Ion-Irradiation resistance of the Orthorhombic Ln_2TiO_5 (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb and Dy) series

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Abstract

The response of Ln_2TiO_5 (where Ln is a lanthanide) compounds exposed to high-energy ions was used to test their suitability for nuclear-based applications, under two different but complementary conditions. Eight samples with nominal stoichiometry Ln_2TiO_5 (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb and Dy), of orthorhombic ($Pnma$) structure were irradiated, at various temperatures, with 1 MeV Kr^{2+} ions *in-situ* within a transmission electron microscope. In each case, the fluence was increased until a phase transition from crystalline to amorphous was observed, termed critical dose D_c .

At certain elevated temperatures, the crystallinity was maintained irrespective of fluence. The critical temperature for maintaining crystallinity, T_c , varied non-uniformly across the series. The T_c was consistently high for La, Pr, Nd and Sm_2TiO_5 before sequential improvement from Eu to Dy_2TiO_5 with T_c 's dropping from 974 K to 712 K.

In addition, bulk Dy_2TiO_5 was irradiated with 12 MeV Au^+ ions at 300 K, 723 K and 823 K and monitored via grazing-incidence X-ray diffraction (GIXRD). At 300 K, only amorphisation is observed, with no transition to other structures, whilst at higher temperatures, specimens retained their original structure. The improved radiation tolerance of compounds containing smaller lanthanides has previously been attributed to their ability to form radiation-induced phase transitions. No such transitions were observed here.

1. Introduction

There has been considerable research into the radiation tolerance of the $\text{Ln}_2\text{Ti}_2\text{O}_7$ series of compounds, which adopt the pyrochlore structure, primarily due to their ability to incorporate actinides and their resistance to damage via exposure to high energy particles.[1-5] The capacity to incorporate actinides into the crystal structure provides a means for the storage of nuclear wastes, especially in the management and disposal of high level wastes (HLW), where actinides are separated from short-lived fission products. The Ln_2TiO_5 series of compounds (where Ln represents lanthanides plus yttrium) may provide an alternative to pyrochlore compounds and have already been investigated for nuclear based applications.[6-8] Due to its relatively large neutron absorption cross section, Dy_2TiO_5 has been incorporated into inert matrix fuel as a neutron absorber.[9] Similarly the Gd_2TiO_5 compound has also been proposed as a burnable absorber [10] and its radiation tolerance has been tested.[11] Other fundamental studies have also probed the radiation resistance of Ln_2TiO_5 materials via heavy ion irradiation.[6, 7, 12, 13]

The Ln_2TiO_5 compounds show a range of structures depending on the lanthanide size, fabrication regime, temperature and pressure. The temperature stability diagram for the Ln_2TiO_5 compounds established by Shepelev and Petrova [14] indicates the polymorphs available for each lanthanide compound; orthorhombic (La to Sm), orthorhombic and hexagonal (Eu and Gd), orthorhombic, hexagonal and cubic (Tb to Ho), and cubic (Er to Lu).

Both La_2TiO_5 and Nd_2TiO_5 can transform from orthorhombic to hexagonal structure type at pressures between 6 to 10 GPa. [15] The smaller lanthanides, from Tb to Lu, may form high temperature cubic polymorphs with long range defect fluorite ($Fm-3m$) and short range defect pyrochlore ($Fd-3m$) symmetry.[16-18]

The orthorhombic $Pnma$ Ln_2TiO_5 compounds have no mixed occupancy between the cation sites. The lanthanide occupies two 7-fold polyhedra consisting of a distorted cube with one oxygen missing and the remaining oxygens slightly rearrange from their ideal cubic positions to compensate. [19] The titanium cation on the other hand adopts atypical co-ordination with oxygen, five, based on a capped octahedron i.e. removal of an apex oxygen, giving rise to an offset square based pyramid. The authors have previously carried out a systematic study of the Ln_2TiO_5 series of compounds with orthorhombic symmetry[20] showing a linear decrease in all cell parameters from La to Dy_2TiO_5 . Significantly, this study shows a deviation in the titanium oxygen bonding behaviour for Tb_2TiO_5 and Dy_2TiO_5 , which may be a destabilising mechanism for their orthorhombic crystal structure.

