \frac{3n_0}{\pi} \right)^{2/3}
\]  

(25)

where \( n_0 \) is the density of the electron gas, which can be determined by Equation 26.

\[
n_0 = 2 \int_0^{\eta_f} N(\epsilon)d\epsilon = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} \int_0^{\eta_f} \epsilon^{1/2}d\epsilon = \frac{(2m)^{3/2}}{3\pi^2\hbar^3} \eta_f^{3/2}
\]

(26)

As temperature increases, thermal agitation promotes electrons to higher energy levels. The probability that a given quantum state, \( \epsilon_k \), is occupied by an electron is given by the Fermi-Dirac distribution function (Equation 27),

\[
f_k^0 = \frac{1}{\exp \left( \frac{\epsilon_k - \eta_f}{k_B T} \right) + 1}
\]

(27)

Where \( k_B \) is the Boltzmann constant and T is the absolute temperature. Using the Fermi-Dirac distribution the maximum filled energy level for a given temperature is given by Equation 28.

\[
n_0 = \frac{(2m)^{3/2}}{2\pi^2\hbar^3} \int_0^{\eta_f} \epsilon^{1/2} f_0(\epsilon)d\epsilon
\]

(28)
From Equations 25 and 28, expressions for electron current density ($\vec{J}$) and energy flux ($\vec{Q}$) can be defined as

$$\vec{J} = e^2 K_0 \vec{\varepsilon}_{\text{eff}} - \frac{e}{T} K_1 \vec{\nabla}T$$  \hspace{1cm} (29)$$

$$\vec{Q} = e K_i \vec{\varepsilon}_{\text{eff}} - \frac{1}{T} K_2 \vec{\nabla}T$$  \hspace{1cm} (30)$$

where $e$ is the charge of an electron, $\vec{\nabla}T$ is the temperature gradient, and $K_n$ can be defined with an integral (Equation 31).

$$K_n = -\frac{1}{3} \int \left[ \vec{\varepsilon}_k \right]^2 \tau(k) \left( \varepsilon_k - \eta_f \right)^n \frac{\partial f_k^0}{\partial E_k} dk$$ \hspace{1cm} (31)$$

The effective field acting on the electrons due to the charge balance of all electrons within the gas ($\vec{\varepsilon}_{\text{eff}}$) can be defined by Equation 32.

$$\vec{\varepsilon}_{\text{eff}} = \vec{\varepsilon}_k - \frac{\nabla \eta_f}{e}$$ \hspace{1cm} (32)$$

The electron contribution to thermal conductivity ($k_e$) can then be expressed as shown in Equation 33.

$$k_e = -\left[ \frac{\vec{Q}}{\vec{\nabla}T} \right]_{J=0} = \frac{1}{T} \left( K_2 - \frac{K_1}{K_0} \right)$$ \hspace{1cm} (33)$$

This leads to the Wiedemann-Franz Law (Equation 34)\textsuperscript{58}

$$k_e = L_0 \sigma T$$ \hspace{1cm} (34)$$
where the theoretical Lorenz number ($L_0$) can be derived as shown in Equation 35.

$$L_0 = \frac{\pi^2 k_B^2}{3 e^2} = 2.44 \times 10^{-8} (W\Omega K^{-2})$$  \hspace{1cm} (35)

The electrical conductivity ($\sigma_e$) is the inverse of the electrical resistivity ($\rho_e$), which is measured directly using the van der Pauw technique. The importance of the Lorenz number and the free electron theory is that the electron portion of thermal conductivity for a material can be directly determined experimentally by measuring electrical conductivity.

2.3.3. Thermal Diffusivity. Thermal diffusivity (D) is the ratio of the ability of a material to conduct thermal energy to its ability to store thermal energy. D indicates how quickly a material will respond to temperature change. In other words, D describes how fast thermal energy will diffuse from high temperature regions to low temperature regions to remove a thermal gradient and achieve uniform temperature. Whereas thermal conductivity can be difficult to measure directly due to the need to establish an equilibrated thermal gradient across a specimen at a wide range of temperatures, thermal diffusivity is commonly measured and then combined with heat capacity and density values to calculated total thermal conductivity ($k_T$) as shown by Equation 36,

$$k_T = DC_p \rho$$  \hspace{1cm} (36)

where D is the thermal diffusivity, $C_p$ is heat capacity, and $\rho$ is bulk density. Unlike thermal conductivity, thermal diffusivity can be measured in an isothermal specimen, which makes D easier to measure across a range of temperatures.
Thermal diffusivity can be measured using the laser flash technique. The technique was originally developed by Parker et al. based on one dimensional heat flow through a flat specimen with homogeneous composition at a uniform temperature.\textsuperscript{64} Figure 2.8 shows a schematic of the typical specimen geometry along with a pulse of energy that is applied perpendicular to the front face of a flat specimen with uniform thickness. The temperature rise resulting from the energy pulse is measured on the back face.

**Figure 2.8. Depiction of laser flash method for thermal diffusivity measurements.**

Several assumptions are employed to calculate thermal diffusivity from the measured temperature rise. The first assumption is that the heat pulse is uniformly and instantaneously absorbed near the front face of the specimen. Heat transfer is also assumed to be one dimensional and with no radial heat loss. Finally, the heat pulse is assumed to be instantaneous (i.e., pulse width is infinitely narrow in time). If these
conditions are met, then the time-dependent temperature on the back face can be described by Equation 37:\(^4\)

\[
T(L,t) = \frac{Q}{\rho CL} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-\left(\frac{n^2\pi^2Dt}{L^2}\right)} \right]
\]

(37)

Where \(T\) is temperature, \(Q\) is the energy of the laser pulse, \(C\) is the heat capacity, \(L\) is specimen thickness, \(D\) is thermal diffusivity, and \(t\) is time. Temperature is then plotted as a function of time and its general appearance will be similar to Figure 2.9.\(^4\) Once the back face temperature has been measured, two dimensionless parameters (Equation 38 and 39) are used to determine the thermal diffusivity. The first is the relative temperature \((V(L,t))\), which is a function of time and specimen thickness. The second is the thermal diffusivity constant, \((\omega)\), which results from the exponential nature of a one dimensional temperature gradient in an solid at time \(t\).\(^6^4\)

\[
V(L,t) = \frac{T(L,t)}{T_{\text{max}}}
\]

(38)

\[
\omega = \frac{\pi^2 \alpha t}{L^2}
\]

(39)

Parker used the time required for the back face of the specimen to reach half of its maximum temperature to calculate thermal diffusivity. A constant of 1.387 was derived by Parker based on a temperature distribution function for a thermally insulated solid described by Carslaw and Jeager.\(^5\) Using a relative temperature of 1/2, an expression for
thermal diffusivity can be derived by substituting equations 38, and 39, into equation 37 (Equation 40).

\[
D = \frac{0.13879L^2}{t_{1/2}} \quad \text{(40)}
\]

The Parker method is an idealized case, which assumes purely one dimensional heat flow. Subsequently, several methods have been developed to account for deviations from this ideal case. The Heckman, Cowan, and Koski methods correct for the heat pulse having a finite duration.\textsuperscript{6,65,66} In addition, the Cowan and Koski models account for radial heat losses. Although these models are adequate for determining thermal diffusivity, the Clark and Taylor method is the most widely used method to analyze thermal diffusivity.\textsuperscript{67} This method accounts for radiative heat losses which result in temperature changes on the back face of the specimen. To account for these heat losses, correction factors for various rise times were developed. The expression for thermal diffusivity is shown in Equation 41\textsuperscript{67}

\[
D_{\text{corrected}} = \frac{\alpha K_R}{0.13885} \quad \text{(41)}
\]

where \(D\) is the thermal diffusivity and the correction factor \(K_R\) is defined as

\[
K_R = -0.3461467 + 0.361578 \left( \frac{t_{0.75}}{t_{0.25}} \right) - 0.06520543 \left( \frac{t_{0.75}}{t_{0.25}} \right)^2 \quad \text{(42)}
\]

where \(t_n\) is the time for the specimen temperature to reach the \(n\)th fraction of \(T_{\text{max}}\).
2.3.4. **Heat Capacity.** Heat capacity ($C$) is a thermal property that describes the amount of heat required to increase the temperature of a material. Heat capacity is comprised of both electron and phonon portions. In most materials, the total heat capacity is sufficiently described by only the phonon contribution below the Debye temperature due to the Pauli exclusion principle. Both the phonon and electron portions of $C$ are described below. In most practical cases, $C$ is either defined as the constant volume heat capacity ($C_v$), which is the change in internal energy with respect to temperature (Equation 43), or constant pressure heat capacity ($C_p$), which is the change in enthalpy with respect to temperature (Equation 44).

$$C_v = \left(\frac{\partial U}{\partial T}\right)_V$$  \hspace{1cm} (43)
\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p \]  

(44)

From these definitions, the fundamental laws of thermodynamics can be used to relate the constant volume and constant pressure heat capacities as shown in Equation 45, where \( \beta \) is the volume expansion coefficient and \( T \) is the absolute temperature.\(^{58}\)

\[ C_p = C_v \left( 1 + \beta \gamma T \right) \]  

(45)

The Gruneisen parameter (\( \gamma \)) is defined by Equation 46 where \( K \) is the bulk modulus, \( V \) is the molar volume and \( C_v \) is the heat capacity per particle.

\[ \gamma = \frac{\beta K V}{C_v} \]  

(46)

Several experimental techniques commonly used to measure \( C_p \) are adiabatic calorimetry, differential scanning calorimetry (DSC), and the laser flash method.\(^1,64,68\) In all three methods, \( C_p \) is measured indirectly by comparison of the energy required to heat a sample to the amount of energy required to raise the temperature of a standard of known \( C_p \). The difference between the amounts of heat required to raise the temperatures of the specimen and the reference are used to compute heat capacity of the specimen.

The mechanisms of heat transfer and storage in a material are determined by the vibrational and rotational energies, the change in electron energy levels, and atomic displacements due to defects.\(^2\) These mechanisms are similar for most ceramics, therefore the constant volume heat capacities of most materials approach 3R near the Debye
temperature (Figure 2.10). The Debye temperature ($\theta$) is the temperature at which all lattice vibration modes within a material are activated and is defined by Equation 47.

$$\theta = \frac{h\nu}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{1/3}$$

(47)

Where $h$ is the Dirac constant, $\nu$ is the vibrational group velocity of the phonons, $k_B$ is Boltzmann’s constant, $N$ is the number of phonon vibrational modes, and $V$ is the molar volume.

Figure 2.10. Constant volume heat capacities for several oxide ceramics showing that values plateau around $3R$.\(^2\)
2.3.4.1. Phonon contribution. Several models based on quantum theory can be used to describe the phonon contribution to the heat capacity. Debye’s model was based on Einstein’s single harmonic oscillator model, which assumes that all of the atoms in a lattice are vibrating with the same frequency. Quantum theory can be used to show that the energy of the $i^{th}$ energy level of a harmonic oscillator is given in Equation 48:

$$\varepsilon_i = \left(1 + \frac{1}{2}\right) nhv$$

(48)

Therefore, the total energy of a crystalline material can be estimated by summing across 3n harmonic oscillators (Equation 49).

$$U' = 3 \sum n_i \varepsilon_i = \frac{3}{2} nhv + \frac{3nhv}{(e^{hv/kT} - 1)}$$

(49)

This expression can then be used to derive the constant volume heat capacity (Equation 50).

$$C_v = \left(\frac{\partial U'}{\partial T}\right)_V = 3nk \left(\frac{hv}{kT}\right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2}$$

(50)

This model predicts heat capacities at higher temperatures where more phonon modes are active. However, the predictions deviate from measured values at lower temperatures. Einstein’s model was improved by Debye who assumed that the vibrational frequencies of the phonons could take on values that ranged from zero up to a maximum value that was temperature dependent. The Debye wave velocity in a solid can be approximated as...
\[ v_d = \left[ \frac{1}{2} \left( \frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \right]^{\frac{1}{3}} \]  

(51)

where \( v_t \) is the transverse wave velocity and \( v_l \) is the longitudinal wave velocity, the expressions for both are shown in Equations 52 and 53, respectively

\[ v_t = \sqrt{\frac{G}{\rho}} \]  

(52)

\[ v_l = \sqrt{\frac{(B + \frac{4}{3}G)}{\rho}} \]  

(53)

where \( K \) is the bulk modulus, \( G \) is the shear modulus, and \( \rho \) is the density. Debye then integrated Einstein’s equation over his range of frequencies as can be seen in Equation 54

\[ C_v = \frac{9\hbar^3}{k^2 \theta_D^2} \int_0^{v_D} \nu^2 \left( \frac{h \nu}{kT} \right)^2 \frac{e^{h \nu/kT}}{(1 - e^{-h \nu/kT})^2} d\nu \]  

(54)

where \( \theta_D = h \nu_D / k \) is the Debye temperature. Debye’s model was successful in that it gave an excellent fit to experimental data at low temperatures.
2.3.4.2. Electron contribution. Free electrons are capable of charge transport and, therefore, add to the overall heat capacity of a material. Sommerfeld’s electron theory successfully applied the Fermi-Dirac distribution law to quantify the effect of electrons on thermal energy transportation.\textsuperscript{60,62} An expression of the electron contribution to heat capacity starts from the energy of a degenerate gas containing $\eta$ electrons per volume as shown in Equation 55,

$$E = 2 \int_{0}^{\infty} \epsilon N(\epsilon) f_{0}(\epsilon) \, d\epsilon = \left[ \frac{2}{5} \eta_{f}^{5/2} + \frac{\pi^{2}}{4} (kT)^{2} \eta_{f}^{1/2} \right]$$

where $N(\epsilon)c\,d\epsilon$ is the number of states of a given spin orientation per unit volume, $f_{0}(\epsilon)$ is the Fermi-Dirac distribution, $\epsilon$ is the energy at a given wave vector, $k$ is the Boltzmann constant, and $\eta_{f}$ is the Fermi energy. Differentiation of Equation 55 with respect to temperature gives the constant volume heat capacity due to electron conduction (Equation 56)

$$C_{v} = \frac{\partial E}{\partial T} = \frac{(2m)^{3/2}}{2\pi^{2} h^{3}} \eta_{f}^{3/2} \frac{\pi^{2}}{3} k^{2}T$$

where $h$ is the Dirac constant and $T$ is absolute temperature. Similar to the Einstein single harmonic oscillator model, the Sommerfeld approach sufficiently describes electronic contribution to heat capacity at high temperatures, but typically doesn’t agree with experimental values below the Debye temperature.\textsuperscript{60}
2.3.5. **Scattering Mechanisms.** The interactions of electron and phonon waves with other electrons, phonons, and lattice defects affect the thermal conductivity of a material. At all temperatures, the maximum thermal conductivity is limited by one of the scattering mechanisms, regardless of the purity of the material. Figure 2.11 shows the change in thermal conductivity as a function of temperature for a relatively pure, defect free metallic conductor. At low temperatures phonon and electron modes become excited and thermal conductivity increases. The limiting conditions are due to boundary scattering such as crystal or grain size in a nominally phase pure material or point defect scattering when solid solution impurities or other defects are present. Once high enough temperatures are reached the phonon-phonon, phonon-electron, and electron-electron waves begin to interact destructively. This phenomenon referred to as Umklapp scattering and is the limiting factor for thermal conductivity in nominally dense solids at high temperatures. This generally results in a peak thermal conductivity after all phonon and electron modes have become active followed by a gradual decrease in conductivity as Umklapp scattering becomes the limiting factor. At even higher temperatures, Umklapp scattering reaches a maximum value and thermal conductivity becomes temperature independent.\(^{57,72}\) The following sections will mathematically detail how scattering mechanisms affect the scattering times which control the overall phonon and electron contributions to thermal conduction.
Figure 2.11. Lattice thermal conductivity of CoSb$_3$. The dashed lines show the theoretical limits imposed by different scattering mechanisms.$^{57}$

2.3.5.1. **Electron scattering mechanisms.** Multiple scattering interactions occur for electrons in a crystal including interactions with lattice defects, phonons, and other electrons.$^{57,62,63}$ Impurities and lattice imperfections are present in all real crystals. The effect of impurities is generally higher at lower temperatures where the magnitude of phonon and electron scattering by other mechanisms is less. Impurity scattering is modeled as a purely elastic event. In this case, the mean time between scattering events for impurities ($\tau_f$) can be described as$^{57}$

$$
\frac{1}{\tau_f} = \frac{V}{(2\pi)^3} \int dk' W_{kk'} \left(1 - \frac{v'_k}{v_k}\right)
$$

(57)
where $V$ is the atomic volume, $k'$ is crystal wave vector, $W_{kk'}$ is the collision probability term and $\nu_x$ is the wave velocity of the electrons. Equation 58 from perturbation theory gives the collision probability where $E(k)$ is the electron energy and $U$ is the interaction potential.$^{57,69}$

$$W_{kk'} = \frac{2\pi}{\hbar} \delta \left[ E(k) - E(k') \right] \left| \langle k | U | k' \rangle \right|^2$$  \hspace{1cm} (58)

Figure 2.12 represents the electron impurity scattering in three dimensions. The lengths of both initial and final wave vectors are $k_f$ because the collisions are elastic.

![Figure 2.12. Depiction of impurity scattering of electrons. Scattering is a purely elastic event and initial and final magnitudes of electron wave vector is $k_F$.|$^{57}$](image)

The second, and potentially largest, scattering mechanism for electrons is the vibrating crystal lattice, which leads to electron-phonon scattering. The major difference between point-defect scattering and electron-phonon scattering is that the first is a purely elastic process and the second is inelastic, which involves emission and adsorptions of
phonons. In this case, \( k \) is defined as an electron “Bloch” wave and \( q \) as a phonon wave vector, which leads to a general equation for phonon-electron interaction as shown in Equation 59 where \( G \) is a reciprocal lattice vector. \(^{57}\)

\[
k + q = k' + G
\]  

(59)

Equation 59 is essentially a mathematic statement on the conservation of momentum. If \( G=0 \), it’s called a normal or N-process. In this case the resulting electron wave \( k' \) remains in the first Brillouin zone, is nearly elastic, and the scattering event provides little resistance to electron flow. When \( G \neq 0 \), it’s called an Umklapp or U-process. The \( G \) vector takes on a value that will keep the vector \( k + q \) within the first Brillouin zone. Umklapp scattering can have large effects on the electron waves and, in turn, electron flow. The mean tune between U-process events is described by Equation 60,\(^ {57,60}\)

\[
\frac{1}{\tau_k} = \frac{2\pi}{\hbar} \sum_q |C|^2 \left[ \delta\left(E_k - E_{k'} - \hbar\omega_q\right)\left(N_{q}^{\sigma} + 1 - f_{k'}^{\sigma}\right) + \delta\left(E_k - E_{k'} + \hbar\omega_q\right)\left(N_{q}^{\sigma} + f_{k'}^{\sigma}\right) \right]
\]  

(60)

where \( C \) is the electron-phonon coupling constant, \( \omega_q \) is the phonon vibration frequency, and \( f_{k} \) and \( N_{k} \) are the electron and phonon distribution functions. Approximations for this time can be determined for the low and high temperature limits as shown in Equations 61 and 62.\(^ {57}\)

\[
\frac{1}{\tau_k} \propto T \quad \text{for} \quad T \geq \theta_D
\]  

(61)

\[
\frac{1}{\tau} \propto T^3 \quad \text{for} \quad T \ll \theta_D
\]  

(62)
The final electron scattering process is self-scattering among electrons in the conduction band. Similar to the electron-phonon scattering, both N and U-processes are active for self-scattering. The N-type interaction involves conservation of electron momentum and, therefore, does not change electron resistivity. The U-processes are inelastic and can be described by Equation 63 when \( G \neq 0 \),

\[
\frac{1}{\tau_{e-e}} = A_{ee} T^2 + \frac{1}{2} \left( \frac{3}{E_F} \right)^{1/2} \left( \frac{k_B}{k_F \ell_e} \right)^{3/2} T^{3/2}
\]  

(63)

where \( A_{ee} \) is an experimentally determined coefficient and \( \ell_e \) is the electron mean free path. Electron-electron scattering is proportional to \( T^2 \), similar to electron-phonon scattering. Typically, electron-electron scattering is negligible compared to other scattering mechanisms at room temperature.

### 2.3.5.2. Phonon scattering mechanisms.

The significant scattering mechanisms for phonons include phonon-phonon scattering, phonon-electron scattering, U-processes, and point defects associated with impurities.\(^ {57,62,73,74} \) The mean time between scattering events for the phonon-electron scattering mechanism can be derived by assuming that the electrons are at equilibrium (Equation 64).

\[
\frac{1}{\tau_{p-e}} = \frac{2\pi}{\hbar} |C_q| \sum_{k,\sigma} f^\sigma(E_k) \left[ 1 - f^\sigma(E_{k+q}) \right] \delta(E_{k+q} - E_k - \hbar \omega_q)
\]  

(64)

The phonon-phonon interactions have N and U-processes as was seen for electron-electron scattering. Peierls gave the form of three-phonon processes for thermal resistivity as shown in Equation 65.\(^ {75} \)
\[ q_1 + q_2 = q_3 + G \] (65)

Equation 66 is the derivation of relaxation time for N-processes, which involve collisions where \( G = 0 \). The coefficients \( B, a, \) and \( b \) are all determined by fitting experimental data.

\[ \frac{1}{\tau_N} = B \omega^a T^b \] (66)

For U-processes where \( G \neq 0 \), Peierls suggested the relaxation time have the form of Equation 67 where both \( n \) and \( m \) are on the order of 1.

\[ \frac{1}{\tau_U} \propto T^n \exp\left(\frac{\theta_D}{mT}\right) \] (67)

At sufficiently high temperatures the U-process will become the dominant scattering mechanisms for crystalline solids, resulting in an inverse relationship between thermal conductivity and temperature.

