Rapid Synthesis and Chemical Durability of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_{207}$ ($0.0 \leq x \leq 2.0$) Sub-Micron Ceramics as Nuclear Waste Forms

Kui Liu

Southwest University of Science and Technology <https://orcid.org/0000-0002-0400-6907>

Kuibao ZHANG (✉ xiaobao320@163.com)

Ting DENG

Southwest University of Science and Technology

Jianjun ZENG

Southwest University of Science and Technology

Daimeng CHEN

Southwest University of Science and Technology

Haiyan GUO

Southwest University of Science and Technology

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Abstract

In this work, Nd^{3+} was used as a surrogate and it was incorporated into $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanocrystalline ceramics to simulate the immobilization of trivalent actinide elements. A series of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) nanocrystalline powders were fabricated by solvothermal method, and then $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ sub-microncrystalline ceramics were prepared by sintering via self-propagating chemical furnace plus quick pressing (SCF/QP). All powders are in defective fluorite structure, and Nd doping hardly change the powder grain size. After analyzing the sintered ceramics, it can be found that the transition from defective fluorite structure to pyrochlore structure occurs when $x \geq 1.5$. The sample density decreases with elevated Nd content, while the grain size gradually enlarges. Besides, the normalized release rates of Nd and Zr elements in the $\text{Nd}_2\text{Zr}_2\text{O}_7$ waste form are kept in low values (below $10^{-5} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$), which exhibits its excellent aqueous stability.

1. Introduction

Crystalline $\text{Gd}_2\text{Zr}_2\text{O}_7$ (GZO) oxide with pyrochlore or defective fluorite structure has been widely used in many fields due to its excellent thermal stability, chemical stability and mechanical properties^[1–4]. GZO ceramic exhibits the characteristics of immobilizing certain actinides and outstanding radiation resistance in term of nuclear waste immobilization, which makes it a promising host material for the safe disposal of high-level radioactive wastes^[5–9].

The GZO oxide can tolerate actinide elements into its crystal structure due to its flexible lattice sites. GZO exhibits the $\text{A}_2\text{B}_2\text{O}_7$ stoichiometry, where the A site can immobilize trivalent nuclides (such as Am) while the B site can immobilize tetravalent nuclides (such as Pu)^[10–12]. According to Subramanian theory, the phase stability is mainly determined by the cation radius ratio (r_A/r_B). The phase structure of $\text{A}_2\text{B}_2\text{O}_7$ can be divided into three different types: disordered defective fluorite structure ($r_A/r_B < 1.46$), ordered pyrochlore structure ($1.46 \leq r_A/r_B \leq 1.78$) and monoclinic crystal structure ($r_A/r_B > 1.78$)^[13]. The r_A/r_B value of GZO is 1.46, which is exactly at the boundary between disordered defective fluorite structure and ordered pyrochlore structure. This characteristic makes its structure unstable and can adapt to a range of structural defects^[14, 15]. Figure 1 depicts the crystal structure of pyrochlore and defective fluorite. The pyrochlore structure is a superstructure derivative of simple fluorite structure (AO_2). It can be written as

$\text{A}_2\text{B}_2\text{O}_6\text{O}'$ and belongs to the space group $Fd\bar{3}m$ ($Z = 8$). A, B, O, O' ions respectively occupy $16c$, $16d$, $48f$ and $8b$ four crystal sites, and the unoccupied $8a$ site corresponds to the oxygen

vacancy. The defective fluorite structure shows the $Fm\bar{3}m$ ($Z = 1$) space group, in which the cation arrangement and oxygen vacancy distribution become disordered^[16–18]. Of course, other factors may also cause disorder of cations and anions, such as sintering temperature, pressure, metal-oxygen bond covalentness and ion irradiation^[19–21]. At present, research reports demonstrate that

the pyrochlore structure formed in GZO at a temperature range of 1300–1500 °C and transformed to defective fluorite structure at temperature higher than 1550 °C [22, 23].

