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Multidimensional Analysis of Nanoscale Phase Separation in Complex Materials Systems

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Propelled by rapid advances in synthesis, characterization, and computational modeling, materials science is fast progressing toward a "materials-by-design" paradigm. While this new approach offers the promise of "designer" materials, it has tended to overlook the complex kinetic limitations that hinder the realization of the targeted materials systems. In particular, while we can envision a very large number of materials combinations, we are unable to synthesize them in practice because existing characterization and modeling approaches fail to capture the inherent complexities of such systems. This shortcoming is amplified by the fundamental disconnect between highly local and volume-averaged structure-property models resulting from electron microscopy and X-ray diffraction investigations, respectively. Our study addresses the grand challenge of multicomponent materials design, using a multidimensional analysis approach to achieve a *predictive* understanding of structure-property relationships in a model system.

Here we explore the model complex oxide, La_2MnNiO_6 (LMNO), which possesses a hierarchy of structural, chemical, and magnetic ordering across multiple length scales. This material shows great promise for next-generation spintronics and thermoelectrics, but its implementation is hindered by a poor understanding of the underlying structure that governs its macroscale magnetic performance [1]. Using aberration-corrected scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (STEM-EDS) we map the onset of cation ordering upon annealing, as shown in Figures 1.A-B. We find that post-annealing can promote extensive cation ordering; however, bond angle mapping using the RevSTEM technique [2] reveals that large structurally-disordered regions remain after annealing, as shown in Figure 1.C. We combine STEM-EDS mapping with the emerging technique of laser-assisted atom probe tomography (APT) to measure a fine distribution of NiO secondary phases, which we visualize with unprecedented clarity in three dimensions, as shown in Figure 2.

To interpret these results, we conduct *ab initio* calculations, which show that the NiO phase is an inevitable result of low-oxygen pressure growth processes that are commonly used in fabrication of complex oxide heterojunctions. We argue that kinetic limitations on the reincorporation of NiO nuclei "locks" them into the film structure during synthesis; the resulting nanoscale network disrupts the long-range ferromagnetic ordering of the matrix, degrading macroscale magnetic properties. This array of experimental and theoretical techniques allows us to better understand the relationship between structure

and magnetic properties, illustrating the need for a new approach to complex materials characterization. [3]

References:

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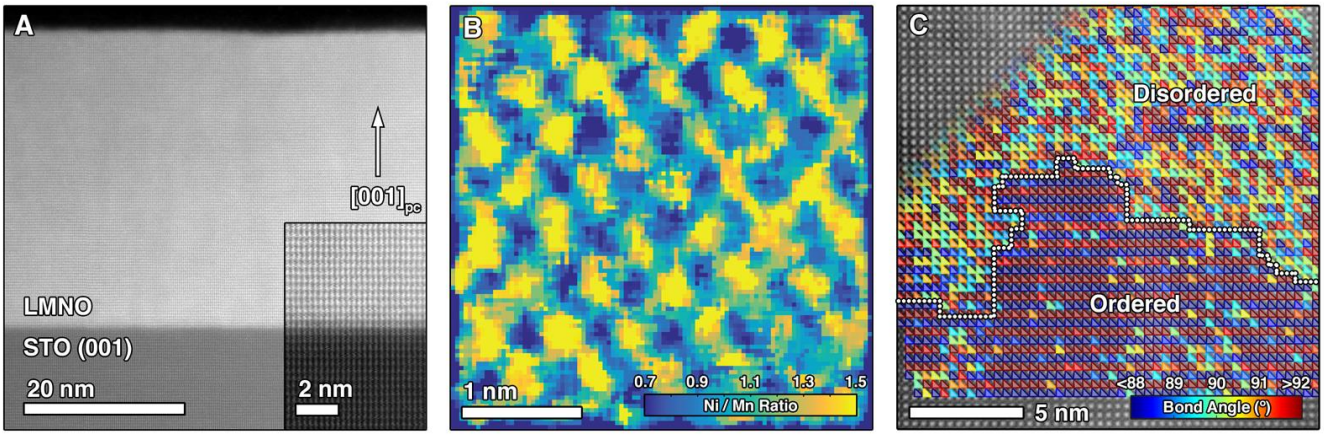

Figure 1. STEM mapping of cation order and extended structural disorder. (A) Representative STEM-HAADF cross-section of the LMNO / STO heterostructure, inset with a high-magnification image of the interface, showing excellent epitaxy and crystallinity. (B) Atomic-level STEM-EDS map of the annealed film, showing clear ordering of the *B*-sites onto Mn and Ni cation planes along the diagonal pseudocubic [111] direction. (C) Intermediate-magnification RevSTEM bond angle map of the annealed film, showing a clear layering of long and short bonds into pseudocubic (001) planes, commensurate with an ordered $P2_1/n$ structure; however, there are extensive disordered regions at larger length scales.

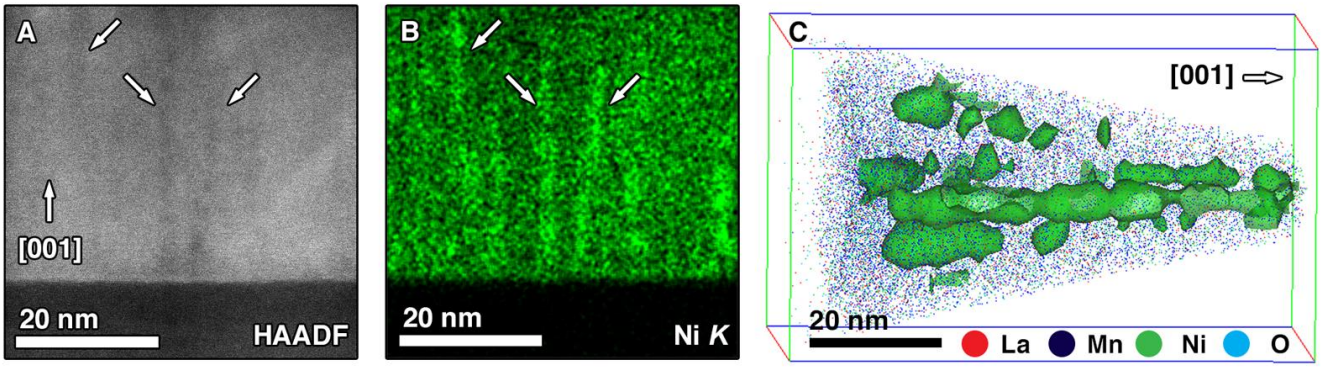

Figure 2. Complementary STEM / APT mapping of NiO secondary phase morphology and composition. (A, B) STEM-HAADF micrograph and corresponding STEM- EDS map of the Ni *K* peak, revealing the presence of several extended, Ni-rich regions (marked with arrows). Images taken along the [110] pseudocubic zone-axis. Images taken along the [110] pseudocubic zone-axis. (C) APT volume reconstruction of a portion of the annealed film; there is a clear distinction between the NiO regions highlighted by the 15 at % Ni isocomposition surface (green) and the LMNO matrix (colored points).

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