High-entropy perovskite RETa₃O₉ ceramics for high-temperature environmental/thermal barrier coatings

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Abstract: Four high-entropy perovskite (HEP) RETa₃O₉ samples were fabricated via a spark plasma sintering (SPS) method, and the corresponding thermophysical properties and underlying mechanisms were investigated for environmental/thermal barrier coating (E/TBC) applications. The prepared samples maintained low thermal conductivity (1.50 W·m⁻¹·K⁻¹), high hardness (10 GPa), and an appropriate Young’s modulus (180 GPa), while the fracture toughness increased to 2.5 MPa·m¹/₂. Nanoindentation results showed the HEP ceramics had excellent mechanical properties and good component homogeneity. We analysed the influence of different parameters (the disorder parameters of the electronegativity, ionic radius, and atomic mass, as well as the tolerance factor) of A-site atoms on the thermal conductivity. Enhanced thermal expansion coefficients, combined with a high melting point and extraordinary phase stability, expanded the applications of the HEP RETa₃O₉. The results of this study had motivated a follow-up study on tantalate high-entropy ceramics with desirable properties.

Keywords: high-entropy ceramics (HECs); tantalates; thermal conductivity; nanoindentation; fracture toughness

1 Introduction

Oxide environmental/thermal barrier coatings (E/TBCs) have been extensively investigated to increase the working temperatures of aircraft engines, gas turbines, and hypersonic vehicles [1–6]. E/TBCs are applied to ceramic/alloy substrates to decrease surface temperatures and prevent damage from high-speed impact particles, molten oxides, and other environmental factors [2–12]. Rare earth (RE) tantalates (RETaO₄, RE₂TaO₇, and RETa₃O₉) are considered novel E/TBCs because of extraordinary thermophysical properties [4,8,13–15]. It has been reported that tantalates have low thermal conductivity and high hardness, melting points, and thermal expansion coefficients. However, tantalates also have clear shortcomings, e.g., RETa₃O₉ has inadequate fracture toughness (1.1–1.5 MPa·m¹/₂) [15]. Diverse methods are used to enhance the properties of RETaO₄ [8,13] and RE₂TaO₇ ceramics [14,16], and our aim is to stimulate the investigation and application of RETa₃O₉ with perovskite structures. Some scholars have identified perovskite oxides as promising E/TBCs, and high-entropy ceramics (HECs) are being studied in various fields [15,17–19]. Wright et al. [20] have reported that HECs of RE₂Zr₂O₇ exhibit low thermal conductivity and high stiffness, and Liu et al. [17] have proven that the thermal properties of perovskite-type
(ABO₃) ceramics can be regulated by entropy engineering. Furthermore, HECs of RE₂SiO₇, RE₃NbO₇, and other RE tantalates have been studied for use as E/TBCs [21–24]. One of the most striking features of HECs is that multifarious properties can be successfully tailored to meet the demands of specific applications.

The structure of HECs is similar to that of high-entropy alloys (HEAs), that is, one or more Wyckoff sites in lattices are occupied by identical or near-identical atoms. In HECs, more than four types of atoms occupy one site, and the configurational entropy is higher than 1.5R (where R denotes the gas constant); the configurational entropy (ΔS_conf) is expressed as ΔS_conf = R × lnN, where N is the number of elements in one sublattice [5,25–27]. The configurational entropy increases with the number of types of atoms in one or more Wyckoff sites in the lattice. Herein, we regulate the configurational entropy by controlling the types of atoms in the lattice. Theoretically, the highest configurational entropy is obtained for some materials when all the elements in a sublattice have the same atomic fraction [28,29]. To date, HECs have been fabricated with many excellent properties, including enhanced hardness and toughness [19], regulation of thermal transportation properties [20,23], increased corrosion resistance [21], and strengthened high-temperature phase stability [10,17]. HECs of RE₃TaO₉ [16], RE₂Zr₂O₇ [20,23], RE₃NbO₇ [22], and RE₃Al₅O₁₂ [30] have also been investigated for use as TBCs, whereas HECs of RE₂Si₂O₇ [21] and RE₂SiO₅ [31] have been investigated for use as EBCs. Currently, multifunctional thermal and environmental barrier integration coatings are used to improve the performance of components of alloys and ceramic matrix composites. A few oxides meet the requirements of multifunctional E/TBCs. Perovskite-type ceramics typically have high melting points [17], low thermal conductivity [15,17,18], regulatable mechanical properties [17,32,33], etc. [34,35]. Accordingly, multifarious perovskite-type oxides have been fabricated to improve the properties and expand the applications [15,17,18,33–36]. In this study, we optimize the properties of HECs of RET₃O₉ (RE = La, Sm, Eu, Gd, Dy, Ho, Er, Tm), Pr₆O₁₇, and Ta₂O₅ with 99.9% purity as raw powders, which had particle sizes less than 10 μm. The weighed powders were mixed by a ball mill (300 r·min⁻¹, 12 h) using alcohol as the dispersion medium, and then placed in a drier at 90 °C for 6 h to evaporate alcohol. The dried powders were maintained at 1600 °C for 10 h to obtain high-purity RET₃O₉ powders. The prepared powders were passed through a 500-mesh sieve, and approximately 2.5 g of the sieved powders were sintered by spark plasma sintering (SPS). The final SPS parameters were 1600 °C for 10 h to obtain high-purity RET₃O₉ powders. The prepared powders were synthesized by a high-temperature sintering process without pressure. We used RE₂O₃ (RE = La, Sm, Eu, Gd, Dy, Ho, Er, Tm), Pr₆O₁₇, and Ta₂O₅ with 99.9% purity as raw powders, which had particle sizes less than 10 μm. The weighed powders were mixed by a ball mill (300 r·min⁻¹, 12 h) using alcohol as the dispersion medium, and then placed in a drier at 90 °C for 6 h to evaporate alcohol. The dried powders were maintained at 1600 °C for 10 h to obtain high-purity RET₃O₉ powders. The prepared powders were passed through a 500-mesh sieve, and approximately 2.5 g of the sieved powders were sintered by spark plasma sintering (SPS). The final SPS parameters were 1600 °C, 100 MPa, 10-min sintering time, and a heating rate of 50 °C·min⁻¹. For comparison, a dense yttria-stabilized zirconia (YSZ) bulk ceramic was synthesized and tested using the same methods.

