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# Alpha-particle irradiation effects on uranium-bearing $Gd_2Zr_2O_7$ ceramics for nuclear waste forms

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ABSTRACT

It is necessary to study the self-irradiation effects of nuclear waste forms under α-decay in the long term storage. In the present work, accelerated irradiation experiments were performed on $(Gd_{1-4x}U_{2x})_2(Zr_{1-x}U_x)_2O_7$ ($x = 0, 0.10, 0.14$) samples using 0.5 MeV alpha-particle irradiation at fluences ranging from $1 \times 10^{14}$ to $1 \times 10^{17}$ ions/cm$^2$ at room temperature. Irradiation induced microstructural evolution was examined by grazing incidence X-ray diffraction (GIXRD), Raman spectroscopy and Field-emission scanning electron microscopy (FESEM). The results show that the main crystal structure is kept, however, weaker structural ordering is leaded as a result of intensified irradiation. And the radiation resistance is enhanced by the growing uranium content in the discussed range. Moreover, the irradiation effects as a function of depth have been discussed. Raman spectra reveal that the vibration intensity of atomic bonds are changed due to increased irradiation. In addition, the microtopography and element distribution have been kept after irradiation.



## 1. Introduction

In the field of nuclear waste immobilization, pyrochlore oxides (with a general formula of $A_2B_2O_7$, and closely related to the fluorite structure $AO_2$) show obvious advantages as host matrix [1–3]. Due to its flexible crystalline structure, considerable amounts of nuclides with poly-types and muti-valence could be incorporated into structure at A or/and B site [4,5]. Furthermore, it shows good thermal stability, mechanical and chemical performance [6]. However, the selection of host materials for nuclear waste is still a complex job depending on the radiation performance, since they show a range of irradiation behavior among hundreds of pyrochlore-related materials [7–10]. Therefore, it is necessary to study the radiation performance of fabricated waste forms before geological disposal for the long-term security [11].

Numerous studies have been focused on the accelerated radiation damage of pyrochlore like materials to simulate the self-irradiation effects, such as lattice expansion [12], mechanical properties evolution [13], and phase transformation [14]. Especially, the phase transformation associated with ions irradiation (i.e., the pyrochlore-to-fluorite structural transition or amorphization) has been intensively researched. For instance, Sickafus et al. discover that fluorites are inherently more radiation resistant than pyrochlores from the aspect of material's propensity to accommodate lattice point defects [7], and this has been confirmed in systems like $Gd_2Zr_2O_7$ and $^{241}Am_2Zr_2O_7$ [15,16]. More detailed evidence focused on the factor of ionic size has been obtained and different critical ionic radii ratios ($r_A/r_B$) have been determined based on varied pyrochlore systems [17,18]. However, the same rule has been found that pyrochlore transforms into a radiation resistant defect-fluorite structure as the ratio ($r_A/r_B$) below the critical value, while the defect-fluorite structure become increasingly unstable with respect to the amorphous state as the ratio goes beyond the critical value. Moreover, J. Lian et al. consider that ionic size and cation electronic configurations (e.g. bond-types) affect the structural distortion from the ideal fluorite structure under a radiation condition [19].

With great appreciation to previous work, the authors find that they are normally concentrated on waste forms with nuclides in a single valence state, and the nuclides usually occupy at a sin-

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gle A or B site. There are scarce researches focused on radiation behavior of those pyrochlore based materials, which simultaneously holding nuclides with different valence at both A and B sites. Particularly, there are no radiation researches based on such a new interesting system $(Gd_{1-4x}U_{2x})_2(Zr_{1-x}U_x)_2O_7$ $(0 \le x \le 0.14)$. This system is designed by simultaneous substitution through two different mechanisms (equivalent substitution for $U^{4+}$ replacing $Zr^{4+}$, and un-equivalent substitution for $U^{6+}$ replacing $Gd^{3+}$) [20]. By this way, up to 38.83 wt.% $U_3O_8$ could be successfully incorporated in the $Gd_2Zr_2O_7$ pyrochlore structure as a single phase. More interestingly, the mentioned system tends to decrease the $r_A/r_B$ ratio with enhanced uranium content, which implies a better radiation resistance than the original pyrochlore according to literature [7].

The motivation of this work was to explore the radiation tolerance of composite $(Gd_{1-4x}U_{2x})_2(Zr_{1-x}U_x)_2O_7$ ($x = 0$, 0.10, 0.14). Alpha-particle irradiation was conducted considering the α-decay of actinides in the long term storage. To assess the radiation performance of these ceramics, GIXRD was taken to study the structure evolution of waste forms as a function of uranium content and irradiation fluences, Raman spectra was collected to get the detailed local information of irradiated samples, and FESEM was performed to distinguish the micro-morphology and element distribution evolution under alpha-particle irradiation.

## 2. Experimental procedure

### 2.1. Fabrication

In this study, polycrystalline $(Gd_{1-4x}U_{2x})_2(Zr_{1-x}U_x)_2O_7$ ($x = 0$, 0.10, 0.14) samples were prepared from $Gd_2O_3$, $ZrO_2$ and $U_3O_8$ by a standard solid state process. All chemicals used in the experimental procedures (Aladdin Chemistry Co. Ltd., Shanghai, China) are A.R. grade. Before weighing, all the raw powders were pre-heated at 700 °C for 12 h to remove the possible moisture and other impurities. Then stoichiometric amounts of the powders were weighed, and ground/mixed in analytically pure ethanol medium. The powders were dried again and then compacted into a pellet form (12 mm diameter and ~2 mm thickness) at a pressure of 10 MPa. The pellets were sintered at 1500 °C for 48 h to fabricate dense bulk ceramics in air atmosphere. More preparation details are displayed in our previous work [20].

