Ti$^{4+}$-incorporated fluorite-structured high-entropy oxide (Ce,Hf,Y,Pr,Gd)O$_{2-\delta}$: Optimizing preparation and CMAS corrosion behavior

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Abstract: Environmental barrier coatings (EBCs) with excellent chemical resistance and good high-temperature stability are of great significance for their applications in next-generation turbine engines. In this work, a new type of high-entropy fluoride-structured oxide (Ce$_{0.2}$Hf$_{0.2}$Y$_{0.2}$Pr$_{0.2}$Gd$_{0.2}$)O$_{2-\delta}$ (HEFO-1) with different Ti$^{4+}$ contents were successfully synthesized. Minor addition of Ti$^{4+}$ could be dissolved into a high-entropy lattice to maintain the structure stable, effectively reducing the phase formation temperature and promoting the shrinkage of bulk samples. Heat treatment experiments showed that all the samples remained a single phase after annealing at 1200–1600 °C for 6 h. In addition, high-entropy (Ce$_{0.2}$Hf$_{0.2}$Y$_{0.2}$Pr$_{0.2}$Gd$_{0.2}$Ti$_{0.2}$)O$_{2-\delta}$ demonstrated great resistance to calcium–magnesium–alumina–silicate (CMAS) thermochemical corrosion. When the content of Ti was increased to $x = 0.5$, the average thickness of the reaction layer was about 10.5 µm after being corroded at 1300 °C for 10 h. This study reveals that high-entropy (Ce$_{0.2}$Hf$_{0.2}$Y$_{0.2}$Pr$_{0.2}$Gd$_{0.2}$Ti$_{0.2}$)O$_{2-\delta}$ is expected to be a candidate for the next-generation EBC materials with graceful resistance to CMAS corrosion.

Keywords: high-entropy ceramics (HECs); fluorite structure; high-temperature stability; calcium–magnesium–alumina–silicate (CMAS) corrosion

1 Introduction

Oxide-/SiC-based ceramic matrix composites (CMCs) are considered to be a candidate material for the next-generation high-temperature components due to their superior performance compared to traditional alloys [1–3]. However, such CMCs are often corroded by molten silicates and water vapor in the working environment, resulting in structural damage [4–6]. At present, it is urgent to develop new environmental barrier coatings (EBCs) to protect the SiC-based CMCs. The EBCs are required to have outstanding corrosion resistance and thermal stability to ensure the normal function in high-temperature airflow and calcium–magnesium–alumina–silicate (CMAS) corrosive environments [7–9]. Therefore, much research has focused on correcting existing deficiencies and developing new systems to meet the requirements of industrial applications.

Highly disordered, multi-component, and entropy-stabilized new systems developed an uncharted advanced material field. High-entropy alloys (HEAs) with at
least five elemental species have been successfully synthesized and have attracted widespread attention due to their predominant physical properties and potential applications [10–12]. Inspired by this concept, high-entropy materials have been broadened to more categories: high-entropy ceramics (HECs), including oxides [13], carbides [14,15], borides [16], silicides [17], and sulfides [18]. The HECs have been found to exhibit better structure stability, enhanced mechanical properties, colossal dielectric constant, amorphous-like thermal conductivity, superionic conductivity, and chemical catalysis properties [19–24]. High-entropy oxide (HEO) (Mg,Ni,Co,Cu,Zn)O has been designed while the entropy stabilization mechanism was first proved in 2015 by Rost et al. [13]. Other disordered ceramic systems rapidly followed, stimulating the addition of more components to obtain materials expressing a blend of properties.

High-entropy fluoride-structured oxides (HEFOs), as a significant part of the HEO system, have received much attention for their composition design and performance. Sarkar et al. [25] prepared several rare earth (RE) element fluoride-structured oxides through nebulized spray pyrolysis (NSP) method and proved that cerium (Ce) cations played a vital role in the stability of a high-entropy system. Enlighten by this study, Ce-containing HEFO systems have emerged successively, and many new entropy-stabilized single-phase HEFOs were synthesized by solid-state reaction method [26–28]. In addition, Ce-free (Zr0.2Pr0.2Y0.2La0.2)O2-δ series single-phase HEOs have also been successfully prepared [29]. Hereafter, some scientific workers studied the influence of metal ions doped on the structures and properties of Ce-based HEFOs. The addition of Mo4+ not only results in a change of the crystal symmetry from Ia-3 to Fm-3m, but also affects the conduction, especially at high temperatures [30]. In addition, Anandkumar et al. [31] found that the photoluminescence spectroscopy emission intensity of (Ce0.2Gd0.2Hf0.2La0.2Zr0.2)O2 increased with the Eu3+ concentration and calcination temperature because Eu3+ ions acted as luminescent centers. The entry of ions makes (Ce0.2Gd0.2Hf0.2La0.2Zr0.2)O2 nanoparticles a promising candidate for imaging and warm-light illumination.

