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Swift heavy ion irradiation-induced amorphization of La₂Ti₂O₇

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ABSTRACT

Polycrystalline La₂Ti₂O₇ powders have been irradiated with 2.0 GeV ¹⁸¹Ta ions up to a fluence of 1×10^{13} ions/cm². Radiation-induced structural modifications were analyzed using synchrotron-based X-ray diffraction (XRD), small angle X-ray scattering (SAXS), Raman spectroscopy and transmission electron microscopy (TEM). An increase in the amorphous fraction as a function of fluence was revealed by XRD and Raman analyses and is evidenced by the reduction in intensity of the sharp Bragg maxima from the crystalline regions. Concurrently, diffraction maxima and vibrational absorption bands broaden with the increasing amorphous fraction. The cross-section for the crystalline-to-amorphous transformation (ion tracks) was determined by quantitative analysis of XRD patterns yielding a track diameter of $d = 7.2 \pm 0.9$ nm. Slightly larger track diameters were obtained directly from TEM images ($d = 10.6 \pm 0.8$ nm) and SAXS analysis ($d = 10.6 \pm 0.3$ nm). High-resolution TEM images revealed that single tracks are entirely amorphous without any outer crystalline, disordered shell as found in pyrochlore oxides of the same stoichiometry. The large ratio of ionic radii of the A- and B-site cations ($r_A/r_B = 1.94$) means that disordering over the A- and B-sites is energetically unfavorable.

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1. Introduction

Pyrochlore oxides (A₂B₂O₇) have been studied in great detail due to their importance in many technological applications, such as a host phase for actinides or as a substrate for superconductors [1–3]. Due to pyrochlore's chemical and structural flexibility, over \sim 450 synthetic pyrochlore oxides have been synthesized with a wide range of chemical and physical properties [4]. Isometric pyrochlore (A₂B₂O₇; $Fd\bar{3}m$, Z = 8, a = 0.9–1.2 nm) is an aniondeficient derivative of the fluorite structure AX_2 (Fm3m), with one-eighth of the anions removed and two types of cations at the A- and B- sites. The A-site cation is eight-coordinated (square antiprismatic), whereas the B-site cation is in octahedral coordination [5,6]. The stability of the pyrochlore structure depends on the radius ratio of the A- and B-site cations, r_A/r_B , [7]. If the radius ratio is below 1.46, pyrochlore can be disordered to a defect fluorite structure, where the A- and B-type cations are randomly distributed over the A- and B-sites, and the oxygen vacancies are disordered on the anion sublattice. However, if the cation ionic radius ratio exceeds 1.78, such as when lanthanum occupies the A-site, the ordered pyrochlore structure is no longer the stable phase for $A_2B_2O_7$, and a monoclinic, layered perovskite ($P2_1$) structure forms, which belongs to a homologous series $A_nB_nO_{3n+2}$ where n = 4 [8].

The structure of La₂Ti₂O₇ consists of alternating layers of corner-sharing TiO₆ octahedra: a layer with corner-sharing TiO₆ bridged to La-cations is topped with corner-sharing TiO₆, with La-cations located in the cavities between the two octahedra. The two layers alternate with a periodic break in between the framework structure. The layers are staggered resulting in β = 98.60°, forming a monoclinic pervoskite structure. A schematic of the structure can be found in Ref. [8].

Although extensive irradiation studies using various ion species and energies have been completed on a variety of $A_2B_2O_7$ compositions, most of these studies were conducted on isometric pyrochlore, with a focus on titanate and zirconate oxides ($A_2Ti_2O_7$ and $A_2Zr_2O_7$) [9–12]. Ion-beam irradiation with swift heavy ions has revealed a complex ion-track morphology for pyrochlores in the Gd₂Zr_{2-x}Ti_xO₇ binary, consisting of nanoscale core–shell structures [9,10,12]. Up to now, no irradiation experiments with GeV ions have been completed on $A_2B_2O_7$ stoichiometries with $r_A/r_B > 1.78$. This paper presents the first detailed investigation of swift heavy ion irradiation damage and single-ion track morphology for the monoclinic perovskite, $La_2Ti_2O_7$. First described in the early

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1950s [13], La₂Ti₂O₇ has numerous technological applications because of its electrical properties, photocatalytic activity, and photoluminescence. With it high-temperature piezoelectric properties, high Curie temperature ($T_c = 1500$ °C), and low dielectric constant ($\varepsilon_r = 42-62$), it is also an excellent candidate material for multifunctional nanostructures [14–16].

