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Mixed Valence Cerium Substitution in Gd_{2-x}Ce_xTi₂O_{7+δ} Pyrochlores

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Highlights:

- Variation of the Ce oxidation state in $Gd_{2-x}Ce_xTi_2O_{7+\delta}$ was investigated
- XPS and XANES confirmed the presence of Ce³⁺ and Ce⁴⁺
- Increase in Ce oxidation state is charge balanced by O intercalation

ABSTRACT: Pyrochlore-type oxides having the formula $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ have been synthesized by ceramic and co-precipitation methods and annealed at 1300 °C under different environments. Rietveld refinement of powder X-ray diffraction (XRD) patterns indicated that the products adopt the pyrochlore-type oxide structure with Ce ions substituting for Gd ions. Analysis of Ce 3d X-ray photoelectron spectroscopy (XPS) spectra confirmed the presence of both Ce³⁺ and Ce⁴⁺, which was corroborated by analysis of Ce L₃-edge X-ray absorption near edge spectroscopy (XANES) spectra. Incorporation of Ce⁴⁺ imparts disorder on the Ti octahedra as observed by analysis of Ti K-edge XANES spectra. Due to the presence of Ce⁴⁺ in the A-site of the pyrochlore-type structure, oxygen is likely intercalated into the vacant anion 8b site to charge balance the system. This intercalation results in an increase of the average Ti coordination number from 6 to between 6 and 7, which leads the formula unit being better represented as $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$.

Keywords: solid-state chemistry, nuclear waste sequestration, x-ray absorption spectroscopy

1. Introduction

The proliferation of high-level nuclear waste represents a challenging environmental concern[1]. Ceramic waste forms have been proposed as a solution to this problem with the radioactive waste products being incorporated into a crystalline structure[1]. A variety of crystal structures and compositions have been studied because of the ability of these structures to incorporate different waste products [2–5]. Pyrochlore-type oxides, with the formula A₂B₂O₇, have been proposed as candidates to incorporate actinide waste products [1,6,7]. Pyrochlore-type oxides are attractive materials due to the resistance of these materials to leaching and radiation damage [8].

Pyrochlore-type oxides (space group F d -3 m) have a very broad range of chemical compositions, with over 500 synthetic compositions being known [9–11]. The 8-coordinate A-site is normally occupied by an ion in the 3+ oxidation state (**Figure 1**). However, 4+ ions have been shown to be stabilized in the A site by the addition of a 2+ ion to maintain charge balance [12,13]. Similarly, the 6-coordinate B-site is normally occupied by a 4+ ion, but both 3+ and 5+ ions have been shown to be stabilized in the B site by the incorporation of either oxygen vacancies or A-site cation vacancies [10,14]. The pyrochlore-type structure can form when the radius ratio of A- to B-site cations is between 1.78 and 1.46 while the defect fluorite structure can form when the radius ratio is \leq 1.46 [7,15]. The pyrochlore-type structure is a derivative of the fluorite crystal system with ordered oxygen vacancies while the defect fluorite structure has randomly distributed oxygen vacancies. The 48f anion position, which is shared between the A- and B- site vertices, is the only atomic position in the structure that is not located at a special position. Thus, changes in the 48f x-coordinate are able to describe distortions of the A- and B-site pyrochlore structure[7].



Figure 1. Pyrochlore crystal structure of $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$. GdO_8 and CeO_8 polyhedra are depicted in magenta. TiO₆ octahedra are depicted in cyan. The structure is projected along the (2 2 2) plane and contains eight formula units.

Cerium is often used as a surrogate for plutonium due to the similarities in the radii and redox properties of these elements [16,17]. Previous work has suggested that when cerium is substituted into Gd₂Ti₂O₇, the solubility limit is reached at Gd_{1.6}Ce_{0.4}Ti₂O₇, it only substitutes for gadolinium, and is only present in the 3+ oxidation state[18]. Additionally, it has been shown that post-synthetic treatment of Ce₂Zr₂O₇ by sodium hypobromite results in partial oxidation of Ce³⁺ to Ce⁴⁺, which results in an excess of oxygen being present in the structure with the final stoichiometry being Ce₂Zr₂O_{7+δ}[19]. This excess oxygen has been suggested to occupy the normally vacant anion 8b site, which is coordinated to the Zr ions. In this

work, it is shown that when Ce is incorporated into $Gd_2Ti_2O_7$, it only substitutes for Gd in the A-site and is present in both 3+ and 4+ oxidations states. The increase in average A-site oxidation state likely results in an oxygen-intercalated pyrochlore (i.e. $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$). The average Ce oxidation state has also been shown in this study to vary depending on the synthesis conditions and/or annealing atmosphere.

