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Structural, Surface and Electrochemical studies of LaNbO_4 based Ionic Conductors

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Declaration

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

Cheng Li Date

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Abstract

In the search for novel solid oxide fuel cell (SOFC) electrolytes, research focus has shifted from conventional materials with high symmetry fluorite and perovskite structures, to those structures with anisotropic conducting paths and defective local environment. Amongst the novel fast ion conductors are the hyperstoichiometric modulated CeNbO_{4+d} phases, which have displayed remarkably oxygen diffusivity in the intermediate temperature region (500 °C to 750 °C). The oxidation of Ce^{3+} to Ce^{4+} , however, leads to undesirable electronic conduction. In addition, the structure and conducting mechanism of the modulated fergusonite phases has been left unexplored due to the structural modulation.

This work thus aims to investigate the crystal structure, phase evolution and transport properties of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$, a structural analogue to $\text{CeNbO}_{4.25}$. The hyperstoichiometric $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases ($x = 0.08\text{--}0.16$) adopt a $(3 + 2)\text{D}$ modulated structure, with cation ordering at the Nb/W site. Using the superspace group $I2/c(a_1,0,\gamma_1)00(a_2,0,\gamma_2)00$, the room temperature crystal structure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ has been refined using the Rietveld method with powder synchrotron diffraction data. The refined structure model suggests extended B-site coordination numbers, ranging from 6 to 8 with a 3 Å cut-off. The additional B-O bonds accommodate the variations in local environment and provide linkages between the NbO_x slabs, forming a 3D network similar to that in $\text{CeNbO}_{4.25}$. *In situ* neutron diffraction has revealed a sequence of structural transformations which has been overlooked in the literature. Compared with the undoped LaNbO_4 , the conductivity of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases is much improved, reaching $8 \times 10^{-3} \text{ S cm}^{-1}$ at 863 °C for $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$. ^{18}O tracer diffusivity measurements have confirmed oxygen ions being the major charge carriers, and an interstitial conducting mechanism has been proposed to explain the improved conductivity.

Despite the huge interest of utilising LaNbO_4 based materials for SOFC electrolyte application, their surface chemistry, which plays an important role in determining electrochemical performance, has been left unexplored. Surface chemistry of acceptor doped LaNbO_4 is investigated using LEIS and SIMS. A Nb and Sr enriched surface layer, approximately 6–7 nm thick, has been identified after annealing $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ at 1000 °C. Isotopic exchange experiments reveal a systematic decrease in isotopic surface concentration after the Sr enriched layer has developed at the surface, highlighting the impact of surface chemistry on the ion transport process.

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List of Acronyms

ASR	Area Specific Resistance
BSE	Backscattered Electron
CGO	$\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x}$
EDX	Energy-Dispersive X-ray Spectroscopy
e.s.d.	Estimated Standard Errors
GOF	Goodness of Fitting
HTXRD	High-Temperature X-ray Diffraction
IT-SOFC	Intermediate-Temperature Solid Oxide Fuel Cell
LEIS	Low Energy Ion Scattering
LNO	Lanthanum nickelate $\text{La}_2\text{NiO}_{4+d}$
LSM	$\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$
LSC	$\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$
LSCF	$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$
MIEC	Mixed Ionic-Electronic Conducting Materials
SE	Secondary Electron
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SOFC	Solid Oxide Fuel Cell
TEC	Thermal Expansion Coefficient
TEM	Transmission Electron Microscopy
ToF	Time-of-Flight
XRD	X-ray Diffraction
YSZ	Yttria-Stabilised Zirconia

Chapter 1. Background

1.1 Energy crisis and global warming

Our civilization has thrived on increasing energy consumption; the total energy demand has grown steadily over time ever since the industrial revolution (Figure 1-1) [1]. There has been a particularly sharp increase in the energy consumption in the past four or five decades, influenced by a significant increase in overall economic activity [2]. Despite the global economic downfall in 2008, the energy market keeps expanding, in part owing to the up-and-coming economies, such as India, whose electricity consumption per capita is still only half that of the global average, and China, which has more than doubled its domestic energy demand since the 1990s, which now seek to contribute further to the ever-growing energy demand [1]. In stark contrast to the growing demand, the resources available are limited. For instance, as reserves of North Sea oil and natural gas were being exhausted, their overall output declined swiftly during the late 1990s, after peak in annual offshore oil output of 400 million barrels in 1985. Furthermore, global oil production, which is generally believed to have peaked at around the year 2000, has long surpassed the rate at which we discover new oil reserves, posing obstacles for continuing economic growth [3].

Even more important than the economic implications are the environmental considerations, as the increase in energy demand puts a huge burden on the global ecosystem. In 2012 alone, more than 9 billion tons of greenhouse gas was released into the biosphere due to human activity [4], which continues to contribute to long term climate change. The human race has started to suffer from the impact of the global climate change: whilst Californians are experiencing one of the severest droughts ever recorded, the Maldives are struggling to keep their islands amidst the rising sea-level [5]. Climate change is a direct threat to the survival of our race. More climate abnormality is destined to come if we fail to limit our environmental

footprint [5]. Unfortunately human beings are far from creative when it comes to conceiving of new ways to generate energy; burning fossil fuels still constitutes the majority of energy generation. To reverse the trend on global climate change, it is imperative that we seek cleaner and more efficient methods for energy generation.

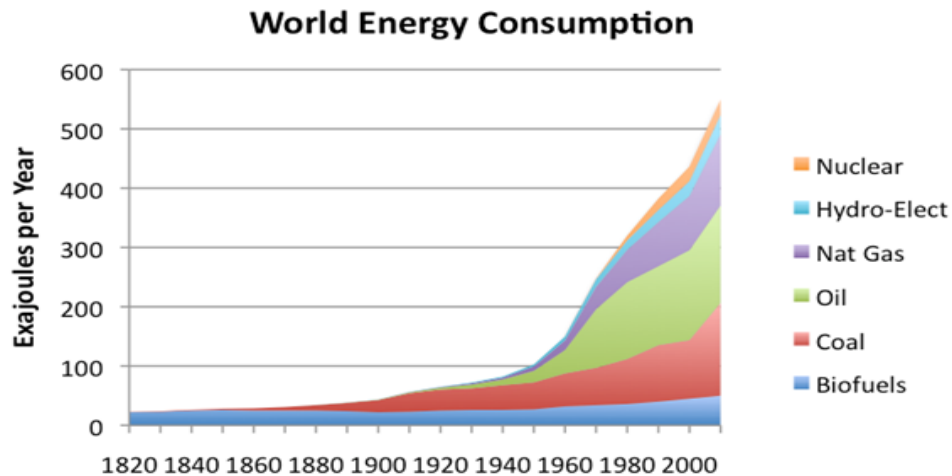


Figure 1-1: Global energy consumption from the industrial revolution to the 2010s. Total energy consumption has increased steadily over the past century, although we still rely heavily on fossil fuel nowadays [1].

1.1 Fuel cell—solution to future energy demand

A fuel cell is an electrochemical device that directly transfers the chemical energy stored in the fuel to electrical power in the grid [6]. Fuel cells are often much more efficient than combustion engines, due to the direct conversion without the combustion process [6]. The efficiency of the cell is not limited by its size, and a small local power generation system for combined heat and power is extremely efficient and desirable [7]. Comparing with conventional combustion engine, the construction of fuel cell stacks requires few moving parts, therefore reliable and long-lasting systems can be expected [8]. In addition, undesirable products such as NO_x , SO_x and particulates are low with fuel cells [7] providing additional environmental benefits. Fuel cells therefore have long been considered to be a systems that could potentially shift global energy generation, away from conventional fossil fuels such as coal, oil and natural gas, towards a cleaner and more sustainable approach [8]. Depending on the design, there are various fuel cell prototypes, such as proton exchange membrane fuel cell, phosphoric acid fuel, direct carbon fuel cell, and the focus of this work solid oxide fuel cell (SOFC).

1.1.1 Solid Oxide Fuel Cell (SOFC)

A solid oxide fuel cell has three main components (shown in Figure 1-2a): an anode, an electrolyte and a cathode. SOFCs utilize electrolytes that conduct oxide ions. The oxygen permeates through the porous cathode which reduces the oxygen to O^{2-} ions. The O^{2-} ions diffuse into the electrolyte across the electrolyte-cathode interface, and then migrate through the electrolyte to the anode side where the oxidation of fuel occurs. The diffusion of oxygen is driven by the difference in oxygen activity across the electrolyte. The electrolyte is electronically insulating therefore the electrical power of the overall reaction is harnessed through the external circuit connecting cathode and anode [9].

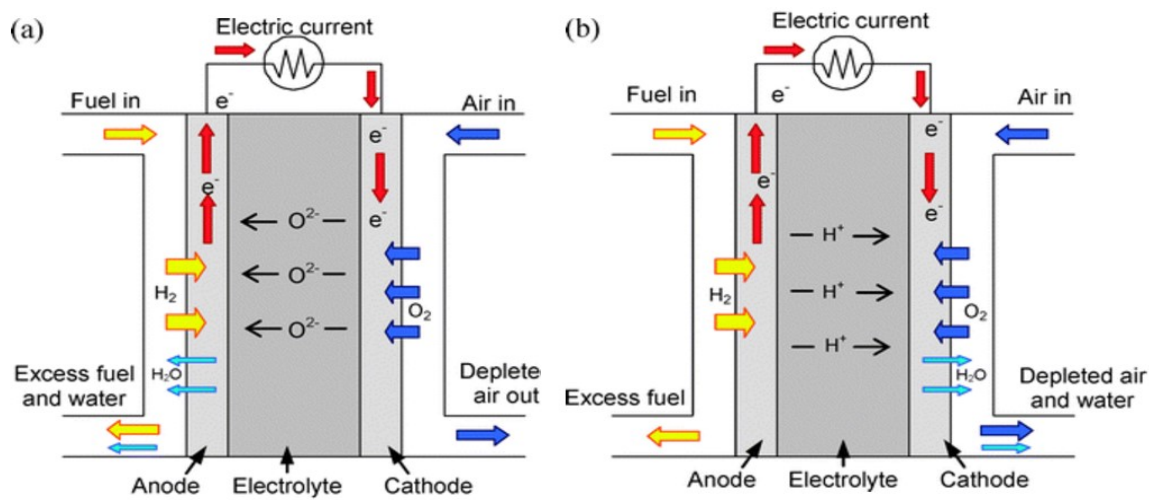


Figure 1-2: Schematics demonstrate the working principle of a SOFC with (a) oxide ion electrolyte and (b) a proton conducting electrolyte. Image is adapted from ref. [10].

Using H_2 as the fuel, the electrochemical reactions at cathode, anode and the overall reaction, are summarized as follows:



Alternatively, in a proton conducting fuel cell, protons, instead of oxygen ions, are transported through the electrolyte, after which they are combined with electrons from the external circuit and form water at the cathode side (shown in Figure 1-2b). Comparing with the fuel cell using an oxide ion conductor, dilution of the fuel at the anode is avoided and better efficiency is expected [9]. The overall reactions are summarized as follows:



1.1.2 Material requirements for fuel cell electrolytes

An operating time of 40000 h is targeted for SOFCs, hence long term stability is required for the fuel cell components [11]. The fuel side of the electrolyte is exposed to low oxygen partial pressures (often $pO_2 < 10^{-15}$ atm [12]), therefore stability under reducing conditions is required. In addition, chemical reaction between different components, which contributes to long-term performance degradation, must be avoided. Apart from that, mechanical compatibility between electrolyte and electrodes is also desirable for the enhancement of thermal cyclability [11]. Most importantly, the electrolyte must have high ionic conductivity combined with negligible electronic conduction under operating conditions. An area specific resistivity (ASR) of less than $0.15 \, \Omega \, \text{cm}^2$ (or $100 \, \Omega \, \text{cm}^2$ for a $15 \, \mu\text{m}$ thick electrolyte) is considered a prerequisite for SOFC electrolyte applications, above which the ohmic loss becomes unacceptable [13]. Limited by the ionic conductivity of the electrolytes, conventional SOFCs using yttria stabilized zirconia (YSZ) electrolyte often operate in the $800 \, ^\circ\text{C}$ to $1000 \, ^\circ\text{C}$ region, which leads to long start-up time and incompatibility at the electrolyte/electrode interface [13]. Furthermore, expensive interconnect components are required for high temperature operation which increases the total cost of fuel cell stacks [13]. Therefore, there is a huge economic incentive to reduce the operating temperature of fuel cells to the intermediate region ($500 \, ^\circ\text{C}$ to $750 \, ^\circ\text{C}$), which in turn poses further challenges to material design.

1.2 Fuel cell electrolyte materials

With the aforementioned stringent material requirements, only a few materials known are able to fulfil the task as fuel cell electrolyte. Conventionally, fluorite and perovskite related structures are used as SOFC electrolytes; however their performance is often restricted by their stability [14–16] as well as limited conductivity [14,17]. Advanced material systems must be explored to fulfil the increasing demands for SOFC electrolyte applications. Recent years have seen the research interest shift towards complex structures with anisotropic conducting pathways [18–21]. In the following section, both conventional electrolytes as well as novel electrolytes with complex structures will be reviewed.

1.2.1 Conventional fuel cell electrolytes

1.1.1.1 Electrolytes with fluorite structure

Fluorite is the classical crystal structure for oxygen ion conducting electrolytes. The structure, with a general formula AO_2 (where A is the tetravalent metal), has a near cubic oxygen sublattice with the cation occupying the alternating octahedral sites (Figure 1-3). Stoichiometric CeO_2 and UO_2 with their large cation size readily crystallise in the cubic symmetry [14], whereas the smaller Zr ion in ZrO_2 needs large dopants (typically Y_2O_3 , CaO or Sc_2O_3 [14,22]) to stabilise the cubic phase. The crystal structure is relatively open and has the capability to accommodate large degrees of distortion introduced by dopants and oxygen nonstoichiometry.

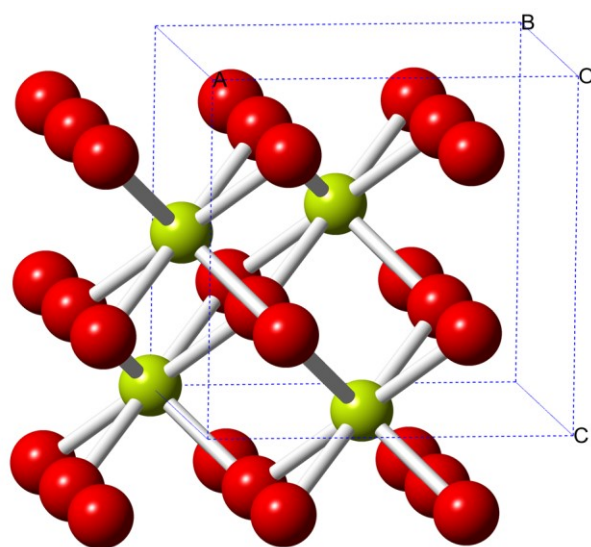


Figure 1-3: Crystal structure of stoichiometric fluorite. The red balls represent oxygen ions, the yellow balls are the tetravalent cations and the blue square represents the unit cell. The fluorite structure has simple cubic lattice with the cations occupying $\frac{1}{2}$ of the octahedral sites.

Stabilized ZrO₂

Stoichiometric ZrO₂ is monoclinic at room temperature and has very modest ionic conductivity [22]. Introduction of an aliovalent dopant such as Y³⁺, Yb³⁺ and Ca²⁺ helps to generate vacancies in the structure (Eqn. 2.10) which facilitate oxygen ion migration [14].



First inspection of Eqn. 1.1 might suggest that increasing dopant concentration is always beneficial for enhancing conductivity as more vacancies, which are the charge carriers in the system, are generated. However, there is an optimal Y₂O₃ dopant level (8 mol% to 11 mol%) above which association between oxygen vacancy and dopant becomes significant and the vacancies become immobile [23]. Similar effects has been observed with other dopants such as CaO and Sc₂O₃, which all have an optimal dopant level [23]. In addition to generating vacancies, the larger dopant stabilizes the high temperature cubic and tetragonal phase, which is only stable above 2340 °C for pure ZrO₂ [22]. With 8 mol% Y₂O₃ dopant, a tetragonal phase is successfully stabilized (YSZ) at room temperature [22]. Typically, the ionic conductivity for YSZ is approximately 0.1 S cm⁻¹ at 1000 °C [23] (Figure 1-4).

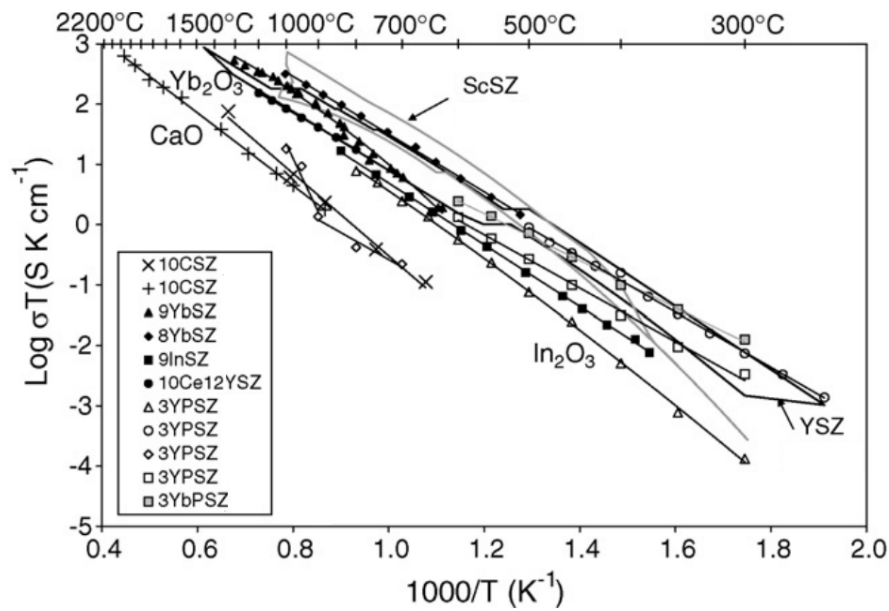


Figure 1-4: Arrhenius plot of ZrO₂ with different dopants. Amongst all the substitutions, Sc₂O₃ has the best performance. Detailed information for individual references of individual compositions can be found in [23]

YSZ with the optimal dopant concentration (around 8 mol% Y₂O₃, 8YSZ) suffers nontrivial decreases in conductivity over time [24]. The degradation is partly due to phase separation as the composition of 8YSZ is located in a two phase field under the typical fuel cell operation conditions [24]. Reduction of Y₂O₃ dopant content to 3 mol% results in improved stability

though at the expense of decreasing ionic conductivity thus requiring a higher operating temperature (800 °C to 1000 °C) [24]. Among all the possible dopants, Sc₂O₃ stabilized ZrO₂ (ScSZ) is a promising solution, which provides increased conductivity and stability compared to YSZ (Figure 1-4) [25]. The increased conductivity is attributed to the smaller mismatch between Sc and Zr, leading to a reduced defect association energy thus improvement of the oxygen mobility [23]. However, Sc is less abundant and much more expensive than Y₂O₃ [11], driving up the material cost for the fuel cell system. YSZ electrolytes are incompatible with lanthanum strontium manganite (LSM, a commonly used cathode) which forms blocking lanthanum zirconate layers [15] and thus further hinders its application as an SOFC electrolyte.

Doped CeO₂

Doped CeO₂ is also a commonly used electrolyte in SOFCs. Comparing with doped ZrO₂, it has better compatibility with cathode materials, and is often applied as an interlayer at the ZrO₂/cathode interface [26]. Comparing with YSZ and ScSZ, improvement in oxygen ion conductivity, particularly below 600 °C has been reported for Gd doped CeO₂ [23]. Similar to ZrO₂, aliovalent dopants are introduced to increase the oxygen vacancy concentration. Among the possible dopants, best performance is achieved with Gd and Sm doped CeO₂ (CGO and CSO) which again is explained in terms of small mismatch between the dopants and the lattice Ce [23,27]. A maximum conductivity is obtained with 20–25 mol% Gd₂O₃ dopant, reaching 0.01 S cm⁻¹ at 600 °C [28]. Further increasing the dopant concentration decreases the mobility of the oxygen vacancies, similar to that observed in doped ZrO₂ [28]. The major drawback of CeO₂ however is its non-negligible electronic conductivity, resulting from the reduction of Ce⁴⁺ to Ce³⁺ at low pO₂ [14]. No clear solution to reduce the electronic conduction has been presented.

δ-Bi₂O₃

Unlike other fluorite phases which require dopants to increase oxygen vacancy concentration, Bi₂O₃ intrinsically has ¼ of the oxygen sites vacant [29]. Due to its unique structure, the high temperature δ-Bi₂O₃ has an impressive oxygen ion conductivity of $\sigma = 2.3 \text{ S cm}^{-1}$ at 800 °C, amongst the highest ever reported [29]. However the oxygen diffusivity of Bi₂O₃ drops by 7 orders of magnitude when transforming into the low temperature α-Bi₂O₃ phase [30]. Consequently, pure Bi₂O₃ has only a small window of operation between the α-δ phase transition temperature at 730 °C and its melting point at 817 °C [31]. Many efforts have been

made to stabilize the high temperature structure using WO_3 , Y_2O_3 and Gd_2O_3 , although the resultant structures generally have significantly lowered ionic conductivity [32,33].

1.1.1.2 Electrolytes with perovskite structure

The crystal structure of an ideal cubic perovskite is shown in Figure 1-5. It has a general formula of ABO_3 and is one of the most well studied solid state systems [34]. An ideal cubic perovskite has two cation sites: the larger A cation is coordinated with 12 oxygen ions whereas the smaller B cation, often a transition metal, sits in the centre of a BO_6 octahedron. The structure is quite accommodating and can facilitate almost all of the elements in the periodic table [35], although departure from the ideal A/B ionic radius ratio often results in the distortion and rotation of the BO_6 polyhedra [34]; as a result, the crystal structure deviates from the perfect cubic symmetry [34].

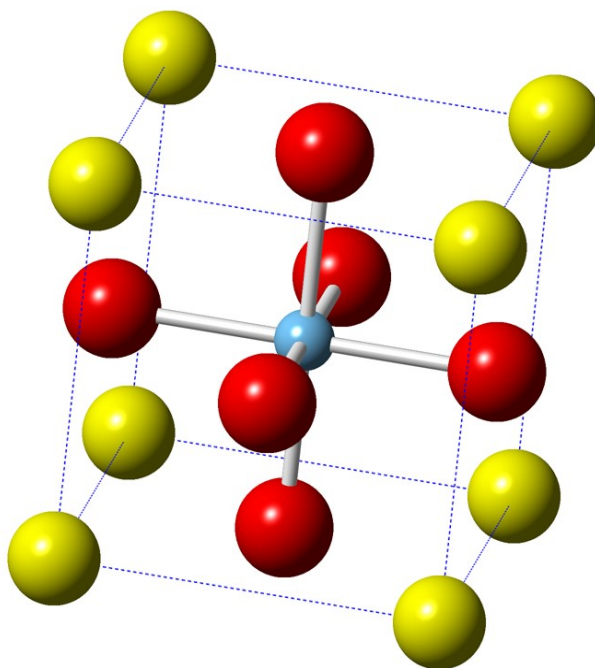


Figure 1-5: Crystal structure of an ideal cubic perovskite; the red, yellow and blue spheres represent oxygen ions, larger A site cations and smaller B site cations, respectively. The A site is coordinated with 12 oxygen ions whereas the B site is coordinated with 6 oxygen ions in the ideal cubic perovskite.

LaGaO₃ based electrolytes

For LaGaO_3 based perovskite, co-doping of Sr at the La site and Mg at the Ga site has been identified as the most efficient method to improve oxygen ion conductivity [36]. Total conductivity of 0.1 S cm^{-1} at 800°C has been reported for $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-d}$ (LSGM) [37], which is comparable to that of ScSZ. Furthermore, it has been demonstrated that the electrical contribution to the total conductivity is negligible when $p\text{O}_2$ varies from 1

to 10^{-20} atm at 800 °C [36]. However, loss of Ga under low oxygen partial pressures, followed by permanent reduction in ionic conductivity is problematic [11]. In addition, LSGM reacts with Ni, the most commonly used anode material, forming a LaNiO_3 and $\text{LaSrGa}_3\text{O}_7$ impurities which are detrimental for the whole cell performance [38]. Phase separation of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-d}$ into La_4SrO_7 and SrLaGaO_4 has been reported after heating at 1000 °C, posing concern for the long-term stability of this electrolyte [16].

$\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$

Most recently, it was discovered that the large leakage currents in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT), a well-known lead-free piezoelectric material, was due to oxygen ion conduction [39]. Doping on the Ti site with 1 at% Mg [39], yielding $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.99}\text{Mg}_{0.01}\text{O}_{3-d}$, further increases the ionic conductivity to a maximum of 0.01 S cm^{-1} at 600 °C [39]. Interestingly, the conduction is suppressed in samples with 1 at% Na deficiency, which supposedly also contains oxygen vacancies. The Na deficient samples with nominal composition $\text{Na}_{0.49}\text{Bi}_{0.5}\text{TiO}_{3-d}$ have a total conductivity of $1.6 \times 10^{-6} \text{ S cm}^{-1}$ at 600 °C, three orders of magnitude lower than that of the stoichiometric phase [40]. The conductivity seems to be limited by the low defect concentration and further optimisation of the chemical composition as well microstructure is required for future study.

BaCeO_3 and BaZrO_3 based proton conductors

Acceptor doped perovskites with the general formula $\text{AB}_{1-x}\text{M}_x\text{O}_{3-d}$ (where A = Ca, Sr, Ba, B = Ce, Zr, Ti, Sn, M = Y and Gd) were the first oxide system investigated extensively for proton conduction [41]. To form the mobile proton species, water from the gas phase is disassociated into a hydroxyl group and a proton; the hydroxyl group occupies an existing vacancy site, which is created to compensate the acceptor dopant with a process similar to Eqn. 2.10; the disassociated proton forms a covalent bond with a lattice oxygen, creating another hydroxyl group [41]. The overall reaction is shown in Eqn. 1.2:



The proton diffusion involves two steps: a rotational motion of proton defects followed by a jump to a nearby oxygen site. Both experiment [42] and simulation [43] suggest that the proton transfer reaction between two lattice oxygen ions is the rate limiting step for long range diffusion. There is still uncertainty in terms of the optimized composition for perovskite based proton conductors, and the reported conductivity data are scattered due to the wide variations of processing conditions and characterization methods [42,44–48]. In general, the

highest proton conductivity of $10^{-1} \text{ S cm}^{-1}$ to $10^{-2} \text{ S cm}^{-1}$ in the 500–600 °C range was reported for 10-25 mol% Y or Gd doped BaCeO_3 and BaZrO_3 [49]. Most recently, there was report of very high bulk conductivity of 0.11 S cm^{-1} at 500 °C in the $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-d}$ thin film electrolyte prepared by pulsed laser deposition [50], providing new strategies to manufacture perovskite based proton conductor.

Unfortunately, BaCeO_3 based electrolytes, which afford the highest proton mobility amongst solid state proton conductors, are not stable in wet or CO_2 containing environments as they readily decompose into hydroxide and carbonate, rendering them unfit for device applications [51]. BaZrO_3 based electrolytes have much improved chemical stability, although their conductivity is about one order of magnitude lower than the BaCeO_3 phase [42,48]. In addition, poor sinterability and high grain boundary resistivity of BaZrO_3 still poses issues for its application. Without the application of advanced manufacturing methods such as spark plasma sintering or hot pressing, sintering temperatures above 1600 °C are often required to obtain dense BaZrO_3 samples [48]. In addition, the grain boundary conductivity is often reported to be 3 - 4 orders of magnitude lower than that of the grain bulk under a wet atmosphere in the 400°C to 500 °C range, restricting the overall performance of the electrolytes [17,52]. The low grain boundary conductivity is often related to the space charge layer at the grain boundary; it is suggested that a positively charged core forms at the grain boundary, which attracts acceptor dopants and creates a proton depletion zone in the near grain boundary region [17,53]. The proton charge carriers have reduced mobility in the depletion zone, leading to a poor specific grain boundary conductivity [17], which is still an unresolved issue for perovskite based proton conductors.

1.2.2 Novel electrolyte materials with complex structure

Conventionally, a large number of equivalent positions is considered a prerequisite for fast ion diffusion [54] and therefore crystal structures (such as fluorite and perovskite phases) with cubic or near cubic symmetry which allow more symmetry-related equivalent sites are sought after for electrolyte applications [14,54]. However, as demonstrated earlier in section 1.2.1, the performance of conventional electrolytes is often limited by their conductivity, stability or availability and new crystal families need to be explored in the search for novel electrolyte materials.

Recently, various anisotropic structure prototypes, including the apatite family [55–57], $\beta\text{-La}_2\text{Mo}_2\text{O}_9$ (LAMOX phase) [20,21] and the hyperstoichiometric melilite structure [18,19],

have been identified to be fast ion conductors. In other cases, fast ion diffusion is realised in a highly complex modulated structure, such as that observed in hyperstoichiometric fergusonite CeNbO_{4+d} phases [58,59]. Unlike the conventional fluorite or perovskite based electrolytes, these novel electrolytes with anisotropic diffusion pathways offer superior ionic conductivity and inspire new concepts for electrolyte design. In the following section, the literature reports on these novel ion conductors with complex structures are reviewed.

1.1.1.3 Apatite family

Chemical compositions of the apatite family can generally be described as $[\text{A}^{\text{I}}]_4[\text{A}^{\text{II}}]_6[(\text{BO}_4)_6][\text{X}]_n$, in which both A^{I} and A^{II} are rare earth or alkaline earth elements that occupy different crystallographic sites, whereas $\text{B} = \text{Ge}, \text{Si}$ or Al and $\text{X} = \text{O}, \text{Cl}, \text{OH}$ and other anion groups [55,60]. Apatites are constructed of an $\text{A}^{\text{I}}_4[(\text{BO}_4)_6]$ framework around the $[001]$ channel (Figure 1-6a). The diameter of the channel is adjusted by the size of the $[\text{A}^{\text{II}}]_6[\text{X}]_2$ hexagonal ring (the red and black ions in the centre of Figure 1-6a) which occupies the tunnel. Introduction of substitution is facilitated by rotating triangular faces of the $[\text{A}^{\text{I}}\text{O}_6]$ with a twisting angle ϕ which leaves the B site coordination essentially undistorted [60].

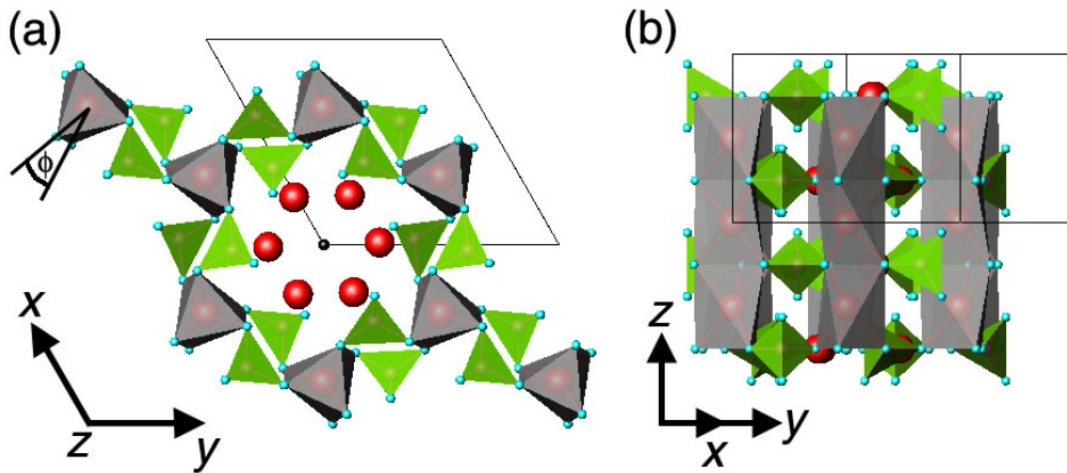


Figure 1-6: Crystal structure of $\text{La}_8\text{Sr}_2(\text{GeO}_4)_6\text{O}_{2-d}$ apatite viewing from (a) $[001]$ direction and (b) $[100]$ direction from ref. [60]. The La and Sr are randomly distributed across the $[\text{A}^{\text{I}}]$ and $[\text{A}^{\text{II}}]$, with the former site shown as the grey polyhedra and the latter represented by the red sphere. The black square shows the unit cell. A twisting angle ϕ (shown in (a)) in the triangular faces of the $[\text{A}^{\text{I}}\text{O}_6]$ is introduced, leaving the B site tetrahedra (green) effectively undistorted.

Among all the possible compositions, La based oxygen excess apatite such as $\text{La}_{10}(\text{GeO}_4)_6\text{O}_3$, $\text{La}_{10}(\text{SiO}_4)_6\text{O}_3$ and $\text{La}_{9.75}\text{Sr}_{0.25}(\text{SiO}_4)_6\text{O}_{3-d}$ have the highest reported conductivity (summarised in Figure 1-7) [61]. The large La ion is believed to enhance the conductivity by expanding the tunnel along which the interstitials diffuse [62,63]. A total conductivity of 0.14 S cm^{-1} at 950°C with good reduction stability down to $p\text{O}_2 = 10^{-21} \text{ atm}$ was reported for $\text{La}_{10}(\text{GeO}_4)_6\text{O}_3$

[62]. Due to the anisotropic nature of the structure, the ionic conduction in apatites is expected to be favoured along the [001] tunnel direction. Indeed, various authors have reported higher conductivity parallel to the c -axis, comparing with the directions perpendicular to the tunnel [64–66]. Nakayama et al., for instance, reported that the conductivity of $\text{Pr}_{9.33}(\text{SiO}_4)_6\text{O}_2$ along the c -axis is $1.3 \times 10^{-2} \text{ S cm}^{-1}$, which is an order of magnitude higher than the conductivity perpendicular to the c direction ($1.2 \times 10^{-3} \text{ S cm}^{-1}$) [64].

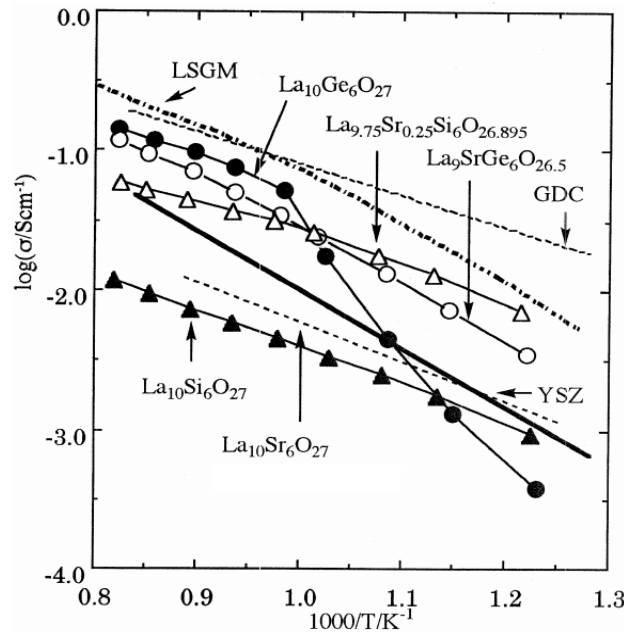


Figure 1-7: Arrhenius plot of the conductivity of silicate and germinate apatites in comparison to conventional electrolytes [62]. Comparing with the YSZ benchmark, superior conductivity was reported for apatites.

The intra-tunnel migration of oxygen might contribute considerably to the total conductivity, especially in the germanate apatites [55]. After investigating the structure of $\text{La}_{10}(\text{GeO}_4)_6\text{O}_3$ using neutron diffraction, Pramana et al. [55] proposed that the composition was better described as $\text{La}_{10}(\text{GeO}_4)_5(\text{GeO}_5)\text{O}_2$ in which the two interstitial oxygen ions were preferably residing at the tunnel wall. The relaxation around the interstitial oxygen transiently converts GeO_4 tetrahedra to GeO_5 bi-pyramids which serves as a reservoir and enables the diffusion in-between tunnels [55]. Similar distortion of SiO_4 to SiO_5 was reported for $\text{La}_8\text{Sr}_2(\text{SiO}_4)_6\text{O}_2$ [67,68], highlighting the importance of local defect structure. A detailed summary of the conductivity of the apatite families can be found in the literature [63,69].

1.1.1.4 β -La₂Mo₂O₉ (LAMOX phase)

Fast ion conductivity in β -La₂Mo₂O₉ phase (LAMOX) was first reported by Lacorre and co-workers; a total ionic conductivity of $6 \times 10^{-2} \text{ S cm}^{-1}$ at 800 °C was reported for the stoichiometric β -La₂Mo₂O₉ which is higher than that of the YSZ benchmark [20]. A phase transition occurs at approximately 580 °C, forming the low temperature α -La₂Mo₂O₉ phase whose conductivity is almost two orders of magnitude lower than β -La₂Mo₂O₉ [20,21].

The lone-pair substitution (LPS) theory has been proposed to explain the seemingly counterintuitive fast ion conduction observed in the LAMOX phase [70]. The concept is built upon the observation that the electronic lone-pair occupies a volume similar to O²⁻ or F⁻ anions. It was speculated that a vacancy is created when replacing a lone-pair cation with a non-lone-pair cation [70]. The crystal structure of β -La₂Mo₂O₉ resembles that of the β -SnWO₄ [20,70] in which Sn contains an electron lone pair. After complete substitution of Sn with La, the LAMOX structure is better described as β -La₂Mo₂O₈₊₁□₁, indicating that one of the oxygen ions is located in the lone-pair position whereas the other lone-pair induced “vacancy” is vacant and available to facilitate fast ion conduction [70]. Albeit an interesting concept, the LPS relies on the assumption that the lone-pair space will be left undistorted when substituting the lone-pair ions. However, it is well known that a lone-pair exerts a stronger repulsive force than O²⁻, and the presence of a lone-pair is often accompanied with a significant distortion of the local symmetry [71,72]. In PbO, for instance, all four of the coordinating oxygen ions are pushed to one side whereas the lone-pair of Pb is projected towards the opposite direction [72]. Therefore, when substituting the lone-pair cation, reconstruction of the local structure is to be expected, and consequently the linkage between the two structures is disturbed.

Another feasible explanation to the high ionic conductivity of β -La₂Mo₂O₉ is its highly defective local structure [73,74]. The low temperature α -La₂Mo₂O₉ phase was solved with a $2 \times 3 \times 4$ expansion of the high temperature β -La₂Mo₂O₉ phase with 312 unique crystallographic positions [73]. The refinement showed a highly varied Mo coordination local environment (Figure 1-8a and b), with a mixed coordination number ranging from 4 to 6 [73]. The varied environment was considered to be a key factor to facilitate fast oxygen diffusion pathways, as both dielectric relaxation studies [75] as well as molecular dynamics simulation [76] indicated that all the available sites participated in the conduction process. Detailed examination of the ordered array of the 216 oxygen positions in α -La₂Mo₂O₉ indicated they were related to the average site occupancy of the high temperature structure: when collapsing

the supercell to the high temperature β - $\text{La}_2\text{Mo}_2\text{O}_9$, a good correlation between the two phases has been identified (Figure 1-8a and b). It is therefore proposed to visualise the β - $\text{La}_2\text{Mo}_2\text{O}_9$ phase as a dynamic time-average of the low temperature α - $\text{La}_2\text{Mo}_2\text{O}_9$ phase, and the defect local structure is inherited by the high temperature phase [73]. The proposition is echoed by the pair distribution function (PDF) analysis of neutron scattering data which reveals a remarkable similarity between the α - and β - $\text{La}_2\text{Mo}_2\text{O}_9$ phases (Figure 1-8c): the local structure of the two phases are almost identical, indicating that rather than a redistribution of the oxygen ions, the α to β phase transition serves to initiate a transit from a stable to a dynamic oxygen lattice [74].

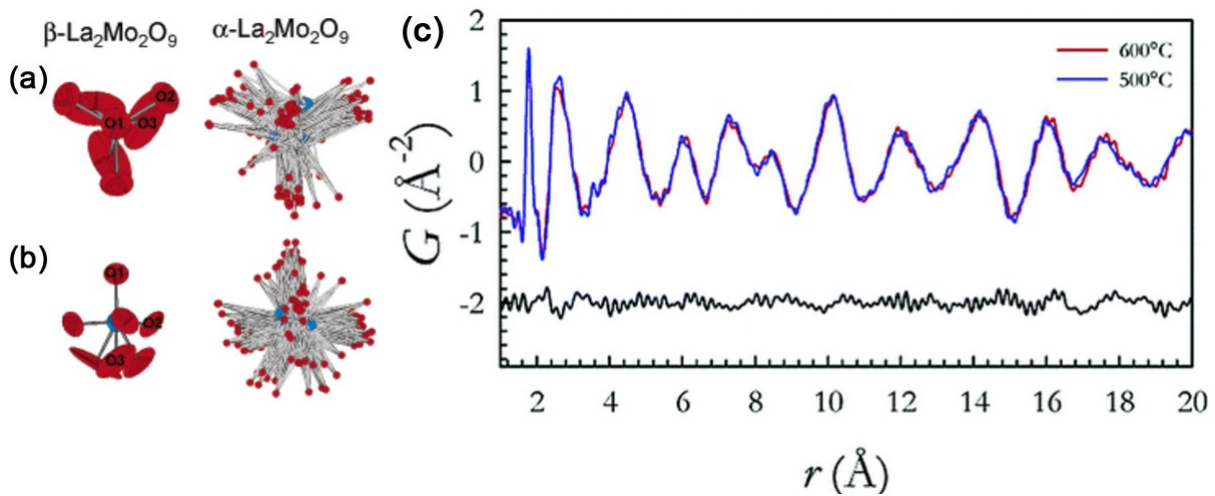


Figure 1-8: Comparison of the Mo coordination environment in α - and β - $\text{La}_2\text{Mo}_2\text{O}_9$, from two mutually perpendicular directions as in (a) and (b)[73]. For β - $\text{La}_2\text{Mo}_2\text{O}_9$, the thermal ellipsoids at 50% probability is shown; for α - $\text{La}_2\text{Mo}_2\text{O}_9$ the superposition of all the independent Mo atoms is plotted. The β - $\text{La}_2\text{Mo}_2\text{O}_9$ can be visualized as a dynamic time average of the low temperature α - $\text{La}_2\text{Mo}_2\text{O}_9$ phase. PDF analysis in (c), highlights the similarity of the local structures between the α - $\text{La}_2\text{Mo}_2\text{O}_9$ at 500 °C and β - $\text{La}_2\text{Mo}_2\text{O}_9$ at 600 °C [74] .

The high Mo^{6+} content unfortunately leaves the material susceptible to reducing atmospheres: in a 5% H_2 /95% Ar mixture, decomposition of $\text{La}_2\text{Mo}_2\text{O}_9$ was observed after annealing at 650–750 °C for 24 h and longer reduction leads to amorphous structures [77]. Many attempts were made to enhance the redox resistance, for instance W substitution was shown to increase the stability limit of the LAMOX phase although the conductivity is inferior compared with the parent phase [77,78].

1.1.1.5 Layered melilite structure

Another hyperstoichiometric oxygen ion conductor is the series of materials that adopts the melilite structure. Melilite has a general formula of $[A]_2[B^I]_2[B^{II}O_7]_2$ in which A is occupied by large divalent alkaline earth or lanthanides and the smaller B sites are occupied by smaller ions (e.g. Si^{4+} , Ga^{3+} , Zn^{2+} , Co^{2+} and Ge^{4+}) [79,80]. The B site polyhedra have two distinctive environments, $B^{II}O_7$ tetrahedral dimers (coloured grey in Figure 1-9) and B^IO_4 tetrahedra (orange in Figure 1-9) which share corners with four neighbouring $B^{II}O_7$ dimers. Overall, B site cations create an extended two-dimensional network which is separated by the interlayer A site (Figure 1-9b) [79]. The mismatch between the layers is accommodated by the rotation of the polyhedra coupled with the displacement of the A site ion, which might lead to incommensurate structures in the melilite family [79–81].

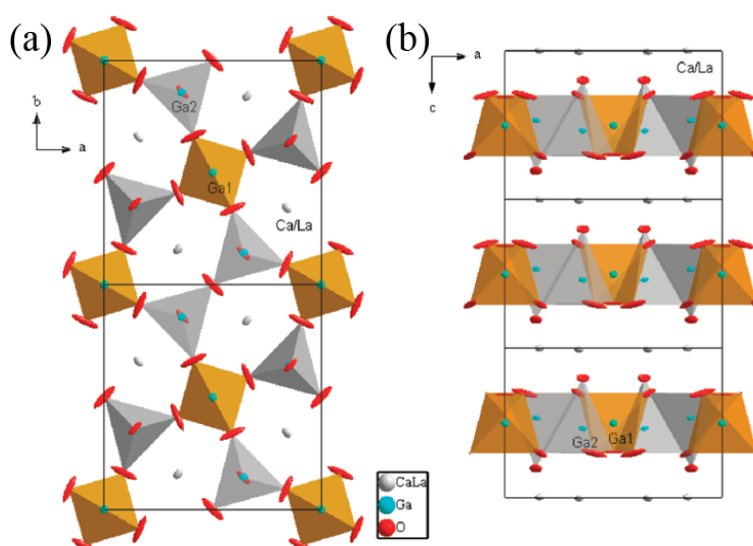


Figure 1-9: Crystal structure of the $[CaLa]_2[Ga]_2[Ga_2O_7]_2$ melilite viewing from (a) $[001]$ and (b) $[010]$ directions. Small Ga cations have two environments, $Ga_2^{II}O_7$ dimers coloured grey and Ga^{IO}_4 tetrahedra coloured orange. The B site polyhedra form a layered network which is separated by larger Ca/La cations as shown in (b). The thermal ellipsoids are drawn with 50% probability, and the black square represents the unit cell [79].

Layered gallium melilites doped with lanthanides have high interstitial oxygen content and thus have good ionic conductivity [18,19]. The interstitial oxygen ions partially occupy the “channel” in the B_3O_7 layer, causing local structures to relax [18]. Unlike the apatite family, in which the BO_4 polyhedra are completely isolated and therefore are not restricted by B-O-B bridging, only $B^{II}O_7$ have a non-bridging terminal in the melilite structure (grey sites in Figure 1-9). Therefore, B^{II} sites have the required flexibility and interstitials are solely bound to B^{II} [18]. The oxygen excess $[Sr_{0.46}La_{1.54}]_2[Ga]_2[Ga_2O_{7.27}]_2$ has a total conductivity of 0.02 S cm^{-1} to 0.1 S cm^{-1} from 600 °C to 900 °C, which surpasses the

$[\text{Sr}_{0.95}\text{La}_{1.05}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_{7.025}]_2$ by two orders of magnitude [82], highlighting the importance of interstitial concentration. Pure oxygen ionic conductivity is maintained within oxygen partial pressures range from 1 to 10^{-24} atm, showing good stability [18]. Due to the relaxation about the interstitial oxygen located in the channel, anisotropic conduction has been reported. At 850 °C, the conductivity along the *ac* plane was reported to be 0.036 S cm^{-1} whereas the conduction perpendicular to the tetrahedron plane is only 0.008 S cm^{-1} for the $[\text{Ca}_{0.50}\text{La}_{1.50}]_2[\text{Ga}]_2[\text{Ga}_2\text{O}_{7.25}]_2$ composition [83].

1.3 Summary

Fuel cell technology provides a scalable, high efficiency and low emission solution to the global energy demand, although there are still significant challenges to overcome before fuel cells can become commercially viable on a large scale. One of the major issues is to enhance the performance of the SOFC electrolytes so that the operating temperature of SOFCs can be reduced to the intermediate temperature region. However, the application of conventional electrolytes with perovskite and fluorite structures is often restricted by their stability [14–16], availability [11] as well as limited conductivity [14,17]. As such, advanced materials systems need to be explored in the search for new SOFC electrolytes.

Recent years have seen a shift in research interest towards materials with complex structures such as the apatite families [55], the LAMOX phases [20] and the melilite families [18]. With their highly deformed local structure and anisotropic conducting paths, these unique structures offer superior ionic conductivity in comparison to conventional electrolytes. Recently, another structural prototype namely the hyperstoichiometric modulated CeNbO_{4+d} phases, with fergusonite/scheelite structure, have received great interest due to their remarkable oxygen ion diffusivity at low temperature [58,59]. In the next chapter the structure, electrical properties and the surface chemistry of scheelite related ionic conductors will be reviewed.

Chapter 2. Literature Review

In the previous chapter, the broader context and background to the research was introduced and it was concluded that advanced material systems must be explored to fulfil the material property requirement for the SOFC and PCFC electrolyte application. Most recently, the fergusonite/Scheelite related materials, with the general formula $(A_{1-x}A_x')B_{1-x}B_x'O_4$, where A, A' = K, Na, Li, Rb, Ag, La, Ca, Sr, Ba, rare earths or vacancy and B, B' = Mo, W, V, Nb among others, have attracted considerable research interest due to their applications as catalysts [84], microwave dielectrics [85], oxide ion conductors [86–88], and optical devices [89–91]. The application of fergusonite related structure solid oxide electrolyte is especially promising as the structure affords remarkable oxygen diffusivity ($CeNbO_{4+d}$ has an oxygen diffusivity around $10^{-7} \text{ cm}^2\text{s}^{-1}$ at 650 °C) [58]. Current project aims to further investigate the crystal structure, transport properties and surface chemistry of $LaNbO_4$ based oxide ion and proton conductors, with the fergusonite crystal structure.

In this chapter, the prototypical crystal structure of fergusonite and its high temperature polymorph, scheelite, is first introduced. Using $LaNbO_4$ as an example, the phase transition between the two polymorphs is discussed. Following that, scheelite related materials with a modulated structure are introduced. Structural modulation is a common theme in the scheelite related materials, and understanding the modulated structure provides the necessary starting point for understanding thus optimizing the properties. Literature reports on the oxide conductivity as well as proton conductivity of scheelite related materials are reviewed, highlighting the state-of-art performance of the scheelite related electrolytes and the limitations for further property optimisation. Finally, the surface chemistry, which has significant impact on their electrochemical properties, of the scheelite related materials is discussed, pinpointing discrepancies in the available literature.

2.1 ABO₄ compounds with the scheelite and fergusonite structures

The ABO₄ formula is very versatile and can facilitate various crystal structures depending on the ionic size and valence of the A and B site cations [92]. Among all the possible crystal structures, this work focuses on the fergusonite and scheelite structures due to their potential applications as ionic conductors [93,94]. The crystal structure and phase transition of LaNbO₄ grants a general description of the crystal structure which is characteristic of the other scheelite related materials [95]. Pure LaNbO₄ has two polymorphs, a low temperature monoclinic fergusonite phase (*m*-LaNbO₄, space group 15, *I*12/*c*1, Figure 2-1a) and a high temperature scheelite phase (*t*-LaNbO₄, space group 88, *I*114₁/*a*, Figure 2-1b) [95,96]. The key difference in symmetry is the four-fold screw axes in *t*-LaNbO₄ phase which corresponds to the two-fold axes in *m*-LaNbO₄. When approaching the phase transition temperature, the lattice parameters of the monoclinic phase a_m and c_m converge towards a_t whereas the β angle approaches 90° [97].

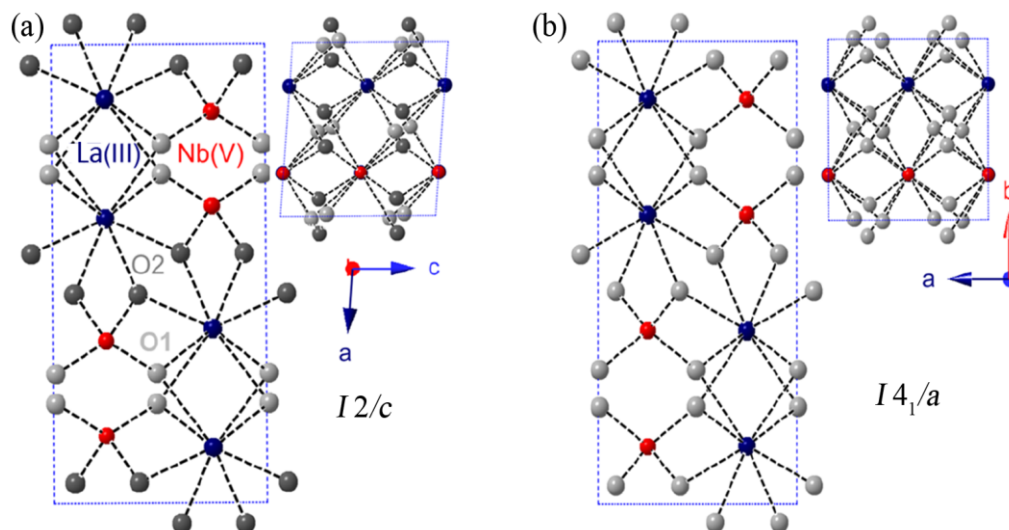


Figure 2-1: Schematics highlighting the polyhedral network of (a) *m*-LaNbO₄ and (b) *t*-LaNbO₄. Two structures have similar polyhedron linkage and a phase transition from monoclinic to tetragonal is achieved by shearing in the a/b plane of the tetragonal phase.

The low temperature fergusonite structure of LaNbO₄ is characterized by the isolated distorted NbO₄ tetrahedron, linked by LaO₈ decahedra (Figure 2-1a). All of the eight oxygen ions in the LaO₈ decahedron are corner shared with NbO₄, whereas the LaO₈ polyhedra share one edge each with four adjacent decahedra [97]. The NbO₄ tetrahedra have two pairs of Nb-O bond distances (coloured differently in Figure 2-1a), and with increasing temperature the difference between them becomes smaller and reduces to 0 above the phase transition temperature [97]. It is worth noting that the fergusonite and scheelite phases are closely

related as the NbO_4 polyhedra have the same linkage network in the two phases (Figure 2-1a and b). The transition between the structure can be envisaged as distortion along the $a_t b_t$ plane in the tetragonal phase, creating the compressed c_m and elongated a_m in the monoclinic phase [95,97]. In the following sections, the term “scheelite related materials” refers to the collection of compositions which adapts either the fergusonite or scheelite structure at room temperature. The stand-only usage of fergusonite or scheelite refers to the specific structure type.

2.2 Modulation in scheelite and related structures

Many of the scheelite related materials adopt a modulated structure, a complex type of structure with hidden symmetry that requires a superspace approach to describe. In order to better understand the crystal structure of the scheelite related material, the basic concept of structural modulation and superspace is introduced, laying the foundation for future discussion. The common feature of the modulated scheelite structures, namely modulation wave(s) that propagates along the $a_t b_t$ plane ($a_m c_m$ plane if the crystal has the monoclinic symmetry), is introduced. The impact of structural modulation on properties is highlighted.

2.2.1 Basics of Structure modulation

The Oxford English Dictionary defines a crystal as an “ordered, three-dimensional arrangement of atoms or molecules within the body of the solid” [98]. Indeed, translational symmetry, thus long-range ordered, in the solid is conventionally considered a prerequisite for the definition of “*crystal*”. In normal crystals the exact same environment is found by moving along any lattice vector [99] (schematically shown in Figure 2-2a).

However it is realized that the crystalline symmetry can also be achieved in a different fashion. Considering the structure showcased in Figure 2-2b, all the atoms are displaced along the a -axis and the magnitude of the displacement is determined by a periodic wave function, which has the atomic position in the original crystal as its sole argument. This wave function is termed as a *modulation function*. In the crystal shown in Figure 2-2b, the period of the function is $3a$. A superlattice, with the same periodicity of the displacive wave function, can be created to fully describe the structure. Alternatively, the new crystal is described by the superimposition of the original structure (also called the *parent structure*) and the modulation wave, leading to the notion of a *commensurate modulated* structure [100]. Building upon the structure shown in in Figure 2-2b, one can easily imagine a situation where

the periodicity of the modulation wave does not match any integer number of the original lattice (Figure 2-2c), resulting an *incommensurate modulated* structure. In this case, all the atoms in the crystal have different environment due to the incompatible periodicity between the modulation wave and the crystal lattice [100] and consequently the translational symmetry of the original crystal breaks down. Remarkably, the translational symmetry of this type of the crystal is preserved in the reciprocal space (Figure 2-2d): the modulation wave manifests itself as additional diffraction spots (often termed as *satellite reflections*) in the diffraction experiment, indicating the hidden symmetry operators.

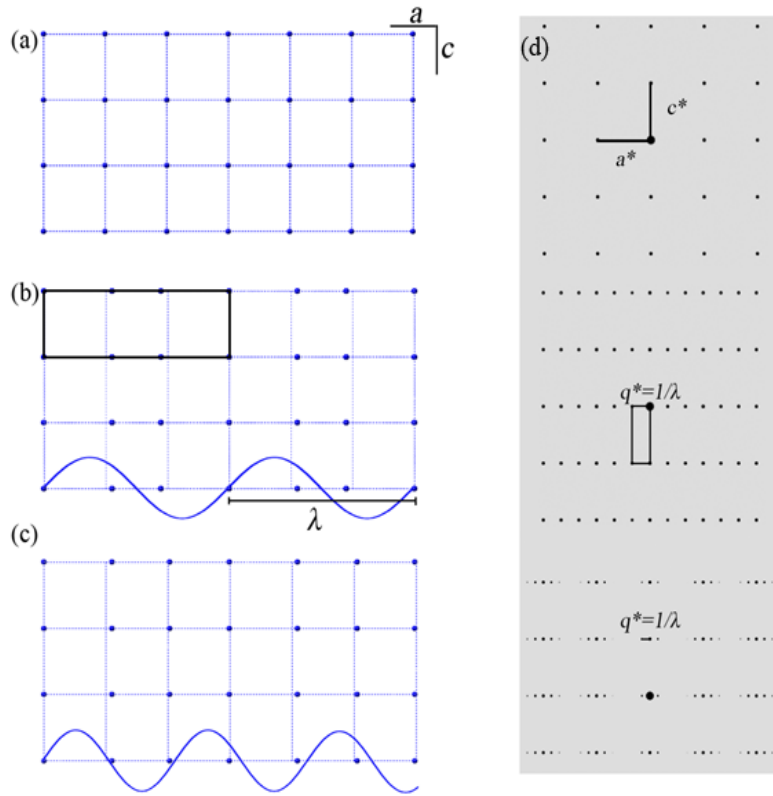


Figure 2-2: Schematics demonstrating the differences between (a) a normal crystal lattice (b) a commensurate modulated crystal with the displacive modulation along the a -axis and (c) an incommensurate modulated lattice. Their corresponding diffraction patterns are shown in (d). The dotted blue squares are the original unit cell, the black square shows the supercell in the commensurate case, and the waves in the bottom of the lattice describes the magnitude of displacement of individual atoms. The translational symmetry of the incommensurate structure is preserved in the reciprocal space.

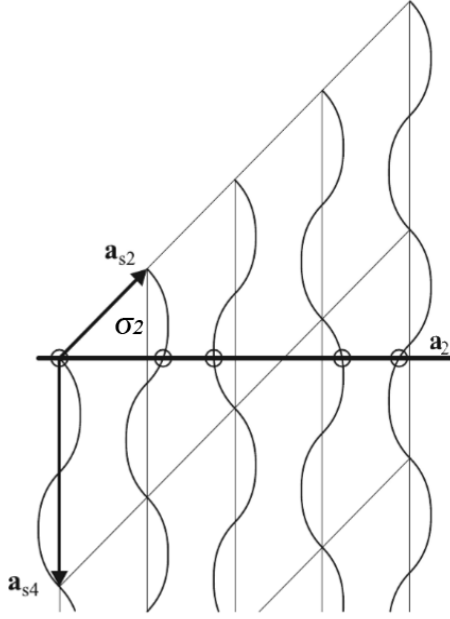
The superspace approach which gives a full description of the symmetry in modulated structures was first introduced by de Wolff [101] and later developed by de Wolff, Janssen and Janner [102]. The theory of superspace groups and higher dimensional crystallography is firmly rooted in the experimental observation that the electron diffraction pattern of the modulated structure has translational symmetry and requires more than three vectors to index (Eqn. 2.1)

$$\mathbf{S} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^* + h_4 \mathbf{q}_i \quad \text{Eqn. 2.1}$$

where $\mathbf{S}$ is the scattering vector, h_i are integer indexations and $\mathbf{a}_i^*$ ($i = 1,2,3$) represent the reciprocal lattice of the parent cell, and $\mathbf{q}_i$, expressed as a linear combination of the reciprocal lattice parameters $\mathbf{a}_i^*$ ($i = 1,2,3$) (Eqn. 2.2) is the additional vector(s) required for indexing. The structure is incommensurately modulated if any of the σ_i is irrational [100].

$$\mathbf{q}_i = \sigma_1 \mathbf{a}_1^* + \sigma_2 \mathbf{a}_2^* + \sigma_3 \mathbf{a}_3^* \quad \text{Eqn. 2.2}$$

The simplest case, which requires only one additional wave vector $\mathbf{q}$ that describes the displacive movement of the ions, is introduced in the following section, although the same formality is easily extended to treat crystals with larger numbers of modulation vector and/or different types of modulation. The superspace approach treat the observed four basic vectors, $\mathbf{a}_i^*$ and $\mathbf{q}$, as the projection of a higher dimensional lattice (with basic vectors $\mathbf{a}_{si}^*$ in reciprocal space) upon the 3D reciprocal space. Similarly, the modulated structure in real space is considered to be the projection of a (3 + 1)D crystal onto the real 3D space (a section of which is shown in Figure 2-3). The forth vector of the higher dimension crystal in real space is defined as $\mathbf{b}$, which is perpendicular to the physical space. Its counterpart in reciprocal space, $\mathbf{b}^*$, is defined to be parallel to $\mathbf{b}$ (therefore is perpendicular to all $\mathbf{a}_i$), and both of them are defined to be unity length: $\mathbf{b} \cdot \mathbf{b}^* = 1$. Based on the above definition, the 4D reciprocal space is defined in Eqn. 2.3, and the corresponding real space construction based on the reciprocity requirement is defined in Eqn. 2.4:



$$\begin{cases} \mathbf{a}_{si}^* = (\mathbf{a}_i^*, 0), & i = 1, 2, 3 \\ \mathbf{a}_{s4}^* = (\mathbf{q}, -\mathbf{b}^*) \end{cases} \quad \text{Eqn. 2.3}$$

$$\begin{cases} \mathbf{a}_{si} = (\mathbf{a}_i, \sigma_i \mathbf{b}), & i = 1, 2, 3 \\ \mathbf{a}_{s4} = (0, \mathbf{b}) \end{cases} \quad \text{Eqn. 2.4}$$

Figure 2-3: Schematic demonstrating the superspace approach to describe the incommensurate modulated structure adapted from [100]. The position of an atom in the 3D real space is the projection, from a $(3 + 1)$ D high dimension supercell, marked by the $\mathbf{a}_{s4}$ and $\mathbf{a}_{s2}$ vectors. The translational symmetry is preserved along the $\mathbf{a}_{s4}$ direction, and the displacement of any atom in real space is a periodic function of its internal axis coordination.

Shown in Figure 2-3, the displacement of the atom (shown as the sinuous wave propagating along $\mathbf{a}_{s4}$) from the parent structure is a function of the coordination of the internal axis $\mathbf{a}_{s4}$. The displacement $\mathbf{u}$, mostly commonly expressed as a Fourier series as in Eqn. 2.5, is a function of the internal coordination x_4 , although any periodic function $\mathbf{u}$ that fulfils Eqn. 2.7 can be used to describe the periodic deviation from the parent structure.

$$\mathbf{u}(x_4) = \sum_n A^n \sin(2\pi x_4) + B^n \cos(2\pi x_4) \quad \text{Eqn. 2.5}$$

in which the A_i^n and B_i^n are the n^{th} order Fourier magnitudes which describes the deviations from the average structure (or the *parent structure*). The internal coordination x_4 is related with the atomic coordinates in the real space by the modulation wave vector $\mathbf{q}$ w Eqn. 2.6:

$$x_4 = \mathbf{q}\bar{\mathbf{x}} = \mathbf{q} \cdot (\mathbf{L} + \mathbf{x}_0) \quad \text{Eqn. 2.6}$$

in which $\bar{\mathbf{x}}$ is the position of an atom in the real space, which consists of, $\mathbf{L}$ lattice vector and $\mathbf{x}_0$ the fractional coordinates in a unit cell. According to Eqn. 2.5, the translational symmetry which corresponds to the observed satellite reflections in Figure 2-2c, is preserved along the internal axis x_4 of the high dimensional crystal as:

$$\mathbf{u}(x_4) = \mathbf{u}(x_4 + 1) \quad \text{Eqn. 2.7}$$

The position of the displaced atom in the real space is expressed as follows:

$$\mathbf{x} = \bar{\mathbf{x}} + \mathbf{u}(x_4) \quad \text{Eqn. 2.8}$$

The same formality is used to describe other types of periodic variations including but not limited to, occupational modulation, charge density modulation, atomic displacement (ADP) modulation or any combination thereof [100,103], and $\mathbf{u}(x_4)$ would represent the corresponding periodic variations. The above example showcases the (3 + 1)D modulated structure where one additional vector is required to fully index the diffraction pattern. The concept is easily generalized for crystals with higher dimensions, creating (3 + 2)D and (3+3)D modulated structures, which require additional modulation vectors to describe the periodic deviation from the average parent structure (Eqn. 2.9), although in this case mixed higher-harmonic coefficients are involved [100]:

$$\begin{aligned} \mathbf{x} &= \bar{\mathbf{x}} + \mathbf{u}(x_4, \dots, x_i) \\ &= \bar{\mathbf{x}} + \sum_{n_1}^{\infty} \dots \sum_{n_{i-3}}^{\infty} A^{n_1 \dots n_{i-3}} \sin 2\pi(x_4 + \dots x_i) + B^{n_1 \dots n_{i-3}} \sin 2\pi(x_4 + \dots x_i) \\ x_i &= \mathbf{q}_i \bar{\mathbf{x}} = \mathbf{q}_i (\mathbf{L} + \mathbf{x}_0) \end{aligned} \quad \text{Eqn. 2.9}$$

2.2.2 Modulated scheelite and related structures

Depending on the composition, size and/or charge of the cations, the scheelite structure can accommodate various prototype structures ranging from unmodulated CaWO_4 [104], to commensurate modulated $\text{Eu}_2(\text{MoO}_4)_3$ [105], to more complicated (3 + 1)D and (3 + 2)D incommensurate modulated $\text{KNd}(\text{MO}_4)_2$ [106], $\text{KSm}(\text{MO}_4)_2$ [107] $\text{Ag}_{1/8}\text{Pr}_{5/8}\text{MO}_4$ [108] and $\text{Na}_{2/7}\text{Gd}_{4/7}\text{MO}_4$ [109].

Despite the variance in the refined space groups, it is proposed that the scheelite phase, modulated or unmodulated, can be derived using the (3 + 1)D incommensurate modulated $\text{KNd}(\text{MO}_4)_2$ as a template [110]. This representation is built upon the observation that the scheelite structure shares a common building block (consisting of A and BO_4 polyhedra, with a cell dimension of $a \approx b \approx 5.5 \pm 0.5 \text{ \AA}$, $c \approx 2a$, all angles are close to 90°), whereas the variations of the modulating function $\mathbf{q}$ generate different structures [110]. Such representation is inspired by previous investigations of the $\text{Bi}_{2+x}\text{Se}_3$ ($x = 0-2$) series: Lind & Lidin described the whole compositional range of these layered compounds using a combination of an identical parent cell (the dark black box in the Bi_2Se_3 phase in Figure 2-4) with a varying $\mathbf{q}$ vector along c axis, despite the difference in unit cell size [111]. The

simplicity of the superspace approach is highlighted in Figure 2-4; construction of huge supercells, which often consist of hundreds of atoms (for instance, in the case of Bi_8Se_9 , an elongated cell with $a = b = 4.23 \text{ \AA}$ and $c = 95.03 \text{ \AA}$ is required), is avoided for the structure solution [111]. The same approach has been applied to generate the temperature dependent polymorphs of $\text{K}_4\text{Yb}(\text{MoO}_4)_4$ [112].

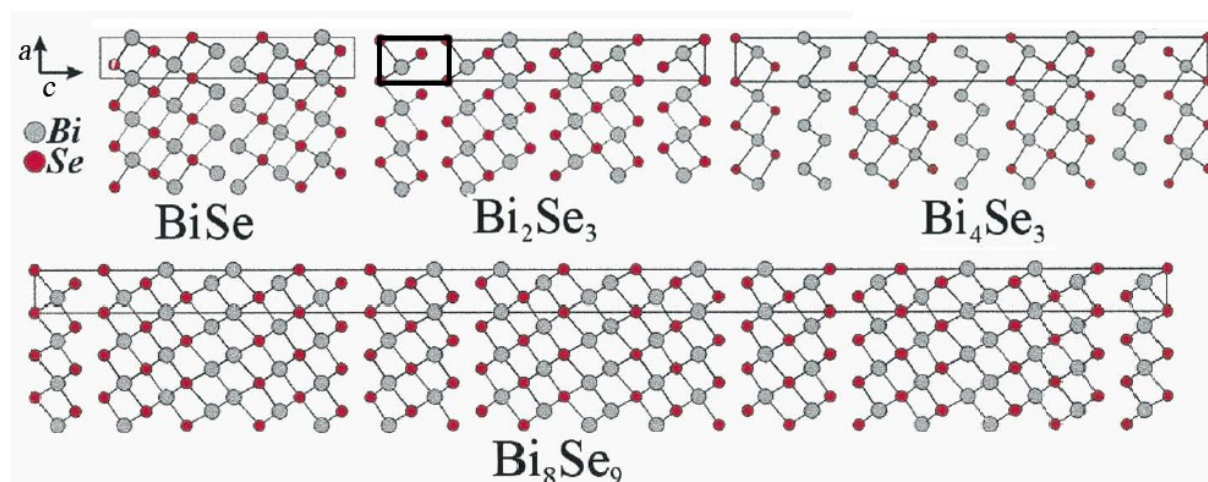


Figure 2-4: Crystal structure of layered $\text{Bi}_{2+x}\text{Se}_3$ ($x = 0-2$) compounds. The difference between the supercell approach and the superspace approach, when describing the structures of the $\text{Bi}_{2+x}\text{Se}_3$ series, is highlighted; the former approach requires the construction of large supercells (light rectangular box) whereas the latter relies on the combination of simple building units (dark rectangular box) and variations in the modulation waves (figure adapted from [111]).

