Effect of He\textsuperscript{2+} Ion Irradiation on the Crystal Structure of Non-stoichiometric Sm\textsubscript{2+x}Zr\textsubscript{2-x}O\textsubscript{7-x/2} (x = 0, 0.2, 0.4, 0.6)

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Abstract. In this paper, a series of non-stoichiometric Sm\textsubscript{2+x}Zr\textsubscript{2-x}O\textsubscript{7-x/2} (x=0, 0.2, 0.4, 0.6) were synthesized by chemical co-precipitation method. He\textsuperscript{2+} ion irradiation experiments were carried out with irradiation energy of 500 KeV and irradiation flux of 5×10\textsuperscript{16} ions/cm\textsuperscript{2}. Effect of He\textsuperscript{2+} ion irradiation on the crystal structure was characterized by XRD, GIXRD, and Raman spectroscopy. The XRD patterns show that all the peaks shift to lower diffraction angles and the characteristic peaks of pyrochlore structure weaken after irradiation, which suggests an expansion of the lattice and the degeneration of pyrochlore structure. Moreover, the GIXRD patterns reveal the existence of an irradiated layer on the surface of the sample.

1. Introduction

According to the statistics, the current annual global productions of low-level and high-level nuclear wastes are about 200,000 m\textsuperscript{3} and 10,000 m\textsuperscript{3} respectively, which show a continuous growing trend [1]. If the nuclear waste leaks into the environment, it will pollute the water, soil and atmosphere, destroying the living environment of human beings. If it gets into the living body, it will cause irreversible radiation damage to the organism through ionization and excitation. Therefore, research on the disposal of radioactive waste has attracted more and more attention in recent years [2,3,4]. The low-level waste and intermediate-level waste is generally cured by cement, asphalt and plastic, and the disposal method is relatively simple. Meanwhile, the most mature treatment method for high-level waste nowadays is glass curing, with which the waste phase is cured with the glass phase, and then buried several hundred meters underground [5,6,7]. However, after several decades, the heat generated by the fission product decay process will destroy the stability of the glass solidified body and cause the leaching of the radionuclide. So people must find a more stable solidified substrate instead of glass.

The pyrochlore structure oxide A\textsubscript{2}B\textsubscript{2}O\textsubscript{7} has a unique crystal structure, high melting point and high chemical stability. Due to these excellent properties, pyrochlore structural oxides can be applied to various aspects such as thermal barrier coatings, solid electrolytes, and catalysts. Moreover, it has been found that it can be used as a candidate matrix for curing radioactive nuclear waste due to its high radiation resistance and complex crystal structure [8,9]. The pyrochlore structure oxide is a face-centered cubic structure, and the space group belongs to Fd-3m. It is very similar to the fluorite structure Fm-3m and can be regarded as a variant of the fluorite structure. The A and B cations in the fluorite structure share an effective crystallographic site, and the oxygen vacancies are randomly distributed. In contrast, the A and B cations in the pyrochlore structure oxide are ordered, and are fixed at two different crystallographic sites, while the oxygen vacancies are at specific sites. The A\textsuperscript{3+} cations are coordinated with 8 oxygen anions, which are 16d site; the B\textsuperscript{4+} cations are coordinated with 6
oxygen anions, which are 16c site; and the oxygen vacancies are at the center of four B\(^{4+}\) cation tetrahedrons, which is 8asite. There are two kinds of oxygen anions at different crystallographic sites. One O' anion is located at the center of four A\(^{3+}\) cationic tetrahedra, which is 8bsite; the other O anion is located at the center of the A\(_2\)B\(_2\) tetrahedron, at the 48f site. The crystal structure diagram is shown in Figure 1.

![Figure 1. Partial unit cell of the pyrochlore structure][10].

