Comparison of short-range order in irradiated dysprosium titanates

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The structural response of Dy\textsubscript{2}TiO\textsubscript{3} oxide under swift heavy ion irradiation (2.2 GeV Au ions) was studied over a range of structural length scales utilizing neutron total scattering experiments. Refinement of diffraction data confirms that the long-range orthorhombic structure is susceptible to ion beam-induced amorphization with limited crystalline fraction remaining after irradiation to \(8 \times 10^{12}\) ions/cm\(^2\). In contrast, the local atomic arrangement, examined through pair distribution function analysis, shows only subtle changes after irradiation and is still described best by the original orthorhombic structural model. A comparison to Dy\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} pyrochlore oxide under the same irradiation conditions reveals a different behavior: while the dysprosium titanate pyrochlore is more radiation resistant over the long-range with smaller degree of amorphization as compared to Dy\textsubscript{2}TiO\textsubscript{3}, the former involves more local atomic rearrangements, best described by a pyrochlore-to-weberite-type transformation. These results highlight the importance of short-range and medium-range order analysis for a comprehensive description of radiation behavior.

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\textbf{INTRODUCTION}

Dysprosium titanate oxide (Dy\textsubscript{2}TiO\textsubscript{3}) is a neutron absorbing material used in control rods in a number of nuclear reactors\textsuperscript{1,2}. It is an attractive nuclear material due to dysprosium’s large thermal neutron absorption cross section, as well as the low thermal expansion, large heat capacity, low swelling under irradiation, high melting point, suppression of outgassing, and chemical compatibility with cladding materials\textsuperscript{3,4}. Within the extreme environment of nuclear applications, materials will be modified across multiple length-scales, from atomic-scale changes to extended long-range defective microstructures. These structural changes will affect thermomechanical and transport properties, which depend strongly on behavior at different length-scales. Therefore, as with all nuclear materials, it is imperative to understand the radiation response of Dy\textsubscript{2}TiO\textsubscript{3} across length scales from the atomic arrangement to the long-range structure.

Dy\textsubscript{2}TiO\textsubscript{3} oxide, like other A\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} (A = trivalent lanthanides, Y\textsuperscript{3+}) materials, commonly occurs in one of three types—an orthorhombic phase of space group Pnma (Fig. 1a), a hexagonal phase of space group P6\textsubscript{3}mmc, and cubic phases reported as Fm-3m, Fd-3m, or F-43m depending on synthesis routes\textsuperscript{5}. The orthorhombic phase is the equilibrium phase of Dy\textsubscript{2}TiO\textsubscript{3} under ambient conditions and it reversibly transforms to a hexagonal high-temperature phase above 1370 °C, followed by a cubic high-temperature phase above 1680 °C, before melting at 1875 °C\textsuperscript{5}. In the orthorhombic phase, Dy\textsubscript{2}TiO\textsubscript{3} exhibits unusual polyhedral geometries with Dy occupying 7-coordinate mono-capped octahedra and Ti occupying 5-coordinate square pyramids\textsuperscript{5}. The radiation response of A\textsubscript{2}BO\textsubscript{5} compounds is often compared and contrasted to that of compositionally-related A\textsubscript{2}B\textsubscript{2}O\textsubscript{7} pyrochlore materials\textsuperscript{5}. These complex oxides, which are also relevant for nuclear applications, adopt either an ordered pyrochlore (Fd-3m) or disordered, defect-fluorite (Fm-3m) phase\textsuperscript{5}. Both phases are derivatives of the ideal fluorite structure, but with two cations and one vacant anion site, which are ordered in pyrochlore and disordered in defect-fluorite\textsuperscript{5}. In the ordered pyrochlore structure, the larger A-cation occupies a 8-coordinate distorted trigonal scalenohedron and the smaller B-cation occupies a 6-coordinate trigonally flattened octahedron\textsuperscript{5}. The adopted structure type is determined by the ratio of cation’s ionic radii (r\textsubscript{A}/r\textsubscript{B}) as well as the cation antisite defect energy. For example, most A\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} compounds exhibit a pyrochlore structure (e.g., Dy\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, Fig. 1b) while some A\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} compounds can only be synthesized with a defect-fluorite structure (e.g., Ho\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7})\textsuperscript{5}.

