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Molecular dynamics calculation of thermal expansion coefficient of a series of rare-earth zirconates

Fan Qun-bo*, Zhang Feng, Wang Fu-chi, Wang Lu

School of Materials Science and Engineering, Beijing Institute of Technology, No. 5, Zhong Guan Cun South Street, Beijing 100081, PR China

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ABSTRACT

To develop more reliable and stable thermal barrier coatings, low thermal conductivity materials with higher thermal expansion coefficients (TECs), like rare-earth zirconates $(A_2Zr_2O_7, A = La, Nd, Sm, Eu, Gd, Er, Yb and Lu)$, have been the focus of a great deal of attention in recent years. But the mechanisms underlying the values of TECs are still poorly understood. In this paper, the TECs of a series of rare-earth zirconates are calculated using molecular dynamics. Two typical crystal structures, pyrochlore and fluorite, are considered. By investigating the potential functions and the equilibrium-location deviations between the atoms, it is found that the Zr–O bond is the most important factor that determines the overall TECs, and the A–O bond plays a secondary role. However, O–O has little effect on the TECs. In addition, the fluorite structure has a relatively higher TEC due to a weaker Zr–O bond. Calculated values are consistent with the experimental observations. Using the method presented in this study, two doped zirconates (Gd_{0.4}Sm_{0.5}Yb_{0.1})₂Zr₂O₇ and Sm₂(Ce_{0.3}Zr_{0.7})₂O₇ are designed and compared. As expected, both of them have higher TECs than undoped Sm₂Zr₂O₇, and doping at the A-site is more efficient than doping at the Zr-site.

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1. Introduction

As the next generation of gas turbine engines develops, the operating temperature gets higher and higher. Generally, thermal barrier coatings (TBCs) with relatively low thermal conductivity are used to insulate the metal substrate of these engines from heat. In addition, materials in TBC applications should possess a thermal expansion coefficient (TEC) that is as high as possible, in order to be close to that of the metal substrate, since a mismatch in the thermal expansion of the coating and the metallic layer is one key factor in the failure of coatings. Recently, scientists have found that rare-earth zirconates [1] ($A_2Zr_2O_7$, A = La, Nd, Sm, Eu, Gd, Er, Yb and Lu) possess good overall properties, having a high TEC and low thermal conductivity, and are expected to be used as next generation thermal barrier coatings. In view of this, an investigation into the underlying physical mechanism of rare-earth zirconates is timely. A study of the TECs of a series of rare-earth zirconates is the main focus of this paper.

In recent years, molecular simulation has been found to be a valid tool to predict TECs of crystals and is ideal for systematically investigating various possible chemical compositions in order to

* Corresponding author. Tel.: +86 10 68912712.

E-mail address: fanqunbo@bit.edu.cn (F. Qun-bo).

identify the TEC trends. Schelling and co-workers [2] successfully predicted several typical rare-earth zirconates using molecular simulations, though the experimental TEC values were consistently larger than the calculated results. Up to now, however, some of the intrinsic physical mechanisms regarding the TECs for rare-earth zirconates are still poorly understood. These include: (i) what kind of factors influence the TEC values of rare-earth zirconates with different phase structures; (ii) which factor is most important; (iii) how does doping other elements into rare-earth zirconates affect TEC values, with a view to developing the next generation of materials for thermal barrier coatings. To this end, classical molecular dynamics (MD) were employed for this paper. Anharmonicity of bondings, phase structures, as well as doping effects, were taken into account.

2. Calculation details

Rare-earth zirconates are usually identified as having one of two typical crystal structures: pyrochlore and fluorite. With increasing temperature, the crystal structure usually transforms from the pyrochlore phase to the fluorite structure, crystallizing in the fd-3 m and fm-3 m space groups, respectively. The crystal structures are shown in Fig. 1. For the pyrochlore zirconate, there are four crystallographically independent atom sites: A³⁺ in 16d at (0.5, 0.5, 0.5),





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Fig. 1. Pyrochlore and fluorite structures of A2Zr2O7.

Table 1Parameters of short-range potentials [5].

