

## Mapping Cation Disorder in Irradiated $\text{Gd}_2\text{Ti}_2\text{O}_7$ Pyrochlore by 4D-STEM

Matthew T. Janish<sup>1</sup>, Matthew M. Schneider<sup>1</sup>, Colin Ophus<sup>2</sup>, Jim Ciston<sup>2</sup>, James A. Valdez<sup>1</sup>, Kenneth J. McClellan<sup>1</sup>, Darrin D. Byler<sup>1</sup>, Di Chen<sup>1</sup>, Yongqiang Wang<sup>1</sup>, Terry G. Holesinger<sup>1</sup> and Blas P. Uberuaga<sup>1</sup>

<sup>1</sup> Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, USA

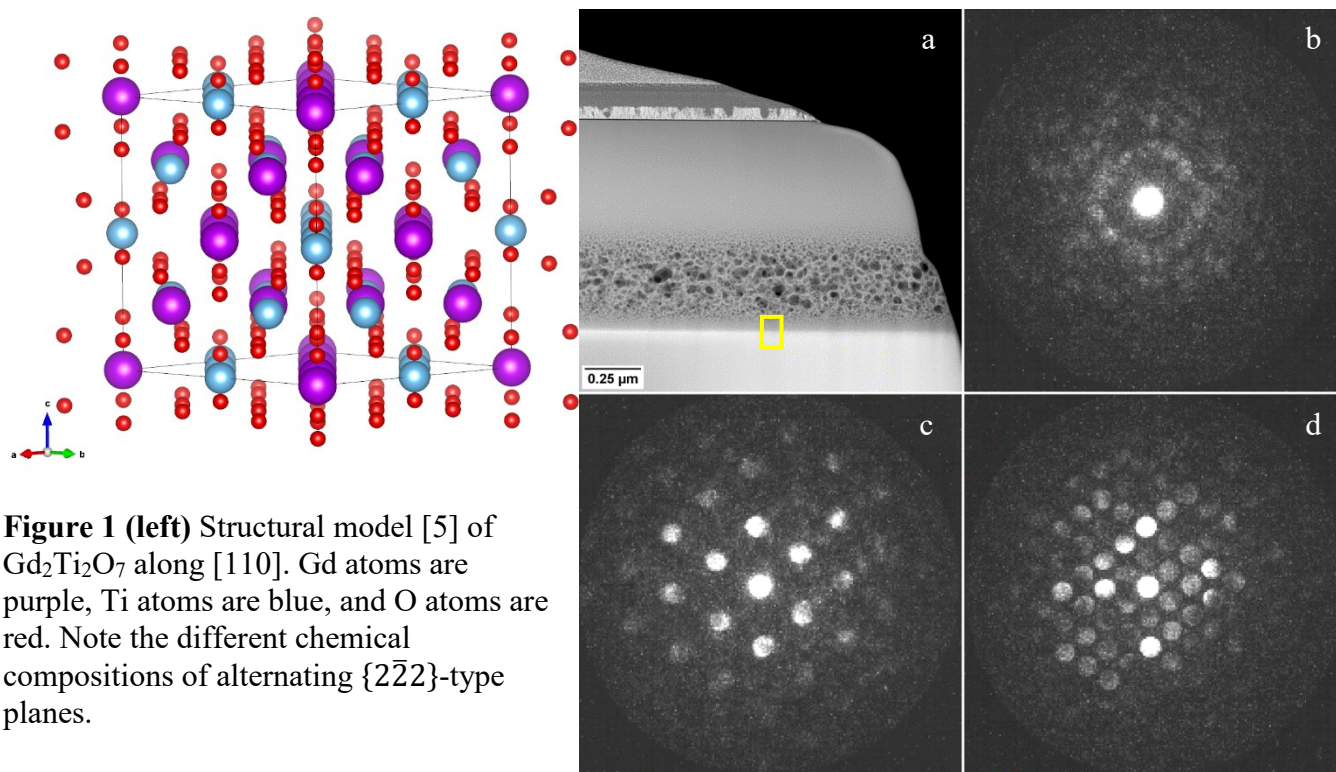
<sup>2</sup> National Center for Electron Microscopy, Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, USA

Pyrochlores have the general formula  $\text{A}_2\text{B}_2\text{O}_7$ , where A is trivalent and usually a rare earth, and B is a tetravalent transition metal. The pyrochlore structure is closely related to that of fluorite; the difference stems from a systematic oxygen vacancy that compensates the lesser charge of the A cation. Arranging the charges appropriately requires a unit cell that is twice as large on a side compared to what is necessary to describe the fluorite structure, and so pyrochlores have lattice constants over 1 nm with eight formula units per cell. The structure of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  (GTO) is shown in Figure 1, with  $a = 1.018$  nm, Gd occupying the 16c sites, Ti on 16d, and O on 8a and 48f (space group  $Fd\bar{3}m$ ); the viewing direction is  $5^\circ$  off  $[110]$  to emphasize the ordering of the cation sublattice. Pyrochlores have generated interest as components of solid nuclear waste forms [1] and as ionic conductors [2].

