FULL PAPER

Theoretical analysis of thermal and mechanical properties of $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ pyrochlores

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First-principles calculations were used to analyze relationship between elastic stiffness and thermal conductivity of $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ pyrochlore oxides. $\text{Eu}_2\text{Hf}_2\text{O}_7$ demonstrated mechanical properties inferior to $\text{Gd}_2\text{Hf}_2\text{O}_7$. $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ belong to quasi-ductile ceramic materials because their G/B ratios are below 0.571 and because of their positive Cauchy pressure values. Thermal conductivity values of $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$, equal to 1.66 and 1.62 W/(m·K) are below that of yttria stabilized zirconia. Thus, $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ pyrochlores are promising as thermal barrier coatings for high-temperature applications, for example, in gas turbine engines.

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Key-words : Oxides, Ceramic, Mechanical properties, Thermal conductivity, First-principles calculations

[Received May 8, 2019; Accepted July 10, 2019]

1. Introduction

Applications of thermal barrier coatings (TBCs) include superalloy protection during their use in high temperature sections of gas turbine engines to ensure long operational life of these components at these conditions.^{1,2)} Currently used industrial TBCs mostly consists of ZrO_2 partially stabilized by 6–8 wt % of Y_2O_3 (YSZ) with thermal conductivity of ~ 2.2 W/(m·K).^{3,4)} However, during thermal cycling, tetragonal-to-monoclinic phase transition may severely impact coating life and limit its functioning at temperatures over 1200°C.¹⁾ As requirements for temperatures of typical gas turbine engines rise, TBCs with better thermal stability as well as lower thermal conductivity are required.^{5–11)}

Oxides with pyrochlore-type structures containing rare earth elements (RE) with a typical formula expressed as $\text{RE}_2\text{B}_2\text{O}_7$ (with B being a tetravalent metal) have many practical uses because of their excellent structural stability, high melting points and thermal expansion coefficients as well as low thermal conductivity in combination with good fracture toughness. Outstanding thermal stability of these materials correlates with the strong bonds between their constituent elements. At the same time, properties like high thermal expansion coefficients, low thermal conductivities and fracture toughness are defined by weak RE-O bonds. Thus, $\text{RE}_2\text{B}_2\text{O}_7$ -type pyrochlores contain alternating weak and strong chemical bonds. Such complex

chemical structure allows pyrochlore oxides to easily accommodate defects,^{6,12)} which makes them excellent candidate materials for high-permittivity dielectrics,¹³⁾ TBCs,^{6,14)} solid electrolytes,¹⁵⁾ nuclear waste hosts,¹⁶⁾ catalysis,¹⁷⁾ etc. Thus, optimization of combination of these diverse properties of pyrochlores while simultaneously keeping their excellent physical, chemical and thermal properties is required.

Pyrochlore-type $\text{RE}_2\text{T}_2\text{O}_7$ oxides with $T = \text{Zr}, \text{Sn}, \text{Hf}, \text{Ti}$, and Ge can be obtained by either replacing half of the T-atoms in the TO_2 fluorite units by RE or by formation of oxygen vacancies, which are often formed to sustain electroneutrality (see Fig. 1).⁶⁾ O-atoms in HfO_6 octahedra [see Fig. 1(b)] are relaxed. Other O atoms [marked in Fig. 1(a) as O1] are positioned at the initial sites. Chemical

Fig. 1. (a) Schematic of the $\text{RE}_2\text{Hf}_2\text{O}_7$ and (b) its HfO_6 octahedron structures.

