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A case for oxygen deficiency in $Gd_2Ti_{2-x}Zr_xO_7$ pyrochlore-type oxides

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ABSTRACT

Pyrochlore-type oxides having the formula $Gd_2Ti_{2-x}Zr_xO_7$ have been studied in the past as potential candidates for the sequestration of nuclear waste elements owing to their chemical robustness and increased resistance to radiation induced damage with greater Zr incorporation. To be used for nuclear waste sequestration applications, all aspects of these materials need to be understood. This is especially the case for the stoichiometry of the materials and the effect of crystal defects. X-ray absorption near-edge spectroscopy (XANES) has been used here to study the local chemical environment of the metal atoms depending on composition. Analysis of Ti K-edge XANES spectra has shown that $Gd_2Ti_{2-x}Zr_xO_7$ ($0 \leqslant x < 2$) can be slightly O-deficient, and that the level of O-deficiency increases with greater Zr incorporation.

1. Introduction

When discussing the longevity of the nuclear power industry, how the nuclear waste generated will be handled must be considered. Spent nuclear fuel can be stored on site at nuclear power facilities and/or in geological repositories [1]. As such, inert host materials are needed which can contain radioactive waste elements for long periods of time [2]. With over 500 synthetic compositions known, transition metal oxides adopting the pyrochlore-type structure (general formula $A_2B_2O_7$) have a diverse chemistry leading to many applications, including nuclear waste sequestration [3]. (Pyrochlore-type materials have also been studied as potential catalysts, as ion conductors for fuel cells, and as thermal barrier coatings [2,4–10].) With naturally occurring pyrochlores containing large amounts of U or Th, and Pu-bearing analogues having been successfully synthesized, the ability of these materials to structurally incorporate actinides makes them desirable as hosts for nuclear waste [8,11,12]. In particular, certain Ti and Zr pyrochlore compositions are ideal for nuclear waste sequestration due to their high chemical durability and resistance to radiation induced damage [10,13]. For example, the titular compounds, $Gd_2Ti_{2-x}Zr_xO_7$, have been found to become increasingly resistant to radiation induced damage with greater Zr incorporation [10].

The pyrochlore-type structure ($Fd\bar{3}m$; see Fig. 1) is an O-deficient superstructure of the fluorite structure-type ($Fd\bar{3}m$) and has two different cation sites, one eighth fewer O atoms, and the unit cell is approximately double in size [8,14]. Larger cations (e.g., rare earth elements; RE^{3+}) are incorporated in the 8-coordinate A-site, with smaller cations, such as Zr^{4+} or Ti^{4+}, occupying the 6-coordinate B-site. Three O sites are present in this structure (48f, 8a, 8b), with two being occupied (48f, 8b) and the third (8a) being unoccupied in a perfectly ordered pyrochlore [8]. The closely related defect fluorite structure ($Fd\bar{3}m$), an oxygen-deficient derivative of the fluorite structure, can also be formed depending on either the composition or experimental conditions [8,11,15,16]. The defect fluorite-type structure results from the cations being randomly distributed on a single site with the single O site being 7/8 occupied.

The governing factor determining the formation of either a pyrochlore- or defect fluorite-type structure is the relative size of the A- and B-site cations, which is generally determined by comparison of the ionic radii of the cations (r_A/r_B) [8,10,11]. As the size of the A- and B-site cations approach unity, greater antisite disorder between the cation sites can occur, leading to the transformation of the pyrochlore structure to the defect fluorite structure. Materials produced at atmospheric pressure can adopt the pyrochlore-type structure when r_A/r_B is between ~1.46 and 1.78, while the defect fluorite-type structure is favoured when $r_A/r_B \leqslant 1.46$ [8,15]. Materials with a ratio near the phase-transition boundary, such as $Gd_2Zr_2O_7$ ($r_A/r_B = 1.46$), can undergo a thermally induced change from one structure to the other, with the defect fluorite-type structure being favoured when higher reaction temperatures are used [8,13,17,18]. Transformation from the pyrochlore to defect fluorite structure is mediated by a shifting of the x coordinate of the 48f O-site along with cation and anion antisite disorder [8,16].

