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Combining STEM Imaging and X-Ray Diffraction for Structure Determination of a New Highly Distorted Infinite-Layer Phase

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High-resolution STEM imaging is an excellent technique for the study of nanoscale structural heterogeneity in complex materials systems. In the case of new and highly distorted structures, it can also play a crucial role in the understanding of the crystal structure itself. The recent discovery of superconducting infinite-layer nickelates has prompted a flurry of research activity directed at those compounds as well as at the synthesis of related transition metal oxide infinite-layer materials in hopes of identifying additional high-temperature superconductors and of elucidating the mechanisms of superconductivity in nickelates and analogous cuprates [1-5].

Calcium cobalt oxide ($CaCoO_2$) has been identified as a possible candidate for such studies and has recently been synthesized by topotactic reduction of $CaCoO_{2.5}$ thin films. While the measured change in out-of-plane lattice parameter upon reduction is consistent with other infinite-layer phases, the precise structure and symmetry may be distinct, especially given the significantly lower Ca:Co ionic size ratio. X-ray structure refinement is often used to determine crystal structure. In the case of these very thin, potentially distorted films, however, structure refinement can be hampered by the large phase space. Here, we report the use of atomic-resolution ADF- and ABF-STEM imaging and precise atomic-position analysis to first narrow the phase space for subsequent x-ray refinement and then to identify the correct structure from multiple plausible refinements.

Figure 1 shows the predicted highly distorted $CaCoO_2$ infinite-layer structure with cation positions measured by ADF-STEM. The top right of Fig. 1 displays cross-sectional ADF-STEM images of the [100] and [110] pseudocubic (pc) zone axes (ZAs) of the film, showing distorted A and B sites. The angstrom-scale distortions of the A and B sites are measured from $[110]_{pc}$ ZA images and confirmed with $[100]_{pc}$ ZA imaging. Using simulated and experimental ABF-STEM imaging, as shown in the bottom right of Fig. 1, we conclude there are indeed no oxygens in the Ca atomic layers and only in-plane distortions of oxygens in the Co atomic layers.

Using the measured cation positions, x-ray scattering peaks were simulated, and a partial refinement was carried out via synchrotron grazing incidence x-ray diffraction (GIXRD), leading to two possible structures with differences only in the oxygen positions, as shown in Fig. 2. To differentiate between these two structure refinements, plan-view STEM imaging was attempted. The challenges associated

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with plan view focused ion beam (FIB) preparation of a ~20 nm thin film are depicted schematically in the left panel of Fig. 2. In order to unambiguously capture the oxygen positions with ABF-STEM imaging and avoid contributions from oxygen in the perovskite substrate, the thinned lamella must be ~20 nm thick and contain a region with the $SrTiO_3$ substrate completely removed. Thinning must therefore be carried out carefully to obtain a small useable region as indicated in the schematic. An SEM image of the final thinned lamella is shown in the bottom left of Fig. 2 with the layers labeled. The bottom right of Fig. 2 shows averaged ADF- and ABF-STEM images of the plan-view lamella containing contrast only form the $CaCoO_2$ film. We conclude that x-ray refinement #1 is consistent with ABF-STEM measurement. We thus successfully identify a new, highly distorted infinite-layer structure by first reducing the phase space for a partial x-ray crystal structure refinement through atomic-resolution cross-sectional STEM imaging. We then identify the correct structure from the resulting candidate refinements using plan-view ABF-STEM imaging [6].

