**An investigation of the electronic structure and structural stability of $\text{RE}_2\text{Ti}_2\text{O}_7$ by
glancing angle and total electron yield XANES**

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Abstract:

Pyrochlore-type oxides ($A_2B_2O_7$) have been investigated for nuclear waste sequestration applications due to their overall resistance to **radiation-induced** structural damage. This damage can be simulated by implanting the materials with high-energy ions to aid in understanding how the structure of a crystalline material responds to radioactive decay of incorporated nuclear waste elements. $RE_2Ti_2O_7$ ($RE=La-Lu$), $Yb_{1.85}Ca_{0.15}Ti_2O_{7-\delta}$, and $Yb_2Ti_{1.85}Fe_{0.15}O_{7-\delta}$ were synthesized by the ceramic method and investigated by Ti K-edge X-ray absorption near edge spectroscopy (XANES) and powder X-ray diffraction before and after being implanted by 2 MeV Au^- ions. Surface sensitive total electron yield (TEY) XANES spectra and glancing-angle (GA) XANES spectra were collected to study the **ion-implanted** materials. It was necessary to use these surface sensitive detection methods because the 2 MeV Au^- ions only implant to ~ 450 nm into the surface of the materials. An effective sample mounting procedure has been developed that uses conductive silver paint to collect high quality TEY-XANES spectra from the damaged surface layer of the implanted pellets so as to minimize charging effects. This investigation has shown that the local coordination number of Ti decreased after implantation, and that the degree of damage observed decreases with decreasing radius of the **RE cation**. The study has also shown that the oxygen vacancies generated by a slight substitution of Ca^{2+} for Yb^{3+} or Fe^{3+} for Ti^{4+} does not considerably affect the resistance of $Yb_2Ti_2O_7$ to **radiation-induced** damage.

Keywords: TEY-XANES (D); GA-XANES (D); Pyrochlore-type oxide (A); Nuclear wasteforms (A); Radiation damage (C); Ion beam implantation (D).

Introduction:

The use of nuclear reactors to supply power to the civilian population has resulted in the production of a considerable stock-pile of radioactive nuclear waste [1-6]. Crystalline materials have been investigated as one strategy for the safe disposal and long-term storage for radioactive nuclear waste [5-9]. A key concern of these materials is the stability of the crystalline structure over thousands of years, which can be affected by the decay of radioactive elements [3,4,9]. The incorporated radioactive nuclear waste elements can release α -particles (β - or γ -particles can also be released depending on the decay mechanism), and be transformed into daughter products during the radioactive decay process [5,6,9]. The α -particles and the daughter products can displace other atoms within the structure of the materials, which (may) result in amorphization [10,11]. This process can also result in the development of crystal defects and swelling of the structure, which can affect the long-term chemical durability of the nuclear wastefrom [5,6,12]. Radiation-induced structural damage can be simulated by implanting the materials with high energy ions (e.g., Au⁻, Kr⁺, and Xe⁺) to better understand how the structure of crystalline materials respond to radioactive decay of incorporated nuclear waste elements [5,7,13-16]. High energy (MeV) ion-implantation can produce a thin amorphous (damaged) layer, which is typically a few hundred nm thick [16,17].

Multiple crystalline oxides are being investigated for nuclear waste sequestration, with pyrochlore-type oxides receiving considerable attention [5,7,18-20]. Pyrochlore-type oxides can be represented by the general formula $A_2B_2O_7$ (Space group: $Fd\bar{3}m$) where A^{3+} and B^{4+} -site cations are in eight and six coordinate sites, respectively. The pyrochlore-type structure is shown in Figure 1. The perfectly ordered pyrochlore structure has three distinct oxygen anion sites within tetrahedral interstices, with one of them being vacant [5,7,22-24]. Cation and anion

anti-site disorder has been observed in materials that adopt this structure and can be caused by: composition; synthesis method; ion beam implantation; or the application of an external pressure [25-29]. The degree of cation anti-site disorder present in a pyrochlore-type material is dependent on the ratio of the A- and B-site cationic radii. When the ionic radius ratio (r_A/r_B) approaches ~ 1.46 , cation anti-site disorder is more likely to occur, which can result in the transformation of the pyrochlore-type structure into the defect fluorite-type structure [5,28,29].

