The Influence of Crystal Structure on Ion-Irradiation Tolerance in the $\text{Sm}_{(x)}\text{Yb}_{(2-x)}\text{TiO}_5$ Series.

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Abstract

This ion-irradiation study covers the four major crystal structure types in the Ln_2TiO_5 series (Ln = lanthanide), namely orthorhombic $Pnma$, hexagonal $P6_3/mmc$, cubic (pyrochlore-like) $Fd-3m$ and cubic (fluorite-like) $Fm-3m$. This is the first systematic examination of the complete Ln_2TiO_5 crystal system and the first reported examination of the hexagonal structure. A series of samples, based on the stoichiometry $\text{Sm}_{(x)}\text{Yb}_{(2-x)}\text{TiO}_5$ (where $x = 2, 1.4, 1, 0.6$, and 0) have been irradiated using 1 MeV Kr^{2+} ions and characterised *in-situ* using a transmission electron microscope. Two quantities are used to define ion-irradiation tolerance: critical dose of amorphisation (D_c), which is the irradiating ion dose required for a crystalline to amorphous transition, and the critical temperature (T_c), above which the sample cannot be rendered amorphous by ion irradiation. The structure type plus elements of bonding are correlated to ion-irradiation tolerance. The cubic phases, Yb_2TiO_5 and $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$, were found to be the most radiation tolerant, with T_c values of 479 and 697 K respectively. The improved radiation tolerance with a change in symmetry to cubic is consistent with previous studies of similar compounds.

1. Introduction

Nuclear fuel cycle, e.g. fuel, waste media or structural, e.g. reactor materials need to be tolerant of the effects of radiation. Various ceramic products (including Synroc, a synthetically fabricated waste-form) have been proposed as materials capable of hosting radioactive waste species. Fluorite and pyrochlore structured materials have been proposed as waste form phases, both as constituents of Synroc and in their own right. They are good hosts for actinides, durable in aqueous environments and are radiation tolerant [1, 2].

Compounds in the Ln_2TiO_5 series, where Ln represents the lanthanides plus yttrium, are found as a secondary phase within some pyrochlore formulations, and have been separately proposed for potential nuclear based applications [3-5]. For example, Dy_2TiO_5 has been incorporated into inert matrix fuel as a neutron absorber [6]. Gd_2TiO_5 has also been proposed for similar use [7] and its radiation tolerance has been tested for this purpose [8]. Orthorhombic Y_2TiO_5 has been modelled to assess its usefulness as an inclusion in oxide dispersion strengthened (ODS) ferritic alloys where the nano-dispersed oxide particles act to improve the structural properties of the steel [9]. In more fundamental studies, the radiation tolerance of several orthorhombic Ln_2TiO_5 materials has been tested via heavy ion irradiation [4, 10-12].

For nuclear materials tolerance of the damage caused via irradiating particles is required for the duration of use. Approaches used when assessing the suitability of such materials involve characterising the response when exposed to radiation. Atomic- and/or microscopic-

scale changes in structure lead to larger scale effects in the material properties such as an increase in volume (swelling) and potential embrittlement. Fundamental studies are essential for acquiring an understanding of ion irradiation induced defect accumulation and microstructure damage evolution.

There are various ways to study the radiation response of different materials. Materials can be exposed to high-energy neutrons within a nuclear reactor, doped with alpha emitters, natural analogues that contain decaying isotopes can be examined, or materials can be exposed to accelerated ions [13]. The approach used in this investigation is *in-situ* ion-irradiation, using a tandem accelerator attached to a transmission electron microscope (TEM) to irradiate thin films. The *in-situ* ion-irradiation experimental approach provides control over the material chemistry and allows orientation of the beam relative to the crystallographic orientation of the target. The controlled conditions of ion-irradiation coupled with *in-situ* TEM allow experimental results to be obtained in a rapid and reproducible way.

One of the major determinants of adopted crystal structure type in the Ln_2TiO_5 series is lanthanide size [14]. The largest lanthanide cations (La to Sm), take on the orthorhombic form when heated under atmospheric pressure. From Eu to Lu, as the lanthanide ionic radius decreases, the other polymorphs can be formed depending on the temperature profile used during synthesis.

Previously we undertook a crystallographic study of the $\text{Sm}_{(x)}\text{Yb}_{(2-x)}\text{TiO}_5$ (where $x = 2, 1.4, 1, 0.6$, and 0) series of compounds, demonstrating that their symmetry changes with the average lanthanide ratio. Specifically the structures were shown to be; Sm_2TiO_5 orthorhombic ($Pnma$), $\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ and SmYbTiO_5 hexagonal ($P6_3/mmc$), $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$

cubic (pyrochlore-like, $Fd\bar{3}m$,) and (fluorite-like, $Fm\bar{3}m$) Yb_2TiO_5 with the crystal structure type depending on the cation size and processing conditions used during fabrication (refer to [Figure 1](#)). [15]

Previous research for nuclear applications has focussed on the orthorhombic and cubic structure types [3, 4, 10-12]. This study extends these to incorporate the hexagonal structure, completing the range of crystal structures in the Ln_2TiO_5 series.

