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Structural response of titanate pyrochlores to swift heavy ion irradiation



Jacob Shamblin ^{a, b}, Cameron L. Tracy ^c, Rodney C. Ewing ^c, Fuxiang Zhang ^d, Weixing Li ^e, Christina Trautmann ^{f, g}, Maik Lang ^{a, *}

^a Department of Nuclear Engineering, University of Tennessee, Knoxville, TN 37996, USA

^b Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996, USA

^c Department of Geological Sciences, Stanford University, Stanford, CA 94305-2115, USA

^d Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

^e CAS Center for Excellence in Tibetan Plateau Earth Sciences and Key Laboratory of Continental Collision and Plateau Uplift, Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100101, China

^f GSI Helmholtzzentrum für Schwerionenforschung, 64291 Darmstadt, Germany

^g Technische Universität Darmstadt, 64287 Darmstadt, Germany

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ABSTRACT

The structure, size, and morphology of ion tracks resulting from irradiation of five different pyrochlore compositions ($A_2Ti_2O_7$, $A = Yb, Er, Y, Gd, Sm$) with 2.2 GeV ^{197}Au ions were investigated by means of synchrotron X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM). Radiation-induced amorphization occurred in all five materials analyzed following an exponential rate as a function of ion fluence. XRD patterns showed a general trend of increasing susceptibility of amorphization with increasing ratio of A- to B-site cation ionic radii (r_A/r_B) with the exception of $Y_2Ti_2O_7$ and $Sm_2Ti_2O_7$. This indicates that the track size does not necessarily increase with r_A/r_B , in contrast with results from previous swift heavy ion studies on $Gd_2Zr_{2-x}Ti_xO_7$ pyrochlore materials. For $Y_2Ti_2O_7$, this effect is attributed to the significantly lower electron density of this material relative to the lanthanide-bearing pyrochlores, thus lowering the electronic energy loss (dE/dx) of the high-energy ions in this composition. An energy loss normalization procedure was performed which reveals an initial increase of amorphous track size with r_A/r_B that saturates above a cation radius ratio larger than $Gd_2Ti_2O_7$. This is in agreement with previous low-energy ion irradiation experiments and first principles calculations of the disordering energy of titanate pyrochlores indicating that the same trends in disordering energy apply to radiation damage induced in both the nuclear and electronic energy loss regimes. HRTEM images indicate that single ion tracks in $Yb_2Ti_2O_7$ and $Er_2Ti_2O_7$, which have small A-site cations and low r_A/r_B , exhibit a core-shell structure with a small amorphous core surrounded by a larger disordered shell. In contrast, single tracks in $Gd_2Ti_2O_7$ and $Sm_2Ti_2O_7$, have a larger amorphous core with minimal disordered shells.

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1. Introduction

Oxides with the pyrochlore structure have the general formula $A_2B_2O_7$ with the A- and B-site cations being 8- and 6-fold coordinated with O, respectively [1,2]. Edge-sharing between these scalenohedra and distorted octahedra yields a cubic unit cell. The crystallography of pyrochlores (Fd-3m space group) is often described as a superstructure with a unit cell composed of eight

fluorite-structure (AX_2) unit cells, but with one eighth fewer anions (a metal:oxygen ratio 4:7 vs. 1:2) resulting in a constitutional vacancy at the 8a Wyckoff position and A- and B-site cations residing at 16d and 16c sites respectively [3,4]. A-site cations typically have an ionic radius of approximately 1 Å while B-site cations are smaller, with ionic radii of approximately 0.6 Å. The ratio of A- to B-site ionic radii (r_A/r_B) governs the structural stability of these compounds, with $A_2^{3+}B_2^{4+}O_7$ -type oxides stable in the ordered pyrochlore structure only when $1.46 \leq r_A/r_B \leq 1.78$ [1,2]. Compositions with an r_A/r_B below this stability range instead adopt a disordered, defect-fluorite structure, while those above form a

* Corresponding author.

E-mail address: mlang2@utk.edu (M. Lang).

monoclinic, layered perovskite-type structure. Owing to their chemical versatility, structural flexibility, and unique defect dynamics, pyrochlores have been extensively investigated for a wide range of applications, including electrolytes in solid oxide fuel cells and nuclear waste forms for the immobilization of Pu and other actinides [5–7]. Ion-beam irradiation experiments are particularly useful for the study of nuclear applications of pyrochlores as they simulate, on short time frames, the effects of self-irradiation of actinide-bearing compounds with, for example, the energetic nuclear fragments produced from fission events.

High-velocity ion projectiles (specific energies above ~ 1 MeV/u) transfer their kinetic energy to a material by electronic excitation and ionization processes [8]. In many insulators, this results in dense concentrations of high-energy electrons and holes within a cylindrical volume around the ion's trajectory. These charge carriers interact with the relatively low-energy atoms over 100 fs–1 ps time-scales driving both subsystems towards equilibrium. Such interactions are complex and not well understood, but proposed mechanisms for the transfer of energy from the electron-hole plasma to the atomic system include the modification of inter-atomic potentials due to the promotion of electrons from bonding to antibonding orbitals, as well as the recombination of electrons with holes via electron-phonon coupling, which locally heats the material ("thermal spike"). This transfer of energy to the atomic subsystem can lead to very high local energy densities (several eV/atom), which cause the displacement of atoms from their initial positions, leading to a wide range of structural modifications. Above a critical ion energy-loss threshold, in many compounds a cylindrical damage region is formed along the paths of each individual ion known as ion track.

Swift heavy ion tracks in pyrochlores are complex and often consist of several distinct, concentric damage zones (*i.e.*, amorphous track core, with disordered fluorite and defect-rich pyrochlore shells) [3,9–11]. The pyrochlore cation ionic radii ratio (r_A/r_B) directly influences the stability of the pyrochlore phase relative to metastable defect-fluorite and amorphous phases, and in turn susceptibility of these materials to irradiation-induced loss of the ordered structure of pyrochlore. More radiation resistant compositions (smaller r_A/r_B) tend to disorder under irradiation to a defect-fluorite structure, but still maintain their crystallinity, while more susceptible compositions (larger r_A/r_B) tend to amorphize [6,10,12,13]. For compositions with intermediate radiation tolerance, the relative cross-sectional areas of the amorphous track core and disordered track shell vary with the cation ionic radius ratio. From a structural point of view, variation in r_A/r_B strongly affects the ability of these materials to incorporate defects into their structure, which is governed by the defect formation energy [12]. If the antisite formation energy is small (A- and B-site cations of similar size, minimizing the structural distortion associated with their site exchange), the cations can readily exchange sites. Along with the displacement of oxygen to 8a constitutional vacancies, this yields a disordered, defect-fluorite structure. When the antisite formation energy is too high (*i.e.*, the A-site cation is significantly larger than the B-site cation), a disordered phase incorporating these defects becomes energetically unfavorable relative to an amorphous phase and the long-range, atomic-scale periodicity of the structure is lost.

