



Response of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ to swift-heavy ion irradiation and annealing

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Abstract—Swift heavy ion (2 GeV ^{181}Ta) irradiation-induced amorphization and temperature-induced recrystallization of cubic pyrochlore $\text{Gd}_2\text{Ti}_2\text{O}_7$ ($Fd\bar{3}m$) are compared with the response of a compositionally-similar material with a monoclinic-layered perovskite-type structure, $\text{La}_2\text{Ti}_2\text{O}_7$ ($P2_1$). The averaged electronic energy loss, dE/dx , was 37 keV/nm and 35 keV/nm in $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$, respectively. Systematic analysis of the structural modifications was completed using transmission electron microscopy, synchrotron X-ray diffraction, Raman spectroscopy, and small-angle X-ray scattering. Increasing ion-induced amorphization with increasing ion fluence was evident in the X-ray diffraction patterns of both compositions by a reduction in the intensity of the diffraction maxima concurrent with the growth in intensity of a broad diffuse scattering halo. Transmission electron microscopy analysis showed complete amorphization within ion tracks (diameter: ~ 10 nm) for the perovskite-type material; whereas a concentric, core-shell morphology was evident in the ion tracks of the pyrochlore, with an outer shell of disordered yet still crystalline material with the fluorite structure surrounding an amorphous track core (diameter: ~ 9 nm). The radiation response of both titanate oxides with the same stoichiometry can be understood in terms of differences in their structures and compositions. While the radiation damage susceptibility of pyrochlore $\text{A}_2\text{B}_2\text{O}_7$ materials decreases as a function of the cation radius ratio r_A/r_B , the current study correlates this behavior with the stability field of monoclinic structures, where $r_{\text{La}}/r_{\text{Ti}} > r_{\text{Gd}}/r_{\text{Ti}}$. Isochronal annealing experiments of the irradiated materials showed complete recrystallization of $\text{La}_2\text{Ti}_2\text{O}_7$ at 775 °C and of $\text{Gd}_2\text{Ti}_2\text{O}_7$ at 850 °C. The annealing behavior is discussed in terms of enhanced damage recovery in $\text{La}_2\text{Ti}_2\text{O}_7$, compared to the pyrochlore compounds $\text{Gd}_2\text{Ti}_2\text{O}_7$. The difference in the recrystallization behavior may be related to structural constraints, i.e., reconstructing a low symmetry versus a high symmetry phase.

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1. Introduction

The $\text{A}_2\text{B}_2\text{O}_7$ pyrochlore structure has been investigated for various technological applications, such as a nuclear wasteform for actinide immobilization, electrolytes for solid oxide fuel cells, and thermal barrier coatings for gas turbines [1–4]. The wide variety of pyrochlore compositions (~ 450 synthetic compositions) results in widely varying chemical and physical properties, as well as its structural diversity, resulting from the different combinations of A- and B-site cations [5,6]. Pyrochlores are structurally isometric ($Fd\bar{3}m$, $Z = 8$, $a = 0.9$ – 1.2 nm), and can be described

as an anion-deficient derivative of the fluorite structure, AX_2 ($Fd\bar{3}m$), with one-eighth of the anions removed and two types of cations ordered on the A- and B-sites [6,7]. The stability of the pyrochlore structure is determined by the cationic radius ratio r_A/r_B . At ambient conditions, the stable pyrochlore structure ($Fd\bar{3}m$) is formed for those with r_A/r_B of 1.46–1.78. If the r_A/r_B drops below 1.46, a disordered fluorite structure ($Fd\bar{3}m$), forms, and when it is above 1.78, such as when La occupies the A-site and Ti occupies the B-site, the structure conforms to a monoclinic, layered-perovskite structure ($P2_1$), which belongs to a homologous series $\text{A}_n\text{B}_n\text{O}_{3n+2}$ where $n = 4$ [8]. Fig. 1 shows the crystal structures of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ projected along the [010] direction. The perovskite, $\text{La}_2\text{Ti}_2\text{O}_7$, contains alternating layers of corner-sharing TiO_6

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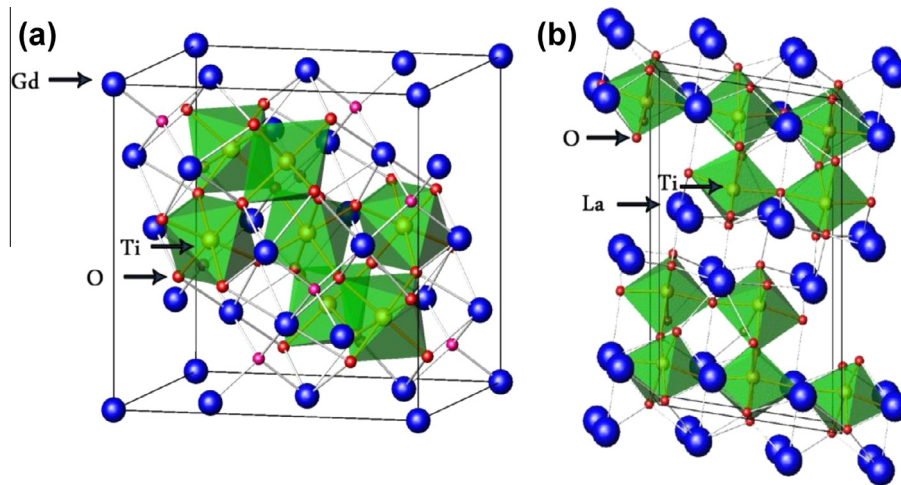