X-ray absorption near edge spectroscopy (XANES) is a powerful technique that provides unique insight into the electronic and structural properties of a material [30,31]. XANES is an **element-specific method** and gives detailed information about the coordination number (CN), oxidation state, and bonding environment of the element of interest [32-34]. The most common measurement methods used to collect XANES spectra are transmission, total electron yield (TEY), and fluorescence yield (FLY) [31,35]. The spectra collected using these different detection methods probe different sampling depths [31]. Transmission and fluorescence XANES measurements are inherently bulk sensitive whereas TEY-XANES measurements are surface sensitive [16,35-37]. Surface charging can be problematic while recording the TEY-XANES spectra from thick pellets of poorly conductive materials [38,39]. Although hard X-ray XANES spectra are generally bulk sensitive, surface sensitive detection methods such as glancing angle XANES and TEY-XANES measurements can be used to probe only the damaged surface layer of **ion-implanted** materials [16,17,35,37,40,41]. In glancing angle XANES (GA-XANES) experiments, the incident X-ray beam angle is set to be just above the critical angle (the angle at which total external reflection occurs) in order to selectively probe the surface layer. The spectra become more surface sensitive as the glancing angle decreases. Previous investigations by this

group (and other groups) have shown how GA-XANES can be used to study the damaged surface layer of ion-implanted materials [16,17,42,43].

Rare-earth titanates ($\text{RE}_2\text{Ti}_2\text{O}_7$; RE (rare-earth)=La-Lu, and Y) have been investigated for the sequestration of nuclear waste due to their resistance to radiation-induced structural damage, which depends on the rare-earth cation present [7,44,45]. $\text{RE}_2\text{Ti}_2\text{O}_7$ crystallites have been examined previously using transmission electron microscopy (TEM) before and after implantation, and this previous study has shown that the resistance to radiation-induced structural damage increases with decreasing radius of the RE cation [7]. Along with stoichiometric materials, oxygen deficient pyrochlore-type materials ($\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$) can also be synthesized by the partial substitution of the A^{3+} or B^{4+} cations by metals that have a lower oxidation state [46-48]. The potential for developing chemically durable pyrochlore-type materials that are resistant to radiation-induced structural damage has led to increased interest in the use of these materials for nuclear waste sequestration applications [7,49-51]. The objective of the present study was to demonstrate the ability of GA-XANES and TEY-XANES studies to probe the damaged surface layer of rare-earth titanate materials. This study has shown how GA-XANES and TEY-XANES, as well as powder XRD, can be used to study how the structural stability of $\text{RE}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$, and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ pellets changes depending on composition. An effective way of collecting TEY spectra from thick pellets of poorly conducting pyrochlore-type oxides has also been tested and is discussed.

2. Experimental

2.1. Synthesis

A series of $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Eu, Gd, Ho, Yb, Y) materials were synthesized by the ceramic method. RE_2O_3 (Alfa Aesar, 99.99 %) and TiO_2 (Alfa Aesar, 99.9%) powders were mixed, ground in stoichiometric amounts, and pressed into pellets at 6 MPa. These pellets were placed in aluminum crucibles and heated in air at 1400 °C over 6-9 days, with intermediate grinding and repelleting until phase purity was achieved. Yb_2O_3 , TiO_2 , and CaCO_3 (EMD, >99%) powders were mixed and first heated to 900 °C to decompose the carbonate before being heated to 1400 °C and then quench cooled in air to synthesize $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$. The method used to synthesize $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ was reported previously [47]. The phase purity of the synthesized materials was confirmed by powder X-ray diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer and a Cu $\text{K}\alpha_{1,2}$ X-ray source. A Rietveld refinement of the powder XRD patterns from some of the synthesized (undamaged) $\text{RE}_2\text{Ti}_2\text{O}_7$ materials was performed using the High Score Plus Software package [52]. The lattice constants, the x-coordinate of O in the 48f position (x_{48f}), the overall thermal factor, and the line shape were all refined during analysis (Table S1). The phase-pure samples were repelletted at 8 MPa after being examined by powder XRD and heated at 1400 °C for 3 days to increase the hardness of these pellets before being implanted by Au^+ ions.

2.2. Ion beam implantation

Ion-implantation of $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Eu, Gd, Ho, Yb, Y), $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$, and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ was performed using the 1.7 MeV Tandetron accelerator located at Interface Science Western (ISW), University of Western Ontario. The ion beam was aligned normal to the

pellet surface during ion-implantation. All materials were implanted by 2 MeV Au⁻ ions to a dose of 5×10^{14} ions/cm² at room temperature.

The Stopping and Range of Ions in Matter (SRIM-2013) software package was used to calculate the depth profiles and defect per ion profiles of the implanted RE₂Ti₂O₇ (RE=Sm, Gd, Yb), Yb_{1.85}Ca_{0.15}Ti₂O_{7-δ}, and Yb₂Ti_{1.85}Fe_{0.15}O_{7-δ} samples [53]. The densities (ρ) of Sm₂Ti₂O₇, Gd₂Ti₂O₇, Yb₂Ti₂O₇, Yb_{1.85}Ca_{0.15}Ti₂O_{7-δ}, and Yb₂Ti_{1.85}Fe_{0.15}O_{7-δ} used in the calculations were 6.17 g/cm³, 6.57 g/cm³, 7.16 g/cm³, 6.89 g/cm³, and 7.46 g/cm³, respectively [46,51]. Ion-implantation depth profile calculations were performed using five thousand (5000) 2 MeV Au⁻ ions and by assuming that the target displacement energies were 25 eV for RE/Ti/Fe/Ca and 28 eV for O. These calculations (Figure 2a and Figure S1 in supporting information) predicted that the ions **penetrate** to a depth of ~100-450 nm for all samples. Profiles of the number of vacancies produced per Au⁻ ion are shown in Figure 2b and Figure S2. These calculations showed that the number of vacancies produced in the material reach a maximum at a depth of ~200 nm, and that the number of vacancies **decreases** dramatically at deeper depths.