In terms of thermal properties, the HEFOs have low thermal conductivity, appropriate thermal expansion coefficient, and high-temperature phase stability [32–35]. For instance, the high-entropy (5RE0.2)Ce2O7 successfully prepared by Xu et al. [36] has a more suitable thermal expansion coefficient and can be better matched to metal substrates. These HEFOs have a lower thermal conductivity (1.52–1.55 W/(m·K)) compared to conventional materials such as La2CeO7 while exhibiting high-temperature sintering resistance. For medium-entropy (ME) oxide ceramics, (Y,Ti)0.1(Zr,Hf,Ce)0.9O2 and (Ta,Ti)0.1(Zr,Hf,Ce)0.9O2 have been designed and prepared by Qiu et al. [37]. The two ME fluorite-structured oxides display significantly lower thermal conductivity compared to yttria-stabilized zirconia (YSZ), with the thermal expansion coefficient close to those of the YSZ and Ni-based superalloys. Importantly, the two ME oxides only formed a penetration layer of 2 µm after CMAS attacking at 1250 °C for 4 h, showing outstanding CMAS resistance. CMAS corrosion behavior, ablation resistance, and thermal expansion coefficient of medium- and high-entropy compositionally complex fluorite oxides were comprehensively investigated by Wright et al. [34]. Suitable thermal conductivity and thermal expansion coefficients are inherent advantages of the HEFOs as thermal protection materials. Nevertheless, their chemical interaction with molten silicates and phase stability are also important points to be explored.

Drawing inspiration from the above studies, we successfully designed and synthesized a series of single-phase (Ce0.2Hf0.2Y0.2Pr0.2Gd0.2Ti0.2)O2-δ (x = 0, 0.3, and 0.5) HEFOs by the solid-state reaction method. X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HR-TEM) were used to characterize the crystal structures and microscopic morphology of the HEFOs. The primary focus of this work was to benchmark the relevant properties of the new class of the HEFOs, including preparation, high-temperature stability, and CMAS corrosion behavior. All the prepared HEFOs based on the high-entropy effect can maintain the phase stability at high temperatures and effectively inhibit the corrosion of the CMAS at 1300 °C, laying a foundation for their application of the EBC materials.

2 Experimental

2.1 Materials and synthesis

As illustrated in Table 1, six metal oxides (Ce, Hf, Y, Pr, Gd, and Ti) were used as basic raw materials for the synthesis of the HEFOs. Commercially available Y2O3...
Table 1 Crystal structures, cationic radii (rc), and corresponding cationic coordination numbers (CNs) of selected oxides

| Oxide          | Crystal structure | rc (Å) | CN |
|----------------|-------------------|--------|----|
| CeO2           | Cubic             | 0.97   | VIII |
| HfO2           | Monoclinic        | 0.83   | VIII |
| Y2O3           | Bixbyite          | 1.019  | VIII |
| Pr6O11         | Cubic             | 0.96   | VIII |
| Gd2O3          | Bixbyite          | 1.053  | VIII |
| TiO2           | Tetragonal        | 0.74   | VIII |
| (Ce0.2Hf0.2Y0.2Pr0.2Gd0.2)O2 | | | |
| (Ce0.188Hf0.188Pr0.188Gd0.188Ti0.06)O2 | | | |

