Preparation and properties of CMAS resistant bixbyite structured high-entropy oxides \( \text{RE}_2\text{O}_3 \) (\( \text{RE} = \text{Sm, Eu, Er, Lu, Y, and Yb} \)): Promising environmental barrier coating materials for \( \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 \) composites

Yanan SUN\(^{a,b}\), Huimin XIANG\(^b\), Fu-Zhi DAI\(^b\), Xiaohui WANG\(^c\), Yan XING\(^d\), Xiaojun ZHAO\(^a\)*, Yanchun ZHOU\(^b\)*

\(^{a}\)School of Materials Science and Engineering, Central South University, Changsha 410083, China  
\(^{b}\)Science and Technology on Advanced Functional Composite Laboratory, Aerospace Research Institute of Materials & Processing Technology, Beijing 100076, China  
\(^{c}\)Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China  
\(^{d}\)New Energy Technology Engineering Laboratory of Jiangsu Province, Nanjing University of Posts and Telecommunications, Nanjing 210023, China

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Abstract: \( \text{Y}_2\text{O}_3 \) is regarded as one of the potential environmental barrier coating (EBC) materials for \( \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 \) ceramic matrix composites owing to its high melting point and close thermal expansion coefficient to \( \text{Al}_2\text{O}_3 \). However, the relatively high thermal conductivity and unsatisfactory calcium–magnesium–aluminosilicate (CMAS) resistance are the main obstacles for the practical application of \( \text{Y}_2\text{O}_3 \). In order to reduce the thermal conductivity and increase the CMAS resistance, four cubic bixbyite structured high-entropy oxides \( \text{RE}_2\text{O}_3 \), including \( (\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \), \( (\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Er}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \), \( (\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Er}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \), and \( (\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \) were designed and synthesized, among which \( (\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \) and \( (\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \) bulks were prepared by spark plasma sintering (SPS) to investigate their mechanical and thermal properties as well as CMAS resistance. The mechanical properties of \( (\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \) and \( (\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \) are close to those of \( \text{Y}_2\text{O}_3 \) but become more brittle than \( \text{Y}_2\text{O}_3 \). The thermal conductivities of \( (\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \) and \( (\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3 \) (5.1 and 4.6 W·m\(^{-1}\)·K\(^{-1}\)) are only 23.8% and 21.5% respectively of that of \( \text{Y}_2\text{O}_3 \) (21.4 W·m\(^{-1}\)·K\(^{-1}\)), while their thermal expansion coefficients are close to those of \( \text{Y}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \). Most importantly, HE \( \text{RE}_2\text{O}_3 \) ceramics exhibit good CMAS resistance. After being attacked by CMAS at 1350 °C for 4 h, the HE \( \text{RE}_2\text{O}_3 \) ceramics maintain their original morphologies without forming pores or cracks, making them promising as EBC materials for \( \text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3 \) composites.

Keywords: high-entropy ceramics; rare earth oxides; low thermal conductivity; thermal expansion coefficient; CMAS resistance

* Corresponding authors.  
E-mail: X. Zhao, Zhaoxj@csu.edu.cn;  
Y. Zhou, yczhou@alum.imr.ac.cn
1 Introduction

Oxide/oxide ceramic matrix composites (CMCs) are promising materials for next generation gas turbine engines [1–6]. Among them, Al2O3/Al2O3 composites are the up-to-date candidates but are restricted by their grain growth, sintering, creep deformation, water vapor recession [7–9], and CMAS corrosion [10–14] in combustion environment. To cope with the degradation problem, environmental barrier coatings (EBCs) have to be applied, which play an important role in protecting Al2O3/Al2O3 composites from water vapor and CMAS attack.

Eligible EBC materials should have several fundamental but essential properties [15–17], i.e., (1) good high temperature phase stability without phase transition and decomposition, (2) good thermodynamic compatibility with substrates, (3) good mechanical strength and damage tolerance, (4) good resistance to water vapor and CMAS corrosion. Materials satisfying the foregoing requirements are potential as preeminent EBCs for Al2O3/Al2O3 composites.

Previous works have demonstrated that Y2O3 is a potential EBC material because of its high melting point (2500 °C) [18] and close thermal expansion coefficient ([(8.6–9.6)×10−6 K−1] [19,20] to Al2O3, ([(8.5–9.0)×10−6 K−1]) [21]. However, the thermal conductivity of Y2O3 at room temperature is relatively high. Meanwhile, the CMAS resistance of Y2O3 is not as satisfactory as expected [22]. Therefore, reducing the thermal conductivity and improving CMAS resistance of Y2O3 is significant.

In the past few years, high-entropy ceramics (HECs) have been proven to have fascinating properties comparing to the single-component materials such as good stability, adjustable thermal expansion coefficient, low thermal conductivity, slow grain growth rate, high hardness and strength, and improved oxidation resistance [17,23–37]. Particularly, compositional disorder and severe lattice distortion can enhance phonon scattering, resulting in lower thermal conductivity. Moreover, improved corrosion resistance can be achieved due to sluggish diffusion.

In order to reduce the thermal conductivity and improve the CMAS resistance of Y2O3, four cubic bixbyite structured high-entropy rare earth oxides, i.e., (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Eu0.2Er0.2Y0.2Yb0.2)2O3, and (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3 were designed and synthesized in this work.

When choosing the compositions, crystal structures and atomic differences were taken into account as the main criteria. Firstly, the constituting oxides are expected to crystallize in similar crystal structures. Secondly, the chosen five kinds of rare earth elements are supposed to have small ionic radius difference but high atomic mass difference. Thus, (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 was designed as the initial composition, wherein five constituting oxides Eu2O3, Er2O3, Lu2O3, Y2O3, and Yb2O3 possess the same crystal structure. Then, in view of the fact that Sm2O3 has two types of crystal structures and its effect on the crystal structure of high-entropy rare earth oxides is unknown, by substituting Eu2O3, Er2O3, and Lu2O3 with Sm2O3 in order, the three compositions, i.e., (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Eu0.2Er0.2Y0.2Yb0.2)2O3, and (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3 were designed.

