High Temperature Effect and Radiation Damage in Yb₄Hf₃O₁₂ Delta Phase Material

M Ado¹,², Q Wang¹*, S A Ibrahim¹,³ and A Ullah¹

¹ College of Nuclear Science and Technology, Harbin Engineering University, Harbin, Heilongjiang, 150001, China
² Nigerian Nuclear Regulatory Authority (NNRA), Abuja, Nigeria
³ Department of Science Laboratory Technology, Binyamin Usman Polytechnic, Hadejia 731101, Jigawa State, Nigeria

Email: mohdado2@gmail.com

Abstract. The development of next generation nuclear energy systems such as Gen-IV and fusion reactors need materials that resist radiation damage effects. Therefore, advanced nuclear reactors require the development of new materials that will satisfy their design specifications. A considerable amount of research has been performed on some crystalline oxides with fluorite related structures (CaF₂) as potential candidates for inert matrix in nuclear fuel and waste forms. Delta phase, another fluorite-related phase structure is a compound produced from ceramic oxide compositions usually in the form of A₄B₃O₁₂ or A₆B₁O₁₂ describe as MₓO₁₂ (where M is a metal representing AB and O is oxygen). In this work, we developed a new Yb₄Hf₃O₁₂ delta phase material using solid-state sintering. The oxide was characterized with an ordered rhombohedral structure called delta phase material. The high-temperature XRD result showed that the phase and structure of the composition remain the same up to the high temperature of 1300°C indicating a non-phase transition, but the lattice parameters values revealed a linear thermal expansion in the volume as the temperature increases. The polycrystalline sample was irradiated with 6keV He⁺ at room temperature to fluences of 7.6 x 10¹⁶ ions/cm² (corresponding to 6.2dpa) to study the radiation tolerance in the compound. The irradiated sample was characterized by transmission electron microscopy (TEM). The result showed no formation of bubble gas but an airy ring was observed in the diffraction pattern indicating that the structure was damaged.

1. Introduction

Crystalline oxides with fluorite (CaF₂) structure or their derivatives display a variety of properties that make them appropriate for nuclear technological applications, such as in inert matrix for advanced nuclear fuels forms and as host materials for immobilization of high-level radioactive waste [1-4]. Over the past decades, numerous studies were focused on oxygen-deficient fluorite structure called delta phase compounds represented as A₄B₃O₁₂ or A₆B₁O₁₂ (A and B represents a metal cation, while O refers to an oxygen anion) [5-14].

A delta (δ) phase is a radiation tolerant compound produced from ceramic oxide compositions usually in the form of A₄B₃O₁₂ or A₆B₁O₁₂ stoichiometry [5, 11]. Both A₄B₃O₁₂ (4:3:12) and A₆B₁O₁₂ (6:1:12) δ-phase compounds can be described with structure compared to MO₂ ideal cubic fluorite compounds.
and M₄O₇ pyrochlores (where M is representing AB and O is oxygen) [8, 9, 15]. The main differences between 4:3:12 and 6:1:12 δ-phase compounds are the cations used to produce their respective stoichiometry with 4:3:12 compounds made from trivalent and tetravalent cations as (A³⁺B⁴⁺O₁₂) while the 6:1:12 compounds incorporate trivalent and hexavalent species as (A⁶⁺B⁶⁺O₁₂) [13, 15-17].

Safety and reliability of nuclear energy systems highly rely on the performance of structural materials under harsh conditions, such as high irradiation dose, high pressure and high-temperature [4, 18]. Therefore, it is necessary to investigate such effect from the microstructure state in order to produce new structural materials with strong mechanical properties, high thermal and phase stabilities, and high irradiation resistance [4, 18, 19]. A lot of studies have been conducted on the radiation tolerance of delta phase materials in the past with phase transformation from ordered rhombohedral δ-phase structure to disordered cubic fluorite phase when exposed to radiation using ion beam [2, 3, 5, 6, 11, 15, 20].