The r_A/r_B dependence of pyrochlore radiation tolerance has been confirmed experimentally for irradiations with both low-energy ions (which deposit energy to a material *via* elastic nuclear collisions) [6,13,14] and high-energy ions (which deposit energy *via* electronic energy loss) [3,9,15–17]. Pyrochlore compounds with relatively large B-site cations (smaller r_A/r_B), such as zirconium, tend to disorder in response to irradiation while those with smaller B-site cations (larger r_A/r_B), such as titanium, instead become

amorphous [3,7,9–11,13]. For swift heavy ions, in particular, the relevance of this point defect-based description to phase behavior within the ion-solid interaction regions is unclear, considering the dense ionization and extreme energy densities typical of the transient energy deposition and "heating" processes. Recent complementary experimental characterizations and molecular dynamics (MD) simulations have shown that the complex track structure may be the result of the rapid quenching of a previously molten phase [18–20]. Formation of the high-temperature defect-fluorite polymorph, that is thermodynamically accessible for low r_A/r_B compounds, is kinetically favored during the quenching process, compared with the more highly-ordered pyrochlore phase. Formation of the disordered phase is energetically unfavorable for compounds with a large r_A/r_B , resulting in amorphization. The diffusion of thermal energy in the radial track direction during quenching and the stabilizing effect of the liquid-solid interface at the track edge on the epitaxial formation of the defect-fluorite phase leads to the unique core-shell morphology of ion tracks in pyrochlore materials.

The size and damage morphology of ion tracks in insulators depends on the energy loss (dE/dx) [3,10], ion velocity [21], and the chemical composition of the target [11,13,22]. For pyrochlores in particular, the effect of chemical composition has typically been studied by replacing the B-site cation to alter the r_A/r_B [3,9–11,20,23]. The $Gd_2Zr_{2-x}Ti_xO_7$ solid solution series ($1.46 \leq r_A/r_B \leq 1.74$) has been extensively studied and the size of the amorphous track core has been shown to decrease as smaller Ti is replaced by larger Zr at the B-site [3,9–11]. The smaller amorphous cores in Zr-rich compositions are surrounded by larger defect-fluorite shells. While the effects of B-site cation substitution are well studied, the effect of changes to the A-site composition has not been adequately addressed. In this systematic study, we investigate the response of the $A_2Ti_2O_7$ ($A = Yb, Er, Y, Gd, \text{ and } Sm$) series to 2.2 GeV ^{197}Au ion irradiation with particular emphasis on amorphization resistance and track morphology.

2. Experimental procedure

Polycrystalline samples of $A_2Ti_2O_7$ ($A = Yb, Er, Y, Gd, \text{ and } Sm$) were investigated to cover a range of r_A/r_B , providing a steady, incremental change in A-site cation ionic radii due to lanthanide contraction. Yttrium was included to assess the importance, if any, of lanthanide 4f orbitals to the radiation response. The pyrochlore samples were synthesized *via* the solid-state reaction method from the binary oxides (A_2O_3 and TiO_2). Powders were mixed using a mortar and pestle in an acetone slurry and pressed into pellets with a hydraulic press, which were fired at 1200 °C for 20 h. The pellets were then reground, pressed, and fired at 1400 °C for an additional 20 h. The final pellets were ground into fine powders (grain size ~ 1 μm) and uniaxially pressed into 40- μm thin platelets with a hydraulic press (surfaces were approximately 3 mm in diameter). The samples were then sintered in a furnace for 24 h at 800 °C to stabilize the platelets and remove any adsorbed water. All starting samples were characterized prior to irradiation by X-ray diffraction. Analysis showed that all compositions contained only the pyrochlore phase with no observable impurities. The irradiation experiments were completed at room temperature at the X0 beamline of the UNILAC linear accelerator at the GSI Helmholtz Center in Darmstadt, Germany using 2.2 GeV ^{197}Au ions. Irradiation was performed for nine ion fluences ranging from 5×10^{10} to 3×10^{13} ions/cm². The projected range for the ^{197}Au ions was determined using the Stopping Power and Range in Matter code (SRIM) and was about 20 μm larger than the 40 μm thickness for all samples (Fig. 1) [24]. The energy loss (dE/dx) due to nuclear collisions is several orders of magnitude less than the electronic energy

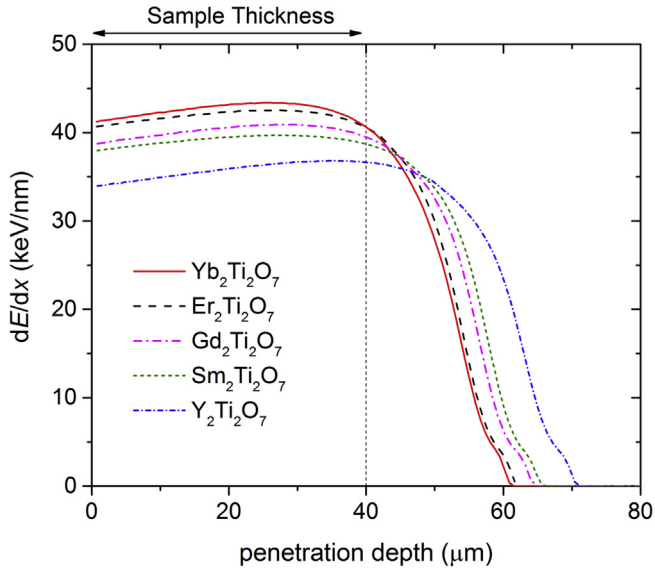


Fig. 1. Electronic energy loss (dE/dx) of 2.2 GeV ^{197}Au ions as a function of ion penetration depth in various titanate pyrochlores. Note that the dE/dx in $\text{Y}_2\text{Ti}_2\text{O}_7$ is noticeably reduced due to its relatively low density (Table 1). The vertical dashed line represents the thickness of the samples used in this study, showing that all ions passed completely through these samples with relatively constant electronic energy loss.

loss across the entire sample and was therefore neglected. The mean electronic dE/dx for all compositions and the variation over the 40- μm thick samples were determined with the SRIM code assuming theoretical density and are summarized in Table 1 and displayed in Fig. 1. The plot shows that ions passed through with nearly constant energy loss. The actual density can be assumed to be lower but this does not significantly affect the energy loss within the grain and only extends the range [25].

The B2 beam line at the Cornell High Energy Synchrotron Source (CHESS) at Cornell University was utilized for angle-dispersive powder XRD measurements. The beam energy was 25 keV ($\lambda = 0.496 \text{ \AA}$) with a spot size of 0.5 mm. All samples were measured in transmission mode and the Debye diffraction rings were recorded using a MAR CCD detector. The two-dimensional MAR images were processed into one-dimensional X-ray diffraction patterns using the FIT2D software [26]. The XRD pattern analysis was completed using the software DatLab [27] focusing on the determination of the fluence-dependent crystalline and amorphous phase fractions. Relative amorphous sample fractions were determined by deconvoluting the XRD patterns into both crystalline (consisting of ordered pyrochlore and disordered, defect-fluorite) and amorphous contributions following a methodology that has been previously described in detail by Lang *et al.* [23]. XRD patterns were analyzed with pseudo-Voigt functions that were fit to the Bragg peaks from crystalline contributions and to the diffuse scattering bands from the amorphous sample regions. A sixth-order polynomial was used to describe the background

evolution, which was subtracted from the pattern. A semi-quantitative assessment of the amorphous fraction was then obtained by taking the ratio of the area from the amorphous scattering bands to the total integrated intensity of the diffraction pattern (amorphous and crystalline). This approach is not an absolute measure of the amorphous sample fraction as the intensity from the amorphous phase is widely spread out over all scattering angles, and is partly discarded in the background subtraction. This peak deconvolution method therefore yields amorphous fractions that are in general smaller than what is measured by other techniques. However, the relative increase of the amorphous phase can still be accurately compared between compositionally and structurally related materials.

