Impact of isovalent and aliovalent substitution on the mechanical and thermal properties of Gd$_2$Zr$_2$O$_7$

S. Zhang$^1$, H. B. Zhang$^2$, F. A. Zhao$^3$, M. Jiang$^1$, H. Y. Xiao$^1$, Z. J. Liu$^4$ & X. T. Zu$^3$

In this study, a density functional theory method is employed to investigate the effects of isovalent and aliovalent substitution of Sm$^{3+}$ on the phase stability, thermo-physical properties and electronic structure of Gd$_2$Zr$_2$O$_7$. It is shown that the isovalent substitution of Sm$^{3+}$ for Gd$^{3+}$ results in the formation of Gd$_2$Zr$_x$Sm$_{1-x}$O$_7$ solid solution, which retains the pyrochlore structure and has slight effects on the elastic moduli, ductility, Debye temperature and band gap of Gd$_2$Zr$_2$O$_7$. As for the aliovalent substitution of Sm$^{3+}$ for Zr$^{4+}$ site, a pyrochlore-to-defect fluorite structural transition is induced, and the mechanical, thermal properties and electronic structures are influenced significantly. As compared with the Gd$_2$Zr$_2$O$_7$, the resulted Gd$_2$Sm$_x$Zr$_{2-x}$O$_7$ compositions have much smaller elastic moduli, better ductility and smaller Debye temperature. Especially, an amount of electrons distribute on the fermi level and they are expected to have larger thermal conductivity than Gd$_2$Zr$_2$O$_7$. This study suggests an alternative way to engineer the thermo-physical properties of Gd$_2$Zr$_2$O$_7$ and will be beneficial for its applications under stress and high temperature.

The rare-earth zirconates, with chemical formula A$_2$Zr$_2$O$_7$ (A = Y or another rare earth elements)$^1$$^2$, exhibit ordered pyrochlore-type structure or defect fluorite-type structure, which is mainly governed by the ionic radii of A$^{3+}$ and Zr$^{4+}$$^3$. They have attracted the attention of many researchers, due to their good chemical and mechanical stability, excellent catalytic activity, high ionic conductivity, ferromagnetism, luminescence as well as strong resistance to amorphization under irradiation$^4$$^8$. Owing to these outstanding properties, the rare-earth zirconates have a wide range of technical applications, e.g., ceramic thermal barrier coating$^9$$^{10}$, oxidation catalyst$^5$$^{11}$, solid electrolyte$^{12}$, hosts of actinides in nuclear waste$^{13}$ and oxygen gas sensor$^{14}$.

Of the zirconate pyrochlores, Gd$_2$Zr$_2$O$_7$ is of special interest due to its good thermo-physical properties$^{15}$$^{19}$. Shimamura et al$.$ have measured the thermal expansion of a series of zirconate pyrochlores employing high-temperature X-ray diffraction and found that the thermal expansion coefficient of Gd$_2$Zr$_2$O$_7$ is larger than other zirconates during the temperature range of 400–1600°C$^{20}$. The thermal conductivity of rare-earth zirconates has been investigated by Wang et al$.$, who reported that the thermal conductivity of 1.15–1.43 W/mK for Gd$_2$Zr$_2$O$_7$ is lower than that of Yb$_2$Zr$_2$O$_7$, Dy$_2$Zr$_2$O$_7$ and 7YSZ between 25°C and 800°C. In recent years, both Liu et al$.$ and Pan et al$.$ reported that, among the (La$_{1-x}$Gd$_x$)$_2$Zr$_2$O$_7$ (0 $\leq x \leq$ 1) systems, the LaGdZr$_2$O$_7$ has the minimum thermal conductivity, which is about 20% lower than that of Gd$_2$Zr$_2$O$_7$$^{18}$. In recent years, both Liu et al$.$ and Pan et al$.$ reported that the thermal diffusivity of (Sm$_{1-x}$Gd$_x$)$_2$Zr$_2$O$_7$ (0 $\leq x \leq$ 1) is lower than those of pure Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$. Especially, Sm$_2$Zr$_2$O$_7$–Gd$_2$Zr$_2$O$_7$ solid solutions have lower Young’s modulus than (La$_{1-x}$Gd$_x$)$_2$Zr$_2$O$_7$ (0 $\leq x \leq$ 1) at room temperature and larger thermal expansion coefficients than (Gd$_{1-x}$Y$_x$)$_2$Zr$_2$O$_7$ (x = 0, 0.1, 0.3, 0.5, 0.7) from 300°C to 900°C$^{18}$. These investigations are mainly experimental studies, and the related theoretical investigations are relatively much fewer$^{27}$$^{28}$.

