Room temperature structure and transport properties of the incommensurate modulated LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$

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Abstract

The crystal structure of a (3 + 2)D incommensurate modulated LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ phase, a novel oxygen ionic conductor, is refined using a combination of synchrotron X-ray diffraction and electron diffraction data. The superspace group $I2/c(α,0,γ)$00($α_20γ_2$)00 ($a = 5.4131(1)$ Å, $b = 11.6432(2)$ Å, $c = 5.2963(1)$ Å, $β = 91.540(1)$°, $q_1 = 0.2847(5)a^* + 0.1098(9)c^*$ and $q_2 = −0.1266(9)a^* + 0.2953(1)c^*$) was chosen for the refinement. Similar to other scheelite type modulated structures, the modulation of LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ stems from the cation occupancy ordering in the $xz$ plane. To facilitate the modulated cation sub-lattice, and to compensate for the difference in their size and charge, the B site polyhedra are distorted by stretching the B-O bond lengths. Consequently, an extension in the B site coordination number from 6 to 8 is observed in the modulated phase. An interconnected 3D network of BO$_x$ polyhedra, similar to that of modulated CeNbO$_{4.25}$, is obtained as a result of the structure modulation, which is not available in the unmodulated parent structure. Tracer diffusivity measurements indicate that the composition is an oxygen ion conductor, which relies on an intersticalcy conduction mechanism. Oxygen tracer diffusivity of $2.46 \times 10^{-9}$ cm$^2$ s$^{-1}$, at 750 °C is reported.
1 Introduction
In the search for novel electrolyte materials, research interest has shifted from conventional materials with high symmetry and large number of equivalent positions to structures with anisotropic conduction paths.1–3 Among the novel oxygen ion conductors, modulated CeNbO$_{4.25}$ has demonstrated remarkable oxygen diffusivity in the 500–650 °C region, a temperature range of interest for SOFC electrolyte application.4,5 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,6 low temperature CeNbO$_{4+d}$ phases are modulated monoclinic phases which have an ordered anion sub-lattice.7 With its highly defective local structure, CeNbO$_{4+d}$ provides an interesting template and a new concept in designing structures with high ionic mobility. However, the undesirable electronic conduction in CeNbO$_{4+d}$ hinders its application as an oxide electrolyte.8 More recently, hyperstoichiometric W doped LaNbO$_4$, a structural analogue to CeNbO$_{4+d}$, demonstrated promising overall conductivity and good reduction stability, and has been proposed for SOFC electrolyte application.9 Despite the interest in its conduction properties, the modulated structure of LaNb$_{1-x}$W$_x$O$_4+d$ has yet to be resolved.9,10 The room temperature structure has been identified to be (3 + 2)D incommensurate modulated,9,11 although no structural solution was available in the literature. Literature reports often treated the structure as being unmodulated,9,10 which risks oversimplifying the crystal structure. Consequently, the interplay between its complex structure and the underlying transport mechanism is not yet well understood.

In this contribution, we provide the structural solution of the LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ composition using electron diffraction and high-resolution powder diffraction and discuss the impact of Nb/W cation ordering on the local structure in the (3 + 2)D incommensurate modulated LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$. The x = 0.12 is of interest since it has the highest conductivity of $8 \times 10^{-3}$ S cm$^{-1}$ at 863 °C, among the W doped LaNbO$_4$ samples (support information). Furthermore, the transport properties of the W doped analogue will be explored.
2 Experimental