High-resolution transmission electron microscopy images (HRTEM) were taken in a FEI Tecnai G2 F20 X operated at 200 keV at Stanford University to study the morphology of ion tracks in $\text{Sm}_2\text{Ti}_2\text{O}_7$, $\text{Y}_2\text{Ti}_2\text{O}_7$, $\text{Er}_2\text{Ti}_2\text{O}_7$, and $\text{Yb}_2\text{Ti}_2\text{O}_7$. HRTEM images were recorded under top-view conditions with the electron beam parallel to both the ion tracks and a major zone axis of the sample. The fluence for TEM samples was limited to 3×10^{11} ions/ cm^2 to prevent track overlap. The samples were thinned down for TEM studies by polishing and subsequent ion milling from the surface opposite to the ion irradiation. Tracks in all studied materials are very stable when subjected to electron beams at low magnifications and even in HRTEM mode. Therefore, sample modification due to the electron beam can be neglected.

3. Results

3.1. Synchrotron X-ray diffraction

Radiation-induced amorphization is evident in the XRD patterns by the reduced intensity of the crystalline diffraction maxima and a simultaneous increase of diffuse scattering bands with increasing ion fluence. These scattering bands, arising from the amorphous phase, are centered at $2\theta \approx 9.5^\circ$, $2\theta \approx 15^\circ$, and $2\theta \approx 19^\circ$ (see corresponding patterns in Fig. 2; the third scattering band was omitted for clarity). The onset of amorphization in the XRD patterns is first evident at a fluence of 1×10^{12} ions/ cm^2 for A = Sm, Gd, Er, and Yb and 2×10^{12} ions/ cm^2 for A = Y. It is difficult to qualitatively determine a trend across the lanthanide titanate series as the variation in radiation response with composition is minor. However, the ratio of amorphous to crystalline scattering intensity is, at any given fluence, greater for A = Sm, Gd than for Er, Yb. This is most evident at an ion fluence of 5×10^{12} ions/ cm^2 , for which $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$ show a more pronounced diffuse contribution to the (222) peak relative to $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$ (Fig. 2). Unlike the larger lanthanide A-site cations, $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$ also show some residual crystallinity at an ion fluence of 8×10^{12} ions/ cm^2 , as indicated by a sharp shoulder within the broad amorphous peak. These results show that amorphization proceeds more rapidly with increasing fluence when larger cations (Gd and Sm) occupy the pyrochlore A-site instead of smaller cations (Yb and Er). $\text{Y}_2\text{Ti}_2\text{O}_7$, which has an A-site cation ionic radius

Table 1

Chemical composition, ratio of cation ionic radii (r_A/r_B), unit cell parameter (a), calculated density (ρ_{calc}), electronic energy loss (dE/dx), extracted amorphous track diameters (XRD d_a), and track diameters normalized by $(dE/dx)^2$ for (Normalized XRD d_a) for titanate pyrochlores studied.

Composition	r_A/r_B	$a = b = c \text{ (\AA)}$	$\rho_{\text{calc}} \text{ (g/cm}^3\text{)}$	$(dE/dx) \text{ (keV/nm)}$	XRD $d_a \text{ (nm)}$	Normalized XRD $d_a \text{ (} 10^{-3} \text{ nm}^3/\text{keV}^2\text{)}$
$\text{Yb}_2\text{Ti}_2\text{O}_7$	1.63	10.23130(6)	6.87	42.5 ± 0.7	5.66 ± 0.46	3.13 ± 0.27
$\text{Er}_2\text{Ti}_2\text{O}_7$	1.66	10.28530(6)	6.61	41.8 ± 0.6	5.70 ± 0.45	3.26 ± 0.26
$\text{Y}_2\text{Ti}_2\text{O}_7$	1.68	10.3004(2)	4.69	35.7 ± 0.9	4.62 ± 0.40	3.62 ± 0.34
$\text{Gd}_2\text{Ti}_2\text{O}_7$	1.74	10.3861(1)	6.18	40.2 ± 0.6	6.23 ± 0.47	3.85 ± 0.30
$\text{Sm}_2\text{Ti}_2\text{O}_7$	1.78	10.4482(1)	5.92	39.1 ± 0.5	5.90 ± 0.51	3.86 ± 0.34

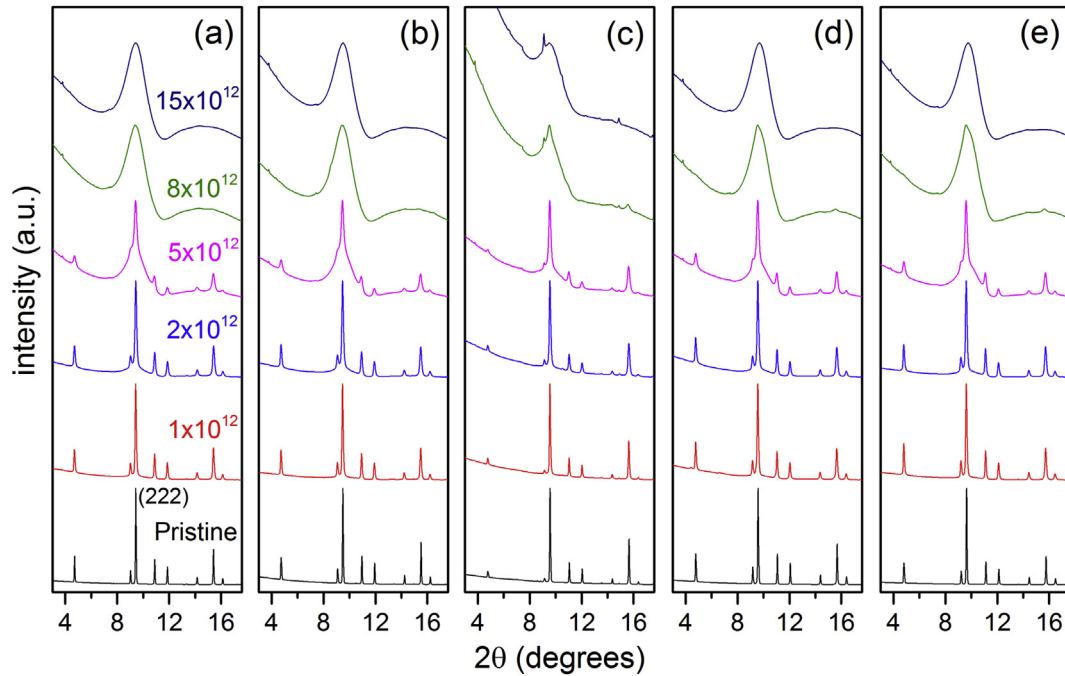


Fig. 2. Synchrotron XRD patterns for (a) $\text{Sm}_2\text{Ti}_2\text{O}_7$, (b) $\text{Gd}_2\text{Ti}_2\text{O}_7$, (c) $\text{Y}_2\text{Ti}_2\text{O}_7$, (d) $\text{Er}_2\text{Ti}_2\text{O}_7$ and (e) $\text{Yb}_2\text{Ti}_2\text{O}_7$ before and after irradiation with 2.2 GeV Au ions to various ion fluences (all units are ions/cm²). All patterns were normalized to the same maximum intensity. The upturn in intensity at low 2θ in the high fluence samples is due the unscattered beam near the beamstop. This is much more prominent in high fluence 4 patterns and all patterns from $\text{Y}_2\text{Ti}_2\text{O}_7$ due to the weaker scattering from the amorphous phase and yttrium relative to the lanthanides, respectively.