1School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu, 610054, China. 2Institute of Nuclear Physics and Chemistry, Chinese Academy of Engineering Physics, Mianyang, 621900, China. 3Institute of Fundamental and Frontier Sciences, University of Electronic Technology and China, Chengdu, 610054, China. 4Department of Physics, Physics, Lanzhou City University, Lanzhou, 730070, China. Correspondence and requests for materials should be addressed to H.Y.X. (email: hyxiao@uestc.edu.cn) or Z.J.L. (email: lzjcaep@126.com)
Very recently, the Th\(^{4+}\) ion incorporation into Gd\(^{3+}\) and Zr\(^{4+}\) sites in Gd\(_2\)Zr\(_2\)O\(_7\) was investigated by first-principles calculations\(^{28}\). Unexpectedly, the aliovalent substitution of Th\(^{4+}\) for Gd\(^{3+}\) turns out to be thermodynamically stable and such substitution even results in better thermo-physical properties than the pure Gd\(_2\)Zr\(_2\)O\(_7\)\(^{28}\). This thus arouses our interest that whether the aliovalent substitution of Ln\(^{3+}\) for Zr\(^{4+}\) sites are energetically and mechanically stable or not? If yes, will the substitution of Ln\(^{3+}\) for Zr\(^{4+}\) sites cause different thermo-mechanical properties from the isovalent substitution of Ln\(^{3+}\) for Gd\(^{3+}\) sites? In this study, we choose Sm\(^{3+}\) as a model and investigate the phase stability and thermo-physical properties of Gd\(_2\)Zr\(_2\)O\(_7\) with isovalent and aliovalent substitution of Ln\(^{3+}\) for Gd\(^{3+}\) and Zr\(^{4+}\) sites by employing the density functional theory (DFT) method. It reveals that the Sm\(_{x}\)Gd\(_{2-x}\)Zr\(_{2}\)O\(_7\) retains the pyrochlore structure and the isovalent substitution of Sm\(^{3+}\) for Gd\(^{3+}\) sites influences slightly the mechanical and thermal properties of Gd\(_2\)Zr\(_2\)O\(_7\). On the other hand, the aliovalent substitution of Sm\(^{3+}\) for Zr\(^{4+}\) sites induces pyrochlore-to-fluorite structural transition and affects significantly the elastic moduli, Debye temperature and thermal conductivity. The presented results provide a new way to tune the thermo-physical properties of Gd\(_2\)Zr\(_2\)O\(_7\) and will have important implications in advancing the further related experimental and theoretical studies for its applications under high temperature.

Figure 1. Variation of (a) lattice constants and (b) positional parameter \(x_{\text{O}48}\) for Sm\(_{x}\)Gd\(_{2-x}\)Zr\(_2\)O\(_7\) and Gd\(_{y}\)Sm\(_{2-y}\)Zr\(_2\)O\(_7\) (0 ≤ \(y\) ≤ 2) as a function of Sm content.

| Compounds                  | \(d < \text{Gd-O}_{48}\>\) | \(d < \text{Gd-O}_{8b}\>\) | \(d < \text{Sm-O}_{48}\>\) | \(d < \text{Sm-O}_{8b}\>\) | \(d < \text{Zr-O}_{48}\>\) |
|----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Gd\(_2\)Zr\(_2\)O\(_7\)   | 2.478                       | 2.263                       | —                           | —                           | 2.083                       |
| Sm\(_{0.5}\)Gd\(_{1.5}\)Zr\(_2\)O\(_7\) | 2.482                      | 2.257                       | 2.497                       | 2.297                       | 2.084                       |
| SmGd\(_2\)Zr\(_2\)O\(_7\)  | 2.485                       | 2.252                       | 2.503                       | 2.289                       | 2.085                       |
| Sm\(_{1.5}\)Gd\(_0.5\)Zr\(_2\)O\(_7\) | 2.495                      | 2.245                       | 2.506                       | 2.286                       | 2.086                       |
| Sm\(_2\)Zr\(_2\)O\(_7\)    | —                           | —                           | 2.514                       | 2.280                       | 2.087                       |
| Gd\(_2\)Sm\(_{0.5}\)Zr\(_{1.5}\)O\(_7\) | 2.482                      | 2.280                       | 2.253                       | —                           | 2.087                       |
| Gd\(_2\)SmZr\(_2\)O\(_7\)  | 2.387                       | 2.309                       | 2.329                       | —                           | 2.124                       |
| Gd\(_2\)Sm\(_{1.5}\)Zr\(_{0.5}\)O\(_7\) | 2.394                      | 2.327                       | 2.299                       | —                           | 2.096                       |
| Gd\(_2\)Sm\(_2\)O\(_7\)    | 2.426                       | 2.341                       | 2.262                       | —                           | —                           |

Table 1. The bonding distances (Å) between atoms in Sm\(_{x}\)Gd\(_{2-x}\)Zr\(_2\)O\(_7\) and Gd\(_{y}\)Sm\(_{2-y}\)Zr\(_2\)O\(_7\) (0 ≤ \(y\) ≤ 2).
Results and Discussion

Structural stability of \( \text{Sm}_y\text{Gd}_{2-y}\text{Zr}_2\text{O}_7 \) and \( \text{Gd}_2\text{Sm}_{2-y}\text{Zr}_y\text{O}_7 \) (0 \( \leq \) \( y \) \( \leq \) 2).