2.3. Micro powder X-ray diffraction

Micro powder XRD (μ-XRD) patterns from the **ion-implanted** samples were collected using the PANalytical Empyrean X-ray diffractometer described in section 2.1. The diffraction patterns were collected to analyze the changes that occur in the long-range crystal structure of these titanate pyrochlore-type oxides after ion-implantation. μ-XRD analysis was performed by reducing the X-ray beam spot size to 200 μm using a mono-capillary collimator. Each implanted pellet was placed on a goniometer stage which permits translation in x-, y- and z-axis directions as well as tilting of the goniometer head. The surface of the implanted pellets was aligned to the

incident X-ray beam using a microscope and diffraction patterns were collected in the 2θ range of 10 - 55° .

2.4. XANES

The Soft X-ray Microcharacterization Beamline (SXRMB, 06B1-1) located at the Canadian Light Source (CLS) was used to collect the Ti K-edge XANES spectra from the damaged and undamaged $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Eu, Gd, Ho, Yb and Y), $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$, and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ materials using a Si(111) monochromator [54]. This beamline provides a photon flux of 10^{11} photons/s and a resolution of 0.5 eV at 4966 eV [54,55]. Spectra from the undamaged materials were collected from powdered materials placed on carbon tape. The **ion-implanted** (i.e., damaged) $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm,Gd,Ho,Yb), $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$, and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ pellets (~ 1 - 2 mm thick) were mounted on the Cu sample holder using carbon tape, and silver paint was used to place the surface of the pellets in electrical contact with the sample holder. All spectra were collected in total electron yield (TEY) mode using a step size of 0.15 eV through the absorption-edge. The angle between the X-ray beam and the implanted pellet was $\sim 85^\circ$ during these measurements [54]. The spectra were calibrated using the K-edge spectrum from Ti metal (4966.0 eV) [55].

Ti K-edge GA-XANES spectra from damaged pellets of $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Gd, and Yb), $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$, and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ were collected using the Pacific Northwest Consortium/X-ray Science Division Collaborative Access Team (PNC/XSD-CAT, Sector 20) bending magnetic beamline (20BM) located at the Advanced Photon Source (APS) [56]. A Si (111) double crystal monochromator with harmonic rejection was used, providing a photon flux of $\sim 10^{11}$ photons/s and a resolution of 0.7 eV at 4966 eV [54,56]. GA-XANES analysis of the

ion-implanted pellets was performed using a vertically focused X-ray beam with a height of 45 μm and a beam width of 2 mm. The X-ray beam angle of incidence on the surface of the pellets was changed using a motor driven Huber (goniometer) stage that permits x-, y-, and z-axis translation as well as rotation of the glancing angle (α) between the X-ray beam and the surface of the sample. The glancing angle (α) was set to the desired value with an accuracy of 0.1° to reach different depths of the implanted pellets during GA-XANES analysis. A web-based program was used to calculate the glancing angles required to reach specific X-ray attenuation depths for photons having energies of 4966 eV (Ti K-edge; Figure 2a and Table 1) [57]. Partial fluorescence yield spectra were collected using a single element vortex silicon drift detector. (The Ti K-edge partial fluorescence spectra collected at different glancing angles were not found to be influenced by absorption effects, which is in agreement with a previous study [17].) Spectra were recorded by stepping the energy in 0.15 eV increments through the absorption edge and calibrated against Ti metal (4966.0 eV) [55]. All XANES spectra discussed here were normalized, calibrated, and analyzed using the Athena software program [58].

3. Results and discussion

3.1. Powder X-ray diffraction before and after ion implantation

Bulk powder XRD and μ -XRD patterns from $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Eu, Gd, Ho, Yb and Y), $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$, and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ before (bulk powder XRD) and after (μ -XRD) being implanted by Au^- ions to a dose of 5×10^{14} ions/ cm^2 are presented in Figure 3 and Figure S3. The XRD patterns of the undamaged materials reported in this study are in good agreement with those reported previously, where the $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Eu, Gd, Ho, Yb and Y) materials adopt the pyrochlore-type structure [7,51]. The lattice constants of the ternary materials (Table 2) were

found to decrease with decreasing ionic radius of the **RE cation** [59]. The lattice constant of $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ was found to be larger than that of $\text{Yb}_2\text{Ti}_2\text{O}_7$ because of the larger ionic radius of Ca^{2+} compared to Yb^{3+} ($r_{\text{Ca}^{2+}}=1.120 \text{ \AA} > r_{\text{Yb}^{3+}}=0.985 \text{ \AA}$) [59]. As was reported previously, the lattice constant of $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ was found to be smaller than that of $\text{Yb}_2\text{Ti}_2\text{O}_7$ because of the decrease in Ti and Fe CN upon Fe^{3+} substitution [47].