Materials used in nuclear applications are required to be tolerant of high energy particle interactions for the duration of their use. In this study, Ln_2TiO_5 specimens were irradiated with high energy heavy ions to simulate radiation effects in such an environment. The controlled conditions of ion-irradiation coupled with *in-situ* characterisation, via transmission electron microscopy

(TEM), allow experimental results to be obtained quickly and in a reproducible way.[21, 22]

The radiation resistance of the orthorhombic Ln_2TiO_5 ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}$ and Y) compounds has been investigated by *Zhang et al.* [12] via *in-situ* Kr 1 MeV ion irradiation studies. They found that the critical temperatures for amorphisation (T_c) of La_2TiO_5 , Sm_2TiO_5 and Nd_2TiO_5 were similar whereas those for Gd_2TiO_5 , Dy_2TiO_5 and Y_2TiO_5 decreased sequentially. The improved tolerance in Gd_2TiO_5 , Dy_2TiO_5 and Y_2TiO_5 was highlighted as arising from an ion-irradiation induced phase transformation from an orthorhombic to cubic defect fluorite structure.

Whittle and co-workers [6] fabricated, characterised and conducted *in-situ* ion irradiation experiments on cubic Y_2TiO_5 , YYbTiO_5 and Yb_2TiO_5 . They found that the T_c decreased, in order, from Y_2TiO_5 to YYbTiO_5 and then to Yb_2TiO_5 . The T_c value for cubic Y_2TiO_5 , 589 K, was similar to the T_c value determined by *Zhang et al.* [12] for orthorhombic Y_2TiO_5 , of 623 K. This is in agreement with *Zhang's* premise that the improved T_c values of the smaller Ln_2TiO_5 compounds may be due to their ability to transform into polymorphs with irradiation.

In this study, we investigate the radiation tolerance of orthorhombic Ln_2TiO_5 compounds. Specifically we fabricated Ln_2TiO_5 compounds ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$ and Dy) and subjected them to both *in-situ* ion-irradiation and bulk *ex-situ* ion-irradiation (Dy_2TiO_5) experiments to provide new and

additional data on their radiation resistance. By investigating the bulk sample ion-irradiation behaviour of Dy_2TiO_5 , we hope to confirm a previously proposed source of improved radiation tolerance [12] in compounds capable of high temperature phase transformations.

As some of these materials have been proposed for nuclear applications, their tolerance to the impact of high energy particles is of interest. The aim of this study was to investigate both the critical dose of irradiating ions required to cause a significant phase transformation from crystalline to amorphous and the energy input, via heat, required to achieve self-annealing sufficient enough to maintain the crystalline structure during the irradiation process. The results of this study can therefore be used to assess the suitability of Ln_2TiO_5 compounds in nuclear applications.

2. Methods

Bulk, polycrystalline Ln_2TiO_5 single-phase samples were each prepared by mixing stoichiometric amounts of Ln_2O_3 ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{and Dy}$), Tb_4O_7 and TiO_2 (99.9% purity). These were then pelletised and consolidated using a cold isostatic press operated at 400 MPa and sintered between 1573 K and 1823 K for 48 hours using a heating and cooling rate of 5 K per minute. One system, Sm_2TiO_5 , could not be fabricated as a bulk single phase material using the oxide route, therefore a floating zone furnace was used to achieve the desired material.[18] Eu_2TiO_5 could not be fabricated to a phase purity of better than 90 %, thus detailed TEM characterisation was

carried out on these specimens pre-irradiation to ensure that only the desired Eu_2TiO_5 single phase was monitored during the *in-situ* ion irradiation experiment.

Scanning Electron Microscopy (SEM) was undertaken using a Zeiss Ultra Plus Gemini operated at 15 keV, and fitted with an in-lens Angle Selective Backscatter electron detector (AsB detector). The SEM was also equipped with an Oxford X-Max Silicon Drift Detector Energy Dispersive X-ray Spectrometer (EDX) and EDX data was collected and analysed using the Oxford INCA Microanalysis software system.

Transmission electron microscopy (TEM) samples consisted of crushed grains dispersed in ethanol then dispensed onto a holey carbon film on a TEM mesh grid. The TEM grids were copper for room temperature to 650 K experiments or molybdenum for temperatures above 650 K. All TEM samples were cleaned with argon (Ar) plasma using a South Bay Technology PC 150 Plasma Cleaner.

A JEOL 2010F operating at 200 keV and fitted with an energy dispersive x-ray analysis system (EDX) was used to characterise pre-irradiated samples. The crystal structure was investigated via selected area electron diffraction (SAED), and the lanthanide to titanium ratio was confirmed using EDX data analysed with the Noran system six software.