In this study, Sm substitution for both Gd-site and Zr-site in \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) with different concentrations are considered, resulting in \( \text{Sm}_y\text{Gd}_{2-y}\text{Zr}_2\text{O}_7 \) and \( \text{Gd}_2\text{Sm}_{2-y}\text{Zr}_y\text{O}_7 \) (\( y = 0, 0.5, 1, 1.5, 2 \)). The geometrical structures of \( \text{Sm}_y\text{Gd}_{2-y}\text{Zr}_2\text{O}_7 \) and \( \text{Gd}_2\text{Sm}_{2-y}\text{Zr}_y\text{O}_7 \) are optimized firstly. In order to test whether local density approximation (LDA)\(^{29}\) or generalized gradient approximation (GGA)\(^{30}\) is more appropriate to describe the exchange-correlation interaction between electrons, both LDA and GGA methods are employed to relax the structures of \( \text{Gd}_2\text{Zr}_2\text{O}_7 \) and \( \text{Sm}_2\text{Zr}_2\text{O}_7 \). For \( \text{Gd}_2\text{Zr}_2\text{O}_7 \), the lattice constant \( a_0 \) and \( x_{\text{O}_{48}} \) obtained by LDA are 10.451 Å and 0.342, respectively, agreeing well with the experimental values of \( a_0 = 10.472 \) Å and \( x_{\text{O}_{48}} = 0.3453 \)\(^{31,32}\). As compared with the LDA results, the values of \( a_0 = 10.641 \) Å and \( x_{\text{O}_{48}} = 0.339 \) calculated by GGA deviate much more from the experimental results. As for \( \text{Sm}_2\text{Zr}_2\text{O}_7 \), the LDA calculations yield a lattice constant of 10.531 Å and an \( x_{\text{O}_{48}} \) parameter of 0.34, which are also comparable with the experimental data of \( a_0 = 10.514 \) Å and \( x_{\text{O}_{48}} = 0.342 \)\(^{31,32}\). On the other hand, the GGA results of \( a_0 = 10.715 \) Å and \( x_{\text{O}_{48}} = 0.337 \) are in bad agreement with the experimental measurement. Obviously, the structural parameters obtained by LDA are in better agreement with experiments than the GGA method. The LDA calculations yield a lattice constant of 10.531 Å and an \( x_{\text{O}_{48}} \) parameter of 0.34, which are also comparable with the experimental data of \( a_0 = 10.514 \) Å and \( x_{\text{O}_{48}} = 0.342 \)\(^{31,32}\). On the other hand, the GGA results of \( a_0 = 10.715 \) Å and \( x_{\text{O}_{48}} = 0.337 \) are in bad agreement with the experimental measurement. Obviously, the structural parameters obtained by LDA are in better agreement with experiments than the GGA method. The LDA method, thus, is employed in all the subsequent calculations. The calculated lattice constant \( a_0 \) and \( x_{\text{O}_{48}} \) for \( \text{Sm}_y\text{Gd}_{2-y}\text{Zr}_2\text{O}_7 \) and \( \text{Gd}_2\text{Sm}_{2-y}\text{Zr}_y\text{O}_7 \) as a function of Sm content are plotted in Fig. 1a and b, respectively. As Sm substitutes for Gd-site in \( \text{Gd}_2\text{Zr}_2\text{O}_7 \), it is found that the resulted \( \text{Sm}_y\text{Gd}_{2-y}\text{Zr}_2\text{O}_7 \) compositions remain the ideal pyrochlore structure. Especially, the lattice constant \( a_0 \) and the \( x_{\text{O}_{48}} \) positional parameter increase linearly with the increasing Sm concentration, suggesting that the lattice parameters of \( \text{Sm}_y\text{Gd}_{2-y}\text{Zr}_2\text{O}_7 \) follow well the Vegard’s law, i.e., \( a(\text{Sm}_y\text{Gd}_{2-y}\text{Zr}_2\text{O}_7) = 2 - \frac{y}{2} \times a(\text{Gd}_2\text{Zr}_2\text{O}_7) + \frac{y}{2} \times a(\text{Sm}_2\text{Zr}_2\text{O}_7) \). These results indicate that the \( \text{Gd}_2\text{Zr}_2\text{O}_7-\text{Sm}_2\text{Zr}_2\text{O}_7 \) solid solution is formed by Sm substitution into Gd-site in \( \text{Gd}_2\text{Zr}_2\text{O}_7 \).

Figure 2. Schematic view of the optimized configurations for (a) \( \text{Gd}_2\text{Zr}_2\text{O}_7 \), (b) \( \text{Sm}_0.5\text{Gd}_{1.5}\text{Zr}_2\text{O}_7 \), (c) \( \text{SmGdZr}_2\text{O}_7 \), (d) \( \text{Sm}_1\text{Gd}_1\text{Zr}_2\text{O}_7 \), (e) \( \text{Sm}_2\text{Zr}_2\text{O}_7 \), (f) \( \text{Gd}_2\text{Sm}_0.5\text{Zr}_1.5\text{O}_7 \), (g) \( \text{Gd}_2\text{SmZr}_2\text{O}_7 \), (h) \( \text{Gd}_2\text{Sm}_1.5\text{Zr}_0.5\text{O}_7 \), (i) \( \text{Gd}_2\text{Sm}_2\text{O}_7 \). The blue, purple, green and red spheres represent Sm, Gd, Zr and O atoms, respectively.
Table 2. Elastic constants (C_{11}, C_{12}, C_{44}, in GPa), bulk modulus (B, in GPa), shear modulus (G, in GPa) and Young's modulus (E, in GPa) of Sm_{x}Gd_{2-x}Zr_{2}O_{7} and Gd_{2}Sm_{x}Zr_{2-x}O_{7} (0 \leq x \leq 2).
agreeing well with the experimental observation. Experimentally, Liu et al. also found that the lattice constants increase linearly with different compositions for (Sm$_x$Gd$_{1-x}$)$_2$Zr$_2$O$_7$ system from $x = 0$ (Gd$_2$Zr$_2$O$_7$) to $x = 1.0$ (Sm$_2$Zr$_2$O$_7$), and the Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ ceramics are infinitely solid solution. As Sm substitutes for Zr-site, i.e. Gd$_{1-x}$Sm$_x$Zr$_2$O$_7$, the lattice constants increase more significantly than the case of Sm$_{1-x}$Gd$_x$Zr$_2$O$_7$ and there is a small deviation from the Vegard’s law. It is noticeable that the $x_{O48}$ of Gd$_{1-x}$Sm$_x$Zr$_2$O$_7$ increases remarkably with the increasing Sm content instead of decreasing as the case of Sm$_{1-x}$Gd$_x$Zr$_2$O$_7$. In A$_2$B$_2$O$_7$ pyrochlores, the $x_{O48}$ positional parameter can be used to describe the degree of distortion of <B-O> octahedron and it is located within the range of 0.3125 to 0.375. Generally, the material with $x_{O48}$ closer to 0.3125 has the ordered pyrochlore