The mechanisms underlying the low thermal conductivity of HECs are attributed to atomic mass difference and lattice distortion. For the electrical insulating HECs, the thermal conductivities are typically determined by a combination of phonon–phonon scattering and defect scattering [38]. The phonon relaxation time τ can be described as

\[ \tau_U(\omega) = \left( \frac{6\pi^2}5 \right)^{1/3} \frac{\text{\textit{M}} V_\text{p}^2}{2 k_B \gamma^2 \omega T^3} \]  

\[ \tau_{PP}^{1/3} = \frac{V_\text{p}^4}{4\pi\nu_\text{p}^2} \left[ \sum_i f_i \left( 1 - \frac{m_i}{m} \right)^2 + \sum_i f_i \left( 1 - \frac{\rho_i}{\rho} \right)^2 \right] \]  

where \( \tau_U \) and \( \tau_{PP} \) refer to Umklapp phonon-phonon scattering and point defect scattering, respectively. In detail, \( \text{\textit{M}} \) is the average mass, \( \nu_\text{p} \) is the phonon group velocity, \( V_\text{p} \) is the phonon phase velocity, \( V \) is the volume per atom, \( \gamma \) is the Grüneisen parameter, \( \omega \) is the phonon frequency, \( f_i \) is the fraction of atoms with mass \( m_i \) and radius \( r_i \) on the site with average mass \( \bar{m} \) and radius \( \bar{r} \). Based on Eq. (1) and Eq. (2), it is reasonable to expect that the thermal conductivity of HE RE2O3 will be reduced compared to Y2O3 owing to big atomic mass difference and lattice distortion in HE RE2O3.

Aiming at reducing the thermal conductivity and improving the CMAS resistance of Y2O3, four cubic bixbyite structured high-entropy rare earth oxides, i.e., (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Eu0.2Er0.2Y0.2Yb0.2)2O3, and (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3 were designed, which have big atomic mass difference and ionic radius difference. These high-
entropy rare earth oxides were synthesized using Sm$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Lu$_2$O$_3$, Y$_2$O$_3$, and Yb$_2$O$_3$ as starting materials, and then the mechanical and thermal properties as well as CMAS resistance were explored to assure their qualification as promising EBC materials for Al$_2$O$_3$/Al$_2$O$_3$ composites.

2 Experimental

2.1 Preparation and characterization of HE RE$_2$O$_3$ powders and bulks

Powders of (Eu$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$, (Sm$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$, (Sm$_{0.2}$Eu$_{0.2}$Er$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$, and (Sm$_{0.2}$Eu$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ were synthesized by the solid state reaction method. Five RE$_2$O$_3$ oxides chosen from six rare earth oxides, i.e., Y$_2$O$_3$, Sm$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$, and Lu$_2$O$_3$ powders (99.9% purity; HWRK Chem. Co., Ltd., Beijing, China) were mixed in equal molar ratios according to the above target compositions. The mixtures were cold pressed into pallets and then calcined at 1600 °C for 4 h in air. After cooling, these pallets were smashed and ball milled for 4 h to obtain fine powders.

Phase identification was performed by an X-ray diffractometer (XRD, D8 advanced, Bruker, Germany) using Cu Kα ($\lambda$ = 1.54178 Å) radiation at a scanning speed of 2 (°)/min. To prove that the as-prepared powders exhibit the cubic bixbyite structure, Rietveld refinement was conducted using TOPAS software (TOPAS, Bruker Corp., Karlsruhe, Germany). In Rietveld refinement, $R$ factor is the sum of weighted and squared differences between observed and calculated intensities at each point in an XRD pattern which is minimized by least squares refinement as [39]:

$$R = \sum_i w_i \left| y_i^{\text{obs}} - y_i^{\text{calc}} \right|^2$$

where $y_i^{\text{obs}}$ and $y_i^{\text{calc}}$ are the observed and calculated intensities at point $i$ respectively, $w_i$ is the weight assigned to each intensity, and $y_i^{\text{calc}}$ can be calculated as follows:

$$y_i^{\text{calc}} = \sum_k (p_k L_k |F_k|^2 G(\Delta\theta_{ik}) P_k) + y_i^{\text{bkg}}$$

where $S$ is a phase-specific scale factor, $p_k$ is the multiplicity factor, $L_k$ is the Lorentz and polarization factor for the $k$th Bragg reflection, $F_k$ is the structure factor for an individual reflection of a particular phase, $G(\Delta\theta_{ik})$ is the reflection profile function, $\Delta\theta_{ik}$ is the Bragg angle for the $k$th reflection, $P_k$ is the preferred orientation function, and $y_i^{\text{bkg}}$ is the refined background. In this way, reliability factors $R_p$ [39] and $R_{wp}$ [40] are built as

$$R_p = \frac{\sum_i |y_i^{\text{obs}} - y_i^{\text{calc}}|}{\sum_i y_i^{\text{obs}}}$$

$$R_{wp} = \left[ \frac{\sum_i (y_i^{\text{obs}} - y_i^{\text{calc}})^2}{\sum_i y_i^{\text{obs}}} \right]^{1/2}$$

wherein lower values indicate higher degree of agreements. The particle size distribution of HE RE$_2$O$_3$ powders was observed in a scanning electron microscope (SEM, Apollo300, CamScan, Cambridge, UK) and analyzed using ImageJ software (open resource) [41] with at least 300 particles were counted.

Bulk HE RE$_2$O$_3$ ceramics were prepared by a spark plasma sintering apparatus (SPS-20T-6-IV, Shanghai Chenhua Science and Technology Co., Ltd., China) at 1500 °C for 10 min under a pressure of 30 MPa. The bulk density was measured by the Archimede’s method. After being polished and thermally etched at 1500 °C for 1 h, microstructures and element distribution of HE RE$_2$O$_3$ ceramics were observed by a scanning electron microscope (SEM, Apollo300, CamScan, Cambridge, UK) equipped with energy dispersive X-ray spectroscopic system (EDS, Inca X-Max 80 T, Oxford, UK). The grain size distribution was analyzed using ImageJ software (open resource) [41] based on the microstructures of the thermally etched surface and at least 300 grains were counted.