### 2.2. Irradiation

The fabricated pellets were prepared for irradiation by cutting them into small pieces (1.6cm × 1.7 cm). The ion-irradiation experiment was performed at room temperature using a 320 kV multi-discipline research platform for highly charged ions at the Institute of Modern Physics, Chinese Academy of Sciences. The 0.5 MeV alpha-particle were implanted at normal incidence using a fluence rate of $1.2 \times 10^{13}$ ions/cm$^2$ s to ion fluences ranging from $1 \times 10^{14}$ to $1 \times 10^{17}$ ions/cm$^2$.

### 2.3. Characterization

The phase structures of the samples before irradiation were characterized by an X-ray diffractometer (X'Per PRO, Netherlands) with Cu Kα radiation (λ = 1.5406 Å). The XRD pattern of the samples was recorded from 2θ = 10 to 80° at a scanning rate of 2°/min. Grazing incidence X-ray diffraction (GIXRD) was performed on a Netherlands Panalytical X-ray diffractometer with Cu Kα radiation, and θ – 2θ geometry. The step size of the scan angle was 0.02°, and the scan range was 10–90° under X-ray incident angles from 0.25° to 10°. The Raman spectra in the range of 100–900 cm$^{-1}$ were recorded with the microspectrometer LeiCa DMLM (InVia, UK). Field-emission scanning electron microscopy (FESEM; Zeiss Ultra-55, Oberkochen, Germany) was utilized to observe the microstructure of the irradiated samples at 5 KV with the theoretical resolution of 1.5 nm. The element distribution was analyzed using energy-dispersive X-ray spectrometer (EDS) attached to the FESEM equipment.

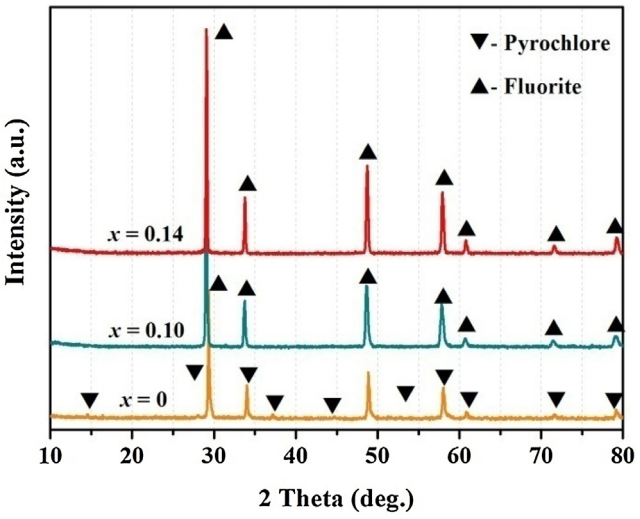


**Fig. 1.** XRD patterns for un-irradiated samples $(Gd_{1-4x}U_{2x})_2(Zr_{1-x}U_x)_2O_7$ ($x = 0$, 0.10, 0.14).

## 3. Results and discussion

### 3.1. Structural analysis through XRD and GIXRD

A series of X-ray diffraction patterns obtained from $(Gd_{1-4x}U_{2x})_2(Zr_{1-x}U_x)_2O_7$ ($x = 0$, 0.1, 0.14) before irradiation are presented in Fig. 1. The sharp peaks of all the considered samples indicate ordered crystal structures. For $Gd_2Zr_2O_7$, the super-lattice peaks at 2θ values of about 14° (111), 28° (311), 37° (331) and 45° (511) are distinguished from samples $x = 0.10$ and $x = 0.14$. These super-lattice peaks suggest a pyrochlore structure for $Gd_2Zr_2O_7$, whereas $x = 0.10$, 0.14 samples crystallize as a defect fluorite structure. And it also suggests that pyrochlore is more ordering in this system before irradiation, even though the super-lattice peaks are weak. The phase difference roots in the fact that $r_A/r_B$ ratios for $x = 0.10$, 0.14 samples (1.08 and 0.95, respectively) have exceeded the range for pyrochore structure (1.46–1.78). Therefore, although pyrochlore are more ordering, the decreased $r_A/r_B$ ratio with enhanced uranium content in this system implies a better radiation resistance than the original pyrochlore according to literature [7].

The irradiation effects on the samples under 0.5 MeV alpha-particle at an ion fluence of $1 \times 10^{17}$ ions/cm$^2$ were investigated as a function of irradiation depth by varying the X-ray grazing incidence angles. Fig. 2 shows the GIXRD patterns obtained from irradiated $(Gd_{1-4x}U_{2x})_2(Zr_{1-x}U_x)_2O_7$ ($x = 0.10$, 0.14) samples at $\gamma = 0.5°$, 1.0°, 1.5°, 2.0°, 2.5°, 3.0° and 10° (the X-ray characterizing depth is 0.193 μm, 0.386 μm, 0.579 μm, 0.771 μm, 0.964 μm, 1.157 μm and 3.838 μm, respectively, calculated by X'Pert program). It could be found that the intensities of the principal diffraction maxima increase with X-ray incident angle. This may attribute to the fact that the damaged areas are mainly focused in a certain shallow surface while the measuring depth increase with the incident angles. According to the SRIM simulated results (shown in Fig. 3), the irradiation affected area mainly focused in the range of about 0–2 μm beneath the surface. At lower $\gamma$ angles, the X-ray collected data comes mainly from the shallow surface of the samples, where the