Figure 4. Variation of elastic moduli for (a) Sm$_{1-x}$Gd$_x$Zr$_2$O$_7$ and (b) Gd$_{1-x}$Sm$_x$Zr$_2$O$_7$ (0 ≤ $y$ ≤ 2) as a function of Sm content. B: bulk modulus; G: shear modulus; E: Young’s modulus.

| Compounds          | G/B   | $A^6$   | $v_m$ (m/s) | $\Theta$ (K) | $\sigma$ |
|--------------------|-------|---------|-------------|--------------|---------|
| Gd$_2$Zr$_2$O$_7$  | Our Cal. | 0.499 | 0.00420 | 4833.5 | 612.9 | 0.286 |
| Exp.$^{19}$        |       |        |            |              |         |
| Exp.$^{20}$        |       |        |            |              | 0.276  |
| Other cal.$^{36}$  |       |        |            |              |         |
| Sm$_{1-x}$Gd$_x$Zr$_2$O$_7$ | 0.505 | 0.00085 | 4855.2 | 614.4 | 0.284 |
| SmGdZr$_2$O$_7$    | 0.504 | 0.00042 | 4864.9 | 614.5 | 0.284 |
| Sm$_{1-x}$Gd$_x$Zr$_2$O$_7$ | 0.504 | 0.00009 | 4880.8 | 615.3 | 0.284 |
| Sm$_2$Zr$_2$O$_7$  | Our Cal. | 0.505 | 0.00063 | 4918.3 | 618.8 | 0.284 |
| Exp.$^{19}$        |       |        |            |              | 0.277  |
| Exp.$^{20}$        |       |        |            |              | 0.278  |
| Other cal.$^{36}$  |       |        |            |              | 0.274  |
| Gd$_{1-x}$Sm$_x$Zr$_2$O$_7$ | 0.428 | 0.097   | 4220.6 | 530.5 | 0.313 |
| Gd$_3$SmZrO$_7$    | Our Cal. | 0.320 | 0.566   | 3583.7 | 447.4 | 0.356 |
| Gd$_{1-x}$Sm$_x$Zr$_2$O$_7$ | 0.270 | 0.920   | 3230.2 | 399.5 | 0.376 |
| Gd$_2$Sm$_2$O$_7$  | Our Cal. | 0.205 | 4.738   | 2786.4 | 341.7 | 0.404 |

Table 3. Pugh’s indicator (G/B), elastic anisotropy index ($A^6$), sound wave velocity ($v_m$ in m/s), Debye temperature ($\Theta$ in K) and Poisson’s ratio ($\sigma$) of Sm$_{1-x}$Gd$_x$Zr$_2$O$_7$ and Gd$_{1-x}$Sm$_x$Zr$_2$O$_7$ (0 ≤ $y$ ≤ 2).
structure and the one with $x_{O48f}$ closer to 0.375 is more likely to undergo a transition from pyrochlore to defect-fluorite structure \(^{31,33-35}\). Our calculations show that the $x_{O48f}$ for Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ with high content of Sm approaches to be 0.375, implying that order-disorder transition may occur in the systems. The schematic view of optimized configurations of Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ is illustrated in Fig. 2. As can be seen in the figure, Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ still maintains the pyrochlore-type structure, while Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ exhibits defective fluorite-type structure due to the significant disordering of the anions. These results suggest that Sm substitution for Gd-site has minor effects on the pyrochlore structure of Gd$_2$Zr$_2$O$_7$, as evidenced by the small changes in the $<\text{Gd-O}>$ and $<\text{Zr-O}>$ bonding distances shown in Table 1. On the other hand, structural transformation from ordered pyrochlore to disordered defect-fluorite structure is induced by the substitution of Sm for Zr-site, which is accompanied by the weakened interaction of $<\text{Sm-O}_{48f}>$ and $<\text{Gd-O}_{8b}>$ bonds (see Table 1).

In the literature, it has been reported that the Madelung binding energy reduces with the increasing $x_{O48f}$ and the thermal expansion increases with the decreasing Madelung binding energy \(^{20}\). Considering that Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ has larger $x_{O48f}$ than Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$, we thus suggest that smaller Madelung binding energy exists in the Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$, and they probably have larger thermal expansion coefficient. Meanwhile, the disordering of oxygen ions in Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ may increase the phonon scattering, which will reduce the mean free path of the phonon and result in small phonon thermal conductivity.

