

# **A-site vacancies and atomic-scale domain boundary structures in polycrystalline solid-state electrolyte $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_3$**

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All-solid-state lithium-ion batteries containing nonflammable solid electrolytes have pronounced advantages over conventional commercial batteries in terms of thermal stability, increased cycle life and energy density, absence of electrolyte leakage, robustness under vibration and physical impacts, and large chemical windows of application. To realize these advantages, an appropriate solid electrolyte must be developed that has a reasonably high lithium ionic conductivity as well as good chemical stability [1]. The perovskite-type compounds  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$  (LLTO), consisting of alternating stacks of La-rich and La-poor layers sandwiched between  $\text{Ti-O}_6$  octahedral sheets along the  $c$  axis, display high bulk conductivity up to  $1.1 \times 10^{-3} \text{ Scm}^{-1}$  ( $x \approx 0.11$ ) at room temperature in single crystal form [2], and hence are promising candidates. For this intrinsically A-site cation-deficient material, the origin of the high ionic conductivity is thought to be related to the high concentration of A-site cation vacancies, and bottleneck caused by octahedral tilting [1], although the formation of domains and domain boundary structures in polycrystalline samples also has a large effect. However, the actual atomic structure of the domains and the domain boundaries in this material, and hence their contribution to the ionic conductivity, are still unclear.

In this study, direct visualization of the atomic structure within the domains and at domain boundaries of thin films of the Li-rich phase  $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_3$  has been performed, utilizing the  $Z$ -contrast high-angle annular dark field (HAADF) and annular bright field (ABF) imaging methods in a spherical-corrected scanning transmission microscope (STEM). Both  $90^\circ$ -oriented and antiphase domain boundaries were frequently observed. Atomic structure analysis based on HAADF images reveals that the irregularly shaped domain boundaries often overlap with one another. Also, many

cation vacancies were observed to be randomly distributed over the A-sites in the La-poor layer, which is thought to be responsible for the severe Ti displacements towards the La-poor layer, resulting in both enhanced Ti-O<sub>6</sub> octahedral tilting and enlarged “oxygen bottleneck” along the pathway for Li-ion migration during charging and discharging. Based on this analysis, the effect of such atomic and microstructural adjustments are discussed in terms of their contribution to the conductivity, in order to provide a comprehensive understanding on the relationship between the microstructure and ionic conductivity of this material.

## References

- [1] S. Stramare, *et. al.*, Chem. Mater. **15** (2003) 3974.  
 [2] Y. Inaguma, *et. al.*, Solid State Commun. **86** (1993) 689.

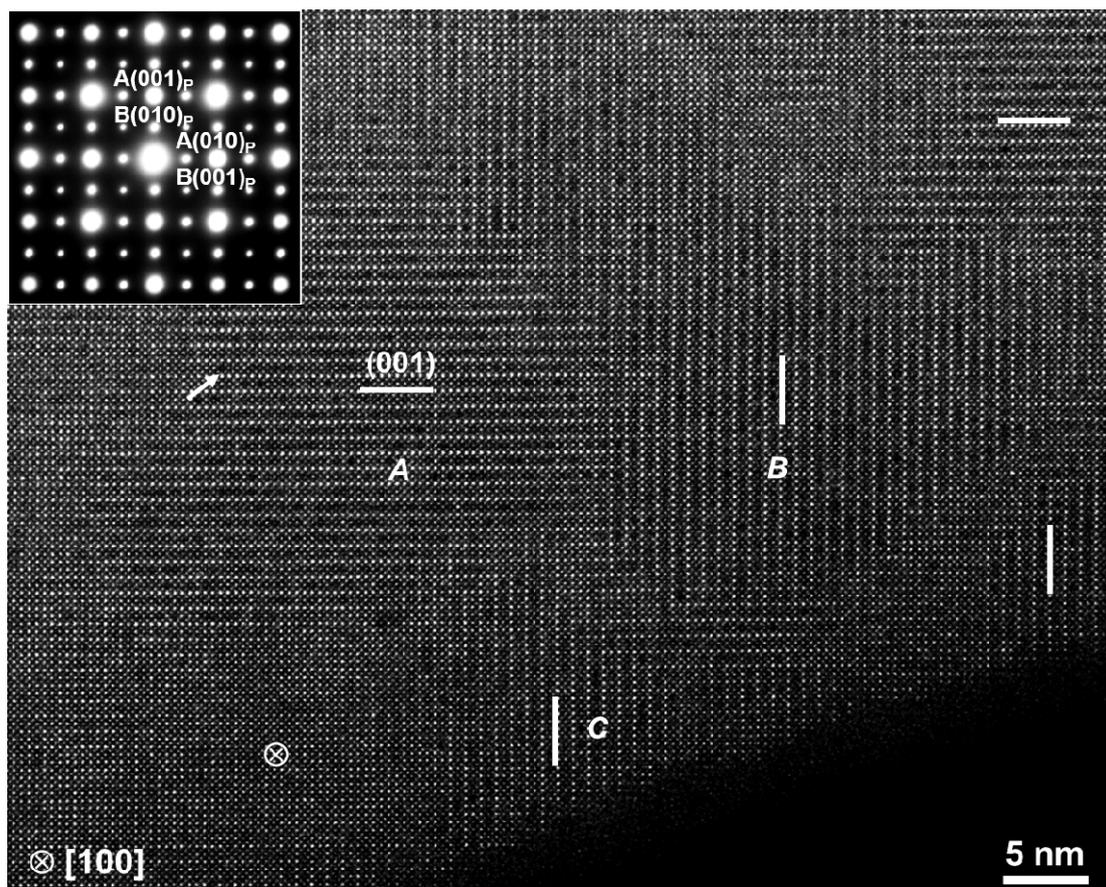


FIG. 1. HAADF image shows both the 90°-oriented (A-B) and antiphase (B-C) domain boundaries in  $\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_3$ . The abundant randomly distributed black spots (with an example arrowed) indicate non-uniform atom contrast on the La2 sites. The inset shows the corresponding SAED pattern taken along the  $[100]$  zone axis.