In recent years, nuclear waste forms based on GZO ceramics have been widely investigated for high-level radioactive wastes [24–26]. Nd^{3+} is usually selected as a surrogate of trivalent actinides to simulate the trivalent nuclide immobilization effect, which can be used for manufacturing or performance evaluation [27]. According to the isomorphism theory, Nd^{3+} is designed to occupy the Gd^{3+} site in the GZO crystal structure since the radius of Nd^{3+} ($r_{\text{Nd}^{3+}} = 1.11 \text{ \AA}$) is close to the equivalently charged Gd^{3+} ($r_{\text{Gd}^{3+}} = 1.05 \text{ \AA}$). Mandal et al. have investigated the phase relation and thermal expansion behavior of $\text{Gd}_2\text{Zr}_2\text{O}_7$ - $\text{Nd}_2\text{Zr}_2\text{O}_7$ system using conventional sintering methods [28]. Since then, Lu et al. have also prepared and characterized $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics using spark plasma sintering (SPS) technology [29]. The sample grain size prepared by the two methods are in the micron scale. Moreover, only the phase structure is characterized while the immobilization properties (such as aqueous stability) are not studied. The preparation and research of nanocrystalline ceramics have also been extensively carried out with the rise of nanocrystalline materials. Compared with large-grain ceramics, nanocrystalline ceramics display more exceptional radiation stability in the field of nuclear waste immobilization [30]. This conclusion is because nanocrystalline ceramics have massive crystal interfaces and grain boundaries. They can act as sinks for the annihilation of point defects (such as interstitials and vacancies) produced by radiation [31, 32]. Therefore, it is of great value to prepare $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics with grain size less than micron scale and to explore its immobilization properties.

In this study, the preparation process of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics with grain size less than a micrometer and the aqueous stability with the maximum Nd doping were studied. In our previous work, GZO nanocrystalline ceramics have been successfully prepared [33]. Thus, $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics were also prepared by a two-step method in this work. The structure and performance evolution of these Nd-doped GZO waste forms were characterized by X-ray diffraction, Raman spectroscopy, scanning electron microscopy and density measurement to understand the microstructural effects of Nd in place of Gd. The aqueous durability of $\text{Nd}_2\text{Zr}_2\text{O}_7$ ceramic was estimated using the static leaching experiment, and the crystal structure of the sample after leaching was characterized and analyzed as well.

2. Experimental Details

2.1 Composition design and preparation of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ceramics

As the previous researchers have completely prepared $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) microcrystalline ceramics, it is determined that Nd^{3+} can wholly replace the Gd^{3+} position in the $\text{Gd}_2\text{Zr}_2\text{O}_7$ structure. Therefore, five x values were designed to obtain detailed information about the structural evolution in this system. The stoichiometric amount of the starting reagents were weighed according to Table 1. All Gd_{2-x}

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$x\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) nanocrystalline powders were prepared by solvothermal methods using $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as the starting materials. All prepared $\text{Gd}_2 - x\text{Nd}_x\text{Zr}_2\text{O}_7$ nanocrystalline powders were calcined at 800 °C for 2 hours to remove impurities and organics. Subsequently, the calcined powder was weighed 1 g and then uniaxially pressed with a steel mold to form a disk with diameter of 10 mm.

Table 1
Composition details for $\text{Gd}_2 - x\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) nanocrystille powders

No.	Designed formula	Amounts of raw materials/g		
		$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	$\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$
1	$\text{Gd}_2\text{Zr}_2\text{O}_7$	5.9296	5.6401	0.0000
2	$\text{Gd}_{1.5}\text{Nd}_{0.5}\text{Zr}_2\text{O}_7$	4.4953	5.7011	1.7501
3	$\text{GdNdZr}_2\text{O}_7$	3.0296	5.7633	2.9423
4	$\text{Gd}_{0.5}\text{Nd}_{1.5}\text{Zr}_2\text{O}_7$	1.5315	5.8268	4.4620
5	$\text{Nd}_2\text{Zr}_2\text{O}_7$	0.0000	5.8920	6.0152

Because the density of $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanocrystalline ceramic obtained by the previous process is only 83.6%, a slight improvement was made to improve its density in this study. Cold isostatic pressing was performed on the pressed disk sample, thereby improving the compactness before sintering. The pressure of 200 MPa was adopted and the pressure was maintained for 200 s during cold isostatic pressing. Finally, the SCF/QP technology was used to obtain $\text{Gd}_2 - x\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics with higher density. The maximum temperature of SCF can reach to 1642 °C, the applied pressure was 50 MPa and the pressing time was 1 min. The entire sintering process was completed within 5 min. Specific powder preparation and sintering processes have been described elsewhere [33].