In this study, we investigate the effect of radiation on YbₓHf₁₋ₓO₁₂ using in situ ion beam irradiation. Also, we measure the effect of temperature on the structure using high temperature X-ray diffraction. The focus of this paper is on AₓB₂O₄ δ-phase compounds with rhombohedral (trigonal) symmetry. This belongs to space group of the fluorite structure whose oxygen vacancies are ordered along (111) direction [2, 5, 8, 17]. The structure has 1/7 of all their cation sites in 6-fold coordination on the site of the trigonal symmetry by oxygen and surrounded by seven oxygen atoms on the remaining 6/7 cations [2, 11].

2. Experimental Procedure

The sample was prepared from metal oxides which includes; hafnia (HfO₂) and yttbia (Yb₂O₃) in masses to form the target compound. HfO₂ was dehydrated in an oven set at 180°C while the rare earth oxide Yb₂O₃ was dehydrated in an oven set at 800°C all for 12 h each. Ball milling was used to mix the powders with a small volume of isopropanol in a stainless steel cup. The dried powder was sieved using 212µm mesh and pressed at a pressure of 110MPa in a 13mm diameter stainless steel die to obtain an equivalent pellet of the composition. A final heat treatment was performed under air at 1500°C for 7days followed by a very slow ramp down 5°C/min to room temperature in a high temperature furnace. The measured density of the sample was 80% of the theoretical value. The pellet of the composition was crushed to a fine powder for the X-ray diffraction (XRD). The High temperature XRD experiment was performed from 30°C (room temperature) to 1300°C and then cooling down by reducing 100°C back to 100°C.

The sample was prepared for irradiation and TEM by crushing the pellet into powder using isopropanol and collecting the suspension on carbon coated copper grid. The irradiated was carried out at room temperature for about 30 minutes to a maximum fluences of 7.6x10¹⁶ He/cm². The projected range of 7.6x10¹⁶ He ions in δ-YbₓHf₁₋ₓO₁₂ was estimated by using the Monte Carlo code SRIM [21].

3. Results and discussion

3.1. High temperature X-ray diffraction (HT-XRD)

A STOE STADI P (Cu, PSD) diffractometer for high resolution operating at 40kV, 35mA was used for the experiment. The image was ideal for high-throughput phase analysis with a mystery white ribbon like material covering -150° 2θ. XRD patterns of the sample are shown in Fig 1. The diffraction patterns observed is in good agreement with that of literature data [15]. The result showed no phase transitions within the considered temperature range but volume expansion was observed with increasing heat because of an increase in the lattice parameters [22].
Figure 1. HT-XRD patterns of Yb$_4$Hf$_3$O$_{12}$ showing an ordered δ-phase composition with peaks of superlattice reflections associated with δ$_1$, δ$_2$, δ$_3$, δ$_4$, δ$_5$ and δ$_6$ at (110), (012), (131), (104), (303) and (024) [15].

The density, unit cell volume and axial angle calculated from the XRD patterns are shown in Table 1. in order to understand whether the average mass of the sample increase or decrease on solid solution formation. The density value in Table 1. was compared with the measured density from the Archimede’s machine.

| Compound   | Lattice system | Possible variation | Density (g/cm$^3$) | Unit cell volume (Å$^3$) | Axial angles |
|------------|----------------|--------------------|--------------------|--------------------------|--------------|
| Yb$_4$Hf$_3$O$_{12}$ | Hexagonal       | Primitive          | 10.644             | 664.4                    | $\alpha=\beta=90^\circ$, $\gamma=120^\circ$ |

3.2. Lattice parameter calculation
The relationship between the temperature and the lattice parameters (that is the unit cells size and volume) are investigated to determine how the structure of the composition changes with increasing temperature. For hexagonal system [23], the unit cell size are;

\[ a = b \neq c \]  \hspace{1cm} (1)

The equation relating the unit cells size, a and c and the distance between the atomic layers, d for hexagonal crystal is given by Miller index [22] below;

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \]  \hspace{1cm} (2)

