

# Understanding Structural Variability Induced by Grain Boundary Doping in SrTiO<sub>3</sub>

H. Yang<sup>1</sup>, Y. Sato<sup>2</sup>, H.S. Lee<sup>2</sup>, Y. Ikuhara<sup>2</sup> and N.D. Browning<sup>3</sup>

<sup>1</sup> Department of Chemical Engineering and Materials Science, University of California–Davis, One Shields Avenue, Davis, CA 95616;

<sup>2</sup> Institute of Engineering Innovation, The University of Tokyo, 2-11-16, Yayoi, Bunkyo, Tokyo 113-8656, Japan;

<sup>3</sup> Chemical and Materials Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99352 USA

Grain boundaries have long been known to have far-reaching effects on the bulk properties of perovskite materials, and effective control of grain boundary structures is highly desirable for improving various properties. It has been well demonstrated that grain boundary doping is a powerful method to alter the atomic and electronic structures of grain boundaries,[1-2] therefore understanding the doping mechanism is highly advantageous for controlling the influence of grain boundary on the bulk properties. In this research, we focus on the doping effects in grain boundaries of SrTiO<sub>3</sub>, which is considered as prototype structure for all perovskites. As for the choice of dopants, a series of dopants with different ionic radii and valence states are considered, and both doped and undoped grain boundaries are prepared with diffusion bonding technique[3].

As a start point, the undoped  $\Sigma 13$  (510)/ [001] grain boundary of SrTiO<sub>3</sub> is investigated. Two different structures have been found, one being a symmetric structure and the other being rigid-body shift structure that contains a rigid-body translation along the boundary plane, as shown in Fig.1a) and b) respectively. Statistically the grain boundary population shows the rigid-body shift structure is the prevalent structure. Besides, compositions in two types are different and the rigid-body shift structure has a Ti-rich nonstoichiometry as compared to the other, and by taking such a composition difference into first principles DFT calculations, both structures are shown to be energy stable structures.

In the case of praseodymium (Pr) doping, interestingly we find mainly one type of atomic structure, as shown in Fig.2. Compared to the undoped case, the Pr doped grain boundary has a very similar structure to the symmetric structure type, but has relative brighter intensities in particular atomic positions in the Z contrast images. The presence of Pr has been analyzed from EELS chemical mapping, and confirms that the brighter intensity is actually the substitution of Pr dopants. Further discussion on the theory calculations and results on grain boundaries with other dopants will be shown in the presentation.

## References

- [1] Buban, J.P., et al., *Science*. 311 (2006) 212.
- [2] Klie, R.F., et al., *Nature*. 435 (2005) 475.
- [3] Yamamoto, T., et al., *J. Am. Ceram. Soc.* 83 (2000) 1527.

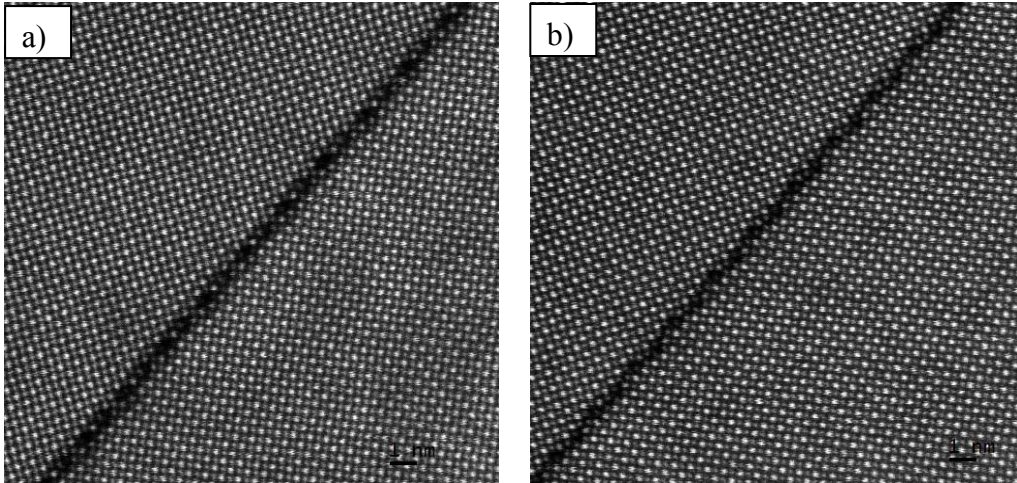


FIG. 1. Average images of two different atomic structures with the structure units overlaid on the left part. From a dataset of over 400 cropped experimental images two atomic structures have been categorized. Of these cropped images, 35% images show a symmetric structure in a); and 65% images show rigid-body shift structure in b).

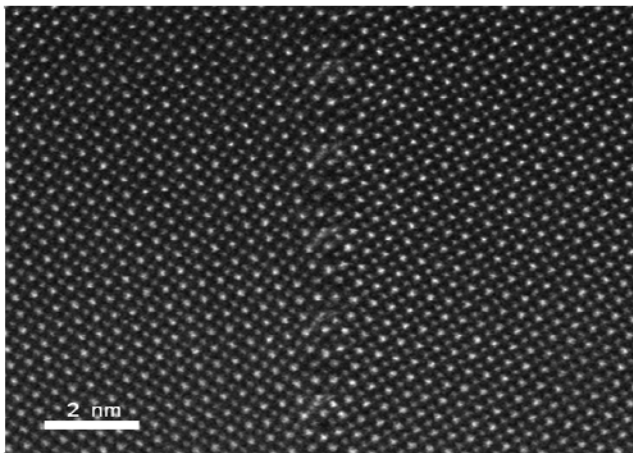


FIG. 2. STEM images of Pr doped  $\text{SrTiO}_3$  grain boundaries. The structure is symmetric across the grain boundary plane, and brighter intensity indicates the presence of Pr in the grain boundary.