(99.9%, 5 μm, Bangru New Material Technology Co., Ltd.), HfO2, TiO2 (99.9%, 5 μm, Zhongyue Metals Material Technology Co., Ltd.), CeO2, Pr6O11 (99.9%, Aladdin Biochemical Technology Co., Ltd.), and Gd2O3 (99.99%, Aladdin Biochemical Technology Co., Ltd.) were purchased and weighed in a stoichiometric ratio. High-entropy (Ce0.2Hf0.2Y0.2Pr0.2Gd0.2)O2−δ (x = 0, 0.3, and 0.5) were synthesized, including (Ce0.2Hf0.2Y0.2Pr0.2Gd0.2)O2−δ (HEFO-1), (Ce0.188Hf0.188Pr0.188Gd0.188Ti0.06)O2−δ (HEFO-2), and (Ce0.18Hf0.18−Y0.18Pr0.188Gd0.188Ti0.06)O2−δ (HEFO-3). The raw materials firstly were calcined at 850 °C to remove moisture, impurities, and undesirable groups. The powders were accurately weighed according to the stoichiometric ratio, and then a planetary ball was milled in ethanol by a polytetrafluoroethylene (PTFE) jar and zirconia ball grinding media (ball-to-powder mass ratio ≈ 10 : 1; QM-3SP2, Nanjing University, China) for 8 h. After drying for at least 12 h, the grinding media was completely removed, and polyvinyl alcohol (PVA) solution was added dropwise to the powders as a binder, and then followed by thorough mixing. As for the Ti4+-incorporated compositions, the powders before ball milling were weighed with TiO2 according to their respective ratios to obtain the relative content of Ti ions of x = 0, 0.3, 0.5 (occupying 5.66% and 9.09% of cationic lattice sites, respectively). The raw powders were pressed into pellets by a diameter of 15 mm in a stainless-steel mold under a cold isostatic pressure of 250 MPa. Then, the consolidated pellets were sintered at 1500 °C for 4 h in a muffle furnace (KSL-1700x, Hefei Kejing Materials Technology Co., Ltd., China). Additionally, the as-sintered samples were coarsely ground with sandpapers of different fineness, and finely polished by a diamond paste of 0.25 μm for testing and characterization.

2.2 Characterization

The crystalline structures of the calcined HEFOs were determined by a X-ray diffractometer (Rigaku, Ultima IV, Japan) utilizing Cu Kα radiation with a step size of 0.01° in 2θ at a scanning rate of 5 (°)/min. Rietveld refinement was done by a general structure analysis system (GSAS) program with CeO2 as crystallographic information file (CIF) structure files to confirm the phase structures and lattice parameters. The sintering shrinkage of the HEFOs at different temperatures was captured by a visual deformation meter (TA-16A01, Tianjin Zhonghuan Electric Furnace, China), and the temperature is raised from 50 to 1500 °C (10–20 °C /min) for 1 h. The theoretical densities of bulk HEFOs were calculated by utilizing the lattice parameters from the XRD refinement, and the actual density was measured by Archimedes drainage method.

The microstructures and chemical uniformity of the synthesized samples were characterized by a scanning electron microscope (LYRA3, TESCAN, Czech Republic) and a transmission electron microscope (Tecnai G2 F30, FEI, USA) equipped with an energy dispersive X-ray spectroscopy (EDS) detector (Oxford Instruments, UK). Sample preparation involves the dispersion of the powdered samples in deionized water (DI) by ultrasonication, and then drop casting the dispersion on the TEM grid and drying at room temperature. An X-ray photoelectron spectroscopy (K-Alpha, Thermo Scientific, USA) with a monochromatic Al Kα anode (1486.7 eV) was used to indicate the valence state of each element in the HEFOs. The photoelectron spectra were taken with a spot size of 400 μm at the pass energy of 50 eV with an energy step of 0.1 eV.

2.3 CMAS corrosion test

To satisfy the application requirements, the ability of the as-prepared HEFOs for resisting the CMAS corrosion was tested in this work. The CMAS with a composition of 33CaO–9MgO–13Al2O3–45SiO2 in the molar ratio was prepared by ball milling method. CaO, MgO, Al2O3, and SiO2 powders were uniformly mixed together according to the above stoichiometric ratio. The average values of the main components of the deposits on an aircraft turboshaft shroud operated in the desert environment were used as a representative component ratio for molten CMAS [38–40]. The original CMAS powders were similarly pressed into a disc with a diameter of 15 mm in a stainless-steel mold under a uniaxial pressure of 4 t, and then pre-annealed at 1200 °C (the mixture was melted at around 1235 °C) to synthesize the main component anorthite (CaAl2Si2O8).
and cyclowollastonite ($\beta$-CaSiO$_3$) [41,42]. Annealed CMAS loading up to $\sim$115 mg/cm$^2$ was placed on top of the bulk HEFOs, and this structure was heated to the corresponding temperatures in a furnace under an air atmosphere. At 1300 °C, some sand was melted and flowed out of the top, resulting in a mass loss. The CMAS loading was finally reduced to $\sim$40 mg/cm$^2$ without affecting the changes observed at the original reaction interface. After annealing, the CMAS-attacked specimens were cut and polished for the SEM characterization to observe the reaction interface morphology.