Cation anti-site disorder can be observed in these materials, and is related to the ratio of the A and B cationic radii. As the ionic radii ratio (r_A/r_B) approaches ~ 1.46 , the A-site and B-site cations may undergo anti-site disorder which can result in a phase transition from the pyrochlore to the defect fluorite structure [5,7,22,60]. The super structural peaks (odd planes) from the XRD patterns were used to differentiate the pyrochlore-phase materials from the defect-fluorite phase materials [60-63]. A decrease in the intensity of the superstructural peaks is generally indicative of cation anti-site disorder; however, the intensities of these peaks relative to the other peaks are also affected by the differences in the scattering power between the A- and B-site cations [34,64]. Rietveld refinement results of the powder XRD patterns collected from some of the undamaged $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm,Gd,Yb) materials are presented in Figure S4 and Table S1 in the supporting information. The refinement results confirmed that all three $\text{RE}_2\text{Ti}_2\text{O}_7$ materials studied in this manner adopted the pyrochlore-type structure. The refinement parameters show that a small decrease in the x_{48f} position of the oxygen anions was observed with decreasing radius of the **RE cation** (Table S1). In pyrochlore-type materials, the TiO_6 octahedral shape is sensitive to the oxygen x_{48f} position parameter [5,7,65,66]. A small decrease in the **oxygen** x_{48f} position parameter with decreasing radius of the **RE cation** suggests that a small distortion of the TiO_6 octahedra occurs with decreasing radius of the **RE cation**.

The examination of diffraction patterns from the $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Eu, Gd, Ho, Yb and Y), $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$, and $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ materials before and after implantation allows for an investigation of how the long-range crystal structure is affected by ion implantation. The lattice parameters did not change because of implantation (Table 2); however, the diffraction patterns from the implanted materials (Figures 3 and S4) clearly show a broadening of the diffraction peaks (e.g., the (222) diffraction peak; see Table 2). The increase in the width of the diffraction peaks could be a result of a decrease in the average crystallite size, but these peaks can also broaden because of the production of defects [67]. The presence of the small hump located near the (222) diffraction peak ($\sim 30^\circ$) in the diffraction patterns from the implanted $\text{RE}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ materials indicates that these materials become partially amorphous after ion implantation (see Figures 3 and S4). The intensity of the amorphous hump located at $\sim 30^\circ$ in the diffraction patterns from the implanted $\text{RE}_2\text{Ti}_2\text{O}_7$ materials gradually decreases with decreasing ionic radii of the RE cation (Sm $\rightarrow$ Yb) [51,68]. It has been previously demonstrated by examination of ion-implanted crystallites of $\text{RE}_2\text{Ti}_2\text{O}_7$ by TEM that these materials become less prone to ion-beam induced amorphization with decreasing ionic radii of the RE cation [7]. As the radius of the RE cation decreases and approaches that of Ti^{4+} , the tendency for the cations to undergo anti-site disorder increases and the materials become more likely to undergo a phase transition from the pyrochlore-type structure to the defect fluorite-type structure because of ion implantation instead of becoming amorphous [7].

3.2. Ti K-edge XANES of the undamaged materials

Normalized Ti K-edge XANES spectra from the undamaged $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm, Eu, Gd, Ho, Yb, and Y) materials are presented in Figure 4. The examination of these spectra has allowed for a study of how the electronic structure of these materials changes depending on

composition. The spectra consist of low intensity, quadrupolar (pre-edge; $1s \rightarrow 3d$; A) excitations and strong, dipolar (main-edge; $1s \rightarrow 4p$; B and C) excitations [69,70]. Three features are observed in the pre-edge region (A_1 , A_2 , and A_3), and result from the excitation of $1s$ electrons to crystal field split $3d$ states ($3d-t_{2g}$ and $3d-e_g^*$) as well as non-local excitations. Feature A_1 and the lower energy region of feature A_2 in the pre-edge region are a result of $1s \rightarrow 3d-t_{2g}$ and $1s \rightarrow 3d-e_g^*$ excitations, respectively. The higher energy region of peak A_2 and all of feature A_3 results from non-local (intersite-hybrid) excitations of $1s$ electrons to d -states of next-nearest neighbour atoms that overlap with Ti $4p$ states of the absorbing atom *via* O $2p$ states [69-72]. All of the features in the spectra have been found to change because of variations in bonding, oxidation state, and CN [34,73,74]. The changes observed in the pre-edge and main-edge features with varying composition are discussed below.