![Projected density of state distribution for Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ (y = 0, 0.5, 1, 1.5, 2). The Fermi level is located at 0 eV.](image)

**Figure 5.** Projected density of state distribution for Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ (y = 0, 0.5, 1, 1.5, 2). The Fermi level is located at 0 eV.
Elastic constants and elastic moduli of Sm\textsubscript{y}Gd\textsubscript{2-y}Zr\textsubscript{2}O\textsubscript{7} and Gd\textsubscript{2}Sm\textsubscript{2-y}Zr\textsubscript{y}O\textsubscript{7} (0 ≤ y ≤ 2). In order to investigate the mechanical properties of SmyGd\textsubscript{2-y}Zr\textsubscript{2}O\textsubscript{7} and Gd\textsubscript{2}Sm\textsubscript{2-y}Zr\textsubscript{y}O\textsubscript{7} compounds, we further calculate their elastic constants based on the optimized structures. For a cubic crystal, there are three independent elastic constants, i.e. C\textsubscript{11}, C\textsubscript{12} and C\textsubscript{44}, where C\textsubscript{11} refers to the uniaxial deformation along the [001] direction, C\textsubscript{12} is the pure shear stress at (110) crystal plane along the [110] direction, and C\textsubscript{44} is a pure shear deformation on the (100) crystal plane\textsuperscript{4}. The values of these three elastic constants for all compounds are summarized in Table 2. For Gd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, our calculated values of C\textsubscript{11}, C\textsubscript{12} and C\textsubscript{44} are 325.6, 126.3 and 94.0 GPa, respectively, which are found to be close to the results of C\textsubscript{11} = 314.2 GPa, C\textsubscript{12} = 126.2 GPa and C\textsubscript{44} = 96.2 GPa for Sm\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}. It should be pointed out that in this study the Gd 4\textsuperscript{f} and Sm 4\textsuperscript{f} electrons are treated as core electrons. In order to investigate if these f electrons will influence the mechanical properties of Gd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and Sm\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, we further consider the Gd 4\textit{f} and Sm 4\textit{f} electrons as valence electrons and carry out LDA + U calculations, in which the effective U values are taken to be 6 eV for Gd 4\textit{f} and 8 eV for Sm 4\textit{f} electrons\textsuperscript{4}. For Gd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, the LDA + U results of C\textsubscript{11} = 316.9 GPa, C\textsubscript{12} = 123.0 GPa and C\textsubscript{44} = 94.7 GPa are very similar to the LDA calculations. In the case of Sm\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}, the calculated C\textsubscript{11} = 276.9 GPa, C\textsubscript{12} = 114.2 GPa, and C\textsubscript{44} = 112.6 GPa are deviated from the LDA results. Further investigation shows that the Sm\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} is elastically anisotropic, which is not consistent with the elastic isotropy of Sm\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7}. Hence, the Gd 4\textit{f} and Sm 4\textit{f} electrons are frozen in our calculations and all the calculations are carried out by the LDA method. These results indicate that Gd\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} and Sm\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} may exhibit very similar mechanical properties.

Figure 6. Projected density of state distribution for Gd\textsubscript{2}Sm\textsubscript{2-y}Zr\textsubscript{y}O\textsubscript{7} (y = 0, 0.5, 1, 1.5, 2). The Fermi level is located at 0 eV.
properties, agreeing well with the experiment carried out by Shimamura et al. The elastic constants reported by Lan et al. employing GGA method are generally smaller than our LDA results, while they also found that the results of Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ are very similar to each other. We find that the mechanical stability criteria, i.e., $(C_{11}-C_{12}) > 0$, $C_{44} > 0$, and $(C_{11} + 2C_{12}) > 0$, are satisfied for all compounds, indicating that Sm-substituted Gd$_2$Zr$_2$O$_7$ compounds are mechanically stable.

The calculated elastic constants for both Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ (0 ≤ $y$ ≤ 2) as a function of Sm content are plotted in Fig. 3. It is noted that Sm substitution for Gd-site results in very small changes in the elastic constants and the mixed Gd$_2$Zr$_2$O$_7$-Sm$_2$Zr$_2$O$_7$ phases have similar values with the pure states. As the Sm substitutes for Zr-site, the values of $C_{11}$ are strikingly decreased with the increasing Sm content, implying that the compositions with high content of Sm are more likely to undergo the uniaxial deformation along the [001] direction. On the other hand, the $C_{12}$ and $C_{44}$ slightly increase and decrease with the Sm incorporation, respectively. Generally, the changes in the elastic constants of Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ are more significant than those of Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$, meaning that the effects of Sm incorporation into Gd-site on the mechanical properties of Gd$_2$Zr$_2$O$_7$ are nearly negligible whereas Sm incorporation into Zr-site has remarkable influence. This may be mainly due to the fact that Gd$^{3+}$ and Sm$^{3+}$ have similar mass (Gd$^{3+}$: 157.25 amu; Sm$^{3+}$: 150.3 amu) and cation size (Gd$^{3+}$: 1.053 Å; Sm$^{3+}$: 1.079 Å) and Sm substitution for Gd-site affects the structural properties of Gd$_2$Zr$_2$O$_7$ slightly, while the mass and radius for Sm$^{3+}$ are largely different from the mass of 91.22 amu and the radius of 0.72 Å for Zr$^{4+}$.