2.2 Characterizations

The calcined powders prepared by the solvothermal method were subjected to transmission electron microscopy (TEM; Zeiss Libra-200FE, Germany). The calcined powders and sintered ceramics were characterized by Cu K α radiation X-ray diffraction (XRD; X'Pert PRO, Netherlands). Raman spectroscopy was performed on the sintered ceramics using a Raman spectrometer (Raman; InVia, Renishaw, Britain) with 785 nm excitation wavelength. Field-emission scanning electron microscopy (FESEM; Zeiss Ultra-55, Oberkochen, Germany) and grain size statistics software (Nano measurer; Fudan University, Shanghai, China) were used to determine the grain size of ceramic samples. The density of samples was tested based on the Archimedes drainage method. The leached samples were analyzed by grazing incidence X-ray diffraction (GIXRD) using an X-ray diffractometer (Bruker; D8 Advance) with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$).

2.3 Aqueous durability

The aqueous durability of $\text{Nd}_2\text{Zr}_2\text{O}_7$ ceramics was evaluated according to the standard MCC-1 method [34]. The selected sample was cut into $5.0 \times 4.3 \times 3.0$ mm, which was polished and suspended with copper wire in the center of PTFE container filled with 80 ml deionized water (pH = 6.5). The vessel was then placed in a kettle and transferred to an oven at 90 °C for 1, 3, 7, 14, 21, 28, 35 and 42 days. The leaching concentrations (C_i) of Nd and Zr elements were measured by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7700 × spectrometer. The normalized elemental leaching rate LR_i ($\text{g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) was obtained using the equation given below:

$$LR_i = \frac{C_i V_i}{f_i S_A t} \quad (1)$$

Where the five variables in the equation represent the concentration of the element i in the leached solutions after leaching experiment (C_i g/ L), the quality percentage of the element i in the specimen (f_i wt%), the surface area of the specimen (S_A , m^2), the volume of the leached solutions (V_i L) and the duration time (t , d).

3. Results And Discussion

3.1 Analysis of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) nanocrystalline powders

The XRD patterns of calcined $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) nanocrystalline powders formed by the solvothermal method are shown in Fig. 2. Interestingly, the diffraction peaks of all powders present basically the same parameters as the JCPDS cards (PDF No. 80-0471 and 78-1289), which indicates that they belong to defective fluorite structure. According to Subramanian theory [13], $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.5 \leq x \leq 2.0$) should be a pyrochlore structure because r_A/r_B values are between 1.46 and 1.54. The cation radius ratio at the A and B sites is based on the following formula:

$$r = \frac{r_A}{r_B} = \frac{\left(\frac{1-x}{2}\right)r_{\text{Gd}^{3+}} + \frac{x}{2}r_{\text{Nd}^{3+}}}{r_{\text{Zr}^{4+}}} \quad (2)$$

Where r is the radius ratio of the cations at the A and B sites; r_A is the average cation radius at the A site, consisting of Gd^{3+} and Nd^{3+} ; $r_{\text{Gd}^{3+}}$ is 1.05 Å, $r_{\text{Nd}^{3+}}$ is 1.11 Å and r_B is equal to $r_{\text{Zr}^{4+}}$ (0.72 Å); x is the matching value in $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$). The above phenomenon occurs due to the influence of surface/interface energy on the Gibbs free energy, so nanocrystalline powders always exist in the form of a high-temperature phase (defective fluorite structure) [35]. In addition, it can be discovered that the diffraction peaks gradually move to a smaller angle as the value of x increases. This occurrence is because the radius of Nd^{3+} is larger than that of Gd^{3+} , which causes the unit cell to expand. The XRD consequences also point out that it is feasible to introduce the simulated radionuclide Nd into the crystal structure using the solvothermal method.

The powders (at $x = 0.0$ and 2.0) were characterized by TEM to study the doping amount influence on the micro-morphology of $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanocrystalline powder (x

= 0.0), while (c) and (d) correspond to $\text{Nd}_2\text{Zr}_2\text{O}_7$ ($x = 2.0$). The crystallite shape of both powders is approximately spherical and the average grain size of the two powders are 6.5 nm and 7.0 nm. According to the fitting calculation of their XRD data by Jade software, the grain size of $\text{Gd}_2\text{Zr}_2\text{O}_7$ and $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanocrystalline powders are 6.4 and 6.9 nm. This conclusion is basically in consistence with the TEM results, which reveals that Nd doping has no significant effect on the micro-morphology of nanopowders prepared by solvothermal method.

