Theoretical and experimental investigation of Xenotime-type rare earth phosphate $\text{REPO}_4$ (RE = Lu, Yb, Er, Y and Sc) for potential environmental barrier coating applications

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The mechanical and thermophysical properties of Xenotime-type $\text{REPO}_4$ (RE = Lu, Yb, Er, Y and Sc) have been theoretically and experimentally investigated for a potential environmental barrier coating (EBC) topcoat application. The results show that the current studied $\text{REPO}_4$ exhibits a quasi-ductile property, suggesting a potential long life expectancy of its made coatings. Further, from the study of underlying parameters governing thermophysical properties of a ceramic, low thermal expansion coefficients (TECs) and low thermal conductivities cannot be achieved simultaneously, due to mutual exclusive nature of above two parameters. $\text{REPO}_4$ has been unveiled to have rather small TECs, attributing partly to its weak lattice anharmonicity, and is thus well-matched with silicon carbide based ceramic matrix composites. Last, the current investigated $\text{REPO}_4$ exhibits very good high-temperature water vapor corrosion resistance, excellent calcium-magnesium aluminosilicates (CMAS) resistance as well as excellent chemical compatibility with silicon bond coats at elevated temperatures. Therefore, the Xenotime-type rare earth phosphates are a promising EBC topcoat material.

In order to achieve a higher thermal efficiency, according to Carnot Cycle, there is endless driving force to increase the inlet temperature of advanced gas turbines. With the increase of operation temperatures, it of course imposes more thermal loads to hot-section components, and hence makes the thermal environment more deteriorate and thus severely challenges corresponding materials. Unfortunately, the conventional nickel based superalloys cannot survive these demanding environments, and silicon carbide based ceramic matrix composites (CMCs) are a promising candidate to replace those superalloys due to a combination of superior properties such as: superior high-temperature mechanical properties, excellent oxidation/thermal shock resistances, high reliability and damage tolerance, low densities, as well as their excellent high temperature stability, which is capable of surviving temperatures higher than 1,400 °C, a temperature well above superalloy’s upper limit. However, one fatal drawback of silicon carbide based CMCs as a gas turbine hot-section component is that they tend to react with high-temperature water vapor, a byproduct of fuel combustion, which results in a rapid recession of CMCs and thus cannot satisfy the reliability and durability criteria for aero-engine application. In this sense, the prevention and protection of silicon carbide based CMCs in high-temperature combustion gases that are both oxidative and rich in water vapor is the core and bottleneck technology.

In order to address above problems, there are mainly two strategies. One is to develop a more oxidation and water–vapor resistant CMCs, such as to employ an oxidation and water vapor-resistant compounds to modify both interphase and matrix of CMCs. This work is still under way. The other strategy is more direct and open.
simple, that is to employ a so-called environmental barrier coating, EBC, to physically isolate the harmful
combustion gases and CMC components. Despite of different functions, EBC is rather similar to thermal
barrier coating (TBC), the main function of latter is to provide a thermal insulation so as to increase working
temperature of gas turbines. Similar to TBC, EBC has at least two layers, which are bond coat and top coat. The
main function of EBC bond coat is to provide sufficient adhesion and oxidation resistance, and silicon is the
common choice in the state-of-art. The problem of Si bond coat is poor oxidation resistance and limited
temperature capability restrained by its melting point, which is around 1,410 °C. To address these issues, a haf-
nium oxide (HfO2) modified Si bond coat is proposed to improve its oxidation resistance by forming a HfSiO4
phase. Meanwhile, a rare earth silicide compound has been proposed as a high-temperature capable bond
catóde by a U.S. patent.

On the other hand, as EBC top coats directly contacts with combustion gases, their main function is to
improve environmental durability. That is to say, EBC top coats have to be both water vapor and calcium-
magnesium aluminosilicates (CMAS) resistant. In addition, as EBC is a prime reliant coating, which indicates
its failure could perhaps lead to a catastrophic consequence, the reliability and durability are of primary
concern. To ensure long durability and good reliability, a low stress level of EBC coating system is mandatory.
In this regard, the thermal expansion coefficient (TEC) matching between top coat and substrate CMCs is a
top priority. A larger TEC of top coats compared to CMC substrates tend to generate tensile stress, which drives
it to form mud cracks during thermal cycling. These mud cracks allow hot corrosive combustion gases directly
attack bond coats or CMC substrates, leading to their rapid failure. Besides, a good phase stability, low elastic
modulus and good sintering resistance of top coats are all favored to produce low stress levels and thus a good
lifespan of relevant EBCs.

To date, there are three generations of EBC top coats developed, which are the first generation mullite (i.e. 
Al2O3·SiO2 oxide mixtures), the second generation BSAS (i.e. BaO·SrO·Al2O3·SiO2 oxide mixtures) and the
timeless rare earth disilicates (RE2Si2O7) or monsilicates (RE2SiO5) with smaller RE cations, i.e. RE including Lu, Yb, Er, 
Y and Sc, for potential EBC topcoat materials. As a result, they are promising EBC topcoats.