between Sm and Yb, was by far the most radiation tolerant composition of the series. This is likely due to its significantly lower density, and thus smaller dE/dx , relative to the other compositions studied (see Table 1).

Concomitant with amorphization, the widths of the diffraction maxima also increase significantly with ion fluence (Fig. 3). Peak broadening can be caused by either irradiation-induced grain fragmentation (size broadening) or by the production of defects in the crystalline fraction that distort the local structure (strain broadening) [28]. There is no clear relation between peak broadening and dE/dx or r_A/r_B , however, it is most prominent in $\text{Sm}_2\text{Ti}_2\text{O}_7$

(largest r_A/r_B) and least prominent in $\text{Y}_2\text{Ti}_2\text{O}_7$ (smallest dE/dx). There is also considerable unit cell expansion as indicated by a shift in the diffraction peaks to lower 2θ with increasing ion fluence (the (222) peak is shown in Fig. 4). Interestingly, the first-order amorphous peak (centered at $2\theta \approx 9.5^\circ$) becomes evident at a 2θ value that corresponds to the position of the (222) maximum in the pristine samples of $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$ but at a higher 2θ in $\text{Er}_2\text{Ti}_2\text{O}_7$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$ (Fig. 4). The position of the amorphous bands directly relates to the mean interatomic spacing within the aperiodic array. An increase in scattering angle indicates that atoms are more tightly packed. This suggests that the relative density change associated with the crystalline-to-amorphous transition in $\text{Er}_2\text{Ti}_2\text{O}_7$

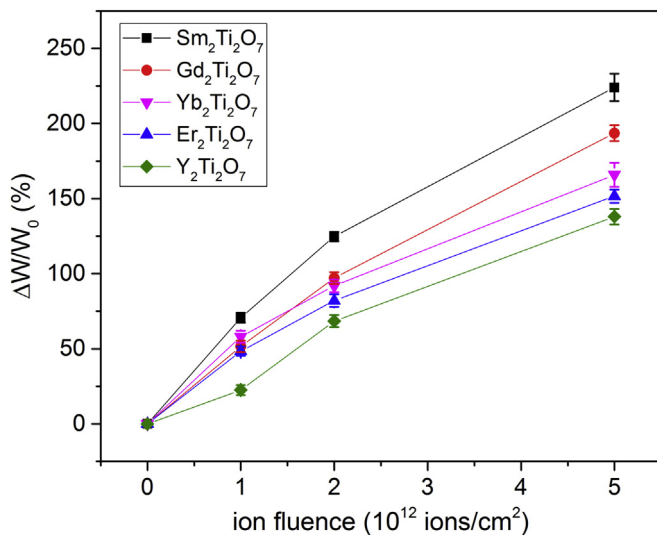


Fig. 3. The relative change in width of the (222) Bragg peak increases as a function of ion fluence for all compositions studied.

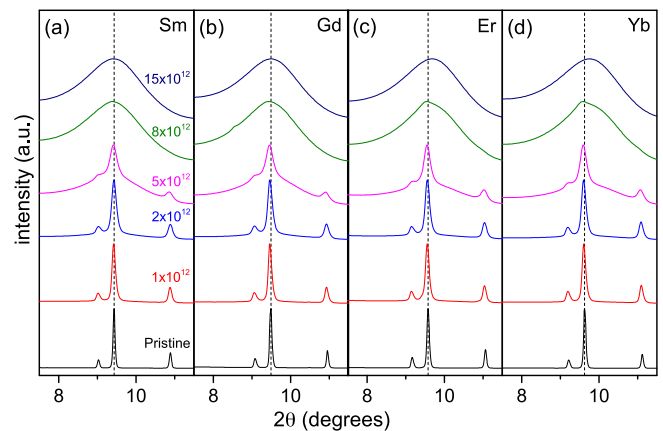


Fig. 4. XRD patterns illustrating the development of the first-order amorphous scattering band for (a) $\text{Sm}_2\text{Ti}_2\text{O}_7$, (b) $\text{Gd}_2\text{Ti}_2\text{O}_7$, (c) $\text{Er}_2\text{Ti}_2\text{O}_7$, and (d) $\text{Yb}_2\text{Ti}_2\text{O}_7$. The ion fluence has units of ions/cm². The vertical dashed lines denote the centroid of the (222) Bragg peak in the pristine samples. The amorphous phase develops at the same scattering angle as the pristine (222) peak for A = Sm and Gd but at higher 2θ for A = Er and Yb.

and $\text{Yb}_2\text{Ti}_2\text{O}_7$ could differ from that in $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$.

In order to obtain a quantitative understanding of the amorphization process, the XRD patterns were deconvoluted into amorphous and crystalline contributions. The amorphous phase fraction of all compositions initially increases linearly with ion fluence, then begins to saturate at higher fluences (illustrated for $\text{Gd}_2\text{Ti}_2\text{O}_7$ in Fig. 5). This fluence dependence is indicative of a direct-impact damage accumulation process [29], which can be modeled by:

$$f_a(\Phi) = A_{\max}(1 - e^{-\sigma\Phi}) \quad (1)$$

with f_a corresponding to the amorphous fraction, σ the cross-sectional area of the amorphous portion of each ion track, Φ the ion fluence, and $A_{\max}$ the saturation amorphous phase fraction, which was fixed at unity. This model represents a damage production mechanism wherein each ion creates an amorphous track as it traverses the target material. With increasing fluence, tracks begin to overlap, eventually leading to complete amorphization of the pyrochlore sample. Alternative models have been proposed for swift heavy ion effects in pyrochlores to account for the overlap of complex track structures with core-shell morphologies [17]. However, the overall trend of the results presented here is in good agreement with a single-impact model. Track diameters were determined using cross-sectional areas extracted from fitting Eq. (1) to the data assuming cylindrical ion-track geometry:

$$\sigma = \pi\left(\frac{d}{2}\right)^2 \quad (2)$$

with d being the effective amorphous track diameter. Uncertainties were calculated by propagating the errors reported through the fitting procedure for multiple deconvolutions. The fitting results for all pyrochlore compositions are summarized in Table 1 and displayed in Fig. 6.