LaNb$_{1-x}$W$_x$O$_{4+d}$ phases were prepared via solid state reaction. All the starting powders were examined with X-ray diffraction (XRD) to ensure that they were single phase. Stoichiometric amounts of starting powders (La$_2$O$_3$ (99.9%), Nb$_2$O$_5$ (99.9%), WO$_3$ (99.5\% all from Sigma-Aldrich) were weighed and then ground together. The La$_2$O$_3$ was pre-treated at 1000 °C for 10 h prior to mixing to produce a dehydrated and decarbonated phase. The powder mixtures were ball milled for 24 h in acetone with zirconia balls to achieve homogeneous mixing. The mixed powder was first calcined under lab air at 1200 °C for 10 h, then milled and calcined again at 1400 °C for 10 h. The chemical composition of the powder was examined using energy dispersive X-ray spectroscopy (EDX) in a scanning electron microscope (SEM, JEOL JSM 6400) and the results are presented in the supporting information (Fig. S1 and Tab. S1). To produce pellets, approximately 0.5 g of powder was weighed and uniaxially pressed under 360 MPa pressure, followed by isostatic pressure at 300 MPa for 1 min. All the samples were sintered at 1400 °C in air for 12 h with the heating/cooling rate set at 10 °C/min.

A JEM-2100F TEM/STEM (JEOL) operated at 200 kV was used to investigate the crystal structure of LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$. Electron diffraction was carried out with powder samples, prepared by dispersing finely ground powder onto a copper grid.

The powder diffraction dataset was obtained at room temperature 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 range of $3.0 \leq 2\theta \leq 20.1^\circ$ ($6.32 \, \text{Å} > d$-spacing $> 0.95 \, \text{Å}$) was used for the refinement. The wavelength of the synchrotron radiation was calibrated using a Si standard prior to the measurement. The Pseudo-Voigt function was used to describe the line profile, and the instrument parameters were obtained by refining the diffraction pattern of a Na$_2$Ca$_3$Al$_2$F$_{14}$ reference gathered using the same geometry and optics. The crystal structure was refined using the JANA2006 program.$^{13}$

The electrochemical impedance spectroscopy (EIS) measurements 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 mV across 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 Ltd, UK).

To investigate oxygen mobility, $^{18}$O tracer diffusivity, after exchanging in an $^{18}$O$_2$ enriched environment, was measured using the line scan method by secondary ion mass spectrometry (SIMS). The samples, which had been polished to a $\frac{1}{4}$ μm surface finish prior to the exchange experiments, were placed in a quartz tube and evacuated to $<5 \times 10^{-7}$ mbar total pressure. The samples were heated to the exchange temperature and pure oxygen with normal isotopic concentration at 200 mbar nominal pressure was introduced into the main chamber. The samples were annealed in the pure oxygen atmosphere; the anneal temperature was set to be at least 10 times longer than the actual exchange process to eliminate any chemical gradient between the solid surface and the gas phase.

After annealing, the samples were allowed to cool to room temperature and once cool the main chamber was again evacuated to high vacuum ($<5 \times 10^{-7}$ mbar pressure). $^{18}$O enriched gas with gas concentration ($C_g$) $\approx$ 54 % (measured by oxidising a Si single crystal) was introduced from the reservoir. The samples were rapidly heated to the exchange temperature, held for the 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 close to the sample and the actual exchange time was calibrated based on the activation energy of diffusion and the thermal profile, according to Killoran.

3 Results and discussion

3.1 Transmission electron microscopy (TEM)

3.1.1 Electron diffraction (ED)

The crystal structure of the LaNb$_{1-x}$W$_x$O$_{4+d}$ samples was investigated using electron diffraction (ED). The electron diffraction patterns of the LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ composition from the low index planes are shown in Figure 1. 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 [111] 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 resulted from double reflection. Double reflection along the unique axis has been observed in KSmMoO$_4$ and KNdMoO$_4$ 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 1: Electron diffraction patterns of the incommensurately modulated LaNb_{0.88}W_{0.12}O_{4+d} phase from [010]* [001]* [101]* and [1-11]*directions. Satellite reflections were observed from the [010]*direction, indicating a (3 + 2)D modulated structure.](image)