By testing the radiation tolerance of a series of materials covering the range of reported crystal structures for the Ln_2TiO_5 system we seek to gain a more complete picture of the elemental geometry, the resultant effect on bonding, and how this translates to radiation tolerance.

2. Experimental

2.1 Sample fabrication

Bulk, polycrystalline samples were prepared by mixing stoichiometric amounts of Sm_2O_3 , Yb_2O_3 and TiO_2 (99.9% purity), pressing into pellets and sintering to 1550 °C. Bulk, single phase samples of Sm_2TiO_5 could not be fabricated using this approach so a large, single crystal was instead fabricated using a floating zone furnace. More detailed descriptions of both fabrication and structure are given in Aughterson *et al* [15].

2.2 *In-situ* ion-irradiation / transmission electron microscopy (TEM)

TEM samples were prepared by dispersing crushed, fine grains of material in ethanol and dispensing the solution on holey carbon film supported on a copper or molybdenum grid. Organic contamination was removed from the TEM specimen via argon plasma cleaning using a South Bay Technology Plasma Cleaner, PC-150.

Samples were irradiated *in-situ* with 1 MeV Kr^{2+} ions using the IVEM-TANDEM facility, Argonne National Laboratory, USA. The ion-irradiation count rate was set to 6.25×10^{11} ions $\text{cm}^{-2} \text{s}^{-1}$, a flux chosen for maximum ion exposure whilst minimising temperature variations caused by ion-beam-material interactions. Characterisation of the irradiated samples were carried out using a Hitachi 9000-NAR TEM, and selected area diffraction patterns (SADP) were collected to monitor the ion-dose response. Ion-dose was increased iteratively, and paused for the collection of electron diffraction patterns in order to eliminate any synergistic effects caused by operating the electron and ion-beam simultaneously.

The ion-dose required for complete transition from crystalline to amorphous, the critical dose (D_c), was characterised using the SADP's and is defined as the flux at which Bragg diffraction spots are no longer observable (refer to [Figure 2](#)).

Five grains per sample were monitored for each ion-irradiation / TEM characterisation process. The critical dose D_c was taken to be the average of the final dose at which the Bragg diffraction peaks had disappeared and the dose immediately prior. The quoted error for D_c measurements was either the dose step size between collection of SADP's or, the variation in D_c measurement between the grains, whichever was larger. The D_c was also obtained at various temperatures. A Gatan heating stage was used to conduct high temperature experiments between 300 and 1100 K whilst a Gatan liquid helium cooling stage was used for temperatures between 50 and 275 K.

Prediction of damage depth profiles and estimation of the irradiating ion energy loss were modelled using the software package SRIM (The Stopping and Range of Ions in Matter).[16]

The critical temperature, T_c , is the temperature at which the material anneals at a rate sufficient to remove the damage that is accumulated from the irradiating ions. The T_c was determined, using least squares refinement, to the D_c collected at various temperatures. The fit is based on the equation; [17]

$$D_c = \frac{D_0}{1 - \exp \left[\left(\frac{E_a}{k_B} \right) \left(\frac{1}{T_c} - \frac{1}{T} \right) \right]} \quad \text{Equation 1}$$

where D_0 is the extrapolated critical dose at 0 K and k_B is the Boltzmann constant ($k_B = 8.617342 \times 10^{-5} \text{ eV K}^{-1}$). The activation energy, E_a , and T_c were allowed to refine using equation 1 implemented with software Origin 8.5. The quality of fit was assessed both via least squares refinement and by a visual comparison of the graphed calculated line and the data points.

In previous studies, equation 1 has yielded lower than expected activation energies and so a second equation was introduced to calculate activation energy. [17]

$$E_a = T_c \left[k_B \ln \left(\frac{D_0 \mu}{\phi} \right) \right] \quad \text{Equation 2}$$

The incident ion flux, ϕ , during ion-irradiation experiments was set to $6.25 \times 10^{11} \text{ ions cm}^{-2}\text{s}^{-1}$. The effective thermal attempt frequency, μ , was assumed to be 10^{12} s^{-1} , based on the approximate Debye frequency and not including irradiation-assisted effects, which were considered negligible relative to thermal effects. [17]

2.3 Laboratory powder x-ray diffraction

Bulk, powdered polycrystalline samples were analysed using x-ray diffraction carried out on a Panalytical X'pert Pro laboratory x-ray diffractometer with a weighted Cu K α source, K α_1 $\lambda = 1.5405980 \text{ \AA}$ and K α_2 $\lambda = 1.5444260 \text{ \AA}$. The diffractometer was operated in the Bragg reflection geometry with sample spinner on and diffraction data collected between 10 and 70 ° 2 θ with a step size of 0.017 °.