2. Experimental

Polycrystalline samples of La2Ti2O7 were synthesized by a sol-gel method, the details of which have been reported elsewhere [17]. With a typical grain size on the order of a few microns, the calculated density was 6.56 g/cm³. The dense pellets were polished (roughness: $\leq 1 \mu m$) without specific orientation down to a thickness of ${\sim}40\,\mu\text{m}$ and subsequently annealed at 800 °C for 24 h to release any absorbed water. After this, specimens were prepared for irradiation by cutting them into small pieces (area: $\sim 0.25 \text{ cm}^2$). The ion-irradiation experiment was performed at room temperature and under vacuum using the X0 beamline of the UNILAC accelerator of the GSI Helmholtz Center for Heavy Ion Research in Darmstadt, Germany. The samples were homogeneously exposed to a defocused cm-sized beam of ¹⁸¹Ta ions with a kinetic energy of 2.0 GeV. The projected range of the projectiles, as calculated using the SRIM 2008 code [18], was approximately 97 µm, which is almost 60 µm larger than the sample thickness; thus, all ions passed completely through the sample. The electronic energy loss, dE/dx, averaged over the entire sample thickness was 24.5 keV/nm, with a variation of 1.5 keV/nm. The nuclear energy loss is neglected because it is about three orders of magnitude less than the electronic energy loss. Several sets of samples were irradiated to fluences in the range of 1×10^{10} – 1×10^{13} ions/cm². A typical fluence uncertainty at the beamline is given by 10-20%.

Samples were characterized before and after irradiation by angle-dispersive synchrotron powder X-ray diffraction measurements (XRD) performed at the beam line B2 of the Cornell High Energy Synchrotron Source (CHESS) of Cornell University. A mono-energetic beam of 25 keV ($\lambda = 0.496$ Å) with spot size of \sim 1 mm was used in transmission mode to analyze ion-induced structural modifications throughout the entire sample thickness. Debye diffraction rings were recorded with a Mar CCD detector, and the integrated two-dimensional patterns were produced with the Fit 2D software [19]. The ion-induced amorphization was quantified by a deconvolution and peak-fitting procedure of XRD patterns, differentiating integrated peak intensity contributions from crystalline and amorphous sample fractions, respectively [20]. Beside the peak area, the fitting procedure also provided the width and position of all diffraction maxima.

Raman spectra were obtained with a Horiba Jobin Yvon (HR800) micro-Raman spectrometer with a 20 mW HeNe-Laser as excitation source (λ = 632.82 nm). The flat polished specimens were measured in backscattering geometry, and the Raman signal was collected from a spot diameter of ~2 µm. The measurement times varied from sample to sample and were optimized to gain maximum intensity (the same procedure was used for the XRD measurements).

Transmission electron microscopy (TEM) was performed using a JEOL 2010F and 3011 to obtain bright-field and high-resolution images and electron diffraction patterns. The irradiated samples were crushed into a fine powder and deposited on a holey carbon TEM grid. The track diameters were measured from bright-field images and high-resolution TEM (HRTEM) images on samples irradiated to a fluence of 1×10^{11} ions/cm² in order to avoid an overlap of individual ion tracks. For the HRTEM imaging, the pre-polished samples were further thinned using mechanical polishing and ion milling providing electron-transparent specimens perpendicular to the incident ion direction (plan view). Fast Fourier transform (FFT) images were additionally obtained from TEM images to characterize the local structural modifications of irradiated La₂Ti₂O₇.