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 \( q_1 \approx 0.29a_I^* + 0.12c_I^* \) and \( q_2 \approx -0.13a_I^* + 0.30c_I^* \) (the subscript \( I \) indicates the \( I \) 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 \( B2/b(\alpha_1,\beta_1,0)00(\alpha_2,\beta_2,0)00,18 \) 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.\(^{19–21}\) Similar domain structures, which are created by rotating about the \( b \) unique axis have also been observed in the LaNb\(_{1-x}\)W\(_x\)O\(_{4+d}\) phases (discussed in the next section). However, the presence of mixed second-order satellite reflections \( q_1 \pm q_2 \) (Figure 1) 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 \(\text{LaNbO}_4\) parent structure. For consistency, the SSG setting is transformed to the \(I2/c\) setting with respect to the \(B2/b\) setting using the transformation matrix \(P = \begin{bmatrix} -1 & 0 & 0 \\ -1 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}\)

\[
\begin{pmatrix} a \\ b \\ c \end{pmatrix}_{I2/c} = P \begin{pmatrix} a \\ b \\ c \end{pmatrix}_{B2/b}
\]

and \(P^T = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ -1 & 1 & 0 \end{bmatrix}\) is used to transform the unit cell in reciprocal space. The transformed SSG is therefore \(I2/c(a_1,0,\gamma_1)00(a_2,0,\gamma_2)00\) 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 centres of symmetry at \((0, 0, 0, 0, 0)\) and \((1/2, 1/2, 1/2, 0, 0)\).

3.1.2 Imaging the modulated structure

The domain structure of the \(\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}\) is shown in Figure 2. 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 \(\text{LaNbO}_4\).\(^{19,20}\) The inset of Figure 2 highlights the structure within a domain, a checker-board pattern composed of pseudo-cells, which are about \(1.6\) nm \(\times\) \(1.6\) nm, was observed.
Figure 2: TEM bright field image of LaNb$_{0.88}$W$_{0.12}$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 3: a) HRTEM image and the corresponding Fourier transformed (FT) pattern of (3 + 2)D incommensurately modulated LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ phase, the inset in the yellow square shows the simulated image using a 10 × 1 × 10 commensurate approximation of the modulated structure using JEMS.$^{22}$ A defocus value $\Delta f = -7.5$ nm and thickness $t = 25$ 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 3a shows the enlarged HRTEM image of the inset in Figure 2. A Fourier transform of the image is also displayed, showing clearly both the satellite reflections and the parent structure. Displacement of the atomic columns (represented as dots in the image), away from the average positions was clearly observed. The HRTEM image suggests an ordered distribution of the W dopant along the xz 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.\textsuperscript{23} 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 xz plane.
Figure 3b). The inset in

Figure 3a shows the simulated pattern based on $10 \times 1 \times 10$ commensurate approximation of the refined structure and will be discussed shortly.

3.2 Incommensurate modulated structure of LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$

3.2.1 Crystal structure of incommensurate modulated LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$

Anisotropic peak broadening in the X-ray diffraction data 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 (-121) 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 (-121) reflection had a shoulder towards higher 2θ whereas broadening towards the opposite direction was observed for the (121) reflection. A similar trend was observed for the other diffraction pairs such as (200) and (002), as well as (-161) and (161) (shown in Figure 4).
Asymmetric peak broadening in diffraction patterns has been previously reported in LaNbO$_4$\textsuperscript{24} YNbO$_4$\textsuperscript{25} and Ce$_{1-x}$Sr$_x$NbO$_4$ (Figure A.3 in ref \textsuperscript{26}), 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.\textsuperscript{27–29} A ferroelastic material exhibits spontaneous strain without the application of external stress which often leads to hkl-dependent diffuse scattering.\textsuperscript{28} As shown in Figure 2, the microstructure of LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ phases consists of domains, similar to those observed in LaNbO$_4$\textsuperscript{19,20} in which they are related by rotation about the unique b axis. The domain structure indicates 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 prototypical tetragonal structure has been proposed by Tsunekawa and Takei\textsuperscript{30} 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 NbO$_4$ polyhedra.\textsuperscript{30} Jian and Wayman proposed that a gradual orientation change within the transition zone lowered the energy requirement for the movement of domain boundaries.\textsuperscript{20} Due to the presence of the domain structure, a distribution of d-spacing at the xz plane was expected, whereas a narrower peak profile for the 0k0 reflections, which are free from strain, is expected.\textsuperscript{31} The domain structure as well as the transition zone are likely to relate to the abnormal peak broadening observed in the XRD pattern,\textsuperscript{31} which disappears after LaNbO$_4$ transforms from the monoclinic fergusonite to the tetragonal scheelite structure.\textsuperscript{24} Study of the acceptor doped LaNbO$_4$ phase reveals similar micro-structure features which suggest that the presence of the transition zone is common for low temperature monoclinic
LaNbO$_4$.\textsuperscript{32} The formality introduced by Stephens\textsuperscript{33} was used to described the anisotropic peak broadening observed in the LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ phase.