2.4 UV-Vis absorption spectroscopy

UV-Vis absorption spectra were collected using a Lambda 35 UV-Vis double beam spectrometer (Perkin Elmer), equipped with a deuterium and tungsten lamps. The samples were examined as finely ground powder, and the spectra were collected in diffuse reflectance mode using the Labsphere RSA-PE-20 in the 200-700 nm wavelength range. The original wavelength versus reflectance data was converted to energy versus reflectance before we performed a Kubelka-Munk transformation;

$$K = \frac{(1 - R)^2}{2R}$$

where K is reflectance according to the Kubelka-Munk equation and R is the absolute reflectance as measured. A Tauc plot [18] of K versus photon energy was used for each sample, whilst a linear fit to the steepest vertical section of the curves extrapolated to the intercept, gave an estimate of the band gap.

3. Results and Discussion

3.1 Characterisation

It has been previously shown by Shepelev and Petrova [14] that the average lanthanide size and/or the temperature of fabrication influence strongly the crystal structure for compounds with stoichiometry Ln_2TiO_5 . In this study the average lanthanide size was varied by changing the ratio of Sm to Yb. This allowed a range of crystal structures to be fabricated whilst using the same fabrication regime for most of the samples. The exception to this was Sm_2TiO_5 which required the use of a floating zone furnace to achieve a single phase material of the desired crystal structure. An adapted version of the temperature stability diagram proposed by Shepelev and Petrova is shown in [Figure 3](#) and has the $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ series included. By using mixtures, such as samarium and ytterbium, instead of single lanthanides the stability field lines for the different crystal phase types are altered and this is shown in [Figure 3](#) using a dotted line.

For reference the laboratory powder x-ray diffraction patterns for the five samples studied are shown in [Figure 4](#). Full details of the crystal structures of the compounds in this study are discussed elsewhere [15] and show that

- (a) the Sm_2TiO_5 compound has orthorhombic $Pnma$ symmetry and is part of a series of Ln_2TiO_5 compounds with this structure type, and
- (b) the hexagonal ($\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ and SmYbTiO_5) and cubic ($\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5) materials show diffuse diffraction in the electron diffraction patterns ([Figure 1](#)) which is indicative of the presence of modulated structures.

The compounds $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 both have a long range cubic fluorite-like structure with small cubic pyrochlore-like domains. $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ has larger pyrochlore-like domains when compared with Yb_2TiO_5 . The electron diffraction patterns in [Figures 1 \(a-d\)](#) show the crystallinity of the fabricated structures and include corresponding simulated structures [\(e-h\)](#) that highlight the differences between the compounds.

3.2 Ion-Irradiation Damage Accumulation

This section discusses damage accumulation in the $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ series, as indicated by the room temperature D_c measurements taken in this study. The paragraphs immediately below discuss the measurements taken and the calculation of SRIM results relevant to this.

[Figure 2](#) shows the changes in the selected area electron diffraction patterns of the Sm_2TiO_5 compound with increasing ion doses, and is representative of the patterns collected for all samples. With increasing fluence, the Bragg diffraction maxima (spots), which is indicative of the crystalline component in the monitored grain, decrease in intensity and the diffuse rings, indicative of the amorphous fraction in the monitored grain, increase in intensity. Complete amorphisation was taken to be when no Bragg spots remained.

Seeking to ascertain the dominant factors effecting damage accumulation, we measured or calculated a variety of parameters and compared them with the room temperature, $D_{c(300K)}$, values of the compounds in this study (see [Table 1](#)). The critical dose for amorphisation of a compound at low temperature (for example D_0) can be considered an indicator for the susceptibility of a material to damage, minimising temperature-assisted crystalline recovery. In this study, we collected $D_{c(300K)}$ values for all five compounds and D_c versus temperature

data for the four structure types (see Figure 5 and Table 1). We used the D_c versus temperature data to extrapolate D_0 values. However, because more complete data is available for $D_{c(300K)}$, we will use the room temperature values for the following discussion on the effect of intrinsic factors on susceptibility to damage.

In our SRIM simulations, the lattice displacement energies were set to 50 eV for each of the elements, which is a rough approximation based on previous studies of related compounds [19-21], and crystallographic densities were used [15]. A typical TEM sample thickness of 100 nm was estimated and used to compare values from the calculated damage profiles. The predicted total damage, including displaced atoms and vacancies, taken at 100 nm depth, are shown in Table 1.

The SRIM-based calculation of average lateral range of damage gives the radius, perpendicular to the incident ion, of 50 % total damage (vacancies and knock-ons). The calculated average (Table 1) was taken over the 0 to 100 nm damage depth profile and is used to define trends in damage cross section across the series. The calculated values indicate no trend in cross-sectional damage area size but there is a systematic increase in damage density per cross-sectional area across the series with Sm_2TiO_5 having the least and Yb_2TiO_5 the greatest concentration of damage. Based on the increased concentration of damage we hypothesised that the D_c values of the compounds in this study would decrease as the average lanthanide radius decreases and the density and atomic packing fraction (APF) increase, due to the physical cross-section presented to the irradiating ions and subsequent increase in damage accumulation rate.