Based on the three elastic constants, the bulk modulus (B), Young’s modulus (E) and shear modulus (G) can be deduced under Voigt-Reuss-Hill (VRH) approximation, i.e., $B = (C_{11}+2C_{12})/3$, $E = 9BG/(3B+G)$, $G = ((C_{11}-C_{12}+3C_{44})^2 + 5(C_{11}+C_{12})C_{44} + 4C_{44})(C_{11}+C_{12}))^{1/2}$. The values of bulk modulus, Young’s modulus and shear modulus are shown in Table 2, together with available experimental and theoretical results in the literature. As compared with the experimental measurement, our calculated elastic moduli for Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ are overestimated slightly. This may be resulted from the employed LDA method, which generally underestimates the lattice constant whereas overestimates the mechanical modulus. Besides, the defects and impurities in the sample experimentally may also lead to the underestimated values of the B and G. Variation of the elastic moduli for Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ with the Sm content is illustrated in Fig. 4. As expected, the elastic moduli for Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ vary slightly with the Sm content since the elastic constants for all compositions are very similar to each other. Different from the case of Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$, the bulk modulus, Young’s modulus and shear modulus for Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ all decrease sharply with the increasing Sm content, especially the Young’s modulus.
Consequently, the Gd$_2$Sm$_2$O$_7$ has the minimum Young’s modulus of 87 GPa, minimum shear modulus of 31 GPa and minimum bulk modulus of 151 GPa. These results indicate that the Gd$_2$Sm$_2$O$_7$ has good compliance due to the lowest bulk modulus and the lowest Young’s modulus, which will produce relatively smaller residual stresses in the coating system under the severe conditions and result in better thermo-mechanical stability.

Elastic anisotropy, ductility and Debye temperature of Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_2$Sm$_{y}$Zr$_{2-y}$O$_7$ (0 ≤ y ≤ 2). The elastic anisotropy, which is correlated with the possibility of the appearance of microcracks, is an important mechanical property of materials. For a crystal, the elastic anisotropy of materials can be evaluated by the $A^U$ (universal elastic anisotropy index), which can be calculated by $A^U = \frac{5}{2} G^V/G^R + B^V/B^R - 6$, with V and R representing the Voigt and Reuss approximation, respectively. The $A^U$ value of zero refers to isotropic

---

Figure 8. Projected and total density of state distribution for Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ obtained by the LDA and LDA+SOC methods. The Fermi level is located at 0 eV.
mechanical properties, otherwise defines the anisotropy. The calculated results are shown in Table 3. Obviously, the values of $A_U$ are very close to zero in the case of Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ ($0 \leq y \leq 2$), which indicates that all compounds are of elastic isotropy. However, the crystals show strong anisotropy in the Gd$_2$SmyZr$_{2-y}$O$_7$ ($0.5 \leq y \leq 2$) system, as the $A_U$ values have large deviation from zero and they increase with the increasing Sm content. The sharp increase from 0.920 for Gd$_2$Sm$_{1.5}$Zr$_{0.5}$O$_7$ to 4.738 for Gd$_2$Sm$_2$O$_7$ may be caused by the pyrochlore-to-defect fluorite structural transition.

Another important mechanical property of materials is the ductility, which is often evaluated by the Pugh’s indicator ($G/B$ ratio). The Pugh’s indicator of 0.5 is a boundary of brittleness or ductility, i.e., if $G/B > 0.5$, the material tends to be brittle; otherwise, the material is ductile. The calculated Pugh’s indicators are presented in Table 3. For the compounds of Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$, the values are close to 0.5, and are located within the range of 0.499 to 0.505. As for Gd$_2$SmyZr$_{2-y}$O$_7$ ($y = 0.5, 1, 1.5, 2$), the $G/B$ values of 0.205–0.428 are much smaller. Obviously, the Gd$_2$SmyZr$_{2-y}$O$_7$ compositions have better ductility than the Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ compounds. The Poisson’s ratio ($\sigma$) can also be used to evaluate the relative ductility of materials. Generally, the $\sigma$ values are close to 0.1 and 0.33 for brittle covalent material and ductile metallic material, respectively. The $\sigma$ values are 0.286 and 0.284 for Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$, respectively, which are comparable with the experimental data of 0.274–0.276 for Gd$_2$Zr$_2$O$_7$ and 0.277–0.278 for Sm$_2$Zr$_2$O$_7$. As shown in Table 3, the Poisson’s ratio is ~0.285 for Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ and vary from 0.313 to 0.404 for Gd$_2$SmyZr$_{2-y}$O$_7$, meaning that the latter compositions are more ductile, which is consistent with the results obtained from the Pugh’s indicator.

In this study, the Debye temperature that is related to the hardness and thermal expansion coefficient of materials is also estimated for Sm-contained Gd$_2$Zr$_2$O$_7$ by

$$\Theta = \frac{\hbar}{4\pi^2} \left( \frac{N_A \rho}{M} \right)^{1/3} v_m$$

Here, $\hbar$ is the Planck’s constant, $k_B$ is the Boltzmann’s constant, $n$ is the number of atoms in molecular, $N_A$ is the Avogadro’s constant, $\rho$ is the density, $M$ is the molecular mass and $v_m$ is the sound wave velocity. The $v_m$ can be deduced by

$$v_m = \left( \frac{3(\rho v_l)^{1/3}}{2v_l + v_t} \right)^{1/3}$$

where $v_l = \left( \frac{\delta + 4G/3}{k_B T} \right)^{1/2}$ is the longitudinal sound velocity and $v_t = \left( \frac{G}{\rho} \right)^{1/2}$ is the transverse sound velocity. As one can see from Table 3, Sm substitution for Gd-site has slight effects on the Debye temperature of Gd$_2$Zr$_2$O$_7$ and all the compositions have very similar results. However, as Sm substitutes for the Zr-site, the Debye temperature decreases considerably with the increasing Sm content. The Gd$_2$Sm$_2$O$_7$ has the lowest Debye temperature of 341.7 K, which is about 44.3% lower than that of Gd$_2$Zr$_2$O$_7$. These results suggest that Sm incorporation into Zr-site causes weaker interaction of chemical bonds and the Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ with high content of Sm will have much larger thermal expansion coefficient than Gd$_2$Zr$_2$O$_7$.