The intensity and absorption energy of the pre-edge (A) and main-edge features (B and C) in Ti K-edge XANES spectra change with changing CN [73-80]. The pre-edge features (A_1 and A_2) resulting from local excitations are very sensitive to changes in CN or a distortion of the local coordination environment [73-78]. Examination of the pre-edge region of Ti K-edge XANES spectra can be useful in determining if the local Ti coordination environment is affected by the radius of the **RE cation** in $RE_2Ti_2O_7$. As the CN changes and/or the local coordination environment around the Ti ion is distorted, the variation in the amount of overlap between Ti $3d$ and Ti $4p$ states can change the dipolar character of the transition [69,71,73,75-78]. For example, a decrease in Ti CN would result in greater overlap of the Ti $3d$ and $4p$ states, which would be observed by an increase in the intensity of the pre-edge peak. However, such changes are not observed in the Ti K-edge spectra (Figure 4a) from the undamaged $RE_2Ti_2O_7$ materials as the **RE**

cation is changed. This result is in agreement with the results of the Rietveld refinement of powder XRD data from $\text{Sm}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{Ti}_2\text{O}_7$, and $\text{Yb}_2\text{Ti}_2\text{O}_7$ (Figure S4).

The intensity of the main-edge region of the Ti K-edge spectra (C) increases with decreasing radius of the RE cation in the $\text{RE}_2\text{Ti}_2\text{O}_7$ system. The intensity of the main-edge feature (C) changes considerably because of variations in the chemical environment around the Ti atoms [73,74,79,80]. An increase in intensity of feature C can be a result of an increase in the number of Ti 4p final states (or Ti 4p-O 2p states) available for 1s electrons to be excited to. The observed change with decreasing radius of the RE cation could be a result of a change in the bonding environment around the Ti atoms with decreasing Ti-O bond length and/or a distortion of the TiO_6 octahedra. This could lead to an increase in the average number of Ti 4p final states (or Ti 4p-O 2p states) available for 1s electrons to be excited to.

The previously reported XANES spectrum from undamaged $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ is presented in Figure 4b along with the spectrum from $\text{Yb}_2\text{Ti}_2\text{O}_7$ [47]. The observed spectral changes (i.e., an increase in intensity of feature A, a decrease in energy of feature B, and a decrease in intensity of feature C) upon Fe^{3+} substitution are a result of a decrease in the Ti CN upon substitution of Ti^{4+} for Fe^{3+} [47]. Similar spectral changes are observed (Figure 4c) in the spectrum from $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ upon substitution of Yb^{3+} for Ca^{2+} . The observed decrease in the Ti CN in $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ indicates that oxygen vacancies are generated in both systems either by substitution of Ti^{4+} for Fe^{3+} or by substitution of Yb^{3+} for Ca^{2+} .

3.3. Ti K-edge XANES from ion-implanted materials

GA-XANES and TEY-XANES spectra were collected from the ion-implanted materials to study how the composition affects the resistance of these materials to structural damage. The 2 MeV Au⁺ ions penetrate through the surface region to a maximum depth of ~450 nm in these rare earth titanate materials (Figure 2a and Figure S1), and defect-per-ion profiles indicate that the largest number of defects would be generated at a depth of ~200 nm (Figure 2b and Figure S2). As such, it was necessary to use surface sensitive detection methods to study how the Ti K-edge XANES spectra from these materials change as a result of ion implantation [16,17]. Examination of these spectra from the implanted RE₂Ti₂O₇, Yb₂Ti_{1.85}Fe_{0.15}O_{7-δ}, and Yb_{1.85}Ca_{0.15}Ti₂O_{7-δ} materials provided important information on the effect of RE ionic radii, metal substitution, and the presence of O-vacancies.

3.3.1. GA-XANES

Ti K-edge GA-XANES spectra were collected using glancing angles that provided X-ray attenuation depths of 100 nm and 450 nm to investigate the effect of ion implantation on the local coordination environment of Ti. Normalized Ti K-edge GA-XANES spectra collected at different glancing angles from RE₂Ti₂O₇ (RE=Sm,Gd,Yb), Yb₂Ti_{1.85}Fe_{0.15}O_{7-δ}, and Yb_{1.85}Ca_{0.15}Ti₂O_{7-δ} implanted by Au⁺ ions to a dose of 5×10¹⁴ ions/cm² are presented in Figure 5. These spectra are compared to the Ti K-edge XANES spectra from the undamaged materials collected in TEY mode.