The *in-situ* ion-irradiation experiments were carried out using the IVEM-TANDEM facility at Argonne National Laboratory and a Hitachi 9000-NAR TEM operated at 300 keV, interfaced with an NEC ion accelerator. A Nd-doped zirconolite was used as a standard reference and its critical amorphisation dose, D_c , at room temperature was measured and compared with previous tests to confirm a correct and consistent flux of 1 MeV Kr^{2+} ions was incident on the area of interest. For all *in-situ* experiments 1 MeV Kr^{2+} ions were incident on the sample at a flux of $6.25 \times 10^{11} \text{ ions cm}^{-2} \text{ s}^{-1}$. This irradiation dose rate was selected in order to give high doses quickly but at a rate low enough to minimise heating of the sample ($<2 \text{ K}$). A total of 5 grains were selected for each critical dose measurement so as to give better statistical confidence in the acquired results. The grains were monitored via bright field images, together with selected area electron diffraction patterns (SAED). The presence of (Bragg diffraction maxima) in the SAED patterns indicates crystallinity within the grain. The samples were alternately dosed with 1 MeV Kr^{2+} ions and monitored with the electron beam. These processes were kept separate to minimise the synergistic effects between the electron and ion beams.

Grains were monitored until all Bragg diffraction peaks had disappeared, indicating the grain was completely amorphous. The average of the final dose, of which the diffraction peaks had disappeared and the dose immediately prior, was taken to be the critical dose, D_c . The quoted error for D_c measurements was either the dose step size between a collection of SAED's or the variation in D_c measurements between the grains, dependent of which

was larger. The D_c was also measured at elevated temperature using a Gatan heating stage between 300 and 1100 K.

Bulk Dy_2TiO_5 samples were ion-irradiated using the ANTARES TANDEM accelerator, within ANSTO. Various ion doses were used ranging from 1×10^{13} to 2.5×10^{14} Au^+ 12 MeV ions / cm^2 at room temperature and 5×10^{13} Au^+ 12 MeV ions / cm^2 at 723 K and 823 K. These samples were analysed using Grazing Incidence X-ray Diffraction (GIXRD) performed at room temperature using a Bruker D8 Advance using a copper x-ray source (weight Cu radiation $\sim 1.5418 \text{ \AA}$). The x-ray angle of incidence was set to 3, 4 and 5 ° and data collected in 0.03 ° steps between 10 to 80 ° 2-theta.

Modelling the damage depth profiles and estimation of the rates of irradiating ion energy losses were calculated using the software package SRIM 2013 (the Stopping and Range of Ions in Matter).[23] For these calculations the densities were taken from ref [24] and all displacement energies set to 50 eV.

3. Results and Discussion

3.1 Quality control and sample characteristics

The purity of the samples used in radiation tolerance experiments was assessed using x-ray diffraction (XRD) and SEM. Resulting XRD patterns showed each fabricated sample was single phase (the exception being Eu_2TiO_5), with indexable reflexions of orthorhombic, $Pnma$ symmetry. Corresponding SEM analyses displayed minor secondary phases within the

matrix material, detected via phase contrast within backscattered electron (BE) images. A grid was placed across the BE image and the grid squares containing any secondary phase were counted and averaged. The results of this process are listed in [Table 1](#). The samples used in the ion-irradiation experiments contained at least 95% of the design phase, except Eu_2TiO_5 , which contained only 90%. The composition of the major phase in each sample was confirmed using EDX spot analysis in at least 3 locations.

Attempts were made to fabricate single phase orthorhombic Ln_2TiO_5 across the entire lanthanide series. It was not possible to fabricate single phase Ho_2TiO_5 and Y_2TiO_5 compounds in the orthorhombic form. Sintering above 1250 °C predominantly produced Ho_2TiO_5 and Y_2TiO_5 compounds with hexagonal symmetry whilst sintering above 1500 °C produced cubic symmetry. The highest yield of orthorhombic Ho_2TiO_5 and Y_2TiO_5 were achieved by heating at 1200 °C for 6 days which gave approximately 30% and 70% orthorhombic Ho_2TiO_5 and Y_2TiO_5 , respectively, with the remainder consisting of $\text{Ho}_2\text{Ti}_2\text{O}_7$ or $\text{Y}_2\text{Ti}_2\text{O}_7$ (pyrochlore) together with un-reacted precursors. To date bulk, polycrystalline, single phase orthorhombic Ho_2TiO_5 and Y_2TiO_5 samples have not been fabricated. Currently published characterisation data has been carried out on single crystals picked out of heterogeneous mixes.[19] Due to the large amount of secondary phase found in Ho_2TiO_5 and Y_2TiO_5 , these samples were not used in this ion-irradiation study. Under these conditions, it was not possible to fabricate compounds of Er_2TiO_5 , Yb_2TiO_5 or Lu_2TiO_5 in the orthorhombic form.

