

Article

Investigation on the Thermal–Mechanical Properties of YbRESiO₅ (RE = Yb, Eu, Gd, Ho, Tm, Lu, Y, Sc): First-Principles Calculations and Thermal Performance Experiments

Shilong Yang ^{1,†}, Tianying Wang ^{2,†}, Kaibin Li ^{1,*}, Weize Wang ^{1,3,*}, Yangguang Liu ¹ and Ting Yang ¹

¹ Key Laboratory of Pressure System and Safety, Ministry of Education, East China University of Science and Technology, Shanghai 200237, China; y84220052@mail.ecust.edu.cn (S.Y.); y10210065@mail.ecust.edu.cn (Y.L.); y10200060@mail.ecust.edu.cn (T.Y.)

² Key Laboratory for Advanced Corrosion and Protection of Aviation Materials, AECC Beijing Institute of Aeronautical Materials, Beijing 100195, China; ty-wang_90@163.com

³ Shanghai Institute of Aircraft Mechanics and Control, Shanghai 200092, China

* Correspondence: y10210064@mail.ecust.edu.cn (K.L.); wangwz@ecust.edu.cn (W.W.)

† These authors have contributed equally.

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Abstract: Environmental barrier coatings are critically needed in the future to safeguard SiC-based ceramic matrix composites (SiC CMCs) used in gas turbines. Element doping of rare earth monosilicates could further improve the properties of the coating. The crystal structure, elastic properties, and resistance to water vapor corrosion of Yb₂SiO₅ and YbRESiO₅ (where RE = Sc, Y, Eu, Gd, Ho, Tm, Lu) were examined in this study using first-principles calculations. When RE is Yb, the material is Yb₂SiO₅. Based on the outcomes of the calculation, we prepared YbRESiO₅ (RE = Sc, Yb, Eu) and studied the thermodynamic properties. The findings show that YbRESiO₅'s resistance to water vapor corrosion is as follows: YbLuSiO₅ < YbEuSiO₅ < YbGdSiO₅ < YbYSiO₅ < Yb₂SiO₅ < YbTmSiO₅ < YbHoSiO₅ < YbScSiO₅. YbScSiO₅ has a lower unit cell volume, average Re–O bond length, and thermal expansion coefficient than Yb₂SiO₅, while YbEuSiO₅ has the reverse pattern. Moreover, of the eight materials, YbScSiO₅ has the greatest elastic modulus and lattice distortion. After doping with Eu, YbEuSiO₅ exhibits a decrease in thermal conductivity by nearly thirty percent compared to Yb₂SiO₅, due to the formation of oxygen vacancies. The development of environmental barrier coating materials may benefit from these discoveries.

Keywords: rare earth monosilicate; environment barrier coating; first-principles calculation; water vapor corrosion resistance; thermal properties

1. Introduction

As the aviation sector develops, thrust–weight ratios increase in new generations, and internal gas temperatures exceed the bearing limits of nickel-based superalloys [1,2]. According to the needs of the current development, the surface temperature of the hot end components of the new generation of aero-engines can reach 1400 °C, while the maximum working temperature of single-crystal nickel-based superalloys is 1100 °C and Ni3Al single-crystals have a high-temperature limit of 1200 °C, so there is an urgent need to develop a new type of material matrix [3]. The most promising high-temperature structural materials to replace nickel-based superalloys in the hot sections of aircraft engines are SiC-based ceramic matrix composites (SiC CMCs) [1,4,5]. SiC CMCs have a high temperature resistance, low density, high strength, high elastic modulus, oxidation resistance, erosion resistance, and crack insensitivity [6]. But in real high-temperature

service conditions, SiC CMCs face substantial hurdles, especially with regard to considerable water vapor corrosion issues [4]. Poor environmental durability still prevents them from being used in combustion environments due to the presence of two chemical degradation mechanisms, recession and thermal corrosion. (i) Recession is the loss of silicon-based ceramics due to repeated oxidation and volatilization when exposed to high-velocity water vapor in a turbine. (ii) Thermal corrosion is caused by alkaline salts in the combustion environment, which form liquid silicates and cause craters in silicon-based ceramics [7–9]. Alkaline salts are salts formed by the reaction of an alkaline metal (e.g., sodium, potassium) or an alkaline earth metal (e.g., calcium, magnesium) with an acid. Experimental results from NASA et al. show that the loss rate of the ceramic surface is about 270 $\mu\text{m}/\text{kh}$ in a combustion environment (1200 °C; pressure 1013.25 KPa; airflow velocity 90 m/s). For the protection of the substrate, environmental barrier coatings (EBCs) must be used. Due to their resistance to water vapor corrosion, high temperature phase stability, and matching thermal expansion coefficient with SiC CMCs substrates, rare earth silicate materials in EBC systems are currently receiving a lot of attention [1,10,11].

EBCs have evolved through three generations since the 1990s [12]. The initial generation of EBC systems, YSZ/Mullite, could not meet the practical application requirements under continuous thermal cycling because of crack propagation, which limited its ability to resist a few hundred hours in a water vapor atmosphere at 1300 °C [13,14]. Later, BSAS ($1-x\text{BaO}-x\text{SrO}-\text{Al}_2\text{O}_3-2\text{SiO}_2$, $0 \leq x \leq 1$) materials with low thermal expansion coefficients ($4 \times 10^{-6}\text{K}^{-1}$ – $5.15 \times 10^{-6}\text{K}^{-1}$, and thus a close match with SiC, $4.02 \times 10^{-6}\text{K}^{-1}$) and a low elastic modulus (60–70 GPa) were used to develop the second generation of EBCs [15]. These materials replaced YSZ as the surface coating, or they enhanced Mullite with BSAS + Mullite to form the BSAS/Mullite/Si system. Unfortunately, at 1584 K, the BSAS material system experiences a glass phase shift that shortens the coating's lifespan by causing cracking [13,14,16]. BASA's volatilization loss for 1000 h at 1400 °C, 6 atm total pressure and 24 m/s gas flow rate is as high as 70 μm . The third-generation rare earth silicate system has a high melting point (1950 °C), a low thermal conductivity ($2.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ – $1.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$), and a coefficient of thermal expansion (6 – $8 \times 10^{-6}\text{K}^{-1}$) similar to that of silicon-based ceramic materials ($5 \times 10^{-6}\text{K}^{-1}$). And according to research, it can serve thousands of hours in a water vapor environment at 1482 °C, with excellent water vapor corrosion resistance. Therefore, rare earth silicate materials are drawing more and more attention [13,14,17–19].

Two distinct crystal phases can be distinguished in RE_2SiO_5 based on variations in rare earth elements (RE). All RE_2SiO_5 are monoclinic and stable as either space group $\text{P}2_1/\text{c}$ or $\text{C}2/\text{c}$, which are generally termed the X1 and X2 structure. RE_2SiO_5 forms the X1 phase when the radius of the rare earth elements ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}, \text{and Gd}$) is bigger, i.e., in the atomic numbers from 57 to 64. RE_2SiO_5 forms the X2 phase when the radius of the rare earth elements ($\text{RE} = \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{and Lu}$) is lower [20], i.e., in the atomic numbers from 66 to 71. According to Mackenzie Ridley's research, RE_2SiO_5 is in the X2 phase when the average radius of rare earth elements is less than 0.95 Å [21]. Two crystal structures are present in rare earth monosilicates; the X1 phase is stable at low temperatures (800–1200 °C) and the X2 phase emerges and is stable at high temperatures (1450–1950 °C) [22]. Volume differences brought forth by changes in the crystal shape affect stress fields and raise the possibility of cracking. Consequently, X2-phase monosilicates at high temperatures (1450–1550 °C) are frequently utilized in Environmental Barrier Coatings (EBCs). RE_2SiO_5 , in X2 phase compounds, includes one silicon atom (Si), five oxygen atoms (O1–O5), and two distinct locations for rare earth elements (RE_1 and RE_2). While the other oxygen atom forms a loose link with the rare earth elements, the four separate oxygen atoms (O1–O4) combine to create a $[\text{SiO}_4]$ tetrahedron with Si. The two distinct rare earth atoms have coordination numbers of 7 and 6, respectively, resulting in the compounds $[\text{REO}_7]$ and $[\text{REO}_6]$. Whereas $[\text{REO}_7]$ and $[\text{REO}_6]$ are comparatively softer, the $[\text{SiO}_4]$ tetrahedral structure is strong and has stiff characteristics. The mechanical and thermal properties of the material are greatly

impacted by these features. The rigidity of the $[\text{SiO}_4]$ tetrahedra endows the material with a higher modulus of elasticity and lower coefficient of thermal expansion, and thus the material typically exhibits better structural stability. In contrast, the weaker bonding of the $[\text{REO}_7]$ and $[\text{REO}_6]$ units allows for increased flexibility of the material, but may result in higher coefficients of thermal expansion and lower moduli of elasticity [20,21,23].

For multi-component rare earth monosilicates, the introduction of rare earth elements needs to be carefully selected, and different rare earth elements will have an impact on the Si-O bond strength and mechanical properties. It has been shown that the strength of the Si-O bond is proportional to the water vapor corrosion resistance of multi-component rare earth monosilicates, and the higher the strength of the Si-O bond, the stronger the water vapor corrosion resistance. For example, K. N. Lee [17] experimentally showed that the water vapor corrosion resistance of Yb_2SiO_5 is greater than that of Lu_2SiO_5 . And Han et al. [24] calculated the Si-O bond length of Yb_2SiO_5 to be 1.6137 Å by the first nature principle, which is smaller than the Si-O bond length of Lu_2SiO_5 of 1.6246 Å [24]. The flexural strength, elastic modulus, and thermal shock resistance of monoclinic Re_2SiO_5 for orthosilicates are dependent on the mass and radius of the rare earth cations, as demonstrated by both experimental and Density Functional Theory (DFT) calculations. For example, according to the experiments, RE_2SiO_5 increases the elastic modulus from Tb_2SiO_5 (143.72 GPa) to Lu_2SiO_5 (171.3 GPa) and the shear modulus from Tb_2SiO_5 (61 GPa) to Lu_2SiO_5 (71 GPa) as the radius of the rare earth elements decreases [7].

In order to study the lattice distortions as well as the mechanical properties of Yb_2SiO_5 and YbRESiO_5 (where RE = Sc, Y, Eu, Gd, Ho, Tm, Lu), we calculated the crystal structures and the elastic properties of the materials using first-principles calculation. Furthermore, the Si-O bond lengths of eight different rare earth monosilicates were simulated to assess the materials' resistance to water vapor corrosion. Additionally, Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 bulk materials were produced utilizing solid-phase reaction techniques based on the outcomes of first-principles calculations in order to precisely investigate the impact of various rare earth cations on the mechanical and thermodynamic properties of the materials. Microstructural analysis and thermodynamic property evaluations of the composite materials were conducted. Last but not least, by investigating the effects of the crystal structure, coefficient of thermal expansion, thermal conductivity, and elastic constants of different rare earth monosilicates, this study may provide a theoretical framework for the creation of novel EBC materials.

