**High-entropy (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ with good high
temperature stability, low thermal conductivity and anisotropic
thermal expansivity**

Zifan ZHAO^{a,b}, Huimin XIANG^a, Heng CHEN^a, Fu-Zhi DAI^a, Xiaohui WANG^c,

Zhijian PENG^{b,*}, Yanchun ZHOU^{a,*}

^a*Science and Technology on Advanced Functional Composite Laboratory, Aerospace
Research Institute of Materials & Processing Technology, Beijing 100076, China*

^b*School of Engineering and Technology, China University of Geosciences, Beijing
100083, China*

^c*Shenyang National Laboratory for Materials Science, Institute of Metal Research,
Chinese Academy of Sciences, Shenyang 110016, China*

Abstract: The critical requirements for the environmental barrier coating (EBC) materials of silicon-based ceramic matrix composites (CMCs) including good tolerance to harsh environments, thermal expansion match with the interlayer mullite, good high-temperature phase stability and low thermal conductivity. Cuspidine-structured rare-earth aluminates RE₄Al₂O₉ have been considered as candidates of EBCs for their superior mechanical and thermal properties, but the phase transition at high temperatures is a notable drawback of these materials. To suppress the phase transition and improve the phase stability, a novel cuspidine-structured rare-earth aluminate solid solution (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ was designed and successfully synthesized inspired by entropy stabilization effect of high entropy ceramics. The as-synthesized (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ exhibits close thermal expansion coefficient

($6.96 \times 10^{-6}/\text{K}$ at 300-1473 K) to that of mullite, good phase stability from 300 K to 1473 K, and low thermal conductivity ($1.50 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ at room temperature). In addition, strong anisotropic thermal expansion has been observed compared to $\text{Y}_4\text{Al}_2\text{O}_9$ and $\text{Yb}_4\text{Al}_2\text{O}_9$. The mechanism for low thermal conductivity is attributed to the lattice distortion and mass difference of the constituent atoms while the anisotropic thermal expansion is due to the anisotropic chemical bonding enhanced by the large size rare earth cations.

Keywords: $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$; high-entropy ceramics; environmental barrier coatings; phase stability; thermal properties

*Corresponding Author.

Tel: +86 10 88524221; Fax: +86 10 6875 9874

Email address:

yczhou@alum.imr.ac.cn (Y.C. Zhou), pengzhijian@cugb.edu.cn (Z. J. Peng)

1 Introduction

Silicon-based ceramic matrix composites (CMCs), such as Si_3N_4 and SiC CMCs, have been considered as candidates to replace superalloys to manufacture the hot section structural components in gas turbine engines due to their superior high-temperature mechanical properties, good durability, excellent creep and oxidation resistance [1,2,3,4,5,6]. However, a key barrier to realizing silicon-based turbine hot section components is the lack of environmental durability of these materials in combustion

environments because the protective silica scale on the surface of silicon-based CMCs can be corroded by high-temperature water vapor and yields volatile products, such as Si(OH)_4 , which will result in the rapid recession of silicon-based CMCs [7,8,9,10,11]. Thus, environmental barrier coatings (EBCs) are necessary for silicon-based CMCs, which can protect the hot section components from the corrosion of high-temperature water vapor [12,13].

Generally, the current prime EBC system of silicon-based CMCs consists of a multiple-layer silicon/mullite/(refractory oxide) coating structure and each layer is under a specific purpose. Silicon as the adhesive layer to bond the substrate and the upper coatings, mullite as the interlayer to reduce the thermal stress between the substrate and the upper coatings, while the refractory oxide as the top layer to protect the underlayer coatings and the substrate from the corrosion of harsh environments [12,13,14]. There are several key requirements for selecting the top refractory oxides, including good tolerance to harsh environments, thermal expansion match with the interlayer and the substrate materials, good phase stability at high temperature, low thermal conductivity, and so on [12,15,16,17]. Particularly, cuspidine-type rare-earth aluminates $\text{RE}_4\text{Al}_2\text{O}_9$ are a class of ceramics that have been considered as potential materials for EBCs of silicon-based CMCs owing to their high melting point, low Young's modulus, good damage tolerance, close thermal expansion coefficients to that of mullite, low thermal conductivity and good resistance to hot gas atmosphere [16,18,19,20,21]. However, one major weakness of $\text{RE}_4\text{Al}_2\text{O}_9$ compounds for EBC application is the high-temperature phase transition with a sudden change in volume,

which can lead to cracking of the coatings in thermal cycling [22,23,24,25]. Therefore, the suppression of phase transformation of $\text{RE}_4\text{Al}_2\text{O}_9$ compounds is of great significance for their applications at high temperature.

In recent years, a new type of ceramics consisting of multi-principal component elements in equal molar or near equal molar but form a single phase, have triggered much attention, which are referred to as high entropy ceramics (HECs) [26,27,28]. These materials exhibit many intriguing properties, such as higher hardness, sluggish grain growth rate, lower thermal conductivity, strong microwave absorption capability and better water-vapor resistance, etc [29,30,31,32,33,34]. More importantly, our previous work indicates that high-entropy ceramics usually possess better high-temperature phase stability than the single-component ceramics owing to the entropy stabilization effect of HECs [35,36], which may provide a new way to improve the phase stability of $\text{RE}_4\text{Al}_2\text{O}_9$ at high temperatures, i.e., through forming high-entropy solid solutions. Consequently, in order to suppress high-temperature phase transformation and reduce thermal conductivity of $\text{RE}_4\text{Al}_2\text{O}_9$ compounds, a novel high-entropy cuspidine-structured rare-earth aluminate solid solution $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ was designed and successfully synthesized in this work. The phase composition, microstructure, phase stability, average linear thermal expansion coefficient, anisotropy of thermal expansion coefficient and thermal conductivity of this new type of high-entropy rare-earth aluminate were investigated synthetically. These fundamental data are of great importance to evaluate the prospect of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ for EBC application. In addition, the mechanisms

for low thermal conductivity and anisotropic thermal expansion will be presented.

