Order-to-disorder phase transformation in ion irradiated uranium-bearing delta-phase oxides $RE_3U_1O_{12}$ ($RE$=Y, Gd, Ho, Yb, and Lu)

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Polycrystalline uranium-bearing compounds $Y_6U_1O_{12}$, $Gd_6U_1O_{12}$, $Ho_6U_1O_{12}$, $Yb_6U_1O_{12}$, and $Lu_6U_1O_{12}$ samples were irradiated with various ions species ($300\text{ keV} \text{ Kr}^+$, $400\text{ keV} \text{ Ne}^+$, and $100\text{ keV} \text{ He}^+$) at cryogenic temperature ($\sim 100\text{ K}$), and the microstructures were examined following irradiation using grazing incidence X-ray diffraction and transmission electron microscopy. The pristine samples are characterized by an ordered, fluorite derivative structure, known as the delta phase. This structure possesses rhombohedral symmetry. Amorphization was not observed in any of the irradiated samples, even at the highest dose ($\sim 65\text{ dpa}$ (displacement per atom)). On the other hand, some of these compounds experienced an order-to-disorder ($O\rightarrow D$) phase transformation, from an ordered rhombohedral to a disordered fluorite structure, at ion doses between 2.5 and 65 dpa, depending on ion irradiation species. Factors influencing the irradiation-induced $O\rightarrow D$ transformation tendencies of these compounds are discussed in terms of density functional theory calculations of the $O\rightarrow D$ transformation energies.

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1. Introduction

Uranium (U) and rare earth (RE) oxides are important materials for nuclear energy applications. RE oxides exhibit considerable solid solubility in nuclear fuel materials made from uranium oxides. RE–U–O solid solutions, which crystallize in structures related to the fluorite ($\text{CaF}_2$) crystal structure [1], are considered as potential fuel candidates for nuclear energy applications. RE oxides exhibit considerable solid solubility in nuclear fuel materials made from uranium oxides. RE–U–O solid solutions, which crystallize in structures related to the fluorite ($\text{CaF}_2$) crystal structure [1], are considered as potential fuel candidates for nuclear energy applications.

In this paper, we report different $O\rightarrow D$ transformation tendencies of the compounds $Y_6U_1O_{12}$, $Gd_6U_1O_{12}$, $Ho_6U_1O_{12}$, $Yb_6U_1O_{12}$, and $Lu_6U_1O_{12}$ under three different ion irradiation conditions. The $U^{4+}$ cations occupy the $3a$ Wyckoff equipoint in $V$-fold, distorted octahedral coordination relative to nearest neighbor O anions, while the $RE^{3+}$ cations occupy the general $18f$ equipoint with $VII$ fold coordination relative to surrounding O anions. The formally vacant anion sites, relative to the ideal $\text{MO}_2$ parent fluorite phase, are located at the $6c$ equipoint positions on the triad axes. There are also small relaxations of the U, RE, and O ions from their ideal fluorite positions. It is important to note that if U and RE cations could randomly swap positions on the cation sublattice sites, and if oxygen ions and oxygen vacancies were to become randomly distributed on all anion sublattice sites, then the cation and anion superlattices associated with delta phase are destroyed and the crystal structure would be indistinguishable (from a diffraction perspective) from the parent fluorite ($\text{MO}_2$) structure. We refer to this crystal structure as the disordered fluorite structure. Since radiation damage inherently involves disordering processes, we might anticipate a radiation-induced order-to-disorder ($O\rightarrow D$) phase transformation, from an ordered rhombohedral to a disordered fluorite phase, in our uranium-bearing delta phase compounds exposed to irradiation. Such a radiation-induced $O\rightarrow D$ transformation has been reported in similar fluorite derivative compounds, such as $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore oxides [5] (where $A$ and $B$ are metal cations and O are oxygen anions) and $\text{A}_2\text{B}_2\text{O}_5$ beta phase oxides [6].

In this paper, we report different $O\rightarrow D$ transformation tendencies of the compounds $Y_6U_1O_{12}$, $Gd_6U_1O_{12}$, $Ho_6U_1O_{12}$, $Yb_6U_1O_{12}$, and $Lu_6U_1O_{12}$ under three different ion irradiation conditions.
conditions: 300 keV Kr⁺, 400 keV Ne⁺, and 100 keV He⁺. We also compare and contrast these experimental results with the O–D transformation energies calculated using density functional theory.