The irradiation environment encountered by nuclear materials is harsh, complex and can be divided into two distinct regimes: (i) low energy ions (keV–MeV range), e.g., recoil nuclei from alpha-decay events, which interact with a material through ballistic collisions (nuclear energy loss regime) and (ii) high energy ions (MeV–GeV range), e.g., fragments from fission events, which interact primarily with the electrons within a material (electronic energy loss regime). A\textsubscript{2}BO\textsubscript{5} compounds have been studied under both irradiation regimes and the lanthanide titanates (Ln\textsubscript{2}TiO\textsubscript{3}), in general, are susceptible to radiation-induced amorphization\textsuperscript{6,10–13}. Tracks with an amorphous core and a disordered shell form in Ln\textsubscript{2}TiO\textsubscript{3} after 1.4 GeV Xe ion irradiation with the amorphization efficiency increasing as a function of Ln cation size\textsuperscript{12}. A similar behavior is observed for low-energy ion irradiation (1 MeV Kr ions) of Ln\textsubscript{2}TiO\textsubscript{3} by a decrease in the critical amorphization dose with increasing Ln cation size\textsuperscript{10,11}, which is equivalent to an increase of the critical amorphization temperature, \(T_c\), above which the material can no longer be amorphized (\(T_c = 400–440°C\) for Dy\textsubscript{2}TiO\textsubscript{3}\textsuperscript{10,11}).

The local order of amorphous and disordered crystalline complex oxides has recently been studied using a variety of newly developed and improved techniques\textsuperscript{14–20}, including Raman spectroscopy, electron energy loss spectroscopy (EELS), extended x-ray absorption fine structure analysis (EXAFS), and neutron total scattering. These techniques have the advantage of providing structural information on local defects and disorder. Irradiation effects in Dy\textsubscript{2}TiO\textsubscript{3} and other titanate compositions have been previously investigated using grazing incidence x-ray diffraction analysis\textsuperscript{10}, transmission electron microscopy (TEM)\textsuperscript{10,11}, and

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...dilatometry techniques. While these studies have provided significant insight into the process of radiation damage in dysprosium titanate, the analytical techniques used have several general shortcomings. For instance, the low interaction cross section of x-rays with low-Z elements, such as oxygen, makes x-ray probes insensitive to radiation damage induced within the oxygen sublattice. In contrast, neutron probes, for which interaction cross sections have no explicit Z-dependence, provide structural information on the cation and oxygen sublattices. Neutron total scattering experiments have recently received more attention due to advent of modern, intense spallation neutron sources with beamlines specifically designed to produce high resolution pair distribution functions (PDFs), such as the Nanoscale Ordered Materials Diffractometer (NOMAD) at the Spallation Neutron Source (SNS)\(^2\). The intense neutron flux of \(\sim 1 \times 10^{8}\) neutrons/cm\(^2\) s reduces the required sample mass for such experiments to \(\sim 50\)–100 mg. This amount of irradiated sample mass is within the achievable range of the largest ion accelerator facilities\(^2\).

