Crystal Structure and Potential Interstitial Oxide Ion Conductivity of LnNbO$_4$ and LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ (Ln = La, Pr, Nd)

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Abstract

Single phase LnNbO$_4$ and LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ (Ln = La, Pr and Nd) were prepared via solid state reaction. The crystal structure of the materials has been investigated by X-ray diffraction and Rietveld refinement. PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ and NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ were found to have the same crystal structure as the parent phases whereas LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ has a modulated structure. Electrical conductivity was studied by AC impedance spectroscopy. Substantial improvements in total conductivity were achieved by W doping on the B-site, with LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ having the highest overall conductivity of 3.0x10$^{-3}$ S cm$^{-1}$ at 800 °C.

Keywords: LaNbO$_4$; oxide ion conductor, impedance spectroscopy, x-ray diffraction

1. Introduction

Rare earth ortho-niobates (with the general formula ReNbO$_4$ (Re = lanthanide)) have been widely investigated due to their potential use as ferroelectrics $^1$, phosphors $^2$ and prospective laser materials$^3$. These materials have also been proposed as potential ionic conductors where two structures types dominate: a high temperature tetragonal scheelite phase and a low temperature monoclinic fergusonite phase which can be viewed as a distorted version of the scheelite structure. Both crystal systems have previously been identified as potential SOFC materials which exhibited excellent conductivity in the intermediate temperature region (600 °C to 800 °C) $^4$-7. Currently, much of the research interest is focused on the acceptor doped ReNbO$_4$ (Re=La, Nd, Gd, Tb) after Haugsrud et al. reported an impressive proton conductivity of 10$^{-3}$ S cm$^{-1}$ at roughly 800 °C for the
Ca doped LaNbO$_4$ system$^{8,9}$. Alternatively, the conductivity of these materials can also be improved by introducing oxygen interstitials into the structure$^6$: it has been reported that the ionic conductivity of CeNbO$_4$, which readily absorbs oxygen on heating due to the partial oxidation of Ce$^{3+}$ to Ce$^{4+}$, reaches 0.01 S cm$^{-1}$ at 800 °C$^6$. It has been demonstrated that the low temperature monoclinic phase (fergusonite, modulated superstructure) has a higher oxygen tracer diffusion coefficient than the crystallographically simpler tetragonal high temperature CeNbO$_4$ phase$^{10}$. Unfortunately, a low transference number which also originates from the oxidation of Ce$^{3+}$, and poor stability, hinder its usage as an electrolyte$^6$.

Rare earth elements such as La and Nd which are more redox stable than Ce also form analogous structures to cerium niobate$^{11,12}$. Additionally, it has been reported that interstitial oxygen ions can be introduced via hexavalently doping at the Nb site$^{13}$. It is thus of great interest to investigate how the structure and conductivity of LnNbO$_4$ (Ln=La, Pr, Nd) compounds can be affected by rare earth substitution. Unfortunately, little information can be retrieved from the literature with regard to the conducting properties of these niobates; therefore, in this study, we investigate the structure and conduction properties of both LnNbO$_4$ and LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$. The effect of ionic radius on the structural and electrical properties was investigated using XRD, structural refinement and impedance spectroscopy.

2. Experimental

2.1 Sample Preparation

Both pure LnNbO$_4$ (Ln=La, Pr and Nd) and 8 wt% W doped LnNbO$_4$ (LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$) were prepared via solid state reaction. All the starting powders were examined with XRD to ensure that they were single phase. Stoichiometric amounts of starting powders (La(OH)$_3$ (99.9%), Nb$_2$O$_5$ (99.9%), WO$_3$ (99.99%) all from Sigma-Aldrich; Pr$_6$O$_{11}$ (99%) from Rhone Poulenc and Nd$_2$O$_3$ (99.9%) from Alfa Aesar) were weighed and then ground together. The powder mixtures were transferred into HDPE bottles and ball milled for 24 hours in acetone with zirconia balls to achieve homogeneous mixing. After the ball milling, the powders were dried in the oven at 100 °C. Approximately 0.5 g of powder was then weighed and uniaxially pressed into a 13 mm die with a pressure of about 360 MPa for each composition. The pellets were then isostatically pressed at 300 MPa for 1 min to achieve higher green density. To sinter the W containing compositions, pellets were buried in powder of the same chemical composition and placed in a platinum crucible to limit
the loss of tungsten. All the samples were sintered at 1400 °C for 12 hours with the heating/cooling rate set at 10 °C/min.