2.2 Mechanical properties of bulk HE RE$_2$O$_3$

Good mechanical properties and damage tolerance are basic requirements for EBC materials. To evaluate the suitability of HE RE$_2$O$_3$ as EBC materials, their mechanical properties were measured. For flexural strength and fracture toughness, at least five samples were tested using a universal testing machine (MTS-Criterio C45.105, USA). The flexural strength of HE RE$_2$O$_3$ was measured through a three-point bending test method with the sample dimension of 3 mm × 4 mm × 36 mm. Fracture toughness $K_{IC}$ was determined using single-edge notched beam (SENB) specimens with the dimension of 3 mm × 6 mm × 36 mm. The
The notch was 3 mm in depth and 0.15 mm in width. The crosshead speed for flexural strength test is 0.5 mm/min and that for $K_{IC}$ determination is 0.05 mm/min. The elastic modulus $E$ was estimated by a residual-indent analysis method. In this method, elastic modulus is a simple function of $E_r$ [42]:

$$\frac{1}{E_r} = 1 - \nu^2 + \frac{1 - \nu^2}{E}$$

(7)

where $E_r$ is the reduced modulus, $E$ and $\nu$ are the elastic modulus and Poisson’s ratio of the specimen, while $E_i$ and $\nu_i$ are the elastic modulus and Poisson’s ratio of the indenter, respectively.

2.3 Thermal properties of bulk HE RE$_2$O$_3$

Thermal conductivity is one of the most important properties for HE RE$_2$O$_3$ that needs to make a breakthrough in this work. Thermal conductivity ($\kappa$) of HE RE$_2$O$_3$ can be calculated from thermal diffusivity ($D_{th}$), heat capacity ($c_p$), and bulk density ($d$) using:

$$\kappa = D_{th} \cdot c_p \cdot d$$

(8)

where $c_p$ was calculated from the data of the constituent oxides (Y$_2$O$_3$, Sm$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$, and Lu$_2$O$_3$) by Neumann–Kopp rule. The thermal diffusivity ($D_{th}$) was measured by a laser flash thermal conductivity apparatus (NETZSCH LFA467, Germany). To achieve such a goal, samples with the size of Ø10 mm × 2 mm were used and were coated by layers of platinum and graphite to prevent heat radiation from penetrating. The average linear thermal expansion coefficient (TEC) was obtained by a vertical high-temperature optical dilatometer (ODHT-1600-50, Expert System Solutions, Modena, Italy) from room temperature to 1673 K using a sample of 3 mm × 4 mm × 15 mm in size.

2.4 CMAS resistance of HE RE$_2$O$_3$

Recently, CMAS corrosion has become a pending teaser which must be taking into consideration when developing EBC materials. To demonstrate the CMAS resistance of HE RE$_2$O$_3$ ceramics, a CMAS composition of 22CaO–19MgO–14AlO$_1.5$–45SiO$_2$ [43] in molar ratio was used in this work. Firstly, homogeneous mixture of CaO, MgO, Al$_2$O$_3$, and SiO$_2$ powders were annealed at 1400 °C for 4 h to obtain CMAS powders. Secondly, by dispersing CMAS powders in ethanol, CMAS slurry was dropped on the polished surfaces of bulk HE RE$_2$O$_3$ ceramics with a loading density of about 77 mg/cm$^2$. After the evaporation of ethanol, the coated samples were heated to 1250 and 1350 °C, respectively, for up to 4 h in a muffle furnace. Finally, the CMAS attacked samples were cut along their midline and the cross-sections were polished for SEM characterization.

3 Results and discussion

3.1 Phase composition and microstructure of HE RE$_2$O$_3$ powders

Figure 1 shows the XRD patterns of HE RE$_2$O$_3$ powders and those of Y$_2$O$_3$, Sm$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$, and Lu$_2$O$_3$. One can see that although the XRD pattern of Sm$_2$O$_3$ is different from those of Y$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$, and Lu$_2$O$_3$, the XRD patterns of the four HE RE$_2$O$_3$ powders are similar to each other and coincide with those of cubic bixbyite structured RE$_2$O$_3$, indicating the formation of cubic bixbyite structured HE RE$_2$O$_3$.

Among the six selected rare earth oxides, Y$_2$O$_3$, Sm$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$, and Lu$_2$O$_3$ can all crystallize in cubic bixbyite structure. Nevertheless, the XRD patterns in Fig. 1 show that Y$_2$O$_3$, Eu$_2$O$_3$, Er$_2$O$_3$, Yb$_2$O$_3$, and Lu$_2$O$_3$ are in cubic bixbyite structure ($Ia\bar{3}$ space group) [44], while Sm$_2$O$_3$ is in monoclinic structure (C2/m space group) [44,45]. Figures 2(a) and 2(b) show the crystal structure of cubic Y$_2$O$_3$ and that of monoclinic Sm$_2$O$_3$, respectively. Figure 2(c) shows the schematic crystal structure of high-entropy RE$_2$O$_3$, which was built based on a 2 × 2 × 2 supercell of Y$_2$O$_3$. In Y$_2$O$_3$, Y atoms are located at 8$a$ (1/4, 1/4, 1/4) and 24$d$ (x, 0, 1/4) and 24$d$ (x, 0, 1/4) sites, while O atoms occupy the 48$e$ (x, y, z) site. In HE RE$_2$O$_3$, five kinds of RE atoms occupy the 8$a$ and 24$d$ sites randomly. Using the structure model of HE RE$_2$O$_3$ in Fig. 2(c), a simulated XRD pattern is obtained as shown in Fig. 2(d). This XRD pattern is very similar to those of cubic bixbyite oxides but with tiny peaks at low angle due to the supercell.