3.2 XRD and Raman analysis of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics

Fig. 4(a) presents the XRD patterns of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics. The original matrix $\text{Gd}_2\text{Zr}_2\text{O}_7$ indicates a defective fluorite structure. This result can be attributed to the high sintering temperature of 1642 °C as $\text{Gd}_2\text{Zr}_2\text{O}_7$ exhibits defective fluorite structure when the sintering temperature is higher than 1550 °C^[23]. Interestingly, the structure of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ceramics starts to change from pyrochlore structure to defective fluorite structure when x value goes beyond 1.0. With the doping of Nd, the cation radius ratio at the r_A/r_B is greater than 1.46 and its structure should theoretically be a pyrochlore structure. However, since the grain size of prepared ceramics is in sub-micron scale and the samples have more grain boundaries and crystal planes, which also affects the Gibbs free energy of the system. So it is still a defective fluorite structure^[35]. The cation radius ratio and the grain size gradually increases with the Nd content when x value goes beyond 1.0, which makes the ceramics form pyrochlore structure. Therefore, the phenomenon of structural change from defective fluorite to pyrochlore appears. In addition, it can be found that the diffraction peaks gradually shift to a small angle with the Nd content increases. This outcome is in accordance with the XRD results of nanocrystalline powders, which can be attributed to lattice expansion caused by Nd doping. The phenomena of this study are somewhat different from previous report^[29]. Lu et al. have used SPS (1700 °C sintering temperature) to prepare ceramics with a grain size of about 9 μm . Transition from defective fluorite structure to pyrochlore structure appears when $x \geq 0.8$. The reason for this difference is that the sub-micron ceramic samples have a greater influence on the Gibbs free energy of the system, and there is also a certain difference in the sintering temperature between the two systems. Thus, the critical point of transition from defective fluorite structure to pyrochlore structure is different between the two studies.

As a supplement and verification of XRD results, the Raman spectroscopy analysis was also conducted to further understand the ordered structure of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ceramics as presented in Fig. 4(b). Firstly, the original matrix $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramic shows three Raman active modes of the defective fluorite structure, including E_g , F_{2g} and A_{1g} ^[36]. When x increases from 0 to 1.0, $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.5 \leq x \leq 1.0$) ceramics also display the same three Raman active modes as above. When $x = 1.5$ and 2.0, $\text{Gd}_{0.5}\text{Nd}_{1.5}\text{Zr}_2\text{O}_7$ and $\text{Nd}_2\text{Zr}_2\text{O}_7$ demonstrate four kinds of pyrochlore structure Raman active modes, which are $E_g + A_{1g} + 2F_{2g}$ ^[37]. In these Raman active modes, A_{1g} corresponds to O-Zr-O bending vibration type, E_g corresponds to Zr-O bending vibration type and F_{2g} corresponds to Zr-O and Gd (Nd)-O stretching vibration type. This result is in line with XRD analysis that the pyrochlore structure appears at $x = 1.5$ and 2.0. Secondly, the Raman

change of force constant caused by Nd doping in the A site. The average cation radius ratio (r_A/r_B) increases from 1.46 to 1.54 with the continuous doping of Nd at the A site. This condition makes the bond force constant of Gd (Nd)-O and Zr-O variations, which leads to the change of ZrO_6 coordination octahedron vibration modes in $Gd_{2-x}Nd_xZr_2O_7$ ceramics [38]. Hence, the Raman vibration peaks generated by these groups shift to lower frequencies as the average r_A/r_B ratio increases.