Previous radiation-damage studies of different pyrochlore oxides using neutron total scattering analysis have revealed local structural changes that are not represented by the average, long-range structure observed by conventional analysis. For example, Shamblin et al. showed that locally-ordered structural motifs are present in irradiated pyrochlore oxides that are arranged such that the structural information from diffraction experiments does not represent the actual local atomic configuration\(^2\). Independent of whether a pyrochlore undergoes an amorphization process during swift heavy ion irradiation (e.g., Dy\(_2\)Sn\(_2\)O\(_7\)) or is disordered to the defect-fluorite structure (e.g., Er\(_2\)Sn\(_2\)O\(_7\)), the short-range structure changes to a weberite-type atomic arrangement\(^2\). This suggests that radiation damage is more complex than previously thought and short-range as well as medium-range analysis with high sensitivity to the anion sublattice must be included in ion-beam studies. The local structural changes induced by ion irradiation of A\(_2\)BO\(_5\) compounds have not been well studied and this work was performed to analyze the amorphization process of Dy\(_2\)TiO\(_5\) across a range of length scales. Swift heavy ions were used to irradiate the material in sufficient quantity for neutron total scattering experiments. The PDFs, produced from the total scattering data, provided information on the local atomic arrangement within the aperiodic phase. The behavior was then compared with the compositionally-related Dy\(_2\)Ti\(_2\)O\(_7\) pyrochlore which also undergoes amorphization under ion irradiation, focusing particularly on changes to the coordination polyhedra and their connectivity.

**RESULTS AND DISCUSSION**

**Long-range structural analysis**

Neutron diffraction data of the Dy\(_2\)Ti\(_2\)O\(_7\) and Dy\(_2\)TiO\(_5\) samples confirm that both starting materials are well crystallized with no discernible impurity phases (Fig. 2). The diffraction data are well-fitted by the expected structures for both samples; the data residual (\(R_w\)) for each is below 5%. After irradiation, both samples display distinct loss of long-range crystallinity evident by reduced peak intensities and strongly increased diffuse scattering (Fig. 2). This agrees well with previous synchrotron x-ray diffraction studies which showed that Ln\(_2\)Ti\(_2\)O\(_7\) and Ln\(_2\)TiO\(_5\) titanate oxides can be readily amorphized by swift heavy ions at room temperature\(^1\)\(^1\)\(^2\)\(^4\). The remaining long-range crystalline phase for each irradiated sample is still well fit using the unirradiated structural model. No peak broadening or shifts are observable, indicative of undamaged pyrochlore with no significant accumulation of defects. The incomplete amorphization in this study can be explained by specifics of the ion-beam experiments. Neutron total scattering experiment requires large sample amounts which can only be achieved by irradiating large areas with a highly defocused beam spot. This may introduce inhomogeneity within the irradiated area and some sample powder may not be fully covered by the ion beam. However, both samples were irradiated under identical beam setting to \(8 \times 10^{12}\) ions/cm\(^2\) and their relative radiation behavior can be compared. Additionally, the scattering information from the unirradiated sample regions can be well separated from those arising from the modified material.
The amorphous background is significantly more pronounced in the Dy₂TiO₅ diffraction pattern with a greater relative Bragg peak-intensity reduction of the remaining crystal-line phase as compared to Dy₂Ti₂O₇. This indicates that the same swift heavy ion irradiation more efficiently amorphizes orthorhombic Dy₂TiO₅, suggesting that the cross-section for amorphization of individual ion tracks is larger than in cubic Dy₂Ti₂O₇. This is in clear contrast to previous studies on these materials using low-energy ions (1 MeV Kr) which demonstrated that within the nuclear energy loss regime A₂TiO₅ compounds are more resistant than corresponding A₂Ti₂O₇ pyrochlore compositions. The long-range behavior observed for Dy₂TiO₅ and Dy₂Ti₂O₇ under swift heavy ion irradiation seems to be a general trend across a range of chemical compositions based on previous published and unpublished data (Fig. 3). Synchrotron x-ray diffraction analysis of A₂TiO₅ and A₂Ti₂O₇ (A = Sm, Gd, and Y) irradiated with 2.2 GeV Au ions under identical conditions shows at each fluence step more pronounced radiation effects for the A₂TiO₅ materials (Fig. 3). This is particularly evident at higher fluences by the diffuse scattering at Q = 1.5–2.5 Å⁻¹ produced by the amorphous phase. These results combined with the present neutron diffraction data consistently show that, within the electronic energy loss regime of swift heavy ions, orthorhombic A₂TiO₅ compounds are more readily amorphized than the corresponding cubic A₂Ti₂O₇ pyrochlore compositions. It remains unclear why this behavior contrasts the response under irradiation with ions of predominantly nuclear energy loss. Previous studies have shown that both nuclear and electronic energy loss regimes induce very similar radiation effects in a range of pyrochlore compositions. It should be noted that ion irradiations in the 

