Strong Irradiation tolerance to amorphization in delta-Sc₄Ti₃O₁₂

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Abstract

Polycrystalline delta-phase Sc₄Ti₃O₁₂ was irradiated under two separate conditions, with 200 keV Ne⁺ or 600 keV Kr³⁺ at cryogenic temperature (~77K) to examine its radiation tolerance to amorphization. Irradiated samples were characterized using grazing incidence X-ray diffraction and cross-sectional transmission electron microscopy. An order-to-disorder (O-D) structural transformation was observed under both ion beam irradiation conditions, but the threshold irradiation doses to produce the O-D transformation differ significantly. The order to disorder phase transformation was completed by a fluence of 2×10^{19} Ne/m² (or a peak dose of ~0.7 dpa) with Ne irradiation, while it was not accomplished until a fluence of 5×10^{20} Kr/m² (or a peak dose of ~93 dpa) with Kr irradiation. This observation was interpreted in terms of greater probability of defect survivability in dilute Ne versus dense Kr ion cascades.

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More interesting aspect in this study, in the basis of so-called “chemical effects”, Ti-bearing oxide $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ should be readily amorphous when exposed to ion irradiation, but no amorphization was observed even after 93 displacements per atom in Kr irradiation. These observations exhibit that the temperature-composition (T-C) phase diagram is a good indicator for radiation tolerance, especially for amorphization.

Introduction

Crystalline oxides with structures related to fluorite (CaF_2) have received considerable attention as potential nuclear fuel forms and waste forms [1-5]. In certain fluorite derivative structures, it has been shown that the structural stability under irradiation highly depends on compounds composition. For instance, in $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore oxides (where A and B are metal cations and O are oxygen anions), compounds with $\text{B} = \text{Zr}$ are found to be far more tolerant to radiation-induced amorphization than those with $\text{B} = \text{Ti}$ [3, 6-9]. Structural changes such as crystalline to amorphous transitions can dramatically affect many properties of a material, including altering mechanical durability, increasing chemical transport in complex oxides, and significant volume changes [10, 11]. Thus identifying materials that are resistant to radiation induced amorphization is very important for their applications in nuclear reactor radiation environment or in nuclear waste forms. Several concepts have been proposed to relate amorphization resistance of a material to various material parameters such as cation ratio, defect formation energy, bond type, electron electro-negativities [2, 11-13]. In contrast to the above-mentioned materials that exhibit amorphization resistance, a concept that relates to titanium containing oxide ceramics sets forth another criterion for amorphization in materials is termed “chemical effects” [11, 14], and states that complex titanate oxides, regardless of their structure and chemistry, can be readily amorphized as demonstrated in $\text{A}_2\text{Ti}_2\text{O}_7$ pyrochlore oxides. Contrasting to the pyrochlore structure ($\text{A}_2\text{B}_2\text{O}_7$), another fluorite derivative oxide with the stoichiometry of $\text{A}_4\text{B}_3\text{O}_{12}$ known as delta (δ) phase has shown exceptional radiation stability [13, 15, 16]. The $\text{A}_4\text{B}_3\text{O}_{12}$ δ -phase compounds tested so far have exhibited no irradiation-induced amorphization susceptibility. Specifically related to this study, to our best knowledge, the amorphization behavior of $\delta\text{-A}_4\text{Ti}_3\text{O}_{12}$ have never been examined under radiation environments.

Here we report our preliminary studies on titanate based delta phase structures of $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ under various ion irradiation conditions. We irradiated the $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ samples using 200 keV Ne^+ or 600 keV Kr^{3+} at cryogenic temperature ($\sim 77\text{K}$) to evaluate its radiation tolerance to amorphization. Using grazing

incidence X-ray diffraction (GIXRD) and cross-section transmission electron microscopy (XTEM), we observed order-to-disorder phase transformation but no amorphization was seen even at the highest dose used (~ 93 dpa at 5×10^{20} Kr/m²). These results are discussed in the context of temperature-composition phase diagram of the compound.