Electronic structure of Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ ($0 \leq y \leq 2$). In order to investigate how Sm incorporation influences the electronic structure of Gd$_2$Zr$_2$O$_7$, the atomic projected density of state (DOS) distribution of Sm$_y$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_2$Sm$_y$Zr$_{2-y}$O$_7$ are analyzed and plotted in Fig. 5 and Fig. 6, respectively.
In Fig. 7a and b, the orbital projected DOS for Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ are also presented. For Gd$_2$Z$_r$O$_7$, the valence band maximum (VBM) are mainly contributed by O 2p states hybridized with Zr 4d, Gd 5d and Gd 5p orbitals, and the conduction band minimum (CBM) are mainly contributed by Zr 4d states and O 2p states. The obtained band gap value of 2.55 eV is comparable with the value of 2.71 eV reported by Wang et al. [50] For Sm$_2$Zr$_2$O$_7$, the DOS distribution is similar to that of Gd$_2$Zr$_2$O$_7$, i.e., the VBM are mainly contributed by O 2p states hybridized with Zr 4d, Sm 5d and Sm 5p states, and the CBM are mainly dominated by Zr 4d states and O 2p states. Considering that Sm and Gd are heavy atoms and the spin–orbit coupling (SOC) may affect the band gap and electronic structure of the investigated systems, we further calculate the density of state distribution of Gd$_2$Zr$_2$O$_7$. Considering that Sm and Gd are heavy atoms and the spin–orbit coupling (SOC) may affect the band gap and electronic structure of the investigated systems, we further calculate the density of state distribution of Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ employing the LDA + SOC method. A comparison of LDA and LDA + SOC results for both compounds is illustrated in Fig. 8. For Gd$_2$Zr$_2$O$_7$, the band gap value of 2.64 eV by LDA + SOC is close to the value of 2.55 eV by LDA method. In the case of Sm$_2$Zr$_2$O$_7$, the band gap values are 2.9 eV and 2.83 eV for LDA + SOC and LDA calculations, respectively. As shown in Fig. 8, the atomic projected and total DOS obtained by LDA with and without spin–orbit coupling exhibit very similar characters for both compounds. These results suggest that the spin–orbit coupling has slight effects on our results and such effects are thus not considered for the mixed states. When Sm substitutes for Gd-site, the Sm 5d orbitals also contribute to the VBM and interacts with the oxygen. Meanwhile, the insulating character of Gd$_2$Zr$_2$O$_7$ is kept and the band gap is broadened with the increasing Sm content, i.e., 2.62, 2.68, 2.76 and 2.83 eV for Sm$_0.5$Gd$_{1.5}$Zr$_2$O$_7$, SmGdZr$_2$O$_7$, Sm$_1.5$Gd$_{0.5}$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$, respectively. In addition, the hybridization of O 2p and Zr 4d is slightly affected by the incorporation of Sm. As for Gd$_{y}$Sm$_{1-y}$Zr$_2$O$_7$, the hybridization of O 2p states with Zr 4d, Gd 5d and Sm 5d orbitals also dominates the VBM. It is interesting to find that Sm incorporation causes electrons distributing on the fermi level and the number of electrons increases with the increasing Sm content. This results in an insulating-to-metallic transition and the Gd$_{y}$Sm$_{1-y}$Zr$_2$O$_7$ has much stronger electronic conductivity than the pure state. In the meantime, the Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ do not have any magnetism, whereas the Gd$_{y}$Sm$_{1-y}$Zr$_2$O$_7$ compositions exhibit strong ferromagnetic states due to the different charge states of Sm and Zr.

Obviously, Sm incorporation into Gd-site and Zr-site of Gd$_2$Zr$_2$O$_7$ causes very different electronic structures, i.e., the Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_{y}$Sm$_{2-y}$Zr$_2$O$_7$ are mainly of insulating and metallic characters, respectively. These results indicate that the thermal conductivity of Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$ are mainly contributed by phonons, while both phonons and electrons contribute to the thermal conductivity of Gd$_{y}$Sm$_{2-y}$Zr$_2$O$_7$.