![Synchrotron x-ray diffraction patterns of titanate oxide samples before and after ion irradiation.](image-url)
nuclear energy loss regime utilized mostly in situ TEM characterization on electron transparent samples (typical thickness <100 nm). The increased surface area in such nanofilms can modify damage formation and recovery as compared to the bulk samples used for this study, which may contribute to the reversed relative radiation response of $A_2TiO_5$ and $A_2Ti_2O_7$ compounds under swift heavy ion and low-energy ion irradiation.

**Short-range structural analysis**

The short-range structures of the unirradiated and irradiated samples were characterized through PDF analysis. Using small-box refinement, the local and intermediate structure of pristine, unirradiated Dy$_2$TiO$_5$ from 1.5 to 20 Å (Fig. 4) was well modeled with the orthorhombic structure used for Rietveld refinement of the diffraction pattern ($R_w = 15\%$). Beyond the nearest-neighbor distance of ~3.3 Å, there is a distinct reduction in peak intensity for the irradiated sample compared with the unirradiated material (Fig. 4). Notably, the peak widths, a measure of disorder, do not change significantly outside this range. Thus, the reduction in intensity is equivalent to a significant decrease in peak area consistent with a crystalline-to-amorphous transformation and associated loss of long-range coordination. The peaks that correspond to the nearest-neighbor coordination polyhedra, however, exhibit only subtle changes after ion irradiation. This is in clear contrast to the changes observed in the PDF of irradiated Dy$_2$Ti$_2$O$_7$ (Fig. 5). While the behavior beyond nearest-neighbor distances of ~3 Å is comparable to that of Dy$_2$TiO$_5$, with amorphization evidenced by reduction in peak area and no change to peak width and shape, ion-beam exposure creates distinct modifications to the local atomic arrangement. The PDF of the unirradiated Dy$_2$Ti$_2$O$_7$ can be best described with the $Fd-3m$ pyrochlore structural model. The PDF of the irradiated Dy$_2$Ti$_2$O$_7$ remains consistent with the unirradiated pyrochlore structural model at larger $r$-values (unirradiated sample regions in agreement with diffraction data), but displays significant changes between 2 and 5 Å. The intensity of the negative peak at ~2 Å is reduced, and the distinct peaks at 2.2 and 2.5 Å are replaced with a single peak at 2.3 Å. The peak at 3.0 Å broadens and shifts to lower-$r$. Similar behavior has been previously reported for several irradiation-induced amorphous pyrochlore compositions, and the PDF of irradiated Dy$_2$Ti$_2$O$_7$ can be best modeled in a range up to ~8 Å with a weberite-type atomic arrangement of space group $Ccmm$. Interestingly, the same local structural transformations are also evident in pyrochlore compositions which are radiation resistant but disorder to a defect-fluorite structure over the long-range. The presence of local ordering in amorphized pyrochlores has also been confirmed using EXAFS, Raman spectroscopy, and EELS. The most significant change in the PDF that occurs in irradiated Dy$_2$TiO$_5$ is a decrease in slope near 3.7 Å caused primarily by a shift of the negative peak near 3.4 Å (Fig. 5). Other subtle changes include a small shift of the first three positive peaks and a slight increase in intensity of the second peak near 3 Å. Despite its lower resistance to irradiation-induced amorphization displayed by the Bragg peak response of the long-range structure, Dy$_2$TiO$_5$ has much less structural modifications at the level of the coordination polyhedra than Dy$_2$Ti$_2$O$_7$.

