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High-Precision Chemical Analysis and Structural Determination of Functional Oxides by STEM-EELS

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Chemical doping of functional complex oxides is perhaps the most widespread means of tailoring their physical properties, which crucially depend on the materials' atomic arrangements at the sub-angstrom scale. Minute changes in their composition can dramatically alter the local atomic configuration and thus transform the physical properties of these oxides. As these effects are often too local to be fully understood through bulk characterization methods, due to the presence of point or extended defects for instance, scanning transmission electron microscopy (STEM) has become a ubiquitous tool in their study, thanks to atomic-resolution Z-contrast imaging and true routine 2D electron energy loss spectroscopy (EELS) chemical mapping. When these techniques are combined with advanced statistical image analysis [1] it is possible to determine statistically the chemical distribution of the different sites in these structures across a range of compositions and to relate those to accurately measured small local atomic displacements generated by these compositional changes.

In this work we present examples of combined STEM/EELS and statistical image analysis in functional complex oxide systems with varying cation contents. All samples were synthesized by the mixed oxide route. The thermoelectric properties of the perovskite system (1-x)$SrTiO_3$-x$La_{2/3}TiO_3$ can be fine-tuned by adjusting the La/Sr ratio, *i.e.* by varying x. HAADF imaging in an aberration-corrected STEM revealed that in the La-rich side of the compound series there are two distinct A lattice sites with strikingly different column intensities (Figure 1a). In combination with 2D EELS mapping it is revealed that one of the two A sites (site A1) is fully occupied by La, while the other (A2) exhibits either a shared occupancy of Sr or La vacancies. Further analysis of the EELS data as well as statistical analysis of the image intensities is used to determine the cation concentration at La-deficient sites. The structural variations derived from image and chemical map analysis are in turn related to fine structure changes in the EELS maps, notably for the Ti $L_{2,3}$ edge (Figure 1b).

Furthermore, the magneto-electric oxide gallium ferrite $Ga_{1-x}Fe_xO_3$, whose spontaneous polarization is dependent on the distortions caused by the structural asymmetry of the cation sites [3], provides another example of combined EELS and image analysis methodology. Analysis of the HAADF image intensities as well as detailed 2D EELS mapping is used to demonstrate that in the intermediate compositions cation intermixing occurs mainly in the Fe2 and Ga2 sites. Advanced image analysis is used to determine the respective displacement of the Fe2 and Ga2 sites with respect to the atomic composition.

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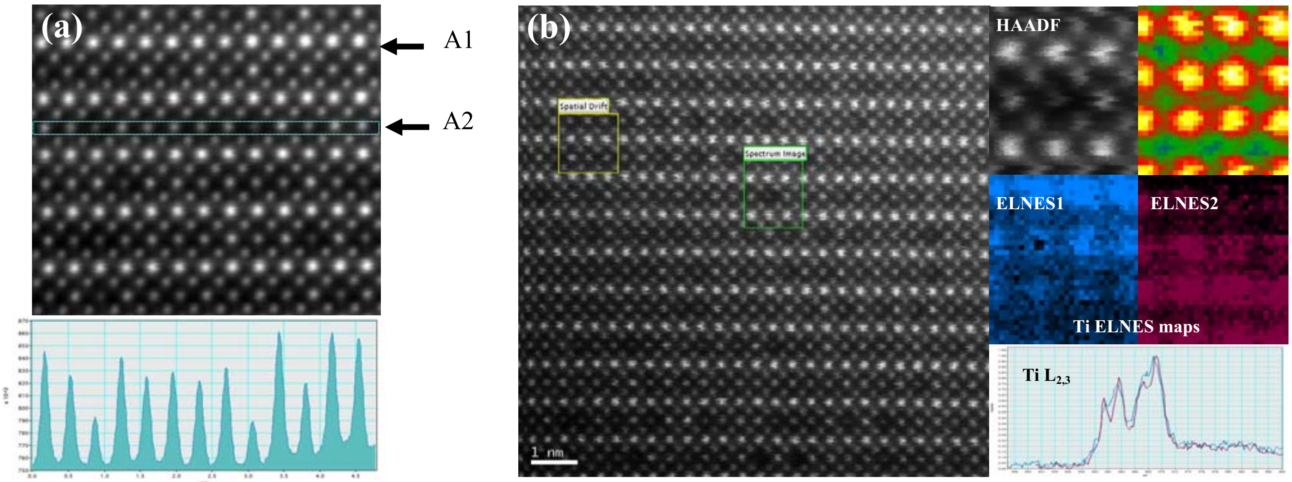