The amorphous track diameter varies with the size of the A-site

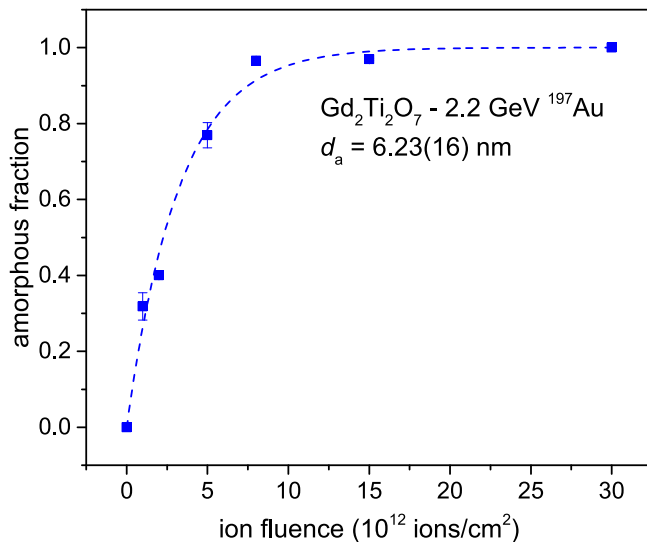


Fig. 5. Amorphous phase fractions for $\text{Gd}_2\text{Ti}_2\text{O}_7$ as a function of ion fluence, extracted from peak deconvolution of XRD patterns. The dashed line represents a fit of the single impact model [Eq. (1)] to the data points. Because all compositions showed complete amorphization at 3×10^{13} ions/cm², the saturation fraction in Eq. (1) was fixed at 1 for all fits. Assuming cylindrical symmetry, the amorphous track diameter extracted from this fitting is 6.2 ± 0.16 nm. Error bars are calculated from multiple deconvolutions at each given fluence and are smaller than the symbols at some points.

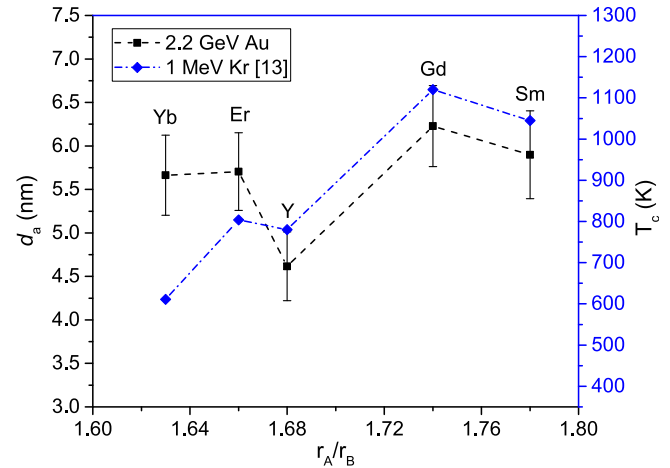


Fig. 6. Amorphous track diameters measured from the peak-fitting procedure for each pyrochlore composition as a function of the cation ionic radii ratio (r_A/r_B) in the present study using 2.2 GeV Au ions (black squares, left axis) and critical amorphization temperatures for the same compounds determined by Lian *et al.* using 1 MeV Kr ions (blue diamonds, right axis) Ref. [13]. Both studies show similar dependence of radiation tolerance on r_A/r_B despite differing energy loss mechanisms (purely electronic vs. mixed electronic/nuclear). $\text{Gd}_2\text{Ti}_2\text{O}_7$ was the most susceptible to amorphization of any composition in either study. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cation with an average diameter that linearly increases as a function of the ionic radius ratio r_A/r_B for $A = \text{Yb}$, Er , and Sm . Two compositions, $\text{Y}_2\text{Ti}_2\text{O}_7$ and $\text{Gd}_2\text{Ti}_2\text{O}_7$, however, fall significantly outside of this trend with appreciably smaller tracks in $\text{Y}_2\text{Ti}_2\text{O}_7$ and larger tracks in $\text{Gd}_2\text{Ti}_2\text{O}_7$. The deviation of $\text{Y}_2\text{Ti}_2\text{O}_7$ can be explained by its large difference in electron density, relative to the other compounds investigated, and the corresponding effect on the electronic dE/dx of the 2.2 GeV Au ions (Table 1). The calculated density is much lower for $\text{Y}_2\text{Ti}_2\text{O}_7$, which leads to a reduced dE/dx across the entire sample thickness as electronic stopping power is directly proportional to target electron density (Fig. 1). This makes compositional analysis quite difficult as even small density variations from one composition to another can cause a relatively large change in amorphous track diameter.

The effect of dE/dx on track size is generally a material-dependent, complex relationship [30,31], but it has been previously shown for $\text{Gd}_2\text{Ti}_2\text{O}_7$ that the diameter of amorphous tracks monotonically increases with the electronic energy loss with approximately $d_a \propto (dE/dx)^2$ dependence (Fig. 7) [3]. Assuming this relation holds for other titanate pyrochlores, it is reasonable to divide the amorphous track diameter extracted through XRD analysis by $(dE/dx)^2$ to effectively normalize the amorphous diameter by the energy loss (Fig. 8). This normalization excludes the effects of dE/dx on track diameter data allowing for direct comparison of the response of two compounds to the deposition of a specific amount of energy. The normalized amorphous track diameter increases monotonically within the r_A/r_B range studied but saturates at high r_A/r_B (Fig. 8).

3.2. High-resolution transmission electron microscopy

High-resolution transmission electron microscopy (HRTEM) images confirm the existence of an amorphous phase within single ion tracks for all compositions studied, consistent with the single-impact model for amorphization. However, the ion track morphology differs significantly among the different compositions (Fig. 9). Cross-sectional imaging shows that tracks in $\text{Yb}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ consist of an amorphous core, indicated by the aperiodic

contrast in the center region of the track, surrounded by a crystalline shell with a structure different from the pyrochlore matrix (the dark ring observed in $\text{Yb}_2\text{Ti}_2\text{O}_7$ is likely caused by strain contrast). Previous experimental and computational investigations have shown that the track shell consists primarily of the disordered, defect-fluorite structure [9,18,32]. This is evident by the epitaxial relation between the defect-fluorite shell with the pyrochlore matrix. $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{O}_7$ display larger amorphous tracks with only a minimal disordered shell observed in $\text{Gd}_2\text{Ti}_2\text{O}_7$. In $\text{Y}_2\text{Ti}_2\text{O}_7$ (not shown) tracks are inhomogeneous consisting of amorphous and disordered regions distributed throughout the ion track cross section.

4. Discussion

4.1. Susceptibility to radiation-induced amorphization

Both XRD and HRTEM analysis show a consistent trend of an increasing amorphous volume produced within an ion track in the lanthanide pyrochlores as a function of increasing r_A/r_B with the exception of $\text{Sm}_2\text{Ti}_2\text{O}_7$. XRD analysis reveals that $\text{Gd}_2\text{Ti}_2\text{O}_7$ has the largest amorphous track diameter (before dE/dx normalization) of any composition studied. The amorphous track diameters extracted through XRD analysis are smaller than those measured with HRTEM for all compositions studied. This is not surprising for reasons described earlier and is consistent with previous studies employing the peak deconvolution method for determining amorphous fractions [3,9,33]. An alternative method for analyzing the amorphous fraction using XRD, described in detail in Ref. [11], involves consideration of only the relative change in crystalline peak area before and after irradiation of the same sample. This approach however, assumes that *all* reduction in Bragg peak area can be attributed to amorphization, which is not fully accurate. Heating a sample will also result in reduced diffraction peak area in the absence of amorphization due to the influence of the Debye-Waller factor [34,35]. In this case, atomic vibrations reduce the periodicity of even a perfect crystal, which lowers the area of Bragg peaks. In addition, local deviations from the average structure (point defects, local distortions, etc.) can also lead to reduced Bragg peak area without amorphization [36,37]. In general, many of the

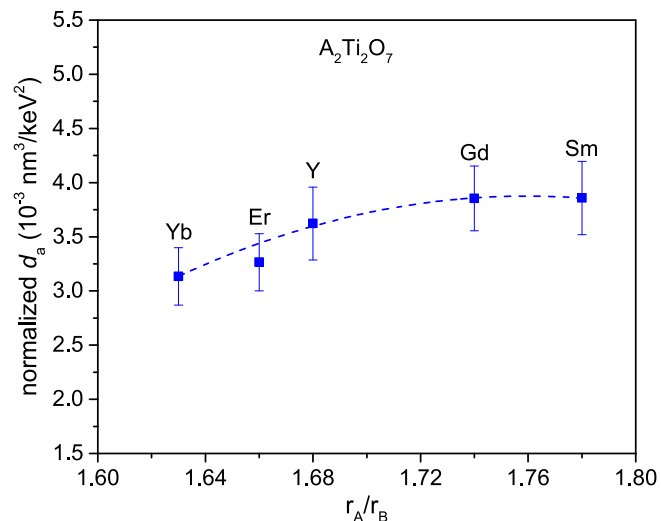


Fig. 8. Amorphous track diameters normalized by $(dE/dx)^2$. The nonlinear dependence on r_A/r_B is in agreement with disordering energy calculations in [39]. The dashed line is a guide to the eye. Error bars were calculated by propagating the variance in dE/dx through the sample with the errors from the peak fitting procedure.

electrons excited during ion-solid interactions travel far beyond the central track region before relaxation, such that a defect-rich halo can be expected within otherwise undamaged pyrochlore matrix [8,9]. These defects also reduce the area of Bragg peaks in the XRD data but are not directly associated with the ion track diameter. As a result, neither approach (described in Ref. [11] or peak deconvolution presented here) gives an absolute diameter value from XRD data that is directly comparable to HRTEM images, but the relative trend among the different compositions should be quite reliable. In fact, even HRTEM images may not fully reflect the actual track size as MD simulations have shown that amorphous ion tracks can be heterogeneous along the ion trajectory [38]. Other contributions to TEM contrast, such as that from strain, can also be misinterpreted as amorphous material. Many tracks must be measured in order to get statistically meaningful information on the amorphous diameter, which is very difficult to obtain with HRTEM images particularly on polycrystalline samples. For this reason, HRTEM was only used to characterize the damage morphology while XRD was used to study the *relative* changes in amorphous track diameter with composition.

Radiation-induced amorphization in the $\text{A}_2\text{Ti}_2\text{O}_7$ series has been previously studied with 1-MeV Kr^+ ions as a function of fluence and irradiation temperature [13]. Kr ions at this specific energy deposit their kinetic energy by electronic as well as nuclear energy loss. For our study, the most relevant information from this irradiation is the critical amorphization temperature, T_c , which is defined as the temperature above which a sample can no longer be amorphized under continuous irradiation due to dynamic defect annealing. Compositions with a higher T_c are considered to be more prone to radiation-induced amorphization. Although critical amorphization temperatures for low-energy ion irradiations and amorphous track diameters from swift heavy ion irradiations are not directly comparable, a similar r_A/r_B dependence was revealed for both parameters and energy-loss regimes (Fig. 6). $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Y}_2\text{Ti}_2\text{O}_7$ both gave rise to discontinuities in the trend of increasing amorphization susceptibility with r_A/r_B , with the unexpectedly high $\text{Y}_2\text{Ti}_2\text{O}_7$ resistance being much more pronounced in the present study. $\text{Gd}_2\text{Ti}_2\text{O}_7$ was the most susceptible to amorphization using both methods of analysis. The consistent behavior of both low- and high-energy ion irradiations with r_A/r_B can be explained by the

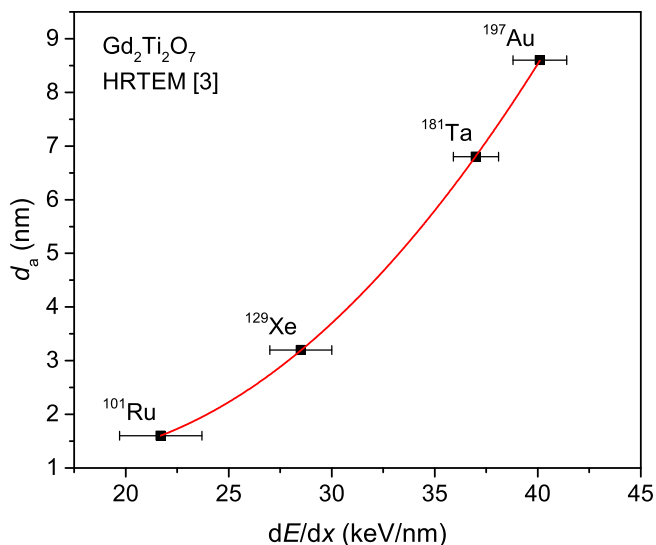


Fig. 7. Amorphous track core diameters for $\text{Gd}_2\text{Ti}_2\text{O}_7$ irradiated with various projectile ions (11.1 MeV/u) measured by HRTEM. The diameters show approximately $(dE/dx)^2$ dependence. The solid line is a guide to the eye. Figure reproduced from Ref. [3].