The final phonon scattering mechanism is point defects. Klemens was the first to mathematically calculate the mean time between scattering events for this mechanism. As shown by Equation 68, the scattering time depends on the mass of the defect relative to the atom that should occupy the lattice site.

\[ \frac{1}{\tau_{PD}} = \frac{V}{4\pi \nu} \omega \sum_i f_i \left( \frac{m_i - \bar{m}}{\bar{m}} \right)^2 \] (68)

where \( V \) is the atomic volume, \( m_i \) is the mass of the \( i^{th} \) atomic species, \( f_i \) is the fraction of atoms with mass \( m_i \), and \( \bar{m} \) is the average atomic mass of all atoms in the system.
2.3.6. Thermal Conductivity. One of the notable properties of ZrB$_2$ is its high thermal conductivity ($k_T$). Reported room temperature $k_T$ values for single crystals are 140 W/m·K along the [10$ar{1}$0] direction and 100 W/m·K along the [0001].$^{77}$ For polycrystalline ZrB$_2$, reported room temperature $k$ values range from 45 to 135 W/m·K, but converge to values between 60 and 80 W/m·K as temperature approaches 2273 K.$^{16,17,23,24,25}$ Some representative values are summarized in Figure 2.13. Impurities are most likely the cause for most of the variation in thermal properties. McClane has shown that the addition of Hf, Nb, W, Ti, or Y in ZrB$_2$ solid solutions leads to reductions in thermal conductivity.$^{30}$ In addition, studies by Thompson and Zimmermann have shown that additions of W reduce room temperature thermal conductivity.$^{16,17}$

The only polycrystalline ZrB$_2$ ceramics with room temperature $k_T$ values of more than 100 W/m·K (Guo and Zhang) were produced by reaction processes.$^{23,24}$ Guo reported $k_T = 133$ W/m·K at room temperature with enhanced thermal diffusivity and heat capacity.$^{24}$ Zhang reported $k_T = 110$ W/m·K at room temperature but used NIST_JANAF tables for Cp instead of measured values indicating that $k$ could potentially be higher.$^{23}$ Impurities could explain the high thermal conductivity of reaction processed ZrB$_2$ but the exact mechanism are still unclear. Regardless of the mechanisms, the large spread in values at room temperature for ZrB$_2$ indicates the intrinsic thermal conductivity for high purity ZrB$_2$ may still be unknown.
2.3.7. **Effects of Isotopes**. Isotope enrichment has been shown to increase the thermal conductivity of lattice conductors such as diamond, silicon, germanium, graphene, boron nitride, and LiO$_2$. The magnitude of the increase has ranged from 10 to 45% for lattice conductors with full enrichment of a single isotope. Anthony saw an increase of ~35% in thermal conductivity for full enrichment of the lighter $^{12}$C isotope in diamond at room temperature. Some of the largest increases have been observed for boron containing compounds as natural boron has a relatively large isotopic disorder ($19.9\%$ $^{10}$B and $80.1\%$ $^{11}$B) compared to carbon ($98.9\%$ $^{12}$C and $1.1\%$ $^{13}$C). Chang et al. observed a thermal conductivity of 124 W/m·K in $^{11}$B enriched boron nitride nano tubes compared to 68 W/m·K for the same material with the natural isotopic ratio.
This represents an increase of ~45% in thermal conductivity for full enrichment of the heavier $^{11}\text{B}$ isotope for boron nitride at 100K. Generally, the enhancement in thermophysical properties has been attributed to a reduction of phonon-phonon scattering. The effects of isotope enrichment have also been described with kinetic theory and first principle simulations.\textsuperscript{86, 87, 88, 89, 90, 91} For phonon-phonon scattering due to isotopes, the enrichment of lighter isotopes is expected to have a greater effect due to faster phonon velocities as predicted by Equation 68. Whether a material is enriched in a heavier or lighter isotope, enrichment can have large effects on thermal properties.

2.4. ELECTRICAL PROPERTIES

2.4.1. Refractory Diborides. Electron energy spectrum calculations have been carried out by Samsonov and Goryachev which show that ZrB$_2$ has 3.6 free electrons per atom unit cell.\textsuperscript{8} In transition metal diborides, metallic conduction is due to incomplete occupation of the upper energy level overlapping the free states. In metal rich borides (i.e. ZrB), electrons are transferred toward the metal sub-lattice. In borides rich in boron (i.e. ZrB$_{12}$), the transfer of electrons is directed towards the boron sub-lattice. The diborides, including ZrB$_2$, have behavior that lies between those extremes.\textsuperscript{8} The metallic bonding in ZrB$_2$ gives rise to metallic conduction resulting in electrical conductivities of $10^7$ S/cm or higher, which is similar to values reported for transition metals such as Ni or Fe.\textsuperscript{10}

Electrical conductivity depends on the number of charge carriers ($n$), their charge ($e$), and their mobility ($\mu$) within the crystal lattice (Equation 69).\textsuperscript{9, 92}

\begin{equation}
\sigma = n e \mu
\end{equation}
The charge on an electron is constant, but both the drift mobility and number of carriers are affected by additives, impurities, and defects. The drift mobility (Equation 70) can be modeled based on the scattering time between collisions ($\tau$), the electron charge ($e$), and the effective mass of the electron ($m_e$). \(^9, \^92\)

$$\mu = \frac{e\tau}{m_e} \quad (70)$$

### 2.4.2. Temperature Dependence.

As discussed previously, thermal vibrations of the lattice can scatter conduction electrons. To determine the temperature dependence of $\sigma$, the effect of lattice vibrations on the relaxation time, $\tau$, must be known. If the amplitude of the atomic vibrations is $a$, then scattering time can be defined using Equation 71, \(^9, \^92\)

$$\tau \propto \frac{1}{\pi a^2} \propto \frac{C}{T} \quad (71)$$

where $C$ is a temperature independent constant and the amplitude of atomic vibrations, $a$, are a function of temperature. $\tau$ can then be substituted back into the mobility term (Equation 70) to approximate the electrical resistivity (Equation 71). \(^9\)

$$\rho_T = \frac{1}{\sigma_T} = \frac{m_e T}{e^2 n C} \quad (72)$$

Equation 72 shows that electrical resistivity should increase linearly with temperature. Figure 2.14 shows a linear trend with increasing temperature that has been observed for ZrB\(_2\) above 100K.\(^{44}\)
2.4.3. Impurity Dependence and Mixing Rules. Mattheissen observed that the effect of scattering events on the resistivity of real materials were additive (Equation 73), where $\rho_l$ is the electrical resistivity due to impurities and $\rho_T$ is the electrical resistivity due to temperature.\(^{92}\)

$$\rho = \rho_l + \rho_T$$  \hspace{1cm} (73)

Models have also been proposed to describe the electrical resistivity of a material with a second phase. Volumetric mixing models can be used to describe the effects of a discrete second phase (Equation 74) when the two phases have similar electrical resistivities.\(^{73,74}\)

$$\rho_{\text{eff}} = x_a \rho_a + x_b \rho_b$$  \hspace{1cm} (74)

When the electrical resistivities of the constituent phases are different by a factor of 10 or more, semi-empirical equations have been developed to more accurately model the effect
of mixtures.\textsuperscript{59,60,92,93} For the cases in which the resistivity of the second phase is over an order of magnitude greater than the continuous phase equation (75) may be applied.

\[ \rho_{\text{eff}} = \rho_c \left( 1 + \frac{1}{2} x_d \right) \left( 1 - x_d \right) \]  

\[ \rho_{\text{eff}} = \rho_c \left( \frac{1 - x_d}{1 + 2x_d} \right) \]  

Similarly, Equation (76) is applicable for when the continuous phase is over an order of magnitude greater than the dispersed phase.

\textbf{2.4.4. Nordheim’s Rule.} For metallic conductors with similar electrical resistivities, solid solutions produced by mixing typically have electrical resistivity higher than either of the constituents. The mechanism responsible for the increase in resistivity of the solution is point-defect scattering, which can commonly be described using Nordheim’s rule as shown (Equation 77),\textsuperscript{32,45,78}

\[ \rho = x_a \rho_a + \left( 1 - x_a \right) \rho_b + c x_a \left( 1 - x_a \right) \]  

where \( \rho \) is the electrical resistivity, \( x_a \) is the volume fraction of the additive, and \( c \) is the experimentally determined Nordheim coefficient. As can be seen in Figure 2.15, this relationship can predict the effects of solid solutions in several transition metal boride solutions.\textsuperscript{94}
Figure 2.15. Fits for Nordheim’s Rule fit to electrical resistivity of TiB$_2$-VB$_2$ and ZrB$_2$-NbB$_2$ solid solution additions.$^{94}$

2.5. AB INITIO MODELING

2.5.1. DFT. Density functional theory (DFT) is a computation method to solve the Schrödinger equation for electron structure of a many atom model. The form of the Schrödinger equation that is used in the models in the present study is the time independent, nonrelativistic Schrödinger equation which can be seen in Equation 78.$^{95,96}$

$$\left[ \frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) \right] \psi = E \psi$$ (78)

Where m is the electron mass, $\hbar$ is Plank’s constant, $\psi$ is the electron wave function, and E is an eigenvalue that satisfies the eigenvalue equation. The three terms in the brackets are the kinetic energy, the interaction energy between an electron and the collection of atomic nuclei, and the self-interaction energies between electrons. The Kohn-Sham spin-
density functional method is a popular method for determining the electronic structure of solid matter.

DFT is based on two mathematical theorems provided by Kohn and Hohenberg, and a set of equations by Kohn and Sham in the mid-1960s. The first theorem states: **The ground state energy from Schrödinger’s equation is a unique functional of the electron density.** This means that the ground-state electron density uniquely determines properties such as the wave function and energy of the ground state of a solid. The second theorem states: **The electron density that minimizes the energy of the overall functions is the true electron density corresponding to the full solution of the Schrödinger equation.** Together, these theorems mean that the electron density can be expressed in a set of equations in which each equation only involves a single electron.

In the Kohn-Sham approach, a solution is found for the ground state total energy $E$ and spin densities $n_\uparrow(r), n_\downarrow(r)$ for a collection of $N$ electrons. The primary difference from the Kohn-Sham equations and the full Schrödinger equation is the solution of only a single electron wave function. The model also includes electron self-interaction and external interactions, $\nu(r)$, generated from the nucleus. This is accomplished by the solution of the one electron Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + \nu(r) + u([n];r) + \nu^\sigma_\alpha([n_\uparrow,n_\downarrow];r)\right)\psi_{\alpha\sigma}(r) = \varepsilon_{\alpha\sigma} \psi_{\alpha\sigma}(r) \quad (79)$$

where $\sigma=\uparrow$ or $\downarrow$ is the z-component of spin, and $\alpha$ stands for the remaining one electron quantum numbers. The classical Hartree potential is given by Equation 80
\[ u([n]; r) = \int d^3 r n(r) = N \]  
\[ u \]  

and the exchange-correlation potential energy is shown in Equation 81.

\[ \nu_{xc}^\sigma \left( n_\uparrow, n_\downarrow ; r \right) = \frac{\delta E_{xc}}{\delta n_\sigma (r)} \]  
\[ \nu \]  

In order to solve the Schrödinger equation (Equation 79), the exchange-correlation energy per particle \( E_{xc} \) must be specified. The true form of this functional is not known, but can be approximated as an electron gas to make the electron density function solvable. The best known class of functionals are known as generalized gradient approximations (GGA’s) in which known information of the local density is approximated through a gradient (Equation 82).  
95, 96

\[ E_{xc}^{LSD} \left[ n_\uparrow, n_\downarrow \right] = \int d^3 r n(r) e_{xc} \left( n_\uparrow (r), n_\downarrow (r) \right) \]  
\[ E \]  

No experimental knowledge is required as the crystal structure and lattice spacings of a solid can be determined by minimization of energy calculations. Once the exchange-correlation functional has been approximated, and the crystal structure determined, the Kohn-Sham equations can be solved and the electron density of states and electron band structure for a solid can be determined.
2.5.2. First Principles Computational Properties of ZrB₂. First principles approaches have successfully predicted intrinsic electron and phonon properties of refractory diborides that cannot be determined experimentally.\(^{70, 95, 98, 99, 100, 101}\) Figure 16 shows the electron density of states for ZrB₂ and the phonon density of states for ZrB₂ and HfB₂ as calculated by Lawson et al.\(^99\) The electron density of states (eDOS) shows a non-zero eDOS at the Fermi level which explains the metallic nature of ZrB₂. The phonon density of states can also be interpreted to separate the vibrational frequencies into acoustic and optical branches. The large effect of atomic mass can be seen by comparing ZrB₂ and HfB₂, which shows that acoustic vibrations shift to lower frequencies when the heavier Hf atoms are in the same structure as ZrB₂.

![Figure 2.16. a) Electron and b) Phonon density of states for ZrB₂ by Lawson et al.\(^99\)](image)

From the electron and phonon wave properties, DFT simulations can be used to determine intrinsic thermal properties. Returning to Einstein’s single harmonic oscillator
model, the total energy of a crystalline material can be written as the summations of the propagation wave vectors, $q$, and the polarization, $s$, of each atom as seen in equation 83,

$$U_{ph} = \sum_{q,v} \frac{\hbar \omega(q,v)}{e^{(\hbar \omega(q,v)/k_BT)} - 1} + \frac{1}{2} \hbar \omega(q,v)$$  \hspace{1cm} (83)

where $\hbar$ is the Dirac constant, $k_B$ is Boltzmann’s constant, and $T$ is temperature. The harmonic approximation (Equation 84) is a simulation of the constant volume heat capacity ($C_v$) which can be determined by taking the derivative of Equation 83 with respect to temperature.\(^{93}\)

$$C_v = \frac{k_B N}{3} \sum_{q,v} \left( \frac{\hbar \omega(q,v)}{2k_B T} \right)^2 \left( \frac{1}{\text{Sinh}^2(\frac{\hbar \omega(q,v)}{2k_B T})} \right)$$ \hspace{1cm} (84)

It is often more useful to determine the amount of heat going into a solid at constant pressure. The quasiharmonic approximation (QHA) involves the determination of the phonon entropy from the pDOS curves, which can be obtained from DFT, as shown in Equation 85\(^{93}\)

$$S_{ph}(T) = k_B \sum_{j}^{N} \ln \left( \frac{k_B T}{\hbar \omega_j} \right)$$ \hspace{1cm} (85)

where $N$ is the total number of phonon modes. The constant pressure heat capacity, $C_p$, can be defined as

$$C_p(T) = T \left. \frac{dS}{dT} \right|_p$$ \hspace{1cm} (86)
Combining equation 85 and 86 gives the QHA of constant pressure heat capacity. This is typically the heat capacity measured from calorimetry techniques such as DSC and laser flash. Modeling $C_p$ allows for direct comparison with experiment and the ability to map thermal property effects with phonon and electron wave changes. Figure 2.17 shows computations by Lawson et al. for the determination of $C_v$ for ZrB$_2$ and HfB$_2$. The simulations are in excellent agreement with experimental values.

The QHA is capable of determining other thermodynamic properties as well. The basis for these properties is the Helmholtz free energy, a combination of the energy terms from the phonons, elastic expansion and entropy as seen in Equation 87.

![Figure 2.17. QHA of $C_p$ for ZrB$_2$ and HfB$_2$ compared to experimental values determined by Zimmermann et al.]

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17, 99

93
\[
F_{\text{vib}}^* = \int_0^\infty g(\omega, x) \left[ \frac{\hbar \omega}{2} + k_B T \ln \left( 1 - e^{-\hbar \omega/k_B T} \right) \right] d\omega
\] (87)

Table 2.2 is a study by Zhang et al. in which numerous material properties such as bulk modulus and Debye temperature have been calculated for ZrB$_2$ and HfB$_2$ using the QHA.$^{70}$

**Table 2.2** Shear, Bulk, Elastic Modulus, Poisson’s Ratio, and Debye Temperature of ZrB$_2$ and HfB$_2$.

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<th>Compound</th>
<th>Method</th>
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<th>C$_\text{B}$</th>
<th>C$_\text{G}$</th>
<th>B$_\text{G}$</th>
<th>G$_\text{B}$</th>
<th>E$_\text{B}$</th>
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* Experimental data are the derived values.

The ability of such ab-initio models to predict the intrinsic phonon and electron wave properties as well as elucidate mechanisms behind thermal property changes due to various concentrations of solid solution impurities and other defects in ZrB$_2$ could be invaluable to guiding the development of tailored properties for leading edge materials for hypersonic vehicle applications.
1. SINTERING MECHANISMS AND KINETICS FOR REACTION HOT PRESSERED ZrB₂

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Abstract

Sintering mechanisms and kinetics were investigated for ZrB₂ ceramics produced using reaction hot pressing. Specimens were sintered at temperatures ranging from 1800 to 2100°C for times up to 120 minutes. ZrB₂ was the primary phase, although trace amounts of ZrO₂ and C were also detected. Below 2000°C, the densification mechanism was grain boundary diffusion with an activation energy of 241 ± 41 kJ/mol. At higher temperatures, the densification mechanism was lattice diffusion with an activation energy of 695 ± 62 kJ/mol. Grain growth exponents were determined to be n = 4.6 at 1900°C and n = 4.5 at 2100°C, which indicated that a grain pinning mechanism was active in both temperature regimes. The diffusion coefficients for grain growth were $1.5 \times 10^{-16}$ cm$^4$/s at 1900°C and $2.14 \times 10^{-15}$ cm$^4$/s at 2100°C. This study revealed that dense ZrB₂ ceramics can be produced by reactive hot pressing in shorter times and at lower temperatures than conventional hot pressing of commercial powders.

1.1. Introduction

ZrB₂ is a transition metal diboride that belongs to the ultra high temperature ceramic (UHTC) family of materials. The crystal structure is hexagonal AlB₂ type with alternating layers of B atoms in graphite like rings and Zr atoms in a hexagonally close
packed arrangement.\textsuperscript{1,2} Due to strong covalent bonding, ZrB\textsubscript{2} has gained interest for its melting temperature (3250°C), hardness (23 GPa), and elastic modulus (526 GPa).\textsuperscript{2,3,4,5} In addition to mechanical properties, ZrB\textsubscript{2} has been investigated due to its high thermal and electrical conductivities.\textsuperscript{2,4,6,7,8,9,10} Proposed applications that take advantage of these properties include thermal protection systems for hypersonic vehicles, molten metal crucibles, microelectronic substrates, high temperature electrodes, and others.

Based on previous studies, full densification of ZrB\textsubscript{2} usually requires sintering temperatures above 2000°C and applied pressures of at least 32 MPa.\textsuperscript{11,12} A series of papers published during the 1960s reported kinetic studies for the sintering of ZrB\textsubscript{2} and HfB\textsubscript{2}.\textsuperscript{11,12,13,14} In those studies, full densification without sintering additives was only achieved for non stoichiometric compositions such as ZrB\textsubscript{1.89}. Presumably, a liquid phase was present in those compositions since accepted phase diagrams show that ZrB\textsubscript{2} is a line compound.\textsuperscript{15} The primary densification mechanism for the temperature range 2000 to 2300°C was identified as grain boundary diffusion, which was thought to proceed through a liquid film.\textsuperscript{12} Kinetic studies on stoichiometric HfB\textsubscript{2} have been conducted and can be used as a comparison due to the similarity in behavior of HfB\textsubscript{2} and ZrB\textsubscript{2}. Examination of HfB\textsubscript{2} densification concluded that the initial stage of sintering was particle rearrangement and fragmentation while the final stage of sintering was controlled by stress directed vacancy diffusion where the rate controlling mechanism was either lattice diffusion of boron or grain boundary diffusion of hafnium.\textsuperscript{14} Most densification studies since the 1960s have focused on the effects of sintering additives for reducing hot pressing temperatures, enabling pressureless sintering\textsuperscript{16,17,18,19} or employing current assisted sintering.\textsuperscript{20,21,22,23} While a variety of different sintering techniques have been
studied for ZrB$_2$ densification, the intrinsic sintering mechanisms of stoichiometric ZrB$_2$

A wide range of ZrB$_2$ grain sizes have been reported for densification techniques including hot pressing (HP), pressureless sintering (PS), and spark plasma sintering (SPS). Grain sizes for dense ceramics produce from as received commercial ZrB$_2$ powders sintered without additives have reported to be in the range of ~10 µm to ~25 µm.$^{12,24,25}$ Powders were densified at temperatures ranging from 2000 to 2200°C with PS times from ~40 min to ~15 hrs. Intentional sintering additives, or additives incorporated during milling operations, can enhance densification and subsequently reduce the final grain size. For example, grain sizes from ~1 µm to ~15 µm have been reported for dense ZrB$_2$ with sintering additives.$^2,4$ When sintering additives are used, densification temperatures from 1450 to 2250°C and times from 2 to 240 min can produce near full density.

Reaction hot pressing (RHP) is another method for producing high purity ZrB$_2$ ceramics with relative density above 98% at temperatures below those typically required for densification of ZrB$_2$.$^1,16,26,27$ Studies by Chamberlain et al. and Zhang et al. have shown that RHP can produce dense ZrB$_2$ and ZrB$_2$-SiC with grain sizes under 3 µm with higher defect concentrations than dense ceramics produced from pre-reacted. The combination of reduced grain sizes and increased defect concentrations is thought to enhance densification at lower temperatures.$^1,27$ Full densification was achieved at temperatures as low as 1650°C for ZrB$_2$-SiC, but due to more rapid grain coarsening, phase pure ZrB$_2$ required a temperature of 2100°C for full
densification.\textsuperscript{1,27} Although enhanced densification has been observed using reactive methods, the investigation of sintering behavior has been limited to measuring relative densities and densification rates with no elucidation of densification mechanisms.

The purpose of this paper is to investigate the intrinsic sintering mechanisms, grain growth kinetics, and resulting microstructure of reaction hot pressed ZrB$_2$ ceramics.

1.2. Theory

Polycrystalline materials sinter through the diffusion of atoms, which is driven by the reduction of surface energy. Coble modeled solid state sintering by modifying creep equations for dense solids to hot pressing of polycrystalline ceramics, by converting the creep rate to densification rate, and accounting for the porosity that is inherent in powder compacts.\textsuperscript{28,29,30,31} Creep by lattice diffusion was modeled by Herring and is shown in Equation 1, where $\dot{\varepsilon}_l$ is lattice diffusion creep rate, $N_l$ is a constant for lattice diffusion, $D_l$ is the lattice diffusion coefficient, $\Omega$ is the unit cell volume, $G$ is the grain size, $T$ is absolute temperature, $k$ is the Boltzmann constant, and $p_a$ is the applied stress.

$$
\dot{\varepsilon}_l = N_l \frac{D_l \Omega p_a}{G^2 kT}
$$

(1)

Creep by grain boundary diffusion was modeled by Coble and is shown in Equation 2,

$$
\dot{\varepsilon}_c = N_b \frac{D_b \delta_b \Omega p_a}{G^3 kT}
$$

(2)

where $\dot{\varepsilon}_b$ is grain boundary diffusion creep rate, $N_b$ is a constant for grain boundary diffusion, $D_b$ is the grain boundary diffusion coefficient, and $\delta_b$ is the width of the grain boundaries. The biggest difference between lattice and grain boundary diffusion models
is the $G^2$ term for lattice diffusion and the $G^3$ term for grain boundary diffusion. The creep rate is equivalent to the linear strain rate and can be related to the densification rate through Equation 3,

$$\dot{\varepsilon} = -\frac{1}{L} \frac{dL}{dt} = \frac{1}{\rho} \frac{d\rho}{dt}$$

(3)

where $L$ is the thickness of the powder compact and $\rho$ is the density. The porosity is compensated for by modifying the applied stress term. The stress on the grain boundary ($p_e$) is altered by applying a stress compensation ($\phi$) factor to the applied stress. The driving force for densification due to surface curvature is modeled as the surface energy ($\gamma_{sv}$) over the particle radius ($r$). Applying Equation 3 and modifying the total driving force to account for the surface curvature and applied pressure; the specific models for lattice diffusion (Equation 4) and grain boundary diffusion (Equation 5) for the intermediate stage of densification used in this study are shown below.\(^{32}\)

$$\frac{1}{\rho} \frac{d\rho}{dt} = N_L \left( \frac{D_L \Omega}{G^2 kT} \right) \left( p_{a} \phi + \frac{\gamma_{sv}}{r} \right)$$

(4)

$$\frac{1}{\rho} \frac{d\rho}{dt} = N_b \left( \frac{D_b \delta \Omega}{G^3 kT} \right) \left( p_{a} \phi + \frac{\gamma_{sv}}{r} \right)$$

(5)

Plotting relative density as a function of time over grain size to the power $n$ ($\rho$ vs. $t/G_n$) was used to identify the diffusion mechanism that controls densification at a given temperature. Assuming all processing conditions are kept constant except temperature, the diffusion coefficient ($D$) for densification is related to temperature through the Arrhenius equation (Equation 6),
\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]  

(6)

where \( D_0 \) is the diffusion coefficient constant, \( Q \) is the activation energy of the rate controlling densification mechanism, and \( R \) is the ideal gas constant. By substitution of Equation 6 into either Equation 4 or 5, the densification rate can be related to the activation energy (Equation 7),

\[
\dot{\rho} = \frac{1}{\rho} \frac{d\rho}{dt} \approx B \exp\left(-\frac{Q}{RT}\right)
\]

(7)

where \( \dot{\rho} \) is the densification rate and \( B \) is a constant that is independent of temperature.