In the current study, we have systematically investigated the mechanical and thermophysical properties of a
Xenotime-type REPO4 with smaller RE cations, i.e. RE including Lu, Yb, Er, Y and Sc, for potential EBC topcoat
applications. First, we employ first-principle calculations to predict elastic constants of REPO4 (RE = Lu, Yb, Er, 
Y and Sc), on the basis of which the mechanical properties can then be calculated. Second, the thermophysical
properties (i.e. thermal expansion coefficients and thermal diffusivities of REPO4) can be measured. From the
discussion of underlying parameters dictating those thermophysical properties, it is for the first time unveiled
that a low thermal expansion coefficient and a low thermal conductivity are mutually exclusive and thus cannot
be achieved simultaneously. Lastly, the water vapor corrosion resistance and chemical compatibility of REPO4
with Si bond coat are experimentially studied to justify them as a potential EBC topcoat.

Methodology
Theoretical calculation methods. The elastic constants of REPO4 (RE = Lu, Yb, Er, Y and Sc) are theo-
retically predicted based on first principles calculations. The calculations are carried out employing the CASTEP
code. The plane wave basis is used under periodic boundary conditions. The kinetic energy cutoff is set to
500 eV for expanding Bloch waves in the reciprocal space. For the energy integrations, a discretized 5×5×5 k
sampling grid is applied in the first irreducible Brillouin zone based on Monkhorst–Pack method. For the
exchange correlation energy, polarized generalized gradient approximation (GGA) is used. The crystal structures
are fully optimized by independently modifying lattice parameters and internal atomic coordinates. The
Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization scheme has been employed to minimize the total
energy and interatomic forces. For the pseudo-atoms, the ultra-soft type pseudopotentials are applied for RE,
F and O atoms to account for the electrostatic interactions between valence electrons and ionic cores. The cri-
tera for convergence in geometry optimization are selected as follows: the difference in total energy within
1×10−6 eV/atom, the ionic Hellmann–Feynman forces within 0.002 eV/Å, the maximum stress within 0.01 GPa
and the maximum ionic displacement within 1×10−4 Å.

Material preparation and characterization. The thermophysical properties (i.e. thermal diffusivity, thermal
expansion coefficient) of REPO4 are experimentially measured from the sintered REPO4 ceramic bulks.
The starting REPO4 (RE = Lu, Yb, Er, Y and Sc) powders and Yb2SiO5, Yb2Si2O7 powders (which are used as a
reference to compare water vapor corrosion rates) are all 99.9% pure, purchased from the Kai-Star Electro-
Optic Materials, Wuxi, China. The powders were cold isostatic pressed at 50 MPa into disk-shaped (12.7 mm in
diameter × 2 mm high) and bar-shaped (5 mm × 5 mm × 25 mm) green compacts. The green compacts were then sintered at 1,500 °C for 20 h in air.

The densities of bulks were measured by Archimedes’ method in distilled water. The phases were examined by X-ray diffraction (XRD, Bruker D8 Advanced, Cu Ka radiation). The thermal diffusivity is measured by means of the laser flash technique, using thermal constant measurement equipment (NETZSCH LFA 427, Bavaria, Germany). The thermal conductivity $k$ (in W/m•K) was calculated from the equation:

$$ k = c_p D \rho $$

where $c_p$ is the specific heat (in J/kg•K), $D$ the thermal diffusivity (in cm²/s), and $\rho$ the density (in g/cm³). The specific heat capacitance is calculated according to the Neumann–Kopp rule by employing standard $c_p$ values extracted from. Thermal expansion coefficients (TECs) were obtained from temperature-dependent changes in the length of the specimens from room temperature to 1,350 °C in air as determined using a vertical high-temperature optical dilatometer (ODITT, Modena, Italy).

The water vapor corrosion behaviors of sintered ceramic bulks were investigated in 50% H₂O/50% O₂ water vapor flowing at a rate of 0.30 cm/s with an atmospheric pressure at 1,500 °C for 80 h. The water vapor was introduced to an alumina tube by O₂ carrier gas bubbling through distilled water heated at 81.7°C. For each compound, at least 3 samples were measured. The chemical compatibility of REPO₄ with conventional silicon bond coat was evaluated by identifying phase compositions of REPO₄ and Si powder mixtures with a weight ratio 7:3 after dwelling at 1,350 °C in air for 20 h.

**Results**

Crystal structure, phase compositions and densities of REPO₄ (RE = Lu, Yb, Er, Y and Sc). Figure 1 shows the typical crystal structure of Xenotime-type rare earth phosphate REPO₄. As shown, REPO₄ exhibits a tetragonal structure consisting of two types of polyhedra, i.e. PO₄ tetrahedra and REO₈ dodecahedra. In addition, the REPO₄ crystals can be considered as the accumulation of vertex-connected PO₄ tetrahedra and REO₈ dodecahedra. In PO₄ tetrahedra, the P atom is surrounded by four O atoms; whereas, in REO₈ polyhedra, the RE atom is surrounded by eight O atoms. As shown in Fig. 1b, each oxygen atom connects two RE atoms and one P atom; whereas, each RE atom or P atom solely connects oxygen atoms, with the former connected to eight oxygen atoms and latter four respectively.

