Probing Cation Antisite Disorder in Gd2Ti2O7 Pyrochlore by Site-specific NEXAFS and XPS

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Disorder in Gd$_2$Ti$_2$O$_7$ pyrochlore 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 1$s$ 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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respectively. 3,7,10–12

shows the experimental geometry relative to the electric field
photon-energy was calibrated to the Ti 2p

dettes for several incidence angles. Spectra were corrected for
sites in Gd2Ti2O7. The energy separation between d$_z^2$ and e$_g$ (crystal
field splitting, 10 Dq) is ~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$_{x^2-y^2}$ 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$_{x^2-y^2}$ 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$_{x^2-y^2}$ 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(2t$_{2g}$)$^3$(1s)${}^{-1}p^6$ and
3d(3e$_{g}$)$(1s)^{-1}p^6$, 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$_{x^2-y^2}$ 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$_3$ in which
Ti$^{4+}$ 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$_7$ from the corresponding Gd$_2$Ti$_2$O$_7$ material employed in spectra before annealing show that Ti$^{4+}$ is being reduced and reflects weaker covalence between Ti sites compared to the earlier results reported by Chen for Gd$_2$Ti$_2$O$_7$ as in TiO$_2$. The large intensity for the transitions to the $2g$ state relative to the $2a$ state within the Gd$_2$Ti$_2$O$_7$ sample shows the clear signature of C surface contamination at $\sim$531 eV prior to sputtering. After light sputtering, the high BE component is almost fully removed, resulting in a single, narrow O 1$s$ peak in spectrum (d). The observed O 1$s$ 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. The spectrum after Ar$^+$-sputtering and annealing under 2$\times$10$^{-6}$Torr of O$_2$ at 875 K, whereas spectra (b-c) were recorded after light- and heavy-Ar$^+$-sputtering, respectively, prior to annealing in O$_2$. Spectra (d-e) were obtained from Gd$_2$Ti$_2$O$_7$ after light Ar$^+$-sputtering and as-received, respectively. The O 1$s$ spectrum (d) was normalized to the intensity of the corresponding spectrum (b). This same normalization was employed for Ti spectrum (d). Spectra (e) were normalized using the same scaling factor relative to O 1$s$ spectrum (d).

FIG. 3. Comparison of the normal ($\theta=0^\circ$) to grazing incidence ($\theta=75^\circ$) Ti 2$p_{3/2}$ and O 1$s$ NEXAFS from Gd$_2$Ti$_2$O$_7$(100). The $\theta=0^\circ$ polarization has the electric field vector (E) of the x rays parallel to the a axis (E//a), whereas for $\theta=75^\circ$, E is nearly parallel to the c axis (E//c).

FIG. 4. Ti 2$p$ and O 1$s$ XPS spectra collected from Gd$_2$Ti$_2$O$_7$(100) [spectra (a-c)] and the Gd$_2$Ti$_2$O$_7$ pyrochlore used in Refs. 11 and 12 [spectra (d-e)]. Spectra (a) was recorded after heavy Ar$^+$-sputtering followed by annealing under 2$\times$10$^{-6}$Torr of O$_2$ at 875 K, whereas spectra (b-c) were recorded after light- and heavy-Ar$^+$-sputtering, respectively, prior to annealing in O$_2$. Spectra (d-e) were obtained from Gd$_2$Ti$_2$O$_7$ after light Ar$^+$-sputtering and as-received, respectively. The O 1$s$ spectrum (d) was normalized to the intensity of the corresponding spectrum (b). This same normalization was employed for Ti spectrum (d). Spectra (e) were normalized using the same scaling factor relative to O 1$s$ spectrum (d).
natorialize 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{3} symmetry with a tetragonal distortion, which is induced by the vacant 8a oxygen sites located in the \textit{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}(100) 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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