



## Structural and crystal chemical properties of rare-earth titanate pyrochlores



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### ABSTRACT

Rare-earth titanates,  $RE_2Ti_2O_7$  (where  $RE$  = a rare-earth) with the pyrochlore structure continue to be investigated for use as potential stable host materials for nuclear and actinide-rich wastes. Accordingly, the present work is directed towards the elucidation of the fundamental structural, physical, and thermochemical properties of this class of compounds. Single-crystals of the rare earth pyrochlores were synthesized using a high-temperature flux technique and were subsequently characterized using single-crystal X-ray diffraction. The cubic lattice parameters display an approximately linear correlation with the  $RE$ -site cation radius. Theoretical calculations of the lattice constants and bond lengths of the subject materials were carried out using density functional theory, and the results are compared to the experimental values. The Sm and Eu titanates exhibit a covalency increase between the  $REO_8$  and  $TiO_6$  polyhedral resulting in a deviation from the increasing linear lattice parameter through the transition series.  $Gd_2Ti_2O_7$  with the  $4f^7$  half-filled  $f$ -orbital  $Gd^{3+}$  sub-shell exhibits the lowest  $48f$  oxygen positional parameter. The coefficient of thermal expansion for the rare-earth titanate series is approximately linear, and it has a range of  $10.1\text{--}11.2 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ . Raman spectroscopy indicated that the  $\sim 530 \text{ cm}^{-1}$  peak associated with the Ti–O stretching mode follows a general trend of decreasing frequency with increasing  $RE$  reduced mass.

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### 1. Introduction

Pyrochlore-structure compounds of the form,  $A_2B_2O_7$ , have been the subject of extensive research due to their broad range of physical, chemical [1], and magnetic properties that depend on the substitution of ions on the A and B cation sites. These compounds are important candidate materials for electrolytes and anodes in solid-oxide fuel cell (SOFC) applications [2]. In fact at  $727 \text{ } ^\circ\text{C}$ , the ionic conductivity of these pyrochlore compositions can reach  $5 \times 10^{-2} \text{ S/cm}$  – a value that is comparable to yttrium stabilized cubic zirconia (YSZ) – an electrolyte for the development of SOFC. Rare-earth titanates,  $RE_2Ti_2O_7$  (where  $RE$  = a rare-earth ion) with the pyrochlore structure also continue to be investigated for use as potential nuclear and actinide waste storage/disposal

forms. They are, in fact, a key component phase in Synroc (synthetic rock)-based pyrochlore-rich ceramics for the proposed geological immobilization of surplus plutonium from dismantled nuclear weapons [3,4], and single-crystals of these materials represent the basis for continuing heavy-particle radiation-damage and actinide-doping investigations. The magnetic behavior of the titanate pyrochlores are also of interest due to their varied and often unconventional magnetic ground states [5]. In these materials, the magnetic  $RE$  ions form a lattice of corner-sharing tetrahedra, which is the 3D archetype for geometric frustration. This frustration underlies a range of exotic disordered magnetic states at low temperature, such as spin-liquid, spin-glass, and spin-ice states.

Pyrochlores are also an important mineral structure-type with pyrochlore minerals occurring in a wide variety of high-temperature geologic settings including pegmatites and other igneous formations that often preferentially incorporate U and Th in their structure. Naturally occurring pyrochlores are often found in the disordered, metamict state due to radiation damage from  $\alpha$ -decay