3.3 Micromorphology and density analysis of $Gd_{2-x}Nd_xZr_2O_7$ ($0.0 \leq x \leq 2.0$) ceramics

Fig. 5 demonstrates the micromorphology of $Gd_{2-x}Nd_xZr_2O_7$ ($0.0 \leq x \leq 2.0$) ceramics sintered by SCF/QP technology. It can be discovered that the grain boundary of ceramics after SCF sintering is clear. The grain shape is approximately spherical and all display a dense microscopic state. The grain size distribution was counted by Nano measure software and the statistical results are depicted in the upper right corner of Fig. 5(a)-(e). The average grain size of the original matrix $Gd_2Zr_2O_7$ is 79 nm, which is in consistent with our previous work [33]. When the x values are 0.5, 1.0, 1.5, and 2.0, the average grain size is 116 nm, 164 nm, 205 nm, and 265 nm. Fig. 5(f) shows the fitting result of XRD datas with Jade software to obtain the grain size. The results indicate that the calculated grain size is in accordance with the SEM grain statistics. The above results indicate that the average grain size of the ceramic samples also gradually enlarges with the Nd doping amount increases. This phenomenon is due to the fact that the atomic radius of Nd is larger than Gd, which leads to the grain size gradually enlarges after sintering. The density measured by the Archimedes drainage method is displayed in Fig. 6. At the same time, the results are compared with previous research [29]. It can be seen that the sample density prepared by the three sintering methods decreases with the increase of Nd content. Density is directly proportional to mass and inversely proportional to volume. As the radius of Nd atom is larger than Gd atom while Nd atom is lighter than Gd atom, the sample density gradually decreases in this system. In addition, the sample density after SCF/QP sintering is between SPS sintering and conventional sintering. However, the grain size of the samples sintered by SPS (1700 °C, 3 min) and conventional sintering (1500 °C, 72 h) is in micron scale. This consequence is due to SPS sintering temperature as high as 1700 °C and conventional sintering time as long as 72 hours. SCF sintering can produce dense samples with sub-micron grain sizes in just a few minutes. The density of $Gd_2Zr_2O_7$ after SCF sintering is $6.17 \text{ g}\cdot\text{cm}^{-3}$. Compared with the previous result of $5.53 \text{ g}\cdot\text{cm}^{-3}$, the improved preparation process did improve the density [33]. $Nd_2Zr_2O_7$ with the largest amount of Nd doping has a density of $5.87 \text{ g}\cdot\text{cm}^{-3}$ and relative density of 90.3%.

3.4 Aqueous durability analysis of $Nd_2Zr_2O_7$ ceramic

It is well known that nuclear waste forms will eventually be disposed in deep geological repositories. The waste forms will inevitably contact with groundwater and aqueous durability is a very important property to evaluate the safety of nuclear waste forms [39, 40]. Standard MCC-1 measurements were performed at 90 °C for 1–42 days to estimate the leaching behavior of $Nd_2Zr_2O_7$ sample. The normalized elemental leaching rates (LR) are depicted in Fig. 7. As the immersion time was extended from 1 day to 42 days, the degree of LR value reduction during the first 28 days is extremely large, which exceeds two orders of

magnitude. But the value gradually stabilizes from the 28th to the 42nd day. The LR_i value for Zr shows a different trend. The LR_{Zr} value decreases significantly in the first seven days. Then, there is a slight fluctuation between the 7th and 42nd days. For short-term leaching tests, fluctuations in LR_i values on the same order of magnitude is a common phenomenon [41]. The leaching values of Nd and Zr on the 42nd day are $1.1 \times 10^{-6} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ and $2.5 \times 10^{-7} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, respectively. Their values are lower than the leaching data of ordinary SYNROC (at the order of 10^{-4} to $10^{-3} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$) [42]. This result demonstrates that $\text{Gd}_2\text{Zr}_2\text{O}_7$ indicates great potential as immobilization matrix of radioactive wastes.

The influence of MMC-1 leaching experiment on the samples phase structure at different depths was further studied by the analysis of GIXRD, which has been used to evaluate the phase structure leaching stability of samples. The GIXRD patterns of $\text{Nd}_2\text{Zr}_2\text{O}_7$ after the MCC-1 leaching experiment are presented in Fig. 8. GIXRD analysis with different incident angles was carried out to achieve the purpose of detecting different depths. The incident angle γ was selected to be 4° , 2° , 1° and 0.5° , and the corresponding detection depths are 1440 nm, 720 nm, 360 nm and 180 nm. These depth values are calculated by the critical angle model, which has been described in the previous work [43]. The $\text{Nd}_2\text{Zr}_2\text{O}_7$ maintains the pyrochlore structure when the incident angle decreases from 4° to 1.0° . However, some characteristic peaks of pyrochlore structure begin to disappear ($2\theta = 60.3^\circ$ and 70.9°) when the incident angle drops to 0.5° . Compared with the original $\text{Nd}_2\text{Zr}_2\text{O}_7$ sample, the characteristic peaks of pyrochlore structure do indeed weaken after leaching, and even some weaker characteristic peaks disappear. This phenomenon demonstrates that the leaching experiment mainly caused slight damage to the crystal structure in the depth range of 180 nm. There is basically no effect in the depth range of more than 360 nm. This conclusion proves that $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanocrystalline ceramics possess excellent aqueous stability in immobilization radioactive wastes.