Experimental Procedure

Polycrystalline δ -Sc₄Ti₃O₁₂ samples were synthesized from TiO₂ and Sc₂O₃ powders (Alfa Aesar, 99.99% purity), by conventional ceramic processing procedures. The TiO₂ and Sc₂O₃ oxide powders started with drying at 800 °C for 12 hours to remove the possible absorbed water. Dried TiO₂ and Sc₂O₃ with corresponding weight were mixed for 4 hours in ZrO₂ Vial by ball-milling, and pressed at pressure of ~ 260 Mpa to form green pellet. Then the green pellets (nominally 13 mm in diameter) were calcined at 1000 °C for 24 hours. Finally, the disk samples were sintered at 1100 °C for 24 hours to achieve densified pellets with $\sim 88\%$ based on the theoretical density of Sc₄Ti₃O₁₂. These pellets were cut using a diamond saw to thickness of ~ 1 mm disks, then the disk samples were polished to a mirror finishing using 1 μ m diamond paste. Pristine samples were examined using X-ray diffraction and were determined to possess the δ -phase structure (S.G. #148, $R\bar{3}$) with $a = 0.90669(157)$ nm and $c = 0.85217(54)$ nm, based on the hexagonal unit cell description of the δ -Sc₄Ti₃O₁₂ ($V = 0.6067(60)$ nm³/unit cell). The measured crystal structure parameters are very close to published values by Rossell ($a = 0.90880(7)$ nm, $c = 0.85443(11)$ nm, $V = 0.6111(2)$ nm³/unit cell) [17].

Ion irradiations were carried out under cryogenic conditions (~ 77 K) in the Ion Beam Materials Laboratory at Los Alamos National Laboratory, using a 200 kV Danfysik High Current Research Ion Implanter. The samples were mounted in a copper plate with silver paste, and then the good thermal conductor copper plate was attached in a steel charmer cooled by liquid Nitrogen. The thermal couple was attached on the copper plate with a measured temperature of about -196 °C within the whole irradiation

period. The 200 keV Ne^+ ions were implanted at normal incidence to ion fluences ranging from 2×10^{19} to 2×10^{20} ions/ m^2 , while 600 keV Kr^{3+} were implanted to ion fluences ranging from 2×10^{20} to 5×10^{20} ions/ m^2 . The irradiation flux for both ions was kept at $\sim 1\text{--}3 \times 10^{16}$ ions/ $\text{m}^2 \cdot \text{s}$ to avoid any potential beam heating effects during ion irradiation. The projected ranges of 200 keV Ne^+ ions and 600 keV Kr^{3+} ions in $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ were estimated using the Monte Carlo code SRIM using the full damage cascades mode (arbitrarily assumed the threshold displacement energies of Sc, Ti and O are 40 eV) [18].

Ion irradiated samples were characterized using grazing incidence X-ray diffraction (GIXRD) and cross-sectional transmission electron microscopy (XTEM). GIXRD measurements were performed using a Bruker AXS D8 Advanced X-ray diffractometer configured in θ - 2θ geometry. The X-ray incidence angle for measurements was chosen to be $\gamma = 0.25^\circ$, so that the estimated X-ray penetration depth is less than 100 nm [15, 19-21], significantly shallower than the projected range of the damage of the different ion beams used. TEM observations were performed using a JEOL-3000 instrument. Selected area electron diffraction (SAED) was used in this study to obtain electron diffraction patterns from sample regions (diameters of ~ 100 nm).

Results

Figure 1 shows the SRIM results for simulations using 200 keV Ne and 600 keV Kr ions into $\text{Sc}_4\text{Ti}_3\text{O}_{12}$. Fig. 1(a,b) shows plots of the ballistic damage (in units of displacement per atom) and implanted Ne and Kr ion concentration as a function of depth in $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ to fluence of 2.0×10^{20} ions/ m^2 respectively. It can be seen that the peak damage for 200 keV Ne is ~ 250 nm versus ~ 180 nm for 600 keV Kr, while the ion peak ranges are ~ 330 nm for 200 keV Ne and ~ 260 nm for 600 keV Kr. Fig. 1(c,d) shows the electronic and nuclear energy loss of 200 keV Ne and 600 keV Kr into $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ as a function of ion depth. We should point out that the electronic energy losses of both ions at the selected energies are somewhat similar (ranging 0.7 to 0.4 keV/nm from sample surface to depth of 100 nm), but the nuclear energy loss of the Kr ions is approximately one order of magnitude greater than that of Ne ions in the observed area.