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bond change and oxygen vacancy appearance upon structure distortion leads to thermal conductivity decrease. Combination of these two variations in pyrochlore chemical structure results in a wide variety of pyrochlores with varying compositions and properties.¹⁸⁾ By systematically studying $\text{La}_2\text{T}_2\text{O}_7$ structures of pyrochlores based on Zr, Ge, Hf, Ti and Sn, Liu et al. deduced their low thermal conductivity values and showed importance of La–O weak bonds in sustaining their good thermal and mechanical characteristics.^{6),19)} Feng et al. found *RE* zirconates and stannates as efficient TBCs.^{20),21)} Yet, despite these studies and their encouraging results, reports on pyrochlore *RE* hafnates are lacking. Thus, in this work, we report theoretical calculations based on plane-wave pseudopotential total energy with the goal to analyze mechanical, elastic and thermal conductivity properties of pyrochlore *RE* hafnates to predict their relevant properties as function of their specific *RE*. Our ultimate goal is to understand how different *REs* affect overall pyrochlore hafnate properties. Our results should provide contribution to understanding function and use of *RE* hafnates as TBCs.

2. Calculation methods

For structure optimization and property analysis, we used quantum ESPRESSO code based on the density functional theory.^{22),23)} To analyze interactions between outer electrons and ionic core, we used ultrasoft pseudo-potential rather than norm conserving pseudo-potential in this paper. First of all, ultrasoft pseudo-potentials own smaller plane-wave basis set and a smaller real-/reciprocal space grids than norm conserving pseudo-potential for the same system, due to the Kohn–Sham orbits can be chosen to be very smooth, being obviously more efficient. Secondly, the scattering properties and their energy derivatives of ultrasoft pseudo-potentials are correct at several energies spanning the range of occupied states, and the transferability can be systematically improved by increasing the number of such energies. And the pseudo-potential itself becomes involved in the self-consistent screening process, thereby improving transferability with respect to changes in charge configuration.^{22),24)} The valence electrons in this paper are Eu $4f^65d^16s^{1.5}6p^{0.5}$, Gd $4f^75d^16s^{1.5}6p^{0.5}$, Hf $4f^{14}6s^26p^05d^2$ and O $2s^22p^4$. Feng et al. reported that U is used to correct the on-site Coulomb interactions for the highly localized $4f$ orbital, and which is not directly related to stress-strain evaluations.²⁵⁾ Therefore, our results in this paper do not add U because the mechanical and thermal properties are nearly independent of U values. To evaluate elastic constants, exchange correlation potential was obtained taking into account spin polarization effect and also using generalized gradient approximation in the form of Perdew–Burke–Ernzerhof.²⁶⁾ Calculations used a supercell with eight $\text{RE}_2\text{Hf}_2\text{O}_7$ units and with $6 \times 6 \times 6$ k-point sampling in reciprocal space as well as 36 Ry cutoff energy for the plane wave basis. We allowed crystal structures to stay relaxed until the individual applied forces were below 0.005 eV/Å.

3. Results and discussion

3.1 Lattice parameters

$\text{RE}_2\text{Hf}_2\text{O}_7$ pyrochlores are part of the $Fd\bar{3}m$ space group (see Fig. 1). *REs* populate $16d$ sites at $(1/2, 1/2, 1/2)$ positions. Hafnium atoms occupy $16c$ sites at $(0, 0, 0)$ positions. O1 and O2 atoms occupy $8b$ sites at $(3/8, 3/8, 3/8)$ positions surrounded by tetrahedrally-coordinated *REs* and $48f$ sites at $(x, 1/8, 1/8)$ positions surrounded by two Hf and two *REs*, respectively. Two sets of independent parameters were implemented to define pyrochlore cell: 1) internal atomic parameter x corresponding to the O_{48f} sites at $(x, 1/8, 1/8)$ positions and 2) regular cell parameters. We optimized equilibrium lattice constants at their corresponding ground states first. Lattice and second-order elastic constants for $\text{RE}_2\text{Hf}_2\text{O}_7$ (with Eu and Gd as *RE*) are shown in Table 1. $\text{Gd}_2\text{Hf}_2\text{O}_7$ lattice constant calculated in this work is equal to 10.55 Å and shows excellent agreement with experimentally obtained literature values (10.51 Å²⁷⁾ and 10.49 Å²⁸⁾) within the reasonable experimental and calculation errors. Thus, all parameters and assumptions used in our optimizations and calculations were reliable.