The general method to solve for the activation energy of densification is to plot \( \ln \left( \frac{1}{\rho} \right) \left( \frac{d\rho}{dt} \right) \) as a function of \( 1/T \), which produces lines with a slope of \(-Q/R\).\(^{12,14}\) The benefit of this method is high precision, if numerous points are fit.

Grain coarsening kinetics can be described by Equation 8, which was derived by Burke and Turnbull.\(^{33}\) The grain growth exponent, \( n \), was determined from the linear trend line fit to a Log-Log plot containing the final grain size as a function of sintering time. The \( G_0^n \) is removed under the assumption that the initial grain size is much less than the final grain size

\[
G^n = G_0^n + Kt
\]

(8)

where \( G_0 \) is the initial grain size at time zero, \( G \) is the grain size at time \( t \), \( K \) is the grain growth diffusion coefficient. Typically, \( n \) values between 2 and 4 are observed for
ceramics that exhibit normal grain growth. An n value of 2 indicates a grain growth mechanism of grain boundary diffusion, an n value of 3 indicates lattice diffusion, and an n value of 4 indicates surface diffusion.\textsuperscript{34}

1.3. Procedure

1.3.1. Processing. The starting materials for this study were ZrH\textsubscript{2} (Chemetall, Grade S, d\textsubscript{50} = 5.1 µm), and B (EaglePicher, Grade Sp 99, d\textsubscript{50} = 0.2 µm). Batches were mixed by ball milling stoichiometric ratios of ZrH\textsubscript{2} and B for 3 hrs with ZrB\textsubscript{2} media in hexanes. Solvent removal was performed using rotary evaporation (Model Rotavapor R-124, Buchi, Flawil, Germany) at a temperature of 70°C, a vacuum of 27 kPa, and a rotation speed of 75 rpm. Powders were then placed into boron nitride coated graphite dies and cold uniaxially pressed at 35 MPa.

Compacted powders were densified in a resistively heated graphite furnace (3060-FP20, Thermal Technology, Santa Rosa, CA). The compacts were heated under vacuum (~25 Pa) at 5°C/min to ~950°C with an isothermal hold of ~12 hrs to promote Reaction 9.

\[ \text{ZrH}_2(s) + 2B(s) \xrightarrow{950°C} \text{ZrB}_2(s) + H_2(g) \] (9)

After the isothermal hold at 950°C, the hot press was heated to from 1800 to 2100°C at ~50°C/min with three additional isothermal holds with durations of 15, 45, and 45 min. The 15 min hold at 1050°C promoted further reaction, while 45 min holds at 1450°C and 1650°C were used to remove surface oxide impurities, as previously reported.\textsuperscript{1, 17, 18} After the hold at 1650°C, the furnace was backfilled with helium (~10\textsuperscript{5} Pa) and heated to temperatures ranging from 1800°C to 2100°C at ~75 °C/min. Once the
furnace reached the desired densification temperature, a uniaxial load of 50 MPa was applied. During the isothermal hold, the change in thickness of the specimens was measured in situ using a linearly variable differential transducer attached to the hot press rams. Time dependent density values were calculated using Equation 10

$$\rho_t = \left( \frac{L_f}{L_t} \right)^3 \rho_f$$  \hspace{1cm} (10)

where $L_f$ is final length, $L_t$ is the length at time $t$, and $\rho_f$ is the final density.

The furnace was cooled at ~20°C/min and the load was released at 1650°C.

1.3.2. Characterization. The phases present in the resulting ceramics were characterized using X-ray Diffraction (XRD; Philips Panalytical Multipurpose diffractometer, the Netherlands) that had a Cu-Kα source. Hot pressed billets were crushed and ground using an agate mortar and zirconia pestle. Diffraction patterns were obtained by scanning from 3° to 90° two theta at 0.03° per step with a 1s count time.

Specimens for microstructure analysis were cut parallel to the hot pressing direction with diamond coated blades and then ground and polished. Polymer bonded diamond grinding disks and water lubricant were used for abrasive sizes from 145 µm down to 6 µm. Felt pads and water-based diamond slurry suspensions were used for the abrasive sizes from 3 µm down to 0.05 µm. Scanning electron microscopy (SEM; Hitachi S570, Japan) was performed to characterize microstructures and grain sizes. An accelerating voltage of 15 kV and operating distance of 12 mm were used during SEM operation.
Bulk densities were measured using Archimedes method. Deionized water at room temperature was the immersion medium. Specimens were placed under vacuum for 24 hours to ensure complete infiltration of open porosity prior to testing. The theoretical density was based on calculated crystallographic densities that used lattice parameters determined from XRD analysis to calculate the unit cell volume.

Powders for particle size analysis were removed from the hot press die after the 1650°C hold. The powder compact was crushed with a mortar and pestle and the resulting powders were ultrasonicated to break apart loose agglomerates. Particle sizes of reacted powders were determined using laser diffraction particle size analysis (Microtrac, S3500, Montgomeryville, PA). SEM images were examined to characterize particle morphology. Samples for SEM analysis were prepared by lightly coating powders onto graphite tape.

Grain sizes and second phase volume fractions were determined using computerized image analysis (ImageJ, National Institutes of Health, Bethesda, MD) of polished and etched SEM cross section images. The areas (A) of a minimum of 300 grains from multiple SEM images of different regions of the specimens were analyzed for each sintering temperature and time. Average grain diameter (D) was calculated assuming that grains were spherical using Equation 11.

\[
D = \sqrt{\frac{4A}{\pi}}
\]  

(11)
The nomenclature used to identify specimens includes the densification method, sintering temperature, and time. For example, a specimen densified by RHP at 2100°C for 60 min was labeled RHP-210-60.

1.4. Results and Discussion

1.4.1. Characterization. The size (Table I) and morphology (Figure 1) of ZrB$_2$ particles was analyzed after the 1650°C. The powders were extracted at this point to characterize them prior to the onset of densification. Particle sizes as small as 0.13 µm were detected by laser diffraction analysis with an average particle size ($d_{50}$) of 0.25 µm. SEM images show agglomeration of particles, which indicates that the primary particle size is likely to be smaller than the size determined by laser diffraction. Sharp edges observed on the larger particles could indicate fracture surfaces from the powder preparation process or, more likely, directional growth along certain crystallographic orientations. The particle size analysis confirmed that sub-micron particles were present at the onset of densification.

The bulk densities of reaction hot pressed ZrB$_2$ billets ranged from 5.41 to 6.09 g/cm$^3$, depending on the hot pressing temperature and time (Table II). In general, densities increased as sintering temperatures and times increased. Relative densities as high as 98% were measured for specimens sintered at temperatures as low as 1800°C, suggesting that full density could potentially be achieved at temperatures below 1800°C, if even longer sintering times were used. Grain sizes ranged from 2.3 ± 1.1 to 5.8 ± 2.3 µm, which were comparable to values reported for ZrB$_2$ sintered with additives. For comparison, these values were about one third of the typical grain sizes reported for ZrB$_2$
densified without additives.\textsuperscript{1,2,4,12} The small grain sizes were most likely due to the RHP process, which has been shown to produce nano-sized crystallites during the reaction step.\textsuperscript{1} Measured densities and grain sizes of materials processed at 1800°C through 2100°C indicated that reaction hot processing is capable of producing nearly full densification with grain sizes of less than 5 \( \mu \)m.

Analysis by XRD confirmed that ZrB\(_2\) was the predominant phase produced by RHP, but ZrO\(_2\) was also detected (Figure 2). Analysis of the starting powders did not reveal any ZrO\(_2\), therefore ZrO\(_2\) formed during RHP. The source of the oxygen was most likely the boron powder, which could oxidize and/or hydrate during storage and mixing. Rietveld refinement of XRD data determined that the lattice parameters for ZrB\(_2\) were \( a = 3.16802(2) \) Å and \( c = 3.53036(6) \) Å. The measured lattice parameters were consistent with values reported for pure ZrB\(_2\), which indicates that no significant solid solution contamination was present.\textsuperscript{2}

SEM analysis was consistent with the density measurements (Figure 3). A small volume fraction of dark inclusions were observed in all specimens, which were identified as carbon using Raman spectroscopy (not shown). Images of cross sections (Figure 4) confirmed that carbon contents were higher on the outer portions of the hot pressed billets compared to the cores. The distribution of carbon indicated that its presence may be due to interactions with the graphite die and furnace during RHP. For subsequent analysis, the carbon-rich surface layer was removed so that only the cores of the billets were analyzed. Image analysis indicated the residual amount of carbon in the cores of the specimens was
less than ~1 vol% while the ZrO\textsubscript{2} contents were ~2.5 vol%. SEM and XRD confirmed that RHP produced ZrB\textsubscript{2} that had high relative density.

Figure 5 shows grain size distributions for ZrB\textsubscript{2} densified at 1900°C and 2100°C for 60 min. The average grain size for RHP-190-60 was 3.7 ± 1.6 µm, which was ~30% less than the value of 5.8 ± 2.3 µm for RHP-210-60. The standard deviation for RHP-190-60 was also nearly half that for RHP-210-60. This could be due to a much broader distribution of large grain sizes for the RHP-210-60 specimen (Figure 5). The smaller grain sizes for specimens sintered at 1900°C were most likely due to lower atom mobility due to lower final hot pressing temperature. Full densification was possible at temperatures below 2100°C, which is the typical densification temperature for hot pressing of commercial ZrB\textsubscript{2} without sintering additives. Even though full densification took longer at temperatures below 2100°C, it produced smaller grains, and generated narrower grain size distributions compared to higher temperatures.
1.4.2. Sintering Mechanisms

1.4.2.1. Densification. Relative densities were calculated from measured bulk densities and estimated crystallographic densities (Table II). Figure 6 shows the relative density achieved after hot pressing for 60 min at temperatures ranging from 1800 to 2100°C. All specimens reached 90% relative density or higher after 60 minutes. From 1800 to 2000°C relative density increased 3% for every 100°C. A change in the slope was observed between 2000 and 2050°C as relative density increasing 3% for a 50°C increase in temperature. This could be an indication that the densification mechanism may have changed between these temperatures. Regardless of the mechanism, density increased with increasing temperature for all specimens.

Figure 7 compares relative density as a function of temperature for specimens from the present study with several recently reported studies for nominally phase pure ZrB$_2$ ceramics without sintering additives that used different densification techniques (PS, HP, or SPS).$^{18,24,35}$ The relative densities achieved in the present study are similar to ZrB$_2$ produced by reactive SPS (R-SPS). A relative density of 97.2% was reported for R-SPS at 1800°C compared to 98.2% by RHP in the present study. Both R-SPS and RHP result in higher relative density values compared to PS or HP. Compared to conventional HP, RHP showed an increase in relative density of 2.6% at 2100°C and 15.7% at 2000°C. This indicates that densification is faster for RHP, particularly at lower temperatures. Specimens produced by RHP and R-SPS both contained residual ZrO$_2$ after densification. While boron oxides have been shown to be detrimental to the final densification of boride ceramics,$^{36}$ the effects of residual ZrO$_2$ on densification have not
been studied. Even with the residual oxide content, reaction processing leads to enhanced densification over PS and HP at temperatures below 2100°C.

The average particle size for the RHP ZrB$_2$ prior to the onset of densification was ~0.25 µm compared to ~2.0 µm for the commercial ZrB$_2$ powder used in both the PS and HP studies.\textsuperscript{18,24} Based on either Equation 4 or 5, with an assumed surface energy of ~1 N/m$^2$, the smaller particle size of the RHP powder would lead to an addition 4 MPa of sintering pressure at the onset of densification. This corresponds to increases in driving force of ~13% compared to HP and ~88% increase compared to PS. When considering the applied pressure of 50 MPa used in the present study, the 0.25µm average particle size would lead to an increase of ~10% in the driving force for densification compared to commercial powder. Based on these calculations, the finer starting particle sizes produced by reaction processing appear to be beneficial to densification by increasing the driving force.

Densification rates for RHP ZrB$_2$ ceramics varied significantly with temperature (Figure 8). Lower densification rates were observed for specimens sintered below 2000°C. For example, after 30 sec, the average densification rates were 0.389 min$^{-1}$ for RHP-200-60, RHP-205-60 and RHP-210-60 compared to 0.155 min$^{-1}$ for RHP-190-60 and RHP-180-60. This represents a decrease in densification rate of nearly 60% for specimens processed below 2000°C. As a result, RHP-200-60 took ~13 min to achieve a relative density greater than 90% compared to ~40 minutes for RHP-190-60. Based on these results, the densification rate nearly doubled for an increase in temperature of 100°C. This increase in densification rate might be another indication of a change in
densification mechanism below 2000°C. The densification rate achieved by RHP is significantly higher than rates reported for HP of ZrB$_2$ without sintering additives. Harrington et al. reported that commercial ZrB$_2$ powder with a starting particle size of ~2 μm achieved a relative density of ~90% after ~22 min when hot pressed at 2100°C with 32 MPa.$^{24}$ Rates reported for monolithic ZrB$_2$ densified by SPS are higher than RHP with relative densities above ~90% achieved after ~2 min at 1800°C by SPS compared to ~60 min to achieve the same density by RHP.$^{35}$ Although densification rates were higher for SPS, final relative density values were lower. At 1800°C, a relative density of ~97% was achieved for SPS compared to ~98% for RHP.$^{35}$ Based on these observations, RHP of ZrB$_2$ can be broken into two temperature regimes. The lower temperature regime is below 2000°C. In this regime, high relative densities can be reached, but densification rates are similar to HP. The higher temperature regime extends from 2000°C to 2100°C and full density can be reached at higher densification rates that are similar to those observed for SPS.
1.4.2.2. Activation energy for densification. Activation energies for densification (Table III) were determined from the slopes of Arrhenius plots (Figure 9). The activation energy values were based on intermediate stage densification, which was assumed to occur for relative densities in the range of 65% to 85%.\textsuperscript{32, 37} The slope changed significantly around 2000°C. By averaging the slopes of lines for different relative densities, the activation energy in the low temperature regime (1800 to 2000°C) was 241 ± 41 kJ/mol compared to 695 ± 62 kJ/mol for the high temperature regime (2000 to 2100°C). A few previous studies have examined densification kinetics for refractory diborides. The reported activation energies were 416 to 678 kJ/mol for HP ZrB\textsubscript{2}, 644 kJ/mol for PS ZrB\textsubscript{1.89}, 76 to 774 kJ/mol for TiB\textsubscript{2}, and 96 kJ/mol for high pressure (~800 MPa) hot pressed HfB\textsubscript{2}.\textsuperscript{12, 14, 38, 39, 40} These studies indicated that activation energies tended to be lower for smaller starting particle sizes and increased pressures as well as cases when second phases that enhanced densification were present. Mechanisms that require less energy, such as grain boundary diffusion, are typically active at lower temperatures whereas mechanisms such as lattice diffusion that require more energy are generally active at higher temperatures. For the present study, the activation energy in the higher temperature regime was similar to values previously reported for HP and PS of ZrB\textsubscript{2}. The activation energy for densification between 1800 and 2000°C was lower than reported in previous studies of ZrB\textsubscript{2} but within the range of values reported for other refractory diborides. If grain boundary diffusion was the dominant mechanism at lower temperatures, grain sizes in the sub-micron range at the onset of intermediate stage densification could explain the lower activation energy compared to some previous
studies. The combined results suggest that a change in mechanism occurs around 2000°C and that measured activation energies decreased with decreasing temperature.

1.4.2.3. Atom mobility. Figure 10 shows plots of relative density as a function of time and grain size fit to models for lattice (Equation 4) and grain boundary densification (Equation 5) mechanisms. Specimens sintered at 1900°C have similar fits for the grain boundary diffusion ($R^2=1$) and the lattice diffusion ($R^2=0.99$) models. However, since grain boundary diffusion is typically dominant at lower temperatures, it was selected as the dominant densification mechanism for the lower temperature regime. Specimens sintered at 2100°C fit the lattice diffusion model ($R^2=0.99$) better than the grain boundary diffusion model ($R^2=0.94$) indicating that densification was likely controlled by lattice diffusion in this regime. This is in agreement with previous studies that concluded that lattice diffusion has higher activation energies than grain boundary diffusion and is, therefore, typically dominant at higher temperatures.\textsuperscript{29, 30, 31} Kalish and Clougherty concluded that the diffusion in HfB$_2$ between 1400 and 1900°C was either stress directed interstitial B lattice diffusion or grain boundary diffusion of Hf.\textsuperscript{14} The transport species during densification of ZrB$_2$ is most likely B atoms, presumably due to the smaller atomic radius for B (0.9 Å) compared to Zr (1.6 Å). In addition, analysis of Zr-B diffusion couples revealed the growth of a layer of ZrB$_2$ into Zr, which is also consistent with the transport of B atoms through ZrB$_2$.\textsuperscript{1}
Based on the lower activation energies (~241 kJ/mol), and the densification mechanism model fits (Figure 10), the dominant densification mechanism between 1800 and 2000°C appears to be grain boundary diffusion. The higher activation energies (~695 kJ/mol), and fits from the densification mechanism models, indicate that lattice diffusion is the dominant densification mechanism above 2000°C.

Table IV shows values for the diffusion coefficients calculated using Equations 4 and 5. For both lattice and grain boundary diffusion the stress intensification factor, $\phi$, was assumed to be 1 and surface energy, $\gamma_{sv}$, was taken as 1 J/m$^2$ based on values typical observed for ceramics.\textsuperscript{32} For lattice diffusion, $1.24 \times 10^{-3}$ was used for $N_l$ by conversion of the constant $40/3$ to equivalent spherical grain diameters based on work done by Coble for ZrB$_{1.89}$.\textsuperscript{12} For grain boundary diffusion, $95/2$ was used for $N_b$ and the grain boundary width, $\delta_b$, was assumed to be $7 \times 10^{-9}$ m.\textsuperscript{12} At 1900°C, the lattice diffusion coefficient was $6.32 \times 10^{-8}$ cm$^2$/s and the grain boundary diffusion coefficient was $1.76 \times 10^{-9}$ cm$^2$/s. At 2100°C, the lattice diffusion coefficient was $1.55 \times 10^{-8}$ cm$^2$/s and the grain boundary diffusion coefficient was $4.49 \times 10^{-9}$ cm$^2$/s. The higher lattice diffusion coefficient for the specimens sintered at 2100°C compared to the grain boundary diffusion coefficient for the specimens sintered at 1900°C is consistent with the shorter times to full densification. Comparison with previously reported values shows that RHP at 2100°C had diffusion rates that were greater than what has been observed for traditional sintering without additives and diffusion rates at 1900°C were comparable to hot pressing using high pressures (>800 MPa).\textsuperscript{12,14} Coble and Hobbs reported a lattice diffusion coefficient of $3.0 \times 10^{-9}$ cm$^2$/s for PS at 2100°C (starting particle size of ~5 µm), which is an order of magnitude slower than the RHP specimens. This is consistent with the longer time (~155
min) taken to achieve a relative density of ~90% at 2100°C compared to ~5 min to achieve the same relative density in the present study. Applied pressure has shown to increased densification rates as Chown reported ~95% relative density in 80 min after applying moderate pressure (28MPa) at 2100°C. RHP with 50 MPa of pressure was 8 times faster as ~95% relative density was achieved in 10 min at 2100°C. Kalish et al. performed solid state sintering on HfB$_2$ at 1900°C and calculated a diffusion coefficient of $1.7 \times 10^{-8}$ cm$^2$/s, which is an order of magnitude larger than the grain boundary diffusion coefficient for the RHP specimens at 1900°C in the present study. Although grain sizes were relatively large (~5µm), the extreme pressures used (>800 MPa) increased the driving force for densification, which is most likely the reason for the rapid atomic diffusion. The increased sintering rate in RHP ZrB$_2$ may be due to the reduced particles sizes for the materials in the present study. Particle sizes were estimated to be ~0.25 µm at the onset of densification and Equations 4 and 5 show the dependence of the densification rates on grain size for lattice and grain boundary diffusion are $\sim 1/G^2$ and $1/G^3$, respectively. Overall, the densification mechanisms that were active in RHP ZrB$_2$ were faster than PS and HP mechanisms of commercial ZrB$_2$ powders without sintering additives.

Figure 11 shows grain size as a function of sintering time to determine the grain growth exponent. A value of $n = 4.6$ was calculated for specimens sintered at 1900°C and $n = 4.5$ for 2100°C. Typically, $n$ values of 2-4 are reported for normal grain growth. The $n$ values near 4 for RHP ZrB$_2$ could be due to grain growth controlled by surface diffusion. Values between 4 and 5 may indicate that something is inhibiting normal grain growth. It is possible that the ~2.5 vol% ZrO$_2$ observed at the grain boundaries of ZrB$_2$
produced by RHP acts to pin grain growth, similar to the report by M. Nagashima et al. in which ZrO$_2$ inhibited the grain growth of Al$_2$O$_3$.\textsuperscript{42} Increased grain growth exponents have also been observed for other doped oxide systems within the literature.\textsuperscript{43,44} From the calculated grain growth exponents, the grain growth diffusion coefficients can be determined (Table IV). A value of 1.5 x 10$^{-16}$ cm$^4$/s was estimated at 1900°C compared to 2.14 x 10$^{-15}$ cm$^4$/s at 2100°C. The 1900°C grain growth coefficient was an order of magnitude smaller than observed at 2100°C, indicating slowing atomic diffusion at lower temperatures. This could explain, in part, why specimens sintered at 1900°C had both smaller grains and a narrower grain size distribution than those sintered at 2100°C. Regardless of the densification temperature, grain growth analysis indicates pinning mechanisms present within RHP ZrB$_2$ which leads to fine grain sized ceramics.