2. Computational Models and Experimental Procedures

2.1. Computational Models

One silicon atom (Si), five oxygen atom sites (O1–O5), and two distinct rare earth atom sites (Yb1 and Yb2) make up the Yb_2SiO_5 unit cell. While the remaining oxygen atom loosely connects with the rare earth atoms, four of the oxygen atoms (O1–O4) form a $[\text{SiO}_4]$ tetrahedron with the silicon atom. The two distinct rare earth atoms have coordination numbers of 7 and 6, respectively, resulting in the formation of $[\text{YbO}_7]$ and $[\text{YbO}_6]$ polyhedra [25]. Therefore, in the actual process, because larger atomic radius elements tend to occupy sites with larger coordination numbers, in the model of Yb_2SiO_5 , to better approximate real conditions, rare earth elements (RE = Eu, Gd, Ho, Tm) with atomic radii larger than Yb were added into the Re1 site, while rare earth elements (RE = Sc, Y, Lu) with atomic radii smaller than Yb were added into the RE2 site [26]. The conventional and primitive cells of Yb_2SiO_5 are shown in Figure 1 a and b, respectively.

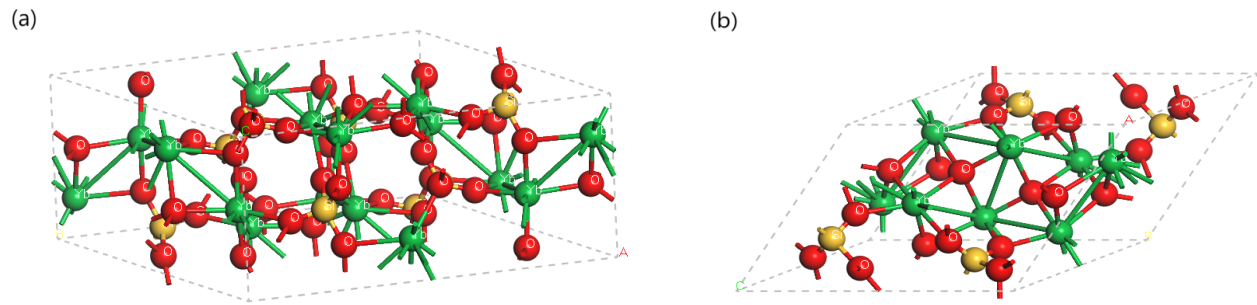


Figure 1. (a) Conventional cell and (b) primitive cell of Yb_2SiO_5 .

CASTEP was used to do computations from first principles. The most stable crystal structure at zero temperature was obtained by geometric optimization of the crystal structure of each rare earth silicate, which was then analyzed before the material's resistance to water vapor corrosion and its thermodynamic properties were assessed. The crystal structure optimization method was carried out by expanding Bloch waves in reciprocal space with a cutoff energy of 450 eV using a plane wave basis set under periodic boundary conditions [27]. The first irreducible Brillouin zone was used as the discrete $2 \times 3 \times 4k$ sample grid for the Monkhorst–Pack technique of energy integration. The first irreducible Brillouin zone is the smallest, uniquely defined region in reciprocal space that contains all the distinct momentum states of a crystal, crucial for simplifying electronic band structure calculations. Regarding exchange–correlation energies, the local density approximation (LDA) was employed [28]. To maximize the crystal structure, separate modifications were performed to the lattice constants and the relative locations of interior atoms. We used the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization approach to minimize both the interatomic forces and the overall energy [29]. We computed the electrostatic interactions between valence electrons and ionic cores using ultra-soft pseudopotentials. Atomic forces within $0.03 \text{ eV/\AA}$, energy differences within $1 \times 10^{-5} \text{ eV/atom}$, maximum stress within 0.05 GPa, and maximum ion displacement within $1 \times 10^{-3} \text{ \AA}$ were the convergence conditions for geometric optimization. A distance of 3 Å was chosen as the Mulliken population cutoff distance (which is the threshold distance used to determine which atomic contributions to electronic charge density are considered significant in the Mulliken population analysis) [24].

By linearly fitting stress against applied homogeneous elastic strains, the elastic constants were found. The strain–stress relationship approach developed by Milman and Warren was used to derive second-order elastic constants [30]. Four sets of uniform strain configurations (which refer to four different strain states applied in various directions and magnitudes to study changes in a material's structure and properties) were used to calculate the 13 independent elastic constants (C_{11} , C_{22} , C_{33} , C_{44} , C_{55} , C_{66} , C_{12} , C_{13} , C_{23} , C_{15} , C_{25} , C_{35} , and C_{46}) of Yb_2SiO_5 . Internal atomic degrees of freedom were optimized to yield the stresses. The linear fitting of computed stresses as a function of strain allowed for the determination of elastic stiffness. Maximum ion displacement differences were defined at $2 \times 10^{-4} \text{ \AA}$, total energy differences within $2 \times 10^{-6} \text{ eV/atom}$, and Hellmann–Feynman force (which is the force on an atom or particle derived directly from the gradient of the potential energy with respect to atomic positions) differences within $0.006 \text{ eV/\AA}$ as the convergence criterion for optimizing internal atomic degrees of freedom. The average sound velocity (v_m), Debye temperature (θ_D), bulk modulus (B), shear modulus (G), Young's modulus (E), and Poisson's ratio (ν) were then calculated using the elastic stiffness constants (c_{ij}) [31].

2.2. Material Preparation and Microstructure Characterization

The Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 bulk materials were prepared using the solid-state reaction method. The raw materials included Sc_2O_3 , Ho_2O_3 , Yb_2O_3 (≥ 99.9 wt.% from Shanghai Maclin Biochemical Technology Co., Ltd., Shanghai, China), and SiO_2 (≥ 99.99 wt.% from Shanghai Maclin Biochemical Technology Co., Ltd.). The powdered raw materials were first placed in crucibles and dried in an oven for two hours at 393 K. After that, they were weighed using a molar ratio of 2:1 for silicon to rare earth elements. After that, a clean stainless-steel tank was filled with the materials, milling balls, and anhydrous ethanol in a mass ratio of 1:2:1. The tank was then subjected to a 10 h ball milling process at 270 revolutions per minute. The slurry that had been ground was dried in ovens for 12 h at 353 K and 393 K. Subsequently, the coarse oxides were crushed into powders using an agate grinding disc and sieved through an 80-mesh screen to achieve fine powders. After that, these fine powders were put into molds measuring $\phi 15$ mm, and they were uniaxially pressed for five minutes at 15 MPa before oil pressure was applied. For thirty minutes, an oil pressure of 300 MPa was applied. To obtain the final products, the samples were sintered for 10 h at 1823 K.

Phase analysis of the sintered samples was carried out with an X-ray diffractometer (XRD, D/max, 2550VB/PC, Rigaku, Tokyo, Japan) filtered with $\text{Cu K}\alpha$ radiation at 18 KV accelerating voltage and 450 mA current. Using a step size of $10^\circ/\text{min}$, the diffraction angles were scanned from 10° to 80° . A scanning electron microscope (SEM, HITACHI S-3400 N, Japan) fitted with an energy-dispersive spectrometer (EDS, AMETEK APOLLO X, Berwyn, PA, USA) was used for microstructural examination.

2.3. Thermal Properties

Using standard metallographic techniques, all samples used in the thermal treatment experiments were cut from sintered bulk silicate.

Using a laser flash analyzer ((NETZSCH, LFA 427, Germany), the bulk silicate's thermal diffusivity was determined throughout a temperature range of 300 K to 1473 K. Sample dimensions were $12.7 \text{ mm} \times 2 \text{ mm}$. To reduce heat radiation, a thin layer of graphite was applied to the samples' two sides prior to testing.

The thermal conductivity (k) of the material was calculated using the following formula, derived from thermal diffusivity (D_{th}), density (ρ), and specific heat capacity (c_p) [32]:

$$k = D_{th} \cdot \rho \cdot c_p \quad (1)$$

Additionally, the density (ρ) was determined using Archimedes' method (which is using the principle of buoyancy to determine the volume of an irregularly shaped object) [33], while the specific heat capacity (c_p) was calculated using the Neumann-Kopp law (which states that the heat capacity of a substance is proportional to the number of atoms or molecules in a compound) [34]. Furthermore, the thermal conductivity of fully dense samples (k_0) was computed [35].

$$k_0 = \frac{k}{1 - \frac{4\psi}{3}} \quad (2)$$

k is the theoretical thermal conductivity, ψ is the porosity. Additionally, thermal expansion coefficient-related parameters of bulk silicates were measured using a vertical high-temperature dilatometer (NETZSCH, DIL 402C, Germany) in the range of 303 K to 1473 K. The formula for calculating the thermal expansion coefficient (α) is as follows [31]:

$$\alpha = \frac{\Delta L}{L \cdot \Delta T} \quad (3)$$

Here, L represents the original length of the sample, and ΔL denotes the length change of the sample under the temperature difference ΔT . The samples used were rectangular rods measuring $2 \text{ mm} \times 6 \text{ mm} \times 11 \text{ mm}$ in the three dimensions.