2 Experimental procedures

2.1 Synthesis of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders

The starting materials used for synthesizing $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders are as follows: $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (RE= Nd, Sm, Eu, Y and Yb) powders (99.9% purity, Aladdin Biochemical Technology Co., Ltd, Shanghai, China), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ powders (99.9% purity, Aladdin Biochemical Technology Co., Ltd, Shanghai, China) and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, pH=12.5, Beihua Fine Chem. Co., Ltd. Beijing, China).

A co-precipitation method was performed to synthesize $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders. Firstly, $\text{RE}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (RE= Nd, Sm, Eu, Y and Yb) powders were weighted in equal molar ratio and mixed, then dissolved in distilled water to form a clear solution with a concentration of 0.3 mol/L. Separately, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ powders were also dissolved in distilled water to form a clear solution with the same molar concentration and then added into the mixed RENO_3 solution with stirring. The molar ratio of total RE elements and Al is $\text{RE}_{\text{total}}: \text{Al}=2:1$. After that, excess aqueous ammonia was added slowly into the mixed solution with vigorously stirring to obtain gel-like precipitants. The precipitants were then filtered and washed with distilled water for several times to ensure impurity ions (NH_4^+ and NO_3^-) were eliminated before being dried in an oven at 383 K for 12 h. Finally, $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders were synthesized by calcining the precursors at 1873 K for 1 h in a muffle furnace. The calcined products were

ball-milled with agate balls for 20 h and then dried in a vacuum oven at room temperature. Fine-particle powders were obtained by screening the calcined products in a 300 mesh sieve.

2.2 Preparation of bulk $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$

Bulk $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ was prepared by using a spark plasma sintering apparatus (SPS-20T-6-IV, Shanghai Chenhua Science and Technology Co. Ltd, China) at 1923 K for 4 min under a pressure of 30 MPa. Details of the preparation process were reported in our previous work [31,32,36]. After sintering, the surface of the bulk sample was ground by silicon carbide sandpapers to remove the carburized layer.

2.3 Characterization of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders and the sintered compacts

The phase compositions of the as-synthesized powders and the sintered compacts were determined by an X-ray diffractometer (XRD, D8 Advanced, Bruker, Germany) using Cu K_α radiation ($\lambda=1.5406 \text{ \AA}$) with a step size of 0.02° . The scanning rate is $2^\circ/\text{min}$. The lattice parameters of as-synthesized $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ were refined by the Rietveld method (TOPAS, Bruker Corp., Karlsruhe, Germany).

The density of the sintered compacts was measured by Archimedes' method. The investigation of the microstructure and the element distributions of the sintered compacts were performed by using a scanning electron microscope (SEM, Apollo300, CamScan, Cambridge, UK) equipped energy dispersive X-ray spectroscopic system (EDS Inca X-Max 80T, Oxford, UK). Before SEM observation, the samples were polished by silicon carbide sandpapers and then thermally etched at 1673 K for 2 h to

ensure the grain boundary is clear.

The investigation of linear thermal expansion of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at 300-1473 K was performed by an optical dilatometer (Misura ODHT 1600-50, Expert System Solutions, Italy). The as-measured sample is a polished rectangular bar with the size of 3 mm $\times$ 4 mm $\times$ 15 mm. A 45° chamfer was cut at one end of the sample. The anisotropic thermal expansion coefficient of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ was investigated by a powder X-ray diffractometer equipped with isothermal sample heating system (XRD, X'Pert MPD Pro Panalytical Holland). $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders were heated from 300 K to 1473 K at a heating rate of 5 K/min, and held for 5 min to achieve temperature equilibration at 100 K intervals, and then the XRD patterns of the sample at the desired temperatures were recorded with a scanning rate of 1°/min. The lattice parameters of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at different temperatures were refined by the Rietveld method. The volumetric thermal expansion coefficient (α_v) and the linear thermal expansion coefficients along principal axes (α_a , α_b and α_c) were obtained by fitting the lattice parameters versus temperature curves of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$.

Thermal diffusivity of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ was investigated by the laser flash method. The as-measured sample is a disk with the size of Ø 10 mm $\times$ 2 mm. Before the measurement, the surface of the sample was sprayed a layer of graphite to prevent heat radiation from penetrating through it. The heat capacity at constant pressure was calculated by Neumann-Kopp rule using the data of its

constituent oxides (Nd₂O₃, Sm₂O₃, Eu₂O₃, Y₂O₃, Yb₂O₃, and Al₂O₃) [37,38]. Thermal conductivity (κ) was calculated by the following equation [39]:

$$\kappa = D_{th} \cdot C_p \cdot d \quad (1)$$

where κ is thermal conductivity, D_{th} is thermal diffusivity, C_p is heat capacity at constant pressure, and d is bulk density of the sample.

3 Results and discussion

3.1 Phase composition and microstructure

The first step for synthesizing high-entropy rare-earth aluminate is choosing the compatible rare-earth elements that warrant the easy formation of phase-pure solid solution. Generally, there are two criteria for selecting the compatible components of high-entropy materials [36]. Firstly, the difference of the ion radius of the selecting elements is small. Secondly, the single-component phases containing the selected elements possess the same or similar crystal structures. Herein, the cation radius and radius difference of the selecting rare-earth elements for the design of high-entropy rare-earth aluminate together with the space group of the single-component phases containing these rare-earth elements are listed in Table 1 [25]. It can be seen that the radius difference of the selected rare-earth elements is less than 13% and that all the single-component RE₄Al₂O₉ (RE= Nd, Sm, Eu, Y and Yb) possess the same crystal structure, which warrant the easy formation of the phase-pure high-entropy rare-earth aluminate. Fig. 1 exhibits the crystal structure of rare-earth aluminate. The high-entropy (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ has the same crystal structure with those of the single-component RE₄Al₂O₉, which crystallizes in a monoclinic structure

with a space group of $P2_1/c$ and five component elements (Nd, Sm, Eu, Y and Yb) occupy the RE sites evenly and randomly [40].