In a previous study, we collected synchrotron powder diffraction data on Ln_2TiO_5 compounds with orthorhombic symmetry and determined the cell parameters and atomic positions using Rietveld refinements [20]. These results were compared to previously published data and are shown in [Figure 1a](#). Here, the unit cell parameters show a linear decrease from lanthanum to dysprosium.

[Figure 1b](#) shows the Ti-O bond lengths of the compounds in this study. The Ti-O5 bond length is constant across the investigated compounds whereas the Ti-O3 bond length is seen to vary linearly with lanthanide ionic radius. The Ti-O1 and Ti-O4 bond lengths show a deviation from the general trend for Dy_2TiO_5 ; and Dy_2TiO_5 and Tb_2TiO_5 respectively. The deviation from titanium-oxygen bonding trends within Tb_2TiO_5 and Dy_2TiO_5 compared with the rest is significant as it may highlight a destabilising mechanism for these compounds. Such a mechanism could allow a structural transition from orthorhombic to hexagonal/cubic polymorphs at elevated temperature or with exposure to irradiating ions.

Shepelev and Petrova [14] created a temperature stability diagram for the Ln_2TiO_5 compounds. [Figure 2](#) is an adapted version of this diagram. *Zhang et al.* [12] suggested that the high relative radiation resistance, lower T_c , for Gd_2TiO_5 , Dy_2TiO_5 and Y_2TiO_5 is due to the smaller lanthanides more easily forming disordered structures. This disordering is related to their capacity to form high temperature phases. The same reasoning has been applied to other systems where phase diagrams were used to predict improved radiation

resistance for those compounds which transition from their original structure to a defect fluorite structure, across a broader temperature range.[25]

The crystallographic data from our previous study [20] were used to calculate the density, which was then used to estimate the electronic to nuclear stopping power ratio, ENSP, (Table 2). The density increased with increasing atomic number, Z, (decreasing lanthanide size) due both to the increase in atomic mass of the lanthanide and the decreasing unit cell size.

The SRIM based calculation of the electronic to nuclear stopping ratio gives an estimate of the dominating stopping force. A high ENSP value indicates electronic, inelastic scattering as the dominant force in energy loss between the ion and lattice, with a low value indicating the dominance of nuclear, elastic scattering. The governing energy loss type has relevance to both the formation and mobility of defects, with defect mobility being a significant driver in determining the rate and extent of re-crystallisation.

3.2 Radiation response

All the Ln_2TiO_5 series of samples that were irradiated *in-situ* using the IVEM-Tandem showed responses similar to those detailed in Figure 3. With increasing dose, the Bragg peaks were observed to diminish in relative intensity and the diffuse rings, indicative of short range order, seen to increase in relative intensity. Figure 3 contains a series of electron diffraction patterns showing the sample's response to accumulated ion irradiation dose.

Figures 3a and 3h are bright field (BF) images of the grain of interest: in this case a crystal of Gd_2TiO_5 , both pre and post ion-irradiated respectively.

Figures 3b-g show the SAED patterns of the grain as the dose is increased from zero to the dose at which the grain was deemed amorphous, where Bragg diffraction maxima are no longer detectable and were replaced by diffuse rings.

For room temperature *in-situ* experiments, there is a correlation between decreasing lanthanide ionic radius and increasing critical dose of amorphisation, D_c , (see Table 2). However, Eu_2TiO_5 and Dy_2TiO_5 deviate from this linear trend with lower and higher than expected D_c values respectively. Tracy *et al.* [13] previously irradiated Ln_2TiO_5 compounds ($\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ and Gd) with 1.47 GeV Xe ions indicating that the volume of amorphous regions within the damage tracks decreased systematically with decreasing lanthanide size. This variation, defined as the amorphisation cross-section was attributed to the variation in rates of epitaxial re-crystallisation from the periphery of the damage region toward the centre. Whilst our $D_{c(300\text{K})}$ results are in general agreement with that work it should be noted the ion-target interaction was significantly different due to the large differences in ion energies. The 1.47 GeV Xe ions used in the work by Tracy *et al.* would lose energy to the target material almost exclusively via electronic losses whereas the electronic to nuclear stopping ratio in our study (Table 2) show a more dominant elastic, nuclear stopping loss of energy. The dominance of electronic stopping will lend to greater deposition of thermal energy and this

influences the mobility of defects, increasing the probability of damage recovery.

