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The crystal structures and corresponding ion-irradiation response for the $Tb_{(x)}Yb_{(2-x)}TiO_5$ series

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ABSTRACT

The Ln_2TiO_5 (Ln = lanthanides and yttrium) compounds find use in nuclear, electronic and battery applications but there is a lack of information correlating the synthesis, structure and properties of these materials. We give an in depth review of the current available literature on the Ln_2TiO_5 compounds. New structural findings of the $Tb_xYb_{2-x}TiO_5$ (x = 0, 0.4, 0.8, 1, 1.2, 1.6, 2) compounds are detailed and their response to 1 MeV krypton ion exposure is discussed. A single phase Tb_2TiO_5 sample with hexagonal symmetry is the first bulk, single phase, mono-lanthanide with this stoichiometry and symmetry to be reported. Thus this work brings together the current literature and illustrates the synthesis-structure-property relationships that are observed in this family.

1. Introduction

The lanthanide titanate compounds of Ln_2TiO_5 stoichiometry exhibit a variety of structures and chemistries, which impacts their properties and hence their suitability for various applications. Ln_2TiO_5 compounds have been used or proposed for use as burnable poisons within the nuclear fuel matrices [1], containment materials for high level radioactive waste [2–8], and ionic conductors for either battery storage [9] or electronic applications [10,11].

Nuclear fuel assemblies can be designed to accommodate excess reactivity, so as to increase nuclear fuel burn-up and extend the usable life of the fuel. The excess reactivity existing in a freshly loaded reactor is balanced by introducing shim or control rods (containing elements or compounds with large thermal neutron absorption cross-sections to soak up excess neutrons) or by adding boron to the reactor coolant. Compounds containing the absorbing elements are known as burnable poisons. Boron carbide and boron-doped steel are currently used in control rods for Russian power water reactors. However radiation induced damage occurs within these absorber materials resulting from the neutron absorption by the ^{10}B isotope, formation of alpha particles, and subsequent helium formation and swelling [1].

Alternative ceramic compounds, many containing lanthanides, have been investigated for use as burnable poisons. Dy_2TiO_5 has been successfully used as a neutron absorber within control rods for both the MIR (Modernised International Reactor) and VVER (Water-Water Energetic Reactor) reactors in Russia for numerous years [1]. The fluorite structured poly-type was found to be best for this application due to the fact it suffers minimal swelling upon exposure to radiation [1]. Pellets designed with varying ratios of Gd_2TiO_5 and $Gd_2Ti_2O_7$ phases were tested for radiation response within the HANARO research reactor and of the four specimens tested three showed no thermal or irradiation induced swelling within experimental error [12].

Nuclear waste needs to be immobilised in a manner which ensures the safety of handling, society and the environment. Currently high level waste (HLW) from the reprocessing of spent nuclear fuel (SNF) and other sources is dispersed in borosilicate glass. However borosilicate glass is not suitable for the long term storage of all HLW streams or for a variety of other nuclear waste streams. Alternative waste form matrices have been studied for several decades including the multi-phase ceramic based waste-forms known as Synroc (Synthetic Rock) [13,14]. A variety of Synroc formulations have been designed to suit a variety of waste-streams, but all formulations incorporate titanate compounds. Studies of natural pyrochlore and zirconolite minerals, which incorporate actinides, show that they are largely radiation tolerant and chemically stable over geological timescales. Consequently, the radiation responses of pyrochlore-structured synthetic titanate compounds have been intensively studied [3,7,15–27]. Some of the Ln_2TiO_5 compounds have a short-range defect-pyrochlore, long-range defect-fluorite structure. Consequently radiation tolerance studies have also been undertaken for some of those compounds [1–3,7,28]. Of

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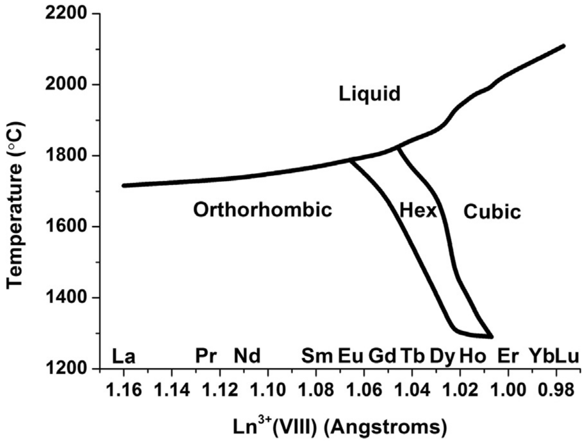

Fig. 1. Temperature stability diagram for the conventional solid oxide route fabrication of bulk Ln_2TiO_5 compounds. This diagram is adapted from that proposed by Shepelev and Petrova [29].

particular interest are those compounds with either pyrochlore, or especially, fluorite structures, which tend to show good radiation tolerance.

1.1. *The structure of bulk Ln_2TiO_5 compounds*

There are a range of polymorphs for the Ln_2TiO_5 system of compounds, with the final phase being dependent on temperature and/or pressure of fabrication and the lanthanide radius size (see Fig. 1) [29]. When fabricated at atmospheric pressure, there are four main polymorphs; orthorhombic *Pnma*, hexagonal *P6₃/mmc*, cubic *Fd-3m* and cubic *Fm-3m* symmetry. Shepelev and Petrova [29] identified a monoclinic *B2/m* phase for the compound Dy_2TiO_5, although there have been relatively few other references to this symmetry for the other Ln_2TiO_5 compounds. In the same study a temperature stability diagram (Fig. 1) was proposed with sintering temperature plotted against lanthanide radius size.