It has come to light that the stable crystal structure of the RE$_2$O$_3$ at room temperature varies with the atomic number of RE [46]. The light rare earth element oxides RE$_2$O$_3$, from La$_2$O$_3$ to Nd$_2$O$_3$, are stable in the form of hexagonal structure (A phase), while the middle rare earth element oxides RE$_2$O$_3$, including Sm$_2$O$_3$, Eu$_2$O$_3$, and Gd$_3$O$_2$, are stable in either monoclinic (B phase) or cubic structure (C phase). The heavy rare earth element oxides RE$_2$O$_3$, from Tb$_2$O$_3$ to
Lu₂O₃, are stable only in cubic structure (C phase). In this work, HE RE₂O₃ powders are synthesized at 1600 °C. Sm₂O₃ and Eu₂O₃ are supposed to transfer from cubic to monoclinic structure when the temperature reaches up to 1600 °C. Theoretically, Sm₂O₃ and Eu₂O₃ obey an ideal transition sequence of cubic (C phase) → monoclinic (B phase) → hexagonal (A phase) → high temperature hexagonal (H phase) → high temperature cubic (X phase). The transition temperatures [46–52] are listed in Table 1.
According to Table 1, the C→B phase transition temperatures of Sm₂O₃ and Eu₂O₃ are in a range of 1153–1348 °C. The phase transition is irreversible [53]. XRD pattern of monoclinic structured Sm₂O₃ in ICSD database [54] and those of Sm₂O₃ before and after heated at 1600 °C for 4 h are shown in Fig. 3. Comparing with Fig. 1, after being heated at 1600 °C for 4 h, there was no phase transition for monoclinic structured Sm₂O₃. In HE RE₂O₃, however, monoclinic structured Sm₂O₃ has been dissolved into the cubic bixbyite structure. Since Sm₂O₃ has a different crystal structure, it demonstrates that materials with different crystal structures can be integrated into a homogeneous solid solution through entropy stabilization. In addition, cubic bixbyite structured Eu₂O₃ is supposed to transfer to a monoclinic structure after being heated at 1600 °C for 4 h. However, it remains in a cubic bixbyite structure in HE RE₂O₃. These facts demonstrate that the structural constraint of high-entropy oxides is effective in restraining phase transition and sustaining the phase stability [55].

![Graph](image)

**Fig. 3** XRD patterns of Sm₂O₃ before and after being heated at 1600 °C for 4 h together with peak positions and intensities in PDF#42-1464 of monoclinic structured Sm₂O₃ [54].

Lattice parameter \(a\) and theoretical density \(d_t\) of the four HE RE₂O₃, i.e., \((Eu_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\), \((Sm_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\), \((Sm_{0.2}Eu_{0.2}Er_{0.2}Y_{0.2}Yb_{0.2})_2O_3\), and \((Sm_{0.2}Eu_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) obtained by Rietveld refinement are listed in Table 2. The average lattice parameter \(a_{av}\) and density \(d_{av}\) of five constituting oxides are also included for comparison. Primarily, the \(R_p\) and \(R_{wp}\) values are less than 10, which indicate good reliability of the refinement. Analyzing of the data in the table, one can find that the refined lattice parameters \(a\) are somewhat smaller than the average lattice parameters \(a_{av}\). And the theoretical densities \(d_t\) of HE RE₂O₃ are lower than the average densities of the constituting oxides \(d_{av}\), from which the deviations are around 2%. From the above results, a conclusion can be drawn that for the HE RE₂O₃, the lattice parameters are not just the average of those the constituting components but are the results of energetic optimization of the structure after they reach thermodynamic equilibrium.

Interestingly, it should be pointed out that during the synthesis procedure, the solubility of \((Sm_{0.2}Eu_{0.2}Er_{0.2} Y_{0.2}Yb_{0.2})_2O_3\) and \((Sm_{0.2}Eu_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) powders changes over holding time. Figure 4 shows the XRD patterns of HE RE₂O₃ powders with different compositions heated for 1, 2, 3, and 4 h. As shown in Figs. 4(c) and 4(d), for \((Sm_{0.2}Eu_{0.2}Er_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) and \((Sm_{0.2}Eu_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\), wherein Sm and Eu co-exist, there are several weak peaks appearing on both sides of the strongest (222) peak compared with \((Eu_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) and \((Sm_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) powders after 1 h heating. With the extension of heating time to 2 and 3 h, these peaks are weakened. XRD patterns of the four specimens that are heated for 4 h converge with each other eventually. Time dependent peak change may be caused by atomic size differences, which results in time dependent solubilities. Sm and Eu are the two largest atoms of the selected rare earth elements with the ionic radii of 0.964 and 0.950 Å [56], respectively, as summarized in Table 3. This fact implies that it takes more time for big atoms to incorporate into a homogeneous solid solution. In terms of the time-independent solubility of \((Eu_{0.2}Er_{0.2} Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) and \((Sm_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) at 1600 °C, \((Eu_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) has the biggest relative atomic mass difference among the four HE RE₂O₃, while \((Sm_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) has the biggest ionic radii difference. Thus, \((Eu_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) and \((Sm_{0.2}Er_{0.2}Lu_{0.2}Y_{0.2}Yb_{0.2})_2O_3\) are consolidated into bulk form and investigated deeply in this work as representatives.

### Table 1  Phase transition temperatures of Sm₂O₃ and Eu₂O₃

| Material      | Transition temperature (°C) |
|---------------|----------------------------|
|               | C→B                        | B→A | A→H | H→X |
| Sm₂O₃         | 1153 [46]                  | 2170 [46] | 2369 [46] | 2526 [46] |
| Sm₂O₃         | 1173–1273 [47]             | 2143 [48] | 2403 [50] | 2523 [50] |
| Sm₂O₃         | 1153 [49]                  | 2173 [50] | 2343 [48] | 2498 [48] |
| Eu₂O₃         | 1348 [46]                  | 2323 [46] | 2413 [46] | 2526 [46] |
| Eu₂O₃         | 1348 [47]                  | 2323 [50] | 2413 [50] | 2523 [50] |
| Eu₂O₃         | 1323 [51]                  | 2323 [52] | 2413 [52] | 2498 [48] |
Table 2  Lattice parameters and densities of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Eu0.2Er0.2Y0.2Yb0.2)2O3, and (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3

| Material                               | \(a\) (Å) | \(a_{av}\) (Å) | \(V\) (Å³) | \(d_t\) (g/cm³) | \(d_{av}\) (g/cm³) | \(R_p\) | \(R_w\) |
|----------------------------------------|-----------|----------------|-----------|----------------|-----------------|--------|--------|
| (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3          | 10.563    | 10.569         | 1178.586  | 7.899          | 7.944           | 4.90   | 6.22   |
| (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3          | 10.575    | 10.583         | 1182.609  | 7.854          | 8.038           | 4.95   | 6.23   |
| (Sm0.2Eu0.2Er0.2Y0.2Yb0.2)2O3          | 10.666    | 10.681         | 1213.402  | 7.453          | 7.590           | 4.90   | 6.69   |
| (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3          | 10.636    | 10.646         | 1203.192  | 7.587          | 7.762           | 6.71   | 8.91   |

Fig. 4  XRD patterns of the as-prepared (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Eu0.2Er0.2Y0.2Yb0.2)2O3, and (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3 powders synthesized at 1600 ℃ from 1 to 4 h.

