

Revealing Unit Cell Level Distortions in Random Oxide Solid Solutions by Scanning Transmission Electron Microscopy and the Projected Pair Distribution Function

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Picometer-scale lattice distortions critically determine a range of properties in oxide solid solutions including ferroelectricity, piezoelectricity, high temperature superconductivity, and thermoelectricity. Through solid solution alloying of constituent elements, these properties can be tailored for specific applications. Direct real-space visualization of local crystal distortions combined with atomic-level chemical information in solid solutions can thus provide key insights towards understanding the interplay between the lattice degrees of freedom.

In this talk, we present an investigation of atomic-level displacements in $(\text{La}_{0.18}\text{Sr}_{0.82})(\text{Al}_{0.59}\text{Ta}_{0.41})\text{O}_3$ (LSAT) where the A sub-lattice contains La/Sr, and the B sub-lattice contains Al/Ta. A spatially averaged face centered cubic unit cell has been determined by diffraction methods for this solid solution. Significant local unit cell distortion, however, is expected due to complex local chemical and charge variation on both A sub-lattice (La^{3+} and Sr^{2+}) and B sub-lattice (Al^{3+} and Ta^{5+}). The recently developed revolving scanning transmission electron microscopy (RevSTEM) technique removes sample drift distortion that enables investigation of picometer-level distortion within the 2D projection of the three dimensional crystal [1]. Figure 1b shows a typical RevSTEM image with evident intensity variation across atom columns. Weak columns are found to be Al-rich B sub-lattice atom columns as confirmed with atomic resolution energy dispersive X-ray spectroscopy (EDS) (Figure 1a). The average nearest like neighbor (NLN) around each atom column of A sub-lattice (Figure 1c) and B sub-lattice (Figure 1b) was calculated using atom column fitting and indexing technique as described in Ref. [2], and then used to render the rounded rectangles representing the magnitude of NLN. Larger unit cells are rendered red while smaller unit cells are rendered blue. Figure 1c and 1d show a significantly larger average NLN variation for A site than B site. Additionally, dark B sub-lattice columns tend to have small unit cells and bright B sub-lattice columns tend to have large unit cells.

Further, we discuss the development and application of the projected pair distribution function (pPDF) to quantify distortion and correlation. This approach enables measurement of a function that is related to the PDF used in diffraction, but obtained directly from real-space atom column locations as schematically shown in Figure 2a. The partial pPDF can be determined for A sub-lattice and B sub-lattice (Figure 2b). The large variation for B sub-lattice than A sub-lattice is confirmed by significantly broader peaks in pPDF for B sub-lattice (Figure 2c). Through correlation analysis, we also will show that A sub-lattice cations move closer to B sub-lattice atom columns that are rich in Al atoms and away from those rich in Ta. We will demonstrate using density function theory (DFT) that the observed distortion is due to the local bonding configuration for the different sub-lattices. The local charge density of oxygen is shown to depend on the nearest B-site atom type, and is ultimately determined to provide the driving force for the structural distortion observed on the A sub-lattice. Finally, we will discuss how this approach may be applied across a range of complex oxides to understand their properties and phenomena [3-4].

References:

- [1] X. Sang and J. M. LeBeau, *Ultramicroscopy* **138** (2014), p. 28.
- [2] X. Sang, A. A. Oni and J. M. LeBeau, *Microscopy and Microanalysis* **20** (2014), p. 176.
- [3] X. Sang et al., *Appl. Phys. Lett.* **106** (2015), p. 061913.
- [4] The authors acknowledge the use and support of the Analytical Instrumentation Facility at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation.

