Radiation Damage in the STEM: A Dose Rate Threshold in Rare Earth Oxides

Aaron C. Johnston-Peck¹ and Andrew A. Herzing¹

¹Materials Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

Radiation damage presents a practical limit to all studies in the electron microscope. Inelastic and elastic interactions between the incident electron beam and specimen can cause atomic displacement, radiolysis, heating, charging, sputtering, and hydrocarbon contamination [1]. In crystalline materials the onset of detectable damage is typically characterized by a critical dose (e/nm²). Here we demonstrate that specific materials (i.e., cerium, terbium, and praseodymium oxides) do not have a critical dose threshold, rather a critical dose rate (e/nm²s) must be exceeded for damage to accumulate.

Prior radiation damage studies of CeO₂ using electron energy loss spectroscopy (EELS) reveal that the electron beam reduces the oxidation state of the cerium ion from +4 to +3 as oxygen vacancies are generated [2]. Using low-angle and high-angle annular dark field STEM (LAADF and HAADF STEM, respectively) imaging and EELS we quantitatively assess the effects of electron beam irradiation in CeO₂ and other rare earth oxides. It was observed the onset of reduction depends on the dose rate (Fig. 1), at sufficiently low dose rates the material does not reduce even when exposed to large doses. As the dose rate increases oxygen vacancies are generated and when the dose rate is sufficiently high CeO₂ transforms to C-Ce₂O₃ as the oxygen vacancies order as shown in Fig. 2. The symmetry of the cerium sub-lattice does not change during this transformation and when the dose rate is lowered the material oxidizes back to CeO₂ without distorting the original morphology of the nanoparticle. CeO₂₋ₓ is able to getter oxygen from the vacuum environment (sample environment pressures of ≈10⁻⁵ Pa to 10⁻⁶ Pa here), therefore, only when the reduction rate is greater than the oxidation rate will damage begin to accumulate. The reduction and oxidation rates are expected to depend on several parameters but will largely be influenced by the dose rate and the partial pressure of oxidizing species, respectively. Further, coating the sample inhibits the reduction process and significantly increases the dose rate threshold. The coating acts as a diffusion barrier and inhibits release of oxygen into the surrounding environment. For the purposes of experimentation this suggests that dose intensive experiments on these specific materials can be executed without altering their structure and generating artifacts in the data when the probe current and other variables that influence reduction are properly controlled.

References:

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FIG. 1. The white-lines ratio of the Ce M\textsubscript{4,5} edges from a single nanocube as a function of cumulative dose under different dose rates.

FIG. 2. HAADF STEM images and FFTs tracking a CeO\textsubscript{2} nanocube [001] as it transforms from its original fluorite structure (a) to the sesquioxide C-Ce\textsubscript{2}O\textsubscript{3} phase (b) and back to its original form (c).