Table 3  Atomic and ionic radii, relative atomic mass, and the relative ionic radius differences of the selected rare earth elements

| Element | Atomic radius (Å) [56] | Ionic radius RE³⁺ (Å) [56] | Coordination number | Ionic radius difference | Mass (g/mol) | Mass difference |
|---------|------------------------|-----------------------------|---------------------|------------------------|--------------|----------------|
| Sm      | 1.814                  | 0.964                       | 6                   | 13.7%                  | 150          | 68.5%          |
| Eu      | 1.984                  | 0.950                       | 6                   | 12.0%                  | 152          | 70.8%          |
| Er      | 1.780                  | 0.881                       | 6                   | 3.9%                   | 167          | 87.6%          |
| Yb      | 1.923                  | 0.858                       | 6                   | 1.2%                   | 173          | 94.4%          |
| Lu      | 1.760                  | 0.848                       | 6                   | 0%                     | 175          | 96.6%          |
| Y       | 1.824                  | 0.892                       | 6                   | 5.2%                   | 89           | 0%             |

SEM images of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 powders and the corresponding statistics of particle size are shown in Fig. 5. It can be seen from Figs. 5(a) and 5(c) that the particle sizes of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are analogous. Following a log-normal distribution in Figs. 5(b) and 5(d), the average particle sizes of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are determined 1.09±0.53 and 1.35±0.62 μm, respectively.

3. 2  Phase composition and microstructure of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 ceramics

Bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 ceramics were prepared by spark plasma sintering at 1500 ℃ under a pressure of 30 MPa for 10 min. For comparison, bulk Y2O3, which was used to obtain its thermal conductivity, was sintered under the same condition. XRD patterns of the three bulks are shown in Fig. 6. For both (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and
Fig. 5  Particle morphologies (a, c) and particle size distributions (b, d) of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 powders.

Fig. 6  XRD patterns of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, and Y2O3. (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, no impurity phase can be identified within the resolution of X-ray diffraction, indicating high phase purity and good high temperature stability of high-entropy (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3.

The densities of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, and Y2O3 measured by Archimede’s method are 7.88, 7.82, and 5.03 g/cm³, respectively, corresponding to 99.8%, 99.6%, and 99.9% of the theoretical values. Figure 7 shows the SEM images of the polished surfaces of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and the distribution of constituting elements. Apparently, there are no micro-pores or micro-cracks in the observed region, revealing high density of the bulk HE RE2O3 ceramics. Moreover, it also can be seen from the figure that the corresponding rare earth elements are uniformly distributed in both bulk (Eu0.2Er0.2Lu0.2
Figure 8 shows the surface microstructures and grain size distributions of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, which were thermally etched at 1500 °C for 1 h. No residual cracks or pores are in sight, whereas the average grain size of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 is less than half of that of (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3. The mean grain sizes of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are 3.55±1.23 and 8.48±3.77 μm, respectively. X-ray diffraction patterns from surfaces of the thermally etched (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are consistent with the original patterns of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, conforming the good high temperature stability of HE RE2O3 ceramics.

3.3 Mechanical properties of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3

Mechanical properties, including Young’s modulus $E$, fracture toughness $K_{IC}$, flexural strength $σ_b$, and Vickers hardness $H_v$ of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are summarized in Table 4. For comparison, the mechanical properties of Y2O3 [57] are also given. The Young’s moduli measured by residual indent method are 205±10.1 and 189±3.7 GPa for (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, respectively, which are higher than that of Y2O3 (181.4 GPa). The higher Young’s modulus can be understood from the difference in lattice parameters $a$ of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 (10.563 Å), (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 (10.567 Å), and Y2O3 (10.604 Å) as shown in Table 2. Smaller lattice parameters of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 indicate stronger bonding, which in turn lead to their slightly higher Young’s modulus than Y2O3.
Table 4 Young’s modulus $E$, fracture toughness $K_{IC}$, flexural strength $\sigma_b$, Vickers hardness $H_v$, damage tolerance $D_t$, and brittleness $B$ of bulk $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$, $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$, and $\text{Y}_2\text{O}_3$.

| Material | $E$ (GPa) | $K_{IC}$ (MPa m$^{1/2}$) | $\sigma_b$ (MPa) | $H_v$ (GPa) | $D_t$ (m$^{1/2}$) | $B$ (μm$^{-1/2}$) |
|----------|-----------|--------------------------|-----------------|-------------|-----------------|------------------|
| $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ | 205±10.1 | 1.67±0.13 | 165.7±0.57 | 7.55±0.04 | 0.254 | 4.521 |
| $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ | 189±3.7 | 1.64±0.11 | 166.1±5.37 | 7.42±0.24 | 0.233 | 4.524 |
| $\text{Y}_2\text{O}_3$ [55] | 181.4 | 2.06 | 122 | 7.60 | 0.374 | 3.689 |