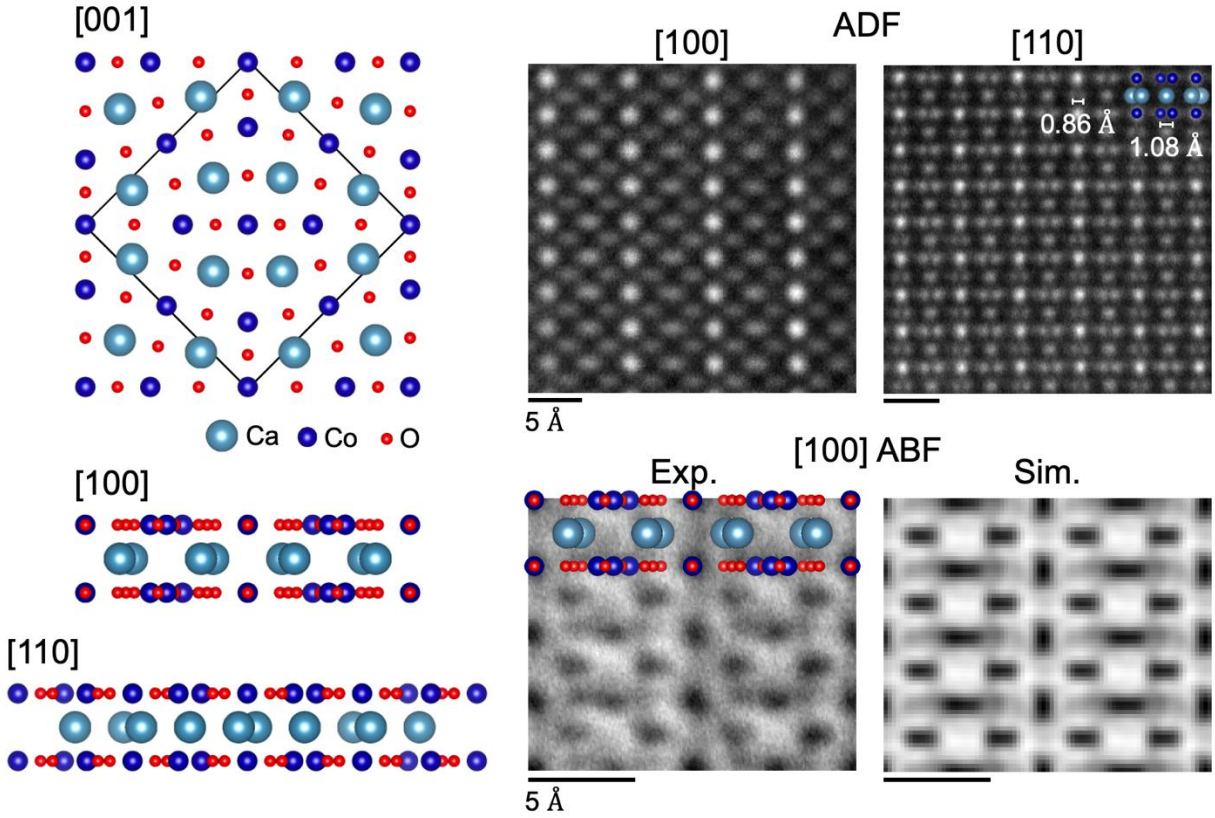

Figure 1. (left) Atomic model for $CaCoO_2$ predicted by STEM measurement projected down the $[001]_{pc}$, $[100]_{pc}$, and $[110]_{pc}$ zone axes. (top right) ADF-STEM images of a $CaCoO_2$ thin film projected along the $[100]_{pc}$ and $[110]_{pc}$ zone axes. Measurements of the distorted cation sites are overlaid on the $[110]_{pc}$ zone axis image along with the corresponding cation model. (bottom right) Experimental and simulated ABF-STEM images of the $[100]_{pc}$ zone axis showing good intensity agreement.

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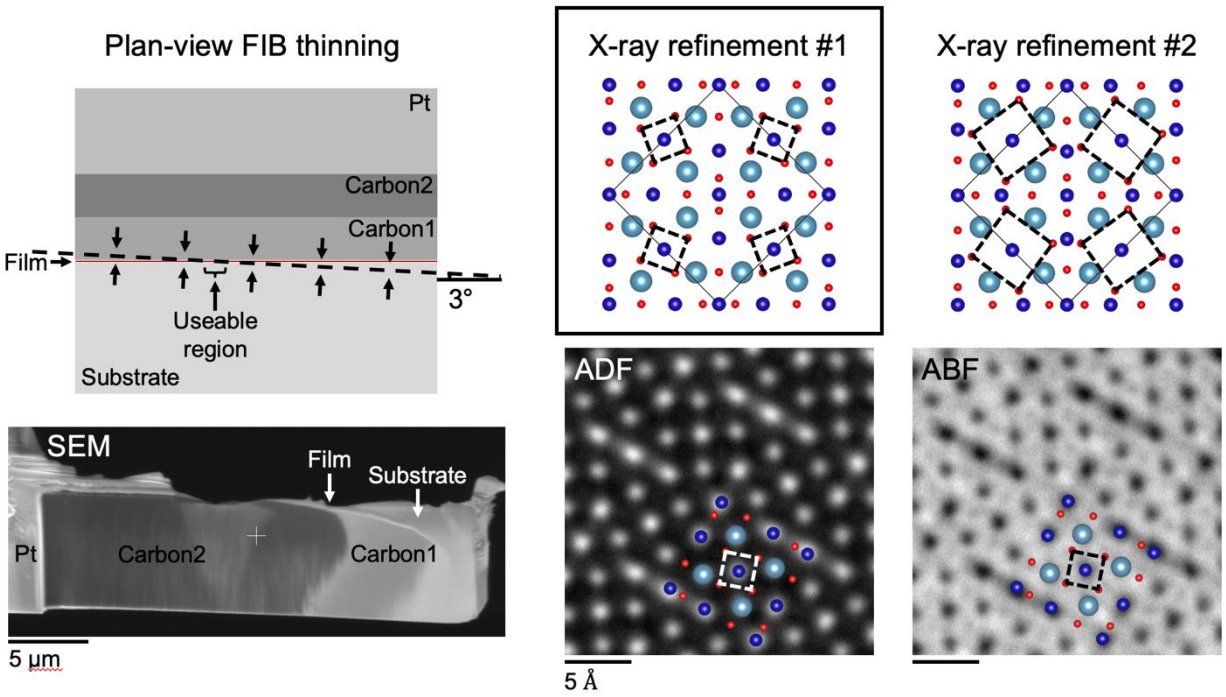

Figure 2. (left) Schematic of a plan-view lamella viewed down the thinned edge of the lamella. The directions orthogonal to the surface of the thinned lamella are indicated with arrows and the usable region consists of the small stretch containing only film, with no substrate and minimal residual carbon. An SEM image of the final lamella is shown below with layers from the schematic labeled. (top right) Two candidate crystal structures for $CaCoO_2$ calculated from x-ray refinement using the cation positions measured by STEM. (bottom right) Averaged plan-view ADF- and ABF-STEM images with x-ray refinement #1 overlaid, showing good experimental match with that structure.

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