3 Results and discussion

3.1 Structural properties

The XRD (Fig. 1(a)) is performed to demonstrate the crystalline structures of the as-synthesized five-component equimolar HEFOs and provided standard PDF cards for the five components. The cubic CeO$_2$, monoclinic HfO$_2$, bixbyite Y$_2$O$_3$, cubic Pr$_6$O$_{11}$, and bixbyite Gd$_2$O$_3$ have provided structural information for these metal oxides. The absence of diffraction peaks indexed to raw metal oxides indicated that Hf, Y, Pr, and Gd all dissolved into cubic CeO$_2$ to form an $Fm-3m$ single-phase fluorite structure. As shown in Fig. 1(b), three HEFOs maintained the stable fluorite structure at room temperature, and all the reflections observed for the HEFOs were analogous to the cubic oxide such as CeO$_2$ with planes corresponding to (111), (200), (220), (311), and (222). More importantly, the vanish of the diffraction peaks ascribed to TiO$_2$ and the shift right of the diffraction peaks with the increase of Ti$^{4+}$ concentration suggested that the vast majority of Ti$^{4+}$ may be incorporated into the HEFO sublattice for the formation of solid solution. According to Bragg diffraction equation: $2d \sin \theta = n\lambda$, where $\lambda$ is the wavelength of the Cu Kα in this work, $d$ is the crystal spacing, and $n$ is an integer, when $\theta$ decreases with the peak shifting to a higher diffraction degree direction, the interplanar spacing of the crystal planes decreases accordingly.

Figure 2 depicts the XRD Rietveld-refined results of three HEFOs after sintering at 1500 °C for 4 h, in which the calculated patterns were in agreement with the experimental patterns. The fitted parameters $R_{wp}$, $R_p$, and $\chi^2$ values were combined with general standards.
to prove that the calculation results were credible and accurate. By comparing with the CIF structure information of cubic CeO2, all the HEFOs conformed to a single cubic fluorite phase. Interestingly, with the Ti4+ content increasing, the calculated lattice parameters decreased accordingly. The result further illustrated the above diffraction peak displacement phenomenon, which may be due to the entry of Ti4+ with a significantly smaller ionic radius into the cation site, resulting in the reduction of the average cation radius and interplanar spacing.

The single-phase HEFO-3 was investigated with the use of X-ray photoelectron spectroscopy (XPS) method, so as to determine the valence states of the ions in fluorite-structured HEFOs. According to the fitted spectra (Fig. 3), Gd and Y elements occurred only in the 3+ valence state [43,44], which is expected. In the case of the Hf element, the characteristic peaks of pure HfO2 were at binding energies (BEs) of 19.1 and 20.7 eV (corresponding to Hf 4f7/2 and Hf 4f5/2, respectively). The deviation of the BE of the Hf element in HEFO-3 was roughly attributed to the interaction between Hf and other elements in the fluorite structure lattice to produce the Hf–RE–O bond [43,45]. The valence of Ce in HEFO-3 was predominantly 3+/4+, and the integral region of Ce4+ dominates, which is consistent with the observed behavior in fluorite structures [46–48]. Here, the blue integral area corresponds to Ce4+, and the orange area corresponds to Ce3+. For the Pr element, the 3+/4+ mixed valence state similar to that of Ce could be clearly observed [49,50]. It is worth noting that the characteristic peak positions of Ti change after entering the high-entropy fluorite structure. The pure TiO2 sample had the single Ti4+ (2p3/2) peak located at the BE of ca. 458.9 eV, which corresponds to the Ti4+ state, but this area is very small. Therefore, it is possible that Ti has been transformed to sub-stoichiometric Ti oxides (the valence of Ti is less than 4+) with a BE of about 457.5 eV. Alternatively, the peak positions were shifted due to the interactions between different cations [47,51]. These variations all indicated strong interactions of Ti4+ with Ce and other elements in the lattice, further demonstrating that the incorporation of TiO2 is not mechanically mixed in the HEFOs.

3.2 Morphology and homogeneity

Micrographs depicting the surfaces of the polished bulk samples are presented in Figs. 4(a)–4(c), and bulk HEFO-1,2,3 are sintered at 1500 ℃ for 4 h. Three HEFOs after the furnace sintering were solid compacts free of obvious cracks with randomly distribution porosity at a relatively low level. The surface profile with grain contours is provided in Fig. S1 in the Electronic Supplementary Material (ESM). Furthermore, no second phase was found in the SEM images and EDS mappings, and all the elements were distributed homogeneously without obvious segregation or clustering. Likewise, for the Ti-containing fractions, six metal elements were randomly and uniformly distributed, and a small amount of doped Ti4+ was not segregated.