To investigate the subtle changes of the local structure in Dy$_2$TiO$_5$ before and after irradiation in more detail, the PDF of the irradiated sample was modeled with the initial orthorhombic, $Pnma$ structure. This structural model describes well the PDF changes between 1.5 and 8 Å ($R_w = 16\%$), despite minor deviations in peak shape and position. The spatial extent of structural changes to the local structure in Dy$_2$TiO$_5$ is similar to the length scale observed by Shamblin et al. and Chung et al. for radiation-induced weberite-type ordering in amorphized Dy$_2Sn_2O_7$ and Dy$_2Ti_2O_7$, respectively. To gain further insight into these local structural changes, induced by the swift heavy ion irradiation of Dy$_2$TiO$_5$, the partial PDF contributions from each atom–atom pair in the corresponding refinements were calculated (individual peaks positions are indicated by arrows in Fig. 6). The region with the most pronounced changes in the PDF profile ($r$-values between 3 and 4 Å) is a superposition of contributions from 4 distinct atom–atom pairs, making it difficult to unambiguously discern the origin of the observed subtle changes in the PDF before and after ion irradiation. The oxygen–oxygen pair correlations at ~3.0 Å and the Dy–Ti nearest-neighbor correlation at ~3.5 Å appear to have the most noticeable changes. These observations combined with the Dy–O and Ti–O nearest-neighbor correlations remaining mostly unchanged after irradiation, suggest that long-range amorphization in Dy$_2$TiO$_5$ is locally...
accompanied by slight distortions of the coordination polyhedra and modification of the connectivity between these structural building blocks. Nevertheless, the polyhedra stay intact and are resistant to irradiation which explains why locally the orthorhombic structural model still describes the atomic arrangement. The short-range structures in the irradiated and unirradiated samples are two variants of the same structural model. This is in clear contrast to the formation of a weberite-type atomic arrangement in irradiated pyrochlore, which requires distinct changes to the coordination polyhedra. In the fully ordered Dy$_2$Ti$_2$O$_7$ pyrochlore structure, Dy is in eightfold coordination and shares multiple polyhedral edges, while Ti is in sixfold coordination and shares all corners (Fig. 1b). The weberite-type arrangement induced by ion irradiation contains similar eightfold coordinated edge sharing Dy and sixfold coordinated corner sharing Ti, but also has sevenfold coordinated edge sharing mixed cation sites. The orthorhombic Dy$_2$Ti$_2$O$_7$ structure has sevenfold coordinated, edge sharing Dy polyhedra and fivefold coordinated Ti-polyhedra sharing 2 corners (Fig. 1a). The smaller number of shared components in the Ti-polyhedra of Dy$_2$Ti$_2$O$_7$ may result in greater structural stability. Further, the Ti-polyhedra in Dy$_2$Ti$_2$O$_7$ have a lower coordination (5-coordinated) as compared to Ti-polyhedra in Dy$_2$Ti$_2$O$_7$ (6-coordinated), which results in stronger bonds in the former as the excess Ti charge is shared between a smaller number of oxygen atoms. This stronger bond stability within the coordination polyhedra is present under irradiation within the long-range amorphization resistance over the highly transient extreme conditions. It remains unclear why a larger degree of amorphization is observed for the compound that largely maintains the local coordination polyhedra. Structural rigidity in Dy$_2$Ti$_2$O$_7$ may also limit the ability of reconnecting individual atomic building blocks to maintain long-range coherency after disruption by the highly transient radiation regime. Thus, changes to the intermediate-range structure induced by the ion irradiation must play an important role in the radiation response of complex oxides. This is supported by a previous study confirming the same weberite-type atomic arrangement in irradiated pyrochlore whether or not the long-range structure is amorphous (e.g., Dy$_3$Sn$_2$O$_7$) or crystalline but disordered (e.g., Er$_3$Sn$_2$O$_7$). Further studies are needed to systematically characterize the atomic-scale behavior of other complex oxides under swift heavy ion irradiation with the aim to identify the structural pathway and role of medium-range structure in the amorphization process.

