A multicomponent \( \gamma \)-type (Gd\(_{1/6}\)Tb\(_{1/6}\)Dy\(_{1/6}\)Tm\(_{1/6}\)Yb\(_{1/6}\)Lu\(_{1/6}\))\(_2\)Si\(_2\)O\(_7\) disilicate with outstanding thermal stability

Luchao Sun\(^a\), Yixiu Lue\(^a\), Xiaomin Ren\(^a,b\), Zenghua Gao\(^c\), Tiefeng Du\(^a\), Zhen Wu\(^a\) and Jingyang Wang\(^a\)

\(^a\)Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, People’s Republic of China; \(^b\)School of Materials Science and Engineering, University of Science and Technology of China, Shenyang, People’s Republic of China; \(^c\)Aerospace Special Materials and Processing Technology Institute, Beijing, People’s Republic of China

ABSTRACT
A multicomponent rare-earth disilicate (Gd\(_{1/6}\)Tb\(_{1/6}\)Dy\(_{1/6}\)Tm\(_{1/6}\)Yb\(_{1/6}\)Lu\(_{1/6}\))\(_2\)Si\(_2\)O\(_7\) has been designed and successfully synthesized following the strategy of high entropy engineering. The as-prepared single-phase 6RE-disilicate possesses a new \( \gamma \)-type crystal structure (monoclinic, \( P2_1/c \)) beyond the \( \alpha \), \( \beta \) and \( \delta \)-type parent structures of six single RE disilicates. Six-species RE cations are homogeneously distributed on RE lattice sites and our multicomponent disilicate demonstrates outstanding thermal stability from room temperature up to around 1900°C. This work extends the knowledge of strategic multicomponent modification of complex ceramics with extremely high phase stability.

IMPACT STATEMENT
The first multicomponent \( \gamma \)-type RE\(_2\)Si\(_2\)O\(_7\), (Gd\(_{1/6}\)Tb\(_{1/6}\)Dy\(_{1/6}\)Tm\(_{1/6}\)Yb\(_{1/6}\)Lu\(_{1/6}\))\(_2\)Si\(_2\)O\(_7\) with outstanding phase stability is developed. It presents the possibility to design complex oxide through the ‘one-from-none’ strategy.

Introduction
Recently, high entropy alloys (HEAs), a new class of materials consisting of multi-principal elements in equal molar or near-equal molar percent but form a single-phase solid solution, has attracted much interest [1,2]. The multicomponent modification was exploited by encompassing four or more principal elements in equiatomic or near-equaiatomic proportions into a single solid solution lattice with a random distribution. In an HEA, the configurational entropy is intentionally used as the driving force to stabilize solid solution alloys with a maximum value of \( S = R \ln N \), where \( N \) is the number of equimolar components and \( R \) is the gas constant [3,4]. At the early ages, studies have been mostly centered on metallic HEAs with simple structures, e.g. face-centered cubic, body-centered cubic and hexagonal close packing crystal structures [5–7]. Most recently, Rost et al. pioneered applying the high entropy concept to ceramic materials and successfully fabricated an entropy-stabilized single-phase rock-salt oxide [8]. After that, several high-entropy ceramics, including high-entropy oxides [9–11], metal diborides [12], carbides [13–18], nitride [19], and silicide [20] have been reported. High-entropy materials generally display interesting mechanical and physical properties, such as higher strength/hardness, high structural stability, superconductivity and colossal dielectric constant [3,21]. These successful explorations demonstrate that the entropy engineering is a particularly effective approach for the design and optimization of advanced ceramic materials.

Inspired by the impressive progress of high entropy engineering, we herein extend the strategy to developing
multicomponent rare earth disilicates with extremely high phase stability. RE-disilicates (RE$_2$Si$_2$O$_7$) are showing promising prospect for multifunctional thermal and environmental barrier coating (TEBC) application due to their matched thermal expansion coefficients with the silicon-based substrates, low thermal conductivity and excellent corrosion resistance in harsh combustion environments [22]. Nevertheless, phase instability of RE$_2$Si$_2$O$_7$ at elevated temperatures, governed by their abundant phase transformation mechanisms, is a well-acknowledged challenge that seriously restricts their engineering applications. It has been reported that RE$_2$Si$_2$O$_7$ show seven polymorphs and, in fact, all RE$_2$Si$_2$O$_7$ except for $\beta$-Yb$_2$Si$_2$O$_7$ and $\beta$-Lu$_2$Si$_2$O$_7$, undergo phase transformation with temperature variations. In this respect, we hope that the high-entropy engineering might be helpful to improve the phase stability of RE-disilicates and to promote their high-temperature performance as environmental barrier coating. Meanwhile, previous works have demonstrated that high entropy or multi-principal element rare-earth silicates are showing some balanced optimal or even extraordinarily enhanced properties compared with those single principal element disilicates, which also heralds some exciting opportunities through high entropy engineering [22,23].