3. Result and Discussion

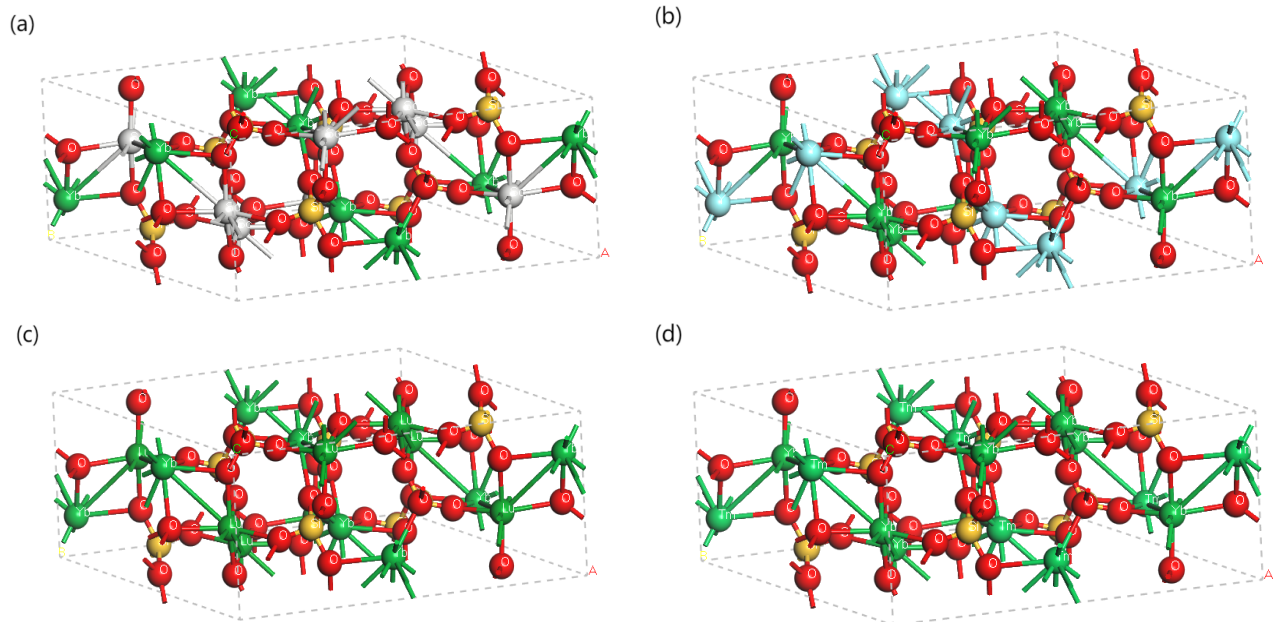
3.1. First-Principles Calculations

After geometric optimization, the computed and theoretical lattice parameters of Yb_2SiO_5 are shown in Table 1. Deviation in this section is defined as the gap between the geometrically optimized lattice parameters of the material and the theoretical lattice parameters. Less than 3% separates the lattice constants from their theoretical values, indicating that the computations are reliable.

Table 1. The lattice parameters of Yb_2SiO_5 after lattice optimization and the theoretical lattice parameters.

Parameter	Yb_2SiO_5 Theory [20]	Yb_2SiO_5 Calculation	Deviation (%)
$a(\text{\AA})$	14.2800	14.1961	0.5021
$b(\text{\AA})$	10.2800	10.0852	1.9052
$c(\text{\AA})$	6.6530	6.5614	1.3013
$\gamma(^{\circ})$	122.200	122.2250	0.0220

The crystal structures of YbRESiO_5 (RE = Sc, Y, Ho, Eu, Tm, Lu, Gd) following geometric optimization are displayed in Figure 2. Due of variations in rare earth element types, the locations of Si and O atoms vary during geometric optimization, leading to changes in lattice constants and subsequently affecting the unit cell volumes. The crystal forms with various rare earth element dopants following geometric optimization are shown in Figure 2.



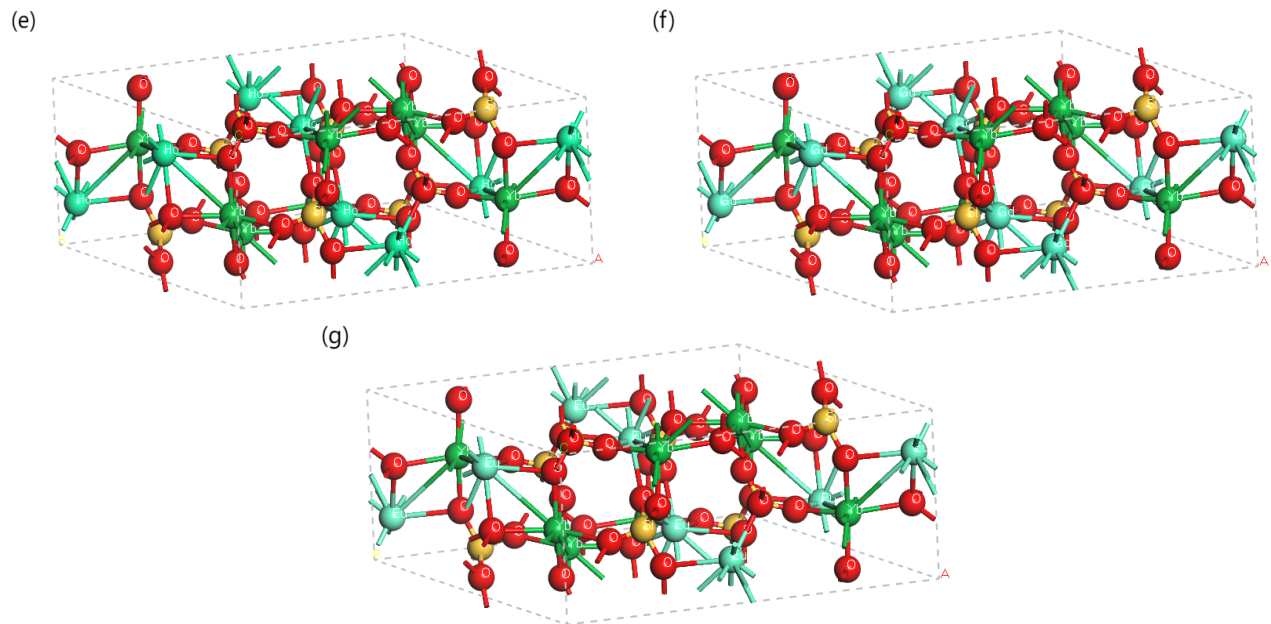


Figure 2. Geometrically optimized crystal structure of YbRESiO₅ (RE = Sc, Y, Lu, Tm, Ho, Gd, Eu). (a) YbScSiO₅, (b) YbYSiO₅, (c) YbLuSiO₅, (d) YbTmSiO₅, (e) YbHoSiO₅, (f) YbGdSiO₅, and (g) YbEuSiO₅.

After geometric optimization with addition of different rare earth elements, Table 2 shows the lattice parameters and unit cell volumes of YbRESiO₅. According to computational analysis, the largest unit cell volume is produced by doping with the largest atomic radius element, Eu, and the smallest unit cell volume is produced by adding the element Sc. The overall trend is YbScSiO₅ (750.4240 Å³) < YbHoSiO₅ (794.8210 Å³) < Yb₂SiO₅ (794.7620 Å³) < YbTmSiO₅ (800.1510 Å³) < YbGdSiO₅ (806.6770 Å³) < YbYSiO₅ (809.2980 Å³) < YbLuSiO₅ (812.4510 Å³) < YbEuSiO₅ (813.6240 Å³).

Table 2. Geometrically optimized lattice parameters of YbRESiO₅ (RE = Sc, Y, Lu, Tm, Ho, Gd, Eu).

Parameter	a (Å)	b (Å)	c (Å)	γ (°)	V (Å ³)
YbYSiO ₅	14.2749	10.1817	6.5710	122.0710	809.2980
YbLuSiO ₅	14.3203	10.1851	6.5834	122.2090	812.4510
YbHoSiO ₅	14.1741	10.1046	6.5834	122.3620	794.8210
YbGdSiO ₅	14.2360	10.1655	6.5936	122.2250	806.6770
YbScSiO ₅	13.9188	9.94632	6.4012	122.1350	750.4240
YbTmSiO ₅	14.1493	10.1100	6.6152	122.2680	800.1510
Yb ₂ SiO ₅	14.1916	10.0858	6.5616	122.2250	794.7620
YbEuSiO ₅	14.2760	10.1632	6.6205	122.2340	813.6240

3.1.1. Crystal Lattice Distortion Calculation

To quantitatively describe the distortion of polyhedra, the following equation is used to calculate the lattice distortion within the material [25]:

$$\Delta d = \frac{1}{n} \sum_n \left\{ \frac{d(\text{MO})_n - [d(\text{MO})_{\text{Re}}]}{[d(\text{MO})_{\text{Re}}]} \right\}^2 \quad (4)$$

Here, $d(\text{MO})_{\text{Re}}$ represents the average bond length of Re-O and Si-O in YbReSiO₅ (Re = Sc, Y, Lu, Eu, Gd, Tm, Ho), while $d(\text{MO})_n$ represents the bond length between the rare earth element (Re) or silicon (Si) and the nth oxygen atom.

Table 3 gives the bond lengths, average bond lengths, and lattice distortions of [SiO₄], [REO₆], and [REO₇] in YbRESiO₅ (RE = Sc, Y, Lu, Eu, Gd, Tm, Ho). We discovered that adding Sc, the element with the smallest atomic radius in our investigation, drastically alters the bond lengths and lattice distortions of the material when compared to Yb₂SiO₅. In comparison to Yb₂SiO₅, YbScSiO₅ has the highest lattice distortions in [REO₆] and [REO₇], rising by approximately 50% and 60%, respectively. It also has the shortest average RE-O bond lengths in [REO₆] and [REO₇]. Compared to Yb₂SiO₅, its average RE-O bond lengths decrease by 0.5% and 4.4%. Conversely, among elements that increase the RE-O bond lengths, adding Eu resulted in the longest RE-O bond lengths in [REO₆] and [REO₇] for YbEuSiO₅, rising by roughly 1.3% and 1.5%, respectively, compared to Yb₂SiO₅.

Table 3. Lattice distortion values of different rare earth monociliate.

Compound	Bond	Polyhedra	Bond Length (Å)	Average Bond Length (Å)	Degree of Distortion (%)
Yb ₂ SiO ₅	RE1-O	[REO ₇]	2.17365, 2.26578, 2.27687, 2.28556, 2.29827, 2.3003, 2.50653	2.30098	1.63300
	RE2-O	[REO ₆]	2.17305, 2.20835, 2.21083, 2.22665, 2.22665, 2.24791	2.21750	0.12334
	Si-O	[SiO ₄]	1.5915, 1.60382, 1.60696, 1.6228	1.60627	0.04824
YbTmSiO ₅	RE1-O	[REO ₇]	2.1845, 2.23035, 2.24948, 2.28916, 2.31377, 2.35425, 2.4962	2.30253	1.68259
	RE2-O	[REO ₆]	2.15346, 2.20741, 2.21105, 2.22142, 2.22615, 2.26116	2.21344	0.20894
	Si-O	[SiO ₄]	1.59125, 1.60026, 1.60967, 1.62292	1.60602	0.05333
YbEuSiO ₅	RE1-O	[REO ₇]	2.22305, 2.26695, 2.31138, 2.31634, 2.32237, 2.36489, 2.50513	2.33001	1.26024
	RE2-O	[REO ₆]	2.15427, 2.22478, 2.23663, 2.25526, 2.26148, 2.29384	2.23771	0.37126
	Si-O	[SiO ₄]	1.59478, 1.60092, 1.61483, 1.61983	1.60759	0.03971
YbGdSiO ₅	RE1-O	[REO ₇]	2.2152, 2.26505, 2.29988, 2.31368, 2.31368, 2.35175, 2.49526	2.32157	1.27335
	RE2-O	[REO ₆]	2.19257, 2.21548, 2.23843, 2.23147, 2.25323, 2.26769	2.23314	0.11984
	Si-O	[SiO ₄]	1.59321, 1.60148, 1.6151, 1.62029	1.60752	0.04468
YbHoSiO ₅	RE1-O	[REO ₇]	2.20092, 2.25368, 2.28601, 2.30648, 2.30662, 2.34039, 2.58406	2.32545	2.37837
	RE2-O	[REO ₆]	2.20766, 2.22172, 2.22778, 2.23061, 2.27294, 2.14123	2.21699	0.31473
	Si-O	[SiO ₄]	1.59119, 1.5994, 1.61279, 1.62194	1.60633	0.05451
YbLuSiO ₅	RE1-O	[REO ₇]	2.17016, 2.28852, 2.28869, 2.30331, 2.30836, 2.31393, 2.52894	2.31456	1.82196
	RE2-O	[REO ₆]	2.21116, 2.23925, 2.24528, 2.25512, 2.25873, 2.26928	2.24643	0.07019
	Si-O	[SiO ₄]	1.59393, 1.60716, 1.60992, 1.61873	1.60744	0.03059
YbScSiO ₅	RE1-O	[REO ₇]	2.15248, 2.21908, 2.23995, 2.2501, 2.28767, 2.29817, 2.59642	2.29198	3.31675
	RE2-O	[REO ₆]	2.11166, 2.02535, 2.08059, 2.11853, 2.13039, 2.17394	2.10674	0.47114
	Si-O	[SiO ₄]	1.59075, 1.5956, 1.60682, 1.61654	1.60243	0.05863
YbYSiO ₅	RE1-O	[REO ₇]	2.17206, 2.28342, 2.29012, 2.29846, 2.30223, 2.30753, 2.54975	2.31480	2.07000
	RE2-O	[REO ₆]	2.19854, 2.23202, 2.23482, 2.23886, 2.24511, 2.25553	2.23415	0.06170
	Si-O	[SiO ₄]	1.5952, 1.60773, 1.60961, 1.61904	1.60620	0.02906