4. Conclusions

In this study, Nd^{3+} was successfully incorporated into $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanocrystalline powder by solvothermal method, and $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics with sub-micron grain size were prepared by SCF/QP sintering technology. $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) nanocrystalline powders are in all defective fluorite structure. In addition, the doping of Nd does not cause changes in the grain size of powders. The XRD and Raman analysis of the sintered ceramics demonstrate that the sample has a defective fluorite structure when $x < 1.5$ while the pyrochlore structure appears when $x \geq 1.5$. Furthermore, the sample density gradually decreases ($6.17\text{--}5.87 \text{ g} \cdot \text{cm}^{-3}$) and the grain size increases from nanometer to sub-micrometer (79–265 nm) as the amount of Nd doping elevates. The $\text{Nd}_2\text{Zr}_2\text{O}_7$ leaching experiment exhibits its promising aqueous stability as the LR_i values are mostly in the range of $10^{-5}\text{--}10^{-7} \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. The sample after leaching displays a slight crystal structure damage in the depth range of 180 nm at the sample surface layer. These results indicate that $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanocrystalline ceramics have great potential for immobilizing trivalent actinide elements.

Declarations

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References

1. Moskal G, Swadźba L, Hetmańczyk M et al (2012) Characterization of microstructure and thermal properties of $\text{Gd}_2\text{Zr}_2\text{O}_7$ -type thermal barrier coating. *J Eur Ceram Soc* 32:2025–2034
2. Aytug T, Paranthaman M, Leonard KJ et al (2005) Assessment of chemical solution synthesis and properties of $\text{Gd}_2\text{Zr}_2\text{O}_7$ thin films as buffer layers for second-generation high-temperature superconductor wires. *J Mater Res* 20:2988–2996
3. Zhang Y, Guo L, Zhao X et al (2015) Toughening effect of Yb_2O_3 stabilized ZrO_2 doped in $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramic for thermal barrier coatings. *Mat Sci Eng A-Struct* 648:385–391
4. Jafar M, Phapale SB, Mandal BP et al (2015) Preparation and structure of uranium-incorporated $\text{Gd}_2\text{Zr}_2\text{O}_7$ compounds and their thermodynamic stabilities under oxidizing and reducing conditions. *Inorg Chem* 54:9447–9457
5. Mandal BP, Banerji A, Sathe V et al (2007) Order–disorder transition in $\text{Nd}_{2-y}\text{Gd}_y\text{Zr}_2\text{O}_7$ pyrochlore solid solution: An X-ray diffraction and Raman spectroscopic study. *J Solid State Chem* 180:2643–2648
6. Lu XR, Long F, Shu XY et al (2015) Phase evolution and chemical durability of co-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramics for nuclear waste forms. *Ceram Int* 41:6344–6349
7. Patwe SJ, Ambekar BR, Tyagi AK (2005) Synthesis, characterization and lattice thermal expansion of some compounds in the system $\text{Gd}_2\text{Ce}_x\text{Zr}_{2-x}\text{O}_7$. *J Alloy Compd* 389:243–246
8. Kumari R, Kulriya PK, Grover V et al (2016) Radiation stability of $\text{Gd}_2\text{Zr}_2\text{O}_7$: effect of stoichiometry and structure. *Ceram Int* 42:103–109
9. Lutique S, Staicu D, Konings RJM et al (2003) Zirconate pyrochlore as a transmutation target: thermal behaviour and radiation resistance against fission fragment impact. *J Nucl Mater* 319:59–64
10. Mandal BP, Banerji A, Sathe V et al (2007) Order–disorder transition in $\text{Nd}_{2-y}\text{Gd}_y\text{Zr}_2\text{O}_7$ pyrochlore solid solution: An X-ray diffraction and Raman spectroscopic study. *J Solid State Chem* 180:2643–2648
11. Wang L, Shu X, Yi F et al (2018) Rapid fabrication and phase transition of Nd and Ce co-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramics by SPS [J]. *J Eur Ceram Soc* 38:2863–2870
12. Sayed FN, Jain D, Mandal BP et al (2012) Tunability of structure from ordered to disordered and its effect on the $\text{Nd}_{2-y}\text{Ho}_y\text{Zr}_2\text{O}_7$ ($0.0 \leq y \leq 2.0$) system. *RSC Adv*

