

## Increased Fluctuation of Interatomic Distances in Distorted Structure of Stoichiometric $\text{LaMnO}_3$ .

Alexander V. Kvit<sup>1,3</sup>, Jie Feng<sup>2</sup>, Andrew B. Yankovich<sup>1,2</sup>, Dane Morgan<sup>1,2</sup> and Paul M. Voyles<sup>1,2</sup>

<sup>1</sup> Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI, 53706, USA

<sup>2</sup> Materials Science Program, University of Wisconsin-Madison, Madison, WI, 53706, USA

<sup>3</sup> Materials Science Center, University of Wisconsin-Madison, Madison, WI, 53706, USA

Non-rigid registration of aberration- corrected scanning transmission electron microscope (STEM) images enables sub-picometer precision in locating atomic column positions under favorable circumstances [1]. Reproducible high precision requires careful alignment of the microscope and selection of the acquisition parameters. Sample mistilt causes systematic variations in interatomic distances, but can be minimized using position-averaged convergent beam electron diffraction (PACBED) to  $<1$  mrad. Low sample drift of  $1 \text{ \AA}/\text{min}$  results in larger field of view after registration. On our microscope, a FEI Titan operated at 200 kV, dwell time of  $12 \mu\text{s}/\text{pixel}$  and for  $256 \times 256$  pixel images is optimal.

We recently found that images of  $\text{LaMnO}_3$  (LMO) film grown on  $\text{DyScO}_3$  (DSO) substrates exhibit an unusual elastic stress relaxation microstructure. They also consistently show precision of 3- 6 pm, measured as the standard deviation of repeated interatomic distances within the image field, despite being acquired under the conditions described above. Here we present evidence that the large spread in interatomic distances is intrinsic to the sample, and that it arises from the nature of stress relaxation in the LMO film.

LMO (*Pnma* space group) is a good lattice match to DSO, but these materials have slightly different thermal expansion coefficients, creating stress in the film due to the change in lattice mismatch with temperature. The stress does not result in interface misfit dislocations. Instead, the film contains domains rotated by  $90^\circ$  with respect to each other and the substrate, as shown in Figure 1a. The different domains have different internal strain. Figure 1b shows a  $2.3^\circ$  tilt between the epitaxial LMO film and DSO substrate; Figure 2a shows a NRR image of a tilted domain, in which the unit cell corner angles are  $92^\circ$  and  $88^\circ$  degrees, not  $90^\circ$ . Figure 2b shows a simulated image of undistorted [100] LMO. The distances between La- atom columns DS0 and DS1 are not equivalent due to presence of oxygen columns on opposite sides of the La columns (see Figure 2e). From simulations,  $\text{DS0} = 2.7575 \text{ \AA}$ ,  $\text{DS1} = 2.8246 \text{ \AA}$ , and  $\text{DS2} = 3.8751 \text{ \AA}$  for 10 nm sample thickness, which is close to thickness estimation from PACBED in the area shown on Figure 2a and 2c. We can distinguish such differences from NRR HAADF image on Figure 2a. Figure 2c shows a NRR low-angle annular bright field (LAABF,  $8.48 - 18.7$  mrad detector angle) image from the same area where oxygen columns can be easily distinguished except those that overlap with La columns. Simulated positions of all columns are shown by circles on experimental LAABF on bottom part of Figure 2c.

Figures 2a and d show obvious elongation of the Mn columns. The La columns do not show such elongation, so the distortion does not arise from probe aberrations or sample mistilt. We therefore suggest that the distortion is a result of changes in octahedral tilt related to the same elastic stress that

changes the La positions. Local variations in these distortions, either randomly or as a function of distance away from the substrate explain the larger intrinsic variability of interatomic distances we observe [2].

## References

[1] A. B. Yankovich, et al., Nat. Commun. **5**, 4155 (2014).

