



## Full length article

## Atomic scale imaging of structural changes in solid electrolyte lanthanum lithium niobate upon annealing



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## ABSTRACT

$\text{La}_{(1-x)/3}\text{Li}_x\text{NbO}_3$  (LLNbO) is a promising electrolyte material for solid-state lithium-ion batteries because it is stable in contact with Li metal and contains a high concentration of intrinsic Li-ion vacancies. One strategy for improving its ionic conductivity and making it more competitive with other solid-state Li-ion electrolytes is to disorder the Li-ion vacancies by appropriate post-synthesis heat treatment, e.g., annealing. In this study, we examine the effects of annealing on single crystals of LLaNbO with Li contents  $x = 0.07$  and  $0.13$  based on simultaneous atomic resolution high angle annular dark field and annular bright field imaging methods using state-of-the-art aberration corrected scanning transmission electron microscopes. It is found that La modulation within A1 layers of the cation-deficient layered perovskite structure becomes more diffuse after annealing. In addition, some La atoms move to A-site positions and O4 window positions in the nominally vacant A2 layer, while O atom columns in this layer become rumpled in the  $[001]_p$  direction, indicating that the  $\text{NbO}_6$  octahedra are more heavily distorted after annealing. The observed crystal structure differences between as-prepared and annealed single crystals explain the drop in Li-ion conductivities of LLaNbO single crystals after heat treatment.

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## 1. Introduction

Because of their high energy density and design flexibility, lithium ion batteries (LIBs) are widely used in portable electronic devices such as laptops, mobile phones, and digital cameras [1–3]. At present, most commercial LIBs use electrolytes made from organic solvents containing a lithium salt. This liquid electrolyte has a number of intrinsic drawbacks, including being a safety hazard: Because the organic electrolyte is flammable, electrolyte leakage or vaporization may result in combustion of the battery [4–6]. Such safety issues are even more critical if LIBs are to be used on a larger scale to power fully electric and plug-in hybrid electric vehicles. In addition, the electrochemical windows of currently available liquid electrolytes are narrow, prohibiting the use of high

voltage cathodes or Li metal as the anode [6–8]. This limits the energy density that can be achieved using this technology. Replacing the liquid electrolyte with a solid-state electrolyte with a wide electrochemical window is one way of overcoming these limitations, while at the same time providing many other advantages, such as better safety, thermal stability, less packaging, and resistance to mechanical shock and vibrations. Consequently, significant efforts are being made to develop all-solid-state lithium ion batteries [7,9–13].

In addition to high Li-ion conductivity, a solid electrolyte needs to be an electronic insulator. Of the many different types of Li-ion solid electrolytes currently known, cation-deficient perovskite type materials are promising because they contain a high concentration of intrinsic cation vacancies through which Li ions are expected to migrate easily. Lanthanum lithium titanates (LLTO) of general formula  $\text{La}_{(2/3-x)}\text{Li}_x\text{TiO}_3$ , for example, exhibit Li-ion conductivities as high as  $10^{-3} \text{ S cm}^{-1}$  at room temperature when  $x$  is around  $0.11$  [14]. However, during charging and discharging, LLTO

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materials can intercalate excess Li ions, resulting in the reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  [15,16]. When this occurs, LLTO becomes electronically conductive, decreasing the battery capacity and potentially short-circuiting the device. This limits the practicality of using LLTO as the electrolyte material in commercial all-solid-state LIBs. Development of more stable A-cation deficient perovskite type oxides, such as lanthanum lithium niobates  $\text{La}_{(1-x)/3}\text{Li}_x\text{NbO}_3$  (LLNbO), in which Ti has been completely replaced by Nb, is one strategy for overcoming this problem.

Because the formal charge of the Nb cation (+5) is higher than that of the Ti cation (+4),  $\text{La}_{1/3}\text{NbO}_3$  contains twice the number of A-cation vacancies per formula unit than  $\text{La}_{2/3}\text{TiO}_3$ , which might be expected to provide a higher Li-ion conductivity when sufficient Li atoms are introduced. Experimentally, however, this is not found to be the case. The highest reported Li-ion conductivity for polycrystalline LLaNbO is around  $4.7 \times 10^{-5} \text{ S cm}^{-1}$  at room temperature [17,18]. This is attributed to the confinement of Li atoms to the La-occupied A1 layers in LLaNbO, making it a 2D ionic conductor, whereas in LLTO La and Li atoms are found in both A1 and A2 layers, enabling 3D diffusion. Although doping LLaNbO with elements such as Sr has been shown to increase the conductivity to  $7.3 \times 10^{-5} \text{ S cm}^{-1}$  [17,19], this is still low compared with LLTO.