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events of nuclides in the decay series of  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  impurities [6,7]. Studies involving Cm-doped  $\text{Gd}_2\text{Ti}_2\text{O}_7$  have shown a crystalline transformation to an amorphous state as a result of alpha-decay of the incorporated Cm [8]. Synthetic  $\text{Gd}_2\text{Ti}_2\text{O}_7$  doped with  $^{244}\text{Cm}$  is, in fact, very susceptible to  $\alpha$ -decay damage and transforms to an amorphous structure after a dose of  $2.3 \times 10^{25}$   $\alpha$ -decays/m<sup>3</sup> [9]. Radiation effects due to bulk doping of actinides result in volume swelling and micro-fracturing due to the increased size of the network as the structure expands. A practical host material for storing actinide waste would, of course, not be an isotropic phase. It would, instead, be an anisotropic polyphase material, and the determination of the thermal expansion for each phase of a pyrochlore-containing host material is essential for waste storage applications to prevent thermo mechanical phase mismatch. The coefficient of thermal expansion (CTE) can be calculated from the lattice parameters as a function of temperature, and the present study presents the first comprehensive determination of the CTE values for the  $\text{RE}_2\text{Ti}_2\text{O}_7$  ( $\text{RE} = \text{Lu-Sm}$  and  $\text{Y}$ ) pyrochlores. Accordingly, precise temperature-related structural data and single-crystal structural and crystal chemical analyses are pertinent to the interpretation of previous and ongoing rare-earth titanate irradiation-induced amorphization, chemical stability and thermo mechanical studies [10].

The pyrochlore,  $\text{A}_2\text{B}_2\text{O}_7$ , structure ( $Fd-3m$ ,  $Z = 8$ ), is an anion-deficient derivative of fluorite,  $\text{AX}_2$  ( $Fm3m$ ,  $Z = 1$ ), with two types of cations ordered on the A- and B-sites and one eighth of the anions removed. The structure can be envisioned as interpenetrating networks of  $\text{BO}_6$  octahedra and  $\text{A}_2\text{O}$  chains of distorted cubes. One-eighth of the oxygen atoms are removed from the fluorite structure giving the pyrochlore formula of  $\text{A}_2^{3+}\text{B}_2^{4+}\text{O}_7$ , in which the A-site contains the large cations (rare-earth ions) and the B-site consists of smaller (e.g., titanium), higher-valence cations. The larger  $\text{RE}^{3+}$  cations are eight-fold coordinated with oxygen and located within a distorted cubic coordination polyhedron. The loss of oxygen atoms causes a reduction in the coordination of the Ti-site cation from eight to six in a distorted octahedron. The general coordinates are shown in Table 1. There are two unique oxygen sites noted by the Wyckoff notation (48f and 8b): the 48f site oxygen at  $(x, \frac{1}{2}, \frac{1}{2})$  is coordinated with two  $\text{Ti}^{4+}$  and two  $\text{RE}^{3+}$  cations, while the 8b site oxygen at  $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$  is in a tetrahedral coordination with only  $\text{RE}^{3+}$  cations. The  $x$  positional parameter for the 48f site oxygen is the only variable coordinate for each rare-earth titanate pyrochlore compound. An unoccupied interstitial site, 8a, is surrounded by four  $\text{Ti}^{4+}$  ions, and the “vacancies” at the 8a site are ordered on the anion sub-lattice.

For the ordered pyrochlore structure,  $\text{A}_2\text{B}_2\text{O}_7$ , the chemical stability is mainly determined by the cation ionic radius ratio ( $r_A/r_B$ ). The larger  $\text{A}^{3+}$  cations are eight-fold coordinated with oxygen and located on the 16c site at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  within the distorted cubic polyhedron. The smaller  $\text{B}^{4+}$  cation is six-coordinated with oxygen and located in a distorted octahedron on the 16d site at (0,0,0). The ionic conductivity that makes these materials of interest for SOFC applications is attributed to the cation disordering at the A and B sites [11].

The essential crystallographic feature of the pyrochlore structure consists of sheets of corner-sharing  $\text{BO}_6$  octahedra parallel to the (111) plane. These sheets are arranged into three- and six-membered rings. When actinides are substituted into the

pyrochlore structure, they preferentially occupy the A-site [12]. This octahedral framework structure is an ideal host in which to substitute actinide elements at the A-site. As a result of the stable bonding, the rare-earth pyrochlores are important candidate ceramic waste forms for actinide immobilization [13], and they are one of the principal host phases being considered for the disposition of Pu from dismantled nuclear weapons [14].

An upper A-cation radius exists, above which the cubic titanate pyrochlore cannot form ( $r_{\text{A}^{3+}} > r_{\text{Sm}^{3+}}$ ,  $\text{RE} = \text{Nd, Pr, and La}$ ), and these compositions then crystallize in the monoclinic space group  $P2_1$  (No. 4).

Rare-earth titanate compounds have previously been characterized using routine powder XRD methods and other physical techniques [15,16]. Prior to the present investigations the synthesis of these compounds, however, has been limited primarily to the formation of powder samples. We have now grown single-crystal samples of the rare-earth titanate pyrochlore series,  $\text{RE}_2\text{Ti}_2\text{O}_7$  ( $\text{RE} = \text{Lu to Sm, and Y}$ ) by using a high-temperature flux technique [17]. The present study investigates the details of the single-crystal structures, plus the coefficients of thermal expansion of this series were determined using high-temperature X-ray diffraction. Spectral characterizations were also made by using Raman spectroscopy.

## 2. Experimental

### 2.1. Crystal growth

Single-crystals of the compounds  $\text{RE}_2\text{Ti}_2\text{O}_7$  ( $\text{RE} = \text{Sm to Lu, plus Y}$ ) were grown at  $T = 1235$  °C in a molten mixture consisting of the specific rare-earth oxide ( $\text{RE}_2\text{O}_3$ ), titanium oxide ( $\text{TiO}_2$ ), and lead fluoride ( $\text{PbF}_2$ ). Octahedral crystals of  $\text{RE}_2\text{Ti}_2\text{O}_7$  up to 3 mm on a side were formed by the slow evaporation of the  $\text{PbF}_2$  flux during a 5-day high-temperature synthesis period. The resulting crystals were yellow to brown in color depending on the particular rare-earth oxide used in the synthesis. The excess  $\text{PbF}_2$  flux that remained on the crystals was superficial and was removed by physical methods before analysis. The growth process was completed in air in a Pt crucible that was placed in a temperature-programmable furnace employing SiC heating elements.

The rare-earth pyrochlore crystal composition was confirmed by a semi-quantitative X-ray fluorescence analysis employing an International Systems Instrument (ISI-40) scanning electron microscope (SEM) equipped with an energy dispersive system (EDS). Trace amounts of lead (Pb) from the  $\text{PbF}_2$  flux were observed on the crystal surface. The majority of the  $\text{PbF}_2$  was physically removed before any further analyses was undertaken, however, and the interior surfaces of fractured crystals did not show traces of lead flux that might have been incorporated in the crystal lattice. Additionally, examination of the crystal samples using polarized light microscopy showed no evidence for impurity phases in the crystal matrix and confirmed the optical homogeneity of the single crystals that were selected for subsequent X-ray diffraction analysis.

### 2.2. Single-crystal X-ray diffraction studies

#### 2.2.1. Collection methods

Intensity data for all of the rare-earth pyrochlore compounds were collected using an Enraf-Nonius CAD4-F auto-diffractometer equipped with a graphite monochromator (take-off angle at  $2.8^\circ$ ). Using Mo  $K\alpha$  radiation ( $\lambda_{\text{mean}} = 0.71073$  Å). The orientation matrix and unit cell lattice parameters were obtained through the application of the CAD4 subroutine program SEARCH [18]. Data sets were collected for each compound in the range of  $3.0 < 2\theta < 56$

**Table 1**  
Atomic positions for  $\text{RE}_2\text{Ti}_2\text{O}_7$  ( $\text{RE} = \text{Lu-Sm}$  and  $\text{Y}$ ).

Atom	Wyckoff notation	x	y	z
RE	16d	1/2	1/2	1/2
Ti	16c	0	0	0
O(1)	48f	x	1/8	1/8
O(2)	8b	3/8	3/8	3/8

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