Density and hardness of Nd-doped zircon ceramics as nuclear waste forms

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Abstract. Zircon ceramics were employed as host material for immobilization of element Nd, which was used as the surrogate of trivalent actinide nuclide. A series of Zr₂ₓNdₓSi₆O₁₈₋ₓ compounds were prepared by solid-state reaction method at 1500 ℃ for 72 h in air and investigated in respect of their physics performances. These performances were characterized by density and hardness. The results show that the density raises as the value of x increases from 0.02 to 0.20. Moreover, the hardness of the Nd-doped ceramic also increase with enhanced Nd content.

1. Introduction

Nuclear energy is one of the most promising energy, which has high energy density than fossil fuels and does not cause air pollution [1-3]. The development and utilization of nuclear energy have brought great economic benefits and social benefits to human beings. However, such nuclear waste from the nuclear industry pose a considerable biological hazard on human beings, and produce a threat to environmental safety at the same time [4, 5]. Thus, safe disposal of these nuclear waste, especial for radioactive nuclides (Uranium, Plutonium, Americium and Thorium), has become more and more important in nuclear industry [6, 7]. In the past, some host materials, like glasses and cements, have been considered for this purpose. Nevertheless, the high leaching rate in glasses and cements limit their further application in the disposal of radioactive waste [8-10]. Moreover, glasses belong to metastable state, which has a tendency to get devitrified at high temperature and pressure [11]. By contrast, composites of mineral analog titanates, named as SYNROC, such as zircon based materials have excellent physical properties, and it is considered as suitable to immobilize nuclear wastes [12].

Zircon (I₄₁/amd, Z = 4) belongs to the island of silicate minerals and tetragonal crystal system, and the theoretic composition consists of 32.8 wt% SiO₂ and 32.8 wt% ZrO₂. Due to its fantastic properties, such as high thermal decomposition temperature (≥ 1500℃), low thermal expansion coefficient (about 4.1 × 10⁻⁶ K⁻¹ at 25-1400℃), good chemical stability as well as the ability to immobilize actinides in the lattices, zircon has been attracted intensive attention in recent years [13, 14]. Zircon in nature (crystalline rocks) contains a certain amount of radioactive elements, as much as UO₂ 5 wt% or ThO₂ 15 wt%, and keeps its structure well after millions of years [15]. In the past 10 years, great progress has been achieved in the research of zircon immobilized Pu and other radioactive elements. A certain amount of radionuclide replaced Zr at the Zr site to synthesize ASiO₄ (A⁴⁺=Zr, Hf, Th, Pa, U, Np, Pu,
and Am) has been investigated by Keller at el. [16, 17].

The aim of the present work is to synthesize a series of Zr\(_2\)-Nd\(_2\)O\(_8\)-0.5Si\(_2\)O\(_8\)-0.5 (0.02 ≤ \(x\) ≤ 0.20) ceramic by gradually substituting Nd for Zr in the composition. The effect of Nd substitution on the density as well as the hardness of the compositions was investigated. The density meter and hardness tester were implemented to measure the density and hardness of the each sintered sample induced by substituting Nd, respectively.

2. Experiment
Nd has so far gained widespread recognition and become representative substitutes for An (An: actinide) owing to their similar ionic radius and ion valence to some actinide elements. Therefore, in the present work Nd is selected as an alternative to simulate the trivalent actinides, and to substitute for Zr in ZrSiO\(_4\) to simulate ceramics solidifying radioactive nuclides like Pu, Am, U and Th.

In the present study, AR grade ZrO\(_2\), CeO\(_2\) and SiO\(_2\) were selected as the starting materials. A series of Zr\(_2\)-Nd\(_2\)O\(_8\)-0.5Si\(_2\)O\(_8\)-0.5 (0.02 ≤ \(x\) ≤ 0.20) were prepared by solid-state reaction method. Before weighing, all the raw powders were heated at 100°C for 6 h to remove adsorptive water. Then stoichiometric amounts of the powders in appropriate ratios were weighed, and ground in analytically pure ethanol medium. The dried powders were compacted in a pellet form (12 mm diameter and ~2 mm thickness) at a pressure of 10 MPa. The pellets were sintered at 1500°C for 72 h in air atmosphere to fabricate dense bulk ceramic at a heating rate of 5 °C/min. The sintered compounds were taken out of the furnace after being naturally cooled to room temperature. Table 1 presents the contents of starting materials for synthesizing Zr\(_2\)-Nd\(_2\)Si\(_2\)O\(_8\)-0.5Si\(_2\)O\(_8\)-0.5 (0.02 ≤ \(x\) ≤ 0.20). Figure 1 shows the T-t curve of the sintering progress.