3.2 Mechanical characteristics

Crystal response to external forces is typically associated with its elastic constants, which also reflects equilibrium state bond strength between individual atoms. Elastic constant is often implemented to obtain Poisson's ratio, Young's as well as shear and bulk moduli. Therefore, elastic constant optimization for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ was our first step in mechanical property simulations (see results in Table 1). Three elastic constants (c_{11} , c_{12} and c_{44}) of cubic crystal structures typically show the following relative mechanical stability:²⁹⁾

$$c_{11} > 0, c_{44} > 0, c_{11} - c_{12} > 0, c_{11} + 2c_{12} > 0 \quad (1)$$

$\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ with cubic structures demonstrated acceptable mechanical stability. Elastic constant c_{11} of $\text{Gd}_2\text{Hf}_2\text{O}_7$ is higher than that of $\text{Eu}_2\text{Hf}_2\text{O}_7$. However, their corresponding c_{12} values (which are, typically, related to the Poisson effect for materials with cubic structures) are the same (see Table 1). c_{11} is related to linear compressive resistance along the x and z axis. Thus, higher c_{11} implies larger compressive resistance under uniaxial stress. c_{44} represents shear resistance in the $[001]$ direction of (010) or (100) planes. Higher c_{44} value for $\text{Eu}_2\text{Hf}_2\text{O}_7$ implies larger shear resistance than that for $\text{Gd}_2\text{Hf}_2\text{O}_7$.

Table 1. Calculated hafnate pyrochlore elastic constants and lattice parameters in comparison with the experimental ones (last column) ($1 \text{ Å} = 10^{-10} \text{ m}$)

Hafnate pyrochlore	Elastic constants			Lattice parameter (Å)	
	c_{11}	c_{12}	c_{44}	a (Calculated)	a (Experimental)
$\text{Eu}_2\text{Hf}_2\text{O}_7$	306.9	105.6	96.2	10.59	10.54 ²⁷⁾
$\text{Gd}_2\text{Hf}_2\text{O}_7$	310.6	105.1	94.7	10.55	10.51 ²⁷⁾ 10.49 ²⁸⁾

Elastic constants (c_{ij}) are somewhat hard to calculate for polycrystalline materials. Thus, their shear (G) and bulk (B) moduli are frequently obtained experimentally. However, these moduli can also be accessed using Voigt-Reuss-Hill approximation, which is an average of the lower Voigt and upper Reuss bounds:^{30)–32)}

$$B_V = \frac{c_{11} + 2c_{12}}{3} \quad (2)$$

$$G_V = \frac{c_{11} - c_{12} + 3c_{44}}{5} \quad (3)$$

$$B_R = \frac{1}{3s_{11} + 6s_{12}} \quad (4)$$

$$G_R = \frac{15}{4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{13} + s_{23}) + 3(s_{44} + s_{55} + s_{66})} \quad (5)$$

$$B_H = \frac{B_R + B_V}{2} \quad (6)$$

$$G_H = \frac{G_R + G_V}{2} \quad (7)$$

Young's modulus (E) and Poisson's ratio (ν) are thus obtained from bulk and shear moduli:³³⁾

$$E = \frac{9B_H G_H}{3B_H + G_H} \quad (8)$$

$$\nu = \frac{3B_H - 2G_H}{2(3B_H + G_H)} \quad (9)$$

Calculated mechanical properties of $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ are presented in **Table 2**. Typically, bulk modulus is related to valence electrons at their bonding states and also corresponds to the ability of a solid to compress under applied hydrostatic pressure. For the materials studied in this work, bulk modulus was higher for Gd-based pyrochlore hafnate. Shear and Young's moduli are related to the stiffness and resistance to transverse deformation, respectively. Shear and Young's moduli as well as Poisson's ratio were almost the same for both hafnates (see Table 1).

G/B ratio and Cauchy pressure (equal to the difference in elastic constants: $c_{12} - c_{44}$) can be used to predict ceramics ductility and/or brittleness.^{5),34)} At G/B ratios above and below 0.571, ceramics are considered brittle and quasi-ductile, respectively. Positive Cauchy pressure is typical for ductile materials while a negative one is typical for intrinsically brittle materials. G/B ratios for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ were calculated to be <0.571 , thus, these hafnates are quasi-ductile. This was confirmed by the positive values of Cauchy pressure of both hafnates.