Figure 2 shows GIXRD patterns obtained from pristine $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ and $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ irradiated with 200 keV Ne^+ ions to fluences ranging from 2.0×10^{19} to 2.0×10^{20} Ne/m^2 . The GIXRD patterns in Fig. 2 indicate that “superlattice” reflections, specifically: $(012)_\delta$, $(021)_\delta$, $(220)_\delta$, $(104)_\delta$, $(312)_\delta$, and $(232)_\delta$ (marked on the graph), these reflections disappear by the surprisingly low fluence of 2×10^{19} Ne/m^2 (0.7 peak dpa). The structure that is left after the superlattice reflections disappear results in a disordered fluorite structured material possessing the principal diffraction maxima (using the rhombohedral setting), of $(211)_\delta$, $(122)_\delta$, $(214)_\delta$ and $(125)_\delta$. These observations suggest that Ne^+ ion irradiation of $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ induces a phase transformation, from an ordered δ -phase to a cubic fluorite phase measured using the X-ray diffraction method. Following transformation, the δ -phase $(211)_\delta$, $(122)_\delta$, $(214)_\delta$ and $(125)_\delta$ reflections are identified with the “parent” cubic fluorite (F) structure (corresponding to $(111)_F$, $(200)_F$, $(220)_F$ and $(113)_F$ reflections). This transformation appears to be the same as the O-D (ordered δ -phase to disordered fluorite) structural transformation observed in previous study by Sickafus et al. [13]. Moreover, the diffraction maxima move to the lower 2θ angle, which means a unit cell swelling, and this swelling is due to the cation and anion disordering [22, 23]. It is interesting to note that despite this O-D structural transformation, no amorphization transformation was observed in the compound, even to the highest fluence of 2×10^{20} Ne/m^2 (7.0 dpa) using a 200 keV Ne^+ ion beam.

Figure 3 shows cross-sectional TEM bright-field micrographs with corresponding SAED patterns, obtained from $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ irradiated with 200 keV Ne^+ ions to a fluence of 2×10^{20} Ne/m^2 . The TEM images reveal that the Ne -ion irradiated regions are ~ 260 nm thick for the fluence of 2×10^{20} Ne/m^2 , which is consistent with the SRIM simulation result shown in Fig. 1(a) with damage peak at ~ 250 nm. TEM observations reveal no evidence of an irradiation-induced amorphous structure, to Ne ion fluences up to 2×10^{20} Ne/m^2 . However, the SAED patterns do reveal evidence for a complete structural transformation at a fluence of 2×10^{20} Ne/m^2 . The SAED pattern obtained from the irradiated region in Fig. 3 is consistent with a cubic fluorite structure, oriented with an epitaxial relationship w.r.t the unirradiated substrate (beam direction $\vec{B} = [012]_F$ in the irradiated region; $\vec{B} = [2\bar{2}1]_\delta$ in the substrate). The TEM observations in Fig. 3 confirm the GIXRD results presented in Fig. 2, indicating that $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ undergoes a structural

transformation induced by the 200 keV Ne^+ ion irradiation, from an ordered δ -phase to a cubic fluorite structure, while no amorphization is observed by a fluence of 2×10^{20} ions/m² (7.0 dpa).

Figure 4 shows GIXRD patterns obtained from pristine $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ and $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ irradiated using 600 keV heavy Kr^{3+} ions to fluences ranging from 2.0×10^{20} to 5.0×10^{20} Kr/m² (~37-93 dpa). The GIXRD patterns obtained at a fluence of 2.0×10^{20} Kr/m² (~37 dpa) show that the “superlattice” diffractions labeling as $(012)_\delta$, $(021)_\delta$, $(220)_\delta$, $(104)_\delta$, $(312)_\delta$, and $(232)_\delta$ were almost unaffected under this irradiation condition. However, the GIXRD patterns obtained from $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ irradiated to a fluence of 5.0×10^{20} Kr/m² (~93 dpa) indicate a structural transformation, i.e. all the “superlattice” diffraction peaks, $(012)_\delta$, $(021)_\delta$, $(220)_\delta$, $(104)_\delta$, $(312)_\delta$ and $(232)_\delta$, were diminished in intensity. Meanwhile the primary fluorite peaks indexed (using the rhombohedral setting) as $(211)_\delta$, $(122)_\delta$, $(214)_\delta$ and $(125)_\delta$ were not affected to a measurable degree, indicating the structure $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ remained intact after irradiation with 600 keV Kr ions to a fluence of 5.0×10^{20} Kr/m² (~93 dpa). Once again, despite the clear observation of an O-D transformation in 600 keV Kr ion irradiated $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$, no amorphization is observed even at the highest fluence used (5×10^{20} Kr/m² or ~ 93 dpa).