2.2 Characterisation

The crystal structures of the obtained samples were investigated using powder X-ray diffraction (D2 Phaser, Bruker) with Cu Kα radiation (λ= 0.15418 nm). A scan speed of 1 s/step with a step size of 0.02° was used over the 2θ range from 20° to 100°. The crystal structure was determined through Rietveld refinement using GSAS-II where possible. Pawley refinement was performed on the LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase, to obtain the lattice parameters for the parent monoclinic structure. The LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase was also characterized with electron diffraction (JEOL FX2100, operating at 200 kV), to investigate the modulated nature of the structure.

The fracture surfaces of the W doped samples were examined using scanning electron microscopy (JEOL JSM-6400). Chemical analysis was carried out with an INCA energy dispersive X-ray spectrometer (EDX) fitted within the SEM. Prior to the SEM, the samples were plasma cleaned (Gatan SOLARIS plasma cleaner, default procedure for TEM sample cleaning) to reduce organic contamination on the surface. All the samples were then coated with carbon as a conducting layer (K975X Thermal Evaporator, Quorum Technologies); the usage of carbon reduces the absorbing effect of the conducting layer and thus improves the accuracy of the chemical analysis. The EDX system was calibrated with a cobalt source prior to the characterisation.

The density of the samples was measured using Archimedes principle prior to impedance spectroscopy and all samples reached 90% to 93% after sintering. To carry out impedance spectroscopy (IS) measurements, both top and bottom surfaces of the sintered pellets were painted with platinum paste. The samples were then heated to 900 °C and held for 1 hour to achieve good adhesion between the conducting Pt layers and the sample. Impedance data over a wide temperature range, from 450 °C to 900 °C, were collected using a Solartron 1260 FRA system. An AC potential of 100 mV was applied over the frequency range 1 MHz – 1 Hz, with 30 data points collected per decade; at each point, 10 s integration time was allowed for data collection. Impedance measurements were conducted both under dry (compressed air ~10$^{-5}$ atm pH$_2$O) and wet (bubbling air through water ~0.02 atm pH$_2$O) conditions to investigate potential proton conduction. The impedance spectra were fitted using the ZView package (v3.2, Scribner Associates) to calculate the conductivity of the sample.
3. Results and discussion

3.1 Structural study

Figure 1 shows the XRD patterns of the various compositions examined in this work. All of the undoped materials had the fergusonite structure at room temperature (space group $I2/c$); no additional peaks were observed, confirming the formation of single phase powders. Rietveld refinement was carried out for all of the undoped samples (results shown in Table 1): the cell parameters of the three phases vary slightly, due to the variation in ionic radius of the Ln site. The W dopant has an evident effect on the structure of the PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ and NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases: peak shifts towards high 2θ values were observed in both systems, though the symmetry remains the same as the parent structure. Rietveld refinement was carried out for the PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ (Figure 2) and NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ (not shown) with the refined lattice parameters presented in Table 1. No additional peaks were observed in the data, indicating single phase formation and a random distribution of the W dopants.

LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ on the other hand has what appears to be a superstructure, characterised by the satellite reflections in the XRD pattern, Figure 3a. Electron diffraction (Figure 3b) of the LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase clearly demonstrates its modulated nature. It is beyond the scope of this report to study in detail the crystallography of this phase, nevertheless, the electron diffraction suggests that the structure is 2d-incommensurately modulated, with modulation vectors $q_1=0.263a^*+0.106c^*$ and $q_2=0.082a^*+0.2427c^*$.

It has been suggested by Cava$^{13}$ that a minimum defect concentration is required to obtain an incommensurately modulated phase (superstructure); in their experiment, 10 wt% W substitution was required to obtain an incommensurately modulated structure in the LaNbO$_4$ system. Due to the complicated nature of the modulated superstructure, only Pawley refinement was carried out for the LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase. It is unclear whether an incommensurately modulated structure can be obtained in the PrNbO$_4$ and NdNbO$_4$ system by increasing the W dopant level, but clearly at 8 wt% no superstructure is formed in these solid solution systems.