In recent years, studies on the radiation resistance of pyrochlore structural oxides have attracted the interest of many researchers. K.E. Sickafus et al [11] found that after irradiation the ordered pyrochlore structure turns to transform to the disordered fluorite structure. Moreover, the cation anti-site defect is most likely to occur during the irradiation process. The closer the radius of the A and B cations, the smaller the formation energy of the cation reverse defect, the stronger the irradiation stability of the pyrochlore. Subsequently, the anti-amorphization ability of pyrochlore oxide under irradiation was correlated with the temperature-composition (T-C) phase diagram which was proposed to predict the radiation resistance of materials by using the phase transition temperature in T-C phase diagram [12]. It has been revealed that the radiation resistance of the pyrochlore increases with the decreasing order-disorder transition temperature. On the other hand, M. Lang et al [13] have irradiated Gd\(_2\)(Zr\(_{1-x}\)Ti\(_x\))\(_2\)O\(_7\) with Xe ions, and found that the irradiation produces an amorphous latent track which decreases with increasing x, and the fluorite structure cladding increases as x increases, which reveals that the irradiation resistance of zirconium titanate pyrochlorite increases with the increase of Zr content under heavy ion irradiation. YH Li and J Zhang et al [14,15] have studied the change in volume of pyrochlore structure under Ne\(^{2+}\) ion irradiation, and found that A\(_2\)Ti\(_2\)O\(_7\) oxide shows an obvious lattice swelling under ion beam irradiation. It is believed that the cationic anti-site defect may be responsible to the lattice swelling of A\(_2\)Ti\(_2\)O\(_7\) oxide. D G Yang et al [16] have studied the effect of ion species on the irradiation of Lu\(_2\)Ti\(_3\)O\(_7\), and found that heavier ions are more likely to induce amorphization and lattice swelling of pyrochlore materials. X R Lu et al [17] have used Xe\(^{20+}\) ions to irradiate Gd\(_2\)Zr\(_2\)O\(_7\)-pyrochlore and Nd\(_2\)Ce\(_2\)O\(_7\) fluorite to study the irradiation resistance of pyrochlore and fluorite materials under the same irradiation conditions. It was found that Gd\(_2\)Zr\(_2\)O\(_7\) shows a pyrochlore-fluorite transition which is accompanied by a slight lattice swelling, where as the fluorite structure Nd\(_2\)Ce\(_2\)O\(_7\) is amorphized.

Nearly all the researches up to now have confirmed that rare earth zirconate pyrochlore have a good radiation resistance [18,19,20,21], especially the Gd\(_2\)Zr\(_2\)O\(_7\) which suffers a pyrochlore-fluorite transition at a low temperature, and shows an excellent radiation resistance performance. However, as a candidate substrate for solidified nuclear waste in the future, not only excellent radiation resistance but also high-nuclear solid solution capability is required. In order to have both of these requirements, the non-stoichiometric pyrochlore material was investigated in this paper. Generally speaking, the solid solution capability of the non-stoichiometric A\(_{2+x}\)B\(_2\)O\(_7\) is expected to increase with the composition parameter x. Since the non-stoichiometry range of Sm\(_2\)Zr\(_2\)O\(_7\) is larger than Gd\(_2\)Zr\(_2\)O\(_7\), the
stoichiometric Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$ was prepared and irradiated by He$^{2+}$ ion beam to investigate the radiation damage behavior and radiation resistance of the material.

2. Experiment

2.1. Fabrication and irradiation

The precursor powder was prepared by chemical co-precipitation method. The specimens was pressed at 300 MPa and then sintered at 1600°C for 10 hour in air to synthesize a series of dense non-stoichiometric Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$ ($x = 0, 0.2, 0.4, 0.6$). Bulk densities of the sintered samples measured according to the Archimedes principle showed that the samples were almost fully densified with densities all above 95%.

The irradiation experiment was carried out at the 320 kV multidiscipline research platform for highly charged ions (Institute of Modern Physics, Chinese Academy of Sciences). Each group of samples was subjected to He$^{2+}$ ion irradiation experiment under the same conditions. The irradiation energy was 500KeV, and the irradiation flux was $5 \times 10^{16}$ ions/cm$^2$.

