

Structural Response of A_2TiO_5 (A = La, Nd, Sm, Gd) to Swift Heavy Ion Irradiation*

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Pyrochlore-structured titanates ($A_2Ti_2O_7$) have been extensively studied as radiation-resistant materials for nuclear fuel cycle applications. Here we investigate related compounds A_2TiO_5 , where A is a lanthanide element. They are orthorhombic at ambient conditions for A-site elements with a lower Z than Ho. The radiation response of A_2TiO_5 in general, and comparison with $A_2Ti_2O_7$ materials is of interest as a means of investigating the role of structure in swift heavy ion-induced amorphization of ternary complex oxides.

Powders of A_2TiO_5 (A = La, Nd, Sm, Gd) were pressed into 40 μm thick pellets and irradiated with 1.47 GeV ^{132}Xe ions at the X0 beamline of the UNILAC accelerator [1]. Irradiation was performed to several fluences in the range 5×10^{10} to 1×10^{13} ions/cm². For the energies used, the nuclear energy loss remained at least three orders of magnitude lower than the electronic energy loss. The ions passed completely through the thin samples, producing damage tracks of cylindrical geometry. All materials were characterized using synchrotron x-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy.

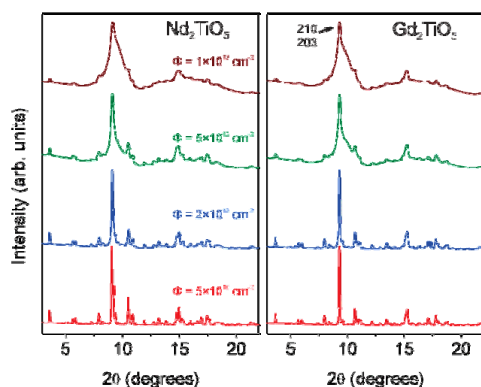


Figure 1: XRD patterns of irradiated Nd_2TiO_5 and Gd_2TiO_5 . The decrease in amorphization with substitution of smaller cations is evident in the (210) and (203) peaks.

Both XRD and Raman spectroscopy showed evidence of increasing amorphization as a function of fluence for all compositions. The Raman spectra exhibited a systematic

decrease in the intensity of the vibrational modes along with growth of a broad band at ~ 750 cm⁻¹, a vibrational mode also observed in pyrochlore titanates following swift heavy ion-induced amorphization. The XRD patterns displayed both peak broadening and the growth of broad peaks at approximately 7-12°, 12-20°, and 22-30° resulting from diffuse scattering by the amorphized sample volume (Fig. 1).

The XRD patterns were analyzed by deconvoluting the intensity and peak area of the crystalline and amorphous contributions. The amorphization cross section per ion was calculated by fitting a direct-impact model to the extracted amorphous volume as a function of irradiation fluence. These cross sections were found to decrease as lanthanides of smaller ionic radius (higher Z) were substituted on the A-site. This relation between the ionic radius ratio of the cations and the amorphization per ion is similar to that previously observed in pyrochlores as a result of their propensity to resist amorphization. The effect is ascribed to the recrystallization of a disordered fluorite structure when the thermal spike region is quenched [2]. The occurrence of this phenomenon in A_2TiO_5 and its dependence on the cation radius ratio was confirmed by high-resolution TEM of single tracks shown in Fig. 2. La_2TiO_5 , for which the cations differ greatly in ionic radius, exhibits only amorphous material within the track while Sm_2TiO_5 features a defect fluorite track shell surrounding the amorphous core. The presence of this non-equilibrium phase suggests that it forms as an intermediate phase during solidification of the melted track and is quenched before further ordering occurs.

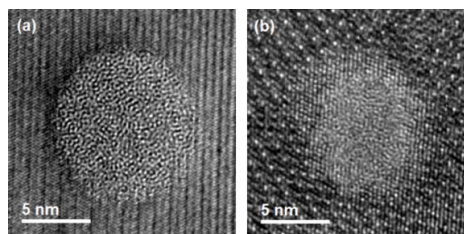


Figure 2: Cross-sectional TEM images of individual tracks in (a) La_2TiO_5 and (b) Sm_2TiO_5 . The latter shows a defect-fluorite shell around the amorphous track core.

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