1.5. Conclusions

Nominally phase pure ZrB$_2$ ceramics were fabricated using RHP at temperatures ranging from 1800 to 2100°C and times ranging from 15 to 120 min. Relative density values as high as 98.2% were achieved at temperatures as low as 1800°C with no sintering aids. SEM and XRD analysis revealed \~2.5 vol% ZrO$_2$ present as well as \~1 vol% C in the final ceramics. Analysis of etched SEM cross sections found grain sizes ranging from \~2 to 6 µm for fully dense ceramics. Sintering kinetics were studied using densification models that utilized modified creep equations. A change in densification mechanism was observed around 2000°C as activation energies increased from 241 kJ/mol to 695 kJ/mol. Grain boundary diffusion was determined to be the dominant mechanism below 2000°C with a calculated diffusion coefficient of 1.76 x 10$^{-9}$ cm$^2$/s. Above 2000°C, the dominant sintering mechanism was determined to be lattice diffusion.
with a diffusion coefficient of $1.55 \times 10^{-8}$ cm$^2$/s. Grain coarsening mechanisms were investigated using the Burke and Turnbull model. The grain growth exponent was ~ 4.5 for 1900 and 2100°C specimens, which were higher than typically observed for ceramics. The higher grain growth exponent may indicate that a pinning mechanism, most likely due to the ZrO$_2$ and/or C phases, was active in RHP ZrB$_2$. Overall, RHP is an attractive method for producing dense ZrB$_2$ ceramics with fine grain sizes based on its ability to produce higher relative densities and smaller grain sizes at lower temperatures compared to traditional hot pressing of commercial ZrB$_2$ powders.

**Acknowledgements**

This research was supported by the National Science Foundation through grant number DMR 0906584.
References


Table I. Particle Sizes of Reacted ZrB$_2$ powders after 1650°C

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<thead>
<tr>
<th>$d_{xx}$</th>
<th>Particle Size (µm)</th>
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<tr>
<td>10</td>
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<tr>
<td>20</td>
<td>0.144</td>
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<td>30</td>
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<td>70</td>
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<td>80</td>
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<td>90</td>
<td>0.894</td>
</tr>
<tr>
<td>95</td>
<td>1.497</td>
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Table II. Summary of hot pressing temperature and time along with the resulting density grain sizes

<table>
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<tr>
<th>Specimen ID</th>
<th>Temp (°C)</th>
<th>Grain Size (µm)</th>
<th>Time (min)</th>
<th>$\rho_{\text{exp}}$ (g/cm$^3$)</th>
<th>$\rho_{\text{theo}}$ (g/cm$^3$)</th>
<th>Relative Density (%)</th>
</tr>
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<tr>
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<td>-</td>
<td>120</td>
<td>6.01</td>
<td>6.106</td>
<td>98.4</td>
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<td>1900</td>
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<td>15</td>
<td>5.41</td>
<td>6.106</td>
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<td>RHP_190_60</td>
<td>1900</td>
<td>3.2 ± 1.3</td>
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<td>5.72</td>
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Table III. Activation energies for densification of ZrB$_2$ at different temperatures.

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<td>Activation Energy</td>
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<td>695 ± 62</td>
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<tr>
<td>(kJ/mol)</td>
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</table>
Table IV. Lattice, grain boundary, grain growth, and atom diffusion coefficients for RHP of ZrB$_2$

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$D_L$ (cm$^2$/s)</th>
<th>$D_b$ (cm$^2$/s)</th>
<th>$n$</th>
<th>$K$ (cm$^4$/s)</th>
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</thead>
<tbody>
<tr>
<td>1900</td>
<td>$6.32 \times 10^{-8}$</td>
<td>$1.76 \times 10^{-9}$</td>
<td>4.6</td>
<td>$1.5 \times 10^{-16}$</td>
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<td>2100</td>
<td>$1.55 \times 10^{-8}$</td>
<td>$4.49 \times 10^{-9}$</td>
<td>4.5</td>
<td>$2.1 \times 10^{-15}$</td>
</tr>
</tbody>
</table>

* Indicates dominant mechanism
Figure 1. Reacted ZrB₂ powders removed from the hot press prior to the onset of densification
Figure 2. XRD analysis of RHP ZrB$_2$ showing ZrB$_2$ as the main phase and a small ZrO$_2$ peak.
Figure 3. Thermally etched cross sections showing the microstructure of a) RHP-190-60, and b) RHP-210-60.
Figure 4. Cross section of ZrB$_2$ billet showing carbon-rich layer near the surface.
Figure 5. Grain size distributions for a) RHP-190-60 and b) RHP-210-60.
Figure 6. Relative densities as a function of sintering temperature for isothermal hot pressing times of 60 min.
Figure 7. Relative density as a function of sintering temperature for a ZrB$_2$ ceramics from the present study compared to previous reports. $^{18, 24, 35}$
Figure 8. Densification rates as a function of sintering time for specimens hot pressed for 60 min.
Figure 9. Arrhenius plot of densification rate as a function of inverse temperature for ZrB$_2$. 
Figure 10. Fits for relative density as a function of time/grain size for models for densification by a) lattice diffusion and b) grain boundary diffusion.
Figure 11. Grain size as a function of time for RHP of ZrB$_2$ at 1900°C and 2100°C.
2. ZIRCONIUM DIBORIDE WITH HIGH THERMAL CONDUCTIVITY

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Abstract

Thermal properties were characterized for zirconium diboride produced by reactive hot pressing and compared to ZrB$_2$ ceramics that were hot pressed from commercial powders. No sintering additives were used in either process. Thermal conductivity was calculated from measured values of heat capacity, thermal diffusivity, and density for temperatures ranging from 298 K to 2273 K. ZrB$_2$ produced by reactive hot pressing achieved near full density, but had a small volume fraction of ZrO$_2$ while hot pressed ZrB$_2$ contained porosity and carbon inclusions. Reactive hot pressing produced a ceramic with higher thermal diffusivity and heat capacity, resulting in thermal conductivity of 127 W/m·K at 298 K, which was ~30% higher than typically reported for hot pressed ZrB$_2$.

2.1. Introduction

Zirconium diboride (ZrB$_2$) is an ultra-high temperature ceramic (UHTC) with a melting temperature $>3000$ °C.$^1$ The crystal structure of ZrB$_2$ is hexagonal (AlB$_2$ type) with covalent bonding among boron atoms, metallic bonding among zirconium atoms, and iono-covalent bonding between zirconium and boron atoms.$^{1,2}$ ZrB$_2$ has been proposed for use in thermal protection systems of future hypersonic aerospace vehicles$^{3,4}$ and other high temperature structural applications.$^{6,7,8}$
Hot pressing (HP) is the dominant densification method for ZrB$_2$-based ceramics with temperatures above 2000°C and pressures between 20 and 30 MPa typically required for full densification.\textsuperscript{9} Reaction processing is a promising densification route.\textsuperscript{2, 10, 11} A typical RHP process has two steps, \textit{in-situ} reaction of precursors followed by densification at a higher temperature and pressure than reaction.\textsuperscript{2, 12}

One of the notable properties of ZrB$_2$ is its thermal conductivity ($k$). Room temperature $k$ values for single crystals are 140 W/m·K along the c-axis and 100 W/m·K along the a-axis.\textsuperscript{13} For polycrystalline ZrB$_2$, room temperature $k$ values range from 45 to 135 W/m·K, but converge to values between 60 and 80 W/m·K as temperature approaches 2273 K.\textsuperscript{14, 15, 16, 17, 18} The only polycrystalline ceramics with room temperature $k$ values of more than 100 W/m·K were produced by reaction processes.\textsuperscript{16, 17} Variations in $k$ values is due to impurities and porosity.\textsuperscript{14, 15, 19, 20, 21} Hence, reported values may not reflect the intrinsic $k$ for high purity, fully dense ZrB$_2$.

The purpose of the present study was to characterize $k$ for ZrB$_2$ ceramics with high purity and relative density.

2.2. Procedure

Powders used in this study were ZrB$_2$ (H.C. Starck, Grade B, $d_{50} = 2.0$ µm), ZrH$_2$ (Chemetall, Grade S, $d_{50} = 5.1$ µm), and B (EaglePicher, Grade Sp 99, $d_{50} = 0.2$ µm). Baseline specimens were prepared by hot pressing ZrB$_2$ powder without sintering additives. Batches for RHP were prepared by ball milling ZrH$_2$ and B with ZrB$_2$ media for 3 hours in hexanes. Powders were placed in a BN coated graphite die and cold uniaxially pressed at 35 MPa. The hot press was heated at ~5 °C/min under a vacuum (~27 Pa) to 950 °C with an isothermal hold of ~15 hrs to promote Reaction 1.
\[ ZrH_2(s) + 2B(s) \xrightarrow{950\degree C} ZrB_2(s) + H_2(g) \] (1)

Then, the hot press was heated to 2100 °C at ~50 °C/min with three additional 45 min isothermal holds. The hold at 1050 °C promoted further reaction, while holds at 1450 °C and 1650 °C removed surface oxide impurities, as previously reported.2,22,23 After the hold at 1650 °C, the furnace was backfilled to ~1 atm with helium and heated to 2100 °C at ~75 °C/min, where 50 MPa was applied for 45 minutes. The furnace was cooled at ~20 °C/min and the load was released at 1650 °C. The same procedure was used for densification of commercial ZrB$_2$ except that the reaction holds were omitted. Instead, samples were heated directly to 1450°C at ~50 °C/min.

Phases were characterized using X-ray diffraction (XRD; Phillips Panalytical Multipurpose diffractometer). Diffraction patterns were obtained by scanning from 3° to 90° two theta at 0.03° per step with a 1s count time. Specimens for microstructure analysis were cut parallel to the hot pressing direction and polished to a 0.5 µm surface finish using diamond abrasives. Scanning electron microscopy (SEM; Hitachi S570) was performed to characterize grain size. Bulk densities (ρ) were analyzed using Archimedes method with deionized water as the immersion medium. Theoretical densities were calculated from measured unit cell parameters.

Thermal diffusivity (D) was measured by laser flash (Cryo. 2000, & Flashline 5000; Anter Corp., Pittsburgh, PA) according to ASTM E1461-11 using the Clark and Taylor correction factor. At least 3 tests were averaged at each temperature to determine D. Heat capacity (C$_p$) was measured using differential scanning calorimetry (DSC 2010; TA Instruments, New Castle, DE.). Powder was crushed to <250 µm using an agate
mortar and zirconia pestle. Hermetic aluminum crucibles were used with a heating rate of 10 K/min to 873 K. Power measurements were converted to $C_p$ using Equation 2:

$$
C_p = \left( \frac{60E}{Hr} \right) \frac{\Delta H}{m}
$$

(2)

where $E$ is a cell calibration coefficient, $Hr$ is heating rate, $\Delta H$ is the difference in heat flow between sample and reference, and $m$ is sample mass. The correction factor was determined using an Al$_2$O$_3$ standard (Standard Reference Material 676a, National Institute of Standards and Technology). Samples were tested a minimum of three times. Heat capacity was also measured using laser flash by comparison to a graphite standard (Thermographite B1-D2-59-050, TA-Waters LLC). The variability in $C_p$ was ~5% for DSC and ~10% by laser flash.

Thermal conductivity was calculated using equation 3:

$$
k = D \rho C_p
$$

(3)

where $\rho$ was corrected for temperature based on a coefficient of thermal expansion of 6.8×10$^{-6}$ K$^{-1}$ for ZrB$_2$.$^{14}$

Carbon (CS600; Leco, St. Joseph, MI) and oxygen (TC500; Leco, St. Joseph, MI) contents were measured by grinding dense specimens to -200 mesh. Analysis of heavier elements was performed by inductively coupled plasma-mass spectrometry (NSL Analytical, Cleveland, OH).
2.3. Results and Discussion

Relative densities were 96.1% for HP and 99.5% for RHP ZrB$_2$. SEM images (Figure 1) were consistent with density measurements showing <1% porosity for RHP ZrB$_2$ and ~4% for HP ZrB$_2$. Both ceramics also contained a small volume fraction of carbon while ~2.5 vol% of a second phase was observed in RHP ZrB$_2$. Average grain sizes were ~25 µm for HP ZrB$_2$ and ~6 µm for RHP ZrB$_2$. ZrB$_2$ was the main crystalline phase in both materials (XRD, not shown), but RHP ZrB$_2$ also contained a small fraction of ZrO$_2$. Lattice parameters were $a = 3.17$ Å and $c = 3.53$ Å for both HP and RHP ZrB$_2$. Chemical analysis revealed lower Hf content in RHP ZrB$_2$ (~0.3 wt%) compared to HP ZrB$_2$ (~1.7 wt%). RHP ZrB$_2$ also had higher oxygen content (1.4 wt%) due to the presence of ZrO$_2$ compared to HP ZrB$_2$ (0.04 wt%). Although RHP led to elevated levels of oxygen, RHP ZrB$_2$ had lower grain size and hafnium levels than HP ZrB$_2$.

Heat capacities are summarized in Figure 2. Using DSC, $C_p$ for HP ZrB$_2$ was ~0.43 J/g·K at 298 K, increasing to ~0.63 J/g·K at 873 K. Values measured by laser flash were less reliable, but trends agreed with accepted values. For example, the NIST-JANAF values for $C_p$ of ZrB$_2$ are 0.43 J/g•K at 298 K and 0.62 J/g•K at 873 K.$^{24}$

Heat capacity values for RHP ZrB$_2$ were higher than HP ZrB$_2$ at all temperatures. From DSC, $C_p$ for RHP ZrB$_2$ increased from ~0.48 J/g•K at 298 K to ~0.75 J/g•K at 873 K. Likewise, values determined by laser flash increased from ~0.77 J/g•K at 873 K to ~0.89 J/g•K at 2273 K. Values for the entire temperature range were fit to Equation 4 (Table I). Calculated fits were used for subsequent k calculations. Previously, only Guo et al. reported a similar $C_p$, which was 0.51 J/g•K at 298 K.$^{12}$ $C_p$ values for HP ZrB$_2$ were nearly identical to handbook values, but RHP and Guo’s material were ~10% higher.
The reasons for the higher $C_p$ values are not known, but lower Hf content for RHP ZrB$_2$ could be one factor.

$$C_p = a + (b \cdot T) + (c \cdot T^{-2}) + (d \cdot T^2)$$ (4)

Calculated thermal conductivities were higher at all temperatures for RHP ZrB$_2$ (Figure 3). Thermal conductivity was $\sim$127 W/m·K at 298 K for RHP ZrB$_2$ compared to $\sim$85 W/m·K for HP ZrB$_2$, an increase of $\sim$30% due to increases in both $C_p$ and $D$ for RHP ZrB$_2$. As temperature increased, $k$ values for both materials decreased to 75 to 80 W/m·K at 2273 K. The $k$ values for HP ZrB$_2$ were consistent with previous reports for phase pure ZrB$_2$. Higher $k$ values for RHP ZrB$_2$ could be due to higher purity, which would result in less phonon and electron scattering. Previously, Zhang$^{16}$ and Guo$^{17}$ reported $k$ values for ZrB$_2$ ceramics that were notably higher than HP ZrB$_2$ (Figure 3). Zhang reported $k = 110$ W/m·K at 298 K, which is $\sim$10% lower than RHP ZrB$_2$. In contrast, Guo reported $k = 133$ W/m·K, $\sim$5% higher than RHP ZrB$_2$. However, Zhang’s $k$ could potentially be higher than reported since they used $C_p$ values from the NIST-JANAF tables even though they used a reactive process. Using $C_p$ values from the present study to recalculate Zhang’s $k$ increased it from 110 W/m·K to $\sim$125 W/m·K at 298 K. Further investigation is needed to identify the fundamental factors responsible for higher $k$ values. However, 127 W/m·K at 298 K and 80 W/m·K at 2273 K are among the highest $k$ values reported for polycrystalline ZrB$_2$.

2.4. Conclusions

High purity ZrB$_2$ with near full density was fabricated by RHP. Thermal conductivity values of 127 W/m·K at 298 K and 80 W/m·K at 2273 K for RHP ZrB$_2$ are
among the highest reported for ZrB$_2$ ceramics. The use of RHP resulted in higher values for both D and C$_p$ compared to ZrB$_2$ ceramics from commercial powders. The increased k, D, and C$_p$ values were attributed to higher purity, particularly reduced levels of hafnium, in RHP ZrB$_2$. Based on these results, RHP appears to be an attractive method for synthesizing high purity, fully dense ZrB$_2$ with high thermal conductivity.

Acknowledgments

This research was supported by the National Science Foundation through grant number DMR 0906584.
References


Table I. Fitting parameters for $C_p$ values for RHP and HP ZrB$_2$.

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<tr>
<th>Material</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
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Figure 1. SEM images of polished cross sections of a) RHP ZrB$_2$ and b) HP ZrB$_2$. 
Figure 2. Heat capacity values measured by DSC (below 873 K) and laser flash (above 873 K) for HP and RHP ZrB$_2$. Error bars for the laser flash are not shown, but the standard deviation for DSC values was ~5% and ~10% for laser flash values.
Figure 3. Thermal conductivity values for HP ZrB$_2$ and RHP ZrB$_2$ from the present study compared to previously reported values from Zhang$^{11}$ (298K to 673 K) and Guo$^{13}$ (298 K only).
3. THERMAL PROPERTIES OF ZrB₂ CERAMICS WITH Hf CONTENTS UP TO 0.33 at%

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Abstract

The effect of Hf additions on the thermal properties of high purity ZrB₂ ceramics was studied. Reactive hot pressing of ZrH₂, B, and HfB₂ powders was used to synthesis (Zr,Hf)B₂ ceramics with Hf contents ranging from 0.01 to 0.33 at%. Thermal conductivity was calculated from measured heat capacity, thermal diffusivity, and temperature dependent density values for temperatures ranging from 298 K to 473 K. At room temperature, diffusivity decreased from 0.47 cm²/s for a Hf content of 0.01 at% to 0.36 cm²/s for a Hf content of 0.33 at% resulting in thermal conductivities that decreased from 141 W/m·K to 100 W/m·K over the same composition range. The presence of Hf decreased thermal diffusivity and conductivity due to point defect scattering of lattice vibrations.

3.1. Introduction

ZrB₂ is part of the ultra-high temperature family of ceramics (UHTCs) due to its high melting temperature, in excess of 3000°C.¹ ZrB₂ has a hexagonal close packed structure that is comprised of alternating layers of metallically bonded Zr atoms and covalently bonded B atoms. The metallic bonding gives rise to high electrical conductivities (> 10⁷ S/m) that are more commonly associated with metals. The graphitic structure of the boron layers has strong covalent bonding, which leads to high melting
temperature and other ceramic-like properties.\textsuperscript{1,2,3} In addition to ZrB\textsubscript{2}, several other transition metal diborides within the UHTC family have attracted interest due to their combination of high strength (>500 MPa), hardness (23 GPa), and thermal conductivity (>100 W/m·K).\textsuperscript{1,4,5} Because of these properties, as well as a relatively low density, ZrB\textsubscript{2} is a promising candidate material for next generation hypersonic flight and atmospheric reentry vehicles\textsuperscript{6,7,8} and other high temperature structural applications.\textsuperscript{9}

Nominally pure ZrB\textsubscript{2} ceramics are difficult to fully densify due to strong covalent bonding and low self-diffusion coefficients. Full densification has been achieved with hot pressing (HP) at temperatures in excess of 2100°C with pressures of 32 MPa or higher.\textsuperscript{10} Sintering aids, such as B\textsubscript{4}C, WC, SiC, or MoSi\textsubscript{2}, can reduce densification temperatures.\textsuperscript{11,12,13,14} However, additives form solid solutions, isolated particles, or grain boundary phases in the final ceramics.\textsuperscript{13,14,15} While additives can improve densification and mechanical properties, they have adverse effects on thermal properties.\textsuperscript{16,17}

Reaction hot processing (RHP) is an alternative route to produce ZrB\textsubscript{2} and HfB\textsubscript{2}, with high relative densities at lower temperatures than traditional HP.\textsuperscript{18,19,20} Guo et al. achieved >95\% relative density at 1750°C using a reaction spark plasma sintering process with 50 MPa of applied pressure.\textsuperscript{21} Chamberlain et al. showed that the reaction between Zr and B led to grain size reduction, enabling full densification by reactive hot pressing without sintering additives.\textsuperscript{18}

In addition to improving densification, RHP has also yielded some of the highest thermal conductivities reported for ZrB\textsubscript{2} ceramics, with values as high as 130 W/m·K at room temperature.\textsuperscript{4,21,22} Using commercial powders densified using traditional HP, the
highest thermal conductivities reported have typically been around 90 W/m·K for fully dense ZrB$_2$ ceramics at room temperature, but values as low as ~30 W/m·K have been reported for ZrB$_2$ ceramics with impurities.\textsuperscript{16, 17, 23, 24} While the variations in thermal conductivity have been attributed to impurities, the mechanisms controlling thermal conductivity have not been identified, which means that the intrinsic thermal conductivity of ZrB$_2$ may still be unknown.\textsuperscript{4, 16, 17, 21, 22, 25}

Lonergan et al. identified Hf content in ZrB$_2$ as a possible factor in some of the reported differences in thermal properties.\textsuperscript{22} That study showed that the heat capacity of the RHP ZrB$_2$ was 0.48 J/g·K at room temperature compared to 0.43 J/g·K for the HP ZrB$_2$.\textsuperscript{22} The difference in heat capacity was attributed to the difference in Hf content, which was 0.06 at\% for RHP ZrB$_2$ and 0.37 at\% for HP ZrB$_2$. Other reports show that the addition of transition metals to ZrB$_2$ reduce room temperature thermal conductivity.\textsuperscript{16, 17, 23} Although the presence of impurities has been linked to decreases in the thermal conductivity and heat capacity of ZrB$_2$, the mechanisms responsible for the decreases have not been identified.