Figure 1. a) Stack-averaged HAADF STEM image showing two distinct A sites in $La_{0.6}Sr_{0.1}TiO_3$ and intensity profile of the A2 site, (b) HAADF STEM survey image of a La-vacancy in the A2 cation site, corresponding atomically-resolved Ti and Ti ELNES maps.

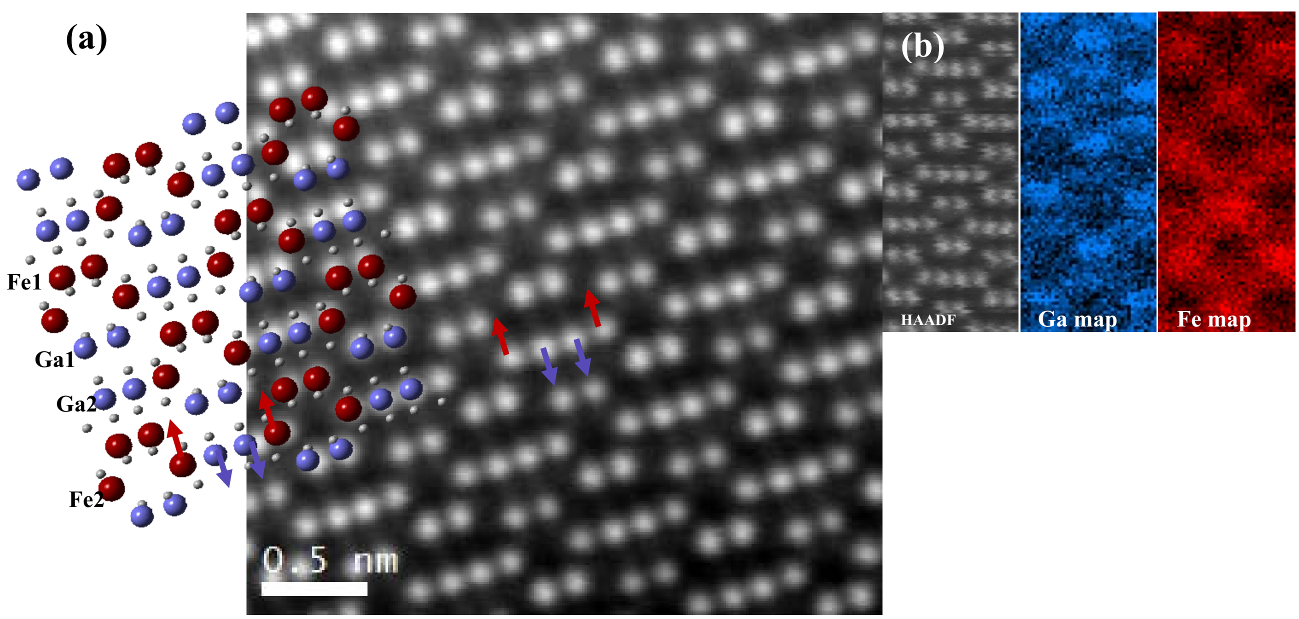

Figure 2. (a) Ball and stick model of gallium ferrite and stack-averaged HAADF image of the $Ga_{1.2}Fe_{0.8}O_3$ composition and (b) atomically resolved Fe map.

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