The difference in the crystal structure among the W doped LnNbO$_4$ might be related to the radius of the rare earth site ions. The rare earth ions are eight fold coordinated in the fergusonite and scheelite structures, as a result, Pr and Nd have a slightly smaller ionic radius comparing with La.
(1.16 Å, 1.126 Å and 1.109 Å respectively for La, Pr and Nd), leading to a more rigidly packed cell. The structural modulation of CeNbO$_{4+d}$ (Ce$^{3+}$ has a slightly larger radius than Pr$^{3+}$ and Nd$^{3+}$) has also been well documented in the literature. The nature of the modulation remains to be explored.

The fracture surfaces of the LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ compounds were examined with scanning electron microscopy, Figure 4. The W doped samples all have similar microstructure: the grains were well shaped and no abnormal grain growth was observed. No secondary phase can be identified which again indicates that the materials under investigation are single phase in agreement with the XRD data. The EDX spectra, Figure 5, confirm the presence of W in all of the LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ samples. Quantification of the cation ratio was attempted using the EDX spectra: at least 20 spectra were recorded for each sample and the obtained data were normalized (Table 2). The oxygen counts could be affected by residual contamination on the surface and thus were not included in the normalization. The results show good agreement with the expected stoichiometry: the cation ratio between A and B site is close to 1 for all the doped samples. This agrees well with the nominal stoichiometry and suggests that the materials incorporate excess oxygen.

3.2 Conductivity of LnNbO$_4$ and LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases (Ln=La, Pr, Nd)

The conduction properties of the LnNbO$_4$ and LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases were investigated using AC impedance spectroscopy. Figure 6 shows an impedance spectrum of the NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ recorded at 450 °C: three responses, namely the bulk response at the left-hand side, the grain boundary response with a maximum at $\sim 10^4$ Hz and an electrode-interface response (the long tail to the right) can be separated from the spectrum based on their characteristic capacitances. A model (shown in the inset of Figure 6) with two constant phase elements was used to estimate the grain boundary and bulk resistance of the samples. The electrode interface response is excluded from the fitting and the total resistance is considered to be the sum of the grain boundary resistance and bulk resistance.

The total conductivity of the LnNbO$_4$ phases is significantly improved by the W substitution: the Arrhenius plot of the total conductivity demonstrates that at least 1.5 orders of magnitude improvement is achieved by the W substitution, regardless of the type of the rare earth elements, Figure 7. Among all the W doped compounds, the LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase has the highest conductivity in the intermediate region, reaching $3.0 \times 10^{-3}$ S cm$^{-1}$ at 800 °C, above which, the conduction curves of LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases tend to converge.
Closer examination of the conduction plot of the doped samples would reveal a change in the activation energy at elevated temperature, Figure 8: for the LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase, the activation energy reduces from 1.57 eV to 0.93 eV at around 600 °C. The change may be related to the fergusonite – scheelite phase transition, which also occurs within this temperature region. It is worth noting that a decrease of activation energy at elevated temperature has also been observed in the lanthanide doped CaWO$_4$ systems (these systems maintain the scheelite structure over the temperature range of interest). It has been suggested that the change in charge carrier species might be responsible for the difference in activation energy in the scheelite systems$^{17}$. The activation energies, Table 3, also vary significantly with composition: at high temperature, the activation energy increases with reduced ionic radius among the LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases; at low temperature, the PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ has the lowest Ea (1.34 eV) while LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ and NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ have a similar value (1.56 eV). The variation in activation energy with composition might result from the difference in ionic radius. In the W containing phases, the lattice could be compressed if an oxygen ion is situated in the interstitial sites in the neighbouring cell. As a result, the migration of the charge carriers may be hindered. Larger rare earth ions, on the other hand, would facilitate a broader lattice framework (as evidenced by the lattice parameters reported in Table 1) which might improve the mobility of the charge carriers.

It is interesting to probe the conducting mechanisms in these phases, especially that of LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ which is shown to be modulated. One of the possible causes for the improved conductivity of the W doped phase might be the introduction of interstitial oxygen into the structure. A similar effect has been observed in the lanthanide doped scheelite structure: the presence of the oxygen ions in these structures was confirmed by a neutron diffraction study and the improvement in conductivity has been associated with the aliovalent doping on the A site$^7$. However, due to the relatively low dopant concentration, a minor amount of vacancy on the A site would also facilitate the charge compensation process. For instance, a Nd$_{0.97}$Nb$_{0.01}$W$_{0.02}$O$_4$ phase would fall within the experimental error of the reported cation ratio in Table 2. Consequently, the charge compensation process remains unclear in these phases and requires further conductivity measurements on nominally cation deficient samples. Proton conduction of the alkaline earth metal doped fergusonite structures has been well documented in the literature$^{8,9}$, although impedance measurements in humidified air (~0.02 atm pH$_2$O) suggest that proton conduction
contributes little to the conductivity enhancement observed in the current phase, as demonstrated in Figure 9.