With the $(3 + 1)\text{D}$ modulated $\text{KNd}(\text{MoO}_4)_2$ as a template, Arakcheeva et al. applied the aforementioned methodology and successfully reproduced various scheelite type structures, including both A site ordering (e.g. $\text{La}_2(\text{MoO}_4)_3$, $\text{K}_2\text{Th}(\text{MoO}_4)$) and B site cation ordering ($\text{Bi}_3[\text{BiO}_4(\text{MoO}_4)_2]$ among many others) [110]. In addition, the structure template successfully predicted the modulated structure of $\text{KEu}(\text{MoO}_4)_2$, whose low angle reflections had been originally left unindexed with an unmodulated structure model [110]. The validity of this approach with the scheelite structure has recently been demonstrated in $\text{Eu}_2(\text{MoO}_4)_3$ [105]. Building on the work of Arakcheeva et al., Morozov et al. further argued that various unmodulated, commensurate modulated and incommensurate modulated scheelite based structures could be generated by utilizing a $(3 + 2)\text{D}$ modulated structure with a superspace group $I4_1/a(a, \beta, 0)00(-\beta, \alpha, 0)00$ as the starting template [109]. Nevertheless, the general structural formalism of the scheelite structure reveals the common origin of the structural modulation: an occupational wave in the ab plane, whose wavelength can be either commensurate or incommensurate, coupled with the displacement of ions to facilitate the change in the bond length. The compositional wave corresponds to the hidden symmetry operator thus is very difficult to recognize using the supercell approach [110].

CeNbO_{4+d} is an interesting example illustrating the interplay between the charge ordering of the cations and the resultant crystal structure. Depending on the oxidation state of Ce and the corresponding interstitial oxygen content, four distinctive phases, namely the unmodulated CeNbO₄ parent structure, an incommensurate phase with nominal composition CeNbO_{4.08} and two commensurate modulated structures (CeNbO_{4.25} and CeNbO_{4.33}) have been identified [113]. The most recent report on the structure of CeNbO_{4.25} revealed an ordered cation network comprised of ordered Ce³⁺ and Ce⁴⁺ cations. Based on the refined oxygen positions, the location of the Ce⁴⁺ ions has been predicted by examining the bond valence sum, and a helical ordering of Ce³⁺ and Ce⁴⁺ along the *c* axis was proposed (Figure 2-5d and e). Comparing with the CeNbO₄ parent phase (Figure 2-5a), the anion sublattice of CeNbO_{4.25} is significantly deformed to accommodate the change in the bond length (Figure 2-5b), resulting in interconnected “NbO_x” polyhedra with coordination numbers extending to 7 and 8 (coloured orange and purple respectively in Figure 2-5b and c), whereas the coordination number is fixed at 6 for the CeNbO₄ parent structure [59]. It is worth pointing out that the wave function of CeNbO_{4.25} has a component along the unique axis: doubling along *b* of the monoclinic cell is required to fully describe the structure [59,113], whereas the modulation wave in most scheelite structures (those reported in [12,13,14,16]) is restricted in the *ac* basal plane. In addition, CeNbO_{4+d} is among the few modulated scheelite related structures that has been reported to be hyperstoichiometric.

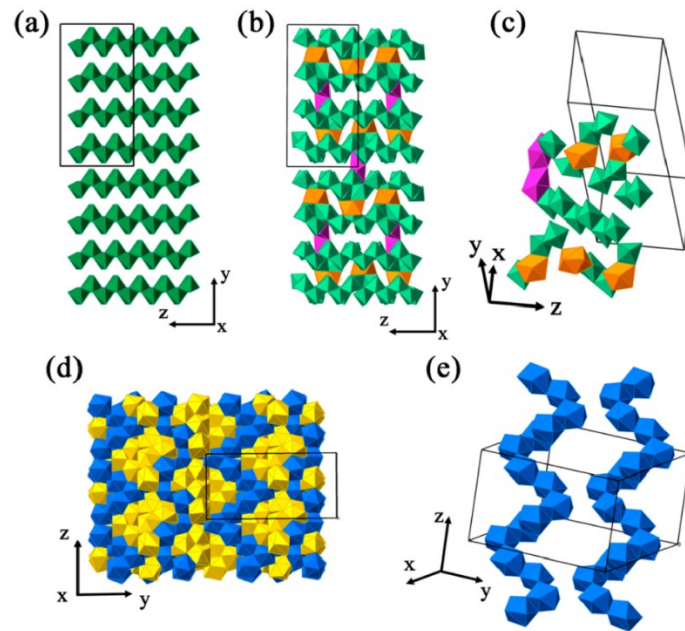


Figure 2-5: NbO_x polyhedra arrangement in a) CeNbO₄ parent structure and b) modulated CeNbO_{4.25} structure. In CeNbO_{4.25} the distorted NbO₆ (green), NbO₇ (purple) and NbO₈ (orange) polyhedra form a connecting network as shown in (c). The ordering of Ce³⁺/Ce⁴ (blue/yellow), leading to a helical network along the *c* axis as shown in (d) and (e) [59].

In contrast to the various stoichiometric modulated phases [110], hyperstoichiometric modulated structures are less commonly observed. A modulated structure was proposed for a 1 mol% La doped PbWO_4 single crystal, however the presented electron diffraction and lattice imaging is of poor quality to support such claim [115]. Another known case of modulated scheelite structure with interstitial content is the recently discovered $\text{La}_6\text{Mo}_8\text{O}_{33}$ phase (better described as $\text{La}_6\Box_2\text{Mo}_8\text{O}_{32+1}$) [116]. The structure has been refined with both cation vacancies and oxygen interstitials ordering. The interstitials were reported to locate near the cation vacancy sites and link two neighbouring $[\text{MoO}_4]$ tetrahedra forming the $[\text{Mo}_2\text{O}_9]^{3-}$ complex. Considering the localized charge of the cation vacancies, it is not surprising that both the A site vacancies and oxygen interstitials are ordered in this structure [116].

The structural modulation has significant impact on the performance of the scheelite related materials. Arakcheeva et al. studied the structure and the luminescence properties of $\text{Na}_x\text{Eu}_{(2-x)/3}\text{MoO}_4$ series and reported a $(3 + 1)\text{D}$ modulated structure with the composition range $0.25 > x > 0.015$. Remarkably, the authors revealed a strong correlation between the density of the Eu^{3+} dimer, which correlates to the modulation wave rather to the composition, and the characteristic luminescence parameters (quantum yield Q_L^{Eu} , which describes the efficiency of the fluorescence process, and the observed lifetimes τ_{obs} , the average time required for the minority carriers to recombine, are shown in Figure 2-6) [117]. Morozov et al. examined $\text{Na}_x\text{Eu}_{(2-x)/3}\text{MoO}_4$ closely with TEM and pointed out that the $x = 0.286$ composition, which previously had been reported to be unmodulated, was actually $(3 + 2)\text{D}$ ordered. The authors proposed that the change in the ordering dimensionality might relate to the local minima in the photoluminescence emission spectra [118].

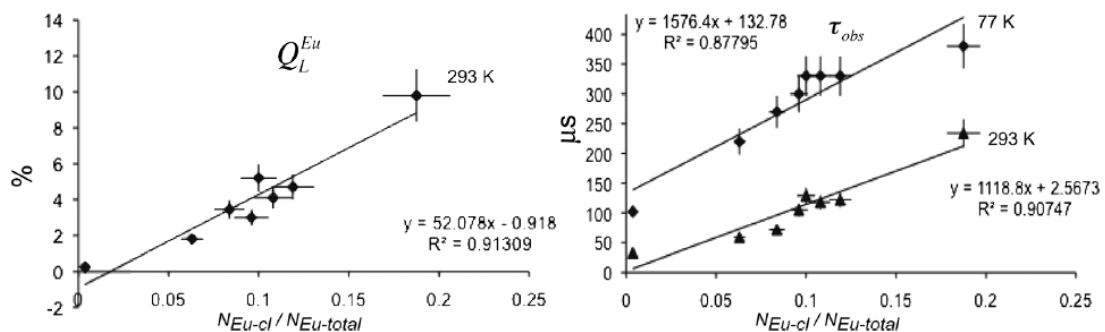


Figure 2-6: Quantum yield Q_L^{Eu} and observed lifetime τ_{obs} as a function of the Eu cluster density in $\text{Na}_x\text{Eu}_{(2-x)/3}\text{MoO}_4$ are shown. The luminescence properties are dependent on the Eu^{3+} dimers density, rather than the Eu^{3+} concentration, showcasing the impact of structural modulation on the luminescence properties. Figure adapts from [117].

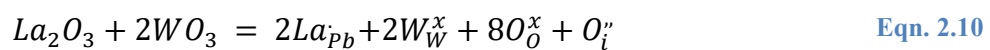
2.2.3 Summary

The superspace approach is a powerful tool that reveals the hidden symmetry of modulated structures. Using the superspace approach, scheelite related structures are described by the combination of a simple building unit and a varied modulation vector q . The occupational modulation with compensating displacement movement is a key feature of the modulated scheelite type materials. Structural modulation has significant impact on the performance of the material, understanding the structure is essential to reveal the property-structure relationship.

2.3 Conductivity of scheelite related materials

2.3.1 Scheelite related materials as oxygen ion conductor

The investigation of the oxygen ion transport properties of scheelite related materials was pioneered by Esaka and co-workers in the early 1990s when they first studied the oxide ion conduction of $PbWO_4$ with various rare earth dopants [86]. Single phase $Pb_{1-x}La_xWO_{4+d}$ were synthesized with La dopant concentration up to 30 at% whereas higher dopant concentrations introduced $\alpha-La_2W_2O_9$ impurity. By comparing the measured density of the sintered powder with the theoretical crystallographic density, it was concluded that the charge compensation was achieved via the introduction of interstitial oxygen ions (Eqn. 2.10) [86]. Interestingly, it has been suggested that at relatively low dopant level (<1 at%) the creation of V_{Pb}'' and La_W''' is energetically favourable and might be the major charge compensation mechanism [119].



Comparing with the $PbWO_4$ parent phase (with $\sigma = 5 \times 10^{-5} \text{ S cm}^{-1}$ at 800°C [14]), the conductivity of the La doped species is significantly improved: a maximum conductivity of $4.2 \times 10^{-2} \text{ S cm}^{-1}$ at 800°C was reported for $Pb_{0.8}La_{0.2}WO_{4+d}$, which is very close to the conductivity of YSZ at this temperature [14]. The measured EMF of the La doped samples is more than 95% of the theoretical value, confirming the ionic nature of the conduction. Enhancement in conductivity was also achieved by doping $PbWO_4$ with other lanthanides such as Pr, Sm and Tb [87,120], whose conductivity are reported in Figure 2-7.

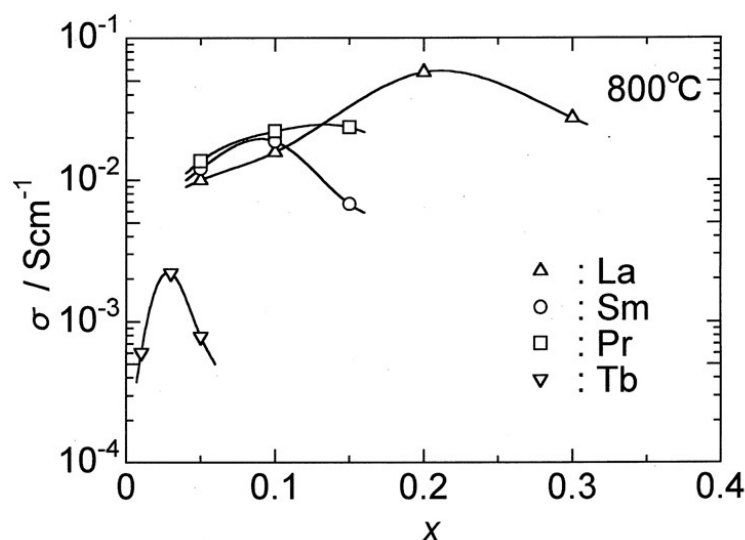


Figure 2-7: Total conductivity of $\text{Pb}_{1-x}\text{Ln}_x\text{WO}_{4+d}$ ($\text{Ln} = \text{La}, \text{Sm}, \text{Pr}$ and Tb) at 800 °C in air, as a function of Ln dopant concentration [87].

It was suggested that the La dopants had two competing effects on the overall conductivity: the dopant would lower the activation energy via depressing the oxide vacancy ordering; on the other hand, deviation from a perfect lattice structure would increase the activation energy [87,121]. Overall, a maximum conductivity was achieved with an optimum dopant level; further increasing the dopant level would in turn see a decrease in the conductivity [87] (as demonstrated in Figure 2-7). Similar doping strategies have been applied to other scheelite structures and the results are summarized in Figure 2-8. Apart from the CeNbO_{4+d} based materials which will be discussed shortly, all the compositions reported here have a transport number close to 1, even in the case of Pr and Tb dopants which are often readily oxidized [120].

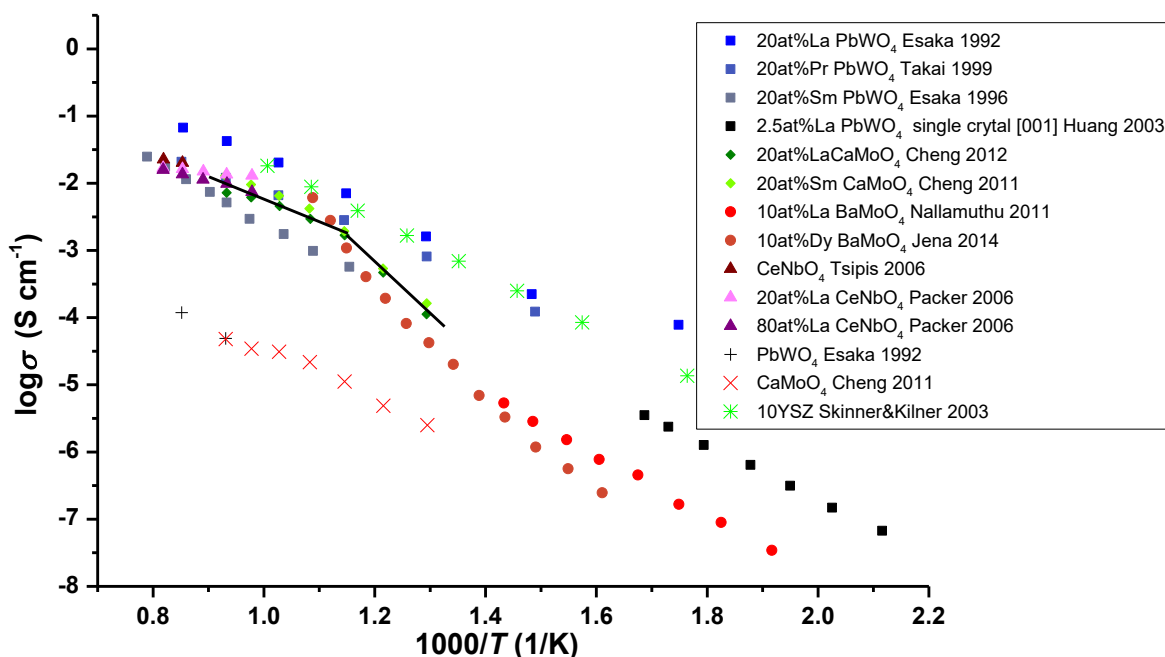


Figure 2-8: Summary of literature report on the oxide ion conductivity of scheelite related materials; apart from the CeNbO₄ and La doped CeNbO_{4+d}, all the other composition have a transfer number close to unity thus have pure ionic conduction. La_{0.2}Pb_{0.8}WO_{4+d} has the highest conductivity amongst the reported compositions, reaching $4.2 \times 10^{-2} \text{ S cm}^{-1}$ at 800 °C, comparable to that of 10YSZ [14]. The dark lines highlight the change in activation energy with increasing temperature in La_{0.2}Ca_{0.8}MoO_{4+d}.

Exemplified by La, Pr and Sm doped PbWO₄ (Figure 2-8), increasing the dopant size seems to have a positive impact on the ionic conduction, which might reflect an open anion sublattice [122]. Larger dopant radius also increases the conductivity in CaMoO₄ and BaMoO₄ based systems, both of which have the scheelite structure. Among all the doped molybdates, the La doped Ca_{0.8}La_{0.2}MoO_{4+δ} has the highest conductivity of $7.3 \times 10^{-3} \text{ S cm}^{-1}$ at 800 °C, lower than that of Pb_{0.8}La_{0.2}WO_{4+d}. The rare earth dopant has different solubility based on the parent phase: for CaMoO₄, single phase is maintained with up to 30 at% La dopants [123], whereas for BaMoO₄, a La₂MoO₆ secondary phase forms with dopant level as low as 10 at% [124]. A PbWO₄ single crystal was prepared to investigate the effect of orientation on the ion transport [119]. Conductivity along the *c* axis of a 2.5 mol% La doped PbWO₄ single crystal was reported to be lower than that of the 20 mol% La doped polycrystalline sample ($1.5 \times 10^{-4} \text{ S cm}^{-1}$ for the polycrystalline [87] comparing with $3.2 \times 10^{-6} \text{ S cm}^{-1}$ for the single crystal at 273 °C [119]); however it is unclear whether the difference results from anisotropy or reduced interstitial content.

A closer examination of the Arrhenius plot of the Ln doped scheelite phases would reveal a variation in activation energy with temperature. For instance, the activation energy saw a decline after the temperature reached 600 °C for the CaWO₄ based phases (from 0.76 eV to 0.46 eV, highlighted by the lack lines in Figure 2-8) [125], whereas no phase transition has

been recorded in this temperature region. It is speculated that association-dissociation of the defects might have occurred, resulting in the difference in activation energy [119,126]. Results from conductivity studies on the La doped PbWO_4 single crystals are in line with this conjecture [126]: the conductivity along the c -axis of 1 mol% La-doped crystal is comparable to that of 2.5 mol% doped single crystal at low temperature. It is suggested that at higher temperature, the vacancies trapped in the $[(\text{La}_\text{W}''' - (\text{La}_\text{Pb}') - \text{V}_\text{O}^{\bullet\bullet})]$ clusters become mobile and start contributing to total conductivity [126,127].

In general, the oxygen excess phases have good stability under reducing atmosphere. At 900 °C, the conductivity of the $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+\delta}$ and $\text{Pb}_{1-x}\text{La}_x\text{MoO}_{4+\delta}$ remained constant when the oxygen partial pressure was lowered to $\sim 10^{-17}$ atm and $\sim 10^{-12}$ atm respectively, and became n-type if the partial pressure was further reduced. On the other hand, impurities formed after exposing the $\text{Ca}_{0.8}\text{Sm}_{0.2}\text{MoO}_{4+\delta}$ phase in H_2 atmosphere at 900 °C for 2 h, indicating a poor reduction resistance [121].

Another interesting example of scheelite related ionic conductor are the modulated CeNbO_{4+d} phases which display a remarkable oxygen diffusivity $6.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 700 °C [58] superior to the well-established YSZ based electrolyte ($3.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 693 °C [128]). Tracer diffusivity measurement indicated a continuous increase in the surface exchange coefficient k^* with temperature (Figure 2-9b), whereas a sharp drop of oxygen diffusivity D^* was observed at around 1073 K (Figure 2-9a), identifying the low temperature structure as an ideal ionic conductor [58]. In addition, the high temperature diffusivity does not follow an Arrhenius type diffusivity model (the region highlighted in the square in Figure 2-9a), which might result from incomplete phase transition between different hyper-stoichiometric CeNbO_{4+d} phases [58]. The drop in diffusivity is particularly interesting considering that CeNbO_{4+d} has modulated monoclinic phases at lower temperature, whereas the high temperature polymorph has unmodulated tetragonal symmetry; anion sites with a high number of equivalent position are often considered necessary for fast ion diffusion [129], whereas the low symmetry phase was report to have high diffusivity in CeNbO_{4+d} .

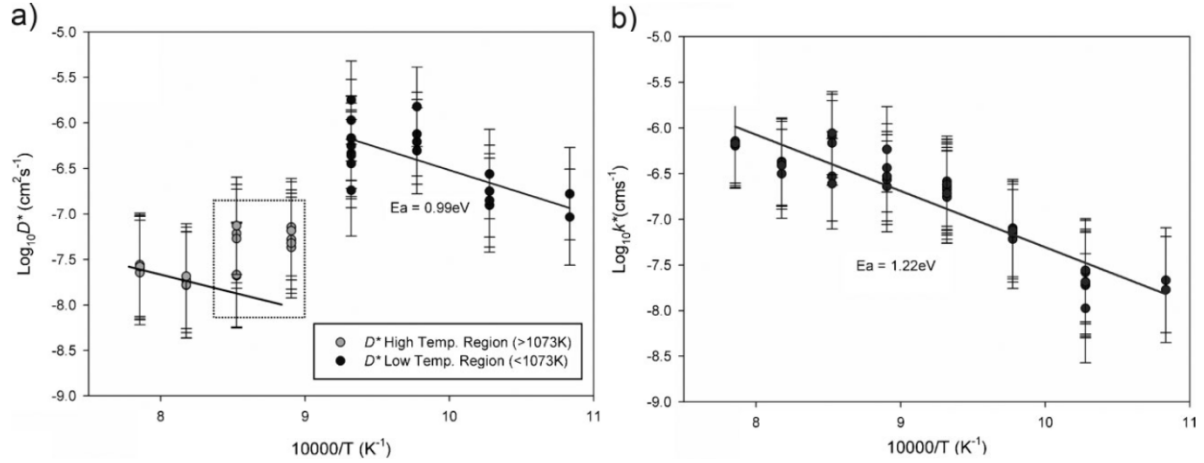
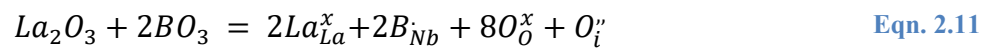


Figure 2-9: Arrhenius plot of a) Oxygen tracer diffusivity D^* and b) surface exchange coefficients k^* in CeNbO_{4+d} . Continued increase of k^* is observed whereas D^* sees a sharp drop round 1073 K, indicating that the low temperature structure has superior oxygen ion diffusivity. The line in (a) is just for a guide of eye; the D^* in the rectangular box might result from incomplete phase transition, which leads to the non-Arrhenius type behaviour [58].

Unfortunately, the electronic conduction due to the oxidation from Ce^{3+} to Ce^{4+} is undesirable for electrolyte applications. Attempts were made to reduce the electronic conduction by substitution of Ce with La [130,131]. It was discovered that the reduction of the electronic conduction is at the expense of reduced interstitial content, thus ionic conductivity. *In situ* neutron scattering data showed that $\text{La}_{0.2}\text{Ce}_{0.8}\text{NbO}_{4+d}$ maintained its interstitial content and formed a structure similar to $\text{CeNbO}_{4.25}$ in the 427 °C to 900 °C range, whereas $\text{La}_{0.8}\text{Ce}_{0.2}\text{NbO}_{4+d}$ transforms directly to a tetragonal phase with $d \approx 0$ at 800 °C. Total conductivity of $1 \times 10^{-3} \text{ S cm}^{-1}$ was recorded for $\text{La}_{0.8}\text{Ce}_{0.2}\text{NbO}_{4+d}$ at 900 °C under static air which is not competitive as an oxygen ion conductor [130]. Substitution on the B-site with V and Ta has also been reported, though the resultant structures show low transference numbers [132,133].

2.3.2 Literature review of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases

An alternative strategy to promote oxygen ion conductivity in the scheelite related materials is to use LaNbO_4 as the starting phase and introduce interstitials via hexavalent dopant at the B-site (Eqn. 2.11), although to date, few have studied the ionic conduction in hyperstoichiometric LaNbO_4 .



Cava [134] first reported the structure and conductivity of W and Th doped LaNbO_4 in the late 1970s. Both W and Th dopants led to the formation of modulated structures which were considered to be iso-structural with the low temperature $\text{CeNbO}_{4.08}$. For W doped LaNbO_4 ,

three distinctive phases have been identified at room temperature (shown in the phase diagram in Figure 2-10): a W solid solution in LaNbO_4 with very low dopant level (about 2 at%), a single phase region of the modulated structure exists with 11 at% to 22 at% dopant, and a line phase with ~60 at% W dopant, whose structure was not defined by Cava [134].

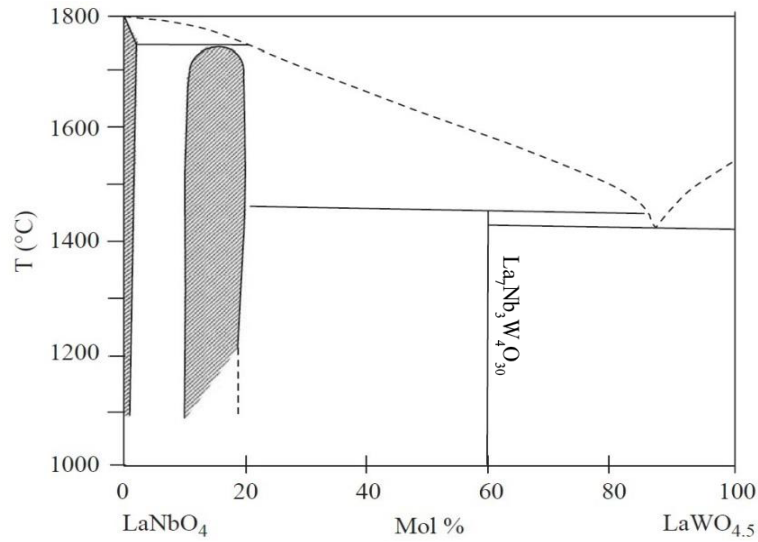


Figure 2-10: Phase diagram of W doped LaNbO_4 system proposed by Cava; single phase region is hatched for clarity; in addition, there is a line phase with nominal composition $\text{La}_7\text{Nb}_3\text{W}_4\text{O}_{30}$ [134]

The modulation was believed to be incommensurate in nature and was isostructural of $\text{CeNbO}_{4.08}$ [134]. A recent study [135] revealed that this line phase has a composition of $\text{La}_7\text{Nb}_3\text{W}_4\text{O}_{30}$ which is regarded as a reduced version of the $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOX) phase. Among Th doped LaNbO_4 , $\text{La}_{0.93}\text{Th}_{0.07}\text{NbO}_{4+d}$ has the highest performance with a total conductivity of $2.6 \times 10^{-2} \text{ S cm}^{-1}$ at 1000 °C, and the conductivity of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series was not reported by the authors [134].

Bayliss [136] studied the stability and transport properties of one of the modulated compositions, $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$. Weight loss of the material is negligible up to 1000 °C and no detectable electronic conduction was observable down to $p\text{O}_2 = 10^{-12}$ bar at 800 °C, indicating a pure ionic contribution as well as promising reduction resistance. The total conductivity of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+\delta}$ was reported to be $\sim 4 \times 10^{-4} \text{ S cm}^{-1}$ at 600 °C which is respectable for an electrolyte whose composition and microstructure has yet to be optimized [136]. A reversible fuel cell with a $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ electrolyte has been fabricated. Using 50 vol% $\text{H}_2\text{O}/50 \text{ vol}\% \text{H}_2$ as the fuel, and at a cell voltage of 0.5 V and 1.3 V for SOFC and SOEC mode respectively, current density of 200 mA cm^{-2} and 250 mA cm^{-2} was reported [137]. However due to the complex structural modulation, many questions were left

unanswered with regard to the structural evolution as well as the conducting mechanism of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series oxygen ion conductors. In addition, other rare earth RENbO_4 systems were largely left unexplored and the variations in their electrical and structural properties with different doping strategies require further investigation.

2.3.3 Scheelite related materials as proton conductor

Recent years saw a huge interest in investigating the proton conduction in acceptor doped fergusonite phases with the general formula $\text{Re}_{1-x}\text{A}_x\text{MO}_{4-d}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}, \text{M} = \text{Nb}$ and Ta), after Haugrud and Norby demonstrated that $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ has a proton conductivity of 0.001 S cm^{-1} at 900°C under wet conditions ($P_{\text{H}_2\text{O}} \approx 2\text{mbar}$) [93] whereas the undoped LaNbO_4 showed no proton conductivity [94]. The acceptor dopant introduces vacancy defects (Eqn. 2.12), which accommodate the intake of proton according to Eqn. 2.13:

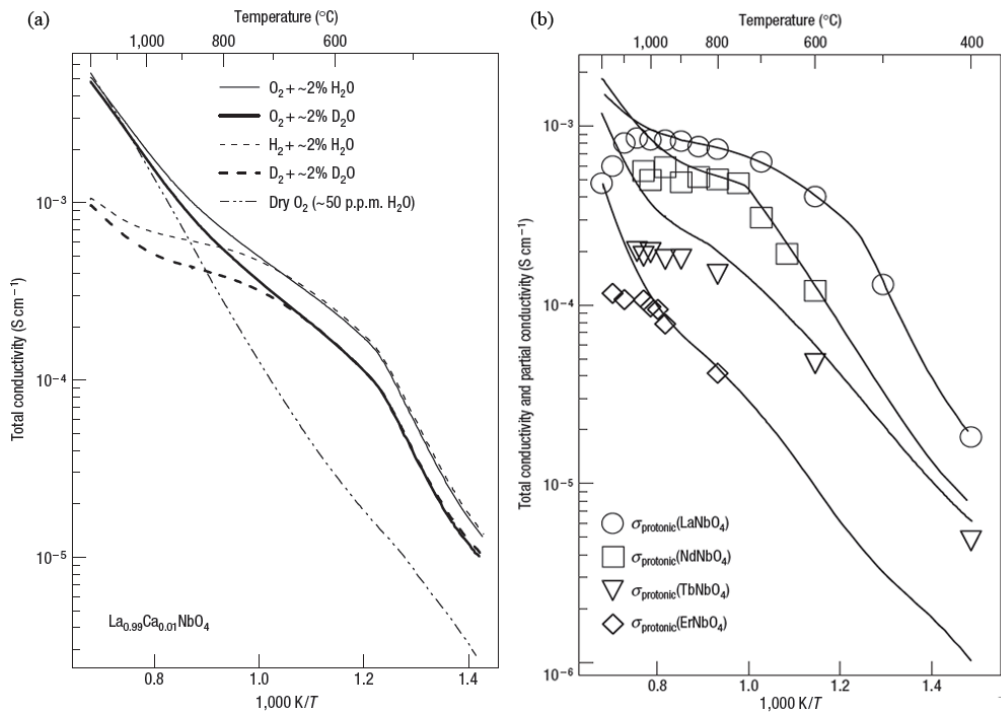
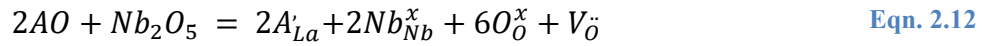


Figure 2-11: Arrhenius plots of (a) Conductivity of $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ under various atmospheres, demonstrating the dominant protonic conduction under humid atmosphere below 800°C (b) total A.C. (straight line in the figure) and partial protonic conductivity of various $\text{RE}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ ($\text{RE} = \text{La}, \text{Nd}, \text{Tb}, \text{Er}$) in wet H_2 atmosphere. The conductivity is predominantly protonic at temperature below 800°C (adapted from [93]).

The conductivity of $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ in wet O_2 was about an order of magnitude higher than that measured under dried O_2 ; in addition, an isotope effect was observed as the conductivity in $\text{D}_2+\text{D}_2\text{O}$ was lower than that measured in $\text{H}_2+\text{H}_2\text{O}$ atmosphere (Figure 2-11a). The isotope effect confirmed that the proton is the major charge carrier in $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ under wet atmosphere below 800 °C [93]. Among all the $\text{Re}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ reported in [93], $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ has the highest proton conductivity (Figure 2-11b), which is comparable to $(\text{Ba}/\text{Sr})\text{CeO}_3$ perovskite [44]. In addition, the ortho-niobate has much better chemical stability in CO_2 containing environments [138], as well as improved mechanical properties [47], making them interesting contenders for proton conducting fuel cell electrolytes.

Fitting of the thermodynamic parameters based on the conduction data revealed the effect of cation size on hydration and conduction process (Table 2-1). The hydration enthalpy is always negative indicating a thermodynamically favoured process; in addition the enthalpy becomes more negative with smaller cation size, suggesting the preserve of water at higher temperature [93]. All the $\text{Re}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ under investigation have similar conduction enthalpies, although the hydrogen mobility decreases with decreasing rare earth sizes, despite a reduced O-O distance thus a shortened jumping distance for the proton [93]. Similar trends were observed in the perovskite based proton conductors, and were attributed to reduced lattice dynamics [93,139].

Table 2-1: Fitted thermal dynamics parameters for $\text{Re}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$. ΔS^0 and ΔH^0 are the entropy and enthalpy of hydration respectively, U_{0,H^+} is the mobility of proton and $\Delta H_{m,H^+}$ the conduction enthalpy. The hydration enthalpy is negative for all the compositions whereas the H mobility increases with increasing rare earth size [93].

Materials	$\Delta S^0(\text{J mol}^{-1} \text{K}^{-1})$	$\Delta H^0(\text{kJ mol}^{-1})$	$U_{0,H^+}(\text{cm}^2 \text{K V}^{-1})$	$\Delta H_{m,H^+}(\text{kJ mol}^{-1})$
$\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$	-120 ± 10	-115 ± 10	35 ± 10	55 ± 5
$\text{Nd}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$	-120 ± 10	-130 ± 10	10 ± 5	50 ± 5
$\text{Gd}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$	-120 ± 10	-145 ± 10	3 ± 2	63 ± 5
$\text{Tb}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$	-130 ± 10	-140 ± 10	5 ± 2	52 ± 5
$\text{Er}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$	-130 ± 10	-165 ± 10	2.5 ± 2	57 ± 5

Literature reports on the proton conductivity of acceptor doped LaNbO_4 are summarized in Figure 2-12. One of the disadvantages of the LaNbO_4 based proton conductors is their low dopant solubility, thus low defect concentration. Bi et al. reported that the conductivity of $\text{La}_{1-x}\text{Ca}_x\text{NbO}_4$ reached its maximum with $x = 0.005$; further increasing the dopant level (from 0.5 at% to 2.5 at%) saw negligible change in the bulk conductivity (σ_{bulk}) and a decrease in grain boundary conductivity, σ_{gb} [140]. The authors ascribed this observation to the low solubility of Ca in the bulk, and speculated the formation of a secondary phase at the grain

boundary when $x > 0.01$, leading to the reduced σ_{gb} [140]. Similar solubility was reported for Sr and Ba dopant in LaNbO_4 [141]. A series of B site dopants in $\text{LaNb}_{1-x}\text{M}_x\text{O}_4$, where M = Ga, Ge, Si, Al, B, P, Zr or Ti, has been explored in an attempt to increase the oxygen vacancy concentration. However, the solubility levels were low ($x < 0.03$) for all the tested dopants. Among all the B sited doped LaNbO_4 , $\text{LaNb}_{0.97}\text{Ti}_{0.03}\text{O}_4$ has the highest total conductivity $\sigma_{\text{total}} = 2.3 \times 10^{-5} \text{ S cm}^{-1}$ at 870 °C, the conduction is predominantly protonic under wet oxidising environment [142].

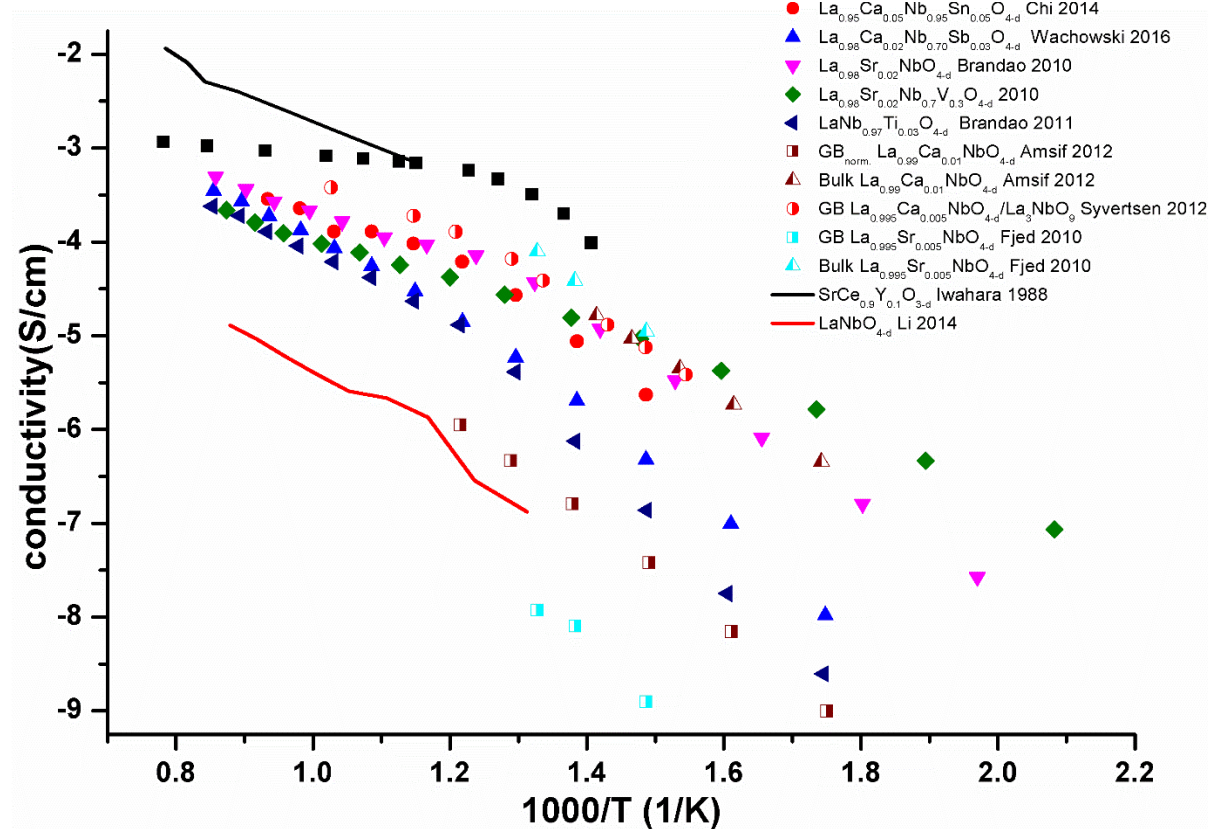


Figure 2-12: Summary of literature reports on the protonic conduction in acceptor doped LaNbO_4 ; apart from the $\text{La}_{0.95}\text{Ca}_{0.05}\text{Nb}_{0.95}\text{Sn}_{0.05}\text{O}_{4-d}$, which was measured under wet H_2 , all the others samples reported here were measured under wet O_2 , ($p(\text{H}_2\text{O}) = 0.025 \text{ bar}$). The blocking effect of grain boundary in $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ [143] and $\text{La}_{0.995}\text{Sr}_{0.005}\text{NbO}_{4-d}$ [88] is highlighted.

Indeed, the LaNbO_4 parent structure lacks the ability to accommodate acceptor substitution; a recent study showed the formation of a Ca enriched secondary phase with a nominal composition $\text{Ca}_{0.96}\text{La}_{1.56}\text{Nb}_{1.48}\text{O}_7$ with the addition of a mere 0.25 mol% CaO. The secondary phase has a tendency to migrate to the surface as larger fraction of the Ca enriched phase was observed at the as-sintered surface, in comparison with the bulk [144]. A similar phenomenon has been recorded in $\text{La}_{0.98}\text{AE}_{0.02}\text{NbO}_{4-d}$ (AE = Ca, Sr and Ba, Figure 2-13). The secondary phases which appear darker in the BSE images were discovered in all the compositions with 2 at% dopant (impurity in $\text{La}_{0.98}\text{Sr}_{0.02}\text{NbO}_{4-d}$ is heighted by the arrows in Figure 2-13b). The

impurity adopts irregular shapes on both the as-sintered surface and the polished surface, and those found on the $\text{La}_{0.98}\text{Ca}_{0.02}\text{NbO}_{4-d}$ and $\text{La}_{0.98}\text{Sr}_{0.02}\text{NbO}_{4-d}$ surface have larger size compared with those found on the polished bulk (Figure 2-13d and e). The impurity is missing from $\text{La}_{0.98}\text{Ba}_{0.02}\text{NbO}_{4-d}$ (Figure 2-13f), which might relate to the volatility of Ba [145]. The secondary phase is not homogeneously distributed and tends to agglomerate into large grains (Figure 2-13c-e). In the bulk of $\text{La}_{0.98}\text{Ba}_{0.02}\text{NbO}_{4-d}$, the impurity forms an interconnected sponge-like network that infiltrates the other phase (Figure 2-13c). All the aforementioned characteristics, as well as the abnormal grain growth of $\text{La}_{0.98}\text{Ba}_{0.02}\text{NbO}_{4-d}$ suggests the presence of liquid phases during the 1400 °C sintering [141].

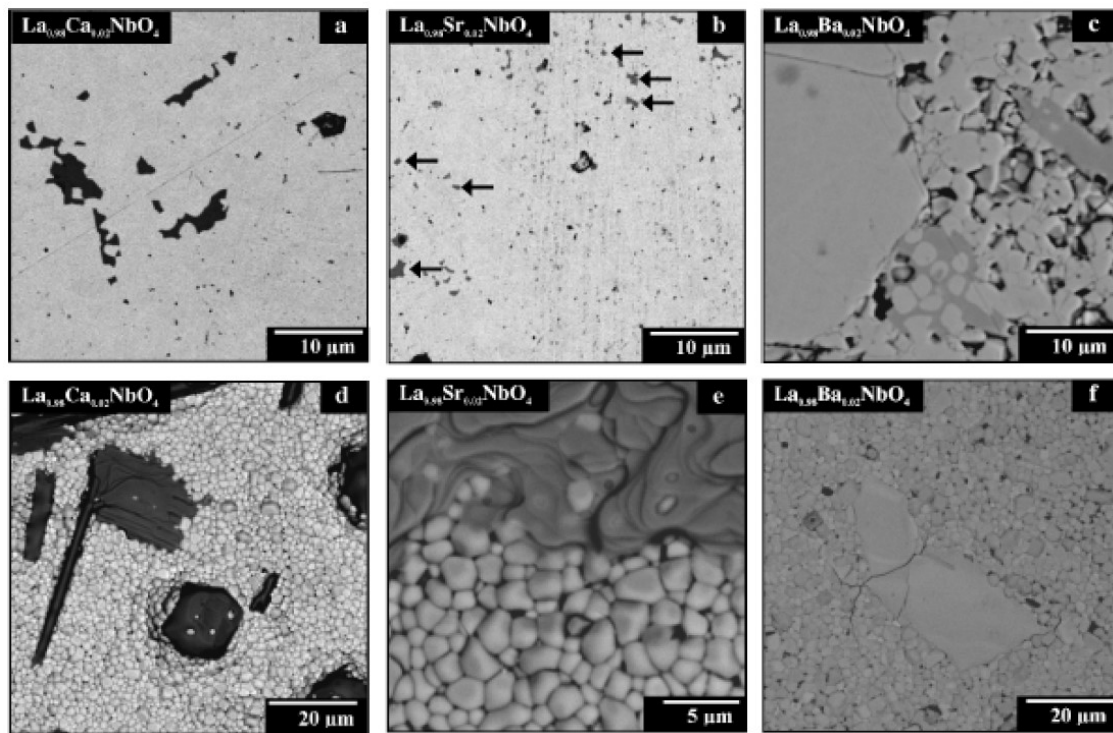


Figure 2-13: BSE images show the surface of (a) $\text{La}_{0.98}\text{Ca}_{0.02}\text{NbO}_{4-d}$ (b) $\text{La}_{0.98}\text{Sr}_{0.02}\text{NbO}_{4-d}$ and (c) $\text{La}_{0.98}\text{Ba}_{0.02}\text{NbO}_{4-d}$ whereas the corresponding polished surfaces are shown in (d)(e)(f). The alkaline earth enriched 2nd phase is darker in the BSE images. Higher fraction of 2nd phase with irregular shape was found on the as sintered surface, suggesting the formation of liquid phase during sintering [141].

Co-doping both the A and B sites does increase the solubility of alkaline earths in LaNbO_4 : 5 at% Ca on the La site is achieved alongside 5 at% Sn doping at the Nb site. A total conductivity of $2.96 \times 10^{-4} \text{ S cm}^{-1}$ was reported at 800 °C in wet N_2 . However, the total conductivity in dry N_2 was reported to be $1.40 \times 10^{-4} \text{ S cm}^{-1}$ at the same temperature, indicating a strong contribution from oxygen ions and holes [146]. Most recently, Harris [147] has demonstrated that CeNbO_{4+d} can accommodate Sr dopant levels up to 15 at%, a huge improvement compared to the LaNbO_4 based system. A reduction in conductivity was

observed when switching from H₂O to a D₂O environment, confirming the proton as the major charge carriers. Coupled with its electrical conduction, Ce_{1-x}Sr_xNbO_{4-d} is an interesting contender for high temperature proton cathode application and requires further investigation [147].

Another hurdle to improve the performance of acceptor doped LaNbO₄ is its blocking grain boundary (highlighted in Figure 2-12): the grain boundary in acceptor doped LaNbO₄ is highly resistive in comparison to the grain bulk, similar to the perovskite based proton conductors such as BaZrO₃ [148,149]. Amsif studied the conductivity of 1 at% Ca doped LaNbO₄, prepared from spray freeze-dried precursors and reported a specific grain boundary conductivity of $5.1 \times 10^{-8} \text{ S cm}^{-1}$ at 400 °C under wet O₂ atmosphere for samples sintered at 1150 °C for 4 h [143]. The bulk conductivity was measured to be $1.2 \times 10^{-5} \text{ S cm}^{-1}$ under the same conditions, almost three orders of magnitude higher than the specific σ_{gb} (Figure 2-12). Increasing the sintering temperature to 1500 °C sees increased grain growth although the specific σ_{gb} shows little change ($6 \times 10^{-8} \text{ S cm}^{-1}$), indicating that the grain boundary make-up has little dependence on the sintering temperature [143]. Similar results were reported for 0.5 at% Ca doped LaNbO₄ measured under an H₂O/Ar mix, and again a large difference between σ_{bulk} and σ_{gb} was reported ($1.1 \times 10^{-5} \text{ S cm}^{-1}$ and $1.1 \times 10^{-9} \text{ S cm}^{-1}$ respectively at 440 °C, Figure 2-12). The grain boundary is blocking for proton conduction, although bright field TEM imaging of boundary revealed no secondary phase along the grain boundary in the 0.5 at% Sr doped LaNbO₄ [88].

The blocking effects of the grain boundary is explained with the space charge theory; a grain boundary consists of a positively charged core and a neighbouring depleted zone with reduced proton concentration is proposed for acceptor doped LaNbO₄ [88]. However, to my knowledge, no experimental evidence has been produced to support this theory. Modification of the space charge layer nevertheless has been attempted by intentionally preparing non-stoichiometric compositions to create heterogeneous interfaces in the LaNbO₄/La₃NbO₇ and LaNbO₄/LaNb₃O₉ ceramic composites. The grain boundary conductivity of the La_{0.995}Ca_{0.005}NbO_{4-d}/La₃NbO₇ (30 vol%) composite showed encouraging grain boundary conductivity [150], unfortunately the total conductivity was not increased, probably due to the reduced La_{0.995}Ca_{0.005}NbO_{4-d} volume fraction.

One of the strategies to enhance the low temperature proton conductivity is to stabilize the high temperature scheelite phase as structures with reduced symmetry are considered to be less optimal for proton conduction [139]; in addition, reduction in activation energy has been

recorded once the acceptor doped LaNbO_4 transformed from the low temperature monoclinic to high temperature scheelite phase [140]. Wachowski et al. investigated the structure evolution of $\text{LaNb}_{1-x}\text{M}_x\text{O}_4$ ($\text{M} = \text{Sb, Ta}$; $x = 0.05\text{-}0.3$), and reported a gradual decrease of the t to m transition temperature with increasing Sb concentration (415°C for $x = 0.05$ to 125°C for $x = 0.25$). The tetragonal structure is stabilized at room temperature with 30 at% Sb substitution [151]. Solubility of the Ca dopant in the $\text{LaNb}_{1-x}\text{Sb}_x\text{O}_4$ compositions was reported to be about 2 at%. The maximum observed proton conductivity was reported to be $\sim 10^{-4} \text{ S cm}^{-1}$ at 800°C for $\text{La}_{0.98}\text{Ca}_{0.02}\text{Nb}_{0.7}\text{Sb}_{0.3}\text{O}_{4-d}$, lower than that of the $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ phase. The conduction was predominantly protonic in an oxidizing wet environment below 800°C and p -type in a dry environment [152]. Brandao et al. studied the stability and conductivity of $\text{La}_{0.98}\text{Sr}_{0.02}\text{Nb}_{1-x}\text{V}_x\text{O}_{4-d}$ and reported a single tetragonal phase at room temperature with a compositional range of $0.325 > x > 0.25$ [142]. The chemical stability of $\text{La}_{0.98}\text{Sr}_{0.02}\text{Nb}_{1-x}\text{V}_x\text{O}_{4-d}$ however is reduced with V doping and a LaVO_4 impurity was identified in $\text{La}_{0.98}\text{Sr}_{0.02}\text{Nb}_{0.7}\text{V}_{0.3}\text{O}_{4-d}$ after annealing in 10% H_2/N_2 gas mixture at 900°C for 5 h [153]. Comparing with $\text{La}_{0.98}\text{Sr}_{0.02}\text{NbO}_{4-d}$, $\text{La}_{0.98}\text{Sr}_{0.02}\text{Nb}_{0.7}\text{V}_{0.3}\text{O}_{4-d}$ showed an improved total conductivity at wet oxidising environment, though the latter was reported to have a higher p -type conduction at elevated temperature ($< 600^\circ\text{C}$ under wet O_2) [153].

2.3.4 Summary

Oxide ion conductors based on hyper-stoichiometric scheelite related materials have demonstrated great potential for SOFC electrolyte application; a maximum conductivity of $4.2 \times 10^{-2} \text{ S cm}^{-1}$ at 800°C was achieved with $\text{Pb}_{0.8}\text{La}_{0.2}\text{WO}_{4+d}$. Most notable are the low temperature modulated CeNbO_{4+d} phases which provide an interesting structure template that offer remarkable oxygen ion diffusivity thus fast ion conduction. However, the undesirable electronic conduction of CeNbO_{4+d} cannot be reduced without compromising its oxygen ion conductivity. Alternatively, the structural template of CeNbO_{4+d} can be exploited by the hyperstoichiometric LaNbO_4 phases with hexavalent dopant at the B site. For instance, preliminary investigation of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ shows promising oxygen conductivity, although the structural evolution of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series have not yet been attempted due to its modulated nature, and its conducting mechanism being not well understood. In addition, other rare earth RENbO_4 systems with various doping strategies should be systematically explored to take full advantage of the CeNbO_4 structural template.

Protons are the major charge carrier under wet atmosphere for the acceptor dopant LaNbO_4 phases. The highest proton conductivity of 0.001 S cm^{-1} at 800°C has been reported for $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_{4-d}$ that is comparable to conventional perovskite structure. In an attempt to enhance the proton conductivity, various dopant strategies were explored and the possibility to stabilize the high temperature structure was verified. The LaNbO_4 parent structure however is not tolerant to substitution and allows only low solubility (typically below 2 at%) for both A site and B site dopant. In addition, the low specific grain conductivity poses a challenge for further optimizing the transport properties.

2.4 Surface studies of scheelite related materials

The surface of oxide systems often adopt unique geometries [154–156] and chemical compositions [157–160] that differ significantly from the bulk. Meanwhile, many properties of the oxide systems, such as adhesion, electron emission, catalysis, and wetting, are dominated by the surface [161]. For instance, the importance of the surface exchange activity relative to the bulk diffusion has been well recognized for $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-d}$ based oxygen permeation membranes [162]. Also, in the YSZ system, direct correlation between surface isotopic concentration and reduced Ca, Si, impurities has been reported, indicating that surface contamination is the rate limiting factor for SOFC electrolytes [160]. Understanding the surface chemistry of scheelite related material, though not a trivial task, but would prove rewarding. In the following section, the origin of the surface segregation is first introduced, and the impact of surface chemistry on the electrochemical performance will be highlighted. Literature reports on the surface of scheelite related materials will be reviewed, pinpointing discrepancies in the reported data.

2.4.1 Surface chemistry in oxide systems—experimental & theory

In oxide systems, the chemical composition of the surface is often modified by dopant segregation. For instance, strontium surface segregation is commonly observed in perovskite based material such as in $\text{La}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ [163], $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ [164,165] and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ (LSC) [166,167] after annealing the samples at elevated temperature (400–1000 °C). The segregation behaviour however is not unique to perovskites; dopant segregation has also been reported in other structure including double perovskite [158,159], layered Ruddlesden-Popper phases [158,168] and fluorite ZrO_2 [79]. De Ridder et al showed that the outermost layer of as-sintered YSZ surface was completely covered by Ca, Na and Si using even the purest starting powder available (<50 ppm). The authors suggested that the impurities would probably originate from the grain boundary which diffuse to the surface during sintering [169]. It is further demonstrated that, beneath the contaminant layer lies an Y enriched segregation layer, which was estimated to be one monolayer thick [169]. The formation of the surface segregation in YSZ is an endothermic process; rather than absorbing the contaminants into the bulk, increasing the annealing temperature raises the surface coverage of the contaminant [160]. Nowotny et al. pointed out the importance of differentiation between the equilibrium segregation process which leads to the thermodynamically stable configuration, and the non-equilibrium segregation process, which is largely affected by the experimental conditions. In the case of equilibrium segregation, stable configuration was reached by the formation of monolayer impurity [170].

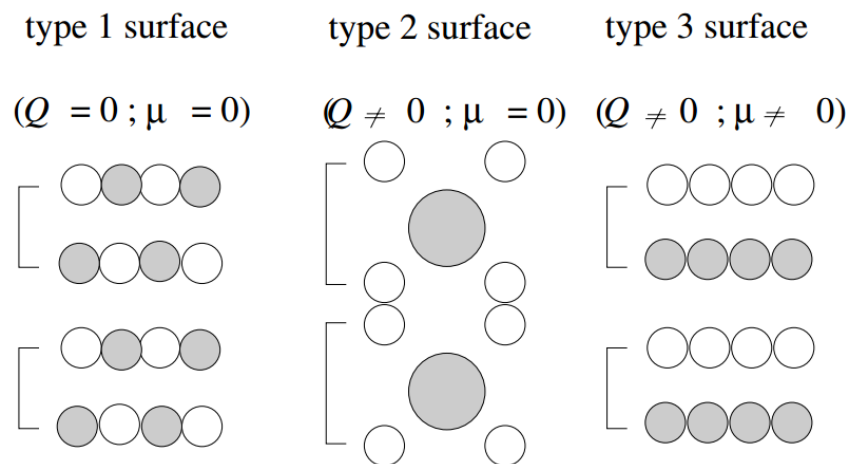


Figure 2-14: Classification of surface by Noguera [155]; Q represents the surface charge and μ is the surface dipole; a surface can have neutral block (type I), has a charged surface but non dipole (type II) or has a surface dipole (type III). The type III surface is unstable and requires substantial reconstruction.

Overbury et al. summarized the thermodynamic argument for surface segregation in binary systems [171]; the creation of new surface is always associated with a positive free energy

change, therefore the surface has a tendency to be enriched by the component with the lower surface energy, creating an unbalanced distribution of constituent species between the bulk and the surface [171]. The difference in the defect formation energy between the surface and bulk creates the space charge layer. Defects that preferentially form at the surface will diffuse into the bulk, this builds up a potential in the near-surface region and leaves the surface enriched with defects of the opposite charge [88,172].

Tasker [173], amongst those who pioneered the investigation of surface chemistry, categorised surfaces into three types (shown in Figure 2-14): type I surface has neutral building blocks ($Q = 0$); type II surface has charged layers but the dipole moments perpendicular to the surface cancel out each other; type III surface has a dipole moment that is perpendicular to the surface plane. He concluded that whereas both type I and II surfaces are stabilized with minor relaxation of underlying layers, the type III surface is considered unstable and requires substantial reconstruction or surface absorption [173]. Noguera later pointed out that a surface could still be polar, thus unstable, even with alternating neutral building blocks [155]. A weak dipole moment perpendicular to the (100) perovskite surface has been measured in SrTiO_3 , due to the partial covalency of the Ti-O bond [155]. The dipole moment is mitigated with creation of point defects and surface reconstruction; depending on the experimental environment, 2×1 , 4×2 and 6×2 reconstruction of the (001) surface has been reported [174].

Apart from the surface polarity, modern atomistic simulation demonstrates that the charge and size difference between the dopant and the host provides the driving force for the surface segregation at the atomic scale [175–177]. Lee et al. studied the surface segregation of various alkaline earths (Ca, Sr and Ba) on the LaMnO_3 surface, and showed that the segregation energy calculated with DFT was overall in good agreement with the sum of the elastic and electrostatic energy contributions [175]. The simulation was supported by surface composition analysis which revealed that among all of the studied compositions, Ca substitution, with the smallest mismatch between the dopant and the host, shows the lowest surface coverage—thus least likely to segregate towards surface [175]. Several authors have reported the effect of stress and polarisation on segregation [164,165,177]. Ding et al. demonstrated that the strontium surface segregation is suppressed by applying an LSM coating on the LSCF, indicating that compression stress on the surface reduces Sr segregation in LSCF [177]. Araki studied the surface segregation of LSCF under 28 MPa bending test, and observed smaller and fewer particles that were enriched with Sr in the areas under

compression stress [165]. Finsterbusch et al. applied 300 mV on a 1.1 mm thick LSCF film and observed higher concentration of Sr on the anode side in comparison to the cathode side. It was proposed that the vacancy gradient driven by the polarization promotes the Sr segregation process [164].

2.4.2 Impact of the segregation on performance

Impact of surface segregation on the electrodes and electrolyte performance has been well documented in the literature. Surface degradation from cation segregation limits the long-term performance and stability of the perovskite based electrode. Chen et al. [178] studied the electronic structure of $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_3$ and discovered an increase in surface band gap (from 2.5 eV for $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_3$ to 3.6 eV for SrFeO_3) with increasing Fe content while the surface Sr concentration increases. The results suggest the inhibition of charge transfer from the bulk to the surface with a higher degree of Sr segregation [178]. Indeed, the dopant segregation has significant impact on the surface exchange process. When studying the transport properties of the $(\text{La}_{1-x}\text{Sr}_x)_2\text{CoO}_4$ epitaxial films, Chen et al. reported no dependence of the surface exchange coefficient on crystallographic orientation, whereas the *ab* plane has an oxygen diffusivity about an order of magnitude higher than that along the *c* axis [168]. Sr surface segregation was observed at both the (001) and (100) terminations of the films, therefore it was speculated that the structural anisotropy is overridden by the surface segregation [168]. Significant reduction of the oxygen reduction reaction (ORR) activity of up to two orders of magnitude was reported in LSC [167,179]. The degradation of ORR activity is believed to be linked with Sr segregation, which forms insulating particles that blocks the charge transfer and the oxygen incorporation pathway [179].

The surface chemistry also impacts the performance of the electrolyte material. Steele proposed three pathways for oxygen diffusion into the electrolyte: 1. direct absorption, dissociation and incorporation at the electrolyte surface, 2. dissociative-adsorption of the oxygen at the cathode which and surface diffuses to the electrolyte and 3. surface reaction of oxygen at cathode followed by bulk diffusion towards electrode electrolyte interface. The electrolyte surface is of utmost importance for both the first and second pathways [180]. For YSZ, a linear correlation between the surface CaO coverage and the surface ^{18}O isotopic fraction after the isotopic exchange has been reported, indicating the blocking effect of the contaminant layer [169]. Isotopic exchange experiments revealed a sharp drop in the isotopic fraction in the near-surface region, indicating the presence of an intermediate layer with a

reduced diffusivity (Figure 2-15a). The diffusivity of the intermediate layer was fitted to be $4.9 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at 500°C whereas the bulk has a diffusivity of $D^* = 1.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ (Figure 2-15b). It was postulated that the intermediate layer has the monoclinic symmetry due to the reduced Y content, as the dopant has segregated towards the surface forming the monolayer Y enriched surface [181].

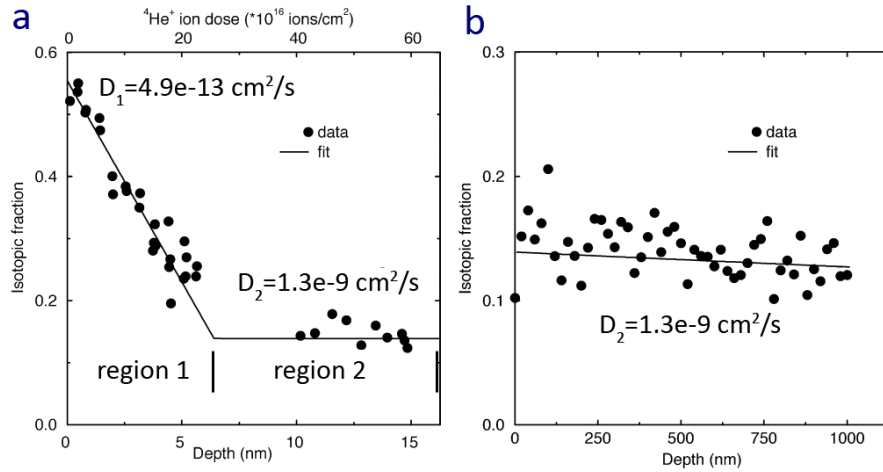


Figure 2-15: Diffusion profiles of 10YSZ (a) at the surface and (b) in the bulk, after exchanging in ^{18}O at 500°C for 10 min. Two distinctive regions are identified in (a): region 1, which is closer to the surface has much reduced oxygen diffusivity comparing with the underlying layers in region 2 [181]. Note the difference in the x-axis scale between the two plots.

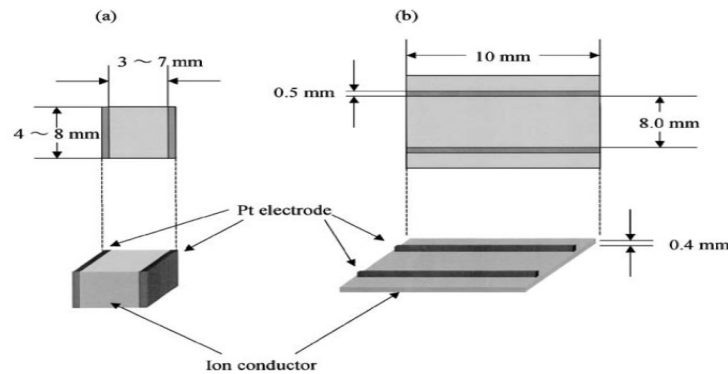


Figure 2-16: Schematics showing the setup to measure the a) bulk and b) surface conductivity used in ref [186].

As discussed in section 2.3.3, the grain boundary is often considered to be blocking for proton transport in acceptor doped LaNbO_4 and BaCeO_3 based proton conductors [182–185]. For Y doped BaCeO_3 , a grain boundary core enriched in Y has been confirmed experimentally and a depletion layer low in H concentration has been proposed based on the space charge theory [185]. Remarkably, Tomita and Hibino demonstrated that the surface layer of 25 mol% Y^{3+} doped BaCeO_3 has total conductivity of $8.24 \times 10^{-3} \text{ S cm}^{-1}$ at 400°C , three times higher than the bulk conductivity (the measurement geometry is shown in Figure

2-16 [186]). The surface is considered to have the same defect profile as half a grain boundary thus is expected to be a blocking layer. Surprisingly, a reduction in activation energy has been observed for the surface conduction (from 0.47 eV to 0.30 eV). Such behaviour is not observed in the YSZ and SDC samples [187]. The results highlight the importance of surface chemistry in determining the transport properties of proton conductors; although it is unclear the contribution of surface layer to the measured conductivity.

2.4.3 Surface studies of scheelite related materials

Despite the significant interest in utilizing scheelite related materials as catalysts, surprisingly little is known about their surface chemistry. Available literature often contains ambiguous and sometimes conflicting information. For instance, the surface composition of BiVO₄ photocatalyst has been reported by several authors using XPS, while some claim Bi enrichment with the Bi/V ratio ranging from 2 [188] to 2.94 [189], others suggest a near stoichiometric BiVO₄ surface [190]. Surface composition of CaWO₄ [191], CaMoO₄ [192] and CdMoO₄ [193] has been reported, although no quantitative cation ratio, nor comparison with the bulk composition is available.

Several reports have focused on the termination of the scheelite surface as well as its interaction with water and hydrogen. Cooper et al. studied the interaction between the scheelite CaWO₄ and water molecules using both atomic simulation and DFT and suggested physisorption of water and the formation of a semi-crystalline hydrous phase [194]. Their simulation also suggested that for the tetragonal scheelite phase, the {101}_t and {001}_t terminations have similar surface energy (0.64 J m⁻² and 0.79 J m⁻² respectively) [194]. Similar results were reported for the stoichiometric fergusonite LaNbO₄, as DFT simulation suggested a relaxed {010}_m plane, crystallographically related to the {001}_t of the scheelite structure, was favoured with the lowest surface energy (0.64 J m⁻² and 76 J m⁻² depending on the termination) [195]. However the H adsorption on this surface was strongly endothermic, and that H₂ splitting is more likely to occur at the less stable {101}_m termination [195]. Yan et al. studied the interaction between the stable {010}_m planes with 2.1 at% oxygen vacancies and water molecules using DFT. It was concluded that, unlike stoichiometric LaNbO₄, the dissociation of water into the proton and hydroxyl pair is spontaneous and favoured on the oxygen vacancy sites [196]. However, this study did not include the dopant in the simulation, neither has it addressed the possibility of surface segregation, which has a significant impact on the surface density of states [178]. It is worth emphasizing that the aforementioned studies,

amongst a few others [197,198], all focused on stoichiometric CaWO_4 and LaNbO_4 whose transport properties are very modest; reports on the surface chemistry of the LaNbO_4 ionic conductors are not available in the literature.

2.4.4 Summary

Many properties of the material, including the surface exchange of ionic conductors, are determined by the surface chemistry which can differ drastically from that of the bulk. In oxide systems, surface modification often manifests itself in the form of dopant segregation, as a result of surface polarity, stress, or a size and charge mismatch between dopant and the lattice. Surface segregation has pronounced effect on the oxygen reduction reaction and the transport properties for SOFC electrodes and electrolyte. Relationship between the long term instability and surface segregation has long been established for perovskite based structures.

However, when it comes to the surface chemistry of scheelite related materials, literature reports often provide confusing and sometimes conflicting information. Partially due to the lack of reliable compositional information, most of the literature concerning the scheelite surface to date focus on simulating the defect-free parent structures whose conductivities are modest. There is a pressing need to survey the surface chemistry of scheelite related materials, which will withhold useful information for property optimisation.

2.5 Chapter Summary

The scheelite related materials offer both rich structural chemistry and transport properties. Both fast oxygen and proton transport can be facilitated by the scheelite/fergusonite structure, depending on the doping strategies adopted. The hyperstoichiometric modulated CeNbO_{4+d} provides an interesting template for oxygen ion conduction [58]. Preliminary investigation on the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$, a structural analogue to CeNbO_4 showed promising results [94,137]. Despite the interest in the literature on the modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$, the modulated structure has yet to be solved. Consequently, the interplay between the interstitial oxygen, its complex structure and the transport property is not established. Doping strategies to produce interstitial containing LaNbO_4 based oxide conductors have not been fully explored to take full advantage of the CeNbO_{4+d} structural template. In addition to the bulk structural study, the surface chemistry of the LaNbO_4 based system, although key to the electrochemical performance, has been largely neglected in the literature. Understanding the surface, a highly

defective interface analogous to the grain boundary, might provide key information to overcome the low grain boundary conductivity in the LaNbO_4 based system.

This work therefore proposed to study the structure, transport properties and surface chemistry of LaNbO_4 based ionic conductors, in an attempt to further understand this promising, interesting but also challenging system. In Chapter 3, the techniques used in this work are introduced; following that the investigation into the room temperature modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ structure is carried out in Chapter 4. Building upon this knowledge, the high temperature phase transition and the structural evolution of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases are discussed, in Chapter 5, shedding light on the conducting mechanism of these hyperstoichiometric phases. Alternative doping strategies and the conducting properties of $\text{La}_{1-y}\text{Y}_y\text{Nb}_{1-x}\text{W}_x\text{O}_{4+d}$ are also reported in Chapter 5. Finally, the surface chemistry of LaNbO_4 based conductor is reported in Chapter 6, with special emphasis on the impact of Sr surface segregation on the proton transport of acceptor doped LaNbO_4 .

Chapter 3. Experimental Techniques

3.1 Sample preparation

The materials investigated in this work were prepared using solid state synthesis. Solid state synthesis is the most common way to produce ceramic solids by heating two or more components in stoichiometric mix at elevated temperature, and allowing the reaction products to form. Before synthesis, the La_2O_3 and SrCO_3 starting powders were treated at 1000 °C and 300 °C respectively for 10 h to remove moisture and carbonates. All the starting powders were examined with X-ray diffraction to ensure that they were single phases. Stoichiometric amounts of those starting powders were weighed using an electric balance with 0.0001 g precision (Sartorius) and then ground together in a pestle and mortar. The powder mixtures were ball milled for 24 h in acetone with zirconia balls to achieve a homogeneous mix. The mixed powders were first calcined under lab air at 1200 °C for 10 h, then crushed, milled and calcined again at 1400 °C for 10 h. The milling process was conducted using a ball-mill with ZrO_2 milling medium (mass ratio between powder and milling medium is approximately 1:5, radius of the ZrO_2 is approximately 7 mm). Phase purity was checked using XRD after each calcination step and the calcination process repeated for 2 to 3 times until no change in phase composition was confirmed.

In the case where pellet samples were required for subsequent characterisation techniques, approximately 0.5 g of powder was weighed and uniaxially pressed under 360 MPa pressure for 1 min, followed by isostatic press at 300 MPa for 1 min. Samples were then sintered at 1400 °C for 12 h with the heating/cooling rate set at 5 °C/min. Prior to the surface analysis, sintered samples were required to be ground and polished. Samples were first ground with SiC papers (600–4000 grade, particle size 16–6 µm, Struers) and then polished with successive grades of diamond polishing media (Type K diamond slurry, particle size 3–0.25 µm, Kemet) to obtain mirror surface finish.

3.2 Thermal analysis

3.2.1 Differential scanning calorimeter/Thermogravimetric analysis (DSC/TG)

In differential scanning calorimeter (DSC) measurement (Figure 3-1), the energy difference required to maintain a balanced temperature between the sample and the reference is recorded as a function of temperature, atmosphere and heating rate. The technique allows the precise measurement of the sample heat capacity and is a powerful tool to study the phase transition behaviour in ceramic materials. The power supply accurately adjusts and records the difference in the heat flow $\Delta_d H$ required to maintain the temperature balance T between the sample and reference. According to Eqn. 3.1, in which dH is the change in enthalpy, the heat absorbed or released during an endothermic or exothermic reaction may be calculated:

$$\frac{\Delta_d H}{dT} = \left(\frac{dH}{dT}\right)_{\text{sample}} - \left(\frac{dH}{dT}\right)_{\text{reference}} \quad \text{Eqn. 3.1}$$

Thermogravimetric analysis measures the weight change of the sample as a function of temperature using a high precision balance (accuracy of 0.0001 g). The change in oxygen stoichiometric of the sample can be inferred from the weight change.

