

## Developing Atomic-scale Understanding of Beam-sensitive Functional Materials

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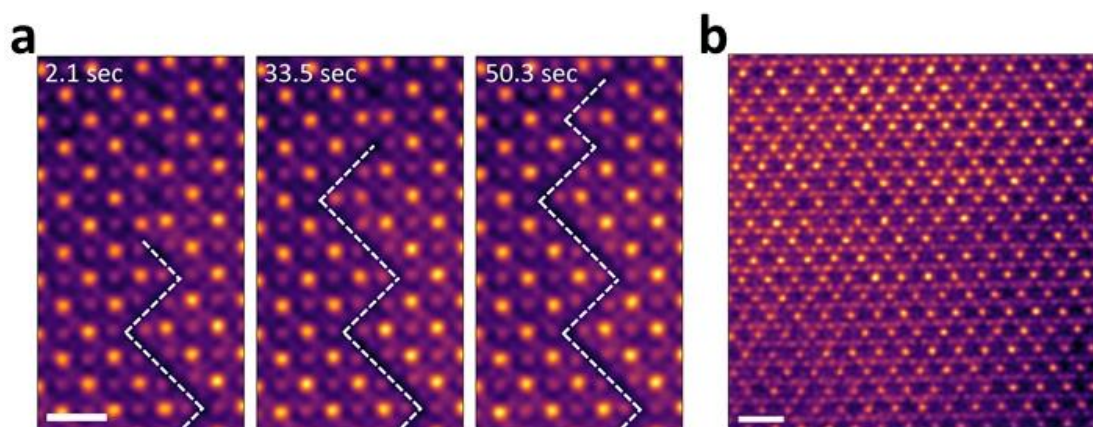
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Atomic-scale characterization of functional materials can enable novel properties and optimization of device performance. For instance, using a combination of electron microscopy and first-principles calculations, we have characterized lead-halide perovskites at the atomic scale and shown that a high concentration of planar faults in lead-halide perovskites can enhance emission stability [1, 2]. Scanning transmission electron microscopes (STEM) have enabled the atomic-scale characterization of a variety of materials. STEM allows simultaneous structural and chemical characterization of a material with high spatial ( $< 1 \text{ \AA}$ ) and energy ( $< 10 \text{ meV}$ ) resolution [3, 4], through the use of a series of analytical detectors and spectrometers. The data collected from these STEM detectors can be interpreted to build a holistic snapshot of material at the atomic scale.

The highly converged electron beam probe in STEM can induce electronic excitations as well as structural changes while irradiating the sample [5]. One major challenge in electron microscopy while investigating intrinsic material properties at the atomic scale is to understand the impact of electron beam irradiation on the sample. Figure 1 shows STEM imaging results for two classes of materials: a lead-halide perovskite used as a light-emitting diode and a spinel oxide used in a multivalent metal-ion battery system. Figure 1a shows the evolution of Ruddlesden-Popper (RP) planar fault in  $\text{CsPbBr}_3$ , while a scanning electron beam probes the sample. The electron beam imparts enough energy to induce atomic rearrangement such that the RP-planar fault propagates through the entire thickness of the crystal. The network of such planar defects significantly alters the emission stability of these lead-halide nanocrystals [1]. Figure 1b shows the cation disorder (variation in the brightness of the atomic columns) in a different class of material – a spinel oxide ( $\text{MgCr}_{1.5}\text{Mn}_{0.5}\text{O}_4$ ). Here, the cation disorder is driven by the Mg-ion transport during an electrochemical reaction resulting in the formation of cation antisite pairs. It is important to understand such structural changes in cathode materials to realize the theoretical operating potentials and further material optimization for multivalent metal-ion battery systems in general.

Here, we will provide an overview of our work on the atomic-scale characterization of beam-sensitive inorganic functional materials with emphasis on perovskite semiconductors for light-emitting diodes and cathode materials for multivalent metal-ion batteries. We will describe the role of these findings in describing macroscopic measurements and device performance [6].



**Figure 1.** (a) Atomic resolution Z-contrast images showing the structural evolution of Ruddlesden-Popper planar faults in  $\text{CsPbBr}_3$  under electron beam irradiation. The real-time in seconds for each frame acquisition is shown on the top-left for each image. The dashed lines in (a) highlight the RP-planar faults for each frame. (b) Atomic resolution Z-contrast image showing cation disorder (variation in the brightness of the atomic columns) in a spinel oxide. Scale bars correspond to 1 nm for (a) and (b).

#### References:

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- [6] A portion of the microscopy research was performed as part of a user proposal at Oak Ridge National Laboratory's (ORNL) Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy (DOE), Office of Science User Facility. This work is supported by the Joint Center for Energy Storage Research (JCESR) and Energy Innovation Hub funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences. This work made use of instruments in the Electron Microscopy Service, specifically JEOL JEM-ARM200CF in the Research Resources Center, University of Illinois at Chicago.