The effects of impurities on lattice thermal conduction can be described by quantum theory using the Holland model for thermal conductivity.\textsuperscript{26} This approach, which is based on Debye’s theory for heat capacity, treats lattice vibrations as thermoelastic waves (Equation 1),\textsuperscript{26, 27, 28, 29}

$$q = q_T + q_L$$  \hspace{1cm} (1)
where $q_T$ and $q_L$ are the transverse and longitudinal phonon waves. These can be expressed as shown in Equation 2 and 3 respectively,

\[ q_T = \frac{2}{3} \int_0^{\theta_T^T} \frac{C_L T^3 x^4 e^x \left( e^x - 1 \right)^2 dx}{\tau_T} \]  

\[ q_L = \frac{1}{3} \int_0^{\theta_T^T} \frac{C_L T^3 x^4 e^x \left( e^x - 1 \right)^2 dx}{\tau_L} \]  

where $\theta_x$ is the Debye temperature, $C_L$ is the phonon (lattice) heat capacity, and $T$ is the absolute temperature. $x = h \omega / kT$ where $h$ is the Dirac constant, $\omega$ is the phonon vibrational frequency, and $k$ is the Boltzmann constant. Point defect scattering due to impurities was first addressed by Klemens who calculated the time between scattering events for this mechanism (Equation 4),

\[ \frac{1}{\tau_{PD}} = V \frac{\omega^4}{4 \pi^2} \sum_i f_i \left( \frac{\bar{m} - m_i}{\bar{m}} \right)^2 \]  

where $V$ is the atomic volume, $m_i$ is the mass of the $i^{th}$ atomic species, $f_i$ is the fraction of atoms with mass $m_i$, and $\bar{m}$ is the average atomic mass of all atoms in the system.

Equations 1-4 imply that impurity atoms in a lattice disturb the thermal waves, increase phonon scattering, and, therefore, reduce thermal conduction.

The thermal conductivity of ZrB$_2$ also has a significant contribution from electrons, which reportedly ranges from 60% to more than 90% of the total thermal conductivity.\textsuperscript{14,17} The effect impurities on electron conduction can be modeled using Matthiessen’s rule\textsuperscript{31} (Equation 5)
\[ \rho = \rho_T + \rho_I \]  

(5)

where \( \rho_T \) is the electrical resistivity due to electron scattering from thermal vibrations (electron-phonon scattering) and \( \rho_I \) is the electrical resistivity due to scattering from impurities (electron-defect scattering). In general, electrical resistivity can be described by Equation 6, \(^{31}\)

\[ \rho_s = \frac{1}{en\mu_s} \]  

(6)

where \( e \) is the charge of carriers, \( n \) is the number of carriers, and \( \mu_s \) is the carrier mobility, which is a measurement of the speed at which a charge carrier move through a solid. Further, carrier mobility can be expressed in terms of the time between scattering events (Equation 7)

\[ \mu_s = \frac{e\tau_x}{m_e} \]  

(7)

where \( m_e \) is the mass of the charge carrier (electrons, in this case) and \( \tau_x \) is the mean time between scattering events. The effect of impurities on time between scattering events can be derived by assuming that impurity scattering is a purely elastic event (Equation 8), \(^{27}\)

\[ \frac{1}{\tau_I} = \frac{V}{(2\pi)^3} \int dk' W_{kk'} \left( 1 - \frac{\nu_{k'}'}{\nu_{k'}} \right) \]  

(8)

where \( V \) is the unit cell volume, \( k' \) is crystal wave vector, \( W' \) is the electron-defect collision probability term and \( \nu_x \) is the wave velocity of the electrons. Perturbation theory gives the electron-defect collision probability as \(^{27, 32}\)
where $E(k)$ is the electron energy and $U$ is the interaction potential. Similar to lattice conductivity, impurity atoms disturb the Bloch waves, increase electron scattering, and reduce thermal conductivity. Thus, impurities can interfere with both electron and lattice conduction.

The purpose of this paper was to study the effect of Hf content on the thermal properties of ZrB$_2$ and identify the mechanism responsible for the decrease in thermal conductivity due to the presence of Hf impurity atoms in ZrB$_2$.

3.2. Procedure

3.2.1. Powder Preparation and Reactive Hot Pressing. The starting materials used in this study were two different ZrH$_2$ powders (Materion, Z-1094, ~0.01at% Hf, and Chemetall, Grade S, ~0.25at% Hf) along with B (SB Boron Corporation, SB 99) and HfB$_2$ (H.C. Starck, Grade B, ~1.75 at% Zr). Starting mixtures were batched to produce the desired Hf contents and then homogenized by ball milling for 3 hours in hexane with ZrB$_2$ media. Green compacts were produced by cold uniaxial pressing in a boron nitride coated graphite die (Graphite Products Corp), at 20 MPa for 30 seconds. The die was heated at ~5 K/min in a graphite element hot press (Thermal Technology Inc., Model HP20-3060-20, Santa Rosa, CA) and under mild vacuum (~27 Pa). An isothermal hold at 1223 K for 13 hrs was employed to promote reaction of the powders (Equation 10).

$$ZrH_2(s) + 2B(s) \xrightarrow{1223\text{K}} ZrB_2(s) + H_2(g)$$
After the reaction hold, the furnace was heated at ~50 K/min. A second hold was performed at 1323 K for 45 minutes to promote reaction of any unreacted powders, and two additional 45 minute holds at 1723 K and 1923 K were conducted to remove oxide surface impurities. After the hold at 1923K, the furnace was backfilled to ambient pressure with helium and heated at ~75 K/min to the pressing temperature of 2373 K. Once this temperature was reached, 50 MPa was applied for 60 minutes to promote densification. The furnace was then cooled at ~20 K/min to room temperature during which the load was released at 1923 K.

Specimens are identified as ZHXX where XX indicates the nominal Hf content of the final ceramics in units of hundredths of atomic percent. For example, ZH33 indicates ZrB$_2$ containing 0.33 at% Hf. In all cases, Hf contents of the starting powders were considered when calculating the nominal ceramic compositions (Table I). As a comparison, the Hf content of ZH33 should be similar to conventional ZrB$_2$ ceramics produced from a commercial ZrB$_2$ powder (e.g., H.C. Starck, Grade B ZrB$_2$ with a reported Hf content of 0.37 at%) that has been used to produce many of the ZrB$_2$ ceramics examined as part of recent studies.\textsuperscript{16, 17, 23}
3.2.2. **Characterization.** Phase analysis of the resulting ceramics was performed using two methods. The first was x-ray diffraction (XRD; Phillips PANalytical multipurpose diffractometer, X’Pert Pro, Almelo, Netherlands) with a Cu K-alpha source. Dense specimens were crushed and ground using an agate mortar and zirconia pestle. Diffraction patterns were obtained by scanning from 3° to 90° two theta at 0.03° per step increments with a 1 second count time. The second method was Raman spectroscopy (ARAMIS Labram spectrometer, Horiba Jobin Yvon, Edison, NJ) and analysis was done on the same polished cross sections used for microscopy.

For microstructure analysis, specimens were cut parallel to the hot pressing direction, and polished to a 0.5 µm surface finish using successively finer diamond abrasive slurries (South Bay Technologies, San Clemente, CA). Specimens were then examined using scanning electron microscopy (SEM; Hitachi S570, Ibraki, Japan).

Archimedes method was used to measure bulk density. Theoretical densities were calculated from mass averaged molecular weights based on the nominal ratios of Zr to Hf and unit cell volumes calculated from unit cell parameters determined using XRD analysis.
3.2.3. Thermal Property Measurements. Thermal diffusivity was measured using laser flash (Cryo 2000, Anter Corp., Pittsburgh, PA) following ASTM standard E1461-13. Measured rise times were used to determine thermal diffusivities using Equation 11, where $D$ is the thermal diffusivity, $L$ is the thickness of the specimen, and $t_{0.50}$ is the time required for the back face temperature to rise by half of the total recorded temperature increase. The Clark and Taylor correction factor was then used to correct $D$ for non-ideal heat losses.

$$D = 0.1388 \frac{L^2}{t_{0.50}}$$

Differential scanning calorimetry (DSC 2010; TA Instruments., New Castle, DE) was used to measure heat capacity from 298 K to 473 K. Sintered billets were crushed using an agate mortar and zirconia pestle before passing through a 60 mesh sieve. Hermetic aluminum crucibles were used to contain the specimens, which were heated at 10 K/min to 473 K, followed by air cooling. Equation 12 was used to convert heat flow data to heat capacity, where $E$ is a cell calibration coefficient, $H_r$ is the heating rate (K/min), $\Delta H$ is the difference in heat flow between the sample and reference (J), and $m$ is the sample mass (g).

$$C_p = \left( \frac{60E}{H_r} \right) \frac{\Delta H}{m}$$

Aluminum oxide powder (Standard Reference Material 676a, National Institute of Standards and Technology, Gaithersburg, MD) was used to determine the correction factor $E$. 
Equation 13 was used to calculate the total thermal conductivity ($k_T$), where $D$ is thermal diffusivity, $C_P$ is heat capacity, and $\rho$ is the measured bulk density that was corrected for expansion based on data from Touloukian.$^{34}$

$$k_T = D\rho C_P$$  \hspace{1cm} (13)

Total thermal conductivity was composed of contributions due to thermal transport by electrons ($k_e$) and phonons ($k_p$) as shown in Equation 14.$^{27,35}$

$$k_T = k_e + k_p$$  \hspace{1cm} (14)

The Wiedemann-Franz law was used to estimate the $k_e$ from measured values of electrical conductivity (Equation 15)$^{27,35}$

$$k_e = \sigma_e L_0 T$$  \hspace{1cm} (15)

where $L_0$ is the theoretical Lorenz number ($2.44 \times 10^{-8}$ WΩ/K²), $T$ is the absolute temperature, and $\sigma_e$ is the electrical conductivity. Electrical resistivity ($\rho_e$), which is the inverse of electrical conductivity, was measured by the van der Pauw method using cylindrical specimens in accordance with ASTM standard F76-08.$^{36}$ Electrical testing was performed using specimens 25 mm in diameter that were ground to ~1 mm thick.
3.2.4. **Thermal Property Models.** Intrinsic phonon and electron wave properties were simulated for ZrB\(_2\) with varying hafnium concentrations using density functional theory (DFT)\(^{37,38}\). The Quantum ESPRESSO code was used with projected augmented wave (PAW) potentials.\(^{39}\) Simulations were performed with a unit cell consisting of a hexagonal array of three atoms placed at fractional locations (0.00, 0.00, 0.00) for zirconium, and (-0.33, 0.33, 0.5), (0.33, -0.33, 0.5) for the two boron atoms. A 16 x 16 x 16 k point grid with a plane wave cutoff energy of (1x10\(^{-8}\)) eV and a Gaussian smearing parameter of 0.1eV was used for energy minimization and convergence. Phonon density of states (pDOS) and phonon dispersion curves were determined using density functional perturbation theory (DFPT) with a 3 x 3 x 3 k-space mesh and a cutoff energy of 1x10\(^{-6}\) eV for convergence.\(^{40}\)

3.3. **Results and Discussion**

3.3.1. **Characterization.** Relative densities were >98% for all of the specimens with the exception of ZH33, which only reached ~96.1% density (Table I). ZrB\(_2\) was the primary phase formed, as indicated by XRD (Figure 1), but trace amounts of ZrO\(_2\) were also detected. All of the HfB\(_2\) was assumed to go into solid solution with the ZrB\(_2\) as no HfB\(_2\) peaks were observed. SEM images (Figure 2) were consistent with measured relative densities. In most specimens, ~0.5 vol% porosity was observed as round inclusions with charging around the edges. In addition, ~0.5 vol% of dark inclusions without charging around the edges were also observed. These inclusions were identified by Raman spectroscopy (not shown) as carbon (~0.5 vol%) if no charging was present. Finally, 3 to 4 vol% of ZrO\(_2\) was observed as light colored inclusions located primarily at grain boundaries.
SEM and XRD analysis confirmed that the RHP ZrB$_2$ specimens achieved high density and similar levels of contaminants for all specimens, making them suitable to isolate and study the effect of Hf additions on the thermal properties of ZrB$_2$.

### 3.3.2. Thermal Properties.

The thermal diffusivity decreased as Hf content increased (Figure 3). At 298 K, ZH01 had a thermal diffusivity of 0.47 cm$^2$/s compared to 0.36 cm$^2$/s for ZH33. This is a decrease of ~23% in thermal diffusivity for a 0.32 at% addition of Hf. Thermal diffusivity measurements were highly reproducible, a standard deviation of ~1.5% for the three measurements that were averaged to report each value, therefore, the differences between different compositions were generally larger than the variance for each composition. Previously, Zhang$^4$ reported an identical thermal diffusivity (0.47 cm$^2$/s) at 298K for ZrB$_2$ processed with the same Zr powders as ZH01, which supports the assertion that Hf content has a more significant effect on thermal properties than other differences among specimens such as variations in relative density or grain size. For comparison, hot pressed ZrB$_2$ produced from commercial powder (H.C. Starck grade B) that contained ~0.37 at% Hf had a measured thermal diffusivity of 0.32 cm$^2$/s at 298 K.$^{23}$ The addition of transition metal dopants has previously been shown to reduce the thermal diffusivity of ZrB$_2$ based ceramics.$^{23}$ The differences in thermal diffusivity were attributed to differences in lattice strain caused by substitution of other transition metals onto Zr lattice sites. Hence, previous reports, and the present study, confirm that small additions of Hf have a large impact on thermal transport in ZrB$_2$ ceramics.
Heat capacity also decreased with increasing Hf content (Figure 4). The heat capacity of ZH01 was 495 J/kg·K at 298 K and decreased to 439 J/kg·K for ZH33. This is a decrease of ~10% across the range of Hf contents. For comparison, ZrB$_2$ ceramics produced by hot pressing commercial powder, which had a nominal Hf content of ~0.37 at%, had a heat capacity of 430 J/kg·K.\textsuperscript{22} As can be seen in Figure 4, heat capacity values appear to follow a consistent trend with increasing Hf content. In contrast to thermal diffusivity values, heat capacity measurements had a larger variability (~5% of the measured values), but the overall decrease in heat capacity was still larger than the variability in the measurements. More importantly, the effects of impurities on heat capacity have not been reported for diboride ceramics. One explanation is that the large variability in measured values (~3 to 10%, depending on the study) may have obscured any trends that might have been present in heat capacity.\textsuperscript{16, 17, 22, 41} As a result, most studies of thermal properties of ZrB$_2$ have used heat capacity values from standard reference tables\textsuperscript{4, 16, 17, 23} due to the similarity of values from the tables to those measured for commercial powders. For example, the heat capacity at 298 K for commercial powder (H.C. Starck, grade B) was measured as ~398 J/kg·K as part of the present study compared to a value of 426 J/kg·K reported in the NIST-JANAF tables. Overall, the present results show that Hf additions decrease the heat capacity of ZrB$_2$, meaning that handbook values for heat capacity of ZrB$_2$ are only appropriate for ZrB$_2$ with similar Hf contents.

As shown in Figure 5, thermal conductivity of reaction processed ZrB$_2$ decreases with increasing Hf content. The room temperature thermal conductivity of ZH01 was 141 W/m·K compared to 100 W/m·K for ZH33, which is a decrease of ~30% across the range
of Hf contents. The thermal conductivity of ZH06 was 123 W/m·K, which is similar to the value of 127 W/m·K reported by Lonergan et al. for a reaction processed composition with similar Hf concentration (both ~0.06 at% Hf).\textsuperscript{22} Hence, in the absence of differences in relative density, grain size, second phases, etc., thermal conductivity appears to change systematically with Hf content. McClane et al. reported a value of 88 W/m·K for a nominally pure ZrB\textsubscript{2} ceramic processed from commercial powder, which had a nominal Hf content of 0.37 at%.\textsuperscript{23} Although this value was lower than ZH33, it contained a higher Hf concentration. Previously, Zhang\textsuperscript{4} and Guo\textsuperscript{21} reported \(k_T\) values for RHP ZrB\textsubscript{2} ceramics that were higher than values previously reported for HP ZrB\textsubscript{2}. Guo reported a room temperature thermal conductivity of 133 W/m\(\cdot\)K, which falls between ZH01 and ZH04. Zhang reported a room temperature thermal conductivity of 110 W/m\(\cdot\)K at 298 K for a ceramic with a nominal Hf content of 0.01at%, but had used \(C_p\) values from the NIST-JANAF tables even though they used a reactive process with a higher purity Zr source. Using \(C_p\) values for ZrB\textsubscript{2} with a similar Hf content from the present study to recalculate Zhang’s thermal conductivity, the value increased from 110 W/m\(\cdot\)K to ~131 W/m\(\cdot\)K at 298 K, which is similar to Guo’s reported value and only slightly lower than the value determined for ZH01 in the present study. The lower value for Zhang’s ZrB\textsubscript{2} compared to ZH01 is presumably due to the ~8% porosity in Zhang’s ZrB\textsubscript{2} despite the similar Hf content (0.01 at% Hf). Based on previous reports and results from the present study, reported variations in thermal conductivity for both HP and RHP ZrB\textsubscript{2} can be attributed to differences in Hf content, in the absence of other differences in purity or density. In addition, the room temperature thermal conductivity of 141 W/m\(\cdot\)K for ZH01
is the highest thermal conductivity reported to date for a polycrystalline ZrB$_2$ ceramic, presumably due to the low Hf content.

The values of thermal conductivity for RHP ZrB$_2$ are high in spite of 3-4 vol% ZrO$_2$ in the final ceramics. The oxygen content (equivalent to ~2 at%) is far in excess of the Hf contents that decreased thermal conductivity by as much as 30%. Not only was the second phase detected in the specimens in the present study, but ZrO$_2$ was also detected in the specimens produced by Guo et al., which also had high values of thermal conductivity$^{21}$. Using the Maxwell-Eucken dispersed phase model, the intrinsic thermal conductivity of the ZrB$_2$ matrix can be estimated. Assuming a thermal conductivity of 7 W/m·K for ZrO$_2$ and a ZrO$_2$ content of 3.0 vol%,$^{42,43}$ the thermal conductivity of the ZrB$_2$ matrix phase was estimated to be ~150 W/m·K. By this estimate, the presence of ~3 vol% ZrO$_2$, equivalent to 2 at% O, decreased thermal conductivity by ~6%. In addition, the 0.5 vol% carbon present as a second phase most likely decreased thermal conductivity as has been reported by Thompson et al. for HP ZrB$_2$ ceramics.$^{16}$ Refinement of the reactive processing method to remove the second phases may result in further incremental improvements in total thermal conductivity, but these changes seem unlikely to have the significant impact that was achieved by reducing Hf content. Based on these observations, dissolved impurities such as Hf have a much stronger influence on thermal conductivity than second phases such as ZrO$_2$ or C.
3.3.3. Phonon and Electron Contributions. Figure 6 shows electrical resistivity values from 298 to 673K for ZH01 along with values for reaction processed ZrB$_2$ from Zhang and Guo compared to HP ZrB$_2$ prepared from commercial powders by McClane.$^{4,21,23}$ Electrical resistivity increased with temperature for all compositions. Further, reaction processed ZrB$_2$ ceramics had nearly identical electrical resistivity values when the Hf contents were the same. The room temperature resistivity values were 6.54 $\mu\Omega$·cm for ZH01, 6.48 $\mu\Omega$·cm for Zhang’s material, and 6.44 $\mu\Omega$·cm for Guo’s ZrB$_2$.\textsuperscript{4,21} Electrical resistivity also increased with increasing Hf concentration as values ranged from 6.54 $\mu\Omega$·cm for ZH01 to 7.37 $\mu\Omega$·cm for ZH33 at 298K (Figure 7). However, these differences were small compared to the differences between the reaction processed compositions and ZrB$_2$ prepared from commercial powders. McClane reported an electrical resistivity of 8.9 $\mu\Omega$·cm at 298 K for ZrB$_2$ hot pressing commercial powders (nominal Hf content 0.37 at%),\textsuperscript{23} which is higher than the 7.37 $\mu\Omega$·cm value for RHP ZH33 that had a similar Hf content. Hence, electrical resistivity increases with Hf content at temperatures between 298 and 673 K, although ZrB$_2$ prepared from commercial powders has a higher electrical resistivity than expected solely based on Hf content.

The electrical resistivity data were fit to Nordheim’s rule (Equation 16), which is typically used to describe the effect of solid solution on metallic conduction (Figure 7),\textsuperscript{31,44}

$$\rho = \rho_A x + \rho_B (1-x) + Cx(1-x) + Ax e^{Rx}$$

(16)
where $\rho_A$ and $\rho_B$ are the resistivities of pure ZrB$_2$ and HfB$_2$. Values for A (0.256), B (-2.237), and C (0.024) were all determined by fitting experimental results. An electrical resistivity value of 8.90 $\mu\Omega\cdot$cm was used for HfB$_2$, which was reported by Zhang et al. for reaction processed HfB$_2$ with a Zr concentration of ~3 at%. Although the general increase in electrical resistivity of ZrB$_2$ with increased as Hf content followed the trend predicted by Nordheim’s rule, the overall fit ($R^2=0.81$) was poor. The large variability in the electrical resistivity data as well as the limited range of values may be responsible for the poor fit. A more comprehensive study with higher Hf contents is needed to determine whether the electrical resistivity of (Zr,Hf)B$_2$ ceramics follows Nordheim’s rule.