**Summary**

In this work, a systematic study based on the DFT method is carried out to investigate the effects of Sm substitution for Gd-site and Zr-site in Gd$_2$Zr$_2$O$_7$ on its structural stability, mechanical properties, Debye temperature and electronic structures. It is shown that the Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$ compositions keep the pyrochlore structure and their lattice parameters follow well the Vegard’s law, indicative of the formation of Gd$_2$Zr$_2$O$_7$·Sm$_2$Zr$_2$O$_7$ solid solution. On the other hand, Sm substitution for Zr-site influences the structure significantly and a pyrochlore-to-defect fluorite structure transition occurs. The Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$ compositions are of elastic isotropy and their elastic moduli, ductility, Debye temperature and band gap vary slightly with the Sm content. However, the Gd$_{y}$Sm$_{2-y}$Zr$_2$O$_7$ compounds show strong elastic anisotropy and their bulk, Young’s and shear moduli all decrease sharply with the increasing Sm content. Consequently, the Gd$_{y}$Sm$_2$O$_7$ has the minimum Young’s modulus of 87 GPa, minimum shear modulus of 31 GPa and minimum bulk modulus of 151 GPa. Meanwhile, both the Pugh’s indicator and Poison’s ratio suggest that the Gd$_{y}$Sm$_2$Zr$_2$O$_7$ have better ductility than the Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$. As the Sm substitutes for Zr-site, the Debye temperature decreases considerably with the increasing Sm content and the Debye temperature of 341.7 K for Gd$_{y}$Sm$_2$O$_7$ is about 44.3% lower than that of Gd$_2$Zr$_2$O$_7$. In addition, the insulating character of Gd$_{y}$Zr$_2$O$_7$ is kept in the system of Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$, while the Gd$_{y}$Sm$_{2-y}$Zr$_2$O$_7$ compositions exhibit metallic characters. Our calculations demonstrate that substituting Sm for Zr-site is an effective approach to tailor the mechanical and thermal properties of Gd$_2$Zr$_2$O$_7$.

**Methods**

In this work, first-principles total energy calculations within the DFT framework are carried out. All calculations are performed with the Vienna Ab-initio Simulation Package (VASP) [51, 52]. The interaction between electrons and ions is described by the projector augmented wave method [52, 53]. All computations are based on a supercell containing 88 atoms. The convergence criteria for total energies and forces are 10$^{-6}$ eV and 10$^{-4}$ eV/Å, respectively. The structural relaxation is carried out at variable volume. In order to determine the values of cutoff energy and k-point sampling, a series of test calculation has been carried out. Figure 9 shows the variation of total energy of Gd$_2$Zr$_2$O$_7$ and Sm$_2$Zr$_2$O$_7$ with cutoff energy and k-point sampling, which leads to our calculation being performed with a 2 × 2 × 2 Monkhorst-Pack k-mesh for Brillouin-zone integrations and a cutoff energy of 600 eV for plane wave. For Sm$_{y}$Gd$_{2-y}$Zr$_2$O$_7$ and Gd$_{y}$Sm$_{2-y}$Zr$_2$O$_7$ (y = 0.5, 1, 1.5), the structure models are constructed by the special quasirandom structure approach [54, 55].

**References**

1. Zhao, F. A., Xiao, H. Y., Jiang, M., Liu, Z. J. & Zu, X. T. A DFT + U study of Pu immobilization in Gd$_2$Zr$_2$O$_7$. *J. Nucl. Mater.* 467, 937–948 (2015).
2. Schelling, P. K., Phillpot, S. R. & Grimes, R. W. Optimum pyrochlore compositions for low thermal conductivity. *Philos. Mag. Lett.* 84, 127–137 (2004).
3. Liu, Z. G., Ouyang, J. H., Zhou, Y. & Xia, X. L. Effect of Sm substitution for Gd on the electrical conductivity of fluorite-type Gd$_2$Zr$_2$O$_7$. *J. Power Sources* 185, 876–880 (2008).
4. Feng, J. et al. Electronic structure, mechanical properties and thermal conductivity of Ln$_2$Zr$_2$O$_7$ (Ln = La, Pr, Nd, Sm, Eu and Gd) pyrochlore. *Acta Mater.* 59, 1742–1760 (2011).
5. Sohn, J. M., Kim, M. R. & Woo, S. I. The catalytic activity and surface characterization of Ln$_2$B$_2$O$_7$ (Ln = Sm, Eu, Gd and Tb; B = Ti or Zr) with pyrochlore structure as novel CH$_4$ combustion catalyst. *Catal. Today* 83, 289–297 (2003).
52. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).

53. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp. Mater. Sci.* **6**, 15–50 (1996).

54. Zunger, A., Wei, S., Ferreira, L. G. & Bernard, J. E. Special quasirandom structures. *Phys. Rev. Lett.* **65**, 353–356 (1990).

55. Jiang, C., Wolverton, C., Sofo, J., Chen, L.-Q. & Liu, Z.-K. First-principles study of binary bcc alloys using special quasirandom structures. *Phys. Rev. B* **69**, 214202 (2004).

56. Jiang, C., Stanek, C. R., Sickafus, K. E. & Uberuaga, B. P. First-principles prediction of disordering tendencies in pyrochlore oxides. *Phys. Rev. B* **79**, 104203 (2009).

57. Guo, L., Li, M., Zhang, Y. & Ye, F. Improved Toughness and Thermal Expansion of Non-stoichiometry Gd$_{2−x}$Zr$_2$O$_7+x/2$ Ceramics for Thermal Barrier Coating Application. *J. Mater. Sci. Technol.* **32**, 28–33 (2016).

**Acknowledgements**

H.Y. Xiao was supported by the NSAF Joint Foundation of China (Grant No. U1530129) and the scientific research starting funding of University of Electronic Science and Technology of China (Grant No. Y02002010401085). Z.J. Liu was supported by National Natural Science Foundation of China (Grant No. 11464025) and the New Century Excellent Talents in University under Grant no. NCET-11–0906. The theoretical calculations were performed using the supercomputer resources at TianHe-1 located at National Supercomputer Center in Tianjin.

**Author Contributions**

H.X. and X.Z. designed the calculations. S.Z. conducted the calculations and wrote the manuscript. F.Z., M.J., Z.L. and H.Zhang contributed the discussion and interpretation of the results. All authors discussed the results and reviewed the manuscript.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

**Publisher’s note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2017