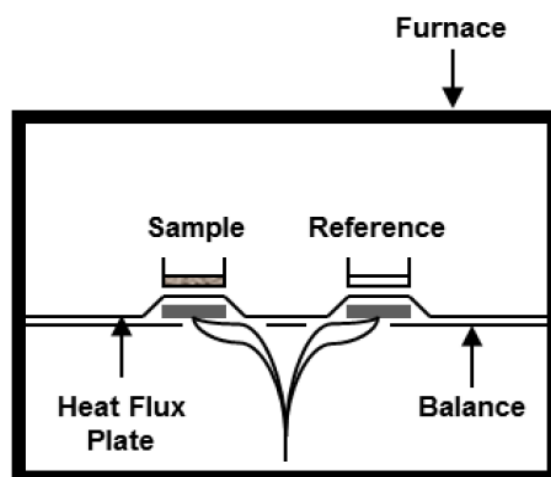


Figure 3-1: Schematic of the DSC/TGA set-up.

Simultaneous DSC/TG measurements were conducted using a NETZSCH STA 449C Jupiter heat flux instrument. Approximately 50 mg sample was loaded into the Pt crucible and the DSC/TG measurements were performed under static air environment from room temperature to 800 °C with a heating rate of 10 °C/min. The instrument was calibrated by measuring under the same conditions with only the sample environment (crucible plus the balance).

3.2.2 Dilatometry

Dilatometry measures the change of sample dimension caused by a physical or chemical process. The samples are in contact with a push rod which connects to a linear viable displacement transducer (LVDT) that records the displacement (Δl) as a function of controlling parameters such as temperature and atmosphere (setup shown in Figure 3-2). Knowing the initial length of the sample, l_0 , the thermal expansion coefficient α (TEC) is computed according to Eqn. 3.2.

$$\alpha = \frac{\Delta l}{l_0} \frac{1}{(T_{final} - T_{initial})} \quad \text{Eqn. 3.2}$$

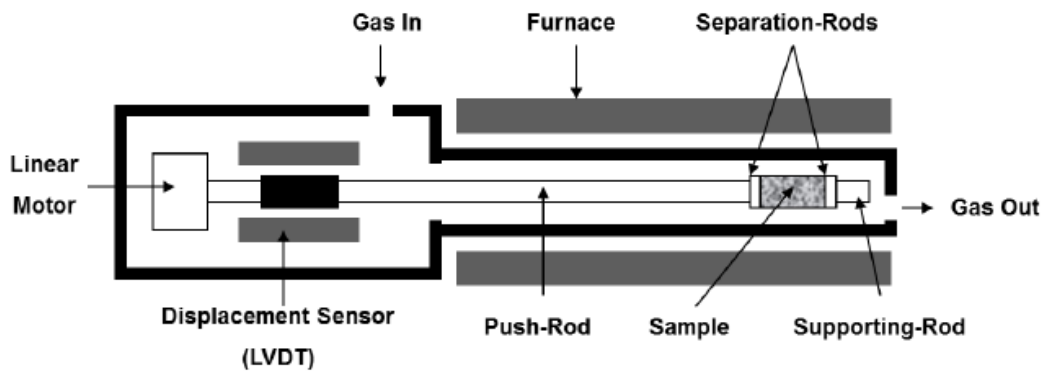


Figure 3-2: Schematic drawing of t dilatometry with a horizontal set-up.

Sintered, rectangular-shape samples with the size approximately 4 mm × 4mm × 25 mm were used for the dilatometry measurements. The samples were prepared using uniaxial press at 350 MPa followed by isostatic press at 300 MPa for 1 min. Samples were sintered at 1400 °C for 10 h and reached more than 95% density. A pure alumina reference was used to calibrate the instrument prior to sample measurement. The length change of the samples from room temperature to 800 °C with a heating rate of 10 °C/min was recorded using a NETZSCH DIL 402 E dilatometry.

3.3 Electron microscopy

3.3.1 Scanning electron microscope (SEM)

Scanning electron microscope (SEM) uses a well-focused electron beam to raster on the sample surface and detects the electrons and X-ray signals generated by the beam-sample interactions. For imaging purposes, two signals, namely the secondary electrons (SEs) and backscattered electrons (BSEs), are most commonly used. Secondary electrons, which are produced by the ejection of outer shell electrons from the inelastic scattering of the incident electron beam, have the lowest energy (<50 eV) thus shortest attenuation length (typically tens of nanometres) among the products of the electron-sample interaction [199]. Therefore, SE yield is sensitive to the surface roughness, porosity and edges, providing topological contrast. Backscattered electrons are produced by the elastic scattering of the beam. The BSE provides compositional contrast, as its intensity depends on the electron density, therefore the atomic number Z , of the samples. In addition to its imaging capability, modern SEM is often equipped with an energy/wave-dispersive X-ray spectroscopy (EDS/WDS) for chemical composition analysis. The electron-sample interaction produces characteristics X-ray radiation, which represents the discrete electron level bound to various atomic cores. Quantitative analysis of the EDX /WDS is performed according to Eqn. 3.3:

$$C_{Sample} = k \cdot C_{Standard} \cdot A \quad \text{Eqn. 3.3}$$

where C_{Sample} and $C_{Standard}$ are the concentration of the element of interest in the samples and standard respectively; the concentration is related by the measured intensity with the k ratio ($k \equiv I_{Sample}/I_{Standard}$), and a correction factor A , which corrects for absorption, X-ray fluorescence and other matrix related effect.

Two SEM instruments were used in this work: a JSM6400 SEM (Jeol), fitted with an EDX detector (Oxford Instruments Ltd), was used mainly for chemical composition analysis; a LEO Gemini 1525 field emission SEM (Zeiss) was employed for imaging purposes. For the JSM6400 SEM, accelerating voltage of 15 keV with 1×10^{-9} nA beam current at approximately 15 μm working distance was used to enhance counting statistics. The EDX was calibrated using a Ag standard prior to the analysis. The LEO Gemini 1525 was operated under 5-10 kV accelerating voltage to achieve optimal lateral resolution. Prior to the SEM

experiment, the insulating samples were coated with carbon (K975X, Turbo-Pumped Thermal Evaporators, Quorum) to prevent charge accumulation at the insulating sample.

3.3.2 Transmission electron microscope (TEM)

Transmission electron microscope (TEM) is a powerful technique that studies the interaction between the high energy electron beam (typically accelerated with 200-400 kV voltage) and a thin sample (typically tens of nanometres thick). The beam transmits through the sample and generates various types of signals (shown in Figure 3-3) providing chemical and structural information of the sample at nano or even atomic scale.

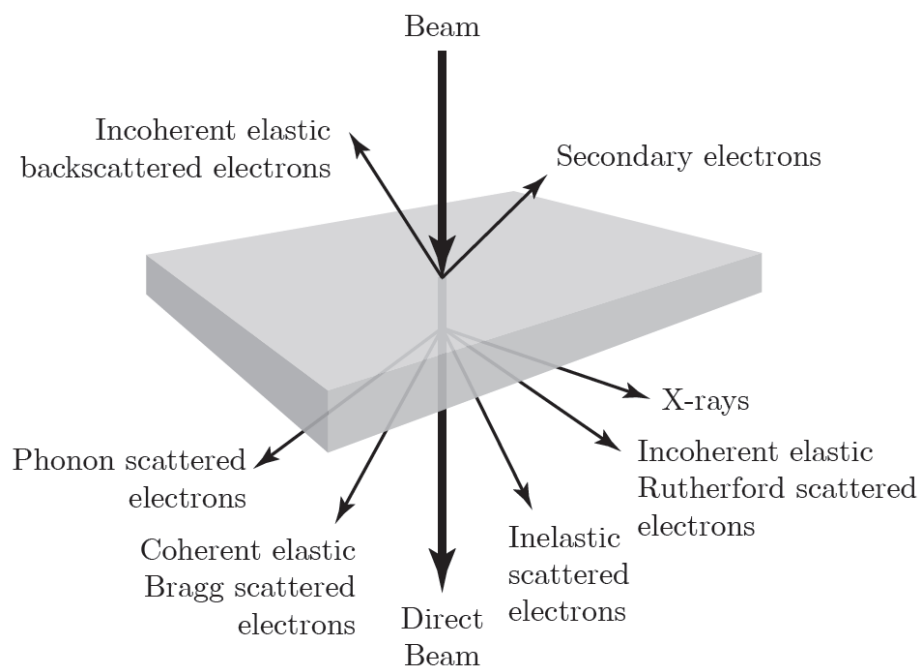


Figure 3-3: Schematic illustrates the products from the sample-beam interaction in TEM.

Conventional TEM operates in a fashion that is similar to optical microscopy, though instead of visible light, the electron wave is used to produce the image and diffraction pattern in TEM. According to Rayleigh [200], the smallest distance Δl that can be resolved in a microscope is expressed in Eqn. 3.4:

$$\Delta l = 1.220\lambda/n \quad \text{Eqn. 3.4}$$

in which λ is the wavelength and n is a constant depending on the geometry of the receiving lenses [200]. Employing electron beams, which have a much shorter wavelength compared to visible light ($\lambda=0.00251$ nm for 200 keV electron, whereas $\lambda = 380\text{--}750$ nm for visible light [200]), grants a huge boost to the theoretical resolution limit. Achieving atomic resolution

during characterization is still a challenging task, and the actual resolution power of the instrument is often constrained by the spherical and chromatic aberrations of the electromagnetic lenses [200].

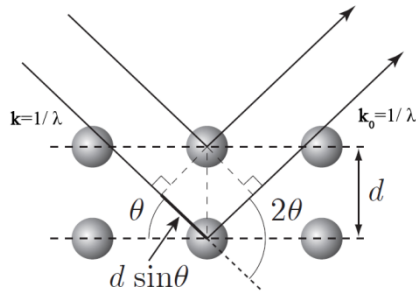
A wide range of products (summarized in Figure 3-3) are created from the electron-sample interaction. Analysis of these products provides a rich body of information about the chemistry, morphology and the crystal structure of the sample. Various imaging modes are available based on the contrast mechanisms. For instance, *bright field* images are produced using direct beam that has not been scattered by the sample. The intensity depends on the attenuation of the electron beam thus providing contrast based on the sample thickness. Alternatively, a *dark field* image forms when the scattered electrons are collected, producing contrast based on the atomic mass, as heavier elements have a higher probability of scattering the electron beam. *High angle annular dark field* (HAADF) is a variation of the *dark field* imaging which, as the name suggests, only collects electrons that have been scattered to higher angles. In addition to imaging, TEM also provides rich structural information with *electron diffraction* (ED) technique. The ED patterns are formed with coherent elastically scattered electrons at the back focal plane of the electromagnetic lenses. Compared with XRD (introduced in section 3.4.3.3), the electron beam is able to probe large reciprocal space, due to its short wavelength. Instead of the parallel beam condition in conventional TEM, modern instruments have the ability to focus the electron beam into a narrow spot which scans the sample in a raster. The operation mode, termed scanning transmission electron microscope (STEM), is similar to SEM, and is often used to probe the local chemical variations using techniques such as EDX and electron energy loss spectroscopy (EELS).

In the current project, a JEM-2100F TEM/STEM (JOEL) operated at 200 kV was used. Powder samples for structural analysis were prepared by grounding the sample in acetone solution which was then dispersed onto a copper grid. Lamellar samples were prepared using a focused ion beam (Helios Nanolab 600) following the procedures described in [201].

3.4 Crystal structural characterization using diffraction techniques

3.4.1 Diffraction theory

Diffraction technique is widely used to study the crystal structure of matters. The position, intensity and the shapes of the Bragg reflections reveal information about the lattice parameters of the crystal, the atomic coordinates as well as sample conditions (such as strain and crystal size of the sample) [99]. The modern diffraction technique is based on the well-known Bragg's law which predicts that the maximum constructive interference occurs when the path difference (P.D.) of the incoming waves are equal to an integer number of the wavelength (Figure 3-4 and Eqn. 3.5), when scattered by a plane of atoms:



$$\text{P.D.} = n\lambda = 2\sin\theta d_{hkl} \quad \text{Eqn. 3.5}$$

Figure 3-4: Schematic highlights the Bragg's diffraction condition for maximum constructive interference.

In Eqn. 3.5, λ is the wavelength of the scattered wave; d_{hkl} is the interplanar distance of the hkl plane, and θ gives the Bragg peak position.

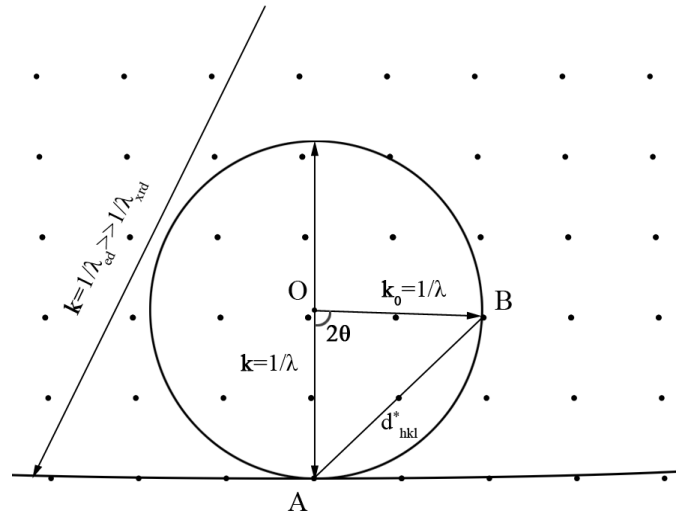


Figure 3-5: Ewald sphere construction demonstrates the Bragg's diffraction condition for X-ray diffraction and electron diffraction in the reciprocal space. The radius of the sphere equals to $1/\lambda$, inverse of the wavelength of the incident waves. OA and OB represents the incoming wave and scattered wave vector whereas AB corresponds to the scattering vector S . The Bragg condition is fulfilled when the Ewald sphere intercepts with the reciprocal lattice point. Similar construction is made for the electron diffraction (introduced in section 3.4.3.3), which utilises much shorter wavelengths thus leads to a sphere with much larger radius.

The Bragg condition is better visualized in reciprocal space with the construction of the Ewald Sphere (shown Figure 3-5). The radius of the sphere is $1/\lambda$, which is equal to the modulus of the wave vector $|k|$. The vectors **OA** and **OB** represent the direction of the incident wave and the scattered wave respectively; the difference between the two wave vectors is defined as the scattering vector **S**. The Bragg condition is satisfied when the sphere intercepts the reciprocal lattice, i.e. $|\mathbf{S}| = \frac{2 \sin \theta}{\lambda} = \frac{1}{d} = |\mathbf{d}^*|$. Therefore, the reflection condition in the reciprocal space is expressed in Eqn. 3.6:

$$\mathbf{k}_0 - \mathbf{k} = \mathbf{S} = \mathbf{d}_{hkl}^* \quad \text{Eqn. 3.6}$$

3.4.2 Structure factor and refinement

The Bragg's law (Eqn. 3.5) and Ewald sphere construction reveals the position of the maximum intensity of the constructive interference whereas the intensity of the reflections $I(\mathbf{S})$ relies on the structure factor $F(\mathbf{S})$ which depends on the scattering power $f(\mathbf{S})$ of all the atoms in the unit cell, and the position of these atoms in the lattice $\mathbf{x}(\mu)$. In an infinite crystal, the overall structure factor $F(\mathbf{S})$ is a sum of all the scattered wave vectors from all the atoms in the lattice, as shown in Eqn. 3.7:

$$F(\mathbf{S}) = \sum_{\mu=1}^n f_{\mu}(\mathbf{S}) \exp[2\pi i \mathbf{S} \mathbf{x}(\mu)] \quad \text{Eqn. 3.7}$$

In X-ray diffraction, $f_{\mu}(\mathbf{S})$ is the angular dependent atomic scattering factor for the atom μ , whereas in neutron it represents the elastic scattering cross-section of the particular atom [99]. The expression is expanded to include the effect of structural modulation, which has been introduced in section 2.2.1, on the structure factor:

$$F(\mathbf{S}) = \sum_1^N \sum_{\mu=1}^n f_{\mu}(\mathbf{S}) \exp[2\pi i (\mathbf{S}(\mathbf{L} + \mathbf{x}(u) + \mathbf{u}^{\mu}(x_4, \dots, x_i)))] \quad \text{Eqn. 3.8}$$

in which $\mathbf{L}$ is lattice vector and $\mathbf{u}^{\mu}(x_4, \dots, x_i)$ is the displacement due to structural modulation as defined in Eqn. 2.5 in section 2.2.1. The structure factor is summed over all N^{th} parent cells due to the lack of translational symmetry in the modulated structure [100].

For both modulated and unmodulated structure, the intensity of the scattering wave vector $I(\mathbf{S})$ is related to the structure factor by Eqn. 3.9:

$$I(\mathbf{S}) = |F(\mathbf{S})|^2 \quad \text{Eqn. 3.9}$$

It is clear from Eqn. 3.7 and Eqn. 3.9 that the structure factor is a complex number whereas the measured scattering intensity is a scalar. Consequently, the phase information of the structure factor is lost during the diffraction experiment, which constitutes the phase problem of crystal structure determination [99].

Rietveld method is the most commonly applied methodology to solve crystal structures. The Rietveld method records the whole diffraction pattern and compares the measured intensity with a model which not only contains information about the crystal structure (space group, lattice parameters, atomic positions *etc.*), but also experimental factors such as scaling parameter, background intensity and peak profiles due to instrumental broadening [202,203]. These parameters are then optimized using a least square procedure, until a best match to the experimental data is found [203].

Although visual inspection of the refined pattern is often considered the most reliable way to determine the quality of fitting, there are several figures of merits which characterize the general quality of fitting [204,205]. The most commonly used figures of merit include the weighted R value R_{wp} , the statistically expected R_{exp} and goodness of fitting χ which are defined in Eqn. 3.10 to Eqn. 3.12 accordingly:

$$R_{wp} = \left\{ \frac{\sum_i w_i [y_i(obs) - y_i(calc)]^2}{\sum_i w_i [y_i(obs)]^2} \right\}^{1/2} \quad \text{Eqn. 3.10}$$

$$R_{exp} = \left[\frac{(N - P)}{\sum_i^N w_i y_i(obs)^2} \right]^{1/2} \quad \text{Eqn. 3.11}$$

$$\chi = R_{wp}/R_{exp} \quad \text{Eqn. 3.12}$$

in which $y_i(calc)$ and $y_i(obs)$ are the calculated and observed intensity at the i^{th} data point; w_i is the weighting factor which depends on standard uncertainty (*s.u.*) of the particular data point; N is the number of observation and P is the number of refined parameters. R_{wp} is numerically minimized during a Rietveld refinement whereas R_{exp} reflects the counting statistics of the data. Generally, low values of R_{wp} and R_{exp} , with the goodness of fitting χ

approaching 1, tend to suggest good structure model with high quality data. However, these figures of merit should not be over interpreted, and no single set of standard exists that guarantees a good fit [205]. Again, one should rely more on the visual inspection of the fitted pattern to identify the discrepancy between the model and the dataset [204,205]. In this work, the structural refinement was carried out using Jana 2006 [206], a software specialized in refinement of high dimensional crystals.

3.4.3 Experiment conditions for the diffraction experiments

3.4.3.1 X-ray powder diffraction (XRD)

Room temperature XRD scattering data were gathered using both a PANalytical X'Pert Pro MPD and a Bruker D2 Phaser diffractometer, with Cu K α radiation, $\lambda = 1.54056 \text{ \AA}$. Typically, a step size of 0.01° from 10° to 100° with a 50 s counting time was used to check for phase purity.

Phase transitions of various LaNbO₄ based ionic conductors were investigated using *in-situ* high temperature PANalytical X'Pert diffractometer (Cu K α_1 radiation with $\lambda = 1.54056 \text{ \AA}$) fitted with a Böhler HDK 2.4 high-temperature chamber. Samples were placed on a Pt heating tape whose temperature was controlled with joule heating. Diffraction patterns were collected from room temperature up to 800°C with the heating rate set to 60°C/min and a rest time of 1 min for thermal equilibrium. The actual temperature of the Pt strip was calibrated by refining the lattice parameter of the Pt. The temperature gradient within the sample was considered negligible due to the low sample mass used in the experiment (less than 0.1 g). Typically, the scan range was set to be 12° to 80° with a 0.02° step size and a counting time of 200 s/step.

3.4.3.2 Synchrotron radiation

Due to the inherent limitations associated with laboratory X-ray equipment (namely, high peak width, low X-ray flux, overlapping intensity), accurate structural information cannot be satisfactorily obtained. These limits can be partially overcome using synchrotron radiation, which provides a high intensity monochromatic source. Room temperature measurements of the LaNb_{0.88}W_{0.12}O_{4+d} composition were conducted on BL04 (MSPD) at Alba Synchrotron, Barcelona, Spain, and the dataset in the range $2.94^\circ \leq 2\theta \leq 20.00^\circ$ was used for the refinement. The measurements were conducted using a wavelength of $0.3308 \text{ \AA}$, which had been calibrated using a Si standard.

3.4.3.3 Electron diffraction (ED)

The diffraction condition for electron diffraction (ED) in TEM may be visualized in the Ewald sphere construction in Figure 3-5. Compared with XRD, the sphere for ED has a larger radius corresponding to the much shortened wavelength employed in electron diffraction: the de Broglie wavelength of an electron with 200 keV energy is approximately 0.0251 Å whereas the wavelength of Cu K α_1 emission (one of the most commonly used lab X-ray sources) is 1.5406 Å, consequently, the scattering vector $\mathbf{S}$ becomes negligible comparing with the wave vector $\mathbf{k}_0$, and the diffraction condition is fulfilled when the wave vector is perpendicular to the reciprocal lattice:

$$\mathbf{k} \cdot \mathbf{d}_{hkl}^* = 0 \quad \text{Eqn. 3.13}$$

The electron diffraction patterns and the modulation wave vectors $\mathbf{q}$ were obtained using a JOEL-2010 microscope operated at 200 kV, equipped with a Gatan double tilt holder. The diffraction pattern was gathered with an objective aperture of 36 nm⁻¹ diameter and beam semi-convergence of 1 mrad. The symmetry of the diffraction pattern was simulated using the CrystalMaker software suite [207].

3.4.3.4 Neutron scattering with a pulsed source

To investigate the structural evolution and the interstitial oxygen position in the modulated LaNb_{1-x}W_xO_{4+d} phases, an *In situ* neutron scattering experiment was carried out on HRPD at ISIS, Oxford, United Kingdom. ISIS utilizes a pulsed neutron source whose operational principle is different from the constant wavelength diffraction experiments.

At ISIS, the neutron flux is generated by bombarding a tungsten target with protons that travel at a fraction of speed of light. The neutrons vary in speed, thus wavelength, according de Broglie equation. The wavelength of a single neutron is related by its velocity (v) by Eqn. 3.14:

$$\lambda = \left(\frac{h^2}{2mE} \right)^{\frac{1}{2}} = \frac{0.003955}{v} = \frac{0.003955t}{L} \quad \text{Eqn. 3.14}$$

where h is the Planck constant; t is the time required for the neutron to travel from its source to the detector (time of flight, ToF.); L is the flight path, which depends on the beamline construction. A linear relationship between the ToF of the neutron and its wavelength is expressed in Eqn. 3.14.

Combining equation Eqn. 3.14 and the Bragg's law yields Eqn. 3.15:

$$t = 505.5569 L d_{hkl} \sin \theta \quad \text{Eqn. 3.15}$$

HRPD instrument uses fixed geometry detectors (fixed θ) and measures the ToF of the neutron, thus records the scattering event with the corresponding d spacing. The scattering conditions for ToF neutron scattering are shown in Figure 3-6. Instead of gathering scattering signals by scanning through θ (i.e. change the position of the detector or the incident beam so that different wave vector $\mathbf{S}$ is recorded), the Bragg condition is fulfilled for all the lattice planes that are in the shaded area. The detector assigns the intensity to the correct wave vector $\mathbf{S}$ by measuring t in Eqn. 3.15.

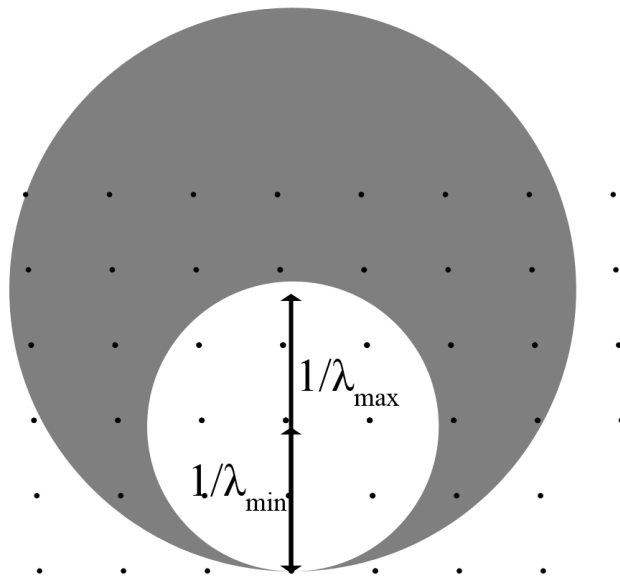


Figure 3-6: Ewald sphere construction showcases the experimental conditions of ToF neutron scattering; all the reciprocal lattices in the shadowed area are probed with the incident neutron wavelength varying from $\lambda_{\min}$ to $\lambda_{\max}$.

In X-ray diffraction, the scattering intensity is directly linked to the electron density thus the atomic number of the atom. Consequently, light elements, such as O, are often difficult to detect using XRD. In addition, atoms with similar Z number are difficult to differentiate using X-rays [99]. Neutrons are charge neutral, thus primarily interact with the nucleus [208]. The scattering intensity is defined similarly to X-rays (see Eqn. 3.7), although the atomic scattering factor f is replaced by the neutron scattering length b . The scattering length of common elements is summarized in Figure 3-7, in which a positive neutron scattering length represents a repulsive Fermi pseudopotential for the neutron scattering (although the true potential might have a very different form). Conversely, a negative scattering length indicates

an attractive pseudopotential [209]. Unlike the atomic scattering factor which increases monotonously with atomic number Z [209], neutron scattering length shows no dependence on the atomic number [210]. Neighbouring elements might have drastically different scattering length; in addition, the scattering power of light elements such as oxygen is comparable to heavy metals, making them “visible” using neutron scattering. A few elements such as V, scattering neutron very weakly, and is used to manufacture the sample environment for *in-situ* neutron scattering experiments.

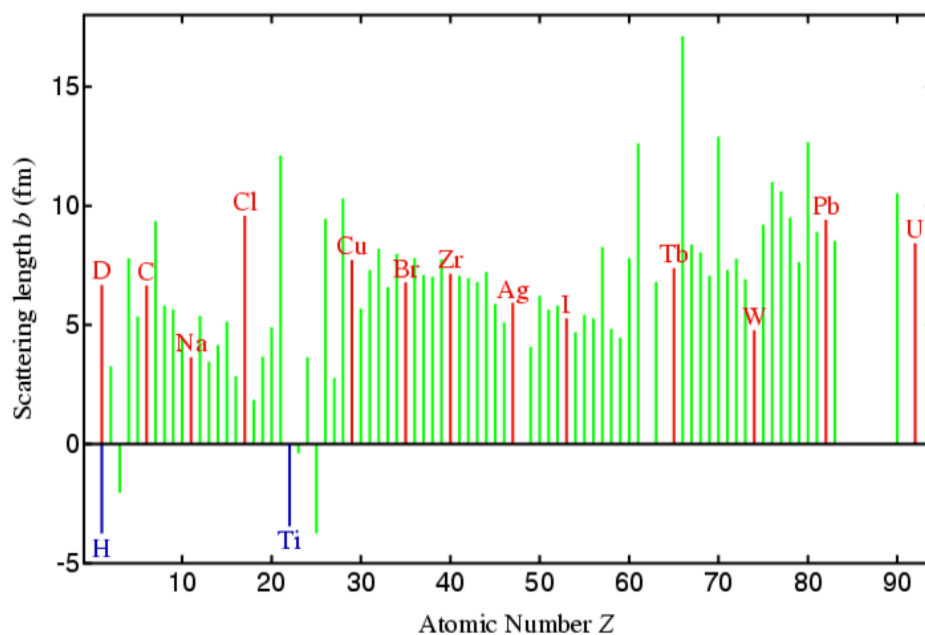


Figure 3-7: Scattering length of selected elements and isotopes. The scattering power of nuclei depends on the strong interaction between the neutron and nucleus and shows no dependence on atomic number [210].

To study the phase transition and to identify the interstitial position of hyperstoichiometric $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases, *in situ* neutron scattering measurements were performed at HRPD beamline at ISIS, the Rutherford Appleton laboratories, UK. Approximately 10 g of sample was placed inside a quartz ampoule, which was heated by a vanadium furnace. Diffraction patterns from room temperature up to 800 °C were gathered; the heating rate was set at 10 °C/min and a 10 min holding time was allowed for thermal equilibrium before each measurement began. For data normalization, signal from the background was measured with an empty ampoule in the furnace environment. Datasets from the backscattered bank ($2\theta \approx 145^\circ$) in the range of $2.6 \text{ \AA} \geq d\text{-spacing} \geq 0.9 \text{ \AA}$ were used for the refinement.

3.5 Surface analysis techniques

3.5.1 Secondary Ion mass spectroscopy (SIMS)

Secondary ion mass spectrometry (SIMS) is a technique that analyses the surface chemical composition using secondary ions generated by bombarding the sample surface with primary ions. The primary ions are accelerated towards the sample surface and their energy (typically 0.5 keV-40 keV) is transferred to the sample with a series of collision, recoil, sputtering and other events (the processes are schematically shown in Figure 3-8). The interaction between the primary ion beam and sample generates charged secondary ion species which are collected with a biased field. The mass of these charged secondary ions are determined with a mass spectrometer. The depth resolution of SIMS depends on the penetration depth of the primary beam, and is often cited to be 1-2 nm [211,212].

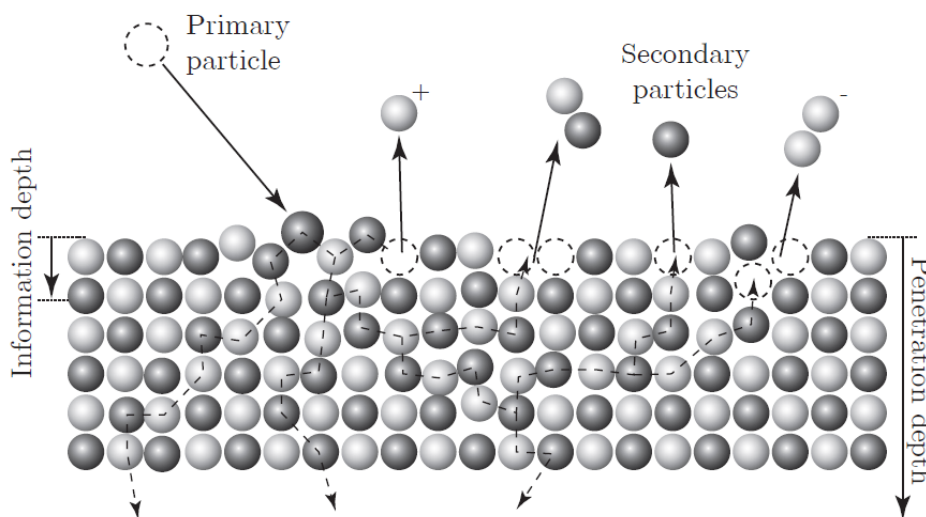


Figure 3-8: Schematics illustrates the interaction between the primary ion and the sample surface during a SIMS experiment [213].

SIMS is a semi-quantitative technique as the secondary ion yield depends heavily on the local composition. The ionisation of the ejected particles occurs at, or very close to, the sample surface, and the probability to generate atom/ion is closely related to local electronic structure. Changing the concentration of the other components in the sample would therefore alter the intensity of the analyte, and such effect is often termed as the “matrix effect” [212]. Due to the chemical similarity between isotopic species (i.e. ^{18}O , ^{17}O and ^{16}O), the difference in their ionisation probability, thus secondary ion yield, is negligible. Therefore, in this work, the SIMS technique is mainly used for the measurement of isotopic diffusion profile (introduced in section 3.7). All the experiments were conducted using a TOF.SIMS⁵(IONTOF)

instrument with a 25 keV Bi⁺ liquid metal primary ion source. A Cs⁺ sputtering gun (1–2 keV), which enhances the O⁻ yield, was used for the oxygen tracer diffusivity measurements whereas an O²⁻ sputtering gun was used and metal oxide molecular species MO⁺ were monitored when investigating the cation distribution of the sample.

3.5.2 Low energy ion scattering (LEIS)

LEIS uses charged primary noble gas ions (He⁺, Ne⁺ or Ar⁺) with energy ranging from 0.5 keV to 8 keV to bombard the surface of the sample. Instead of detecting the secondary ion leaving the surface as in SIMS, noble gas projectiles recoiled from the surface are captured by the detector where their final energy is measured. Assuming the collision is purely elastic, the resultant energy of the noble gas is a function of the primary ion energy, the scattering geometry and the mass of the target ion, expressed in Eqn. 3.16:

$$E_f = \left(\frac{\cos\theta \pm \sqrt{h^2 - \sin^2\theta}}{1 + h} \right) E_0 \quad \text{Eqn. 3.16}$$

where θ is the scattering angle shown in Figure 3-9; $h = m_2/m_1$ is the mass ratio between the primary ion and the target ion; E_f and E_0 are the energy of the projectile before and after the scattering process respectively.

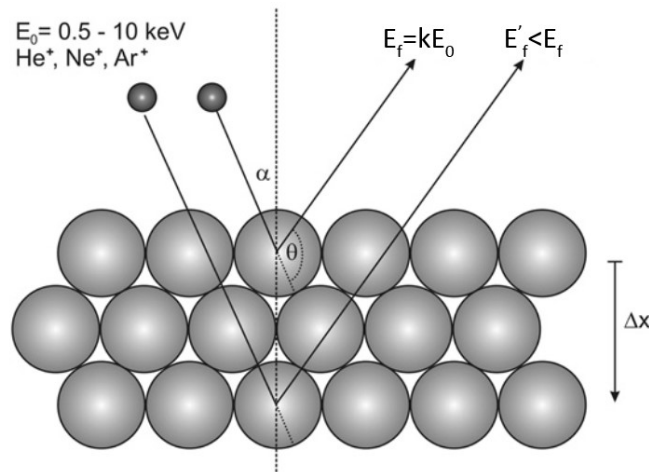


Figure 3-9: Schematics illustrates the sample-ion interaction during LEIS experiments. After scattering elastically from the outermost layer, the resultant energy E_f of the primary ion is a function of the mass of the target on the surface. Alternatively, ions might survive the interaction with the in-depth layers, leading to reduced scattered energy E'_f and background signal [161].

With fixed geometry and known primary ion energy, the mass of the target ion can be calculated from the energy of the projectile. In real experiments, inelastic collision occurs and ions emerging from in-depth layers after surviving the reionization process would have a

reduced kinetic energy (E_f' as shown in Figure 3-9) and contribute to the low energy background of the spectrum.

LEIS is a powerful technique that has the ability to probe the chemical composition of the outermost atomic layer. The high surface sensitivity stems from the neutralization behaviour of the primary noble gas ions: once penetrating deep into the sample, the noble gas has a high probability to be neutralized thus become undetectable when re-emerging from the sample surface [161]. Reionization after scattering from the in-depth layer is possible, especially on metal oxide surface in the presence of oxygen [161]. However, reionization is often accompanied with other inelastic processes and does not contribute to the elastic scattering peak. Brongersma gives a comprehensive review of the physical characteristics of the various neutralization and reionization processes in LEIS [161].

Unlike the SIMS technique, whose ion yield has a strong dependence on the surrounding chemical composition, the overwhelming majority reports of quantified LEIS data shows no sign of matrix effects (summarized in [161]) although the physics underlying the absence of the matrix effect is still not clear. Due to the absence of the matrix effect, LEIS is considered a quantitative technique that gives the true chemical composition of the outermost surface, although standards are often required for quantification. The ion yield A_i^+ in a LEIS experiment is governed by the following expression:

$$A_i^+ = N_0 \cdot c_i \cdot \left(\frac{d\sigma}{d\Omega}\right)_i \cdot d\Omega \cdot \eta_i^+ \cdot P_i^+ \cdot t \quad \text{Eqn. 3.17}$$

where N_0 is the number of primary ions; c_i is the concentration of target ions on the surface; $\left(\frac{d\sigma}{d\Omega}\right)_i$ is element dependent scattering cross-section, which describes the possibility for a scattering event to occur; $d\Omega$ is the solid angle, determined by the geometry of the detectors; η_i^+ represents the detector efficiency; P_i^+ is the ionization fraction that describes the survival probability of the primary ion after the scattering event, and t is the acquisition time.

A Qtac100 LEIS instrument (IONTOF Inc.) was used to study the surface composition of LaNbO_4 based ionic conductors. The geometry of the instrument is shown in Figure 3-10; a primary ion gun is positioned perpendicular to the sample surface whereas a ring detector gathers the scattered ions with a 145° scattering angle. The instrument is also equipped with a sputtering gun, with a 59° incident angle towards the surface, for *in situ* cleaning and depth profiling. Prior to the LEIS analysis, the surface of the sample was cleaned, sequentially using acetone, isopropanol and distilled water, to remove organic contaminants. After

transferring the samples into the LEIS instrument, the samples were cleaned again *in situ* using atomic oxygen or low dose of Ar^+ sputtering to remove the outermost contaminant layer. High vacuum of 10^{-8} mbar was maintained in the main chamber during the surface analysis experiment.

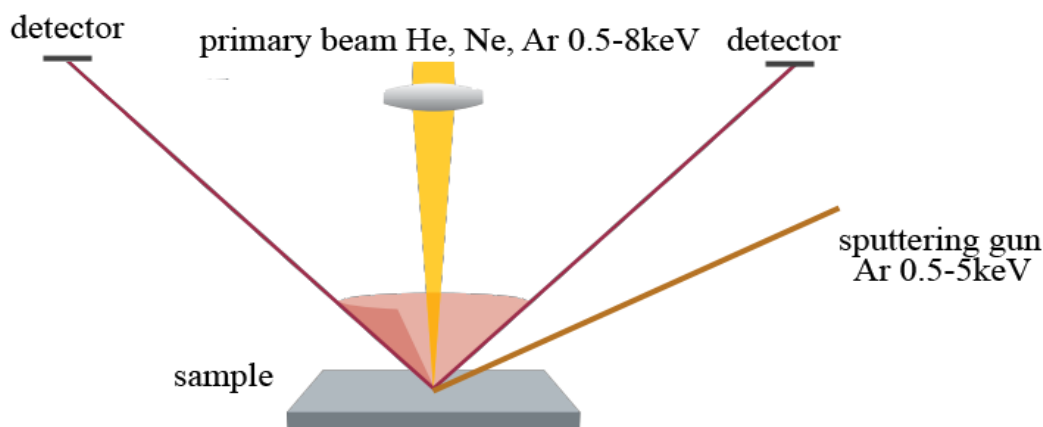


Figure 3-10: Schematics showing the measurement geometry of the Qtac100 LEIS instrument; a primary beam is fixed perpendicular to the sample surface, whereas the sputtering gun has a 59° incidence. The scattered ions with 145° scattering angle are collected by the detector [214].

During a typical LEIS experiment, a “survey spectrum” using 3 keV He^+ primary beam was first gathered to characterize the remaining contamination on the surface after the cleaning process. He^+ is able to scatter from common light element contaminants, such as C and O. However, He^+ primary ions suffer low mass sensitivity when scattered from heavier elements Eqn. 3.16. Quantification data were acquired using a 7 keV Ne^+ beam which affords better mass separation between the heavy cations according to Eqn. 3.16. To ensure that LEIS experiment occurs in the “static region”—the state at which the surface is considered to be unmodified, the dose density of the primary beam must be restricted. The sample surface is considered to be unmodified if less than 1% of the surface atoms have been altered, which corresponds to $10^{13}/\text{cm}^2$ atomic density [212]. Therefore the primary beam dose was restricted to be below $3 \times 10^{14}/\text{cm}^2$ and $2 \times 10^{13}/\text{cm}^2$ respectively for He^+ and Ne^+ primary ions during the data acquisition to satisfy this requirement. Quantification of the LEIS data relied on an internal reference, namely the stoichiometric bulk composition which was obtained by sputtering away the surface layers, and the detailed experimental conditions for the LEIS measurements are established in Chapter 6.

3.5.3 X-ray photoelectron spectroscopy (XPS)

Another surface analysis technique that has been employed was X-ray photoelectron spectroscopy (XPS). The samples are irradiated with X-rays which excite electrons from the inner shells. The kinetic energy of the escaping electrons, which is sensitive to both the bond valence and the bonding environment, is measured by the detector. In order to reach the detector from the sample, a photoelectron must survive any inelastic collision and recombination events. Therefore the signal from the surface is much stronger than that generated from the in-depth layers, making XPS a surface sensitive technique. In this work, XPS spectra were gathered on a Thermo Scientific K-Alpha⁺ X-ray Photoelectron Spectrometer, which uses a monochromated, microfocused Al K α X-ray source ($h\nu = 1486.6$ eV) and a 180° double focusing hemispherical analyser with a 2D detector. The X-ray source was operated with a 6 mA emission current and 12 kV anode bias. Data were collected at 200 eV pass energy for survey and 20 eV pass energy for core level and valence band spectra using an X-ray spot size of 400 μm^2 . A flood gun was used to minimize sample charging. All data were analysed using the Advantage software package.

3.6 Electrochemical impedance spectroscopy (EIS)

3.6.1 Theory of impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measures the frequency dependent complex impedance by applying an alternating voltage V and records the current response I . The frequency dependent complex impedance of the sample is defined as the ratio between the voltage and the current:

$$Z = V/I \quad \text{Eqn. 3.18}$$

in which Z is the complex impedance whereas V and I are both vectors under alternating current (AC) conditions, as defined in Eqn. 3.19:

$$\begin{aligned} V &= |V|e^{i(\omega t + \phi V)} \\ I &= |I|e^{i(\omega t + \phi I)} \end{aligned} \quad \text{Eqn. 3.19}$$

in which ω is the frequency of the AC; $|V|$ and $|I|$ are the magnitudes for the voltage and current whereas ϕV and ϕI are their corresponding phase angles. The definition of

impedance Z is an extension of direct current (DC) resistance R under AC conditions; impedance Z has a magnitude as well as a phase component. The magnitude of the impedance determines the ratio between the magnitude of V and I whereas the phase records the difference between the phase angles ϕV and ϕI . The concept of complex impedance is necessary due to the presence of non-resistance components, such as capacitors and inductors, which leads to the phase difference between V and I [215].

The electrochemical performance of ceramic electrolytes is routinely investigated using EIS. The electrical response of a single grain is analogous to a pair of resistance (R) and capacitor (C) components connected in parallel. Under the electric field, a grain behaves like a resistor as the charge carriers move along the field direction, constituting a current that is proportional to the field strength. In the meantime, the grain also displays capacitive behaviour, as polarization develops due to the alignment of charge ions under the alternating electric field. Applying the same argument, the electric response of grain boundaries can also be described as RC components in parallel. The capacitance of the grain boundary component is however much higher than that of the grain, reflecting the reduced thickness of the grain boundary, assuming the grain boundary and grain bulk have similar chemical composition thus relative permittivity [216]. Based on the brick layer model [215], a ceramic material can be visualized as individual grains connected with a network of grain boundaries. Consequently the overall electrical response of the sample is simplified as two RC in series (shown in Figure 3-11), with an additional contribution sample-electrode interface response.

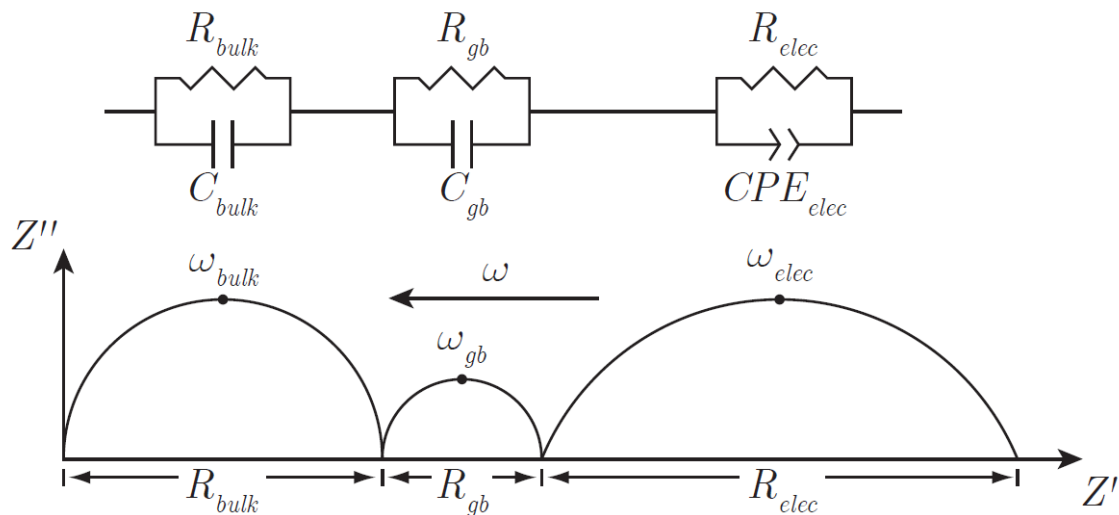


Figure 3-11: Schematic demonstrates the EIS response of an electrolyte with Pt electrodes painted on the surface. The response from different part of the sample is differentiated based on the characteristics capacitance $C=1/R\omega$.

The real and imaginary part of the impedance through a wide range of frequencies is recorded in the Nyquist plot. Contributions from various electrochemical processes are distinguished by their characteristic frequencies ($\omega = 1/RC$, summarized in Table 3-1). Consequently, a separation of grain interior and grain boundary contribution to the total conduction is possible using the EIS measurements. In summary, EIS measurements are able to differentiate the response from grain boundary, grain interior and other contribution by examining the characteristic frequency whereas the frequency dependent response is absent in direct current (DC) based measurements.

Table 3-1: Characteristic capacitance value and the potential interpretations [216].

Capacitance / F	Phenomenon Responsible
10^{-12}	Bulk conduction
10^{-11}	minor, second phase
10^{-11} – 10^{-8}	grain boundary conduction
10^{-10} – 10^{-9}	bulk ferroelectric
10^{-9} – 10^{-7}	surface layer
10^{-7} – 10^{-5}	sample-electrode interface
10^{-4}	electrochemical reactions

3.6.2 Experimental conditions

The EIS measurements (setup shown in Figure 3-12) were carried out with a two-probe geometry: two Pt mesh electrodes connecting a frequency response analyser (Solartron 1260FRA) were attached to the opposite sides of the sample. The magnitude of the AC wave was set at 0.5 V cross the sample and the corresponding current as a function of frequency was recorded by the FRA. The response in the frequency range from 1 MHz to 1 Hz with 30 points per decade was probed, and an integration time of 1 s at each frequency was allowed for data acquisition. The temperature profile of the sample was controlled by SMaRT impedance measurement software (SMaRT, v 3.3.0, Solartron analytical).

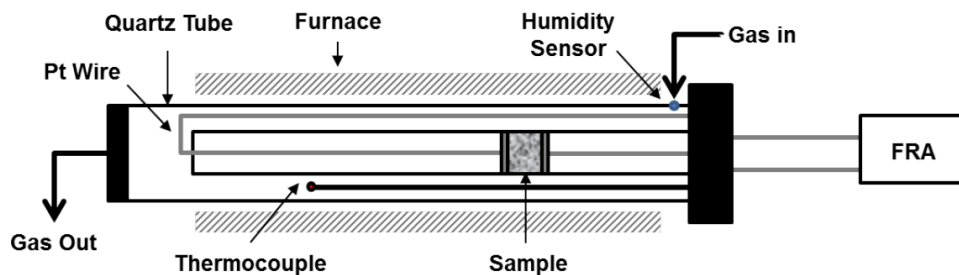


Figure 3-12: Schematic of the sample environment for the EIS measurements.

For a typical measurement, the impedance was measured from 400 °C to 900 °C with a 50 °C interval. Once the set temperature had been reached, the samples were kept isothermal for one hour to allow for thermal equilibrium. The actual sample temperature was actively monitored by a thermocouple placed closely to the sample. When measuring the acceptor doped LaNbO_4 , compressed air was passed through a humidifier which was linked to the gas inlet of the sample holder. The relative humidity of the sample environment was monitored with a humidity sensor (SHT75 Sensirion Sensor). Interpretation of the impedance data was achieved by the construction of equivalent circuit using ZView software suite (v3.2, Scribner Associates Inc.).

3.7 Transport property measurement

3.7.1 Diffusion Theory

Depending on the type of charge carriers in the ionic conductor, there are three diffusion mechanisms for oxygen ion transport, as schematically shown in Figure 3-13. Conventional oxygen ion conductors such as YSZ and LSGM rely on the vacancy diffusion mechanism in which diffusion is achieved by subsequent jump of oxygen ion into neighbouring vacancy sites (Figure 3-13a). The diffused oxygen ion leaves its original position vacant which facilitates future jumps, and thus long range diffusion. Alternatively, interstitial mechanisms (Figure 3-13b and c) dominate if interstitial oxygen is created for charge compensation. There are two types of interstitial diffusion mechanisms, direct and indirect. For the direct interstitial mechanism (Figure 3-13b), interstitials diffuse into the available interstitial sites; whereas for the indirect interstitial mechanism or interstitialcy mechanism (Figure 3-13c), the interstitials knock a lattice oxygen into another interstitial position, the process is then repeated leading to long-range transport. The apatite [55] and melilite [18] based oxygen ion conductors, which have been introduced in section 1.2.2, have fast diffusion pathways for the interstitial oxygen ions.

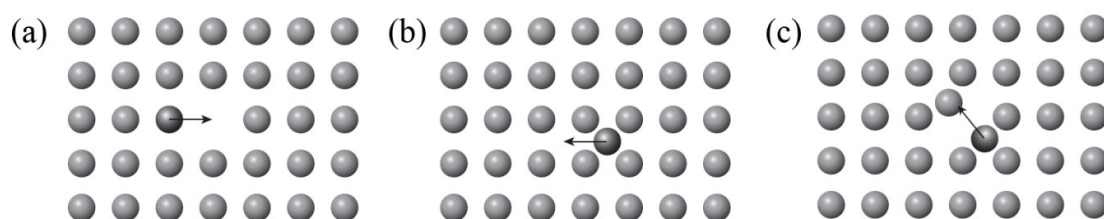


Figure 3-13: Schematics demonstrate three different diffusion mechanisms, namely (a) the vacancy diffusion mechanism (b) the direct interstitial diffusion and (c) the indirect interstitial or interstitialcy mechanism.

Both ionic conductivity and diffusion are limited by the same factor—the mobility of the ions—one can thus relate the diffusivity D to the ionic conductivity σ_{ion} with the Nernst-Einstein relationship, which links the diffusivity to the ionic contribution to total conductivity [217]:

$$\sigma_{ion} = \frac{z_{ion}^2 e^2 C D}{kT} \quad \text{Eqn. 3.20}$$

where σ_{ion} is the ionic contribution to conduction, z_{ion} is the number of charges of the mobile ion, e is the charge of a free electron, C is the concentration of the charge carrier, and D is the diffusivity of the charge carrier, which is the solution to Fick's second law of diffusion:

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x} \left(D \frac{\delta C}{\delta x} \right) \quad \text{Eqn. 3.21}$$

in which x is the distance away from the diffuser and t is the time for diffusion.

3.7.2 Oxygen tracer self-diffusivity measurement

Experimentally, the self-diffusivity of an isotopic tracer D^* , instead of the diffusion coefficient D is measured using the isotopic exchange method. These two parameters are related by a correlation factor f (Eqn. 3.22), which describes the interaction between subsequent jumps. The correlation factor depends on the structure as well as the charge carrier concentration, and equals to unity if the charge carriers behave like free gas i.e. have no interaction. [217].

$$D^* = f D_{self} \quad \text{Eqn. 3.22}$$

The technique to measure oxygen tracer diffusivity, using ^{18}O labelling tracer with a SIMS instrument, was pioneered by Kilner and Steele in the 1970s [218]. The principal of the technique is to introduce isotopic tracer into a dense material in the absence of a chemical gradient, and then obtain a concentration profile of the tracer as a function of the penetration depth. When exposing the solid samples to ^{18}O enriched gas, the ^{18}O tracer flux into the samples is counterbalanced by a similar flux across the gas/solid interface, leading a tracer concentration profile to be characterized with a mass spectrometer (the procedure is shown in Figure 3-14).

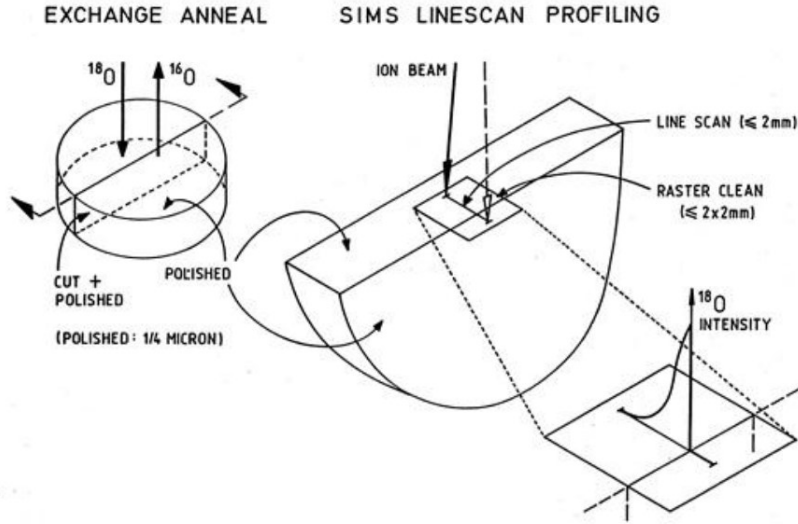


Figure 3-14: Experimental procedures to obtain a diffusional profile using the SIMS line-scan method [224].

Assuming the flux between the gas and solid phase is proportional to the difference in concentration, a boundary condition for Fick's second law is defined in Eqn. 3.23 [218,219]:

$$-D^* \frac{dC(x, t)}{dx} = k^*(C(x, t) - C_g) \quad \text{Eqn. 3.23}$$

in which D^* describes the mobility of tracer in the material, whereas the surface exchange coefficient k^* describes the speed at which the oxygen moves between the gas and solid interface; $C(x, t)$ and C_g are the concentration of tracer in the solid and gas phase respectively [217,220]. Assuming constant concentration in the gas phase, the Crank's solution to diffusion in the semi-infinite medium with the above boundary condition is given in Eqn. 3.24 [219]:

$$\begin{aligned} C'(x, t) &\equiv \frac{C(x, t) - C_{bg}}{C_g - C_{bg}} \\ &= \operatorname{erfc}\left(\frac{x}{2\sqrt{D^*t}}\right) - \left[\exp\left(\frac{k^*x}{D^*} + \frac{k^{*2}t}{D^*}\right) \right. \\ &\quad \times \left. \operatorname{erfc}\left(\frac{x}{2\sqrt{D^*t}} + \sqrt{\frac{k^{*2}t}{D^*}}\right) \right] \end{aligned} \quad \text{Eqn. 3.24}$$

in which $C'(x, t)$ is the normalized isotopic fraction; C_{bg} is the background isotopic concentration of ^{18}O ; $C(x, t)$ is the isotopic concentration which is a function of the distance

x to the free surface and the calibrated diffusion time t . By fitting the concentration profile $C'(x, t)$ obtained from SIMS measurements, to Eqn. 3.24, the transport properties D^* and k^* are extracted.

Oxygen tracer diffusivity measurements were conducted for $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ based oxygen ion conductors to determine the mobility of oxygen ions and the ionic contribution to the total conductivity. The apparatus for tracer diffusivity exchange is schematically shown in Figure 3-15. The sample, which had been polished to a $\frac{1}{4} \mu\text{m}$ surface finish prior to the exchange experiment, were placed in a quartz tube and evacuated to $<5 \times 10^{-7}$ mbar pressure. The samples were heated to the exchange temperature and pure oxygen with normal isotopic concentration with 200 mbar nominal pressure was introduced into the main chamber. The samples were annealed in the pure oxygen; the annealing temperature was set to be at least 10 times longer than the actual exchange process to eliminate the chemical gradient between the solid surface and the gas phase.

After the annealing, the samples were allowed to cool to room temperature when the main chamber was evacuated to high vacuum again ($<5 \times 10^{-7}$ mbar pressure). ^{18}O enriched gas with $C_g \approx 54\%$ (measured by oxidising a single crystal Si) was introduced from the reservoir. The samples were rapidly heated to the exchange temperature, held for desired duration and quickly quenched to room temperature by removing the roll-on tube furnace. During the exchange experiment, the sample temperature was closely monitored by a thermocouple placed closely to the sample and the actual exchange time was calibrated based on the activation energy of diffusion and the thermal profile, according to Killoran [221] and de Souza [222].

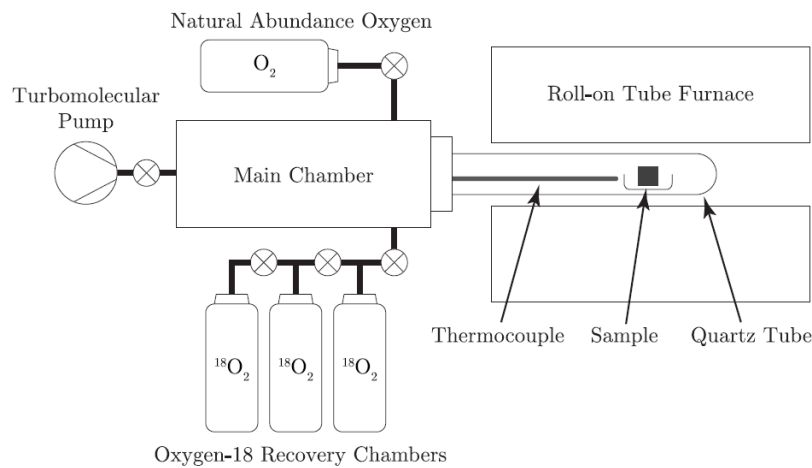


Figure 3-15: Schematic of the experimental apparatus used in ^{18}O tracer diffusivity measurements [223].

The process of extracting the diffusion profile is shown in Figure 3-14. The annealed samples were cut perpendicular to the exchange surface. The newly exposed surface was polished to $\frac{1}{4}$ μm surface and characterized using the TOF-SIMS instrument (introduced in section 3.5.1). By monitoring the intensity of the ^{16}O and the tracer ^{18}O , the diffusion profile was revealed using the “line-scan” technique. Alternatively, the diffusion profile was obtained using a “depth-profile” method; layers of material (typically a few nanometres thick) is removed with the sputtering gun in the SIMS instrument, and the corresponding isotopic fraction as a function of sputtering does, was recorded with TOF-SIMS.

The diffusivity of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ based oxygen ion conductor was measured in the temperature range from 500 $^{\circ}\text{C}$ to 750 $^{\circ}\text{C}$, a range of interest for SOFC application. The exchange time was selected so that the diffusion length $L = 2\sqrt{D^*t}$ falls in the range of 150–200 μm , allowing enough data points with good spatial resolution during the SIMS line scan.

3.7.3 Isotopic exchange with D_2O wet exchange

To evaluate the impact of surface layers on the transport properties, isotopic exchange in humidified environment using D_2O tracer (99%, C/D/N Isotopes Inc., UK) was conducted. The general procedure is very similar to the $^{16}\text{O}/^{18}\text{O}$ exchange process: a pre-annealing step in H_2O with normal isotopic concentration to eliminate chemical activity gradient, followed by isotopic exchange to introduce D_2O tracer. The wet exchange was performed in a modified version of the dry exchange rig and the setup is schematically shown in Figure 3-16. The exchange tube, as well as the water inlet is wrapped with heating tape to prevent condensation. Various thermocouples were in place to make sure than the water bath had the lowest temperature in the whole exchange system. The water bath was set at 51–55 $^{\circ}\text{C}$, which according to saturated vapour pressure of water, corresponds to a $\text{H}_2\text{O}/\text{D}_2\text{O}$ partial pressure of approximately 120 mbar to 150 mbar in the exchange rig. The wet exchange experiment was conducted at 450 $^{\circ}\text{C}$ with an exchange time of 1 h to investigate the impact of surface layer on the proton transport in acceptor doped LaNbO_4 .

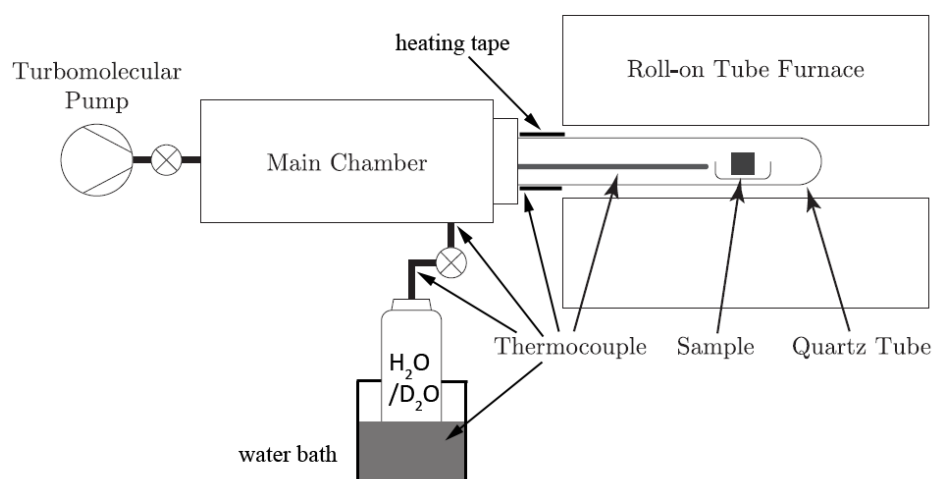


Figure 3-16: Schematic of the experimental apparatus used for D_2O wet exchange measurements, adapted from Figure 3.27 in [223].

Chapter 4. Room temperature structure of the hyperstoichiometric modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases

4.1 Introduction

Hyperstoichiometric, modulated CeNbO_{4+d} has remarkable oxygen diffusivity in the 500–650 °C region, a temperature range of interest for SOFC electrolyte application [58,225]. Unlike traditional perovskite and fluorite based oxygen ion conductors, which rely on cubic and cubic related crystal systems with large numbers of equivalent crystallographic positions [129], low temperature CeNbO_{4+d} phases are modulated monoclinic phases which have an ordered anion sub-lattice [59]. With its highly defective local structure, CeNbO_{4+d} provides an interesting template and a new concept in design structures high ionic mobility. However, the undesirable electronic conduction in CeNbO_{4+d} hinders its application as oxide electrolyte [131]. Most recently, hyperstoichiometric W doped LaNbO_4 , a structural analogue to CeNbO_{4+d} that demonstrates promising overall conductivity and good reduction stability, has been proposed for SOFC electrolyte application [136,226]. Despite the interest in its conduction properties, the modulated structure of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ has yet to be resolved [136,137,226]. Available reports often treated the structure as being unmodulated [137,226], which risk oversimplifying the crystal structure. Consequently, the interplay between the interstitial oxygen, its complex structure and the underlying transport mechanism is yet well understood. To shed light on the complicated incommensurate modulated structure, the room temperature structure of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series ($x = 0.01\text{--}0.20$) is investigated in this chapter. Single phase modulated structure is identified for the $x = 0.08, 0.12$ and 0.16 compositions. Their modulation vectors, $\mathbf{q}$, are determined from electron diffraction studies. The structure

of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition is further investigated using synchrotron X-ray diffraction to improve the resolution of weak satellites yielded by the modulated crystal. A structural model, which contains highly defective but interconnecting NbO_x polyhedra, whose coordination numbers range from 6 to 8, is proposed for the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition, a first attempt to resolve its $(3 + 2)\text{D}$ modulated structure.

4.2 Room Temperature Structure of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series

Six compositions ($x = 0.01\text{--}0.20$) and undoped LaNbO_4 were prepared using solid state reaction and the resultant powders were characterized with XRD (patterns shown

Figure 4-1).

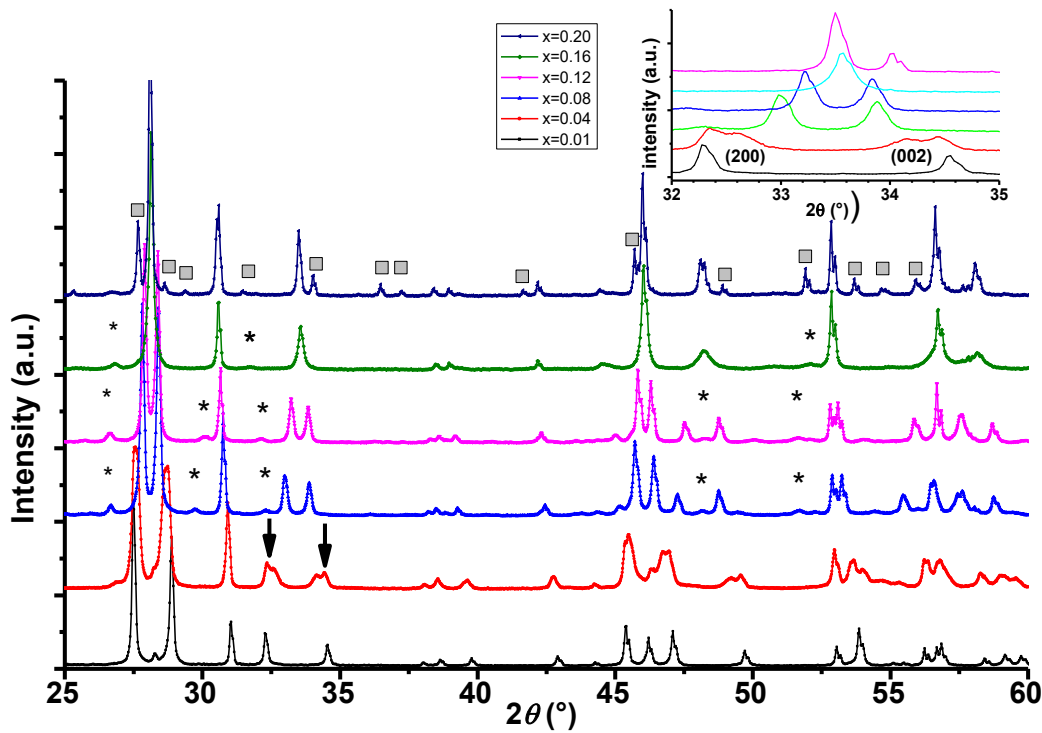


Figure 4-1: Room temperature XRD patterns of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series ($x = 0.01\text{--}0.20$). W solid solution forms with 1 at% W dopant. Satellite reflections of the modulated structures (marked by the asterisks) were observed in the $x = 0.08\text{--}0.16$ compositions. The $x = 0.20$ composition has a $\text{La}_2\text{W}_2\text{O}_9$ secondary phase (marked by the “ $\blacksquare$ ”). The inset shows the enlarged pattern from 32° to 35° in 2θ emphasizing the (200) and (002) reflections with increasing dopant level.

Profile fitting indicates the formation of a single phase W solid solution in 1 at% W doped LaNbO_4 , with; all the peaks being ascribed to the monoclinic phase with space group $I12/c1$ (space group 15, $I2/c$ for short). Identified by the overlapping of peaks (as those marked by the arrows), the $x = 0.04$ composition is in a biphasic region, consisting of a modulated phase and a W solid solution. Further increasing the dopant level ($\text{W} = 8 \text{ at } \% \text{ to } 16 \text{ at } \%$) reaches

another single-phase region. Additional peaks, resulting from the modulated structure first reported by Cava et al [134] and later investigated by Bayliss et al. [136], are marked with “*” in the diffraction patterns (Figure 4-1). With increasing dopant level, the β angle of the monoclinic phase decreases gradually, whereas the lattice parameters a and c converge, making those reflections related by a two-fold axis merge (i.e. (200) and (002) reflections which are highlighted in the inset in (Figure 4-1). The gradual transition of the parent structure from monoclinic to pseudo-tetragonal symmetry with increasing W dopant is consistent with the literature [134], which reported a tetragonal line phase with approximately 22 at% W substitution. Sample with nominal composition $\text{LaNb}_{0.80}\text{W}_{0.20}\text{O}_{4+d}$ contained a large proportion of a secondary phase whose reflections were marked “x” in the diffraction pattern (Figure 4-1). A search of the literature suggested that the W enriched $\text{La}_2\text{W}_2\text{O}_9$ phase, which is an analogue of the $\text{La}_2\text{Mo}_2\text{O}_9$ structure [227], led to the best fitting to the pattern. The refined lattice parameters of the parent phases, determined using the Le Bail method, are reported in Table 4-1.

Table 4-1: Lattice parameters of LaNbO_4 and $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ determined using the Le Bail method.

x in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	$\theta(^{\circ})$
0, LaNbO_4 [228]	5.5651(1)	11.523(1)	5.2034(1)	94.071(1)
0, LaNbO_4 this work	5.5634(3)	11.5218(6)	5.2027(3)	94.058(4)
0.01	5.5552(2)	11.5206(3)	5.2051(2)	93.909(5)
0.04	5.4801(3)	11.5767(7)	5.2677(4)	92.429(8)
0.08	5.4253(2)	11.6240(4)	5.2893(2)	91.715(7)
0.12	5.3920(2)	11.6588(3)	5.2964(1)	91.390(5)
0.16	5.3534(2)	11.6871(4)	5.3363(2)	90.295(9)
0.20*	5.3492(3)	11.6849(5)	5.3472(3)	90.010(4)

*the lattice parameters of the primary phase for the $x = 0.20$ composition are reported here.

The phase diagram proposed by Cava [134] (shown in Figure 2-10 in section 2.3.2) predicted a similar compositional range for the modulated structure; single phase modulated structure formed with 11 at% to 22 at% W dopant, although it was unclear from the literature the exact number of compositions investigated within this range. Ferrara et al. [226] studied the structure of $\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ and reported that both compositions crystallised in a modulated structure, in good agreement with the current results. The following section focuses on the $x = 0.12$ composition, whose modulated structure will be investigated in detail.

4.3 Chemical analysis

The polished surface of a $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ sample is shown in Figure 4-2, demonstrating the microstructure of a typical ceramic sample. Chemical composition of the sample was probed using energy dispersive X-ray spectroscopy (EDX), and the average atomic percentage of the modulated compositions, obtained by averaging more than 10 spectra, is reported in Table 4-2. Overall, the cation concentration is in reasonable agreement with the expected stoichiometry and no secondary phase was observed in the back scattered images within the detection limit of the instrument (Figure 4-2b), indicating chemically homogeneous samples have been obtained.