In this study, a multicomponent $\gamma$-type (Gd$_{1/6}$Tb$_{1/6}$ Dy$_{1/6}$Tm$_{1/6}$Yb$_{1/6}$Lu$_{1/6}$)$_2$Si$_2$O$_7$ disilicate (hereinafter referred to as (6RE$_{1/6}$)$_2$Si$_2$O$_7$ for brevity) was designed and synthesized. The crystal structure, microstructure, and high-temperature phase stability of as-prepared (6RE$_{1/6}$)$_2$Si$_2$O$_7$ were investigated through XRD, SEM, TEM, EDS and TG/DTA methods. The crystal structure and high-temperature phase stability of the as-prepared material were investigated in detail. Furthermore, the possible mechanism of the phase formation and phase stability of (6RE$_{1/6}$)$_2$Si$_2$O$_7$ are highlighted and discussed.

**Materials and methods**

Commercially available powders, RE$_2$O$_3$ (RE = Gd, Dy, Tm, Yb and Lu), TbzO$_7$ (Rear-Chem. Hi-Tech. Co., Ltd., Huizhou, China) and SiO$_2$ (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were used to synthesize (Gd$_{1/6}$Tb$_{1/6}$Dy$_{1/6}$Tm$_{1/6}$Yb$_{1/6}$Lu$_{1/6}$)$_2$Si$_2$O$_7$. The powders were mixed according to the stoichiometry of (6RE$_{1/6}$)$_2$Si$_2$O$_7$ and then ball milled 24h in a Si$_3$N$_4$ jar, with Si$_3$N$_4$ balls and ethanol as media. The obtained powders were synthesized at 1550°C for 6h to get (6RE$_{1/6}$)$_2$Si$_2$O$_7$. For bulk materials, the as-synthesized (6RE$_{1/6}$)$_2$Si$_2$O$_7$ powders were placed in a BN-coated graphite mold and hot pressed at 1800°C for 2h under a pressure of 30 MPa. The phase composition of (6RE$_{1/6}$)$_2$Si$_2$O$_7$ was determined using an X-ray diffractometer (D/Max-2400, Rigaku, Tokyo, Japan). Rietveld refinement method was employed for the crystal structure analysis using the General Structural Analysis System (GSAS) program [24,25]. Microstructures of bulk samples were observed with a scanning electron microscope (SUPRA 55, Zeiss, Oberkochen, Germany) equipped with an electron-dispersive spectrometer (EDS). Atomic occupations were characterized by a double aberration-corrected electron microscope with an energy dispersive X-ray spectrometer (Thenis Titan G2 cubed 60-300, FEI, Hillsboro, USA). A thermogravimetry/differential thermal analysis (TG/DTA) device (STA 449 F3, NETZSCH, Selb, Germany) was employed to measure the TG-DTA curve of (6RE$_{1/6}$)$_2$Si$_2$O$_7$ from room temperature to 1630°C in helium atmosphere. The melting point was measured by a self-developed melting point testing system equipped with an infrared high precision thermometer under the protection of argon atmosphere.

**Results and discussion**

The XRD pattern of (6RE$_{1/6}$)$_2$Si$_2$O$_7$ powders is shown in Figure 1(a). All the detected peaks match with those of $\gamma$-type Y$_2$Si$_2$O$_7$ (PDF#42-0167), illustrating that (6RE$_{1/6}$)$_2$Si$_2$O$_7$ is a pure and single-crystalline disilicate with $\gamma$-type structure. XRD peak positions of the single principal element RE$_2$Si$_2$O$_7$ are also presented here for reference. Interestingly and surprisingly, none of these single principal element parental disilicates shows $\gamma$-type structure at ambient pressure [26–28]. Specifically, Gd$_2$Si$_2$O$_7$, Tb$_2$Si$_2$O$_7$ and Dy$_2$Si$_2$O$_7$ possess $\alpha$-type as low-temperature structure and $\delta$-type as high-temperature structure; Tm$_2$Si$_2$O$_7$ exhibits $\alpha$-type as low-temperature structure and $\beta$-type as high-temperature structure; while Yb$_2$Si$_2$O$_7$ and Lu$_2$Si$_2$O$_7$ only have the $\beta$-type structure [27]. It should be pointed out that, unstable $\gamma$-type structures for Tm$_2$Si$_2$O$_7$, Yb$_2$Si$_2$O$_7$ and Lu$_2$Si$_2$O$_7$ were observed under a pressure of 40 kbar [26]. To the best of our knowledge, this ‘one-from-none’ phase formation phenomenon, in terms of polymorphic crystal structure, is a brand-new discovery in the design of multicomponent or high entropy ceramics, and provides new wisdom in the fabrication and property optimization of complex ceramics.