Fig. 2 shows the XRD pattern of as-synthesized $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders, the data of single-component $\text{RE}_4\text{Al}_2\text{O}_9$ (RE= Nd, Sm, Eu, Y and Yb) obtained from ICDD/JCPDS cards are also exhibited for comparison. Clearly, the as-synthesized powders are phase-pure and only a monoclinic phase was detected, indicating that a solid solution $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is formed. For the single-component $\text{RE}_4\text{Al}_2\text{O}_9$, the diffraction peaks shift to the higher angle direction with the decrease of RE^{3+} radius ($\text{Nd}^{3+} \rightarrow \text{Yb}^{3+}$). While the diffraction peaks of high-entropy $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ are lying in the middle of those of five single-component phases, which proves that five RE^{3+} with different ion radius homogenously occupy the RE site of the solid solution. Rietveld refinement was performed by using TOPAS software to obtain the information about the lattice parameters of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$. The results are presented in Table 2 and compared with the data of the single-component $\text{RE}_4\text{Al}_2\text{O}_9$ (RE= Nd, Sm, Eu, Y and Yb) obtained from ICDD/JCPDS cards. It can be seen that the refined lattice parameters (a , b and c) of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ are larger than those of $\text{Y}_4\text{Al}_2\text{O}_9$ and $\text{Yb}_4\text{Al}_2\text{O}_9$ but smaller than those of $\text{Nd}_4\text{Al}_2\text{O}_9$, $\text{Sm}_4\text{Al}_2\text{O}_9$ and $\text{Eu}_4\text{Al}_2\text{O}_9$. Based on the refined lattice parameters, the theoretical density of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is calculated to be 6.06 g/cm^3 , which is between the data of five single-component phases.

Fig. 3 illustrates the XRD pattern of the as-sintered

(Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ compact. Clearly, the phase composition of the as-sintered compact is unchanged compared with that of the as-synthesized powders, indicating that (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ possesses good thermal stability. Fig. 4 displays the SEM image of the as-sintered (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ compact after thermally etched at 1673 K for 2 h and the corresponding EDS mappings of rare-earth elements (Nd, Sm, Eu, Y and Yb). No pores and cracks can be found from the observation region, indicating that the as-sintered compact has a high relative density. The experimental density of the as-sintered compact measured by Archimedes' method is 6.02 g/cm³ and the corresponding relative density is 99%. It also can be found that the containing rare-earth elements are uniformly distributed in the grains, indicating that (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ is a homogeneous solid solution.

3.2 Phase stability and thermal expansion behavior

The linear thermal expansion curve of (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ measured at 300-1473 K is illustrated in Fig. 5. It is evident that the expansion of bulk (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ increases linearly with the increase of the temperature and no abrupt volume change was found, which indicates that (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ has good phase stability at the measured temperature range. Noting that the single-component Sm₄Al₂O₉ and Eu₄Al₂O₉ exhibit reversible phase transition with abrupt volume change at 1317 K and 1387 K respectively [25]. This phase transition is harmful for the materials applied in the high temperature environment due to the sudden change in volume will reduce the thermal shock

resistance of the materials and cause the cracking of coatings in thermal cycling. Thus, good phase stability of high-entropy $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ renders it more suitable for high temperature applications.

In addition, the thermal expansion versus temperature curve in Fig. 5 can be fitted by using a linear function: $\Delta L/L_0 \times 100\% = 6.96 \times 10^{-6} T(\text{K}) - 0.25$, with a reliability value of $R^2 = 0.999$. The linear thermal expansion coefficient of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is determined in terms of the slope of the curve and calculated to be $6.96 \times 10^{-6} / \text{K}$ at 300-1473 K, which is in between those of $\text{Y}_4\text{Al}_2\text{O}_9$ ($7.37 \times 10^{-6} / \text{K}$) [19] and $\text{Yb}_4\text{Al}_2\text{O}_9$ ($6.27 \times 10^{-6} / \text{K}$) [16], and close to that of the interlayer phase of EBC system, mullite ($5\text{-}7 \times 10^{-6} / \text{K}$) [41].

To investigate the anisotropy of the thermal expansion of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$, the XRD patterns of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders at different temperature were recorded and are exhibited in Fig. 6. It can be seen that there is no phase transformation detected when the temperature increases from 300 K to 1473 K, further proving that $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ has good phase stability at high temperature. While the diffraction peaks of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ gradually shift to the lower angle direction with the increase of temperature, which indicates that the lattice parameters of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ changes when the temperature increases. The lattice parameters of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at different temperature were obtained by fitting the XRD patterns in Fig. 6 according to the Rietveld refinement method. Fig. 7 shows the normalized lattice parameters of

(Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ at 300-1473 K. Clearly, the lattice parameter a , b , c and the unit cell volume V monotonously increase as the temperature increases from 300 K to 1473 K. The volumetric thermal expansion coefficient (α_v), namely, the relative change in volume when the temperature rises by 1 K, is defined by the following equations [42]:

$$\alpha_v = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right) \quad \text{or} \quad V(T) = V_0 \exp \left[\int \alpha_v(T) dT \right] \quad (2),$$

where $\alpha_v(T)$ is the temperature-dependent volumetric thermal expansion coefficient, V_0 is the volume of unit cell at 300 K. $\alpha_v(T)$ tends to be a constant at high temperature and thus the equation (2) can be simplified as :

$$\ln(V / V_0) = \alpha_v (T - T_0) \quad (3).$$

Based on the equation (3), the volumetric thermal expansion coefficient (α_v) of (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ can be obtained by fitting the data in Fig. 7. Moreover, the linear thermal expansion coefficients along three crystallographic directions (α_a , α_b , and α_c) were also calculated in the same way. Table 3 shows the anisotropic thermal expansion coefficients (α_a , α_b , and α_c) and volumetric thermal expansion coefficient (α_v) of (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ together with those of Y₄Al₂O₉ [19]. Clearly, the volumetric thermal expansion coefficient (α_v) of (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ (24.40×10^{-6} /K) is slightly higher than that of Y₄Al₂O₉ (23.37×10^{-6} /K), while the anisotropy of thermal expansion coefficients of (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ is much stronger than that of Y₄Al₂O₉. To obtain an intuitive and complete representation of the anisotropic thermal expansion coefficients of (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉, the variation of thermal expansion