The ion-induced atomic-scale changes in both amorphizable materials appear to be subtle in their appearance, but they are indicative of two distinct amorphization processes. While ion-induced modifications occur over picosecond timeframes and neutron measurements are only performed on the fully quenched damaged structure, the present results lead to the following conclusions with regard to amorphization in Dy$_2$Ti$_2$O$_7$: (i) atomic bonds are disrupted and reconnected to form weberite-type coordination polyhedra and (ii) these weberite-type building blocks are randomized across the intermediate-range structure resulting in the loss of long-range coherency. In contrast, (i) appears to be different in Dy$_2$Ti$_2$O$_7$ with only subtle changes to the coordination polyhedra after bond disruption and reconnection. The higher rate of amorphization in this material must be related to a very efficient randomization of the same structural building blocks over the intermediate-range structure. This indicates that ion-induced modifications at the intermediate-range structure play an important role in long-range amorphization by rearrangement of local structural building blocks and the associated loss of their connectivity. Under intense ion irradiation, Dy$_2$Ti$_2$O$_7$ will maintain its long-range structure to much higher ion fluences than Dy$_2$Ti$_2$O$_7$ until it becomes fully amorphous (Figs. 2 and 3). However, the latter performs much better in terms of maintaining the local atomic bonding environment (Fig. 5). The local transformation to weberite-type domains in Dy$_2$Ti$_2$O$_7$ with coexisting pyrochlore domains involve a larger structural mismatch as compared with Dy$_2$Ti$_2$O$_7$ which retains a much more homogenous structural environment during build-up of amorphization. If the same structural behavior is present under irradiation within the nuclear energy loss regime remains an open question. The use of Dy$_2$Ti$_2$O$_7$ as control rod material entails intense neutron irradiation and damage that is more closely related to 1 MeV Kr ion irradiation. The 2.2 GeV Au ion irradiation was chosen in
this study to reach the large sample mass required for neutron characterization. Similar studies should be completed on these materials after irradiation within a nuclear reactor which would also provide access to a sufficiently large amount of irradiated bulk material for neutron characterization. Such experiments would reveal the atomic-scale processes related to amorphization induced in the nuclear energy loss regime, shedding light on the question why $A_2TiO_5$ compounds are more resistant to amorphization under low energy ion irradiation, while $A_2Ti_2O_7$ compounds have a greater resistance when exposed to swift heavy ions.

METHODS

Sample preparation and ion-beam experiments
Polycrystalline dysprosium titanate oxides ($Dy_2TiO_3$ and $Dy_2Ti_2O_7$) were prepared with conventional solid-state methods. Stoichiometric quantities of dysprosium sesquioxide ($Dy_2O_3$) and titanium dioxide ($TiO_2$) powders were obtained from Alpha Aesar (99.9% purity) and mixed in acetone. These mixtures were then formed into pellets with a uniaxial hydraulic press. The as-pressed pellets were sintered at 1200 °C for 20 h, ground into powder, repressed, and heated at 1400 °C for an additional 20 h. The resulting material was subsequently reground into powder for use in ion-beam irradiation and neutron characterization experiments. Laboratory x-ray diffraction was utilized for quality control after synthesis and the obtained starting materials were pure orthorhombic ($A_2TiO_5$) and cubic ($A_2Ti_2O_7$) structures, respectively.