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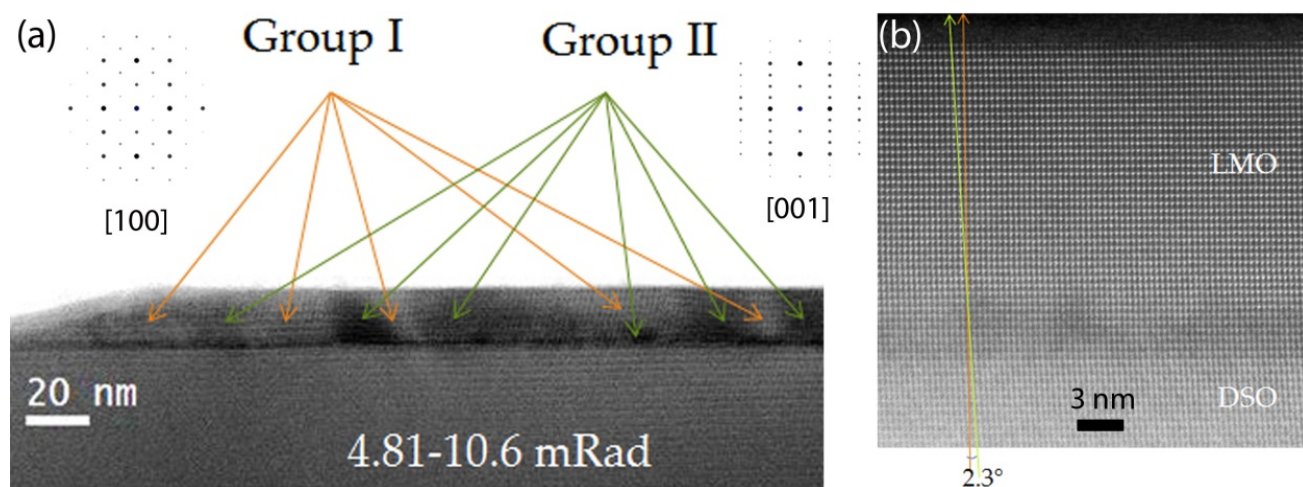


Figure 1. (a) LAABF STEM image shown domains with [100] and [001] orientations; (b) Consequence of lateral stress between DSO substrate and LMO film: distortion of LMO structure and tilt of 2.3°. The image is taken in [100] zone axis.

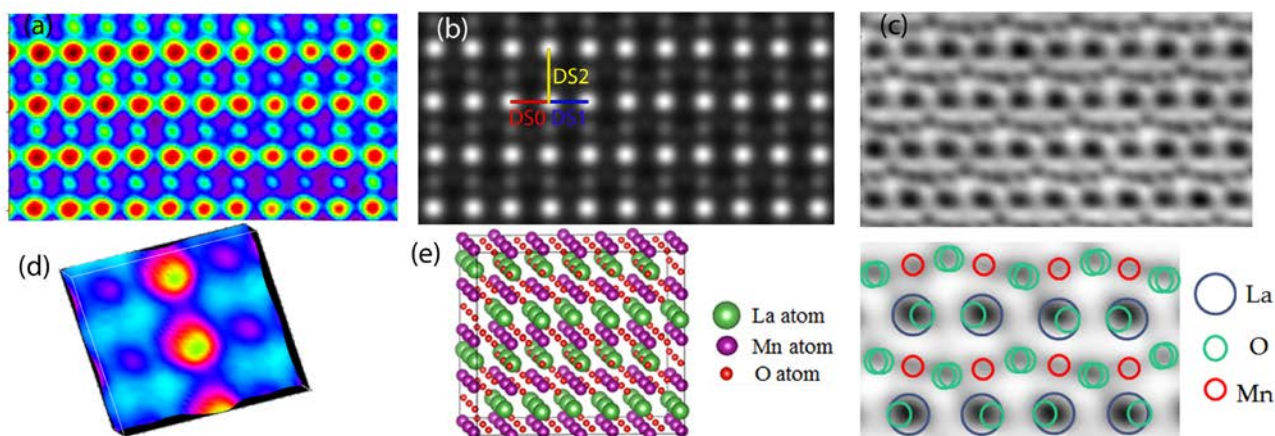


Figure 2. (a) NRR HAADF STEM image of LMO domain in [100] zone axis; (b) Simulated HAADF STEM image; with labeled distances between La columns DS0, DS1, and DS2; (c) NRR LAABF STEM image; circles show good correlations with simulated positions of O, Mn and La columns; (d) Zoomed NRR HAADF STEM image: elongation of Mn columns; (e) Simulated position of all columns.