Phase and Microstructure of (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ (0 ≤ x ≤ 0.35) Compounds

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Abstract—In order to investigate the compounds with the general formula (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$, a series of compositions were fabricated by high temperature solid state reaction at 1500°C under atmosphere pressure for 72 h. XRD and SEM were exploited to characterize the crystal structure and microstructure of the synthetic samples. The results indicate that all the (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ samples exhibit a single pyrochlore structure. The microstructure of the specimen is relatively dense, and the grain size is in the range of 4–5μm.

Keywords— (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$; solid state reaction; phase; crystal structure; microstructure

I. INTRODUCTION

Pyrochlores are regarded as promising matrices for the immobilization of actinides produced in nuclear power plants\(^1\). The pyrochlores are complex oxides with general formula of A$_2$B$_2$O$_6$. In most cases A is a trivalent rare-earth ion and B may be 3d, 4d, or 5d transition element. The space group of the pyrochlore is cubic Fd-3m\(^2\). The A$_2$B$_2$O$_6$ can be treated as A$_2$B$_2$O$_6$O‘ and it can be regarded as composed of two interpenetrating networks: a corner shared BO$_6$ octahedral network and an A$_2$O‘ network\(^3-4\). In addition, when the ordering of A$^{3+}$ and B$^{4+}$ is disturbed, the phase transition will happen from the pyrochlore structure to the defect fluorite structure\(^5\). As we know, a good host matrix should have excellent physical and chemical properties. Pyrochlore Gd$_2$Zr$_2$O$_7$ has aroused significant attention of the world due to its high thermal stability, high chemical resistance and durability\(^6-8\). It has been found that Gd$_2$Zr$_2$O$_7$ are extremely stable under high and low energy radiation environments owing to lower $r_A/r_B$ radius ratio\(^9-10\). In consideration of these extensive characters and applications, the pyrochlore Gd$_2$Zr$_2$O$_7$ has been widely researched.

Since the past 50 year, over 1400 Mt of Pu and substantial quantities of the “minor” actinides, such as Am, Np and Cm, have been generated in nuclear reactors\(^11\). The long-lived actinides are among the most important contributors to the calculated exposures to humans over the long periods envisioned for geological disposal, and after several hundred years, the radiotoxicity of disposed nuclear fuel is dominated by actinides\(^11\). Considering the safety of the public, it is essential to develop modern and safer technologies to incorporate all these nuclear wastes.

Therefore, in this paper, we will investigate the feasibility of Gd$_2$Zr$_2$O$_7$ used for the disposal of actinides. According to the theory of isomorphism, the substitution is more likely to happen when two cations show similar ionic radius and equal ionic valence. For pyrochlore Gd$_2$Zr$_2$O$_7$, Gd can be taken place by another trivalent rare earth elements such as Nd$^{3+}$, Eu$^{3+}$, and Th$^{3+}$, etc.\(^11\) In addition, the eight coordination ionic radius of Nd$^{3+}$ is 0.1099 nm, while Am$^{3+}$ is 0.109 nm. Therefore, Nd$^{3+}$ was used as surrogate material for Am$^{3+}$ to investigate the fabrication of (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$. A series of specimens were to be fabricated by high temperature solid state reaction. The crystal structure and microstructure will be shown by XRD and SEM studies.

II. EXPERIMENTAL PROCEDURE

(Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ ceramics were fabricated by a high temperature solid state reaction process. Gadolinium oxide powder (Shanghai Aladdin Co. Ltd., purity≥99.99%), zirconium oxide powder (Chengdu KESH Chemical, purity≥99.99%), and neodymium oxide powder (Shanghai Aladdin Co. Ltd., purity≥99.99%) were adopted as the starting reagents. All the raw powders were heated at 120°C for 2h to remove moisture. Then stoichiometric amounts of the powders in appropriate ratios were weighed and mixed in the agate mortar with analytically pure alcohol medium. Subsequently, the powders were dried again and compacted in a pellet form (12 mm diameter and ~2 mm thickness) under 10 MPa pressure. The starting materials for syntheses of (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ compounds are shown in Table 1. Finally, these pellets were heated at 1500°C for 72h to obtain dense bulk ceramics in air atmosphere. The heating rates were 5°C per minute in all the annealing steps.