coefficients as a function of crystal orientation is necessary. Fig. 8 exhibits the surface contour of the thermal expansion coefficients of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ and the planar projections of the thermal expansion coefficients on (001), (010), and (100) crystallographic planes. It can be seen that the anisotropy of thermal expansion coefficients of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is clearly illustrated and the anisotropy of thermal expansion coefficients on (010) plane is stronger than those on (001) and (100) planes. The maximum and minimum values of thermal expansion coefficients are $10.60 \times 10^{-6}/\text{K}$ and $4.87 \times 10^{-6}/\text{K}$ (α_{11} and α_{33}), respectively. The strong anisotropy of thermal expansion coefficients of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ can be explained by the crystal structure feature of $\text{RE}_4\text{Al}_2\text{O}_9$. Fig. 9 exhibits the planar projections of the crystal structure of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ on (001), (010), and (100) crystallographic planes. It can be seen that the arrangement of RE atoms along the a and b axes is much denser than that along the c axis. Thus, the fluctuation of the lattice parameters a and b is much stronger than that of the lattice parameter c when the RE^{3+} radius changes, which is demonstrated by the relative change regularity of the lattice parameters of $\text{RE}_4\text{Al}_2\text{O}_9$ compounds. Fig. 10 shows the relative change of the lattice parameters of $\text{RE}_4\text{Al}_2\text{O}_9$ ($\text{RE} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Y}$ and Yb) as a function of RE^{3+} radius, the data were obtained from ICDD/JCPDS cards and are listed in Table 2. As the RE^{3+} radius increase, the relative change of the lattice parameters a and b are much larger than that of the lattice parameter c , which will result in the anisotropy of bonding strength, i.e., the bonds along the a and b axes are weaker than that along the c axis. Quantitatively description of this bonding

anisotropy is accessible by estimating the bond energy of HE $\text{RE}_4\text{Al}_2\text{O}_9$ and $\text{Y}_4\text{Al}_2\text{O}_9$ using a simply theory called chemical bonding theory (CBT). Due to the similarity in crystal structure, the calculation procedure for parameters of all chemical bonds in HE compound is the same as that in $\text{Y}_4\text{Al}_2\text{O}_9$, and for detail description, one may refer to ref. [18]. The chemical parameters for each bond of two materials are listed in Table 4 (Worth noting that the listed bond energies for HE $\text{RE}_4\text{Al}_2\text{O}_9$ are the average ones, since the bond length (l^μ) around different rare earth atom is different). For both materials, the covalency (f_c^μ) and bond energies (U^μ) of Al-O bonds are significantly larger than those of RE-O bonds, demonstrating stronger bonding nature of Al-O tetrahedron. Large bond energy also leads to less contribution of AlO_4 tetrahedron to total thermal expansion, and the chemical environments around RE atoms determine the expansion behavior of HE $\text{RE}_4\text{Al}_2\text{O}_9$. With different RE atoms incorporating in the structure, the bond strength of all RE-O bonds varies accordingly. However, the energy changing for different RE-O bonds is quite anisotropic, e.g. the response of RE1-O3, RE1-O7, RE1-O2, and RE1-O1 is more evident than the rest RE1-O bonds. The spatial configuration of RE1-O polyhedra is shown in Fig. 11(a). Clearly, the bonds with large energy degradation are almost parallel with ab plane, leading to the increase of anisotropy in bonding strength between ab plane and c direction. For other three RE sites listed in Table 4, the same situation is observed, the RE-O bonds along ab plane are disturbed notably than that along c direction. Since the thermal expansion of $\text{RE}_4\text{Al}_2\text{O}_9$ is determine by RE-O bonds, increase of anisotropy of RE-O bonds along different direction will eventually result in the increase of anisotropy in thermal

expansion. In addition, the same variety trend was also found from the Young's modulus of $\text{RE}_4\text{Al}_2\text{O}_9$ compounds. The anisotropy of Young's modulus of $\text{Yb}_4\text{Al}_2\text{O}_9$ is weaker than that of $\text{Y}_4\text{Al}_2\text{O}_9$ due to Yb^{3+} has a smaller radius than Y^{3+} , which also proves that $\text{RE}_4\text{Al}_2\text{O}_9$ with large RE^{3+} radius exhibits the strong anisotropy of bonding strength [16,18].

3.3 Thermal conductivity

Table 5 shows the thermal diffusivity, heat capacity, bulk density and thermal conductivity of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ measured at room temperature. Clearly, the thermal conductivity of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at room temperature is as low as $1.50 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is 55% lower than that of $\text{Y}_4\text{Al}_2\text{O}_9$ ($3.31 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). This value is also much lower than those of other candidate EBC materials, such as Y_2SiO_5 ($1.86 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [43], Yb_2SiO_5 ($2.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [44], $\gamma\text{-Y}_2\text{Si}_2\text{O}_7$ ($4.91 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [42] and $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ ($4.31 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) [45]. The low thermal conductivity of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is likely attributed to the high-entropy effect [28]. For opaque dielectric materials, the major process that leads to a finite thermal conductivity is phonon scattering and the extent of phonon scattering depends on the anharmonicity of the lattice vibrations [46]. Based on the Umklapp phonon-phonon scattering mechanism [47,48]:

$$\kappa_a = \frac{(6\pi^2)^{2/3}}{4\pi^2} \frac{\overline{M}_s^3}{TV^{2/3}\gamma^2} \left(\frac{1}{N^{1/3}} \right) \quad (4)$$

where κ_a is thermal conductivity of acoustic contribution, $\overline{M}$ is average mass, v_s is averaged speed of sound, T is temperature, V is volume per atom, γ is Grüneisen parameter, N is atoms per primitive cell. For $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$, five