Substituting the peaks [110] and [003] for h, k and l respectively in equation (2) yields;

\[ a = 2d \]  \hspace{1cm} (3)
\[ c = 3d \]  \hspace{1cm} (4)

Calculating the separation distance, d using the Bragg’s Law [22] with the angles of the diffraction, $\theta$ from the crystal as;

\[ d = \frac{n\lambda}{2\sin \theta} \]  \hspace{1cm} (5)
The order of reflection, n = 1, wavelength, \( \lambda = 1.504\text{Å} \) for the XRD machine and \( \theta = 18.8^\circ \) for peak [110]. Therefore, d is;

\[
d = \frac{n\lambda}{2\sin \theta} = \frac{1.504\times10^{-10}}{2\sin(18.8^\circ/2)}
\]

(6)

And d, is also calculated at \( \theta = 30.5^\circ \) for peak [003] as;

\[
d = \frac{n\lambda}{2\sin \theta} = \frac{1.504\times10^{-10}}{2\sin(30.5^\circ/2)}
\]

(7)

Equation (6) and (7) are repeated for different temperature values from 30\(^\circ\)C (room temperature) to 1300\(^\circ\)C to calculate different unit cells size values of, a, c and volume, V after substitution in equation (3) and (4) as shown in Table 2.

| Table 2. Lattice parameter values |
|----------------------------------|
| \( T (^\circ C) \) | \( 2\theta [110] \) | \( 2\theta [003] \) | \( d(\text{m}[110]) \times 10^{-10} \) | \( d(\text{m}[003]) \times 10^{-10} \) | \( a(\text{m}) \times 10^{-10} \) | \( c(\text{m}) \times 10^{-10} \) | \( V(\text{m}^3) \times 10^{-30} \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 30              | 18.76           | 30.5            | 4.61            | 2.86            | 9.23            | 8.58            | 591             |
| 100             | 18.64           | 30.44           | 4.64            | 2.86            | 9.29            | 8.59            | 599             |
| 200             | 18.88           | 30.42           | 4.58            | 2.87            | 9.17            | 8.60            | 588             |
| 300             | 18.86           | 30.42           | 4.59            | 2.87            | 9.18            | 8.60            | 589             |
| 400             | 18.86           | 30.4            | 4.59            | 2.87            | 9.18            | 8.60            | 589             |
| 500             | 18.78           | 30.38           | 4.61            | 2.87            | 9.22            | 8.61            | 594             |
| 600             | 18.86           | 30.38           | 4.59            | 2.87            | 9.18            | 8.61            | 590             |
| 700             | 18.7            | 30.4            | 4.63            | 2.87            | 9.26            | 8.60            | 597             |
| 800             | 18.98           | 30.48           | 4.56            | 2.86            | 9.12            | 8.58            | 581             |
| 900             | 18.68           | 30.64           | 4.63            | 2.85            | 9.27            | 8.54            | 592             |
| 1000            | 18.74           | 30.48           | 4.62            | 2.86            | 9.24            | 8.58            | 593             |
| 1100            | 18.58           | 30.24           | 4.66            | 2.88            | 9.32            | 8.65            | 608             |
| 1200            | 18.56           | 30.18           | 4.66            | 2.89            | 9.33            | 8.67            | 610             |
| 1300            | 18.76           | 30.14           | 4.61            | 2.89            | 9.23            | 8.68            | 601             |
Figure 2. The lattice parameters plot against temperature from the values calculated in Table 2. in (a) the unit cell, a, at $\theta = 18.8^\circ$ along the [110] peak, (b) the unit cell, c, at $\theta = 30.5^\circ$ along the [003] peak and (c) the unit cell volume, V along the two peaks.
The values in Table 2. are used to plot the unit cell values against the temperature in Fig. 2. The thermal expansion varies linearly with increasing temperature as indicated by the volume in Fig. 2(c). Examining the lattice expansion is necessary in order to get an insight into the cause of atomic displacement which highly modifies the crystal structure in a composition. This may lead to phase transition or amorphization in the composition with potential nuclear engineering applications [2, 3, 24]. The lattice thermal expansion also induces fuel-cladding interactions and causes fuel pin failure in some cases [24].