Small-angle X-ray scattering (SAXS) measurements were performed in transmission mode on a virgin sample and a sample irradiated to a fluence of 1×10^{11} ions/cm² at the Australian Synchrotron in Melbourne, Australia. Samples were measured as irradiated, i.e. no further sample preparation was required. A mono-energetic beam of 11 keV ($\lambda = 1.127$ Å) with a spot size of ~0.1 × 0.2 mm² was used, and the distance between the sample and the CCD detector was ~1610 mm. The camera length was determined using a silver behenate standard, and the absolute scattering was calibrated using a glassy carbon standard. Data were collected using a Pilatus 1 M detector for a q-range of 0.01– 0.4 Å⁻¹. The sample was placed on a 3-axis goniometer which allowed precise alignment in the X-ray beam; SAXS images were taken with tracks positioned between 5° and 10° with respect to the X-ray beam direction.

3. Results

3.1. Transmission electron microscopy (TEM)

The irradiated, crushed grains for the TEM analysis were randomly oriented, thus the tracks could be imaged in all orientations (e.g., perpendicular to or along their length). Bright-field TEM images are shown in Fig. 1(a) where the tracks are clearly visible due to their darker contrast with respect to the surrounding matrix. The diameter of the tracks was measured by visually estimating the position of the parallel boundaries between the modified contrast and the unchanged matrix for about 20 tracks. The mean diameter and standard deviation was $d = 10.8 \pm 0.8$ nm. Bright field images at lower magnification provide a means for determining the average diameter of a large number of tracks. In order to obtain information on the damage structure within the ion tracks, we also analyzed the tracks with HRTEM. The size $(d = 10.2 \pm 0.7 \text{ nm})$ of the individual amorphous ion tracks in La₂Ti₂O₇ were consistent with the values determined from bright-field images (Fig. 1(b)). The HRTEM image indicates a direct transition from a crystalline-toamorphous structure without a distinct disordered shell around the amorphous core, as has been described for some A2Ti2O7 pyrochlore compositions [9,10,21,22]. The amorphous structure within the tracks in La₂Ti₂O₇ was confirmed by FFT analyses, as shown in insets 1 and 2 of Fig. 1(b). The dark ring along the edge of the track in the HRTEM image is likely due to the strain contrast of the amorphous tracks surrounded by the crystalline matrix.

3.2. Small angle X-ray scattering (SAXS)

The SAXS image of the irradiated sample shows long streaks that are characteristic of swift heavy ion tracks of high aspect ratio (Fig. 2(a)) [23]. The SAXS images from a virgin sample and an irradiated sample with ion tracks tilted by $\sim 10^{\circ}$ with respect to the Xray beam are shown in Fig. 2(a). The anisotropy in the scattering signal is caused by the high aspect ratio of the tracks, which are only a few nanometers in diameter and up to tens of micrometers in length. Data reduction was completed by masking the streaks and subtracting the background from the data of the virgin sample. The scattering intensity profiles due to the ion tracks and virgin sample are plotted in Fig. 2(b). The track intensities were analyzed with several cylindrical models. The simplest and best fitting model assumes an electron density within the tracks that is constant but different from the matrix, with sharp boundaries (details of which has been published elsewhere, [24,25]). A polydispersity of the diameter with a Gaussian distribution of σ_d width was in-



Fig. 1. (a) Bright-field TEM image of single ion tracks in $La_2Ti_2O_7$ induced by 2.0 GeV ¹⁸¹Ta ions at a fluence of 1×10^{11} ions/cm². (b) HRTEM reveals the amorphous track morphology, which is supported by FFT analyses within (inset 1: amorphous) and outside (inset 2: monoclinic perovskite) the track region, respectively. Track diameters measurements by (a) bright-field TEM ($d = 10.8 \pm 0.8$ nm) and (b) HRTEM ($d = 10.2 \pm 0.7$ nm) yield very consistent values.

cluded in the SAXS model in order to account for deviations from perfectly identical parallel cylindrical tracks. These deviations could be due to roughness of the matrix-track boundaries and variation of the diameter along the length of the track (a result of the decrease in dE/dx as the ion loses energy along its trajectory). From the model fits, as shown in Fig. 2(b), the average track diameter was obtained: $d = 10.6 \pm 0.3$ nm, which is in excellent agreement with TEM measurements, and the polysdispersity gives $\sigma_{\rm d}$ = 1.4 ± 0.4 nm.