rare-earth atoms with different atomic mass and bonding strengths share RE-site in the crystal structure, resulting in the increase of the structural complexity. Correspondingly, the number of atoms per primitive cell (N value) of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ increases and its thermal conductivity decreases. On another hand, point defects scattering is also a dominant process that giving rise to the low thermal conductivity of high-entropy materials. Based on the point defects scattering mechanism [49,50]:

$$\kappa_L = \frac{1}{3} \int_0^{\omega_{\max}} C_s(\omega) v_g(\omega)^2 \tau(\omega) d\omega \quad (5)$$

$$\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi v_p^2 v_g} \left(\sum_i f_i \left(1 - \frac{m_i}{\bar{m}}\right)^2 + \sum_i f_i \left(1 - \frac{r_i}{\bar{r}}\right)^2 \right) \quad (6)$$

where κ_L is lattice thermal conductivity, $C_s(\omega)$ is spectral heat capacity, τ is phonon relaxation time, ω is phonon frequency, v_p is phonon phase velocity, v_g is phonon group velocity, f_i is the fraction of atoms with mass m_i and radius r_i that reside on a site with average mass and radius ($\bar{m}$ and $\bar{r}$), respectively. It can be found from equations (5) and (6) that scattering by point defects arises from the fluctuations of mass and strain within the lattice. For $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$, the server lattice distortion caused by high-entropy effect will result in the increase of the fluctuations of mass and strain within the lattice [51]. This can lead to the intensification of phonon scattering and decrease the thermal conductivity of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$.

For a desirable EBC material, possessing good phase stability from room temperature to the service temperature is essential. Meanwhile, thermal expansion

matches with those of the substrate and the interlayer is also required to minimize the thermal stress and ensure that the coating does not crack in thermal cycling. The investigation on the thermal properties of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ in this work ascertain that $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ exhibits good phase stability at high temperature, close thermal expansion coefficient to that of the interlayer mullite and extremely low thermal conductivity. These results indicate that $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is a promising candidate EBC material of silicon-based structural ceramics.

4 Conclusions

In this work, a novel high-entropy cuspidine-structured rare-earth aluminate ceramic $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ was designed and successfully synthesized. The investigation of the phase composition and the microstructure proves that the synthesized $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is a phase-pure solid solution with uniform component distribution. $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ exhibits good high-temperature phase stability and no phase transition is detected from 300 K to 1473 K. The linear thermal expansion coefficient of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at 300-1473 K is $6.96 \times 10^{-6} / \text{K}$, which is close to that of the interlayer mullite of EBC system. The anisotropy of thermal expansion coefficient of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ is stronger than that of $\text{Y}_4\text{Al}_2\text{O}_9$ due to the anisotropy of bonding strength of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$. The volumetric thermal expansion coefficient and the anisotropic thermal expansion coefficients of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ are $\alpha_v = 24.40 \times 10^{-6} / \text{K}$, $\alpha_a = 10.59 \times 10^{-6} / \text{K}$, $\alpha_b =$

$8.93 \times 10^{-6} / \text{K}$, $\alpha_c = 5.66 \times 10^{-6} / \text{K}$. $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ exhibits low thermal conductivity owing to the intensification of phonon scattering caused by high-entropy effect. The thermal conductivity of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at room temperature is $1.50 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, which is 55% lower than that of $\text{Y}_4\text{Al}_2\text{O}_9$. Good high-temperature phase stability, close thermal expansion coefficient to that of the interlayer mullite and extremely low thermal conductivity of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ make this material promising as candidate EBC material of silicon-based structural ceramics.

Acknowledgements

We acknowledge financial supports from the National Natural Science Foundation of China under grant No. 51672064 and No. 51972089.

References

-
- [1] Klemm H. Silicon nitride for high-temperature applications. *J Am Ceram Soc* 2010, **93**: 1501-1522.
 - [2] Naslain R, Christin R. SiC-matrix composite materials for advanced jet engines. *MRS bull* 2003, **28**: 654-658.
 - [3] Naslain R. Design, preparation and properties of non-oxide CMCs for application in engines and nuclear reactors: an overview. *Compos Sci Technol* 2004, **64**: 155-170.
 - [4] Becher PF, Hsueh CH, Angelini P, *et al.* Toughening Behavior in whisker-reinforced ceramic matrix composites. *J Am Ceram Soc* 1988, **71**: 1050-1061.

-
- [5] Igawa N, Taguchi T, Nozawa T, *et al.* Fabrication of SiC fiber reinforced SiC composite by chemical vapor infiltration for excellent mechanical properties. *J Phys Chem Solids* 2005, **66**: 551-554.
- [6] Jacobson NS. Corrosion of silicon-based ceramics in combustion environments. *J Am Ceram Soc* 1993, **76**: 3-28.
- [7] Smialek JL, Robinson RC, Opila EJ, *et al.* Jacobson, SiC and Si₃N₄ scale volatility under combustor conditions. *Adv Compos Mater* 1999, **8**: 33-45.
- [8] Klemm H, Taut C, Wötting G. Long-term stability of nonoxide ceramics in an oxidative environment at 1500°C. *J Eur Ceram Soc* 2003, **23**: 619-627.
- [9] Tortorelli PF, More KL. Effects of high water-vapor pressure on oxidation of silicon carbide at 1200°C. *J Am Ceram Soc* 2003, **86**: 1249-1255.
- [10] More KL, Tortorelli PF, Walker LR, *et al.* High-temperature stability of SiC-based composites in high-water-vapor-pressure environments. *J Am Ceram Soc* 2003, **86**: 1272-1281.
- [11] Opila EJ. Oxidation and volatilization of silica formers in water vapor. *J Am Ceram Soc* 2003, **86**: 1238-1248.
- [12] Lee KN. Current status of environmental barrier coatings for Si-Based ceramics. *Sur Coat Technol* 2000, **133-134**: 1-7.
- [13] Lee KN, Fox DS, Bansal NP. Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si₃N₄ ceramics. *J Eur Ceram Soc* 2005, **25**: 1705-1715.
- [14] Richards BT, Wadley HNG. Plasma spray deposition of tri-layer environmental barrier coatings. *J Eur Ceram Soc* 2014, **34**: 3069-3083.
- [15] Lee KN, Miller RA. Development and environmental durability of mullite and mullite/YSZ dual layer coatings for SiC and Si₃N₄ ceramics. *Sur Coat Technol* 1996, **86-87**: 142-148.
- [16] Xiang HM, Feng ZH, Li ZP, *et al.* Crystal structure, mechanical and thermal properties of Yb₄Al₂O₉: A combination of experimental and theoretical investigations. *J Eur Ceram Soc* 2017, **37**: 2491-2499.
- [17] Lee KN, Miller RA, Jacobson NS. New generation of plasma-sprayed mullite coatings on silicon-carbide. *J Am Ceram Soc* 1995, **78**: 705-710.
- [18] Zhou YC, Xiang HM, Lu XP, *et al.* Theoretical prediction on mechanical and thermal properties of a promising thermal barrier material: Y₄Al₂O₉. *J Adv Ceram*