| Target compounds | Additive amount of raw materials/g |
|------------------|----------------------------------|
|                  | ZrO\(_2\) | Nd\(_2\)O\(_3\) | SiO\(_2\) |
| Zr\(_{1.98}\)Nd\(_{0.02}\)Si\(_2\)O\(_7\)-99 | 1.9908 | 0.0274 | 0.9805 |
| Zr\(_{1.96}\)Nd\(_{0.04}\)Si\(_2\)O\(_7\)-98 | 1.9659 | 0.0548 | 0.9781 |
| Zr\(_{1.94}\)Nd\(_{0.06}\)Si\(_2\)O\(_7\)-97 | 1.9411 | 0.0820 | 0.9757 |
| Zr\(_{1.92}\)Nd\(_{0.08}\)Si\(_2\)O\(_7\)-96 | 1.9163 | 0.1090 | 0.9733 |
| Zr\(_{1.90}\)Nd\(_{0.10}\)Si\(_2\)O\(_7\)-95 | 1.8917 | 0.1359 | 0.9709 |
| Zr\(_{1.88}\)Nd\(_{0.12}\)Si\(_2\)O\(_7\)-94 | 1.8671 | 0.1627 | 0.9685 |
| Zr\(_{1.86}\)Nd\(_{0.14}\)Si\(_2\)O\(_7\)-93 | 1.8450 | 0.1896 | 0.9673 |
| Zr\(_{1.84}\)Nd\(_{0.16}\)Si\(_2\)O\(_7\)-92 | 1.8206 | 0.2161 | 0.9649 |
| Zr\(_{1.82}\)Nd\(_{0.18}\)Si\(_2\)O\(_7\)-91 | 1.7963 | 0.2426 | 0.9625 |
| Zr\(_{1.80}\)Nd\(_{0.20}\)Si\(_2\)O\(_7\)-90 | 1.7744 | 0.2692 | 0.9613 |
The density of each sintered sample was measured by a full automatic density meter (GH-120D) based on the Archimedes principle. As much as possible to improve the accuracy of the solidified body density test values, the density testing were carried out for three times, and then take the average value as the density value of the sample. The micro-hardness test was carried out on Vickers Hardness Tester Hv-1000A with a diamond tip at a test load of 500 g and dwelling time of 15 s. In order to improve the accuracy of hardness test of the solidified samples, the test were randomly selected in 3 different locations, and then take the average value as the sample hardness value.

3. Results and discussion

The density and hardness are closely related, which are important indexes to evaluate the performance of ceramic materials. As a highly radioactive waste material, it is better to have a larger density and higher hardness [18]. Table 2 lists the tested density of Zr$_{2-x}$Nd$_x$Si$_2$O$_{8-0.5x}$ (0.02 ≤ $x$ ≤ 0.2) compounds and Figure 2 shows the relation curve between the densities and $x$ in Zr$_{2-x}$Nd$_x$Si$_2$O$_{8-0.5x}$ (0.02 ≤ $x$ ≤ 0.2).

Figure 2 shows the relation curve between the densities and $x$ in Zr$_{2-x}$Nd$_x$Si$_2$O$_{8-0.5x}$ (0.02 ≤ $x$ ≤ 0.2). It could be found that the density value display a gradual increase as the content Nd increase in the solid solution. The highest density achieved as 3.784 g·cm$^{-3}$ for Zr$_{1.80}$Nd$_{0.20}$Si$_2$O$_{7.90}$, while the lowest density is obtained as 3.223 g·cm$^{-3}$ for Zr$_{1.98}$Nd$_{0.02}$Si$_2$O$_{7.99}$. The reason for this is mainly due to the relative atomic weight of the element. The relative atomic weight of Nd (144.242) is greater than that of Zr (91.224) and trivalent simulated nuclide Nd can completely replace Zr in the solidified crystal lattice [19]. So the density of Nd-doped ceramics increases with the amount of simulated nuclide Nd.

Table 2. Tested density of Zr$_{2-x}$Nd$_x$Si$_2$O$_{8-0.5x}$ (0.02 ≤ $x$ ≤ 0.2) compounds.

| Target compounds     | Tested density / g·cm$^{-3}$ | 1    | 2    | 3    | 4    | 5    | Average |
|----------------------|------------------------------|------|------|------|------|------|---------|
| Zr$_{1.90}$Nd$_{0.02}$Si$_2$O$_{7.99}$ | 3.209 | 3.206 | 3.265 | 3.232 | 3.205 | 3.223 |
| Zr$_{1.96}$Nd$_{0.00}$Si$_2$O$_{7.98}$ | 3.300 | 3.313 | 3.332 | 3.286 | 3.215 | 3.289 |
| Zr$_{1.94}$Nd$_{0.06}$Si$_2$O$_{7.97}$ | 3.296 | 3.361 | 3.404 | 3.396 | 3.361 | 3.364 |
| Zr$_{1.92}$Nd$_{0.08}$Si$_2$O$_{7.96}$ | 3.402 | 3.415 | 3.395 | 3.33  | 3.408 | 3.390 |
| Zr$_{1.90}$Nd$_{0.10}$Si$_2$O$_{7.95}$ | 3.434 | 3.368 | 3.381 | 3.379 | 3.425 | 3.397 |
Figure 2. Relation curve between the densities and \( x \) in Zr\(_{2-x}\)Nd\(_x\)Si\(_2\)O\(_8\)-0.5\( x \) (0.02 ≤ \( x \) ≤ 0.2).