13. Subramanian MA, Aravamudan G, Rao GVS (1983) Oxide pyrochlores—a review. *Prog Solid State Chem* 15:55–143
14. Ewing RC, Weber WJ, Lian J (2004) Nuclear waste disposal—pyrochlore ($A_2B_2O_7$): nuclear waste form for the immobilization of plutonium and "minor" actinides. *J Appl Phys* 95:5949–5971
15. Sattonnay G, Thome L, Monnet I et al (2012) Effects of electronic energy loss on the behavior of $Nd_2Zr_2O_7$ pyrochlore irradiated with swift heavy ions. *Nucl Instrum Meth B* 286:254–257
16. Lian J, Wang L, Chen J et al (2003) The order-disorder transition in ion-irradiated pyrochlore. *Acta Mater* 51:1493–1502
17. Lee YH, Sheu HS, Deng JP et al (2009) Preparation and fluorite-pyrochlore phase transformation in $Gd_2Zr_2O_7$. *J Alloy Compd* 487:595–598
18. Kong L, Karatchevtseva I, Gregg DJ et al (2013) $Gd_2Zr_2O_7$ and $Nd_2Zr_2O_7$ pyrochlore prepared by aqueous chemical synthesis. *J Eur Ceram Soc* 33:3273–3285
19. Zhao M, Ren X, Pan W (2015) Mechanical and thermal properties of simultaneously substituted pyrochlore compounds $(Ca_2Nb_2O_7)_x(Gd_2Zr_2O_7)_{1-x}$. *J Eur Ceram Soc* 35:1055–1061
20. Kumar NRS, Shekar NVC, Sahu PC (2008) Pressure induced structural transformation of pyrochlore $Gd_2Zr_2O_7$. *Solid State Commun* 147:357–359
21. Aluri ER, Hayes JR, Walker JDS et al (2014) Investigation of the structural stability of ion-implanted $Gd_2Ti_{2-x}Sn_xO_7$ pyrochlore-type oxides by glancing angle x-ray absorption spectroscopy. *J Phys Chem C* 118:7910–7922
22. Zhou L, Huang Z, Qi J et al (2015) Thermal-Driven Fluorite–Pyrochlore–Fluorite Phase Transitions of $Gd_2Zr_2O_7$ Ceramics Probed in Large Range of Sintering Temperature. *Metall Mater Trans A* 47:623–630
23. Wang J, Nakamura A, Takeda M (2003) Structural properties of the fluorite- and pyrochlore-type compounds in the Gd_2O_3 - ZrO_2 system $xGdO_{1.5}-(1-x)ZrO_2$ with $0.18 \leq x \leq 0.62$. *Solid State Ionics* 164:185–191
24. Ewing RC. Nuclear waste forms for actinides, *Proc. Natl. Acad. Sci. U.S.A* 1999, **96**: 3432–3439
25. Lang M, Zhang F, Zhang J et al (2010) Review of $A_2B_2O_7$ pyrochlore response to irradiation and pressure. *Nucl Instrum Methods Phys Res Sect B Beam Interact Mater Atoms* 268:2951–2959
26. Gregg DJ, Zhang Y, Middleburgh SC et al (2013) The incorporation of plutonium in lanthanum zirconate pyrochlore. *J Nucl Mater* 443:444–451
27. Sattonnay G, Sellami N, Thomé L et al (2013) Structural stability of $Nd_2Zr_2O_7$ pyrochlore ion-irradiated in a broad energy range. *Acta Mater* 61:6492–6505
28. Mandal BP, Tyagi AK. Preparation and high temperature-XRD studies on a pyrochlore series with the general composition $Gd_{2-x}Nd_xZr_2O_7$, *Cheminform* 2007, 437: 0–263