Fig. 3 XPS spectra of each cationic element in HEFO-3.
The combination results of the XRD patterns and SEM–EDS mappings indicated that a series of bulk HEFOs \((\text{Ce}_{0.2}\text{Hf}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Ti}_{0.2})\text{O}_{2-\delta}\) have been successfully synthesized. Figures 4(d) and 4(e) show the HR-TEM images of HEFO-3 particles, in which the interlacing of different crystal plane orientations of the fluorite structure is clearly visible. In addition, the interplanar spacing of the \((200)\) plane calculated from the lattice stripes in Fig. 4(d) is 0.254 nm, and the decrease in this value corresponds to the decrease in the interplanar spacing shown by the XRD results. Dark areas appear in some regions in Fig. 4(e), possibly due to the overlap of different crystallographic planes or the uneven distribution of local elements. To further analyze the formation of high-entropy single phase and the homogeneity of elemental distribution at a microscopic scale, a selected area electron diffraction (SAED) pattern and EDS mappings of HEFO-3 are given in Fig. 4(f) and 4(g), respectively. It was evident that the diffraction rings in the SAED pattern could be assigned to the face-centered cubic (fcc) structure, and the homogeneity of the distribution of all elements was proved in the EDS analysis of the selected regions.

3.3 Formation of high-entropy phases

The morphological shrinkage of HEFO-1 and HEFO-3 during the heating and holding process were shown in Fig. 5. The sample was rapidly heated to 800 °C (20 °C/min) in the visual deformation meter, and then heated to 1500 °C (10 °C/min) and kept for 1 h. The volume of the samples decreased slightly as the temperature increased from 800 to 1300 °C, which may be related to the polymerization disappearance of pores. As shown in Fig. 5(a), when the temperature reaches 1400 °C, the surface of the sample block appears to uplift slightly and disappears at about 1500 °C. This phenomenon may be caused by the uneven heating of the samples in short term. The temperatures at the edges were slightly higher than that at the center.
causing the edges of the sample to start shrinking first. The slight uplift of the samples at a macroscopic level was attributed to the difference in the shrinkage rate. As the temperature raised to 1500 ℃ and the holding process started, the shrinkage rate tends to be uniform throughout the sample. All the samples in this work were prepared at 1500 ℃, and again Fig. 6 shows that all three HEFO phase formation temperatures were in the range of 1400–1500 ℃. This stage was accompanied by a sharp shrinkage of size, as depicted in Figs. 5(b) and 5(c), corresponding to the formation of the high-entropy single phase. In addition, the sample entered a stable contraction period again during the heat preservation process of 1500 ℃, and gradually became dense with the increase of the holding time.

The height and width change ratios and shrinkage ratio of the HEFO-1 and HEFO-3 at different temperatures are shown in Table 2. The maximum shrinkage rate of HEFO-3 could even reach 32.52% after holding at 1500 ℃ for 1 h. Similar to the phenomenon indicated in Fig. 5, HEFO-3 (containing Ti⁴⁺) shrank more than HEFO-1 (without Ti⁴⁺) at most temperatures. Comparative tests have shown that the addition of Ti⁴⁺ can effectively promote the densification process for

Table 2 Width and height change ratios, and corresponding calculated volume shrinkage ratios for HEFO-1 and HEFO-3 in sintering process at 1300, 1400, and 1500 ℃ (selected data is final size of sample after being kept at 1500 ℃ for 1 h, and sample size before sintering is 15 mm in diameter and 1 mm in height)

| No. | Composition | Size       | Temperature |
|-----|-------------|------------|-------------|
|     |             | Width (%)  | 1300 ℃     | 1400 ℃ | 1500 ℃ |
| HEFO-1 | (Ce₀.1Hf₀.1Y₀.1Pr₀.1Gd₀.1)O₂−δ | 97.01 | 94.40 | 93.61 |
| HEFO-3 | (Ce₀.18Hf₀.18Y₀.18Pr₀.18Gd₀.18Ti₀.1)O₂−δ | 98.42 | 85.81 | 79.94 |
|      |             | Height (%) | 102.39 | 100.59 | 93.41 |
|      |             | Volume shrinkage (%) | 3.79 | 10.36 | 18.15 |
|      |             |           | 1300 ℃ | 1400 ℃ | 1500 ℃ |
| HEFO-1 | (Ce₀.1Hf₀.1Y₀.1Pr₀.1Gd₀.1)O₂−δ | 102.39 | 100.59 | 93.41 |
| HEFO-3 | (Ce₀.18Hf₀.18Y₀.18Pr₀.18Gd₀.18Ti₀.1)O₂−δ | 97.20 | 116.08 | 105.59 |
|      |             | Volume shrinkage (%) | 5.85 | 14.53 | 32.52 |
(Ce$_{0.2}$Hf$_{0.2}$Y$_{0.2}$Pr$_{0.2}$Gd$_{0.2}$Ti$_{0.2}$)$_2$O$_{2-\delta}$ high-entropy system under the same matrix composition and sintering conditions. The bulk HEFO-3 samples had higher volume shrinkage and higher densities compared to HEFO-1 after holding at 1500 °C for 1 h.