In this study, the average RE-O bond lengths in [REO₆] polyhedra for the eight different rare earth monosilicates are ordered as follows: YbScSiO₅ (2.10674 Å) < YbHoSiO₅ (2.21699 Å) < YbTmSiO₅ (2.21344 Å) < Yb₂SiO₅ (2.21750 Å) < YbLuSiO₅ (2.24643 Å) < YbGdSiO₅ (2.23314 Å) < YbEuSiO₅ (2.23771 Å). In [REO₇] polyhedra, the average RE-O

bond lengths are ordered as: YbScSiO_5 (2.29198 Å) < Yb_2SiO_5 (2.30098 Å) < YbTmSiO_5 (2.30253 Å) < YbYSiO_5 (2.31480 Å) < YbLuSiO_5 (2.31456 Å) < YbHoSiO_5 (2.32545 Å) < YbGdSiO_5 (2.32157 Å) < YbEuSiO_5 (2.33001 Å). The lattice distortion in $[\text{REO}_7]$ is ranked as follows: YbEuSiO_5 (1.26024‰) < YbGdSiO_5 (1.27335‰) < Yb_2SiO_5 (1.63300‰) < YbTmSiO_5 (1.68259‰) < YbLuSiO_5 (1.82196‰) < YbYSiO_5 (2.07000‰) < YbHoSiO_5 (2.37837‰) < YbScSiO_5 (3.31675‰). The lattice distortion in $[\text{REO}_6]$ polyhedra is ranked as: YbYSiO_5 (0.06170‰) < YbLuSiO_5 (0.07019‰) < YbGdSiO_5 (0.11984‰) < Yb_2SiO_5 (0.12334‰) < YbTmSiO_5 (0.20894‰) < YbHoSiO_5 (0.31473‰) < YbEuSiO_5 (0.37126‰) < YbScSiO_5 (0.47114‰). Among the eight rare earth monosilicates, YbScSiO_5 has the biggest lattice distortion and the shortest RE-O bond length. We relate this to the considerable difference in atomic radii between Yb and Sc elements. Additionally, the introduction of various elements also affects the lattice distortion of $[\text{SiO}_4]$ tetrahedra, but because of their rigid nature, the amplitude of variation is not significant in this study and thus is not discussed in detail here. YbScSiO_5 exhibits the largest lattice distortion and shortest RE-O bond length as a result of this heterogeneity in rare earth cation radii.

3.1.2. Water Vapor Corrosion Resistance

Testing the water vapor corrosion resistance in environments similar to combustion but without alumina is necessary because the majority of current experiments on environmental barrier coatings for water vapor corrosion are carried out in alumina tubes, and there are reports that alumina contamination may alter the water vapor corrosion resistance of RE_2SiO_5 [9]. It is difficult, though, to carry out useful research in such hot conditions without adding alumina materials. Thus, in order to acquire theoretical information on the water vapor corrosion resistance of eight materials, this work uses first-principles calculations. It has been demonstrated that using first-principles calculations to predict the properties of compounds with various components but the same crystal structure works well [24]. For example, the strength of the Si-O linkages can reflect the water vapor corrosion resistance of $\text{RE}_2\text{Si}_2\text{O}_7$ with the same crystal structure.

The Si-O bonds in rare earth silicates are broken down by steam during high-temperature water vapor corrosion, which corrodes environmental barrier coatings by Si-O degradation. The pace of corrosion is slower if the Si-O bonds are generally stable; on the other hand, the rate of corrosion is higher if the Si-O bonds are weak. As a result, by determining the strength of the Si-O linkages, the water vapor corrosion resistance of rare earth monosilicates may be compared [36]. Si-O bond density, which is defined as the ratio of Si-O bond energy to Si-O bond length, usually directly correlates with the strength of Si-O bonds. Determining the Si-O bond information through first-principles calculations on materials enables evaluation of the water vapor corrosion performance of various rare earth monosilicates.

Eight distinct rare earth monosilicates are shown in Figure 3 and Table 4 along with their Si-O bond densities, Milliken populations, and Si-O bond lengths. Our calculations show that, out of the eight materials, YbScSiO_5 has the highest resistance to water vapor corrosion because it has the shortest Si-O link length (1.60243 Å), the highest Milliken population (0.63500), and the greatest bond density (0.3963 Å⁻¹). Following Eu addition, YbEuSiO_5 has the longest Si-O bond length (0.61000 Å); nevertheless, it also has a lower Milliken population (0.61000) and bond density (0.3794 Å⁻¹) than Yb_2SiO_5 , suggesting that it is less resistant to water vapor corrosion than Yb_2SiO_5 . The water vapor corrosion resistance of Yb_2SiO_5 is generally enhanced by adding Sc, Ho, and Tm, and decreased by doping with Gd, Eu, Y, and Lu. Overall, the ranking of water vapor corrosion resistance among the eight different rare earth monosilicates is as follows: YbLuSiO_5 (0.3764 Å⁻¹) < YbEuSiO_5 (0.3794 Å⁻¹) < YbGdSiO_5 (0.3810 Å⁻¹) < YbYSiO_5 (0.3811 Å⁻¹) < Yb_2SiO_5 (0.3844 Å⁻¹) < YbTmSiO_5 (0.3851 Å⁻¹) < YbHoSiO_5 (0.3860 Å⁻¹) < YbScSiO_5 (0.3963 Å⁻¹).

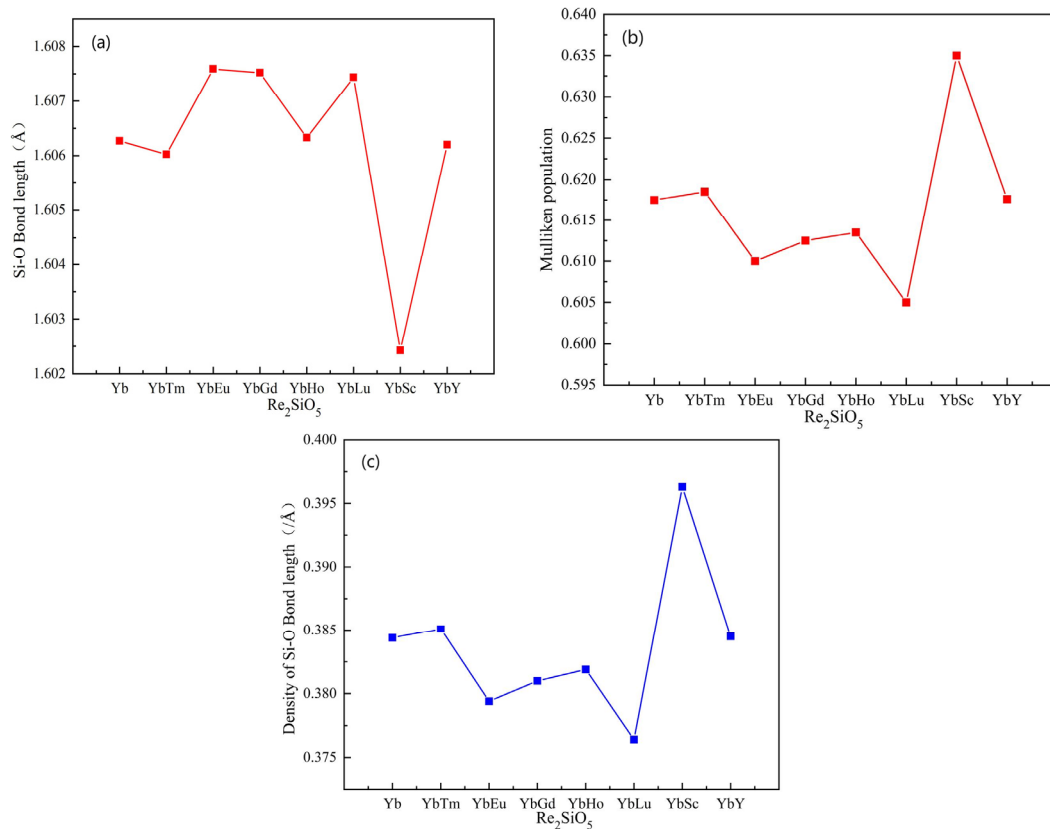


Figure 3. (a) Si-O bond lengths, (b) Milliken population, and (c) density of Si-O bonds for YbRESiO₅ (RE = Yb, Sc, Y, Lu, Tm, Ho, Gd, Eu).

Table 4. Si-O bond information for YbRESiO₅ (RE = Yb, Sc, Y, Lu, Tm, Ho, Gd, Eu).