The measured room temperature fracture toughness of bulk $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are 1.67±0.13 and 1.64±0.11 MPa m$^{1/2}$, respectively, which are lower than that of $\text{Y}_2\text{O}_3$ (2.06 MPa m$^{1/2}$). The flexural strengths of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are 165.7±0.57 and 166.1±5.37 MPa, respectively, which are higher than that of $\text{Y}_2\text{O}_3$ (122 MPa). Lower fracture toughness and higher flexural strength than $\text{Y}_2\text{O}_3$ indicate that $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are more brittle. The Vickers hardness of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are 7.55±0.04 and 7.42±0.24 GPa, which are close to that of $\text{Y}_2\text{O}_3$ (7.60 GPa). Brittleness index [58] in Eq. (9):

$$B = \frac{H}{K_{IC}} \quad (9)$$

and damage tolerance expressed in Eq. (10) [59]:

$$D_t = \frac{K_{IC} \cdot E}{\sigma_b \cdot H} \quad (10)$$

are quantitative measure of brittleness and damage tolerance, respectively. The values of brittleness of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are 4.521 and 4.524 μm$^{-1/2}$, respectively, which are higher than that of $\text{Y}_2\text{O}_3$ (3.689 μm$^{-1/2}$). The values of damage tolerance of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are 0.254 and 0.233 m$^{1/2}$, which are lower than that of $\text{Y}_2\text{O}_3$ (0.374 m$^{1/2}$). The relatively high brittleness and low damage tolerance values of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ imply that $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are more brittle than $\text{Y}_2\text{O}_3$. Although the damage tolerances $D_t$ of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ are lower than $\text{Y}_2\text{O}_3$, they are still close to that of $\text{Y}_4\text{Al}_2\text{O}_9$ (0.25 m$^{1/2}$), a candidate thermal barrier coating material [60], which still warrant their resistance to damage.

Figure 10 compares the fracture surfaces of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ after fracture toughness test. It can be seen that both of the fracture surfaces exhibit a combination of intragranular fracture (blue arrows indicate characteristic zone of intragranular fracture, while red arrows indicate characteristic zone of intergranular fracture).

Fig. 10 Fracture surfaces of (a) $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and (b) $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ (blue arrows indicate characteristic zone of intragranular fracture, while red arrows indicate characteristic zone of intergranular fracture).

3. 4 Thermal properties of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$

Thermal properties are key parameters to judge the qualification of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ as EBC materials. The linear thermal expansion curves of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ and $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ is the result of grain size difference. The average grain size of $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ is 8.48±3.77 μm, which is more than twice of that of $(\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$ (3.35±1.23 μm). When fracture occurs, cracks have to extend across the interior of grains in $(\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3$, forming cleavage steps.
proves the good high temperature stability of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 in the testing temperature range. As shown in Figs. 11(a) and 11(b), the thermal expansion coefficients of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 determined by linear fitting are 8.09×10^{-6} K^{-1} (R^2 = 0.997) and 7.95×10^{-6} K^{-1} (R^2 = 0.993), respectively, which are close to those of Y2O3 ((8.6–9.6)×10^{-6} K^{-1}) [19,20] and Al2O3 ((8.5–9.0)×10^{-6} K^{-1}) [21]. The difference between TECs of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 may result from the difference of their chemical bonding [58,61].

Table 5 compares the thermal expansion coefficients (TECs) of the selected cubic bixbyite structured rare earth oxides [53]. In general, the TECs of HE RE2O3 are slightly smaller than those of single component rare earth oxides, which distribute in a range of (8.2–8.9)×10^{-6} K^{-1}. This fact implies that the TECs of HE RE2O3 stem from complex synergism of the component rare earth oxides instead of the average of them. Basically, thermal expansion of materials originates from anharmonic vibration of lattice at finite temperatures, which is closely related to the bond strength of chemical bond. Since the TECs of HE RE2O3 are smaller than those of the constituting rare earth oxides, the RE–O bonds in HE RE2O3 are statistically stronger than the RE–O bonds in single phase RE2O3. The enhanced Young’s modulus of HE RE2O3 is a clear indication of stronger bonding than in the single component rare earth oxides RE2O3 since it is a direct reflection of chemical bonding.

The measured thermal diffusivities Dth, calculated heat capacities c_p, and the room temperature thermal conductivities κ of HE RE2O3 and Y2O3 are listed in Table 6. The room temperature thermal diffusivities of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are 1.92×10^{-6} and 1.88×10^{-6} m²·s⁻¹, respectively. And the room temperature thermal conductivities

| Material | Dth (10⁻⁶ m²·s⁻¹) | c_p (J·mol⁻¹·K⁻¹) | κ (W·m⁻¹·K⁻¹) |
|----------|-----------------|-----------------|----------------|
| (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 | 1.92 | 109.55 | 5.1 |
| (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 | 1.88 | 108.19 | 4.6 |
| Y2O3 | 5.23 | 102.32 | 21.4 |

Fig. 11 Thermal expansion curves of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 measured from room temperature to 1673 K.

Fig. 12 Thermal diffusivities of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 measured from room temperature to 1173 K.
of \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) and \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) are 5.1 and 4.6 \(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\), respectively. One can see that the thermal diffusivities and thermal conductivities of \(\text{HE RE}_2\text{O}_3\) are much lower than those of \(\text{Y}_2\text{O}_3\) (5.23 \(\times\) \(10^{-6}\) \(\text{m}^2 \cdot \text{s}^{-1}\) and 21.4 \(\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}\)). Figure 12 shows the thermal diffusivities measured from room temperature to 1173 K. Curve fitting of the scatters of \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) and \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) yields:

\[
D_{\text{th1}} = 2.74 - 3.41 \times 10^{-3}T + 1.51 \times 10^{-6}T^2
\]

for \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) \hspace{1cm} (10)

\[
D_{\text{th2}} = 2.67 - 3.27 \times 10^{-3}T + 1.50 \times 10^{-6}T^2
\]

for \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) \hspace{1cm} (11)

wherein \(R^2\) is 0.986 and 0.991 respectively. Heat capacities \(c_{p1}\) and \(c_{p2}\) as functions of temperature for \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) and \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) calculated by Neumann–Kopp rule yield (as shown in Fig. 13):

\[
c_{p1} = 122.72 + 14.4 \times 10^{-3}T - 1.55 \times 10^{-6}T^2
\]

for \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) \hspace{1cm} (12)

\[
c_{p2} = 123.66 + 13.0 \times 10^{-3}T - 1.60 \times 10^{-6}T^2
\]

for \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) \hspace{1cm} (13)

