

Synchrotron x-ray diffraction analysis of gadolinium and lanthanum titanate oxides irradiated by xenon and tantalum swift heavy ions

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ABSTRACT

A synthetic cubic pyrochlore, $\text{Gd}_2\text{Ti}_2\text{O}_7$ ($Fd\bar{3}m$) irradiated with swift heavy ions is compared with a compositionally-related composition $\text{La}_2\text{Ti}_2\text{O}_7$ ($P2_1$), which has a monoclinic, layered, perovskite-type structure. Irradiation experiments were performed at the GSI Helmholtz Center with ^{181}Ta ions and ^{129}Xe ions at specific energies of 11 MeV/amu. At these energies the ions pass entirely through the sample thickness of $\sim 40\ \mu\text{m}$. Angle-dispersive synchrotron powder x-ray diffraction (XRD) measurements were completed and an increasing ion-induced amorphization with increasing ion fluence was for both phases. The ion track cross-sections for the radiation-induced crystalline-to-amorphous transformation, as determined from the evolution of the integrated peak intensities as a function of fluence, reveal that $\text{La}_2\text{Ti}_2\text{O}_7$ (track diameter, $d \sim 7.2\ \text{nm}$ with ^{181}Ta and $5.1\ \text{nm}$ with ^{129}Xe) is more susceptible to amorphization than $\text{Gd}_2\text{Ti}_2\text{O}_7$ ($d \sim 6.2\ \text{nm}$ with ^{181}Ta and $4.6\ \text{nm}$ with ^{129}Xe). The radiation response of the two titanate compounds can be understood in the context of their different structures and cation ionic radius ratios r_A/r_B , where the susceptibility of radiation of titanate pyrochlores is proportionate with this radius ratio. The higher electronic linear energy loss of the ^{181}Ta ions as compared with ^{129}Xe ions leads to a consistent increase of volume amorphized per ion in both materials, which manifests as a larger track diameter.

INTRODUCTION

The highly localized energy deposition caused by swift heavy ions with has been used to study the radiation response of two compositionally-related complex oxides. Such energetic ions transfer their energy to the electrons along the ion path via electronic excitation and ionization (electronic energy loss). The deposited energy is subsequently transferred to atoms in the target material through electron-phonon coupling associated with non-radiative decay of electrons from the conduction band, driving the material close to the ion path to far-from-equilibrium states. The energy density produced in many materials near the ion trajectory exceeds the binding energy, leading to complex structural modifications [1]. In many insulators, cylindrical damage zones, or ion tracks, are observed after irradiation if the energy loss exceeds a critical value [2]. The size and damage morphology of tracks depends on the ion linear energy loss, dE/dx and the thermal and electrical properties of the target material [3]. In this study, two compositionally-related compounds, $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$, were chosen as the target materials. $\text{A}_2\text{B}_2\text{O}_7$ -type pyrochlore phases have been identified as potential host matrices for the immobilization of nuclear waste, an application for which their response to ionizing radiation is of significant

relevance [4-6]. The wide range of combinations exhibited by these material, due to flexibility in the A- and B-site cations, make the pyrochlore structure unique with over 500 compositions identified, with a wide range of chemical and physical properties [7,8]. If the A-and B-site cations are chosen such the cationic radius ratio, r_A/r_B , is between 1.46 and 1.78, the compound conforms to an isometric pyrochlore structure-type ($Fd\bar{3}m$, $Z = 8$, $a = 0.9\text{-}1.2\text{nm}$). This is an anion-deficient derivative of the ideal fluorite structure AX_2 ($Fm\bar{3}m$), with one-eighth of the anions replaced by ordered vacancies and two types of cations ordered on the A- and B-sites [8,9]. When r_A/r_B exceeds 1.78, however, such as when lanthanum occupies the A-site in a titanate compound (e.g. $r_A/r_B = 1.92$ for $\text{La}_2\text{Ti}_2\text{O}_7$), the ordered pyrochlore structure is no longer thermodynamically stable and the compound adopts a new structure, a monoclinic-layered perovskite structure ($P2_1$), where layers of TiO_6 periodically repeat with La cations located in the cavities between the TiO_6 octahedra. Previous swift heavy ion studies demonstrated that titanate pyrochlores are generally less stable to swift heavy ion irradiation than pyrochlores with larger B-site cations, such as Zr, and undergo a crystalline-to-amorphous phase transformation, as compared with zirconate pyrochlore that undergo an order-disorder transformation without amorphization [10-12]. In the present work, we report the radiation responses of $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$ irradiated with swift heavy ions of different electronic energy loss. Synchrotron x-ray diffraction was used to study how the structure of the closely related $\text{A}_2\text{B}_2\text{O}_7$ compositions affects the radiation response over a range of energy loss.