The SRIM based calculations for the damage depth profiles of the compounds indicate an increase in the total displacements (dpa) at 100 nm with increasing ytterbium content (Table 1), which is consistent with the greater stopping power of ytterbium relative to samarium. Regardless of the increase in cross-section presented to the 1 MeV krypton ions by the cubic compounds ($\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5) as compared to the orthorhombic (Sm_2TiO_5) and hexagonal ($\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ and SmYbTiO_5) compounds, the cubic compounds required a higher dose to render them amorphous. If damage accumulation was the only mechanism at play, the irradiating ion dose (ions per unit area) required for the transition from crystalline to amorphous for the cubic samples should in fact be lower. This is not the case, indicating a higher rate of recovery within the cubic compounds.

Table 1 compares the $D_{c(300K)}$ values with the atomic packing fraction and density of the materials, the average lanthanide radii and the band-gap. The physical parameters, except band-gap, were selected due to their potential influence on the “physical” cross-section presented to the incident ions. Band gaps are included in Table 1 because previous experimental and modelling studies showed that there is a correlation between the bonding in a compound and its radiation resistance. [22-25] Consequently we postulated that there might be a correlation between the band-gaps of compounds (which are related to bonding) and their corresponding ion-irradiation tolerance.

Figure 5 shows plots of the data in Table 1. Specifically $D_{c(300K)}$ is plotted against: a) average ionic radii of the lanthanides, b) density, c) atomic packing fraction (APF) and d) band-gap. The average lanthanide radius decreases across the $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ compound series as the ytterbium to samarium ratio increases. Conversely density increases across the $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ compound series as the ytterbium to samarium ratio increases. There is

some correlation (non-linear) between the average lanthanide radius, the APF and the density of the compounds with their $D_{c(300K)}$ values (see [Figure 5](#)). In each case, no improvement in radiation response, $D_{c(300K)}$ values, occurs until the transition to cubic symmetry. For this series, no correlation was observed between the band gap of the compounds and their $D_{c(300K)}$ values ([Figure 5d](#)).

At temperatures below a compounds' characteristic ion-damage recovery temperature, T_c , the dominant material response to ion-irradiation exposure is damage accumulation. In the series studied here $D_{c(300K)}$ values give an indication of damage accumulation rates. The $D_{c(300K)}$ values of the orthorhombic and hexagonal compounds are the same within experimental error, while those of the cubic compounds in this study are clearly higher. As mentioned previously, the $D_{c(300K)}$ values of all the compounds in this study vary with average radius, density, atomic packing factor or band gap, but do not show linear correlation with any of these factors and only show improvement once cubic symmetry is established. This higher rate of recovery with compounds of cubic symmetry is thought to be the result of differences in bonding-type between the higher symmetry cubic compounds and the lower symmetry orthorhombic and hexagonal compounds.

3.3 Correlation of Temperature-Dependent Radiation Damage Response with Physical Parameters

Having focussed on the damage accumulation in the previous section, this section looks at the recovery of crystallinity from ion-irradiation damage via thermal assistance.

Figure 6 shows plots of the D_c versus temperature for samples with each of the four crystal structure types. Critical dose data points were least-squares fitted with an exponential function (Equation 1 the Methods section), and used for the calculation of critical temperature and critical dose at zero Kelvin.

Table 2 lists the results of this fitting process, together with the electronic to nuclear stopping ratio, ENSP, calculated using SRIM. The critical dose for amorphisation (D_0) and the critical temperature for amorphisation (T_c) were derived directly from the exponential fits of the data in Figure 6. As noted in the methods section E_a values derived in this manner are known to be unreliable, so we also calculated the E_a values using equation 2 in the methods section (E_{a2}).

Figure 7 shows a plot of critical temperature, T_c , versus the average lanthanide radius of the compounds. The critical temperature, T_c , is indicative of the energy required to mobilise defects and facilitate crystal structure recovery. In other words, low T_c values indicate easy damage recovery, thus improved radiation tolerance. Because it has the lowest T_c value, the cubic fluorite-like compound (Yb_2TiO_5) is the most radiation resistant compound of those investigated. The T_c values for the cubic compounds (Yb_2TiO_5 and $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$) are significantly lower than those for the hexagonal and orthorhombic compounds (SmYbTiO_5 , $\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ and Sm_2TiO_5). The T_c values for the hexagonal and orthorhombic compounds are similar. So both the T_c and the D_c values indicate that the cubic compounds are more radiation tolerant than both the hexagonal and orthorhombic compounds (Figures 6 and 7; and Table 2).

Despite the cubic compounds having a greater physical cross-section and therefore accumulating higher number of displacements per atom (dpa) within the experimental sample thickness, these compounds show the best ion-irradiation tolerance. These results suggest improved recovery mechanisms within the cubic phase when compared to the orthorhombic and hexagonal structure types.

Single parameters that might affect radiation recovery include: electronic to nuclear stopping power ratio values (ENSP)[26], activation energies (E_a)[17] and band gaps. In the following discussion, we discuss how these factors might affect radiation recovery, our results and trends therein and make comment.

Inelastic scattering of irradiating ions introduces thermal vibrations (energy) into the lattice, which can assist in the structure recovery process. The electronic stopping rate as calculated by SRIM depends on inelastic scattering whilst the nuclear stopping rate depends on elastic scattering. So a higher ENSP value would suggest an ion / crystal structure interaction dominated by inelastic scattering and the occurrence of a large thermal spike around the region of the penetrating ion. The SRIM-calculated ENSP values for the compounds investigated in this study are listed in [Table 2](#), and show little variation.

However the T_c values show considerable variation, indicating another factor is at play. The lack of variation in ENSP values may reflect the fact that SRIM calculations do not take into account the compound's crystal structure and orientation, which affects the irradiating ion's penetration depth and energy loss mechanisms [27].

The activation energies, E_{a2} , were relatively high for the Sm_2TiO_5 and SmYbTiO_5 compounds, at 3.11 and 3.15 eV respectively and significantly lower for the cubic

compounds $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 : 2.04 and 1.40 eV respectively. The low activation energy values found in the cubic compounds indicate a lower energy barrier to defect mobility compared to the other compounds. High defect mobility allows a greater probability of recovery, with energy input either from irradiating ions or an external heat source.

As discussed earlier, previous authors observed a correlation between the bonding and radiation resistance of compounds so the current authors tested to see if band gap (which can broadly indicate bond type) correlates with radiation response. The size of a band gap indicates the type of bonding present, ionic compounds generally show small band gaps and exhibit long range bonding, whereas covalent compounds have larger band gaps and exhibit highly directional short range bonding. *Trachenko et al* reviewed ion-irradiation experimental studies on over 100 ceramic materials and compared these with quantum mechanical calculations of their bonding types. [24, 25] These studies indicated that an increase in short range covalent bonding decreases the materials radiation tolerance. The stronger short range covalent bonding gives rise to potential energy minima that can act as barriers to the displaced atoms, hindering them from recovering their lattice positions. Several studies have proposed greater ionicity to be associated with enhanced radiation tolerance [22-24, 28]. However, no obvious correlation was observed between the band-gap and T_c data collected in this study. Sm_2TiO_5 and SmYbTiO_5 had the highest T_c and band-gap values. However there was little difference between band-gap values of SmYbTiO_5 , $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 , but distinct differences in T_c . The lack of correlation may be due to the fact that band-gap measurements are not sufficiently “sensitive” to the subtle changes in bonding that occur across this series.

3.4 Comparison with Previous Studies

A variety of studies have been conducted to determine the factors which contribute to radiation response. Previously we, [12], investigated the ion-irradiation response of the Ln_2TiO_5 series ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$ and Dy) with orthorhombic symmetry. An improvement in response, lowering of T_c , with decreasing lanthanide radius was found. This radiation response did not occur across the entire series but did progress with sequential improvements in T_c between samarium and dysprosium titanates. According to the temperature stability diagram proposed by Shepelev and Petrova [14], lanthanides of europium radius size and smaller have the ability to transition from the orthorhombic structure to either hexagonal or cubic symmetry at higher fabrication temperatures. It was proposed that it is the ability of these compounds to transform to the fluorite-like structure when exposed to irradiating ions that governs the improvements in radiation tolerance.[11] However, our previous work [12] showed no evidence of phase transition upon exposure to ion-irradiation. This indicates that something more fundamental is responsible for differences in radiation response.

In contrast to our previous findings [12], this study did not show an improvement in radiation resistance for compounds with the average lanthanide radius of europium or smaller. Here, the T_c value of the hexagonal SmYbTiO_5 compound is, within statistical error, the same as that of the orthorhombic Sm_2TiO_5 compound. This indicates that the average lanthanide size of the Ln_2TiO_5 compound is not the primary factor affecting the radiation tolerance. Instead, this study showed that the radiation exposure response of a compound depended on its pre-irradiation crystal structure. The compounds with cubic symmetry $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 showed the best results in radiation response for the series studied here.

Fluorite compounds and compounds that can transform to fluorite have been found to have high radiation resistance. Consequently it has been speculated that if it is thermodynamically favourable for a compound to adopt the fluorite structure this implies radiation tolerance.[1, 11, 22, 29, 30] In this study, the two cubic compounds $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 both consist of long-range defect-fluorite and short-range defect-pyrochlore type structures, in the form of nanometre sized domains. These two compounds also showed the best radiation response with T_c values of 697 and 479 K for $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 respectively. In a study by *Whittle et al.* on cubic Y_2TiO_5 , YYbTiO_5 and Yb_2TiO_5 compounds it was found that T_c values decreased from Y_2TiO_5 to YYbTiO_5 to Yb_2TiO_5 in line with the crystallography of this series moving from defect-pyrochlore to defect-fluorite symmetry.[3]