To further confirm the formation of the novel $\gamma$-type phase, we carried out the Rietveld refinement of XRD pattern for (6RE$_{1/6}$)$_2$Si$_2$O$_7$ powders using General Structural Analysis System (GSAS) program. The crystal structure of $\gamma$-Y$_2$Si$_2$O$_7$ (monoclinic, P2$_1$/c) was adopted as the starting structural model [28]. Rietveld refinement profiles are schematically shown in Figure 1(b)
Figure 1. (a) XRD pattern of (Gd1/6Tb1/6Dy1/6Tm1/6Yb1/6Lu1/6)2Si2O7, along with the standard X-Ray diffraction patterns of RE2Si2O7 (RE = Y, Gd, Tb, Dy, Tm, Yb and Lu) and (b) Rietveld refinement of XRD pattern for (Gd1/6Tb1/6Dy1/6Tm1/6Yb1/6Lu1/6)2Si2O7.

Table 1. Refined lattice parameters from the XRD Rietveld analysis of (Gd1/6Tb1/6Dy1/6Tm1/6Yb1/6Lu1/6)2Si2O7, in comparison with data of single principal element RE2Si2O7.

| Compound | Structure | Space group | a (Å) | b (Å) | c (Å) | β (°) |
|----------|-----------|-------------|-------|-------|-------|-------|
| γ-(6RE1/6)2Si2O7 | monoclinic | P2₁/c | 4.683 | 10.83 | 5.572 | 95.98 |
| γ-Y2Si2O7 [28] | monoclinic | P2₁/c | 4.688 | 10.84 | 5.582 | 96.03 |
| δ-Gd2Si2O7 [27] | orthorhombic | Pna2₁ | 13.87 | 5.053 | 8.301 | 90.00 |
| δ-Tb2Si2O7 [27] | orthorhombic | Pna2₁ | 13.80 | 5.036 | 8.200 | 90.00 |
| δ-Dy2Si2O7 [27] | orthorhombic | Pna2₁ | 13.73 | 5.030 | 8.205 | 90.00 |
| α-Gd2Si2O7 [27] | triclinic | P₁ | 6.624 | 6.679 | 12.13 | 89.79 |
| α-Tb2Si2O7 [27] | triclinic | P₁ | 6.623 | 6.684 | 12.10 | 89.85 |
| α-Dy2Si2O7 [27] | triclinic | P₁ | 6.639 | 6.691 | 12.15 | 89.81 |
| β-Tm2Si2O7 [27] | monoclinic | C2/m | 6.818 | 9.104 | 4.679 | 101.8 |
| β-Yb2Si2O7 [27] | monoclinic | C2/m | 6.789 | 9.067 | 4.681 | 101.8 |
| β-Lu2Si2O7 [27] | monoclinic | C2/m | 6.760 | 9.051 | 4.685 | 101.9 |

with R-factors of Rp = 4.79% and Rwp = 5.82%. The refined lattice parameters of (6RE1/6)2Si2O7 are listed in Table 1, together with the data of those single principal element RE2Si2O7 for comparison. It is indicated that (6RE1/6)2Si2O7 crystallizes in a monoclinic cell (space group P2₁/c) with lattice parameters a = 4.683 Å, b = 10.83 Å, c = 5.572 Å and β = 95.98°. These results clearly demonstrate that the as-prepared (6RE1/6)2Si2O7 is isostructural with γ-type Y2Si2O7 and distinctly differs from those single principal element RE2Si2O7 (RE = Gd, Tb, Dy, Tm, Yb and Lu) reported with the α-, β- or δ-type structures.