- 2. Experimental Section
 - 2.1 Synthesis and Powder XRD
 - 2.1.1. Synthesis of $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ Materials by the Ceramic Method

 $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ pyrochlore-type materials were synthesized using Gd_2O_3 , TiO₂, and CeO₂ or $Ce(NO_3)_3 \cdot 6H_2O$ as precursors. Stoichiometric amounts of the precursors were thoroughly mixed using a mortar and pestle and pressed into pellets at ~6 MPa. The pellets were loaded into an alumina boat, placed into a tube furnace, and heated to 1300 °C under an atmosphere of N₂(g) (PraxAir; 99.99%) or air at a rate of 100 °C/hr and held at this temperature for 72 hours. Samples that were heated under air were quench cooled after the 72-hour heating cycle. Samples heated under N₂(g) were allowed to cool to room temperature over 12 hours. The samples were then reground, pelleted, and heated under the same conditions for an additional 72 hours. All samples produced by this method were brown in color.

2.1.2. Synthesis of Gd_{1.6}Ce_{0.4}Ti₂O₇₊₈ Materials by a Co-precipitation Method

Samples synthesized by the co-precipitation method (designated as "p" below) were synthesized by dissolving $Gd(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9%), $Ce(NO_3)_3 \cdot 6H_2O$, and titanium (IV) tertbutoxide (Sigma-Aldrich, deposition grade) in 1 M nitric acid, followed by the addition of NH₄OH (concentrated; 28 wt. %) dropwise until the pH reached 10 and a white precipitate formed. The precipitate was filtered and washed with deionized water and allowed to dry in air overnight before being pressed into a pellet and heated under the same conditions as the ceramic samples described above. All samples produced by this method were brown in color. **Table 1** contains a list of the sample names and starting materials,

synthesis method, and annealing atmospheres used to synthesize all pyrochlore-type materials discussed herein.

2.1.3. Synthesis of Standard Materials

 $Gd_2Ce_2O_7$, a standard sample containing Ce^{4+} , was synthesized using Gd_2O_3 (Alfa Aesar; 99.99%) and CeO_2 (Sigma-Aldrich; 99.9%). Stoichiometric amounts of the precursors were thoroughly mixed using a mortar and pestle and pressed into pellets at ~6 MPa. The pellets were loaded into an alumina boat, placed into a tube furnace, and heated to 1300 °C under air at a rate of 100 °C/hr and held at this temperature for 72 hours. The pellets were removed from the furnace and quench cooled in air.

CePO₄, a standard sample containing only Ce³⁺, was synthesized by dissolving 1.197 g of Ce(NO₃)₃·6H₂O (Alfa Aesar; 99.5%) in 50 mL of deionized water and adding 0.20 mL of H₃PO₄ (Fisher Scientific, 85%). This solution was allowed to reflux overnight and the solution was filtered to collect a white precipitate, which was annealed under air at 1100 °C for 3 days and quench cooled to room temperature.

Table 1. List of pyrochlore-typ	e samples showing	g differences in	n synthesis	methods,	starting	materials,
and annealing atmospheres						

Sample Name	Synthesis Method	Starting Materials	<u>Annealing</u> Atmosphere
$\begin{array}{l} Gd_{1.6}Ce_{0.4}Ti_{2}O_{7+\delta}\\ (Ce^{3+}/N_{2}) \end{array}$	Ceramic	Gd ₂ O ₃ , Ce(NO ₃) ₃ , TiO ₂	N ₂
$\begin{array}{c} Gd_{1.6}Ce_{0.4}Ti_{2}O_{7+\delta}\\ (Ce^{4+}/N_{2}) \end{array}$	Ceramic	Gd ₂ O ₃ , Ce(NO ₃) ₃ , TiO ₂	N_2
$\begin{array}{l} Gd_{1.6}Ce_{0.4}Ti_{2}O_{7+\delta}\\ (Ce^{4+}/air) \end{array}$	Ceramic	Gd ₂ O ₃ , CeO ₂ , TiO ₂	Air
$\begin{array}{l} p\text{-}Gd_{1.6}Ce_{0.4}Ti_{2}O_{7\text{+}\delta}\\ (Ce^{3\text{+}}\!/N_{2}) \end{array}$	Co-precipitation	Gd(NO ₃) ₃ , Ce(NO ₃) ₃ , Ti(OC ₄ H ₉) ₄	N_2

2.1.4. Powder X-ray Diffraction

Powder XRD patterns were collected using a Panalytical Empyrean powder XRD equipped with a Co K $\alpha_{1,2}$ (1.79 Å) source. High quality power X-ray diffraction patterns were collected from Gd₂Ti₂O₇, Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce³⁺/N₂), Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/air), and p-Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce³⁺/N₂) samples. The patterns were collected using a 2 θ range of 5-120° and a step size of 0.017 °. The patterns were analyzed by performing a Rietveld refinement. The parameters included in the refinement were scale factor, zero shift, lattice parameter, Caglioti scattering coefficients, O 48f x-coordinate, and overall isotropic thermal factor (B_{OVL}). The patterns were refined using the X'Pert HighScore Plus software program [20].

2.2 XPS

XPS spectra from Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/N₂), Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/air), and Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce³⁺/N₂) were collected using a Kratos AXIS Supra X-ray photoelectron spectrometer equipped with an Al K α (1487 eV) X-ray source located in the Saskatchewan Structural Sciences Center, University of Saskatchewan. High resolution Ce 3d and C 1s XPS spectra were collected using a pass energy of 40 eV, a step size of 0.05 eV, and an appropriately sized energy window. All spectra were collected with the charge neutralizer turned on and were calibrated by setting the binding energy of the C 1s peak from adventitious carbon to 284,8 eV. The XPS spectra were analyzed using the CasaXPS software program [21].

2.3 XANES

The Ti K-edge and Ce L_3 -edge XANES spectra were collected using beamlines located at the Advanced Photon Source synchrotron radiation facility, Argonne National Laboratory. Spectra were collected using the 20-BM and 9-BM beamlines. Both beamlines were equipped with a Si (1 1 1) monochromator. Samples were prepared as powders sealed between layers of Kapton tape and collected in partial fluorescence and transmission modes using a 13-element Ge detector and N₂-filled ionization

chambers, respectively. The Ti K-edge XANES spectra were calibrated using Ti metal (4966 eV) and the Ce L₃-edge XANES spectra were calibrated using Cr metal (5989 eV). The resolution of the Ti Kedge XANES spectra was 0.7 eV or 0.5 eV when collected using the 20-BM beamline or the 9-BM beamline, respectively. The resolution of the Ce L₃-edge XANES spectra was 0.8 eV or 0.6 eV when collected using the 20-BM beamline or the 9-BM beamline, respectively. All XANES spectra were calibrated, normalized, and analyzed using the Athena software program [22]. Linear Combination Fitting of the Ce L₃-edge XANES spectra was also performed using the Athena software program. Error in the LCF data was determined by manually fitting each component to a composition where the intensities matched that of the experimental spectra.

3. Results and Discussion

3.1. Structure

X-ray diffraction patterns from the Ce-substituted Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} pyrochlore-type materials show that the products are majority single-phase (**Figure 2**); however, the Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce³⁺/N₂) and Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/N₂) samples contained a small amount of TiO₂ (2 wt. %) and CeO₂ (2 wt. %), while the Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/air) sample contained a moderate amount of CeO₂ (7 wt. %). Rietveld refinement of the XRD patterns from the Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} series was performed to determine if there were any changes in the pyrochlore-type crystal structure based on changes in starting materials, synthesis methods, or annealing atmosphere. The model system was based on Ce substituting for Gd in the A-site. The Rietveld refinements performed using this structural model are shown in **Figure 2** and **Figure S1** in the Supporting Information section. The refinement results (Table 2) indicate that the experimental patterns agreed well with the model system. Upon closer inspection of the XRD patterns of the pyrochlore-type materials (**Figure 3**), a shift in peak position to lower 2 θ values (larger unit cell) was observed for samples that were annealed in N₂(g) when compared to the unsubstituted pyrochlore (Gd₂Ti₂O₇). Substitution of Ce³⁺ for Gd³⁺ should result in an expansion of the pyrochlore lattice as the

ionic radius of Ce^{3+} (1.14 Å) in an 8-coordinate environment is larger than Gd^{3+} (1.05 Å) [23]. However, the XRD patterns of samples that were annealed in air were shifted to higher 20 values (smaller unit cell) when compared to the XRD pattern from the unsubstituted pyrochlore material (**Table 2**). This could indicate that there is partial oxidation of Ce^{3+} to Ce^{4+} , which would result in a contraction of the lattice due to the smaller size of Ce^{4+} (0.97 Å) compared to Gd^{3+} in an 8-coordinate environment [23]. Another possibility is that Ce^{4+} substitutes for Ti^{4+} in the B-site. While there was a small amount of TiO_2 (2%) present in these materials, Ce substituting for Ti in the B-site would result in a large amount of TiO_2 (12%) present in the final product. Also, attempts to refine the diffraction patterns to include the possibility of Ce substituting for Ti in the B-site were unsuccessful (**Figure S2**), indicating that Ce only substitutes for Gd in the A-site.



Figure 2. (Top) XRD pattern and Rietveld refinement of $Gd_{1.6}Ce_{0.4}Ti_2O_7$ (Ce³⁺/N₂). (Bottom) XRD Patterns of cerium-substituted pyrochlores synthesized using different annealing conditions and starting materials. CeO₂ and TiO₂ impurities are indicated by (*).

Parameters	Gd ₂ Ti ₂ O ₇	$\begin{array}{c} Gd_{1.6}Ce_{0.4}Ti_{2}O_{7+\delta}\\ (Ce^{3+}/N_{2}) \end{array}$	$\frac{Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}}{(Ce^{4+}/N_2)}$	$\begin{array}{c} Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}\\ (Ce^{4+}/air) \end{array}$	$\begin{array}{c} p\text{-} \\ Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta} \\ (Ce^{3+}\!/N_2) \end{array}$
a (Å)	10.1843(5)	10.197(1)	10.1956(9)	10.175(1)	10.1911(8)
48f O (x)	0.420(5)	0.421(1)	0.420(5)	0.42(1)	0.426(7)
B _{OVL}	0.(2)	1.7(4)	1.0(4)	1.(1)	0.7(4)
R _{wp}	7.17403	8.08379	8.3056	14.71565	10.1271
R _{exp}	5.23556	6.05142	5.4437	11.75847	6.8719
χ^2	1.87759	1.7845	2.32785	1.56624	2.17178

Table 2. Rietveld refinement parameters	for	Gd _{2-x} Ce _x T	$i_2O_{7+\delta}[24].$
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Figure 3. Zoomed in view of the (222) powder XRD peak from the pyrochlore-type materials showing the change in peak position that occurred when the annealing atmosphere was changed. The red line indicates the $k\alpha_1$ peak position for $Gd_2Ti_2O_7$.

3.2. X-ray Photoelectron Spectroscopy

Analysis of the power XRD patterns from these materials indicated that the lattice constants varied depending on the synthetic conditions used, which could result from a variation in the Ce oxidation state. The samples annealed in air were exposed to an oxidizing environment that could result in the formation of Ce⁴⁺. While the Ce-containing precursor used to form the $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ (Ce⁴⁺/N₂) sample did not contain any Ce⁴⁺ to begin with, and was annealed in an inert environment, the starting material, Ce(NO₃)₃·6H₂O, contained both NO₃⁻ and H₂O, which are oxidizing agents, which could lead to the partial oxidation of Ce^{3+} to Ce^{4+} . Additionally, it is likely that the $N_2(g)$ used contained a small amount of water. The effect of these different oxidizing conditions on the ratio of Ce^{3+}/Ce^{4+} in substituted pyrochlores is not known. Ce 3d XPS spectra have been shown to be sensitive to changes in Ce oxidation state.[25] Ce 3d XPS spectra were collected from the pyrochlore-type materials and appropriate standards to study how the Ce oxidation state changes depending on synthesis conditions and are shown in Figure 4. The spectrum from CePO₄ is presented to show the spectral features that would be expected from a Ce³⁺-bearing material. The spectrum consists of two pairs of spin-orbit split peaks and associated shake-up satellites. The Ce $3d_{5/2}$ component is labeled u_0 and the associated shake-up satellite peak is labeled u_1 , while the Ce $3d_{3/2}$ component is labeled u_0 ' and the shakeup satellite is labeled u₁' in **Figure 4**. Ligand to metal charge transfer shake-up peak satellites result from the donation of a valence electron from neighboring O atoms into the conduction band of the Ce atoms [26]. The Ce 3d XPS spectrum from CeO₂ is also presented in Figure 4 and is consistent with what would be expected for spectra from Ce⁴⁺-bearing materials, with three pairs of spin-orbit split peaks and associated shake-up satellites that result from the different final states of Ce^{4+} (i.e., $4f^0$, $4f^1$, and $4f^2$) [27]. The Ce $3d_{5/2}$ components are labeled as

 v_0 , v_1 , and v_2 , and the Ce $3d_{3/2}$ components labeled as v_0 ', v_1 ', and v_2 ' in **Figure 4** [23, 24]. The peak labeled as v_2 ' is diagnostic of the presence of Ce⁴⁺[25].



Figure 4. Ce 3d XPS spectra from of $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ (Ce⁴⁺/N₂), $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ (Ce⁴⁺/air), and $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ (Ce³⁺/N₂) materials synthesized using different conditions. The Ce 3d XPS spectra from Ce⁴⁺ (CeO₂) and Ce³⁺ (CePO₄) standards are also shown.

The Ce 3d XPS spectra from the Ce-substituted pyrochlore-type materials can be compared to the spectra from the two standard materials to determine the relative amount of each oxidation state present based on the difference in peak intensities and binding energies of the Ce³⁺ and Ce⁴⁺ spectral features. In the Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce³⁺/N₂) sample, the u₀/u₁ and u₀'/u₁' intensity ratios

are similar to that of CePO₄. This indicates that the primary oxidation state of Ce is 3+ in this sample; however, some Ce⁴⁺ is also present, which can be observed by the presence of peak v₂'. In the Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/N₂) sample, the intensity of peak v₀ is higher than the intensity of peak u₀, indicating that there is more Ce⁴⁺ in this sample when compared to Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce³⁺/N₂). This is corroborated by an increase in the peak height of v₂'. This indicates that materials synthesized using a Ce⁴⁺ containing precursor contain some Ce³⁺ after annealing in air. When comparing the spectra from the Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/N₂) and Gd_{1.6}Ce_{0.4}Ti₂O_{7+ δ} (Ce⁴⁺/air) samples, the peaks associated with Ce⁴⁺ are higher in intensity in the sample annealed in air. This indicates that the materials annealed under air have more Ce⁴⁺ than the materials annealed under N₂(g).

3.3. XANES

3.3.1. Ce L₃-edge XANES

Ce L₃-edge XANES spectra have been shown to be sensitive to changes in oxidation state and these spectra were collected to confirm the Ce 3d XPS results presented above. The Ce L₃edge XANES spectra from Ce³⁺ (CePO₄) and Ce⁴⁺ (Gd₂Ce₂O₇) standard materials are shown in **Figure 5**. The Ce L₃-edge spectrum from Gd₂Ce₂O₇ consists of four main features while the spectrum from CePO₄ consists of one feature. The feature in the Gd₂Ce₂O₇ spectrum labeled B₁ is a pre-edge feature that results from the $2p \rightarrow 4p$ quadrupolar transition. Features B₂, B₃, and B₄ result from dipolar $2p \rightarrow 5d$ transitions in which the final state 4f occupancies change to 4f², 4f⁴, and 4f⁰, respectively [28]. The Ce³⁺ component is similar in energy to feature B₂ and results from the excitation of a 2p electron to a 5d state [28]. The Ce L₃-edge XANES spectra from the Gd_{1.6}Ce_{0.4}Ti₂O_{7+δ} materials are shown in **Figure 6**. The materials synthesized using a Ce³⁺ precursor have a higher intensity of the Ce³⁺ feature compared to the materials synthesized using

a Ce^{4+} precursor. Additionally, the materials annealed under $N_2(g)$ have a higher intensity Ce^{3+} feature compared to the materials annealed under air.



Figure 5. Ce L₃-edge XANES spectra of Ce^{3+} (CePO₄) and Ce^{4+} (Gd₂Ce₂O₇) standards.



Figure 6. Comparison of Ce L₃-edge XANES spectra from the $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ materials.

The Ce L₃-edge XANES spectra from the Gd_{1.6}Ce_{0.4}Ti₂O_{7+δ} materials were fitted using a linear combination fitting (LCF) method involving two standards, CePO₄ and Gd₂Ce₂O₇, and the results are shown in **Figure 7** and in **Table 3**. The LCF results indicate that the p-Gd_{1.6}Ce_{0.4}Ti₂O_{7+δ} (Ce³⁺/N₂) sample contained the most Ce³⁺ (~70 %) but that there was still a moderate amount of Ce⁴⁺ (~30 %) present (**Figure 7a**). The ceramic sample, Gd_{1.6}Ce_{0.4}Ti₂O_{7+δ} (Ce³⁺/N₂) (Figure 7b), contained similar amounts of Ce³⁺ (~67%) and Ce⁴⁺ (~33%) as the sample synthesized by the co-precipitation method. Additionally, when the starting material was changed to CeO₂ (Figure 7d) and the sample was annealed under N₂(g), the Ce³⁺ (~48%) and Ce⁴⁺ (~52%) content were roughly equal. Changing the annealing atmosphere to air (Figure 7c), resulted in a large increase in the Ce⁴⁺ (~75%) content of the material. While this sample had 7% CeO₂ present, as discerned from the XRD pattern, it does not account for all of the Ce⁴⁺

determined by analysis of the Ce L_3 XANES spectrum, which indicates that a substantial amount of Ce⁴⁺ is present in this sample. The results of the LCF fits were consistent with the XPS analysis of these materials presented above.



Figure 7. Fitted Ce L₃-edge XANES spectra from $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ materials synthesized using different conditions.

Sample description	<u>Ce^{3+} (%)</u>	<u>Ce^{4+} (%)</u>
$Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta} (Ce^{3+}/N_2)$	67	33
$Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta} (Ce^{4+}/N_2)$	52	48
$Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$ (Ce ⁴⁺ /air)	25	75
$p\text{-}Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}\ (Ce^{3+}/N_2)$	70	30

Table 3. LCF results from the Ce L₃-edge XANES spectra. All values have an error of $\pm 5\%$.

3.2 Ti K-edge XANES

A variation in the Ce⁴⁺/Ce³⁺ ratio in these materials would suggest that a change in the local coordination environment would occur as a result in a variation in the O stoichiometry to charge balance the system. Ti K-edge XANES spectra were collected to study how the changes in the Ce⁴⁺/Ce³⁺ ratio affected the Ti coordination environment. The Ti K-edge XANES spectra from the Gd_{1.6}Ce_{0.4}Ti₂O₇₊₈ materials are presented in **Figure 8**. Ti K-edge XANES spectra have been shown to be sensitive to both changes in oxidation state and coordination number [29,30]. There are two distinct regions present in Ti K-edge XANES spectra, which are referred to as the pre-edge (< 4977 eV) and the main-edge (> 4977 eV) regions. The pre-edge region results from 1s \rightarrow 3d quadrupolar transitions and consists of three distinct features, which are labeled as A₁, A₂, and A₃ in Figure 8. Feature A₁ and A₂ are primarily due to the excitation of 1s electrons to crystal field split 3d t_{2g} and eg^{*} states when studying Ti⁴⁺ in an octahedral environment [29–31]. Feature A₃ results from the excitation of 1s electrons to 3d orbitals of next-nearest-neighbor Ti atoms that are hybridized with Ti 4p states on the absorbing atom through bridging O 2p orbitals [29–31]. The intensities of the pre-edge features are very sensitive to changes in coordination number

due to changes in the amount of d- and p-orbital overlap that occurs in different coordination environments [29].

The energies of the pre-edge features of the pyrochlore materials are consistent with Ti⁴⁺ in a 6-coordinate environment [29]. However, all pre-edge features are more intense in the spectra from the Ce-substituted pyrochlore materials in comparison to the unsubstituted pyrochlore, Gd₂Ti₂O₇, as shown in **Figure 8**. While it has been reported that an increase in the pre-edge intensity is indicative of a decrease in the coordination number from 6, a 6-coordinate centrosymmetric environment with distorted octahedral geometry represents a minimum intensity of this pre-edge feature [29,32]. The loss of inversion symmetry as the distorted octahedral geometry shifts to higher or lower coordination results in an increase of the amount of 3d and 4p overlap. Thus, any change in coordination that breaks the inversion symmetry of the distorted octahedral geometry will result in an increase in the intensity of the pre-edge peak due to the increase in p-orbital character, which results in an increase in the dipolar character of the transition [32].



Figure 8. Ti K-edge XANES spectra of the $Gd_{2-x}Ce_xTi_2O_{7+\delta}$ materials synthesized under different synthetic conditions. The inset shows an expanded view of the pre-edge region.

Incorporation of Ce⁴⁺ into the pyrochlore structure must be charged balanced either by cation vacancies or by the intercalation of oxygen into vacant anion sites. There are two vacant anion sites in the pyrochlore structure, the 8b and 32e sites.[33] The 8b site is tetrahedrally coordinated to four B-site ions in the pyrochlore structure, while the 32e site is octahedrally coordinated to 3 A-site ions and 3 B-site ions [19]. Previous studies of the Ce₂Zr₂O_{7+ δ} system showed that when $\delta \leq 0.2$, the intercalated oxygen occupies the 8b site, but also displaces oxygen from the 8a site.[19] When $\delta > 0.2$, the site occupancy of 8a increases as the 8b site is saturated[19].

This led to an increase in the average coordination number of the Zr ions to somewhere between 6 and 7[19].

 Ce^{4+} incorporation into the pyrochlore structure could result in the intercalation of oxygen into the vacant 8b site surrounding the Ti atoms, resulting in 7-coordinate Ti, which charge balances the system. The intercalation of these O atoms around the Ti coordination environment increase the amount of overlap between the Ti 3d and 4p orbitals, resulting in an increase in the intensity of the pre-edge features. The lattice parameters, as determined by Rietveld Refinement, do not follow a linear trend as expected. If Vegard's Law was followed, the materials with the highest concentration of Ce^{4+} would have the smallest lattice constant, and the materials with lowest concentration of Ce^{4+} would have the largest lattice constant. This deviation could be due to the competing effect of oxygen intercalation which should result in expansion of the lattice and lattice contraction due to Ce^{4+} incorporation. These competing effects are the likely reason as to why the lattice constants reported in Table 2 do not follow Vegard's Law.

4. Conclusions

Cerium substitution in $Gd_2Ti_2O_7$ pyrochlore-type materials results in the formation of single-phase products having the formula, $Gd_{1.6}Ce_{0.4}Ti_2O_{7+\delta}$, with Ce substituting for Gd in the A-site. The Ce exists in the A-site with both 3+ and 4+ oxidation states present, which could be charge balanced by the incorporation of excess oxygen into the vacant anion 8b site. The relative amounts of Ce³⁺ and Ce⁴⁺ can be varied based on the oxidation state of the Ce-containing starting material, the synthetic method used, and the annealing environment. The versatility of the pyrochlore structure to incorporate multiple oxidation states of the same element could be important for the sequestration of plutonium, which primarily occurs in +3 and +4 oxidation states.

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6. Declaration of Interest

The authors declare no competing financial interest.

Supporting information available: Rietveld refinement patterns, example of Rietveld refinement with Ce substituting in the B-site of the pyrochlore structure.

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