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 anisotropic displacement parameters (ADP). Their site occupancy, $p^\lambda$, for atom $\lambda$ at the Nb/W site, as a function of the internal coordination $t$ and $u$, is expressed in Equation 1:

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

Equation 1

in which $p_0^\lambda$ is the nominal site occupancy for Nb and W, which are 0.88 and 0.12 respectively based on the chemical analysis presented in Table S1; $p_n^\lambda$ is the Fourier magnitude along the $n^{th}$ wave function. Although higher order satellite reflections were clearly observed in the electron diffraction pattern (Figure 1), 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, $p_{c1}^{Nb} = -p_{c1}^{W}$, so that the overall occupancy $p^\lambda$ remains constant regardless of any change in the internal $t$-$u$ space, i.e. all the sites in the real space have full occupancy. The refinement converged with improved fitting parameters, $R_p = 8.5\%$ and $R_{wp} = 10.8\%$ for the whole pattern, compared with the structural model with only the parent structure ($R_p = 10.9\%$ and $R_{wp} = 14.3\%$). The refined pattern is shown in Figure 5, whereas the experimental conditions, the refined parameters of the parent structure and the Fourier magnitudes of the modulated phase are summarized in Table 1-Table 3 respectively.
Figure 5: Rietveld refinement of synchrotron powder diffraction data of LaNb$_{0.88}$W$_{0.12}$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 $R_p = 8.3\%$ and $R_{wp} = 10.6\%$ were reported. The major difference between the model and the fitting resulted from the asymmetric peak shape reported in Figure 4. The strongest modulation peaks are marked in the Figure.

The $t$-$u$ plot of the residual electron density map in the vicinity of the cation sites is shown in Figure 6. For the La site, the maximum residual density of $-2 \text{ eÅ}^{-3}$ 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 slight negative density might therefore result from the background.\textsuperscript{34} A higher residual level ($-3.5 \text{ eÅ}^{-3}$) at the Nb site was registered, which may be related to the Nb/W occupational modulation.
Figure 6: 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 eÅ⁻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 7. The occupancy of W varied continuously with internal coordinate and reached its maximum of approximately 40 at% at around $t = 0.45, u = 0.95$.

Figure 7b), more than three times higher than the bulk nominal concentration (12 at%). The slightly negative occupancy of W at around $(t, u) = (0, 0.5)$ 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 Error! Reference source not found.a). Slight negative cation occupancy was reported in other (3 + 2)D modulated scheelite structures,\textsuperscript{35} and was ascribed to inaccurate occupancy wave functions, using only the sine/cosine waves. Indeed, previous reports on (3 + 1)D modulated scheelite KSm(MO$_4$)$_2$\textsuperscript{16} and KNd(MO$_4$)$_2$\textsuperscript{17}, 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.\textsuperscript{16}