The XRD patterns of the HEFOs prepared at different temperatures are shown in Fig. 6. The single-phase formation temperature and other related information of all the samples are listed in Table 3. The diffraction peaks at adjacent positions have not been merged, and the characteristic peaks other than the fluorite structure were present in all three groups of the samples at 1350 °C. HEFO-2 formed a single-phase structure at 1450 °C, while HEFO-3 containing more Ti$^{4+}$ already formed a single phase only at 1400 °C. To investigate the decrease in the formation temperature of the Ti$^{4+}$-containing HEFOs, such differences were understood from the perspective of Gibbs mixing free energy ($\Delta G_{\text{mix}}$). Generally, the $\Delta G_{\text{mix}}$ shown in Eq. (1) was used as a criterion to determine the stability of a system.

Following Boltzmann’s hypothesis, the configurational entropy ($\Delta S_{\text{config}}$) is calculated by Eq. (2) [52]:

$$
\Delta G_{\text{mix}} = -T \Delta S_{\text{config}}
$$

(1)

$$
\Delta S_{\text{config}} = -R \left[ \sum_{i=1}^{N} \chi_i \ln \chi_i^{\text{cation-site}} + \sum_{j=1}^{M} \chi_j \ln \chi_j^{\text{anion-site}} \right]
$$

(2)

where $\Delta H_{\text{mix}}$ is the mixed enthalpy, $T$ is the temperature, $R$ is the ideal gas constant (8.314 J/(mol·K)), $N$ ($M$) is the number of ion species, and $\chi_i$ ($\chi_j$) is the mole fraction of various ions (the only anion site is O on this occasion). The calculated $\Delta S_{\text{config}}$ for HEFO-3 (1.77$R$) was higher than that for HEFO-2 (1.74$R$) or HEFO-1 (1.61$R$). This means that the synthesis temperature of Ti$^{4+}$-containing components reduced as the configurational entropy increased [53,54]. The high-entropy system often had critical temperatures during the preparation, below which the high-entropy single phases could not be obtained. However, the high-entropy phase was not formed instantaneously at a certain temperature. Each component was dissolved in a definite order as the temperature increased [29], and the existence of Ti$^{4+}$ increased the configurational entropy of the high-entropy system and reduced the temperature required for synthesis.

### 3.4 Thermal stability

As a key attribute of the EBC materials, to investigate the thermal stability of the HEFOs, three groups of samples were heat treated at different temperatures. The XRD patterns of the HEFOs after heating at different temperatures (1200–1600 °C) for 6 h are shown in Fig. 7. Compared with those without annealing, all the heat-treated specimens were free of second-phase diffraction peaks after holding at 1600 °C, and

| Table 3 | Detail information of HEFOs |
|---|---|---|---|---|---|
| No. | Composition | Single phase | Lattice parameter (Å) | Theoretical density (g/cm$^3$) | Relative density (%) | Transition temperature (°C) |
| HEFO-1 | (Ce$_{0.2}$Hf$_{0.2}$Y$_{0.2}$Pr$_{0.2}$Gd$_{0.2}$)$_2$O$_{2-\delta}$ | Yes | 5.362 | 7.301 | 92.325 | 1500 |
| HEFO-2 | (Ce$_{0.18}$Hf$_{0.18}$Y$_{0.18}$Pr$_{0.18}$Gd$_{0.18}$Ti$_{0.06}$)$_2$O$_{2-\delta}$ | Yes | 5.347 | 7.010 | 94.667 | 1450 |
| HEFO-3 | (Ce$_{0.18}$Hf$_{0.18}$Y$_{0.18}$Pr$_{0.18}$Gd$_{0.18}$Ti$_{0.1}$)$_2$O$_{2-\delta}$ | Yes | 5.332 | 6.823 | 95.076 | 1400 |

