

## Damage evolution in Au-implanted $\text{Ho}_2\text{Ti}_2\text{O}_7$ titanate pyrochlore

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### ABSTRACT

Damage evolution at room temperature in  $\text{Ho}_2\text{Ti}_2\text{O}_7$  single crystals is studied under 1 MeV  $\text{Au}^{2+}$  ion irradiation by Rutherford backscattering spectroscopy along the  $(001)$  direction. For a better determination of ion-induced disorder profile, an iterative procedure and a Monte Carlo code (McChasy) were used to analyze ion channeling spectra. A disorder accumulation model, with contributions from the amorphous fraction and the crystalline disorder, is fit to the Ho damage accumulation data. The damage evolution behavior indicates that the relative disorder on the Ho sublattice follows a nonlinear dependence on dose and that defect-stimulated amorphization is the primary amorphization mechanism. Similar irradiation behavior previously was observed in  $\text{Sm}_2\text{Ti}_2\text{O}_7$ . A slower damage accumulation rate for  $\text{Ho}_2\text{Ti}_2\text{O}_7$ , as compared with damage evolution in  $\text{Sm}_2\text{Ti}_2\text{O}_7$ , is mainly attributed to a lower effective cross section for defect-stimulated amorphization.

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### 1. Introduction

Pyrochlore materials, due to the remarkable elemental versatility in the  $\text{A}_2\text{B}_2\text{O}_7$  crystal structure, are considered for a wide range of applications, such as fuel cells [1,2], catalysts [3,4], and immobilization of actinide-rich nuclear waste [5–7] or excess plutonium [8,9]. Considerable self-radiation damage from alpha decay in actinide-bearing phases can result in amorphization, macroscopic swelling and order-of magnitude increase in dissolution rates [10–13], and these changes in structure and chemical durability affect long-term performance of the actinide waste forms [9–15]. Studies of actinide-doped [11,12,16] and natural pyrochlores [17], indicate that pyrochlores with Ti, Nb, and Ta as the major B-site cations become amorphous as a result of the gradual accumulation of alpha-recoil collision cascades. However, such studies are time consuming, and only limited data under a few sets of experimental conditions are available. Heavy-ion irradiation studies [6,13,18–28] have been used to more rapidly evaluate radiation effects on a wide range of pyrochlore compositions that generally confirm the results for the actinide-doped pyrochlores or natural minerals.

In general, alpha decay of actinide elements produces high-energy alpha particles and low-energy heavy recoil nuclei (alpha recoils) [15]. The alpha particles with energies of 4.5–5.8 MeV, due to smaller mass, have relatively less radiation impact. The heavy recoil nuclei (alpha recoils) with energies of 70–100 keV account for most of the crystal damage produced through elastic scattering collisions. Since nuclear stopping at the damage peak resulting from heavy-ion irradiation, such as Au ion, is similar to the nuclear stopping of alpha recoils ( $\sim 5$  keV/nm), the damage evolution at the damage peak under heavy-ion irradiation provides a reasonable simulation of the damage evolution behavior due to alpha-recoil collision cascades. Accumulation of alpha decay damage may lead to serious disorder or even a crystalline to amorphous transition. Such phase transformation may enhance the ceramic aqueous dissolution and produce a large swelling leading to cracks or even fragmentation of the waste form. Since both effects may increase the actinide release, it is important to understand and predict the behavior of the pyrochlore materials in a radiation environment.

Considerable transmission electron microscope (TEM) studies have been carried out to characterize the temperature dependence of the critical dose for amorphization [6,13,24–28], few studies have quantitatively investigated the damage evolution behavior as a function of irradiation dose [20–23] at different temperatures, particularly in relevant pyrochlore phases. In this work, quantitative characterization of damage accumulation in holmium titanate

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( $\text{Ho}_2\text{Ti}_2\text{O}_7$ ) single crystals as a function of irradiation dose is carried out using ion-channeling methods, which should lead to a better understanding of the amorphization and damage evolution processes.

## 2. Experimental procedures

The  $\text{Ho}_2\text{Ti}_2\text{O}_7$  single crystals used in current work were grown by a floating zone technique using an infrared image furnace at the University of Warwick, UK [29]. The pyrochlore crystal was sectioned along the (1 0 0) plane. The polished samples were characterized by high-resolution X-ray diffraction (HRXRD) and a series of pole figure measurements. Samples exhibiting large single crystal regions were then selected for the irradiation experiments. Some material was crushed for powder XRD, which revealed no evidence for the existence of secondary or minor phases.

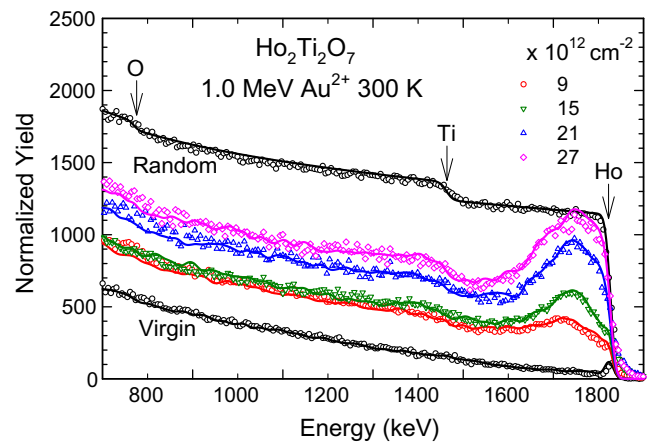
The Au irradiations and subsequent ion beam analysis of damage accumulation in the  $\text{Ho}_2\text{Ti}_2\text{O}_7$  single crystals were carried out using the 3.0 MV tandem accelerator facility within Environmental Molecular Sciences Laboratory (EMSL) at the Pacific Northwest National Laboratory (PNNL). Each sample was mechanically mounted to a molybdenum plate using molybdenum spring-loaded clips, with a chromel–alumel thermocouple clamped to the sample surface. The samples were irradiated with 1.0 MeV  $\text{Au}^{2+}$  ions at 300 K  $7^\circ$  off the (0 0 1) direction. The ion fluences are chosen from  $2 \times 10^{12}$  to  $3.1 \times 10^{13} \text{ Au}^+ \text{ cm}^{-2}$ , which produced damage states that ranged from relatively minor disorder to a fully amorphous layer. The beam energy was chosen to produce shallow damage that could be readily measured by the ion channeling technique. For each ion fluence, the local dose at the damage peak, in displacements per atom (dpa), was determined using the Stopping and Range of Ions in Matter (SRIM) 2008 code [30] under full-cascade mode, assuming a theoretical density of  $6.926 \text{ g/cm}^3$  and threshold displacement energies of 50 eV for Ho, Ti and O atoms [10]. The conversion factor at the damage peak from ion fluence ( $10^{14} \text{ Au}^+ \text{ cm}^{-2}$ ) to dose (dpa) is 0.438 under the irradiation conditions of this study.