3.3. X-ray diffraction (XRD)

Synchrotron XRD was used to observe beam-induced structural changes in La2Ti2O7. XRD patterns displaying the evolution of La2Ti2O7 diffraction maxima as a function of fluence, from 1×10^{10} to 1×10^{13} ions/cm² are shown in Fig. 3(a). Over the range of fluence, the Bragg maxima intensities significantly decrease with increasing ion fluence. Concomitantly, there is an ingrowth of a broad, diffuse-scattering background, confirming the crystalline-to-amorphous transformation. This transformation is accompanied by a pronounced broadening of the diffraction peaks. The diffuse scattering of the amorphous phase for La₂Ti₂O₇ is similar to that reported for swift heavy ion-irradiated cubic pyrochlore [10,26] with the main peak between 8° and 11° 2 θ . At the maximum fluence, all sharp diffraction maxima from crystalline



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Fig. 2. (a) SAXS image of a La₂Ti₂O₇ virgin sample (1) and an irradiated sample with 2.0 GeV 181 Ta ions to a fluence of 10^{11} ions/cm² (2). (b) SAXS intensities s of La₂Ti₂O₇ before (circles) and after (squares) irradiation with 2.0 GeV ¹⁸¹Ta ions to a fluence of 1×10^{11} ions/cm² as a function of the scattering vector q. The scattering intensity of the tracks was extracted from the anisotropic scattering images after background removal using the unirradiated sample. The solid line shows the fits based on models in which the tracks are solid cylinders with sharp boundaries. The mean track diameter is $d = 10.6 \pm 0.3$ nm. For display purposes, the intensity profiles of the virgin and irradiated samples were multiplied by a respective factor of 0.5 and 2 in the vertical axis.

sample regions have vanished, which is indicative of complete amorphization.

A quantitative analysis of the amorphous fraction as a function of the irradiation fluence was completed (Fig. 3(a)). The amorphous fraction systematically increases with irradiation fluence with an initial linear increase, and a gradual evolution onto a plateau as the amorphization reaches saturation due to substantially overlapping tracks. From the selectively analyzed amorphous fraction, the damage evolution is well described by a direct-impact model of the form:

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

where f_A represents the amorphous fraction at a given fluence (Φ), and σ is the cross-sectional area of the amorphous track produced by each individual ion [27]. The cross-sectional area determined from the model fit through the experimental data is $\sigma = 41.1 \pm$ 7.4 nm², with a track diameter of $d = 7.2 \pm 0.9$ nm, assuming cylindrical track geometry. This diameter indirectly deduced from the XRD data is about 70% of the diameter directly obtained from the TEM images.

3.4. Raman spectroscopy

The Raman spectrum of La₂Ti₂O₇ is rather complex with relatively broad vibrational modes that partly overlap (Fig. 4). After



Fig. 3. (a) XRD patterns of La₂Ti₂O₇ irradiated with 2.0 GeV ¹⁸¹Ta ions for selected fluences from 1×10^{10} to 1×10^{13} ions/cm² (bottom to top). Amorphizaion increasing as a function of fluence is evident by the decrease in intensity of crystalline sharp diffraction maxima concomitant with the growth of broad amorphous peaks. (b) Amorphous fraction determined from quantitative analysis of XRD patterns as a function of fluence. The solid curve represents the fit of a single impact model (inset) to the experimental data.