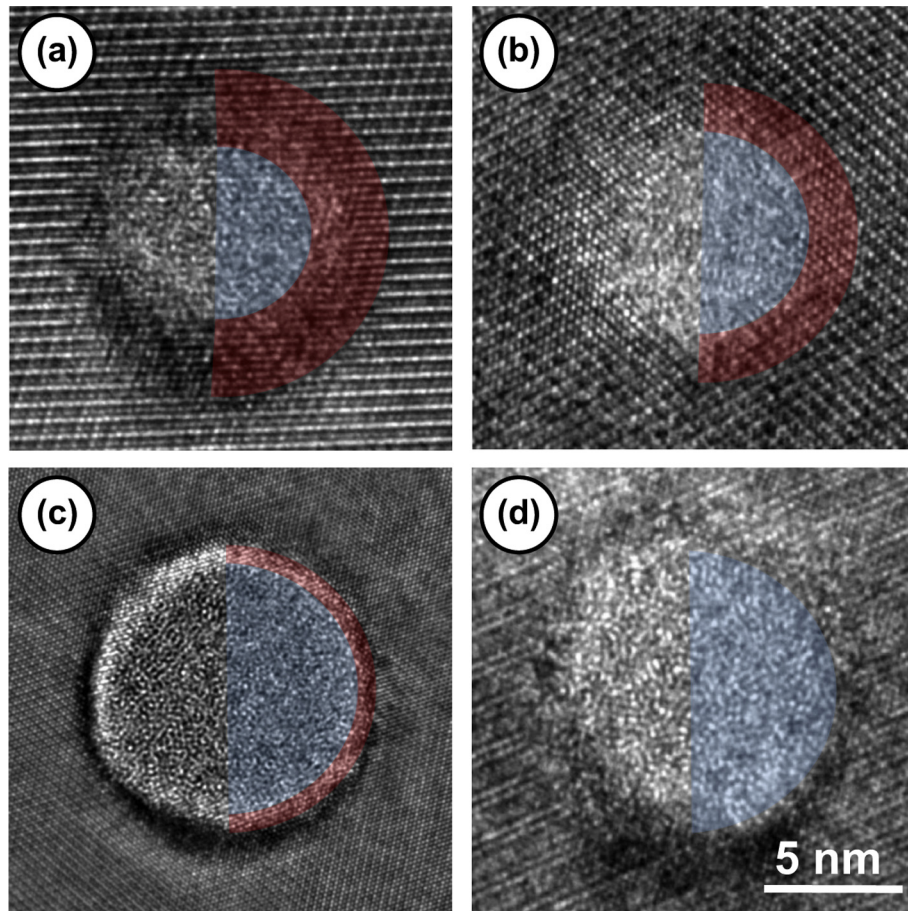


Fig. 9. HRTEM images of single 2.2 GeV ion tracks in (a) $\text{Yb}_2\text{Ti}_2\text{O}_7$, (b) $\text{Er}_2\text{Ti}_2\text{O}_7$, (c) $\text{Gd}_2\text{Ti}_2\text{O}_7$, and (d) $\text{Sm}_2\text{Ti}_2\text{O}_7$. Ion tracks in $\text{Yb}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ consist of a small amorphous core surrounded by a large disordered shell while in $\text{Gd}_2\text{Ti}_2\text{O}_7$ the amorphous core is larger and the disordered shell smaller. Ion tracks in $\text{Sm}_2\text{Ti}_2\text{O}_7$ are completely amorphous. The blue and red transparencies are guides to the eye to delineate the core and shell respectively. *HRTEM image of $\text{Gd}_2\text{Ti}_2\text{O}_7$ was taken from Ref. [3]. The scale bar in (d) applies to all boxes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

disordering energetics of pyrochlore from first-principles calculations on the disordering energy for a range of pyrochlore compositions [39]. The disordering energy, $\Delta E_{\text{disorder}}$, was defined as the energy difference between the fully-ordered pyrochlore and fully-disordered defect-fluorite structure. The formation of the defect-fluorite structure is unfavorable for compositions with a high $\Delta E_{\text{disorder}}$, which instead amorphize under irradiation. The disordering energy for titanate pyrochlores was shown to have a nonlinear dependence on A-site cation radius. $\Delta E_{\text{disorder}}$ initially increases with increasing r_A but shows a maximum at $\text{Gd}_2\text{Ti}_2\text{O}_7$ before decreasing for larger A-site cations. This is in agreement with the critical amorphization temperature trend observed in Ref. [13] and our XRD analysis, particularly when the amorphous track diameter is normalized by dE/dx (Fig. 8). Although $\text{Gd}_2\text{Ti}_2\text{O}_7$ does not exhibit the largest normalized track diameter among the compounds investigated, this value is within error of that of $\text{Sm}_2\text{Ti}_2\text{O}_7$, and we do observe a saturation of the normalized diameter with larger r_A . This suggests that the same disordering-energy effect plays a key role in radiation resistance of pyrochlore compounds regardless of the mechanism of energy loss (i.e., electronic vs. nuclear).

The nonlinear trend observed in titanate pyrochlores is in contrast to previous results from experiments in which the B-site cation was varied. Swift heavy ion studies on $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ pyrochlores have shown that these compounds become increasingly susceptible to amorphization as the titanium content at the B-site (x) is increased [3,9,23]. Bright-field TEM (BFTEM) measurements

revealed that the *total* diameter of ion tracks (core + shell) resulting from irradiation with 1.47 GeV ^{129}Xe ions increases linearly as a function of r_A/r_B [9]. However, it was originally suggested that the *amorphous* diameter extracted through XRD analysis (applying the same peak deconvolution) showed a non-linear dependence with r_A/r_B similar to that shown in the present study. This non-linearity was mainly attributed to $\text{Gd}_2\text{Zr}_2\text{O}_7$ which has a singularity behavior with no measurable amorphization, and this composition was therefore discarded in later studies for the description of amorphous track diameters [3]. A linear dependence was postulated for the amorphous track core as a function of r_A/r_B , especially considering the fact that BFTEM images of *total* track diameter (i.e., including the fluorite shell) showed a linear behavior. However, particularly after normalization with $(dE/dx)^2$, the amorphous track diameter in $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$ still appears to be curved with increasing r_A/r_B even when neglecting $\text{Gd}_2\text{Zr}_2\text{O}_7$ (see Fig. 10). This trend when varying the B-site cation is thus in agreement with the data in the present study of changing the A-site cation. This shows that r_A/r_B is a major parameter determining the radiation resistance in pyrochlores, independently of how this parameter is changed.

A similar swift heavy ion study on orthorhombic A_2TiO_5 oxides ($A = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}$) irradiated with 1.47 GeV Xe ions also exhibited a linear dependence of total track diameter on r_A/r_B as measured by BFTEM [40]. Although the uncertainty is relatively high, XRD analysis suggests that the amorphous core diameter initially increases with increasing r_A/r_B , but also saturates at high r_A/r_B ,

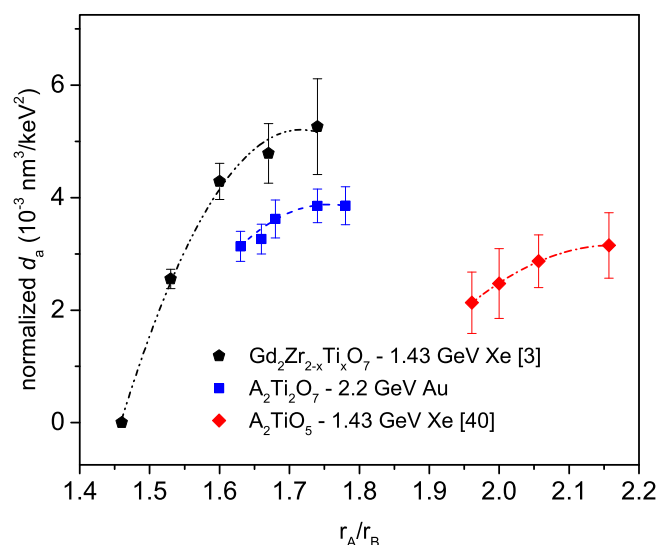


Fig. 10. Comparison between amorphous track diameters (normalized by $(dE/dx)^2$) extracted through XRD analysis in isometric pyrochlore ($A_2Ti_2O_7$ ($A = Yb, Er, Y, Gd, Sm$)) in the present study and $Gd_2Zr_{2-x}Ti_xO_7$ in Ref. [3]) and orthorhombic A_2TiO_5 in Ref. [40]. Normalization was performed to account for dE/dx variations due to the different densities across the sample series, however, all studies also display a nonlinear dependence on r_A/r_B before normalization. Larger uncertainties in Refs. [3] and [40] are largely due to increased variance in dE/dx across the sample.

analogous to the behavior of titanate pyrochlores in this study (Fig. 10). This is interesting because both systems show a linear increase in *total* track diameter (measured by BFTEM in Refs. [40] and [3]) but a curved dependence in *amorphous* track diameter despite having differing crystal structures. This may be indicative of the generality of the importance of r_A/r_B on the radiation resistance and susceptibility to amorphization on complex ternary oxides.