The damage evolution was investigated by the relative disorder determined by backscattering spectroscopy (RBS) along the (0 0 1) channel direction. Helium ions of 2.0 MeV were used as probing beam and the backscattering angle was  $150^\circ$ . Energy calibration of  $E \text{ (keV)} = E \text{ (ch)} \times 2.045 \text{ (keV/ch)} + 71.4 \text{ (keV)}$  is used to convert to an energy spectrum. For ion-beam induced damage, the backscattering yield is primarily due to interstitials within channels, unaligned atoms in amorphous domains, and unaligned atoms due to local strain from dislocations. The ion-channeling methods are not as sensitive to vacancies, antisite defects, or the cation and anion disorder; however, the influence of such defects may be noticeable by the increase of dechanneling fraction. The disordering measured in the present study by ion channeling is disorder associated with anions and cations on non-crystalline sites.

## 3. Results and discussion

### 3.1. Damage accumulation

Channeling RBS spectra for the irradiated samples along the (1 0 0) direction in  $\text{Ho}_2\text{Ti}_2\text{O}_7$  are shown in Fig. 1. For clarity purpose, only the result from ion fluences of  $9 \times 10^{12}$ ,  $1.5 \times 10^{13}$ ,  $2.1 \times 10^{13}$ ,  $2.7 \times 10^{13} \text{ cm}^{-2}$  are included, which illustrates the general statistics for other irradiated samples. The random and channeling spectra from a virgin area are also included to indicate the fully amorphous and essentially defect-free states, respectively. The ratio of the backscattering yield in the virgin spectrum to the yield in the random spectrum just below the surface peak,  $\chi_{\text{min}}$ ,



**Fig. 1.** A series of (1 0 0)-aligned RBS spectra for  $\text{Ho}_2\text{Ti}_2\text{O}_7$  samples under 1.0 MeV Au irradiation at room temperature to ion fluences from  $9 \times 10^{12}$  to  $2.7 \times 10^{13} \text{ cm}^{-2}$ . Random and channeling spectra from a virgin area are also included. For clarity purpose, every three data points are shown. Backscattered He ions from the sample surface are marked for the Ho, Ti and O sublattices, respectively. The lines are the simulation results from the McChasy code.

is  $\sim 3.7\%$ , which indicates the good quality of the crystal. The emergence of the damage peaks in the channeling spectra indicates the presence of disorder that causes backscattering of the channeled ions. As shown in Fig. 1, the increase in disorder on the Ho and Ti sublattices with increasing ion fluences is evident. Because the damage accumulation starts from the surface and increases with ion fluence, the surface peak cannot be resolved.

In order to obtain a quantitative damage profile, an iterative procedure [31–35] is applied to determine the dechanneling component of the RBS spectra as a function of depth. Because the backscattering yield due to the ion-beam-induced disordering is much more evident from the Ho sublattice, all analyses of cation disordering were performed on that part of the spectrum. For each ion fluence, a set of three spectra is needed to determine the corresponding disorder profile: the measured channeling spectra from both the irradiated sample and the virgin sample, as well as the random spectrum [32]. Both the normalized spectra,  $V(x)$  and  $\eta(x)$ , from the virgin spectrum and the damaged spectrum can be achieved by normalizing the corresponding channeling spectra to the random spectrum. The dechanneling component,  $R(x)$ , starts from a point,  $x_0$ , on the normalized virgin spectrum near the beginning of the damaged region, where the dechanneling component  $R(x_0)$  is assumed to be zero.

$$R(x) = V(x) + [1 - V(x)] \times \left( 1 - \exp \left[ -\sigma_D \times \sum_{x+1}^{x_0} \left[ \frac{\eta(x+1) - R(x+1)}{1 - R(x+1)} \right] \right] \right) \quad (1)$$

The iterative procedure [32] successively moves in depth to the next channel, as described in Eq. (1), to determine the dechanneling function,  $R(x)$ , which enables the separation of the direct backscattering contribution from the displaced atoms at that depth. The parameter,  $\sigma_D$ , is the only adjustable parameter that is related to dechanneling cross section for the disorder along the axial channel direction, and can be determined when the dechanneling component  $R(x)$  overlaps with the normalized channeling spectrum  $\eta(x)$  after the damage peak. After separation of the dechanneling component from the direct backscattering contribution,  $\eta(x) - R(x)$ , the profile of the relative Ho disorder is then derived by  $[\eta(x) - R(x)] / [1 - R(x)]$ . The continuous amorphous state determined by RBS corresponds to a relative disorder level of 1.0, where the aligned spectrum overlaps with the random spectrum.

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