Fig. 4. Raman spectra of La₂Ti₂O₇ irradiated with 2.0 GeV ¹⁸¹Ta ions for fluences with between 1×10^{10} and 1×10^{13} ions/cm² (bottom to top). The intensity of all Raman modes associated with the crystalline fraction decreases systematically with increasing fluence, indicative of radiation-induced amorphization.

irradiation to different fluences (Fig. 4 bottom to top), all crystalline vibrational modes broaden and decrease in intensity with increasing irradiation, which is in good agreement with the XRD

results (Fig. 3(b)). This behavior has been also observed for other complex oxides and was attributed to ion-induced amorphization [9,10,12,26] At the maximum fluence of 1×10^{13} ions/cm², none of crystalline vibration modes were detected. Only a broad peaklike structure with a maximum at \sim 750 cm⁻¹ remains, which has been also observed in previous ion-beam experiments and may be related to the formation of an amorphous phase [9–10,12,26]. Another weak broad band is noticeable at \sim 800 cm⁻¹, and it exists over the entire fluence range, although the peak intensity decreases and width broadens with increasing fluence. The overall background significantly grows with increasing fluence, and therefore, guantitative analysis of the amorphous fraction from the Raman data was not done. Nevertheless, the evolution of the intensity profiles confirms that the intensities of the crystalline vibrational modes decrease in a systematically with increasing fluence.

4. Discussion

Based on the decrease of diffraction maxima and absorption band intensities, XRD and Raman spectroscopy independently confirm substantial amorphization in La₂Ti₂O₇ by irradiation with 2.0 GeV tantalum ions. Raman analysis is not useful for quantifying the crystalline-to-amorphous transformation because the vibrational modes are broad and overlapping, and this is further complicated by the pronounced increase of an asymmetric background (Fig. 4). The XRD data were quantitatively analyzed by fitting the evolution of the amorphous fraction with increasing fluence (Fig. 3(a)) using a single-impact model (Fig. 3(b)) [27]. The application of this model is supported by the observation of individual amorphous ion tracks by HRTEM (Fig. 2(b)). The track diameter deduced from XRD analysis, $d = 7.2 \pm 0.9$ nm, is ~ 30 percent smaller as compared with the direct size measurements from TEM images. Such pattern has been reported before for pyrochlores and was attributed to the complex track morphology [9]. This is because the diameter as measured by XRD represents only the amorphous core, while the TEM diameter includes the outer disordered track shell [9]. In this study, no distinct disordered shell was evident in HRTEM, thus both XRD and TEM track diameters should be similar. A possible source of uncertainty in the XRD analysis is from the uncertainty in the fluence: while TEM diameters are directly determined by individual ion tracks, the XRD diameters are indirectly deduced from fluence-dependent data. Top-view, low magnification TEM images have been used to estimate the areal track density in a sample irradiated to a nominal fluence of 1×10^{11} ions/cm². The limited statistical set of tracks indicated that the actual fluence was about a factor of two lower than expected, which accounts for the smaller track diameters as measured by XRD. Independently of the uncertainty in fluence, the treatment of XRD patterns and, in particular, the determination of the amorphous sample fraction is not straightforward. Due to the complex and unknown relationship between integrated XRD-peak intensities and crystalline/amorphous phase distribution, this method is not a precise measurement of the actual amorphized volume [28]. Additional contributions, such as defects and related strain effects will impact the behavior of XRD maxima upon irradiation. When discussing track cross-sections, as deduced from XRD data, all contributing factors should be considered in detail, because the crystalline-toamorphous transformation cannot be fully described by a simple analysis of increasing and decreasing integrated peak intensities.

The tracks sizes obtained from bright-field TEM, high-resolution TEM, and SAXS analysis are in excellent agreement. The mean diameters and standard deviations for bright field TEM are: $d = 10.8 \pm 0.8$ nm; HRTEM: $d = 10.2 \pm 0.7$ nm; SAXS: $d = 10.6 \pm 0.3$ nm. The fact that SAXS technique is sensitive to the density difference

between the crystalline and amorphous domains means that it is a sensitive measure of the amorphous track core, confirming that the track diameter is \sim 10 nm.