The pre-edge (A) and main-edge features (B,C) in the Ti K-edge GA-XANES spectra from RE₂Ti₂O₇ (RE=Sm,Gd,Yb), Yb₂Ti_{1.85}Fe_{0.15}O_{7-δ}, and Yb_{1.85}Ca_{0.15}Ti₂O_{7-δ} were found to change significantly upon ion implantation (Figure 5). The intensity of the pre-edge feature (A)

increased while the intensity and energy of the main-edge feature (B,C) decreased as a result of ion implantation. All of these changes are a result of a decrease in the Ti CN [73-78]. As was stated in section 3.2, a decrease in CN can lead to an increased dipolar character of the transition by increased mixing of p- and d-states, which results in an increase in the pre-edge peak intensity. The decrease in the energy and intensity of the two main-edge features (B and C) in the spectra presented in Figure 5 from the damaged materials are a result of greater final-state relaxation effects and the reduced number of Ti 4p-O 2p final states available for 1s electrons excited to, respectively, and are a result of a reduction of the Ti CN [73,74,77,78,81]. As was stated in a previous report, the observed decrease in Ti CN does not indicate significant loss of O^{2-} from the materials after ion implantation, but instead suggests that the atoms become disordered in the near surface region of these materials upon ion implantation [17].

Analysis of the GA-XANES spectra collected at different glancing angles from **ion-implanted** $Sm_2Ti_2O_7$, $Yb_2Ti_2O_7$, $Yb_2Ti_{1.85}Fe_{0.15}O_{7-\delta}$, and $Yb_{1.85}Ca_{0.15}Ti_2O_{7-\delta}$ (Figure 5) shows that more damage occurs (i.e., the Ti CN decreases) near the surface (X-ray attenuation depth of 100 nm) compared to deeper into the material (X-ray attenuation depth of 450 nm). This observation is in agreement with the calculated **defect-per-ion profiles** presented in Figure 2b and Figure S2. Examination of the GA-XANES spectra collected from the **ion-implanted** $RE_2Ti_2O_7$ (RE=Sm,Gd,Yb) materials using a glancing angle that provides an X-ray attenuation depth of 450 nm (Figure 6a) shows that the $RE_2Ti_2O_7$ materials show an increase in resistance to structural damage with decreasing radius of the **RE cation**. This assessment is based on the observation of a decrease in intensity of the pre-edge and an increase in the energy and intensity of the main-edge as the RE cation was changed from Sm to Gd to Yb. As the radius of the **RE cation** decreases and approaches the radius of Ti^{4+} , the tendency for the cations to undergo anti-

site disorder increases and the materials are more likely to undergo a phase transition from the pyrochlore-type structure to the defect-fluorite-type structure because of ion implantation instead of becoming amorphous [5,7,51]. The observation by GA-XANES that $\text{Yb}_2\text{Ti}_2\text{O}_7$ is more resistant to **radiation-induced** damage compared to $\text{Sm}_2\text{Ti}_2\text{O}_7$ or $\text{Gd}_2\text{Ti}_2\text{O}_7$ is in agreement with a previous study that used TEM to monitor the radiation resistance of crystallites of these materials [7].

The effect of metal substitution (A-site and B-site substitution) and the presence of oxygen vacancies on the structural stability of $\text{Yb}_2\text{Ti}_2\text{O}_7$ was studied by comparing the GA-XANES spectra from **ion-implanted** $\text{Yb}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ (Figure 6b). No significant differences in the spectra were observed, which suggests that the number of oxygen vacancies generated by a slight substitution of Ca^{2+} for Yb^{3+} or a slight substitution of Fe^{3+} for Ti^{4+} does not considerably affect the resistance of $\text{Yb}_2\text{Ti}_2\text{O}_7$ to **radiation-induced** structural damage. This result was verified by analysis of Ti K-edge TEY-XANES spectra from the implanted materials (*vide infra*).

3.3.2. TEY-XANES

Surface-sensitive Ti K-edge TEY-XANES spectra were also collected from the implanted materials. The TEY-XANES spectra from the implanted materials have been compared to the spectra from the undamaged materials, and the normalized spectra are shown in Figure 7. Charging effects can be problematic while acquiring TEY spectra from thick pellets of insulating materials [35]. These issues can be resolved by mounting the pellet to an electrically grounded sample holder using conductive silver paint to connect the surface of the pellet to the holder to increase the conductivity of the sample [35,37,82]. The effect of this mounting procedure on the

quality of the TEY spectra collected is demonstrated in Figure 8 by comparison of Ti K-edge spectra before normalization from a pellet of **ion-implanted** $\text{Sm}_2\text{Ti}_2\text{O}_7$ connected to the holder using only carbon tape or using carbon tape *and* silver paint.