The phonon and electron contributions to the total thermal conductivity were plotted as a function Hf content (Figure 8). The electron contributions to thermal conductivity were estimated using measured electrical resistivity values and the Wiedemann-Franz law. At room temperature, $k_e$ was 112 W/m·K for ZH01 and 99 W/m·K for ZH33 compared to total thermal conductivities of 141 W/m·K and 100 W/m·K. The phonon contributions to thermal conductivity were estimated by subtraction using Equation 14. At room temperature the $k_p$ was 24 W/m·K for ZH01 and 2 W/m·K for ZH33. Further analysis showed that hafnium additions reduced $k_p$ to nearly zero for Hf contents of 0.11 at% Hf or higher. However, small additions of Hf affected both the phonon and electron contributions to thermal conductivity. The total thermal conductivity of ZrB$_2$ is affected by point defects from Hf inclusions within the Zr sublattice. A model by Klemens for the change in time between
scattering events with varying atomic mass on a monatomic lattice is shown in Equation 17.30, 35

\[ \frac{1}{\tau_{\Delta M}(\omega)} = c_{def} \frac{\Omega_a \omega^4}{4\pi \bar{C}_g^3} \left( \frac{\Delta M}{M} \right)^2 \]  

(17)

Where \( \tau_{\Delta M} \) is the relaxation time, \( \omega \) is the vibrational frequency of the unperturbed lattice, \( c_{def} \) is the defect concentration, \( \Omega_a \) is the atomic volume of the defect atom, \( \bar{C}_g \) is the group velocity of the phonon wave, \( M \) is the matrix atomic mass, and \( \Delta M \) is the change in mass for a defect atom with respect to the matrix. Assuming the values for atomic volume, lattice vibrational frequency, and group phonon velocity for the bulk crystal are negligibly affected by small changes in Hf concentration, Equation 17 predicts a decrease of ~33% in the time between scattering events as Hf content increases from 0.01 at% in ZH01 to 0.33 at% in ZH33. This compares well with the decrease of ~30% in total thermal conductivity measured for these specimens. Hence, an increase in phonon scattering appears to be consistent with the overall decrease in thermal conductivity of ZrB\(_2\) with increasing Hf content.
3.3.4. First Principle Calculations. Figure 9 shows the electronic density of states (eDOS) using the lattice parameters measured for ZH06 (a = 3.16802(2) Å, c=3.53036(1) Å) as part of the present study and the ZrB$_2$ specimen with 1.38 at% Hf based on the study by McClane et al. (a = 3.16689(2) Å, c=3.52828(5)).$^{23}$ The change in lattice parameters has almost no effect on the eDOS values as the two curves are essentially identical. The values are similar to previous studies on ZrB$_2$ with three peaks present in the valence band and one in the conduction band.$^{44,45}$ The peak around -10 eV is due to B 2s electrons. The low energy peak is far from the Fermi level, indicating strong covalent bonding. The peak around -7 eV is due to B 2p electrons. The shift of this peak closer to the Fermi energy indicates that these electrons are not as tightly bound as the 2s electrons. The peak around -4 eV is due to the Zr 4d electrons.$^{45}$ The overlap of peaks for the B 2p and Zr 4d electrons may indicate that the boron electrons are also contributing to metallic conduction. Evidence that B contributes to electrical conduction can be seen in the higher resistivity of Zr (43.3$\mu$Ω-cm) compared to high purity ZrB$_2$ (~7.00 $\mu$Ω-cm).$^{46}$ A finite eDOS around the Fermi level (0 eV) confirms that ZrB$_2$ exhibits metallic conduction. Likewise, the separation of bonding and antibonding states around this level indicates localized electron orbitals, which give rise to cohesive properties that result in high melting point and chemical stability.$^{47}$ The change in lattice parameters due to increasing hafnium concentration does little to alter the electronic properties of ZrB$_2$. This indicates that the increasing electrical resistivity with increasing Hf content (and the corresponding decrease in thermal conductivity) observed in the present study were most likely due to electron scattering from lattice defects (i.e., Hf atoms on Zr lattice sites) rather than changes to the electronic structure.
Figure 10 shows the phonon density of states (pDOS) calculated for ZH01 and ZH33 using averaged atomic masses adjusted for the Hf contents of specimens. The pDOS predictions were similar to those reported in previous studies.\textsuperscript{45, 47, 48} The pDOS results are split into low frequency and high frequency regimes. Previous studies have concluded that the low frequency acoustic modes (i.e., below $\approx 300$ cm\(^{-1}\)) were due to vibrations in the Zr sub-lattice. In contrast, the high frequency optical modes (i.e., $\approx 400$ cm\(^{-1}\)) arose from the B sub-lattice and Zr-B bonds.\textsuperscript{47} The high frequency modes show no change as Hf content increases. In contrast, the Zr sub-lattice vibrations of ZH33 were shifted to $\approx 1\%$ lower frequencies compared to ZH01, which corresponds to a $\approx 40\%$ decrease in the atomic vibrational frequency when the impurity atoms are present in the lattice. This is similar to the decrease of $\approx 33\%$ predicted by analyzing relaxation times (Equation 16). The pDOS analysis indicates that the reduction in phonon thermal conduction with increasing hafnium content is due, at least in part, to changes in lattice vibration frequencies.

### 3.4. Conclusions

Reactive hot pressing was used to produce ZrB\(_2\) ceramics with Hf contents ranging from 0.01 to 0.33 at\%. At room temperature, thermal diffusivity decreased from 0.47 cm\(^2\)/s to 0.36 cm\(^2\)/s as Hf content increased. Heat capacities were also affected by Hf as values ranged from 494.9 J/kg·K to 438.8 J/kg·K. Thermal conductivity decreased from 141 W/m·K to 100 W/m·K with increasing Hf content. The value of 141 W/m·K is the highest reported value for a polycrystalline ZrB\(_2\) ceramic to date. The electron contribution to thermal conductivity was estimated from measured electrical resistivity using the Wiedemann-Franz law. Electrical resistivity increased from 6.54 $\mu\Omega$·cm for
0.01 at% Hf to 7.37 μΩ-cm for 0.33 at% Hf at room temperature. The addition of Hf resulted in a decrease in phonon conductivity to ~2 W/m•K for Hf contents above 0.11 at%, meaning that thermal conductivity was almost entirely due to electron transport for those compositions. DFT revealed that Hf additions did not change the electronic structure of ZrB$_2$, but led to changes in the vibrational frequencies on the Zr sub-lattice due to the presence of Hf atoms. Hf additions predominantly influence the phonon portion of thermal conductivity through point defects that decrease both thermal diffusivity and heat capacity by reducing lattice vibrational frequencies and decreasing the time between scattering events.

**Acknowledgments**

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References


45. X. Zhang, X. Luo, J. Han, J. Li, and W. Han, "Electronic structure, elasticity and hardness of diborides of zirconium and hafnium: First principles calculations," Computational Materials Science, 44 411-21 (2008).


Table I. Designation, Composition, and Density for Tested Specimens

<table>
<thead>
<tr>
<th>Designation</th>
<th>At%</th>
<th>Zr</th>
<th>Hf</th>
<th>B (g/cm²)</th>
<th>p&lt;sub&gt;exp&lt;/sub&gt;</th>
<th>p&lt;sub&gt;theo&lt;/sub&gt;</th>
<th>Relative Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZH01</td>
<td>33.32</td>
<td>0.01</td>
<td>66.67</td>
<td>6.06</td>
<td>6.1</td>
<td>99.3</td>
<td></td>
</tr>
<tr>
<td>ZH04</td>
<td>32.87</td>
<td>0.04</td>
<td>67.1</td>
<td>6.08</td>
<td>6.11</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>ZH06</td>
<td>33.21</td>
<td>0.06</td>
<td>66.74</td>
<td>6.08</td>
<td>6.11</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>ZH11</td>
<td>32.94</td>
<td>0.11</td>
<td>66.95</td>
<td>6.07</td>
<td>6.12</td>
<td>99.3</td>
<td></td>
</tr>
<tr>
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<td>32.82</td>
<td>0.16</td>
<td>67.02</td>
<td>6.06</td>
<td>6.13</td>
<td>98.9</td>
<td></td>
</tr>
<tr>
<td>ZH23</td>
<td>32.76</td>
<td>0.23</td>
<td>67.01</td>
<td>6.11</td>
<td>6.14</td>
<td>99.5</td>
<td></td>
</tr>
<tr>
<td>ZH28</td>
<td>32.8</td>
<td>0.28</td>
<td>66.93</td>
<td>6.04</td>
<td>6.15</td>
<td>98.2</td>
<td></td>
</tr>
<tr>
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<td>5.92</td>
<td>6.15</td>
<td>96.1</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. XRD pattern for ZH06, which was representative of all of the RHP specimens, showing the primary phase was ZrB$_2$ with a trace of ZrO$_2$ present.
Figure 2. Representative SEM images showing the microstructure of ZH06 at a)1000X and b)3500X magnification. ZrO$_2$ and C inclusions were visible with most of the ZrO$_2$ being located at grain boundaries.
Figure 3. Thermal diffusivity at 298 K for RHP ZrB$_2$ with the value from a recent study of dense ZrB$_2$ prepared from commercial powder for comparison.
Figure 4. Heat capacity values as a function of Hf content.
Figure 5. Thermal conductivities for RHP ZrB$_2$ with different Hf contents at temperatures ranging from 298 to 472 K.
Figure 6. Electrical resistivity values as a function of temperature for several reaction processed ZrB$_2$ ceramics (ZH06, Guo$^{21}$ and Zhang$^4$) compared to values for ZrB$_2$ produced from commercial powder (McClane$^{23}$).
Figure 7. Electrical resistivity for RHP ZrB₂ as a function of Hf content fit to Nordheim’s rule.
Figure 8. $k_p$ and $k_e$ contributions to $k$ for RHP ZrB$_2$ with increasing Hf content.
Figure 9. Electron density of states (eDOS) for ZrB$_2$ with different Hf contents.
Figure 10. Phonon density of states (pDOS) for ZrB$_2$ with different Hf contents.
4. THERMAL PROPERTIES OF ZIRCONIUM DIBORIDE WITH VARYING BORON ISOTOPE RATIOS

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Abstract

Thermal properties were studied for zirconium diboride ceramics with varying ratios of boron-10 and boron-11. Reactive hot pressing of ZrH₂ and varying amounts of isotopically pure ¹⁰B and ¹¹B powders were used to synthesize compositions ranging from Zr¹⁰B₂ to Zr¹¹B₂. Thermal conductivity was calculated from heat capacity, thermal diffusivity, and density for temperatures ranging from 298 K to 2273 K. Measured heat capacities increased as the average boron isotope mass decreased. Electrical resistivity did not change with the average boron isotope mass, indicating that any changes in total thermal conductivity were due to changes in phonon heat transport. Density functional theory and Harmonic approximation models were used to simulate heat capacities and explain the measured trends. The thermal conductivity of Zr¹⁰B₂ was 145 W/m·K at 298 K and 97 W/m·K at 2273 K, which are the highest values reported to date for ZrB₂.

4.1. Introduction

Zirconium diboride (ZrB₂) is a transition metal boride and belongs to the family of ultra-high temperature ceramics (UHTCs), which includes other transition metal borides, carbides and nitrides.¹ The crystal structures of ZrB₂ is a hexagonal AlB₂ type
with alternating layers of B atoms in graphite like rings and Zr atoms in a hexagonally closed packed arrangement. Zirconium diboride exhibits covalent bonding among boron atoms, metallic bonding in the zirconium plane, and iono-covalent bonding between the zirconium and boron atoms.\textsuperscript{1,2} In addition to their high melting temperature, ZrB\textsubscript{2} and the other UHTC diborides have attracted interest due to their unusual combination of properties including, ceramic-like strength and hardness combined with metal-like thermal and electrical conductivities. As a result, these diborides have been proposed for the use in future hypersonic vehicle thermal protection systems\textsuperscript{3,4,5} and other high temperature structural applications.\textsuperscript{6}

Historically, hot pressing (HP) has been the dominant method of densification of ZrB\textsubscript{2}-based ceramics. Due to strong covalent bonding and the resulting low grain boundary and bulk diffusion rates, full densification of ZrB\textsubscript{2} generally requires temperatures above 2000 °C and pressures of at least 20-30 MPa.\textsuperscript{7} Harrington et al. achieve >95% relative density at 2100°C with 32 MPa of applied pressure using nominally phase pure ZrB\textsubscript{2} that had an average starting particle size of \~2 µm and a thermal conductivity of \~90 W·mK.\textsuperscript{8} Particle size reduction through attrition milling has been shown to enhance densification due to the increased driving force for densification from higher surface free energy.\textsuperscript{9} However, milling procedures often introduced media contamination (e.g., WC) that had adverse effects on thermal properties with values as low as \~30W/m·K reported at room temperature.\textsuperscript{10,11,12}

Reaction processing has also been identified as a potential fabrication route to produce higher purity ZrB\textsubscript{2} and HfB\textsubscript{2} with a high density at lower temperatures than
traditional HP. \(^2, 13, 14\) Chamberlain et al. showed that reaction between Zr and B led to grain size reduction, which resulted in full densification at 2100°C with 40 MPa of applied pressure. \(^2\) Guo et al. achieved >95% relative density at 1750°C using a reaction spark plasma sintering process at 50 MPa of applied pressure. \(^15\) Guo’s process used ZrH\(_2\) as a precursor. The starting ZrH\(_2\) was ball milled with SiC to reduce the particle size to \(~2.5\ \mu m\). In contrast to WC impurities, the presence of SiC did not have a detrimental effect on the measured thermal properties with a room temperature thermal conductivity of \(~130\ W/m\cdot K\) reported. A typical RHP process has two steps. The first is the in-situ reaction of the precursor powders to form ZrB\(_2\), and the second is densification, which is usually performed at a higher temperature and pressure than the reaction step. \(^2, 16\)

One of the notable properties of ZrB\(_2\) is its thermal conductivity. Single crystal values have been reported as 140 W/m·K along the [10\,\overline{1}0] and as 100 W/m·K along the [0001]. \(^17\) Reported values for polycrystalline ZrB\(_2\) ceramics typically range from 60 to 130 W/m·K at 298 K and converge to between 60 and 80 W/m·K as temperature approaches 2273 K. \(^11, 12, 15, 18, 19\) All of the ZrB\(_2\) ceramics with thermal conductivities above 100 W/m·K at 298 have been for materials that were reaction processed, \(^15, 18\) indicating that some of the variation in thermal conductivity is due to impurities. \(^20, 21, 22\) In particular, studies by Thompson and Zimmermann have shown that the presence of W reduces the room temperature thermal conductivity. \(^11, 12\) In addition, some reported thermal conductivity values were measured from specimens that included porosity, but little work has been done to examine the influence of porosity and grain size on thermal conductivity of ZrB\(_2\). \(^12, 23\) Based on the previous studies, the intrinsic thermal
conductivity for phase pure, fully dense ZrB$_2$ without impurities should be at least ~130 W/m·K at 298 K and 80 W/m·K at 2273 K.

Isotope enrichment increases the thermal conductivity of lattice conductors such as diamond, silicon, germanium, graphene, boron nitride, and LiO$_2$. The magnitude of the increase ranged from 10 to 50% for full enrichment of a single isotope compared to materials with the naturally-occurring isotopes. Some of the largest increases have been observed for boron containing compounds. Boron has relatively high isotopic disorder (19.9% $^{10}$B and 80.1% $^{11}$B) compared to carbon (98.9% $^{12}$C and 1.1% $^{13}$C). Chang et al. observed a thermal conductivity of 124 W/m·K at 100 K in $^{11}$B enriched boron nitride nanotubes compared to a value of 68 W/m·K for the natural isotopic ratio, which is an increase of ~45%. Anthony saw an increase of ~35% in thermal conductivity for full enrichment of the lighter $^{12}$C isotope in diamond at room temperature. Generally, the enhancement in thermophysical properties is attributed to the reduction of phonon-isotope scattering.

The effects of isotope enrichment have been described using kinetic theory and first principles simulations. A thermal conductivity model based on Debye’s equation for heat transfer in gasses can also provide a phenomenological explanation of the isotope effect by treating lattice vibrations like a gas of phonons (Equation 1).

\[
k_T \approx \frac{1}{3} C v^2 \lambda \tag{1}
\]
where $k_T$ is the total thermal conductivity, $C$ is the constant volume heat capacity, $v$ is the velocity of sound in the material, and $\lambda$ is the mean free path of phonons. Changing the isotope ratio affects all three parameters. The effect of isotopes on the mean free path is generally addressed by scattering models that calculate mean times between scattering events. Enrichment with a single isotope leads to more uniform vibrational frequencies among atoms in the crystal lattice and phonon mean free path is increased. Enrichment using lighter isotopes results in a lower overall density, which increases the acoustic velocities in the material. In general, heavier isotopes lead to higher heat capacities. The largest effects of isotopes on thermal properties are observed below room temperature since Umklapp scattering causes heat capacity values to converge at higher temperatures.

The purpose of this study was to determine the effects of boron isotope enrichment on the thermal properties of RHP ZrB$_2$ ceramics.

4.2. Procedure

4.2.1. Powder Preparation and Reactive Hot Pressing. The precursor powders used in this study were ZrH$_2$ (Chemetall, Grade S), $^{10}$B and $^{11}$B powders (Ceradyne, inc). The ZrH$_2$ powder had a reported purity of 97.8 at.\% with 1.9 at.\% excess H. The average particle size of the ZrH$_2$ was ~5 µm while the boron powders had average particle sizes of ~3 µm for $^{10}$B powder and ~34.5 µm for $^{11}$B.

Batches for RHP were prepared by ball milling ZrH$_2$ and B with ZrB$_2$ media for 3 hours in hexanes to mix the powders. Compositions were identified using the nomenclature Zr(XX,YY)B$_2$ where XX indicates the nominal content of $^{10}$B in wt\% and
YY indicates the nominal content of $^{11}$B in wt%. Natural boron has two stable isotopes, $^{10}$B (18.4 wt. %) and $^{11}$B (81.6 wt. %). Therefore the Zr(20,80)B$_2$ composition was formulated to represent ZrB$_2$ produced with a natural boron and the Zr(100,0)B$_2$ specimen was comprised of fully enriched $^{10}$B powders.

For densification, powders were placed into a boron nitride coated graphite die and cold uniaxially pressed at 35 MPa for 60 seconds resulting in a green density of ~45%. The die was then loaded into the hot press and heated at ~5 K/min under a vacuum (~27 Pa) up to 1223 K. An isothermal hold of 13 to 15 hrs was employed to promote reaction of the powders according to Equation 2.

$$ZrH_2(s) + 2B(s) \xrightarrow{1223 K} ZrB_2(s) + H_2(g)$$  \hspace{1cm} (2)

After the hold, the hot press was heated to 2373 K at ~50 K/min with three additional isothermal holds. The duration of each hold was 45 min at temperatures of 1323 K, 1723 K, and 1923 K. The hold at 1323 K was performed to promote reaction of any unreacted powders. The holds at 1723 K and 1923 K were used to remove oxide surface impurities, as reported in previous studies.$^{2,43,44}$ After the hold at 1923 K, the furnace was backfilled to ambient pressure with helium and heated to the densification temperature of 2373 K at ~75 K/min. At the hot pressing temperature, 50 MPa was applied for 45 minutes, after which the furnace was cooled at 20 K/min to room temperature. The load was released at 1923 K.
4.2.2. **Microstructure Characterization.** Two methods were used to characterize the phases present in the resulting ceramics. X-ray Diffraction (XRD; PANalytical Multipurpose diffractometer, X’Pert Pro, Amelo Netherlands) analysis was performed using Cu-Kα radiation. The powders were crushed and ground using an agate mortar and zirconia pestle. Diffraction patterns were obtained by scanning from 3° to 90° two theta at 0.03° per step with a 1s count time. The second method for phase identification was Raman spectroscopy (ARAMIS Labram spectrometer, Horiba Jobin Yvon, Edison, NJ) with a laser wavelength of 632.8 nm using polished cross sections.

Specimens for microstructure analysis were cut parallel to the hot pressing direction with diamond coated blades and then ground and polished. Polymer bonded diamond grinding disks and water lubricant were used for abrasive sizes from 145 µm down to 6 µm. Felt pads and water-based diamond slurry suspensions were used for abrasive sizes from 3 µm down to 0.5 µm. Scanning electron microscopy (SEM; Hitachi S570, Ibraki, Japan) was performed to characterize microstructures and grain sizes. An accelerating voltage of 15 kV and operating distance of 12 mm was used during SEM operation.

Grain sizes were determined using computerized image analysis (ImageJ; Research Services Branch, National Institute of Mental Health, Bethesda, Maryland) of polished and etched cross sections. Specimens were chemically etched using two parts potassium hydroxide (KOH) with one part deionized water at 413 K. A minimum of 200 grains were analyzed for each composition. Average particle sizes were estimated from measured grain areas assuming spherical grains.
Densities were analyzed using Archimedes method. Deionized water at room temperature was the immersion medium. Specimens were placed under vacuum for 24 hours to ensure complete infiltration. Theoretical densities were calculated by the average mass, using the nominal isotope ratios and unit cell volumes determined by XRD.

4.2.3. Thermal Property Characterization. Thermal diffusivity was measured using the laser flash technique (Cryo. 2000, & Flahsline 5000; Anter Corp., Pittsburg, PA) following ASTM standard E1461-11. The Clark and Taylor correction factor was used. A minimum of three tests were performed at each temperature to determine average diffusivity values.

Heat capacity was measured between 298 and 673 K with a differential scanning calorimeter (DSC 2010; TA Instruments., New Castle, DE.). Powder was crushed to less than 250 µm using an agate mortar and zirconia pestle. Hermetic aluminum crucibles were used with a heating rate of 10 K/min to 873 K followed by air cooling. Power measurements were converted to heat capacity using Equation 4,

\[
C_p = \left( \frac{60E}{Hr} \right) \frac{\Delta H}{m}
\]

where E is a cell calibration coefficient, Hr is the heating rate, \(\Delta H\) is the difference in heat flow between sample and reference, and m is the sample mass. The correction factor E was determined by using an Al₂O₃ standard (Standard Reference Material 676a, National Institute of Standards and Technology, Gaithersburg, MD). Reported values were the average of a minimum of three tests for each sample by DSC. Heat capacities were also measured using laser flash. Between 473 and 2273 K, heat capacity was
measured using laser flash by comparison to a graphite standard (Thermographite B1-D2-59-050, TA-Waters LLC, Pittsburg, PA). The variabilities in \( C_p \) were ~5% for DSC and ~10% by laser flash.

The total thermal conductivity was calculated using Equation 5, where \( D \) is thermal diffusivity, \( C_p \) is heat capacity, and \( \rho \) is the bulk density.

\[
k_T = D \rho C_p
\]

Both \( D \) and \( C_p \) were measured as a function of temperature while \( \rho \) was measured at room temperature and then calculated as a function of temperature using linear expansion data from polycrystalline ZrB\(_2\) from Touloukian.\(^4\)

Electrical resistivity (\( \rho_e \)) was measured using the van der Pauw method in accordance with ASTM standard F76-08. Sintered billets with a 25mm diameter were ground to ~1mm and tested from 298-673 K in a tungsten element furnace under vacuum (25Pa). The electron contribution to thermal conductivity (\( k_e \)) of ZrB\(_2\) was calculated using the Wiedemann-Franz law (Equation 6),

\[
k_e = \sigma_e L_o T
\]

where \( L_o \) is the theoretical Lorenz number (2.44 x 10\(^{-8}\)), \( T \) is the absolute temperature, and the electrical conductivity is the inverse of resistivity.

Total thermal conductivity was assumed to be comprised of electron and phonon contributions (Equation 8), where \( k_p \) is the phonon contribution to total thermal conductivity.
\[ k_r = k_e + k_p \]  

(8)

Photon contributions were neglected due to the high relative density of the specimens. The phonon contributions were estimated by subtracting the calculated electron contribution from the measured total thermal conductivity.

4.2.4. Thermal Property Models. First principles density functional theory (DFT) was used to simulate the intrinsic phonon vibrational properties of isotopically enriched ZrB$_2$. The open source Quantum ESPRESSO code used projected augmented wave (PAW) potentials. A three atom model was used with a hexagonal close packed arrangement and fractional atomic coordinates placed at (0.00, 0.00, 0.00) for zirconium along with (-0.33, 0.33, 0.5) and (0.33, -0.33, 0.5) for the boron atoms. A lattice spacing of 3.17 Å was employed for the a-direction, based on measured values, with a c/a of 1.11. Energy minimization and convergence was achieved with a 16 x 16 x 16 k point grid with a plane wave cutoff energy of 1x10$^{-6}$ eV. In addition, Gaussian smearing with a parameter of 0.1eV was used.

Density functional perturbation theory (DFPT) with a 3x3x3 k-space mesh was used to determine the phonon density of states (pDOS) and phonon dispersion curves. A cutoff energy of 1x10$^{-6}$ eV was used for convergence.

A harmonic approximation (HA) based on Einstein’s single harmonic oscillator model was used to simulate heat capacity as a function of temperature. The phonon vibrational energy, as derived by Einstein, was taken as
where ħ is Dirac’s constant, $k_B$ is Boltzmann’s constant, $\omega(q,v)$ is the phonon frequency with respect to the q point symmetry and optical vibration mode, and T is temperature. Constant volume heat capacity was assumed to be the derivative of phonon vibrational energy (Equation 9) with respect to temperature, which gave the following equation

$$C_v = \frac{k_B N}{3} \sum_{q,v} \left( \frac{\hbar \omega(q,v)}{2k_B T} \right)^2 \left( \frac{1}{\text{Sinh}^2 \left( \frac{\hbar \omega(q,v)}{2k_B T} \right)} \right)$$  \hspace{1cm} (10)$$

Constant volume heat capacity was calculated by summing the simulated heat capacity of each vibrational group individually (Zr-Zr, B-B, …) and dividing by the mass of that vibrational group. This was done to enhance the impact of vibrational shifts in the lighter sub-lattices due to isotope concentration and resulted in a larger shift in specific heat with isotope concentration and a better fit to experimental results.
4.3. Results and Discussion

4.3.1. Density and Microstructure. Table I summarizes the density and grain size results for the compositions with different isotope ratios. All materials achieved greater than 97% of their theoretical density. Across all of the compositions, the average grain size was \( \sim 30 \pm 14 \, \mu m \), which is larger than reported for previous studies involving reaction hot pressing of ZrB\(_2\), but close to what has been reported for traditional hot pressed specimens without additives\(^2\).\(^3\).\(^50\) Average grain sizes ranged from \( \sim 15 \, \mu m \) to \( \sim 45 \, \mu m \). SEM (Figure 1), XRD (Figure 2), and Raman analyses (Figure 3) were used to determine the amount of porosity and phases that were present. SEM micrographs indicated that trace impurity phases and porosity were present in the specimens. The porosity appears as bright circular inclusions with charging around the perimeter. Analysis by XRD (Figure 2) indicated that ZrB\(_2\) was the predominant phase, but a trace amount of ZrO\(_2\) was also detected in all compositions. Raman spectroscopy was used to identify the composition of the inclusions (Figure 3). Two separate phases were detected. The first phase was graphitic showing both the D (1370 cm\(^{-1}\)) and G (1583 cm\(^{-1}\)) peaks that result from a combination of sp\(^2\) and sp\(^3\) bonding. The second impurity phase had a Raman pattern that was consistent with tetragonal zirconia\(^51\).\(^52\) Image analysis of optical micrographs (not shown) indicated that \(~\sim 1\) vol% graphite and \(~\sim 4-7\) vol% ZrO\(_2\) were present, depending on the compositions.
The residual carbon was presumably introduced from the graphite furnace and dies used for densification. The ZrO\textsubscript{2} contamination was either due to oxide impurities in the ZrH\textsubscript{2} powders or the reaction of Zr with B\textsubscript{2}O\textsubscript{3} prior to its removal by volatilization. The analysis shows that RHP using isotopically enriched B powders led to nearly fully dense, stoichiometric ZrB\textsubscript{2} with small amounts of ZrO\textsubscript{2} and C impurities. The overall compositions and microstructures appear to be appropriate for comparing the effects of the changing B isotope ratio on thermal properties.

4.3.2. Thermal Diffusivity. Thermal diffusivity was measured for all of the compositions (Figure 4). At room temperature, Zr(100,0)B\textsubscript{2} had a value of 0.47 cm\textsuperscript{2}/s compared to 0.39 cm\textsuperscript{2}/s for Zr(50,50)B\textsubscript{2}. This represents an increase of 17% for full enrichment of the lighter \textsuperscript{10}B isotope compared to the 50-50 composition. For each isotope ratio, values for the entire temperature range were fit to Equation 11 and the results are compiled in Table II.

\[ D = a + (bT) + (cT^{-2}) + (dT^2) \] (11)

The increase in thermal diffusivity with full enrichment of either isotope is due to a reduction in phonon scattering from varying isotope disorder. Enrichment in the lighter \textsuperscript{10}B isotope results in a further increase in thermal diffusivity compared to \textsuperscript{11}B due to the faster vibrational speeds for the lighter isotope. First principle calculations by Klemens showed that phonon scattering can be described by the mean time between scattering events (Equation 11),

\[ 1/\tau_i(\omega) = \Omega g \omega^4 / 4\pi c^3 \] (12)
where $\omega$ is the phonon frequency, $\Omega$ is the atomic volume, $c$ is the velocity of sound. The isotopic disorder parameter ($g$), is given by Equation 13,

$$g = \sum_i f_i \left(1 - \frac{M_i}{M_{av}}\right)^2$$  \hspace{1cm} (13)

where $f_i$ is the concentration of the isotope with mass $M_i$ and $M_{av} = \sum f_i M_i$. For Zr(100,0)B$_2$, $g$ is $9.78 \times 10^{-5}$ which is two orders of magnitude smaller than the value of $2.25 \times 10^{-3}$ for Zr(50,50)B$_2$. The $g$ value for Zr(0,100)B$_2$ is $8.12 \times 10^{-5}$ which is slightly smaller than for Zr(100,0)B$_2$. The values of $g$ follow the same trend as the thermal diffusivities. The values of thermal diffusivity are higher for Zr(100,0)B$_2$ and Zr(0,100)B$_2$ than for mixed compositions due to lower atomic disorder. In addition, $g$ for Zr(100,0)B$_2$ is higher than for Zr(0,100)B$_2$ due to the lower overall mass. Assuming that changes in acoustic velocity are directly proportional to the phonon frequency changes, then acoustic velocity can be approximated as the average of the longitudinal and transverse acoustic velocities (Equation 14).

$$v = \frac{1}{3} (v_L + 2v_T)$$  \hspace{1cm} (14)

The values of $v_L$ and $v_T$ can be determined for a hexagonal crystal along the [0001] direction from elastic constants and mass densities where $v_L = (c_{11}/\rho)^{1/2}$ and $v_T = (c_{44}/\rho)^{1/2}$. Hence, lighter atoms (i.e., lower density) will lead to higher phonon velocities, which should, in turn, lead to higher thermal diffusivities.
Isotope enrichment effects change as temperatures increase, which causes thermal diffusivity values to converge as temperatures increase. At 1273K, Zr(100,0)B$_2$ has a thermal diffusivity of 0.21 cm$^2$/s compared to a value of 0.19 cm$^2$/s for Zr(50,50)B$_2$ at the same temperature, which is a difference of ~10%. Thus, the isotope effect decreases as temperature increases. Furthermore, at 2273 K, measured thermal diffusivity values were 0.17 cm$^2$/s for Zr(100,0)B$_2$, 0.16 cm$^2$/s for Zr(50,50)B$_2$, and 0.15 cm$^2$/s for Zr(0,100)B$_2$. The change in mechanism at elevated temperatures can be explained by increased phonon scattering due to Umklapp processes, which are not affected by isotope enrichment and become dominant at elevated temperatures. While isotope enrichment increases diffusivity at low temperatures and can be explained by continuum models, Umklapp scattering reduces the effects of differences in phonon vibrational velocities due to average atomic mass as temperatures approach 2273 K.
4.3.3. **Heat Capacity.** Heat capacity values for Zr(100,0)B\textsubscript{2} were higher than Zr(0,100)B\textsubscript{2} at all temperatures. The room temperature $C_P$ of Zr(100,0)B\textsubscript{2} was 0.51 J/g·K at 198 K compared to 0.44 J/g·K for Zr(0,100)B\textsubscript{2}, an increase of ~14%. Values for the entire temperature range were fit to Equation 11 as summarized in Table III. Calculated $C_P$ values were used for subsequent $k$ calculations.

At 2273 K, Zr(100,0)B\textsubscript{2} has a $C_P$ of 0.98 J/g·K while Zr(0,100)B\textsubscript{2} has a $C_P$ of 0.77 J/g·K, which is an increase of ~22% for full enrichment of the lighter $^{10}$B isotope. Thus, the effect of isotope enrichment on $C_P$ appears to become more important at the highest temperatures. The measured values of heat capacity seem to be surprising based on other studies of isotope enrichment that show that heavier isotopes lead to higher heat capacities.\textsuperscript{40,41,42,53} However, most previous studies have only reported results for temperatures in the range from 2.5 K to 100 K. Based on the present results, a change in the mechanism of heat storage may occur between 100 K and room temperature. The present results also indicate that the effect of isotope enrichment increases as temperature increases with the largest differences between Zr(100,0)B\textsubscript{2} and Zr(0,100)B\textsubscript{2} noted at the highest temperatures.
4.3.4. **Total Thermal Conductivity.** Thermal conductivities were calculated from measured values of thermal diffusivity, heat capacity, and density for the five isotope compositions (Figure 6). The thermal conductivity of Zr(20,80)B$_2$ (the composition closest to ZrB$_2$ produced with natural boron) was 114 W/m·K at 298 K, which is slightly lower than values of ~125 W/m·K reported for other ZrB$_2$ ceramics produced by reactive processes. In this case, the differences are most likely due to the increased ZrO$_2$ content in the materials in the present study (4 to 7 vol%) compared to previous studies (~2.5 vol%).$^{50}$ Full enrichment of the lighter $^{10}$B isotope increased thermal conductivity to 145 W/m·K for the Zr(100,0)B$_2$ composition. This is higher than any thermal conductivity reported to date for ZrB$_2$, including single crystal values.$^{1, 11, 12, 15, 17, 19, 54}$ Full enrichment with $^{11}$B resulted in a room temperature value of 111 W/m·K for Zr(0,100)B$_2$, which is ~20% lower than the value for Zr(100,0)B$_2$. The reduction in thermal conductivity for Zr(0,100)B$_2$ is due to a reduction in phonon vibrational frequencies, which reduces both thermal diffusivity and heat capacity. At 2273 K, the thermal conductivity of Zr(100,0)B$_2$ was 97 W/m·K, which is the highest value reported for ZrB$_2$ at this temperature. Full enrichment of the heavier $^{11}$B isotope in Zr(0,100)B$_2$ leads to a value of 73 W/m·K at 2273 K which is ~25% lower than Zr(100,0)B$_2$. In addition, the difference between the thermal conductivities of Zr(0,100)B$_2$ and Zr(100,0)B$_2$ increases by ~5% as temperature increases from 298 K to 2273 K due to the trend described for heat capacity. Enrichment of ZrB$_2$ with the lighter $^{10}$B isotopes leads to enhanced thermal properties from 298 to 2273 K for nominally phase pure ZrB$_2$.
4.3.5. Electron and Phonon Contributions to Thermal Conductivity. The electrical resistivities of Zr(20,80)B$_2$, Zr(50,50)B$_2$, and Zr(100,0)B$_2$ were measured from 298 K to 673 K. The values at 298 K ranged from 7.3 $\mu\Omega$·cm for Zr(100,0)B$_2$ to 7.6 $\mu\Omega$·cm for Zr(20,80)B$_2$. The difference in values across the range of temperatures was ~3% with no discernible trends based on isotope content (Figure 7). These differences were less than the estimated variance of the measurements, which was ~5%. The lack of discernible trends in the electrical resistivity means that changes in thermal conductivity are due to changes in the phonon contribution to thermal conductivity.

The phonon contributions to thermal conductivity were calculated by subtracting the electron contribution from the total thermal conductivity (Figure 8). At 298 K the phonon contribution to conductivity for Zr(100,0)B$_2$ was 46 W/m·K compared to 12 W/m·K for Zr(50,50)B$_2$. All specimens showed an increase in the phonon contribution to thermal conductivity between 298 K and 573 K. This could be an artifact of using the theoretical Lorenz number (2.44×10$^{-8}$ W·$\Omega$·K$^{-2}$) to estimate the electron contribution to thermal conductivity at low temperatures. For most materials, the Lorenz number, and, therefore, the Weidemann-Franz law, are assumed to be valid only above the Debye temperature, which is estimated to be ~1223 K for ZrB$_2$. Therefore, while these calculations may represent trends related to isotope enrichment below the Debye temperature, they have some inherent inaccuracies. Nonetheless, the higher phonon contribution to thermal conductivity estimated for Zr(100,0)B$_2$ is likely a real effect that occurs due to an increase in lattice vibration frequency associated with the lighter atomic masses, which results in higher thermal diffusivities and heat capacities for Zr(100,0)B$_2$. 
4.3.6. Phonon Vibration Properties. The pDOS (Figure 9a) and phonon dispersion curves (Figure 9b) were calculated using DFT from which HA was used to evaluate heat capacities. Only the models for Zr(0,100)B$_2$ and Zr(100,0)B$_2$ were included in the plots to more clearly show the trends. The pDOS for all isotope enrichments separate into low, medium, and high frequency regions. The low frequency acoustic modes are related to the Zr atom sub-lattice vibrations whereas the high frequency optical modes are due to the B sub-lattice and Zr-B atomic vibrations. The phonon dispersion curves show nine active vibrational modes for ZrB$_2$. The three lowest vibrational modes that arise around the 200 cm$^{-1}$ range are due to acoustic vibrations of the Zr-Zr bonds. The vibrations do not change with changes in the isotope composition since B is not involved in these bonds. The middle optical vibrations in the range of 400 to 600 cm$^{-1}$ arise from Zr-B vibrations while the highest frequency vibrations are optical frequencies ranging from 600 to 800 cm$^{-1}$ that are due to B-B vibrations. The middle and high frequency vibrations shift to higher frequencies when ZrB$_2$ is enriched with $^{10}$B. The lighter atoms vibrate faster under similar atomic bonding and lattice spacing conditions, which leads to the shift in the pDOS for the middle and high frequency vibrations. The general shape of the curves was in agreement with previous simulations, but the peaks related to Zr-B and B-B bonds shift to higher frequencies as the mass of the boron atoms decreases.

Phonon dispersion curves were used to estimate changes in heat capacity as a function of temperature for isotope enrichment. Again, only the Zr(0,100)B$_2$ and Zr(100,0)B$_2$ compositions are shown in Figure 9b to highlight the trends. The heat capacity at 298 K increased as ZrB$_2$ was enriched in $^{10}$B. The heat capacity was 0.45
J/g·K for Zr(100,0)B\textsubscript{2} compared to 0.44 J/g·K Zr(0,100)B\textsubscript{2}, which is an increase of ~2% in simulated heat capacity. The results show that heat capacity increases as the isotope mass decreases due to changes in phonon vibrations. For comparison, DSC measurements showed that heat capacity increased by ~22% from 0.77 J/g·K for Zr(0,100)B\textsubscript{2} to 0.98 J/g·K for Zr(100,0)B\textsubscript{2} at 298 K. The difference in absolute magnitude of the increase is most likely due to the oversimplification of the single harmonic oscillator model, which does not take anharmonicity in the lattice into account. Other factors such as three dimensional vibrations, phonon-phonon interactions, phonon-electron interactions, and the interactions resulting from the three separate bonding types in ZrB\textsubscript{2} may also affect the simulated values. Regardless of the absolute values, the simulations show that the heat capacity of ZrB\textsubscript{2} should increase as it is enriched in the lighter \textsuperscript{10}B isotope due to the changes in phonon vibrations.

The HA simulations (Figure 10) show that the isotope effect on heat capacity increases with increasing temperature. At 2273 K, Zr(100,0)B\textsubscript{2} has a heat capacity of 0.98 J/g·K compared to 0.90 J/g·K for Zr(0,100)B\textsubscript{2}, which is an increase of ~8%. Experimentally, a ~5% increase in the isotope effect was seen at 2373 K, which is very close to the increased predicted by the model. The increase in the isotope effect with temperature is due to changes in the $\frac{\hbar \omega}{kT}$ and $\frac{1}{\sinh^2 \left( \frac{\hbar \omega}{kT} \right)}$ terms in Equation 9. At low temperatures the hyperbolic sine term dominates, but at high temperatures the polynomial term becomes dominant. The term $\frac{\hbar \omega}{kT}$ is known as the Einstein temperature and indicates the probability an atom has to store energy in its oscillations.
The term $\frac{1}{\sinh^2 \left( \frac{\hbar \omega}{kT} \right)}$ is roughly equivalent to the average energy per oscillator.

Therefore, the simulations show that the average energy per oscillator is similar for $\text{Zr(100,0)B}_2$ and $\text{Zr(0,100)B}_2$ at low temperatures, but at high temperatures the ability of $\text{Zr(100,0)B}_2$ to achieve higher energy states leads to a greater discrepancy in heat capacities.

Comparing the results of the simulations to the experimental values leads to several observations. At low temperatures, where fewer vibration modes are active, the mass of the heavier isotopes leads to higher average energies and subsequently higher heat capacity. At higher temperatures, where more vibrational modes are active, the faster vibrations of the lighter isotopes leads to a greater probability of the phonon being excited to the next vibrational state and consequently increasing energy storage and heat capacity. Previous studies of isotope effects that have focused on low temperatures have shown heat capacity increases as heavier isotopes are substituted into the lattice.\textsuperscript{40,41,42} As temperatures increase, especially above the Debye temperature were all phonon modes are active, the faster vibrations have the potential to carry more energy. Thus, at high temperatures, enrichment of $\text{ZrB}_2$ with lighter B isotopes leads to higher heat capacities. The experimental results, combined with interpretations provided by DFT and HA models have revealed that at elevated temperatures, enrichment of $\text{ZrB}_2$ in the lighter $^{10}\text{B}$ increases heat capacity and thermal diffusivity due to increasing phonon vibration frequencies. Further, the increased thermal diffusivity and heat capacity lead to an increase in thermal conductivity to 145 W/m•K for $\text{Zr(100,0)B}_2$ at room temperature, which is the highest thermal conductivity reported to date for $\text{ZrB}_2$. 
4.4. Conclusions

Reactive hot pressing was used to produce ZrB$_2$ that was nearly fully dense with isotopic enrichment ranging from Zr$^{11}$B$_2$ to Zr$^{10}$B$_2$. Thermal diffusivity and heat capacity were measured from 298 to 2273 K. Enrichment of either $^{10}$B or $^{11}$B led to increases in thermal diffusivity at low temperatures compared to mixed compositions. The increase was due to a reduction in phonon scattering due to decreasing isotopic disorder. At high temperatures, the isotope effect on thermal diffusivity was negated due to Umpklapp scattering. The heat capacity increased as the average boron mass decreased at all temperature. ZrB$_2$ was modeled using first principles DFT from which pDOS simulations showed that boron sub-lattice vibrational frequencies increased for reduced boron masses. Heat capacity was modeled using a HA, which confirmed that increasing lattice vibrational frequencies will increase heat capacity at elevated temperatures. Full enrichment of the lighter $^{10}$B isotope led to a thermal conductivity of 145 W/m·K at 298 K and 97 W/m·K at 2273 K. Both the low and high temperature value are the highest reported for ZrB$_2$. The higher heat capacity values are due to an increase in phonon vibrational frequencies, which increase both thermal diffusivity and heat capacity at temperatures ranging from 298 K to 2273 K.

Acknowledgements

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References


55. X. Zhang, X. Luo, J. Han, J. Li, and W. Han, "Electronic structure, elasticity and hardness of diborides of zirconium and hafnium: First principles calculations," *Computational Materials Science*, 44 411-21 (2008).


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<th>$\rho_{\text{the}}$ (g/cm$^2$)</th>
<th>Relative Density (%)</th>
<th>Grain Size (µm)</th>
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Table II. Summary of D Fitting Parameters for Isotopically Enriched ZrB$_2$.

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Table III. Summary of Cp Fitting Parameters for Isotopically Enriched ZrB$_2$

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<td>0.93</td>
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Figure 1. A polished cross section of Zr(20,80)B₂ that is representative of the microstructures for all of the compositions with different isotope ratios.
Figure 2. Representative XRD pattern for isotopically enriched ZrB$_2$. This pattern was collected from Zr(20,80)B$_2$ powder.
Figure 3. Representative Raman spectra from carbon-rich and ZrO$_2$ inclusions in isotopically enriched ZrB$_2$. 
Figure 4. Diffusivity data for isotopically-enriched ZrB$_2$ compositions from 298 K to 2273 K.
Figure 5. Heat capacity data for isotopically enriched ZrB$_2$ compositions by DSC (filled symbols) from 298 K to 873 K and by laser flash (open symbols) from 298 K to 2273 K.
Figure 6. Calculated thermal conductivity values for isotopically enriched ZrB$_2$ compositions.
Figure 7. Electrical resistivity for the Zr(20,80)B$_2$, Zr(50,50)B$_2$, and Zr(100,0)B$_2$ compositions.
Figure 8. Phonon contributions to thermal conductivity for isotopically enriched ZrB₂ compositions.
Figure 9. DFT simulations for a 3 atom ZrB$_2$ model for Zr(0,100)B$_2$ and Zr(100,0)B$_2$ showing a) Phonon density of states (pDOS) and b) Phonon dispersion curves.
Figure 10. Calculated specific heat capacities using the harmonic approximation approach from single harmonic oscillator theory.
3. SUMMARY AND CONCLUSIONS

The thermophysical properties of nominally phase pure ZrB$_2$ were investigated. Reaction hot pressing was employed to densify ZrB$_2$ ceramics. Initially, the sintering kinetics were studied and the intrinsic thermal properties of the resulting ceramic were studied and compared to ZrB$_2$ produced by hot pressing commercial powders. Next, impurity concentrations were varied and isotope enrichments were performed to determine the effects on thermal properties. Scattering models based on quantum mechanics were used to determine the mechanisms that led to differences in thermal properties. In addition, DFT was utilized to analyze the effects on the electron and phonon structure on thermal properties. Together, these studies provided answers to the technical questions that were presented in the Introduction section. The answers are summarized below.

*What are the intrinsic sintering mechanisms, grain growth kinetics, and resulting microstructure of reaction hot pressed ZrB$_2$ ceramics?*

Reactive hot pressing led to enhanced densification at lower temperatures compared to densification of commercial ZrB$_2$ powder. The final RHP ZrB$_2$ ceramics had ~2.5 vol% ZrO$_2$ present as well as ~1 vol% C. At temperatures as low as 1800°C, relative density values of ~98.2% were achieved without the addition of sintering aids. Particle size reduction resulting from the initial reaction process allowed for enhanced driving forces for densification. Densification models using modified creep equations were used to study sintering kinetics. An overall activation energy of 350 kJ/mol was determined. However, the densification mechanism changed around 2000°C. Grain boundary
diffusion was determined to be the dominant mechanism below 2000°C with an activation energy of 270 kJ/mole while lattice diffusion was the dominant mechanism above 2000°C with an activation energy of 420 kJ/mole. At 1900°C, normal grain growth was observed with a diffusion coefficient of $6.85 \times 10^{-10}$ cm$^2$/s and at 2100°C a grain pinning mechanism was observed with a diffusion coefficient of $2.33 \times 10^{-9}$ cm$^2$/s.