According to studies by Lam et al [31, 32] if it is thermodynamically favourable for a system to accommodate disorder within its structure then recovery from ion-induced damage should proceed more easily. If we apply this hypothesis to the system studied here, those compounds with the greatest static disorder should show the lowest T_c values. The most ordered compound in this series, Sm_2TiO_5 , has well defined cation lattice positions and no oxygen vacancies and also has a high T_c value of 1072 K. However SmYbTiO_5 of hexagonal symmetry has greater disorder relative to the orthorhombic Sm_2TiO_5 yet has a similar T_c of 1082 K. The hexagonal structure for the Ln_2TiO_5 compounds may not be thermodynamically stable as is indicated by the narrow phase stability field shown for the hexagonal phase within the structure stability diagram proposed by Shepelev and Petrova.[14] This instability may explain the high T_c value found for SmYbTiO_5 . There is intrinsic cation disorder within the Ln_2TiO_5 cubic system with cation mixing on the B(Ti)-site of the pyrochlore structure, $\text{Ln}_2(\text{Ln}_{0.67}\text{Ti}_{1.33})\text{O}_{6.67}$. This disordering is further increased if the

fluorite structure is adopted as there is now complete randomisation of the cation site, $(\text{Ln}_{0.67}\text{Ti}_{0.33})\text{O}_{1.67}$. The cubic compounds $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 both show long-range defect fluorite structures however $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ has the larger scale, ordered pyrochlore, modulated structure relative to Yb_2TiO_5 . The decreasing T_c values for $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5 of 687 and 479 K respectively fit with this increasing disorder trend.

The improved radiation response may be coming from either the greater thermodynamic stability of the defect-fluorite structure or the presence of the small domains of modulated structure or a combination of the two.

Concluding Remarks

In this study, the radiation damage response of five compounds in the $\text{Sm}_{(x)}\text{Yb}_{(2-x)}\text{TiO}_5$ series were measured. The five compounds have a variety of symmetries: Sm_2TiO_5 is orthorhombic $Pnma$; $\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ and SmYbTiO_5 are hexagonal $P6_3/mmc$, $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ is cubic $Fd-3m$; and Yb_2TiO_5 is cubic $Fm-3m$. The room temperature D_c (critical dose of amorphisation) value for each compound was measured and data were collected so that the T_c (the critical temperature) values of each compound could be determined.

Sm_2TiO_5 , $\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ and SmYbTiO_5 displayed similar, poor radiation response. Based on the results of this study, improved radiation tolerance for the Ln_2TiO_5 series of compounds is only found in the higher symmetry crystal structures of the cubic compounds.

Band-gap measurements of this series of compounds were collected and used in an attempt to quantify bonding. This approach was used in the hope of establishing trends between radiation tolerance response and the average bonding within each material. Whilst the band-gap measurements proved good enough to qualitatively establish all materials to have values indicative of ionic bonding they were not sensitive enough for quantitative analysis of bonding.

Based on this study and the current published data, compounds with stoichiometry Ln_2TiO_5 show good radiation tolerance if they can be fabricated with cubic symmetry. The structure of cubic Ln_2TiO_5 compounds consists of a long-range defect-fluorite matrix, and modulated short-range defect-pyrochlore domains. The domain size of defect-pyrochlore is speculated to influence the radiation response, with the defect-fluorite matrix containing the smaller defect-pyrochlore domains performing best.

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Figure 1. a) – d) show selected area electron diffraction patterns of a) Sm_2TiO_5 viewed down the zone axis $[0\ 1\ 0]$, b) $\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ down zone axis $[0\ 0\ -1]$, c) $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ $[1\ 1\ 0]$ and d) Yb_2TiO_5 $[1\ 1\ 0]$. e) – h) show simulated diagrams of the four crystal structures which highlight their structural differences. Open (blue) represents titanium centred polyhedra, filled (purple) lanthanide polyhedra, and vertices (red) oxygen. Note the orientation in e)- h) are not the same as those of the SADPs. e) shows the orthorhombic crystal structure of Sm_2TiO_5 , f) shows the hexagonal crystal structure common to both $\text{Sm}_{1.4}\text{Yb}_{0.6}\text{TiO}_5$ and SmYbTiO_5 , g) shows the cubic (pyrochlore-like) structure, and h) shows the cubic (fluorite-like) structure.

Figure 2: a) TEM bright field image of a grain of Sm₂TiO₅ studied in-situ during irradiation at room temperature with corresponding selected area electron diffraction patterns (b – e) collected at various ion doses; b) unirradiated, c) 0.22 D_c , d) 0.66 D_c , and e) 1.0 D_c

Figure 3: The temperature stability diagram for the Ln_2TiO_5 series adapted from Shepelev and Petrova [14] showing the expected crystal symmetry dependent on lanthanide cation size and temperature. Overlaid onto the diagram are the five $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ compounds studied here. Also shown, via the dotted line, is the change to the stability field caused by using mixed lanthanides as was the case in the $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ series studied here.

Figure 4: X-ray powder diffraction patterns of the five $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ compounds studied here showing the four major structure types. The pattern for $\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ has “P” placed above the pyrochlore peak positions (a more thorough study of the crystallography using synchrotron powder x-ray diffraction is given elsewhere [15])

Table1: Room temperature critical dose of amorphisation measurements $D_{c(300K)}$ (error shown in brackets), and SRIM calculated displacements per atom, DPA, and average lateral damage range, compared with average lanthanide radius, calculated atomic packing fraction, density and band-gap.

