

## Direct Determination of Dopant Site-Selectivity in Ordered Perovskite Titanate Polycrystals

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A variety of physical properties and resulting functionalities of many pristine materials are drastically altered by additives or dopants even if their concentration is only of a few atomic percents. Remarkable variations of electrical properties in silicon-based semiconductors, oxide-type superconductors and dielectrics as well as of mechanical properties in metals and structural ceramics are the well-known examples that demonstrate the significance of such external additives. In contrast to covalently bonded compounds, added aliovalent cations can act as either donors or acceptors in complex oxides with multiple components, depending on which host cation in the lattice is replaced<sup>7</sup>. Therefore, to determine the site-selectivity of dopants directly and precisely in the unit cell of such ionic systems is the first crucial step toward the better understanding and systematic estimation of ultimate materials performance by doping.

As has been already recognized well in most of the ABO<sub>3</sub>-type perovskite oxides, a cation in the A site, which is coordinated with 12 oxygen ions, is usually larger than the other in the B site, which is octahedrally coordinated with six oxygen ions. Thus, a plausible substitutional site for a cation dopant in the lattice can be estimated simply by comparison of its ionic radius with those of the host cations, following the well-known Pauling's first rule that states the number of coordinated anions for a stable configuration in ionic crystals. For example, if the added cation dopant were sufficiently smaller than the A-site host cation, it would be substituted for the octahedral interstitial B site so as to reduce the overall lattice strain energy. In contrast to the simple perovskites, however, such a selectivity issue between the cation sites for a dopant can be fairly sophisticated in the complex perovskite oxides that consist of more than one composition in either A or B site (or both). Therefore, one is not able to simply make a prediction for the site occupation any longer without directly probing the exact location of dopants at an atomic scale.

Taking (Ca<sub>1/4</sub>Cu<sub>3/4</sub>)TiO<sub>3</sub>, which has recently attracted much attention due to the high dielectric permittivity [1,2] and the strong nonlinear current-voltage behavior [3], as a complex perovskite oxide in this study, we experimentally show that the doped aliovalent La cations are preferentially substituted for Ca although 75% of the A sites are composed of Cu. STEM with a spherical aberration corrector and scanning EELS analysis were utilized both for the direct visualization and for the chemical identification of each atomic column. The present study thus suggests that the imaging based on the aberration-corrected STEM combined by the EELS can be utilized as a powerful tool that reveals the atomic-level distribution of cation dopants in complex oxides.

### References

- [1] M. A. Subramanian et al., *J. Solid State Chem.* **151** (2000) 323.
- [2] C. C. Homes et al., *Science* **293** (2001) 673.
- [3] S.-Y. Chung et al., *Nature Mater.* **3** (2004) 774.

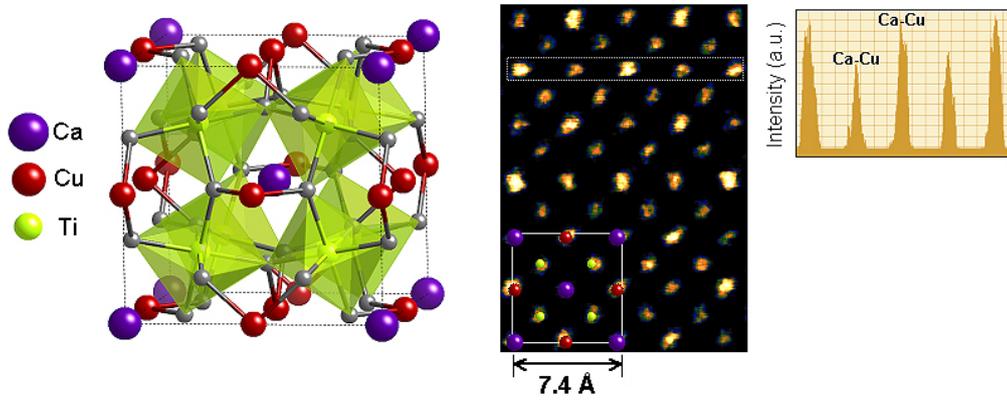


FIG. 1. Crystal structure of  $(\text{Ca}_{1/4}\text{Cu}_{3/4})\text{TiO}_3$  and its HAADF-STEM image.

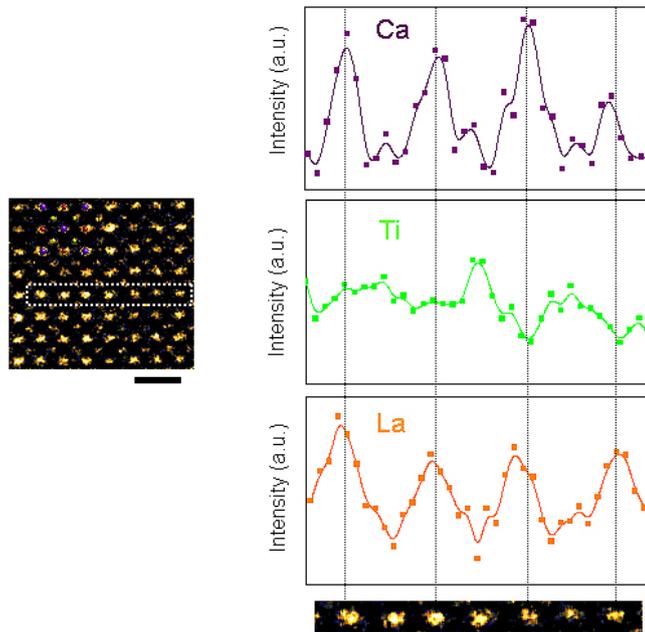


FIG. 2. HAADF-STEM image of La-doped  $(\text{Ca}_{1/4}\text{Cu}_{3/4})\text{TiO}_3$  and intensity profiles for Ca-L<sub>2,3</sub>, Ti-L<sub>2,3</sub>, and La-M<sub>4,5</sub> edges from EELS spectra. The scale bar is 7.4 Å.