Random mixing of the cation sublattice is important to both of these applications, the first because self-irradiation of a waste form will cause mixing over time, and the second because the ionic conductivity of pyrochlores is related to disorder on the cation sublattice. The more the cations mix, the less systematic the oxygen vacancy needs to be to maintain local charge neutrality, and the more mobile it is. Although GTO amorphizes readily under irradiation of any kind, it does pass through a defect-fluorite phase in the process that retains none of the pyrochlore superstructure.

Here we describe an experiment devised to quantify and map the degree of disorder on the cation sublattice in pyrochlore materials at the nanoscale using four-dimensional scanning transmission electron microscopy (4D-STEM) [3]. A GTO single crystal was grown using the float-zone method with a  $\langle 100 \rangle$  growth direction, oriented with a Laue diffractometer, and sectioned into samples with a  $\{110\}$  surface plane. The samples were polished and irradiated with 200 kV He ions to a fluence of  $10^{17}$  ions/cm<sup>2</sup>. TEM specimens were lifted out from the irradiated surface using a Thermo Scientific Helios 600 focused ion beam (FIB) instrument, also with a  $\{110\}$  foil plane. A low-magnification Z-contrast STEM image of a typical specimen is presented in Figure 2a. The 4D-STEM data was acquired on the TEAM I microscope at the National Center for Electron Microscopy. Scans were performed across the bottom interface, encompassing the pristine pyrochlore below the He ions' range and the irradiated material above.

The boxed region of Figure 2a indicates the area used to collect the 4D-STEM data. The other frames of the figure are three convergent-beam electron diffraction (CBED) patterns from different regions of the specimen: amorphous (2b), defect-fluorite (2c), and pyrochlore (2d). By quantifying the ratio of the intensity of the pyrochlore superlattice reflections to that of the main fluorite reflections for every pattern in the scanning nanobeam diffraction dataset, a map of the degree of disorder on the cation sublattice can be generated with a spatial resolution limited by the step size of the scan— in this case, 1 nm. A library approach was used in this case, with each experimental pattern compared iteratively with a dictionary of simulated convergent-beam electron diffraction patterns generated for calculated structures with varying degrees of disorder, using the  $\mu\text{STEM}$  simulation package [4].



**Figure 1 (left)** Structural model [5] of  $\text{Gd}_2\text{Ti}_2\text{O}_7$  along [110]. Gd atoms are purple, Ti atoms are blue, and O atoms are red. Note the different chemical compositions of alternating  $\{2\bar{2}2\}$ -type planes.

**Figure 2 (right)** (a) Low-magnification Z-contrast image of a typical GTO FIB specimen. From top to bottom, the layers are ion-beam-deposited Pt, electron-beam-deposited Pt, Au-Pd for conductivity in the FIB/SEM, amorphous GTO, amorphous GTO with pores and bubbles from He accumulation, defect-fluorite GTO, and pristine pyrochlore GTO. The boxed region indicates where 4D-STEM data was collected. CBED patterns from the 4D-STEM dataset representing (b) the amorphous layer, (c) the defect-fluorite layer, and (d) the pyrochlore layer are also presented.

## References

1. TG Holesinger, JA Valdez, MT Janish, Y Wang, and BP Uberuaga, *Acta Mater.* **164** (2019), p. 250.
2. CR Kreller, JA Valdez, TG Holesinger, J Morgan, Y Wang, M Tang, FH Garzon, R Mukundan, EL Brosha, and BP Uberuaga, *J. Mater. Chem. A* **7** (2019), p. 3917.
3. C Ophus, P Ercius, M Sarahan, C Czarnik, and J Ciston, *Microsc. Microanal.* **20:S3** (2014), p. 62.
4. LJ Allen, AJ D'Alfonso, and SD Findlay, *Ultramicroscopy* **151** (2015), p. 11.
5. K Momma and F Izumi, *J. Appl. Crystallogr.* **44** (2011), p. 1272.
6. Work at the Molecular Foundry was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. JC and CO acknowledge support from the DOE Early Career Research Program. Project funding was provided by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division under award LANLE4BU. Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is managed by Triad National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under contract 89233218CNA000001.