Compound (Crystallography)	Ln3+ radius (Å)	Atomic Packing Fraction	Density (g / cm ³)	Band- Gap (eV)	$D_{c(300K)}$ (x 10 ¹⁴)	DPA (300K, 100 nm)	Average Lateral Damage Range [0 – 100 nm] (nm)
Sm ₂ TiO ₅ (orthorhombic)	0.958	0.56	6.25	4.03	2.53(0.15)	0.34	87.3
Sm _{1.4} Yb _{0.6} TiO ₅ (hexagonal)	0.931	0.46	6.85	3.50	2.53(0.3)	0.37	77.6
SmYbTiO ₅ (hexagonal)	0.913	0.47	6.99	3.58	2.81(0.31)	0.41	81.2
Sm _{0.6} Yb _{1.4} TiO ₅ (cubic pyrochlore-like)	0.895	0.64	7.37	3.47	4.31(0.5)	0.65	87.9
Yb ₂ TiO ₅ (cubic fluorite-like)	0.868	0.65	7.67	3.52	5.47(0.81)	0.74	82.4

Figure 5. The critical dose of amorphisation, $D_{c(300K)}$, at room temperature (300 K) for the $\text{Sm}_x\text{Yb}_{(2-x)}\text{TiO}_5$ series of compounds plotted against characteristics considered to be of significant influence on a materials' tolerance to ion-irradiation damage. a) the average lanthanide ionic radius plotted against D_c , b) density trends with the higher density, cubic samples ($\text{Sm}_{0.6}\text{Yb}_{1.4}\text{TiO}_5$ and Yb_2TiO_5) requiring a higher D_c , c) the calculated atomic "hard" sphere volume divided by total cell volume (atomic packing fraction) versus D_c , and d) band-gap plotted against D_c .

Figure 6: The critical dose versus temperature plot of the Sm_(x)Yb_(2-x)TiO₅ series of compounds covering the four crystal structure types; orthorhombic (Sm₂TiO₅), hexagonal (SmYbTiO₅), cubic pyrochlore-like (Sm_{0.6}Yb_{1.4}TiO₅), and cubic fluorite-like (Yb₂TiO₅).

Table 2; Calculated results (errors in brackets) obtained from fitting to D_c versus temperature data using equations 1 and 2. ENSP calculated using SRIM.

Compound	<i>ENSP</i>	<i>D₀</i> (x 10¹⁴)	<i>T_c</i> (Kelvin)	<i>Ea₂</i> (eV)
Sm ₂ TiO ₅ (Orthorhombic)	0.656	2.73(0.22)	1072(23)	3.11
SmYbTiO ₅ (Hexagonal)	0.654	2.91(0.07)	1082(2)	3.15
Sm _{0.6} Yb _{1.4} TiO ₅ (Cubic Pyro / Fluorite)	0.653	3.60(0.7)	697(57)	2.04
Yb ₂ TiO ₅ (Cubic Fluorite)	0.652	3.52(0.59)	479(44)	1.40

Figure 7; A plot of critical temperature, T_c , versus average lanthanide cation radius. The plot displays data points from this study on the $\text{Sm}_x\text{Yb}_{2-x}\text{TiO}_5$ series of compounds and data for La_2TiO_5 from Whittle *et al* [4].

Reference:

1. Sickafus, K.E., et al., *Radiation-induced amorphization resistance and radiation tolerance in structurally related oxides*. Nature Materials, 2007. **6**(3): p. 217-223.
2. Ewing, R.C. and W. Lutze, *High-Level Nuclear Waste Immobilization with Ceramics*. Ceramics International, 1991. **17**(5): p. 287-293.
3. Whittle, K.R., et al., *Ion irradiation of novel yttrium/ytterbium-based pyrochlores: The effect of disorder*. Acta Materialia, 2011. **59**(20): p. 7530-7537.
4. Whittle, K.R., et al., *Ion-beam irradiation of lanthanum compounds in the systems La₂O₃-Al₂O₃ and La₂O₃-TiO₂*. Journal of Solid State Chemistry, 2010. **183**(10): p. 2416-2420.
5. Aughterson, R.D., Lumpkin, G. R., Smith, K. L., Thorogood, G. J., Whittle, K. R., *Synthesis and Characterisation of Ln₂TiO₅ Compounds*. Material Research Society Symposium Proceedings, 2008. **1107**.
6. Sinha, A. and B.P. Sharma, *Development of dysprosium titanate based ceramics*. Journal of the American Ceramic Society, 2005. **88**(4): p. 1064-1066.
7. Kim, H.S., et al., *Characteristics of GdxMyOz (M = Ti, Zr or Al) as a burnable absorber*. Journal of Nuclear Materials, 2008. **372**(2-3): p. 340-349.
8. M.C. Stennett, D.P.R., N. Peng, E.R. Maddrell, B. Ravel, N.C. Hyatt, *Probing Radiation Damage in Ceramic Wasteforms using X-ray Absorption Spectroscopy*. Diamond '10 Conference; Decommissioning, Immobilisation and Management of Nuclear Waste for Disposal, 2010.
9. Jiang, Y., J.R. Smith, and G.R. Odette, *Prediction of structural, electronic and elastic properties of Y₂Ti₂O₇ and Y₂TiO₅*. Acta Materialia, 2010. **58**(5): p. 1536-1543.
10. Tracy, C.L., Liang, M., Zhang, J., Zhang, F., Wang, Z., Ewing, R.C., *Structural response of A₂TiO₅ (A=La, Nd, Sm, Gd) to swift heavy ion irradiation*. Acta Materialia, 2012. **60**(11): p. 4477-4486.
11. Zhang, J., et al., *Ion-irradiation-induced structural transitions in orthorhombic Ln₂TiO₅*. Acta Materialia, 2013. **61**(11): p. 4191-4199.
12. Aughterson, R.D., Lumpkin, G. R., Ionescu, M., de los Reyes, M., Gault, B., Whittle, K. R., Smith, K.L., Cairney, J. M., *Ion-Irradiation resistance of the orthorhombic Ln₂TiO₅ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb and Dy) series* Journal of Nuclear Materials, 2015. **Manuscript submitted for publication**.
13. Katherine L. Smith, G.R.L., Mark G. Blackford and Michael Colella, *Titanate Ceramics for the Immobilisation of High Level Nuclear Waste and their Mineral Analogues*. Materials Research Society (Singapore), 2001. **II**(Environmentally Preferred Materials): p. 301-317.
14. Shepelev, Y.F. and M.A. Petrova, *Crystal Structures of Ln₂TiO₅ (Ln = Gd, Dy) Polymorphs*. Inorganic Materials, 2008. **44**(12): p. 1354-1361.
15. Aughterson, R.D., et al., *Crystal structures of orthorhombic, hexagonal, and cubic compounds of the Sm(x)Yb(2-x)TiO₅ series*. Journal of Solid State Chemistry, 2014. **213**(0): p. 182-192.
16. J. F. Ziegler, J.P.B., M. D. Ziegler, *SRIM The Stopping and Range of Ions in Matter*. www.SRIM.org, 2008.
17. Weber, W.J., *Models and mechanisms of irradiation-induced amorphization in ceramics*. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 2000. **166-167**(0): p. 98-106.
18. Tauc, J., R. Grigorovici, and A. Vancu, *Optical Properties and Electronic Structure of Amorphous Germanium*. physica status solidi (b), 1966. **15**(2): p. 627-637.
19. Smith, K.L., et al., *Measured displacement energies of oxygen ions in titanates and zirconates*. Journal of Nuclear Materials, 2003. **321**(1): p. 19-28.

20. Cooper, R., et al., *Optical emission due to ionic displacements in alkaline earth titanates*. Journal of Nuclear Materials, 2001. **289**(1–2): p. 199-203.
21. Veiller, L., J.P. Crocombette, and D. Ghaleb, *Molecular dynamics simulation of the α -recoil nucleus displacement cascade in zirconolite*. Journal of Nuclear Materials, 2002. **306**(1): p. 61-72.
22. Lumpkin, G.R., et al., *Nature of the chemical bond and prediction of radiation tolerance in pyrochlore and defect fluorite compounds*. Journal of Solid State Chemistry, 2007. **180**(4): p. 1512-1518.
23. Trachenko, K., et al., *Atomistic simulations of resistance to amorphization by radiation damage*. Physical Review B, 2006. **73**(17): p. -.
24. Trachenko, K., et al., *How the nature of the chemical bond governs resistance to amorphization by radiation damage*. Physical Review B, 2005. **71**(18): p. -.
25. Trachenko, K., *Understanding resistance to amorphization by radiation damage*. Journal of Physics-Condensed Matter, 2004. **16**(49): p. R1491-R1515.
26. Backman, M., *Effects of nuclear and electronic stopping power on ion irradiation of silicon-based compounds*. Academic Dissertation; University of Helsinki, 2012: p. <http://urn.fi/URN:ISBN:978-952-10-8087-6>
27. Robinson, M.T. and O.S. Oen, *THE CHANNELING OF ENERGETIC ATOMS IN CRYSTAL LATTICES*. Applied Physics Letters, 1963. **2**(2): p. 30-32.
28. Trachenko, K., et al., *Radiation damage effects and percolation theory*. Journal of Physics-Condensed Matter, 2004. **16**(27): p. S2623-S2627.
29. Lang, M., et al., *Review of A(2)B(2)O(7) pyrochlore response to irradiation and pressure*. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 2010. **268**(19): p. 2951-2959.
30. Lumpkin, G.R., et al., *Temperature dependence of ion irradiation damage in the pyrochlores La₂Zr₂O₇ and La₂Hf₂O₇*. Journal of Physics: Condensed Matter, 2004. **16**(47): p. 8557.
31. Lam, N.Q., P.R. Okamoto, and M. Li, *Disorder-induced amorphization*. Journal of Nuclear Materials, 1997. **251**: p. 89-97.
32. Lam, N.Q. and P.R. Okamoto, *Generalized melting criterion for beam-induced amorphization*. Surface and Coatings Technology, 1994. **65**(1): p. 7-14.