The higher D_c value for Dy_2TiO_5 is indicative of improved recovery mechanisms. Eu_2TiO_5 with a room temperature D_c of 1.63×10^{14} ions / cm^2 deviates more significantly from the linear trend. Difficulties in fabrication of Eu_2TiO_5 in single phase form may be indicative of thermodynamic instability for the Eu_2TiO_5 orthorhombic structure. Whilst a value for the enthalpy of formation is not directly quoted for Eu_2TiO_5 , in research published by *Kandan et al* [26], the heat capacity values are significantly higher than those found for La, Nd and Gd_2TiO_5 by *Hayun and Navrotsky* [27]. This suggests that the enthalpy of formation for Eu_2TiO_5 is more positive, indicating a less stable structure.

Here we measured the dose of irradiating particles required to render each material amorphous, D_c , at a range of temperatures and used these values to ascertain the energy necessary to recovery of crystallinity (critical temperature of amorphisation, T_c). The critical temperature, T_c , of each compound was determined by fitting to experimentally determined D_c measurements collected at various temperatures to the function [28];

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

where D_0 is the calculated critical dose of amorphisation 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 , D_0 and T_c , were allowed to refine using equation 1. The fit was performed using a least squares refinement implemented in Origin 8.5. A plot of such fits overlayed on experimental results is shown in [Figure 4](#). The goodness of fit between calculation and data was assessed both via least squares refinement and a visual comparison of the graphed calculated line versus data points as shown in [Figure 4](#).

It is generally accepted that equation 1, whilst yielding acceptable values for T_c and D_0 has yielded unrealistically low activation energies due to the kinetics of recovery having 2 components, thermal and irradiation based. Thus a second equation was introduced for activation energy calculations [28];

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

Here, the incident ion flux, ϕ , during the 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^{13} s^{-1} based on the approximate Debye frequency and not including irradiation assisted effects which were considered negligible relative to thermal effects.[28]

Calculated values from the data displayed in [Figure 4](#) are shown in [Table 2](#).

T_c is the temperature above which a sample cannot be rendered amorphous.

So a sample with a low T_c value indicates good ion-irradiation tolerance. In comparing the eight samples, Dy_2TiO_5 gave the best radiation tolerance results, with the lowest T_c of 712 K. The larger lanthanide compounds (La_2TiO_5 , Pr_2TiO_5 , Nd_2TiO_5 and Sm_2TiO_5) had the highest T_c values before sequential improvement from Sm_2TiO_5 to Dy_2TiO_5 .

Figure 5 shows the T_c versus lanthanide radii of the compounds investigated in this study, along with those by *Zhang et al.* [12] and *Whittle et al.*[6] There is a significant discrepancy between the values measured for La_2TiO_5 and Sm_2TiO_5 by the current authors and *Zhang et al.* Such a discrepancy can possibly arise from the temperatures used in the study.

Compounds with higher T_c values, often require data collected to high temperatures to ensure the calculated T_c values are as reliable as possible.

Figure 6 shows two fits of the D_c versus temperature plots for the Pr_2TiO_5 compound. The line of best fit calculated with all 5 collected D_c values asymptote at a lower temperature, 1115 K, than that calculated using the four lower temperature D_c values 1236 K.

The sequential improvement in T_c values with smaller lanthanides continues (Figure 5) from Nd_2TiO_5 to Dy_2TiO_5 and Y_2TiO_5 .

3.3 Factors influencing Radiation Tolerance

Damage evolution can be governed by two competing factors: defect formation and defect recovery energies. At high temperatures, thermal energy

assists defect recovery. The T_c values of La_2TiO_5 , Pr_2TiO_5 , Nd_2TiO_5 and Sm_2TiO_5 are all high, above 1050 K, whereas those compounds between Eu_2TiO_5 to Y_2TiO_5 show sequential decreasing T_c concurrent with decreasing lanthanide size (Figure 5).