All of the features observed in the Ti K-edge TEY-XANES spectra from $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE=Sm,Gd,Ho,Yb), $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ changed upon ion implantation (Figure 7). **The reasons for the changes in the spectra from the ion-implanted materials are the same as those presented in section 3.3.1, where the changes in the GA-XANES spectra are described.** It should be noted that all of the TEY-XANES spectra were collected using the same angle of incidence of the X-rays to the surface of the pellets ($\sim 85^\circ$). Because of this, it is difficult to compare how the spectra from the $\text{RE}_2\text{Ti}_2\text{O}_7$ materials changed depending on the **RE cation** present as the sampling depths were all slightly different. However, the spectra collected from **ion-implanted** $\text{Yb}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ *can* be compared, as the substitution of the A- or B-site cation was minor and it is not expected that this would greatly affect the X-ray attenuation depth or the depth at which electrons would travel through the surface. A comparison of the TEY-XANES spectra from the implanted $\text{Yb}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ materials (Figure 9) reveals no significant differences as a result of a slight substitution of Ca^{2+} for Yb^{3+} or Fe^{3+} for Ti^{4+} , which is in agreement with the equivalent GA-XANES spectra (see Figure 6b). The examination of GA-XANES and TEY-XANES spectra from these rare-earth titanate materials has shown that the damaged surface layer of **ion-implanted** pellets could be studied using either measurement method.

4. Conclusions

GA-XANES, TEY-XANES, and XRD have been used to study how the structural stability of pyrochlore-type oxides changes depending on composition. The examination of Ti K-edge XANES spectra from the implanted $\text{RE}_2\text{Ti}_2\text{O}_7$ materials has shown that these materials have a greater resistance to ion-induced structural damage with decreasing ionic radii of the RE cation, which is in agreement with a previous TEM study of these materials [7]. This study has also shown that oxygen vacancies generated in the structure of $\text{Yb}_2\text{Ti}_2\text{O}_7$ by a slight substitution of Yb^{3+} for Ca^{2+} or Ti^{4+} for Fe^{3+} does not significantly affect the radiation resistance of this material. An effective sample mounting procedure for collecting high quality TEY-XANES spectra from thick pellets was also reported in this study. This investigation has demonstrated the ability of GA-XANES and TEY-XANES to probe the surface layer of materials that have been damaged by ion implantation. These techniques will be useful for the development of materials that can be used to sequester nuclear waste.

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Tables

Table 1. Calculated glancing angles required to give specific X-ray attenuation depths for photons having energies of 4966 eV (Ti K-edge).

Sample	Ti K-edge (4966 eV)	
	X-ray attenuation depth (nm)	Glancing angle
Sm ₂ Ti ₂ O ₇	100	1.0°
	450	3.8°
	4835	45°
Gd ₂ Ti ₂ O ₇	100	1.1°
	450	4.5°
	4088	45°
Yb ₂ Ti ₂ O ₇	100	1.5°
	450	6.1°
	3013	45°
Yb ₂ Ti _{1.85} Fe _{0.15} O _{7-δ}	100	1.5°
	450	6.4°
	2889	45°
Yb _{1.85} Ca _{0.15} Ti ₂ O _{7-δ}	100	1.4°
	450	5.8°
	3187	45°

Table 2. Lattice constants from the undamaged and damaged materials along with the full width at half maximum (FWHM) of the (222) diffraction peak

Sample	Average A-site ionic radius (Å) [59] ^a	Undamaged		Dose: 5×10 ¹⁴ ions/cm ²	
		a (Å)	FWHM of the (222) diffraction peak	a Å	FWHM of the (222) diffraction peak
Sm ₂ Ti ₂ O ₇	1.079	10.2318(3)	0.0581°	10.2390	0.2787°
Eu ₂ Ti ₂ O ₇	1.066	10.2043(1)	0.0571°	10.2095	0.2800°
Gd ₂ Ti ₂ O ₇	1.053	10.1851(1)	0.0878°	10.1850	0.3049°
Ho ₂ Ti ₂ O ₇	1.015	10.1000(2)	0.0584°	10.0845	0.2465°
Y ₂ Ti ₂ O ₇	1.019	10.0962(1)	0.0542°	10.0340	0.2414°
Yb ₂ Ti ₂ O ₇	0.985	10.0296(3)	0.0615°	10.0960	0.2552°
Yb ₂ Ti _{1.85} Fe _{0.15} O _{7-δ} [47]	0.985	10.0268(1)	0.0816°	10.0350	0.2833°
Yb _{1.85} Ca _{0.15} Ti ₂ O _{7-δ}	0.995	10.0385(6)	0.2476°	10.0470	0.2505°

^aThe ionic radius of Ti⁴⁺ is 0.605 Å [59].

Figure Captions:

Figure 1: A portion of the pyrochlore-type structure of $\text{Yb}_2\text{Ti}_2\text{O}_7$ is shown. The structure consists of YbO_8 in distorted cubic polyhedra (dark grey), distorted TiO_6 octahedra (light grey), and O atoms (dark grey spheres) occupy tetrahedral interstitial sites. (This structure was generated using the VESTA program [21].)