2 Experimental

2.1 Material fabrication

HEP RET₃O₉ powders were synthesized by a high-temperature sintering process without pressure. We used RE₂O₃ (RE = La, Sm, Eu, Gd, Dy, Ho, Er, Tm), Pr₆O₁₇, and Ta₂O₅ with 99.9% purity as raw powders, which had particle sizes less than 10 μm. The weighed powders were mixed by a ball mill (300 r·min⁻¹, 12 h) using alcohol as the dispersion medium, and then placed in a drier at 90 °C for 6 h to evaporate alcohol. The dried powders were maintained at 1600 °C for 10 h to obtain high-purity RET₃O₉ powders. The prepared powders were passed through a 500-mesh sieve, and approximately 2.5 g of the sieved powders were sintered by spark plasma sintering (SPS). The final SPS parameters were 1600 °C, 100 MPa, 10-min sintering time, and a heating rate of 50 °C·min⁻¹. For comparison, a dense yttria-stabilized zirconia (YSZ) bulk ceramic was synthesized and tested using the same methods.

2.2 Structure identification

The X-ray diffractometer (MiniFlex 600, Rigaku, Japan) was applied to confirm the crystal structures and lattice constants of the HEP RET₃O₉. The X-ray diffraction (XRD) 2θ angle was ranged between 20° and 60°, and the scanning speed was 5 (°) min⁻¹. The exact lattice constants, unit cell volumes, and theoretical densities of each sample were computed from the XRD patterns. The scanning electronic microscope (SEM, JSM-7800F, JEOL, Japan) and the energy-dispersive spectroscopy (EDS, 6751A-6UUS-SN, Thermo Scientific, USA)
were used to probe the surface structures. We used SEM and EDS to observe the grain sizes, pores, cracks, and elemental distributions.

2.3 Mechanical property testing

The hardness ($H$) and fracture toughness ($K_{IC}$) were determined by the lengths of indentation diagonal ($d$) and the indentation crack ($c$) using a hardness tester (DHV-100Z-CCD, SZNG, China). Each sample was tested 10 times, the minimum and maximum results were removed, and the remaining results were used to calculate the average values. The fracture toughness increased with the surface fracture energy ($\Gamma$), and was calculated as below [37, 38]:

$$K_{IC} = 0.018 \sqrt{\frac{E}{H}} \frac{F}{c^{1.5}} \quad (2)$$

$$\Gamma = \frac{2\zeta^2 Fd^2}{c^3} \quad (3)$$

where $F = 4.9$ N, $\zeta = 0.016$, and $E$ denotes the Young’s modulus measured using the ultrasonic equipment (UMS-100, TECLAB, France) [39]:

$$E = \frac{\rho V_l^2 (3V_t^2 - 4V_i^2)}{V_i^2 - V_t^2} \quad (4)$$

where $\rho$ is the sample density, and $V_l$ and $V_t$ are the longitudinal and transverse acoustic velocities, respectively.

To eliminate the effect of the microstructure on the mechanical properties, the nano-Young’s modulus ($E_N$) and nano-hardness ($H_N$) were simultaneously measured using the nanoindentation device (iNano instrument, iMicro, USA). During the nanoindentation test, we applied both $E$ and $H$ mapping (three-dimensional (3D) mapping) and advanced dynamic $E$ and $H$ (single-point test) models, where the highest test load was 100 mN. A total of $30 \times 30 = 900$ points were tested over a $300 \mu m \times 300 \mu m$ area at intervals of 10 $\mu m$ during the 3D mapping measurement. The advanced dynamic $E$ and $H$ tests were used to determine how the hardness and Young’s modulus varied with the indentation load and depth, and the results were analysed.

2.4 Thermal property testing

The thermal expansion coefficients (TECs) were calculated based on the elongation caused by increasing the temperature that was measured by a thermomechanical analysis device (TMA 402 F3, NETZSCH, Germany). The thermal diffusivity ($\lambda$, 25–900 °C) was measured using the laser reflection device (LFA 457, NETZSCH, Germany), and the thermal conductivity ($k$) was calculated from $\lambda$, density ($\rho$), porosity ($\phi$), and heat capacity ($C_p$) as follows [40]:

$$k = \frac{\lambda \rho C_p}{1 - 4\phi / 3} \quad (5)$$

The phonon mean free path ($l$) was calculated using the relationship between the thermal diffusivity ($\lambda$) and the mean acoustic velocity ($V_m$) [40–42]:

$$l = \frac{3\lambda}{V_m} \quad (6)$$

The mean acoustic velocity ($V_m$) was calculated from $V_l$ and $V_t$ [39]:

$$V_m = \left[ \frac{1}{3} \left( \frac{1}{V_l^3} + \frac{2}{V_t^3} \right) \right]^{-\frac{1}{3}} \quad (7)$$

3 Results and discussion

3.1 Crystal structures

Figure 1(a) shows that the main XRD peaks of the four HEP RETaO$_9$ samples coincide with PDF#52-0567 with the P4/mmm space group. A RETaO$_4$ precipitate (PDF#24-0379) is detected in 5HPE-2, 6HEP-3, and 6HEP-4, whereas the minor peaks at 2$\theta$ angles of 25°–30° for 5HEP-1 are associated with a different RETaO$_4$ phase (PDF#19-1013). The weak peaks of RETaO$_4$ indicate that the RETaO$_4$ content is too low to dominate the thermophysical properties of the prepared samples. In Ref. [43], the crystalline temperature of YTaO$_4$ is reported to be approximately 840 °C, and this low crystalline temperature may be the cause of the RETaO$_4$ precipitate in the prepared HEP samples. The lattice of RETa$_3$O$_9$ (RE1/3TaO$_3$) with the P4/mmm space group is treated as a defect perovskite (A$_{1/3}$BO$_3$-type) structure when a 1/3 vacancy is created in the RE cationic sublattice, as shown in Fig. 1(b). Each Ta is surrounded by six oxygens to form a [TaO$_6$] octahedron, and the octahedra are connected to each other at the corners. These octahedrons are twisted structures, because the Ta–O bond lengths vary. The distortion degree of perovskites depends on the octahedral twist. Normally, the tolerance factor ($t$) is an indicator of the
Fig. 1 Characterization of the crystal structure of (La$_{1/5}$Pr$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-1), (Gd$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Er$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-2), (La$_{1/6}$Sm$_{1/6}$Eu$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-3), and (Eu$_{1/6}$Gd$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Er$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-4): (a) normalized XRD patterns; (b) $2 \times 2 \times 1$ unit cell, where the grey ball represents an A-site $2/3$ RE atom with a $1/3$ vacancy, the blue ball represents a B-site Ta atom, and the purple ball represents an oxygen atom.

Table 1 Design composition, sample name, lattice parameters ($a$, $b$, and $c$), unit cell volume ($V$), theoretical density ($\rho_0$), and porosity ($\phi$) of HEP RETa$_3$O$_9$ ceramics

| Composition                          | Sample   | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $\rho_0$ (g·cm$^{-3}$) | $\phi$ (%) |
|--------------------------------------|----------|---------|---------|---------|-------------|-------------------------|-----------|
| (La$_{1/5}$Pr$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ | 5HEP-1   | 3.878   | 3.878   | 7.850   | 118.081     | 7.89                    | 1.5       |
| (Gd$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Er$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ | 5HEP-2   | 3.854   | 3.854   | 7.864   | 116.796     | 8.06                    | 1.3       |
| (La$_{1/6}$Sm$_{1/6}$Eu$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ | 6HEP-3   | 3.902   | 3.902   | 7.803   | 118.834     | 7.86                    | 2.0       |
| (Eu$_{1/6}$Gd$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Er$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ | 6HEP-4   | 3.854   | 3.854   | 7.837   | 116.396     | 8.07                    | 2.2       |

Lattice stability and distortion degree of perovskite structures [29,32]:

$$ t = \frac{r_A + r_O}{\sqrt{2(r_{Ta} + r_O)}} $$  \hspace{1cm} (8)

where $r_A$, $r_O$, and $r_{Ta}$ are the effective ionic radii of RE$^{3+}$, O$^{2-}$, and Ta$^{5+}$ ions, respectively. Perovskite oxides have a stable lattice when $t$ ranges from 0.8 to 1, and they may crystallize into an orthorhombic phase for $t$ less than 0.9 [29,32]. The tolerance factors of the HEP RETa$_3$O$_9$ are proportional to the A-site ionic sizes, and are 0.871, 0.855, 0.866, and 0.856 for 5HEP-1, 5HEP-2, 6HEP-3, and 6HEP-4, respectively. Among the four prepared samples, 5HEP-2 has the maximum lattice distortion degree based on the minimum tolerance factor. The results presented in Table 1 and Fig. 1(b) indicate that the length of the $c$-axis is almost twice that of the $a$- and $b$-axes, because HEP RETa$_3$O$_9$ is an orthorhombic phase. Usually, the lengths of the $a$-, $b$-, and $c$-axes of ABO$_3$-type perovskites are almost equal (corresponding to a cubic phase), and the structures of the HEP RETa$_3$O$_9$ are also called double-perovskite structures [18]. Herein, the $2 \times 2 \times 1$ unit cell of HEP RETa$_3$O$_9$ is similar to that of cubic ABO$_3$ perovskites.

3.2  Microstructures

The four HEP bulk samples are polished using diamond sandpapers, and then held at 1400 °C for 3 h to observe the surface grains and elemental distributions by SEM and EDS. In Fig. 2, most grains are smaller than 5 μm, and the RE elements are homogeneously distributed in the prepared samples. The prepared HEP samples have smaller grains than the single-rare-earth RETa$_3$O$_9$, and grain refinement is achieved in the HEP RETa$_3$O$_9$ samples [15]. The mean grain sizes are 5–7 μm for the single-rare-earth RETa$_3$O$_9$ ceramics and less than 2 μm for the HEP samples. Thus, the corresponding reduction in the grain size is higher than 50%, and we investigate the effect of this reduction on the material properties. Some nanoscale grains are found in 5HEP-2, 6HEP-3, and 6HEP-4, and it is inferred that these grains...
constitute the RETaO₄ precipitate. We used the backscattered electron (BSE) model to analyse the grains, and no difference was found between nano- and micron-scale grains. The RETaO₄ and RETa₃O₉ phases are comprised of the same elements, and the grains of these phases have the same atomic contrast. Furthermore, the EDS results show no elemental segregation. The XRD, SEM, and EDS analyses imply that we can neglect the influence of RETaO₄ on the properties of the prepared samples. In Table 1, the porosities of the prepared samples are 1%–3%, which are lower than those of the samples synthesized via a solid-state reaction [15]. Hence, dense and high-purity HEP RETa₃O₉ ceramics can be fabricated via an SPS process. The grain size, grain boundary density, cracks, and pores affect the properties of structural ceramics, as discussed in the following sections.

3.3 Mechanical properties

As shown in Table 2, the HEP RETa₃O₉ ceramics have a Young’s modulus (E), hardness (H), and toughness (KIC) of 130–180 GPa, 7–10 GPa, and 1.8–2.5 MPa·m¹/², respectively. YSZ has a high Young’s modulus than those of YSZ and La₂Zr₂O₇ (230 GPa) [6], and 6HEP-4 has the highest toughness (2.5±0.4 MPa·m¹/²). The HEP ceramics and single-rare-earth RETa₃O₉ have similar Young’s moduli (140–200 GPa) and hardness (7.0–10.0 GPa), whereas the toughness of the HEP RETa₃O₉ is 1.8–2.5 MPa·m¹/². Figures 4(a)–4(c) show that the hardness–Young’s modulus, toughness–Young’s modulus, and toughness–hardness curves are not linear. The results presented in Fig. 4(d) and Table 2 indicate that the toughness is proportional to the surface fracture energy. Equation (3) shows that the surface fracture energy is related to the lengths of indentation and cracks, and is an intrinsic feature of these materials. To study the ductile and brittle features of the four samples, we calculate the G/B ratio, where G and B represent the shear and bulk moduli, respectively [39,45]:

\[
B = \frac{E}{3(1-2\nu)}
\]

\[
G = \frac{E}{2(1+\nu)}
\]

where \(\nu\) is the Poisson’s ratio, as measured by ultrasonic equipment. Materials with a G/B ratio less than 0.57 are brittle, and materials with a G/B ratio higher than...
Table 2  Young’s modulus and nano-Young’s modulus ($E$ and $E_N$), hardness and nano-hardness ($H$ and $H_N$), fracture toughness ($K_{IC}$), mean acoustic velocity ($V_m$), surface fracture energy ($\Gamma$), and $G/B$ ratio of HEP RETa$_3$O$_9$ ceramics

| Sample | $E_N$ (GPa) | $H_N$ (GPa) | $V_m$ (m·s$^{-1}$) | $E$ (GPa) | $H$ (GPa) | $K_{IC}$ (MPa·m$^{-1/2}$) | $\Gamma$ (J·m$^{-2}$) | $G/B$ |
|--------|-------------|-------------|-------------------|-----------|-----------|--------------------------|----------------------|-------|
| 5HEP-1 | 178.9±8.7   | 10.8±0.6    | 3270.5±17.3       | 172.5±11.5 | 9.0±0.3   | 1.8±0.4                  | 19.1±7.2             | 0.55  |
| 5HEP-2 | 143.3±12.7  | 10.0±1.3    | 2945.5±5.4        | 139.2±8.6 | 7.3±1.3   | 2.0±0.3                  | 27.2±8.5             | 0.59  |
| 6HEP-3 | 156.7±5.3   | 10.4±0.6    | 3214.1±10.6       | 157.8±10.9 | 9.1±0.3   | 2.1±0.3                  | 25.6±7.8             | 0.62  |
| 6HEP-4 | 180.5±13.6  | 10.6±1.1    | 3215.3±28.1       | 172.8±8.2 | 9.0±0.4   | 2.5±0.4                  | 32.7±10.0            | 0.61  |

Fig. 3  Comparison of Young’s modulus, hardness, and fracture toughness of (La$_{1/5}$Pr$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-1), (Gd$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Er$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-2), (La$_{1/6}$Sm$_{1/6}$Eu$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-3), (Eu$_{1/6}$Gd$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Er$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-4) ceramics, and YSZ.

Fig. 4  Relationships among the mechanical properties of (La$_{1/5}$Pr$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-1), (Gd$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Er$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-2), (La$_{1/6}$Sm$_{1/6}$Eu$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-3), and (Eu$_{1/6}$Gd$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Er$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-4) ceramics: (a) hardness–Young’s modulus, (b) fracture toughness–Young’s modulus, (c) fracture toughness–hardness, and (d) fracture toughness–surface fracture energy.
0.57 are ductile [45]. Table 2 shows that the $G/B$ ratio increases from 0.55 to 0.62, indicating that a brittle-ductile transition occurs with the difference in composition among the four HEP samples. The brittle-ductile transition is considered to increase the toughness. Small grains increase the hardness based on the Hall-Petch principle. The Young’s modulus of the HEP samples are lower than those of the HECs of RE$_2$NbO$_7$ (210 GPa) [22] and RE$_2$Zr$_2$O$_7$ (240 GPa) [20], and close to those of the HECs of RE$_2$SiO$_5$ (170 GPa) [31] and ABO$_3$ (180 GPa) [17]. The relatively low Young’s modulus of the HEP samples is attributed to their parent single-rare-earth RETa$_3$O$_9$ ceramics, where a comparatively low modulus promotes thermal stress reduction for high-temperature E/TBC applications [46].

3.4 Nanoindentation

The nano-Young’s modulus ($E_N = 140–180$ GPa) and hardness ($H_N = 10–11$ GPa) are shown in Table 2 and Fig. 5. The slightly higher mean values measured by nanoindentation than those tested by normal methods (Fig. 5(a)) may be due to the indentation-size effect [47–49]. Figure 6 shows the 3D mapping of $E_N$ and $H_N$, where there are slight variations over the testing area because microstructure defects (pores and cracks) and test error can produce fluctuations in $E_N$ and $H_N$. In Fig. 7, most of the nano-Young’s modulus and hardness results are located around the mean values, and the hardness increases with the modulus. XRD patterns show that there are few precipitated RETaO$_4$ ceramics in the prepared samples, and SEM, EDS, and nanoindentation results jointly indicate the excellent compositional uniformity of the HEP RETa$_3$O$_9$. Furthermore, the differences in the Young’s modulus of each sample tested by different methods in this study are less than 4%. The aforementioned results prove that the presence of a small quantity of precipitated RETaO$_4$ ceramics does not affect the Young’s modulus, hardness, and toughness of the HEP RETa$_3$O$_9$. Normally, increases in the Young’s modulus and acoustic velocity reflect increases in the phonon propagation speed and thermal conductivity, which is discussed in Section 3.5 Thermal properties.

The results of the advanced dynamic $E$ and $H$ tests using nanoindentation are shown in Figs. 5(b)–5(f), where the investigated parameters include the hardness, Young’s modulus, indentation depth, and load. The indentation depth is proportional to the load, which has a maximum value of 100 mN in the current study. The $H_N$ and $E_N$ values for indentation depths less than 100 nm
Fig. 6 3D mapping of Young’s modulus ($E$) and hardness ($H$) for HEP RETa$_3$O$_9$ ceramics: (a, b) (La$_{1/5}$Pr$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-1), (c, d) (Gd$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Er$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-2), (e, f) (La$_{1/6}$Sm$_{1/6}$Eu$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-3), and (g, h) (Eu$_{1/6}$Gd$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Er$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-4).

are not considered here because the indenter appearance is not self-similar, and the contact area is indeterminate at small indentation depths (low indentation loads) [47]. $H_N$ and $E_N$ decrease as the depth and load increase, for test depths beyond 100 nm or loads heavier than 15 mN. During the nanoindentation continuous stiffness test (using the advanced dynamic $E$ and $H$ model), the decrease in the strain gradient results in weakened hardening as the indentation depth and load increase [48–52]. In addition to the strain gradient, other factors affect the hardness and modulus of some materials. The grain size (the grain boundary density), pore, crack, and surface roughness may affect the hardness, toughness, and modulus. Considering the relative density and purity of the HEP RETa$_3$O$_9$, macro-defects should have little effect on the hardness and modulus, that is, the strain gradient is the predominant factor. The relationships between the Young’s modulus and depth/ load are shown in Figs. 5(d) and 5(f), respectively, and their slopes indicate the decreasing rate of the strain gradient in conjunction with increments of load/depth. In addition to the surface micro-defects, the internal micro-defect density affects the modulus and toughness of the prepared ceramics. The results of the advanced dynamic $E$ and $H$ tests show that the internal micro-defect density of the HEP RETa$_3$O$_9$ decreases in the order of 5HEP-1 > 5HEP-2 > 6HEP-3 > 6HEP-4, based on the decrease in the modulus with increasing depth.

3.5 Thermal properties

Figure 8(a) indicates that the thermal diffusivity of the HEP RETa$_3$O$_9$ samples initially decreases with the
increase of temperature, and then clearly increases at high temperatures (≥ 500 °C). Figure 8(b) shows that the thermal conductivity of the HEP RETaO₉ exhibits a similar temperature dependence to that of the corresponding single-rare-earth samples, which is caused by a high concentration of A-site cation vacancies and thermal radiation [15,53]. Increases in thermal conductivity caused by thermal radiation have been reported for YSZ [34], La₂Zr₂O₇ [54], RETaO₄ [42], RE₂SiO₅ [31], and ABO₃ perovskite ceramics [17]. Evidently, the prepared samples have lower thermal conductivity than those of SrZrO₃ [55], YSZ [44], and many

Fig. 7 Distributions of numerical values of nano-Young’s modulus and hardness for HEP RETaO₉ ceramics: (a–c) \((\text{La}_{1/3}\text{Pr}_{1/3}\text{Dy}_{1/3}\text{Ho}_{1/3}\text{Tm}_{1/3})\text{TaO}_9\) (5HEP-1), (d–f) \((\text{Gd}_{1/5}\text{Dy}_{1/5}\text{Ho}_{1/5}\text{Er}_{1/5}\text{Tm}_{1/5})\text{TaO}_9\) (5HEP-2), (g–i) \((\text{La}_{1/6}\text{Sm}_{1/6}\text{Eu}_{1/6}\text{Dy}_{1/6}\text{Ho}_{1/6}\text{Tm}_{1/6})\text{TaO}_9\) (6HEP-3), and (j–l) \((\text{Eu}_{1/6}\text{Gd}_{1/6}\text{Dy}_{1/6}\text{Ho}_{1/6}\text{Er}_{1/6}\text{Tm}_{1/6})\text{TaO}_9\) (6HEP-4).
Fig. 8 Thermal properties of (La$_{1/5}$Pr$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-1), (Gd$_{1/5}$Dy$_{1/5}$Ho$_{1/5}$Er$_{1/5}$Tm$_{1/5}$)Ta$_3$O$_9$ (5HEP-2), (La$_{1/6}$Sm$_{1/6}$Eu$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-3), and (Eu$_{1/6}$Gd$_{1/6}$Dy$_{1/6}$Ho$_{1/6}$Er$_{1/6}$Tm$_{1/6}$)Ta$_3$O$_9$ (6HEP-4) ceramics: (a) thermal diffusivity, (b) thermal conductivity, (c) phonon mean free path, and (d) thermal properties compared with other oxides in Refs. [6,10,14,15,17,23,42,44,53–58].