In the original concept, the notion of ‘high entropy’ was derived from the configurational entropy of $S = R \ln N$ for a N-component system, which implies that all the elements are present in an approximately random solid solution phase and any material that is not homogeneous or that forms multiple phases is not a high-entropy material [5]; thus, the search for single-phase solid solutions has come to strongly emphasized in the field of high-entropy materials. To address this issue, a representative composition and microstructural characterization of the bulk multicomponent RE-disilicate was carried out and the results are presented in Figure 2. Figure 2(a) presents the SEM images of the sample surface with corresponding EDS mapping. We can see that (6RE1/6)2Si2O7 possesses a dense microstructure with quite little porosity, while the elemental mapping results confirm the homogeneous distribution of elements in this ceramic. Furthermore, aberration-corrected scanning transmission electron microscopy (STEM), which enable the synergistic characterization of materials at the atomic level, was also employed to characterize the phase constitution at the atomic scale here. Figure 2(b) presents the STEM high-angle annular dark-field (HAADF) images and corresponding selected compositional maps from EDS for (6RE1/6)2Si2O7, providing a visual and direct observation of the compositional homogeneity at the nanoscale.

The previous findings not only confirm the regenerated single-phase γ-type structure of (6RE1/6)2Si2O7, but also provide convincing evidence of the approximately random elements distribution in this solid solution. Herein, we notice that the underlying ‘one-from-none’ phase selection mechanism of this novel multicomponent γ-phase RE-disilicate, is still worth further discussion.
First, for a multicomponent material, the mixing configurational entropy $\Delta S_{\text{mix}}$ is determined as:

$$\Delta S_{\text{mix}} = -R \sum_{i=1}^{N} c_i \ln c_i,$$

where $R$ is the gas constant, $n$ is the cation species number and $c_i$ is the atomic percentage. The ideal maximum $\Delta S_{\text{mix}} = -R \ln N$ is reached at equicomposition $c_i = 1/N$ for each $i$ [4,8]. So, the equimolar six-species RE cations in $(\text{6RE}1/6)_{2}\text{Si}_2\text{O}_7$ will help to increase the mixing configurational entropy as well as to enhance the stability of the $\gamma$-phase RE-disilicate. At the same time, the average RE$^{3+}$ cation radius and its neighboring coordination with oxygen atom, as well as the compound formation enthalpy may also influence the phase determination in multicomponent or high entropy engineering process, as proposed in recent works [29,30]. These mechanisms may coordinatively affect the phase stability and as an exciting result, a new stable multicomponent phase is fabricated. As mentioned above, the RE-disilicate group possesses extensive polymorphism, most of which are characterized to show complex and low-symmetrical crystals. For example, in Table 1, the crystal structures of $\alpha$-, $\beta$-, $\gamma$-, and $\delta$-type RE-disilicates belong to space group $P\bar{1}$-$P1$, $C2/m$, $P2_1/c$, and $Pna2_1$, respectively. All these crystals consist of isolated $\text{Si}_2\text{O}_7$ double tetrahedra and $(\text{REO}_n)$ polyhedron and the major difference of these polymorphs comes from the geometric arrangement of $\text{Si}_2\text{O}_7$ tetrahedra and $(\text{REO}_n)$ polyhedron. These polymorphs further result in the low phase transformation barrier and then abundant phase transformation in RE-disilicates, which crucially restricts their applications and has long been regarded as a critical challenge. On the other hand, the discrepancies among these polymorphic structures are much smaller compared with those in traditional high-entropy alloys (in FCC, BCC and HCP structure) and consequently, provide RE$_2$Si$_2$O$_7$ disilicates a typical and interesting model with diverse possibilities in connection with high entropy engineering [27].

During the formation of $(\text{6RE}1/6)_{2}\text{Si}_2\text{O}_7$, the change in the local cation size (RE$^{3+}$) will modify the atomic size misfit and vary the cation-oxygen distances in $(\text{REO}_n)$ polyhedron, which will in turn influence the Si–O bonds in $\text{Si}_2\text{O}_7$ tetrahedra, and finally affect the coordination geometry and phase selection.

Considering the potential high-temperature TEBE application of RE-disilicates, it is essential to evaluate the high-temperature stability of this novel material. The TG/DTA curves of $(\text{6RE}1/6)_{2}\text{Si}_2\text{O}_7$ from room
Figure 3. (a) TG/DTA plots of \((\text{Gd}_{1/6}\text{Tb}_{1/6}\text{Dy}_{1/6}\text{Tm}_{1/6}\text{Yb}_{1/6}\text{Lu}_{1/6})_2\text{Si}_2\text{O}_7\) and (b) XRD patterns of specimens after calcined at 1800 and 1900°C for 2 h.