3.3. Transmission Electron Microscope (TEM)
Yb₄Hf₃O₁₂ sample was irradiated with 6keV Helium ion using a JEOL 2000FX machine operating at 200kV at a MIAMI research facility, University of Huddersfield, UK.

![Cross-sectional micrograph showing under focus TEM image with corresponding SAED patterns obtained from irradiated Yb₄Hf₃O₁₂ sample with 6 keV He⁺ ions to a fluence of 7.6x10¹⁶ ions/cm² (at 6.2dpa).](image)

**Figure 3.** Cross-sectional micrograph showing under focus TEM image with corresponding SAED patterns obtained from irradiated Yb₄Hf₃O₁₂ sample with 6 keV He⁺ ions to a fluence of 7.6x10¹⁶ ions/cm² (at 6.2dpa).
Fig. 4. SRIM simulation results obtained from 6keV He ions into Yb₄Hf₃O₁₂ for damage profile and projectile ion distribution to a fluence of 7.6x10¹⁶ He/cm².

Fig. 3. shows the unirradiated room temperature image of Yb₄Hf₃O₁₂ composition before the beginning of the experiment with no cavities or bubbles formation in the crystalline diffraction pattern. After 30 minutes of He irradiation with fluences of 7.6x10¹⁶ ions/cm², the image changes by showing an airy ring in the diffraction indicating an amorphous material suggesting that the crystalline structure was damaged after the irradiation. Fig. 4. Shows the SRIM result for simulation using 6keV He ion in Yb₄Hf₃O₁₂ with plots of ballistic damage (in displacement per atom units) and He ion concentration as a function of depth in the sample to fluence of 7.6x10¹⁶ ions/cm². The results show that a peak dose of 6.2dpa is produced at a depth of 38nm with an ion concentration of 16.3% at a depth of 66nm. The penetration of He ions into the sample at a depth of 38nm with a concentration of 16.3% is low because of the energy of 6keV He (light) that was used in the experiment. The finding is in agreement with the previous studies that the defect induced by light ion irradiation possess high survival ability than heavy ion irradiation [3].

4. Conclusion

Polycrystalline delta phase Yb₄Hf₃O₁₂ compounds was produced using solid-state sintering. The oxide was further characterized with an ordered rhombohedral structure called delta phase material. The compositions demonstrated a strong phase stability under high temperature XRD at 1300°C. The compound exhibited a non-phase transition but the lattice parameters indicate a linear thermal expansion as the temperature increases. The sample was irradiated with 6keV He⁺ to a maximum fluences of 7.6x10¹⁶ ions/cm² (6.2dpa) at room temperature. The TEM results shows no formation of gas bubble or otherwise but an airy ring was observed in the diffraction patterns indicating that the crystalline structure of the material was damage as a result of the irradiation. These structural observations of the composition can be used to understand radiation damage effect in the material. The findings of the Yb₄Hf₃O₁₂ compound observed in the investigation is consistent with the fact that both metals ceramics succumb to an ion spectrum effect as established in previous studies. Further investigation is currently underway.
with 300keV He ion on the Yb$_4$Hf$_3$O$_{12}$ compound in order to develop new material with potential application as actinide hosts for advanced nuclear fuel or waste forms.

5. References

[1] R. C. Ewing, W. J. Weber, and J. Lian, "Nuclear waste disposal-pyrochlore (A2B2O7): Nuclear waste form for the immobilization of plutonium and "minor" actinides," Journal of Applied Physics, Review vol. 95, no. 11 I, pp. 5949-5971, 2004, doi: https://doi.org/10.1063/1.1707213.

[2] J. Wen et al., "Heavy and light ion irradiation damage effects in δ-phase Se$_4$Hf$_3$O$_{12}$," Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 365, pp. 325-330, 2015, doi: https://doi.org/10.1016/j.nimb.2015.04.011.

