# Crystal Structure, Cation Occupancy and Vacancy Ordering in Thermoelectric $(1\text{-}x)SrTiO_3\text{-}xLa_{1/3}NbO_3$: A STEM-EELS Study

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Thermoelectric energy conversion is widely recognized as a promising technology both for electric power generation in terms of waste heat recovery and for cooling of various electronic devices [1]. $SrTiO_3$ based perovskites are among a number of candidate materials for such thermoelectric applications [2]. For the first time, we demonstrate the successful synthesis of $(1\text{-}x)SrTiO_3\text{-}xLa_{1/3}NbO_3$ ceramics that exhibit excellent thermoelectric properties and we have used STEM-EELS in order to assess the quantitative effects of composition on the structure and properties of these materials.

Ceramics with the composition $(1\text{-}x)SrTiO_3\text{-}xLa_{1/3}NbO_3$ (x=0.0, 0.1, 0.2, 0.3, 0.9 and 1) were synthesized by the mixed oxide route. Lattice images were obtained along <100> orientations using a Nion UltraSTEM100 aberration-corrected scanning transmission electron microscope (STEM) operated at 100kV to determine the precise crystal structure of the $La_{1/3}NbO_3$ end-member of this series and to visualize the cation and vacancy distribution in the lattice when the composition is varied. Electron Energy Loss Spectroscopy (EELS) chemical mapping was used to determine more quantitatively the distribution of cations in the structure.

Combining HAADF and EELS data for compositions 0.1<x<0.3 shows that the distribution of La and vacancies in the A-site of cubic $SrTiO_3$ is random. A-site vacancy rich columns, which are created in the structure because of the addition of A-site deficient $La_{1/3}NbO_3$, were clearly observed. No evidence of short range or long range ordering between Sr, La and vacancies was detected for 0.1<x<0. Similarly, the distribution of Nb in the B-site of the perovskite structure was found to be random. For the $La_{1/3}NbO_3$ end member and $0.9La_{1/3}NbO_3\text{-}0.1SrTiO_3$, it was found that the unit cell along c-axis is doubled ($c=2_{aperovskite}$) and there are two distinct lattice sites. One was determined to be fully vacant (A1-site) while the other site is shared between La and vacancies (A2-site). The A2-site sharing between La and vacancies is non uniform (Figure 1 and Figure 2). This is in contrast with the A2-site occupancy model for this structure, proposed from results obtained via x-ray techniques. It is shown that the diffuse diffraction spots observed in the [111] direction is due to a clustering of vacancies. The effect of the fabrication atmosphere on the Ti bonding will also be presented, through the analysis of EELS near-edge fine structure. [3].

References:
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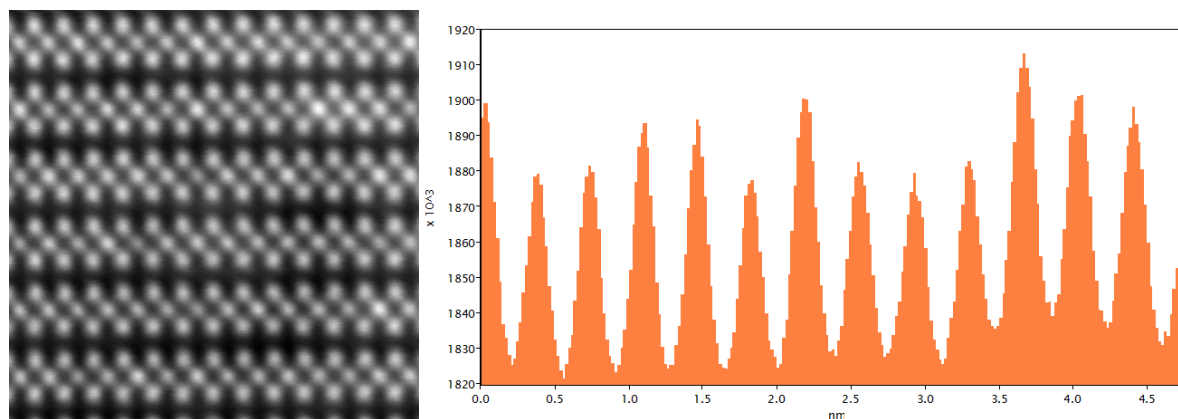
**Figure 1.** HAADF image and intensity profile along the A1 cation sites in the $La_{1/3}NbO_3$ en member demonstrating an apparently random distribution of La and vacancies.
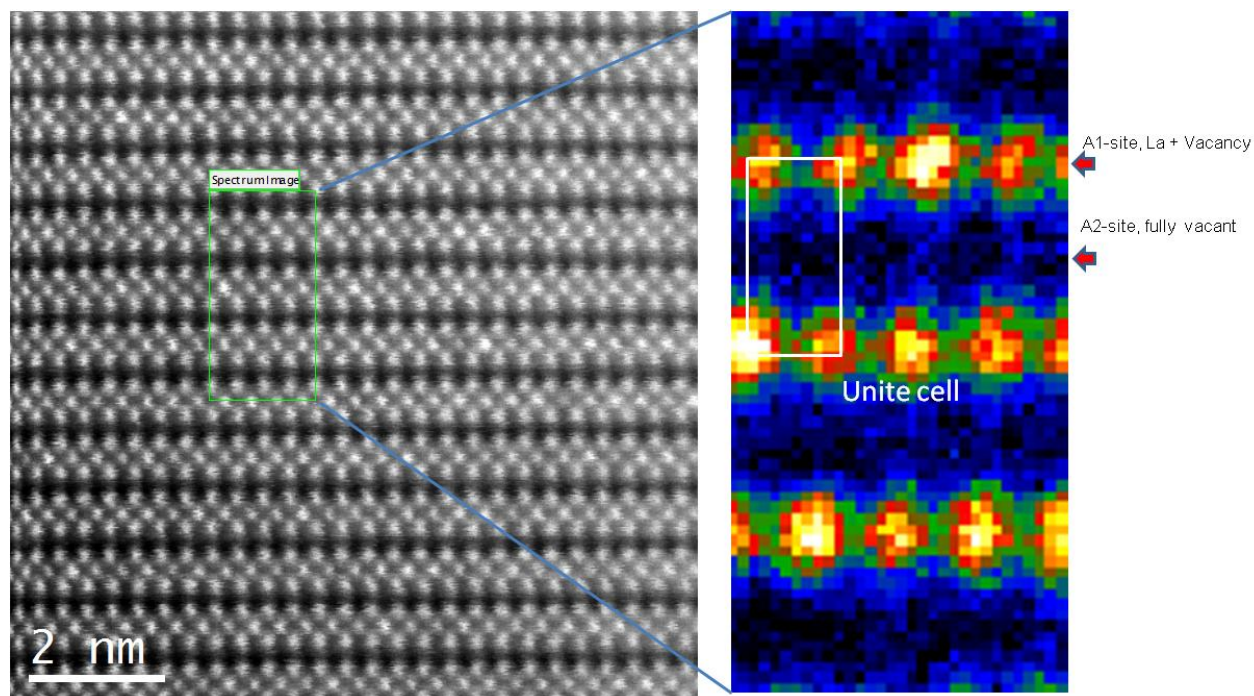


**Figure 2.** La EELS map confirming the intensity analysis: the site intensity distribution at the A1-site in the $La_{1/3}NbO_3$ en member is non-uniform while no intensity is observed at all at the A2-sites, suggesting they are fully vacant in this structure.