-
- 2015, **4**: 83-93.
- [19] Zhou YC, Lu XP, Xiang HM, *et al.* Preparation, mechanical, and thermal properties of a promising thermal barrier material: $\text{Y}_4\text{Al}_2\text{O}_9$. *J Adv Ceram* 2015, **4**: 94-102.
- [20] Morán-Ruiz A, Vidal K, Larrañaga A, *et al.* Characterization of $\text{Ln}_4\text{Al}_2\text{O}_9$ ($\text{Ln}=\text{Y}$, Sm , Eu , Gd , Tb) rare-earth aluminates as novel high-temperature barrier materials. *Ceram Int* 2018, **44**: 8761-8767.
- [21] Lee KN. Environmental barrier coatings for SiC_f/SiC . In: N.P. Bansal, J. Lamon (Eds.), *Ceramic Matrix Composites: Materials, Modeling and Technology*, 1st ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 2015.
- [22] Yamane H, Ogawara K, Omori M, *et al.* Thermal expansion and athermal phase transition of $\text{Y}_4\text{Al}_2\text{O}_9$ ceramics. *J Am Ceram Soc* 1995, **78**: 1230-1232.
- [23] Gervais M, Douy A. Solid phase transformation and melting of the compounds $\text{Ln}_4\text{Al}_2\text{O}_9$ ($\text{Ln}=\text{Gd}$, Dy , Y). *Mater Sci Eng B* 1996, **38**: 118-121.
- [24] Yamane H, Sakamoto T, Kubota S, *et al.* Preparation and phase transition of $\text{Gd}_4(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_9$ solid solutions. *J Mater Sci* 2001, **36**: 307-311.
- [25] Yamane H, Ogawara K, Omori M, *et al.* Phase transition of rare-earth aluminates ($\text{RE}_4\text{Al}_2\text{O}_9$) and rare-earth gallates ($\text{RE}_4\text{Ga}_2\text{O}_9$). *J Am Ceram Soc* 1995, **78**: 2385-2390.
- [26] Rost CM, Sachet E, Borman T, *et al.* Entropy-stabilized oxides. *Nat Commun* 2015, **6**: 8485.
- [27] Chen K, Pei X, Tang L, *et al.* A five-component entropy-stabilized fluorite oxide. *J Eur Ceram Soc* 2018, **38**: 4161-4164.
- [28] Miracle DB, Senkov ON. A critical review of high entropy alloys and related concepts. *Acta Mater* 2017, **122**: 448-511.
- [29] Yan XL, Constantin L, Lu YF, *et al.* $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})\text{C}$ high-entropy ceramics with low thermal conductivity. *J Am Ceram Soc* 2018, **101**: 4486-4491.
- [30] Zhao ZF, Xiang HM, Dai FZ, *et al.* $(\text{La}_{0.2}\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2})_2\text{Zr}_2\text{O}_7$: A novel high-entropy ceramic with low thermal conductivity and sluggish grain growth rate. *J Mater Sci Technol* 2019, **35**: 2647-2651.
- [31] Zhao ZF, Chen H, Xiang HM, *et al.* $(\text{Y}_{0.25}\text{Yb}_{0.25}\text{Er}_{0.25}\text{Lu}_{0.25})_2(\text{Zr}_{0.5}\text{Hf}_{0.5})_2\text{O}_7$: A defective fluorite structured high entropy ceramic with low thermal conductivity and close thermal expansion coefficient to Al_2O_3 . *J Mater Sci Technol* 2019, **39**:

- [32] Zhao ZF, Xiang HM, Dai FZ, *et al.* (La_{0.2}Ce_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2})PO₄: A high-entropy rare-earth phosphate monazite ceramic with low thermal conductivity and good compatibility with Al₂O₃. *J Mater Sci Technol* 2019, **35**: 2892-2896.
- [33] Chen H, Zhao B, Zhao ZF, *et al.* Achieving strong microwave absorption capability and wide absorption bandwidth through a combination of high entropy rare earth silicide carbides/rare earth oxides. *J Mater Sci Technol* 2020, **47**: 216-222.
- [34] Dong Y, Ren K, Lu Y, *et al.* High-entropy environmental barrier coating for the ceramic matrix composites. *J Eur Ceram Soc* 2019, **39**: 2574-2579.
- [35] Zhao ZF, Xiang HM, Dai FZ, *et al.* (TiZrHf)P₂O₇: An equimolar multicomponent or high entropy ceramic with good thermal stability and low thermal conductivity. *J Mater Sci Technol* 2019, **35**: 2227-2231.
- [36] Zhao ZF, Chen H, Xiang HM, *et al.* High-entropy (Y_{0.2}Nd_{0.2}Sm_{0.2}Eu_{0.2}Er_{0.2})AlO₃: A promising thermal/environmental barrier material for oxide/oxide composites. *J Mater Sci Technol* 2020, **47**: 45-51.
- [37] Leitner J, Voňka P, Sedmidubský D. Application of Neumann-Kopp rule for the estimation of heat capacity of mixed oxides. *Thermochim Acta* 2010, **497**: 7-13.
- [38] Barin I. Thermochemical data of pure substances, 3rd ed., *VCH Verlagsgesellschaft mbH, Weinheim, Germany*, 2008.
- [39] Parker WJ, Jenkins RJ, Butler CP. Flash method of determining thermal diffusivity, heat capacity, and thermal conductivity. *J Appl Phys* 1961, **32**: 1679-1984.
- [40] Zhan X, Li Z, Liu B, *et al.* Theoretical prediction of elastic stiffness and minimum lattice thermal conductivity of Y₃Al₅O₁₂, YAlO₃ and Y₄Al₂O₉. *J Am Ceram Soc* 2012, **95**: 1429-1434.
- [41] Schneider H, Fischer RX, Schreuer J. Mullite: crystal structure and related properties. *J Am Ceram Soc* 2015, **98**: 2948-2967.
- [42] Sun ZQ, Zhou YC, Wang JY, *et al.* Thermal property and thermal shock resistance of γ -Y₂Si₂O₇. *J Am Ceram Soc* 2008, **91**: 2623-2629.
- [43] Sun ZQ, Li MS, Zhou YC. Thermal properties of single-phase Y₂SiO₅. *J Eur Ceram Soc* 2009, **29**: 551-557.

-
- [44] Lu MH, Xiang HM, Feng ZH, *et al.* Mechanical and thermal properties of Yb_2SiO_5 : A promising material for T/EBCs applications. *J Am Ceram Soc* 2016, **99**: 1404-1411.
- [45] Wang SB, Lu YR, Chen YX. Synthesis of single-phase $\beta\text{-Yb}_2\text{Si}_2\text{O}_7$ and properties of its sintered bulk. *Int J Appl Ceram Technol* 2015, **12**: 1140-1147.
- [46] Slack GA. Nonmetallic crystals with high thermal conductivity. *J Phys Chem Solids* 1973, **34**: 321-335.
- [47] Slack GA. The thermal conductivity of nonmetallic crystals. *Phys Rev B Solid State* 1979, **34**: 1-71.
- [48] Toberer ES, Zevalkink A, Snyder GJ. Phonon engineering through crystal chemistry. *J Mater Chem* 2011, **21**: 15843-15852.
- [49] Chung JD, Mcgaughey AJH, Kaviany M. Role of phonon dispersion in lattice thermal conductivity modeling. *J Heat Transfer* 2004, **126**: 691-696.
- [50] Klemens PG. The scattering of low-frequency lattice waves by static imperfections. *Proc Phys Soc* 1955, **68**: 1113-1128.
- [51] Dai FZ, Wen B, Sun YJ, *et al.* Theoretical prediction on thermal and mechanical properties of high entropy $(\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{C}$ by deep learning potential. *J Mater Sci Technol* 2020, **43**: 168-174.

Figures and Table captions

Fig. 1 Crystal structure of rare-earth aluminate.

Fig. 2 XRD pattern of as-synthesized $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders together with the data of single-component $\text{RE}_4\text{Al}_2\text{O}_9$ (RE= Nd, Sm, Eu, Y and Yb) obtained from ICDD/JCPDS cards.

Fig. 3 XRD pattern of the as-sintered $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ compact.

Fig. 4 SEM image of the as-sintered $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ compact after thermally etched at 1673 K for 2 h and the corresponding EDS mappings of rare-earth

elements (Nd, Sm, Eu, Y and Yb).

Fig. 5 Linear thermal expansion curve of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ measured at 300-1473 K.

Fig. 6 XRD patterns of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders at different temperatures.

Fig. 7 Normalized lattice parameters of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at 300-1473 K.

Fig. 8 Surface contour of the thermal expansion coefficients of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ and planar projections of the thermal expansion coefficients on (001), (010), and (100) crystallographic planes.

Fig. 9 Planar projections of the crystal structure of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ on (001), (010), and (100) crystallographic planes.

Fig. 10 Relative change of the lattice parameters of $\text{RE}_4\text{Al}_2\text{O}_9$ (RE= Nd, Sm, Eu, Y and Yb) as a function of RE^{3+} radius.

Fig. 11 Spatial configuration of RE-O polyhedra for (a) RE1, (b) RE2, (c) RE3, and (d) RE4 site, respectively.

Table 1 Space group, cation radius and radius difference of $RE_4Al_2O_9$ for design of high-entropy rare-earth aluminates (The data are obtained from the database of Materials Studio program, ©Accelrys Inc., San Diego, USA, 2014).

Space group		Rare-earth elements	Cation radius (Å)	Radius difference (%)
$RE_4Al_2O_9$	$P2_1/c$	Nd	0.98	12.64
		Sm	0.96	10.34
		Eu	0.95	9.20
		Y	0.90	3.45
		Yb	0.87	0

Table 2 Refined lattice parameters, relative change of lattice parameters and theoretical density of high-entropy (Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})₄Al₂O₉ together with those of the single-component RE₄Al₂O₉ (RE= Nd, Sm, Eu, Y and Yb) obtained from ICDD/JCPDS cards.

Phase	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\Delta a/a_{Yb}$ (%)	$\Delta b/b_{Yb}$ (%)	$\Delta c/c_{Yb}$ (%)	$\beta(^{\circ})$	<i>d</i> (g/cm ³)
HE RE ₄ Al ₂ O ₉	7.511	10.573	11.172	3.20	2.55	1.20	109.1	6.06
Nd ₄ Al ₂ O ₉	7.725	10.846	11.306	6.14	5.20	2.41	109.3	6.63
Sm ₄ Al ₂ O ₉	7.520	10.700	11.190	3.33	3.78	1.36	108.9	6.99
Eu ₄ Al ₂ O ₉	7.533	10.696	11.180	3.50	3.74	1.27	108.8	6.76
Y ₄ Al ₂ O ₉	7.379	10.469	11.116	1.39	1.54	0.69	108.6	5.28
Yb ₄ Al ₂ O ₉	7.278	10.310	11.040	0	0	0	108.3	8.30

Table 3 Anisotropic thermal expansion coefficients (α_a , α_b , and α_c) and volumetric thermal expansion coefficient (α_v) of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ together with those of $\text{Y}_4\text{Al}_2\text{O}_9$.