<table>
<thead>
<tr>
<th>TABLE 1: THE STARTING MATERIALS FOR SYNTHESES OF (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ Compounds</th>
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<td>Target compounds</td>
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<td>Gd$<em>{1.5}$Nd$</em>{0.5}$Zr$_2$O$_7$</td>
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<td>Gd$<em>{1.7}$Nd$</em>{0.3}$Zr$_2$O$_7$</td>
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<td>Gd$<em>{1.9}$Nd$</em>{0.1}$Zr$_2$O$_7$</td>
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<td>Gd$_{2}$Zr$_2$O$_7$</td>
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Crystal-phase of the synthesized samples were characterized by X-ray diffraction (XRD, XPert Pro, Netherlands) with Cu Ka radiation ($\lambda$=1.5406 Å). The XRD pattern of sample was recorded from 2θ = 10–70° at a scanning rate of 2°/min. The microstructure of the sintered samples was observed by scanning electron microscope (SEM, Ultra 55, Germany).
III. RESULTS AND DISCUSSION

The XRD patterns of all the (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ ceramics containing different amount of Nd$_2$O$_3$ were recorded and analyzed. Some representative patterns are shown in Fig. 1. It comes to a conclusion that all the samples were successfully fabricated at 1500°C for 72h. Meanwhile, based on the appearance of strong diffraction peaks at 2θ = 29.45°, 34.20°, 49.04° and the presence of supper-lattice peaks at 2θ = 14.5°, 28.17°, 37.2°, 44.7°, 51.3° (using Cu Kα radiation as radiation source), all the products exhibit a single pyrochlore structure.

Many previous researches have indicated that the degree of structural disordering in the solid solutions mainly depend on the ionic radius ratio of A and B cations. And the stabilization of pyrochlore structure is under the limit of the range of $r_A/\overline{r_B}$ ($r_A$ and $r_B$ are the ionic radii of the A and B cations, respectively). According to Subramanian and Aravamudan[2], the pyrochlore structure will form when the range of RR (RR = $r_A$/ $r_B$) is between 1.46 to 1.78, and the fluorite structure will appear when the RR is lower than 1.46. In our studies, the ionic radii of Gd$^{3+}$ and Nd$^{3+}$, in eight-fold coordination, are 1.053 and 1.109Å, respectively, while the ionic radii of Zr$^{4+}$, in six-fold coordination, is 0.72 Å[15]. The range of $r_A/\overline{r_B}$ varies from 1.46 to 1.49, which is within the limiting radius ratio required for the stabilization of pyrochlore structure. Therefore, all the samples revealed a single pyrochlore structure.

![Figure 1. XRD patterns of (a)Gd$_{1-x}$Nd$_x$Zr$_2$O$_7$, (b)Gd$_{1-x}$Nd$_x$Zr$_2$O$_7$, and (c)Gd$_2$Zr$_2$O$_7$ at room temperature](image)

Fig.2. shows some representative microstructures of (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ solid solutions. The samples are relatively dense with only a few pores from the micrograph. And it can be seen clearly that the grain boundary is clean and no other impurities are found which is in good accordance with the XRD pattern in Fig. 1. In addition, the average grain size is in the range of 4-5μm.

![Figure 2. Representative microstructure of (a) Gd$_{1.3}$Nd$_{0.7}$Zr$_2$O$_7$ and (b) Gd$_{1.5}$Nd$_{0.5}$Zr$_2$O$_7$ ceramics.](image)

IV. CONCLUSIONS

In this manuscript, a series of (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ ($0 \leq x \leq 0.35$) compounds were sintered by high temperature solid reaction at 1500°C under air atmosphere for 72 h. The sintered (Gd$_{1-x}$Nd$_x$)$_2$Zr$_2$O$_7$ solid solutions exhibit a single phase of pyrochlore type structure by the XRD analysis. Moreover, the results of SEM indicate that the microstructures of as-sintered samples are relatively dense and the grain boundary is clean. The grain size mainly ranges from 4 to 5μm.

V. ACKNOWLEDGEMENT

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