Compound	Bond Average (Å)	Population of Bond	Density (Å ⁻¹)
Yb ₂ SiO ₅	1.60627	0.61750	0.3844
YbTmSiO ₅	1.60603	0.61850	0.3851
YbEuSiO ₅	1.60759	0.61000	0.3794
YbGdSiO ₅	1.60752	0.61250	0.3810
YbHoSiO ₅	1.60620	0.6200	0.3860
YbLuSiO ₅	1.60744	0.60500	0.3764
YbScSiO ₅	1.60243	0.63500	0.3963
YbYSiO ₅	1.60630	0.61720	0.3811

3.1.3. Elastic Constants

The elastic constants of YbRESiO₅ (RE = Yb, Eu, Gd, Ho, Tm, Lu, Y, Sc) that were determined using first-principles techniques are shown in Table 5. The average sound velocity, Debye temperature, bulk modulus, shear modulus, and Young's modulus of Yb₂SiO₅ are all markedly increased by the equimolar addition of Sc, while the addition of Gd has the reverse effect. Poisson's ratio is the lowest when adding Ho. The order of magnitude for average sound velocity is as follows: YbGdSiO₅ (2875.6370 m/s) < YbEuSiO₅ (3027.7198 m/s) < YbHoSiO₅ (3047.4524 m/s) < YbTmSiO₅ (3115.4777 m/s) < Yb₂SiO₅ (3116.0476 m/s) < YbLuSiO₅ (3136.1570 m/s) < YbYSiO₅ (3282.3078) < YbScSiO₅ (3669.7119 m/s). The ranking of the Debye temperature is YbGdSiO₅ (367.7621 K) < YbEuSiO₅ (392.4537 K) < YbHoSiO₅ (394.2189 K) < YbTmSiO₅ (395.7621 K) < Yb₂SiO₅ (400.2373 K) < YbLuSiO₅ (403.6193 K) < YbYSiO₅ (419.4569 K) < YbScSiO₅ (481.4030 K). The ranking of Young's modulus is YbGdSiO₅ (125.8217 Gpa) < YbEuSiO₅ (134.4732 Gpa) < YbHoSiO₅

(139.7532 Gpa) < YbYSiO₅ (145.4985 Gpa) < YbTmSiO₅ (145.6084 Gpa) < YbLuSiO₅ (151.7248 Gpa) < Yb₂SiO₅ (153.4019 Gpa) < YbScSiO₅ (162.0600 Gpa).

Table 5. Elastic constants of YbRESiO₅ (RE = Yb, Tm, Eu, Gd, Lu, Ho, Sc, Y).

Compound	ν_m (m/s)	θ_D (K)	B (Gpa)	G (Gpa)	E (Gpa)	ν
Yb ₂ SiO ₅	3116.0476	400.2373	116.9618	59.8568	153.4019	0.2696
YbTmSiO ₅	3115.4777	395.7621	105.4786	57.3296	145.6084	0.2699
YbEuSiO ₅	3027.7198	392.4537	102.4466	57.1057	134.4732	0.2677
YbGdSiO ₅	2875.6370	367.7621	92.0294	49.4669	125.8217	0.2721
YbLuSiO ₅	3136.1570	403.6193	106.2719	60.1105	151.7248	0.2621
YbHoSiO ₅	3047.4524	394.2189	97.2663	55.4342	139.7532	0.2605
YbScSiO ₅	3669.7119	481.4030	126.2605	63.0056	162.0600	0.2861
YbYSiO ₅	3282.3078	419.4569	95.0679	53.6648	145.4985	0.2625

Studies have indicated that the atomic number of the rare earth element has a substantial impact on the elastic modulus and flexural strength of X2-RE₂SiO₅ samples. This discovery could be explained by the rare earth element's decreased ionic radius increasing rare earth–oxygen interactions. In X2-RE₂SiO₅ samples, the bond strength can be represented by the cation field strength (CFS) [7]. The calculation formula for CFS is as follows [37]:

$$CFS = Z_c / r_c^2 \quad (5)$$

Z_c represents the cation charge, and r_c^2 represents the cation radius squared.

It is clear from the data in Table 6 that when the ionic radius of rare earth elements falls, so does the bonding strength between oxygen and rare earth in X2-RE₂SiO₅. Consequently, the cation field strength (CFS) of cations having larger radii, including Gd³⁺, Eu³⁺, Ho³⁺, Tm³⁺, and Y³⁺, is lower than that of Yb₂SiO₅. As a result, when adding cations such as Gd³⁺, Eu³⁺, Ho³⁺, Tm³⁺, and Y³⁺, the Young's modulus lowers. Of the eight rare earth monosilicates, the element Sc³⁺ with the shortest cation radius has the highest CFS and, consequently, the highest Young's modulus. The findings of the computed elastic modulus, however, do not quite match the CFS ranking. This disparity can be explained by the fact that materials containing Yb frequently show aberrant characteristics in comparison to other lanthanide elements, such as a different melting and boiling point and density. This observation might be explained by the fact that Yb ([Xe]4f¹⁴6s²) has a closed-shell atomic configuration, meaning that there are only two 6s valence electrons accessible for chemical bonding [7].

Table 6. CFS of rare earth cations in YbRESiO₅ (RE = Yb, Sc, Y, Lu, Tm, Ho, Gd, Eu).

Compound	Average Ionic Radius	CFS
Yb ₂ SiO ₅	0.86	4.056
YbTmSiO ₅	0.865	4.009
YbEuSiO ₅	0.905	3.662
YbGdSiO ₅	0.9	3.370
YbHoSiO ₅	0.88	3.387
YbLuSiO ₅	0.855	4.104
YbScSiO ₅	0.835	4.303
YbYSiO ₅	0.875	3.918

3.2. Phases and Microstructure of Sintered Bulk Materials

Three materials' XRD patterns are displayed in Figure 4: Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅. There is no second phase in the prepared silicate bulk materials, according to

the measured diffraction peaks between the prepared monosilicates and the standard PDF of the Yb_2SiO_5 card (97-000-4446). Shifts in the diffraction peaks of YbScSiO_5 and YbEuSiO_5 relative to the standard Yb_2SiO_5 PDF card are detected upon doping Yb_2SiO_5 with Sc and Eu. The diffraction peaks move to larger angles when the smaller cation radius element (Sc^{3+}) is incorporated into Yb_2SiO_5 . This is due to a change in lattice parameters. On the other hand, adding a higher cation radius element (Eu^{3+}) increases the lattice parameters and causes the peaks of diffraction to move to smaller angles. These outcomes agree with the XRD patterns in Figure 4 and the simulated computations in Table 2. The unit cell volume of Yb_2SiO_5 drops by 5.1% when equal moles of Sc are added, but increases by 2.3% when doped with the same moles of Eu. Consequently, YbScSiO_5 ($750.4240 \text{ \AA}^3$) < Yb_2SiO_5 ($794.7620 \text{ \AA}^3$) < YbEuSiO_5 ($813.6240 \text{ \AA}^3$) is the order in which the unit cell volumes of the three materials are arranged.

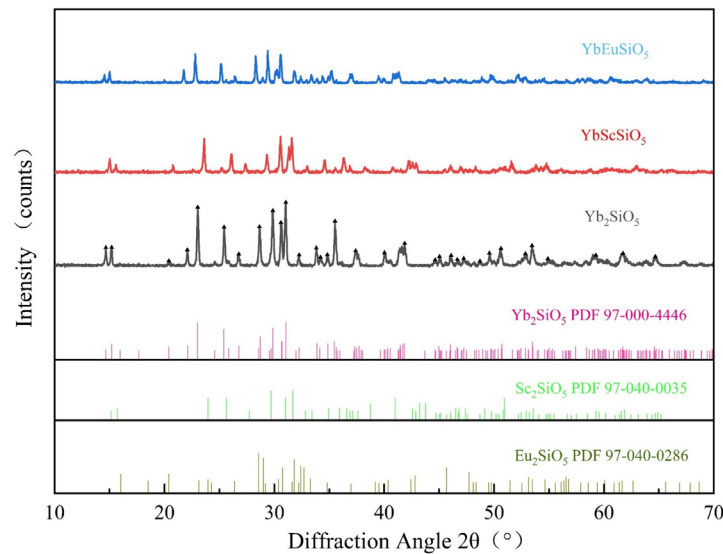


Figure 4. XRD patterns of YbReSiO_5 (Re = Yb, Sc, Eu).

As seen in the XRD patterns in Figure 4, which show no further phases, the produced rare earth monosilicates often have few pores and no noticeable fissures. Furthermore, porosity levels within 5% were demonstrated by the density and porosity calculations of Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 , as indicated in Table 3. The microstructures of cross-sections of the materials Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 are displayed in Figure 5. A homogeneous distribution of elements is revealed by EDS scans of the elemental distribution in the three materials (Figure 6). When paired with the XRD results shown in Figure 4, these results show that the Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 sample preparation procedures were accurate and produced materials that were reasonably pure. The results of various densities and porosities of the three materials are shown in Table 7.

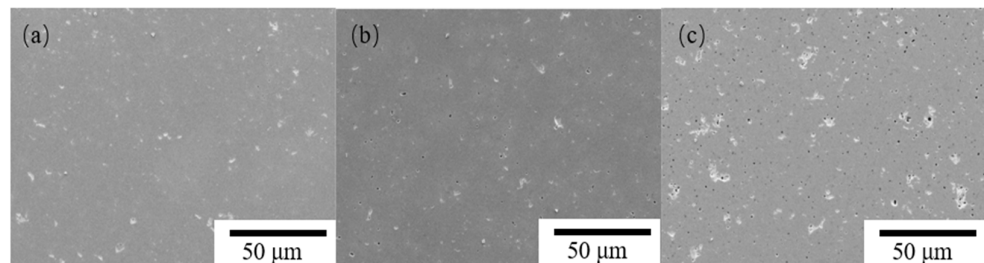


Figure 5. (a) Microstructure of Yb_2SiO_5 , (b) microstructure of YbScSiO_5 , and (c) microstructure of YbEuSiO_5 .

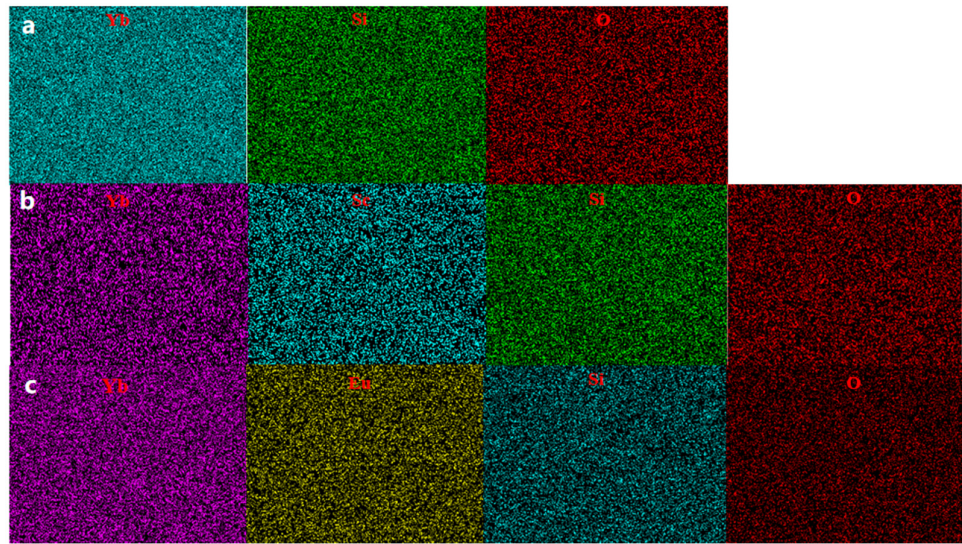


Figure 6. (a) Element distribution of Yb_2SiO_5 , (b) element distribution of YbScSiO_5 , and (c) element distribution of YbEuSiO_5 .