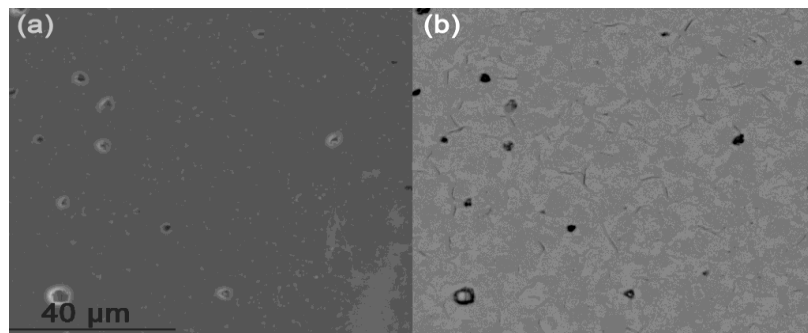


Figure 4-2: SEM micrographs showcase the microstructure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ using (a) secondary electron (SE) signals and (b) backscattered electron (BSE) signals. No secondary phase was visible from the BSE image.

The valence state of the W in the modulated compositions was examined using an X-ray photoelectron spectroscopy (XPS). The results indicate that the W $4f$ core level was dominated by W^{6+} , although some contribution from W^{5+} was also observed (Appendix a). It is therefore concluded that $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ compounds with desired stoichiometry have been successfully synthesized and introduction of oxygen interstitials (Eqn. 4.1) is assumed to be the predominant charge compensation process.

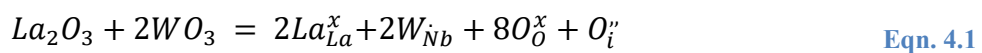


Table 4-2: Chemical composition of selected $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases characterized using EDX and XPS. The quantified atomic percentage was obtained by averaging ten spectra. Nominal concentrations are shown in bold.

$\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ composition	La(at%)	Nb(at%)	W(at%)	W $4f$ core, $\text{W}^{6+}/(\text{W}^{5+} + \text{W}^{6+})$
$x = 0.08$	50	46	4	0.88 ± 0.01
	50.5 ± 1.6	45.7 ± 1.2	3.8 ± 0.4	
$x = 0.12$	50	44	6	0.9 ± 0.01
	50.7 ± 2.2	42.9 ± 1.5	6.4 ± 0.9	
$x = 0.16$	50	42	8	0.91 ± 0.01
	49.4 ± 1.6	42.2 ± 1.2	8.4 ± 0.7	

4.4 Structural analysis using TEM

4.4.1 Electron diffraction (ED)

The crystal structure of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ samples was investigated using electron diffraction (ED). The electron diffraction patterns of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition from the low index planes are shown in Figure 4-3. Overall, the average structure was successfully indexed using the $I2/c$ space group. Reflections $h0l$ with $h \neq 2n$, $l \neq 2n$ were observed from the $[101]^*$ and $[1\bar{1}1]^*$ directions, which are forbidden in this space group. However, the intensity of such reflections was systematically lower than other reflections, and the reflections disappeared on tilting the sample, indicating these reflections were resulted from double reflection. Double reflection along the unique axis has been observed in KSmMoO_4 [107] and KNdMoO_4 [106] systems, probably due to the well aligned cations along the incident beam direction. It is therefore concluded that the body centring symmetry I was preserved in the modulated structure.

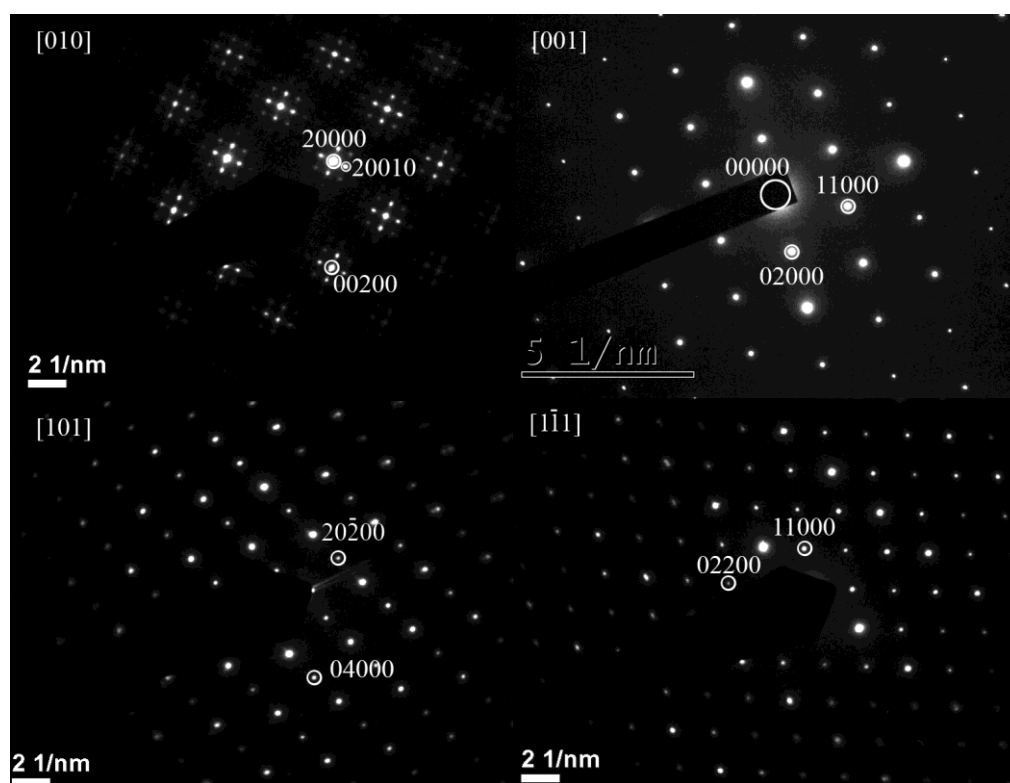


Figure 4-3: Electron diffraction patterns of the incommensurately modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase from $[010]^*$, $[001]^*$, $[101]^*$ and $[1\bar{1}1]^*$ directions. Satellite reflections were observed from the $[010]^*$ direction, indicating a $(3 + 2)\text{D}$ modulated structure.

The diffraction pattern from the $[010]^*$ direction requires 5 independent vectors to index, indicating that the structure is indeed modulated. The satellite reflections of the

incommensurate modulated structure were indexed using two wave vectors $q_1 \approx 0.290(5)a_I^* + 0.123(2)c_I^*$ and $q_2 \approx -0.130(3)a_I^* + 0.300(4)c_I^*$ respectively (the subscript *I* indicates that *I* setting of the parent cell), whereas no modulation along the *b* axis was observed (no additional reflections from the $[010]^*$ pattern). The only superspace group (SSG) that is consistent with the observed modulation waves, and the parent structure point group is the $B2/b(\alpha_1, \beta_1, 0)00(\alpha_2, \beta_2, 0)00$ [229], with no additional centre of symmetry in the two internal axes (marked as *t* and *u* in the following discussion).

The ferroelastic domains in the low temperature LaNbO_4 phase have been well documented in the literature [230–232]. Similar domain structures, which are created by rotating about the *b* unique axis has also been observed in the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases (discussed in the next section). However the presence of mixed second-order satellite reflections $q_1 \pm q_2$ (Figure 4-3) confirms that the observed diffraction resulted from a (3 + 2)D modulated phase, rather than the combination of twinned crystals and a (3 + 1)D modulated structure. The selected SSG adopts the $B2/b$ parent group symmetry, whereas the body-centred setting, $I2/c$, was more conventionally used to describe the low temperature fergusonite LaNbO_4 parent phase. For consistency, the SSG setting is transformed to the $I2/c$ setting with respect to the $B2/b$ setting

using the transformation matrix $\mathbf{P} = \begin{vmatrix} -1 & 0 & 0 \\ -1 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix}$

$$(a \ b \ c)_{I2/c} = (a \ b \ c)_{B2/b} \mathbf{P}$$

and $\mathbf{P}^{-1} = \begin{vmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ -1 & 1 & 0 \end{vmatrix}$ is used to transform the unit cell in reciprocal space. The transformed

SSG is therefore $I2/c(\alpha_1, 0, \gamma_1)00(\alpha_2, 0, \gamma_2)00$ and the new symmetry operators are (x, y, z, t, u) , $(-x, y, -z+1/2, t, u)$, $(-x, -y, -z, -t, -u)$, $(x, -y, z+1/2, -t, -u)$ with additional centering at $(0, 0, 0, 0, 0)$ and $(1/2, 1/2, 1/2, 0, 0)$ respectively.

4.4.2 Imaging the modulated structure

Domain structure of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ is shown in Figure 4-4. The domains varied in size from 30 nm to 100 nm and clear contrast between the domain walls and the surrounding domains was observed. The image was taken from the $[010]$ axis of the sample, indicating a domain wall that is parallel to the unique *b* axis, which is consistent with other reported

domain structure in LaNbO_4 [230,231]. The inset of Figure 4-4 highlights the structure within a domain, a checker-board pattern composed of pseudo-cells, which are about $1.6 \text{ nm} \times 1.6 \text{ nm}$, was observed.

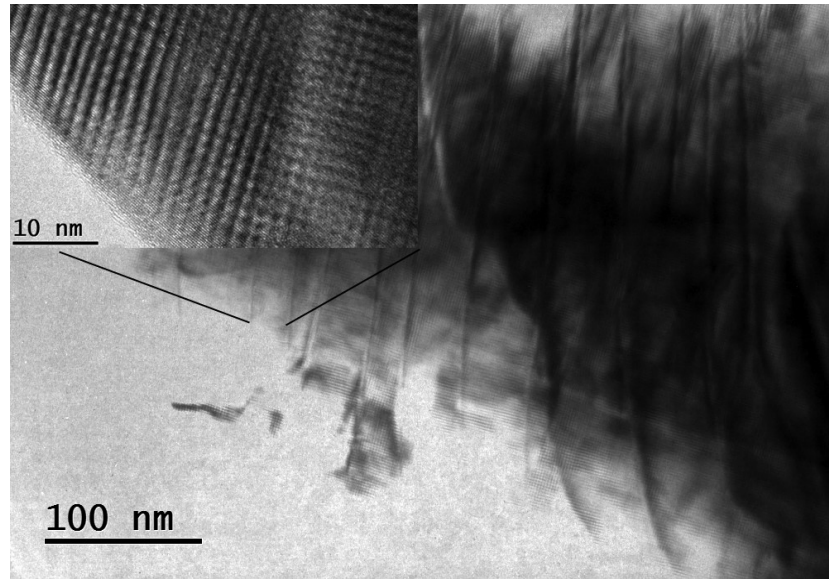


Figure 4-4: TEM bright field image of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$, showcases the twinning/domain structure viewed from the unique axis $[010]$ direction. Inset is an enlarged view within a domain, highlighting a checker-board pattern due to the structural modulation.

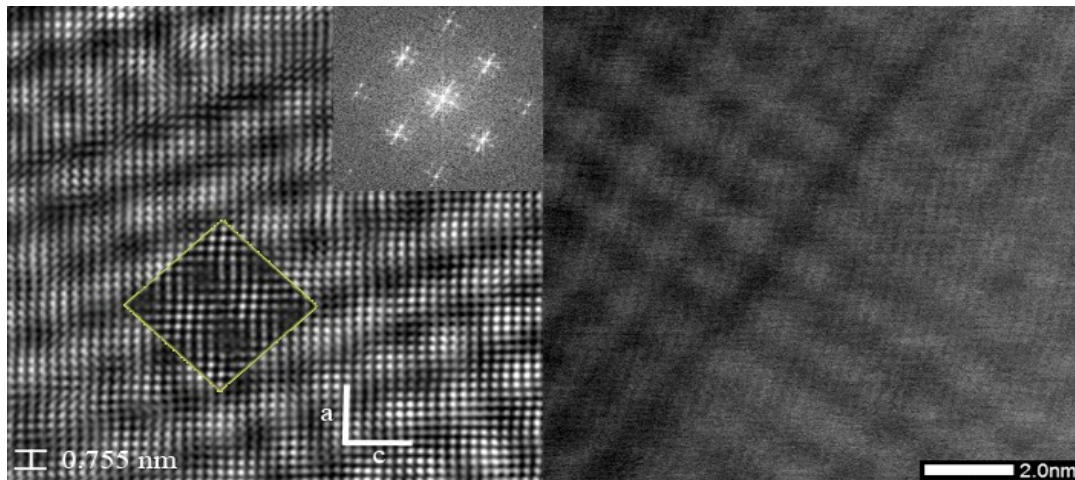


Figure 4-5: a) HRTEM image and the corresponding Fourier transformed (FT) pattern of $(3 + 2)\text{D}$ incommensurately modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase, the inset in the yellow square shows the simulated image using a $10 \times 1 \times 10$ commensurate approximation of the modulated structure using JEMS [233]. A defocus value $\Delta f = -7.5 \text{ nm}$ and thickness $t = 25 \text{ nm}$ was used for the simulation; both the displacive as well as the occupational modulation was recreated from the simulation. b) HAADF image of the same region, confirming the occupational modulation in the structure. Both images were taken from the unique b axis $[010]$

Figure 4-5a shows the enlarged HRTEM image of the inset in Figure 4-4. Fourier transform of the image is also displayed, showing clearly the satellite reflections and thus confirming that the observed image is a superimposition of the average parent structure and the structural

modulation. Displacement of the atomic columns (represented as dots in the image), away from the average positions was clearly observed. The contrast between the atomic columns indicates an ordered distribution of the W dopant along the *ac* plane. To confirm the origin of the modulation wave being occupational, the same area was examined using high angle annular dark field imaging (HAADF) in the scanning transmission electron microscopy (STEM) mode, which is highly sensitive to the atomic number (*Z*) variations in the sample [200]. A checker-board pattern, similar to the HRTEM image was observed. The contrast between the atomic columns therefore confirms the difference in average atomic numbers between the columns, proving the presence of the occupancy modulation along the *ac* plane (Figure 4-5.b). The inset in Figure 4-5a shows the simulated pattern based on $10 \times 1 \times 10$ commensurate approximation of the refined structure and will be discussed in section 4.5.3.

4.5 Refinement of the modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ using synchrotron powder diffraction

4.5.1 Refinement of the parent structure

To further investigate the structure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$, synchrotron powder diffraction data was obtained from the MSPD beamline at the ALBA light source, Barcelona, Spain. A photon wavelength of 0.3308 Å was used and the data in the $2\theta = 3.0^\circ$ to 20.1° 2θ range ($6.32 \text{ Å} > d\text{-spacing} > 0.95 \text{ Å}$) was used for the refinement. The Pseudo-Voigt function was used to describe the line profile, and the instrument parameters were obtained by refining the diffraction pattern of a $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ reference [234], gathered using the same geometry and optics. To refine the parent structure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$, the lattice parameters and zero position were first refined with the Le Bail method, followed by the refinement of atomic positions and atomic displacement parameters (ADP) using the Rietveld method. The space group, lattice parameters and the atomic positions of the parent LaNbO_4 phase (ICSD No. 73390, ref.[235]) were used as input for the refinement.

The W and Nb sites were constrained to have identical positions and atomic displacement parameters (ADP) whereas the Nb/W ratio was fixed to the nominal composition (12 at% W at Nb site). The position of all the heavy cations was first refined prior to the refinement of the oxygen positions. Employing the anisotropic ADPs of the cations resulted in an improvement of the goodness of fit parameters from $R_p = 0.118$ and $R_{wp} = 0.152$ to $R_p = 0.109$ and $R_{wp} = 0.143$. The refinement suggested strong anisotropic ADPs of cations, for instance

U_{11} and U_{33} of La were refined to be $0.016 \text{ \AA}^2$ and $0.033 \text{ \AA}^2$ respectively, whereas the U_{22} which corresponds to the movement along the unique axis was refined to be only $0.005 \text{ \AA}^2$. The anisotropic nature of the ADPs hints at displacive modulation along the ac plane due to the effect of structural modulation. The site occupancy of La was also refined and results suggested 99.3 % occupancy, showing good agreement with the expected composition. Despite a minor improvement in the fitting quality (from $R_p = 0.109$ and $R_{wp} = 0.143$ to $R_p = 0.107$ and $R_{wp} = 0.139$), the refinement returns negative U_{22} and large U_{33} ($0.18 \text{ \AA}^2$) for the O2 site, when refining its anisotropic ADPs. The refinement of the parent structure was therefore concluded without refining the anisotropic ADPs of the oxygen ions, and the refined pattern is shown in Figure 4-6.

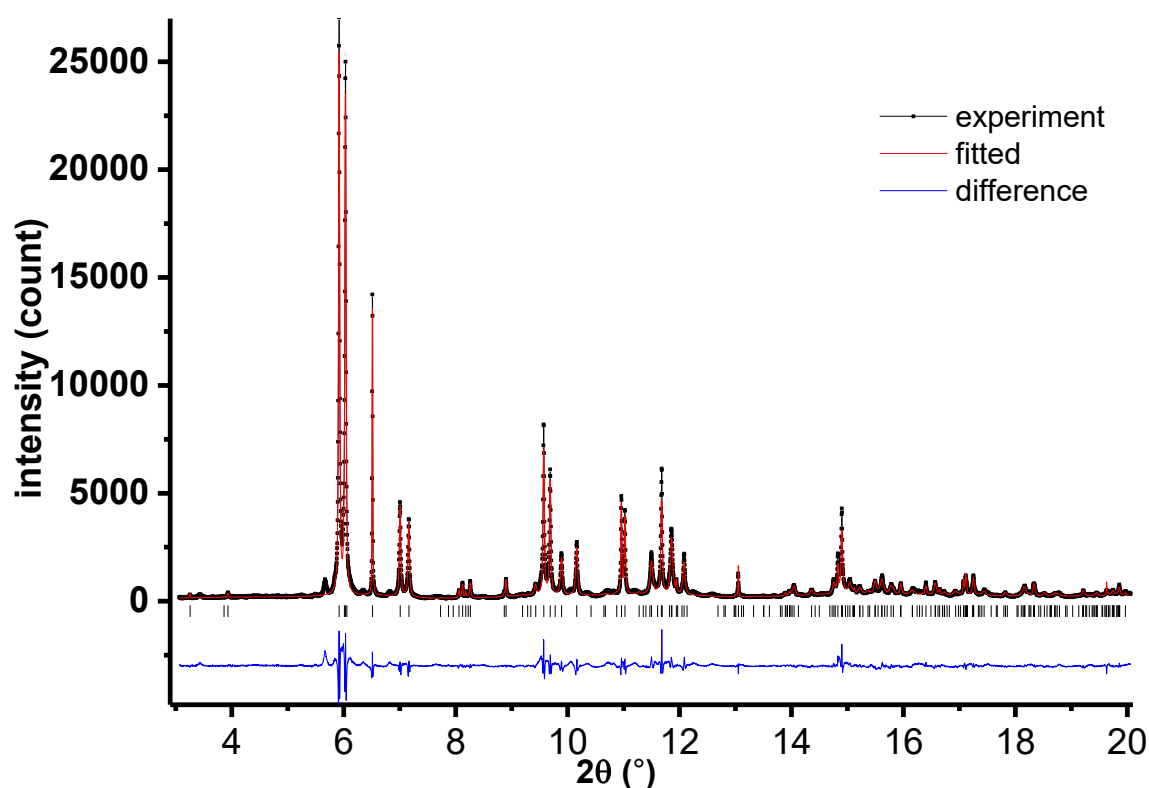


Figure 4-6: Plot of Rietveld refinement results of synchrotron diffraction data of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ refined using only the parent phase space group. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black vertical lines mark the theoretical Bragg peak positions of the parent structure. Final goodness of fit parameters $R_p = 0.107$ and $R_{wp} = 0.139$ were achieved. Clearly, intensity from the modulation peaks have not been accounted in the refinement.

Anisotropic peak broadening was observed in the system during the refinement. It was noticed that the $0k0$ planes, which are perpendicular to the unique b -axis, had a systematically smaller full width at half maximum (FWHM) compared with other diffraction peaks. For instance, both the (040) and (080) had FWHM of approximately 0.010° whereas the FWHM

for the peaks with the highest intensity were almost doubled (approximately 0.018° for $(\bar{1}21)$ and (121) reflections).

Closer examination of the diffraction pattern indicates not only that peaks were broadened anisotropically, the broadening was also asymmetric and the direction of the broadening appeared to relate to its Miller index. For instance, the $(\bar{1}21)$ reflection had a shoulder towards higher 2θ whereas broadening towards the opposite direction was observed for the (121) reflection. A similar trend has been observed for the other diffraction pairs such as (240) and (042) , as well as $(\bar{1}61)$ and (161) (shown in Figure 4-7).

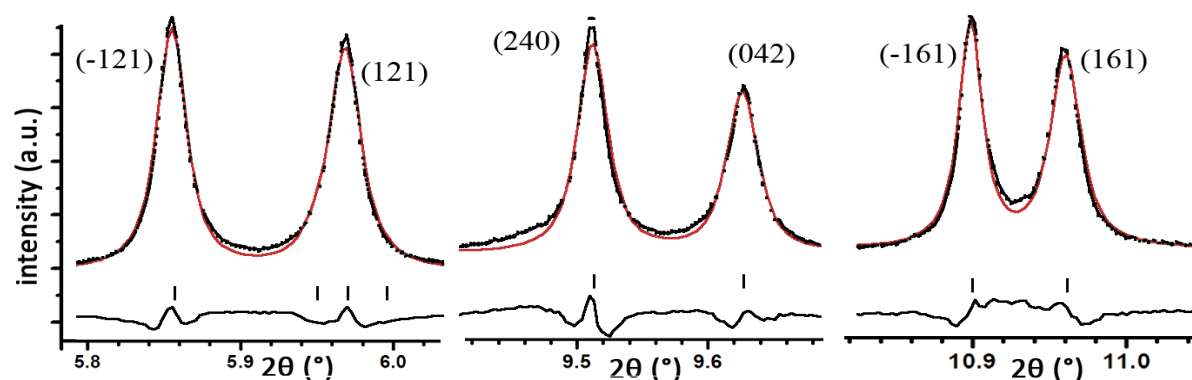


Figure 4-7: Enlarged view of selected reflections based on the refinement of the parent phase shown in Figure 4-6; asymmetric peak broadening was observed, leading to an increased background between those crystallographically related reflections. The red and black lines on top are modelled and measured values respectively whereas the difference plot is shown in the bottom. The shoulder of the (240) reflection resulted from the modulated structure, which was not included in the structural model.

Asymmetric peak broadening in diffraction patterns has been previously reported in LaNbO_4 [96] YNbO_4 [236] and $\text{Ce}_{1-x}\text{Sr}_x\text{NbO}_4$ (Figure A.3 in [147]), all of which have the low temperature LaNbO_4 fergusonite structure. However, the origin of the broadening has not been addressed. It is speculated that the asymmetric broadening is related to the twinning in the low temperature ferroelastic phase, which causes an asymmetric peak profile in ferroelastic crystals [237–239]. A ferroelastic material exhibits spontaneous strain without the application of external stress which often leads to hkl -dependent diffuse scattering [238]. As shown in Figure 4-4, the microstructure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phases consists of domains which are related by rotation about the unique b axis, similar to that observed in LaNbO_4 [230,231], indicating the ferroelastic nature of the material.

The ferroelastic domain structure in LaNbO_4 has been investigated by various authors. A transition zone between the domains, which on average has the prototype tetragonal structure has been proposed by Tsunekawa and Takei [240], to explain the domain wall structure in LaNbO_4 . The authors suggested that the transition zone bounded the neighbouring domains

by rotating and distorting the NbO₄ polyhedra [240]. Jian and Wayman proposed that a gradual orientation change within the transition zone lowered the energy requirement for the movement of domain boundary [231]. Due to the presence of the domain structure, a distribution of *d*-spacing at the *ac* plane was expected, whereas a narrower peak profile for the 0*k*0 reflections, which are free from strain, is expected [97]. The domain structure as well as the transition zone are likely to relate to the abnormal peak broadening observed in the XRD pattern [97], which disappears after LaNbO₄ transforms from monoclinic fergusonite to tetragonal scheelite structure [96]. Study of the acceptor doped LaNbO₄ phase reveals similar micro-structure features which suggest that the presence of the transition zone is common for low temperature monoclinic LaNbO₄ [88]. The method introduced by Stephens [241] was used to described the anisotropic peak broadening observed in the LaNb_{0.88}W_{0.12}O_{4+d} phase.

4.5.2 Refinement of the modulated structure of LaNb_{0.88}W_{0.12}O_{4+d}

The refinement of the displacive modulation was executed along with the refinement of the occupational modulation. The Nb/W sites were set to have the same positions and ADP. Their site occupancy, p^λ , for atom λ at the Nb/W site, as a function of the internal coordination t and u , is expressed in Eqn. 4.2:

$$p^\lambda = p_0^\lambda + p_{c1}^\lambda \cos(2\pi t) + p_{c2}^\lambda \cos(2\pi u) \quad \text{Eqn. 4.2}$$

in which p_0^λ is the nominal site occupancy for Nb and W, which are 0.88 and 0.12 respectively based on the chemical analysis presented earlier; p_n^λ is the Fourier magnitude along the n^{th} wave function. Although higher order satellite reflections were clearly observed in the electron diffraction pattern (Figure 4-3), the intensity of these reflections in the powder diffraction was weak, therefore only the magnitudes of the first order wave function were refined. To maintain the overall B site occupancy, the occupancy wave vectors for Nb and W were set to be complementary, $p_{c1}^{\text{Nb}} = -p_{c1}^{\text{W}}$, so that the overall occupancy p^λ remains constant regardless of any change in the internal t - u space, i.e. all the site in the real space has a full occupancy. The refinement converged with improved fitting parameters, $R_p = 0.085$ and $R_{wp} = 0.108$ for the whole pattern, compared with the structural model with only the parent phase ($R_p = 0.109$ and $R_{wp} = 0.143$). The refined pattern is shown in Figure 4-8, whereas the experimental conditions, the refined parameters of the parent phase and the Fourier

magnitudes of the modulated phase are summarized in Table 4-3, Table 4-4 and Table 4-5 respectively.

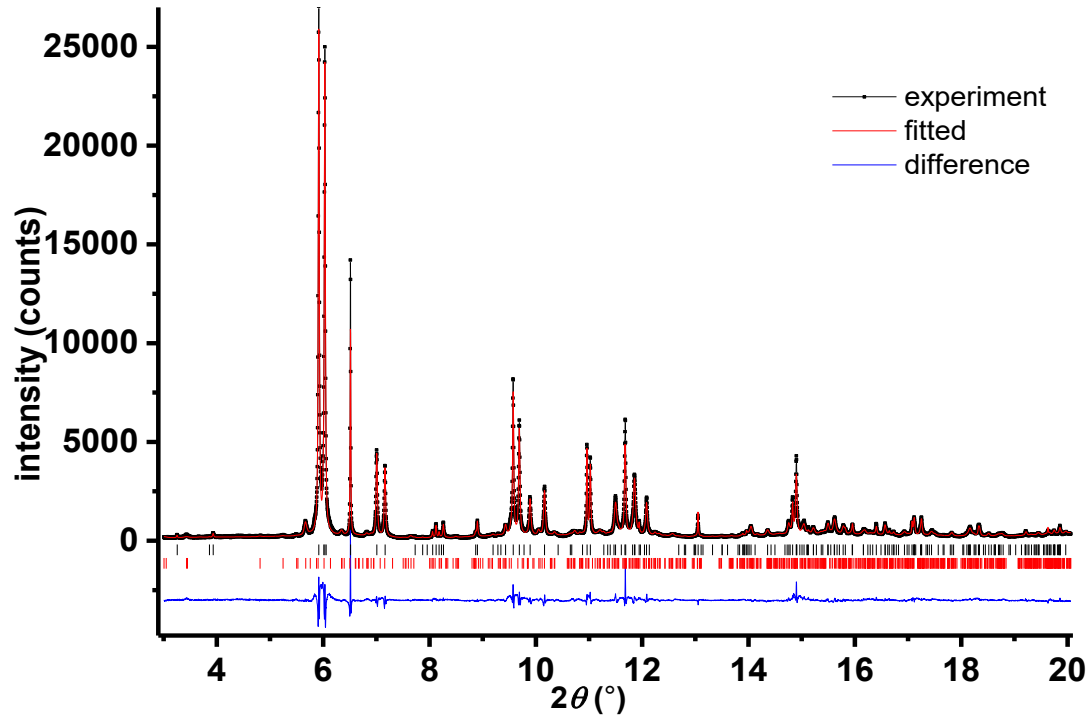


Figure 4-8: Rietveld refinement of synchrotron powder diffraction data of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$, using the superspace group $I2/c(\alpha_1, 0, \gamma_1)00(\alpha_2, 0, \gamma_2)00$. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black and red vertical lines mark the theoretical peak position of the parent structure and the modulated structure respectively. Final fitting with $R_p = 0.083$ and $R_{wp} = 0.106$ were reported. The major difference between the model and the fitting resulted from the asymmetric peak shape reported in Figure 4-7.

Table 4-3: Summary of the experimental conditions.

Composition	$\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$
Space group	$I2/c(\alpha_1, 0, \gamma_1)00(\alpha_2, 0, \gamma_2)00$
Temperature	300 K
a b c ($\text{\AA}$) β ($^\circ$)	5.4131(1) 11.6432(2) 5.2963(1) 91.540(1)
V ($\text{\AA}^3$)	333.682(11)
Modulation waves	$q_1 = 0.2847(5)a^* + 0.1098(9)c^*$ $q_2 = -0.1266(9)a^* + 0.2953(1)c^*$
Data collection	
Instrument	MSPD at ALBA cell
Data range	$2\theta = 3.0^\circ$ to 20.1°
Wavelength	$\lambda = 0.3308 \text{ \AA}$
Reflections (all/observed)	1024/948
among them	
Main Reflections (observed/unobserved)	209/207
1 st order (observed/unobserved)	815/746
Quality of fitting	$R_p = 0.083$ and $R_{wp} = 0.106$ GOF=1.63

Table 4-4: Refined parameters of the parent structure.

	Occ.	x	y	z	U11	U22	U33	U12	U13	U23
La	0.994(12)	0	0.25	0.625	0.019(2)	0.0157(13)	0.031(3)	0	-0.004(2)	0
Nb/W	0.88/0.12	0	0.25	0.125	0.019(3)	0.051(3)	0.008(4)	0	-0.003(2)	0
O1	1	0.231(2)	0.0343(7)	0.076(2)				0.007(2)		
O2	1	0.163(2)	0.2064(8)	0.483(3)				0.005(2)		
Cation site	Average bond length (Å)				Bond valence sum (BVS)					
La			2.523					3.11		
Nb/W			1.834					5.13		

Table 4-5: Atomic coordinates, and the Fourier amplitude of the displacive and occupancy wave functions in the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase.

site	Fourier magnitudes	x	y	z
La		0	0.6273(2)	0.25
	$s,1^*$	0	0.002(1)	0
	$c,1$	-0.018 (1)	0	0.036(2)
	$s,2$	0	-0.001(2)	0
	$c,2$	0.010(3)	0	0.002(4)
Nb/W		0	0.1175(3)	0.25
	$s,1$	0	0.006 (1)	0
	$c,1$	-0.019(2)	0	0.043(2)
	$s,2$	0	0.002(1)	0
	$c,2$	0.012(2)	0	0.007(3)
	p_{c1}, p_{c2}^{**}	0.185(12), -0.160(18)		
O1		0.232(2)	0.035(1)	0.078(2)
	$s,1$	0.022(5)	0.003(2)	0.019(6)
	$c,1$	-0.010(6)	0.005(3)	0.038(7)
	$s,2$	0.002(9)	-0.005(5)	0.020(10)
	$c,2$	0.009(10)	0.004(6)	-0.009(12)
O2		0.164(2)	0.207(1)	0.484(2)
	$s,1$	-0.006(6)	0.002(3)	0.009(7)
	$c,1$	-0.022(7)	-0.011(3)	0.070(4)
	$s,2$	0.033(10)	-0.009(4)	-0.008(10)
	$c,2$	0.039(10)	0.008(4)	-0.027(8)

* s, c stands for Fourier magnitude of sin and cos wave described in Eqn. 2.9 respectively; the number describes the wave vectors: the 1st wave is along q_1 direction and the 2nd wave is along q_2 direction

** $p = p_0 + p_{c1}\cos(2\pi t) + p_{c2}\cos(2\pi u)$, in which p_0 is the site occupancy of the parent structure. p_{c1}, p_{c2} are the Fourier magnitude for the occupational waves; t, u are the coordinates in the internal axes; both the Fourier magnitude of the displacive and the occupational wave follow the format described in Eqn. 2.9.

The t - u plot of the residual electron map in the vicinity of the cation sites is shown in Figure 4-9. For the La site, the maximum residual density of $-2 \text{ e}\text{\AA}^{-3}$ was observed. Refining the site occupancy indicated that the La site is fully occupied (occupancy = 99.4(1.2) %), and showed no improvement in the residual map. The slightly negative residual density might therefore result from the background [55]. A higher residual level ($-3.5 \text{ e}\text{\AA}^{-3}$) at the Nb site was registered, which might relate to the Nb/W occupational modulation.

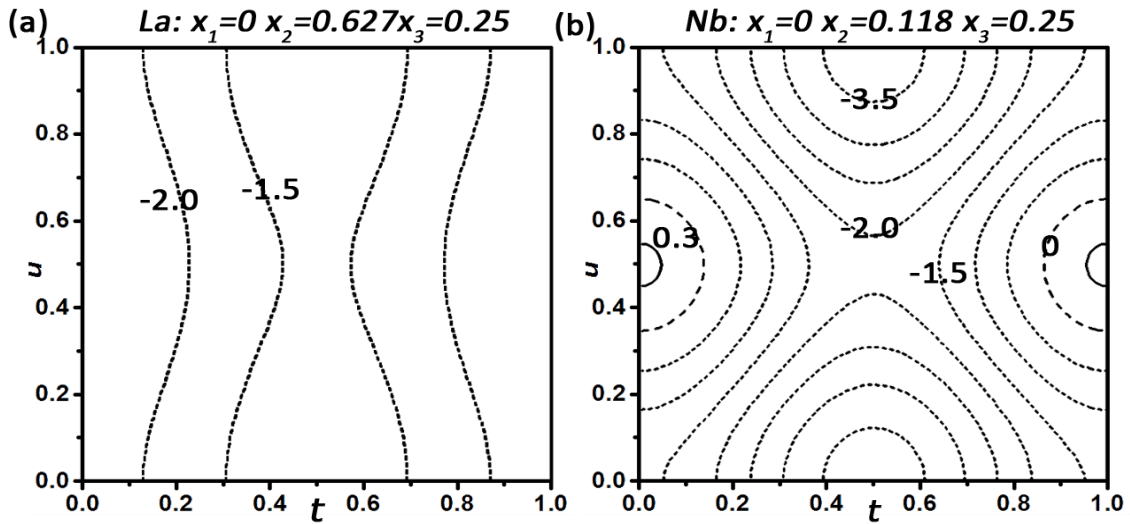


Figure 4-9: The t - u plot of the residual electron density in the vicinity of (a) La and (b) Nb. Overall the La site showed smaller difference between the model and the experiment. Contours level is $0.5 \text{ e}\text{\AA}^{-3}$ for both images.

Based on the refinement, site occupancy mapping, as a function of the internal coordinates t and u , is plotted in Figure 4-10. The occupancy of W varied continuously with internal coordinate, and reaches its maximum of approximately 40 at% at around $t = 0.45$, $u = 0.95$ (Figure 4-10b), more than three times higher than the bulk nominal concentration (12 at%). The slightly negative occupancy of W at around $(t, u) = (0, 0.5)$ (Figure 4-10b) is probably because the actual change in occupancy of the B sites is more abrupt than a single sine wave. Consequently, the magnitude of the sine wave is overestimated in an attempt to provide a reasonable fitting, leading to a negative occupancy at the position where Nb was predicted to have the highest occupancy (at $(t, u) = (0, 0.5)$ in Figure 4-10a). Small negative cation occupancy was reported in other $(3 + 2)$ D modulated scheelite structure [109], and was ascribed to inaccurate occupancy wave functions, using only the sine/cosine waves. Indeed, previous reports on $(3 + 1)$ D modulated scheelite $\text{KSm}(\text{MO}_4)_2$ [107] and $\text{KNd}(\text{MO}_4)_2$ [106], indicated that a combination of crenel function and sine function, which resulted in a sharper transition in the occupancy map, provided a better fit for the experimental data [107]. With such complication in this system, i.e. $(3 + 2)$ D modulation, and the unavailability of the

single crystal diffraction data for better accuracy, refinement of higher order Fourier waves that include more independent variables was not attempted for the refinement of this powder diffraction data.

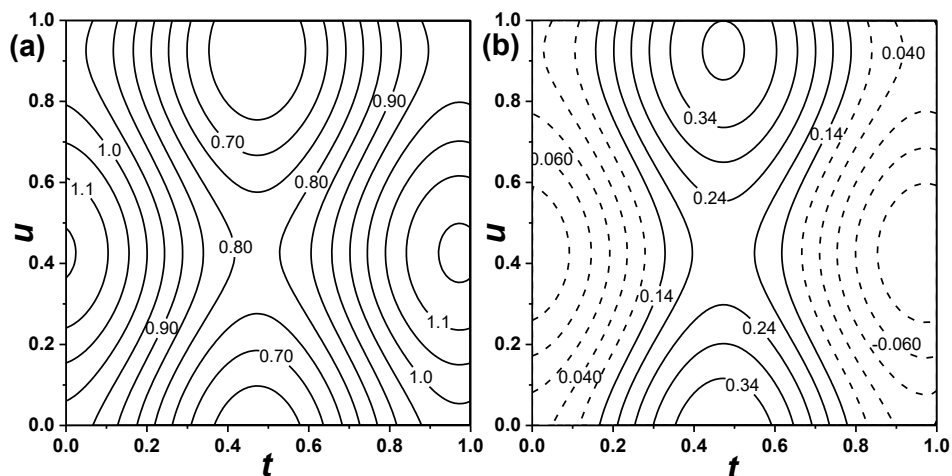


Figure 4-10: Variations of the (a) Nb and (b) W occupancy represented in the t - u plot. The occupancy of Nb varies from 1.2 to 0.60 whereas the W site occupancy was set to be complementary. Full, dot and dash lines represents positive, zero and negative values of occupancy. The contours are 0.05 in both maps.

Due to the difference in the electronegativity between Nb^{5+} and W^{6+} , partial ordering of the B site cations leads to the relaxation of the local coordination environment. Consequently, the cation ordering is accommodated by the periodic displacive movement of both the cations and anions, to compensate for the bond valence sum. Similar displacive movement has been observed in other modulated scheelite structures [90,107,108,110,242]. The movement is described by the Fourier magnitudes of the displacive waves, which are summarized in Table 4-5. Based on the refinement, the variations of the average bond length at the Nb and La sites were calculated and are represented in the t - u plot (Figure 4-11). The bond lengths between Nb and the 4 nearest neighbouring oxygen were averaged, showcasing the change in the bonding environment of the B site tetrahedra. Eight La-O bonds were included (Figure 4-11b) reflecting the larger ion size of La^{3+} .

The variation of the B site bond length correlates well with the occupancy map reported in Figure 4-10; the average Nb/W-O bond length reaches its minimum of 1.810 Å at approximately $t = 0.32$, $u = 0.1$ which coincides with the maximum W occupancy. Indeed, the ions located along the $t \approx 0.5$ strip have slighter shorter average bond length comparing with their neighbours, which agrees well with the W occupancy map (Figure 4-10b), which predicts increased W occupancy at these positions. The difference in average B-O bond length reflects the reduced ionic radius and increased charge of W^{6+} in comparison with Nb^{5+} .

(0.42 Å versus 0.48 Å in IV coordination environment [243]). The B site polyhedra nonetheless seem relatively rigid comparing with the La coordination as the latter was predicted to have a larger variation in average bond length as shown in Figure 4-11b (note the total scales are the same for the two plots). The average bond length ranges from 2.48 Å to 2.58 Å for La-O, despite the cation ordering occurs at the Nb/W site where the Nb/W-O bond lengths were predicted to vary from 1.83 Å to 1.89 Å. The La-O polyhedra are related with the B site by corner sharing with 8 neighbouring NbO₄ tetrahedra; it seems the stretching and bending distortion of the Nb-O and W-O bonds collectively lead to a significant cooperative change in the bonding environment of La-O. Similar trends in average bond length have been observed in other modulated scheelite, such as Na_{2/7}Gd_{4/7}MoO₄ [109] Eu₂(MoO₄)₃ [244] and KSm(MO₄)₂ [107], in which a larger variation of bond length at the A site than of the B site was suggested, although all the compounds have the occupational modulation at the A sites.

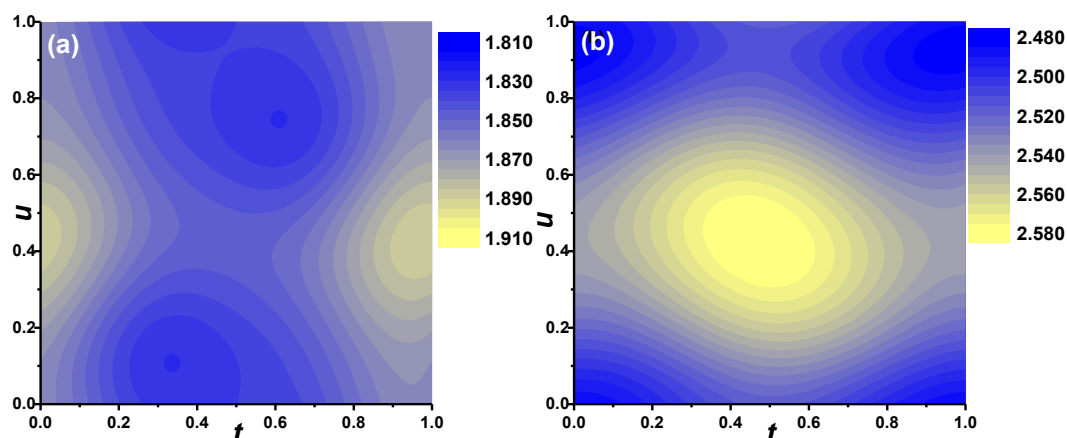


Figure 4-11: Bond length map of (a) Nb/W site and (b) La site, both image are plotted with the same scale. Although the occupancy modulation occurred at the B site, a larger variation in the average bond length was observed at the La site. The average bond length for Nb-O and La-O are 1.834Å and 2.523 Å respectively, as reported in Table 4-4.

The bond valence sum (BVS) calculated according to [245,246], describes the “bond strength” in ionic components, and provides a convenient method to check the chemical sensibility of the refined structural model [245,246]. For the BVS calculation, bond lengths up to 3 Å, which consists of the next nearest neighbours in NbO_x polyhedra, were included and the results are plotted in Figure 4-12. Unsurprisingly, good correlation between B site occupancy and the BVS was obtained from the refinement. Minimum BVS of 4.5 was observed at $(t, u) = (0, 0.5)$ where the Nb occupancy was estimated to be the highest; on the other hand, maximum BVS of 5.45 was observed at around $t = 0.45, u = 0.10$, a coordinate of highest W occupancy. The variations in the La-O bond length lead to a significant variation in the BVS of La, ranging from 2.7 to 3.6 in the refined model. Literature reported a La valence from 2.8

[247] to 3.3 [248] in La-Nb-O systems, covering the low end of the reported BVS. The maximum BVS might relate to particular La sites that are over-bonded.

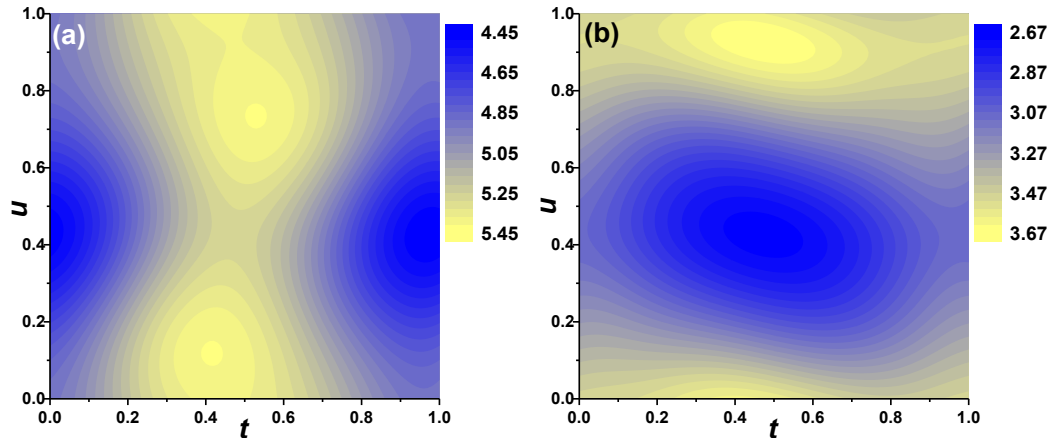


Figure 4-12: Bond Valence Sum map of (a) Nb/W site and (b) La site, both image are plotted with the same scale. Higher BVS along the $t = 0.5$ strip was observed, which corresponds to the increased W occupancy reported in Figure 4-10b. A BVS ranging from 2.7 to 3.6 was reported for La, slightly higher than the reference range (2.8-3.3 Å).

4.5.3 Real space representation of the refined structure

The t - u plots of the average bond length and the BVS mapping, presented in the earlier section, highlight the correlation between the cation modulation and the varied local environment. A reasonable variation of bond lengths and BVS was obtained and thus confirms the validity of the structural model. In the following section, the refined structure is displayed in real space using a commensurate approximation, in an attempt to provide a more intuitive and informative way to present the refined structural model.

A $10 \times 1 \times 10$ commensurate approximation of the refined $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ incommensurate modulated structure is drawn, from three mutually perpendicular directions, in Figure 4-13, Figure 4-14b and Figure 4-15. The cation ordering and the distortion of the B site tetrahedra, based on the structural refinement, are visualized. In these figures, the B site polyhedra are coloured based on their coordination number: green, blue and orange polyhedra represent 6, 7 and 8 coordination oxygen respectively. The distribution of the W substitution in the commensurate approximation is depicted in Figure 4-13b; polyhedra with more than 20 at% W occupancy are coloured grey to highlight the partially ordered B site in the approximated structure (Figure 4-13b). The distribution of the W enriched clusters follows a checker-board pattern pointing along the $q_1 \pm q_2$ directions in the real space (arrows in Figure 4-13b). Indeed, simulation based on the commensurate approximation (inset in Figure 4-5a) successfully recreates the contrast between atomic columns as well as the wavy displacement

of the cation observed in the HRTEM and HAADF image, indicating that a reasonable fit was obtained from the structural analysis.

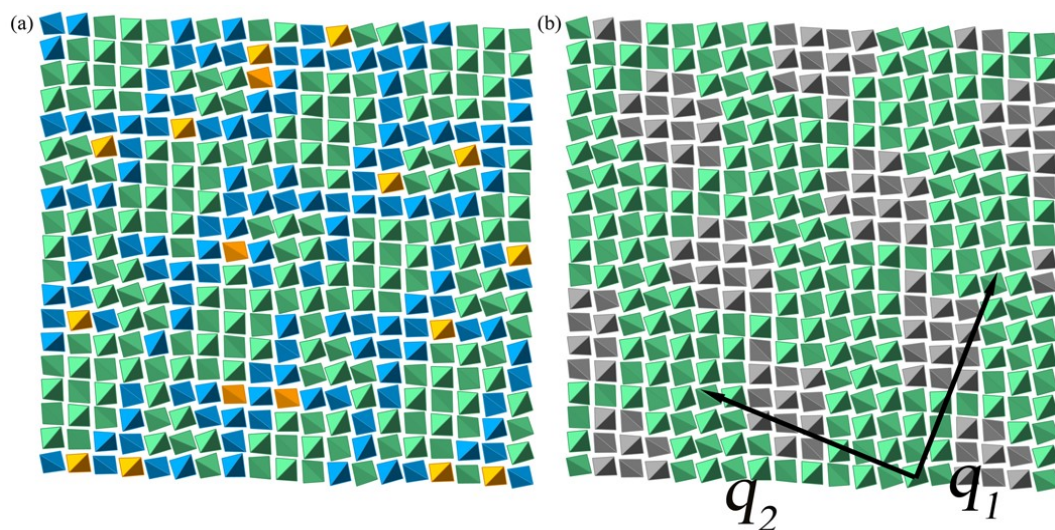


Figure 4-13: A $10 \times 1 \times 10$ commensurate approximation of the refined structure viewed from the [010] direction; (a) the variations in the Nb-O coordination number are highlighted; the cut-off bond length was set at 3 Å and green blue and orange polyhedra present 6, 7 and 8 coordination oxygen respectively; it should be noted only the four closest oxygen ions are shown for clarity; (b) the segregation of W dopant in the structure is highlighted, B site with more than 20 at% W is coloured grey in this plot.

The arrangement of the B site polyhedra, along mutually perpendicular a and c axes, is shown in Figure 4-14 and Figure 4-15 respectively. The parent structure (Figure 4-14a and Figure 4-15a) and the modulated structure (Figure 4-14b and Figure 4-15b) are plotted with a cut-off bond length of 3 Å. In the parent structure, the Nb polyhedra adapt a $4 + 2$ coordination: the 4 shorter bonds (~ 1.8 Å) construct the tetrahedral environment whereas the two longer bonds (~ 2.5 Å) create edge sharing NbO_6 slabs along the c axis. The slabs are translated by the 2_1 axes parallel to c , creating a layered structure. However, no interconnection between the NbO_x slabs is available in the parent structure (Figure 4-14a and Figure 4-15a). On the other hand, the coordination number of Nb/W polyhedra in the modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase ranges from 6 to 8, due to the fluctuations of the local environment. Consequently, the NbO slabs are interconnected by corner sharing polyhedra, especially those with a coordination number higher than 6 (coloured blue and orange in Figure 4-15b). The additional coordination oxygen ions extend the parent structure to an interconnected 3D network, not only in the ac basal plane but also along the unique axis. Such extension of NbO_x coordination polyhedra has been observed in the modulated $\text{CeNbO}_{4.25}$ phase which facilitates the incorporation of interstitial oxygen, and is believed to correlate with the oxygen transport in $\text{CeNbO}_{4.25}$ [249].

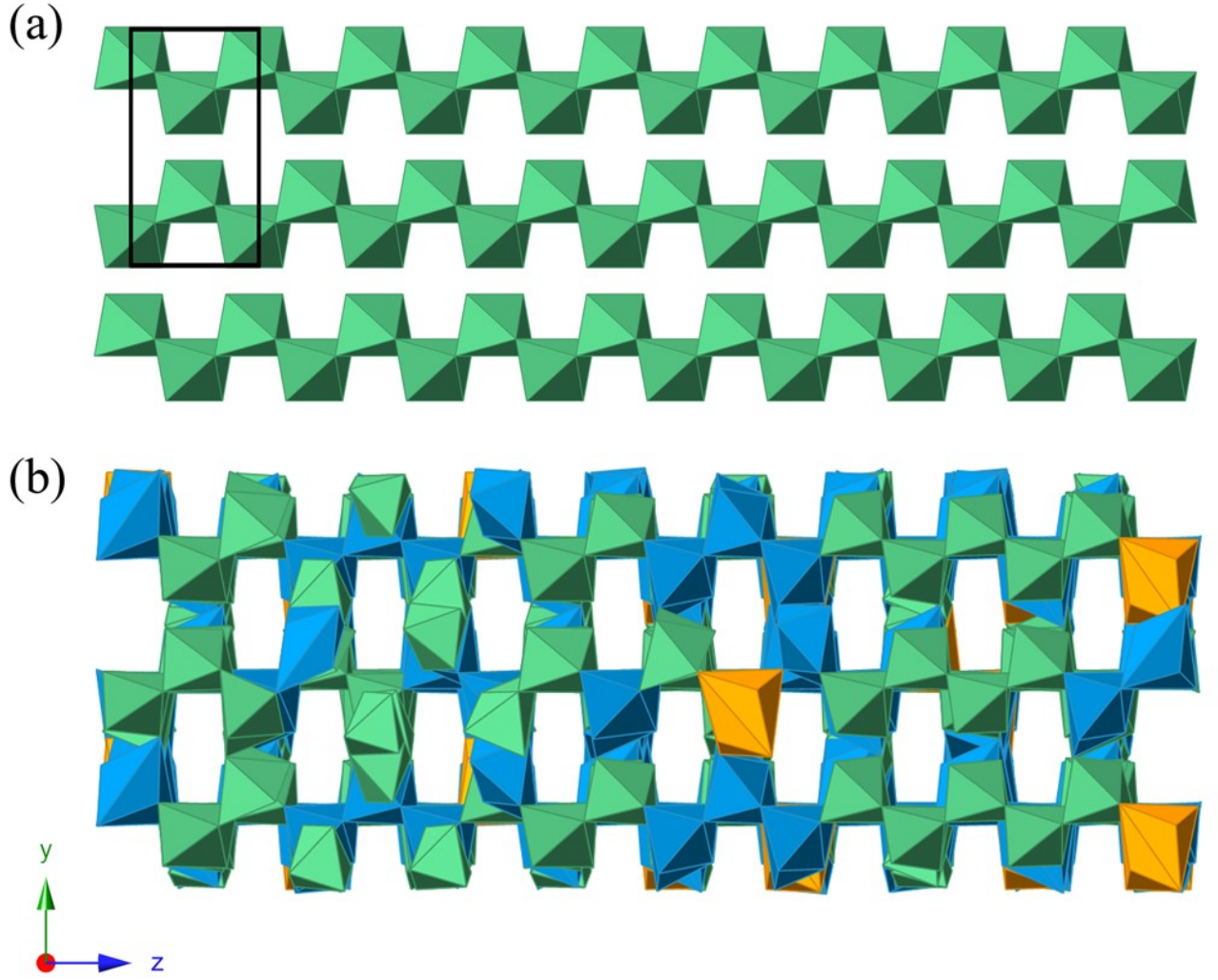


Figure 4-14: (a) Real space image of a $10 \times 1 \times 10$ supercell of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ parent structure, and (b) a $10 \times 1 \times 10$ commensurate approximation of the refined modulated structure, from [100]; interconnectivity between NbO slab along y direction is established due to the displacive movement of the oxygen, which is absent from the parent structure. The same colour scheme from Figure 4-13a is used.

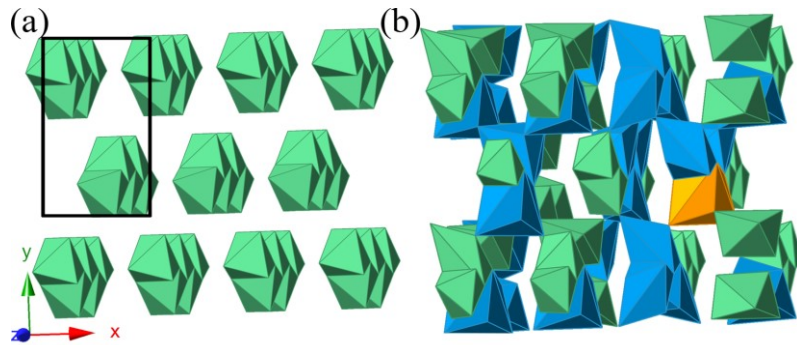


Figure 4-15: (a) Real space image of a $10 \times 1 \times 10$ supercell of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ parent structure, and (b) a $10 \times 1 \times 10$ commensurate approximation of the refined modulated structure, from a direction that is slightly tilted away from [001] of the parent structure (about 2°); connectivity of the coordination polyhedra in the ac plane is highlighted. The same colour scheme from Figure 4-13a is used.

4.6 Conclusions

In an attempt to further explore the modulated $\text{CeNbO}_{4.25}$ structural template, the hyperstoichiometric $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series ($x = 0.01\text{--}0.20$) were successfully synthesized using a solid-state reaction. The composition range $x = 0.08\text{--}0.16$ was identified to have a $(3 + 2)\text{D}$ modulated structure.

Direct imaging of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases using TEM revealed that the modulated phases have ferroelastic domains similar to that observed in the low temperature LaNbO_4 parent phase. In addition, Z contrast was observed using both HRTEM and HAADF, indicating that the structural modulation stems from the occupational modulation at the Nb/W site at the ac plane. The modulation wave vectors $\mathbf{q}$ were extracted using electron diffraction and were used as an input to refine synchrotron X-ray diffraction data of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition. Asymmetric, anisotropic peak broadening was observed when refining the parent structure, and this observation is ascribed to the residual strain in the ferroelastic domains. Rietveld refinement of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ structure was attempted using the superspace group $I2/c(\alpha_1, 0, \gamma_1)00(\alpha_2, 0, \gamma_2)00$; fitting parameters of $R_p = 0.085$ and $R_{wp} = 0.108$ were obtained despite the presence of an asymmetric peak profiles. The cation-oxygen bond lengths, as well as the bond valence sum of the refined model, were examined. Good consistency between the refined value and previous literature reports was achieved, justifying the proposed structural model.

Commensurate approximation was constructed to showcase the refined structure in real space. The refinement proposed a distorted B site coordination environment: both the cations and the oxygen ions are displaced to facilitate the W/Nb occupational modulation. In addition, the variations in B-O bond length lead to a change in the coordination number, which ranges from 6 to 8 in the modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase, while the parent phase has a fixed coordination number of 6 with a cut-off bond length of 3 Å. The increased coordination number provides linkage between the isolated NbO_x slabs, forming a 3D network which is considered to facilitate fast oxygen diffusion in the analogous $\text{CeNbO}_{4.25}$ phase.

Chapter 5. Structural evolution of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases and their transport properties

5.1 Introduction

In the previous chapter, the low temperature crystal structure of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition was studied in detail. As a result of the occupational modulation, a highly defective local structure with interconnecting Nb/ WO_x slabs was highlighted in the low temperature phase. Apart from the low temperature structure, the crystal phase of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ at intermediate temperatures (500–750 °C) is also of interest, as the CeNbO_{4+d} prototype phases have demonstrated remarkable oxygen diffusivity in this temperature region [58]. However, the high temperature structure of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ is not well understood, due to the complex modulated structure; literature reports often treated the high temperature structure as an unmodulated structure [226,250]. It is of interest to verify the high temperature structure of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system and to investigate whether the highly defective local structure, which is considered beneficial to facilitate fast ion conduction [59,251], is preserved at the intermediate temperature range. In addition, there is a pressing need to understand the charge carrier(s) and the conducting mechanism, which remains unclear in these hyperstoichiometric compounds

Building on the room temperature structural analysis presented in the previous chapter, this chapter proceeds to investigate the phase evolution and the transport properties of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system. Key structural features, including the complex phase transition behaviour of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series as well as the position of the interstitial oxygen, are addressed using

thermal analysis and diffraction techniques (*in situ* X-ray and neutron diffraction). Subsequently, the transport properties of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ are probed using electrochemical impedance spectroscopy (EIS) and ^{18}O isotopic exchange, to gain insight of the conducting mechanism. Finally, in an effort towards further exploring the structural template of the CeNbO_{4+d} phase, the effect of A site cations on the conduction of hyperstoichiometric LaNbO_4 is investigated by studying the structure and conductivity of $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ compounds.

5.2 Thermal Analysis of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$

5.2.1 Thermogravimetric Analysis (TGA)

The mass change of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series from room temperature to 900 °C was investigated using thermogravimetric analysis (TGA) under static lab air and the results are plotted in Figure 5-1.

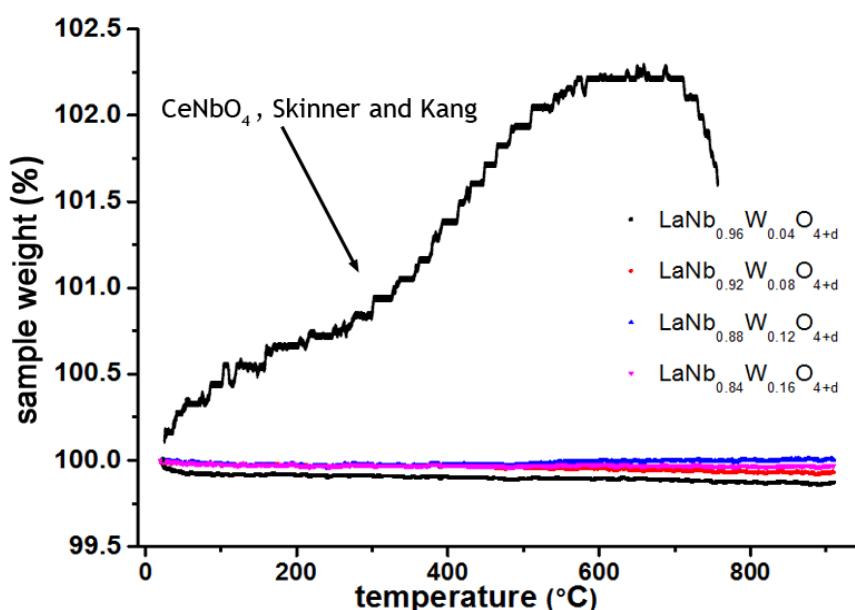


Figure 5-1: TGA measurement of various $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ samples from room temperature to 800°C under lab air, the CeNbO_4 reference adapted from [252] is also shown.

Unlike the CeNbO_{4+d} phases which have a weight gain of approximately 2.05 wt% from room temperature to 600 °C [252], TGA measurements of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ compositions indicated no significant weight change from room temperature to 900 °C. In CeNbO_{4+d} , the weight change is related to the oxidation of Ce^{3+} to Ce^{4+} , accompanied by introduction of interstitial oxygen; the W dopant in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ on the other hand, seems less susceptible to reduction and all measurements showed only a small drift of about 0.1% weight change up

to 900 °C. The drift is mostly likely associated with instrumental effects. A small weight loss of about 0.15% was observed in $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ upon heating (<50 °C) which is probably due to the loss of adsorbed water. Overall the TGA measurements suggest no detectable change in sample mass from the room temperature to 900 °C, indicating good thermal stability and a stable valence state of W^{6+} , which is consistent with a previous report [136].

5.2.2 Dilatometry

Dilatometry curves of the LaNbO_4 reference as well as the modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ compositions, in the temperature range from 200 °C to 900 °C, are shown in Figure 5-2. For the undoped LaNbO_4 , two distinct regions, corresponding to the low temperature monoclinic phase and the high temperature tetragonal phases respectively, are well separated. A sharp decrease in the thermal expansion rate was observed and was attributed to the monoclinic (*m*) to tetragonal (*t*) phase transition [132]. The phase transition temperature was determined by first extrapolating the linear part of the expansion curve (the red lines in Figure 5-2a) and then finding the intersection between the low and high temperature regions. The phase transition temperature (T_{tr} , reported in Table 5-1) was estimated to be 490 ± 10 °C for the undoped LaNbO_4 which is in good agreement with references [132,232].

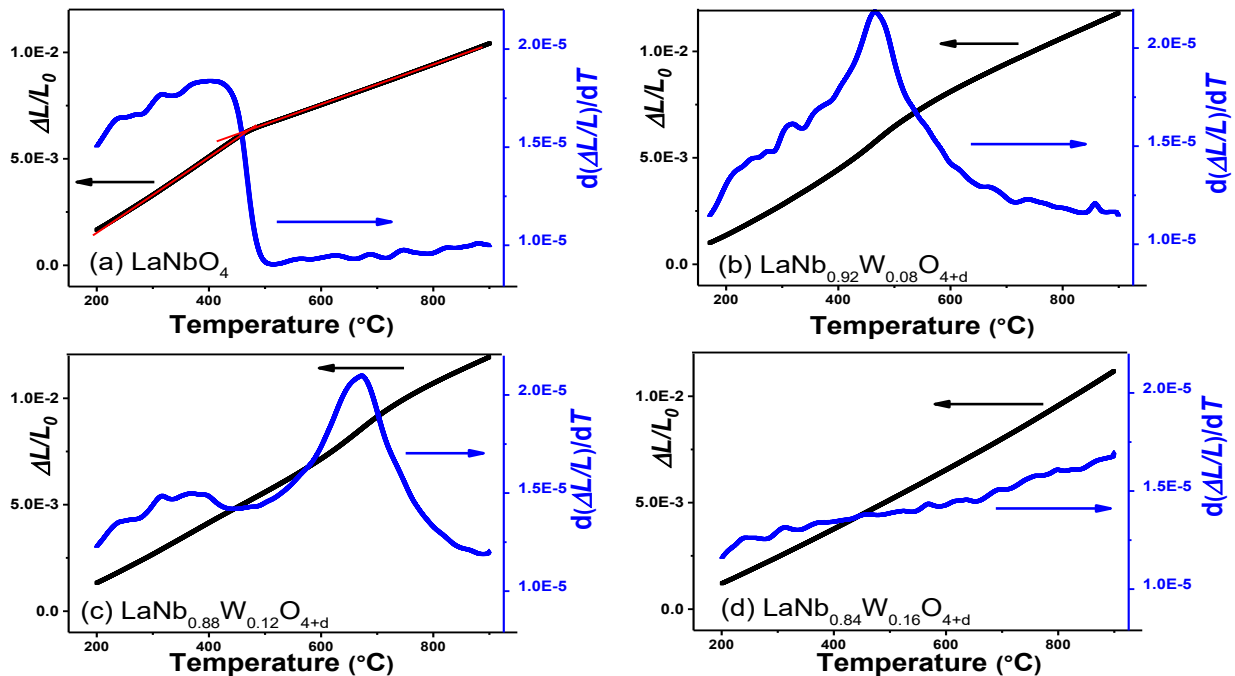


Figure 5-2: Dilatometry curves show the length change and the linear expansion rate as a function of temperature for (a) LaNbO_4 reference and various $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ compounds with (b) $x = 0.08$ (c) $x = 0.12$ and (d) $x = 0.16$. The phase transition in LaNbO_4 was determined by intercepting of the linear part of the expansion curve, highlighted by the red lines in (a).

The thermal mechanical behaviour of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ compositions, however is more complicated; instead of a sudden decrease of the thermal expansion rate approaching the phase transition, the change in $\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$ and $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ was less abrupt (Figure 5-2b and c). For samples with 8 at% to 12 at% W dopant, the thermal expansion rate increased gradually before reaching a transition point, after which a slow decrease in the expansion rate was observed. Such a transition was absent from the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition (Figure 5-2d). The thermal expansion coefficients (TECs, reported in Table 5-1), before and after the transition, were obtained by averaging the length change of the samples over the respective temperature regions. Comparing with the LaNbO_4 parent phase, the W dopant reduces the discrepancy in TEC between the low and high temperature regions (reported in Table 5-1). For fuel cell applications, a sudden change in TEC promotes mismatch between the electrolyte and electrode during the start-up stage and thus often leads to mechanical failure [6]; dilatometry results therefore suggest improved mechanical stability of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ electrolyte with W substitution. In addition, the TEC of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases are higher than the conventional electrolyte (i.e. the TEC of $\text{Ce}_{0.9}\text{G}_{0.1}\text{O}_{2-d}$ is $\sim 12 \times 10^{-6}/\text{K}$ from room temperature to 800°C [253]) and has a closer match with conventional electrodes such as LSCF of $16.6 \times 10^{-6}/\text{K}$ from room temperature to 650°C [254] indicating that the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases have suitable mechanical properties to function in fuel cells. The origin of the transition points (those observed in Figure 5-2b and c) will be discussed in section 5.3.

Table 5-1: Thermal expansion coefficients of the LaNbO_4 and various $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ compositions determined based on the dilatometry measurements in Figure 5-2.

Composition	TEC high temperature ($10^{-6}/\text{K}$)	TEC low temperature ($10^{-6}/\text{K}$)	T_{tr} ($^\circ\text{C}$)	references
LaNbO_4	17.3	9.3	490 ± 10	this work
	17.3	7.1	510 ± 10	[132]
	14.0	8.4	504 ± 10	[232]
$\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$	17.5	12.7	468 ± 5	this work
$\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$	16.2	13.1	669 ± 5	
$\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$	14.5		-	

5.3 *In situ* high temperature XRD (HTXRD) analysis of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series

5.3.1 High temperature XRD

The evolution of the structure and the phase transition of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ ($x = 0.04\text{--}0.16$) from room temperature to $850\text{ }^\circ\text{C}$, a temperature range of interest for SOFC applications, was investigated using *in situ* high temperature X-ray diffraction utilising Cu K_α radiation. The complexity of the phase transition behaviour is well illustrated by the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition (shown in Figure 5-3); at room temperature, the composition is in a biphasic area of the phase diagram, which consists of a modulated monoclinic phase and a W solid solution in LaNbO_4 . Increase the temperature to $300\text{ }^\circ\text{C}$ sees the formation of a single modulated phase, although the intensity of the satellite reflections decreased rapidly with further heating and became undetectable after reaching $400\text{ }^\circ\text{C}$. Similar to the undoped LaNbO_4 , the monoclinic (*m*) to tetragonal (*t*) phase transition of the parent structure in $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ occurs at $500\text{--}550\text{ }^\circ\text{C}$, above which the structure remains tetragonal within the experimental temperature range (Figure 5-3). The completeness of the phase transition was determined by the full width at half maximum (FWHM) of the main reflections: the peak width of the monoclinic phase is consistently wider than the tetragonal phase, especially close to the phase transition temperature where both *m* and *t* phase were observed. The step size of the experiment is set at 0.02° in 2θ ensuring sufficient resolution power in determining the peak width.

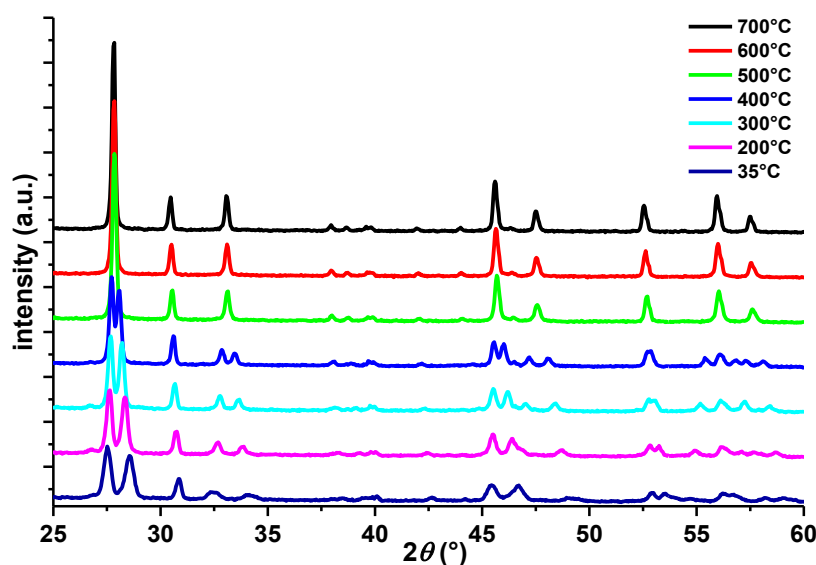


Figure 5-3: Selected high temperature XRD patterns of the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition from room temperature to $700\text{ }^\circ\text{C}$.