29. Lu XR, Shu XY, Wang L et al (2018) Microstructure evolution of rapidly fabricated $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) by spark plasma sintering. *Ceram Int* 44:2458–2462
30. Chang YQ, Guo Q, Zhang J et al (2013) Irradiation effects on nanocrystalline materials. *Front Mater Sci* 7:143–155
31. Chimi Y, Iwase A, Ishikawa N et al (2001) Accumulation and recovery of defects in ion-irradiated nanocrystalline gold. *J Nucl Mater* 297:355–357
32. Shen TD, Feng S, Ming T et al (2007) Enhanced radiation tolerance in nanocrystalline MgGa_2O_4 . *Appl Phys Lett* 90:749–763
33. liu K, zhang KB, deng T et al (2020) Preparation of $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanoceramics from two-step thermal treatment and the aqueous durability analysis. *Ceram Int* 46:13040–13046
34. Smith KL, Lumpkin GR, Blackford MG et al (1992) The durability of synroc. *J Nucl Mater* 190:287–294
35. Wuensch BJ, Eberman KW, Heremans C et al (2000) Connection between oxygen-ion conductivity of pyrochlore fuel-cell materials and structural change with composition and temperature. *Solid State Ion* 129:111–133
36. Glerup M, Nielsen OF, Poulsen FW et al (2001) The structural transformation from the pyrochlore structure, $\text{A}_2\text{B}_2\text{O}_7$, to the fluorite structure, AO_2 , studied by Raman spectroscopy and defect chemistry modeling. *J Solid State Chem* 160:25–32
37. Michel D, Jorba MPY, Collongues R (1976) Study by Raman spectroscopy of order-disorder phenomena occurring in some binary oxides with fluorite-related structures. *J Raman Spectrosc* 5:163–180
38. Wang J, Wang JX, Zhang YB et al (2019) Order-disorder phase structure, microstructure and aqueous durability of $(\text{Gd}, \text{Sm})_2(\text{Zr}, \text{Ce})_2\text{O}_7$ ceramics for immobilizing actinides[J]. *Ceram Int* 45:17898–17904
39. Smith KL, Lumpkin GR, Blackford MG et al (1992) The durability of synroc. *J Nucl Mater* 190:287–294
40. Zhang Y, Stewart MWA, Li H et al (2009) Zirconolite-rich titanate ceramics for immobilisation of actinides-waste form/HIP can interactions and = chemical durability. *J Nucl Mater* 395:69–74
41. zhang KB, peng heS (2018) L, et al. Self-propagating synthesis of $\text{Y}_{2-x}\text{Nd}_x\text{Ti}_2\text{O}_7$ pyrochlore and its aqueous durability as nuclear waste form[J]. *Scr Mater* 146:300–303
42. Lu XR, Fan L, Shu XY et al (2015) Phase evolution and chemical durability of co-doped $\text{Gd}_2\text{Zr}_2\text{O}_7$ ceramics for nuclear waste forms. *Ceram Int* 41:6344–6349
43. liu K, zhang KB, deng T, et al. Heavy-ion irradiation effects of $\text{Gd}_2\text{Zr}_2\text{O}_7$ nanocrystalline ceramics as nuclear waste immobilization matrix, *J. Nucl. Mater* 2020, **538**: 152236.

Figures

(a)

(b)

Figure 1

Crystal structures of pyrochlore and defective fluorite: (a) one-eighth unit cell of pyrochlore structure, (b) defective fluorite structure.

Figure 2

XRD patterns of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) nanocrystalline powders calcined at 800 °C for 2 h.

Figure 3

Transmission electron microscopy (TEM) images of the calcined $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ nanocrystalline powders: (a)-(b) $x=0.0$, (c)-(d) $x=2.0$.

Figure 4

Characteristics of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics sintered by SCF/QP: (a) XRD results, (b) Raman analysis.

Figure 5

(a)-(e) are SEM images and grain size statistics of $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics, (f) is a line chart of grain size under different doping levels.

Figure 6

Density variation as a function of neodymium loading in $\text{Gd}_{2-x}\text{Nd}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 2.0$) ceramics under three different sintering methods.

Figure 7

Normalized release rates of Nd³⁺ and Zr⁴⁺ in Nd₂Zr₂₀7 waste form.

Figure 8

GIXRD patterns at different incidence angles of Nd₂Zr₂O₇ ceramic after leaching.