2.2. Characterization

XRD scans of the samples were performed by an X-ray diffractometer (Bruker D8 Advance, Germany) with a Cu K$_\alpha$ radiation. The scanning range is $2\theta$ = 10°~ 90° with a scanning speed of 4°/min and a step size of 0.02°. Raman spectra of the samples were recorded using a microscopic confocal Raman spectrometer (LabRAM HR Evolution, HORIBA JobinYvon, France) to analyze the changes in structure before and after irradiation. The excitation wavelength was 633 nm and the full power of the incident beam is 7500 μW/cm$^2$. To ascertain the homogeneity of the samples, at least three spots for each sample were detected with a scan time of 20 seconds. The signal was collected and accumulated for a two-times scan.

Figure 2. Unirradiated XRD patterns of Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$

3. Results and discussion

3.1. XRD analysis

XRD patterns of unirradiated samples is shown in Figure 2. It can be seen that all the peaks systematically shift to lower diffraction angles as x increases, which suggests a systematic expansion of lattice parameter. Since the ionic radius of Sm$^{3+}$ ions (~1.079 Å) is larger than that of Zr$^{4+}$ ions (~0.59 Å), the substitution of Sm$^{3+}$ ions for Zr$^{4+}$ ions with the increase of x should be responsible to the
systematic lattice expansion, which indicates the formation of the solid solution of Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$ ($x = 0, 0.2, 0.4, 0.6$) as we expected.

Moreover, it can also be seen from the figure that the characteristic peaks (311), (331) and (511) of pyrochlore structure gradually get weaken as $x$ increases. When $x \leq 0.4$, the pyrochlore structure remains though getting weaken. When $x = 0.6$, the characteristic peaks completely disappear. This indicates that the samples gradually transform from the ordered pyrochlore structure to the disordered fluorite structure, which is consistent with the phase diagram of the SmO$_{1.5}$-ZrO$_2$ system calculated by Wang et al [22,23]. As we know, the stability of A$_2$B$_2$O$_7$ pyrochlore oxides is mainly related to the ratio of the cation radius of A and B ions $r_A/r_B$. When $r_A/r_B$ is in the range from 1.46 (Gd$_2$Zr$_2$O$_7$) to 1.78 (Sm$_2$Ti$_2$O$_7$), the A$_2$B$_2$O$_7$ compound shows a cubic pyrochlore structure. When $r_A/r_B < 1.46$, it turns to be a disordered defect fluorite structure. When $r_A/r_B > 1.78$, the structure of the A$_2$B$_2$O$_7$ compound is monoclinic structure [24, 25, 26, 27]. So, as $x$ increases, the excess Sm$^{3+}$ ions will occupy the B-site to substitute for Zr$^{4+}$ ions, resulting in a decrease of the $r_A/r_B$ ratio and cause the phase transition from pyrochlore structure to fluorite structure.

![Figure 3](image-url)

**Figure 3.** (a) XRD patterns of Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$; (b) (222) Peak partial enlargement; (c) (662) Peak partial enlargement.
XRD patterns of the samples before and after irradiation are shown in Figure 3. After the irradiation, the diffraction peaks of all the samples shift to lower diffraction angles compared with the peaks of the unirradiated samples, as shown in Figure 3(b). It can be attributed to the lattice swelling due to the He$^{2+}$ irradiation. Similar to the case of A$_2$Ti$_2$O$_7$\cite{14, 15}, the cationic anti-site defects may be the main contributor to the swelling. Moreover, the occurrence of cationic anti-site defects may be accompanied by the anti-site of O ions at 48f site and 8a site. The occupation of O ions at 8a site as an interstitial will lead to the expansion of the lattice.

On the other hand, the high-angle peaks of the irradiated sample seem to show a significant splitting, as shown in Figure 3(c). The breakdown of pyrochlore structure is not expected for the He$^{2+}$ irradiation. One reasonable interpretation is that the irradiated layer is so thin that X-ray can easily penetrate it. The apparent splitting of peaks may be the superposition of diffraction peaks of the irradiated layer and underlying unirradiated layer.

3.2. GIXRD and Raman analysis
To verify the assumption above, Grazing-Incidence X-Ray Diffraction (GIXRD) was used to investigate the irradiated layer. GIXRD patterns before and after irradiation of all the samples are shown in Figure 4. It can be seen from the figure that the GIXRD patterns show a similar change after irradiation with the XRD patterns. However, the peak splitting seems to disappear in the GIXRD patterns, which supports the assumption that He$^{2+}$ irradiation results in a very thin irradiated layer on the surface of the samples.