The amount of cation antisite disorder that occurs in the $Gd_2Ti_{2-x}Zr_xO_7$ system depending on composition has been investigated in the past with somewhat conflicting results [18–20]. Analysis of powder X-ray diffraction data from these materials

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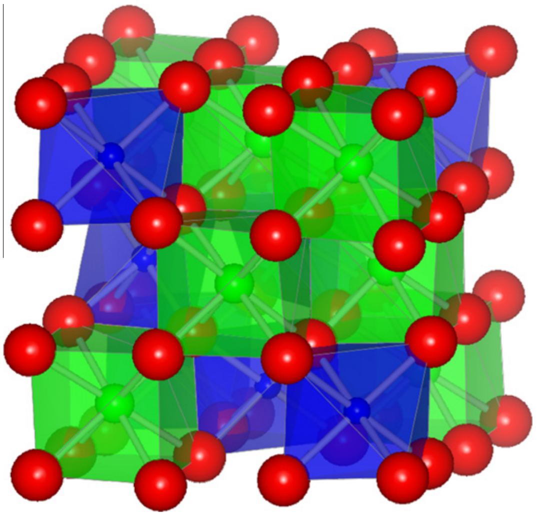

Fig. 1. A portion of the cubic pyrochlore unit cell is shown [14]. The 8-coordinate A-site is presented in green while the 6-coordinate B-site is presented in blue. The O atoms are shown as red spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

suggests that Ti and Zr can increasingly occupy the A-site with greater Zr incorporation [19,20]. However, an examination of Ti $L_{2,3}$- and O K-edge X-ray absorption near-edge spectra instead suggested that Ti remained in the B-site and that only Zr and Gd underwent antisite disorder as the Zr concentration increased [18]. Owing to the sensitivity of X-ray absorption near-edge spectra to changes in coordination, and the difficulty in assigning site occupancies to three different cations across two crystallographically different sites by Rietveld analysis of powder X-ray diffraction data, it is presumed in this present study that Ti preferentially occupies the B-site in these compounds regardless of the concentration of Zr. This suggestion can also be made by comparing the ionic radii of the smaller Ti^{4+} ions to the larger Zr^{4+} and Gd^{3+} ions, as cation antisite disorder generally occurs when the A- and B-site ions are closer in size [8,21].

While the $Gd_2Ti_{2-x}Zr_xO_7$ system has been studied independently by infrared and Raman spectroscopy, X-ray diffraction (XRD), X-ray absorption spectroscopy, and computational methods; few studies have investigated the effect of composition on the local coordination environment of the RE and transition-metal atoms [3,13,17,18]. A thorough understanding of the effect of composition on the local structure of these atoms is important to optimizing the material properties for all of the applications mentioned previously. In particular, knowledge of the local structure (coordination number; CN) is invaluable when investigating how the incorporation of actinides influences the properties and structural stability of the material over time.

One method of probing the local coordination environment of an element is by use of X-ray absorption spectroscopy (XAS), which can be further subdivided into X-ray absorption near-edge spectroscopy (XANES: provides information on charge, bond environment, and the local coordination environment of an atom) and extended X-ray absorption fine-structure analysis (EXAFS: provides information on the local structure of the absorbing atom). Although XAS studies of $Gd_2Ti_{2-x}Zr_xO_7$ have been performed in the past, these studies have focused on different interests, such as the effects of radiation induced damage, cation disorder, or the pyrochlore to defect-fluorite phase transition [13,17,18,22]. In this study, Ti K-, Zr K-, and Gd L_3-edge XANES spectra from a series of $Gd_2Ti_{2-x}Zr_xO_7$ ($0 \leqslant x < 2$) oxides are presented and show that this material can be O-deficient, with the average Ti CN being slightly less than six when the Zr concentration in the material is high.

2. Experimental

2.1. Synthesis and X-ray diffraction

A series of compounds from the $Gd_2Ti_{2-x}Zr_xO_7$ system ($0 \leqslant x \leqslant 2$) were synthesized by stoichiometric reaction of the parent binary oxides (Gd_2O_3, Alfa Aeser, 99.99%; TiO_2–Rutile, Alfa Aeser, 99.99%; ZrO_2, Alfa Aeser, 99.978%). The materials were synthesized by first mixing the binary oxides using an agate mortar and pestle, followed by pressing a pellet of the mixture using a pressure of ~6 MPa ($x > 0$) or ~0.5 MPa ($x = 0$). Each sample was heated in an alumina crucible from 600 °C to 1300 °C over 5 h and held at this temperature for approximately two days. Samples were quench cooled in air, ground, pelleted, and re-heated at 1300 °C for another two days. This process was repeated until a phase-pure compound was formed. All samples were quench cooled in air after receiving the final heat treatment. Pyrochlore-type materials are usually synthesized using higher annealing temperatures (e.g., 1500–1600 °C); however, it has been found here, and in other studies, that these materials can be formed phase-pure at lower temperatures [10,16,18,19]. In addition to these materials, $Yb_{2-x}Ca_xTi_2O_{7-\delta}$, which also adopts the pyrochlore-type structure, was synthesized as part of this study. Yb_2O_3 (Alfa Aesar, 99.9%), $CaCO_3$ (EMD, >99%), and TiO_2 were mixed as described above and the pellet was first heated to 900 °C to decompose the carbonate before being heated to 1400 °C and then quench cooled in air.

Ba_2TiO_4, which contains Ti in a (4-coordinate) distorted tetrahedral environment, and $Ba_2TiSi_2O_8$, which contains Ti in a (5-coordinate) square pyramidal environment, were synthesized to act as references to aid with the analysis of Ti K-edge XANES spectra [23,24]. Ba_2TiO_4 was synthesized by mixing $BaCO_3$ (Alfa Aesar; 99.95%) and TiO_2 (Alfa Aesar; 99.6%), and heating a pressed-pellet of these materials at 800 °C for 19 h and then at 1200 °C for 22 h, at which point phase-purity was achieved. $BaCO_3$, TiO_2, and SiO_2 (Alfa Aesar; 99.99%) were mixed in stoichiometric proportions and pressed into a pellet to synthesize $Ba_2TiSi_2O_8$. The pellet was first heated at 800 °C for ~19 h before the temperature was increased to 1200 °C, and the pellet was held at this temperature for ~40 h with intermediate grinding and re-pelleting before finally being quench cooled in air. Powder XRD was performed using a PANalytical Empyrean diffractometer and a Cu Kα X-ray source to determine phase purity and lattice constants for all compounds synthesized.

2.2. Ti K-edge XANES

Ti K-edge spectra were collected using beamlines located at the Canadian Light Source (CLS) and the Advanced Photon Source (APS; Argonne National Laboratory) synchrotron radiation facilities. The Soft X-ray Microcharacterization Bending Magnet beamline (SXRMB; 06B1-1) was used to collect spectra at the CLS using a Si (111) monochromator [25]. The samples examined were powdered and pressed on C tape before being loaded into the vacuum chamber, and spectra were collected in total-electron yield mode. Spectra were also collected at the APS using the Pacific Northwest Consortium/X-ray Science Division Collaborative Access Team (PNC/XSD-CAT) bending magnet beamline (20BM), also using a Si (111) monochromator [26]. Powdered samples were spread as a thin layer between two pieces of Kapton tape, and multiple layers were used to maximize absorption. Spectra were collected in partial fluorescence yield and transmission modes using a 13-element Ge detector and N_2-filled ionization chambers, respectively. The resolution of the Ti K-edge spectra collected using SXRMB was 0.5 eV when the excitation energy was 5000 eV, while it was 0.7 eV for the spectra collected using the PNC/XSD-CAT beamline. (Note that these resolutions only reflect on the beamlines themselves, and do not include the effect of core-hole lifetime effects, which could further broaden the spectra.) The Ti K-edge spectra were collected in 0.15 eV steps through the main edge and calibrated using Ti powder (CLS) or Ti foil (APS), with the absorption-edge energy set to 4966 eV [27].

2.3. Zr K- and Gd L_3-edge XANES

Spectra from the Zr K- and Gd L_3-edges were also collected at the APS using the PNC/XSD-CAT (20BM) beamline. Sample preparation was the same as for the Ti K-edge spectra collected using this beamline, and spectra were collected in transmission and partial fluorescence yield modes simultaneously for both edges. The incident ionization chamber contained 100% $N_{2(g)}$, while the transmission and reference ionization chambers contained a mixture of $Ar_{(g)}$ and $N_{2(g)}$. Multiple scans of each spectrum were collected with 0.3 eV and 0.15 eV steps through the Zr K- and Gd L_3 absorption-edges, respectively. The resolution of the spectra is 2.5 eV when the excitation energy is 18000 eV (Zr K-edge), while it is 1.0 eV when an excitation energy of 7200 eV is used (Gd L_3-edge). As for the Ti K-edge spectra, the energy resolutions listed here do not include the effects of core-hole lifetime broadening. The Zr K-edge spectra were calibrated using Zr foil as a reference standard with the absorption-edge energy set to 17998.0 eV [27]. As Gd foil was not available, a spectrum from Gd_2O_3 was first calibrated using Fe foil (absorption-edge energy = 7112 eV) and Gd_2O_3 was then used as a reference standard for all other spectra with the absorption-edge energy set to 7246.0 eV [27]. All XANES spectra