The overall track size of swift heavy ion tracks in monocliniclayered perovskite La2Ti2O7 is comparable to track diameters induced by ion of similar dE/dx in cubic $Gd_2Ti_2O_7$ pyrochlore [29] and orthorhombic La₂TiO₅ [26]. Tracks in La₂Ti₂O₇ consist of amorphous cylinders. Based on the HRTEM images, the interface between the amorphous core and the crystalline matrix is rather sharp; there is no evidence of a surrounding halo of disordered material. This is in good agreement with the track structure observed in La₂TiO₅ by Tracy el al., [26], but is distinctively different from most cubic pyrochlores, where a defect-fluorite structures shell surrounds the amorphous track core [6,16–19]. The existence of defect-fluorite structured track regions in titanate pyrochlores was explained by molecular dynamics (MD) calculations [29,30] as being the result of damage recovery and epitaxial recrystallization at the interface of a molten track and the surrounding pyrochlore matrix. The recrystallization was shown to advance from the outer (cooler) boundary of the molten area towards the inner (hotter) central region at the late stage of the track-formation process [29,30]. Determined by the quench rate of the specific pyrochlore composition, the formation of the disordered fluorite phase may not be complete, leading to complex core-shell track morphology. This mechanism is apparently absent in La₂Ti₂O₇. Tracy et al., attributes the lack of a track shell in La₂TiO₅ to insufficient thermodynamic stability of a disordered phase [26]. The present study supports this conclusion, as the large difference in the ionic radii of La and Ti prevent disordering over the cation sites, making the defect-fluorite structure energetically unfavorable. The energetic barrier to recrystallization into a disordered phase during the thermal spike, explains the reason that monoclinic A₂B₂O₇ perovskite is less radiation resistant than the isometric compositions of the same stoichiometry. In the pyrochlore binary, $Gd_2Zr_{2-x}Ti_xO_7$, which covers almost the entire pyrochlore stability field with their $r_{\rm A}/r_{\rm B}$, compositions with a high Zr-content (small $r_{\rm A}/r_{\rm B}$ ratio) displayed a track morphology dominated by the defect-fluorite structured shell. The Ti-rich pyrochlores (large r_A/r_B ratio), in contrast, show a pronounced amorphous track core [9]. Monoclinic perovskite, A₂B₂O₇ provides an example of an extension of this trend. With a cation ionic radius ratio of $r_{\text{La}}/r_{\text{Ti}}$ = 1.94, ion tracks are entirely amorphous, while tracks of the Ti end-member Gd₂Ti₂O₇, with a ratio of $r_{\rm Gd}/r_{\rm Ti}$ = 1.74, still have a thin disordered shell around the amorphous core [9]. The relatively poor radiation tolerance of lanthanum titanates was also evident in ion-beam experiments using low-energy ions in the keV–MeV energy range [31].

5. Conclusion

The radiation-induced crystalline-to-amorphous phase transformation in La₂Ti₂O₇ perovskite was investigated by combining irradiations with 2.0 GeV ¹⁸¹Ta ions, up to a fluence of 1×10^{13} ions/cm², with complementary analytical techniques: synchrotron XRD, Raman spectroscopy, TEM bright-field imaging, high-resolution-TEM and SAXS. Single ¹⁸¹Ta ion tracks have a diameter $d = 10.6 \pm 0.8$ nm, $d = 10.6 \pm 0.3$ nm and $d = 7.2 \pm 0.9$ nm, as measured by TEM, SAXS and XRD, respectively. Based on high-resolution TEM images, single ion tracks are entirely amorphous without a surrounding shell of the disordered fluorite phase, such as has been found in related isometric A₂B₂O₇ compositions. The

absence of formation of a recrystallized, disordered phase during track quenching may be due to the energetic barriers to disordering cations that have different ionic radii. In the absence of forming a disordered, but still crystalline material, phases like La₂Ti₂O₇ are very sensitive to radiation-induced amorphization.

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