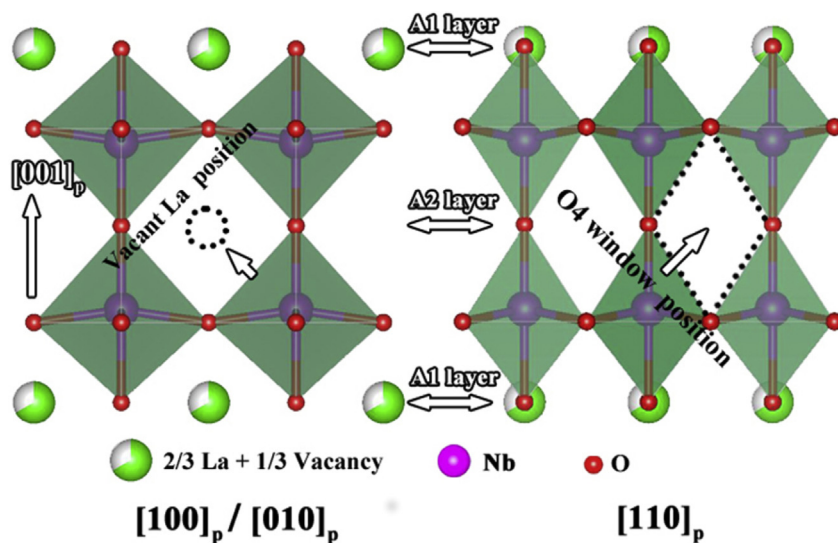
In the case of LLTO, post-synthesis heat treatment is known to affect the microstructure significantly, altering the Li-ion conductivity [20–24]. A similar sensitivity of the domain structure to thermal history has also been observed in A-deficient layered perovskites  $\text{Th}_{0.25}\text{NbO}_3$  [25,26] and  $\text{U}_{0.25}\text{NbO}_3$  [27]. Disordering the layered structure of LLaNbO to produce a more uniform distribution of Li ions (and vacancies) and hence higher Li-ion conductivity similar to that of LLTO might thus be expected to be achievable through appropriate thermal treatment. To the best of our knowledge, however, no such studies have been reported for LLaNbO so far. Given the structural similarities between LLaNbO and LLTO, it is worth examining the effect of heat treatment on the former to gain new insights into the Li-ion conduction mechanism so that its microstructure, ion conductivity, and long-term durability can be optimized.

The Li-free end member of the LLaNbO system,  $\text{La}_{1/3}\text{NbO}_3$ , possesses an orthorhombic structure (space group *Cmmm*;  $a = 7.82 \text{ \AA}$ ,

$b = 7.84 \text{ \AA}$ ,  $c = 7.91 \text{ \AA}$ ) [28]. As illustrated in Fig. 1, La atoms are partitioned into alternating layers in the  $[001]_p$  (where subscript p refers to the primitive cubic pseudo-perovskite structure) direction, namely a partially occupied A layer (the A1 layer) with an average site occupancy factor of 2/3, and a completely vacant layer (the A2 layer). La can be substituted by Li (3 Li atoms replacing 1 La atom), and, according to X-ray diffraction (XRD) analysis, as the Li content,  $x$ , is increased from 0 to 0.25 the average crystal symmetry changes, from orthorhombic to tetragonal and finally to pseudo-cubic [17]. At the same time, the unit-cell volume contracts by around 2.3% [29]. XRD analysis, however, is unable to provide any details about the local atomic structure in these highly defective materials.

To investigate the intrinsic transport behavior in LLaNbO, we grew LLaNbO single crystals by a directional solidification method, as previously reported [30]. By eliminating grain boundaries, which in general impede Li-ion migration [31–33], the Li-ion conductivity of LLaNbO can be enhanced significantly (e.g.,  $\sigma_{\text{ion}} = 2.2 \times 10^{-4} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$  in the case of a single crystal with  $x = 0.08$ ). Previous studies using high resolution methods such as transmission electron microscopy showed that LLaNbO exhibits a number of important nanostructural features such as a modulated distribution of La atoms and vacancies within A1 layers and nanodomains [18,34,35]. Examining local atomic configurations in pseudo-ordered perovskites in detail is thus necessary to completely understand and optimize the structures and properties of these complex materials [36].

Transmission electron microscopy (TEM) is a powerful method for characterizing detailed nanostructural features, especially since the development of aberration correctors now enables materials to be observed with atomic resolution. In this work, we present a detailed investigation of pristine and annealed LLaNbO single crystals using atomic-resolution high angle annular dark field (HAADF) and annular bright field (ABF) imaging techniques simultaneously in a scanning transmission electron microscope. Based on these observations, the influence of local structure on Li-ion conductivity in the LLaNbO system can be inferred. Such information is expected to aid rational design of these materials, enabling the Li-ion conductivity of LLaNbO to be improved through post-synthesis thermal treatment.



**Fig. 1.** Crystallographic projections of the average structure of layered perovskite  $\text{La}_{0.33}\text{NbO}_3$  along  $[100]_p$ /  $[010]_p$  (left) and  $[110]_p$  (right) zone axes showing vacant La positions and O4 window positions, respectively. Subscript p refers to the primitive cubic pseudo-perovskite structure. The partially occupied and completely unoccupied cation layers are labeled A1 and A2 layer respectively.

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