Figure 4. Schematics of the polymorphic transformation temperatures and melting points of \(\text{RE}_2\text{Si}_2\text{O}_7\) disilicates.

Temperature to 1630°C in flowing helium are plotted in Figure 3(a). The DTA curve shows no obvious exothermic or endothermic peaks and the TG curve reveals no intense weight change, which indicates that there was no decomposition or phase transition within the testing temperature range. To estimate the thermal stability of \((\text{6RE}_{1/6})_2\text{Si}_2\text{O}_7\) at even higher temperatures, we further heated the sample at 1800 and 1900°C for 2 h. The XRD patterns of samples after calcined are presented in Figure 3(b). It is seen that all the detected peaks could be indexed to the diffraction data of \(\gamma\)-type \(\text{Y}_2\text{Si}_2\text{O}_7\) (PDF#42-0167), suggesting there was no polycrystalline transformation for \((\text{6RE}_{1/6})_2\text{Si}_2\text{O}_7\) even after annealed at 1800 and 1900°C. These results validate the excellent thermal stability of the present multicomponent \((\text{6RE}_{1/6})_2\text{Si}_2\text{O}_7\).

Melting point was determined by a self-developed melting point testing system to quantitatively evaluate the high-temperature stability of this newly discovered \((\text{6RE}_{1/6})_2\text{Si}_2\text{O}_7\). In Figure 4 we collected the polymorphs and the transition temperatures of RE-disilicates according to [27,31]. The upper ends of these columns represent the melting points of \(\text{RE}_2\text{Si}_2\text{O}_7\), corresponding to the higher values reported in [27,31]. It should be noticed that some of the melting points plotted here was measured by Pt 10% Rh-Pt thermocouple, which will lead to certain deviation in the present comparison. The results show that \((\text{6RE}_{1/6})_2\text{Si}_2\text{O}_7\) begins to melt at temperatures about 1907–1935°C, which are obviously higher than those of single principal element \(\text{RE}_2\text{Si}_2\text{O}_7\). That is to say, \((\text{6RE}_{1/6})_2\text{Si}_2\text{O}_7\) demonstrates the highest melting point among all documented \(\text{RE}_2\text{Si}_2\text{O}_7\). Moreover, seven polymorphic forms (\(\alpha, \beta, \gamma, \delta, A, G\) and \(F\)) could be observed in the disilicate groups. Explorations of the polymorphisms have reached one emerging consensus that phase transitions in \(\text{RE}_2\text{Si}_2\text{O}_7\) are closely related to the ionic radius or the electronic configurations of \(\text{RE}^{3+}\). Most \(\text{RE}_2\text{Si}_2\text{O}_7\) exhibits two or more polymorphic structures upon temperature variation, except for \(\text{Lu}_2\text{Si}_2\text{O}_7\) and \(\text{Yb}_2\text{Si}_2\text{O}_7\), which only possess type \(\beta\) structure from
room temperature to melting points [26,27]. The as-prepared \((6\text{RE})_{1/6}\gamma_3\text{Si}_2\text{O}_7\) is, up to now, the only discovered \(\gamma\)-type disilicate that could maintain phase stability from room temperature to melting point. These results demonstrate the significant effects of multicomponent RE element modification that could contribute to the phase selection control and phase stability optimization in RE-disilicates.

**Conclusions**

In this work, a novel \(\gamma\)-type \((\text{Gd}_{1/6}\text{ Tb}_{1/6}\text{ Dy}_{1/6}\text{ Tm}_{1/6}\text{ Yb}_{1/6}\text{ Lu}_{1/6})_2\text{Si}_2\text{O}_7\) disilicate was designed and synthesized following the high entropy engineering concept. The as-obtained material is a single \(\gamma\)-phase \(\text{RE}_2\text{Si}_2\text{O}_7\) with a monoclinic structure \((P2_1/c)\) and homogeneous chemical composition distribution exhibiting structural stability up to 1900°C, which is highly promising for TEBC applications. The outstanding thermal stability of the as synthesized \((6\text{RE})_{1/6}\gamma_3\text{Si}_2\text{O}_7\) disilicate demonstrates the impressive effect of multicomponent design strategy in driving the phase selection and phase stabilization in RE-disilicates. Furthermore, we observed a brand-new ‘one-from-none’ high entropy engineering approach, in terms of polycrystalline structure, for the first time. We expect that this work could extend the knowledge of phase formation mechanism for multicomponent ceramics and provide an inspiring opportunity to the design and exploration of complex ceramics with extreme high thermal stability.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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