EXPERIMENTAL DETAILS

Polycrystalline samples of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ were synthesized by a sol-gel method, the details of which have been reported elsewhere [13]. The calculated densities were 6.56 g/cm^3 for $\text{Gd}_2\text{Ti}_2\text{O}_7$ to 5.82 g/cm^3 for $\text{La}_2\text{Ti}_2\text{O}_7$. All samples were polished down to a thickness of $\sim 40\text{ }\mu\text{m}$. The ion irradiation experiment was performed at the beamline X0 of the UNILAC linear accelerator at the GSI Helmholtz center for Heavy Ion Research in Darmstadt, Germany. At room temperature under vacuum, all samples were entirely exposed to a defocused cm-sized beam of ^{181}Ta and ^{129}Xe ions with kinetic energies of 2.0 GeV and 1.4 GeV, respectively. The projected range of the projectiles was calculated using the SRIM 2008 code [14] and was for each irradiation experiment significantly larger than the sample thickness [Fig. 1]. The two sets of samples were irradiated to fluences in the range of $1\times 10^{10} - 1\times 10^{13}\text{ ions/cm}^2$. Samples were characterized before and after irradiation by angle-dispersive synchrotron powder X-ray diffraction (XRD) measurements performed at the beamline B2 of the Cornell High Energy Synchrotron Source (CHESS) of Cornell University. A mono-energetic beam of 25 keV ($\lambda = 0.496\text{ }\text{\AA}$) with a spot size of $\sim 1\text{ mm}$ was utilized to analyze structural transformations induced by swift heavy ions. Debye diffraction rings were recorded with a Mar CCD detector, and integrated two-dimensional patterns were produced with the Fit 2D software [15]. The contributions of the crystalline and amorphous phases to the XRD patterns were then deduced by a deconvolution procedure in which peak-fitting of the sharp and diffuse diffraction maxima, described in detail elsewhere [12], was used to quantitatively represent amorphous fraction of the two compounds as a function of fluence.

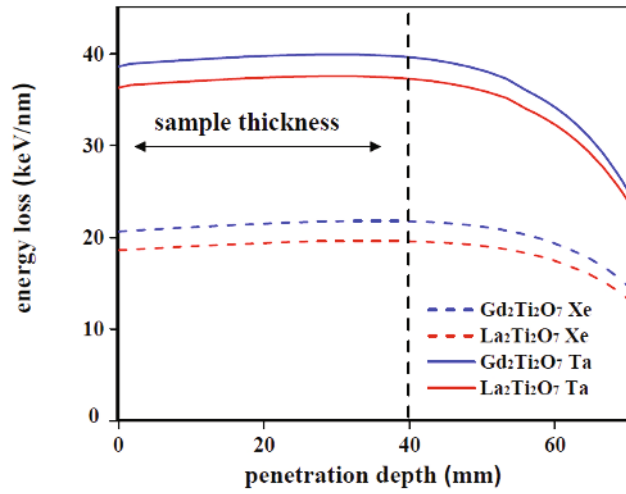


Fig.1. Electronic energy loss of ^{181}Ta and ^{129}Xe ions for $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ as a function of penetration depth calculated with the SRIM-2008 code¹⁴. The energy loss of both ions in both materials is relatively constant across the entire sample thickness, producing uniform ion tracks for analysis.