The lattice parameters of the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition, obtained using the Le Bail method, are plotted in Figure 5-4. The subscript “*m*” and “*t*” indicate the monoclinic and tetragonal structure respectively. It should be pointed out that the b_m axis was chosen as the unique axis for the monoclinic phase which coincide with the c_t axis in the tetragonal unit cell. The choice of unique axes is made to avert any confusion when comparing the literature reported data, which adopt the same cell choice [136]. Approaching the phase transition temperature T_{lr} , a_m decreases while c_m increases, resulting in the merging of monoclinic symmetry related peaks in the XRD pattern to tetragonal. The b_m increases almost linearly with temperature, while the β angle decreases gradually and becomes 90° above the transition temperature (demonstrated for the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition in Figure 5-4a and b).

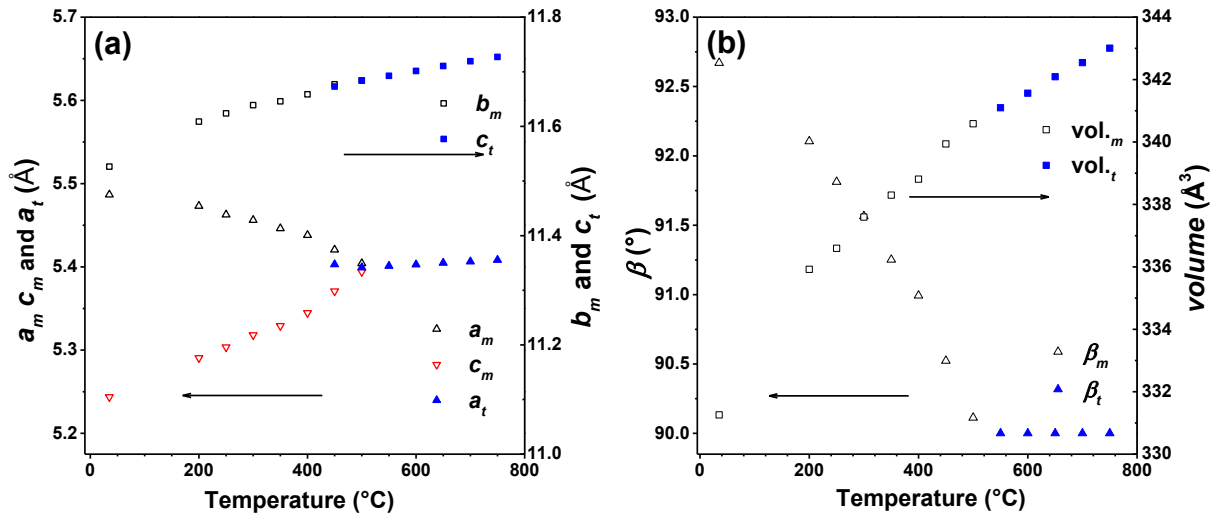


Figure 5-4: Refined lattice parameters (a) and cell volume (b) of the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition as a function of temperature, Error bars are smaller than symbols. The subscript “*m*” and “*t*” refers to the monoclinic and tetragonal structure respectively.

The *m* to *t* transition temperature of the parent phase varies with the W dopant concentration. For instance, the XRD pattern of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition recorded at 400 °C is better fitted with a tetragonal model, as the monoclinic model fails to assign the peak intensities correctly. The modulation reflections (the position of the modulation peak with the highest intensity is marked with an arrow in Figure 5-5) however were still observable in the intermediate tetragonal phase, albeit its intensity decreases rapidly with increasing temperature. The peak becomes indistinguishable from the background above 650 °C. At this temperature, an unmodulated high temperature tetragonal phase formed, similar to the high temperature parent structure of LaNbO_4 .

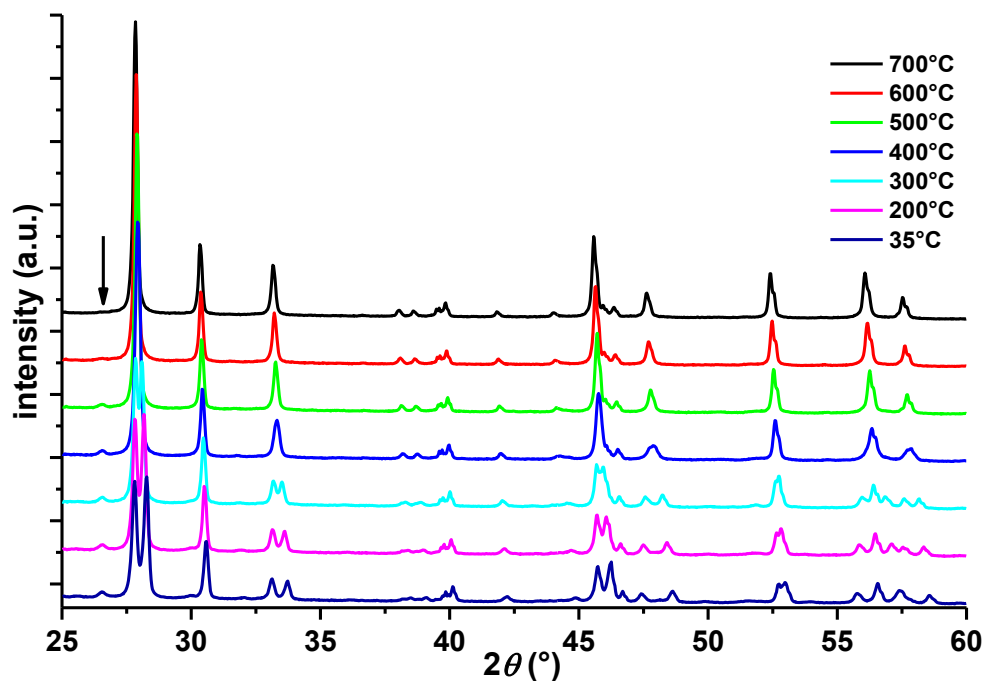


Figure 5-5: Selected high temperature XRD patterns of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase, the position of the satellite reflection with highest intensity is highlighted by the arrow.

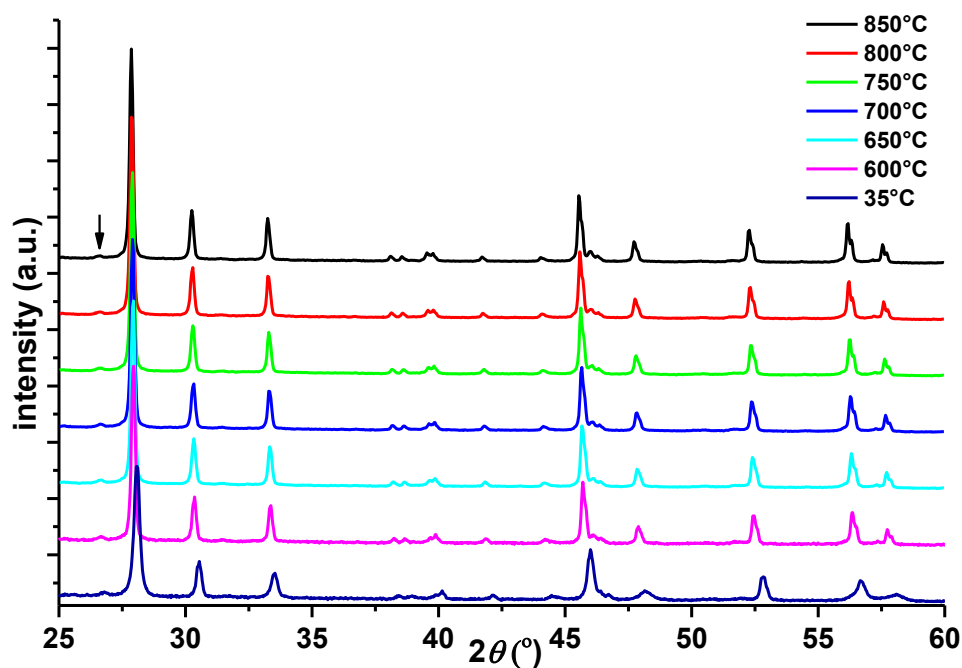


Figure 5-6: Selected high temperature XRD patterns of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition from room temperature to 850 °C. Unlike other compositions, the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ phase remains modulated at 850 °C.

Further increasing the dopant level ($W = 16$ at%) sees the formation of a tetragonal parent phase with some residual monoclinic phase at room temperature, confirmed by refinement of high resolution neutron scattering data (Figure 5-6 and Figure 5-7).. The co-existence of two phases has been reported by various authors when studying the phase transition of rare earth

niobates and has been ascribed to temperature gradient [255], grain size distribution [97] and the residual strain in the ferroelastic monoclinic phase [255]. The two phase region observed in $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ at room temperature is probably due to a size or a strain effect.

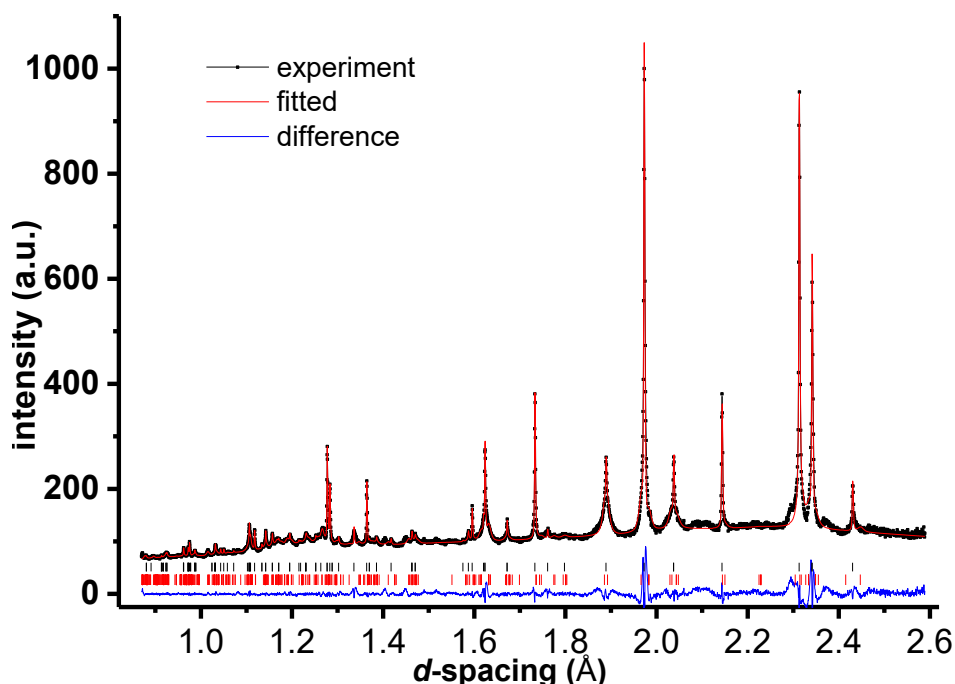


Figure 5-7: Room temperature neutron scattering data of the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition refined with a two phase model containing both the m and t phases. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black and red vertical lines mark the theoretical Bragg peak positions of the tetragonal phase and the monoclinic phase respectively.

The intensity of the monoclinic reflections in $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ decreased sharply on heating and the structure remained modulated through the whole temperature range (up to 850 °C, as shown in Figure 5-6) whereas other composition has transformed to the unmodulated parent tetragonal structure at this temperature. Based on the HTXRD data, two phase transitions have been identified in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$: the transition of parent structure symmetry from monoclinic to tetragonal, similar to that observed in the LaNbO_4 ; and the transition between a modulated phase and an unmodulated phase.

5.3.2 Estimating the phase transition temperature using Landau theory

Landau theory on the 2nd order phase transition predicted that the free energy of a system in the vicinity of the phase transition could be expressed as a Taylor expansion of the order parameter Q [256]. The theory also predicted that, when approaching the phase transition from low temperature, the variation of the order parameter Q with temperature follow the following form:

$$Q = \left(\frac{T_{tr} - T}{T_{tr}} \right)^{1/2} \quad (T \leq T_{tr}) \quad \text{Eqn. 5.1}$$

in which the T is the temperature of the system; T_{tr} is the transition temperature where the discontinuity of second order thermodynamic parameter occurs [256]. When studying the ferroelastic to paraelastic transition, Aizu demonstrated a linear relationship between the order parameter Q and the temperature dependent spontaneous strain ε_s , of the system [257]:

$$\varepsilon_s = Q/k = \left(\frac{T_{tr} - T}{T_{tr}} \right)^{1/2} \cdot 1/k \quad \text{Eqn. 5.2}$$

in which k is a constant. In LaNbO₄ system, the spontaneous strain ε_s describes the difference in lattice parameters between the low temperature monoclinic phase and a hypothetical low temperature tetragonal phase (termed as the *prototype phase*) [257]. The detailed calculation of the spontaneous strain is demonstrated in Appendix b.

It has been widely reported that the transition between the low temperature monoclinic and high temperature tetragonal phase in rare earth niobates is indeed a second-order ferroelastic to paraelastic transition, therefore Landau theory has been employed to predict the phase transition temperature in LaNbO₄ [97,240,258]. The low temperature phase of LaNbO₄ has ferroelastic domains that are related by rotating about the unique axis by $\sim 90^\circ$ and the phase transition is completed by the domain wall movement which merges neighbouring domains [259,260]. Similar domain structure (i.e. domain size and domain wall orientation) was observed in the LaNb_{1-x}W_xO_{4+d}, as presented in the previous chapter (Figure 4-4 in section 4.4.2), indicating a phase transition process resembling LaNbO₄.

Having interweaving micro-domains which are in two related orientation states that can be shifted readily from one to the other with movement of atoms, the LaNb_{1-x}W_xO_{4+d} phases too fit Aizu's definition of a ferroelastic crystal [257,261]. In addition, the gradual transition of the lattice parameters as well as the cell volume (showcased in Figure 5-4b) suggests that the

phase transition is indeed secondary order [132,262]. Therefore Landau theory was applied to predict the phase transition temperature when the symmetry of the parent phase transits from monoclinic to tetragonal.

By fitting the temperature and the spontaneous strain according to Eqn. 5.1, the phase transition temperature between the low temperature ferroelastic monoclinic parent phase and the high temperature paraelastic tetragonal parent phase was predicted, and the results are reported in Table 5-2 and Figure 5-8. Note, the transition temperature for the $x = 0.16$ composition was not fitted, as the prototypic phase has already formed at room temperature for this composition (Figure 5-7).

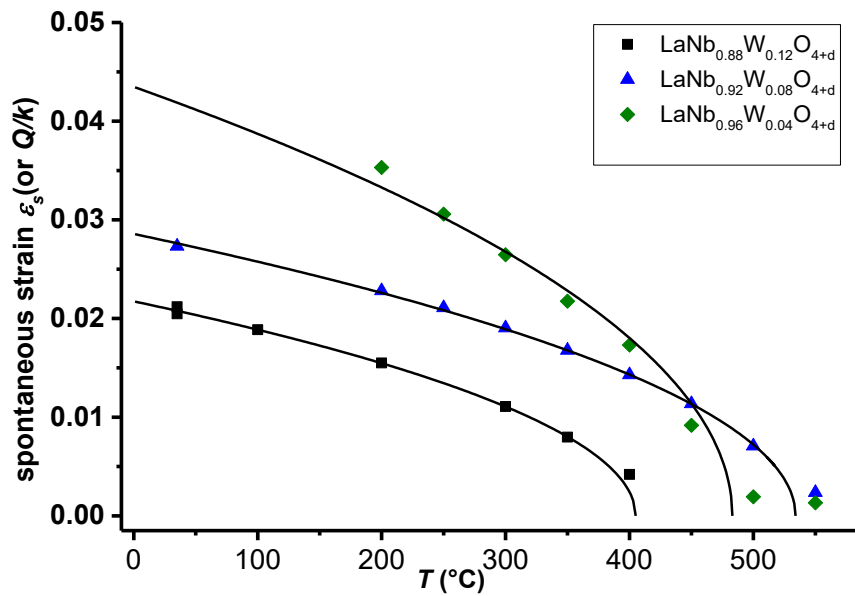


Figure 5-8: Evolution of spontaneous strain ε_s as a function of temperature, fitted to the Landau theory for second order phase transition (Eqn. 5.2). The fitting parameters are reported in Table 5-2.

Table 5-2: Transition temperatures T_{tr} and k factor, fitted using Eqn. 5.2 for various $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases.

compositions	k	T_{tr} (°C)
$\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$	21.4	468
$\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$	35	534
$\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$	46	405

Based on the analysis presented so far, the Nb rich corner of the LaNbO_4 - $\text{LaWO}_{4.5}$ phase diagram is tentatively proposed in Figure 5-9. The solid lines in the phase diagram indicate the single phase boundary; the dotted line separates the monoclinic and tetragonal parent phase, whereas the dash line is the boundary between modulated structure and unmodulated structure. The monoclinic to tetragonal transition temperature of the parent structure was

determined based on Landau theory of second order phase transition, whereas the modulated to unmodulated transition temperature was estimated based on the diffraction experiment. The peak temperatures of the thermal expansion rate from the dilatometry measurements (Figure 5-2) are also marked on the phase diagram. It is unsurprising that the Landau theory is applicable for the modulated structure, despite the complexity of the modulation. The order parameter—spontaneous strain for the LaNbO_4 based electrolytes—characterizes the distortion of the lattice which can be envisioned as the displacement of the atoms in different parent structure [231,257]. Therefore, when the parent structure of the modulated phases transits from monoclinic to tetragonal symmetry, reduction of order parameter followed similar trend of LaNbO_4 [257].

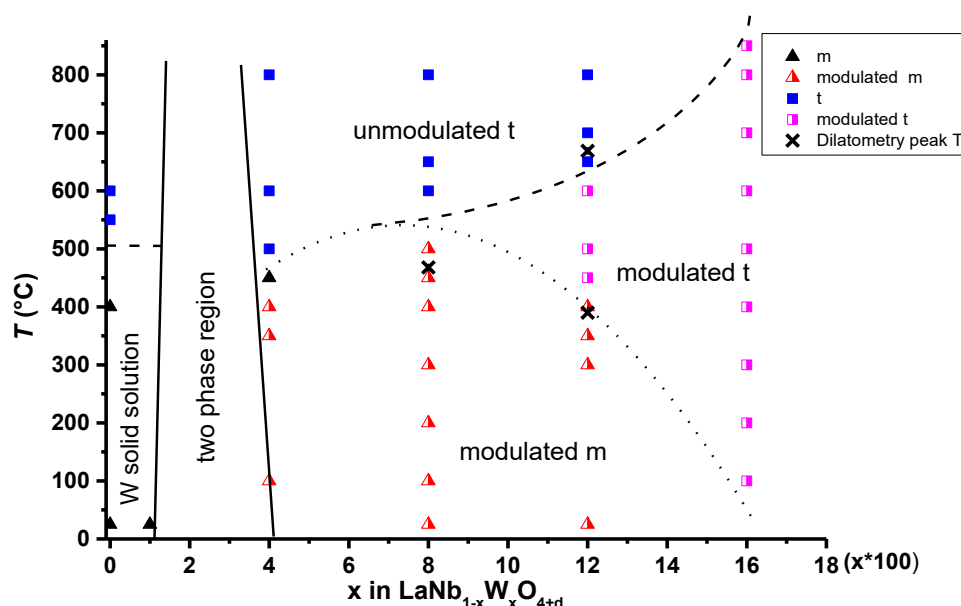


Figure 5-9: Proposed phase diagram of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system, highlights the complexity of the system. The solid lines signify the boundaries between biphasic region and the single phase region. The dotted line was based upon the transition temperature reported in Table 5-2, and separates the phases with monoclinic and tetragonal parent structures; the dash line marks the separation between the modulated phases and the unmodulated structure. All the lines are just guidance for the eyes. The “peak” temperatures from the expansion rate reported in Figure 5-2 are marked as “x” on the proposed phase diagram.

It is interesting to note the correlation between the “peak” temperature during dilatometry and the phase transition temperature obtained from diffraction. For instance, the expansion rate of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition first peaked at ~ 390 °C and later at ~ 670 °C (Figure 5-2c), which corresponds well with two phase transition of the $x = 0.12$ composition. In addition, no abrupt change of shrinkage rate was observed in the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition (Figure 5-2d), which coincides with the absence of a phase transition in this composition. Such correlation however is missing in $\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$, as the dilatometry peak temperature is

about 50-70 °C below the modulated to disorder transition. Still, it is not unreasonable to assume that the modulated to disorder phase transition would affect the thermal expansion of the material. As demonstrated earlier in Chapter 4, the Nb/W-O local environment of the modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase differs significantly from its parent structure. When varying the temperature, both the magnitude and the direction of the $\mathbf{q}$ vectors are expected to change [263], leading to variations of bond lengths and bond angles in addition to the thermal effect. The accumulation of the change would, on a macroscopic scale, perturb expansion rate. In analogy to the ferroelastic to paraelastic transition of the parent LaNbO_4 structure, it is logical to assume that the impact of modulation on the linear expansion rate will be at an extremum when the order-disorder transition occurs. Indeed, the peak temperatures of the dilatometry seem to coincide with the transition temperatures between the modulated structure and unmodulated structure in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ (Figure 5-9); it is therefore speculated that the removal of the structural modulation would introduce a subtle change in the expansion behaviour; however further experiments are required to verify this conjecture.

Theories of the modulated phase transition have been devised to explain the transition between the high temperature incommensurate phase and the low temperature commensurate structure (normally referred to as the “lock-in phase”, often observed below room temperature) [264–266] and provide great assistance in understanding the phase transition in those structures with charge density wave ordering and magnetic ordering [267–269]. However, the phase transition in modulated structure at elevated temperature has been overlooked. The proposed phase diagram highlights the complexity of structural variation in the modulated system, and calls for future investigation.

5.3.3 Interesting observations of the phase transition behaviour in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$

The phase transition reported in Figure 5-9 occurs in a temperature range that is of interest to SOFC electrolyte application. Therefore a detailed structural study is required, in an effort to understand the impact of modulation on the conductivity of the sample. Indeed, there have been many reports of the room temperature modulated scheelite phase [79,90,108,109,242] whereas the high temperature modulation in the fergusonite related structure has been overlooked. To investigate the high temperature structure and to extract the wave vector of the high temperature modulated phase, a $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ pellet was quenched from above

the phase transition temperature (furnace temperature 800 °C) directly into liquid nitrogen, in an attempt to “freeze” the high temperature phase.

Surprisingly, the XRD pattern of the quenched sample (after grinding it into powder) has the identical monoclinic symmetry to that of the furnace cooled sample (shown in Figure 5-10). The only marked difference was its slightly broadened peaks (most clearly seen in the 55° to 60° region), which probably relate to a hysteresis in phase transition. The quenched sample also has a slightly higher intensity for the modulation reflections in comparison with the furnace cooled sample.

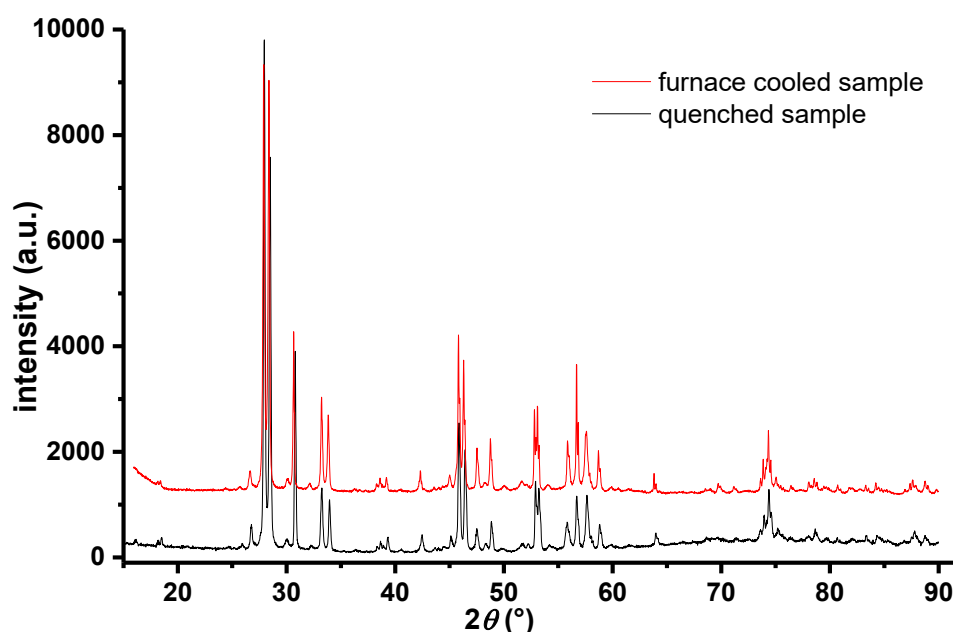


Figure 5-10: Comparison between a $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ sample which has been quenched from 800 °C into liquid nitrogen and a furnace cooled sample; no tetragonal phase was stabilized by quenching the sample.

Based on the refinement results and the TEM study of the room temperature structure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$, it has been confirmed that the modulation results from the cation ordering at the B site (discussed in Chapter. 4). On the other hand, it is also clear from the *in situ* high temperature XRD data (Figure 5-5) that the structure is unmodulated at elevated temperature (i.e. 800 °C). Cation diffusion is therefore required to realize the transition from the unmodulated high temperature phase, in which the W dopant is randomly distributed, to the modulated structure with cation ordering at room temperature. The quenching experiment, however, suggests that the diffusion of the B site cation is extremely fast, as the phase transition finished in just a few seconds, a speed comparable to martensitic phase transition [96]. This observation is particularly interesting as the cations are often considered immobile due to their relatively high charge numbers and thus strong interactions with the

surrounding [270]. However it should be noted that the gasification of the liquid nitrogen during the quenching process might lead to a cooling rate that is slower than expected.

Recent reports suggest that both the trivalent A site cation [271,272], and the WO_x^- ($x < 4$) polyanion [273,274] are mobile in $\text{A}_{3-d}(\text{WO}_4)_3$, an A-site deficient variant of the scheelite structure. To explain the diffusion of B site cation, in the scheelite niobates and molybdates, Neiman proposed a diffusion process involving shape-insertion and conformational changes of the BO_{4-x} tetrahedra, in the presence of oxygen vacancies [274]. The self-diffusion coefficient of Mo in PbMoO_4 was estimated to be $1 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at 780°C [274], which corresponds to a diffusion length of approximately 20 nm after 5 s. However, the presence of vacancies on either the cation or the oxygen sites are required to facilitate the cation diffusion at the A and B site respectively; these defects might be created due to nonstoichiometry and as a consequent of charge compensation mechanisms other than the creation of oxygen interstitial in the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases. Further study that focuses on the local structure variations during the transition is required to gain better insight of the transition process.

5.4 *In situ* Neutron Scattering of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$

One of the key features of the structure is the presence of the interstitial oxygen, introduced by the W^{6+} dopant. Naturally, the position of the interstitial oxygen and its interaction with the neighbouring ions are important for the conduction process. Information about the interstitial site is unfortunately not accessible using the HTXRD due to the low scattering power of oxygen. In addition, the data obtained suffers from high background intensity; it is therefore very difficult to yield detailed structural information, apart from the lattice parameters and the phase transition temperature. The neutron scattering cross-section of oxygen, on the other hand, is comparable to that of Nb, La and W [275], and therefore the structural evolution of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ phases was investigated using *in situ* neutron scattering and the search for the interstitial oxygen position in the latter composition at 500°C was attempted.

5.4.1 *In situ* neutron scattering of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$

The structure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ in the 600°C to 650°C range was first examined. This temperature range is of interest, as the HTXRD result hinted a phase transition between a modulated and an unmodulated tetragonal phase (Figure 5-9). Using the Rietveld method, the neutron scattering pattern of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ recorded at 600°C in static air was first

refined with the parent $I4_1/a$ space group and the fitting is reported in Figure 5-11. After refining the lattice parameters and the peak profile, the atomic position and the isotropic atomic displacement parameters (ADPs) were first refined while site occupancy of all the elements was fixed according to the nominal composition. Constraints on the occupancy were then released, although the Nb/W ratio was still fixed at 88 at%/12 at% at the B site, following the chemical analysis presented earlier (section 4.3). No significant deviation from ideal stoichiometry was reported and the refinement of the parent structure finally converged to $R_p = 0.028$ and $R_{wp} = 0.032$. Visual inspection of the refined pattern revealed additional peaks, indicating the presence of superstructure at elevated temperature, consistent with the HTXRD data (Figure 5-5). These peaks (such as those at $d = 2.30\text{--}2.40$ Å, $d = 1.25\text{--}1.30$ Å, highlighted by the arrows in the inset of Figure 5-11) were not detected by the in-house X-ray diffractometer highlighting the oxygen sensitivity of the HRPD diffractometer. The presence of superstructure must be addressed before the interstitial position can be pinpointed as both superstructure and the interstitial contribute to the observed peak intensity at the parent phase reflection position [100]. It should be noted that the increased background in the low d -spacing is a result of the sample environment; a quartz ampoule instead of the vanadium sample can was used for the *in situ* neutron diffraction to avoid reducing environment [208].

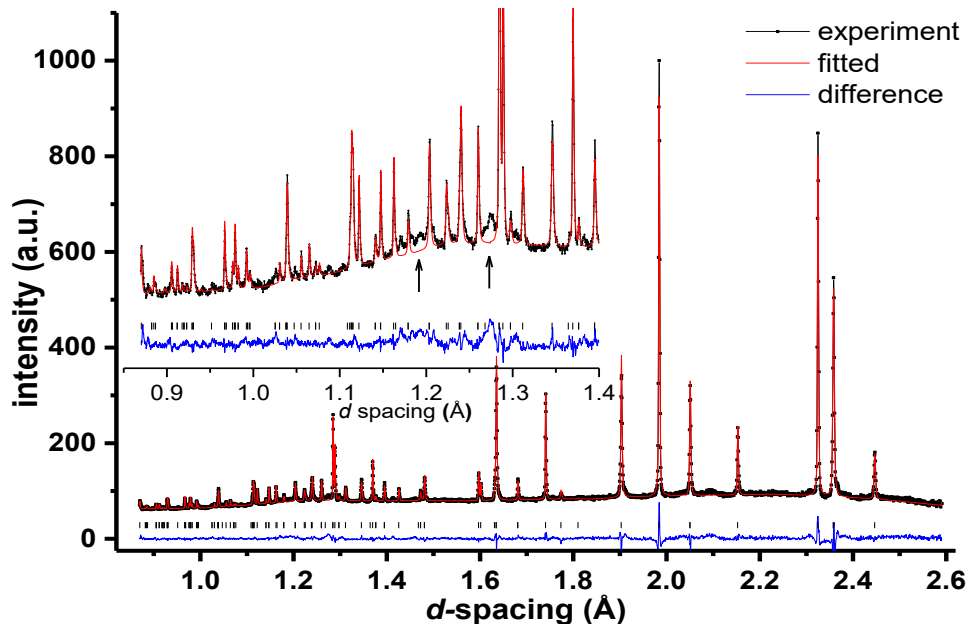


Figure 5-11: Rietveld refinement of neutron powder scattering data of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition at 600°C. Only the average structure was refined using the $I4_1/a$ space group; additional reflections were observed, indicating the presence of superstructure. Refinement converged with $R_p = 0.028$ and $R_{wp} = 0.032$. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black ticks mark the theoretical Bragg peak position. The inset shows the enlarged pattern in the d -spacing of 0.84 Å to 1.40 Å range. The arrows highlight the missing intensity that has not been accounted for using the unmodulated parent structure model.

Based on the space group of the parent structure, the superspace group $I4_1/a(\alpha, \beta, 0)00(-\beta, \alpha, 0)00$ was chosen for the refinement of the superstructure. There were other superspace groups available which are derived from same parent group [229] however the other choices all have a modulation component along the unique axis (c_t), which is inconsistent with the modulation waves in the low temperature structure; the electron diffraction and powder diffraction data presented in the previous chapter (Figure 4-3 in section 4.4.1) showed that the occupational modulated waves in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases propagate along the ab basal plane, similar to other modulated members of the scheelite family [107,108,110]. The chosen superspace group was used in the literature to refine the $(3 + 2)\text{D}$ modulated $\text{Na}_{2/7}\text{Gd}_{4/7}\text{MoO}_4$ scheelite [109] and $\text{CaEu}(\text{MoO}_4)_4$ [242].

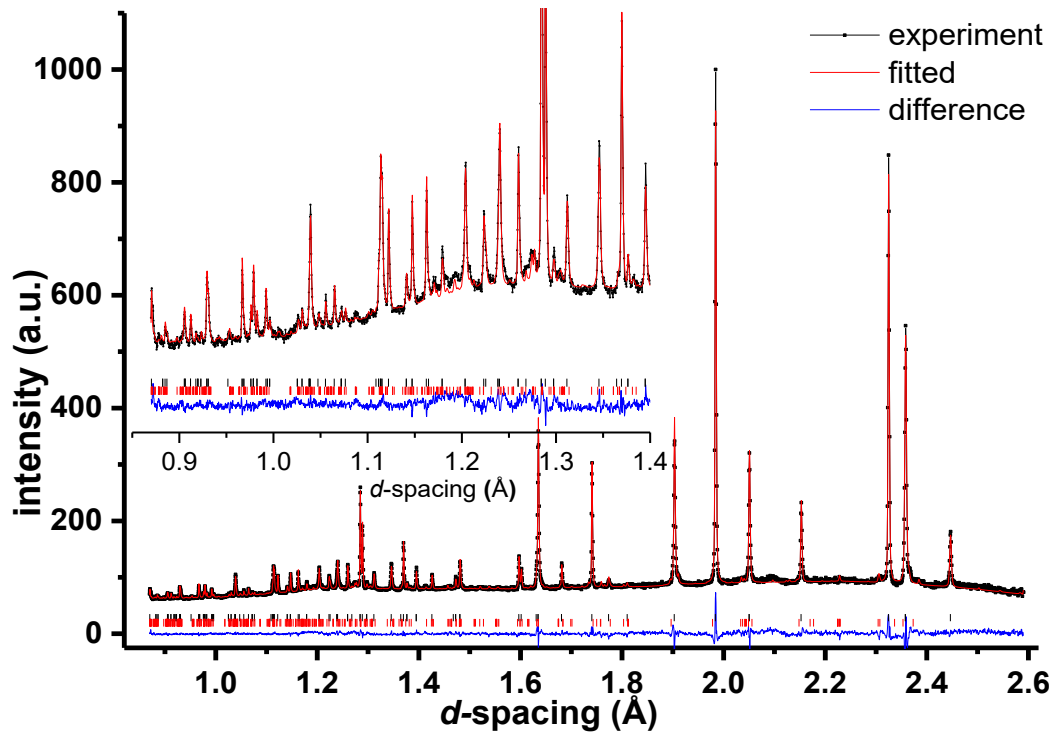


Figure 5-12: Rietveld refinement of neutron powder scattering data of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition at 600°C using the superspace group $I4_1/a(\alpha, \beta, 0)00(-\beta, \alpha, 0)00$. Improved fitting with $R_p = 0.022$ and $R_{wp} = 0.024$ were obtained, by including the structural modulation in the model. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black ticks mark the theoretical Bragg peak position. The inset shows the enlarged pattern in the d -spacing of $0.84 \text{ \AA}$ to $1.40 \text{ \AA}$ range.

To refine the modulated phase, the q vectors obtained from the room temperature electron diffraction, and the Fourier magnitudes of the low temperature $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ structure were used as the input for the subsequent refinement. Only first order modulation waves were refined as the majority of the higher order reflections had intensity lower than the 3σ detection limit. Nb and W were set to have identical fractional coordinates, ADP and displacive modulation amplitude whereas their occupational waves were set to keep the

overall sum constant. The magnitude of the modulation waves was initially fixed at 0.2, which was later released during the final stage of the refinement. It is interesting to notice that more modulation peaks with better resolution were observed in the neutron diffraction pattern. One of possible reasons for the difference is the variation in scattering power for X-ray and neutron: in the latter case the scattering power of oxygen is comparable to that of the heavy cation. This observation provides indirect evidence that the oxygen sublattice is modulated. The 748 observed peaks allowed the refinement of 33 independent parameters, including the anisotropic displacement parameters. The refinement finally converged with $R_p = 0.022$ and $R_{wp} = 0.023$. The introduction of modulation waves made up the difference between the model and the pattern observed in Figure 5-11, which led to an overall improved fitting. The refined occupancy shows good consistency with the expected nominal composition (Table 5-4). The ADPs were refined using anisotropic model and reasonable values were obtained. The refined pattern is shown in Figure 5-12, and the experimental conditions, the refined parameters of the parent phase and the modulated phase are summarized in Table 5-3, Table 5-4 and Table 5-5 respectively.

It should be noted that despite the improved fitting, there is residual intensity which has not been accounted for using the modulated structure model. Part of the discrepancy is related to the asymmetric peak shape discussed in the previous section, but the quality of the refinement results was restricted by the data statistics and the number of reflections available. The fitted model therefore needs to be examined to make sure that the results are chemically and physically sensible, and present a reasonable local coordination environment.

Table 5-3: Summary of the experimental conditions for the *in situ* neutron scattering reported in Figure 5-12.

Composition	LaNb _{0.88} W _{0.12} O _{4+d}
Space group	$I4_1/a(\alpha, \beta, 0)00(-\beta, \alpha, 0)00$
Temperature	873 K
a b c (Å)	5.37466(8) 5.37466(8) 11.72917(18)
V (Å ³)	338.821(9)
modulation waves	$q_1 = 0.3033(3)a^* + 0.1177(4)b^*$ $q_2 = -0.1177(4)a^* + 0.3033(3)b^*$
data collection	
instrument	HRPD at ISIS
data range	$d = 2.5889 \text{ Å to } 0.8696 \text{ Å}$
resolution	$\Delta d/d = 4 \times 10^{-4}$ [208]
Reflections (observed/unobserved)	748/330
number of refined parameters	33
quality of fitting	$R_p = 0.022$, $R_{wp} = 0.023$ GOF = 1.09

Table 5-4: Summary of the refined atomic parameters of the average structure reported in Figure 5-12.

	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La	0.991(8)	0	0.25	0.625	0.0397(12)	0.0397(12)	0.0176(13)	0	0	0
Nb/W	1	0	0.25	0.125	0.0356(14)	0.0356(14)	0.0390(01)	0	0	0
O	0.995(6)	0.2407(4)	0.0910(3)	0.0414(2)	0.0544(14)	0.0690(01)	0.0382(10)	0.0150(1)	0.0088(11)	0.0230(13)
Cation site	Average bond length (Å)					Bond valence sum (BVS)				
La	2.524					3.10				
Nb/W	1.835					5.03				

Table 5-5: Refined Fourier magnitudes for the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase at 600 °C.

site		x	y	z
La	position	0	0.25	0.625
	$s,1^*$	0	0	-0.0030(7)
	$c,1$	-0.0123(15)	0.0220(11)	0
	$s,2$	0	0	0.0032(6)
	$c,2$	0.0220(11)	-0.0123(15)	0
Nb/W	position	0	0.25	0.125
	$s,1$	0	0	0.0088(8)
	$c,1$	-0.0076(16)	0.0218(13)	0
	$s,2$	0	0	-0.0088(8)
	$c,2$	-0.0218(13)	-0.0076(16)	0
	p_{c1}, p_{c2}^{**}	-0.25(6), -0.25(6)		
O	position	0.240(1)	0.092(3)	0.042 (1)
	$s,1$	-0.0008(18)	0.0043(16)	0.0031(7)
	$c,1$	-0.0022(19)	0.0334(15)	0.0036(7)
	$s,2$	-0.0001(15)	-0.0040(2)	-0.0034(7)
	$c,2$	-0.0289(13)	-0.0143(19)	0.0021(8)
Distance (Å)		average	min	max
La-O		2.533	2.462	2.572
Nb-O		1.832	1.772	1.902

* s, c stands for Fourier magnitude of sin and cos wave described in Eqn. 2.9 respectively; the number describes the wave vectors: the 1st wave is along q_1 direction and the 2nd wave is along q_2 direction

** $p = p_0 + p_{c1}\cos(2\pi t) + p_{c2}\cos(2\pi u)$, in which p_0 is the site occupancy of the parent structure. p_{c1} , p_{c2} are the Fourier magnitude for the occupational waves; t,u are the coordinates in the internal axes; both the Fourier magnitude of the displacive and the occupational wave follow the format describe in Eqn. 2.9.

The nuclear density and the residual density maps, in the vicinity of the Nb and La sites, were examined (Figure 5-13). Overall, the residual density is about 1–2% of the observed density, indicating good fitting quality. Similar procedures were used to conduct the refinement of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ data at 500 °C and 550 °C in the (3 + 2)D structural model and the results

are reported in a crystallographic information file (CIF), which can be found in the supplemental information.

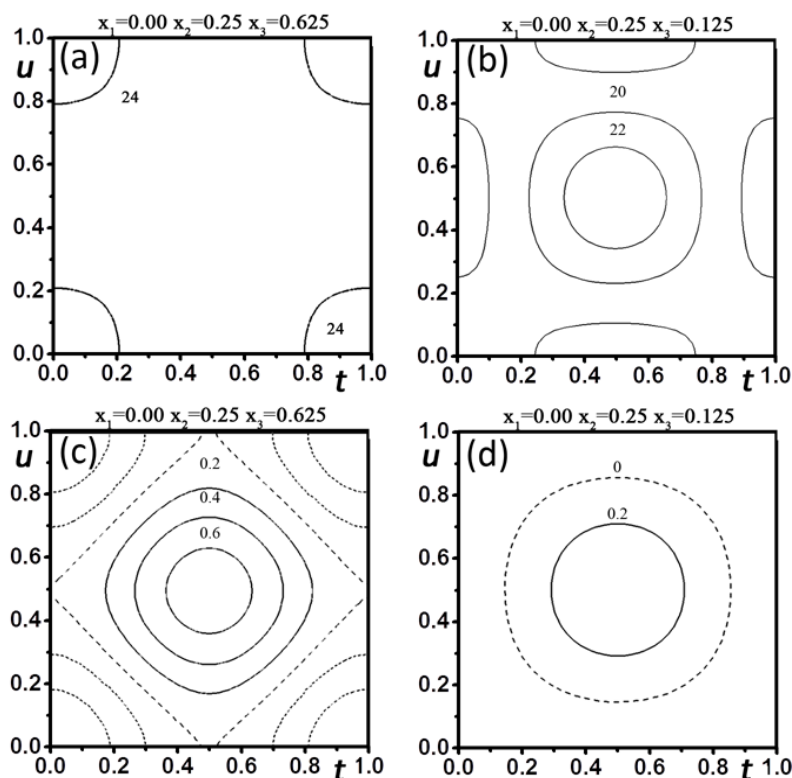


Figure 5-13: Observed nucleus density maps in the vicinity of (a) La and (b) Nb; and the corresponding difference nucleus density maps in (c) and (d), as a function of the internal coordinates. The contour in (a) and (b) is $2 \text{ fm } \text{\AA}^{-3}$ whereas in (c) and (d) is $0.2 \text{ fm } \text{\AA}^{-3}$. Overall a residual level approximately 1-2% of the observed nucleus density was registered, indicating good fitting quality.

When refining the pattern gathered at 650°C , the fitting parameters improve little with the inclusion of structural modulation, due to the lowered intensity and increased width of the satellite reflections (Figure 5-14). The diffraction patterns still have unresolved intensity using only the unmodulated parent structure, for instance, those reflections between $1.19 \text{ \AA}$ and $1.27 \text{ \AA}$ which are absent from the 800°C pattern (shown in Figure 5-15). These fine features have reduced intensity, which is not surprising as the phase diagram based on the HTXRD data suggest a modulated to unmodulated phase transition occurs in this temperature range. The broadening of the reflections might reflect an intermediate state between the long-range ordered modulated structure and the high temperature unmodulated phase, although closer examine of the local structure is necessary to verify this hypothesis. The reduced intensity, hence worsened signal to noise ratio, makes the fitting with the modulated structural model less reliable; the refinement was nevertheless attempted using $(3 + 2)\text{D}$ structural model for the 650°C pattern and the fitting is shown in Figure 5-14 (fitting parameters again reported in the supplemental information). Overall, the neutron scattering

data suggests that the transition temperature in $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ reported in Figure 5-9 should be shifted to a slightly high temperature (600–650°C). Further increasing the temperature saw the reduction of the intensity of the satellite reflections, and no satellite reflections were observed for the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition at 800 °C (Figure 5-15) which is consistent with the HTXRD observation presented earlier in Figure 5-9.

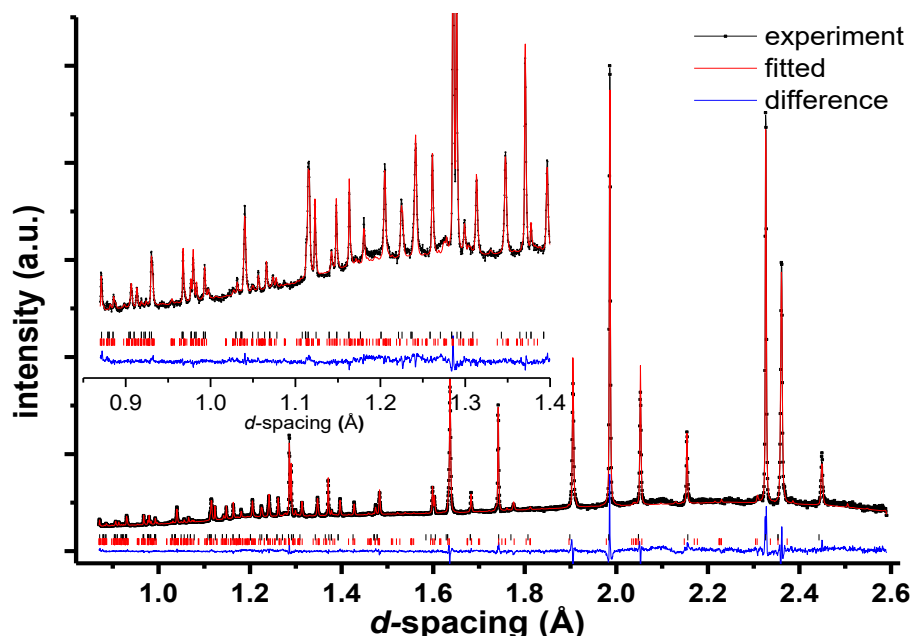


Figure 5-14: Rietveld refinement of neutron powder scattering data of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase at 650 °C using the superspace group $I4_1/a(\alpha, \beta, 0)00(-\beta, \alpha, 0)00$. Good fitting with $R_p = 0.022$ and $R_{wp} = 0.023$ was achieved. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black and red vertical lines mark the theoretical peak position of the parent structure and the modulated peaks respectively. The inset shows the enlarged pattern in the 0.84 Å to 1.4 Å range.

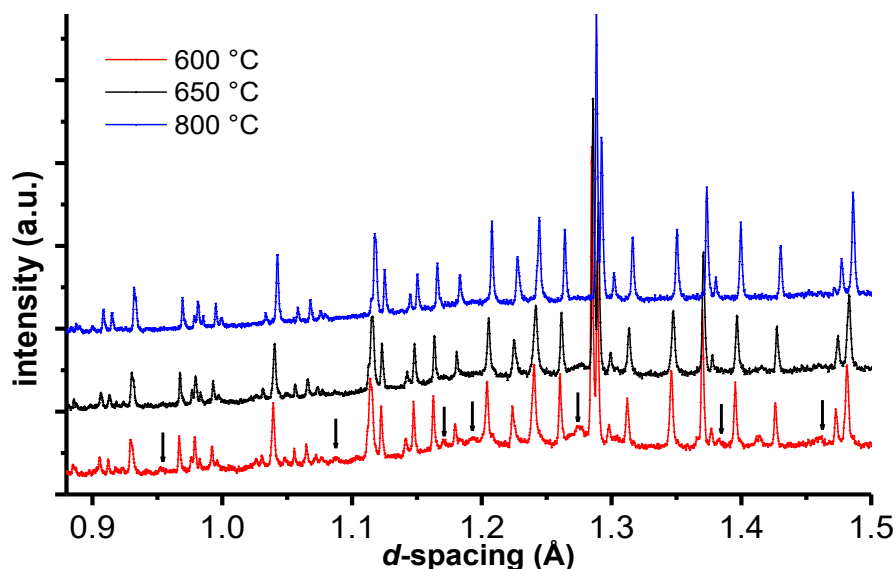


Figure 5-15: Neutron scattering data in the 0.88 to 1.50 Å range of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition gathered at 600–800 °C. The intensity of the satellite reflections (marked by the arrows in the figure) reduces with increasing temperature, and the structure becomes unmodulated at 800 °C.

5.4.2 *In situ* neutron scattering of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$

The same procedures described in the previous section were carried out to refine the structure of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$. Unlike the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition, which goes through a phase transition from modulated structure to unmodulated structure between 650 °C to 800 °C, neutron scattering data confirmed that the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition maintains its modulated structure up to 800 °C. All the patterns gathered between 500 °C and 800 °C were refined using the same $(3 + 2)\text{D}$ superspace group $I4_1/a(\alpha, \beta, 0)00(-\beta, \alpha, 0)00$. In Figure 5-16, the refined pattern of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ phase at 800 °C is shown, highlighting the stability of the structural modulation.

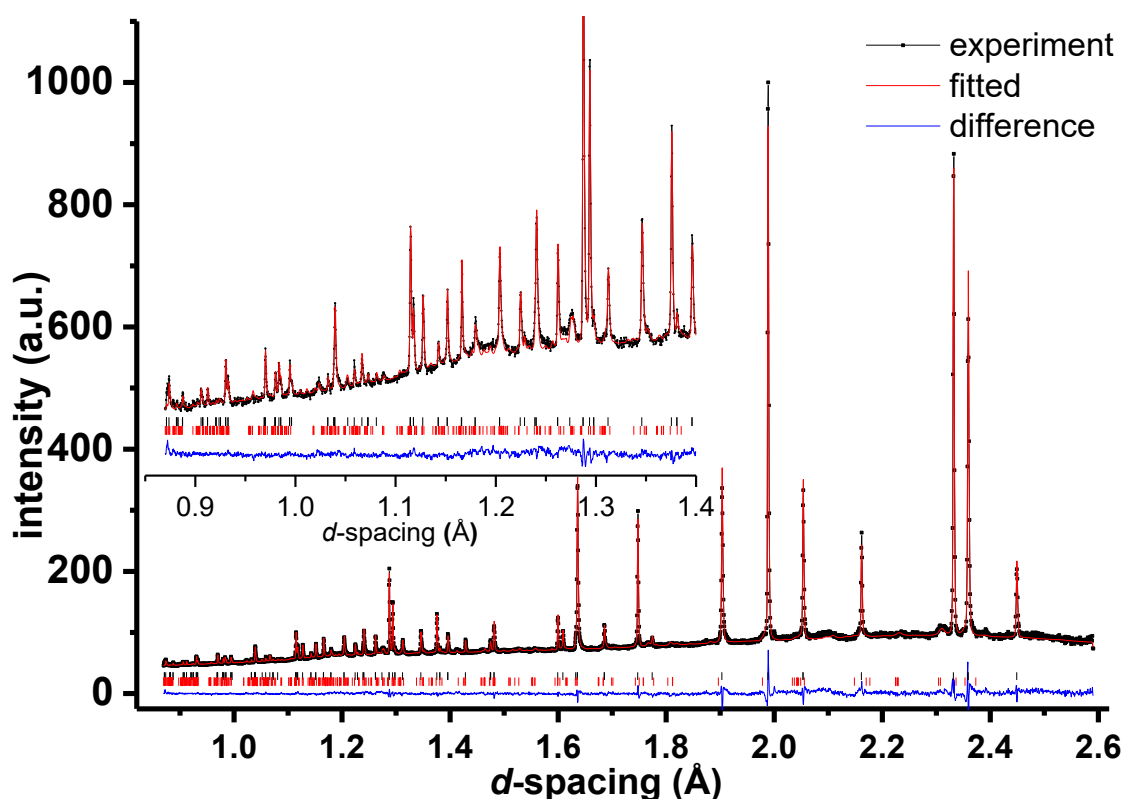


Figure 5-16: Rietveld refinement of neutron powder scattering data of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ at 800 °C, using the superspace group $I4_1/a(\alpha, \beta, 0)00(-\beta, \alpha, 0)00$. Good fitting with $R_p = 0.022$ and $R_{wp} = 0.023$ were obtained. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black and red vertical lines mark the theoretical peak position of the parent structure and the modulated peaks respectively. The inset shows the enlarged pattern in the 0.84 Å to 1.40 Å range.

When refining the occupational magnitude of W/Nb, the occupational wave magnitude which used that of the $x = 0.12$ composition as an input. The refinement showed little improvement of the fitting (R_p change from 0.022 to 0.0217), while a large negative occupancy (< -0.8) in the t - u section was observed, making the model physically unrealistic. The occupational modulation therefore was fixed at 0.2 and -0.2 respectively for Nb and W for the refinement of entire neutron scattering dataset for the $x = 0.16$ composition. Data with higher quality

(preferably single crystal diffraction data), is required to allow for higher order modulation waves to provide an accurate description of the cation ordering.

5.4.3 Locating Oxygen interstitial in $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$

The role of the interstitial oxygen, in the conduction process in the hyperstoichiometric scheelite related compositions, has been highlighted with previous experimental [87,276] and DFT atomic simulation [226] reports. Correlated interstitialcy diffusion has been proposed to explain the long range oxygen transport in the hyperstoichiometric scheelite compounds [226]. The diffusion process starts with an interstitial oxygen knocking a lattice oxygen into a neighbouring interstitial site, followed by the removal of another lattice oxygen into interstitial site by the newly created interstitial oxygen, and thus continue the diffusion process [226]. After the modulated structure of the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ has been attempted (showcased in the previous section 5.4.2), refinement of the interstitial position is carried out based on the neutron scattering data of the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition gathered at 500 °C (the CIF file is reported in the supplemental information). The composition was selected due to its nominal interstitial concentration being higher than other W doped phases, and the temperature is of interest for SOFC electrolyte application.

Determining the interstitial positions however is no trivial task, and the accuracy of the results is often restricted by the high dynamic mobility and the low concentration of the interstitial oxygen [276]. Consequently, the reported interstitial positions in the hyperstoichiometric scheelite structures are scattered. For instance, when studying the modulated CeNbO_{4+d} phases, Thompson et al. predicted the empty eight-coordinate fluorite site as the interstitial positioned, which would result in minimal disturbance to the neighbouring ions [113]. The position reported by Thompson et al. is equivalent to the (0, 0.25, 0.375) position with the current cell choice (red spheres in Figure 5-17). Similar positions was predicted by Takai and co-workers [276] who, using neutron diffraction data, predicted that the interstitial preferentially located at the 8e Wyckoff position (0, 0.25, 0.325) in La doped PbWO_4 . The authors pointed out that the refined occupancy is only 1/3 of the expected value, and suggested that the interstitial could occupy other 8e positions by varying the *z* coordinate (along the arrow direction shown in Figure 5-17), leading to a diffused distribution of the occupancy. The implication of structural modulation on the interstitial position is however overlooked in these reports [226]. It was not until most recently that Pramana et al. showed that, instead of treating the interstitial position as an additional

crystallography position in the parent structure, an expanded supercell which includes the interstitials as lattice oxygen gave a more accurate description of the modulated $\text{CeNbO}_{4.25}$ structure [59]. According to Pramana, the difference between the lattice oxygen and “interstitial” is obscure; all the oxygen ions form an ordered supercell, which are displaced from their positions in the parent structure, to accommodate the ordered $\text{Ce}^{3+}/\text{Ce}^{4+}$ ions (as shown in Figure 2-5 [59]). Indeed, an ordered anion network is often observed to accompany the ordered cations sublattice in the occupational modulated scheelite phases [59,83,116,277].

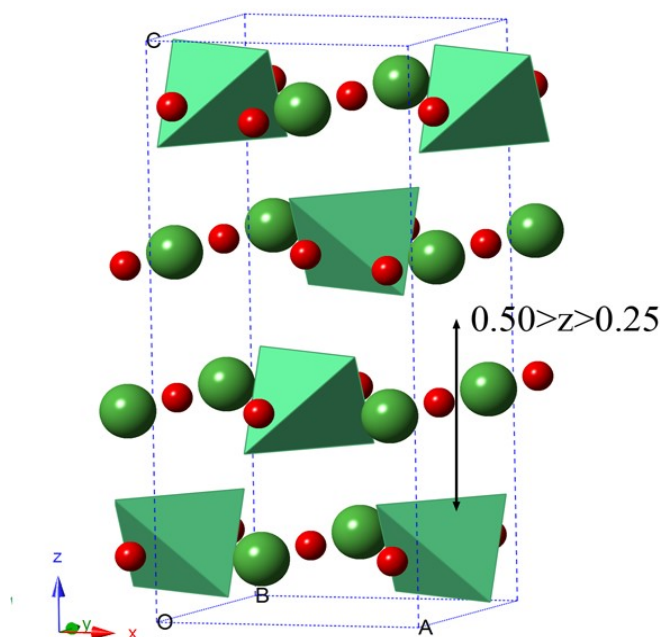


Figure 5-17: Proposed interstitial (shown as red spheres) positions in $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ based on ref. [113] and [276]. The green sphere represents La^{3+} ion whereas the Nb is shown in its polyhedral form. The interstitial is assumed to locate along $(0, 0.25, z)$ and the occupancy at various z position (in the range $0.26 < z < 0.48$, shown by the black arrow) was refined and reported in Figure 5-18. The z range was selected to ensure a minimum 1.5 Å separation from neighbouring ions.

To pinpoint the interstitial position in the hyperstoichiometric $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases, the methodology proposed in ref. [276] was followed to investigate the interstitial site in $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$. The interstitials were assumed to locate at the 8e position $(0, 0.25, z)$, as other positions are either occupied (4a and 4b were occupied by Nb and La respectively) or too close to the cation (the 8c and 8d for instance). The isotropic displacement U_{iso} , of the proposed interstitial site, which is highly correlated with the site occupancy [205], was fixed at 0.04 Å^2 based on the refined U_{iso} of the lattice oxygen (reported in Table 5-4). The z position was varied from 0.26 to 0.48 to keep a minimum distance of 1.5 Å away from neighbouring ions (Figure 5-18), and the occupancy at each specific position was refined. Constraint on the oxygen position was then released and the interstitials were allowed to move freely within the lattice. The occupancy and the position were simultaneously refined,

and the refinement converged to the (0.274, 0.104, 0.223) position. However the refinement returned a large negative occupancy which indicates that the current result is a false local minimum and should be discarded.

The refined occupancy (reported in Figure 5-18) is much lower than the expected full occupancy (0.02 which would correspond to 0.08 interstitial oxygen ion per unit cell). Indeed, the refined occupancy is barely above 0 with larger uncertainty at most z positions. It is therefore speculated that unlike the apatite [55], melilite [80] and hyperstoichiometric La doped PbWO_4 [278], in which interstitial oxygen is localized at specific crystallographic positions, the interstitial oxygen assumes a rather diffuse distribution in the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ system at 500 °C.

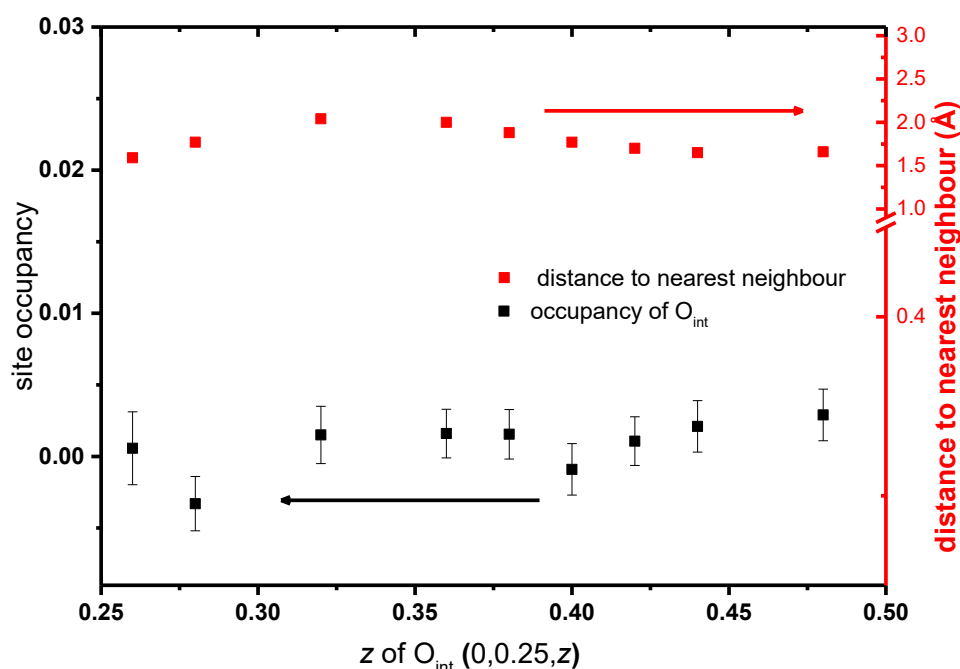


Figure 5-18: Refined oxygen occupancy in $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ at 500 °C, as a function of proposed coordination (0, 0.25, z). The full site occupancy is 0.04 at the site which corresponds to a nominal 0.08 interstitial content per formula unit. The distance to the nearest neighbour is also plotted, the selected interstitial sites is at least 1.5 Å away from any neighbour.

One of the explanations for this observation is that the interstitials have good mobility at the test temperature (500 °C), and thus delocalizes along the conducting pathway leading to a reduced occupancy at any particular crystallographic site. Alternatively, the interstitial might be modulated due to the cation ordering, as the ordering of the anion network is expected from the cation ordering [116,242,279]. In the latter case, the difference between the interstitial sites and the normal sites becomes minor as both sites contribute to accommodating the varying cation coordination environment. The argument for modulated

interstitial sites has been made in the structural solution of $\text{CeNbO}_{4.25}$, which requires an expanded supercell with nominal composition $\text{Ce}_{12}\text{Nb}_{12}\text{O}_{51}$, to describe [59]. The presence of a modulated interstitial site would dilute the local occupancy due to its displacive movement. Current prediction of a diffuse distribution of the interstitial content is nevertheless not inconsistent with the literature reports: most of the experimental [276] and simulation [226] reports to date focus on the structure at room temperature whereas the mobility of oxygen is expected to increase with increasing sample temperature. It is also recognized that charge compensation with A and B site vacancy is also possible which would further reduce the interstitial content in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ [122]. Further experimental and simulation study however is required to thoroughly investigate the interstitial oxygen distribution in the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ structure.

5.4.4 Summary of the *in situ* neutron scattering study

The phase transition of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ was investigated using high resolution *in situ* neutron scattering. The high temperature modulated tetragonal phase predicted by HTXRD was confirmed. A structural model using superspace group $I4_1/a(\alpha, \beta, 0)00(-\beta, \alpha, 0)00$ was proposed to resolve the structure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ in the 500 °C to 650 °C range. Further increasing the temperature to 800 °C saw an unmodulated tetragonal phase, which was refined with the parent $I4_1/a$ space group. Despite the similarity in the chemical composition, the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ phase maintained the modulated structure within the experimental temperature range (up to 800 °C). Refinement of the interstitial oxygen position in the $x = 0.16$ composition was attempted and the results suggest a non-localized distribution of interstitial oxygen, which is similar to that observed in the modulated $\text{CeNbO}_{4.25}$ phase [59].

5.5 Transport properties of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$

In the previous section, the phase transition of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series has been examined in detail. The transport properties of this promising electrolyte material are investigated using electrochemical impedance spectroscopy (EIS) and ^{18}O isotopic exchange in the following section. The nature of the charge carrier and the conducting mechanism is discussed based on the transport properties measurements.

5.5.1 Impedance spectroscopy measurements

The electrical properties of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series, as well as the LaNbO_4 reference, were investigated using impedance spectroscopy. A typical experiment probed the frequency range from 1 MHz to 1 Hz with 30 data points per decade. At each frequency, 5 s acquisition time was used to ensure good data quality. The impedance spectrum of $\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$ measured at 450 °C is shown in Figure 5-19. A model, consisted of two constant phase elements (CPEs) (shown in the inset of Figure 5-19), was used to describe the contribution from grain boundary and grain bulk of the sample respectively.

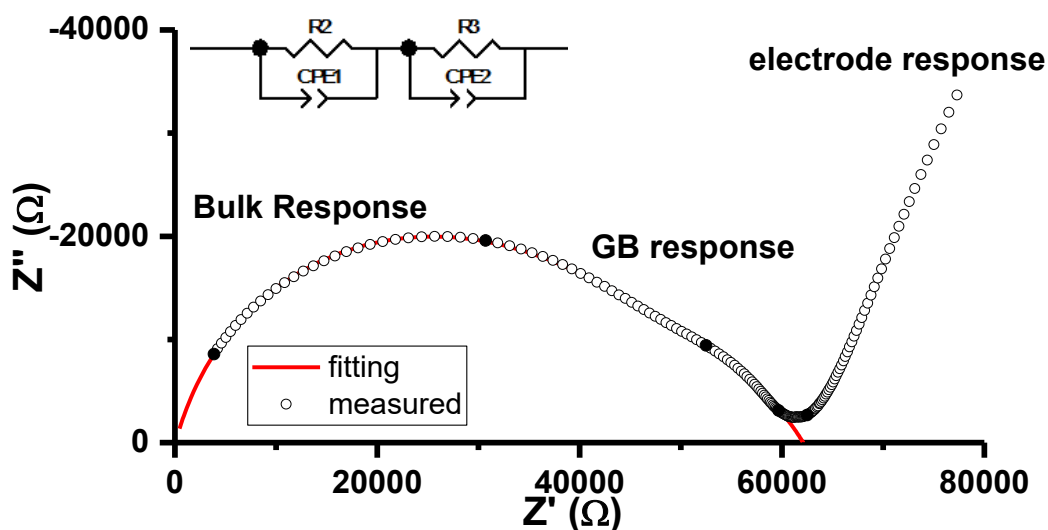


Figure 5-19: A typical impedance spectrum: a $\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$ sample measured at 450 °C; the hollow circles show the measured value whereas the solid circles marks the response, from left to right, at 10^6 Hz, 10^5 Hz and 10^4 Hz respectively; the red line shows the fitting results using the model in the inset.

The W substitution has significant impact on the total conductivity of the sample (reported in Figure 5-20); with only 1 at% W dopant, the conductivity of $\text{LaNb}_{0.99}\text{W}_{0.01}\text{O}_{4+d}$ sees an increase of 1.5 orders of magnitude at 800 °C comparing with the parent phase. It is interesting to note that the effect of the dopant is much less prominent at lower temperature, as the conductivity of $\text{LaNb}_{0.99}\text{W}_{0.01}\text{O}_{4+d}$ is very close to LaNbO_4 below 550 °C. The

similarity of the conductivity suggests the interstitials, the assumed charge carriers, are immobile at low temperature. A change in the slope of the conductivity was observed in the LaNbO_4 at $\sim 530^\circ\text{C}$, correlating well with the phase transition temperature (490°C reported in Table 5-1). Similar change in activation is also observed in the $\text{LaNb}_{0.99}\text{W}_{0.01}\text{O}_{4+d}$ sample, though at a higher temperature ($\sim 750^\circ\text{C}$).

The modulated phases have different conducting behaviours. The total conductivity of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series increases with dopant level and reached its maximum with 12 at% dopant level. The $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition has a total conductivity of $8 \times 10^{-3} \text{ S cm}^{-1}$ at 863°C under lab air, comparable with the value reported for other fergusonite related systems [86,87].

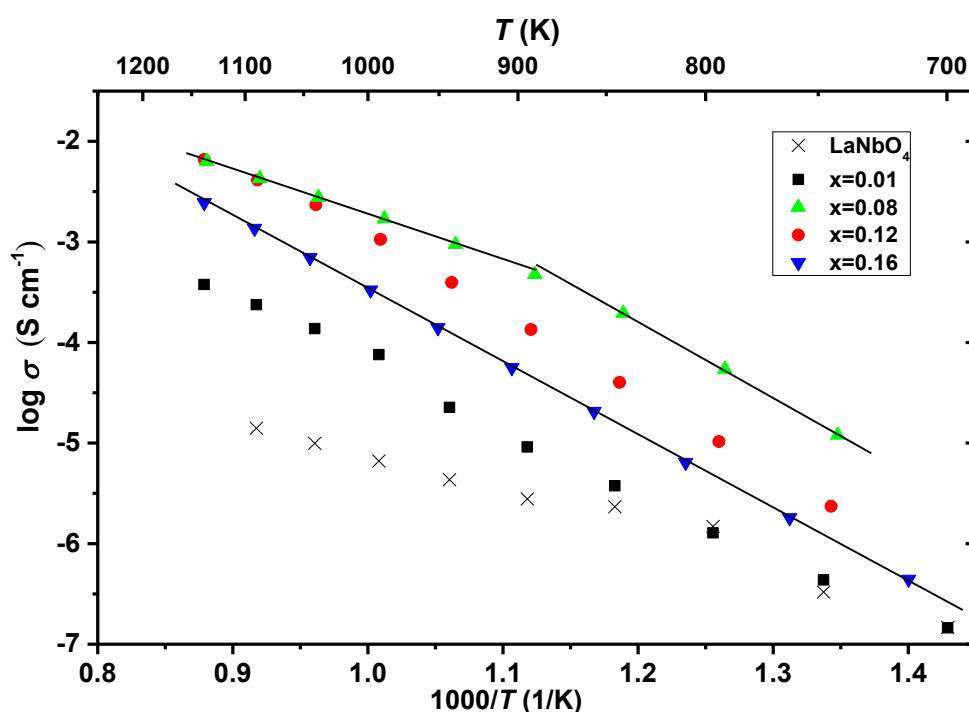


Figure 5-20: Total conductivity of $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases in comparison with the LaNbO_4 reference measured under static air. The solid lines highlight the different behaviour between $\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ compositions: the former has two distinctive regions with different E_a whereas the latter has a fixed E_a .

The overall conductivity of $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition is the lowest among the modulated phases throughout the temperature range (400°C to 800°C). This observation is particularly interesting considering the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition is expected to have the highest oxygen interstitial content, the assumed charge carriers. Indeed, the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition behaved quite differently comparing with other phase; throughout the temperature range: $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ had unique activation energy for conduction (1.43 eV) whereas two distinctive regions were identified for other compositions

(E_a summarized in Table 5-6). At the lower temperature region, the activation energy for the modulated phases is similar, disregarding the dopant concentration. The observation suggests that, rather than the dopant level, it is the structural modulation that decides the conduction properties in the low temperature region. The lack of variation in E_a for the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition is consistent with the structure analysis, which indicates that the composition remains to be modulated from room temperature to 800 °C.