Based on high resolution TEM images and SAED data, *Zhang et al.* [12] proposed that the low T_c values for Ln_2TiO_5 compounds containing smaller lanthanides arises from short range phase transitions these compounds undergo from orthorhombic to cubic (defect fluorite) prior to amorphisation. In support of this hypothesis, Zhang documented SAEDs for the irradiated Gd_2TiO_5 specimen, held around its T_c , showing diffraction maxima matching that of the defect fluorite symmetry.

Hayun et al. [27] examined the formation enthalpies of orthorhombic La_2TiO_5 , Nd_2TiO_5 and Gd_2TiO_5 compounds, determining a trend in decreasing thermodynamic stability (more positive values for enthalpy of formation energies) with decreasing lanthanide radius size from La to Gd. This trend agrees with the temperature-composition diagram created by Shepelev and Petrova.[14]

The temperature-composition diagram shows it is possible for compounds of Ln_2TiO_5 stoichiometry to form polymorphs if the lanthanide radius is of europium size and smaller. Those Ln_2TiO_5 compounds that have a more thermodynamically stable defect fluorite structure should have an increased tolerance to ion-irradiation damage. This is not a new hypothesis; in fact,

compounds adopting the pyrochlore structure have been shown to have improved radiation response with an increase in thermodynamic stability for the formation of defect fluorite structures.[29-31]

Empirically the stability of the defect fluorite structure is based upon cation radii ratios. In compounds with the nominal stoichiometry $A_2B_2O_7$ (A = lanthanides, B = Ti, Zr, Hf, Sn), as the cation radius ratio lowers, the defect fluorite structure becomes more stable. As a consequence compounds, which can adopt the more thermodynamically stable defect fluorite structure type show improved radiation tolerance.[4, 32, 33] If the same trend is applied to those of Ln_2TiO_5 stoichiometry then, the smaller the lanthanide, the more thermodynamically stable the defect fluorite structure should be, thus should show improved radiation response. Previous studies on the crystallography of the smaller lanthanide titanates (Ho_2TiO_5 and Yb_2TiO_5) have shown these consist of long-range defect fluorite and short-range defect pyrochlore structures.[16, 18] The smaller the lanthanide, the more dominant the long-range defect fluorite structure becomes.

Based on these studies and the improved radiation response, decreasing T_c , from Nd_2TiO_5 to Sm_2TiO_5 to Eu_2TiO_5 to Gd_2TiO_5 to Tb_2TiO_5 to Dy_2TiO_5 to Y_2TiO_5 it seems reasonable to propose that the ease of phase transition is linked to relative radiation resistance.

Using HRTEM/SAED alone to study the phase transition in damaged samples is problematic. As a TEM foil is rendered amorphous, its SAED pattern is

comprised of contributions from both the crystalline and the amorphous components within the sample. Consequently it is possible for weaker diffraction maxima to be lost within the amorphous contribution in the SAED pattern, while the stronger diffraction peaks are still evident. Such an effect can lead to false interpretations in changes of symmetry. Furthermore, if nano-domains of defect fluorite were created by irradiation, the SAED patterns would likely show indications of a ring pattern, reflecting misalignment of the domains.

We sought to confirm the proposition that Ln_2TiO_5 compounds, containing smaller lanthanide cations, undergo symmetry changes with dose, by examining the amorphisation of Ln_2TiO_5 compounds using Grazing Incidence x-ray diffraction (GIXRD). Two approaches were used for bulk Dy_2TiO_5 samples exposed to 12 MeV Au^+ ions;

1. Samples held at room temperature and exposed to a series of ion doses between 1×10^{13} to 2.5×10^{14} ions / cm^2 and
2. Samples held at 450 °C and 550 °C and exposed to a dose of 5×10^{13} ions / cm^2

GIXRD patterns from the pre- and post-irradiated samples were collected (Figures 7 (a) and (b)).

In Figure 7 (a) the four major peaks within the patterns from the orthorhombic, *Pnma* symmetry were closely investigated; (203), (210), (013) and (413). A user defined background was subtracted from each pattern, followed by

pattern fitting with Gaussian peaks to determine peak locations and height. In [Table 3](#), our data show that there is some variation with dose in the peak ratios of these four major reflections but the ordering in regards to reflection strength remained constant. There is a significant decrease in peak intensity with dose and with the final dose of 2.5×10^{14} Au⁺ ions / cm² the peak from reflection (013) could no longer be resolved. There was no evidence for peaks which could be ascribed to the cubic ($Fm\bar{3}m$) fluorite structure phase. The consistent orthorhombic peak ratios and lack of peaks with cubic $Fm\bar{3}m$ symmetry with dose indicate Dy₂TiO₅ does not undergo a long range phase transition from orthorhombic, before it is rendered amorphous.