Powders of $Dy_2TiO_3$ and $Dy_2Ti_2O_7$ were pressed into milled cylindrical depressions in aluminum platelets with diameters of 10 mm and depths of 50 μm. Six of these platelets per sample composition were irradiated simultaneously to a fluence of $8 \times 10^{17}$ ions/cm$^2$, with a flux of $1 \times 10^9$ ions/cm$^2$ s chosen to minimize sample heating. Irradiation was performed at room temperature with 2.2 GeV Au ion projectiles and a 5 x 5 cm$^2$ beam spot. The sample mass per holder was determined according to SRIM calculations16 to ensure homogeneous energy deposition throughout the sample (ions completely penetrated the sample platelets). Because the ion energy was in the GeV range, the nuclear energy loss was negligible in comparison to the electronic energy loss (about three orders of magnitude lower). The electronic energy loss per unit path length ($dE/dx$) was nearly identical for both materials with $42 \pm 2$ keV/nm for $Dy_2TiO_3$ and $43 \pm 3$ keV/nm for $Dy_2Ti_2O_7$, assuming a theoretical density of 6.94 g/cm$^3$ for $Dy_2TiO_3$ and 6.87 g/cm$^3$ for $Dy_2Ti_2O_7$ ($dE/dx$ given as average value ± maximum deviation within the chosen sample depth). The sample thickness was limited to ensure full penetration of swift heavy ions utilizing ion-range calculations based on the SRIM code applying a density correction factor. The density of the powder samples was estimated to be 60% theoretical density, a value that has been shown to be an upper limit obtained by uniaxial powder compression at room temperature15. More detailed information regarding the sample preparation and ion irradiation procedure is provided elsewhere16,17. After ion irradiation, the pressed sample compacts were removed from the Al holders with a dull needle and were reground into fine powder with an agate mortar and pestle.

Neutron total scattering experiments and structural analysis
Neutron total scattering experiments were performed on the irradiated and pristine powders at the NOMAD instrument, Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL)13. A total of ~75 mg of each powder was utilized for the neutron measurements using 2 mm diameter quartz capillaries (0.01 mm wall thickness) as sample containment. Measurements were performed at room temperature for 2 h and the $^3$He detectors were calibrated using scattering data from silicon and diamond powder. The scattering data were corrected for multiple scattering and absorption18 and background correction was obtained by subtracting the scattering from an empty 2 mm reference quartz capillary. Details of this process are described elsewhere17. The structure function, $S(Q)$, was created by normalizing the corrected intensity to the scattering intensity from vanadium. The PDF, $G(r)$, was created with STOQ18 using a Fourier transformation of $S(Q)$:

$$G(r) = \frac{2}{\pi} \int_0^{Q_{\text{max}}} Q[S(Q) - 1]\sin Qr dQ$$

(1)

where $Q_{\text{min}}$ and $Q_{\text{max}}$ equaled 0.5 and 26.0 Å$^{-1}$, respectively, for the measurements performed in this study. $Q$ is defined by:

$$Q = \frac{4\pi\sin(\theta)}{\lambda}$$

(2)

where $\theta$ is the scattering angle and $\lambda$ is the neutron wavelength. The average long-range structure of the samples was examined using Rietveld refinement of the diffraction data employing the GSAS-II software package19–21. The expected $Dy_2TiO_3$ orthorhombic structure (space group 62, Pnma) and the expected $Dy_2Ti_2O_7$ pyrochlore structure (space group 227, Fd-3m) for the unirradiated reference materials were obtained from the Inorganic Crystal Structure Database (ICSD). Refinement was performed using the diffraction data from detector banks 3 and 5 of the 6 banks at the NOMAD instrument which provided a balance of $Q$-range and resolution. Sequential structural refinements were performed using a 6 factor Chebyshev background curve, a scale factor, lattice parameters, lattice positions, isotropic thermal displacement parameters subject to the symmetry constraints of the chosen model, and a strain term. Initially, the pristine sample data were refined; then, the refined structure was used as a starting point for the refinement of the irradiated sample data.

The local structure of the samples was analyzed through real-space small-angle refinement using the PDFgui program22 by fitting a structure model to the obtained PDF. The PDF describes the relative probability of interatomic distances compared to that expected for uniformly distributed atoms. Therefore, a positive peak at a distance, $r$, in the PDF arise from pairs of atoms $r$ distance apart. However, titanium nuclei possess a negative neutron scattering length, and thus the Dy-Ti and O-Ti pair correlations manifest as negative peaks in the neutron PDF23. The $Dy_2TiO_3$ small-angle refinements were performed through sequential fits of a scale factor, lattice parameters, lattice position variables, a single isotropic thermal displacement parameter for each element, and an atomic correlation factor. To approximate the amorphous phases, the PDF of the irradiated samples were also refined with the “spjiometer” parameter which corresponds to the spatial extent of the nanoparticle. The $Dy_2TiO_3$ refinements were performed using a scale factor, lattice parameters, lattice position variables, all symmetry-allowed distinct isotropic and anisotropic thermal parameters, and an atomic correlation factor16. The starting structural configuration for each data set was taken from the GSAS-II refinement of the respective long-range structure. For neutron PDF data of ion irradiated samples, alternate phases were investigated as potential models for the post-irradiation local structures. These included a website-type phase (space group Ccmn), as well as some other phases related to the chemical composition of the material (e.g., the cubic F-43m structure for $Dy_2TiO_3$).