Table 5-6: Summary of the activation energy of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series.

Composition	E_a at low T (eV)	E_a at high T (eV)
$\text{LaNb}_{0.99}\text{W}_{0.01}\text{O}_{4+d}$	1.21 ± 0.03	1.05 ± 0.01
$\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4+d}$	1.58 ± 0.01	0.89 ± 0.05
$\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$	1.49 ± 0.02	1.29 ± 0.03
$\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$	1.43 ± 0.02	

It is also noted that the activation energy obtained for the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases is higher than that of the hyperstoichiometric scheelite phases reported by Esaka et al. (typically about than 0.8 eV). One of the possible explanations is the ordering of the anion network in the low temperature structure. Periodic displacive movement of the lattice oxygen is an essential part of the structure solution to modulated scheelite phases [106,107]. Indeed refinements of the neutron scattering data suggest that the anion sublattice in the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system is modulated up to 650 °C in $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and to 800 °C in $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ (reported in section 5.4). Additional activation energy is required to overcome the ordered oxygen lattice to facilitate oxygen diffusion [87,121]. A reduction in activation energy for oxide ion conductor has been reported in the LAMOX phases [280,281], and $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ perovskite [39,40], when transforming from the low temperature ordered phase to the disordered high temperature structure. It is worth noting that the ordered oxygen network might enhance *anisotropic* oxygen transport via the creation of a low energy pathway network, along which significant ionic conduction is possible [83,282]. At this stage, no conduction path was identified in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases, as no residual nucleus density that forms a conducting pathway, was observed in the neutron scattering data.

5.5.2 ^{18}O Tracer Diffusivity Measurements

The total conductivity obtained using EIS contains contribution from different charge carriers (i.e. holes, electrons and ions). To identify the major charge carrier and the conducting mechanism in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$, ^{18}O tracer diffusivity measurements (introduced in section 3.7.2) were conducted for the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition, which has the highest total conductivity amongst the modulated phases.

Preliminary results shows very low surface ^{18}O concentration (typically $C'(0,t) < 1\%$ after exchange at $700\text{ }^\circ\text{C}$ for 3600 s), an indication of lack of electronic conductivity. The low concentration hinders an accurate determination of the tracer diffusivity D^* , as surface concentration at least an order of magnitude higher than the natural abundance (0.2% [283]) is considered necessary to obtain an accurate solution to the Fick's diffusion equation [284]. To resolve this issue, the polished samples were sputter coated with Pt before the exchange experiment. The surface exchange coefficient, which in this case represents the exchange efficiency of the Pt coating instead of the sample surface, has little importance for the current study and is therefore not reported. The diffusion profile was obtained using a secondary ion mass spectrometry (SIMS) using the line scan technique (Figure 3-14). The resultant ^{18}O concentration profile was fitted to Crank's solution of diffusion in a semi-infinite medium (Eqn. 3.24) [219] to extract D^* . The diffusion profile of a $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ sample exchanged at $750\text{ }^\circ\text{C}$ for 1320 s and its corresponding fitting to the Crank's solution is shown in Figure 5-21. High surface isotopic concentration ($C'(0,t) = 30\%$) was obtained with the Pt coating and a good fitting with low residual was achieved.

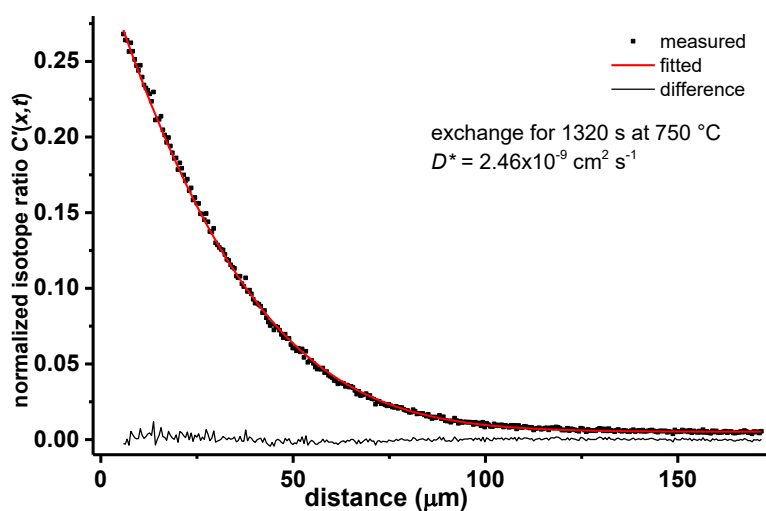


Figure 5-21: ^{18}O tracer diffusion profile of a $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ sample exchanged at $750\text{ }^\circ\text{C}$ for 1320 s . The fitting and the difference profile are shown as red and black lines, respectively. Good fitting to the Crank's solution, with low residual was achieved.

The Arrhenius plot of oxygen tracer diffusivity of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition is shown in Figure 5-22, along with CeNbO_{4+d} and YSZ references. Despite the scattered data, probably due to sample variance, it is evident that CeNbO_{4+d} has superior diffusivity at lower temperature comparing with YSZ benchmark. The low temperature diffusivity of CeNbO_{4+d} is unexpectedly high considering the low temperature phases, namely the hyperstoichiometric $\text{CeNbO}_{4.25}$ and $\text{CeNbO}_{4.08}$ are modulated [58,225], highlighting the potential of the CeNbO_{4+d} structural template.

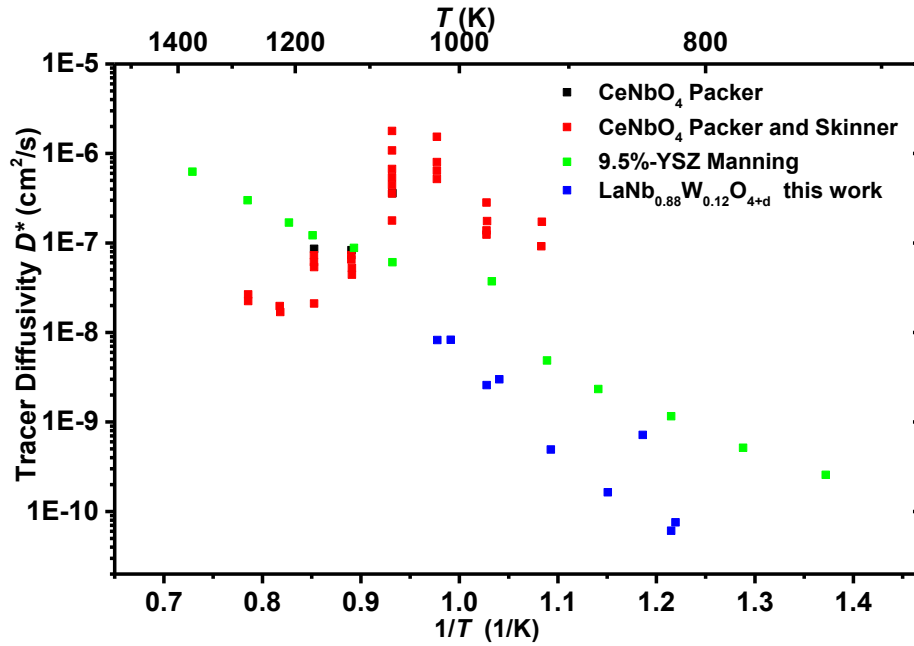


Figure 5-22: Arrhenius plot of the oxygen tracer diffusivity of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ in comparison with the diffusivity of CeNbO_{4+d} [58,225] and YSZ [285].

Despite having the same parent structure, the diffusivity of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase is about 2 orders of magnitude lower than that of CeNbO_{4+d} in the 600 °C to 700 °C range (Figure 5-22). To understand the difference in diffusivity, thus oxygen ion conductivity, between various hyperstoichiometric fergusonite, the conducting mechanism in $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ is first studied using the Nernst-Einstein relation (Eqn. 5.3) which establishes the connection between the ionic conductivity and the self-diffusivity of the charge carrier:

$$\sigma_{ion} = \frac{z_{ion}^2 e^2 C D}{kT} \quad \text{Eqn. 5.3}$$

in which z_{ion} is the number of charge on the oxygen ion, C is the charge carrier concentration, D is the self-diffusivity, which describes the average mobility of the charger carrier in the structure; and the other parameters have their usual meaning.

Assuming oxygen ions are the major charge carriers in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system, self-diffusivity is expressed as follows:

$$D[O] = D_{\text{int}} [O_i''] + D_{\text{lattice}} [O_{\text{lattice}}] \quad \text{Eqn. 5.4}$$

in which D_{int} and D_{lattice} describe the diffusivity of the lattice oxygen and interstitials respectively; whereas $[O_i'']$ and $[O_{\text{lattice}}]$ are their respective concentration. The self-diffusivity D and the tracer diffusivity D^* , which is measured using the isotopic exchange method (Figure 5-22), is related by a correlation factor f (Eqn. 5.5). The correlation factor describes the interaction between subsequent jumps and equals to unity if the charge carriers behave like free gas and have no interaction. The correlation factor depends on the structure as well as the charge carrier concentration, and is often considered to be unity for interstitial diffusion mechanism [217]. The correlation factor is therefore treated as 1 in the current discussion.

$$D^* = fD_{\text{self}} \quad \text{Eqn. 5.5}$$

If the material conducts *via* the interstitial mechanism, the interstitials constantly jump between different interstitial sites whereas the lattice oxygen is immobile, resulting in $D_{\text{int}} \gg D_{\text{lattice}}$, and the charge carrier concentration C equals to the oxygen interstitial content (Eqn. 5.6):

$$C = [O_i''] \quad \text{Eqn. 5.6}$$

In the scenario where the mobility of the interstitials is comparable to that of the lattice oxygen, all the oxygen are considered as charge carrier, leading to the expression in Eqn. 5.7 [217]. Such scenario is similar to that of the interstitialcy mechanism where cooperative movement of an interstitial and at least one lattice oxygen is required [217].

$$C = [O] \quad \text{Eqn. 5.7}$$

Under these two different assumptions, the $D_{\sigma\text{-lattice}}$ and $D_{\sigma\text{-int}}$ calculated using Eqn. 5.3, using the charge carrier concentration presented in Eqn. 5.6 and Eqn. 5.7, is plotted in Figure 5-23.

$$D_{\sigma} = \frac{\sigma_{\text{DC}} k_b T}{q^2 C} \quad \text{Eqn. 5.8}$$

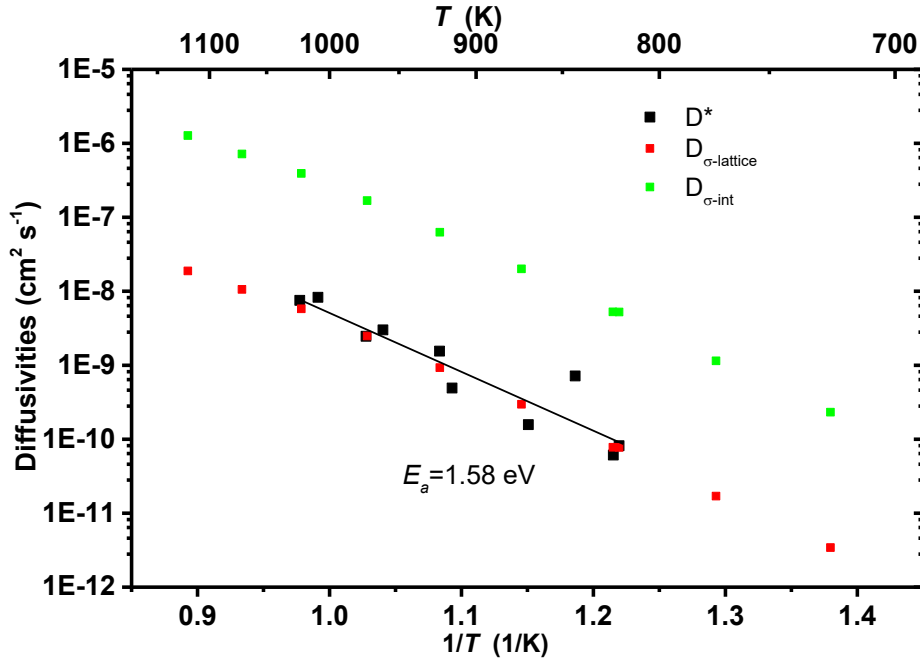


Figure 5-23: Arrhenius plot shows the comparison between D^* and D_σ in $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ in the 500°C to 750 °C range. D_σ is estimated using two models: $D_{\sigma\text{-lattice}}$ was calculated assuming all the oxygen ions in the structure are mobile and $D_{\sigma\text{-int}}$, assuming only the interstitial are mobile. The second model fits better with the tracer diffusivity D^* . The black line shows the activation energy for diffusion, $E_a = 1.58$ eV which is in excellent agreement with the activation for conduction reported in Table 5-6.

The measured tracer diffusivity values D^* is more than two orders magnitude higher than the $D_{\sigma\text{-int}}$, whereas excellent agreement between D^* and $D_{\sigma\text{-lattice}}$ was obtained. The results indicate that the long range diffusion is attained by a cooperative movement of the oxygen which is similar to that of the interstitialcy mechanism. The activation energy for diffusion in this temperature range is 1.58 eV, which is in excellent agreement with the activation energy of total conductivity (1.49 eV, reported in Table 5-6), confirming that oxygen ions are the major charge carriers in the system. The result is consistent with previous simulation which suggests a low interstitial formation energy in the hyperstoichiometric fergusonite phases [226,286] and is the first piece of experimental evidence that supports the interstitialcy transport mechanism in the hyperstoichiometric rare earth niobates system predicted using DFT [226]. The above analysis also indicates that all the lattice oxygen has similar mobility therefore no direct correlation between the interstitial concentration and the overall conductivity is expected, which partially justify the low conductivity of the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition (reported in Figure 5-20), which was assumed to have the highest charge carrier concentration.

It should be stressed however, increased interstitial content is probably still beneficial due to its effect in introducing higher degrees of polyhedra distortion, similar to that observed in the

LAMOX based fast ion conductor [74]. The modulated CeNbO_{4+d} phases are expected to maintain high interstitial content (0.25 interstitial per formula unit comparing with 0.06 in $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$) between 657 °C and 775 °C [287], a temperature range coincides with the maximum diffusivity [58]. The insertion of the interstitials in CeNbO_{4+d} leads to extended NbO coordination environment and a broadened Nb-O bond length distribution in the 2Å-3Å range (Figure 5-24b), which corresponds to the bonds with the next nearest neighbours [249]. Variations in Nb/W-O bond length was also observed in the modulated $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ at 600 °C, though limited to a narrower distribution (Figure 5-24c). The difference in the bond length distribution is closely related to the local structure: $\text{CeNbO}_{4.25}$ has sinusoidal bridging oxygen that facilitates oxygen transport along the *b* axis (Figure 2-5 reported in section 2.2.2) [59,136] whereas the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase has lower degree of connectivity along this direction, which might be responsible for the lowered diffusivity reported in Figure 5-22.

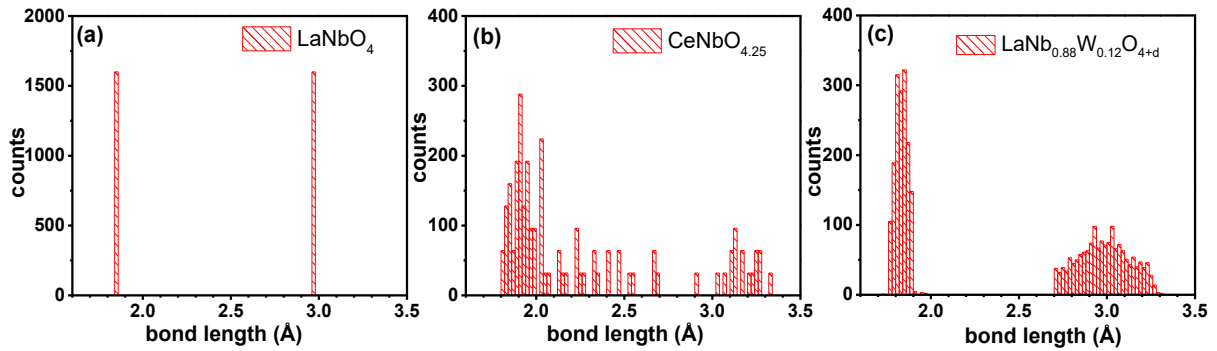


Figure 5-24: Bond length distribution of Nb(W)-O in (a) undoped LaNbO_4 (b) $\text{CeNbO}_{4.25}$ and (c) $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$. Higher degree of connectivity in the 2Å-3Å range was found for the two modulated structure as shown in (b) and (c), whereas the coordination of Nb and O in LaNbO_4 is segmented into two unique values within the first two nearest-neighbours. Comparing with $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$, a wider variation in bond length was observed in $\text{CeNbO}_{4.25}$, probably related to its higher interstitial content. The bond length in (a) was obtained from a $10 \times 10 \times 1$ supercell in LaNbO_4 based on the refined neutron data reported in the appendix. The $\text{CeNbO}_{4.25}$ bond length was generated based on the structure solution in [59]. The $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ bond length was a $10 \times 10 \times 1$ commensurate approximation of the 600 °C modulated structure reported in Figure 5-12.

It is also interesting to notice the difference in conductivity between $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$, despite their similarity in composition. The modulated $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ phase is stable up to 800 °C which might reflect a strong bonding between the W dopant and O, thus a lowered jump probability for the oxygen ions [288]. The average structure model alone seems insufficient to explain the difference in performance between the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ compositions and a detailed examination of the local structure might be required [251,289].

5.6 Structure and conductivity of $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$

In the previous section, it was concluded that the extrinsic defect concentration, namely the interstitial content, has little impact on the overall conductivity in the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases. Other criteria that control oxygen ion conductors such as the size of the lattice, the available free volume V_f [288] and the dimension of the conducting pathway [288,290] need to be examined to identify the factor that controls the ionic conductivity in hyperstoichiometric LaNbO_4 phases. In the following section, the effect of A site cation on the conduction of hyperstoichiometric LaNbO_4 is investigated by studying the structure and conductivity of $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ compounds. Y dopant was chosen as YNbO_4 has the smallest A site to oxygen ratio (r_A/r_x), amongst the ABO_4 compounds with the fergusonite structure [92]; whereas W dopant is selected to introduce oxygen interstitial. The structural evolution and the conductivity of $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ compositions ($x = 0.1, 0.2, 0.3, 0.5, 0.7$ and 1) are studied, in an attempt to further explore the CeNbO_{4+d} structural template.

5.6.1 Structural evolution of $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$

The room temperature XRD data of the $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ series are shown in Figure 5-25, and the refined lattice parameters are reported in Table 5-7. Refinement of the XRD patterns was conducted using the fergusonite parent structure (space group 15, $I2/c$). For the $x = 0.1$ and 0.2 compositions, additional reflections (highlighted by the asterisk in Figure 5-25) and a shoulder at the parent (031) (-121) peaks was observed at room temperature, indicating the formation of secondary phases. Indeed, EDX microanalysis reveals a W and La enriched phase with the $\text{La}:\text{W} \approx 2:1$ (inset in Figure 5-26b) in the $x = 0.1$ and $x = 0.2$ composition. Search of the ICSD database returns various LaO-WO_3 compounds and the La_2WO_6 reported in [291] provided a good fit with the X-ray data using Le Bail refinement. The intensity of the 2nd phase reduces with increasing temperature, and a single monoclinic phase was obtained after heating the sample to above 300°C (Appendix c). It is interesting to note that the structure transforms from the modulated phase to an unmodulated structure with minimal Y (10 at%) doping at the La site. Overall, increasing in the Y dopant level leads to a reduction in the cell volume from $333.66 \text{ \AA}^3$ for $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ to $294.06 \text{ \AA}^3$ for $\text{YNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$. Meanwhile the β angle increases from 91.539° to 93.890° (Table 5-7). The change in the lattice parameters and cell volume is consistent with the smaller ionic radius of Y^{3+} ($1.02 \text{ \AA}$ for Y^{3+} comparing with 1.16 for La^{3+} with VIII coordination[243]), which stabilizes the monoclinic phase [292,293].

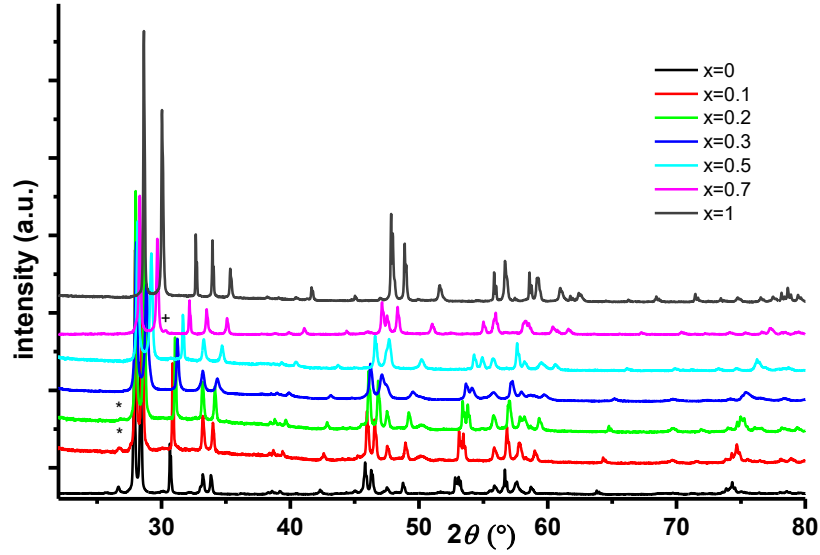


Figure 5-25: Room temperature XRD patterns of various $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ compositions. The “*” marks the impurity La_2WO_6 phase in $x = 0.1$ and $x = 0.2$, whereas the “+” marks another impurity of unknown structure in the $x = 0.7$ composition.

Table 5-7: Refined lattice parameters of the $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$.

x	a (Å)	b (Å)	c (Å)	θ (°)	V (Å ³)
0	5.413(2)	11.643(1)	5.296(1)	91.539(2)	333.66(3)
10	5.392(1)	11.581(1)	5.275(1)	91.555(4)	329.42(2)
20	5.396(1)	11.507(1)	5.249(2)	91.873(1)	325.74(2)
30	5.397(2)	11.438(2)	5.224(1)	92.263(1)	322.21(1)
50	5.386(1)	11.287(3)	5.173(2)	92.967(5)	314.09(2)
70	5.357(2)	11.121(3)	5.123(2)	93.792(2)	304.51(2)
100	5.288(1)	10.957(1)	5.087(1)	93.890(2)	294.06(2)

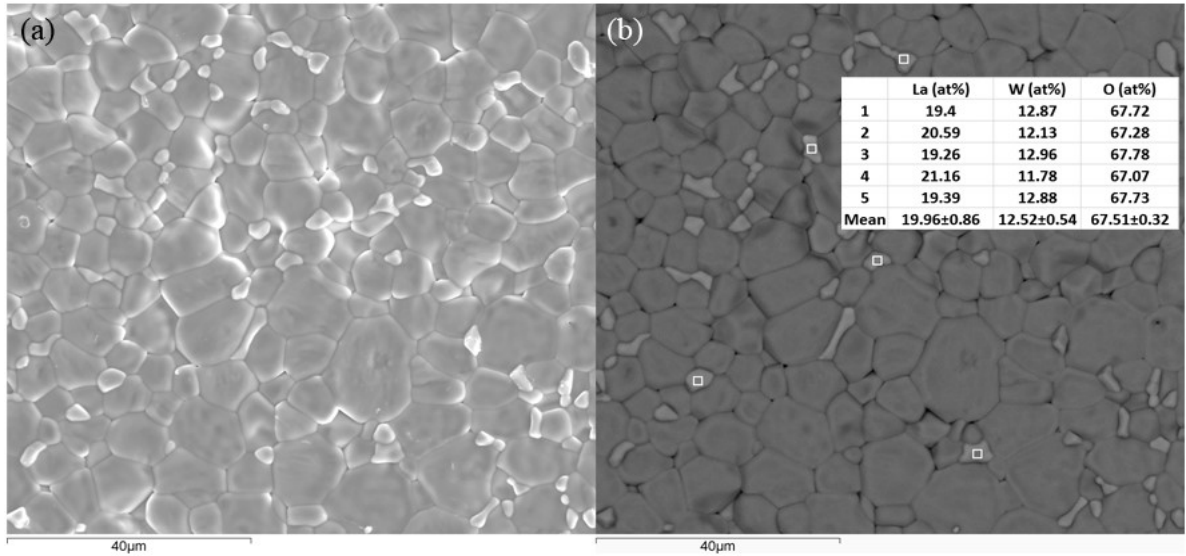


Figure 5-26: (a) secondary electron (SE) and (b) back scattered electron (BSE) image of the as-sintered surface of the $x = 0.1$ composition. Impurity phase that segregated towards triple point at the grain was observed in the BSE image. The chemical composition of the impurity (position of the spectrum shown highlighted as the white squares) was characterized using EDX and the results indicate the impurity is La and W enriched with molar ratio $\text{La}:\text{W} \approx 2:1$.

Increasing the dopant level sees the stabilization of the fergusonite structure; the $x = 0.3$ and $x = 0.5$ phases in the $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ series were successfully refined using the $I2/c$ parent structure and no secondary phase was observed within the detection limit of the instrument. Further increasing the Y dopant level to $x = 0.7$ leads to another impurity (plus mark in Figure 5-25). The impurity phase is W enriched although its exact composition was unclear from the EDX analysis and consequently no match was found from the structural database that fits with the current data. Increasing the sample temperature to $550\text{ }^\circ\text{C}$ sees the major phase transition to the tetragonal structure however the impurity still exists after heating the sample up to $900\text{ }^\circ\text{C}$. The phase diagram of the $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ compositions is therefore presented in Figure 5-27, whereas the corresponding crystal structure and lattice parameters are summarized in Appendix c.

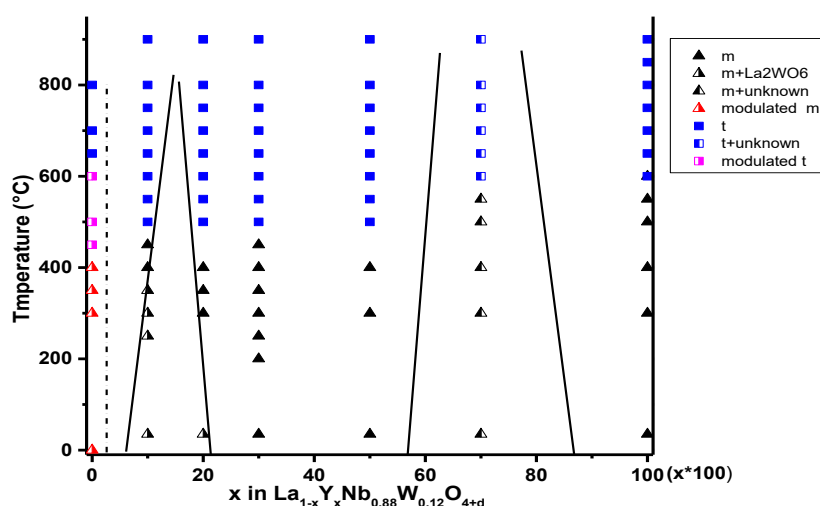


Figure 5-27: Proposed phase diagram of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system, showing the phase transition behaviour between the monoclinic to tetragonal transition as well as the modulated to unmodulated transition; the lines separating different phases are just guidance for the eyes.

5.6.2 Conductivity of $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$

Considering the low fraction of the impurity phase (as shown in Figure 5-26 and the low intensity in XRD pattern), the electrochemical performance of the samples is dominated by the Y, W co-doped LaNbO_4 , therefore, the total conductivity of the $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ series was measured using impedance spectroscopy and the results are reported in Figure 5-28. The $\text{YNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ pellet was not dense enough (less than 90% of the theoretical density) therefore the result is not reported. Overall, a clear dependence of total conductivity on Y concentration was observed; continuously decrease in conductivity with increasing Y substitution is evident. Amongst the Y doped compositions, $\text{La}_{0.9}\text{Y}_{0.1}\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ has the highest conductivity reaching $3 \times 10^{-3} \text{ S cm}^{-1}$ at $800\text{ }^\circ\text{C}$. In fact, both the $x = 0.1$ and $x = 0.2$

compounds have an overall conductivity similar to $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$, although at temperature above 560 °C, the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition has higher conductivity. Further increasing the Y concentration sees a sharp drop of total conductivity; the total conductivity for the $x = 0.7$ composition is approximately $1 \times 10^{-4} \text{ S cm}^{-1}$ at 800 °C, more than one order of magnitude lower than that of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ benchmark. The correlation between cation size and conductivity is similar to that reported in PbWO_4 and CaWO_4 , in which highest conductivity was reported with the largest La^{3+} dopant [86,87]. It is suggested, despite closer distance to the nearby neighbour, smaller cation leads to insufficient space for the oxygen to pass through the diffusion barrier, thus lower the overall conductivity [87].

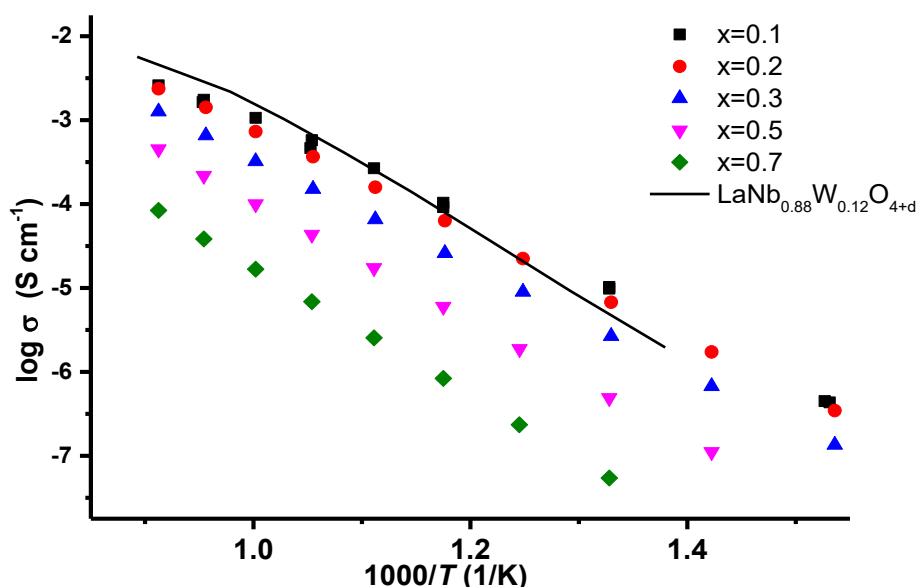


Figure 5-28: Arrhenius plot shows the conductivity of various $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ compositions. Overall, the conductivity of the solid solution decreases with increasing Y content.

5.7 Chapter summary

In this chapter, the structure evolution and transport properties of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series at elevated temperature (from room temperature up to 800 °C) have been investigated. Using *in situ* diffraction techniques and thermal analysis, a sequence of transformation in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ between a modulated monoclinic phase, a modulated tetragonal phase and an unmodulated tetragonal phase, which was overlooked in the literature, now has been revealed. Landau theory has been successfully applied to predict the transition temperature of the parent structure and a phase diagram of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series is proposed based on the current study. Quenching of the modulated structure unveiled a rapid phase transition

dynamics, although it is still unclear at this stage how the ordered cation network facilitates the rapid phase transition. *In situ* neutron scattering experiments were conducted to investigate the structural evolution of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ compositions in detail. Modulation peaks were observed and the structure of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition below 650 °C was successfully refined using a $I4_1/a(\alpha,\beta,0)00(-\beta,\alpha,0)00$ superspace group. The $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition, on the other hand, maintains its modulated structure till 800 °C. Attempts were made to pinpoint the position of the interstitial oxygen in the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition at 500 °C, although the refinement suggests a non-localized distribution of the interstitial oxygen. It is possible that an extended structural model that incorporates interstitials as lattice ions is required to fully describe the structure.

Total conductivity was measured using impedance spectroscopy and a significant improvement in total conductivity was achieved with W dopant. Among all the W doped compositions, $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase was reported to have the highest conductivity of $8 \times 10^{-3} \text{ S cm}^{-1}$ at 863 °C, comparable to other fergusonite systems. Tracer-diffusivity using ^{18}O was conducted and the diffusivity was measured to be $2.46 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 750 °C in $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$. Good agreement of the activation energy between the impedance and diffusivity measurements confirm that the major charge carrier is oxygen in the hyperstoichiometric $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system. The measurements also produced the first piece of experimental evidence for the interstitialcy diffusion mechanism in hyperstoichiometric rare earth niobates.

To further exploit the $\text{CeNbO}_{4.25}$ structural template, and to investigate the effect of size of A site cation on the structure and conductivity in niobates, $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ ($x = 0, 0.1, 0.2, 0.3, 0.5, 0.7$ and 1) phases were prepared and characterized. Overall, the total conductivity of the Y and W co-doped LaNbO_4 phases decreases with increasing Y content. The conductivity of $\text{La}_{0.3}\text{Y}_{0.7}\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ is approximately $1 \times 10^{-4} \text{ S cm}^{-1}$ at 800 °C, more than one order magnitude lower than the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$. Larger cation which promises an open structure seems beneficial for the interstitial transport.

Chapter 6. Surface chemistry of LaNbO_4 based proton conductors

6.1 Introduction

In the previous chapters, the modulated structure, phase evolution and the transport properties of the hyperstoichiometric $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases have been investigated in detail. This chapter therefore proceeds to investigating the surface chemistry, which, as shown in section 2.4.2, determines the surface exchange and transport process in electroceramics. Preliminary characterization (reported in Appendix d) of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phase revealed no surface dopant segregation. Therefore, this chapter will focus on the surface chemistry of acceptor doped LaNbO_4 which exhibits high protonic mobility and excellent chemical stability in wet and CO_2 containing environment [93]. Proton conductivity of approximately $10^{-3} \text{ S cm}^{-1}$ at $\sim 950^\circ\text{C}$ has been recorded for 1 at% Ca doped LaNbO_4 , which is comparable to the conventional perovskite based high temperature proton conductors [93]. The surface compositions of mixed ionic-electronic conductors (MIECs) [158] and oxygen ion conductors might differ significantly from the bulk stoichiometry, demonstrated by the reports on perovskite [163,165,294,295] and Ruddlesden-Popper phases [159,296]. In contrast to the well-established bulk transportation mechanism [88,93,195,297,298], the surface chemistry of acceptor doped LaNbO_4 is less well understood.

Low energy ion scattering (LEIS, introduced in section 3.5) is a powerful technique that yields the chemical compositions of the outermost atomic layer. Utilizing this technique, the surface chemistry of 1 at% Sr doped LaNbO_4 (nominal composition $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$) will be studied in this chapter. The experimental conditions for LEIS measurements, i.e. the cleaning procedure, the sputtering rate calibration and the quantification procedure, are first

to be established. The variations of surface chemistry with sintering and annealing conditions (temperatures, durations) will be investigated using both LEIS and secondary ion mass spectrometry (SIMS). A theory based on phase separation, similar to that observed at the YSZ surface [181], is proposed to explain the observed dopant segregation behaviour. The impact of surface dopant segregation on protonic transport is investigated using the D₂O isotopic exchange technique (introduced in 3.7.3).

6.2 Preliminary characterization

6.2.1 X-ray fluorescence (XRF)

The La_{0.99}Sr_{0.01}NbO_{4-d} samples were prepared using conventional solid state synthesis and the Sr content of the sample was checked using X-ray fluorescence (XRF). Prior to the measurement, the Sr intensity was calibrated using a series of reference samples prepared by thoroughly mixing dried La₂O₃, Nb₂O₅ and SrCO₃ powders to a desired stoichiometry (red line in Figure 6-1). A linear relationship between the Sr *Lα* line intensity and the expected Sr concentration was established, indicating that the matrix effects for the Sr *Lα* signal is negligible in this Sr concentration range (<1 at%). Based on the linear fitting, the Sr concentration of the calcinated powder was estimated to be 1.05 ± 0.04 at%, in good agreement with the expected dopant value (1 at% Sr in LaNbO₄).

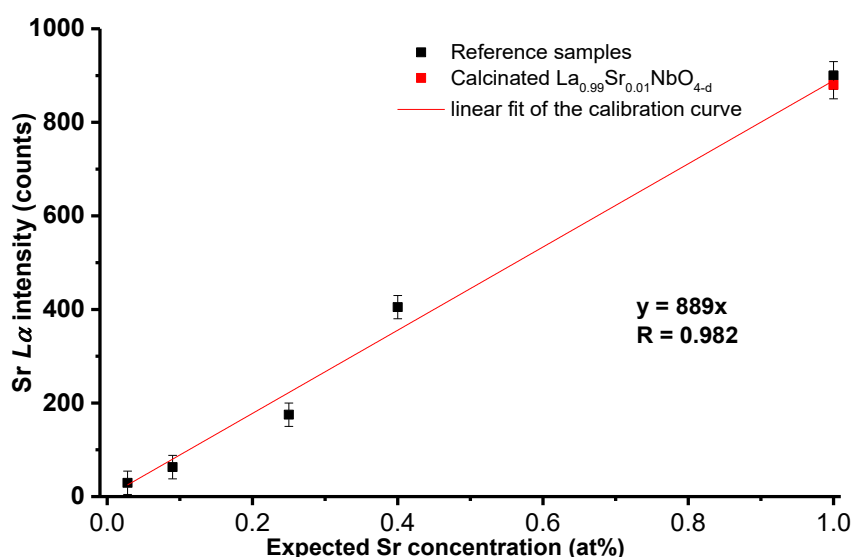


Figure 6-1: Calibration curve for Sr (black marks) and the measured Sr intensity for the La_{0.99}Sr_{0.01}NbO_{4-d} sample (red mark) using XRF; the reference samples were prepared by thoroughly mixing La₂O₃, Nb₂O₅ and SrCO₃ to obtain the expected Sr cation concentration (from 0.03% to 1%).

6.2.2 X-ray diffraction (XRD)

Using Le Bail method [299], the lattice parameters of both the LaNbO_4 and the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ compositions were successfully refined using the $I12/c1$ space group, that of the low temperature fergusonite structure [97]. All the reflections of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ phase are assigned to this space group, although its peak profile is slightly broadened comparing with the parent LaNbO_4 (Figure 6-2). No secondary peaks were detected within the resolution power of the instrument, indicating that current dopant level did not exceed the solubility limit. Indeed, higher Sr solubility in LaNbO_4 has been reported in the literature: Mokkelbost [228] studied $\text{La}_{1-x}\text{Sr}_x\text{NbO}_{4-d}$ ($x = 0, 0.05$ and 0.02) and reported no secondary phase with 2 at% Sr dopant, thus concluded the solubility limit of Sr is approximately 2 at% [228]. It is therefore concluded that single phase $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ was successfully synthesized.

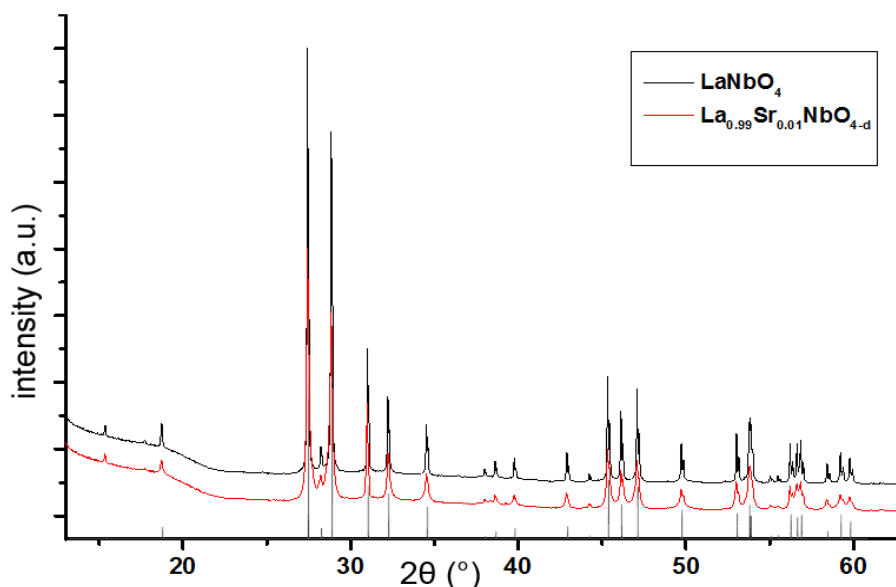


Figure 6-2: Powder diffraction patterns of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ and LaNbO_4 samples ($13^\circ < 2\theta < 65^\circ$); both compositions were refined using the $I2/c$ space group (grey marks show the peak positions) and no secondary phase was detected within the resolution power of instrument.

The refined lattice parameters are summarized in Table 6-1, and show good agreement with literature report [228]. The reported cell volumes show little dependence on the Sr concentration despite the ionic radius difference between the Sr^{2+} and La^{3+} (1.26 Å and 1.16 Å for Sr^{2+} and La^{3+} respectively, at VIII coordination [243]). The change in the lattice parameters induced by the Sr^{2+} might be compensated with the formation of oxygen vacancies [228].

Table 6-1: Lattice parameters of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ and LaNbO_4 phases using the Le Bail method.

composition	a (Å)	b(Å)	c (Å)	β (°)	cell vol. (Å ³)
$\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ (this work)	5.5590(1)	11.5269(3)	5.2018(1)	93.980(2)	332.52(3)
LaNbO_4 (this work)	5.5634(3)	11.5218(6)	5.2027(3)	94.058(4)	332.67(5)
$\text{La}_{0.995}\text{Sr}_{0.005}\text{NbO}_{4-d}$ [228]	5.5649(3)	11.527(5)	5.2039(2)	94.045(4)	332.98(5)
$\text{La}_{0.98}\text{Sr}_{0.02}\text{NbO}_{4-d}$ [228]	5.5631(2)	11.5293(3)	5.2051(2)	94.020(2)	333.03(4)
LaNbO_4 [228]	5.5651(1)	11.523(1)	5.2034(1)	94.071(1)	332.84(3)

6.2.3 Electrical impedance spectroscopy (EIS)

Impedance measurements of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ composition are reported in Figure 6-3. The total conductivity of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ under wet compressed air ($P_{\text{H}_2\text{O}} \approx 2$ mbar) is improved, comparing with that measured under dry condition (~ 1 bar compressed air dried with 98 vol% H_2SO_4 , $P_{\text{H}_2\text{O}} < 0.01$ mbar). The improvement was most clearly observed below 600 °C; the total conductivity increased from $1.3 \times 10^{-6} \text{ S cm}^{-1}$ to $9.4 \times 10^{-6} \text{ S cm}^{-1}$ at 440 °C when switching from dry to wet condition. The huge difference between the dry and wet measurements indicates that protons are the major charge carriers under wet environment in this temperature region, and the difference is therefore ascribed to proton conduction (blue triangle marks in Figure 6-3). The improvement at higher temperature however, is less pronounced, corresponding to a reduced proton concentration in $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ above 600 °C, reflecting the decreased saturated proton concentration [298].

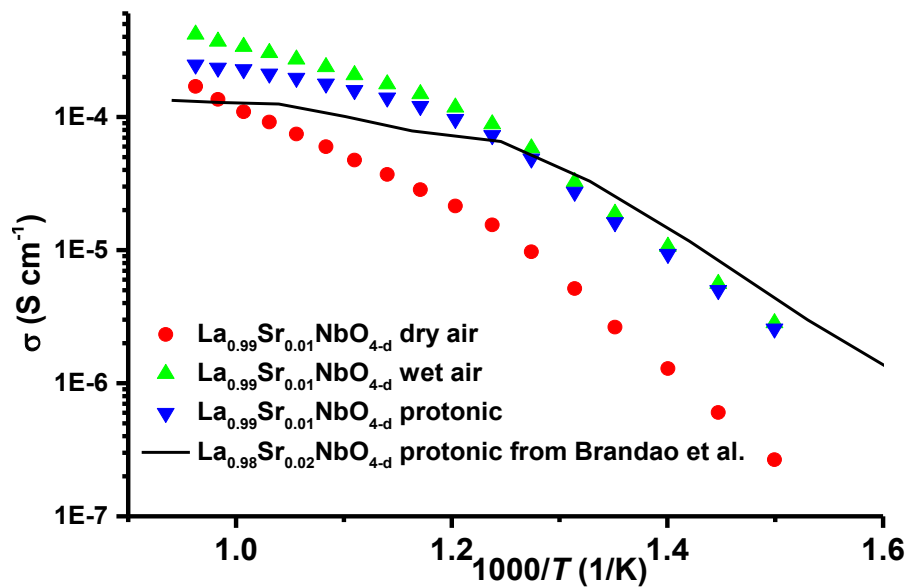


Figure 6-3: Arrhenius plot of the conductivity of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ under dry ($P_{\text{H}_2\text{O}} < 0.01$ mbar) and wet atmospheres ($P_{\text{H}_2\text{O}} \approx 2$ mbar); the conduction is predominantly protonic under wet conditions below 560 °C. Protonic conductivity from [153] is plotted for comparison.

The measured proton conductivity is comparable to literature (black line in Figure 6-3), especially at the low temperature region. The slightly higher conductivity reported in this work, at the high temperature region (above 530 °C), might be attributed to the variance in the temperature profile: both measurements were conducted during the cooling process to ensure low remnant water concentration in samples during the dry measurement. The literature measurement started at a higher temperature comparing to the current study (900 °C and 780 °C respectively), and consequently, the equilibrium proton concentration might not be established during the following measurements thus lead to a lower conductivity value. Acceptor dopant is required to create vacancies that facilitate the water intake in LaNbO_4 based ceramics [47,93], and undoped LaNbO_4 was reported to have negligible proton conductivity [94]. The observed proton conduction would thus indicate successful incorporation of the Sr dopant in the LaNbO_4 crystal.

6.2.4 Transmission electron microscope (TEM)

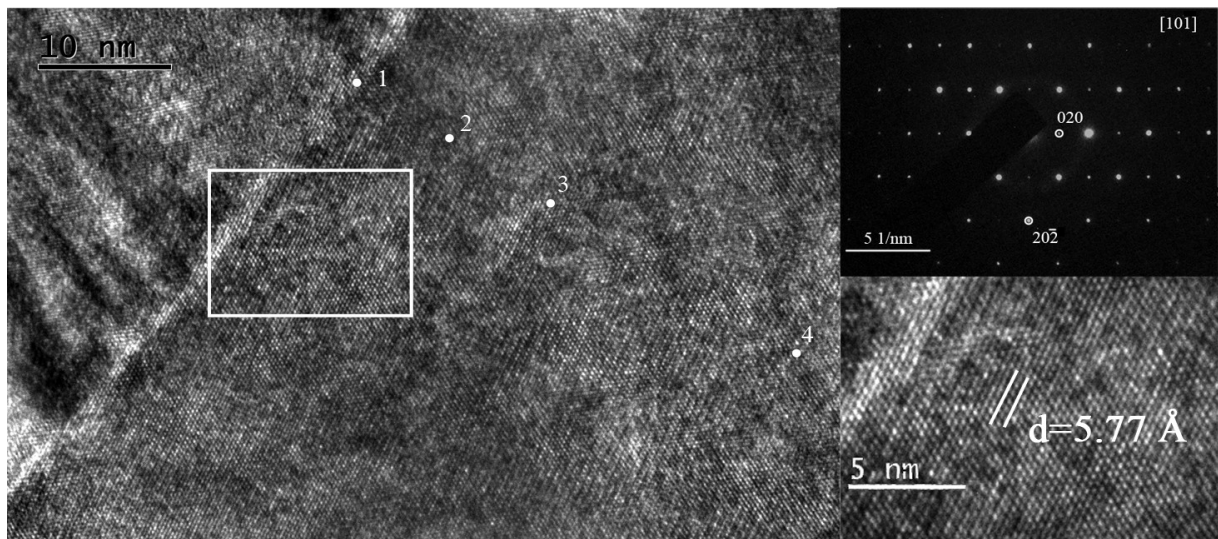


Figure 6-4: HRTEM image of as-sintered $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$, revealing the grain boundary structure; the electron diffraction pattern shows the orientation of the right size grain, the enlarged HRTEM image on the right side corner shows a well-crystallized grain boundary.

The grain boundary, an interface similar to the free surface [300], of an as-sintered $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ sample was studied using transmission electron microscope. The high-resolution TEM (HRTEM) image of the grain boundary structure is shown in Figure 6-4. The incident beam is parallel to the [101] zone axis of the grain crystallised in $I2/c$ space group on the right side of the image (its diffraction pattern shown in the inset). The incident beam direction is not in any particular zone axes of the grain on the left side of the image. The

d -spacing along the 020 plane was measured to be $5.77 \pm 0.1 \text{ \AA}$ (shown in the inset) which agrees very well with the d -spacing obtained from the Le Bail method, $5.76 \text{ \AA}$ (lattice parameters reported in section 6.2.2). The interface between the two grains, highlighted in the inset, is well crystallized and no glassy grain boundary phase was observed. Current results suggest that there is no secondary phase precipitation at the grain boundary.

Point analysis of the chemical composition was carried out using EDX in STEM mode (spot size 0.5 nm). The EDX spectra, from the grain boundary towards the grain bulk, are reported in Figure 6-5, whereas their corresponding positions are marked on Figure 6-4. The intensity of the Sr $L\alpha$ and $K\alpha$ lines (at 1.807 keV and 14.165 keV respectively) decreases steadily from grain boundary and becomes constant when it is approximately 20 nm away from the grain boundary core (spectrum no. 4 in Figure 6-5). The EDX spectra suggest an enrichment of Sr dopant towards the grain boundary. The unmarked peaks in the $1\text{-}2 \text{ keV}$ range resulted from copper sample holder and the Ga implantation during the TEM lamellae fabrication [201].

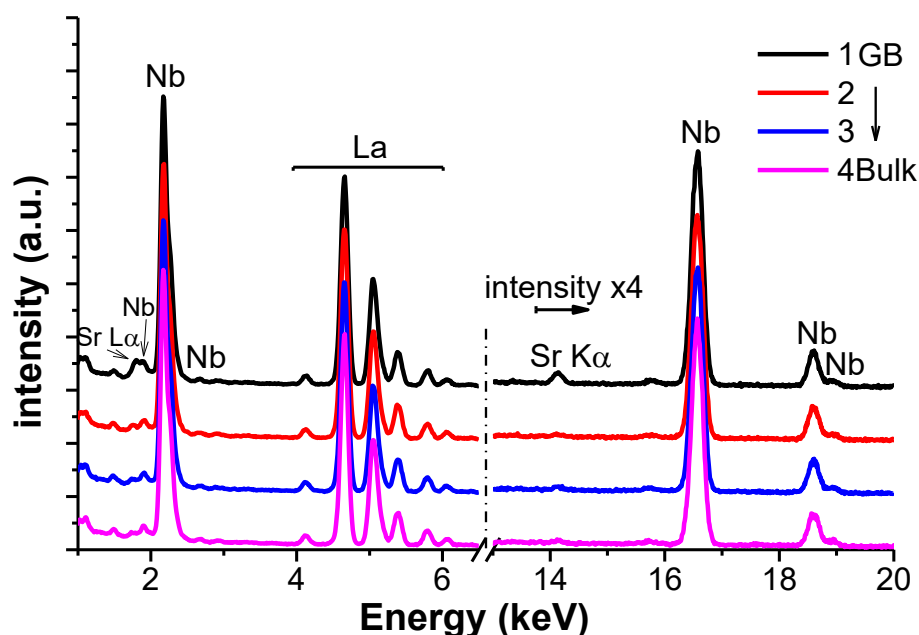


Figure 6-5: EDX spectra highlighting the variations in chemical compositions from grain boundary towards the grain interior. The spectra in the 14 keV to 20 keV range have been highlighted to demonstrate the decrease of Sr $K\alpha$ line intensity. The numbers refer to the positions of the point analysis which are marked in Figure 6-4. Overall, higher Sr intensity was observed near the grain boundary comparing with the bulk.

The conductivity of the acceptor doped LaNbO_4 is constrained by the blocking grain boundary and the reported grain boundary conductivity is often orders of magnitude lower than that of the bulk [88,143]. Several authors have speculated that the reduced grain boundary conductivity is related to the formation of a space charge layer at the grain boundary; a positive charged grain boundary core forms at the grain boundary, resulting in a

proton depletion zone in which the proton charge carriers have reduced mobility [88,301]. The space charge theory further predicts that the negatively charged dopant (A'_{La}) would segregate towards the grain boundary and partially compensate for the positively charged grain boundary core [53].

Only a few authors have attempted to characterize the grains of the acceptor doped LaNbO_4 using TEM. Using high resolution STEM and EELS, Palisaitis et al. reported the formation of a Sr enriched cubic secondary phase in the Sr, Al co-doped $\text{La}_{0.99}\text{Sr}_{0.01}\text{Nb}_{0.99}\text{Al}_{0.01}\text{O}_{4-d}$ [302]. Fjeld et al. investigated the chemical composition of 0.5% Sr doped LaNbO_4 *along* the grain boundary and concluded that the grain was free from glassy secondary phase; however chemical analysis *across* the grain boundary was not reported [88]. Other reports have mainly focused on the twinning structure and stacking faults of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ grains [230,303]. This is the first report on the chemical composition of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ system which confirms the Sr segregation towards the grain boundary, as proposed by the space charge theory.

6.2.5 Summary

Acceptor doped LaNbO_4 with nominal composition $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ has been successfully synthesized. The Sr dopant level was estimated to be 1.05 ± 0.04 at% using XRF, which is below the solubility limit. The structure of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ was successfully refined in the $I12/c1$ space group and the refined lattice parameters agree well with the literature. Impedance measurements confirmed that the major charge carriers were protons below 600 °C under a wet atmosphere ($P_{\text{H}_2\text{O}} \approx 2$ mbar). Chemical analysis of the grain boundary composition using EDX in STEM showed increased Sr concentration towards the grain boundary, and thus provided new evidence for the existence of the space charge layer.

6.3 Surface chemistry of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ (LSNO)

As introduced in section 2.4.2 in the literature review, surface chemistry plays an important role in determining the activity of electrolyte materials. Unlike the bulk transport properties, which have been well characterized for the LaNbO_4 based proton conductor [88,93,195,297,298], surface chemistry of the system has rarely been explored. Another rationale to study the surface chemistry is its resemblance with grain boundary chemistry. Segregation towards the solid-gas interface (surface) and towards the solid-solid interface (grain boundary) shares similar driving forces [300], albeit the latter is more difficult to study and modify. Due to the similarity between these two interfaces, surface chemistry study might provide insight into the grain boundary chemistry thus helps to devise new method to modify the interface.

The LEIS technique has excellent surface sensitivity and provides quantitative chemical information about the outermost atomic layer. Interpretation of LEIS data, though rewarding, is not a trivial task as its signals are affected by various experimental factors (geometry, surface topology, contaminants etc. [161]). In the following section, the experimental procedures for the LEIS measurements, namely the cleaning protocol, the quantification procedure and the sputtering rate calibration, are first established. The surface chemistry of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ samples is then studied using both LEIS and SIMS. Variations of surface composition with annealing temperatures and sintering conditions are presented. Finally, a possible mechanism for the observed Sr segregation is proposed.

6.3.1 Cleaning procedure for low energy ion scattering (LEIS)

The oxide surface is extreme active and is prone to adsorption of contaminants. A simple thermodynamic calculation based on Hertz-Knudsen formula suggests that it takes approximately 10^{-9} s to form a monolayer of contaminants under ambient pressure [211]. The contamination of the outermost layer is therefore almost inevitable during sample transfer. To counter this challenge and to ensure that the data obtained by LEIS measurements is a representation of the “true” surface of the oxide, the samples are cleaned *in situ* in the vacuum chamber prior to data acquisition. Surface spectra after two cleaning procedures, namely cleaning with atomic oxygen plasma and with low dose Ar^+ sputtering, were obtained using 4 keV He^+ primary ion to compare the effectiveness of the cleaning methods.

The surface spectra after different cleaning times under oxygen plasma are shown in Figure 6-6a (note the sputtering yield is presented in absolute values in this figure). The intensity of the oxygen peak clearly increased with prolonged cleaning time, due to the implantation of atomic oxygen, as well as the exposure of the underlying oxide surface previously covered by hydrocarbon impurities. Other impurity species, such as F, Na, Si and Ca, appeared at the surface layer after 40 min cleaning. A tailing of the background towards low energy was observed, creating a “hump” background in the 750 eV to 2000 eV energy range. The background is attributed to the reionization of the primary ions, which was also observed in the Ar^+ cleaned samples (Figure 6-6b).

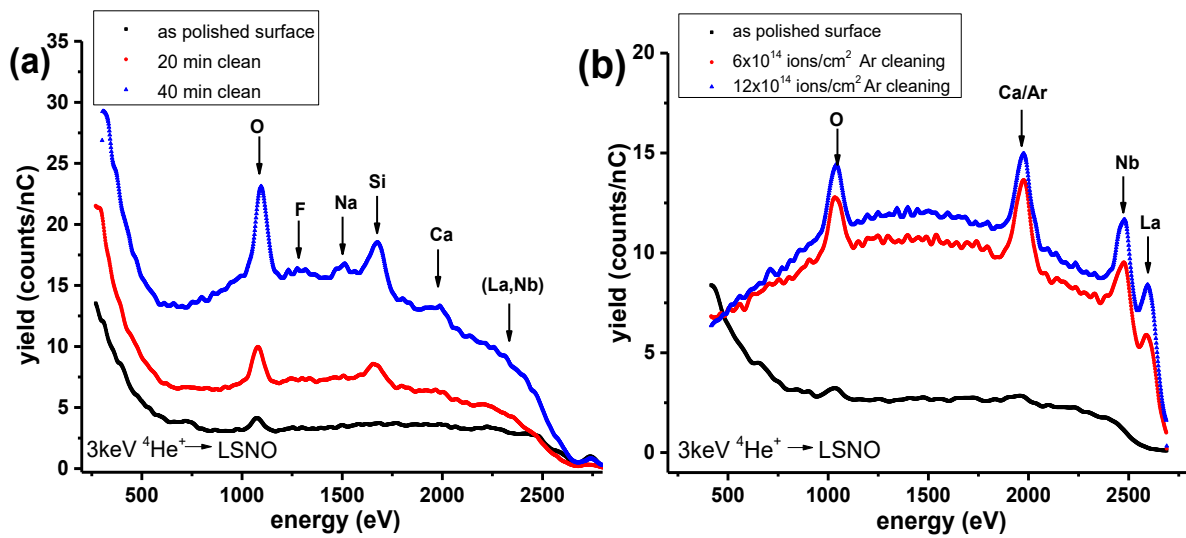


Figure 6-6 Surface spectra after cleaning the as-polished $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ sample using a) atomic oxygen and b) $0.5\text{ keV } \text{Ar}^+$ sputtering. Surface contaminants are effectively removed by $6 \times 10^{14}/\text{cm}^2$ Ar^+ cleaning, whereas inorganic contaminants were clearly observed on the plasma cleaned surface. Note the difference in the scale of y axis.

Unfortunately, the background level for the oxygen cleaned sample is considerably higher than the Ar^+ sputtering counterpart (note the difference in scale between Figure 6-6a and b). This increased in-depth signal is associated with the enhanced ionization probability of the noble gas projectiles from in-depth collision, in the presence of oxygen [161]. In addition, the oxygen cleaned sample had an exponential decay of the background in the low energy region ($<c.a. 600\text{ eV}$), which mostly resulted from the secondary ions rather than the surface scattering events [161]. The signal is most likely to result from residual organic layers with loose packed structure, which gives rise to higher secondary ion yields, whereas such background was not observed in the Ar^+ cleaned samples. The most significant difference between the cleaning techniques lies in their ability to remove inorganic contaminants. No clear peak for either Nb or La was observed at the theoretical peak position after 40 min

oxygen plasma cleaning; although a gradual increase in intensity towards low energy was observed (Figure 6-6a,). This signal is generated from in-depth layers, indicating that the La and Nb species were still beneath the impurity oxide layers (CaO, SiO₂ etc.). Such contaminants are often observed on the outermost surface of oxides, for instance, de Ridder et al. [160] reported a complete surface coverage with SiO₂, CaO and Na₂O impurities on the YSZ surface, even using the starting powders of highest purity (<50 ppm SiO₂, CaO).

A different area of the same sample was used to test Ar⁺ sputter cleaning. The resultant LEIS spectra (Figure 6-6b) suggest an ion dose of 6×10^{14} ions/cm² 0.5 keV Ar⁺ is sufficient to remove the impurities and to reveal the underlying Nb and La species. Assuming the sputtering yield of the Ar⁺ beam to be 1 [158], the dose density suggests that the impurity on the surface was approximately a monolayer thick (i.e. 1×10^{15} /cm²). Similar thickness of the impurity layer was reported in YSZ systems [160,304]: Aoki [305] found a 0.3 nm thick impurity layer on Ca stabilised zirconia; de Ridder [160] commented that the formation of impurities was limited to one monolayer if the driving force was to reduce surface energy, rather than phase separation. For La_{0.99}Sr_{0.01}NbO_{4-d} samples cleaned under Ar⁺ sputtering, further increasing the sputtering time does not change the peak profile significantly nor does it have a detectable impact on the relative intensity of the peaks of interest (Figure 6-6b). The 2000 eV peak probably results from the Ar⁺ implantation of the sputtering beam.

In summary, the Ar⁺ sputtering procedure is more effective in removing the surface impurities and in revealing the cation species of interest whereas the oxygen plasma inevitably implants additional oxygen which enhances the ionization fraction P^+ [161,306] and consequently complicate the interpretation of the peak intensity/surface ion coverage. Therefore, to ensure the accuracy and reproducibility of the results, an Ar⁺ cleaning procedure was adopted; the surface spectra shown in the following sections were obtained after cleaning the surface using *c.a.* 6×10^{14} /cm² dose density of 0.5 keV Ar⁺.

6.3.2 LEIS sputtering rate calibration

To calibrate the sputtering rate of the Ar⁺ ion, the sputtering yield of the Ar⁺ beam was estimated by measuring the geometry of the resultant sputtering crater. A sample was sputtered with the 0.5 keV Ar⁺ for 4200 s. The crater size was set at 400 μm by 400 μm; the current of the sputtering gun was measured at 90 nA both before and after the sputtering, suggesting a stable beam current during the sputtering. The total sputtering dose was

therefore $1.5 \times 10^{18}/\text{cm}^2$. The geometry of the resultant crater was examined using a Zygo interferometer (Figure 6-7a). The low energy Ar^+ beam has a finite size (about $50 \mu\text{m}^2$), therefore the crater assumes a spherical rather than rectangular shape. The depth of the crater was measured to be $0.35 \mu\text{m}$. Based on the Le Bail refinement presented in Table 6-1, the theoretical density of the material is 5.881 g/cm^3 , whereas the measured density was 5.580 g/cm^3 , approximately 95% of the theoretical density. Therefore, a total of 1.8×10^{15} atoms have been removed during the sputtering process, and the estimated sputtering rate is 2 atoms per incident Ar^+ ion. The sputtering rate is assumed to be constant throughout the whole profile disregarding variations in the chemical compositions and preferential sputtering.

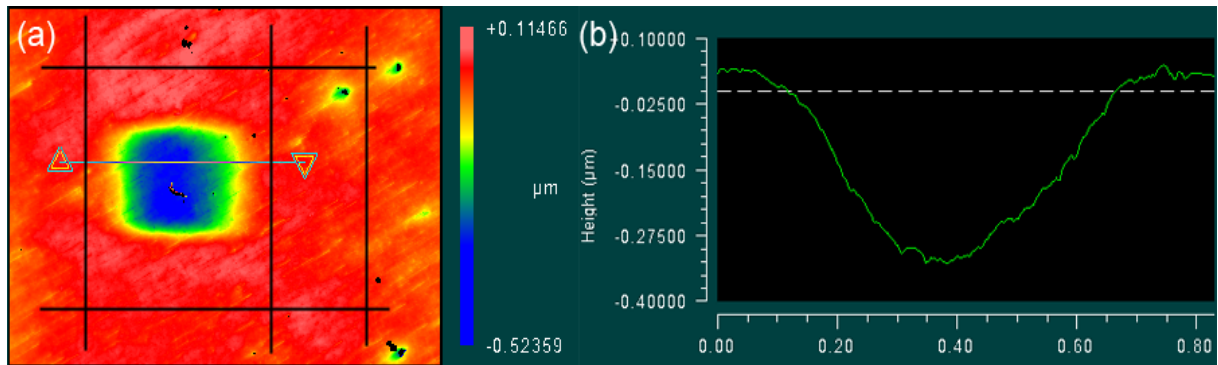


Figure 6-7: (a) Sputtering crater after exposing to 90nA, 0.5 keV Ar^+ beam for 4200 s, the white line indicates the position where the profile in (b) is obtained. The thick black line indicates the positions of the surface profiles reported in Table 6-2.

The surface roughness of the polished $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$, based on the five profiles highlighted in Figure 6-7a, is summarized in Table 6-2. Good surface finish with peak-valley difference of less than 100 nm was obtained, both the root mean square roughness and average roughness was less than 20 nm, indicating good surface quality which would have little impact on the LEIS intensity [161].

Table 6-2: Surface finish of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ after polishing.

Profile	$P-V^*/\text{nm}$	R_{ms}^{**}/nm	R_a^{***}/nm
1	69	17	15
2	100	19	24
3	100	20	16
4	72	13	10
5	94	17	14
average	87 ± 15	17.2 ± 2.7	15.8 ± 5.1

*. P-V: peak-valley, the difference between the maximum and minimum

**. R_{rms} : root mean square roughness $R_{rms} = \sqrt{\frac{1}{n} \sum_{i=1}^n (R_i - \bar{R})^2}$

***. R_a : average roughness $R_a = \frac{1}{n} \sum_{i=1}^n |R_i - \bar{R}|$

The sputtering rate was also simulated using the “The Stopping and Range of Ions in Matter” (SRIM) software suite [307]. The density and the stoichiometry of the surface layer were assumed to be identical to the bulk material. Based on the current measurement geometry, the simulation suggests a sputtering rate of 3.4 atoms per incident Ar^+ (conditions and results of the simulation are summarized in Table 6-3). The twofold difference between the experiment and simulation yield is not unreasonable [158], considering the simulation does not consider the chemical bonding in the sample during the calculation [307].

Table 6-3: Summary of the sputtering yield obtained by SRIM simulation.

composition		Conditions			Yield/incident Ar^+				
$\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$	density	incident angle	Energy		La	Nb	Sr	O	total
	5.88 g/cm ³	59°	0.5 keV		0.34	0.24	0.01	2.79	3.38

6.3.3 Quantification of LEIS data

Figure 6-8 demonstrates the quantification procedure to analyse the LEIS data. The binary collision events were described using a Gaussian peak, whose position is determined according to Eqn. 3.16. The shape of the peak has been corrected based on the isotopic fraction. The broadening of the binary collision peaks is most likely due to instrumental effects (energy distribution of primary ion, finite area of detectors etc. [161]).

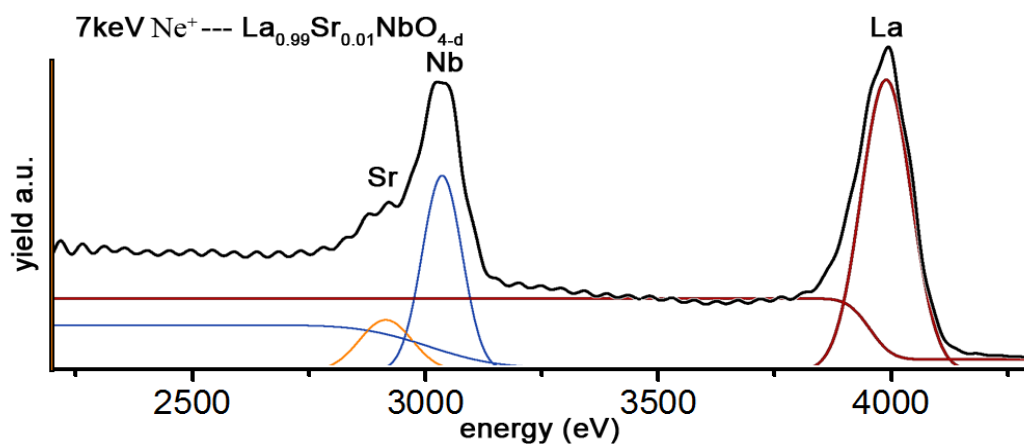


Figure 6-8: A typical LEIS spectrum demonstrating the quantification process. A Gaussian peak describes the surface scattering process whereas the signal generated by collisions with the in-depth layers is described using an error function. The surface concentration was calculated using only the binary collision peaks.

An error function was applied to fit the background which primarily resulted from the collision between the primary ions and the in-depth layers. The position of the error function was constrained to be 20–25 eV less than the theoretical binary peak position. The energy

difference corresponds to the first ionization energy of He^+ and Ne^+ [283], and represents the energy loss during the reionization process of the primary ion after it has interacted with the sub-surface atoms. The height and width of the binary collision peaks and the error functions are fitted until a global minimum in the residual intensity is reached.

To translate the integrated peak intensity to surface coverage, or surface atomic density, a reference is required to account for the variance in ionization efficiency of different ions [157]. In this work, an internal standard was obtained by sputtering the sample surface with a high dose of Ar^+ , until the cation peak intensities became constant [158]. Assuming the absence of matrix effects [161], the surface cation ratio can then be calculated based on the nominal bulk stoichiometry. A depth-profile for an as-polished $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ sample is shown in Figure 6-9. A stable Nb/La peak intensity ratio was observed, indicating that the newly-exposed surface after polishing was indeed stoichiometric. Fluctuation of Nb/La peak intensity was observed for the first few data points, which probably relates to the residual contaminants after the low Ar^+ dose exposure ($<10^{15}/\text{cm}^2$). Rather than reporting the surface peak intensity (I_A of element A), which is affected by the ionization probability of individual elements, the normalized cation ratio (defined in Eqn. 6.1), which reflects the surface stoichiometry of the oxide, is reported in the following sections.

$$[A] = \frac{I_A}{I_{\text{bulk}}} [A]_{(\text{bulk})}$$

Eqn. 6.1

$$\text{normalized cation ratio} \equiv [A] / [B]$$

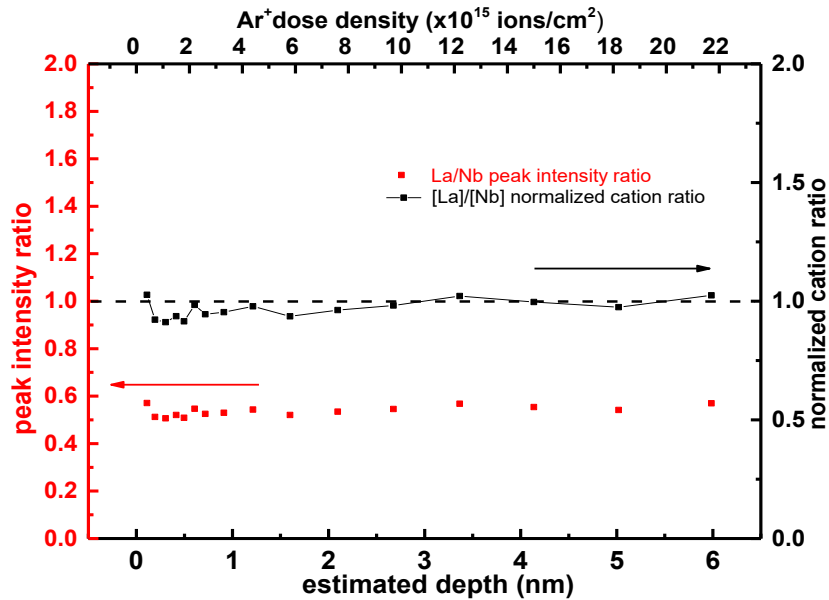


Figure 6-9: LEIS profile shows the integrated peak area ratio, and the normalized cation ratio for Nb/La in the as-polished $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ reference. Constant Nb/La ratio was observed for the as-polished $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ sample indicating that the newly exposed surface after polishing is indeed stoichiometric. The dash line represents the bulk composition.

