

# Atomic and Electronic Structures in Perovskite-Related $\text{LaTiO}_{3.41}$

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Depending on the cation ratio and oxygen concentration, many phases with different perovskite-related structures exist in the lanthanum titanates (La-Ti-O) [1]. In most of them the titanium ion is tetravalent (4+); but interesting transport, electric and magnetic properties are expected for smaller valencies, i.e. trivalence (3+), by forming non-empty 3d band configurations [2]. The titanium valency in the  $\text{LaTiO}_x$ , where the cation ratio is fixed at 1, is believed to be strongly related with the transition from metallic to insulating nature by changing only the oxygen stoichiometry  $x$ . Here we characterize the atomic structure and microstructure of the  $\text{LaTiO}_{3.41}$  synthesized by the floating zone process exhibits a semiconducting behavior ascribed to its unique atomic arrangement and electronic states, by combining conventional TEM and atom-resolved aberration-corrected STEM-EELS with first principle calculation.

The  $\text{LaTiO}_{3.41}$  has a monoclinic layered structure, of which characteristic units are chains of vertex-sharing  $\text{TiO}_6$  octahedra, connected via their apical oxygen atoms and oriented along  $a$ -axis as shown schematically in Fig. 1(a). The periodic contrast in HRTEM images taken from both  $a$ - and  $b$ -axes is consistent with the monoclinic feature in the structure. In order to understand the atomic structure such as cation sites and estimate their chemical environments, high-angle annular-dark-field (HAADF) STEM observation was carried out as shown in Fig. 2. By marking the Ti atoms (in a yellow flame) from 1 to 5 and corresponding  $\text{TiO}_6$  octahedra drawn by white flames in Fig. 2(a), it is found that this unit is periodic based on the perovskite structures distorted locally. It is also noted that despite the Ti sites 1 and 2 appear to have similar chemical environment, i.e. deviating from the orthorhombic perovskite  $\text{LaTiO}_3$  by elongation in  $c$ -axis direction, the local distortion is different. This also applies to the Ti sites 4 and 5. The site 3 appears to have a similar environment as that of the  $\text{LaTiO}_3$ . By examining EELS elemental mapping at atomic resolution and acquiring individual spectrum from the Ti sites in  $\text{TiO}_6$  octahedra, we found that the Ti atoms in the position 3, which has a similar structural environment to that of the  $\text{LaTiO}_3$ , display a trivalence. The Ti sites 1, 2, 4 and 5 display a nearly tetravalency, since the splitting of  $L_3$  and  $L_2$  peaks in the Ti- $L_{3,2}$  spectra are readily visible. However, the valence of Ti in position 2 and 4 differ that of the Ti in 1 and 5 by revealing a notably lower edge onset energy, indicating the local valence state is yet not tetravalent, but slightly lower than that, which could be explained by the distortion of the  $\text{TiO}_6$  octahedra from the HAADF image. This unique atomic structures and electronic valence states are in good agreement with theoretical calculations and are likely to be responsible for the metal-insulating transition behavior in  $\text{LaTiO}_x$ . Hereafter, further extensive first principle calculations may reveal that the  $\text{LaTiO}_{3.41}$  with 2D layered structure and 1D  $\text{TiO}_6$  octahedral chain exhibits an unexpected state with point Fermi surface, and that valence charge is confined largely to within one atomic layer, identifying the quantum confinement effect.

## References

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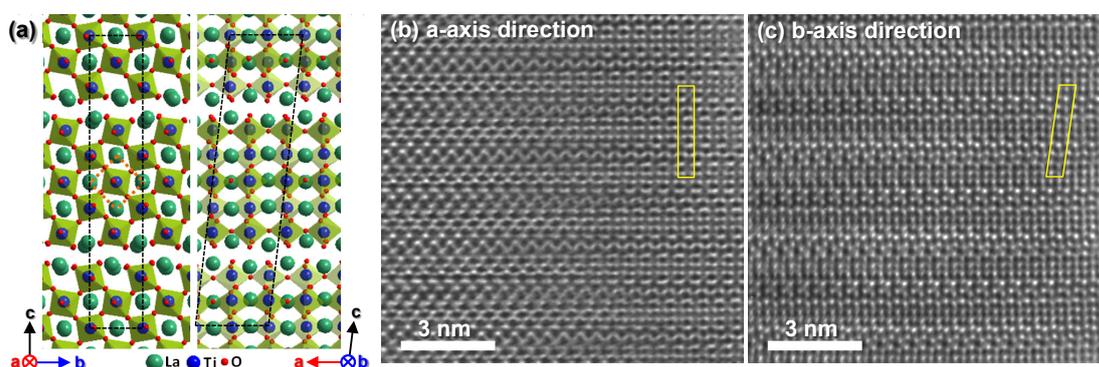


FIG. 1. (a) Crystal structure (the unit cell is outlined by dotted lines), and HRTEM images of the  $\text{LaTiO}_{3.41}$  taken from both (b)  $a$ -axis and (c)  $b$ -axis directions.

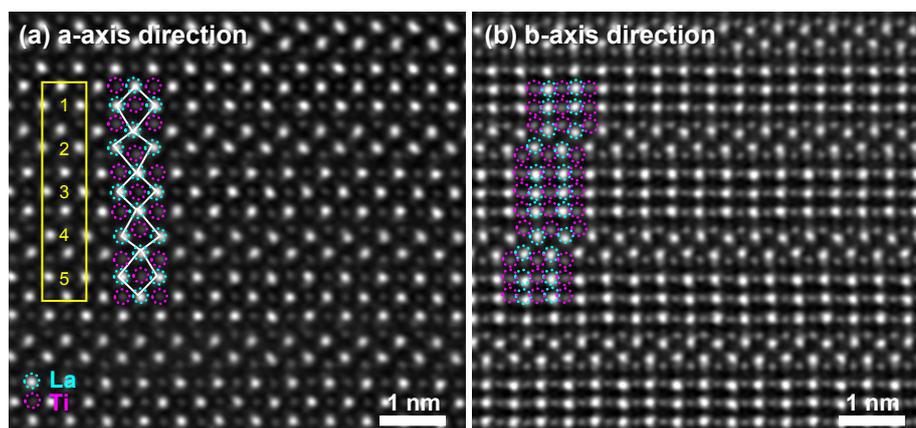


FIG. 2. HAADF-STEM images of the monoclinic  $\text{LaTiO}_{3.41}$  taken from both (a)  $a$ -axis and (b)  $b$ -axis directions. The La and Ti cation atoms are labeled in indigo and magenta, respectively. The white four-sided frames in (a) represent the vertex-sharing  $\text{TiO}_6$  octahedra. (It is noted that distortion of octahedron at Ti site 3 is negligible.)