**Fig. 7** XRD patterns of (a) HEFO-1, (b) HEFO-2, and (c) HEFO-3 after heated to 1200, 1300, 1400, and 1600 °C for 6 h as well as the unannealed ones.
the organization remained stable even at a temperature higher than the sintering temperature. For other annealing temperatures, no phase transformation was observed, demonstrating the outstanding thermal stability of the prepared material. Complex factors determined the stability mechanism of the high-entropy system at high temperatures. The phase stability of the high-entropy system at high temperatures may be attributed to the change of $\Delta G_{\text{mix}}$. Enthalpy and entropy play diametrically opposed roles in thermodynamic changes: on the one hand, the rise of mixing enthalpy hinders the stability of sublattices; on the other hand, configurational entropy promotes the formation of the solid solution. According to Eq. (1), the $T\Delta S_{\text{config}}$ term increases faster than the $\Delta H_{\text{mix}}$ term at high annealing temperatures, and the $\Delta S_{\text{config}}$ compensation dominates the single-phase stability [55,56]. The $\Delta S_{\text{config}}$ of the same system remains unchanged, and the increase in the temperature causes a decrease in $\Delta G_{\text{mix}}$. This phenomenon contributes to further enhancing the system stability. With the addition of Ti$^{4+}$, the $\Delta S_{\text{config}}$ gradually increases, which further expands the $T\Delta S_{\text{config}}$, so as not to negatively affect the phase stability.

3.5 CMAS corrosion behavior

To explore the ability of the as-prepared HEFOs for resisting the molten CMAS corrosion, all the samples were corroded at 1300 °C for 10 h by a muffle furnace. The reaction layer microscopic cross-sectional morphologies were observed, as shown in Fig. 8. It can be seen that a gray corrosion layer with obviously different morphologies was formed at the reaction interface, and its thickness declined gradually with the increase of the Ti content. The average penetration depth measured from the bottom of residual sand layer to the connection between the reaction layer and the HEFO decreases gradually, from about 18.6 µm (HEFO-1) to 12.8 µm (HEFO-2), and then to 10.5 µm (HEFO-3). Moreover, closer examination of the HEFO–CMAS infiltrate revealed that the stick-like second phase was attached vertically to the apparent reaction layer. These stick-like substances all appeared in the three groups of HEFOs, and their morphology was highly similar. The crystal in the residual CMAS could be attributed to the reaction of large amounts of molten calcium and silicon in the CMAS with the RE elements in the HEFOs to form apatite crystal [57–59].

The surface morphology of the samples after the CMAS corrosion is shown in Fig. 9(a). A large number of stick-like crystal grains were distributed on the surface with no regularity for orientation and size. The sample powders and CMAS were homogeneously mixed and annealed at 1300 °C for 10 h to further confirm the permeation reaction products. Mixed HEFO–CMAS powders with a CMAS mass fraction of 10% were used to simulate the reactive interfacial composition environment for sand corrosion of bulk materials. Figure 9(b) shows the presence of the apatite phase in all the HEFOs, which corresponds to the phase observed in the SEM images. Therefore, Ca$_2$(RE)$_8$(SiO$_4$)$_6$O$_2$ with an apatite structure was identified as a major by-product. Similar to those in Refs. [60,61], high concentrations of the RE elements help to prevent further penetration through crystallization during the reaction. This major mechanism was further demonstrated by the compositional analysis, as shown in Fig. 9(c), with fluctuations in the compositional content of the four positions. The RE and a small amount of Ti were still detected in the small stick-like grains at Spot 1, suggesting that elements such as Ca and Si enter the HEFOs at high temperatures, while both RE and Ti will reverse dissolve into the CMAS and participate in the reaction.

![Fig. 8](image-url) Polished cross-sectional SEM images of (a) HEFO-1, (b) HEFO-2, and (c) HEFO-3 after contacting with molten CMAS at 1300 °C for 10 h.
In view of the superiority of HEFO-3 under CMAS corrosion conditions, the cross-sectional morphology after the reaction of 10 h at 1500 °C was examined, as shown in Fig. 10(a). The depth of the reactive interfacial layer was significantly thickened to about 83.8 µm due to the increase in the temperature. The bottom of the gray reaction layer was enlarged, as shown in Fig. 10(b), and still has a similar dense distribution of the stick-like apatite as well as the CMAS penetration in the voids. The aggregation distribution of each element in the corresponding region could be observed by the EDS mapping analysis results (Fig. 10(c)). The RE was mainly distributed in the apatite crystal, and no Ti-rich phase was detected to be present. Ca and Si are concentrated in the CMAS and also exist in the apatite phase. In particular, similar to the RE, the element Ti was uniformly dispersed in the reaction layer. This interesting phenomenon has further supported the dissolution mechanism of Ti, but its exact form remains uncertain. The HEFOs have a high concentration of the RE elements, which is the main mechanism for their corrosion resistance. In addition, the presence of Ti further hindered the progress of corrosion, and a small amount of Ti was dissolved into the CMAS and apatite layer.