6.3.4 Effect of annealing conditions on $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ surface

The as-polished samples were annealed in the 600 °C to 1000 °C range under static air, to encourage the stoichiometric surface to reconstruct into a thermodynamically stable state. Several samples were annealed at 1000 °C for prolonged periods of time to investigate the dynamics of potential segregation process. All these samples are labelled as “annealed” in the following sections. It is also interesting to investigate the surface without the polishing process, as previous literature states stress would affect the segregation of a dopant [308]. The surface of the “as-sintered” samples was therefore characterized without polishing process. In LEIS analysis, primary ions with higher mass and higher energy grants better mass resolution [161], therefore a 7 keV Ne^+ primary beam, which affords a separation between the Sr and Nb peaks, was used for the quantification of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ surface chemistry.

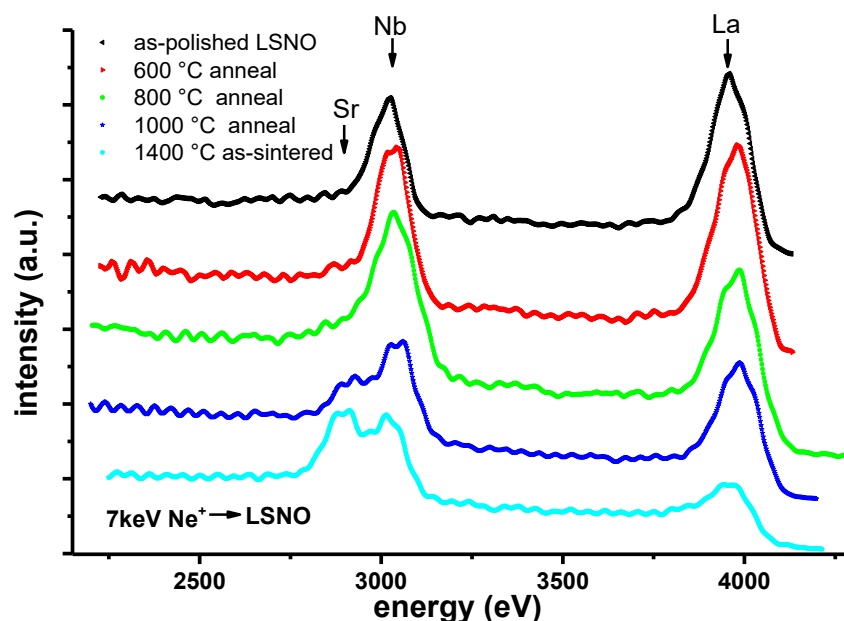


Figure 6-10: LEIS surface spectra of LSNO samples after annealing under static air at 600–1000 °C for 10 h. The surface spectrum of the as-polished sample is also shown as a reference. Significant Sr segregation was observed after annealing the sample above 800 °C. Note the spectra have been shifted vertically for clarification and therefore do not represent the true ion yield.

The LEIS spectra from the outermost surface of various $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ samples annealed at 600 °C to 1000 °C are shown in Figure 6-10. The surface spectrum of the as-polished $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ reference is also shown to demonstrate the impact of annealing temperature. For the 600 °C annealed sample, the La/Nb peak intensity ratio is very similar to that of the as-polished sample; no Sr peak was observed within the detection limit. Depth profiling of the sample (will be reported in Figure 6-12) revealed that the surface composition was very

similar to that of the bulk. Comparing with the 600 °C annealed sample, the peak shape of the 800 °C annealed sample was different: a shoulder at lower energy was observed. It is possible that the signal results from collision between the incident ions and Nb from the in-depth layers, however this assumption is unlikely considering such a feature is missing in the 600 °C annealed and the as-polished samples. Alternatively, the signal might result from enrichment of Sr on the surface, which was clearly observed for the 1000 °C annealed sample. After 1000 °C annealing, the Nb signal from the outermost surface was much weaker whereas a strong Sr signal was observed. Based on Figure 6-10, the onset temperature for the observed Sr segregation in $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ was estimated to be between 600°C to 800 °C. Sr segregation was also observed in the as-sintered samples, which is unsurprising considering that the sintering temperature (1400 °C) is much higher than the highest anneal temperatures (1000 °C). Interestingly, the intensity of the Sr peak of the as-sintered sample was comparable with those annealed at 1000 °C, indicating that the surface chemistry is sensitive to the processing routine, as well as thermal history of the material.

The surface spectra of the 1000 °C annealed sample after prolonged Ar^+ sputtering are shown in Figure 6-11a. Clear reduction in Sr intensity was observed with increasing sputtering dose while the intensity of Nb and La peaks increased gradually. After normalizing the peak intensity to the bulk peak intensity (following Eqn. 6.1), the cation ratio between A and B sites as a function of sputtering dose is plotted in Figure 6-11b. Two distinguished regions are identified (separated by the vertical dashed line in Figure 6-11b): a Sr enriched but La deficiency layer of approximately 6–7 nm thick was observed in the near surface layers. Further sputtering resulted in the plateauing of the cation ratio, which soon became indistinguishable from the nominal bulk composition. Comparing with the bulk composition (shown as the horizontal lines in Figure 6-11b), the Sr/Nb cation ratio on the 1000 °C annealed $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ surface is about 2 times higher, whereas the La concentration is much lowered, leaving the surface A-site deficient with nominal composition close to $\text{La}_{0.3}\text{Sr}_{0.02}\text{NbO}_x$.

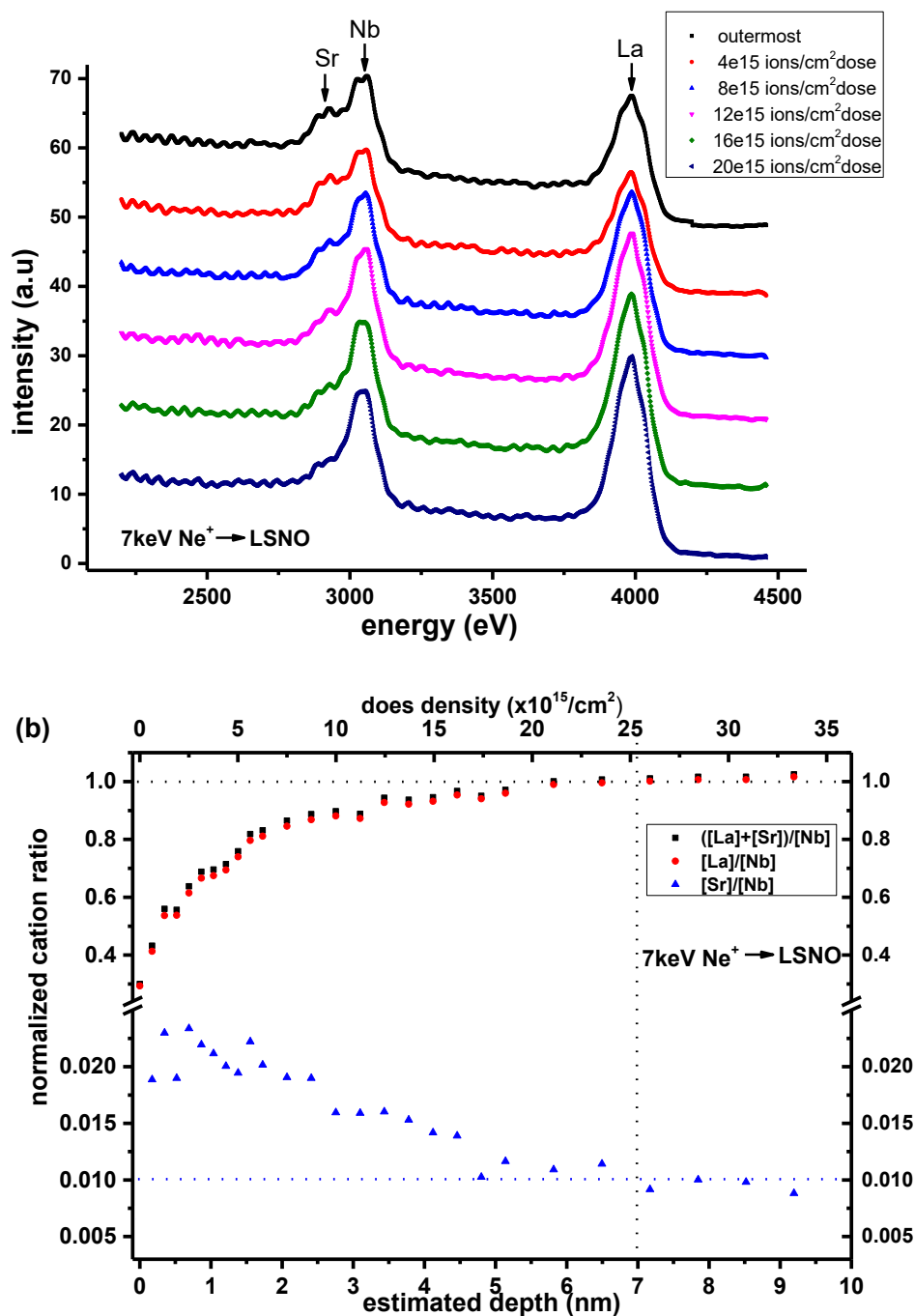


Figure 6-11: a) LEIS depth profile of a 1000 °C annealed sample showing the evolution of chemical composition as a function of sputtering dose and b) normalized cation ratio revealing a Sr enriched but La deficient layer approximately 6-7 nm thick at the surface. The horizontal lines in (b) showcase the bulk composition whereas the vertical line signalling the depth where the bulk stoichiometry has been reached.

To confirm the onset of the segregation temperature estimated by LEIS (those shown in Figure 6-11a), the same sample sets were investigated using secondary ion mass spectrometry (SIMS), which promises better counting statistics. The normalized intensities of LaO⁺, NbO⁺ and Sr⁺ secondary ions (normalized to the total intensity), which are the species with the highest ion yields for corresponding cations, are reported in Figure 6-12. All the SIMS depth-

profiles show an initial increase in the normalized intensity which is highlighted in the hatched area in Figure 6-12a, (for the 600 °C annealed sample, the top few atomic layers were sputtered unintentionally). This sharp change in ion yield resulted from the pre-equilibrium region in which the surface chemical composition, and thus ion yields, is constantly modified by the sputtering ion implantation [211]. Therefore, the obtained signals were not representative of the composition in this pre-equilibrium region [211,309]. The thickness of the pre-equilibrium region depends on the projected range of the sputtering ion, and was estimated (with SRIM [307]) to be approximately 2.4 nm under the current beam condition (1 keV O_2^-). The estimated thickness agrees well with the experimental observation; for the as-polished sample, stable LaO^+ and Sr^+ signals were recorded outside the first 3 nm layers (Figure 6-12a), indicating a stoichiometric surface composition, which is consistent with the LEIS depth profile reported in Figure 6-11.

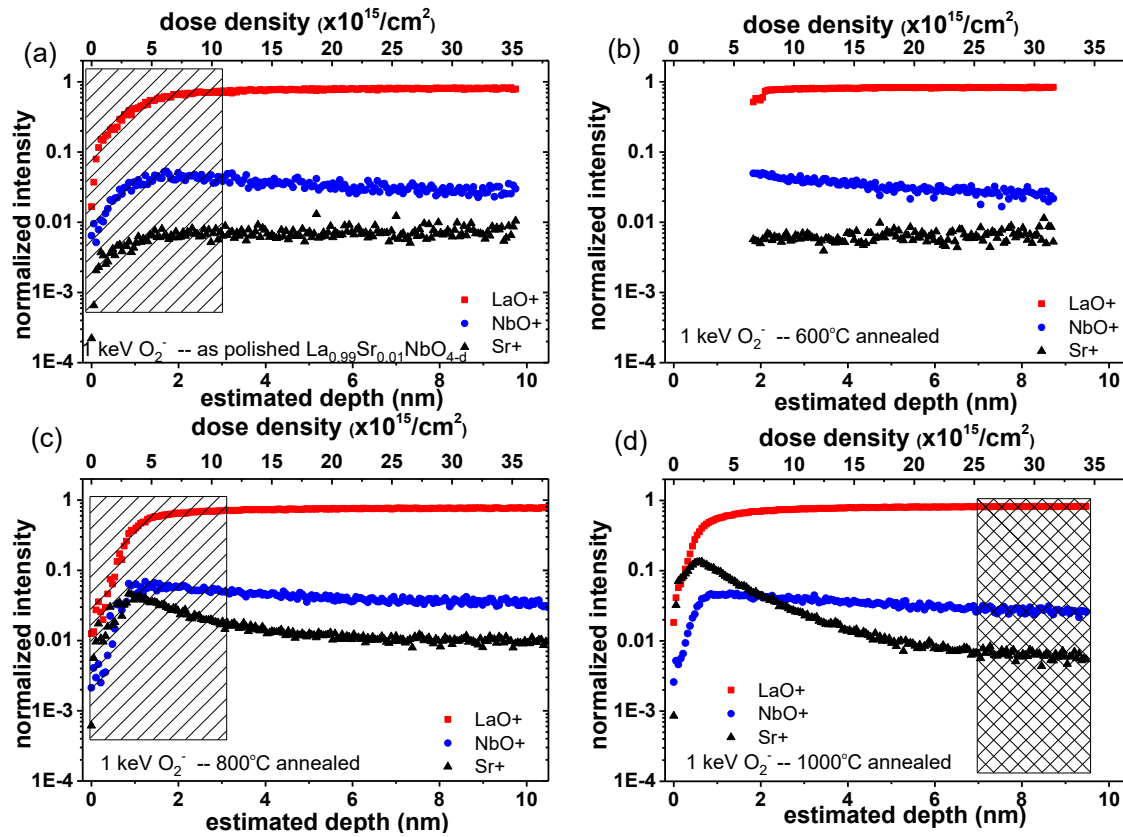


Figure 6-12: SIMS depth profiles of (a) as-polished (b) 600 °C (c) 800 °C and (d) 1000 °C annealed $La_{0.99}Sr_{0.01}NbO_{4-d}$ samples. Segregation of Sr towards the surface was observed in sample annealed above 800 °C, in good agreement with the LEIS data (Figure 6-10). The hatched region in (a) and (c) is the pre-equilibrium region within which the ion yields vary significantly with the implant of sputtering. The double hatched region in (d) is the bulk composition estimated based on the LEIS results in Figure 6-11, slight decrease in Sr concentration was observed within this region indicating that the surface Sr concentration might be underestimated in the LEIS result.

The NbO^+ signal, on the other hand, decreased continuously with sputtering dose, which might relate to the sputtering process, although the actual cause of this trend is unclear. Similar to the as-polished sample, steady Sr^+ and LaO^+ signals were observed for the 600 °C annealed sample, indicating this temperature is too low to initiate cation diffusion towards the surface, again showing good consistency with the LEIS results (the spectrum in Figure 6-10).

For the 800 °C annealed sample, a clear decrease in the Sr^+ intensity was observed outside of the pre-equilibrium region; increasing the annealing temperature saw a shaper drop in Sr^+ intensity for the 1000 °C annealed sample, indicating a higher Sr surface concentration (note all the intensity is plotted in log scale). The double hatched area in Figure 6-12d corresponds to the bulk region predicated by LEIS; a small but non-negligible downward trend was observed for the normalized Sr^+ intensity in the 1000 °C annealed sample. This trend is difficult to detect in the LEIS depth profile, due to the low primary ion yield with low Sr concentration (i.e. the last two spectra in Figure 6-11b). It is therefore speculated that the bulk Sr concentration was underestimated using the LEIS data, and a slightly higher Sr concentration on the surface is expected. It should be emphasized, that SIMS is a qualitative technique and the ion intensity cannot be converted to surface cation concentration due to the matrix effect [212]. Nevertheless, good consistency of the segregation onset temperature as well as segregation layer thickness was found between the LEIS and SIMS data.

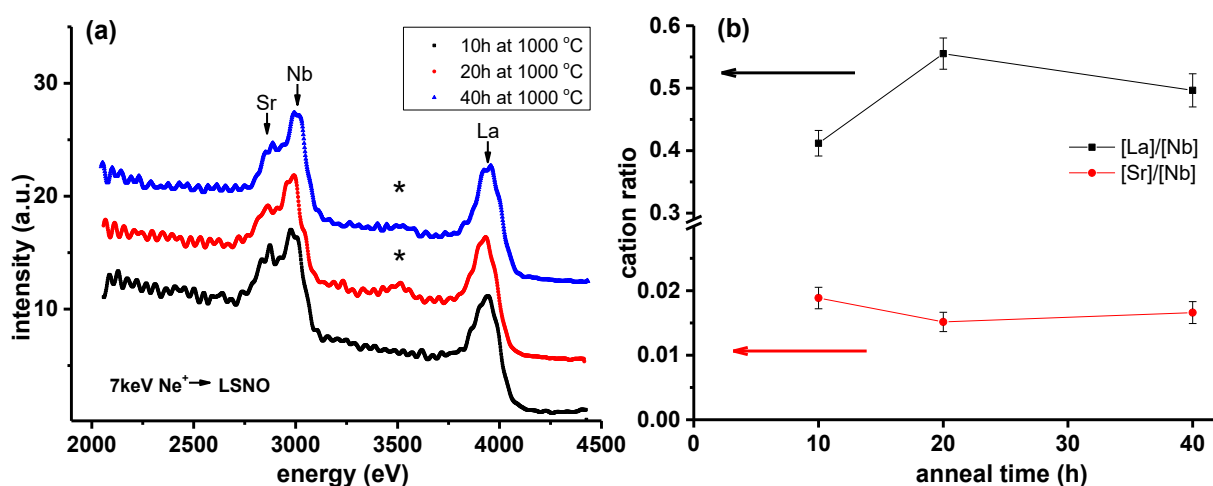


Figure 6-13: (a) LEIS surface spectra of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ annealed at 1000 °C for 10–40 h, and their corresponding surface cation ratios in (b). The peaks at 3500 eV (marked by asterisks in a) correspond to Sn and Sb, which probably originate from furnace contamination. No significant change in the surface composition was observed with prolonged annealing time, indicating the surface reaches equilibrium after 10 h annealing at 1000 °C.

To investigate the dynamics of the segregation process, various $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ samples were annealed at 1000 °C from 10 to 40 h; the resultant LEIS surface spectra and

depth-profiles are reported in Figure 6-13 and Figure 6-14 respectively. The surface spectra show little variations with extended annealing time: no significant change in peak intensity was observed when extending the annealing time from 10 h to 40 h. An additional peak at 3500 eV was observed for those samples annealed for 20 h and longer, which corresponds to Sn or Sb. The peak is most likely to originate from furnace contamination, although it is possible that Sn and Sb has a slow segregation rate and only becomes detectable with longer annealing time. Unlike the surface spectra shown in Figure 6-10, which highlight the sensitivity of segregation behaviour to annealing temperatures, the annealing time has limited impact on the segregation behaviour. This observation indicates a rapid Sr segregation dynamic which reaches a stable state after 10 h annealing at 1000 °C.

The quick segregation dynamics is confirmed with the depth profiles reported in Figure 6-14. Overall, the [La]/[Nb] cation ratio demonstrated little variation with prolonged annealing times, albeit the 10 h annealed sample seemed to have a lower [La]/[Nb] ratio in the first 1-2 nm surface layer, compared with those annealed for longer. The [Sr]/[Nb] ratio, on the other hand, is more scattered, due to the low Sr intensity. Still, a similar trend was observed between different annealing times; using Nb as a standard, the Sr surface concentration was estimated to be approximately 2 at%, which then gradually decreased to the bulk level with an increasing sputtering dose. No clear dependence of the surface compositions on the annealing times was found in the current study (reported in Figure 6-13b). In addition, segregation layers of similar thickness (approximately 6–7 nm) formed with varied annealing time; again confirm that the surface reaches an equilibrium state in less than 10 h when being annealed at 1000 °C.

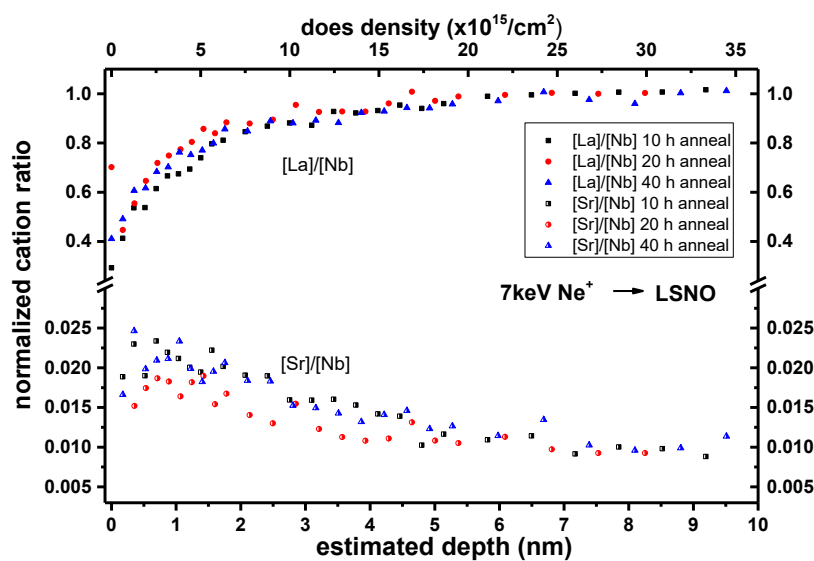


Figure 6-14: LEIS depth profile of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ annealed at 1000 °C for 10–40 h; the segregation behaviour did not vary significant with increasing annealing time.

In electrochemical ceramic system, the Sr surface segregation is often considered harmful, and is related to the long-term degradation of electrochemical performance [167,168,179]. Therefore, it is of interest to investigate whether the surface segregation observed in the as-sintered samples can be avoided. One of the apparent solutions is to vary the sintering temperatures which, depending on the enthalpy of the segregation, would change the equilibrium surface concentration [160], thus has the potential to suppress the observed Sr segregation. The sintering temperature of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ samples were therefore varied from 1350 °C to 1450 °C, and the resultant surface spectra are displayed in Figure 6-15. Enrichment of Sr at the outermost layer persists, when increasing the sintering temperatures from 1350 °C to 1450 °C. Quantification of the surface spectra (summarized in Table 6-4) registers an increase in La coverage and a decrease in Sr concentration with increasing sintering temperature. Increasing the sintering temperature directs the surface composition towards the bulk stoichiometry. High sintering temperature seems beneficial for suppressing the Sr surface segregation although the 1450 °C sintered sample is nevertheless still La site-deficient with Sr segregation.

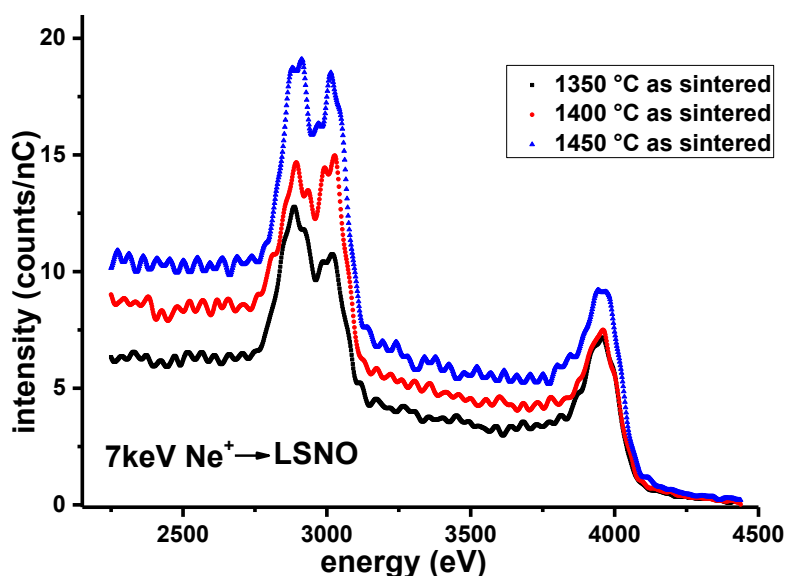


Figure 6-15: LEIS surface spectra of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ sintered at different temperatures for 10 h.

Table 6-4: Surface composition of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ samples prepared under different sintering conditions.

conditions	[La]/[Nb](%)	[Sr]/[Nb] (%)
1450 °C, 10 h sintering	52.7 ± 2.7	2.0 ± 0.2
1400 °C, 10 h sintering	42.3 ± 2.1	2.5 ± 0.2
1350 °C, 10 h sintering	40.0 ± 1.7	3.5 ± 0.2

6.3.5 Possible mechanism for Sr surface segregation in $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$

To summarize the findings presented in the previous section, Sr surface segregation was observed on $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ surface, after be annealed at temperatures above 800 °C. The onset of the annealing temperature was between 600 °C and 800 °C, and the thickness of the segregation layer was estimated to be approximately 6–7 nm after annealing at 1000 °C for 10 h. No enhancement of Sr segregation on the surface was observed after extending the annealing time from 10 h to 40 h at 1000 °C, indicating rapid segregation dynamics. Increasing the sintering temperature from 1350 °C to 1450 °C supresses, but does not eliminate Sr segregation. This is the first report on the surface chemistry and Sr segregation in substituted LaNbO_4 , although Sr dopant segregation has been extensively reported in other oxides such as RP phases $(\text{La}_{2-x}\text{Sr}_x)\text{CoO}_4$ [168], $(\text{La}_{2-x}\text{Sr}_x)\text{NiO}_4$ [310], and various perovskite phases $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-d}$ [311], $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-d}$ [163,295], $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-d}$ [165,294] and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-d}$ [162,312]. In these compositions, the Sr segregation is often accompanied by A site termination. Indeed, preferential A site termination was reported in stoichiometric phases without Sr dopant, such as in polycrystalline RP La_2NiO_4 [158] PrLaNiO_4 [294], and in double perovskite $\text{GdBaCo}_2\text{O}_{5+d}$, $\text{PrBaCo}_2\text{O}_{5+d}$ [159,296] amongst others. The $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ system on the other hand, behaves quite differently: despite the Sr segregation, the surface is overall A site deficient, and Nb has a higher surface coverage than the stoichiometric bulk composition (reported in Figure 6-11 and Figure 6-14).

One of the major differences between the perovskite structure and the scheelite related structure is the tolerance to dopants. Perovskite based structures have the ability to accommodate high levels of substitution (20 mol% Sr or even higher for those investigated in [158,162,168,311,312]) by BO_6 octahedral tilting and distortion [34], whereas the acceptor dopant solubility in LaNbO_4 is relatively low [132]. The solubility of Sr has been reported to be approximately 1 at%, above which 2nd phase starts to precipitate [88,93,141,297]. It is therefore postulated that, in addition to the size and charge mismatch between the dopant and the lattice ion which promotes dopant segregation [175,177], phase separation at the surface, due to the increased Sr concentration and its low solubility [141], leads to the unique segregation behaviour in the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ system. Analogy can be drawn between the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ and the YSZ systems; in the latter case, de Ridder reported the formation of Y deficient monoclinic phase at the near surface region due to the Y segregation towards the outermost layer [181]. The phase separation argument has been proposed to explain the La surface termination in La_2NiO_4 ; Wu et al. calculated the free energy of various LaO-NiO

compounds (La_2O_3 , La_2NiO_4 , $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_4\text{Ni}_3\text{O}_{10}$, and NiO) from 300 to 1373 K and concluded that the decomposition of La_2NiO_4 phase into higher order RP phase and La_2O_3 was thermodynamically favoured, leading to the observed La termination at the surface [313]. Experimental observations of higher order RP phases at the near surface region are consistent with the numerical calculation [158,314].

The segregation process of the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ system is therefore tentatively proposed in Figure 6-16. After the polishing process, a stoichiometric surface, free from segregation, is obtained, confirmed by the SIMS and LEIS measurements (Figure 6-10 and Figure 6-12). However, chemical analysis indicate that the grain boundary is still enriched with Sr dopant (Figure 6-4), possibly due to the space charge effect [88,301] (illustrated as the grey layer in-between the grains in Figure 6-16a). The stoichiometric surface however is not stable, provoking the diffusion of Sr towards the surface when annealed above 800 °C. Diffusion along the grain boundary might be the predominant pathway due to the relatively high Sr concentration, as well as the highly defective structure [270,315] (solid arrows in Figure 6-16b). In addition, high density twinning boundaries might also contribute to the observed segregation behaviour below the ferroelastic to paraelastic phase transition [316]. Upon arriving at the surface, the additional Sr provokes the phase separation into a mix of LaNbO_4 , $\text{Sr}_2\text{Nb}_2\text{O}_7$ and other Sr or Nb enriched phases, according to the $\text{SrO-La}_2\text{O}_3\text{-Nb}_2\text{O}_5$ ternary phase diagram [317], which explains the high Nb concentration in the near surface layers. The $\text{Sr}_2\text{Nb}_2\text{O}_7$ secondary phase has been reported by Mokkelbost after sintering the samples with nominal composition $\text{La}_{0.98}\text{Sr}_{0.02}\text{NbO}_{4-d}$ at 1500 °C for 6 h [141].

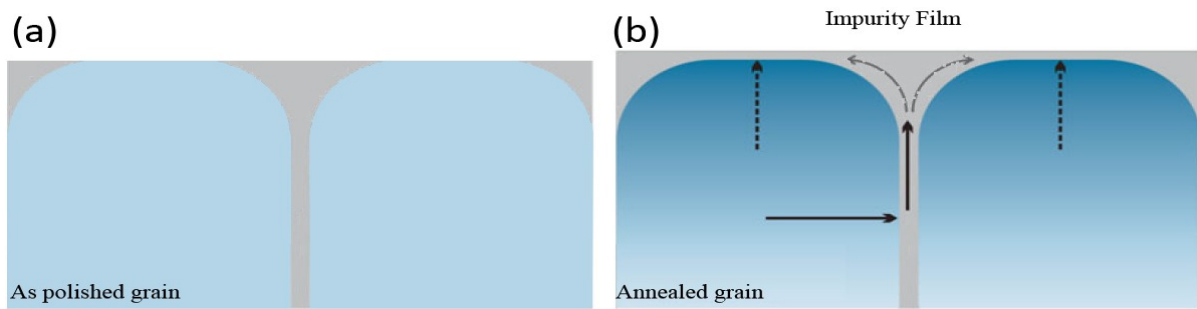


Figure 6-16: Schematics demonstrating the proposed segregation mechanisms in $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$. (a) The as-polished surface is stoichiometric and free from segregation; although the grain boundary is still enriched with Sr (b) the annealing process allows the localized dopant to diffuse towards surface, provoking the formation of Sr enriched impurity layers on the surface.

The onset temperature for segregation (between 600 °C and 800 °C) and rapid segregation dynamics (reported in the previous section 6.3.4) in $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ material is somewhat slower than that reported for perovskite. For instance, Téllez et al. reported a significant increase in A site coverage after annealing the polished $\text{GdBaCo}_2\text{O}_{5+d}$ at 400 °C for only 1 h [159]. Extending the annealing temperature to 8 h and 24 h however showed little increment in A site surface coverage [296]. Finally, it is unsurprising that the as-sintered samples also have a Sr enriched layer, considering the sintering temperatures are much higher than the onset of segregation.

6.4 Impact of Sr segregation on the transport properties—wet exchange of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$

Surface chemistry is crucial for the electrochemical performance. For instance, the surface segregation layer is detrimental for YSZ and many oxide ion electrolytes, as it blocks the oxygen exchange between the solid and gas phases [168,169,179]. The surface analysis presented earlier in this chapter demonstrated that the surface chemistry of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ was altered by annealing conditions, thermal history and sintering conditions. A Sr enriched, La deficient surface layer of about 6–7 nm thick formed after annealing the sample at 1000 °C for 10 h. Due to the low onset temperature for the segregation formation, the surface composition of samples prepared with normal sintering conditions ($T > 1350$ °C) was similar to that of the annealed sample.

The following section proceeds to investigate impact of surface segregation on the transport properties of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ proton conductors. To achieve this aim, isotopic exchange using D_2O tracer was conducted. The surface chemical composition after the wet exchange was first qualitatively studied with SIMS, confirming the presence of a Sr enriched surface layer after exchange. Following that, the impact of surface layer on transport properties was investigated by exchanging $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ at 450 °C and studying the resultant isotopic profile.

6.4.1 Line scan approach

The experimental conditions for the D₂O exchange experiment are shown in Figure 6-17. The polished samples were first annealed in lab air at 800 and 1000 °C for 10 h to introduce different level of Sr segregation, after which the D₂O exchange followed. The exchange temperature is limited to 450 °C, to prevent development of the segregation layer during the exchange. The as-polished samples, which have a stoichiometric surface, were also exchanged at the same conditions as a reference.

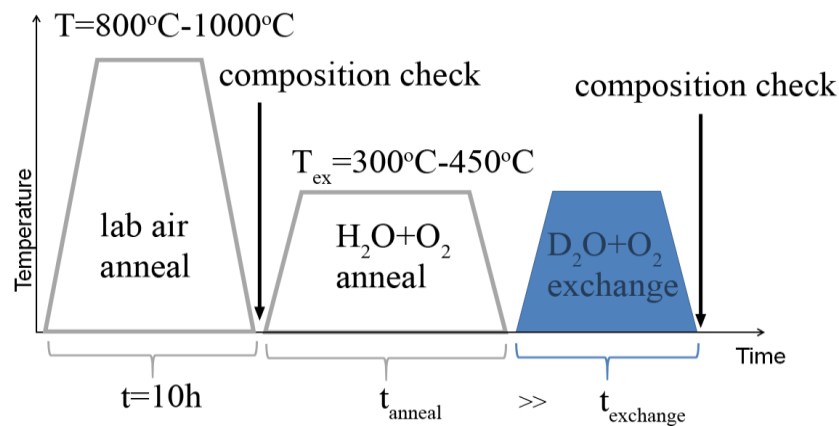


Figure 6-17: Temperature profile of the wet exchange experiment; note that the exchange temperature was set to be 450 °C, to prevent additional segregation during the wet anneal experiment.

The cation distribution was checked using SIMS after the wet exchange and the results for those exchanged at 450 °C for 1 h are shown in Figure 6-18. For the as-polished samples, no Sr profile was observed before the wet exchange (Figure 6-12a), and a slight decrease in Sr intensity with sputtering was observed in the exchanged sample (arrow in Figure 6-18a). It is possible that the wet environment promotes the segregation process and encourages Sr to diffuse towards the surface at a temperature (450 °C) lower than that required in the normal lab air (600 to 800 °C), although the trend is not very clear due to low Sr counts.

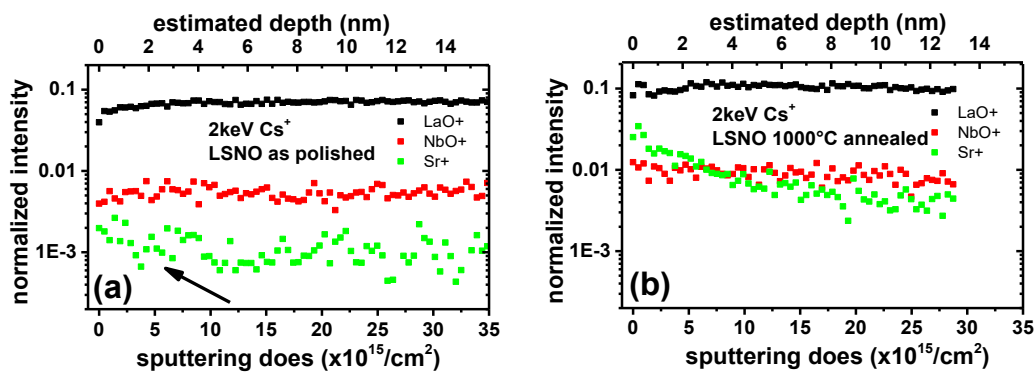


Figure 6-18: SIMS depth profiles display the cation distribution in (a) as-polished and (b) 1000 °C annealed LSNO sample after D₂O wet exchange at 450 °C for 1 h. Sr segregation towards the surface was observed after the wet exchange in the annealed sample.

For the 1000 °C annealed samples, a clear Sr profile was observed both before and after the wet exchange experiments (Figure 6-12d and Figure 6-18b), indicating that the surface layer was stable under the wet exchange environment. In addition, the thickness of the segregation layer was maintained at approximately 7 nm after the wet exchange process, similar to that before the exchange experiment (Figure 6-11).

Part of a typical SIMS spectrum of a $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ sample after wet exchange is shown in Figure 6-19. Owing to the extreme high mass resolution of the instrument, separation between $^{18}\text{O}^-$ (mass = 17.9992 u [318]) and OD^- (mass = 18.0085 u [318]) was readily achieved. The D^- (mass = 2.0136 u [318]) yield is extremely low under both Cs^+ and O^{2-} sputtering beams; OD^- was therefore chosen as the tracer to obtain a diffusion profile. The background level of OH^- due to adsorbed gas on the surface was measured using an unexchanged sample under the same beam conditions and chamber residual pressure.

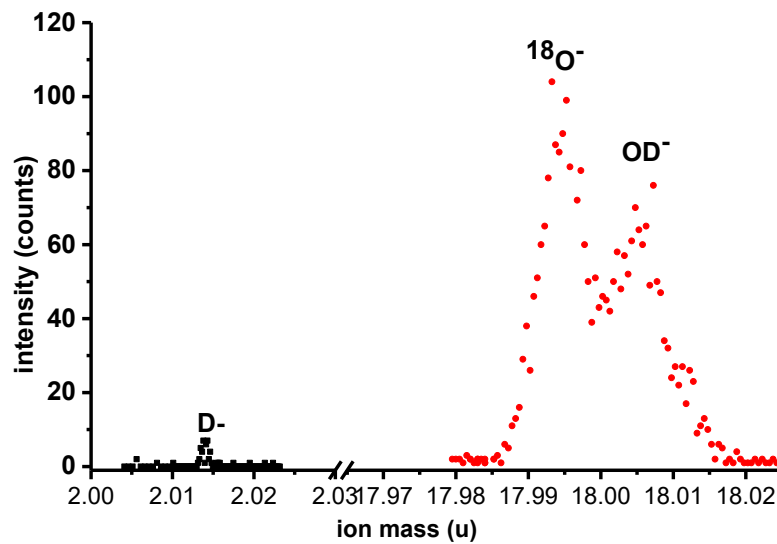


Figure 6-19: Part of a SIMS spectrum, demonstrating the mass separation between the $^{18}\text{O}^-$ and OD^- signals.

The isotopic fraction $C(x,t)$ is expressed in Eqn. 6.2 in which I_{OD^-} and I_{OH^-} represent the intensity of the corresponding secondary ion signal.

$$C(x,t) = \frac{I_{\text{OD}^-}}{I_{\text{OD}^-} + I_{\text{OH}^-}} \quad \text{Eqn. 6.2}$$

For fitting of Crank's solution to Fick's 2nd law of diffusion in a semi-infinite medium, the normalized isotopic fraction $C'(x,t)$ is needed, as expressed in Eqn. 6.3:

$$C'(x,t) = \frac{C(x,t) - C_{bg}}{C_{gas} - C_{bg}} \quad \text{Eqn. 6.3}$$

where C_{bg} is the natural abundance of deuterium D, the theoretical value is 0.0115% [319]; C_{gas} is the isotopic fraction in the exchange gas, which is 95%.

The diffusion profile of an as-polished sample after exchange at 450 °C for 1800 s is shown in Figure 6-20. The isotopic fraction $C'(x,t)$ varies from 0.5% to 2.0%, which is well above the natural abundance (0.0115%) of deuterium, indicating successful incorporation of the deuterium specie. A general decreasing trend of normalized isotopic concentration away from surface was observed (highlighted as the red line in Figure 6-20); however the overall intensity of the OD⁻ species was very low, resulting in significant uncertainty in the normalized isotopic fractions. The low natural abundance brings additional challenges when determining the tail of the profile, and both of these factors hinder the accurate determination of D^* and k^* . Switching the sputtering beam between Cs⁺, O₂⁻ and Ar⁺ ions was attempted and both positive and negative spectra were gathered, though no improvement in the data quality was achieved. Fitting to Eqn. 6.3 was attempted though no stable solution was found for the diffusion profile. Future work is therefore required to optimize the wet exchange condition for the La_{0.99}Sr_{0.01}NbO_{4-d} based proton conductor.

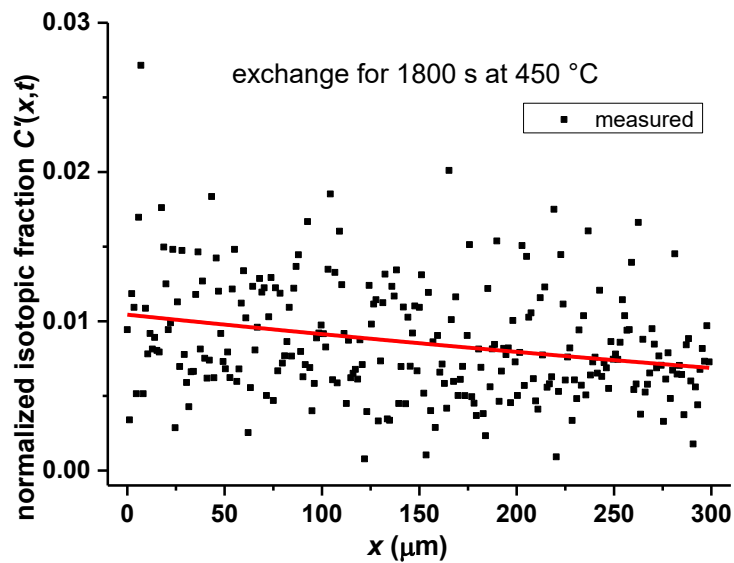


Figure 6-20: A diffusion profile of La_{0.99}Sr_{0.01}NbO_{4-d} after exchanging at 450°C for 1800s, no stable solution was found for the diffusion profile due to low isotopic fraction. The red line highlights the decreasing isotopic fraction away from the sample surface and is only a guide for the eye.

6.4.2 Surface isotopic concentration

The line-scan technique did not produce a satisfactory diffusion profile suitable for fitting. Alternatively, the depth-profile approach was used to study the surface isotopic concentration. It should be emphasized that the diffusion coefficient of the current material is not suitable for depth profile; according to Nernst-Einstein relation (Eqn. 3.20) and the impedance measurements shown in Eqn. 5.3, the proton diffusivity is estimated to be $D^* = 2.33 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 450 °C. Given 15 min as the shortest exchange time that is considered reasonable under the current experimental setup [213], the diffusion length $L = 2\sqrt{D^*t}$ is estimated to be 90 μm which is significantly longer than the depth-profile length (limited to $\sim 10 \mu\text{m}$ using the TOF-SIMS instrument [320]).

Current experiments therefore primarily focus on obtaining the surface isotopic concentration (given in Eqn. 6.4) which is Crank's solution at $x = 0$ and can be rewritten as a function of the dimensionless parameter h' (Eqn. 6.5).

$$C'(x, t) = \text{erfc}\left(\frac{x}{2\sqrt{D^*t}}\right) - \left[\exp\left(\frac{k^*x}{D^*} + \frac{k^{*2}t}{D^*}\right) \times \text{erfc}\left(\frac{x}{2\sqrt{D^*t}} + \sqrt{\frac{k^{*2}t}{D^*}}\right)\right] \quad \text{Eqn. 6.4}$$

$$C'(0, t) = 1 - \exp(h'^2) \times \text{erfc}(h') \quad \text{Eqn. 6.5}$$

$$\text{where } h' = \sqrt{k^{*2}t/D^*}$$

Based on Crank's solution, a linear correlation between $\log C'$ and $\log h'$ is predicted (highlighted in the inset of Figure 6-21 and Eqn. 6.6), when the overall isotopic concentration is low ($C'(0, t) < 10\%$, whereas $C'(0, t) \leq 5\%$ under the current experimental conditions) [220]; under this condition, the approximation in Eqn. 6.6 is obtained:

$$\log C'(0, t) \approx \log h' \quad \text{Eqn. 6.6}$$

Rearranging Eqn. 6.6 gives rise to Eqn. 6.7, which describes the relationship between the surface isotopic concentration and the transport parameters D^* and k^* :

$$\frac{C'(0, t_1)}{C'(0, t_2)} \approx \frac{h'_1}{h'_2} = \frac{k_1^*}{k_2^*} \sqrt{\frac{D_2^* t_1}{D_1^* t_2}} \quad \text{Eqn. 6.7}$$

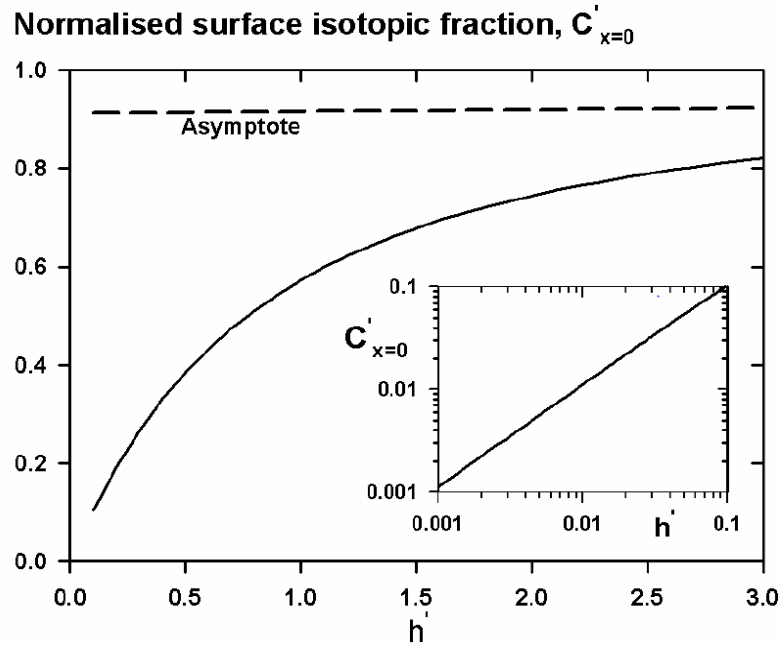


Figure 6-21: The relationship between the dimensionless h' parameters and the surface concentration $C'(0,t)$. When the surface isotopic concentration ($C'(0,t) < 10\%$), a linear relationship between $\log C'$ and $\log h'$ is expected (shown in the inset). Figure adapted from ref. [220].

To obtain the surface concentration, depth profiling of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ samples was carried out and a typical depth profile of an as-polished sample exchanged at 450°C for 1 h is shown in Figure 6-22.

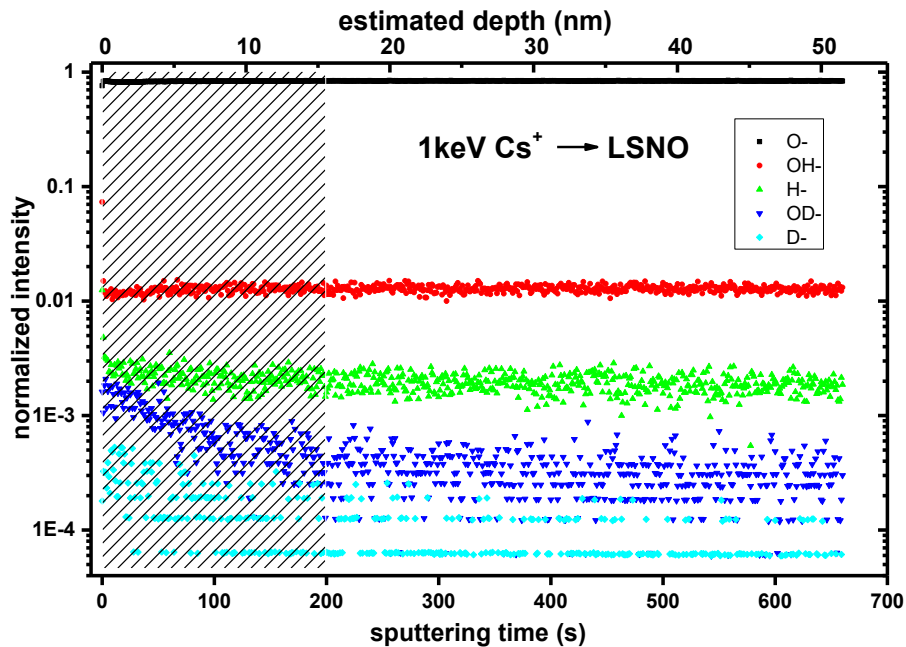


Figure 6-22: SIMS depth profile, showing the normalized intensity of various species as a function of sputtering time; increased OD- intensity was observed at the surface (shaded area in the first 15 nm region), which might relate to the formation of water adsorbed layer. The shaded area represents the surface of the samples which is excluded for the quantification of the surface tracer concentration, all the intensity is normalized to the total counts.

It is noted that the intensity of OD⁻ and D⁻ dropped with initial sputtering which then reached a stable level with increasing sputtering dose. One of the possible explanations for this observation is the absorption of water molecules on the oxide surface; the physisorbed water can accumulate to a few layers on top of the oxide surface and results in an increased isotopic signal [223,321] after the final exchange process in the D₂O. Alternatively, the Sr enriched surface layer might have very low proton diffusivity, and thus leads to an accumulation of tracer in the near-surface region, similar to that observed in YSZ [181]. The signal from the surface enriched layer (the hatched region in Figure 6-22) is considered not representative of the actual surface isotopic concentration, and was excluded from the quantification.

The surface isotopic fraction as a function of annealing conditions is plotted in Figure 6-23. Overall, prolonged exchange time leads to higher surface isotopic concentration, which is expected according to Eqn. 6.7. For the as-polished samples, the isotopic fraction after 2 h exchange was about 1.5 times higher than that exchanged for 1 h, which agrees well with Eqn. 6.7 which predicts a 1.4 times increment.

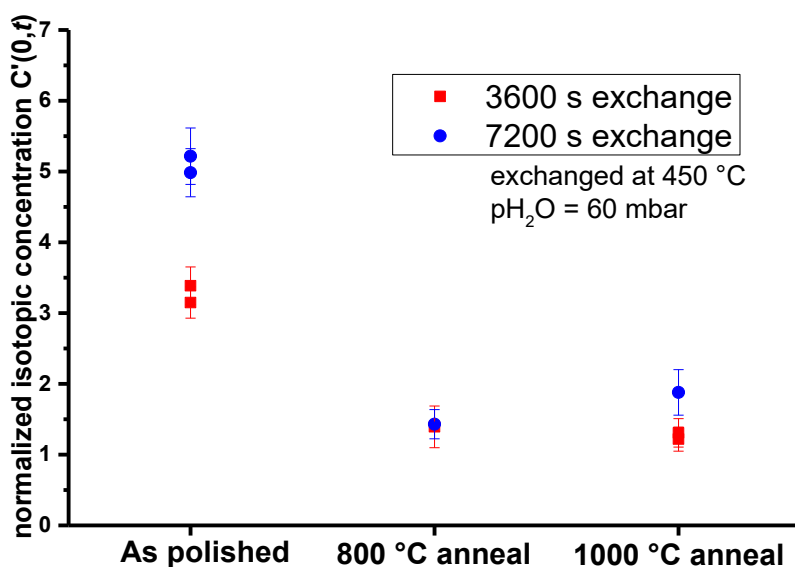


Figure 6-23: Normalized surface tracer concentration after exchange at 450 °C with different exchange time. The as-polished samples which are free from Sr segregation have a higher surface isotopic concentration than their annealed counterparts.

Under the current exchange conditions, the isotopic fraction of the as-polished samples is consistently higher than their annealed counterparts. Coupled with the surface chemistry analysis, it is proposed that the presence of a Sr-enriched layer is blocking to the wet exchange process. Interestingly, it is noted that the 800 °C annealed samples have similar surface isotopic fraction as the 1000 °C annealed sample, although higher Sr surface coverage was confirmed for the latter (Figure 6-10). It seems that the relatively small amount

of Sr segregation is sufficient to suppress the proton surface exchange process, highlighting the importance of the composition at the outermost layer. Assuming the surface layer does not alter the tracer diffusivity D^* , a 50% reduction in the surface exchange coefficient is predicted, according to Eqn. 6.7, after Sr segregation layer has developed.

6.4.3 Implications of Sr surface segregation for proton transport

Regardless of the surface chemistry composition, the normalized isotopic fraction of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ after wet exchange was low (less than 5 %), indicating that the proton diffusion is limited by the surface exchange process. Surface-limited diffusion was often reported for fast ionic conductors such as YSZ [322] and the LAMOX family [323]. Liu et al reported a “flat” tracer profile, similar to that reported in Figure 6-20, and very low (less than 1%) normalized isotopic fraction in LAMOX [323].

The Sr enriched surface layer further impedes the surface exchange process, which reflects a low proton intake of the Sr enriched surface layer. The reduced surface isotopic concentration might be linked with the low proton conductivity of the surface phases. For instance, the total conductivity of $\text{Sr}_2\text{Nb}_2\text{O}_7$, one of the proposed surface phases, was reported to be mixed electronic and ionic with $\sigma = 3.2 \times 10^{-5} \text{ S cm}^{-1}$ at 1000 °C, although no proton conduction was recorded [324,325]. The conductivity data for other potential impurity phases such as $\text{Sr}_2\text{Nb}_5\text{O}_9$ [326] and $\text{Sr}_4\text{Nb}_{17}\text{O}_{26}$ [327] are not available. Proton conduction was reported in $\text{Sr}_{4.5}\text{Nb}_{1.5}\text{O}_{8.25}$ and $\text{Sr}_4\text{Nb}_2\text{O}_9$ [328], however the high Sr/Nb ratio is inconsistent with the surface composition obtained from the LEIS data (Figure 6-14b and Table 6-4), making them unlikely candidate of surface phase. The blocking effect of the Sr enriched phases might be understood in terms of reduced oxygen vacancy concentration. The formation of impurities eliminates the oxygen vacancies in the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ fergusonite phase, thus block the water intake pathway between the gas phase and the oxide surface, a process similar to those reported in [167,168,179]. Unfortunately, the transport parameters were not obtained from the diffusion measurements, due to the low isotopic fraction. Exchange conditions must be optimized, to gain a better understanding of the interplay between the surface chemistry and the diffusion process.

6.5 Chapter Summary

Single phase $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ was successfully synthesized. Its structure was refined in the $I12/c1$ space group and the refined lattice parameters are in good agreement with the literature reports. Impedance measurements confirmed that the major charge carriers were protons below 600 °C under wet atmosphere ($P_{\text{H}_2\text{O}} \approx 2$ mbar). Chemical analysis using TEM showed that the grain boundaries were enriched with Sr, providing new evidence for the existence of the space charge layer in acceptor doped LaNbO_4 .

The experimental procedures for LEIS, namely the cleaning process, the sputtering rate calibration and the quantification process have been successfully established. After that, the surface chemistry of $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$, and its evolution with annealing and sintering conditions were investigated using LEIS and SIMS. A Sr enriched but La deficient surface layer, approximately 6–7 nm thick was identified on the $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ surface, the first report on the surface chemistry of acceptor doped LaNbO_4 . The onset of the Sr segregation was estimated to be between 600 °C and 800 °C, and a thermodynamically stable surface, with a nominal composition close to $\text{La}_{0.3}\text{Sr}_{0.02}\text{NbO}_x$, formed after annealing at 1000 °C for less than 10 h. Surface layers with similar composition were observed in the as-sintered samples: increasing the sintering temperature from 1350 °C to 1450 °C reduced but did not eliminate the segregation layer. Unlike perovskite systems in which the Sr segregation is accompanied by overall A site termination [163,295,311], the surface of the annealed $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ is La, thus A-site, deficient. This unique segregation behaviour is explained in terms of phase separation. The as-polished stoichiometric surface is not stable and encourages Sr diffusion towards the surface during annealing. Upon arriving at the surface, the solubility limit is likely to be surpassed, provoking a phase separation into a mixture of LaNbO_4 , $\text{Sr}_2\text{Nb}_2\text{O}_7$ and other Sr or Nb enriched phases, leading to the observed surface compositions.

Isotopic exchange experiments using D_2O tracer were carried out between 350 °C and 450 °C to investigate the impact of surface layers on proton transport. Diffusion profiles were obtained by the line-scan technique, although the isotopic fraction was too low to provide a stable fitting. Instead, isotopic concentration at the surface was quantified; a systematic decrease in normalized isotopic concentration was reported, after the Sr enriched layer had developed at the surface. The formation of Sr enriched impurities might have eliminated the surface oxygen vacancies in $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$, and thus blocks the water intake pathway between the gas phase and the underlying oxide.

Chapter 7. Conclusions and Future works

The crystal structure, transport properties and the surface chemistry of LaNbO_4 based ionic conductors have been investigated for their potential application as SOFC electrolytes. $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series ($x = 0.01\text{--}0.20$) were successfully synthesized using solid state reaction in an attempt to further explore the structural templates of CeNbO_{4+d} phases, which have been reported to facilitate remarkable oxygen diffusivity of $6.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 700°C . The $x = 0.08\text{--}0.16$ compositions were identified to have a $(3 + 2)\text{D}$ incommensurate modulated structure using electron diffraction. Direct imaging with HRTEM and HAADF indicates that the structural modulation in these phases is a result of the Nb/W cation ordering. The ordering is accommodated by the displacive movements of neighbouring ions to facilitate the varied local environment. Using the modulation wave vectors $\mathbf{q}$ determined using electron diffraction, the structure of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition was refined using the $I2/c(\alpha_1, 0, \gamma_1)00(\alpha_2, 0, \gamma_2)00$ superspace group, with synchrotron powder diffraction data. Final fitting parameters of $R_p = 0.085$ and $R_{wp} = 0.108$ were achieved using Rietveld method, despite the presence of asymmetric peak profile. The bond length and the bond valence sum (BVS) mapping, as a function of the internal t - u space, was examined; reasonable variations in bond length and BVS were observed, justifying the proposed structure model. A real space $10 \times 1 \times 10$, based on the refined incommensurate structure, has been constructed, providing a good match with the HRTEM image. The commensurate approximation revealed a highly distorted B site environment, with coordination numbers ranging from 6 to 8. The additional Nb/W-O bonds in the modulated structure provide linkages between the NbO_x slabs, which are isolated in the LaNbO_4 parent phase, forming an interconnected 3D polyhedral network similar to that observed in $\text{CeNbO}_{4.25}$.

This work proceeded to investigate the structural evolution of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series (from room temperature up to 800 °C) using thermal analysis and *in situ* X-ray and neutron diffraction. Based on the diffraction data, a series of transformations between a modulated monoclinic phase, a modulated tetragonal phase and an unmodulated tetragonal phase has been identified, highlighting the complexity of the phase transition behaviour in the modulated fergusonite/scheelite phases, which has previously been overlooked in the literature. Landau theory has been applied to predict the tetragonal to monoclinic phase transition temperature of the parent phase and a phase diagram of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ series was proposed. *In situ* neutron scattering experiments were conducted to investigate in detail the structural evolution of the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ compositions in the 500–800 °C region. The structure of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ below 650 °C was successfully refined using a $I4_1/a(\alpha,\beta,0)00(-\beta,\alpha,0)00$ superspace group. Above this temperature, an unmodulated tetragonal structure forms. Increasing the dopant level to saw the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition maintain its modulated structure at 800 °C. Attempts were made to pinpoint the position of the interstitial oxygen in the $x = 0.16$ composition at 500 °C, although the refinement suggests a non-localized distribution of the interstitial oxygen.

The transport properties of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases were investigated using electrochemical impedance measurements and ^{18}O tracer isotopic exchange. Comparing with the LaNbO_4 parent structure, huge improvement in total conductivity was achieved with W dopant, reaching $8.0 \times 10^{-3} \text{ S cm}^{-1}$ at 863 °C for $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$; its diffusivity was measured to be $2.46 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 750 °C. Good agreement of the activation energy for oxygen transport between the impedance and diffusivity measurements confirms that the oxygen ions are the major charge carrier in the hyperstoichiometric $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system. The measurements provide the first piece of experimental evidence for an interstitialcy diffusion mechanism in $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$. To investigate the effect of A site cation size on the conductivity of hyperstoichiometric LaNbO_4 , $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ ($x = 0, 0.1, 0.2, 0.3, 0.5, 0.7$ and 1) phases were synthesized and characterized. Overall, the conductivity of the Y and W co-doped LaNbO_4 decreases with increasing Y content; larger cation which promises an open structure seems beneficial for the total conductivity.

The surface chemistry of acceptor doped $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$, and its evolution with annealing and sintering conditions, was investigated using LEIS and SIMS. The LEIS experimental procedures, which consist of *in situ* Ar^+ sputtering cleaning, calibration of the Ar^+ sputtering rate and data quantification, are first established. A Sr and Nb enriched but La deficient

surface layer, with the nominal composition $\text{La}_{0.3}\text{Sr}_{0.02}\text{NbO}_x$, was identified after annealing the polished samples at 1000 °C for 10 h, the first report on surface dopant segregation behaviour in acceptor doped LaNbO_4 . The thickness of the segregation layer was estimated to be 6–7 nm, below which the bulk composition is restored. The onset of the segregation was estimated to be between 600 °C and 800 °C; a thermodynamically stable surface was created after annealing at 1000 °C for less than 10 h. Interestingly, surface layers with similar composition were observed in the samples sintered at 1400 °C for 10 h. Increasing the sintering temperature from 1350 °C to 1450 °C reduced, but failed to eliminate, the segregation layer. The observed segregation behaviour was explained based on a phase separation theory. The polishing process exposes a stoichiometric surface which is thermodynamically unstable, and thus provokes Sr segregation upon annealing. After the Sr dopant has arrived at the surface, its solubility limit is likely to be surpassed, thus leading to the formation of Sr enriched surface layers. Isotopic exchange experiments using D_2O tracer were conducted at 450 °C to investigate the impact of segregation layers on proton transport. A systematic decrease in surface isotopic concentration was observed after the Sr enriched layer had developed at the surface. It is postulated that the formation of stoichiometric impurities might eliminate the surface oxygen vacancies, and thus block the water intake pathway between the gas phase and the oxide surface.

Future Work

The current study has focused on the crystal structure and the transport properties of W doped LaNbO_4 whereas the next steps lie in further understanding the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ system and in the exploration of other hyperstoichiometric ReMO_4 compositions. With such complication in the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ structure, i.e. (3 + 2)D modulation, diffraction data using single crystal, which promises better accuracy, is highly desirable. For instance, using single crystal diffraction data, higher orders of Fourier magnitudes of the modulation waves can be included in the structure model, which would provide more accurate description of the occupational wave vector. In addition, the low temperature $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$ composition can be further explored to locate the interstitial position in the structure. Investigation of the local structure, which combines with average structure information yielded using diffraction technique, would further provide insight into the conducting process. It is also interesting to present a detailed investigation in the variations of modulation vectors as a function of temperature for the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$, whose incommensurate structure shows high stability with temperature. Apart from continuing the structural studies of the modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phase, another key goal is to synthesize other LaNbO_4 based hyperstoichiometric phases to further explore the $\text{CeNbO}_{4.25}$ structural prototype. Potential candidates include various rare earth elements at the A site, as well as Mo and Ru dopant at B site.

Current work has seen the first report on the surface segregation behaviour in the acceptor doped $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ protonic conductor; however, limited by the slow surface exchange rate thus low tracer concentration, proton diffusion profile was not obtained. Consequently, the diffusivity of the surface layer has not been established. The exchange temperature and time therefore must be fine-tuned to optimize the exchange conditions, under which surface exchange coefficient, k^* , and diffusivity, D^* could be directly extracted. In this work, the surface chemistry after annealing under static air was characterized; it is of great interest to investigate the impact of annealing atmospheres. For instance, annealing under real application environments, i.e. under increased water partial pressure, or under CO_2 and SO_2 , would yield information about the long-term degradation process of the material. Finally, one of the interesting implications of current finding lies in the application of acceptor doped LaNbO_4 for thin film electrolyte, which inherently has large surface/bulk ratio. Preliminary effort has been made to fabricate $\text{La}_{0.99}\text{Sr}_{0.01}\text{NbO}_{4-d}$ thin films using PLD. Impact of thin film fabrication conditions on the surface chemistry is to be established.

References

- 1 BP Global, *BP Statistical Review of World Energy June 2016*, <http://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html>, Date Accessed: June.2016.
- 2 J. W. Sun, *Energy Econ.*, 1998, **20**, 85–100, 10.1016/S0140-9883(97)00012-1.
- 3 H. R. Johnson, P. M. Crawford and J. W. Bunger, *Strategic significance of America's oil shale resource: Volume 2--oil shale resources technology and economics*, <http://repository.icse.utah.edu/dspace/handle/123456789/10015>, Date Accessed: July.2016.
- 4 T. A. Boden, G. Marland and R. J. Andres, "*Global, Regional, and National Fossil-Fuel CO2 Emissions*" 2013, 10.3334/CDIAC/00001_V2013.
- 5 S. Y. Wang, L. Hipps, R. R. Gillies and J. H. Yoon, *Geophys. Res. Lett.*, 2014, **41**, 3220–3226, 10.1002/2014GL059748.
- 6 S. C. Singhal and K. Kendall, "*High-temperature solid oxide fuel cells: fundamentals, design, and applications*", 1st Edition, Elsevier B.V. 2003.
- 7 R. J. Braun, S. A. Klein and D. T. Reindl, *J. Power Sources*, 2006, **158**, 1290–1305, 10.1016/j.jpowsour.2005.10.064.
- 8 P. T. Moseley, *J. Power Sources*, 2001, **93**, 285, 10.1016/S0378-7753(00)00571-1.
- 9 J. Larminie and A. Dicks, "*Fuel Cell Systems Explained*", 2nd Edition, John Wiley & Sons Ltd, 2000, 10.1016/S0378-7753(00)00571-1.
- 10 L. Malavasi, C. A. J. Fisher and M. S. Islam, *Chem. Soc. Rev.*, 2010, **39**, 4370–4387, 10.1039/b915141a.

- 11 E. Ivers-Tiffée, A. Weber and D. Herbstritt, *J. Eur. Ceram. Soc.*, 2001, **21**, 1805–1811, 10.1016/S0955-2219(01)00120-0.
- 12 S. Shen and M. Ni, *Int. J. Hydrogen Energy*, 2015, **40**, 5160–5168, 10.1016/j.ijhydene.2015.02.074.
- 13 B. C. Steele and A. Heinzl, *Nature*, 2001, **414**, 345–352, 10.1038/35104620.
- 14 S. J. Skinner and J. A. Kilner, *Mater. Today*, 2003, **6**, 30–37, 10.1016/S1369-7021(03)00332-8.
- 15 M. Chen, Y. L. Liu, A. Hagen, et al., *Fuel Cells*, 2009, **9**, 833–840, 10.1002/fuce.200800129.
- 16 S. Tao, F. W. Poulsen, G. Meng and O. T. Sørensen, *J. Mater. Chem.*, 2000, **10**, 1829–1833, 10.1039/b003890n.
- 17 J. M. Polfus, T. S. Bjørheim, T. Norby and R. Bredesen, *J. Mater. Chem. A*, 2016, **4**, 7437–7444, 10.1039/C6TA02067D.
- 18 X. Kuang, M. A. Green, H. Niu, et al., *Nat. Mater.*, 2008, **7**, 498–504, 10.1038/nmat2201.
- 19 M. R. Li, X. Kuang, S. Y. Chong, et al., *Angew. Chem. Int. Ed. Engl.*, 2010, **49**, 2362–2366, 10.1002/anie.200906220.
- 20 P. Lacorre, F. Goutenoire, O. Bohnke, et al., *Nature*, 2000, **404**, 856–858, 10.1038/35009069.
- 21 V. V. Kharton, F. M. B. Marques and A. Atkinson, *Solid State Ion.*, 2004, **174**, 135–149, 10.1016/j.ssi.2004.06.015.
- 22 P. Aldebert and J.-P. Traverse, *J. Am. Ceram. Soc.*, 1985, **68**, 34–40, 10.1111/j.1151-2916.1985.tb15247.x.
- 23 J. W. Fergus, *J. Power Sources*, 2006, **162**, 30–40, 10.1016/j.jpowsour.2006.06.062.
- 24 R. P. O. Hayre and F. B. Prinz, "*Fuel Cell Fundamentals*", 3rd Edition, John Wiley & Sons, 2016.
- 25 O. Yamamoto, Y. Arati, Y. Takeda, et al., *Solid State Ion.*, 1995, **79**, 137–142, 10.1016/0167-2738(95)00044-7.
- 26 S. Charojrochkul, K. L. Choy and B. C. H. Steele, *Solid State Ion.*, 1999, **121**, 107–113,

- 10.1016/S0167-2738(98)00536-0.
- 27 H. Yahiro, K. Eguchi and H. Arai, *Solid State Ion.*, 1989, **36**, 71–75, 10.1016/0167-2738(89)90061-1.
- 28 D. J. Seo, K. O. Ryu, S. Bin Park, et al., *Mater. Res. Bull.*, 2006, **41**, 359–366, 10.1016/j.materresbull.2005.08.012.
- 29 J. B. Goodenough, *Annu. Rev. Mater. Res.*, 2003, **33**, 91–128, 10.1146/annurev.matsci.33.022802.091651.
- 30 R. D. Bayliss, S. N. Cook, S. Kotsantonis, et al., *Adv. Energy Mater.*, 2014, **4**, 1301575, 10.1002/aenm.201301575.
- 31 P. Patnaik, "*Handbook of Inorganic Chemicals*", McGraw-Hill 2003.
- 32 T. Takahashi, T. Esaka and H. Iwahara, *J. Appl. Electrochem.*, 1977, **7**, 299–302, 10.1007/BF01059169.
- 33 T. Takahashi, T. Esaka and H. Iwahara, *J. Appl. Electrochem.*, 1975, **5**, 197–202, 10.1007/BF01637269.
- 34 P. M. Woodward, *Acta Crystallogr. B*, 1997, **53**, 44–66, 10.1107/S0108768196012050.
- 35 C. A. Hancock, R. C. T. Slade, J. R. Varcoe and P. R. Slater, *J. Solid State Chem.*, 2011, **184**, 2972–2977, 10.1016/j.jssc.2011.08.040.
- 36 T. Ishihara, *Solid State Ion.*, 1998, **113–115**, 593–600, 10.1016/S0167-2738(98)00390-7.
- 37 K. Huang, M. Feng and J. B. Goodenough, *J. Am. Ceram. Soc.*, 1996, **79**, 1100–1104, 10.1111/j.1151-2916.1996.tb08554.x.
- 38 K. Huang, J.-H. Wan and J. B. Goodenough, *J. Electrochem. Soc.*, 2001, **148**, A788, 10.1149/1.1378289.
- 39 M. Li, M. J. Pietrowski, R. a De Souza, et al., *Nat. Mater.*, 2014, **13**, 31–5, 10.1038/nmat3782.
- 40 M. Li, H. Zhang, S. N. Cook, et al., *Chem. Mater.*, 2015, **27**, 629–634, 10.1021/cm504475k.
- 41 K. D. Kreuer, *Annu. Rev. Mater. Res.*, 2003, **33**, 333–359, 10.1146/annurev.matsci.33.022802.091825.