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 7: 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 represent 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 displacement of both the cations and anions, to compensate for the bond valence sum. Similar displacement has been observed in other modulated scheelite structures.$^{36-38}$ The movement is described by the Fourier magnitudes of the displacive waves, which are summarized in Table 3. 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 8). 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 8b) 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 7; the average Nb/W-O bond length reaches its minimum of 1.810 Å at approximately $t = 0.32, u = 0.10$ 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 (b), 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$^{39}$). The B site polyhedra nonetheless seem relatively rigid in comparison with the La coordination as the latter was predicted to have a larger variation in average bond length as shown in Figure 8b (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 occurring 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 NbO$_4$ 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 phases, such as Na$_{27}$Gd$_{47}$MoO$_{43}$ Eu$_2$(MoO$_4$)$_3$ and KSm(MO$_4$)$_2$, 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.
The bond valence sum (BVS), calculated according to Brown\textsuperscript{41}, describes the “bond strength” in ionic components, and provides a convenient method to check the chemical sensibility of the refined structural model. For the BVS calculation, bond lengths up to 3 Å, which consists of the next nearest neighbours in NbO\textsubscript{x} polyhedra, were included and the results are plotted in Figure 8. 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 1.834 Å and 2.523 Å respectively, as reported in Table 2.

Figure 9. 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\textsuperscript{42} to 3.3\textsuperscript{43} 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 9: Bond Valence Sum map of (a) Nb/W site and (b) La site, both images 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

3.2.2 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.

Figure 7b. A BVS ranging from 2.7 to 3.6 was reported for La, slightly higher than the reference range (2.8-3.3 Å).
A $10 \times 1 \times 10$ commensurate approximation of the refined LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ incommensurate modulated structure is drawn, from three mutually perpendicular directions,
Figure 11b and Figure 12. The size of the commensurate approximation is to accommodate the wavevector in real space ($q_{\text{real}} = -3a + 10c$). The cation ordering and the distortion of the B site tetrahedra, based on the structural refinement, are visualized. The In these figures, the B site polyhedra are coloured based on their coordination number: green, blue and orange polyhedra represent 4+2, 4+3 and 4+4 coordination oxygen respectively. The distribution of the W substitution in the commensurate approximation is depicted in
Figure 10b: polyhedra with more than 20 at% W occupancy are coloured grey to highlight the partially ordered B site in the approximated structure.

Figure 10b). The distribution of the W enriched clusters follows a checker-board pattern pointing along the $q_1 \pm q_2$ directions in real space (Figure 2). Indeed, simulation based on the commensurate approximation (inset in Figure 3a) successfully recreates the contrast between atomic columns as well as the wave-like displacement of the cation observed in the HRTEM and HAADF images, indicating that a reasonable fit was obtained from the structural analysis.
Figure 10: 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 4+2, 4+3 and 4+4 oxygen coordination 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
The parent structure and the modulated structure 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 11a and Figure 12a). On the other hand, the coordination number of Nb/W polyhedra in the modulated LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ phase ranges from $4+2$ to $4+4$, 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 12b).

Figure 12b). The additional coordinating oxygen ions extend the parent structure to an interconnected 3D network, not only in the $xz$ basal plane but also along the unique axis. Such extension of NbO$_x$ coordination polyhedra has been observed in the modulated CeNbO$_{4.25}$ phase which facilitates the incorporation of interstitial oxygen, and is believed to correlate with the oxygen transport in CeNbO$_{4.25}$.

$^7$
Figure 11: (a) Real space image of a $10 \times 1 \times 10$ supercell of LaNb$_{0.88}$W$_{0.12}$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 displacement of the oxygen, which is absent from the parent structure. The same colour scheme from Figure 10a is used.
Figure 12: (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; connectivity of the coordination polyhedra in the $xz$ plane is highlighted. The same colour scheme from

Figure 10a is used.