RESULTS AND DISCUSSION

A series of synchrotron XRD patterns for both compounds, following irradiation to various ion fluences, are displayed in Fig. 2. The unirradiated $\text{Gd}_2\text{Ti}_2\text{O}_7$ has an ordered pyrochlore structure, evinced by the pronounced diffraction maxima of the pyrochlore superstructure, such as those seen at $2\theta \sim 5^\circ$ for (111). These pyrochlore peaks are absent in $\text{La}_2\text{Ti}_2\text{O}_7$, which exhibits a monoclinic perovskite structure at room temperature. After irradiation to the same fluences by the two different ions, XRD spectra of the two compounds reveal the distinct effect of electronic energy loss on their structures (Fig.2). In both compounds, the intensities of all sharp crystalline diffraction maxima are gradually reduced, and the peak width increases greatly with increasing fluence. The diffuse scattering of the amorphous phase also becomes apparent with increasing fluence, especially at $2\theta \sim 9^\circ$, confirming the crystalline-to-amorphous transition induced by swift heavy ion irradiations in agreement with previous studies [10,12]. Full amorphization is achieved for both compositions at the highest fluence achieved (1×10^{13} ions/cm²), which is typical of titanate pyrochlores. This observation was also noted in previous studies, which suggest that the transfer of energy from electrons to atoms leading to the extreme local heating along the ion path can produce amorphous core tracks by rapid quenching [16,17]. Whether such tracks will have crystalline-to-crystalline or crystalline-to-amorphous phase transitions depends on the target material and the energetics and kinetics of the phase transition pathways accessible to them at these high, transient energy densities. While titanate pyrochlores in our study display a crystalline-to-amorphous phase transition, zirconate pyrochlores ($\text{A}_2\text{Zr}_2\text{O}_7$) irradiated with swift heavy ions [10,11] often exhibit a predominantly crystalline-to-crystalline phase transition, in which the materials disorder into a defect-fluorite structure with little or no amorphization. The latter materials are of great interest today as they are promising candidates for nuclear waste management applications where radiation resistance is essential [18]. The absence of order-disorder phase transitions in $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ is a result of their high r_A/r_B values, which is explained below.