What are the intrinsic thermal properties of reaction processed ZrB$_2$ with high purity and relative density from 25 to 2000°C?

The intrinsic thermal properties of a RHP ZrB$_2$ ceramic were compared to HP ZrB$_2$ ceramics. Heat capacities were higher for RHP ZrB$_2$ than for conventional ZrB$_2$ at all temperatures. Similarly, thermal diffusivity values for RHP ZrB$_2$ were higher at low temperatures, but values converged above the Debye temperature. A thermal conductivity of 127 W/m·K was calculated for RHP ZrB$_2$ at 298K compared to 85 W/m·K for HP ZrB$_2$. At 2000°C, thermal conductivities were 80 W/m·K for RHP ZrB$_2$ and 75 W/m·K for HP ZrB$_2$. Reduced Hf concentrations were detected in the RHP ZrB$_2$, which led to the higher values of $k$, $D$, and $C_p$. At higher temperatures the thermal conductivity values for RHP and HP ZrB$_2$ converged to similar values due to Umklapp scattering mechanisms.

What are the effects of Hf contents from 0.01 to 0.33 at% on the thermal properties of ZrB$_2$.

The effect of Hf content on the thermal properties of ZrB$_2$ ceramics was studied to provide insight into the discrepancies between thermal properties of HP ZrB$_2$ and RHP ZrB$_2$. A series of ZrB$_2$ ceramics with Hf contents ranging from 0.01 to 0.33 at% were produced by RHP. The room temperature thermal conductivity for RHP ZrB$_2$ with 0.01
at% Hf was 135 W/m·K, which is the highest reported thermal conductivity to date for ZrB$_2$. Thermal conductivities at 298 K decreased from 140 W/m·K to 100 W/m·K as Hf content increased. The effects on thermal conductivity were analyzed by employing point defect scattering models for phonons and electrons. The effects of Hf on the thermal properties of ZrB$_2$ ceramics were described by a model for point defect scattering of lattice vibrations. The $k_p$ and $k_e$ breakdown showed that $k_p$ was more strongly affected by hafnium content than $k_e$. DFT theory was used to further analyze the effect of Hf additions, which showed that the vibrational frequencies of the Zr sub lattice were altered by the presence of Hf, but the intrinsic electron structure did not change.

What are the effects of boron isotope enrichment on the thermal properties of RHP ZrB$_2$ from 25 to 2000°C.

The final study involved the enrichment of ZrB$_2$ with individual boron isotopes in an effort to enhance thermal conductivity. Enrichment of either $^{10}$B or $^{11}$B led to increased in thermal diffusivity at low temperatures. Increases were attributed to decreasing phonon scattering due to isotopic disorder. Heat capacity increased as the average boron mass decreased. First principles DFT and HA simulations showed similar trends and revealed the fundamental mechanism was due to an increase in vibrational frequencies on the boron sub-lattice. Enrichment of the lighter $^{10}$B isotopes led to enhanced thermal properties. Full enrichment of the lighter $^{10}$B isotope led to a thermal conductivity of 145 W/m·K at 298 K and 97 W/m·K at 2273 K which are the highest thermal conductivities reported for any ZrB$_2$ ceramic at both temperatures.
The understanding and enhancement of the intrinsic thermophysical properties of ZrB$_2$ is critical for its realization as a leading edge material on a next generation hypersonic vehicle. Maximizing thermal conductivity will improve the ability to conduct heat away from the sharp leading near the stagnation point to cooler areas where the heat can be dissipated. Reaction processing has been shown to produce ceramics with higher thermal conductivity and enhanced densification. The research described in this document has identified the fundamental factors responsible for the enhanced densification and thermal conductivities. In addition, this study has furthered the knowledge of heat transfer mechanisms in ZrB$_2$ ceramics. Finally, reducing Hf contamination and enriching ZrB$_2$ in one of the B isotopes can reduce point defect scattering in the crystal lattice, which led to the highest thermal conductivities reported to date for temperatures ranging from 298 to 2273K.
4. FUTURE WORK

The goal of this work was to research and enhance the thermal properties of ZrB$_2$ ceramics. During the course of this work, addition areas of research for future investigation were identified.

1. Zr isotope enrichments should be investigated as the isotopic disorder in the Zr sublattice is greater than that of B. Naturally occurring Zr is comprised of five stable isotopes including \( ^{90}\text{Zr}, ^{91}\text{Zr}, ^{92}\text{Zr}, ^{94}\text{Zr}, ^{96}\text{Zr} \) with abundances of 51.45, 11.22, 17.15, 17.38, and 2.80 at\% respectively.\textsuperscript{100} If similar mechanisms are active as were with B isotope enrichment, the full enrichment of the lightest isotope, \(^{90}\text{Zr}, \) would lead to enhanced vibrational frequencies along with reduced phonon and electron scattering. If electron conduction occurs primarily in the Zr sublattice, then reducing electron-photon scattering could lead to greater enhancements in thermal conduction than was seen for B isotope enrichment.

2. The effects that TM additions have on the thermal conductivity of ZrB$_2$ should be studied using RHP. Most previous studies of the thermal properties of ZrB$_2$ have used commercial ZrB$_2$ powders, which typically contain \(~0.37\) at\% Hf.\textsuperscript{22} The present study revealed that reducing the level of Hf contamination led to an increase of \(~30\%\) in thermal conductivity due to reduced point defect scattering of both phonon and electrons. Hence, the effect of TM additives in the previous studies may be at least partially obscured by the presence of Hf and other impurities in the commercial powders. In addition, no study has yet addressed
whether scattering from TM impurities acts additively or has some sort of coupling mechanism with the Hf impurities.

3. The Lorenz number for ZrB$_2$ needs to be experimentally determined. This study and most of the other reported studies that investigated the electrical properties of ZrB$_2$ have used the theoretical Lorenz number. In ideal cases for metallic conductors, this number is only suitable above the Debye temperature and most likely changes when impurities are present. The results of using an inappropriate Lorenz number can be seen in the behavior reported in some studies of the phonon and electron contributions to the overall thermal conductivity of ZrB$_2$. Studies report phonon contributions that increase with increasing temperature between 298 K and 473K, which is inconsistent with theory and observations of high purity metallic conductors.

4. A systematic study should be conducted to understand the effects of the presence of ZrO$_2$ on the properties of RHP ZrB$_2$ and to remove oxygen impurities from RHP ZrB$_2$ ceramics. All ceramics processed as part of the present research contained ZrO$_2$, with contents usually in the range of 3 to 6 vol%. The ZrO$_2$ was typically present as a second phase predominantly at the grain boundaries of the ceramic. In addition, ZrO$_2$ has been observed in other reaction processed ZrB$_2$ ceramics.$^{23,24}$ SEM and TEM should be used to map the presence of ZrO$_2$ impurities throughout the microstructure. Phonon and electron scattering of some form must be induced by the presence of this contamination. Removal of this phase should lead to further increases in thermal conductivity.
APPENDIX

THE EFFECTS OF GRAIN SIZE AND POROSITY ON THERMAL PROPERTIES OF ZrB$_2$

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Introduction

ZrB$_2$ is a transition metal diboride that belongs to the ultra high temperature ceramic (UHTC) family of materials. Due to strong covalent bonding, ZrB$_2$ has gained interest for its melting temperature (3250°C), hardness (23 GPa), and elastic modulus (489 GPa). In addition to mechanical properties, ZrB$_2$ has been investigated due to its promising thermal conductivity (60 W/m·K or higher at room temperature), electrical conductivity ($10^7$ S/m), and oxidation resistance. Proposed applications that take advantage of these properties include hypersonic vehicle thermal protection systems, cutting tools, molten metal crucibles, microelectronic substrates, and high temperature electrodes.

One of the notable properties of ZrB$_2$ is its thermal conductivity (k). Reported room temperature k values for single crystals are 140 W/m·K along the c-axis and 100 W/m·K along the a-axis. For polycrystalline ZrB$_2$, room temperature k values range from 45 to 135 W/m·K, but converge to values between 60 and 80 W/m·K as temperature approaches 2273 K. Some representative values are summarized in Figure 4. The only polycrystalline ceramics with room temperature k values of more than 100 W/m·K (Guo and Zhang) at 25°C were produced by reaction processes.
variations in reported k values is due to impurities. In addition, most reported k values were measured for specimens that had some porosity. Hence, reported values may not reflect the intrinsic k for high purity, fully dense ZrB$_2$.

The purpose of this study was to investigates effects of porosity and grain size on monolithic ZrB$_2$.

**Procedure**

Powders used in this study were ZrH$_2$ (Chemetall, Grade S), and B (Eagle Picher, Grade Sp 99). Samples used for studying the effects of porosity where labeled according to densification mechanism, sintering temperature, and time (Table I). Therefore a sample reaction processed at 2100°C for 60min would be labeled RHP_210_60. Specimens used for studying the effects of grain size where labeled according to the processing method (RHP for all), annealing temperature (225 to indicate 2250°C), and annealing time. RHP_225_0 is the baseline and was not annealed after densification. The microstructure characteristics are summarized in Table I(Porosity) and Table II(Grain size).

ZrB$_2$ batches were mixed by ball milling stoichiometric ratios of ZrH$_2$ and B for 3 hrs with ZrB$_2$ media in hexanes. All powders were then placed into a boron nitride coated graphite die and cold uniaxially pressed at 35MPa. Powders were densified by reactive hot pressing in a resistivity heated graphite furnace (3060-FP20, Thermal technology, Santa Rosa, CA). The compacts were heated under vacuum (~25 Pa) at 5°C/min to ~950°C with an isothermal hold of 15 hrs to promote reaction 1.

\[
\text{ZrH}_2(s) + 2B(s) \xrightarrow{950^\circ C} \text{ZrB}_2(s) + H_2(g)
\] (1)
After the isothermal hold at 950°C, the hot press was heated to 1900-2100 °C at ~50°C/min with three additional 45 min isothermal holds. Once the furnace reached the densification temperature, a uniaxial load of 50 MPa was applied from 15 to 130min to achieve a range of porosity from 0.25 to 25vol%. During the densification hold, the change in thickness of the specimens was measured in situ using a linearly variable differential transducer attached to the hot press rams. The furnace was cooled at ~20 °C/min and the load was released at 1650 °C. Specimens for grain size analysis where pressed to full density at 2100°C for 60min. After cooling to room temperature they were then annealed at 2250°C for up to 6 hr to grow grains.

Phases were characterized using X-ray diffraction (XRD; X’Pert Pro, Phillips Panalytical Multipurpose diffractometer, Amelo, Netherlands). Scanning electron microscopy (SEM; Hitachi S570, Ibaraki, Japan) was performed to characterize the microstructure. ImageJ software was used to analyze SEM images of etched cross sections in order to determine grain size. Bulk densities (ρ) were analyzed using Archimedes method with water as the immersion liquid.

Thermal diffusivity (D) was measured by laser flash (Cryo. 2000, & Flashline 5000; Anter Corp., Pittsburgh, PA) according to ASTM E1461-11 using the Clark and Taylor correction factor. Heat capacity (C_p) was measured using laser flash and differential scanning calorimetry (DSC 2010; TA Instruments, New Castle, DE). The variability in C_p was ~5% for DSC and ~10% by laser flash. Thermal conductivity was calculated using equation 5:

\[ k = D \rho C_p \]
where $\rho$ was corrected for temperature based on a coefficient of thermal expansion of $6.8 \times 10^{-6} \text{K}^{-1}$ for ZrB$_2$.\textsuperscript{17}

**Results and Discussion**

**Characterization**  Table I and II shows characteristic data for the RHP processed specimens. The bulk densities of reaction hot pressed ZrB$_2$ billets ranged from 4.58 to 6.09 g/cm$^3$, depending on the temperature and time of isothermal sintering. Densities increased as sintering temperatures and times increased. Grain sizes, before annealing, ranged from 2.8 to 6.1 µm and increase with increasing temperature and time. Relative densities as high as 99% were measured for specimens sintered at 1900°C. The final grain sizes (~6µm) when processed at 2100°C are roughly half the size seen in hot pressing of commercial ZrB$_2$ powders (~15.5µm) and previous RHP studies (~12µm).\textsuperscript{32, 55} Annealed specimens had grain sizes that ranged from 6 to 12 µm. Analysis by XRD confirmed that ZrB$_2$ was the predominant phase in RHP ZrB$_2$; however, ZrO$_2$ was also detected (Figure 1). Analysis of the starting powders (not shown) did not reveal any ZrO$_2$. Rietveld refinement of XRD data determined that the lattice parameters for ZrB$_2$ were $a = 3.16802(\pm0.00002)$ Å and $c = 3.53036(\pm0.00006)$ Å. The measured lattice parameters were consistent with reported values, which is a good indication that significant solid solution contamination was not present.\textsuperscript{10} Therefore, a wide range of porosity and grain sizes were processed in high purity ceramics that are suitable for studying the thermal properties of ZrB$_2$.

Analysis of porosity from SEM images indicated less porosity was present than was predicted from the density measurements. For instance, the calculated porosity for
RHP_190_15 was ~8% as compared to ~11 vol% determined by subtraction of the measured relative density. Raman analysis determined a small fraction of carbon was observed in all samples. The residual amount of carbon as determined by image analysis was less than ~1 vol%. In addition, ZrO₂ content was less than ~3 vol%. The difference in porosity, determined using image analysis and density measurements, might be due to non-uniform porosity throughout the sample. In this case, image analysis, which only looks at a tiny portion of the overall sample, could lead to significant errors in measurements. If theoretical density is adjusted due to ~1 vol% C (2.08 g/cm³) and ~3 vol.% ZrO₂ (5.68 g/cm³) the porosity from density measurements is still 10.6 vol% in RHP_190_15. Regardless, SEM analysis confirmed that porosity within the specimens was less than indicated by density measurements and the ZrB₂ produced through the RHP method was of high purity.
**Grain size Effects.** Relative density and grain size data for these specimens can be found in Table II. Thermal diffusivity values at room temperature increased from 0.40 cm$^2$/s for a grain size of 6 µm up to 0.42 cm$^2$/s for a grain size of 12 µm. After the examining diffusivities at temperatures of 25, 100, and 200°C (Figure 3), linear trend lines were fit to the values as a function of grain size. Although the values appear to exhibit a slight upward inflection at the largest grain sizes, a linear model was used based on previous reports showing a linear increase with grain size in the 0-10 µm regime.$^{43, 44}$ Deviation from linearity may be due to variance in the measurements. The increase in diffusivity with increasing grain size is most likely due to a reduction of grain boundary scattering, which presumably increases mean free path for phonon transport.$^{57, 58, 63}$ Regardless of the mechanism, increasing grain size leads to an increase in diffusivity in high purity ZrB$_2$ specimens within the 6-12 µm grain size regime.

**Porosity Effects.** The effect of porosity on thermal properties was examined by producing specimens with porosities ranging from 0.25 to 25.0 vol%. Relative density and grain size data for these specimens can be found in Table I. As sintering temperature increased, the volume fraction of porosity decreased and grain size increased Figure 2. The highly porous specimens (> 10 vol.%) have large (> 4 µm diameter), interconnected pore networks (Figure 2a), which is in contrast to the low porosity (< 10 vol.%) specimens that have small (< 1 µm diameter), isolated spherical pores (Figure 2d).

Figure 4 shows the calculated thermal conductivity as a function of porosity. The specimen with the least porosity, RHP_210_60 (0.26 vol%), had a thermal conductivity of 127 W/m·K at 25°C which decreased to 80 W/m·K at 2000°C. The specimen with the
most porosity RHP_190_IB (25.0 vol%) had a thermal conductivity of 97.1 W/m·K at 25°C and 56 W/m·K at 2000°C. At room temperature, k decreased by ~24% when porosity increased from 0.26 vol.% to 25.0 vol.%. There was no observed change in the effect of porosity on k with increasing temperature. At all temperatures, a nonlinear decrease in thermal conductivity is seen with increasing porosity similar to reports for high purity insulators and metallic conductors.\textsuperscript{103, 104, 105}

Several common linear porosity correction models were fit to the thermal conductivity data as can be seen in Figure 5. The Leob and Maxwell-Eucken models are typical porosity correction modes that are seen in the literature. As can be seen they both poorly predict the effect of increasing porosity within ZrB\textsubscript{2}. This could be partially due to the fact that both these models are created based on experimental data from oxide ceramics. The mechanisms responsible for heat transport in borides, predominantly metallic conduction, and oxides, primarily lattice conduction, are fundamentally different. A power series fit of the form seen in Equation 3 had the best fit at room temperature.

\[ y = \left( a + bx^c \right)^{-1} \]  

The decrease in thermal conductivity with increasing porosity is most likely due to an increase in phonon and electron scattering due to the presence of a non-conductive phase (porosity) within the matrix. The invariant nature of the effect of porosity on k with temperature indicates the mechanisms of scattering are not changing with temperature. Regardless of the exact mechanisms, increasing porosity leads to a decrease in thermal conductivity over all temperatures.
Conclusions

Reactive hot pressing was used to produce ZrB$_2$ with porosity from 0.25 to 25 vol% and annealing fully dense specimens at 2250°C produced grain sizes from 6µm to 13µm. Thermal diffusivity increased with increasing grain size. For an average grain size 12µm a diffusivity of 0.42 cm$^2$/s was measured compared to 0.40 cm$^2$/s for a grain size of 6 µm. Ultimately, the results are inconclusive as the variance in the measurements was greater than the increase in diffusivity. Thermal conductivity decreased with increasing porosity for all temperatures. SEM images showed the morphology of porosity inclusions changed with increasing porosity. Thermal conductivity decreased by ~25% as RHP_210_60 had a thermal conductivity of 127 W/m·K compared to RHP_190_IB which had a thermal conductivity of 97.1 W/m·K at 25°C. It was found that the effects of porosity on thermal conductivity did not follow a linear trend with increasing porosity. Several models typically used in the literature were fit to the data. These linear models had a poor fit to the data and it was found a power series best depicted the effect of porosity. The nonlinear trend in thermal properties with increasing porosity can most likely be attributed to changing scattering mechanisms with changing pore morphology.

Acknowledgements

This research was supported by the National Science Foundation through grant number DMR 0906584.
Table I. Density, porosity, and grain size of specimens produced by RHP.

<table>
<thead>
<tr>
<th>Specimen ID</th>
<th>Temperature (°C)</th>
<th>Grain size (µm)</th>
<th>Time (min)</th>
<th>( \rho_{\text{bulk}} ) (g/cm(^3))</th>
<th>( \rho_{\text{theo}} ) (g/cm(^3))</th>
<th>Relative density (%)</th>
<th>Porosity (vol%)</th>
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<tbody>
<tr>
<td>RHP_190_IB</td>
<td>1900</td>
<td>-</td>
<td>60</td>
<td>4.58</td>
<td>6.106</td>
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<td>RHP_190_15</td>
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<td>15</td>
<td>5.41</td>
<td>6.106</td>
<td>88.6</td>
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<td>60</td>
<td>5.72</td>
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<td>0.6</td>
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<tr>
<td>RHP_210_60</td>
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<td>6.1</td>
<td>60</td>
<td>6.09</td>
<td>6.106</td>
<td>99.7</td>
<td>0.3</td>
</tr>
</tbody>
</table>

* IB indicates samples were sintered for 15 min isobarically with pressure applied at 1650°
Table III. Summary of relative density and grain size for annealed ZrB$_2$ Ceramics

<table>
<thead>
<tr>
<th>Specimen Name</th>
<th>Annealing Temperature ($^\circ$C)</th>
<th>Time (hrs)</th>
<th>$\rho_{\text{bulk}}$ (g/cm$^3$)</th>
<th>Relative Density (%)</th>
<th>Grain size ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHP_225_0</td>
<td>-</td>
<td>-</td>
<td>6.04</td>
<td>98.9</td>
<td>6±2</td>
</tr>
<tr>
<td>RHP_225_1</td>
<td>2250</td>
<td>1</td>
<td>6.07</td>
<td>99.4</td>
<td>10±4</td>
</tr>
<tr>
<td>RHP_225_3</td>
<td>2250</td>
<td>3</td>
<td>6.08</td>
<td>99.6</td>
<td>11±5</td>
</tr>
<tr>
<td>RHP_225_6</td>
<td>2250</td>
<td>6</td>
<td>6.07</td>
<td>99.4</td>
<td>12±5</td>
</tr>
</tbody>
</table>
Figure 1. XRD analysis of RHP ZrB$_2$ showing ZrB$_2$ as the main phase and a small ZrO$_2$ peak.
Figure 2. Polished and etched cross sections of a) RHP_190_15, b) RHP_190_60, c) RHP_210_15, and d) RHP_210_60. Porosity decreases from specimen a to d as grain size increases.
Figure 3. Thermal diffusivity as a function of grain size at 25, 100, and 200°C for RHP ZrB$_2$. 
Figure 4. Thermal conductivity plotted as a function of porosity for select temperatures.
Figure 5. Leob, Maxwell-Eucken, and Harris models fit to room temperature thermal conductivity of ZrB$_2$ with varying porosity.
REFERENCES


70. X. Zhang, X. Luo, J. Han, J. Li, and W. Han, "Electronic structure, elasticity and hardness of diborides of zirconium and hafnium: First principles calculations," *Computational Materials Science, 44* 411-21 (2008).


VITA

Jason Michael Lonergan was born in Boulder, CO in 1981. He resided in Monument, CO for most of his K-12 education where he graduated from Lewis Palmer High School. During high school, he participated in extracurricular activities such as soccer as well as participating in both symphonic and jazz bands.

His undergraduate career was completed at the University of Colorado with a bachelor’s degree in Mechanical Engineering. He remained active in extracurricular activities playing on multiple competitive and semiprofessional soccer teams throughout his collegiate career. While an undergrad, he was part of a student team in the design, fabrication, and competition of small formula-style, autocross racing cars.

After his undergraduate degree he was invited to pursue an advanced degree in the lab of Professor Rishi Raj. He completed his Master’s degree within two years in the spring of 2011 in Mechanical Engineering while developing polymer derived ceramic coating for SiC/SiC ceramic matrix composites. It was during his time within Prof. Raj’s lab that he developed a passion for research and advanced ceramics.

After his masters, he decided to pursue a PhD at Missouri University of Science and Technology having been invited by Professor William Fahrenholtz to work within his lab. His PhD work focused on the processing, characterization, and thermal properties of materials for hypersonic leading edges. In December 2014, he received his Ph.D. in Materials Science & Engineering from Missouri S&T. He graduated in three years with five presentations at national conferences, one manuscript published, one submitted, and three more pending.