Discussion

Figure 5 shows idealized (unrelaxed) oxygen layers of pristine and irradiated for the crystal structure of $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$, where we envision the compound as consisting of layers of atoms stacked along the c -axis of the hexagonal unit cell with lattice constant a . Based on the layer model [24], 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) as shown. Therefore, the atomic super-ordering that is characteristic of $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$, arise from special atomic arrangements on the O sublattice. Upon ion irradiation, the metal layers still remain fully-dense, triangular atom nets (with cation ions disordered), while the O layer results in a rearrangement of the O atoms. Actually, the interstices in the O layers evolve during irradiation, from ordered to random arrangements. Eventually, when the concentration of

Frenkel pairs is sufficient, the 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 $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$, induced by ion irradiation. This transformation is likely equivalent to the thermal transformation of $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ based on its phase diagram in Fig. 6, where the O-D transformation occurs at a temperature of $\sim 1150^\circ\text{C}$. Actually, the ion irradiation-induced defects increase the energy of irradiation sample as the arrow shown, which is similar to heating the sample. The high dose irradiated structure of $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ is likely very similar to this high temperature phase.

Another interesting aspect of the results presented in this investigation is the apparent “spectrum effect” which was also observed in previous studies [15, 25]. The spectrum effect we are referring to is in the δ -phased materials, light ions were shown to be more effective in producing order to disorder phase transformations than heavy ion irradiation. In the 200 keV Ne^+ ion irradiation experiments presented here, the O-D transformation is complete by a peak displacement damage dose of ~ 0.7 dpa (2×10^{19} Ne/m^2) from the GIXRD patterns in Fig. 2, whereas in the 600 Kr^{3+} irradiation experiments, the “superlattice” diffraction peaks in $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ remains unchanged at a damage dose of ~ 37 dpa (2×10^{20} Kr/m^2) in Fig. 4, and furthermore, even at the highest dose of 93 dpa, the smaller $(104)_\delta$ and $(312)_\delta$ reflections can still be observed. Thus, the results presented here indicate that the ballistic damage necessary to induce the O-D transformation in Kr is significantly greater than in the case of the lighter Ne ions. The observed “spectrum effect” is explained from using two concepts [15, 25]. First, the heavy Kr ion irradiation creates much denser Frenkel pair cascades as compared to the dilute cascades using Ne irradiation, the Frenkel pairs within the dense cascades have higher probabilities (due to their proximity and concentration with one and other) to harmlessly recombine within the cascade. In other words, the defects induced by light ion irradiation, such as Ne, possess higher survival ability than heavy Kr ion irradiation. Secondly, in the O-D transformation, the $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ was partially disordered during the sample synthesis from study of Rossel [17], so the O atom movements play a more important role to the final change in structure. It is well known that a better match in atomic masses between projectiles and target atoms will

transfer ion kinetic energy more effectively during the collision, e.g. the kinematic efficiency factor is 0.987 for Ne on O, compared to 0.538 for Kr on O.

The most important observation in this study is that no amorphization is observed in this delta phase titanate oxide under ion irradiations. In Fig. 2 the GIXRD examination shows $(111)_F$, $(200)_F$, $(220)_F$ and $(113)_F$ diffractions to a fluence of 2×10^{20} Ne/m² (~7 dpa), and no any evidence of amorphization halo, even though the “supperlattice” diffraction peaks of $(012)_\delta$, $(021)_\delta$, $(220)_\delta$, $(104)_\delta$, $(312)_\delta$, and $(232)_\delta$ all disappear, characteristic of an O-D phase transformation. After finishing GIXRD measurement, the sample is cut to make cross-section TEM observation. Fig. 3 shows the cross-section TEM observations. The SAED patterns indicate that no amorphization have taken place in the irradiation region, even though an O-D phase transformation is evident when comparing the SAED patterns of the irradiation layer and the underneath substrate, consistent with GIXRD results shown in Fig.2. Higher dose irradiation using 600 keV Kr ions to a dose of ~93 dpa showed no amorphization in $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ compounds as shown in Fig. 4. Such a high radiation-resistance to amorphization in $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ under cryogenic temperature (~77K) is not anticipated according to the so-called “chemical effects” [2, 8, 11, 26], in which all complex titanate oxides, regardless of their structure and chemistry, should readily amorphize upon an irradiation as low as ~1 dpa, based on ion irradiation in $\text{Lu}_2\text{Ti}_2\text{O}_7$ pyrochlore structure [8]. The high radiation tolerance of $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ to amorphization observed above suggests that one may need to rethink the so-called “chemical effect” when dealing with radiation damage in complex titanate oxides. Meanwhile, the T-C phase diagram characteristics may be a better indicator for radiation damage to amorphization. To our best knowledge, it is the first observed complex titanate oxides that cannot be amorphized by high radiation damage (~93 dpa) under cryogenic temperature.