3.3 $^{18}\text{O}$Tracer diffusivity of $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$

To shed light on the nature of the charge carriers and the conducting mechanism of $\text{LaNb}_{1-x}\text{W}_{x}\text{O}_{4+d}$, $^{18}\text{O}$ tracer diffusivity measurements were conducted for the $\text{LaNb}_{0.88}\text{W}_{0.12}\text{O}_{4+d}$ composition in the 550 °C to 750 °C range. Initial results show very low surface $^{18}\text{O}$ concentration (typically $C'(0,t) < 1\%$) after the isotopic exchange experiments...
which prohibits accurate determination of the tracer diffusivity $D^*$. The polished samples were therefore sputter coated with Pt to enhance the oxygen exchange at the surface. The tracer diffusion profiles were obtained using secondary ion mass spectrometry (SIMS) using a line scan technique.\textsuperscript{14} To extract $D^*$, the $^{18}$O concentration profile was fitted to Crank’s solution of Fick’s 2\textsuperscript{nd} law in a semi-infinite medium.\textsuperscript{44} The $^{18}$O diffusion profile of the LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ sample (exchanged at 750 °C for 1320 s) and the corresponding fitting is shown in Figure 13. With the high surface isotopic concentration ($C'(0,t) = 30\%$), good agreement between the fitting and the experimental data was achieved.

Figure 13: $^{18}$O tracer diffusion profile of a LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ sample exchanged at 750 °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.
An Arrhenius plot of oxygen tracer diffusivity of LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$, compared with CeNbO$_{4+d}$ and YSZ references, is shown in

![Arrhenius plot](image)

Figure 14. From the plot, it is evident that CeNbO$_{4+d}$ has superior diffusivity at lower temperature compared with the YSZ benchmark, despite the scattered data probably due to sample variance. The low temperature diffusivity of CeNbO$_{4+d}$ is unexpectedly high considering the low temperature phases, namely the hyperstoichiometric CeNbO$_{4.25}$ and CeNbO$_{4.08}$ are modulated, highlighting the potential of the CeNbO$_{4+d}$ structural template.

Having similar room temperature structure with CeNbO$_{4+d}$, the diffusivity of the LaNb$_{0.88}$W$_{0.12}$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 14: Arrhenius plot of the oxygen tracer diffusivity of LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ in comparison with the diffusivity of CeNbO$_{4+d}$ and YSZ.$^{15}$

To understand the difference in diffusivity, thus oxygen ion conductivity, between various hyperstoichiometric fergusonite phases, the conducting mechanism in LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ is probed using the Nernst-Einstein equation (Equation 2), which establishes the connection between the ionic conductivity and the self-diffusivity of the charge carrier:
\[ \sigma_{\text{ion}} = \frac{z_{\text{ion}}^2 e^2 CD}{kT} \]  

Equation 2

in which \( z_{\text{ion}} \) 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 charge carrier in the structure; and the other parameters have their usual meaning.

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

\[ D[O] = D_{\text{int}}[O_i] + D_{\text{lattice}}[O_{\text{lattice}}] \]  

Equation 3

in which \( D_{\text{int}} \) and \( D_{\text{lattice}} \) describe the diffusivity of the lattice oxygen and interstitials respectively; whereas \([O_i]\) and \([O_{\text{lattice}}]\) are their respective concentrations. The self-diffusivity \( D \) and the tracer diffusivity \( D^* \), which is measured using the isotopic exchange method, is related by a correlation factor \( f \) (Equation 4), which describes the interaction between subsequent jumps. The correlation factor is unity if the charge carriers behave like a 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 an interstitial based diffusion mechanism.\(^{46}\) The correlation factor is considered to be unity for the current discussion.

\[ D^* = fD_{\text{self}} \]  

Equation 4

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 \( C \) is equal to the oxygen interstitial content (Equation 5):

\[ C = [O_i] \]  

Equation 5

In the scenario where the mobility of the interstitials is comparable to that of the lattice oxygen, all the oxygen ions are considered as charge carriers, leading to the expression in Equation 6.\(^{46}\) Such a scenario is similar to that of the interstitialcy mechanism where cooperative movement of an interstitial and at least one lattice oxygen is required.\(^{46}\)

\[ C = [O] \]  