Figure 2 shows the XRD patterns of sintered REPO₄ (RE = Lu, Yb, Er, Y and Sc) ceramic bulks. The measured patterns of REPO₄ are compared with the standard XRD spectra of LuPO₄ (ICDD PDF No. 43-0003), suggesting that single REPO₄ phases have been formed. With an increase of ionic radius of rare earth element (from Sc to Y), the diffraction peaks are expected, according to the Bragger’s law, to shift to lower angle. It is worth pointing out that, whereas the cationic sizes of Lu³⁺, Yb³⁺, Er³⁺, Y³⁺ are more or less in the same order, the ionic size of Sc³⁺ is considerably smaller than that of the above four cations. As a result, ScPO₄ shows an XRD pattern dramatically shifted to higher 2θ angles, which is distinctive from the XRD patterns of the other four rare earth phosphates. Table 1 shows the measured, theoretical and relative densities of REPO₄ (RE = Lu, Yb, Er, Y and Sc). As shown, the sintered pellets have achieved a high relative density, more than 97% of theoretical density.

The predicted elastic constants of REPO₄ (RE = Lu, Yb, Er, Y and Sc) from first principles calculations. Table 2 shows the predicted elastic constants of REPO₄ (RE = Lu, Yb, Er, Y and Sc) from first-principle calculations. As shown, no negative $C_{ij}$ value is obtained for these compounds, suggesting that these crystal structures are all stable. For those tetragonal structures such as the current Xenotime-type rare earth phosphates, $C_{22} = C_{11}$ and $C_{33} = C_{11}$. As shown in Table 2, the values of $C_{11}$ and $C_{22}$ are lower than those of $C_{33}$, indicating that the chemical bonds are identical in the directions of [100] and [010] but they are weaker than those in the [001] direction.
direction for current studied REPO₄ compounds. In fact, both RE–O and P–O bonds in Xenotime-type REPO₄ crystal structures can be divided into two groups, which are longer and shorter bonds respectively. Understandably, those shorter RE–O and P–O bonds tend to generate a stronger covalent character than those longer ones. Referring to the crystal structure of REPO₄, the shorter bonds are aligned mainly along the [001] direction. As a result, the calculated C₃₃ values are larger than those of C₁₁ and C₂₂.

For the pure shear Cᵢⱼ constants, the present calculations show that, for all REPO₄ structures currently investigated, C₅₅ and C₄₄ are significantly larger than C₆₆, suggesting that there are probably soft P-O and RE-O bonds on the (001) plane but rigid P-O and RE–O bonds on the (001) and (010) planes. It further indicates shear deformation is easier to take place on the (001) plane. For the other non-diagonal elastic constants, their values are relatively small. The off-diagonal elements also reflect the deviation of atomic force constants from those of central type. For the crystal dominated by central forces, Cauchy's relation implies that C₁₂ = C₆₆, C₁₃ = C₅₅, C₁₅ = C₄₄ and C₁₆ = C₃₃. Applying these conditions to REPO₄ compounds, they exhibit weak many-body forces such as angular and torsional interactions. To sum up above discussions, for Xenotime-type REPO₄ compounds, tensile and compressive deformation takes place primarily along the [100] and [010] directions whilst shear deformation takes place primarily on the (001) plane.

**Figure 2.** XRD patterns of sintered REPO₄ ceramic bulks (RE = Lu, Yb, Er, Y and Sc). ScPO₄ shows a pattern dramatically shifted to higher 2θ angles, attributing to a much smaller cationic size of Sc⁴⁺ than the other four rare earth elements.

**Table 1.** The measured, theoretical and relative density of REPO₄ (RE = Lu, Yb, Er, Y and Sc).

| Compound  | ScPO₄ | YPO₄ | ErPO₄ | YbPO₄ | LuPO₄ |
|-----------|-------|------|-------|-------|-------|
| Experimental density (g/cm³) | 3.78  | 4.38 | 6.05  | 6.95  | 6.92  |
| Theoretical density (g/cm³)  | 3.89  | 4.48 | 6.20  | 7.10  | 6.17  |
| Relative density (%)         | 97.2  | 97.7 | 97.6  | 97.9  | 97.5  |

**Table 2.** Elastic constants Cᵢⱼ (in GPa) of REPO₄ (RE = Lu, Yb, Er, Y and Sc) from first principles calculations.

| Compound | ScPO₄ | YPO₄ | ErPO₄ | YbPO₄ | LuPO₄ |
|----------|-------|------|-------|-------|-------|
| C₁₁      | 285.9 | 399.2| 265.7 | 245.7 | 326.9 |
| C₁₂      | 22.1  | 18.5 | 28.8  | 26.1  | 32.6  |
| C₁₃      | 89.5  | 80.2 | 86.3  | 81.0  | 111.0 |
| C₂₂      | 285.9 | 399.2| 265.7 | 245.7 | 326.9 |
| C₃₃      | 300.0 | 407.7| 367.1 | 326.5 | 403.8 |
| C₄₄      | 93.6  | 71.3 | 78.5  | 68.3  | 80.4  |
| C₅₅      | 285.9 | 399.2| 265.7 | 245.7 | 326.9 |
| C₆₆      | 41.9  | 32.8 | 22.5  | 19.8  | 31.9  |
The measured thermophysical properties of $\text{REPO}_4$ ($\text{RE} = \text{Lu, Yb, Er, Y and Sc}$).