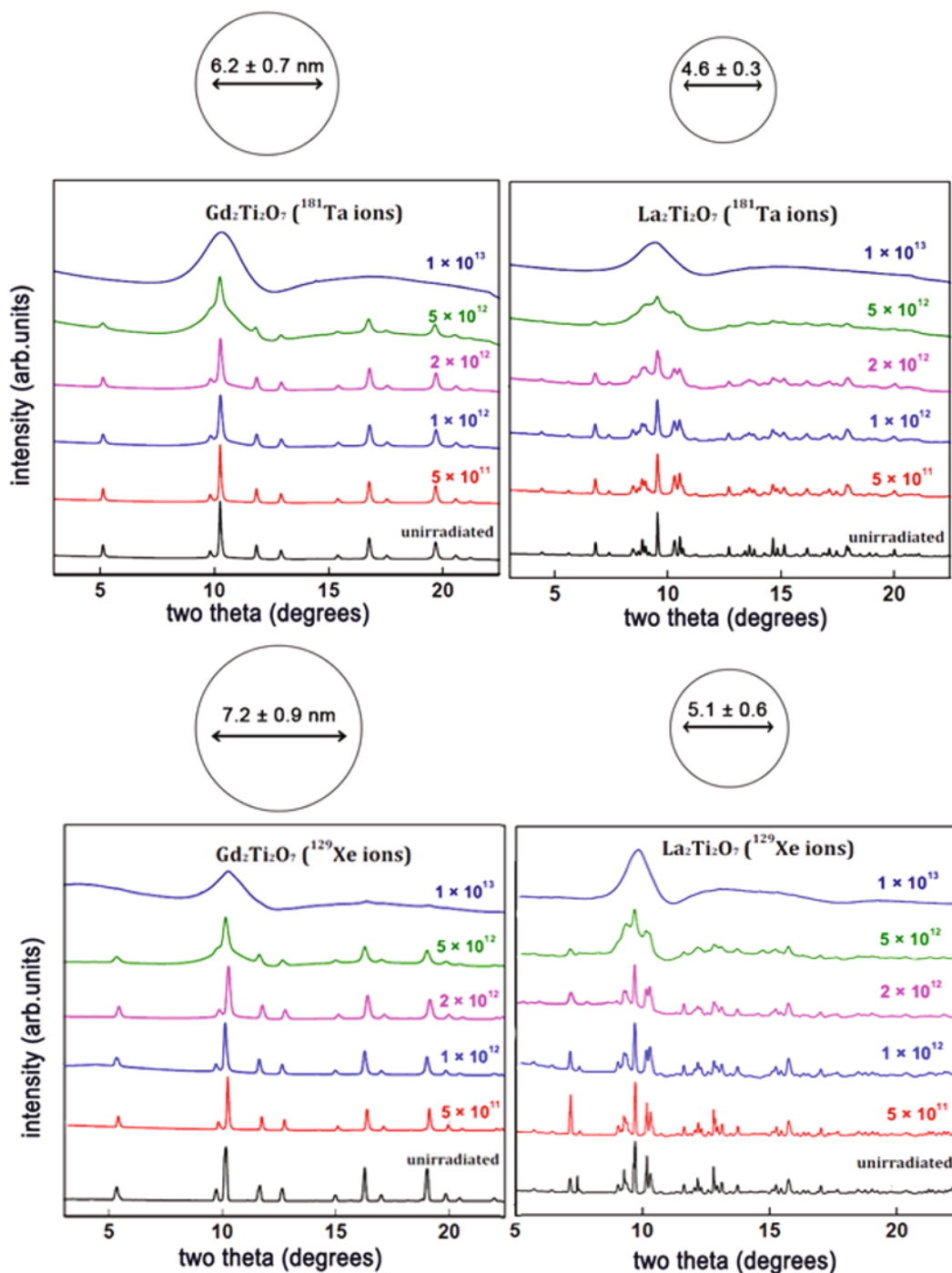


Fig. 2. XRD patterns of two compounds irradiated with ^{181}Ta and ^{129}Xe ions. The sizes of amorphous tracks of both compounds irradiated with the two different ions are represented in circles above the XRD spectra. (color online).

A subtle trend exists that for a given fluence, the amorphous phase fraction is slightly larger in the Ta- irradiated materials as compared with the Xe-irradiated compounds, and the trend is consistent for both $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$. The larger damage from Ta irradiation is more obvious when the XRD patterns are quantitatively analyzed by deconvolution of diffraction

peaks and diffuse scattering from the amorphous phase. The relative amount of the amorphous sample fraction as deduced from the XRD patterns is displayed in Fig 3. Both compounds display an initial linear increase of the amorphous fraction as a function of fluence, followed by saturation as the amorphous tracks begin to overlap. For Ta-ion irradiation, the extent of amorphization for a given fluence is always greater than that of Xe-ion irradiation, which is indicative of larger amorphous tracks produced by Ta-irradiation. Ta-irradiated compounds resulting in bigger track radii compared to the Xe-irradiated ones can be attributed to the difference in the ion energy loss. For $\text{Gd}_2\text{Ti}_2\text{O}_7$, the averaged electronic energy loss, dE/dx , for Ta irradiation is 37 keV/nm, which is higher than that of 28 keV/nm for Xe irradiation. The same trend applies for $\text{La}_2\text{Ti}_2\text{O}_7$, with values of 35 keV/nm for Ta irradiation, and 26 keV/nm for Xe irradiation. With higher dE/dx , Ta-irradiation exhibits a greater ion energy loss, and the increase in energy deposition introduces more damage to a larger volume of the targeted materials.

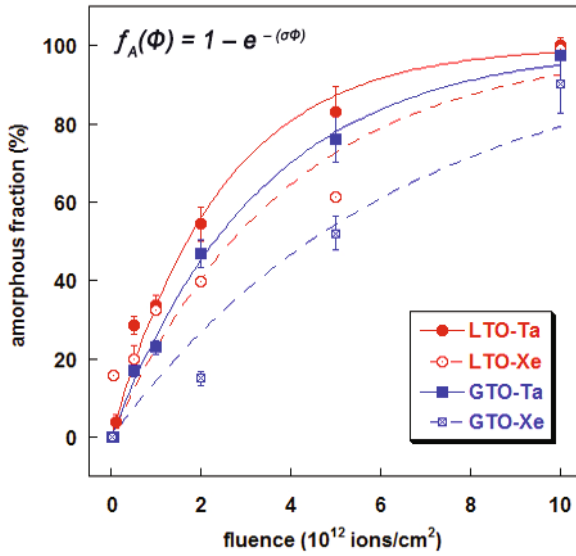


Fig. 3. Amorphous phase fractions deduced from quantitative analysis of XRD patterns as a function of fluence. The error bars indicate the uncertainty from the fitting procedure. (color online)