Equation 6
Under these two different assumptions, the $D_{\sigma \text{-lattice}}$ and $D_{\sigma \text{-int}}$ calculated from Equation 7, using the charge carrier concentration presented in Equation 5 and Equation 6, is plotted in

$$D_{\sigma} = \frac{\sigma_D e k_B T}{q^2 C}$$

Equation 7

Figure 15
Figure 15: Arrhenius plot shows the comparison between $D^*$ and $D_\sigma$ in LaNb$0.88$W$0.12$O$_{4+d}$ in the 500°C to 750 °C range. $D_\sigma$ 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

![Arrhenius plot image]

Figure 14.

The measured tracer diffusivity values $D^*$ are more than two orders of magnitude higher than $D_{\sigma\text{-int}}$, whereas excellent agreement between $D^*$ and $D_{\sigma\text{-lattice}}$ was obtained. The results indicate that long range diffusion is attained by a cooperative movement of the oxygen similar to an interstitialcy mechanism. The activation energy for diffusion in this temperature range is 1.56 eV, which is in excellent agreement with the activation energy of total conductivity (1.49 eV, reported in Figure S2), providing further evidence that the oxygen ions are the major charge carriers in the system. Current analysis is consistent with previous simulation that suggests a low interstitial formation energy in the hyperstoichiometric fergusonite phases$^{9,47}$ and provides the first piece of experimental evidence that supports the interstitialcy transport mechanism in the hyperstoichiometric rare earth niobate system. More interestingly, the above analysis also indicates that all the lattice oxygen sites have similar mobility and therefore no direct correlation between the interstitial concentration and the overall conductivity is to be expected. Current results thus reaffirm the assumption that fergusonite is a valid template to design oxygen ion conductors.
Having established that LaNb$_{1-x}$W$_x$O$_{4+d}$ and CeNbO$_{4+d}$ conduct through a similar mechanism, it is curious to notice the huge difference in their diffusivities, despite both displaying similar structural features. It is possible that the difference might reside in different local structure which is critical in facilitating ion transport$^1$. In addition, the current study focuses on the room temperature structure, whereas investigation into the high temperature crystal structure is required to fully understand the difference in oxygen diffusivity.

4 Conclusion

The room temperature structure of the modulated LaNb$_{0.88}$W$_{0.12}$O$_{4+d}$ phase has been shown to adapt a distorted local structure, using a combination of transmission electron microscope and diffraction techniques. Refinement using the superspace group $I2/c(\alpha_1,0,\gamma_1)00(\alpha_2,0,\gamma_2)00$ leads to a final fitting parameters of $R_p = 8.5\%$ and $R_{wp} = 10.8\%$, despite the presence of asymmetric peak profiles. The W substitution induces an occupancy modulation along the $xz$ plane and leads to a distortion of the B site coordination polyhedron. Consequently, the coordination number of B site ranges from 6 to 8, with a 3 Å bond shell distance, leading to connected NbO$_x$ slabs running along the $xz$ plane.

Similar to the CeNbO$_{4+d}$ template, an interstitialcy diffusion is suggested as the dominant mechanism, as both the lattice oxygen and the interstitial sites are predicted to have similar mobility. Oxygen tracer diffusivity of $2.46 \times 10^{-9}$ cm$^2$ s$^{-1}$, at 750 °C was reported with an activation energy of 1.56 eV. These observations offer experimental insight into the conduction mechanisms of these complex oxide systems and indicate that the scheelite phases with complex modulated structure are valid candidates for the development of new oxygen conductors.
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Tables