**Thermal diffusivity/ conductivity of $\text{REPO}_4$ ($\text{RE} = \text{Lu, Yb, Er, Y and Sc}$).** Figure 3 shows the thermal diffusivity (a) and calculated specific heat capacitance (b) of $\text{REPO}_4$. As shown, rare earth phosphates $\text{REPO}_4$ exhibit thermal diffusivities lower than 3 mm²/s from 1,200 K to 1773 K. By using density values (Table 1) and thermal diffusivity and specific heat capacitance shown in Fig. 3b, thermal conductivities of $\text{REPO}_4$ can be calculated according to Eq. (1), and are shown in Fig. 4. From it, the following trends can be found. First, the thermal conductivities of $\text{REPO}_4$ are generally decreasing with an increase of temperature. This is a typical feature for a ceramic whose heat transport is dictated by the phonon–phonon Umklapp scattering. Second, a heavier rare earth element of $\text{REPO}_4$, for instance, RE = Er, Yb, Lu, tends to generate lower thermal conductivity than those of lighter rare earth elements. Indeed, these three $\text{REPO}_4$ compounds with heavier rare earth elements have almost overlapping thermal conductivity-temperature curves, i.e. very similar thermal conductivity values.

**Thermal expansion coefficient of $\text{REPO}_4$ ($\text{RE} = \text{Lu, Yb, Er, Y and Sc}$).** Figure 5 exhibits the measured thermal expansion coefficients of $\text{REPO}_4$ ($\text{RE} = \text{Lu, Yb, Er, Y and Sc}$) ceramic bulks. As a comparison, the TECs of typical SiC-based CMCs, $\text{Yb}_2\text{Si}_2\text{O}_7$ and $\text{Yb}_2\text{SiO}_5$, representatives of third generation EBC topcoat materials, are also included. As shown, the TECs of $\text{REPO}_4$ are rather close to those of $\text{Yb}_2\text{Si}_2\text{O}_7$, a compound that is thought to have good TEC matching with SiC based CMCs, suggesting that $\text{REPO}_4$ currently investigated probably has a good TEC matching with SiC based CMCs.
Discussions

From the perspective of potential EBC applications, the following three aspects have to be taken into accounts. Firstly, from the mechanical aspect, a smaller elastic modulus together with a quasi-ductile behavior of an EBC topcoat material tends to produce a longer lifespan of its made coatings. From the elastic constants as unveiled in “The predicted elastic constants of REPO₄ (RE = Lu, Yb, Er, Y and Sc) from first principles calculations” section, different kinds of modulus (or mechanical parameters) can be calculated, such as bulk (B), shear (G), elastic (E) modulus respectively, as well as Poisson’s ratio, B/G ratio, the latter two of which usually hints the extent of ductility of a material. Secondly, the thermophysical properties of EBC topcoat are usually of prior concern. The preliminary results in “The measured thermophysical properties of REPO₄ (RE = Lu, Yb, Er, Y and Sc)” section suggests a heavy rare earth element of REPO₄ tends to generate lower thermal conductivity, whilst a smaller rare earth element of REPO₄ (i.e. ScPO₄) tends to have a higher TEC. The underlying mechanisms need further investigation. Last but not least, the water vapor resistance, the thermochemical compatibility issues of REPO₄ have to be examined and justified as a potential EBC topcoat candidate. The following parts are to be discussed from the above three aspects.

Mechanical properties of REPO₄ (RE = Lu, Yb, Er, Y and Sc). As shown in Table 2, the elastic constants Cᵢⱼ can be obtained from first principle calculations. In fact, REPO₄ has 13 independent elastic constants, i.e., C₁₁, C₂₂, C₃₃, C₄₄, C₅₅, C₆₆, C₁₂, C₁₃, C₂₃, C₁₅, C₂₅, C₃₅, and C₄₆. Based on these elastic constants, the bulk modulus B, shear modulus G and Young’s modulus E of REPO₄ can be further calculated. According to Voigt approximations 35–37, the bulk and shear moduli can be calculated from elastic constants as:

\[ B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{12} + C_{13} + C_{23}), \]  

(2)

and

\[ G_V = \frac{1}{15}(C_{11} + C_{22} + C_{33} - C_{12} - C_{13} - C_{23}) + \frac{2}{5}(C_{44} + C_{55} + C_{66}); \]  

(3)

By contrast, on the basis of Reuss approximation, the bulk and shear moduli can be calculated from compliance matrix components as:

\[ B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})}, \]  

(4)

and

\[ G_R = \frac{1}{4(S_{11} + S_{22} + S_{33} - S_{12} - S_{13} - S_{23}) + 3(S_{44} + S_{55} + S_{66})}. \]  

(5)

where Sᵢᵢ refers to the components of the elastic compliances that can be obtained through the inversion of the elastic constants \( S_{ij} = C_{ij}^{-1} \) tensor. Both the Voigt and Reuss averaging methods assume that strains and stresses are continuous in polycrystals and can produce respectively the upper and lower bounds of the effective bulk and shear moduli for polycrystals. On the contrary, the Voigt–Reuss–Hill (VRH) approach combines the upper and lower bounds, assuming that the average Voigt and Reuss elastic moduli are a good approximation of the macroscopic elastic moduli. The bulk modulus \( B_{VRH} \) and shear modulus \( G_{VRH} \) based on Voigt–Reuss–Hill approximation can be calculated as follows:
In the following context, we employ $B_{\text{VRH}}$ and $G_{\text{VRH}}$ as the calculated bulk modulus and shear modulus. In addition, according to Ref.\textsuperscript{38}, the Young's modulus $E$ and Poisson's ratio $\nu$ can be calculated on the basis of $B_{\text{VRH}}$ and $G_{\text{VRH}}$\textsuperscript{39} as follows:

$$B_{\text{VRH}} = \frac{1}{2} (B_V + B_R),$$  

(6)

$$G_{\text{VRH}} = \frac{1}{2} (G_V + G_R).$$  

(7)

Table 3 shows the calculated bulk modulus $B$, shear modulus $G$, and Young's modulus $E$, Poisson's ratio $\nu$, and $B/G$ ratio. As a comparison, the measured bulk moduli of rare earth phosphates are also included. Figure 6 plots the variation of bulk, shear and Young's modulus of $\text{REPO}_4$ versus the radius of rare earth elements. From it, the following trends can be found. Firstly, with an increase of ionic radius of rare earth element $\text{RE}^{3+}$, except for the calculated bulk modulus of $\text{ScPO}_4$, the calculated Young's, bulk and shear modulus decreases till Yb, and then increases. In other words, YbPO$_4$ is predicted to have the lowest above three moduli. Interestingly, this trend is perfectly conforming to the measured bulk modulus from other work\textsuperscript{32,38,40,41} as shown the dash curve in Fig. 6, which confirms the validity of current calculation. The only discrepancy lies in that a much lower bulk modulus of $\text{ScPO}_4$ is predicted compared to the measured value.

In addition, if we closely examine the Poisson's ratio and $B/G$ ratio, we can find rare earth phosphates $\text{REPO}_4$ are rather ductile and even show some plastic deformation that is rare for ceramics, which is desirable for EBC.

Table 3. Elastic moduli $B$, $G$, and $E$ (in GPa), Poisson's ratio $\nu$, $B/G$ ratio, and Vickers hardness $H_V$ (in GPa) in the Hill approximation. Experimental bulk moduli are included as a comparison.

| Compound | ScPO$_4$ | YPO$_4$ | ErPO$_4$ | YbPO$_4$ | LuPO$_4$ |
|----------|----------|----------|----------|----------|----------|
| $B$      | 140.2    | 173.2    | 144.1    | 129.3    | 170.4    |
| $B_{\text{exp}}$ | 203 ± 7\textsuperscript{38} | 186 ± 5\textsuperscript{42} | 168 ± 4\textsuperscript{42} | 150 ± 5\textsuperscript{38} | 169.3\textsuperscript{38} |
| $G$      | 84.4     | 87.2     | 68.8     | 61.8     | 80.9     |
| $E$      | 210.8    | 224.1    | 178.1    | 160.0    | 209.6    |
| $\nu$    | 0.25     | 0.28     | 0.29     | 0.29     | 0.29     |
| $B/G$    | 1.66     | 1.99     | 2.09     | 2.09     | 2.11     |

Figure 6. The plot of calculated bulk ($B$), shear ($G$) and Young's ($E$) moduli of $\text{REPO}_4$ versus cationic radius of $\text{RE}^{3+}$.

$$E = \frac{9 B_{\text{VRH}} G_{\text{VRH}}}{3 B_{\text{VRH}} + G_{\text{VRH}}},$$  

(8)

$$\nu = \frac{3 B_{\text{VRH}} - 2 G_{\text{VRH}}}{2 (3 B_{\text{VRH}} + G_{\text{VRH}})}.$$  

(9)
application. As we know, the Poisson's ratio reflects the capability of a material to resist deformation in different directions, and a greater Poisson's ratio usually yields a better plasticity and ductility of a material. For instance, the Poisson's ratio of metals is usually greater than 0.3. By contrast, the Poisson's ratio of ceramics is usually below 0.3. For example, the Poisson's ratios of zirconia (ZrO₂), lanthanum zirconate (La₂Zr₂O₇) and alumina are 0.27, 0.25 and 0.23 respectively. Except for ScPO₄, the Possion's ratios of the other rare earth phosphate currently investigated are in the range of 0.28–0.29, which is comparable to most intermetallic compounds. This suggests REPO₄ are relatively plastic and ductile.

Furthermore, the B/G value further supports the above conclusion. The B/G value can be taken as a criterion to distinguish a material whether it has a good ductility or not. In general, materials with a B/G value below 1.75 tend to have poor ductility, whereas, materials with a B/G value above 2.0 tend to have excellent ductility. The B/G values of REPO₄ except ScPO₄ are in a range of 1.99–2.11, which lies in the plastic and ductile region. The Possion's ratio and B/G value of ScPO₄ are 0.25 and 1.66 respectively, indicating that it might possess a typical feature of ceramic brittleness. As a comparison, the Possion's ratio and B/G value of RE₂SiO₅ are in the range of 0.20–0.25 and 1.46–1.73 respectively, which are lower than values of REPO₄, suggesting they exhibit a more brittle nature than currently investigated REPO₄. By contrast, the Possion's ratio and B/G value of RE₂Si₂O₇ are in the range of 0.30–0.31 and 2.33–2.35 respectively, suggesting that RE₂Si₂O₇ might possess even better behavior than REPO₄ in terms of toughness. In fact, it is worth pointing out that, due to such quasi-ductile behavior of RE₂Si₂O₇ and REPO₄, they have been proposed as a novel interphase candidate for SiC/SiC interphase so as to improve oxidation resistance of interphase, replacing conventional layered PyC or BN which are highly susceptible to oxidation at low temperatures.

To sum up, in terms of modulus, YbPO₄ exhibits lowest value, which perhaps suggests it might provide best strain tolerance of its made coating and is thus desirable for EBC topcoat application. Meanwhile, from quasi-ductile perspective, ErPO₄, YbPO₄ and LuPO₄ exhibit excellent behavior, suggesting they might produce durable coatings.

Thermophysical properties of REPO₄ (RE = Er, Yb, Lu, Y and Sc). According to, the Grüneisen parameter γ, which is a reflection of lattice anharmonicity, is closely related to the thermophysical properties of a material, such as thermal conductivity and thermal expansion coefficient. Based on the formalism developed in, the Grüneisen parameter γ can be calculated according to the following equation:

\[ \gamma = \frac{M a \omega_D^3}{(2664.8 \times A)} \]

in which \( M \), \( a \), \( \omega_D \) are average atomic mass, size in the lattice and Debye characteristic frequency respectively, while \( A \) is a parameter that can be obtained by curve fitting of thermal conductivity (\( k \)) versus temperature (\( T \)) curves (refer to Fig. 7) according to Eq. (11):

\[ k = \frac{A}{3T_1} + \frac{2A\sqrt{T_1}}{3T_1^{1.5}}, \]

where \( A \) and \( T_1 \) are characteristic parameters. In fact, Eq. (11) depicts the thermal conductivity of a lattice without any point defects, where phonon–phonon Umklapp scattering is the dictating factor to define its thermal conductivity. In fact, according to, \( A/3T_1 \) in Eq. (11) represents the minimal lattice thermal conductivity, \( k_{\text{min}} \), neglecting thermal radiation effects, and can be further expressed as follows:
\[ k_{\text{min}} = \frac{A}{3T_1} = \xi \sqrt{\frac{E}{aM\gamma}}. \]  \hspace{1cm} (12)
measured TEC values might originate from the slight temperature dependence of density $\rho$ and bulk modulus $B$, which is neglected in current calculations.

By comparing Eqs. (12) and (13), it is again affirmed that the Grüneisen parameter $\gamma$ has an important role in determining both thermal conductivity $k$ and thermal expansion coefficient $\alpha$. In addition, the modulus, which is a reflection of bond strength, is another parameter affecting both $k$ and $\alpha$. Different from thermal barrier coating application, which requires a topcoat material desirably having lower $k$ and higher $\alpha$, EBC topcoat material needs to have lower $k$ but lower $\alpha$, as a result of relatively low TEC of common SiC based CMCs (refer to Fig. 5). According to Eqs. (12) and (13), theoretically a low thermal conductivity and high thermal expansion (which is desirable for TBC application) can be achieved simultaneously. However, unfortunately, a low thermal conductivity and low thermal expansion coefficient are exclusive, and thus cannot be achieved simultaneously. This suggests that, for the selection of EBC topcoat material, a compromise of $k$ and $\alpha$ (or, a compromise of lattice anharmonicity and bond strength) would be recommended, which is distinctive from the selection of TBC topcoat material where materials with strong lattice anharmonicity and weak bonding are favored.

The justification of $\text{REPO}_4$ (RE = Lu, Yb, Er, Y and Sc) for potential EBC topcoat application. Except the mechanical and thermophysical properties, the high temperature stability, the CMAS resistance, as well as water vapor resistance of a candidate EBC topcoat are also important factors. Hence, we discuss these properties of xenotime-type $\text{REPO}_4$ (RE = Lu, Yb, Er, Y and Sc) as follows.

As discussed in $^{21-23}$, rare earth phosphates exhibit excellent CMAS resistance, attributed to a dense and crack-free layer formed on the surface of $\text{REPO}_4$ as a result of their reaction with molten CMAS. These dense layers suppress the further penetration of CMAS melts$^{23}$. In addition, the xenotime-type $\text{REPO}_4$ (RE = Lu, Yb, Er, Y and Sc) exhibits very good high-temperature stability, as shown in Fig. 9, which illustrates the DSC curves of current investigated rare earth phosphates measured in ambient atmosphere up to 1,400 °C. As shown, there are no endothermic or exothermic peaks detected for $\text{REPO}_4$ (RE = Lu, Yb, Er, Y and Sc), suggesting they have very good phase stability up to 1,400 °C. However, for Er$\text{PO}_4$, there is a peak around 1,350 °C, suggesting that there might be a phase transformation around this temperature.

As a potential EBC topcoat material, the water vapor corrosion resistance is a key factor. Table 5 exhibits the water vapor corrosion rates of $\text{REPO}_4$ at a normalized condition of 50% H$_2$O-balance O$_2$ vapor with a flow of 0.3 cm/s and a total pressure of 1 atm at 1,500 °C for 80 h.

![Figure 9. The DSC curves of $\text{REPO}_4$ powders (RE = Lu, Yb, Er, Y and Sc).](image)

![Table 5. Comparison of corrosion rate constants of $\text{REPO}_4$ (RE = Lu, Yb, Er, Y and Sc). As a comparison, the values of $\text{Yb}_2\text{SiO}_5$ and $\text{Yb}_2\text{Si}_2\text{O}_7$ are also included. The normalized conditions are 50% H$_2$O-balance O$_2$ vapor with a flow of 0.3 cm/s and a total pressure of 1 atm at 1,500 °C for 80 h.](table)

| Compound     | $\text{ScPO}_4$ | $\text{YPO}_4$ | $\text{ErPO}_4$ | $\text{YbPO}_4$ | $\text{LuPO}_4$ | $\text{Yb}_2\text{SiO}_5$ | $\text{Yb}_2\text{Si}_2\text{O}_7$ |
|--------------|----------------|---------------|----------------|----------------|----------------|--------------------------|--------------------------|
| Corrosion rate constants ($\times 10^{-4}$ mg/cm$^2$ h) | 2.32 ± 0.91 | 2.51 ± 1.33 | 4.08 ± 1.87 | 4.31 ± 1.92 | 1.89 ± 1.03 | 7.46 ± 3.24 | 11.02 ± 3.91 |

Regarding the data shown in Table 5, there is a concern raised from the execution of high temperature water vapor test by use of an alumina tube furnace. Unfortunately, a reaction product Al$_6$RE$_2$O$_{12}$ has been found on the surface of bulk samples after high temperature water vapor corrosion test. The formation mechanism of byproduct Al$_6$RE$_2$O$_{12}$ is likely to be two steps as shown in the Chemical Formula (R1) and (R2). Firstly, the solid...
Al₂O₃ from alumina tube reacts with water vapor to form gaseous Al(OH)₃. Secondly, the gaseous Al(OH)₃ then reacts with REPO₄ to form solid Al₅RE₃O₁₂.

By combining Chemical Formula (R1) and (R2), we then can reach Chemical Formula (R3).

As these chemical reactions would probably affects weight loss or gain during water vapor corrosion test of REPO₄ bulk samples, we would firstly evaluate the potential effect on weight change of these reactions. According to Chemical Formula (R3), the ingest of alumina from the environment will lead to weight gain, whilst the formation of gaseous product P₂O₅ will cause weight loss. Hence, the weight change is dependent on these two factors. As the weight of 2.5 molar ingested Al₂O₃ is slightly higher than that of 1.5 molar gaseous P₂O₅, this reaction would result in a gentle increase of weight. According to Chemical Formula (R3), the reaction of 3 molar REPO₄ will lead to a weight gain of 42 g. Table 6 shows weight gain percentage relative to the REPO₄ mass according to a thorough reaction conforming to Formula (R3), i.e. all REPO₄ has been consumed by Al₂O₃.

| REPO₄  | Weight of 3 molar REPO₄ (g) | Weight gain (g) | Weigh gain percentage relative to REPO₄ mass (%) |
|--------|----------------------------|-----------------|-----------------------------------------------|
| LuPO₄  | 810                        | 42              | 5.2                                           |
| YbPO₄  | 804                        | 42              | 5.2                                           |
| ErPO₄  | 787                        | 42              | 5.3                                           |
| YPO₄   | 551.7                      | 42              | 7.6                                           |
| ScPO₄  | 420                        | 42              | 10                                            |

Table 6. The weight gain and weight gain percentage relative to original REPO₄ mass, assuming a thorough reaction according to Chemical Formula (R3), i.e. all REPO₄ has been consumed by Al₂O₃.

![XRD patterns of REPO₄ mixed with silicon after heat treatment at 1,350 °C for 20 h: (a) 17° ≤ 2θ ≤ 80°; (b) 25° ≤ 2θ ≤ 28°.](image)

Figure 10. XRD patterns of REPO₄ mixed with silicon after heat treatment at 1,350 °C for 20 h: (a) 17° ≤ 2θ ≤ 80°; (b) 25° ≤ 2θ ≤ 28°.

As these chemical reactions would probably affects weight loss or gain during water vapor corrosion test of REPO₄ bulk samples, we would firstly evaluate the potential effect on weight change of these reactions. According to Chemical Formula (R3), the ingest of alumina from the environment will lead to weight gain, whilst the formation of gaseous product P₂O₅ will cause weight loss. Hence, the weight change is dependent on these two factors. As the weight of 2.5 molar ingested Al₂O₃ is slightly higher than that of 1.5 molar gaseous P₂O₅, this reaction would result in a gentle increase of weight. According to Chemical Formula (R3), the reaction of 3 molar REPO₄ will lead to a weight gain of 42 g. Table 6 shows weight gain percentage relative to the REPO₄ mass according to a thorough reaction conforming to Formula (R3), i.e. all REPO₄ has been consumed by alumina. As shown, given all REPO₄ has been consumed to form Al₅RE₃O₁₂, only a 5–10% weight gain would be generated. However, in reality, only a small amount of REPO₄ reacts with Al₂O₃ from the alumina tube to form Al₅RE₃O₁₂. Hence, a negligible weight gain, at least smaller than the error bar, would be generated due to the above byproduct formation. Therefore, the current obtained water vapor resistance data are still reliable.

Finally, the chemical compatibility between REPO₄ (RE = Lu, Yb, Er, Y and Sc) and Si bond layer is further investigated. After annealing of 30 wt.% silicon and REPO₄ powders at 1,350 °C for 20 h, the powder mixtures are then subject to x-ray diffraction and their patterns are shown in Fig. 10a. As shown, the characteristic peaks of Moganite-type SiO₂, as indicated in Fig. 10a, have been present. In Fig. 10b, which is a high magnitude XRD pattern of 25° ≤ 2θ ≤ 28°, the XRD peaks of Xenotime-type REPO₄ denoting (2 0 0) planes are systematically shifting towards lower 2θ angles with an increase of cationic radius of RE, which is consistent with Bragg’s law. By contrast, the peak positions of (-1 1 2) planes of Moganite-type SiO₂ keep relatively unchanged. There are no
impurity peaks except the above two phases, suggesting that the current investigated REPO₄ is thermochemically compatible with the silicon bond coat.

**Conclusion**

The mechanical and thermophysical properties of Xenotime-type REPO₄ (RE = Lu, Yb, Er, Y and Sc) have been thoroughly investigated by first-principle calculations and experimental studies respectively with a potential environmental barrier coating application. The main conclusions are as follows. First, from calculations, large Poisson’s ratio and big B/G ratio are predicted for currently investigated rare earth phosphate compounds except ScPO₄, suggesting that they have some sort of quasi-ductile behavior, which is perhaps beneficial to the durability and lifespan of their made coatings. Second, from the study of underlying parameters governing thermophysical properties of a ceramic, it suggests that, a low thermal expansion coefficient (which yields a good TEC matching of EBC with SiC-based CMC substrates) and a low thermal conductivity (which provides perhaps a good thermal insulation of EBC) are unfortunately exclusive, and thus not possible to achieve simultaneously. For EBC application, a good TEC match of topcoats and substrates is perhaps more important than thermal insulation properties, suggesting a weak lattice anharmonicity of a lattice might be beneficial. However, a weak lattice anharmonicity, i.e. strong lattice harmony might result in strong bonds, i.e. larger elastic modulus, which might be detrimental to the strain tolerance of its coatings. This suggests that a compromised value of TEC and thermal conductivities of a topcoat material is more favorable. In fact, the current studied REPO₄ exhibits a very good TEC match with SiC-based CMCs, particularly for those heavier rare earth elements. Third, the current investigated REPO₄ exhibits very good high-temperature water vapor corrosion resistance, excellent CMAS resistance as well as excellent chemical compatibility with silicon bond coats at elevated temperatures. By considering the above three aspects, it is proposed that Xenotime-type rare earth phosphates are a promising EBC topcoat material.

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Author contributions
Y.W. conceived the idea, J.H. conducted the experiments and the calculations, Wang and Han wrote the text, J.H. drew Figs. 1, 2 and 6, 9, 10. Y.W. drew Figs. 3, 4, 5, 7 and 8. Y.W., R.L., F.W. reviewed the whole manuscript.

Competing interests
The authors declare no competing interests.

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