Compounds	α_a (10^{-6} /K)	α_b (10^{-6} /K)	α_c (10^{-6} /K)	α_v (10^{-6} /K)
HE $\text{RE}_4\text{Al}_2\text{O}_9$	10.59	8.93	5.66	24.40
$\text{Y}_4\text{Al}_2\text{O}_9$	7.34	7.54	7.61	23.37

Table 4 Chemical parameters of each bond for RE₄Al₂O₉ and Y₄Al₂O₉ by chemical bond theory.

Bond	Y ₄ Al ₂ O ₉			HE RE ₄ Al ₂ O ₉		
	l^μ (Å)	f_c^μ	U^μ (kJ·mol ⁻¹)	l^μ (Å)	f_c^μ	U^μ (kJ·mol ⁻¹)
RE1-O3	2.0622	0.12	930	2.0931	0.13	919
RE1-O8	2.0917	0.12	999	2.0967	0.13	997
RE1-O7	2.2460	0.22	950	2.2778	0.22	940
RE1-O2	2.3991	0.12	897	2.4330	0.12	887
RE1-O6	2.5124	0.12	865	2.5247	0.12	862
RE1-O1	2.6015	0.12	841	2.6395	0.12	831
RE1-O5	2.8560	0.11	779	2.8723	0.12	775
RE2-O2	1.9238	0.18	1306	1.9509	0.18	1292
RE2-O3	2.1103	0.16	1116	2.1377	0.16	1105
RE2-O9	2.2430	0.17	1162	2.2482	0.17	1160
RE2-O1	2.3228	0.29	1130	2.3519	0.29	1119
RE2-O4	2.4799	0.16	1074	2.4936	0.16	1069
RE2-O7	2.5044	0.16	1065	2.5410	0.16	1053
RE3-O8	2.1966	0.12	962	2.2225	0.12	953
RE3-O2	2.2160	0.12	955	2.2279	0.12	951
RE3-O4	2.2762	0.12	935	2.3098	0.12	925
RE3-O8	2.4375	0.12	886	2.4467	0.12	884
RE3-O5	2.5367	0.12	858	2.5473	0.12	855
RE3-O6	2.5893	0.12	844	2.6255	0.12	835
RE3-O9	2.7703	0.11	799	2.8103	0.12	789
RE4-O3	2.1601	0.12	974	2.1866	0.12	965
RE4-O6	2.2073	0.12	958	2.2223	0.12	948
RE4-O9	2.2141	0.12	956	2.2381	0.12	953
RE4-O9	2.2888	0.12	931	2.3177	0.12	922
RE4-O8	2.4787	0.12	874	2.5148	0.12	864
RE4-O1	2.5418	0.12	857	2.5544	0.12	853
RE4-O7	2.7460	0.11	804	2.7523	0.12	803
Al1-O4	1.7267	0.57	2297	1.7314	0.58	2290
Al1-O3	1.8286	0.35	2097	1.8457	0.35	2082
Al1-O5	1.8338	0.39	2275	1.8644	0.39	2246
Al1-O2	1.9883	0.38	2146	1.9975	0.38	2136
Al2-O6	1.5632	0.41	2539	1.5703	0.41	2529

Al2-O5	1.6917	0.40	2407	1.7201	0.40	2377
Al2-O7	1.7978	0.39	2307	1.8114	0.39	2292
Al2-O1	1.8279	0.39	2280	1.8348	0.39	2272

Table 5 Thermal diffusivity (D_{th}), heat capacity (C_p), bulk density (d) and thermal conductivity (κ) of $(Nd_{0.2}Sm_{0.2}Eu_{0.2}Y_{0.2}Yb_{0.2})_4Al_2O_9$ measured at room temperature.

D_{th} (mm ² /s)	C_p (J·mol ⁻¹ ·K ⁻¹)	d (g/cm ³)	κ (W·m ⁻¹ ·K ⁻¹)
0.62	306.92	6.02	1.50

Fig. 1 Crystal structure of rare-earth aluminate.

Fig. 2 XRD pattern of as-synthesized $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders together with the data of single-component $\text{RE}_4\text{Al}_2\text{O}_9$ (RE= Nd, Sm, Eu, Y and Yb) obtained from ICDD/JCPDS cards.

Fig. 3 XRD pattern of the as-sintered $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ compact.

Fig. 4 SEM image of the as-sintered $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ compact after thermally etched at 1673 K for 2 h and the corresponding EDS mappings of rare-earth elements (Nd, Sm, Eu, Y and Yb).

Fig. 5 Linear thermal expansion curve of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ measured at 300-1473 K.

Fig. 6 XRD patterns of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ powders at different temperatures.

Fig. 7 Normalized lattice parameters of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ at 300-1473 K.

Fig. 8 Surface contour of the thermal expansion coefficients of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ and planar projections of the thermal expansion coefficients on (001), (010), and (100) crystallographic planes.

Fig. 9 Planar projections of the crystal structure of $(\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Eu}_{0.2}\text{Y}_{0.2}\text{Yb}_{0.2})_4\text{Al}_2\text{O}_9$ on (001), (010), and (100) crystallographic planes.

Fig. 10 Relative change of the lattice parameters of $\text{RE}_4\text{Al}_2\text{O}_9$ (RE= Nd, Sm, Eu, Y and Yb) as a function of RE^{3+} radius.

Fig. 11 Spatial configuration of RE-O polyhedra for (a) RE1, (b) RE2, (c) RE3, and (d) RE4 site, respectively.