Fig. 1. Unit cell of (a) $\text{Gd}_2\text{Ti}_2\text{O}_7$ ($Fd\bar{3}m$) and (b) $\text{La}_2\text{Ti}_2\text{O}_7$ ($P2_1$).

octahedra: a layer with corner-sharing TiO_6 bridged with La cations is topped with corner-sharing TiO_6 , with La cations located in the interstices between the two octahedra. Within a single unit cell, the two layers are periodically repeated with $\beta = 98.60^\circ$, forming a monoclinic-layered perovskite structure.

The structural response of pyrochlore-structured complex oxides and related phases to high-energy heavy ion irradiation is of significant interest, due to the applications of these materials as wasteforms for the immobilization and disposal of radionuclides. In order to understand compositional and structural influences on radiation effects, extensive ion-beam irradiation studies using various ion species and energies have been completed on a wide variety of $\text{A}_2\text{B}_2\text{O}_7$ compositions [9–17]. Irradiation experiments with swift heavy ions of initial energies in the range of MeV to GeV, which deposit energy into a material mainly through electronic excitation and are useful for simulating the effects of nuclear fission fragment irradiation, were mainly performed on titanate and zirconate pyrochlores [9–12]. These studies emphasize that the radiation tolerance of pyrochlores is proportional to r_A/r_B , and that tolerant materials show disordering to a fluorite structure rather than amorphizing under irradiation. In the present work, we report the effects of swift heavy ion irradiation and high temperature on the perovskite compound, $\text{La}_2\text{Ti}_2\text{O}_7$, for comparison to their effects on the pyrochlore compound, $\text{Gd}_2\text{Ti}_2\text{O}_7$, in order to understand how structures affect these closely related compositions. The two compounds find applications in a variety of areas. $\text{Gd}_2\text{Ti}_2\text{O}_7$ has been proposed as an actinide nuclear wasteform [1,3]. Most applications of $\text{La}_2\text{Ti}_2\text{O}_7$ are due to its electrical properties, photocatalytic activity, photoluminescence, high-temperature piezoelectric nanostructures with its high Curie temperature ($T_c = 1500^\circ\text{C}$), and low dielectric constant ($\epsilon_r = 42\text{--}62$), making the material a multifunctional candidate [18–20]. This paper presents a detailed investigation of swift heavy ion irradiation damage and annealing behavior in the monoclinic-layered perovskite $\text{La}_2\text{Ti}_2\text{O}_7$ and cubic $\text{Gd}_2\text{Ti}_2\text{O}_7$ pyrochlore. The two compounds' response to irradiation and temperature is discussed in terms of ionic sizes of the cations, topology and thermodynamic stability.

2. Experimental

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 [21]. The typical grain size of the samples was several microns, and the measured densities of $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ were 6.56 g/cm^3 and 5.82 g/cm^3 , respectively. The dense pellets were polished (roughness: $\leq 1\text{ }\mu\text{m}$) without specific orientation down to a thickness of $\sim 40\text{ }\mu\text{m}$ and subsequently annealed at 800°C for 24 h to evaporate absorbed water. Samples were then cut into small pieces with an area of $\sim 0.25\text{ cm}^2$ for irradiation. The ion irradiation experiment was performed at the beamline X0 of the UNILAC linear accelerator (GSI Helmholtz Center) in Darmstadt, Germany. At room temperature under vacuum, all samples were entirely exposed to a defocused cm-sized ^{181}Ta beam with an ion energy of 2.0 GeV. These energetic particles travel through solids in a roughly linear manner, producing high aspect ratio, cylindrical “ion tracks” of damage material, typically several nanometers in diameter and tens of micrometers in length. This damage can be considered a result of rapid heating of the material inside an ion track through energy deposition to its electrons, which can result in local melting and subsequent quenching as this thermal energy is conducted radially outwards from the track core. The projected ranges of the projectiles, as calculated using the SRIM 2008 code [22], for $\text{Gd}_2\text{Ti}_2\text{O}_7$ and $\text{La}_2\text{Ti}_2\text{O}_7$ are approximately $58\text{ }\mu\text{m}$ and $62\text{ }\mu\text{m}$, respectively. This is about $20\text{ }\mu\text{m}$ larger than the entire sample thickness, indicating that all impinging ions passed completely through the sample (Fig. 2). The averaged electronic energy loss, dE/dx , in the $\text{Gd}_2\text{Ti}_2\text{O}_7$ sample was 37 keV/nm and in $\text{La}_2\text{Ti}_2\text{O}_7$, 35 keV/nm . The nuclear energy loss is neglected because it is about three orders of magnitude less than the electronic energy loss. The two sets of samples were prepared and irradiated to different fluences between 1×10^{10} and 1×10^{13} ions/ cm^2 . The typical uncertainty for the absolute fluence value of a specific irradiation experiment is 10–20%. Because both samples were, for a given fluence, simultaneously irradiated and the fluence series were completed with identical beam settings, the relative error in fluence is minimal. Isochronal

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