Table 7. Theoretical density ρ (RE_2SiO_5), mass fraction ω (RE_2SiO_5), ω (SiO_2), experimental density ρ (Exp.), bulk density (d), and porosity (ψ) of Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 .

Compound	$\rho(\text{RE}_2\text{SiO}_5)$ ($\text{g}\cdot\text{cm}^{-3}$)	$\omega(\text{RE}_2\text{SiO}_5)$ (wt.%)	$\omega(\text{SiO}_2)$ (wt.%)	$\rho(\text{Exp.})$ ($\text{g}\cdot\text{cm}^{-3}$)	d (%)	ψ (%)
Yb_2SiO_5	7.28	86.77	13.23	7.12	97.80	2.20
YbEuSiO_5	5.76	81.57	18.43	5.49	95.31	4.69
YbScSiO_5	6.69	86.13	13.87	6.40	95.66	4.34

3.3. Thermal Performance Test

3.3.1. Thermal Conductivity

Figure 7 shows the thermal expansion coefficients and specific heat capacities of Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 within the temperature range of 300 K to 1473 K. For these three rare earth monosilicates, the thermal expansion coefficients often decrease with increasing temperature, which is consistent with the typical trend of phonon thermal conductivity [25,38]. Both the thermal conductivity and the thermal expansion coefficient, however, exhibit a rising trend at 800 °C, most likely as a result of radiation heat transfer effects, which have also been noted in other tests [39]. Consequently, statistics on laser thermal conductivity above 800 °C should be regarded as approximations. The thermal diffusivity of Yb_2SiO_5 ranges from $0.470 \text{ mm}^2\cdot\text{s}^{-1}$ to $0.788 \text{ mm}^2\cdot\text{s}^{-1}$ between 300 K and 1473 K. YbScSiO_5 exhibits a thermal diffusivity ranging from $0.506 \text{ mm}^2\cdot\text{s}^{-1}$ to $0.751 \text{ mm}^2\cdot\text{s}^{-1}$. The lowest thermal expansion coefficient is shown by YbEuSiO_5 , which ranges from $0.352 \text{ mm}^2\cdot\text{s}^{-1}$ to $0.610 \text{ mm}^2\cdot\text{s}^{-1}$.

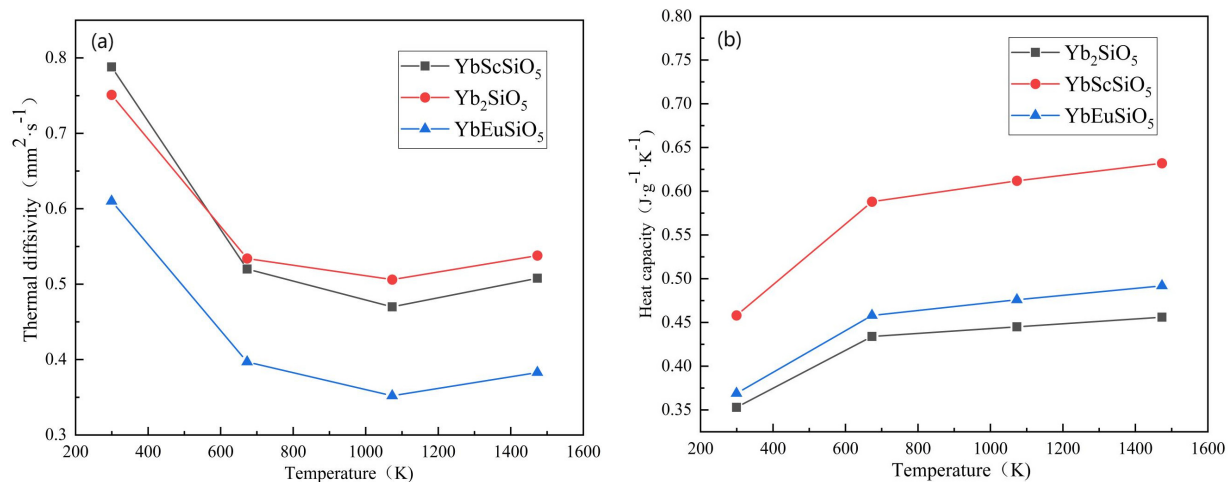


Figure 7. (a) Thermal diffusivity of Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅, (b) specific heat capacity of Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅.

Three distinct rare earth monosilicates' actual and theoretical thermal conductivities are displayed in Figure 8. In this investigation, the porosity of all three samples stayed below 5%. The estimated theoretical value of $2.17 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for Yb₂SiO₅ at ambient temperature closely matches the reported value of $2.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ for Yb₂SiO₅ in the literature [40]. The theoretical thermal conductivity of Yb₂SiO₅ at normal temperatures is $2.07 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. Microstructural variations, such as variations in grain size and the impact of infrared radiation at high temperatures, may be the cause of the poorer thermal conductivity and thermal diffusivity of Yb₂SiO₅ in this investigation. Additionally, YbScSiO₅ has a range of $1.85 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $1.67 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, YbEuSiO₅ exhibits the lowest thermal conductivity among the three materials, ranging from $1.44 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $1.07 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, and Yb₂SiO₅ varies from $2.07 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $1.52 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. Overall, the addition of Sc elements results in very little change in thermal conductivity and thermal diffusivity; at 650 K, YbScSiO₅ exhibits slightly higher values than Yb₂SiO₅, but before this temperature, the tendency is the opposite. On the other hand, YbEuSiO₅'s diffusivity and thermal conductivity dramatically drop with the addition of Eu. The experiment's observation of radiation heat transfer may be the cause of the rise in thermal conductivity at 1073 K.

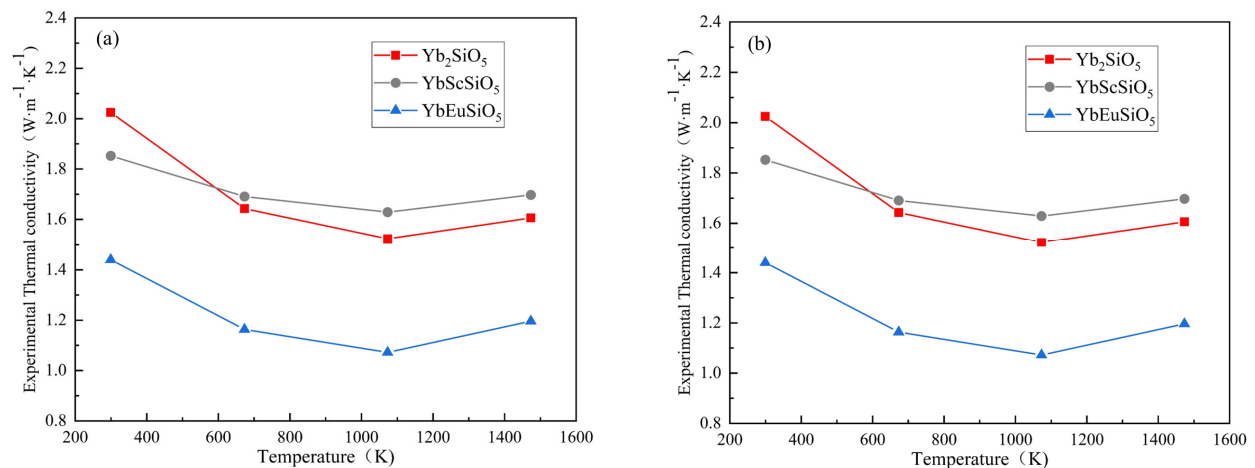


Figure 8. (a) Experimental thermal conductivity of Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅, (b) theoretical thermal conductivity of Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅.

This study states that the thermal conductivity of Sc_2SiO_5 material is 1.67 times greater than that of Yb_2SiO_5 and varies from $2.50 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $3.50 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ between 400 K and 1673 K. Eu_2SiO_5 has a lower thermal conductivity than Yb_2SiO_5 , ranging from $1.50 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $1.25 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. As a result, it drops to $1.25 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, which is less than Yb_2SiO_5 [26,35]. Thus, it can be deduced that there may be a positive correlation between the thermal conductivity of rare earth monosilicate materials doped with binary equimolar elements and the thermal conductivity of their parent materials. Additionally, YbScSiO_5 and YbEuSiO_5 exhibit greater specific heat capacity than Yb_2SiO_5 , with the inclusion of Sc elements having a particularly notable effect. Yb_2SiO_5 with Sc may somewhat raise the material's thermal conductivity, while doping the material with Eu may result in a minor drop in thermal conductivity. Nonetheless, the square root of thermal conductivity and phonon scattering coefficient are inversely proportional in materials with added point defects because of the large lattice distortion in YbScSiO_5 and the adherence to phonon heat transfer principles in those materials. Higher phonon scattering coefficients can result from larger lattice distortions and mismatched rare earth cation weights and radii. This could account for YbScSiO_5 's weaker thermal diffusivity and conductivity than Yb_2SiO_5 at temperatures lower than 600 K.

The outer electron structure of Eu, which is $4f^7 6s^2$, is another factor contributing to YbEuSiO_5 's lowest thermal conductivity. Its outer electron structure becomes $4f^7$ when it loses two electrons. Based on Hund's rule, $4f^7$ is in a stable half-filled state. Eu^{2+} ions, which encourage the creation of oxygen vacancies and drastically lower thermal conductivity, may therefore be present in YbEuSiO_5 [26].

Overall, compared to Yb_2SiO_5 , the insertion of Sc components exhibits little overall change in thermal conductivity and thermal diffusivity. On the other hand, compared to Yb_2SiO_5 , the addition of Eu elements leads to much decreased thermal diffusivity and thermal conductivity because of the development of oxygen vacancies. In particular, YbEuSiO_5 has a minimum thermal conductivity of $1.07 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ in the temperature range of 303 K to 1473 K, which is 29% less than Yb_2SiO_5 's ($1.52 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). Moreover, YbEuSiO_5 's ($1.44 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $1.07 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) thermal conductivity fluctuates less in this temperature range than Yb_2SiO_5 's ($2.07 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ to $1.52 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). Furthermore, the stability of the temperature and stress fields is aided by the low range of thermal conductivity parameters. For materials that are monosilicate, these elements are essential.

3.3.2. CTE

Figure 9 shows the coefficient of thermal expansion (CTE) and $\Delta L/L$ curves of Yb_2SiO_5 , YbScSiO_5 , and YbEuSiO_5 from 303 K to 1473 K. Compared to Yb_2SiO_5 , YbEuSiO_5 exhibits an increasing trend in $\Delta L/L$, while YbScSiO_5 shows a decreasing trend. Here, ΔL is the only representation of the change because L , the original length, is a constant. In contrast to Yb_2SiO_5 , the effects of Sc and Eu doping on ΔL are opposite. In order to get precise coefficients of thermal expansion for monosilicate materials, as shown in Figure 8, it is noted that, for Yb_2SiO_5 , the CTE varies between $5.86 \times 10^{-6} \text{ K}^{-1}$ and $8.05 \times 10^{-6} \text{ K}^{-1}$ over the 600 K to 1473 K temperature range. The results of this investigation closely match those of Tian et al. and mistakes lower than $0.5 \times 10^{-6} \text{ K}^{-1}$ can often be ignored, as they are most likely the result of experimental and sampling mistakes. The addition of Eu to YbEuSiO_5 raises its CTE in comparison to Yb_2SiO_5 , while Sc doping lowers the CTE of YbScSiO_5 , following the $\Delta L/L$ trends. YbScSiO_5 and YbEuSiO_5 show CTE values of $5.64 \times 10^{-6} \text{ K}^{-1}$ to $7.56 \times 10^{-6} \text{ K}^{-1}$ and $6.16 \times 10^{-6} \text{ K}^{-1}$ to $8.6 \times 10^{-6} \text{ K}^{-1}$, respectively, throughout the 600 K to 1473 K range. Compared to Yb_2SiO_5 , the addition of Sc lowers the material's overall CTE as well as the amplitude of its temperature-dependent CTE variation. On the other hand, Eu's introduction has the opposite impact.

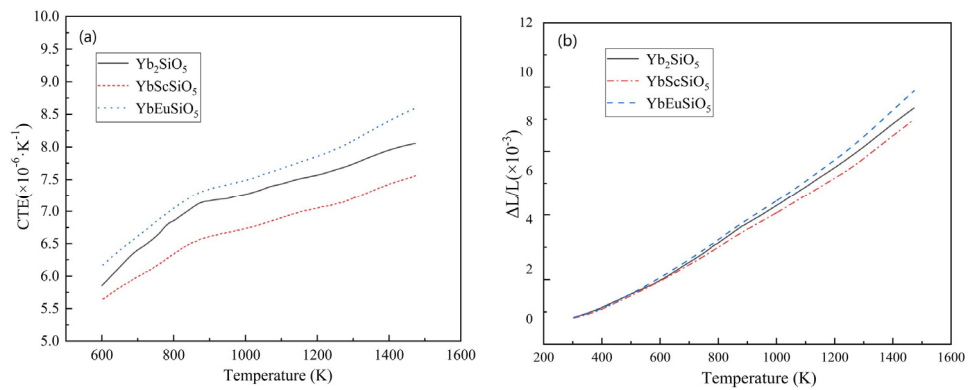


Figure 9. (a) Thermal expansion coefficient (CTE) of Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅, (b) $\Delta L/L$ curves of Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅.

The coefficient of thermal expansion (CTE) of YbScSiO₅ doped with Sc is often lower than that of Yb₂SiO₅, but the CTE of YbEuSiO₅ doped with Eu is higher. YbScSiO₅ has the lowest CTE at 1473 K, $7.56 \times 10^{-6} \text{ K}^{-1}$, 7% less than Yb₂SiO₅, whereas YbEuSiO₅ has the greatest CTE at $8.6 \times 10^{-6} \text{ K}^{-1}$, 7.5% more than Yb₂SiO₅.

The coefficient of thermal expansion (CTE) of rare earth monosilicates should be correlated with the parent silicate, based on the experimental data presented in this work [31]. Based on Mackenzie et al.'s research, we discovered that Sc₂SiO₅ has a thermal expansion coefficient between $4 \times 10^{-6} \text{ K}^{-1}$ and $6 \times 10^{-6} \text{ K}^{-1}$ in the 200 °C to 1200 °C temperature range. This is much lower than that of Yb₂SiO₅. As reported by Chen et al., we discovered that the thermal expansion coefficient of Eu₂SiO₅ is significantly larger than that of Yb₂SiO₅ in the temperature range of 200 °C to 1200 °C, ranging from $7 \times 10^{-6} \text{ K}^{-1}$ to $8.5 \times 10^{-6} \text{ K}^{-1}$ [26,40]. This could be the reason for the difference in material CTE seen when doping Yb₂SiO₅ with Sc versus Eu. Because this phenomenon is not examined in further detail in the current work, more theoretical and experimental research is required to validate it.

4. Conclusions

The crystal structure, elastic constants, Si-O bond lengths, and bond energies of YbRESiO₅ (RE = Yb, Eu, Gd, Ho, Tm, Lu, Y, Sc) were investigated in this work using first-principles calculations. Using a solid-state reaction, dense polycrystalline ceramics of Yb₂SiO₅, YbScSiO₅, and YbEuSiO₅ were created. The created ceramic samples were subjected to thermal tests. The following is a summary of the primary conclusions:

- (1) According to first-principles calculations, the crystal structure and elastic properties of Yb₂SiO₅ are affected differently when equimolar amounts of rare earth elements RE (RE = Eu, Gd, Ho, Tm, Lu, Y, Sc) are added. In particular, doping the material with Eu, which has the largest atomic radius, and Sc, which has the smallest, seems to have opposite effects. While YbEuSiO₅ has the opposite behavior, YbScSiO₅ has the biggest lattice distortion, average sound velocity, Debye temperature, and Young's modulus. It also has the least average RE-O bond length and unit cell volume. The material's Young's modulus is increased when Yb₂SiO₅ is doped with Sc, mostly as a result of an increase in cation field strength and a decrease in average cation radius.
- (2) The Si-O bond lengths and bond energies of YbRESiO₅ (RE = Yb, Eu, Gd, Ho, Tm, Lu, Y, Sc) were calculated using first-principles methods. The seven aforementioned elements can be divided into two groups based on the outcomes of the simulation: In comparison to Yb₂SiO₅, one group (Gd, Eu, Y, and Lu) decreases the bond energy and lengthens the Si-O bond when replacing Yb, which lowers the material's resistance to oxygen and water corrosion. When doped, the other group (Sc, Ho, and Tm) shortens the Si-O bond and lengthens the bond energy, improving the material's resistance to oxygen and water corrosion.

- (3) According to thermal conductivity measurements, below 600 K, YbScSiO₅ has somewhat less thermal diffusivity and thermal conductivity than Yb₂SiO₅. They are marginally greater than Yb₂SiO₅ beyond 600 K, but the overall difference is negligible. When Eu is added, YbEuSiO₅ exhibits much reduced thermal conductivity and diffusivity in comparison to Yb₂SiO₅. In particular, for YbEuSiO₅, the minimum thermal conductivity is 1.072 W·m⁻¹·K⁻¹ between 400 °C and 1200 °C, while for Yb₂SiO₅, it is 1.52 W·m⁻¹·K⁻¹. This indicates that when YbEuSiO₅ is compared to Yb₂SiO₅, its minimum thermal conductivity decreases by 29.4%. The primary cause of YbEuSiO₅'s notable reduction in thermal conductivity is the addition of Eu, which results in the introduction of oxygen vacancies.
- (4) Coefficient of thermal expansion (CTE) testing results show that YbScSiO₅ has a lower CTE than Yb₂SiO₅, but adding Eu raises the CTE of YbEuSiO₅. In particular, at 1473 K, YbScSiO₅ exhibits the lowest CTE (7.56×10^{-6} ·K⁻¹) compared to Yb₂SiO₅ (7% lower) at the same temperature. YbEuSiO₅, on the other hand, has the highest CTE at 8.6×10^{-6} ·K⁻¹, which is 7.5% more than Yb₂SiO₅. According to an analysis of the experimental data, there may be a positive correlation between the base material and the CTE of multi-component silicates.

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References

- Liao, W.; Tan, Y.; Zhu, C.; Teng, Z.; Jia, P.; Zhang, H. Synthesis, microstructures, and corrosion behaviors of multi-components rare-earth silicates. *Ceram. Int.* **2021**, *47*, 32641–32647. <https://doi.org/10.1016/j.ceramint.2021.08.160>.
- Chen, H.; Xiang, H.; Dai, F.-Z.; Liu, J.; Zhou, Y. High entropy (Yb_{0.25}Y_{0.25}Lu_{0.25}Er_{0.25})₂SiO₅ with strong anisotropy in thermal expansion. *J. Mater. Sci. Technol.* **2020**, *36*, 134–139. <https://doi.org/10.1016/j.jmst.2019.07.022>.
- Yang, Z.; Yang, K.; Wang, W.; Yang, T.; Fang, H.; Qiang, L.; Zhang, X.; Zhang, C. Investigation of Thermal Shock Behavior of Multilayer Thermal Barrier Coatings with Superior Erosion Resistance Prepared by Atmospheric Plasma Spraying. *Coatings* **2022**, *12*, 804. <https://doi.org/10.3390/coatings12060804>.
- More, K.L.; Tortorelli, P.F.; Ferber, M.K.; Keiser, J.R. Observations of Accelerated Silicon Carbide Recession by Oxidation at High Water-Vapor Pressures. *J. Am. Ceram. Soc.* **2008**, *83*, 211–213. <https://doi.org/10.1111/j.1151-2916.2000.tb01172.x>.
- Opila, E.J. Oxidation and Volatilization of Silica Formers in Water Vapor. *J. Am. Ceram. Soc.* **2004**, *86*, 1238–1248. <https://doi.org/10.1111/j.1151-2916.2003.tb03459.x>.
- Opila, E.J.; Smialek, J.L.; Robinson, R.C.; Fox, D.S.; Jacobson, N.S. SiC Recession Caused by SiO₂ Scale Volatility under Combustion Conditions: II, Thermodynamics and Gaseous-Diffusion Model. *J. Am. Ceram. Soc.* **2004**, *82*, 1826–1834. <https://doi.org/10.1111/j.1151-2916.1999.tb02005.x>.
- Tian, Z.; Zheng, L.; Wang, J.; Wan, P.; Li, J.; Wang, J. Theoretical and experimental determination of the major thermo-mechanical properties of RE₂SiO₅ (RE = Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) for environmental and thermal barrier coating applications. *J. Eur. Ceram. Soc.* **2016**, *36*, 189–202. <https://doi.org/10.1016/j.jeurceramsoc.2015.09.013>.

8. Fan, W.; Zou, B.; Fan, C.; Wang, Y.; Cai, X.; Tao, S.; Xu, J.; Wang, C.; Cao, X.; Zhu, L. Fabrication and oxidation resistant behavior of plasma sprayed Si/Yb₂Si₂O₇/LaMgAl₁₁O₁₉ coating for Cf/SiC composites at 1673K. *Ceram. Int.* **2017**, *43*, 392–398. <https://doi.org/10.1016/j.ceramint.2016.09.171>.
9. Rohbeck, N.; Morrell, P.; Xiao, P. Degradation of ytterbium disilicate environmental barrier coatings in high temperature steam atmosphere. *J. Eur. Ceram. Soc.* **2019**, *39*, 3153–3163. <https://doi.org/10.1016/j.jeurceramsoc.2019.04.034>.
10. Raj, R. Fundamental research in structural ceramics for service near 2000 °C. *J. Am. Ceram. Soc.* **1993**, *76*, 2147–2174. <https://doi.org/10.1111/j.1151-2916.1993.tb07750.x>.
11. Ren, X.; Tian, Z.; Zhang, J.; Wang, J. Equiatomic quaternary (Y_{1/4}Ho_{1/4}Er_{1/4}Yb_{1/4})₂SiO₅ silicate: A perspective multifunctional thermal and environmental barrier coating material. *Scr. Mater.* **2019**, *168*, 47–50. <https://doi.org/10.1016/j.scriptamat.2019.04.018>.
12. Price, J.R.; Van Roode, M.; Stala, C. Ceramic Oxide-Coated Silicon Carbide for High Temperature Corrosive Environments. *Key Eng. Mater.* **1992**, *72–74*, 71–84.
13. Cao, G.; Wang, Y.-H.; Ding, Z.-Y.; Yang, H.-L.; Liu, Z.-G.; Ouyang, J.-H.; Wang, Y.-M.; Wang, Y.-J. Tunable corrosion resistance of rare-earth monosilicate to molten calcia-magnesia-aluminosilicate glass by RE-doping strategy. *Corros. Sci.* **2022**, *202*, 110319. <https://doi.org/10.1016/j.corsci.2022.110319>.
14. Lee, K.N.; Miller, R.A. Oxidation Behavior of Mullite-Coated SiC and SiC/SiC Composites under Thermal Cycling between Room Temperature and 1200–1400 °C. *J. Am. Ceram. Soc.* **2005**, *79*, 620–626. <https://doi.org/10.1111/j.1151-2916.1996.tb07920.x>.
15. Cojocaru, C.V.; Kruger, S.E.; Moreau, C.; Lima, R.S. Elastic Modulus Evolution and Behavior of Si/Mullite/BSAS-Based Environmental Barrier Coatings Exposed to High Temperature in Water Vapor Environment. *J. Therm. Spray Technol.* **2011**, *20*, 92–99.
16. Cojocaru, C.V.; Lévesque, D.; Moreau, C.; Lima, R.S. Performance of thermally sprayed Si/mullite/BSAS environmental barrier coatings exposed to thermal cycling in water vapor environment. *Surf. Coat. Technol.* **2013**, *216*, 215–223. <https://doi.org/10.1016/j.surfcoat.2012.11.043>.
17. Lee, K.N.; Fox, D.S.; Bansal, N.P. Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si₃N₄ ceramics. *J. Eur. Ceram. Soc.* **2005**, *25*, 1705–1715. <https://doi.org/10.1016/j.jeurceramsoc.2004.12.013>.
18. Nasiri, N.A.; Patra, N.; Horlait, D.; Jayaseelan, D.D.; Lee, W.E. Thermal Properties of Rare-Earth Monosilicates for EBC on Si-Based Ceramic Composites. *J. Am. Ceram. Soc.* **2016**, *99*, 589–596.
19. Xu, Y.; Hu, X.; Xu, F.; Li, K. Rare earth silicate environmental barrier coatings: Present status and prospective. *Ceram. Int.* **2017**, *43*, 5847–5855. <https://doi.org/10.1016/j.ceramint.2017.01.153>.
20. Felsche, J. *The Crystal Chemistry of the Rare-Earth Silicates*; Springer: Berlin/Heidelberg, Germany, 1973; pp. 99–197.
21. Ridley, M.J.; Tomko, K.Q.; Tomko, J.A.; Hoglund, E.R.; Howe, J.M.; Hopkins, P.E.; Opila, E.J. Tailoring thermal and chemical properties of a multi-component environmental barrier coating candidate (Sc_{0.2}Nd_{0.2}Er_{0.2}Yb_{0.2}Lu_{0.2})₂Si₂O₇. *Materialia* **2022**, *26*, 101557. <https://doi.org/10.1016/j.mtla.2022.101557>.
22. Wang, Y.; Niu, Y.; Zhong, X.; Shi, M.; Mao, F.; Zhang, L.; Li, Q.; Zheng, X. Water vapor corrosion behaviors of plasma sprayed RE₂SiO₅ (RE = Gd, Y, Er) coatings. *Corros. Sci.* **2020**, *167*, 108529. <https://doi.org/10.1016/j.corsci.2020.108529>.
23. Qian, B.; Wang, Y.; Zu, J.; Xu, K.; Shang, Q.; Bai, Y. A review on multicomponent rare earth silicate environmental barrier coatings. *J. Mater. Res. Technol.* **2024**, *29*, 1231–1243. <https://doi.org/10.1016/j.jmrt.2024.01.170>.
24. Han, J.; Wang, Y.; Liu, R.; Jiang, D. Study on water vapor corrosion resistance of rare earth monosilicates RE₂SiO₅ (RE = Lu, Yb, Tm, Er, Ho, Dy, Y, and Sc) from first-principles calculations. *Heliyon* **2018**, *4*, e00857. <https://doi.org/10.1016/j.heliyon.2018.e00857>.
25. Xiang, H.; Feng, Z.; Zhou, Y. Mechanical and thermal properties of Yb₂SiO₅: First-principles calculations and chemical bond theory investigations. *J. Mater. Res.* **2014**, *29*, 1609–1619. <https://doi.org/10.1557/jmr.2014.201>.
26. Chen, Z.; Tian, Z.; Zheng, L.; Ming, K.; Ren, X.; Wang, J.; Li, B. (Ho_{0.25}Lu_{0.25}Yb_{0.25}Eu_{0.25})₂SiO₅ high-entropy ceramic with low thermal conductivity, tunable thermal expansion coefficient, and excellent resistance to CMAS corrosion. *J. Adv. Ceram.* **2022**, *11*, 1279–1293. <https://doi.org/10.1007/s40145-022-0609-z>.
27. Segall, M.D.; Lindan, P.J.D.; Probert, M.J.; Pickard, C.J.; Hasnip, P.J.; Clark, S.J.; Payne, M.C. First-principles simulation: Ideas, illustrations and the CASTEP code. *J. Phys. Condens. Matter* **2002**, *14*, 2717–2744. <https://doi.org/10.1088/0953-8984/14/11/301>.
28. Ceperley, D.M.; Alder, B.J. Ground state of the electron gas by a stochastic method. *Phys. Rev. Lett.* **1980**, *45*, 566–569. <https://doi.org/10.1103/PhysRevLett.45.566>.
29. Pfrommer, B.G.; Côté, M.; Louie, S.G.; Cohen, M.L. Relaxation of Crystals with the Quasi-Newton Method. *J. Comput. Phys.* **1997**, *131*, 233–240. <https://doi.org/10.1006/jcph.1996.5612>.
30. Milman, V.; Warren, M.C. Elasticity of hexagonal BeO. *J. Phys. Condens. Matter* **2000**, *13*, 241–251.
31. Li, K.; Wang, W.; Yang, S.; Liu, Y.; Yang, T. First-principles calculations and thermal-mechanical experimental studies on middle-entropy rare-earth disilicates. *Ceram. Int.* **2024**, *50*, 22290–22305. <https://doi.org/10.1016/j.ceramint.2024.03.329>.
32. Leitner, J.; Chuchvalec, P.; Sedmidubský, D.; Strejc, A.; Abrman, P. Estimation of heat capacities of solid mixed oxides. *Thermochim. Acta* **2002**, *395*, 27–46. [https://doi.org/10.1016/S0040-6031\(02\)00177-6](https://doi.org/10.1016/S0040-6031(02)00177-6).
33. Bruce, D.; Paradise, P.; Saxena, A.; Temes, S.; Clark, R.; Noe, C.; Benedict, M.; Broderick, T.; Bhate, D. A critical assessment of the Archimedes density method for thin-wall specimens in laser powder bed fusion: Measurement capability, process sensitivity and property correlation. *J. Manuf. Process.* **2022**, *79*, 185–192. <https://doi.org/10.1016/j.jmapro.2022.04.059>.

34. Leitner, J.; Voňka, P.; Sedmidubský, D.; Svoboda, P. Application of Neumann–Kopp rule for the estimation of heat capacity of mixed oxides. *Thermochim. Acta* **2010**, *497*, 7–13. <https://doi.org/10.1016/j.tca.2009.08.002>.
35. Charvat, F.R.; Kingery, W.D. Thermal Conductivity: XIII, Effect of Microstructure on Conductivity of Single-Phase Ceramics. *J. Am. Ceram. Soc.* **2006**, *40*, 306–315. <https://doi.org/10.1111/j.1151-2916.1957.tb12627.x>.
36. Hao, S.; Oleksak, R.P.; Doğan, Ö.N.; Gao, M.C. Computational Design of High-Entropy Rare Earth Disilicates as Next-Generation Thermal/Environmental Barrier Coatings. *Acta Mater.* **2023**, *258*, 119225. <https://doi.org/10.1016/j.actamat.2023.119225>.
37. Menke, Y.; Peltier-Baron; Hampshire, S. Effect of rare-earth cations on properties of sialon glasses. *J. Non Cryst. Solids* **2000**, *276*, 145–150.
38. Giri, A.; Braun, J.L.; Rost, C.M.; Hopkins, P.E. On the minimum limit to thermal conductivity of multi-atom component crystalline solid solutions based on impurity mass scattering. *Scr. Mater.* **2017**, *138*, 134–138. <https://doi.org/10.1016/j.scriptamat.2017.05.045>.
39. Wright, A.J.; Wang, Q.; Huang, C.; Nieto, A.; Chen, R.; Luo, J. From high-entropy ceramics to compositionally-complex ceramics: A case study of fluorite oxides. *J. Eur. Ceram. Soc.* **2020**, *40*, 2120–2129. <https://doi.org/10.1016/j.jeurceramsoc.2020.01.015>.
40. Ridley, M.; Gaskins, J.; Hopkins, P.; Opila, E. Tailoring thermal properties of multi-component rare earth monosilicates. *Acta Mater.* **2020**, *195*, 698–707. <https://doi.org/10.1016/j.actamat.2020.06.012>.

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