2. Experimental procedure

Polycrystalline Y₆U₁O₁₂, Gd₆U₁O₁₂, Ho₆U₁O₁₂, Yb₆U₁O₁₂, and Lu₆U₁O₁₂ samples were synthesized from Y₂O₃, Gd₂O₃, Ho₂O₃, Yb₂O₃, Lu₂O₃ powders from Alpha Aesar (99.9%–99.99% purity), and UO₂ powder from Bio-Analytical Industries, by conventional ceramic processing procedures [7]. XRD measurements on these samples showed that the sintered pellets consisted of phase-pure RE₆U₁O₁₂. Ion irradiations were performed at cryogenic temperature (~100 K) in the Ion Beam Materials Laboratory at Los Alamos National Laboratory, using a Danfysik high current ion implanter operating at 150 kV. The 300 keV Kr⁺, 400 keV Ne⁺, and 100 keV He⁺ ions were implanted at normal incidence using a dose rate of 1 × 10¹⁶ ions/m²s to fluences of 2 × 10²⁰ Kr/m², 1 × 10²⁰ Ne/m², and 1 × 10²¹ He/m². Irradiated samples were analyzed using both grazing incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM). GIXRD measurements were performed using a Bruker AXS D8 Advanced X-ray diffractometer at a grazing incidence angle of π/3°, 1°, and 1° for Kr, Ne, and He irradiated samples, respectively. Under these conditions, X-rays are scattered from the near-surface of these samples within a depth significantly shallower than the range of these ions (calculated ion ranges are ~200 nm for Kr, ~700 nm for Ne, ~600 nm for He, based on SRIM simulations [7]); X-ray penetration estimates are based on the critical angle formula from Ref. [8]. Thus, we believe that our GIXRD measurements interrogate only the irradiated volume near the sample surface. Irradiated samples were prepared in cross-sectional geometry for TEM examination using a focused-ion-beam (FIB) instrument. TEM investigations were performed using a Philips CM-30 instrument operating at 300 kV.

3. Results and discussion

Fig. 1 shows grazing incidence X-ray diffraction (GIXRD) patterns obtained from U-bearing compounds before and after 300 keV Kr⁺, 400 keV Ne⁺, and 100 keV He⁺ ion irradiations. In all of the GIXRD patterns shown in Fig. 1, there are five prominent diffraction peaks labeled “F”. We will refer to these reflections as parent fluorite peaks (these peaks index as {111}, {200}, {220}, {311}, and {222}, respectively, assuming a structure with a fluorite unit cell). These peaks are the only allowed reflections in the angular range shown (20–70°) for an oxide with the fluorite crystal structure. All other diffraction maxima in the patterns shown in Fig. 1 are fluorite structural derivative or “superlattice” reflections labeled “R”. These peaks are due to the rhombohedral δ-phase. Specifically, these extra peaks arise from three particular features of the 6:1:12 δ-phase: (1) a small rhombohedral distortion from the ideal cubic symmetry associated with the parent fluorite structure; (2) an ordered arrangement of A¹⁺ and U⁶⁺ cation on the cation sublattices; and (3) an ordered arrangement of vacancies on the oxygen sublattice.

GIXRD results in Fig. 1 can be summarized as follows:

(1) Fig. 1a. Before irradiation, Gd₆U₁O₁₂ is initially an ordered δ-phase. Upon ion irradiations almost all R peaks associated with the fluorite structural derivative disappear and only F peaks remain. This is true for the following irradiation conditions: (1) 2 × 10²⁰ Kr/m² (corresponding to 55 dpa); (2) 1 × 10²⁰ Ne/m² (corresponding to 3.5 dpa); and (3) 1 × 10²¹ He/m² (corresponding to 2.5 dpa). The irradiated Gd₆U₁O₁₂ is transformed to a disordered fluorite under these irradiations. Another important result is that no irradiation-induced amorphization was observed in the irradiated Gd₆U₁O₁₂ samples. Similar structural evolution was observed in ion irradiated Yb₆U₁O₁₂ (data not shown here).

(2) Fig. 1b. Before irradiation, Lu₆U₁O₁₂ is initially an ordered δ-phase. Upon ion irradiations some of the R peaks remain, while others exhibit diminished intensity. This is true for the following irradiation conditions: (1) 2 × 10²⁰ Kr/m² (corresponding to 65 dpa); (2) 1 × 10²⁰ Ne/m² (corresponding to 4 dpa); and (3) 1 × 10²¹ He/m² (corresponding to 2.5 dpa). We interpret these results as indicative of a partial O–D phase transformation in Lu₆U₁O₁₂. Once again, no amorphization was observed in the irradiated Lu₆U₁O₁₂ samples. Similar structural evolution was observed in ion irradiated Ho₆U₁O₁₂ and Y₆U₁O₁₂ (data not shown here).