Eventually, thermal conductivities of \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) and \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) follow the relationship as

\[
\kappa_1 = \frac{943.4}{T} + 1.8 \hspace{1cm} \text{for} \hspace{1cm} \text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3
\]

\[
\kappa_2 = \frac{787.5}{T} + 2.1 \hspace{1cm} \text{for} \hspace{1cm} \text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3
\]

with \(R^2\) equals to 0.973 and 0.973, respectively. As shown in Fig. 14, the thermal conductivities of \(\text{HE RE}_2\text{O}_3\) and \(\text{Y}_2\text{O}_3\) decrease with temperature. More importantly, the thermal conductivities of \(\text{HE RE}_2\text{O}_3\) within the measured temperature range are evidently lower than that of \(\text{Y}_2\text{O}_3\). The relatively lower thermal conductivities are caused by a combination of lattice distortion, mass differences of atoms, and composition disorder, as shown in Eqs. (1) and (2). According to the ionic radii of rare earth elements and relative atomic mass that are listed in Table 3, ionic radius difference, which is related to lattice distortion, in \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) is larger than that in \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\). On the opposite, atomic mass difference in \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) is higher than that in \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\). In \(\text{HE RE}_2\text{O}_3\), different RE atoms homogeneously occupy the \(8a\) and \(24d\) cation sites of the cubic bixbyite structure, leading to severe lattice distortion. Meanwhile, different kinds of atoms bring large mass differences compared with single component \(\text{Y}_2\text{O}_3\). Low thermal conductivities and close thermal expansion coefficients to \(\text{Al}_2\text{O}_3\) render \(\text{HE RE}_2\text{O}_3\) ceramics promising as suitable EBCs for \(\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3\) CMCs to replace \(\text{Y}_2\text{O}_3\).

### 3.5 CMAS resistance

CMAS resistance is a critical requirement for EBC coatings. In this work, CMAS corrosion resistance of bulk \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) and \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) ceramics was tested at 1250 and 1350 °C for up to 4 h and the cross-sectional morphologies are shown in Fig. 15. One can find that the cross-sections of bulk \((\text{Eu}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) and \((\text{Sm}_{0.2}\text{Er}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_2\text{O}_3\) after CMAS attack are quite similar, presenting a triple-layer structure, i.e., the CMAS layer, a transition layer, and the \(\text{HE RE}_2\text{O}_3\) substrate layer.
from top to bottom. As shown in Figs. 15(a) and 15(b), after CMAS corrosion at 1250 °C for 4 h, there is only a smooth reaction layer between the CMAS layer and the HE RE2O3 substrate layer, which are 2.62±0.61 and 3.08±0.77 µm, respectively. When the corrosion temperature increases to 1350 °C, it can be observed from Figs. 15(c) and 15(d) that the reaction layers turned to be rugged with burrs. The visible reaction layers increase to about 5.31±1.72 and 6.47±2.18 µm, respectively. Meanwhile, the substrates of HE RE2O3 ceramics still remain relatively glossy without pores or cracks caused by CMAS attack. The morphology integrity of the attacked HE RE2O3 ceramics indicate their better CMAS resistance than Y2O3 [22], YSZ [22, 62], REPO4 (RE = Nd, Sm, Gd) [62], Ba2REAlO5 (RE = Yb, Er, Dy) [63], and high-entropy RE2Si2O7 [64].

Table 7 compares the thicknesses of the reaction layers of several common TBC/EBC materials that are attacked by CMAS under different conditions. After being corroded at 1250 °C for 4 h, thickness values of the reaction layers upon the CMAS deposited (Eu0.2 Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 ceramics (with a concentration of about 77 mg/cm2) are only 2.62±0.61 and 3.08±0.77 µm, which are less than a half of the values in REPO4 (RE = Nd, Sm, Gd) [62] and Ba2REAlO5 (RE = Yb, Er, Dy) [63] (with a concentration of about 15 mg/cm2). After being corroded at 1250 °C for 1 h, MOCVD YSZ coating possessed a 5 µm-thick reaction layer while YSZ pellet infiltrated by CMAS for 4 h has a reaction layer with a depth of 50 µm.

Table 7  Thickness of the reaction layers of several thermal/environmental barrier coating materials after CMAS attack under different conditions

| Material                  | Temperature and duration | CMAS composite             | CMAS loading and loading methods | Thickness of reaction layers |
|---------------------------|--------------------------|-----------------------------|----------------------------------|------------------------------|
| MOCVD Y2O3 coating [22]  | 1250 °C, 1 h             | 35.3CaO–9.6MgO–6.9Al2O3–48.2SiO2 | 30 mg/cm² by powder depositing   | 30 µm                        |
| MOCVD YSZ coating [22]   | 1250 °C, 1 h             | 35.3CaO–9.6MgO–6.9Al2O3–48.2SiO2 | 30 mg/cm² by powder depositing   | 5 µm                         |
| YSZ pellet [62]           | 1250 °C, 4 h             | 22CaO–19MgO–15Al2O3–44SiO2 | 15 mg/cm² by suspension dropping | ~50 µm                       |
| LnPO4 pellets [62]        | 1250 °C, 4 h             | 22CaO–19MgO–15Al2O3–44SiO2 | 15 mg/cm² by suspension dropping | 10–15 µm                     |
| Ba2REAlO5, pellets [63]   | 1250 °C, 4 h             | 22CaO–19MgO–14Al2O3–45SiO2 | ~15 mg/cm² by slurry dropping    | 10–15 µm                     |
| High-entropy RE2Si2O7 [64]| 1500 °C, 4 and 50 h      | 33CaO–9MgO–13Al2O3–45SiO2 | 30 mg/cm² by suspension coating  | ~300 µm                      |
| High-entropy RE2O3 (this work) | 1250 °C, 4 h             | 22CaO–19MgO–14Al2O3–45SiO2 | ~77 mg/cm² by slurry dropping    | 2.62±0.61 µm, 3.08±0.77 µm    |
| High-entropy RE2O3 (this work) | 1350 °C, 4 h             | 22CaO–19MgO–14Al2O3–45SiO2 | ~77 mg/cm² by slurry dropping    | 5.31±1.72 µm, 6.47±2.18 µm    |
EDS linear scanning along the white lines in Fig. 16 displays the relative amount of constituting elements from CMAS to HE RE$_2$O$_3$ that were heated at 1350 °C for 4 h. The undulate distributions of elements match with the changes of morphologies which could be distinguished by colors. Mg and Al have infiltrated into HE RE$_2$O$_3$ substrates largely, leaving Si behind them, while Ca remains mostly in the CMAS layer. As for rare earth elements, Y seems to be eagerly to climb upward while the other four elements are similar and remain mostly in the substrates of HE RE$_2$O$_3$. To figure out the reaction mechanism, samples half-coated by CMAS were designed as shown in Fig. 17(a). In Figs. 17(b) and 17(c), a step appears at the transition zone of each sample, revealing that the reaction mechanism is characterized by the diffusion from CMAS to HE RE$_2$O$_3$.

