Probing Cation Antisite Disorder in Gd$_2$Ti$_2$O$_7$ Pyrochlore by Site-specific NEXAFS and XPS

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Probing cation antisite disorder in Gd$_2$Ti$_2$O$_7$ pyrochlore by site-specific near-edge x-ray-absorption fine structure and x-ray photoelectron spectroscopy


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Disorder in Gd$_2$Ti$_2$O$_7$ is investigated by near-edge x-ray-absorption fine structure (NEXAFS) and x-ray photoelectron spectroscopy (XPS). NEXAFS shows Ti$^{4+}$ ions occupy octahedral sites with a tetragonal distortion induced by vacant oxygen sites. O 1s XPS spectra obtained with a charge neutralization system from Gd$_2$Ti$_2$O$_7$(100) and the Gd$_2$Ti$_2$O$_7$ pyrochlore used by Chen et al. [Phys. Rev. Lett. 88, 105901 (2002)], both yielded a single peak, unlike the previous result on the latter that found two peaks. The current results give no evidence for an anisotropic distribution of Ti and O. The extra features reported in the aforementioned communication resulted from charging effects and incomplete surface cleaning. Thus, a result confirming the direct observation of simultaneous cation-anion antisite disordering and lending credence to the split vacancy model has been clarified.

Pyrochlore materials are potentially useful for a range of technological applications. In particular, their use in solid oxide fuel cells and as host matrices for actinide wastes are receiving increasing attention because of the recent discoveries showing that the isovalent substitution of Zr for Ti in Gd$_2$Ti$_2$O$_7$ results in a four to five orders-of-magnitude increase in the oxygen ion conductivity at 875 K and in resistance to energetic particle irradiation. The mechanisms responsible for the large increase in these properties have been investigated by several experimental and theoretical methods. These studies show that the increase in the ionic conductivity in pyrochlore is most likely due to the increased oxygen vacancies at the 48f site as a result of cation and anion disordering, which are responsible for the increased ionic conductivity. The increased radiation tolerance is attributed to the ease of rearrangement and relaxation of Gd, Zr, and O ions/defects within the crystal structure, which inhibits amorphization by causing the irradiation-induced defects to relax and form cation antisite defects and anion Frenkel defects. However, there is limited direct evidence for the presence of cation antisite disorder in a highly ordered pyrochlore structure.

Recently, Chen et al. reported on the disorder in Gd$_2$(Ti$_{1−x}$Zr$_x$)$_2$O$_7$ pyrochlores measured by laboratory x-ray photoelectron spectroscopy (XPS), and the results provided direct evidence that cation antisite disorder occurs simultaneously with anion disorder. A key piece of information in these studies is the O 1s XPS spectra for Gd$_2$Ti$_2$O$_7$, which exhibits a broad feature with two components centered at binding energies (BEs) of ~526 and 531 eV. These component peaks were attributed to oxygen ions coordinated solely to Gd$^{3+}$, or to both Gd$^{3+}$ and Ti$^{4+}$ ions, respectively. The BE difference of ~5 eV between the two oxygen species is large for a single-phase compound. To obtain XPS spectra, Chen et al. Ar$^+$-sputtered the surface, which removes contaminants but can preferentially deplete lighter elements from the surface region and induce defects/disorder. Although annealing under an oxygen partial pressure recovers the full oxygen stoichiometry and surface order in pyrochlore materials, the O 1s XPS feature has been shown to be insensitive to sputtering and subsequent annealing.

In light of the XPS results from Refs. 11 and 12, the nature of disorder in Gd$_2$Ti$_2$O$_7$ pyrochlore has been re-examined using a multi-technique approach investigating the Ti 2p and O 1s of Gd$_2$Ti$_2$O$_7$(100) by site-specific near-edge x-ray-absorption fine structure (NEXAFS) and XPS, as well as XPS of the same Gd$_2$Ti$_2$O$_7$ (and other pyrochlore compositions) employed in Refs. 11 and 12. NEXAFS involves electronic transitions originating from a selected atomic core level to unoccupied electronic states, which permits the determination of site-specific unoccupied electronic structure and site symmetry by use of linearly polarized x-rays. Laboratory XPS is used to provide information pertaining to the occupied electronic density of states from both pyrochlore materials that can be compared to the results from Refs. 11 and 12. The NEXAFS herein have about the same surface sensitivity as the XPS measurements.

Single crystals of Gd$_2$Ti$_2$O$_7$ were grown by the floating zone technique using an infrared image furnace. The pyrochlore structure of the Gd$_2$Ti$_2$O$_7$ single crystal was confirmed by x-ray diffraction (XRD) and a series of pole figure measurements. Part of the crystal was powdered to measure the bulk lattice parameter ($a=1.01857$ nm) and confirmed the absence of secondary or minor phases. The Gd$_2$Ti$_2$O$_7$ single crystal was cut and polished to obtain a (100) surface to better than 1°. The preparation and characterization of
respectively.\textsuperscript{3,7,10–12} Tetrahedrally coordinated to two-of-each Gd\textsuperscript{3+} and Ti\textsuperscript{4+}, and four Gd\textsuperscript{3+} cations, respectively (Refs. 3, 7, and 10–12). The experimental geometry of Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} pyrochlore used from Refs. 11 and 12 has been described.\textsuperscript{11,12,15} Pyrochlores in general exhibit stoichiometry and are a derivative of fluoro-rute, SrTiO\textsubscript{3} predominantly result from transitions to the final states, \((2p_{3/2})^{-1}d^{1}p^{6}\) and \((2p_{3/2})^{-1}d^{3}(3d_{x})^{-1}p^{6}\), respectively. The energy separation between \(t_{2g}\) and \(e_{g}\) (crystal field splitting, 10 Dq) is \(\sim 2.2, \sim 2.3,\) and \(\sim 2.4\) eV for TiO\textsubscript{2}, Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, and SrTiO\textsubscript{3}, respectively. Comparison of Ti 2p NEXAFS from Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, TiO\textsubscript{2}, and SrTiO\textsubscript{3} shows that Ti is tetravalent and occupies sites of O\textsubscript{h} symmetry in Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}. The \(e_{g}\) states, which consist of \(d_{z^2}\) and \(d_{x^2−y^2}\) orbitals, are directed toward ligand anions and are sensitive to deviations from Ti O\textsubscript{h} symmetry. Consequently, the splitting of \(e_{g}\) states into \(d_{z^2}\) and \(d_{x^2−y^2}\) for Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} is similar to TiO\textsubscript{2} and is dissimilar to SrTiO\textsubscript{3} in which Ti has perfect O\textsubscript{h} site symmetry. This confirms that Ti occupies sites with distorted O\textsubscript{h} symmetry in Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}. The energy separation between the \(d_{z^2}\) and \(d_{x^2−y^2}\) orbitals of the \(e_{g}\) states is 1.0 and 1.2 eV for Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and TiO\textsubscript{2}, respectively. This is a measure of the degree of distortion from pure O\textsubscript{h} site symmetry and the Ti sites in Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} are slightly less distorted than in TiO\textsubscript{2}.

The O 1s transitions identified as \(t_{2g}\) and \(e_{g}\) in the NEXAFS spectra of Fig. 2 for TiO\textsubscript{2}, Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, and SrTiO\textsubscript{3} result from transitions to the final states, \(3d(2p_{3/2})^{-1}(1s)^{-1}p^{6}\) and \(3d(3e)^{1}(1s)^{-1}p^{6}\), respectively, where \((1s)^{-1}\) denotes a hole in the O 1s shell. The 10 Dq is 2.8, 2.7, and 2.5 eV for TiO\textsubscript{2}, Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}, and SrTiO\textsubscript{3}, respectively. The difference between the crystal field splitting observed in the Ti 2p and O 1s NEXAFS arises from the non-symmetric splitting of the \(e_{g}\) states into \(d_{z^2}\) and \(d_{x^2−y^2}\) states which introduces complications in determining the 10 Dq from the Ti NEXAFS. This is substantiated by the close agreement of the 10 Dq observed in Ti 2p and O 1s NEXAFS for SrTiO\textsubscript{3} in which Ti\textsuperscript{4+} is in perfect O\textsubscript{h} site symmetry. Comparison of the O 1s NEXAFS from Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} to TiO\textsubscript{2}, SrTiO\textsubscript{3}, and GdO\textsubscript{2} suggests that the oxygen ions coordinated to Gd\textsuperscript{3+} also contribute to the intensity in the vicinity of \(e_{g}\) states derived from the TiO\textsubscript{6} octahedron for Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}.

The normal incidence \((\theta=0^\circ)\) NEXAFS spectra of Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7}(100), where \(E\) of the x rays is parallel to the \(a\) axis (\(E||a\)) are compared in Fig. 3 to the spectra measured at grazing incidence \((\theta=75^\circ)\) where \(E\) is nearly parallel to the
The Ti XPS spectra from Gd$_2$Ti$_2$O$_7$ show that Ti$^{4+}$ is being reduced and the intensity reduction for the transitions to $t_E$ in spectral intensity for energy directly projected toward oxygen anions, split into lower of Ti and O in $t$ found. However, the intensities for the transitions to $d_{x^2-y^2}$ state within the $t_{2g}$ states for Ti$^{4+}$ and O$^{2-}$ states are located in the $d_{xy}$ plane adjacent to TiO$_6$ octahedron provide unoccupied density that also contributes to the octahedron geometry. The decrease in spectral intensity for $E||c$ geometry compared to the $E||a$. The intensity reduction for the transitions to $t_{2g}$ states is also larger than for the $e_g$ states in the Ti 2p NEXAFS. A similar intensity reduction is observed for the transition to the $d_{2z^2-r^2}$ state relative to the $d_{3z^2-r^2}$ state within the $e_g$ states. The decrease in intensity of the corresponding spectrum ($E||c$).

The results of this investigation, employing site-specific-NEXAFS and XPS to obtain corroborative information from two independent Gd$_2$Ti$_2$O$_7$ pyrochlores, including the same material used in the previous studies, contrast to the earlier results reported by Chen et al. for Gd$_2$Ti$_2$O$_7$. The most difference between the results of the investigations is associated with the O 1s XPS spectra from the two pyrochlore materials examined in the current study that both yield a single, narrow peak at 529.6 eV with $\sim 1.5$ eV FWHM characteristic of Ti-O in Gd$_2$Ti$_2$O$_7$, whereas the previous study yielded broad O 1s features. The O 1s XPS spectra from the current study are also consistent with the corresponding NEXAFS spectra for Gd$_2$Ti$_2$O$_7$. Thus, the O 1s XPS spectra reported by Chen et al. consisting of a broad peak (4 eV) composed of two components ($\sim 526$ eV and 531 eV BE) assigned to oxygen ions coordinated solely to Gd$^{3+}$ and to both Gd$^{3+}$ and Ti$^{4+}$ ions can be attributed to experimental complications difficult to discern when working with pyrochlores. The current results also ra-
tionalize why the components of the O 1s XPS features of Refs. 11 and 12 do not reflect the statistical distribution of oxygen sites as cross-sectional effects should be minimal and this is clearly not the case. Finally, the single peak found throughout in the current investigation reconciles the previously observed 5 eV O 1s chemical shift, which is somewhat large for similar metal-oxygen species in a single-phase material.

The discrepancies in the results between the current investigation and those from Chen et al.,11,12 clearly arise from complications due to the combination of surface charging effects and surface cleanliness during the previous XPS measurements. This has been confirmed by direct comparison of XPS spectra that were measured in the same spectrometer utilizing a charge neutralization system to negate charging effects and by careful observation of the surface contamination levels. The O 1s spectra in Refs. 11 and 12 exhibited peaks at BEs of ~526 and 531 eV that were shifted by charging and from surface hydrocarbon contamination, respectively. It is also interesting to note the surface preparation methodology used in the studies of Refs. 11 and 12 might be thought to have resulted in non-stoichiometric or disordered Gd2Ti2O7 surfaces exhibiting broadened O 1s XPS features. However, based on knowledge from previous studies on pyrochlores13 and the current work concerning the O 1s XPS spectra recorded after Ar⁺-sputtering prior to annealing, the resultant O 1s core level feature should not be appreciable broadened (see Fig. 4). Lastly, the information provided by the NEXAFS spectra is in complete agreement with results of the XPS and the use of the TFY detection mode for the NEXAFS measurements completely avoids charging complications.

The site-specific NEXAFS show that Ti³⁺ ions in Gd2Ti2O7 occupy sites of O2 symmetry with a tetragonal distortion, which is induced by the vacant 8a oxygen sites located in the ab plane adjacent to TiO6 octahedra. Combined with the O 1s XPS spectra that show a single narrow peak characteristic of pristine Ti-O, as well as representative Ti 2p XPS spectra in both Gd2Ti2O7(100) and in the exact same Gd2Ti2O7 pyrochlore used in Refs. 11 and 12, no evidence was found for an anisotropic distribution of Ti and O sites. The XPS and NEXAFS results are consistent for both Ti and O, and do not identify two distinct oxygen species corresponding to unique oxygen sites. The current results provide strong evidence that the observations of two different oxygen sites in Gd2Ti2O7 by XPS with an O 1s BE difference of ~5 eV by Chen et al.,11,12 stem from experimental complications arising from sample charging and surface cleanliness. Therefore, the Gd2Ti2O7 XPS results from Chen et al.11,12 that provided direct evidence supporting the observation of simultaneous cation antisite disordering - anion disordering and lent partial support to the validity of the split vacancy model in pyrochlore materials have been clarified.

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