To obtain anisotropic properties of our pyrochlores, we analyzed Young's modulus behavior in different directions. Surface anisotropy contours for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ are shown in **Fig. 2**. Typically, very regular sphere shape implies very strong isotropy. On contrary, irregular one implies strong anisotropy. Young's modulus value of $\text{Gd}_2\text{Hf}_2\text{O}_7$ reveals stronger anisotropic effects in different orientations comparing to that of $\text{Eu}_2\text{Hf}_2\text{O}_7$.

Elastic anisotropy of materials with cubic lattice structures can be illustrated using Zener anisotropy ratio (Z) equal to $Z = 2c_{44}/(c_{11} - c_{12})$.^{19),35)} It also determines maximum Young's modulus direction. Materials with Z equal to one are considered isotropic, thus, their Young's moduli are not related to crystal orientation. Maximum Young's modulus for materials with cubic structures is along $[111]$ and $[100]$ directions for $Z > 1$ and $Z < 1$, respectively.

We applied Zener anisotropy ratio to describe $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ properties. We calculated Young's modulus as function of its crystallographic orientation in the $[100]$, $[110]$ and $[111]$ directions using the following formula for the Young's modulus variation (E) applicable to cubic crystals:^{19),35)}

Table 2. Calculated mechanical moduli (in GPa), Poisson's and G/B ratios as well as Zener anisotropy ratio for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$

	B_H	G_H	E_H	ν	G/B	$c_{12} - c_{44}$	Z
$\text{Eu}_2\text{Hf}_2\text{O}_7$	172.7	98.0	247.1	0.26	0.567	9.4	0.9557
$\text{Gd}_2\text{Hf}_2\text{O}_7$	173.6	97.8	247.1	0.26	0.564	10.4	0.9216

Fig. 2. Surface contours of direction dependent Young's moduli of (a) $\text{Eu}_2\text{Hf}_2\text{O}_7$ (b) $\text{Gd}_2\text{Hf}_2\text{O}_7$ (c) anisotropic Young's moduli for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$.

Fig. 3. Surface contours of direction dependent shear moduli of (a) $\text{Eu}_2\text{Hf}_2\text{O}_7$ and (b) $\text{Gd}_2\text{Hf}_2\text{O}_7$.

$$\frac{1}{E_0} = \frac{c_{11} + c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} \quad (10)$$

$$\frac{2}{F_0} = \frac{-2c_{12}}{(c_{11} - c_{12})(c_{11} + 2c_{12})} + \frac{1}{c_{44}} \quad (11)$$

$$\frac{1}{E} = \frac{l^4 + m^4 + n^4}{E_0} + \frac{2(m^2n^2 + n^2l^2 + l^2m^2)}{F_0} \quad (12)$$

where l , m and n are directional cosines of angles along the x , y and z directions, respectively. One can express directional cosines for this system as:

$$l = \cos \theta \quad (13)$$

$$m = \frac{\sin \theta}{\sqrt{2}} \quad (14)$$

$$n = \frac{\sin \theta}{\sqrt{2}} \quad (15)$$

where, θ is the angle between $[110]$ and $[100]$ directions.

By applying these equations to our pyrochlore hafnates, we obtained the following Zener anisotropy ratios: 0.9557 for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and 0.9216 for $\text{Gd}_2\text{Hf}_2\text{O}_7$ (see Fig. 3). Maximum and minimum E values were 252.8 and 243.4 GPa for $\text{Eu}_2\text{Hf}_2\text{O}_7$, respectively, 257.5 and 240.4 GPa for $\text{Gd}_2\text{Hf}_2\text{O}_7$, respectively. They were along $[100]$ and $[111]$ directions, respectively, for both pyrochlore hafnates (see Fig. 2).