![Figure 4. (a) GIXRD images of Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$ ;(b) (222) Peak partial enlargement.](image)

The GIXRD patterns after irradiation have also compared with XRD patterns, as shown in Figure 5. The peak position in GIXRD patterns is consistent with that of the left peak in XRD patterns, which may correspond to the irradiated layer. On the other hand, the stronger peak on the right in XRD patterns can be considered to correspond to the underlying unirradiated layer, which is also evidenced by the comparison of XRD patterns before and after irradiation in Figure 3(c).

To further investigate the effect of irradiation on the crystal structure, Raman spectra before and after irradiation of all the samples are shown in Figure 6. It can see from the figure that the samples with x = 0, 0.2 show a typical Raman line of pyrochlore structure before irradiation, whereas the sample with x = 0.6 is completely fluorite structure, with an ambiguous characteristic spectrum for the sample with x=0.4.

After He$^{2+}$ irradiation, it does not seem to change much for the Raman spectra of all the samples, though the intensities of the lines decrease distinctly. Interestingly, a peak at about 670 cm$^{-1}$ which is a very weak peak before irradiation becomes remarkable after irradiation. Moreover, it increases as x increases, which indicates that it is related to the disordered fluorite structure. That may mean that
both the increase of x and He$^{2+}$ irradiation lead to the degeneration of pyrochlore structure, which is accompanied by the enhancement of the Raman line at about 670 cm$^{-1}$. However, all the samples are not amorphized after irradiation.

Figure 5. Comparison of XRD and GIXRD peaks of Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$ after irradiation.

Figure 6. (a) Raman spectra of unirradiated Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$; (b) Raman spectra of irradiated Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$. 
3.3. Irradiation analysis

In order to quantitatively investigate the effect of He$^{2+}$ irradiation on the non-stoichiometric ratio Sm$_{2+x}$Zr$_{2-x}$O$_{7-x/2}$, the peak intensity and peak position of XRD patterns before and after irradiation were determined and analyzed. The intensity of characteristic peak (311) was used to estimate the disorder degree of pyrochlore structure. To eliminate the systematic error, the intensity ratio of the peak (311) to the peak (400) before and after irradiation was compared, as shown in Figure 7(a). It can be seen that the I$_{311}$/I$_{400}$ decreases significantly with the increasing $x$, which suggests the remarkable degeneration of pyrochlore structure. After irradiation, the I$_{311}$/I$_{400}$ gets lower than that before irradiation, and the sample with $x = 0.4$ transforms from pyrochlore structure to fluorite structure. The decrease rates of I$_{311}$/I$_{400}$ before and after irradiation as a function of $x$ were shown in Figure 7(b). It shows an accelerated decrease of I$_{311}$/I$_{400}$ with the increasing $x$.

Furthermore, the shifts of two strong peaks (222) and (400) after irradiation are shown in Figure 7(c). It can be seen that the peak shift to low diffraction angles increases with the increasing $x$ for the samples with pyrochlore structure, whereas the sample with fluorite structure show a lower peak shift. This may suggest a different mechanism of structure variation under irradiation for pyrochlore structure and fluorite structure. For the samples with pyrochlore structure, the crystal energy decreases with the increasing $x$ due to the increase of weaker Sm-O bonds instead of Zr-O bonds, which may facilitate the formation of anti-site defects and enhance the lattice expansion. It seems that the difference in structure results in the decrease of peak shift for the sample with fluorite structure compared to the pyrochlores.
4. Conclusions
In this paper, a series of dense Sm_{2+x}Zr_{2-x}O_{7-x/2} (x=0, 0.2, 0.4, 0.6) samples were synthesized and irradiated with a He^{2+} ion beam with an energy of 500 KeV and a flux of 5 \times 10^{16} ions/cm^2. It is concluded that under light ion irradiation conditions, the lattice will expand after irradiation, and the degree of expansion increases with x for pyrochlore. On the other hand, GIXRD patterns reveal the existence of an irradiated layer on the surface of the sample.

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