Figure 3. Vickers hardness test photos of some samples.

Table 3. Vickers hardness of Zr\(_{2-x}\)Nd\(_x\)Si\(_2\)O\(_8\)-0.5\( x \) (0.02 ≤ \( x \) ≤ 0.2) samples.

| Target compounds      | Hardness / kg·mm\(^{-2}\) | Average   |
|-----------------------|-----------------------------|-----------|
| \( Zr_{1.98}Nd_{0.02}Si_2O_{7.99} \) | 413.03 366.052 352.355 | 377.146   |
| \( Zr_{1.96}Nd_{0.04}Si_2O_{7.98} \) | 453.237 441.261 465.171 | 453.223   |
| \( Zr_{1.94}Nd_{0.06}Si_2O_{7.97} \) | 453.73 447.216 458.27 | 453.072   |
| \( Zr_{1.92}Nd_{0.08}Si_2O_{7.96} \) | 543.438 440.531 486.665 | 490.211   |
| \( Zr_{1.90}Nd_{0.10}Si_2O_{7.95} \) | 521.59 512.187 503.317 | 512.365   |
| \( Zr_{1.88}Nd_{0.12}Si_2O_{7.94} \) | 728.826 660.721 660.085 | 683.211   |
| \( Zr_{1.86}Nd_{0.14}Si_2O_{7.93} \) | 732.336 699.195 809.206 | 746.912   |
| \( Zr_{1.84}Nd_{0.16}Si_2O_{7.92} \) | 803.128 894.931 952.408 | 883.489   |
| \( Zr_{1.82}Nd_{0.18}Si_2O_{7.91} \) | 933.39 1093.815 916.077 | 981.091   |
| \( Zr_{1.80}Nd_{0.20}Si_2O_{7.90} \) | 1145.181 1063.015 1024.197 | 1077.464  |
Figure 3 shows part of Vickers hardness test photos, which reveals the process of the testing. Table 3 gives a series of Vickers hardness test results, and Figure 4 displays the relation curves between $H_v$ and $x$ of Zr$_2$Nd$_{0.02}$Si$_2$O$_{7.99}$ (0.02 ≤ $x$ ≤ 0.2) compounds. The results show that the Vickers hardness of Zr$_2$Nd$_{0.02}$Si$_2$O$_{7.99}$ (0.02 ≤ $x$ ≤ 0.2) samples ranges from 377.146 kg·mm$^{-2}$ for Zr$_{1.98}$Nd$_{0.02}$Si$_2$O$_{7.99}$ to 1077.464 kg·mm$^{-2}$ for Zr$_{1.80}$Nd$_{0.20}$Si$_2$O$_{7.90}$. From Figure 4, it can be clearly seen that with the increase in the amount of Nd$_2$O$_3$, Vickers hardness value appears to be gradually increasing trend. By using the linear equation $y = a + bx$, the Vickers hardness can be linear fitted by the $x$ in the sample. The linear relationship is expressed as $H_v = 229.45 + 3996.96x$, and the $R^2$ value is greater than 0.8739, indicating that Vickers hardness and the content of Nd directly have a good linear relationship.

4. Conclusions
A series of Zr$_2$Nd$_{0.02}$Si$_2$O$_{7.99}$ compounds were prepared by solid-state reaction method at 1500℃ for 72 h in air. The density tests show that the density of Zr$_2$Nd$_{0.02}$Si$_2$O$_{7.99}$ (0.02 ≤ $x$ ≤ 0.20) compounds ranges from 3.223 to 3.784 g·cm$^{-3}$, and with increasing of simulated nuclide Nd, the density increased gradually. From the hardness results, it can be found that the hardness of Zr$_2$Nd$_{0.02}$Si$_2$O$_{7.99}$ (0.02 ≤ $x$ ≤ 0.20) compounds extent from 377.146 kg·mm$^{-2}$ to 1077.464 kg·mm$^{-2}$. Vickers hardness of Zr$_2$Nd$_{0.02}$Si$_2$O$_{7.99}$ (0.02 ≤ $x$ ≤ 0.20) compounds increase gradually with the increase of Nd$_2$O$_3$ content. Vickers hardness and $x$ value has linear fitted as $H_v = 229.45 + 3996.96x$, and the $R^2$ value is greater than 0.87.

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