Conclusions

In summary, $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ has shown to succumb to an irradiation-induced order-to-disorder (O-D) crystal structure transformation, following 200 keV Ne⁺ ion or 600 keV Kr³⁺ ion irradiations under

cryogenic temperature. However, the observed O-D transformation threshold dose under 200 keV Ne ion irradiation (<0.7 dpa) is found significantly less than that using 600 keV Kr ion irradiation (> 37 dpa). This enhanced O-D transformation efficiency in the Ne versus Kr ion irradiation experiments is speculated to be due to a result of higher defect survivability in dilute Ne versus dense Kr ion cascades. More importantly, it is found that $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ is resistant to amorphization up to at least the highest dose used (~ 93 dpa), which is not consistent with the so-called “chemical effects” for complex titanate based oxides. The T-C phase diagrams of Sc_2O_3 - TiO_2 are used to imply its high radiation tolerance to amorphization. These observations exhibit the T-C phase diagram is a good indicator for radiation tolerance.

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Figure Captions

Figure 1. SRIM simulation results obtained from 200 keV Ne and 600 keV Kr ions into $\text{Sc}_4\text{Ti}_3\text{O}_{12}$. (a) damage profile and projectile ion distribution of 200 keV Ne implantation into $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ to a fluence of $2.0 \times 10^{20} \text{ Ne/m}^2$, (b) damage and concentration distribution of 600 keV Kr implantation into $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ to a fluence of $2.0 \times 10^{20} \text{ Kr/m}^2$, (c) nuclear and electronic energy loss for 200 keV Ne irradiation into $\text{Sc}_4\text{Ti}_3\text{O}_{12}$, (d) nuclear and electronic energy loss for 600 keV Kr irradiation into $\text{Sc}_4\text{Ti}_3\text{O}_{12}$.

Figure 2. GIXRD patterns obtained from pristine $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ and $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ irradiated with 200 keV Ne^+ ions to fluences of 2.0×10^{19} and $2.0 \times 10^{20} \text{ Ne/m}^2$ at a fixed grazing incidence angle relative to the sample of, $\gamma = 0.25^\circ$ (peak displacement damage of ~ 0.7 and 7 dpa).

Figure 3. Cross-sectional bright-field TEM images with corresponding SAED patterns obtained from polycrystalline $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ irradiated with 200 keV Ne^+ ions to a fluence of $2 \times 10^{20} \text{ Ne/m}^2$ (~ 7 peak dpa).

Figure 4. GIXRD patterns obtained from pristine $\delta\text{-Sc}_4\text{Ti}_3\text{O}_{12}$ and $\text{Sc}_4\text{Ti}_3\text{O}_{12}$ irradiated with 600 keV Kr^{3+} ions to fluences between 2.0×10^{20} and $5.0 \times 10^{20} \text{ Kr/m}^2$ (patterns obtained at a fixed grazing incidence angle relative to the sample, $\gamma = 0.25^\circ$). The peak displacement damage doses for these fluences are 37 and 93 dpa.

Figure 5. Layer stacking model representations of the pristine oxygen layer with “O vacancies” ordered arranged and irradiated oxygen layer with an O vacancy (square symbol highlighted red) and an O interstitial (sphere highlighted red) introduced into the atom pattern (Note: this diagram is a visual aid only, an adjacent Frenkel pair is not a stable defect configuration).

Figure 6. Phase diagram of $\text{Sc}_2\text{O}_3\text{-TiO}_2$ system.

Figure 1.

Figure 2.

Figure 3

Figure 4

Figure 5

Figure 6