Fig. 2 shows cross-sectional TEM bright-field micrographs with corresponding microdiffraction (μD) patterns, obtained from Gd₆U₁O₁₂ irradiated under the following conditions: (1) 300 keV
Kr+ to a fluence of $2 \times 10^{20}$ Kr/m$^2$ (Fig. 2a); (2) 400 keV Ne+ to a fluence of $1 \times 10^{20}$ Ne/m$^2$ (Fig. 2b); and (3) 100 keV He+ to a fluence of $1 \times 10^{21}$ He/m$^2$ (Fig. 2c). The μD patterns obtained from the irradiated regions in Figs. 2a, b, c are consistent with a single phase, cubic fluorite structure, oriented with an epitaxial relationship w.r.t the unirradiated substrate. In Figs. 2a, b the beam direction is $\vec{B} = [\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ in the irradiated region and $\vec{B} = [\frac{1}{2} \frac{1}{2} \frac{1}{2}]$ in the substrate (the latter using 3-index, hkl, hexagonal indices). In Fig. 2c, the beam direction is $\vec{B} = [013]$, in the irradiated region and $\vec{B} = [1 \overline{1} 2]$, in the substrate. TEM observations in Fig. 2 corroborate the GIXRD results presented in Fig. 1a, indicating that Gd$_6$U$_1$O$_{12}$ experiences an O–D structural transformation induced by Kr/Ne/He ion irradiations, from an ordered δ-phase to a structure indistinguishable from a cubic fluorite. Also, TEM observations revealed no evidence for an irradiation-induced amorphous structure under irradiations. The nature of the O–D transformation is described below.

The irradiation-induced O–D transformation observed in the δ-compounds in this study, can be readily visualized with the aid of a layer-stacking model for the crystal structure of δ-RE$_6$U$_1$O$_{12}$. This model is shown in Fig. 3, where we envision the δ-phase as consisting of layers of atoms stacked along the c-axis of the hexagonal unit cell. There are 3 metal (M) layers and 6 oxygen (O) layers per hexagonal unit cell. The M layers can be described as fully-dense, triangular atom nets, while the O layers are based on triangular atom nets, but with ordered arrangements of interstices (“missing” O atoms) [9]. Experimental studies of δ-RE$_6$U$_1$O$_{12}$ indicate that the RE and U atoms within the M layers are fully ordered (see, e.g., Ref. [3] for δ-Y$_6$U$_1$O$_{12}$). Essentially, the M sublattice in δ-RE$_6$U$_1$O$_{12}$ consists of a pseudo-cubic-close-packed arrangement of cations, where 6/7 of the M atoms in each M layer are RE atoms arranged in a $3^{4.6}$ Archimedean tiling pattern [9]. The remaining 1/7 M atoms in each M layer are U atoms and these U atoms fill the “holes” in the RE $3^{4.6}$ Archimedean tiling pattern. This defines the super-ordering in δ-RE$_6$U$_1$O$_{12}$ compounds due to cation “patterning”. In addition, there is also atomic super-ordering in δ-RE$_6$U$_1$O$_{12}$ compounds, due to special atomic arrangements on the O sublattice. The anions in each O layer in a δ-compound are arranged in a $3^{4.6}$ Archimedean tiling pattern, just like the RE atoms in the M layers [9]. This pattern is shown in Fig. 3. O atom “patterning” produces a super-periodicity of the O sublattice, compared to a cubic fluorite compound. In a cubic MO$_2$ fluorite-structured oxide, the O layers consist simply of fully-dense, triangular atom nets (same as the M layers).

The O–D structural transformation in δ-RE$_6$U$_1$O$_{12}$ compounds, induced by ion irradiation, apparently is due to rearrangements of atoms on both the M and O sublattices. If cation antisite defects are formed under irradiation on the M sublattices (RE and U atoms exchange positions on the RE and U sublattices, respectively), then the $3^{4.6}$ Archimedean tiling patterns of RE atoms in the M layers are disturbed. Similarly, if Frenkel pairs form under irradiation on the O sublattice (O atoms and corresponding vacant O sites exchange positions) then the $3^{4.6}$ Archimedean tiling patterns in the O layers are disturbed. The atomic “patterns” in the M and O layers evolve during irradiation, from ordered to random arrangements. Eventually, when the concentration of cation

![Fig. 2. Cross-sectional TEM bright-field images and corresponding microdiffraction (μD) patterns obtained from Gd$_6$U$_1$O$_{12}$ irradiated with (a) 300 keV Kr to a fluence of $2 \times 10^{20}$ Kr/m$^2$, (b) 400 keV Ne to a fluence of $1 \times 10^{20}$ Ne/m$^2$, and (c) 100 keV He to a fluence of $1 \times 10^{21}$ He/m$^2$.](image-url)
antisite and anion Frenkel pairs is sufficient, the M and O layers, from a diffraction perspective, become indistinguishable from triangular atom nets. By consequence, the irradiated structure comes to resemble a cubic fluorite structure. This is the nature of the \(O-D\) transformation in \(\delta\)-\(\text{RE}_6\text{U}_1\text{O}_{12}\) compounds, induced by ion irradiation.