Figure 18 presents the XRD patterns of the surfaces of HE RE$_2$O$_3$ after CMAS attack at 1250 °C for 1, 2, and 4 h, and at 1350 °C for 4 h, corresponding to curves (2)–(5), respectively. In Fig. 18(a), wherein HE (Eu$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ was attacked by CMAS, the only phase that could be identified was CaSiO$_3$ (in $P2_1/a$ space group), even though the as-marked CaSiO$_3$ phase only matches the position with a shift to lower angle. In detail, curves (2) and (3) are similar despite a new strong peak at $2\theta \approx 37^\circ$ appears in curve (3), which also exists in curve (4). However, most of the peaks still remain unknown, demonstrating that the phase compositions of the surface of (Sm$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ after CMAS attack are more complex.

In order to identify the compositions of reaction products on the CMAS attacked surfaces of HE RE$_2$O$_3$ ceramics, powders of CMAS and HE RE$_2$O$_3$ were mixed with a mass ratio of 1:2 and then heated at 1350 °C for 4 h. The XRD patterns of (Eu$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ and (Sm$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ powders after reaction with CMAS powders are shown in Fig. 19, wherein rare earth aluminate RE$_3$Al$_5$O$_{12}$, Ca$_2$(SiO$_4$), and Ca$_2$RE$_3$(SiO$_4$)$_6$ oxyapatites [65,66] are identified. However, XRD patterns of these three phases cannot match any of the unknown peaks in Fig. 18. The mismatch between XRD patterns in Fig. 18 and Fig. 19 might be related to reaction methods. The XRD patterns shown in Fig. 19 are from the reaction of (Eu$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ and (Sm$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ powders with CMAS powders, while the XRD patterns shown in Fig. 18 are from reaction of the surfaces of bulk (Eu$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ and (Sm$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ with CMAS. For powder reaction, the reactants were well-mixed. As a result, the reaction was sufficient. While for the surface attack, it can be seen from Fig. 16 that the relative amounts of

![Fig. 16](image-url) Relative amount of constituting elements in CMAS and HE RE$_2$O$_3$ substrates: (a) (Eu$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ and (b) (Sm$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ after CMAS attack at 1350 °C for 4 h.

![Fig. 17](image-url) (a) Schematic diagram of the designed half-coated sample, and SEM images of the transition zone of (b) (Eu$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$ and (c) (Sm$_{0.2}$Er$_{0.2}$Lu$_{0.2}$Y$_{0.2}$Yb$_{0.2}$)$_2$O$_3$, demonstrating the reaction occurs on the HE RE$_2$O$_3$ side through CMAS attack.
Fig. 18 XRD patterns of the surfaces of bulk (a) (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (b) (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 after CMAS attack at 1250 °C for 1, 2, and 4 h and at 1350 °C for 4 h.

Fig. 19 XRD patterns of the (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 powders after reacting with CMAS powders at 1350 °C for 4 h.

constituting elements in CMAS that permeated into HE RE2O3 substrates are different. The rapid diffusion of Mg and Al than other elements towards HE RE2O3 may cause the reaction products on the surface different from those of powder reaction. Furthermore, the CMAS loading on HE RE2O3 is about 0.77 mg/cm², which is more than four times thicker than that on REPO₄ (RE = Nd, Sm, Gd) [62] and Ba₂REAlO₅ (RE = Yb, Er, Dy) [63] (with a concentration of about 15 mg/cm²). Thus, the XRD patterns from the surfaces of HE RE2O3 are different from those on REPO₄ (RE = Nd, Sm, Gd) and Ba₂REAlO₅ (RE = Yb, Er, Dy) and also from those of powder reactions.

4 Conclusions

In this study, four cubic bixbyite structured high-entropy rare earth oxides, including (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3, (Sm0.2Eu0.2Er0.2Y0.2Yb0.2)2O3, and (Sm0.2Eu0.2Lu0.2Y0.2Yb0.2)2O3 were designed and successfully synthesized using a solid state reaction method. And bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 ceramics were prepared via spark plasma sintering. The densities of bulk (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 ceramics are 7.88 and 7.82 g/cm³, respectively. The HE RE2O3 ceramics crystallize in cubic bixbyite structure with an Ia3 space group despite the fact that one of the raw materials, i.e., Sm₂O₃, is in monoclinic structure with a C2/m space group, which proves that materials with different crystal structures can be integrated into a high symmetry structure through entropy stabilization. (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 exhibit close mechanical properties and superior thermal properties to Y₂O₃. It is worth highlighting that the room temperature thermal conductivities of (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are 5.1 and 4.6 W·m⁻¹·K⁻¹, respectively, which are only about 23.8% and 21.5% of that of Y₂O₃ (21.4 W·m⁻¹·K⁻¹). More importantly, high-entropy (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 ceramics have good CMAS resistance. After attacking by CMAS at 1350 °C for 4 h, the thicknesses of the reaction layers are only 5.31±1.72
and 6.47±2.18 μm, respectively, and the HE RE2O3 substrates still remain pore-free and crack-free. Close mechanical properties to Y2O3, low thermal conductivities, close thermal expansion coefficient to Y2O3 and Al2O3, and good CMAS resistance indicate that (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 are promising EBC materials for Al2O3/Al2O3 CMCs. However, we must acknowledge that high-entropy (Eu0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 and (Sm0.2Er0.2Lu0.2Y0.2Yb0.2)2O3 ceramics are more brittle than Y2O3, which needs further attention in other high-entropy ceramics.

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