In [Figure 7 \(b\)](#) the GIXRD patterns are from Dy₂TiO₅ samples held at 300 K, 723 K and 823 K during exposure to 12 MeV Au ions. As with the room temperature irradiation, high temperature irradiation shows no evidence for a phase transition to defect fluorite in the GIXRD pattern. In fact, it is shown that long-range orthorhombic symmetry is maintained during bulk irradiation when the sample is held at these elevated temperatures.

The GIXRD results indicate that the recovery mechanism for the Ln₂TiO₅ orthorhombic series is something other than a transition to defect fluorite upon exposure to irradiating ions.

One explanation for the trend of improving radiation response with smaller lanthanide size arises from the thermodynamic stability trends of the Ln₂TiO₅ orthorhombic series. Previous studies of the thermodynamic stability of the

Ln_2TiO_5 compounds within the orthorhombic series suggest smaller lanthanides give less stable orthorhombic structures. This thermodynamic stability trend should give T_c values moving in the opposite direction, increasing T_c with decreasing Ln radius, from what has been found in this study, decreasing T_c with decreasing Ln radius.

A first principles investigation of the Ln_2TiO_5 orthorhombic series using the density functional theory approach showed a trend toward slightly enhanced “covalency” in local bonding across the series from La to Dy.[34] Previous studies of irradiation trends in families of ceramic compounds have associated improved radiation tolerance, lower T_c values, with an increase in “ionicity” (decrease in “covalency”).[35, 36] The T_c results from this study, i.e. lower T_c with greater covalency, are a counter to the argument of improved tolerance with greater ionicity.

A fundamental explanation for the improved radiation response with smaller lanthanides in the Ln_2TiO_5 series is under development, using alternative techniques such as density functional theory on the damage evolution and recovery mechanisms. However, the results here provide new insights into this system.

Concluding Remarks

The almost complete series of orthorhombic Ln_2TiO_5 compounds were investigated for radiation tolerance. This radiation tolerance, as defined by critical temperature, T_c , showed sequential improvement in, lowering of T_c

with decreasing lanthanide size for lanthanides of smaller radius than samarium.

The grazing incidence x-ray diffraction data of Dy_2TiO_5 showed that the long-range orthorhombic structure of the smallest lanthanide in this series was maintained when exposed to heavy ions and held at elevated temperature. This suggests that an ion-irradiation induced phase transition to a defect-fluorite structure, as proposed previously, does not take place.

Whilst a fundamental explanation for this observed radiation response is not yet available, future radiation tolerance studies on the Ln_2TiO_5 compounds should focus on the smaller lanthanides, as current radiation response studies indicate that these show the greatest promise for nuclear-based applications.

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Figure 1. Cell parameter and titanium to oxygen bond length data were taken from the ref [20] study on Ln_2TiO_5 orthorhombic crystallography. a) the cell parameters (*b* not shown) are shown to increase linearly with increasing lanthanide radius, b) the titanium to oxygen bond lengths vary significantly from trend with the Tb_2TiO_5 and Dy_2TiO_5 compounds, which may be indicative of the driving mechanism for a phase transition from the orthorhombic to

hexagonal or cubic structures (trend lines are fitted to bond lengths purely to aid the eye).

Table 1. Phase purity of studied Ln_2TiO_5 samples as measured via SEM BE images and EDX analysis.

Sample	Secondary Phase
La_2TiO_5	~ 2% $\text{La}_4\text{Ti}_3\text{O}_{12}$
Pr_2TiO_5	~ 3.5% $\text{Pr}_2\text{Ti}_2\text{O}_7$
Nd_2TiO_5	~ 5% $\text{Nd}_2\text{Ti}_2\text{O}_7$
Sm_2TiO_5	Single phase
Eu_2TiO_5	~ 10% $\text{Eu}_2\text{Ti}_2\text{O}_7$
Gd_2TiO_5	Single phase
Tb_2TiO_5	Single phase
Dy_2TiO_5	~ 5% $\text{Dy}_2\text{Ti}_2\text{O}_7$

Figure 2. The temperature stability diagram adapted from Shepelev and Petrova [14] for the series of compounds with Ln_2TiO_5 stoichiometry.