DATA AVAILABILITY

The authors declare that all other data supporting the findings of this study are available within the paper. Raw data were generated at the Spallation Neutron Source large-scale facility. Derived data supporting the findings of this study are available from the corresponding author upon request.

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REFERENCES

1. Sinha, A. & Sharma, B. P. Development of dysprosium titanate based ceramics. J. Am. Ceram. Soc. 88, 1064–1066 (2005).
2. Risovany, V. D., Varlachova, E. E. & Soslov, D. N. Dysprosium titanate as an absorber material for control rods. J. Nucl. Mater. 300 (2000) https://doi.org/10.1016/S0022-3115(00)00129-X.
3. Panneerselvam, G. et al. Thermophysical measurements on dysprosium and gadolinium titanates. J. Nucl. Mater. 327, 220–225 (2004).
4. Lee, B.-H., Kim, H.-S., Lee, S.-H. & Sohn, D.-S. Measurement of the thermal properties of gadolinium and dysprosium titanate. Thermochim. Acta 445, 100–104 (2007).
5. Shepelev, Y. F. & Petrova, M. A. Crystal structures of Ln$_2$TiO$_5$ (Ln = Gd, Dy) polymorphs. Inorg. Mater. 44, 1354–1361 (2008).
6. Yang, D. Y. et al. Structural and radiation effect of Er-stuffed pyrochlore Er$_2$(Ti$_2$O$_7$)$_{1-x}$ (0 < x < 0.667), Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 356–357, 69–74 (2015).
7. Subramanian, M. A., Aravamudan, G. & Subba Rao, G. V. Oxide pyrochlores—a review. Prog. Solid State Chem. 15, 55–143 (1983).
8. Exwing, R. C., Weber, W. J. & Lian, J. Nuclear waste disposal-pyrochlore (A2B6O15): nuclear waste form for the immobilization of plutonium and ‘minor’ actinides. J. Appl. Phys. 95, 5949–5971 (2004).
9. Sickafus, K. E. et al. Radiation tolerance of complex oxides. Science 289, 748–751 (2000).
10. Shamblin, J. et al. Probing disorder in isometric pyrochlore and related complex oxides. Acta Mater. 61, 4191–4199 (2013).
11. Zhang, F. et al. Ion-irradiation-induced structural transitions in orthorhombic Ln3Ti2O7. Solid State Chem. 258, 108–116 (2018).
12. Sattonnay, G. et al. Key role of the short-range order on the response of the titane pyrochlore Y2Ti2O7 to irradiation. Phys. Rev. B 94, 224109 (2016).
13. Park, S. et al. Swift-heavy ion irradiation response and annealing behavior of A2TiO5 (A = La, Pr, Nd, Gd, Tb and Dy). J. Solid State Chem. 227, 60–67 (2015).
14. von Dreele, R. B. General structure analysis system (GSAS). Rep. LAUR 86-748 (1986).
15. Tucker, M. G., Keen, D. A., Dove, M. T., Goodwin, A. L. & Hui, Q. RMCPro: a computer program for studying nanocrystals. Comput. Mater. Sci. 75 (2012).
16. Sickafus, K. E. et al. Radiation tolerance of complex oxides. Acta Mater. 61, 4191–4199 (2013).
17. Pauling, L. The principles determining the structure of complex ionic crystals. J. Am. Chem. Soc. 51, 1010–1026 (1929).
18. Lang, M. et al. Unpublished data.