Figure 2: (a) A plot of the ion beam implantation depth profile from $\text{Yb}_2\text{Ti}_2\text{O}_7$ calculated using SRIM-2013 is shown. The calculation was performed using 5000 Au^+ ions with the ion beam energy being 2 MeV. A plot of glancing angle *versus* X-ray attenuation depth for $\text{Yb}_2\text{Ti}_2\text{O}_7$ is also included in the figure and was calculated for photons having an energy of 4966 eV (Ti K-edge). (b) A plot of the number of vacancies produced per Au^+ ion (defect-per-ion profile) in $\text{Yb}_2\text{Ti}_2\text{O}_7$ by a 2 MeV beam of 5000 Au^+ ions is presented.

Figure 3: Bulk and micro powder XRD patterns from $\text{RE}_2\text{Ti}_2\text{O}_7$ (RE= Sm, Eu, Gd, Ho, Y, and Yb, respectively) are shown before and after the materials were implanted by Au^+ ions to a dose of 5×10^{14} ions/cm². The odd lattice planes (super structural peaks) from the pyrochlore-type structure are marked by an asterisk (*) and the amorphous hump located near the (222) diffraction peak in the patterns from the damaged materials are indicated by an arrow.

Figure 4: (a) Ti K-edge XANES spectra from the $\text{RE}_2\text{Ti}_2\text{O}_7$ system. Feature A represents the pre-edge region and is shown in the inset. Features B and C represent the main-edge region. No changes were observed in the pre-edge region (A) with decreasing radius of the **RE cation**. The intensity of the main-edge feature (C) increases with decreasing RE ionic radius. The change in intensity of feature C with decreasing radius of the **RE cation** is indicated by an arrow. (b) Ti K-edge XANES spectra from $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$. The changes of the features

(A,B,C) observed in the spectra because of the substitution of Ti^{4+} for Fe^{3+} are marked by arrows.

(c) Ti K-edge XANES spectra from $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ and $\text{Yb}_2\text{Ti}_2\text{O}_7$. The changes of the features (A,B,C) observed in the spectra because of the substitution of Yb^{3+} for Ca^{2+} are marked by arrows.

Figure 5: Ti K-edge GA-XANES spectra collected at various glancing angles from (a) $\text{Sm}_2\text{Ti}_2\text{O}_7$, (b) $\text{Gd}_2\text{Ti}_2\text{O}_7$, (c) $\text{Yb}_2\text{Ti}_2\text{O}_7$, (d) $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and (e) $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ implanted to a dose of 5×10^{14} ions/cm² are presented along with the spectra from the undamaged samples. The glancing angles used were chosen so as to attain X-ray attenuation depths of 100 nm and 450 nm. The change in intensity of features A and C, and the change in energy of feature B observed in the spectra with decreasing glancing angle (i.e., decreasing X-ray attenuation depth) are indicated by arrows.

Figure 6: (a) Ti K-edge GA-XANES spectra from the implanted $(\text{Sm,Gd,Yb})_2\text{Ti}_2\text{O}_7$ materials at a glancing angle providing an X-ray attenuation depth of 450 nm are shown. Arrows mark the changes observed in the spectra as the RE was changed from Sm to Gd to Yb. (b) Ti K edge GA-XANES spectra from **ion-implanted** $\text{Yb}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ are shown. The glancing angle used to collect these spectra was adjusted to give an X-ray attenuation depth of 450 nm.

Figure 7: Ti K edge TEY-XANES spectra from (a) $\text{Sm}_2\text{Ti}_2\text{O}_7$, (b) $\text{Gd}_2\text{Ti}_2\text{O}_7$, (c) $\text{Ho}_2\text{Ti}_2\text{O}_7$, (d) $\text{Yb}_2\text{Ti}_2\text{O}_7$, (e) $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and (f) $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ implanted to a dose of 5×10^{14} ions/cm² are shown along with the spectrum from the undamaged materials. The changes observed in the spectra because of implantation are indicated by arrows.

Figure 8: Ti K edge TEY-XANES spectra before normalization from a pellet of $\text{Sm}_2\text{Ti}_2\text{O}_7$ implanted to a dose of 5×10^{14} ions/cm² and connected to the sample holder using only carbon tape or using carbon tape *and* silver paint. The quality of TEY spectra collected improved by mounting the pellet to the holder using conductive silver paint.

Figure 9: Ti K edge TEY-XANES spectra from the implanted $\text{Yb}_2\text{Ti}_2\text{O}_7$, $\text{Yb}_2\text{Ti}_{1.85}\text{Fe}_{0.15}\text{O}_{7-\delta}$, and $\text{Yb}_{1.85}\text{Ca}_{0.15}\text{Ti}_2\text{O}_{7-\delta}$ materials are shown. No significant changes were observed in the spectra from the implanted materials because of the partial substitution of Ti^{4+} for Fe^{3+} or Yb^{3+} for Ca^{2+} .

Figures:

Figure 1:

Figure 2:

Figure 3:

Figure 4:

Figure 5:

Figure 6:

Figure 7:

Figure 8:

Figure 9: