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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.

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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 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
the Gd$_2$Ti$_2$O$_7$ pyrochlore used from Refs. 11 and 12 has been described. Pyrochlores in general exhibit A$_2$B$_2$O$_6$O’(Fd$ar{3}$m) stoichiometry and are a derivative of fluorite structure, but with two cations and one-eighth fewer anions. The unit cell contains 8 formula units and 4 nonequivalent sites. Fixing the origin at the B cation as in Fig. 1, the atoms A, B, O and O’ occupy 16d, 16c, 48f, and 8b sites, respectively.\(^{3,7,10–12}\)

Single crystals of TiO$_2$(110), SrTiO$_3$(100), and Gd$_2$O$_3$ powder were utilized as NEXAFS references. Site-specific Ti 2p and O 1s NEXAFS were measured at Beamline 9.3.2 of the Advanced Light Source (ALS) at LBNL.\(^{16}\) Figure 1 shows the experimental geometry relative to the electric field vector ($E$) of the linearly polarized x rays is indicated (Ref. 16).

The O 1s transitions identified as $t_2g$ and $e_g$ in the NEXAFS spectra of Fig. 2 for TiO$_2$, Gd$_2$Ti$_2$O$_7$, and SrTiO$_3$ result from transitions to the final states, (2p$_{3/2}$)$^{-1}$d$^1p^6$ and (2p$_{3/2}$)$^{-1}$d$^13(e_g)$p^6, respectively. The energy separation between $t_2g$ and $e_g$ (crystal field splitting, 10 Dq) is approximately -2.2, -2.3, and -2.4 eV for TiO$_2$, Gd$_2$Ti$_2$O$_7$, and SrTiO$_3$, respectively. Comparison of Ti 2p NEXAFS from Gd$_2$Ti$_2$O$_7$, TiO$_2$, and SrTiO$_3$ shows that Ti is tetravalent and occupies sites of O$_h$ symmetry in Gd$_2$Ti$_2$O$_7$. The $e_g$ states, which consist of d$_{z^2}$ and d$_{x^2}$, orbitals, are directed toward ligand anions and are sensitive to deviations from Ti O$_h$ symmetry. Consequently, the splitting of $e_g$ states into d$_{z^2}$ and d$_{x^2}$ for Gd$_2$Ti$_2$O$_7$ is similar to TiO$_2$ and is dissimilar to SrTiO$_3$, in which Ti has perfect O$_h$ site symmetry. This confirms that Ti occupies sites with distorted O$_h$ symmetry in Gd$_2$Ti$_2$O$_7$. The energy separation between the d$_{z^2}$ and d$_{x^2}$-orbitals of the $e_g$ states is 1.0 and 1.2 eV for Gd$_2$Ti$_2$O$_7$ and TiO$_2$, respectively. This is a measure of the degree of distortion from pure O$_h$ site symmetry and the Ti sites in Gd$_2$Ti$_2$O$_7$ are slightly less distorted than in TiO$_2$.

The O 1s transitions identified as $t_2g$ and $e_g$ in the NEXAFS spectra of Fig. 2 for TiO$_2$, Gd$_2$Ti$_2$O$_7$, and SrTiO$_3$ result from transitions to the final states, 3d(2p$_{3/2}$)$^{1}(1s)^{-1}p^6$ and 3d(3e$^g$)$^{1}(1s)^{-1}p^6$, 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$_2$, Gd$_2$Ti$_2$O$_7$, and SrTiO$_3$, 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$_{x^2}$-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$_3$ in which Ti is in perfect O$_h$ site symmetry. Comparison of the O 1s NEXAFS from Gd$_2$Ti$_2$O$_7$ to TiO$_2$, SrTiO$_3$, and Gd$_2$O$_3$ suggests that the oxygen ions coordinated to Gd$^{3+}$ also contribute to the intensity in the vicinity of $e_g$ states derived from the TiO$_6$ octahedron for Gd$_2$Ti$_2$O$_7$.

The normal incidence ($\theta=0^\circ$) NEXAFS spectra of Gd$_2$Ti$_2$O$_7$(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$_7$ indicate intensity reduction for the transitions to $t_2$g states in both Ti 2p and O 1s NEXAFS which induces the tetragonal distortion. Energy levels directly projected toward oxygen anions, split into lower and higher energy states for TiO$_6$ octahedron provide unoccupied density that also contributes to the geometry. The vacant $8a$ oxygen sites located adjacent to the TiO$_6$ octahedron provide unoccupied density that also contributes to the intensities of the transitions to $t_{2g}$ and $e_g$ states. The large intensity for the transition to the $t_{2g}$ state relative to the $d_{z^2}$ and $d_{x^2-y^2}$ states unlike the $d_{xy}$ and $d_{yz}$ states. The decrease in spectral intensity for $E||c$ compared to the $E||a$ geometry reflects weaker covalence between Ti($d_{z^2}$) and O($p_z$) along the $c$ axis with an elongated Ti-O distance providing additional support for a tetragonal distortion of the TiO$_6$ octahedron in Gd$_2$Ti$_2$O$_7$ as in TiO$_2$. The $e_g$ states, which are directly projected toward oxygen anions, split into lower energy $d_{z^2}$ and higher energy $d_{x^2-y^2}$ states unlike the $t_{2g}$ states. The vacant $8a$ oxygen sites located adjacent to the TiO$_6$ octahedron provide unoccupied density that also contributes to the intensities of the transitions to $t_{2g}$ and $e_g$ states.

The large intensity for the transitions to $t_{2g}$ and $e_g$ states for $E||a$ compared to the $E||c$ geometry suggests that oxygen sites are located in the $a-b$ plane adjacent to TiO$_6$ octahedra in Gd$_2$Ti$_2$O$_7$ which induces the tetragonal distortion.

Figure 4 shows the Ti 2p and O 1s XPS spectra recorded from Gd$_2$Ti$_2$O$_7$(100) at different Ar$^+$-sputtering times along with spectra after annealing under O$_2$, as well as the spectra from the corresponding Gd$_2$Ti$_2$O$_7$ material employed in Refs. 11 and 12 as-received and after light Ar$^+$ sputtering. The Ti XPS spectra from Gd$_2$Ti$_2$O$_7$(100) show significant differences related to the duration of Ar$^+$ sputtering. The spectra before annealing show that Ti$^{4+}$ is being reduced and give evidence for the preferential removal of oxygen from the surface. The spectrum after Ar$^+$ sputtering and annealing in 2 x 10$^{-6}$ Torr of O$_2$ at 875 K, shows characteristics of Ti$^{4+}$ indicating recovery of the fully stoichiometric surface. All of the O 1s XPS spectra collected [except for spectrum (c)] reveal a single peak at 529.6 eV with a full width at half maximum (FWHM) of ~1.5 eV regardless of Ar$^+$-sputtering time or if the pyrochlore has been annealed under O$_2$, although there is a slight decrease in spectral intensity before annealing. The O 1s spectrum (e) from the as-received Gd$_2$Ti$_2$O$_7$ sample shows the clear signature of C surface contamination at ~531 eV prior to sputtering. After light sputtering, the high BE component is almost fully removed, resulting in a single, narrow O 1s peak in spectrum (d). The observed O 1s feature at 529.6 eV for the Gd$_2$Ti$_2$O$_7$ materials is similar to that observed for TiO$_2$. These results agree with previous XPS and NEXAFS studies of TiO$_2$ surfaces that indicate oxygen is preferentially sputtered while Ti at the surface is reduced.

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. Both yield a single, narrow peak at 529.6 eV with ~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 from Gd$_2$Ti$_2$O$_7$(100). Thus, the O 1s XPS spectra reported by Chen et al. consisting of a broad peak (>4 eV) composed of two components (~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-
notionalize 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.\textsuperscript{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 Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} surfaces exhibiting broadened O 1s XPS features. However, based on knowledge from previous studies on pyrochlores\textsuperscript{13} and the current work concerning the O 1s XPS spectra recorded after Ar\textsuperscript{+}-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 Ti\textsuperscript{4+} ions in Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} occupy sites of O\textsubscript{6} symmetry with a tetragonal distortion, which is induced by the vacant 8a oxygen sites located in the ab plane adjacent to TiO\textsubscript{6} 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 Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} and in the exact same Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} 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 Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} by XPS with an O 1s BE difference of \(~5\) eV by Chen et al.\textsuperscript{11,12} stem from experimental complications arising from sample charging and surface cleanliness. Therefore, the Gd\textsubscript{2}Ti\textsubscript{2}O\textsubscript{7} XPS results from Chen et al.\textsuperscript{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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