To gain some insight into the disordering process under irradiation, we performed first-principles calculations to determine the \(O-D\) phase transformation energies in these U-bearing \(\delta\)-phase compounds (results shown in Fig. 4). In order to estimate the \(O-D\) energetics of \(\text{RE}_6\text{U}_1\text{O}_{12}\) (\(\text{RE}=\text{Y, Lu, Ho, Gd, and Yb}\)) \(\delta\)-phases, we have also considered a fully disordered version of the delta phase, i.e., the \((\text{RE}_{6/7}\text{U}_{1/7})(\text{O}_{6/7}\text{V}_{1/7})_2\) defect-fluorite structure (where \(\text{V}\) represents an oxygen vacancy). Here, both the cations and anions are randomly distributed on their respective sublattices. We adopted the special quasirandom structure (SQS) approach [10–12] to adequately reproduce the statistics of such a disordered structure in a relatively small (thus computationally feasible) 76-atom periodic supercell (see Ref. [13] for details on construction of the two-sublattice SQS). First-principles calculations are performed using the all-electron projector augmented wave (PAW) method [14] within the generalized gradient approximation of Perdew, Burke, and Ernzerh of (PBE-GGA) [15], as implemented in Vienna ab initio simulation package (VASP) [16]. According to our convergence tests, a plane wave cutoff energy of 400 eV and a \(2 \times 2 \times 2\) \(k\)-point sampling are sufficient to give converged results. By computing the quantum mechanical forces and stress tensor, the lattice parameters and internal atomic positions of all structures are fully optimized using a conjugate-gradient scheme. Finally, the \(O-D\) disordering energy can be obtained from the total energy difference between the fully ordered ground state delta-phase structure and the SQS, based on which the \(O-D\) transition temperature can be further estimated [13]. Fig. 4 shows the calculated \(O-D\) energies for the \(\text{RE}_6\text{U}_1\text{O}_{12}\) compounds examined in this study. \(\text{Gd}_6\text{U}_1\text{O}_{12}\) and \(\text{Yb}_6\text{U}_1\text{O}_{12}\) compounds have lower \(O-D\) energies compared to other three compounds. This might indicate that the \(O-D\) phase transformation may occur more readily in these two delta phase compounds. This is, in fact, what was found in the experimental results presented here.
Finally, it is noteworthy that our results may indicate an ion species spectrum effect w.r.t. radiation-induced damage accumulation. Though we did not perform a systematic investigation of spectrum effects in this study, our results seem to indicate that defect survivability (damage efficiency) is enhanced under light ion (He or Ne) compared to heavy ion (Kr) irradiation conditions. Similar enhanced defect survivability under light ion irradiation conditions was recently found in the 4:3:12 \( \delta \)-phase compounds \( \text{Sc}_4\text{Zr}_3\text{O}_{12} \) \[17\]. This appears to be a somewhat of unusual behavior for ceramic compounds. Work is in progress to further elucidate spectrum effects in U-bearing, \( \text{RE}_6\text{U}_1\text{O}_{12} \) \( \delta \)-phase oxides.

4. Conclusion

We performed 300 keV Kr\(^{+}\), 400 keV Ne\(^{+}\), and 100 keV He\(^{+}\) ion irradiation experiments under cryogenic conditions (100 K) on the following polycrystalline \( \delta \)-phase compounds: \( Y_6\text{U}_1\text{O}_{12}, \text{Gd}_6\text{U}_1\text{O}_{12}, \text{Ho}_6\text{U}_1\text{O}_{12}, \text{Yb}_6\text{U}_1\text{O}_{12}, \) and \( \text{Lu}_6\text{U}_1\text{O}_{12} \). GIXRD measurements and TEM observations revealed no evidence for irradiation-induced amorphization of these uranium-bearing compounds, up to a maximum dose of 65 dpa. On the other hand, some of these compounds experienced a partial or full order-to-disorder (O–D) phase transformation. The disordering tendencies predicted by DFT calculations (particularly, the O–D transformation energies), are consistent with the experimental results. This concurrence between theory and experiment may help us to predict the radiation damage tolerance (or damage sensitivity) of specific ceramic compounds. In turn, this will help us to develop new materials as actinide hosts for advanced nuclear fuel or waste forms.

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References