The activation energy of the LnNbO$_4$ phases (reported in Table 3, the PrNbO$_4$ dataset was too scattered to yield a meaningful value at low temperature) does not share the same trend with the LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ system. However, there are still some interesting features that call for future study. For instance, the conductivity of the LaNbO$_4$ jumped nearly an order of magnitude at 600 °C, the nature of this abnormal behaviour remains to be explored. To our knowledge, the conductivity of PrNbO$_4$ and NdNbO$_4$ has not been previously reported. It is still unclear how the slight change in the ionic radius would bring about 2 orders of magnitude of improvement in conductivity in the intermediate temperature region.

4. Conclusions

Single phase LnNbO$_4$ and LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ (Ln = La, Pr and Nd) were prepared via solid state reaction. All the LnNbO$_4$, as well as PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ and NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ have a monoclinic fergusonite structure at room temperature while the LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase is incommensurably modulated. Results from the Rietveld refinement reveal an anisotropic expansion of the unit cell in the PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ and NdNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases, despite the lack of ordering in the structure. Conductivity of LnNbO$_4$ is significantly improved with W dopants: a 1.5 order of magnitude increase was obtained for LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$, reaching 3.0x10$^{-3}$ Scm$^{-1}$ at 800 °C. The activation energy of the LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ varies significantly with the size of the rare earth and temperature: larger ions tend to have lower activation energy, while LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase has higher activation energy in low temperature region, possibly resulting from the additional ordering in the structure.

Acknowledgments

The authors are very grateful for Dr. Stevin Pramana, Imperial College London, who helped to carry out the electron diffraction work.
References


Table 1: Refined cell parameters of the LnNbO$_4$ and LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases:

<table>
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<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
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</thead>
<tbody>
<tr>
<td>LaNbO$_4$</td>
<td>5.5682(1)</td>
<td>11.5273(4)</td>
<td>5.2057(1)</td>
<td>94.068(5)</td>
</tr>
<tr>
<td>LaNb$<em>{0.92}$W$</em>{0.08}$O$_{4.04}$</td>
<td>5.4253(2)</td>
<td>11.6240(4)</td>
<td>5.2893(2)</td>
<td>91.975(7)</td>
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<tr>
<td>PrNbO$_4$</td>
<td>5.4702(2)</td>
<td>11.2787(3)</td>
<td>5.1506(2)</td>
<td>94.478(4)</td>
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<td>PrNb$<em>{0.92}$W$</em>{0.08}$O$_{4.04}$</td>
<td>5.4809(5)</td>
<td>11.3874(9)</td>
<td>5.1632(5)</td>
<td>93.924(8)</td>
</tr>
<tr>
<td>NdNbO$_4$</td>
<td>5.4696(2)</td>
<td>11.2840(3)</td>
<td>5.1488(2)</td>
<td>94.510(3)</td>
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<tr>
<td>NdNb$<em>{0.92}$W$</em>{0.08}$O$_{4.04}$</td>
<td>5.4562(5)</td>
<td>11.3209(10)</td>
<td>5.1517(5)</td>
<td>93.969(8)</td>
</tr>
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</table>

a. Results obtained by Pawley refinement
Table 2: Normalized atomic ratio of the cations in various LnNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phases

<table>
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<tr>
<th></th>
<th>Ln%</th>
<th>Nb%</th>
<th>W%</th>
</tr>
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<tr>
<td>LaNb$<em>{0.92}$W$</em>{0.08}$O$_{4.04}$</td>
<td>50.4±0.7</td>
<td>44.6±0.6</td>
<td>4.9±0.4</td>
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<tr>
<td>PrNb$<em>{0.92}$W$</em>{0.08}$O$_{4.04}$</td>
<td>49.2±0.5</td>
<td>46.3±0.5</td>
<td>4.5±0.2</td>
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<tr>
<td>NdNb$<em>{0.92}$W$</em>{0.08}$O$_{4.04}$</td>
<td>49.0±0.6</td>
<td>46.5±0.6</td>
<td>4.5±0.2</td>
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<tr>
<td>Theoretical</td>
<td>50.0</td>
<td>46.0</td>
<td>4.0</td>
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Table 3: Variation of activation energy with temperature and composition (all in eV)