The temperature stability diagram in Fig. 1 indicates that the following statements can be made about the Ln_2TiO_5 series of compounds;

- Those containing large radii Ln elements (lanthanum to samarium) have only orthorhombic symmetry.
- Europium and gadolinium Ln_2TiO_5 compounds can have orthorhombic or hexagonal symmetry.
- Terbium, dysprosium, and holmium compounds can have orthorhombic, hexagonal or cubic symmetry.
- Erbium to lutetium compounds only form in cubic symmetry.

The Ln_2TiO_5 compounds containing the larger lanthanides and fabricated at atmospheric pressure normally adopt the orthorhombic, space group *Pnma* (62), symmetry. This is isostructural with the orthorhombic Y_2TiO_5 discovered by Mumme and Wadsley [30]. Of the three cation sites, the larger lanthanide occupies two sites, each seven co-ordinated, consisting of scalenohedra, minus an oxygen atom, which creates the deformed cube. The third site is exclusively occupied by titanium and has a unique five co-ordinated square based pyramid polyhedron in which the titanium atom is slightly offset from the base. The polyhedra are predominantly edge shared and this creates rhombic and triangular tunnels along the b axis, based on *Pnma* symmetry. It was these tunnels that were highlighted as a potential source of ion conduction in a previous lithium and sodium ion battery study [9].

With the Ln_2TiO_5 compounds containing europium to holmium (and yttrium) there is a small stability field for the hexagonal, space group *P6₃/mmc* (194), symmetry which is isostructural with the beta phase beryllium nitride β-Be_3N_2. There are two fixed cation sites, with the first Wyckoff position, 2a fully occupied by the lanthanide. However the second site, 2c, has mixed occupancy of lanthanide and titanium. All atoms are on special crystallographic sites with the exception of one of the two anion sites, the oxygen z(4f). All sites are fully occupied with the exception of the mixed cation B-site with an approximate vacancy of 20% [29]. These vacancies act to balance charge and so the percentage varies depending on the oxidation states of the cations and anions present [31]. The lanthanides reside within octahedra, whilst the mixed titanium and lanthanide B-site reside in a trigonal bi-pyramid. The polyhedra are arranged in an alternating layered A-site, B-site fashion with the overall structure being made up of six-layer repeat that is close packed with the mixed cation site located on the third and sixth layers [29]. The polyhedra connect via corner sharing across the layers and predominantly edge sharing within the layers.

For the Ln_2TiO_5 compounds with smaller radii lanthanides, from terbium to lutetium, cubic symmetry is found. The sintering temperatures and cooling rates have a large influence on the final dominant form, i.e., cubic symmetry consisting of either the defect-pyrochlore or defect-fluorite type structures.

The materials that are isostructural with pyrochlore have cubic, space group *Fd-3m* (227), symmetry [32]. Assuming the most common cation oxidation states Ln^{3+} and Ti^{4+} are achieved for the Ln_2TiO_5 stoichiometry, there will be inherent oxygen vacancies within the pyrochlore structure. Pyrochlore structured compounds would normally have the stoichiometry of $Ln_2Ti_2O_7$ rather than the Ln_2TiO_5 [$Ln_2(Ti_{1.33}Ln_{0.67})O_{6.67}$]. For the pyrochlore structure, there is only one variable positional parameter, the oxygen x(48f). Usually, in the ideal pyrochlore structure origin choice 2, the O(2) *8a*-site is not occupied, although, due to the cubic Ln_2TiO_5 compounds having been described as long-range fluorite, short-range pyrochlore, it is possible for some oxygen to be found occupying this site [33]. The pyrochlore structure consists of an A-site occupied by the lanthanide, eight co-ordinated, forming scalenohedra linked via edge sharing, and a B-site shared by lanthanide and titanium forming octahedra that are linked via corner sharing. The scalenohedra and octahedra link via edge sharing, with these polyhedra forming two interpenetrating networks. This mixing on the B-site is unusual for pyrochlore structures, as one of the major defining differences between the pyrochlore and fluorite structures is the ordering of cations onto different sites for the former and the disordered nature of the cations for the latter.

The pyrochlore structure is a 2 × 2 × 2 supercell of fluorite. The complete disordering of cations usually requires their respective ionic radii to be similar. This means that the smaller lanthanides, i.e., the ones tending toward the titanium radius size, tend to form fluorite more easily when compared with the larger lanthanides. An empirically derived cation radius ratio has been developed to indicate stability fields for pyrochlore and defect-fluorite formation for $A_2B_2O_7$ compounds. Radius ratios $r_A / r_B < 1.46$ should result in fluorite, and ratios from 1.46 to 1.78 should result in the pyrochlore symmetry [32]. For lanthanides terbium to lutetium it has been shown that it is possible to fabricate the Ln_2TiO_5 compound with cubic, *Fm-3m* (225), symmetry [34]. Compared with the ideal fluorite cation to anion ratio (MX_2), the Ln_2TiO_5 compounds ($MX_{1.67}$) have significant anion vacancies.

The ideal fluorite structure consists of an eight co-ordinated cation site creating edge sharing cubic polyhedra. However the significant vacancies intrinsic to the Ln_2TiO_5 compound with fluorite symmetry require distortion of the polyhedra. A thorough description of the fluorite Ln_2TiO_5 structure is yet to be realised due to the slightly incommensurate pyrochlore phase that is also present [33], and the complexity of diffuse scattering within electron diffraction patterns [31].

1.2. *$Ln_2Ti_2O_7$ to Ln_2TiO_5*

Lau et al. fabricated single phase cubic (defect fluorite) Ln_2TiO_5 compounds, with Ln from terbium to lutetium, by using high