3.3 Thermal properties

Working temperatures of gas turbine engines are significantly higher than Debye temperature of ceramics applicable as TBCs. Thermal conductivities of the best TBC candidates should approach their minimum values. Thus, TBCs should be selected out of materials with the least value of thermal conductivity. The thermal conductivity of insulators was mainly determined by the phonon behaviors. For the theoretical calculations of thermal conduc-

tivity, two approaches were applied in this work. The details of these two approaches Clarke model and Slack's equation are explained as following. Clarke model was employed to predict the minimum thermal conductivity at high temperatures over Debye temperature. According to Clarke model, the minimum thermal conductivity ($\kappa_{\min}$) and Debye temperature (θ_D) were expressed by:^{6),36)}

$$\kappa_{\min} = 0.87\kappa_B \left(\frac{M}{n\rho N_A} \right)^{-2/3} \sqrt{\left(\frac{E}{\rho} \right)} \quad (16)$$

$$\theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} v_m \quad (17)$$

where k_B is the Boltzmann's constant, E is the Young's modulus, ρ is the density, N_A is the Avogadro's number, n is the number of atoms in the molecule, M is molecular weight and h is Planck's constant. Average sound velocity v_m can be calculated as follows:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3} \quad (18)$$

$$v_l = \left[\left(B + \frac{4}{3}G \right) \frac{1}{\rho} \right]^{1/2} \quad (19)$$

$$v_s = \left(\frac{G}{\rho} \right)^{1/2} \quad (20)$$

Where v_l and v_s are longitudinal and transverse sound velocities, respectively. Both v_l and v_s are related to shear modulus and density.

As the minimum thermal conductivity is the lowest limit of thermal conductivity values defined above Debye temperature, the predicted values can only be used for the evaluation of high temperature thermal conductivities. Furthermore, the calculation of the minimum thermal conductivity using Clarke's model does not include the

Table 3. Sound velocity, Debye temperature, minimum and 1600 K thermal conductivities for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$

	v_s (km/s)	v_l (km/s)	v_m (km/s)	θ_D (K)	$\kappa_{\min}$	κ_{1600}
$\text{Eu}_2\text{Hf}_2\text{O}_7$	3.21	5.65	3.57	554.5	1.08	1.66
$\text{Gd}_2\text{Hf}_2\text{O}_7$	3.17	5.59	3.52	549.7	1.08	1.62

contributions from the non-acoustic modes, since the contribution of the optical modes to the thermal conductivity is considered very limited at high temperatures.

For the high temperature applications of TBC materials, the temperatures of interest are often much above the Debye temperature. At this case, the Clarke's model is suitable. Here, the minimum thermal conductivity is the low limit of the thermal conductivity of the studied materials, which can be reached at high temperatures much higher than their Debye temperature.

The temperature dependence of lattice thermal conductivity is calculated from Slack's equation:³⁷⁾

$$\kappa = A \frac{\overline{M}\theta_D\delta^3}{\gamma^2 n^{2/3} T} \quad (21)$$

where $\overline{M}$ is the mean atomic mass, δ^3 the average volume of one atom in the primitive unit cell, θ_D the Debye temperature, T the absolute temperature, n the number of atoms per primitive unit cell, γ is the Gruneisen constant defined as $\gamma = (3/2)[(1 + \nu)/(2 - 3\nu)]$, and A is a coefficient defined as $A_{(\gamma)} = (5.720 \times 10^7 \times 0.849)/[2 \times \{1 - (0.514/\gamma) + (0.228/\gamma^2)\}]$.

In the present calculation, Slack has shown that if the thermal conductivity of one compound is known at its Debye temperature, then the thermal conductivity of other compounds having the same crystal structure at their Debye temperatures can be calculated directly using a simple scaling relation. The contribution of phonon transport to thermal conductivity, is called lattice thermal conductivity, in which the optic branches with small group velocity are generally ignored. Slack's approach is to enumerate the different phonon modes that a particular crystal structure can possess and account for the contributions to the thermal conductivity of every phonon in the structure. Meanwhile, Slack's work was a major step forward in advancing understanding the effects of crystal structure and atomic weight on thermal conductivity. The investigation of the thermal conductivity within a wide range of temperature will provide a comprehensive viewpoint of the heat conduction in a solid.