4.2. Ion track morphology

The core-shell morphology has been associated in several studies with localized “melting” and rapid recrystallization/quenching processes following swift heavy ion penetration. MD thermal spike simulations have previously reproduced the core-shell morphology observed in $Gd_2Ti_2O_7$ [18]. The amorphous core is produced by the rapid quenching of a “molten” state while the shell forms due to epitaxial recrystallization at the molten/solid interface explaining why the disordered shell and surrounding pyrochlore matrix have matching crystallographic orientations. The energy density and cooling rate strongly influence the track morphology, as rapid cooling will lead to a predominantly amorphous track while slower cooling will enhance the formation of the disordered phase. Ions of higher energy loss (at a given velocity) induce a higher energy density within a track which leads to a more rapid cooling and predominately amorphous tracks. This has been shown for tracks in $Gd_2Ti_2O_7$, which exhibit a core-shell morphology that changes as a function of energy loss [3]. The recrystallization rate in pyrochlore depends also (at least partially) on the disordering energy and the materials propensity to accommodate disorder [18]. Compositions with a small disordering energy (the disordered phase is favored) recrystallize more rapidly than those with a large disordering energy. The recrystallization rate in these compositions often exceeds the cooling rate leading to a smaller degree of amorphization. For example, MD simulations of ion tracks in $Gd_2Zr_2O_7$ and $Gd_2Ti_2O_7$ showed that the recrystallization rate is significantly enhanced in $Gd_2Zr_2O_7$ relative to $Gd_2Ti_2O_7$ because of its smaller disordering energy due to more

similarly sized cations [18].

Tracks in $Yb_2Ti_2O_7$ and $Er_2Ti_2O_7$ induced by 2.2 GeV Au ions (Fig. 9) display core-shell morphologies similar to those observed for Ti-containing compositions in the $Gd_2Zr_{2-x}Ti_xO_7$ solid solution series [3,9,11]. The same general trend is observed in the present study, as the amorphous core becomes larger and the disordered shell less pronounced with increasing r_A/r_B . Interestingly, $Sm_2Ti_2O_7$ shows no evidence of a disordered shell even though the energy loss (Fig. 1) and the calculated disordering energy in Ref. [39] are less than that of $Gd_2Ti_2O_7$. This could indicate that the recrystallization rate is affected more strongly by r_A/r_B than energy deposition.

The A-site cation seems to have noticeable effects on the position of the 1st order amorphous band in the XRD patterns (Fig. 4). The first amorphous peak develops at higher 2θ relative to the (222) Bragg peak in pristine $Yb_2Ti_2O_7$ and $Er_2Ti_2O_7$, but the two appear at nearly the same scattering angle for $Gd_2Ti_2O_7$ and $Sm_2Ti_2O_7$ (Fig. 4). This suggests that the amorphous core may be denser for $A = Yb$ and Er compared with Gd and Sm . This could be caused by an under-dense fluorite shell for $A = Yb$ and Er , relative to the surrounding pyrochlore matrix, as volumetric expansion upon disordering would cause the track shell to exert a compressive force onto the track core. An under dense shell has been confirmed experimentally for Gd_2TiZrO_7 irradiated with 120-MeV U ions, which displays a core-shell morphology by HRTEM [17]. More recently, high angle annular dark field imaging and molecular dynamics simulations have also shown that cation-cation spacing is increased in the defect fluorite shell relative to the bulk pyrochlore [41]. However, at high fluences for which $Yb_2Ti_2O_7$ and $Er_2Ti_2O_7$ are completely amorphous, the 1st order amorphous band still appears at higher scattering angles relative to the pristine (222) peak in the corresponding unirradiated samples. If the amorphous band shift was caused solely by a compressive shell, it should be assumed to relax back towards the position of the pristine (222) peak once the tracks have amorphized the entire sample and eliminated the compressive force of the disordered shells. Therefore, more efficient packing for compositions with similarly sized cations ($Yb_2Ti_2O_7$ and $Er_2Ti_2O_7$) may also contribute to densify the amorphous phase and explain the observed band shifts.

Similar to track sizes (Fig. 10), the morphology of tracks in orthorhombic A_2TiO_5 compounds shows a consistent behavior with the titanate pyrochlore in this study. In agreement with the results of this study, cation ratios with a smaller r_A/r_B (Sm_2TiO_5) in Ref. [40] resulted in an amorphous core surrounded by a disordered, defect-fluorite shell while the composition with the largest r_A/r_B (La_2TiO_5) showed larger, completely amorphous tracks. This indicates that the recrystallization kinetics within ion tracks is strongly dependent on the chemical composition of the complex oxide, in particular, the cation ionic radius ratio r_A/r_B .

5. Conclusions

Polycrystalline samples of the $A_2Ti_2O_7$ composition with $A = Yb, Er, Y, Gd$, and Sm were irradiated with 2.2 GeV ^{197}Au ions. This A-site substitution provides an A- to B-site cation ionic radius ratio ranging from 1.63 to 1.78. $Y_2Ti_2O_7$ showed much more amorphization resistance than the rare-earth containing samples due to the smaller electronic energy loss associated with its lower density. XRD analysis revealed that $Gd_2Ti_2O_7$ is the most readily amorphized composition among the titanate pyrochlores. Normalization of amorphous track diameters by the electronic energy loss shows an initial increase of amorphous track size with r_A/r_B that saturates for ionic radius ratios above $Gd_2Ti_2O_7$. This agrees with previous experiments using low-energy ions [13] and with first-principles calculations on disordering energy [39] suggesting that the same

disordering energy operates in both the nuclear and electronic energy loss regime. HRTEM demonstrates that ion tracks in $\text{Sm}_2\text{Ti}_2\text{O}_7$ and $\text{Er}_2\text{Ti}_2\text{O}_7$ (smaller r_A/r_B) display a pronounced core-shell morphology (amorphous core surrounded by a defect-fluorite shell) while $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{Sm}_2\text{Ti}_2\text{O}_7$ (larger r_A/r_B) have larger amorphous cores surrounded by minimal shells. Thus, r_A/r_B is clearly a dominating factor in predicting track size and damage morphology, which even extends to other compositionally related complex oxides. This is independent of whether the A- or B-site cation is altered.

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