other oxides [57,58]. Note that HEP RETa$_3$O$_9$ and HECs ABO$_3$ (Zn$_{0.1}$Ca$_{0.1}$Sr$_{0.4}$Ba$_{0.4}$ZrO$_3$) [17] exhibit similar thermal conductivity, which implies that amorphous-like thermal conductivity may be a common feature of HEP oxides. Furthermore, the thermal conductivity of the HEP samples is lower than those of HECs of RE$_2$SiO$_5$ [31] and RE$_3$Al$_5$O$_{12}$ [30], and close to those of HECs of RE$_2$Zr$_2$O$_7$ [20]. The lower the thermal conductivity of an HEP sample, the higher the thermal insulation performance is. The temperature dependence of the phonon mean free path ($l$) shown in Fig. 8(c) is similar to that of the thermal diffusivity, which further suggests the presence of thermal radiation. Figure 8(d) shows that the TECs range from $8.0 \times 10^{-6}$ to $10.1 \times 10^{-6}$ K$^{-1}$ (1473 K), which exceeds those of GdTa$_3$O$_9$ ($3.6 \times 10^{-6}$ K$^{-1}$), SmTa$_3$O$_9$ ($5.0 \times 10^{-6}$ K$^{-1}$), and DyTa$_3$O$_9$ ($7.5 \times 10^{-6}$ K$^{-1}$), and lattice relaxation may be the predominant factor in the enhanced thermal expansion of the HEP samples [15]. The enhanced TECs of the HEP RETa$_3$O$_9$ can expand applications of these materials, e.g., as EBCs on the surface of Al$_2$O$_3$ fibre-enhanced Al$_2$O$_3$ ceramic matrix composites (Al$_2$O$_3$/Al$_2$O$_3$ with TECs of $8.5 \times 10^{-6}$–$9.0 \times 10^{-6}$ K$^{-1}$) because of matched TECs [10]. In addition, no phase transition is detected during the TECs test up to 1200 °C, which demonstrates the extraordinarily high-temperature phase stability of the prepared HEP RETa$_3$O$_9$ ceramics. Obviously, the TECs of the RETa$_3$O$_9$ are successfully regulated in the fabricated HECs, which exhibit outstanding phase stability.

Figure 8(d) shows that the HEP RETa$_3$O$_9$ oxides have higher TECs compared with those of RE$_2$SiO$_5$ ($6.3 \times 10^{-6}$–$9.0 \times 10^{-6}$ K$^{-1}$) [58] and La$_3$Zr$_2$O$_7$ ($9.0 \times 10^{-6}$ K$^{-1}$) [6] and lower thermal conductivity compared with various E/TBCs [6,10,14,15,17,23,42,44,53–58]. HECs typically have lower thermal conductivity compared with their parent ceramics; however, this trend is not borne out for HEP RETa$_3$O$_9$. The point defect phonon scattering principle is not applicable for analysing the thermal transport properties of the prepared samples because of (1) the formation of random solid solutions, (2) severe lattice distortion, and (3) the cocktail effect of HECs [59,60]. As the $E/k$ ratio reflects the phonon scattering rate, an increase in $E/k$ causes a decrease in the thermal conductivity. The $E/k$ ratio is $113.8$, $92.6$, $96.9$, and $114.1$ GPa·W$^{-1}$·m·K$^{-1}$ for 5HEP-1 (k:
1.52 W·m\(^{-1}\)·K\(^{-1}\), 5HEP-2 (\(k: 1.50\) W·m\(^{-1}\)·K\(^{-1}\)), 6HEP-3 (\(k: 1.63\) W·m\(^{-1}\)·K\(^{-1}\)), and 6HEP-4 (\(k: 1.56\) W·m\(^{-1}\)·K\(^{-1}\)), respectively. Herein, the prominent differences in the Young’s modulus, \(E/k\) ratio, and acoustic velocity among the four HEP ceramics do not noticeably affect the thermal conductivity. Grain refinements are found in the prepared samples: Fig. 2 shows that most grains are micron-sized and are therefore considerably larger than the nanoscale phonon mean free path. Herein, the phonon scattering strength from the grain boundary is not taken into account. The increasing degree of lattice distortion may decrease the thermal conductivity, where the distortion degree is reflected by the tolerance factor (\(t\)). In the HEP \(\text{RE}_2\text{O}_9\), fluctuations in the disorder parameters for the electronegativity (\(\delta_A^{\varepsilon}\)), ionic radius (\(\delta_A^{r}\)), and atomic mass (\(\delta_A^{m}\)) in the A-site sublattice may change the thermal conductivity [17,61,62]:

\[
\delta_A^{\varepsilon} = \sum_i c_i \left( 1 - \frac{e_i}{\bar{e}_A} \right)^2 \tag{11}
\]

\[
\delta_A^{r} = \sum_i c_i \left( 1 - \frac{r_i}{\bar{r}_A} \right)^2 \tag{12}
\]

\[
\delta_A^{m} = \sqrt{\sum_i c_i \left( 1 - \frac{m_i}{m_A} \right)^2} \tag{13}
\]

where \(c_i\) denotes the atomic ratio of the \(i\)th RE element; \(e_i\) denotes the electronegativity of the \(i\)th RE element, and \(\bar{e}_A\) denotes the mean electronegativity of an A-site atom; \(r_i\) denotes the ionic radius of the \(i\)th RE element, and \(\bar{r}_A\) denotes the mean ionic radius of an A-site atom; \(m_i\) denotes the atomic mass of the \(i\)th RE element, and \(\bar{m}_A\) indicates the mean atomic mass of an A-site atom. Table 3 displays the values of the aforementioned parameters. The variation trends in the thermal conductivity with \(t\), \(\delta_A^{\varepsilon}\), \(\delta_A^{r}\), and \(\delta_A^{m}\) are shown in Fig. 9. No regular variation trends are found

| Sample    | \(r_A\) (nm) | \(t\) | \(\delta_A^{\varepsilon}\) | \(\delta_A^{r}\) | \(\delta_A^{m}\) |
|-----------|--------------|------|----------------|----------------|----------------|
| 5HEP-1    | 0.109        | 0.871| 0.082          | 0.072          | 0.050          |
| 5HEP-2    | 0.105        | 0.855| 0.024          | 0.069          | 0.014          |
| 6HEP-3    | 0.108        | 0.866| 0.065          | 0.065          | 0.041          |
| 6HEP-4    | 0.105        | 0.856| 0.036          | 0.063          | 0.019          |

Fig. 9 Variation trends in thermal conductivity with different parameters of (La\(_{1/5}\)Pr\(_{1/5}\)Dy\(_{1/5}\)Ho\(_{1/5}\)Tm\(_{1/5}\)Ta\(_2\)O\(_9\)) (5HEP-1), (Gd\(_{1/5}\)Dy\(_{1/5}\)Ho\(_{1/5}\)Er\(_{1/5}\)Tm\(_{1/5}\)Ta\(_2\)O\(_9\)) (5HEP-2), (La\(_{1/6}\)Sm\(_{1/6}\)Eu\(_{1/6}\)Dy\(_{1/6}\)Ho\(_{1/6}\)Tm\(_{1/6}\)Ta\(_2\)O\(_9\)) (6HEP-3), and (Eu\(_{1/6}\)Gd\(_{1/6}\)Dy\(_{1/6}\)Ho\(_{1/6}\)Er\(_{1/6}\)Tm\(_{1/6}\)Ta\(_2\)O\(_9\)) (6HEP-4) ceramics: A-site atomic disorder parameters of (a) electronegativity, (b) ionic radius, and (c) atomic mass; (d) tolerance factor.
for the thermal conductivity with the aforementioned four parameters; thus, more HEP specimens should be fabricated and tested to identify variation laws. The four investigated samples clearly exhibit low thermal conductivity and high TECs, and they are therefore candidate E/TBCs.

4 Conclusions

Four novel A-site equiatomic HEP RETa3O9 ceramics are fabricated via a two-step sintering process, and the corresponding thermophysical properties are investigated and analysed as candidate E/TBCs for high-temperature applications. The contributions of this study are presented below:

1) Dense and high-purity HEP RETa3O9 bulk ceramics are successfully fabricated via SPS, and XRD, SEM, EDS, and 3D nanoindentation results demonstrate the excellent compositional homogeneity of all the samples.

2) The tolerance factor of the prepared HEP samples depends on the ionic radius of RE3+, where the tolerance factor ranging from 0.8 to 0.9 shows that the samples have stable double-perovskite structures.

3) HEP RETa3O9 has a moderate Young’s modulus (140–180 GPa) and hardness (7–10 GPa), and the brittle–ductile transition results in increased toughness (1.8–2.5 MPa·m1/2).

4) Enhanced TECs (8.0 × 10−6–10.1 × 10−6 K−1 at 1473 K) expand the applications of RETa3O9, and a high melting point and extraordinary phase stability ensure high-temperature applications.

5) A low thermal conductivity (1.5–2.0 W·m−1·K−1) indicates excellent thermal insulation by HEP RETa3O9 ceramics, and the results of this study have inspired a future study on tantalate HECs with desirable properties.

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