Table 3 shows calculated values of sound velocity, 1600 K and minimum thermal conductivities for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$. Typically, material with high shear modulus and low density will have large sound velocity. Average sound velocities for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ were calculated to be 3.57 and 3.52 km/s, respectively. Minimum thermal conductivities ($\kappa_{\min}$) for both pyrochlore hafnates were calculated to be equal to 1.08 W/(m·K), which is below the minimum thermal conductivity value of HfO_2 . Such difference was attributed to the weak La–O bonds in our pyrochlore hafnates.⁶⁾

Fig. 4. Thermal conductivities of $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ as function of the temperature.

The Debye temperature is an essential characteristic associated with material physical properties (e.g. elastic constant, specific heat and melting temperature). Vibrational excitations are typically caused only by acoustic vibrations at low temperatures. Thus, the Debye temperature determined from elastic constants directly correlates with the specific heat. Chemical bonding strength can also be characterized based on the Debye temperature value: materials with stronger chemical bonds typically demonstrate higher Debye temperature values. The Debye temperature for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ were calculated to be equal to 554.5 and 549.7 K, respectively (see Table 3). The lower the value of the Debye temperature, the smaller thermal conductivity of the material is. Thus, one can expect $\text{Gd}_2\text{Hf}_2\text{O}_7$ to have thermal conductivity lower than that of $\text{Eu}_2\text{Hf}_2\text{O}_7$.

We also analyzed thermal conductivity temperature dependence (see **Fig. 4**). Calculated thermal conductivities of $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ at 300 K were 8.87 and 8.64 W/(m·K), respectively. As temperature increased, thermal conductivities decreased. Thermal conductivity values at 1600 K dropped to 1.62 and 1.66 W/(m·K) for $\text{Gd}_2\text{Hf}_2\text{O}_7$ and $\text{Eu}_2\text{Hf}_2\text{O}_7$, respectively. Calculated thermal conductivity values for both compounds are lower relative to YSZ ³⁶⁾ [equal to 2.2 W/(m·K)] and, at the same time, are comparable with the values of *RE* zirconate pyrochlores ($\text{La}_2\text{Zr}_2\text{O}_7$, $\text{Sm}_2\text{Zr}_2\text{O}_7$, $\text{Nd}_2\text{Zr}_2\text{O}_7$ and $\text{Gd}_2\text{Zr}_2\text{O}_7$).^{38),39)} Thus, $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ are promising TBCs.

4. Conclusions

Structures, thermal conductivities and elastic stiffness of $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ pyrochlore hafnates were obtained by first-principles simulations. Lattice constants, thermal conductivities, mechanical moduli as well as elastic constants strongly depend on *RE* type in $\text{RE}_2\text{Hf}_2\text{O}_7$. Lattice constant for cubic Eu-pyrochlore hafnate was larger than for Gd-based one. Bulk modulus of $\text{Eu}_2\text{Hf}_2\text{O}_7$ was calculated to be lower than of $\text{Gd}_2\text{Hf}_2\text{O}_7$. Zener

anisotropy ratio was 0.9557 for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and 0.9216 for $\text{Gd}_2\text{Hf}_2\text{O}_7$. We predicted thermal conductivity values for $\text{Eu}_2\text{Hf}_2\text{O}_7$ and for $\text{Gd}_2\text{Hf}_2\text{O}_7$ at 1600 K to be 1.66 and 1.62 W/(m·K), both of which are lower than that of YSZ. G/B ratios below 0.571 and positive Cauchy pressure indicated good damage tolerance of both pyrochlore hafnates. Therefore, $\text{Eu}_2\text{Hf}_2\text{O}_7$ and $\text{Gd}_2\text{Hf}_2\text{O}_7$ pyrochlores are promising candidates as next generation TBCs.

Acknowledgements This work was financially supported by the National Key Research and Development Program of China (No. 2017YFB0902100).

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