[3] J. Zhang et al., "Strong irradiation tolerance to amorphization in delta-Sc$_4$Ti$_3$O$_{12}$," Journal of Nuclear Materials, vol. 459, pp. 265-269, 2015, doi: https://doi.org/10.1016/j.jnucmat.2015.01.057.

[4] H. Liu, D. Y. Yang, W. Zhang, C. G. Liu, Y. Xia, and Y. H. Li, "Response of the physical properties of δ-Y$_6$WO$_{12}$ and Y$_6$UO$_{12}$ to pressure," Computational Materials Science, vol. 134, pp. 201-205, 2017/06/15 2017, doi: https://doi.org/10.1016/j.commatsci.2017.03.049.

[5] J. A. Valdez, M. Tang, and K. E. Sickafus, "Radiation damage effects in δ-Se$_4$Zr$_3$O$_{12}$ irradiated with Kr$_2^+$ ions under cryogenic conditions," Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 250, no. 1-2, pp. 148-154, 2006, doi: https://doi.org/10.1016/j.nimb.2006.04.098.

[6] M. Ishimaru, Y. Hirotsu, M. Tang, J. A. Valdez, and K. E. Sickafus, "Ion-beam-induced phase transformations in δ - Sc$_4$Zr$_3$O$_{12}$," Journal of Applied Physics, vol. 102, no. 6, p. 063532, 2007/09/15 2007, doi: https://doi.org/10.1063/1.2783892.

[7] K. E. Sickafus et al., "Radiation-induced amorphization resistance and radiation tolerance in structurally related oxides," Nat Mater, vol. 6, no. 3, pp. 217-23, Mar 2007, doi: https://doi.org/10.1038/nmat1842.

[8] K. E. Sickafus et al., "Compositional analyses of ion-irradiation-induced phases in δ-Sc$_4$Zr$_3$O$_{12}$," Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 266, no. 12-13, pp. 2892-2897, 2008, doi: https://doi.org/10.1016/j.nimb.2008.03.227.

[9] M. Tang, J. A. Valdez, and K. E. Sickafus, "Ion irradiation damage effects in δ-phase Y$_6$W$_1$O$_{12}$," Journal of Nuclear Materials, vol. 376, no. 2, pp. 247-250, 2008/05/31/ 2008, doi: https://doi.org/10.1016/j.jnucmat.2008.03.008.

[10] M. W. Blair et al., "Charge compensation in an irradiation-induced phase of δ-Se$_4$Zr$_3$O$_{12}$," Journal of Materials Science, vol. 44, no. 17, pp. 4754-4757, 2009/09/01 2009, doi: https://doi.org/10.1007/s10853-009-3722-2.

[11] C. R. Stanek, C. Jiang, B. P. Uberuaga, K. E. Sickafus, A. R. Cleave, and R. W. Grimes, "Predicted structure and stability ofA$_4$B$_3$O$_{12}$$\delta$-phase compositions," Physical Review B, vol. 80, no. 17, pp. 174101-11, 2009, doi: https://doi.org/10.1103/PhysRevB.80.174101.

[12] M. Tang et al., "Radiation damage effects in the uranium-bearing δ-phase oxide Y$_6$U$_1$O$_{12}$," Journal of Nuclear Materials, vol. 389, no. 3, pp. 497-499, 2009/06/01/ 2009, doi: https://doi.org/10.1016/j.jnucmat.2009.02.001.

[13] M. Tang, J. A. Valdez, B. P. Uberuaga, and K. E. Sickafus, "Irradiation - Induced Amorphization and Order - Disorder Transformation in the Tungsten δ - phase Oxides Yb$_6$W$_1$O$_{12}$ and Y$_6$W$_1$O$_{12}$," AIP Conference Proceedings, vol. 1099, no. 1, pp. 973-976, 2009, doi: https://doi.org/10.1063/1.3120205.