Species	A (ev)	ho (Å)	C (ev Å ⁶
0 ²⁻ -0 ²⁻	35686.18	0.2010	32.00
$Zr^{4+}-O^{2-}$	1402.57	0.3312	5.10
La ³⁺ -O ²⁻	2266.26	0.3276	23.25
Nd ³⁺ -0 ²⁻	2148.14	0.3227	22.59
$Sm^{3+}-O^{2-}$	2074.70	0.3215	21.49
$Eu^{3+}-O^{2-}$	2468.00	0.3114	20.59
$Gd^{3+}-O^{2-}$	2214.40	0.3154	19.90
$Er^{3+}-O^{2-}$	2115.00	0.3111	17.55
$Yb^{3+}-O^{2-}$	2251.26	0.3052	16.57
$Lu^{3+}-O^{2-}$	2062.99	0.3086	16.87

 Zr^{4+} in 16c at (0, 0, 0), O^{2-} in 48f at (x, 0.125, 0.125) and O^{2-} in 8b at (0.375, 0.375, 0.375). Fluorite zirconate, however, has only two crystallographically independent atom sites: Zr^{4+} in 4a at (0, 0, 0), and O^{2-} in 4b at (0.5, 0.5, 0.5). In contrast to the ordered pyrochlore structure, the fluorite phase is characterized by a disordered structure due to the randomly distributed oxygen vacancies. The two kinds of crystal structures for serial rare-earth zirconates were optimized in GULP [3] and imported to the molecular dynamics code Materials Explorer [4] for further calculation.

In Materials Explorer, the linear TEC of a material can be calculated using Eq. (1), in which $\frac{da}{dT}$ can be acquired by calculating lattice constants under different temperatures.

$$\alpha = \frac{1}{a_0} \left[\frac{da}{dT_p} \right] \tag{1}$$

where α is the linear TEC and a_0 is the initial lattice constant at room temperature.

The simulation was performed in the NTP ensemble using the Parrinello-Rahman method at different fixed temperatures with the Nose-Hoover thermostat. A Buckingham-type pair-wise potential function was employed to describe short-range interatomic energy and force, of the form [5]:

$$S_{ij} = A \exp(-\frac{r}{\rho}) - \frac{C}{r^6}$$
⁽²⁾

where A, ρ and C are three adjustable parameters (Table 1). It might be noted that all the MD calculations were performed assuming that the potentials were portable. So, the Buckingham potentials fitted different phase structures and doping compositions. In reality, portability of the Buckingham potentials is reasonable for covalent bonds and has been successfully used in modeling ordered pyrochlore structures and disordered fluorite structures [6]. Supercells of $6 \times 6 \times 6$ for each rare-earth zirconate were used in the simulation, which were first thermalized at room temperature for 30 ps and then heated to 2000 K with a timestep of 0.5 fs.

3. Results and discussion

Some of the calculated TECs of serial pyrochlore-structured rare-earth zirconates were compared with the available experimental results [7–10], as shown in Table 2. It can be seen that the calculated values are consistently smaller. In the present study, all the calculations were based on ideal perfect crystal structures. However, there inevitably exists some defects in the practical experimental samples, like voids, disbonds, and grain boundary cracks, which might weaken the atomic bonds and contribute to a certain degree to higher TEC values.

To reveal the underlying mechanism of TECs of serial rare-earth zirconates, the anharmonicity of atom pairs was investigated by analyzing the equilibrium-location deviations. Equilibrium-location deviations relative to the ground state for different bonds or atom pairs reflect the anharmonicity of the atomic vibration or

 Table 2

 Comparison of TECs from simulations and experiments.

Materials	Cal. (10 ⁻⁶ K ⁻¹)	Exp. (10^{-6} K^{-1})
La ₂ Zr ₂ O ₇	7.82	9.1 [7]
$Nd_2Zr_2O_7$	7.80	9.5 [8]
Sm ₂ Zr ₂ O ₇	7.77	10.8 [9]
$Gd_2Zr_2O_7$	7.91	11.6 [10]



Fig. 2. Sm-O potential energies at different distances and thermal equilibrium positions.

asymmetry of interatomic potentials, which also contribute to the TECs of pyrochlore zirconates. Supposing there was a bond in which the interatomic potential was harmonic, the thermal expansion coefficient would be zero.

Based on the parameters listed in Table 1, the potential energy values at different atom pair distances can be plotted. Fig. 2 shows the Sm–O potential energies at different distances. The discrete points represent the equilibrium points at a series of temperatures. This shows that with an increase in temperature, the Sm–O bond deviates gradually from the ground state equilibrium-location to reach a new thermal stability. Therefore, higher equilibrium-location deviations account for relatively higher TECs. Based on the data in Fig. 2, the equilibrium-location deviations for different po-



Fig. 3. Equilibrium-location deviations for different potential energy differences, relative to the ground state.