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<tr>
<th>Composition</th>
<th>$E_a$ at low $T$</th>
<th>$E_a$ at high $T$</th>
<th>Composition</th>
<th>$E_a$ at low $T$</th>
<th>$E_a$ at high $T$</th>
</tr>
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<tbody>
<tr>
<td>$\text{LaNb}<em>{0.92}\text{W}</em>{0.08}\text{O}_{4.04}$</td>
<td>1.57±0.05</td>
<td>0.93±0.02</td>
<td>$\text{LaNbO}_4$</td>
<td>1.37±0.04</td>
<td>0.71±0.03</td>
</tr>
<tr>
<td>$\text{PrNb}<em>{0.92}\text{W}</em>{0.08}\text{O}_{4.04}$</td>
<td>1.34±0.03</td>
<td>1.00±0.06</td>
<td>$\text{PrNbO}_4$</td>
<td>N/A</td>
<td>0.95±0.03</td>
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<tr>
<td>$\text{NdNb}<em>{0.92}\text{W}</em>{0.08}\text{O}_{4.04}$</td>
<td>1.56±0.04</td>
<td>1.20±0.04</td>
<td>$\text{NdNbO}_4$</td>
<td>0.89±0.04</td>
<td>0.72±0.02</td>
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Figure 1 XRD patterns of LnNbO₄ and LnNb₀.₉₂W₀.₀₈O₄.₀₄ compounds under investigation; at room temperature, the LnNbO₄ under investigation, PrNb₀.₉₂W₀.₀₈O₄.₀₄ and PrNb₀.₉₂W₀.₀₈O₄.₀₄ all have a monoclinic fergusonite structure while LaNb₀.₉₂W₀.₀₈O₄.₀₄ has a superstructure.
Figure 2: Rietveld refinement results for the PrNb$_{0.92}$W$_{0.08}$O$_{4.04}$ phase; the cross marks the observed pattern whereas the green line is the calculated results; the blue line beneath the pattern marks the difference between the calculation and the observation.
Figure 3 a) XRD patterns of LaNbO₄ and LaNb₀.₉₂W₀.₀₈O₄.₀₄ phases, with the inset highlighting the satellite peaks at low angles resulting from additional ordering on introduction of W.

Figure 3 b) Electron diffraction pattern of the LaNb₀.₉₂W₀.₀₈O₄.₀₄ phases from [010] zone axis of the parent phase; a modulation structure, characterized by the satellite reflections is clearly observed; the direction of the modulation vectors were also marked on the image.
Figure 4 Backscatter SEM images showing the fracture surface of the a) \(\text{LaNb}_{0.92}\text{W}_{0.08}\text{O}_{4.04}\) b) \(\text{PrNb}_{0.92}\text{W}_{0.08}\text{O}_{4.04}\) and c) \(\text{NdNb}_{0.92}\text{W}_{0.08}\text{O}_{4.04}\) samples; no secondary phase was observed.
Figure 5 EDX spectra confirming the presence of W in the a) LaNb₀.₉₂W₀.₀₈O₄.₀₄ b) PrNb₀.₉₂W₀.₀₈O₄.₀₄ and c) NdNb₀.₉₂W₀.₀₈O₄.₀₄ samples
Figure 6 Impedance spectrum of NdNb$_{0.02}$W$_{0.08}$O$_{4.04}$ 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, $10^7$ Hz and $10^8$ Hz respectively; the red line shows the fitting results using the model in the inset.
Figure 7 Arrhenius plot of the total conductivity of LnNbO₄ and LnNb₀.₉₂W₀.₀₈O₄.₀₄ phase (Ln = La, Nd, Pr). Note: only LaNbO₄ in humidified air could be identified in the current literature.¹⁸
Figure 8 Arrhenius plot of the LaNb$_{0.92}$W$_{0.08}$O$_{4.04}$ illustrating the change of activation energy at high temperature.
Figure 9 Conductivity of a LaNb$_{0.92}$W$_{0.08}$O$_4$ sample in dry air and wet air; no enhancement in conductivity was observed in the wet condition, suggesting that the photonic conduction has little contribution to the improvement in conductivity.