

Studying Dynamics of Oxygen Vacancy Ordering in Epitaxial $\text{LaCoO}_3 / \text{SrTiO}_3$ Superlattice with Real-Time Observation

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Oxygen vacancies in perovskite oxides are of great interest both from fundamental viewpoint - due to their effect on electronic and magnetic properties of oxides - and from applications viewpoint - due to their importance for solid oxide fuel cells. In the latter case, understanding the dynamic behavior of vacancies is crucial. Oxygen vacancy (V_o) ordering can substantially affect local structure and ionic conductivity of the oxide matrix. Recently, Kim et al. have reported that local oxygen content and thus vacancy ordering can be quantified using lattice expansion via atomic position mapping in high angle annular dark field (HAADF) images with unit cell resolution in the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ system.[1] The composition studied in [1] is remarkably beam resistant, however, in other related compounds such as LaCoO_3 (LCO) exposure to the electron beam can lead to the emergence of vacancy ordering in previously disordered matrix. Adapting Kim et al. approach to a dynamic setting, we explore V_o behavior in the PLD grown $\text{LaCoO}_3/\text{SrTiO}_3$ (LCO/STO) superlattices and LCO films by HAADF and annular bright field (ABF) STEM.

We demonstrate how beam exposure causes the development of the V_o ordering in LCO blocks of the LCO/STO superlattice manifesting as lattice expansion. The initial and final images of LCO/STO superlattice observed in [001] projection are shown in Figs. 1(A,B). Oxygen-depleted layers appear darker than stoichiometric ones and have larger lattice spacings. These changes are even more apparent in the atomic position maps generated from Figs. 1(A, B) (Figs.1(C,D)). Quantitative analysis of time dependent data suggests that the vacancies are primarily redistributed, rather than generated, by the electron beam. Notably, once oxygen depletion/lattice expansion takes place at some point in the LCO layer, it propagates in the lateral direction, likely due to lattice strain caused by non-uniform vacancy ordering.

To better visualize local structure changes inside LCO caused by V_o ordering, we examine the superlattice samples in [110] projection. In these conditions we can track the formation of 1D V_o channels along [110] direction and lateral Co shifts that accompany perovskite to brownmillerite transformation.[2] Figs. 2(A, B) show the close-up of one LCO block before (A) and after (B) the beam exposure. Lattice spacing map (Fig. 2(C)) generated from Fig. 2(B) shows localized expansion, while lateral displacement map (Fig. 2(D)) shows alternating, brownmillerite-like character of Co-Co shifts in the same layer. A schematic of these lattice changes is given in Fig. 2E.

When the same approach is applied to 15 u.c. LCO film, e-beam exposure results in a sequence of phase transformations, starting from disordered perovskite LaCoO_{3-x} to a 2:1 brownmillerite $\text{La}_3\text{Co}_3\text{O}_{8-x}$ to eventually 1:1 brownmillerite $\text{La}_2\text{Co}_2\text{O}_{5-x}$. Quantitative analysis shows that in this case electron beam causes vacancy injection as well as redistribution, suggesting that STO layers serve as barriers to oxygen

transport out of the film. Kinetics of the ordering as well as implications for controlled beam-driven phase-transformations at an atomic scale will be discussed.

References

- [1] Y.-M. Kim et al., *Nature materials* **11**, 888 (2012).
 [2] T. G. Parsons et al. *Chemistry of Materials* **21**, 5527 (2009).
 [3] Research supported by the U.S. Department of Energy (DOE), Basic Energy Sciences (BES), Materials Sciences and Engineering Division, by Center for Nanophase Materials Sciences, which is supported at ORNL by DOE BES, and through a user project supported by ORNL's Center for Nanophase Materials Sciences (CNMS), which is sponsored by the Scientific User Facilities Division, DOE BES.

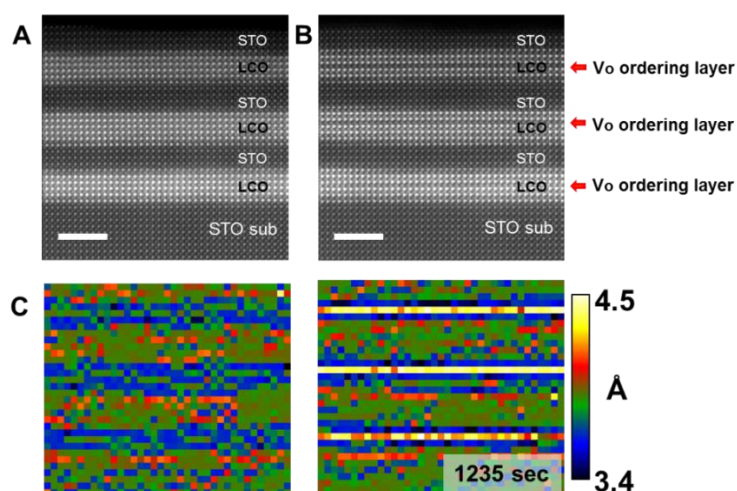


Figure 1. HAADF images of LCO/STO superlattice along $[100]_{pc}$ direction (A) as-grown and (B) after electron beam exposure for 1235 seconds. (C) Atomic position maps generated from (A) and (B) show that lattice expansion indicative of vacancy ordering develops in the LCO blocks.

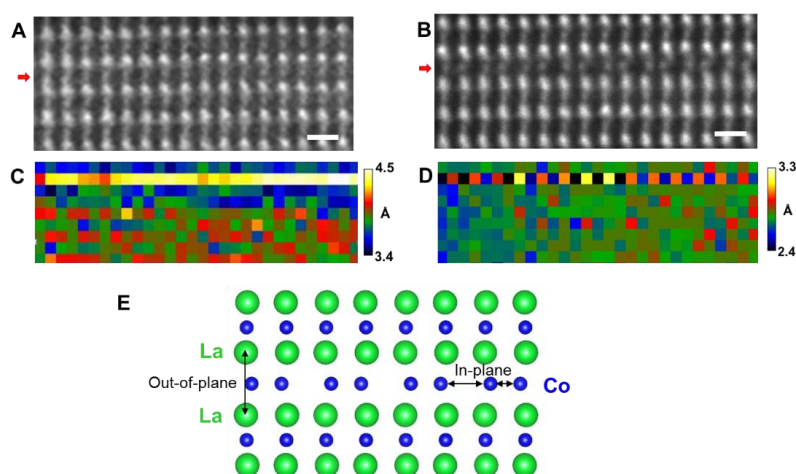


Figure 2. HAADF images of an LCO block in LCO/STO superlattice down $[110]$ direction (A) initial state and (B) after beam exposure. (C) out-of-plane La spacing map generated from (B). (D) in-plane Co-Co spacing map generated from (B). (E) Atomic model illustrating lattice changes shown in (C,D).