- 42 K. D. Kreuer, T. Dippel, Y. M. Baikov and J. Maier, *Solid State Ion.*, 1996, **86–88**, 613–620, 10.1016/0167-2738(96)00221-4.
- 43 W. Münch, G. Seifert, K. D. Kreuer and J. Maier, *Solid State Ion.*, 1996, **86–88**, 647–652, 10.1016/0167-2738(96)00229-9.
- 44 H. Iwahara, *Solid State Ion.*, 1988, **28–30**, 573–578, 10.1016/S0167-2738(88)80104-8.
- 45 T. Yajima, H. Kazeoka, T. Yogo and H. Iwahara, *Solid State Ion.*, 1991, **47**, 271–275, 10.1016/0167-2738(91)90249-B.
- 46 H. Iwahara, T. Yajima, T. Hibino, et al., *Solid State Ion.*, 1993, **61**, 65–69, 10.1016/0167-2738(93)90335-Z.
- 47 K. D. Kreuer, *Solid State Ion.*, 1997, **97**, 1–15, 10.1016/S0167-2738(97)00082-9.
- 48 L. Bi and E. Traversa, *J. Mater. Res.*, 2013, **29**, 1–15, 10.1557/jmr.2013.205.
- 49 H. Iwahara, H. Uchida and N. Maeda, *J. Power Sources*, 1982, **7**, 293–301, 10.1016/0378-7753(82)80018-9.
- 50 D. Pergolesi, E. Fabbri, A. D’Epifanio, et al., *Nat. Mater.*, 2010, **9**, 846–852, 10.1038/nmat2837.
- 51 S. V. Bhide, *J. Electrochem. Soc.*, 1999, **146**, 2038, 10.1149/1.1391888.
- 52 M. Shirpour, R. Merkle and J. Maier, *Solid State Ion.*, 2012, **225**, 304–307, 10.1016/j.ssi.2012.03.026.
- 53 M. Shirpour, B. Rahmati, W. Sigle, et al., *J. Phys. Chem. C*, 2012, **116**, 2453–2461, 10.1021/jp208213x.
- 54 J. C. Boivin, *Int. J. Inorg. Mater.*, 2001, **3**, 1261–1266, 10.1016/S1466-6049(01)00118-0.
- 55 S. S. Pramana, W. T. Klooster and T. J. White, *Acta Crystallogr. Sect. B Struct. Sci.*, 2007, **63**, 597–602, 10.1107/S0108768107024317.
- 56 R. Ali, M. Yashima, Y. Matsushita, et al., *Chem. Mater.*, 2008, **20**, 5203–5208, 10.1021/cm7035234.
- 57 C. Argirusis, E. Jothinathan, G. Sourkouni, et al., *Solid State Ion.*, 2014, **257**, 53–59, 10.1016/j.ssi.2014.01.035.
- 58 R. J. Packer and S. J. Skinner, *Adv. Mater.*, 2010, **22**, 1613–1616,

- 10.1002/adma.200902692.
- 59 S. S. Pramana, T. Baikie, T. An, et al., *J. Am. Chem. Soc.*, 2016, **138**, 1273–1279, 10.1021/jacs.5b11373.
- 60 P. Berastegui, S. Hull, F. J. Garc  Garc  and J. Grins, *J. Solid State Chem.*, 2002, **168**, 294–305, 10.1006/jssc.2002.9724.
- 61 E. J. Abram, D. C. Sinclair and A. R. West, *J. Mater. Chem.*, 2001, **11**, 1978–1979, 10.1039/b104006p.
- 62 H. Arikawa, H. Nishiguchi, T. Ishihara and Y. Takita, *Solid State Ion.*, 2000, **136–137**, 31–37, 10.1016/S0167-2738(00)00386-6.
- 63 E. Kendrick, M. S. Islam and P. R. Slater, *J. Mater. Chem.*, 2007, **17**, 3104–3111, 10.1039/B704426G.
- 64 S. Nakayama and M. Highchi, *J. Mater. Sci. Lett.*, 2001, **20**, 913–915, 10.1023/A:1010928800227.
- 65 M. Higuchi, Y. Masubuchi, S. Nakayama, et al., *Solid State Ion.*, 2004, **174**, 73–80, 10.1016/j.ssi.2004.05.028.
- 66 Y. Masubuchi, M. Higuchi, S. Kikkawa, et al., *Solid State Ion.*, 2004, **175**, 357–360, 10.1016/j.ssi.2003.12.029.
- 67 J. E. H. Sansom, J. R. Tolchard, M. S. Islam, et al., *J. Mater. Chem.*, 2006, **16**, 1410–1413, 10.1039/b600122j.
- 68 A. Jones, P. R. Slater and M. S. Islam, *Chem. Mater.*, 2008, **20**, 5055–5060, 10.1021/cm801101j.
- 69 P. R. Slater, J. E. H. Sansom and J. R. Tolchard, *Chem. Rec.*, 2004, **4**, 373–384, 10.1002/tcr.20028.
- 70 P. Lacorre, *Solid State Sci.*, 2000, **2**, 755–758, 10.1016/S1293-2558(00)01106-7.
- 71 L. M. Schoop, L. M chler, C. Felser and R. J. Cava, *Inorg. Chem.*, 2013, **52**, 5479–5483, 10.1021/ic400381g.
- 72 A. Walsh, D. J. Payne, R. G. Egdell and G. W. Watson, *Chem. Soc. Rev.*, 2011, **40**, 4455–4463, 10.1039/c1cs15098g.
- 73 I. R. Evans, J. A. K. Howard and J. S. O. Evans, *Chem. Mater.*, 2005, **17**, 4074–4077,

- 10.1021/cm050049+.
- 74 L. Malavasi, H. Kim, S. J. L. Billinge, et al., *J. Am. Chem. Soc.*, 2007, **129**, 6903–6907, 10.1021/ja071281e.
- 75 X. P. Wang and Q. F. Fang, *Phys. Rev. B*, 2002, **65**, 64304, 10.1103/PhysRevB.65.064304.
- 76 C. J. Hou, Y. D. Li, P. J. Wang, et al., *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2007, **76**, 14104, 10.1103/PhysRevB.76.014104.
- 77 D. Marrero-López, J. Canales-Vázquez, J. C. Ruiz-Morales, et al., *Electrochim. Acta*, 2005, **50**, 4385–4395, 10.1016/j.electacta.2005.02.002.
- 78 J. A. Collado, M. A. G. Aranda, A. Cabeza, et al., *J. Solid State Chem.*, 2002, **167**, 80–85, 10.1006/jssc.2002.9622.
- 79 F. X. Wei, T. Baikie, T. An, et al., *Inorg. Chem.*, 2012, **51**, 5941–5949, 10.1021/Ic300585t.
- 80 F. Wei, T. Baikie, T. An, et al., *J. Am. Chem. Soc.*, 2011, **133**, 15200–15211.
- 81 F. Rothlisberger, F. Seifert and M. Czank, *Eur. J. Miner.*, 1990, **2**, 585–594, 10.1127/ejm/2/5/0585.
- 82 C. I. Thomas, X. Kuang, Z. Deng, et al., *Chem. Mater.*, 2010, **22**, 2510–2516, 10.1021/cm903132w.
- 83 F. Wei, H. Gasparyan, P. J. Keenan, et al., *J. Mater. Chem. A*, 2015, **3**, 3091–3096, 10.1039/C4TA05132G.
- 84 H. Fu, C. Pan, L. Zhang and Y. Zhu, *Mater. Res. Bull.*, 2007, **42**, 696–706, 10.1016/j.materresbull.2006.07.017.
- 85 S. H. Yoon, D. W. Kim, S. Y. Cho and K. S. Hong, *J. Eur. Ceram. Soc.*, 2006, **26**, 2051–2054, 10.1016/j.jeurceramsoc.2005.09.058.
- 86 T. Esaka, T. Mina-ai and H. Iwahara, *Solid State Ion.*, 1992, **57**, 319–325, 10.1016/0167-2738(92)90165-L.
- 87 T. Esaka, *Solid State Ion.*, 2000, **136–137**, 1–9, 10.1016/S0167-2738(00)00377-5.
- 88 H. Fjeld, D. M. Kepaptsoglou, R. Haugsrud and T. Norby, *Solid State Ion.*, 2010, **181**, 104–109, 10.1016/j.ssi.2009.04.019.

- 89 D. Logvinovich, A. Arakcheeva, P. Pattison, et al., *Inorg. Chem.*, 2010, **49**, 1587–1594, 10.1021/ic9019876.
- 90 V. A. Morozov, A. Bertha, K. W. Meert, et al., *Chem. Mater.*, 2013, **25**, 4387–4395, 10.1021/cm402729r.
- 91 V. A. Morozov, A. V. Arakcheeva, P. Pattison, et al., *Chem. Mater.*, 2015, **27**, 5519–5530, 10.1021/acs.chemmater.5b01622.
- 92 N. Clavier, R. Podor and N. Dacheux, *J. Eur. Ceram. Soc.*, 2011, **31**, 941–976, 10.1016/j.jeurceramsoc.2010.12.019.
- 93 R. Haugrud and T. Norby, *Nat. Mater.*, 2006, **5**, 193–196, 10.1038/nmat1591.
- 94 C. Li, R. D. Bayliss and S. J. Skinner, *Solid State Ion.*, 2014, **262**, 530–535, 10.1016/j.ssi.2013.12.023.
- 95 W. I. F. David, *Mater. Res. Bull.*, 1983, **18**, 749–756, 10.1016/0025-5408(83)90103-4.
- 96 Y. Kuroiwa, H. Muramoto, T. Shobu, et al., *J. Phys. Soc. Japan*, 1995, **64**, 3798–3803.
- 97 P. Sarin, R. W. Hughes, D. R. Lowry, et al., *J. Am. Ceram. Soc.*, 2014, **97**, 3307–3319, 10.1111/jace.13095.
- 98 Oxford English Dictionary, *Oxford English Dictionary Online*, <http://dictionary.oed.com>, Date Accessed: June.2016.
- 99 C. Hammond, "*The Basics of Crystallography and Diffraction*", 3rd Edition, Oxford University Press, USA, 2009, 10.1088/0957-0233/13/2/708.
- 100 S. van Smaalen, "*Incommensurate Crystallography*", 1st Edition, Oxford Scholarship, 2008, 10.1093/acprof:oso/9780198570820.001.0001.
- 101 P. M. De Wolff, *Acta Crystallogr. Sect. A*, 1974, **30**, 777–785, 10.1107/S0567739474010710.
- 102 P. M. De Wolff, T. Janssen and A. Janner, *Acta Crystallogr. Sect. A*, 1981, **37**, 625–636, 10.1107/S0567739481001447.
- 103 J. Zussman, *Mineral. Mag.*, 1986, **50**, 355–355, 10.1180/minmag.1986.050.356.38.
- 104 M. I. Kay, B. C. Frazer and I. Almodovar, *J. Chem. Phys.*, 1964, **40**, 504–506, 10.1063/1.1725144.
- 105 J. Martinez-Garcia, A. Arakcheeva, P. Pattison, et al., *Philos. Mag. Lett.*, 2009, **89**,

- 257–266, 10.1080/09500830902802657.
- 106 V. A. Morozov, A. V. Arakcheeva, G. Chapuis, et al., *Chem. Mater.*, 2006, **18**, 4075–4082, 10.1021/cm0605668.
 - 107 A. Arakcheeva, P. Pattison, G. Chapuis, et al., *Acta Crystallogr. Sect. B Struct. Sci.*, 2008, **64**, 160–171, 10.1107/S0108768108001870.
 - 108 V. A. Morozov, A. V. Mironov, B. I. Lazoryak, et al., *J. Solid State Chem.*, 2006, **179**, 1183–1191, 10.1016/j.jssc.2005.12.041.
 - 109 V. Morozov, A. Arakcheeva, B. Redkin, et al., *Inorg. Chem.*, 2012, **51**, 5313–5324, 10.1021/ic300221m.
 - 110 A. Arakcheeva and G. Chapuis, *Acta Crystallogr. Sect. B Struct. Sci.*, 2008, **64**, 12–25, 10.1107/S010876810705923X.
 - 111 H. Lind and S. Lidin, *Solid State Sci.*, 2003, **5**, 47–57, 10.1016/S1293-2558(02)00080-8.
 - 112 A. Arakcheeva and G. Chapuis, *Acta Crystallogr. Sect. B Struct. Sci.*, 2006, **62**, 52–59, 10.1107/S0108768105034671.
 - 113 J. G. Thompson, R. L. Withers and F. J. Brink, *J. Solid State Chem.*, 1999, **143**, 122–131, 10.1006/jssc.1998.8096.
 - 114 V. Morozov, A. Arakcheeva, B. Redkin, et al., *Inorg. Chem.*, 2012, **51**, 5313–5324, 10.1021/ic300221m.
 - 115 Q. Lin, X. Feng and J. Chen, *J. Alloys Compd.*, 2000, **307**, 245–248.
 - 116 V. Brizé, S. Georges, S. Kodjikian, et al., *J. Solid State Chem.*, 2004, **177**, 2617–2627, 10.1016/j.jssc.2004.03.016.
 - 117 A. V. Arakcheeva, D. Logvinovich, G. Chapuis, et al., *Chem. Sci.*, 2012, **3**, 384, 10.1039/c1sc00289a.
 - 118 V. A. Morozov, B. I. Lazoryak, S. Z. Shmurak, et al., *Chem. Mater.*, 2014, **26**, 3238–3248, 10.1021/cm500966g.
 - 119 H. Huang, X. Feng, W. Zhu, et al., *J. Phys. Condens. Matter*, 2003, **15**, 5689–5695, 10.1088/0953-8984/15/33/303.
 - 120 T. Esaka, R. Tachibana and S. Takai, *Solid State Ion.*, 1996, **92**, 129–133,

- 10.1016/S0167-2738(96)00462-6.
- 121 J. Cheng, C. Liu, W. Cao, et al., *Mater. Res. Bull.*, 2011, **46**, 185–189, 10.1016/j.materresbull.2010.11.019.
- 122 S. Takai, K. Sugiura and T. Esaka, *Mater. Res. Bull.*, 1999, **34**, 193–202, 10.1016/S0025-5408(99)00010-0.
- 123 J. Cheng, W. Bao, C. Han and W. Cao, *J. Power Sources*, 2010, **195**, 1849–1853, 10.1016/j.jpowsour.2009.10.017.
- 124 N. Nallamuthu, I. Prakash, N. Satyanarayana and M. Venkateswarlu, *Mater. Res. Bull.*, 2011, **46**, 32–41, 10.1016/j.materresbull.2010.10.001.
- 125 J. Cheng, C. Tian and D. Zhao, *J. Solid State Electrochem.*, 2011, **16**, 753–758, 10.1007/s10008-011-1423-7.
- 126 W. L. Zhu, X. Q. Feng, Y. L. Huang, et al., *Phys. Status Solidi Appl. Res.*, 2002, **193**, 211–216, 10.1002/1521-396X(200209)193:2<211::AID-PSSA211>3.0.CO;2-B.
- 127 H. Huang, X. Feng, Z. Man, et al., *J. Appl. Phys.*, 2003, **93**, 421–425, 10.1063/1.1519956.
- 128 P. Manning, *Solid State Ion.*, 1996, **93**, 125–132, 10.1016/S0167-2738(96)00514-0.
- 129 T. Ishihara, H. Arikawa, T. Akbay, et al., *J. Am. Chem. Soc.*, 2001, **123**, 203–209, 10.1021/ja0014537.
- 130 R. J. Packer, P. A. Stuart and S. J. Skinner, *J. Solid State Chem.*, 2008, **181**, 1445–1455, 10.1016/j.jssc.2008.03.016.
- 131 R. J. Packer, S. J. Skinner, A. A. Yaremchenko, et al., *J. Mater. Chem.*, 2006, **16**, 3503, 10.1039/b606261j.
- 132 F. Vullum, F. Nitsche, S. M. Selbach and T. Grande, *J. Solid State Chem.*, 2008, **181**, 2580–2585, 10.1016/j.jssc.2008.06.032.
- 133 E. V. Tsipis, V. V. Kharton, N. P. Vyshatko, et al., *J. Solid State Chem.*, 2003, **176**, 47–56, 10.1016/S0022-4596(03)00342-6.
- 134 R. J. Cava, R. S. Roth, T. Negas, et al., *J. Solid State Chem.*, 1981, **40**, 318–329, 10.1016/0022-4596(81)90398-4.
- 135 F. Goutenoire, S. Kodjikian and E. Suard, *J. Solid State Chem.*, 2005, **178**, 2811–2817,

- 10.1016/j.jssc.2005.06.020.
- 136 R. D. Bayliss, "*Synthetic, Structural and Electrochemical Studies of Superstructured Rare-Earth Niobates*", Ph.D. thesis, Department of Materials, Imperial College London, 2014.
- 137 M. A. Laguna-Bercero, R. D. Bayliss and S. J. Skinner, *Solid State Ion.*, 2014, **262**, 298–302, 10.1016/j.ssi.2013.11.039.
- 138 M. J. Scholten, J. Schoonman, J. C. van Miltenburg and H. A. J. Oonk, *Solid State Ion.*, 1993, **61**, 83–91, 10.1016/0167-2738(93)90338-4.
- 139 K. D. Kreuer, *Solid State Ion.*, 1999, **125**, 285–302, 10.1016/S0167-2738(99)00188-5.
- 140 Z. Bi, J. Peña-Martínez, J. H. Kim, et al., *Int. J. Hydrogen Energy*, 2012, **37**, 12751–12759, 10.1016/j.ijhydene.2012.06.014.
- 141 T. Mokkelbost, I. Kaus, R. Haugrud, et al., *J. Am. Ceram. Soc.*, 2008, **91**, 879–886, 10.1111/j.1551-2916.2007.02232.x.
- 142 B. A. D., J. Gracio, G. C. Mather, et al., *J. Solid State Chem.*, 2011, **184**, 863–870, 10.1016/j.jssc.2011.02.012.
- 143 M. Amsif, D. Marrero-López, J. C. Ruiz-Morales, et al., *J. Eur. Ceram. Soc.*, 2012, **32**, 1235–1244, 10.1016/j.jeurceramsoc.2011.11.027.
- 144 G. E. Syvertsen, A. Magrasó, R. Haugrud, et al., *Int. J. Hydrogen Energy*, 2012, **37**, 8017–8026, 10.1016/j.ijhydene.2011.10.113.
- 145 E. Kendrick, K. S. Knight, M. S. Islam and P. R. Slater, *Solid State Ion.*, 2007, **178**, 943–949, 10.1016/j.ssi.2007.05.002.
- 146 X. Chi, Z. Wen, J. Zhang and Y. Liu, *Solid State Ion.*, 2014, **268**, 326–329, 10.1016/j.ssi.2014.06.013.
- 147 C. Harris, "*Structure, redox and transport properties of acceptor doped cerium niobates*", Ph.D. thesis, Department of Materials, Imperial College London, 2015.
- 148 F. Iguchi, T. Tsurui, N. Sata, et al., *Solid State Ion.*, 2009, **180**, 563–568, 10.1016/j.ssi.2008.12.006.
- 149 L. Bi, E. Fabbri, Z. Sun and E. Traversa, *Energy Environ. Sci.*, 2011, **4**, 1352, 10.1039/c0ee00387e.

- 150 G. Syvertsen and C. Estournès, *J. Am. Ceram. Soc.*, 2012, **95**, 1563–1571, 10.1111/j.1551-2916.2012.05101.x.
- 151 S. Wachowski, A. Mielewczyk-Gryn and M. Gazda, *J. Solid State Chem.*, 2014, **219**, 201–209, 10.1016/j.jssc.2014.07.041.
- 152 S. Wachowski, A. Mielewczyk-Gryń, K. Zagórski, et al., *J. Chem. Inf. Model.*, 2013, **53**, 1689–1699, 10.1017/CBO9781107415324.004.
- 153 A. D. Brandão, I. Antunes, J. R. Frade, et al., *Chem. Mater.*, 2010, **22**, 6673–6683, 10.1021/cm102705e.
- 154 G. Kresse, O. Dulub and U. Diebold, *Phys. Rev. B*, 2003, **68**, 1–15, 10.1103/PhysRevB.68.245409.
- 155 C. Noguera, *J. Phys. Condens. Matter*, 2000, **12**, R367--R410, 10.1088/0953-8984/12/31/201.
- 156 F. J. Giessibl, *Science*, 1995, **267**, 68–71, 10.2307/2886041.
- 157 H. H. Brongersma, M. de Ridder, A. Gildenpfennig and M. M. Viitanen, *J. Eur. Ceram. Soc.*, 2003, **23**, 2761–2767, 10.1016/S0955-2219(03)00287-5.
- 158 J. Druce, H. Téllez, M. Burriel, et al., *Energy Environ. Sci.*, 2014, **7**, 3893–3599, 10.1039/C4EE01497A.
- 159 H. Téllez, J. Druce, Y. W. Ju, et al., *Int. J. Hydrogen Energy*, 2014, **39**, 20856–20863, 10.1016/j.ijhydene.2014.06.102.
- 160 M. De Ridder, A. G. J. Vervoort, R. G. Van Welzenis and H. H. Brongersma, *Solid State Ion.*, 2003, **156**, 255–262, 10.1016/S0167-2738(02)00754-3.
- 161 H. H. Brongersma, M. Draxler, M. de Ridder and P. Bauer, *Surf. Sci. Rep.*, 2007, **62**, 63–109, 10.1016/j.surfrep.2006.12.002.
- 162 H. J. M. Bouwmeester, H. Kruidhof and A. J. Burggraaf, *Solid State Ion.*, 1994, **72**, 185–194, 10.1016/0167-2738(94)90145-7.
- 163 H. Dulli, P. A. Dowben, S. H. Liou and E. W. Plummer, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2000, **62**, 629–632, 10.1103/PhysRevB.62.R14629.
- 164 M. Finsterbusch, A. Lussier, J. A. Schaefer and Y. U. Idzerda, *Solid State Ion.*, 2012, **212**, 77–80, 10.1016/j.ssi.2012.02.006.

- 165 W. Araki, T. Yamaguchi, Y. Arai and J. Malzbender, *Solid State Ion.*, 2014, **268**, 1–6, 10.1016/j.ssi.2014.09.019.
- 166 Y. Orikasa, E. J. Crumlin, S. Sako, et al., *ECS Electrochem. Lett.*, 2014, **3**, F23–F26, 10.1149/2.006404eel.
- 167 G. M. Rupp, A. Limbeck, M. Kubicek, et al., *J. Mater. Chem. A*, 2014, **2**, 7099–7108, 10.1039/c3ta15327d.
- 168 Y. Chen, H. Téllez, M. Burriel, et al., *Chem. Mater.*, 2015, **27**, 5436–5450, 10.1021/acs.chemmater.5b02292.
- 169 M. De Ridder, R. G. Van Welzenis, H. H. Brongersma, et al., *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, 2002, **190**, 732–735, 10.1016/S0168-583X(01)01268-X.
- 170 J. Nowotny, C. C. Sorrell and T. Bak, *Surf. Interface Anal.*, 2005, **37**, 316–324, 10.1002/sia.2023.
- 171 S. H. Overbury, P. A. Bertrand and G. A. Somorjai, *Chem. Rev.*, 1975, **75**, 547–560, 10.1021/cr60297a001.
- 172 K. Lehovec, *J. Chem. Phys.*, 1953, **21**, 1123, 10.1063/1.1699148.
- 173 P. W. Tasker, *J. Phys. C Solid State Phys.*, 1979, **12**, 4977–4984, 10.1088/0022-3719/12/22/036.
- 174 N. Erdman, K. R. Poeppelmeier, M. Asta, et al., *Nature*, 2002, **419**, 55–58, 10.1038/nature01010.
- 175 W. Lee, J. W. Han, Y. Chen, et al., *J. Am. Chem. Soc.*, 2013, **135**, 7909–7925, 10.1021/ja3125349.
- 176 A. Chronos, B. Yildiz, A. Tarancón, et al., *Energy Environ. Sci.*, 2011, **4**, 2774, 10.1039/c0ee00717j.
- 177 H. Ding, A. V Virkar, M. Liu and F. Liu, *Phys Chem Chem Phys*, 2013, **15**, 489–496, 10.1039/c2cp43148c.
- 178 Y. Chen, W. Jung, Z. Cai, et al., *Energy Environ. Sci.*, 2012, **5**, 7979, 10.1039/c2ee21463f.
- 179 M. Kubicek, A. Limbeck, T. Frömling, et al., *J. Electrochem. Soc.*, 2011, **158**, B727,

- 10.1149/1.3581114.
- 180 B. C. H. Steele, *Solid State Ion.*, 1997, **94**, 239–248, DOI: 10.1016/S0167-2738(96)00510-3.
 - 181 M. De Ridder, R. G. Van Welzenis, H. H. Brongersma and U. Kreissig, *Solid State Ion.*, 2003, **158**, 67–77, 10.1016/S0167-2738(02)00759-2.
 - 182 K. D. Kreuer, S. Adams, W. Münch, et al., *Solid State Ion.*, 2001, **145**, 295–306, 10.1016/S0167-2738(01)00953-5.
 - 183 S. B. C. Duval, P. Holtappels, U. F. Vogt, et al., *Solid State Ion.*, 2007, **178**, 1437–1441, DOI 10.1016/j.ssi.2007.08.006.
 - 184 Y. Yamazaki, R. Hernandez-Sanchez and S. M. Haile, *Chem. Mater.*, 2009, **21**, 2755–2762, 10.1021/cm900208w.
 - 185 C. Kjøseth, H. Fjeld, Ø. Prytz, et al., *Solid State Ion.*, 2010, **181**, 268–275, 10.1016/j.ssi.2010.01.014.
 - 186 A. Tomita and T. Hibino, *Sci. Technol.*, 2004, **9**, 2493–2497.
 - 187 T. Hibino, A. Hashimoto, M. Suzuki and M. Sano, *J. Phys. Chem. B*, 2001, **105**, 11399–11401, 10.1021/jp0124342.
 - 188 T. S. Sinclair, B. M. Hunter, J. R. Winkler, et al., *Mater. Horiz.*, 2015, **2**, 330–337, 10.1039/C4MH00156G.
 - 189 Z. Zhao, H. Dai, J. Deng, et al., *Cuihua Xuebao/Chinese J. Catal.*, 2013, **34**, 1617–1626, 10.1016/S1872-2067(12)60632-9.
 - 190 H. He, S. P. Berglund, A. J. E. Rettie, et al., *J. Mater. Chem. A*, 2014, **2**, 9371–9379, 10.1039/c4ta00895b.
 - 191 W. Wang, P. Yang, S. Gai, et al., *J. Nanoparticle Res.*, 2010, **12**, 2295–2305, 10.1007/s11051-010-9850-4.
 - 192 X. Liu, L. Li, H. M. Noh, et al., *RSC Adv.*, 2015, **5**, 9441–9454, 10.1039/C4RA12183J.
 - 193 R. Adhikari, S. Malla, G. Gyawali, et al., *Mater. Res. Bull.*, 2013, **48**, 3367–3373, 10.1016/j.materresbull.2013.05.019.
 - 194 T. G. Cooper and N. H. De Leeuw, *Surf. Sci.*, 2003, **531**, 159–176, 10.1016/S0039-6028(03)00362-5.

- 195 K. Hadidi, R. Hancke, T. Norby, et al., *Int. J. Hydrogen Energy*, 2012, **37**, 6674–6685, 10.1016/j.ijhydene.2012.01.065.
- 196 F. Y. Yan, Z. G. Liu, J. H. Ouyang and M. F. Yan, *Int. J. Hydrogen Energy*, 2014, **39**, 1457–1462, 10.1016/j.ijhydene.2013.11.018.
- 197 D. M. Kepaptsoglou, K. Hadidi, O.-M. Løvvik, et al., *Chem. Mater.*, 2012, **24**, 4152–4159, 10.1021/cm302317f.
- 198 K. Hadidi, T. Norby, O. M. Løvvik and A. E. Gunnæs, *Int. J. Hydrogen Energy*, 2012, **37**, 8033–8042, 10.1016/j.ijhydene.2011.11.032.
- 199 J. Goldstein, D. E. Newbury, D. C. Joy, et al., "*Scanning Electron Microscopy and X-ray Microanalysis*", 3rd Edition, Springer, 2003.
- 200 D. B. Williams and C. B. Carter, "*Transmission Electron Microscopy*", 1st Edition, Springer, 1996.
- 201 J. Mayer, L. a Giannuzzi, T. Kamino and J. Michael, *MRS Bull.*, 2007, **32**, 400–407, 10.1557/mrs2007.63.
- 202 L. Dünkel, *Zeitschrift für Phys. Chemie*, 1997, **198**, 273–274, 10.1524/zpch.1997.198.Part_1_2.273.
- 203 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65–71, 10.1107/S0021889869006558.
- 204 B. H. Toby, *Powder Diffr.*, 2006, **21**, 67–70, 10.1154/1.2179804.
- 205 L. B. McCusker, R. B. Von Dreele, D. E. Cox, et al., *J. Appl. Crystallogr.*, 1999, **32**, 36–50, 10.1107/S0021889898009856.
- 206 V. Petříček, M. Dušek and L. Palatinus, *Zeitschrift für Krist.*, 2014, **229**, 345–352, 10.1515/zkri-2014-1737.
- 207 CrystalMaker Software Ltd, *CrystalMaker for Windows*, <http://www.crystalmaker.com/>.
- 208 R. M. Ibberson, W. I. F. David and K. S. Knight, *High Resolution Powder Diffractometer (HRPD) at ISIS. A User Guide*.
- 209 B. L. Henke, E. M. Gullikson and J. C. Davis, *At. Data Nucl. Data Tables*, 1993, **54**, 181–342, 10.1006/adnd.1993.1013.
- 210 Industrial Materials Group, *Powder Diffraction on the WEB*, <http://pd.chem.ucl.ac.uk/pd/welcome.htm>, Date Accessed: July.2016.

- 211 S. Fearn, "*An Introduction to Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and its Application to Materials Science*", Morgan & Claypool Publishers, 2015, 10.1088/978-1-6817-4088-1.
- 212 J. C. Vickerman and I. S. Gilmore, "*Surface Analysis – The Principal Techniques 2nd Edition*", 2nd Edition, John Wiley & Sons, 2009.
- 213 S. N. Cook, "*Single and Multi-Layered Thin Film Oxides for Potential Fuel Cell Applications*", Ph.D. thesis, Department of Materials, Imperial College London.
- 214 ION.TO F GmbH, *Qtac-100 Brochure*, https://www.iontof.com/download/IONTOF_Qtac_Brochure.pdf, Date Accessed: Sep.2016.
- 215 E. Barsoukov and J. R. Macdonald, "*Impedance Spectroscopy: Theory, Experiment, and Applications*", 2nd Revised Edition, Wiley-Blackwell, 2005, 10.1002/0471716243.
- 216 J. T. S. Irvine, D. C. Sinclair and A. R. West, *Adv. Mater.* 1990 2132–138.
- 217 H. Mehrer, "*Diffusion in solids: fundamentals, methods, materials, diffusion-controlled processes*", Springer Berlin Heidelberg, 2007, 10.1007/978-3-540-71488-0.
- 218 J. A. Kilner, B. C. H. Steele and L. Ilkov, *Solid State Ion.*, 1984, **12**, 89–97, 10.1016/0167-2738(84)90134-6.
- 219 J. Crank, "*The Mathematics of Diffusion*", Oxford University Press 1979.
- 220 R. J. Chater, "*Oxygen self-diffusion and surface exchange measurements of the polycrystalline oxide (La_{0.8}Sr_{0.2})(Cr_{0.2}Fe_{0.8})O_{3-d} using Secondary Ion Mass Spectrometry*", Ph.D. thesis, Department of Materials, Imperial College London, 2014.
- 221 D. R. Killoran, *J. Electrochem. Soc.*, 1962, **109**, 170–171, 10.1149/1.2425354.
- 222 R. A. De Souza, J. A. Kilner and J. F. Walker, *Mater. Lett.*, 2000, **43**, 43–52, 10.1016/S0167-577X(99)00228-1.
- 223 J. Liu, "*Mass Transport and Electrochemical Properties of La₂Mo₂O₉ as a Fast Ionic Conductor*", Department of Materials, Imperial College London, 2010.
- 224 R. J. Chater and D. S. McPhail, *Appl. Surf. Sci.*, 2004, **231–232**, 834–839, 10.1016/j.apsusc.2004.03.135.
- 225 R. J. Packer, E. V. Tsipis, C. N. Munnings, et al., *Solid State Ion.*, 2006, **177**, 2059–

- 2064, 10.1016/j.ssi.2006.03.044.
- 226 C. Ferrara, A. Mancini, C. Ritter, et al., *J. Mater. Chem. A*, 2015, **3**, 22258–22265, 10.1039/c5ta06575e.
- 227 D. Marrero-López, J. Peña-Martínez, J. C. Ruiz-Morales and P. Núñez, *J. Solid State Chem.*, 2008, **181**, 253–262, 10.1016/j.jssc.2007.11.024.
- 228 T. Mokkelbost, Ø. Andersen, R. A. Strøm, et al., *J. Am. Ceram. Soc.*, 2007, **90**, 3395–3400, 10.1111/j.1551-2916.2007.01904.x.
- 229 H. T. Stokes, B. J. Campbell and S. Van Smaalen, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2011, **67**, 45–55, 10.1107/S0108767310042297.
- 230 O. Prytz and J. Taftø, *Acta Mater.*, 2005, **53**, 297–302, 10.1016/j.actamat.2004.09.023.
- 231 L. Jian and C. M. Wayman, *J. Am. Ceram. Soc.*, 1996, **79**, 1642–1648, 10.1111/j.1151-2916.1996.tb08776.x.
- 232 T. Mokkelbost, H. L. Lein, P. E. Vullum, et al., *Ceram. Int.*, 2009, **35**, 2877–2883, 10.1016/j.ceramint.2009.03.041.
- 233 P. A. Stadelmann, *JEMS - EMS java version, 2004.*, <http://www.jems-saas.ch/>.
- 234 G. Courbion and G. Ferey, *J. Solid State Chem.*, 1988, **76**, 426–431, 10.1016/0022-4596(88)90239-3.
- 235 S. Tsunekawa, T. Kamiyama, K. Sasaki, et al., *Acta Crystallogr. Sect. A*, 1993, **49**, 595–600, 10.1107/S0108767392013035.
- 236 K. Jurkschat, P. Sarin, L. F. Siah and W. M. Kriven, *Adv. X-ray Anal.*, 2004, **47**, 357–362.
- 237 P. Scardi and M. Leoni, *J. Appl. Crystallogr.*, 1999, **32**, 671–682, 10.1107/S002188989900374X.
- 238 T. K. Wallace, R. H. Colman and A. C. McLaughlin, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8672–7, 10.1039/c2cp43732e.
- 239 O. Eibl, *Phys. C Supercond. its Appl.*, 1990, **169**, 441–450.
- 240 S. Tsunekawa and H. Takei, *Phys. Status Solidi*, 1978, **50**, 695–702, 10.1002/pssa.2210500240.
- 241 P. W. Stephens, *J. Appl. Crystallogr.*, 1999, **32**, 281–289,

- 10.1107/S0021889898006001.
- 242 A. M. Abakumov, V. A. Morozov, A. A. Tsirlin, et al., *Inorg. Chem.*, 2014, **53**, 9407–9415, 10.1021/ic5015412.
- 243 R. D. Shannon, *Acta Crystallogr. Sect. A*, 1976, **32**, 751–767, 10.1107/S0567739476001551.
- 244 A. M. Abakumov, V. A. Morozov, A. A. Tsirlin, et al., *Inorg. Chem.*, 2014, **53**, 9407–15, 10.1021/ic5015412.
- 245 I. D. Brown, *Chem. Soc. Rev.*, 1978, **7**, 359, 10.1039/cs9780700359.
- 246 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B, Struct. Sci.*, 1985, **41**, 244–247, 10.1107/S0108768185002063.
- 247 L. Carrillo, M. E. Villafuerte-Castrejón, G. González, et al., *J. Mater. Sci.*, 2000, **35**, 3047–3052, 10.1023/A:1004863715548.
- 248 K. P. F. Siqueira, J. C. Soares, E. Granado, et al., *J. Solid State Chem.*, 2014, **209**, 63–68, 10.1016/j.jssc.2013.10.015.
- 249 S. S. Pramana, T. Baikie, T. An, et al., 2016, 4–10, 10.1021/jacs.5b11373.
- 250 M. A. Laguna-Bercero, R. D. Bayliss and S. J. Skinner, *Solid State Ion.*, 2014, **262**, 298–302, 10.1016/j.ssi.2013.11.039.
- 251 L. Malavasi, *Dalt. Trans.*, 2011, **40**, 3777–3788, 10.1039/c0dt01355b.
- 252 S. J. Skinner and Y. Kang, *Solid State Sci.*, 2003, **5**, 1475–1479, 10.1016/j.solidstatesciences.2003.09.001.
- 253 G. Corbel, S. Mestiri and P. Lacorre, *Solid State Sci.*, 2005, **7**, 1216–1224, 10.1016/j.solidstatesciences.2005.05.007.
- 254 Q. Xu, D. Huang, F. Zhang, et al., *J. Alloys Compd.*, 2008, **454**, 460–465, 10.1016/j.jallcom.2006.12.132.
- 255 M. Huse, A. W. B. Skilbred, M. Karlsson, et al., *J. Solid State Chem.*, 2012, **187**, 27–34, 10.1016/j.jssc.2011.12.025.
- 256 L. D. Landau, *Zh. Eks. Teor. Fiz.*, 1937, **7**, 19–32, 10.1038/138840a0.
- 257 K. Aizu, *J. Phys. Soc. Japan*, 1970, **28**, 706–716, 10.1143/JPSJ.28.706.
- 258 A. Mielewczyk-Gryn, K. Gdula-Kasica, B. Kusz and M. Gazda, *Ceram. Int.*, 2013, **39**,

- 4239–4244, 10.1016/j.ceramint.2012.09.102.
- 259 Ø. Prytz, "*Phase separation, transformation and domain formation in LaNbO₄ supersaturated with Sr, A TEM study*", Candidatus scientiarum thesis, Department of Physics, University of Oslo, 2003.
 - 260 G. Brunauer, H. Boysen, F. Frey and H. Ehrenberg, *J. Phys. Condens. Matter*, 2002, **135**, 135–144.
 - 261 K. Aizu, *Phys. Rev. B*, 1970, **2**, 754–772, 10.1103/PhysRevB.2.754.
 - 262 A. Mielewczyk-Gryn, S. Wachowski, K. I. Lilova, et al., *Ceram. Int.*, 2015, **41**, 2128–2133, 10.1016/j.ceramint.2014.10.010.
 - 263 P. Bak, *Rep. Prog. Phys.*, 1982, **45**, 587, 10.1088/0034-4885/45/6/001.
 - 264 W. L. McMillan, *Phys. Rev. B*, 1976, **14**, 1496–1502, 10.1103/PhysRevB.14.1496.
 - 265 M. Grabowski and K. R. Subbaswamy, *Phys. D Nonlinear Phenom.*, 1982, **5**, 348–358, 10.1016/0167-2789(82)90028-8.
 - 266 T. Chattopadhyay, K. D. Liss and T. Brückel, *J. Magn. Magn. Mater.*, 1998, **177–181**, 1058–1060, 10.1016/S0304-8853(97)00797-X.
 - 267 C. Chen and S.-W. Cheong, *Phys. Rev. Lett.*, 1996, **76**, 4042–4045, 10.1103/PhysRevLett.76.4042.
 - 268 K. Nakanishi and H. Shiba, *J. Phys. Soc. Japan*, 1977, **43**, 1839–1847, 10.1143/JPSJ.43.1839.
 - 269 G. Ghiringhelli, M. Le Tacon, M. Minola, et al., *Science*, 2012, **337**, 821–825, 10.1126/science.1223532.
 - 270 M. Kubicek, G. M. Rupp, S. Huber, et al., *Phys. Chem. Chem. Phys.*, 2014, **16**, 2715–26, 10.1039/c3cp51906f.
 - 271 N. Imanaka, Y. Kobayashi, K. Fujiwara, et al., *Chem. Mater.*, 1998, **10**, 2006–2012, 10.1021/cm980157e.
 - 272 G. Adachi, N. Imanaka and S. Tamura, *J. Alloys Compd.*, 2001, **323–324**, 534–539, 10.1016/S0925-8388(01)01138-0.
 - 273 Y. Zhou, S. Adams, R. P. Rao, et al., *Chem. Mater.*, 2008, **20**, 6335–6345, 10.1021/cm800466y.

- 274 A. Y. Neiman, *Solid State Ion.*, 1996, **83**, 263–273, 10.1016/0167-2738(95)00247-2.
- 275 V. F. Sears, *Neutron News*, 1992, **3**, 26–37, 10.1080/10448639208218770.
- 276 S. Takai, S. Touda, K. Oikawa, et al., *Solid State Ion.*, 2002, **148**, 123–133.
- 277 J. Hadermann, O. Perez, N. Creon, et al., *J. Mater. Chem.*, 2007, **17**, 2344–2350, 10.1039/B701449J.
- 278 S. Takai, T. Nakanishi, K. Oikawa, et al., *Solid State Ion.*, 2004, **170**, 297–304, 10.1016/j.ssi.2004.03.008.
- 279 P. K. Davies, *Curr. Opin. Solid State Mater. Sci.*, 1999, **4**, 467–471, 10.1016/S1359-0286(00)00002-4.
- 280 D. S. Tsai, M. J. Hsieh, J. C. Tseng and H. Y. Lee, *J. Eur. Ceram. Soc.*, 2005, **25**, 481–487, 10.1016/j.jeurceramsoc.2004.03.020.
- 281 S. Georges, F. Goutenoire, O. Bohnke, et al., *J. New Mater. Electrochem. Syst.*, 2004, **7**, 51–57, 10.1002/chin.200449225.
- 282 A. Chroneos, D. Parfitt, J. A. Kilner and R. W. Grimes, *J. Mater. Chem.*, 2010, **20**, 266–270, 10.1039/b917118e.
- 283 M. L. Williams, "*CRC Handbook of Chemistry and Physics, 76th edition*", 76th Edition, CRC Press, 1996, 10.1136/oem.53.7.504.
- 284 R. J. Chater, S. Carter, J. A. Kilner and B. C. H. Steele, *Solid State Ion.*, 1992, **53–56**, 859–867, 10.1016/0167-2738(92)90266-R.
- 285 P. Manning, *Solid State Ion.*, 1997, **100**, 1–10, 10.1016/S0167-2738(97)00345-7.
- 286 Q. Lin, X. Feng and Z. Man, *Phys. Rev. B*, 2001, **63**, 134105, 10.1103/PhysRevB.63.134105.
- 287 T. Negas, R. S. Roth, C. L. McDaniel, et al., *Mater. Res. Bull.*, 1977, **12**, 1161–1171, 10.1016/0025-5408(77)90170-2.
- 288 M. Mogensen, D. Lybye, N. Bonanos, et al., *Solid State Ion.*, 2004, **174**, 279–286, 10.1016/j.ssi.2004.07.036.
- 289 C. Tealdi, E. Quartarone, P. Mustarelli and L. Malavasi, *Nanoscale*, 2015, **7**, 2221–4, 10.1039/c4nr05647g.
- 290 J. A. Kilner and R. J. Brook, *Solid State Ion.*, 1982, **6**, 237–252, 10.1016/0167-

2738(82)90045-5.

- 291 M.-H. H. Chambrier, S. Kodjikian, R. M. Ibberson and F. Goutenoire, *J. Solid State Chem.*, 2009, **182**, 209–214, 10.1016/j.jssc.2008.09.010.
- 292 D.-W. Kim, D.-K. Kwon, S. H. Yoon and K. S. Hong, *J. Am. Ceram. Soc.*, 2006, **89**, 3861–3864, 10.1111/j.1551-2916.2006.01302.x.
- 293 C. Quinn and R. Wusirika, *J. Am. Ceram. Soc.*, 1991, **74**, 431–432, 10.1111/j.1151-2916.1991.tb06902.x.
- 294 J. Druce, T. Ishihara and J. Kilner, *Solid State Ion.*, 2014, **262**, 893–896, 10.1016/j.ssi.2013.09.010.
- 295 S. Ponce, M. A. Peña and J. L. G. Fierro, *Appl. Catal. B Environ.*, 2000, **24**, 193–205, 10.1016/S0926-3373(99)00111-3.
- 296 H. Téllez, J. Druce, J. a Kilner and T. Ishihara, *Faraday Discuss.*, 2015, **182**, 1–13, 10.1039/C5FD00027K.
- 297 R. Haugrud and T. Norby, *Solid State Ion.*, 2006, **177**, 1129–1135, 10.1016/j.ssi.2006.05.011.
- 298 H. Fjeld, K. Toyoura, R. Haugrud and T. Norby, *Phys. Chem. Chem. Phys.*, 2010, **12**, 10313–9, 10.1039/c002851g.
- 299 A. Le Bail, *Powder Diffr.*, 2005, **20**, 316–326, 10.1154/1.2135315.
- 300 P. Scanlon, R. A. M. Bink, F. P. F. van Berkel, et al., *Solid State Ion.*, 1998, **112**, 123–130, 10.1016/S0167-2738(98)00198-2.
- 301 T. Norby, *Mrs Bull.*, 2009, **34**, 923–928, Doi 10.1557/Mrs2009.214.
- 302 J. Palisaitis, M. E. Ivanova, W. A. Meulenberg, et al., *J. Eur. Ceram. Soc.*, 2015, **35**, 1517–1525, 10.1016/j.jeurceramsoc.2014.11.010.
- 303 M. Ivanova, S. Ricote, W. A. Meulenberg, et al., *Solid State Ion.*, 2012, **213**, 45–52, 10.1016/j.ssi.2011.06.012.
- 304 K. V. Hansen, K. Norrman and M. Mogensen, *Surf. Interface Anal.*, 2006, **38**, 911–916, 10.1002/sia.2314.
- 305 M. Aoki, Y.-M. Chiang, I. Kosacki, et al., *J. Am. Ceram. Soc.*, 1996, **79**, 1169–1180, 10.1111/j.1151-2916.1996.tb08569.x.

- 306 W. L. Baun, *Phys. Rev. A*, 1978, **17**, 849–853, 10.1103/PhysRevA.17.849.
- 307 J. F. Ziegler, M. D. Ziegler and J. P. Biersack, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*, 2010, **268**, 1818–1823, 10.1016/j.nimb.2010.02.091.
- 308 W. Araki, M. Miyashita and Y. Arai, *Solid State Ion.*, 2016, **290**, 18–23, 10.1016/j.ssi.2016.04.003.
- 309 D. Briggs, "*Surface Analysis by XPS and Static SIMS*", Cambridge University Press, 1998.
- 310 M. Burriel, S. Wilkins, J. P. Hill, et al., *Energy Environ. Sci.*, 2014, **7**, 311, 10.1039/c3ee41622d.
- 311 J. Druce, *ECS Trans.*, 2015, **66**, 61–68, 10.1149/06602.0061ecst.
- 312 Z. Feng, Y. Yacoby, M. J. Gadre, et al., *J. Phys. Chem. Lett.*, 2014, **5**, 1027–1034, 10.1021/jz500293d.
- 313 J. Wu, S. S. Pramana, S. J. Skinner, et al., *J. Mater. Chem. A*, 2015, **3**, 23760–23767, 10.1039/C5TA03759J.
- 314 N. Gauquelin, T. E. Weirich, M. Ceretti, et al., *Monatshefte fur Chemie*, 2009, **140**, 1095–1102, 10.1007/s00706-009-0146-2.
- 315 S. P. Harvey, R. A. De Souza and M. Martin, *Energy Environ. Sci.*, 2012, **5**, 5803, 10.1039/c1ee02740a.
- 316 R. W. Balluffi, *J. Electron. Mater.*, 1992, **21**, 527–553, 10.1007/BF02669167.
- 317 Z. K. Huang, D. S. Yan, T. Y. Tien and I. W. Chen, *Mater. Lett.*, 1991, **11**, 286–290.
- 318 G. Audi, A. H. Wapstra and C. Thibault, *Nucl. Phys. A*, 2003, **729**, 337–676, 10.1016/j.nuclphysa.2003.11.003.
- 319 H. Craig, *Science*, 1961, **133**, 1833–4, 10.1126/science.133.3467.1833.
- 320 J. A. Kilner, S. J. Skinner and H. H. Brongersma, *J. Solid State Electrochem.* 201115861–876.
- 321 S. Raz, K. Sasaki, J. Maier and I. Riess, *Solid State Ion.*, 2001, **143**, 181–204, 10.1016/S0167-2738(01)00826-8.
- 322 R. A. De Souza, M. J. Pietrowski, U. Anselmi-Tamburini, et al., *Phys. Chem. Chem.*

- Phys.*, 2008, **10**, 2067–72, 10.1039/b719363g.
- 323 J. Liu, R. J. Chater, B. Hagenhoff, et al., *Solid State Ion.*, 2010, **181**, 812–818, 10.1016/j.ssi.2010.04.009.
 - 324 A. L. Podkorytov, M. I. Pantyukhina, S. A. Shtin and V. M. Zhukovskii, *Inorg. Mater.*, 2000, **36**, 1282–1284, 10.1023/A:1026650202677.
 - 325 M. Fukuhara, C. Y. Huang, A. S. Bhalla and R. E. Newnham, *J. Mater. Sci.*, 1991, **26**, 61–66, 10.1007/BF00576033.
 - 326 K. Iwasaki, H. Yamane, S. Kubota, et al., *J. Alloys Compd.*, 2002, **339**, 268–274, 10.1016/S0925-8388(01)02008-4.
 - 327 V. G. Zubkov, V. A. Pereliaev, A. P. Tyutyunnik, et al., *J. Alloys Compd.*, 1997, **256**, 129–139, 10.1016/S0925-8388(96)03024-1.
 - 328 R. Glöckner, A. Neiman, Y. Larring and T. Norby, *Solid State Ion.*, 1999, **125**, 369–376, 10.1016/S0167-2738(99)00197-6.
 - 329 J. L. Schlenker, G. V. Gibbs and M. B. Boisen, *Acta Crystallogr. Sect. A*, 1978, **34**, 52–54, 10.1107/S0567739478000108.

Appendix

Appendix a. X-ray photoelectron spectroscopy (XPS) study of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$

The survey spectra of modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ samples are displayed in Figure A-1. All the expected core levels are visible; small amounts of C 1s and N 1s detected, probably due to surface contaminant.

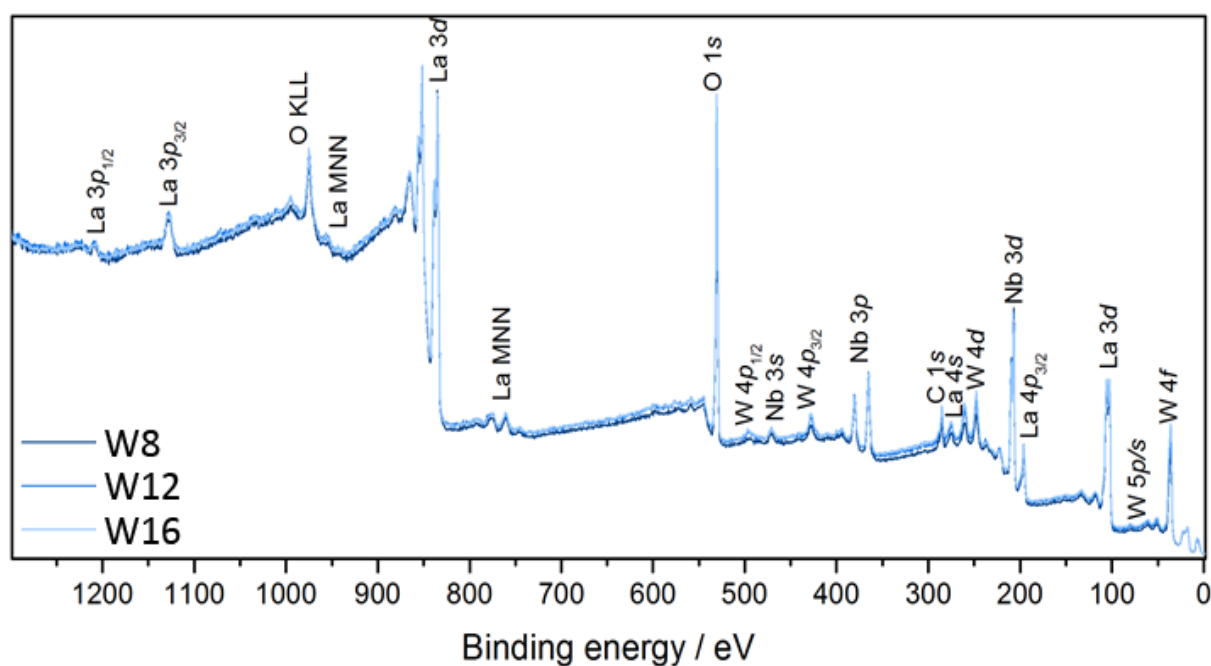
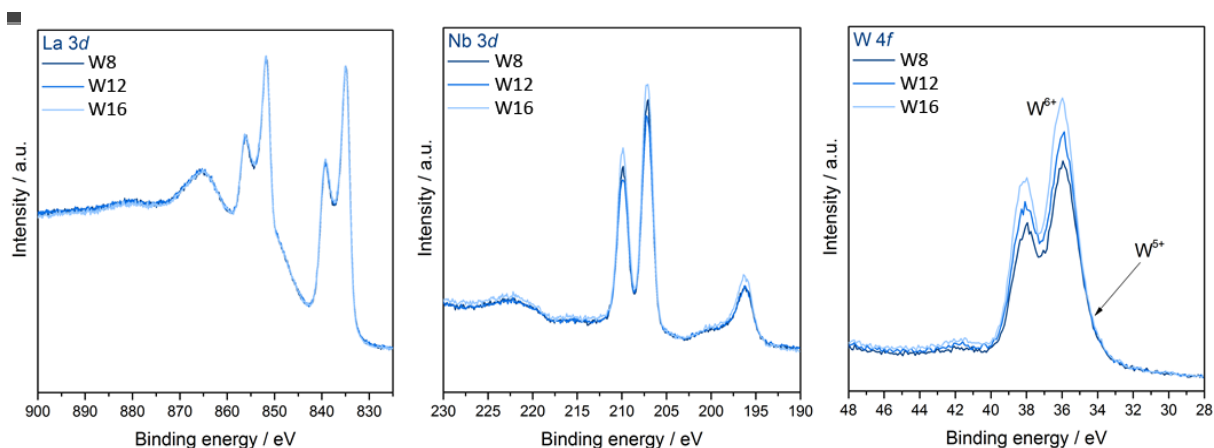


Figure A-1: Survey spectra of various modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ samples

The core level of the cations in the modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases is shown in ■Figure A-2, in which all the intensity is normalized to the corresponding La 3d level. The W 4f core level was dominated by W^{6+} , but contribution from W^{5+} is visible (shoulder to lower bonding energy highlighted by an arrow).



■Figure A-2: Core level of the cations in the modulated $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+d}$ phases; all the intensity is normalized to the corresponding La 3d level.

Appendix b. Calculating the spontaneous strain in the monoclinic LaNbO₄ phase

According to Aizu [257,261], a crystal is said to be ferroelastic when it has two (or more) orientation states ($S_1, S_2, S_3 \dots S_n$) in the absence of external stress, which can be shifted from one to another with slight movement of atoms. A strain tensor relates the ferroelastic phase to the prototypic phase, whose lattice parameters are obtained by extrapolating from the high temperature measurements. In the monoclinic to tetragonal transition in LaNbO₄, there are two states which are related by the rotation along the unique b axis by 90° [97]:

$$\varepsilon(S_1) = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & 0 \\ \varepsilon_{21} & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix} \quad \text{Eqn. A.1}$$

$$\varepsilon(S_2) = R\varepsilon(S_1)R^T$$

According to Schlenker [329], who derived the expression for strain tensor component based on the lattice parameters, the strain components ε_n in LaNbO₄ are expressed in Eqn. A.2:

$$\begin{aligned} \varepsilon_{11} &= c_m \sin \beta_m^* / a_t - 1 \\ \varepsilon_{22} &= a_m / b_t - 1 \\ \varepsilon_{33} &= b_m / c_t - 1 \\ \varepsilon_{12} = \varepsilon_{21} &= -\frac{1}{2} \left(\frac{c_m \cos \beta_m^*}{a_t} \right) \end{aligned} \quad \text{Eqn. A.2}$$

in which the subscripts m and t represent the monoclinic phase and the tetragonal phase of the LaNbO₄; β_m^* is reciprocal β angle of the monoclinic phase. a, b, c are the lattice parameters.

Based on definition of spontaneous strain proposed by Aizu [257], the magnitude of the spontaneous strain must be (a) independent of the choice of coordinates system (b) the same for all the orientation state (S) in the ferroelastic phase and (c) zero through the temperature range for the prototype phase.

Based on these requirements, Aizu defined spontaneous strain tensors $\varepsilon^s(S_i)$ of state S_i as follows:

$$\varepsilon^s(S_i) = \varepsilon(S_i) - \frac{1}{n} \sum_1^n \varepsilon(S_n) \quad \text{Eqn. A.3}$$

in which $\varepsilon(S_i)$ is the strain of the S_i state in Eqn. A.1. In the prototype phase $S_1 = S_2 = S_3 \dots = S_n$ leading to $\varepsilon^s = 0$. Rearrange Eqn. A.1 and Eqn. A.3 yields the expression of spontaneous strain for LaNbO_4 :

$$\varepsilon^s(S_1) = \begin{pmatrix} -\varepsilon_{11}^s & \varepsilon_{12}^s & 0 \\ \varepsilon_{12}^s & \varepsilon_{11}^s & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{Eqn. A.4}$$

$$\varepsilon^s(S_1) = -\varepsilon^s(S_2)$$

where $\varepsilon_{11}^s = \frac{1}{2}(\varepsilon_{11} - \varepsilon_{22})$ and $\varepsilon_{12}^s = \varepsilon_{12}$. The magnitude of the spontaneous strain is then:

$$|\varepsilon^s| = \sqrt{2[(\varepsilon_{11}^s)^2 + (\varepsilon_{12}^s)^2]} \quad \text{Eqn. A.5}$$

The lattice parameters of the prototype phase required for the calculation of spontaneous strain were obtained by extrapolating the measured lattice parameters of the high temperature tetragonal phase. The lattice parameters of the prototype phase for the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition is shown in Figure A-3 and the corresponding spontaneous strain which was utilized for the fitting to Eqn. 5.1 in section 5.3.2, and the results are reported in Table A-1.

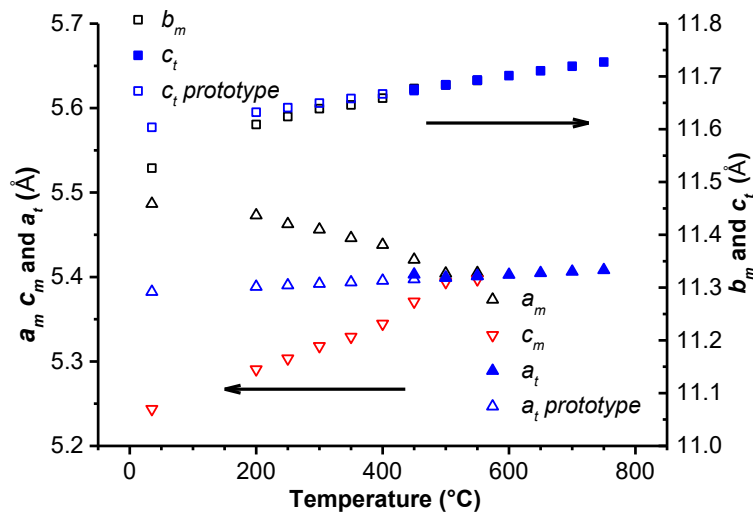


Figure A-3: lattice parameters of the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition. The lattice parameters of the prototype phase (hollow symbols in the plot) were obtained by extrapolating from the measurements of the high temperature tetragonal phase.

Table A-1: Calculated spontaneous strain in the $\text{LaNb}_{0.96}\text{W}_{0.04}\text{O}_{4+d}$ composition, using Eqn. A.1 to Eqn. A.5.

	monoclinic phase				prototype phase		strain					
T (°C)	a_m (Å)	b_m (Å)	c_m (Å)	$\theta(^{\circ})$	a_t/b_t (Å)	c_t (Å)	ε_{11}	ε_{22}	ε_{12}	ε^s_{11}	ε^s_{12}	ε^s
35	5.4867	11.5263	5.2436	92.6697	5.3825	11.6035	-0.0269	0.0194	-0.0227	-0.0231	-0.0227	0.0458
200	5.4731	11.6088	5.2906	92.1047	5.3885	11.6322	-0.0188	0.0157	-0.0180	-0.0173	-0.0180	0.0353
250	5.4627	11.6239	5.3035	91.8123	5.3903	11.6408	-0.0166	0.0134	-0.0156	-0.0150	-0.0156	0.0306
300	5.4562	11.6388	5.3181	91.5655	5.3921	11.6495	-0.0141	0.0119	-0.0135	-0.0130	-0.0135	0.0265
350	5.4462	11.6458	5.3292	91.2513	5.3939	11.6582	-0.0122	0.0097	-0.0108	-0.0110	-0.0108	0.0218
400	5.4381	11.6587	5.3447	90.9929	5.3957	11.6668	-0.0096	0.0079	-0.0086	-0.0087	-0.0086	0.0173
450	5.4206	11.6770	5.3708	90.5228	5.3975	11.6755	-0.0050	0.0043	-0.0045	-0.0046	-0.0045	0.0092
500	5.4042	11.6838	5.3940	90.1129	5.3992	11.6842	-0.0010	0.0009	-0.0010	-0.0009	-0.0010	0.0019
550	5.4048	11.6924	5.3972	90.0704	5.4011	11.6927	-0.0007	0.0007	-0.0006	-0.0007	-0.0006	0.0013

Appendix c. Lattice parameters of the $\text{La}_{1-x}\text{Y}_x\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ phase obtained from Le Bail refinement using *in situ* HTXRD diffraction data

Table A-2: Lattice parameters of the $\text{La}_{0.9}\text{Y}_{0.1}\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition.

Temperature (°C)	monoclinic				tetragonal		phase
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	c (Å)	
35	5.3962	11.6171	5.3010	91.572			m+ La_2WO_6
250	5.3859	11.6133	5.3004	91.046			m+ La_2WO_6
300	5.3818	11.6146	5.3125	90.910			m+ La_2WO_6
350	5.3768	11.6277	5.3258	90.728			m+ La_2WO_6
400	5.3821	11.6289	5.3394	90.455			m
500					5.3609	11.6553	t
550					5.3638	11.6596	t
600					5.3666	11.6620	t
650					5.3694	11.6670	t
700					5.3720	11.6813	t
750					5.3750	11.6903	t
800					5.3775	11.6982	t
900					5.3823	11.7153	t

Table A-3: Lattice parameters of the $\text{La}_{0.8}\text{Y}_{0.2}\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition.

Temperature (°C)	monoclinic				tetragonal		phase
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	c (Å)	
35	5.3971	11.5069	5.2490	91.903			m+ La_2WO_6
300	5.3773	11.5473	5.2903	91.051			m
350	5.3668	11.5578	5.3083	90.718			m
400	5.3568	11.5618	5.3312	90.259			m
450	5.3529	11.5732	5.3382	90.259	5.3431	11.5742	m+t
500					5.3454	11.5822	t
550					5.3476	11.5900	t
600					5.3499	11.5981	t
700					5.3545	11.6143	t
800					5.3620	11.6311	t
900					5.3642	11.6492	t

Table A-4: Lattice parameters of the $\text{La}_{0.7}\text{Y}_{0.3}\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition.

Temperature (°C)	monoclinic				tetragonal		phase
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	c (Å)	
35	5.3977	11.4382	5.2250	92.259			m
200	5.3708	11.4667	5.2536	91.499			m
250	5.3600	11.4742	5.2686	91.114			m
300	5.3420	11.4838	5.2898	90.623			m
350	5.3378	11.4917	5.3120	90.293			m
400	5.3381	11.5096	5.3171	90.189			m
450	5.3321	11.5147	5.3209	90.121			m
500					5.3286	11.5242	t
550					5.3304	11.5317	t
600					5.3330	11.5402	t
650					5.3351	11.5481	t
700					5.3375	11.5569	t
750					5.3401	11.5654	t
800					5.3425	11.5744	t

Table A-5: lattice parameters of the $\text{La}_{0.5}\text{Y}_{0.5}\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition.

Temperature (°C)	monoclinic				tetragonal		phase
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	c (Å)	phase
35	5.3877	11.2839	5.1694	93.040			m
300	5.3375	11.3337	5.2339	91.392			m
400	5.2980	11.3485	5.2792	90.272			m
500					5.2941	11.3688	t
550					5.2962	11.3772	t
600					5.2980	11.3845	t
650					5.2999	11.3923	t
700					5.3020	11.4003	t
750					5.3042	11.4085	t
800					5.3063	11.4165	t
900					5.3105	11.4328	t

Table A-6: lattice parameters of the $\text{La}_{0.3}\text{Y}_{0.7}\text{Nb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition.

Temperature (°C)	monoclinic				tetragonal		phase
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	c (Å)	
35	5.3597	11.1243	5.1245	93.816			m+unknown
300	5.3388	11.1587	5.1559	92.864			m+unknown
400	5.3256	11.1788	5.1788	92.262			m+unknown
500	5.2946	11.1940	5.2150	91.179			m+unknown
550	5.2630	11.1922	5.2456	90.268			m+unknown
600					5.2594	11.2127	t+unknown
650					5.2613	11.2209	t+unknown
700					5.2636	11.2290	t+unknown
750					5.2654	11.2364	t+unknown
800					5.2673	11.2442	t+unknown
900					5.2717	11.2604	t+unknown

Table A-7: lattice parameters of the $\text{YNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition.

Temperature (°C)	monoclinic				tetragonal		phase
	a (Å)	b (Å)	c (Å)	β (°)	a (Å)	c (Å)	
35	5.2880	10.9566	5.0871	93.890			
400	5.2743	11.0029	5.1263	92.701			m
500	5.2595	11.0120	5.1449	92.016			m
600	5.2020	11.0237	5.2012	90.305			t+m
650					5.2048	11.0238	t+m
700					5.2126	11.0488	t+m
750					5.2172	11.0646	t
800					5.2173	11.0647	t
850					5.2192	11.0716	t
900					5.2210	11.0782	t

Appendix d. Surface analysis of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$

The LEIS surface spectra of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ annealed from 600 °C to 1000 °C, as well as that of the as-polished sample, are shown in Figure A-4. The surface chemistry of the annealed samples displayed minor deviation from the as-polished surface: slightly increases in W and Nb concentration was observed for the 600 °C annealed sample, although the accuracy of the data is limited by the low peak intensity of W. In addition, Bi/Pb peak was observed at the 600 °C annealed surface, which is likely to originate from furnace contamination. Slight increase of W concentration on the surface was observed in the 800 °C sample, although the quantification indicates that the 1000 °C sample has the same stoichiometry of the as-polished sample. Overall, no clear trend of surface chemistry with annealing temperatures was observed. Though there are still peculiarities worth further investigation, current investigation will however focuses on acceptor doped LaNbO_4 which exhibits significant surface segregation.

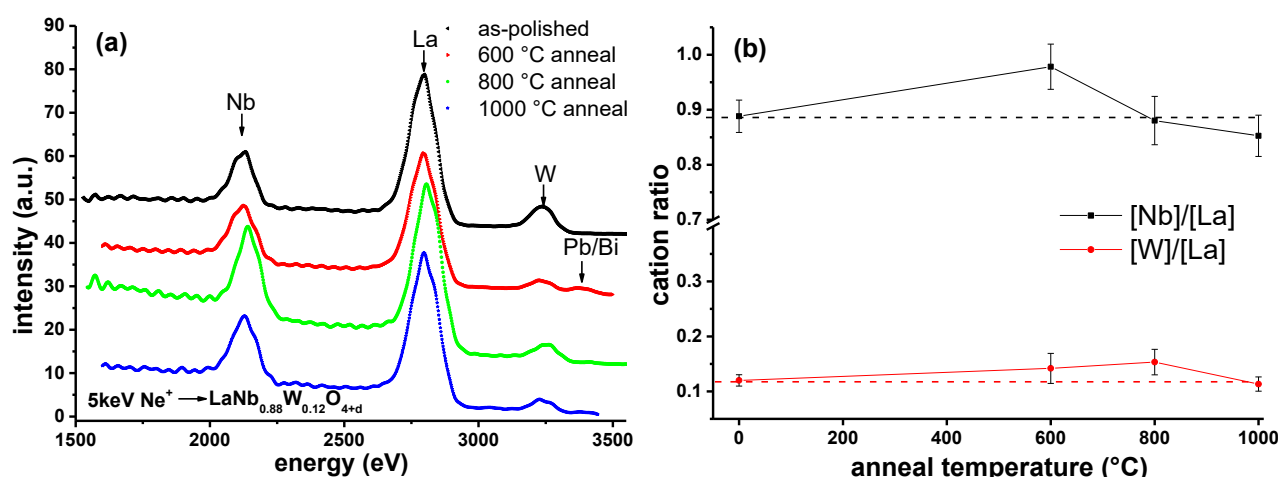


Figure A-4: (a) LEIS surface spectra of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ samples annealed at different temperatures and (b) the corresponding surface cation composition after normalizing to La. The dash lines in (b) indicate the ideal bulk stoichiometry. No clear trend of surface chemistry with annealing temperatures was observed.

Supplemental Information

The refined structures of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4+d}$, using *in situ* neutron scattering are reported as crystallographic information files (CIF), which can be accessed through the Imperial College library service at <http://www.imperial.ac.uk/admin-services/library/>.