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**Atomic Scale Mapping of Phase Segregation at CMR Grain Boundaries in
the Scanning Transmission Electron Microscope**

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The future harnessing of colossal magnetoresistance in manganese oxides necessarily relies on acquiring a deep understanding of their physical/chemical properties at the atomic scale. These are quite complex materials due to the interplay of electron, lattice and spin degrees of freedom. For this reason, the mechanisms underlying CMR are still far from understood. It has been suggested that strong electron-electron correlations may lead to a microphase separation of clusters with stronger and weaker doping levels than the average value for the material [1]. Much research has been devoted to the study of such nanoscale phase separation and related order-disorder transitions, as well as their effects on the physical properties of interest. However, detailed studies on the nature of such phase separation and on the relationship between structure, chemistry and properties at the atomic scale are still needed. The understanding of the relations between electronic properties and macroscopic behavior requires the use of probes with atomic resolution. Aberration correction in the Scanning Transmission Electron Microscope (STEM) is pushing the achievable spatial resolution for imaging and spectroscopy into the sub-angstrom regime, allowing the properties of defects and interfaces to be probed with unprecedented detail. The combination of atomic-resolution Z-contrast scanning transmission electron microscopy and electron energy loss spectroscopy (EELS) provides a powerful method to link the atomic and electronic structure of solids to their macroscopic properties, enabling the local investigation of the relationship between electronic structure and epitaxial strain, structural disorder and phase separation.

Strain fields in thin films allow tuning the physical properties in a controlled way and also modifying the aforementioned phase separation. This work presents atomically resolved studies of CMR films grown on bicrystal substrates. Grain boundaries in CMR materials, like the one shown in figure 1, are of tremendous interest due to their low-field magnetoresistant properties [2]. Their physical properties are certainly influenced by small size active regions such as the dislocation cores. High spatial resolution EELS provides the key to understand their behavior through correlations with the local chemistry, lattice strains around the grain boundary and/or the electronic structure around the dislocation cores. A noticeable segregation of Ca ions at the dislocation cores has been detected by means of EELS (as shown in figure 2), accompanied with a change in the Mn formal oxidation state. These changes locally move the oxide into a completely different region of the phase diagram, having a strong effect on its magnetic properties. These and other similar experiments aimed to study phase segregation will be presented.

- [1] E. Dagotto, T. Hotta, A. Moreo, *Phys. Rep.* **344**, (2001), 1.
 [2] J.Z. Sun and A. Gupta, *Annual Review of Material Science* **28**, (1998), 45.
 [3] This research was sponsored by the Laboratory Directed Research and Development Program of ORNL, managed by UT-Batelle, LLC, for the U.S. Department of Energy under Contract No. DE-AC05-00OR22725.

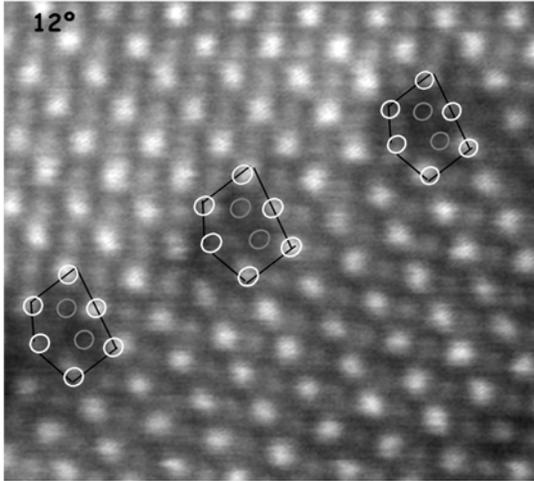


FIG. 1: Z-contrast image of a 12° grain boundary in LCMO taken along the pseudocubic axis. Dislocation core units have been highlighted for clarity. La/CaO columns are marked with white circles, while MnO columns are depicted with grey circles.

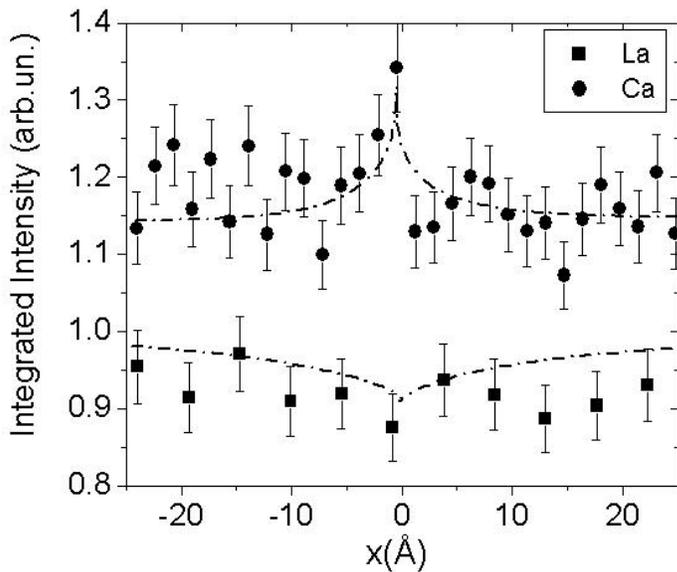


FIG. 2: Integrated Ca (circles) and La (squares) EELS signals, showing the profiles of Ca/La concentration across a dislocation core in a 12° grain boundary.