Figure 3. (a) a BF image, and SAED patterns of a microcrystal of Gd_2TiO_5 , (b) before irradiation (dose = $0 D_c$), after (c) $0.2 D_c$, (d) $0.3 D_c$ (e) $0.4 D_c$, (f) $0.7 D_c$, (g) $1.0 D_c$ and (h) BF image of amorphous grain at $1.0 D_c$.

Figure 4. Critical dose of amorphisation, measured at various temperatures, is plotted for 8 compounds with Ln_2TiO_5 stoichiometry ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{and Dy}$). Lines of best fit, based on equation 1, were calculated and are overlaid across the data points.

Table 2. Ln_2TiO_5 sample characteristics calculated from crystallographic data, and literature ionic radius values [37] are compared with *in-situ* ion irradiation data and corresponding calculated fits using equations 1 and 2. The corresponding errors are shown in brackets.

Compound	Ln^{3+} (VII) Ionic Radius (Å)	Density (g/cm^3)	ENSP	$D_{c(300\text{K})}$ ($\times 10^{14}$)	D_{c0} ($\times 10^{14}$)	T_c (K)	E_a (eV) Eqn 2
La_2TiO_5	1.10	5.44	0.808	1.8 (0.36)	1.6 (0.1)	1070 (23)	3.3
Pr_2TiO_5	1.06	5.73	0.714	2.22 (0.25)	2.0 (0.4)	1115 (2)	3.4
Nd_2TiO_5	1.05	5.90	0.698	2.41 (0.22)	2.1 (0.4)	1143 (81)	3.5
Sm_2TiO_5	1.02	6.25	0.656	2.53 (0.16)	2.7 (0.2)	1072 (23)	3.3
Eu_2TiO_5	1.01	6.38	0.658	1.63 (0.18)	1.7 (0.1)	974 (2)	3.0
Gd_2TiO_5	1.00	6.59	0.717	2.53 (0.16)	2.6 (0.6)	962 (1)	3.0
Tb_2TiO_5	0.98	6.75	0.679	2.34 (0.47)	2.6 (0.5)	889 (15)	2.8
Dy_2TiO_5	0.97	6.95	0.628	3.52 (0.47)	4.1 (0.7)	712 (40)	2.2

Figure 5. Critical temperature of amorphisation plotted against lanthanide radius for the series of orthorhombic Ln_2TiO_5 compounds. The data from this study is compared with previously published data from *Zhang et al.* [12] and *Whittle et al.* [6]. Linear lines to our data are to guide the eye only.

Figure 6. A plot of D_c versus temperature for the compound Pr_2TiO_5 . The same data is plotted twice; once with the full data set and the other missing the final high temperature data point. The two fits to the data diverge due to differences in the final high temperature data point.

Figure 7. The GIXRD patterns (a) from a series of Dy_2TiO_5 irradiated at various doses (ions / cm²) with Au^+ 12 MeV ions, (b) for Dy_2TiO_5 irradiated to 5×10^{13} ions / cm² whilst held at 300, 723 and 823 K (data has background subtracted and peaks normalised). In (a) reflection markers for two polymorphs of Dy_2TiO_5 , orthorhombic ($Pnma$)[24] and cubic ($Fm\bar{3}m$) (lattice parameters are modified from *Lau et al* [38]), are shown as (blue) vertical markers below the series of patterns. Vertical (red) lines mark the positions for reflections of $Fm\bar{3}m$ symmetry to aid the eye in identifying the expected peak

positions if this phase was present. Several major peak positions for both phases are indexed.

Table 3. Integrated peak intensities from grazing incidence x-ray diffraction data for the Dy₂TiO₅ compound bulk irradiated with Au⁺ 12 MeV ions to various doses. The table shows variations in relative peak intensities compared with the major orthorhombic peak reflection (2 1 0).

Dose (ions/cm ²)	$(I(210)_{\text{Dose } x} / I(210)_{\text{Dose } 0}) * 100$	$I(203)/I(210) * 100$	$I(013)/I(210) * 100$	$I(413)/I(210) * 100$
0	100	84	26	31
1×10^{13}	36	79	17	26
2.5×10^{13}	19	80	17	28
5×10^{13}	9	58	19	29
1×10^{14}	6	80	19	34
2.5×10^{14}	6	84	-	16