Table 3

TECs of serial rare-earth zirconates in the fluorite and pyrochlore phases.

Materials	Pyrochlore (10^{-6} K^{-1})	Fluorite (10^{-6} K^{-1})
Nd ₂ Zr ₂ O ₇	7.80	9.71
Sm ₂ Zr ₂ O ₇	7.77	9.55
Eu ₂ Zr ₂ O ₇	7.81	8.88
$Gd_2Zr_2O_7$	7.91	9.18
Er ₂ Zr ₂ O ₇	8.00	9.02
Yb ₂ Zr ₂ O ₇	7.99	9.37
$Lu_2Zr_2O_7$	8.57	9.39

Table 4

TECs of two doped rare-earth pyrochlore zirconates.

Materials	TEC (10^{-6} K^{-1})
(Gd _{0.4} Sm _{0.5} Yb _{0.1}) ₂ Zr ₂ O ₇	7.89
Sm ₂ (Ce _{0.3} Zr _{0.7}) ₂ O ₇	8.23

tential energy differences relative to the ground state can also be plotted.

Fig. 3 shows the equilibrium-location deviations versus different potential energy differences relative to the ground state for Zr–O, O–O, and serial A–O bonds. Among these different atom pairs, or bonds, it is found that the Zr–O bond is the most important factor in determining the overall TECs of different pyrochlore zirconates, and the A–O bond plays a secondary role. However, O– O has little effect on the TECs.

To compare the TEC differences between pyrochlore and fluorite structures, the TECs of a series of pyrochlore-structured and fluorite-structured rare-earth zirconates were calculated, as shown in Table 3. Since $La_2Zr_2O_7$ is stable with a pyrochlore phase structure even at elevated temperatures, its fluorite counterpart was not considered in this paper. As shown in Table 3, the TECs of fluorite structures are higher than those of pyrochlore structures, and the underlying reason can be explained by the structures shown in Fig. 4.

Fig. 4 shows the pyrochlore structure and the fluorite structure of $\text{Er}_2\text{Zr}_2\text{O}_7$. It can be seen that the minimum-length bond in the fluorite structure is the Zr–O bond, which at 2.2985 Å is longer than in the pyrochlore structure (2.0324 Å). The longer the bond is, the weaker the bond is. Correspondingly, the minimum-length bond of a crystal structure reflects the strongest bonding strength in the crystal structure. In addition, for the same chemical composition with different phase structures, the anharmonicity effects are approximately the same since the same set of potential parameters are used. In such a case, the weaker the bonding strength, the larger the TEC. So, bonding strength is another important factor that affects TECs. Therefore, the fluorite structure has a higher TEC.

To further investigate the doping effects on TECs, two doped zirconates with complex pyrochlore structures were modeled and calculated: $(Gd_{0.4}Sm_{0.5}Yb_{0.1})_2Zr_2O_7$ and $Sm_2(Ce_{0.3}Zr_{0.7})_2O_7$. These TEC values are listed in Table 4.

It can be seen from Table 4 that the A-site doped pyrochlore zirconate $(Gd_{0.4}Sm_{0.5}Yb_{0.1})_2Zr_2O_7$ has a smaller TEC than that of the Zr-site doped pyrochlore zirconate. In addition, the TECs of these two structures are larger than that of undoped $Sm_2Zr_2O_7$ (Table



Fig. 4. Crystal structure of Er₂Zr₂O₇.

2). The reason for this is that doping weakens the bonding strength and the Zr–O bond is stronger than the A–O bond. Thus, in order to develop a novel material with a higher TEC, Zr-site doping is recommended.

4. Conclusions

The TECs of serial rare-earth zirconates were successfully calculated using classic molecular dynamics. It was proved that the Zr–O bond plays a primary role in thermal expansion due to anharmonicity of the atomic vibration. For the same composition, the fluorite structures always have higher TECs relative to the corresponding pyrochlore structures due to a weaker bonding strength. Zr-site doping in rare-earth zirconates was found to be more effective than A-site doping for developing a new thermal barrier material with a higher TEC.

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