Table 1: Summary of the experimental conditions.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>LaNb0.88W0.12O4+d</td>
</tr>
<tr>
<td>space group</td>
<td>I2/c(α1,0,γ1)00(α2,0,γ2)00</td>
</tr>
<tr>
<td>Temperature</td>
<td>298 K</td>
</tr>
<tr>
<td>a b c (Å) (\beta) (°)</td>
<td>5.4131(1) 11.6432(2) 5.2963(1) 91.540(1)</td>
</tr>
<tr>
<td>(V (Å^3))</td>
<td>333.682(11)</td>
</tr>
<tr>
<td>modulation waves</td>
<td>(q_1^* = 0.2847(5)\alpha^* + 0.1098(9)c^*)</td>
</tr>
<tr>
<td></td>
<td>(q_2^* = -0.1266(9)\alpha^* + 0.2953(1)c^*)</td>
</tr>
</tbody>
</table>

| Data collection                  | MSPD at ALBA cell            |
| Data range                       | 2\(\theta\) = 3.0° to 20.1°  |
| Wavelength                       | \(\lambda = 0.3308 \text{ Å}\) |

| Reflections (all/observed)       | 1024/948                     |
| among them,                      |                              |
| Main Reflections (all/observed)  | 209/207                      |
| 1\textsuperscript{st} order (all/observed) | 815/746                     |
| \(R, R_w\) for Bragg reflections \((R_{all})\) | 9.34%, 9.15%               |
| among them,                      |                              |
| Main Reflections \((R, R_w)\)    | 6.4%, 8.4%                   |
| \(q_1\) 1\textsuperscript{st} order \((R, R_w)\) | 12.1%, 9.5%                 |
| \(q_2\) 1\textsuperscript{st} order \((R, R_w)\) | 15.1%, 9.3%                 |
| \(R_p, R_{wp}\)                  | 8.5%, 10.8%                  |

Table 2: Refined parameters of the parent structure.

<table>
<thead>
<tr>
<th>Element</th>
<th>Occ.</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U11</th>
<th>U22</th>
<th>U33</th>
<th>U12</th>
<th>U13</th>
<th>U23</th>
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<tbody>
<tr>
<td>La</td>
<td>0.994(12)</td>
<td>0</td>
<td>0.25</td>
<td>0.625</td>
<td>0.019(2)</td>
<td>0.0157(13)</td>
<td>0.031(3)</td>
<td>0</td>
<td>-0.004(2)</td>
<td>0</td>
</tr>
<tr>
<td>Nb/W</td>
<td>0.88/0.12</td>
<td>0</td>
<td>0.25</td>
<td>0.125</td>
<td>0.019(3)</td>
<td>0.051(3)</td>
<td>0.008(4)</td>
<td>0</td>
<td>-0.003(2)</td>
<td>0</td>
</tr>
<tr>
<td>O1</td>
<td>1</td>
<td>0.231(2)</td>
<td>0.0343(7)</td>
<td>0.076(2)</td>
<td>0.019(3)</td>
<td>0.051(3)</td>
<td>0.008(4)</td>
<td>0</td>
<td>0.007(2)</td>
<td>0</td>
</tr>
<tr>
<td>O2</td>
<td>1</td>
<td>0.163(2)</td>
<td>0.2064(8)</td>
<td>0.483(3)</td>
<td>0</td>
<td>0.005(2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cation site</th>
<th>Average bond length (Å)</th>
<th>Bond valence sum (BVS)</th>
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<tbody>
<tr>
<td>La</td>
<td>2.523</td>
<td>3.11</td>
</tr>
<tr>
<td>Nb/W</td>
<td>1.834</td>
<td>5.13</td>
</tr>
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</table>
Table 3: Atomic coordinates, and the Fourier amplitude of the displacive and occupancy wave functions in the LaNb\(_{0.88}\)W\(_{0.12}\)O\(_4+d\) phase.

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

\(^*\)s, c stands for Fourier magnitude of sin and cos wave of the displacive waves respectively; the number describes the wave vectors: the 1\(^{st}\) wave is along \(q_1\) direction and the 2\(^{nd}\) 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