The evolution of the amorphous fraction in the two compositions can be described by an exponential equation based on a direct-impact model [19]:

$$f_A(\Phi) = 1 - e^{-(\sigma\Phi)}$$

where f_A represents the amorphous fraction as a function of fluence (Φ) and σ is the cross-sectional area of the amorphous track produced by individual swift heavy ions. Fitting the equation to the XRD data of the two compounds helps estimate the cross-section, σ , (and the corresponding diameters) of the ion tracks [Fig.3]. The corresponding effective track diameters, d , of the amorphous track zone, with the assumption of cylindrical track symmetry ($\sigma = \pi (d/2)^2$), is 6.2 ± 0.7 nm and 4.6 ± 0.3 nm for $\text{Gd}_2\text{Ti}_2\text{O}_7$ and 7.2 ± 0.9 nm and 5.1 ± 0.6 nm for $\text{La}_2\text{Ti}_2\text{O}_7$ irradiated with ^{181}Ta and ^{129}Xe , respectively [Fig.2]. Note that the qualitative nature of the method used to determine the amorphous fraction is not a direct comparison of the track diameters as determined using other characterization techniques, such as transmission electron microscopy, that allow for direct imaging of the tracks. However, our results are comparable to the previous studies where the track radii were deduced from transmission electron microscopy in terms of the overall trend of decreasing degree of amorphization attributed to the reduction of the A-site cation size. Furthermore, consistent application of this technique allows for accurate

determination of relative trends in track diameters as is useful in the comparison of the radiation responses of multiple materials. Therefore the relative comparison between the two materials and the two ions is consistent and effectively display the effects of structure and ion stopping power.

For both Ta and Xe irradiation, damage cross sections for $\text{La}_2\text{Ti}_2\text{O}_7$ compared to those of $\text{Gd}_2\text{Ti}_2\text{O}_7$ are greater by $\sim 14 \pm 4 \%$, suggesting that the relative radiation response of both materials is consistent over a range of energy loss. An increase in swift heavy ion irradiation tolerance seen for $\text{Gd}_2\text{Ti}_2\text{O}_7$ can be attributed to its lower r_A/r_B ratio ($r_A/r_B = 1.74$) compared to that of $\text{La}_2\text{Ti}_2\text{O}_7$ ($r_A/r_B = 1.92$) – an observation that is comparable to that found in related pyrochlore compositions [20-23]. This indicates that it is easier for a compound to recover these complex structures when it can accommodate some degree of disorder by having cations that are similar in size (a cation antisite has lower energy when r_A/r_B is smaller). While this has been shown for pyrochlore in which the order-disorder transition occurs [10,11, 21-23], it seems to also be true for structurally distinct complex oxides like $\text{La}_2\text{Ti}_2\text{O}_7$, suggesting that susceptibility to radiation as a function of radius ratio may move beyond the stability field of the pyrochlore structure. The same trend noted for A_2BO_5 compounds further highlight the general feature of r_A/r_B ratio in compositionally-related complex oxides [20].

CONCLUSIONS

The response of a cubic pyrochlore $\text{Gd}_2\text{Ti}_2\text{O}_7$ and a monoclinic-layered perovskite structure $\text{La}_2\text{Ti}_2\text{O}_7$ to swift heavy ion irradiations has been investigated using synchrotron x-ray diffraction. For both Ta and Xe ions irradiations, a consistent behavior was observed in that $\text{La}_2\text{Ti}_2\text{O}_7$ has a higher susceptibility to radiation damage with increasing fluence compared with $\text{Gd}_2\text{Ti}_2\text{O}_7$. This is attributed to cationic radius ratio of the two compounds. $\text{Gd}_2\text{Ti}_2\text{O}_7$, with a lower r_A/r_B , conforms to an ordered, pyrochlore structure that can disorder into a defect-fluorite structure that recrystallizes from the melt region of ion tracks [12], whereas $\text{La}_2\text{Ti}_2\text{O}_7$, with a higher r_A/r_B , forms a monoclinic layered perovskite structure that is more easily damaged upon irradiation due to the less favorable kinetics of ordering and recovery of a melted track region to the crystalline phase. The greater track damage cross sections for Ta-irradiated compounds were noticed and are attributed to the higher energy regime created by Ta, as opposed to Xe, and highlight the dominant role of dE/dx in track formation.

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