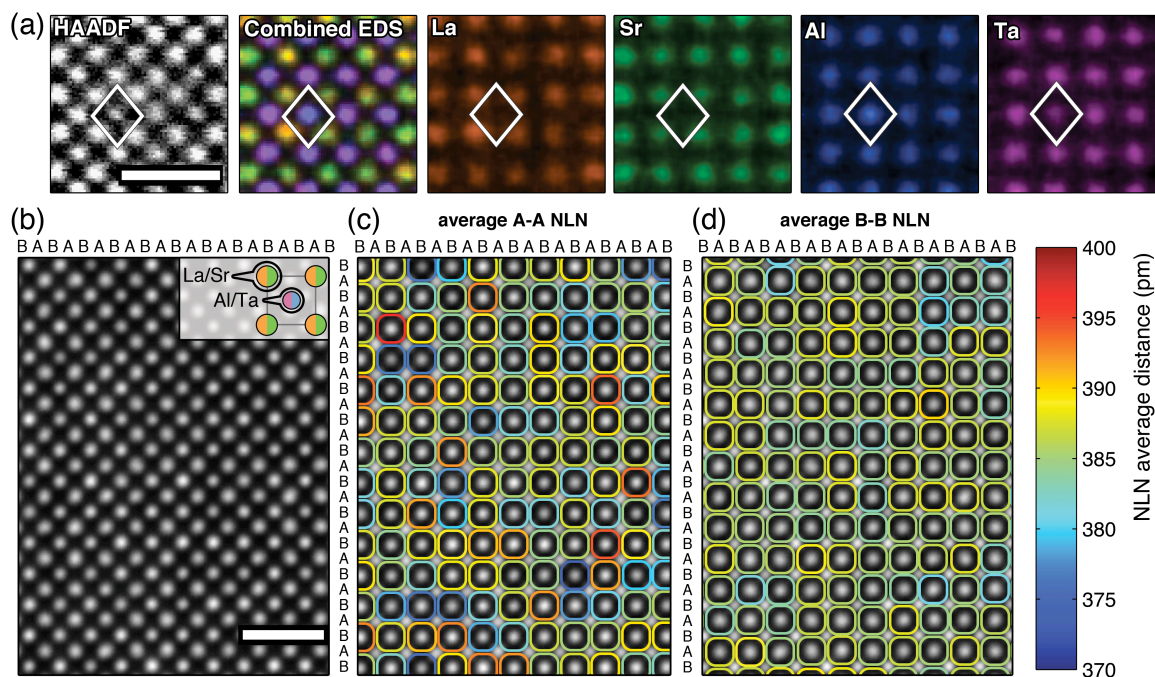


Figure 1. (a) Atomic resolution EDS highlighting Al-rich column with dark intensity in HAADF (b) sub-section of a RevSTEM image along $\langle 100 \rangle$ with the labels ‘A’ and ‘B’ denoting the corresponding sub-lattices. Average A-A (c) and B-B (d) NLN distance around each sub-lattice atom column. The indicated scale bars represent 1 nm.

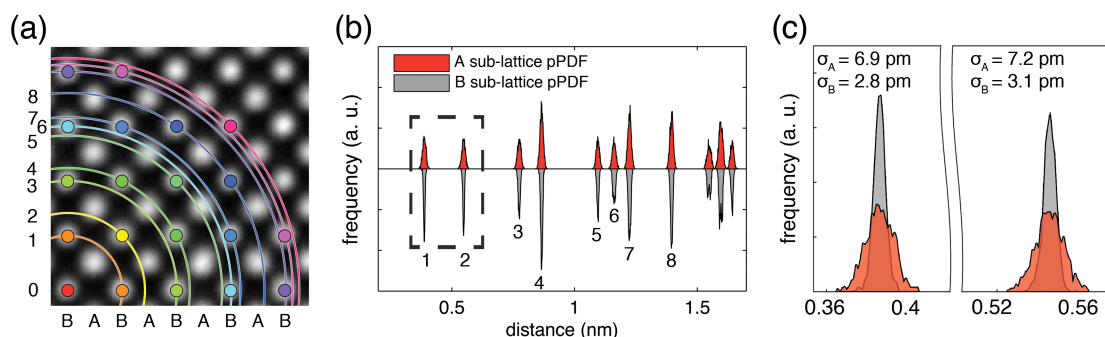


Figure 2. (a) Schematic of projected pair distribution function (pPDF). (b) pPDFs for A (red) and B (gray) sub-lattices calculated based on n^{th} like-neighbor atom columns. (c) Comparison of first and second nearest like-neighbor peaks.