[14] M. Tang et al., "Swift heavy ion irradiation-induced microstructure modification of two delta-phase oxides: Se$_4$Zr$_3$O$_{12}$ and Lu$_4$Zr$_3$O$_{12}$," Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, vol. 268, no. 19, pp. 3243-3247, 2010, doi: https://doi.org/10.1016/j.nimb.2010.05.099.

[15] J. Wen et al., "Ion irradiation induced order-to-disorder transformation in δ-phase Lu$_4$Hf$_3$O$_{12}$," Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with
[16] J. Zhang, Y. Wang, M. Tang, J. Won, J. A. Valdez, and K. E. Sickafus, "Order-to-disorder transformation in δ-phase Sc4Zr3O12 induced by light ion irradiation," Journal of Materials Research, vol. 25, no. 2, pp. 248-254, 2010, doi: https://doi.org/10.1557/JMR.2010.0027.

[17] M. Tang et al., "Structure and mechanical properties of swift heavy ion irradiated tungsten-bearing delta-phase oxides Y6W1O12 and Yb6W1O12," Journal of Nuclear Materials, vol. 425, no. 1, pp. 193-196, 2012/06/01/ 2012, doi: https://doi.org/10.1016/j.jnucmat.2011.11.029.

[18] K. Jin, H. Bei, and Y. Zhang, "Ion irradiation induced defect evolution in Ni and Ni-based FCC equiatomic binary alloys," Journal of Nuclear Materials, vol. 471, pp. 193-199, 2016, doi: https://doi.org/10.1016/j.jnucmat.2015.09.009.

[19] N. R. Sanjay Kumar, N. V. Chandra Shekar, and P. C. Sahu, "Pressure induced structural transformation of pyrochlore Gd2Zr2O7," Solid State Communications, vol. 147, no. 9, pp. 357-359, 2008/09/01/ 2008, doi: https://doi.org/10.1016/j.ssc.2008.06.028.

[20] J. Zhang, Y. Q. Wang, J. A. Valdez, M. Tang, and K. E. Sickafus, "Irradiation induced order-disorder phase transformation in A4Zr3O12 (A=Sc, Lu and Dy)," Journal of Nuclear Materials, vol. 419, no. 1-3, pp. 386-391, 2011, doi: https://doi.org/10.1016/j.jnucmat.2011.08.004.

[21] J. F. Ziegler and J. P. Biersack, "The Stopping and Range of Ions in Matter," in Treatise on Heavy-Ion Science: Volume 6: Astrophysics, Chemistry, and Condensed Matter, D. A. Bromley Ed. Boston, MA: Springer US, 1985, pp. 93-129, doi: https://doi.org/10.1007/978-1-4615-8103-1_3.

[22] T. Richard, Crystals and Crystal Structures. West Sussex, England: John Wiley & Sons Ltd, 2006, pp. 114-152, doi: https://doi.org/10.1080/15421400701431661.

[23] H. Li et al., "Investigation of the structure and photoluminescence properties of Eu3+ ion-activated Y6WxMo(1 − x)O12," Journal of Materials Chemistry, 10.1039/C0JM03656K vol. 21, no. 12, pp. 4531-4537, 2011, doi: https://doi.org/10.1039/C0JM03656K.

[24] R. Vauchy, R. C. Belin, J.-C. Richaud, P. J. Valenza, F. Adenot, and C. Valot, "Studying radiotoxic materials by high temperature X-ray diffraction," Applied Materials Today, vol. 3, pp. 87-95, 2016/06/01/ 2016, doi: https://doi.org/10.1016/j.apmt.2016.03.005.

Acknowledgments
The authors would like to thank the Microscopes and Ion Accelerators for Materials’ Investigations (MIAMI) Facility, University of Huddersfield, UK for their support in conducting the irradiation experiment. Mohammed Ado wishes to express his profound gratitude to the government of the Federal Republic of Nigeria through the Petroleum Technology Development Fund (PTDF) and Chinese Government through China Scholarship Council (CSC) for their financial support in the pursuit of his studies.