At 1300 °C, the reaction behavior of TiO₂ with the CMAS was investigated individually. As shown in Fig. 11, in addition to the CMAS and TiO₂, two different crystals were presented in the reaction cross-section, labeled A and B. The crystal A scattered in the CMAS was shown to be the Ti-rich phase without Ca, Al, and Si elements, in accordance with the EDS mapping.
Besides, the crystal B concentrates at the reaction interface and gradually penetrates into TiO₂. According to the elemental distributions, the crystal B is presumed to be anorthite (CaAl₂Si₂O₈). Moreover, the distribution of Ti in the CMAS has uniformly distributed particles in addition to the aggregated phase. The appearance of the crystal A further proves that the dissolution mechanism of Ti is similar to that of the RE. However, the difference is that Ti prefers to exist in the form of Ti-rich phase or dissolved Ti particles rather than react directly with the CMAS. No Ti-rich crystal was formed after the dissolution of Ti in the CMAS, which may be related to the higher concentrations and consumptions of the CMAS by the RE. This mechanism favors the crystallization process, which is likely to be the main reason for the massive formation of anorthite (CaAl₂Si₂O₈) [62].

To further confirm the main reaction mechanism, the cross-sections of HEFO-3 and CMAS reactions were carefully examined (the interface macroscopic morphology and defects are shown in Fig. S2 in the ESM). The local SEM morphology images and EDS point element analysis results are shown in Fig. 12. Spots A and D were the unreacted HEFO and residual CMAS, respectively. Spot B was the junction of the reaction layer and HEFO, including elements RE, Hf, Ti, and a large amount of Si and Ca. In addition, the gray stick-like substance (Spot C) contains the RE, Ca, and Si, which was the apatite crystal formed by the reaction of the CMAS and the RE. The difference in the content of Ti and Hf in the reaction layer indicates that both elements are equally involved in reverse osmosis, but the dense apatite phase caused by the RE elements still dominates.
The EDS elemental analysis results for Ti and RE elements are shown in Fig. 12(b). The ratio of Ti/(RE + Ti) at Positions 1–5 showed a downward trend. This phenomenon indicated that the RE elements closer to the reaction interface were more soluble than Ti and reacted with the CMAS to form the apatite. The dissolution of Ti located near the reaction interface was confirmed by means of the EDS line analysis (Fig. S3 in the ESM). The results proved that Ti in the high-entropy system was more inclined to stay in the lattice to maintain the stability of the structure than the RE elements, and a small amount of Ti in the CMAS exists not in the Ti-rich phase but in the form of the dissolved Ti particles. These dissolved Ti may have the effect of promoting reactive crystallization, thereby effectively improving the resistance of the HEFO to the CMAS permeation.

4 Conclusions

In this work, high-entropy fluorite structural oxides with different Ti⁴⁺ contents \((\text{Ce}_{0.2}\text{Hf}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Ti}_{0.2-x})\text{O}_{2-\delta}\) were successfully designed and synthesized through the solid-state reaction method with conventional sintering. The prepared HEFOs had a single-phase structure, and the addition of Ti⁴⁺ did not destroy the consistency of the original structure. The single-phase samples exhibited high crystallinity, and the elements were well distributed in the bulk HEFOs. The volume shrinkage of the Ti-containing HEFO increased significantly after sintering at 1500 °C. However, macroscopic deformation occurred during the heating process, which indicates that the preparation of the bulk HEFOs should be performed at a slower heating rate (< 10 °C/min). The incorporation of Ti into a high-entropy lattice increased the configurational entropy, and thus reduced the single-phase formation temperature. The single-phase stability and high-temperature resistance of the HEFOs were excellent, and no phase transition occurred when annealed at high temperatures (1200–1600 °C). Importantly, the HEFOs effectively resisted the corrosion of the molten CMAS at 1300 °C, and the average thickness of the reaction layer gradually decreased to a minimum of 10.5 µm. The inverse dissolution and lattice stabilization of Ti may have promoted the crystallization at the reaction interface rather than direct reaction with CMAS. High concentrations of RE elements were still the mainstay of corrosion reaction, but the use of Ti element has played a significant role in improving the corrosion resistance of HEFOs. Based on functionality, the performance of \((\text{Ce}_{0.2}\text{Hf}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Ti}_{0.2})\text{O}_{2-\delta}\) provides the basis for their application in long-term high-temperature molten silicate environments.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

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