Electronic Supplementary Material (ESI) for Dalton Transactions.

Room temperature structure and transport properties of the incommensurate modulated $LaNb_{0.88}W_{0.12}O_{4.06}$ - Supplemental information

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Surface morphology and chemical composition of various $LaNb_{1-x}W_xO_{4+d}$ samples was verified using SEM. The polished surface, observed using both SE and BES signal, of a $LaNb_{0.88}W_{0.12}O_{4.06}$ sample is presented in Figure S1. No contrast from elemental difference was observed, indicating a homogeneous distribution of the dopant. Chemical composition of the samples was probed using energy dispersive X-ray spectroscopy (EDX). The average composition was obtained by averaging more than 10 spectra, each taken from 200 μm x 200 μm areas (Table S1). 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.

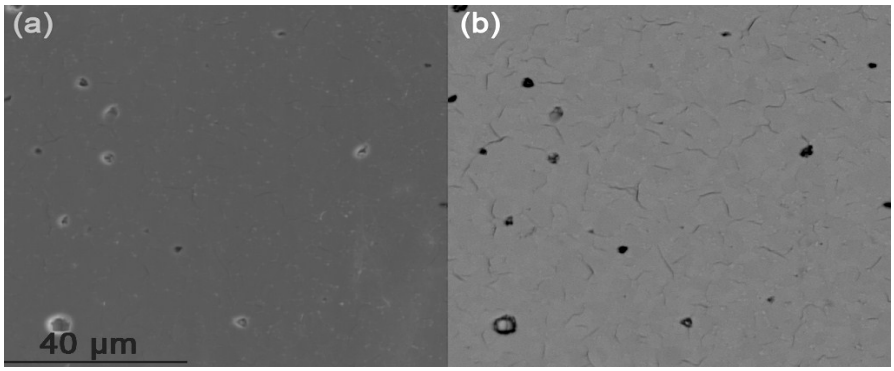

Figure S1: SEM micrographs showcase the microstructure of $LaNb_{0.88}W_{0.12}O_{4.06}$ using (a) secondary electron (SE) signals and (b) backscattered electron (BSE) signals. No secondary phase was visible from the BSE image.

Table S1: Chemical composition of selected $LaNb_{1-x}W_xO_{4+d}$ phases characterized using EDX and XPS. The quantified atomic percentage was obtained by averaging ten spectra. Nominal concentrations are shown in bold.

$LaNb_{1-x}W_xO_{4+d}$ composition	La(at%)	Nb(at%)	W(at%)
x = 0.12	**50**	**44**	**6**
	50.7 ± 2.2	42.9 ± 1.5	6.4 ± 0.9

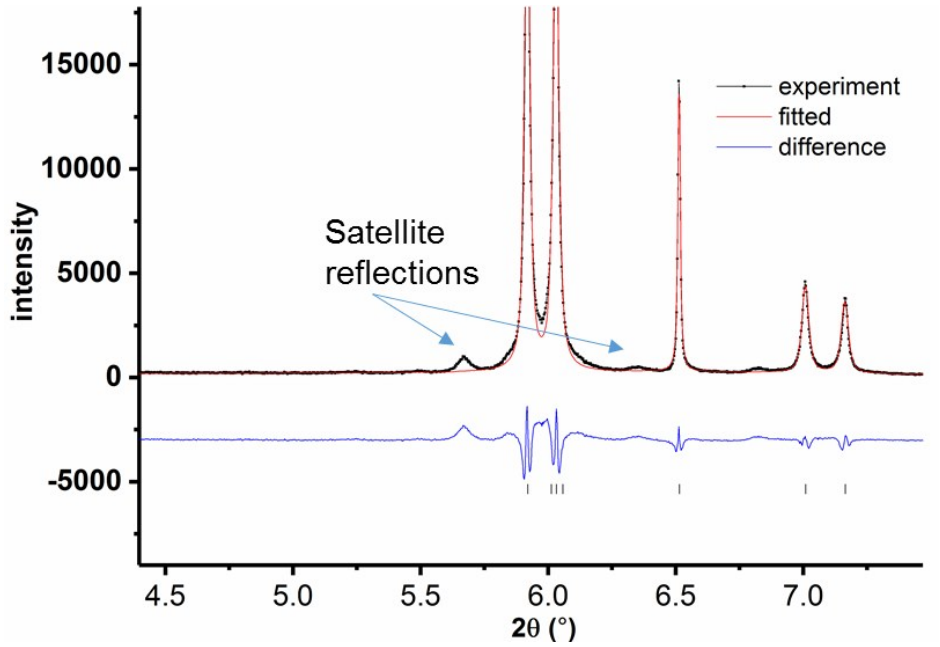

Figure S2: Snapshot of the Rietveld refinement results obtained from synchrotron diffraction data of the $LaNb_{0.88}W_{0.12}O_{4.06}$ phase refined using only the parent phase space group. Black, red and blue lines show the experimental data, modelled data and the difference plot respectively. The black vertical lines mark the theoretical Bragg peak positions of the parent structure. Final goodness of fit parameters R_p = 10.7% and R_{wp} = 13.9% were achieved. Intensity attributable to the satellite peaks associated with the modulated structure are indicated.

The modulated phases have different conducting behaviours, Figure S3. The total conductivity of the $LaNb_{1-x}W_xO_{4+d}$ series increases with dopant level and reached its maximum with 12 at% dopant level. The $LaNb_{0.88}W_{0.12}O_{4.06}$ composition has a total conductivity of 8×10^{-3} S cm^{-1} at 863

°C under lab air, comparable with the value reported for other fergusonite related systems. Activation energy for the x = 0.12 composition was 1.49 eV and 1.29 eV respectively for the high and low temperature region.

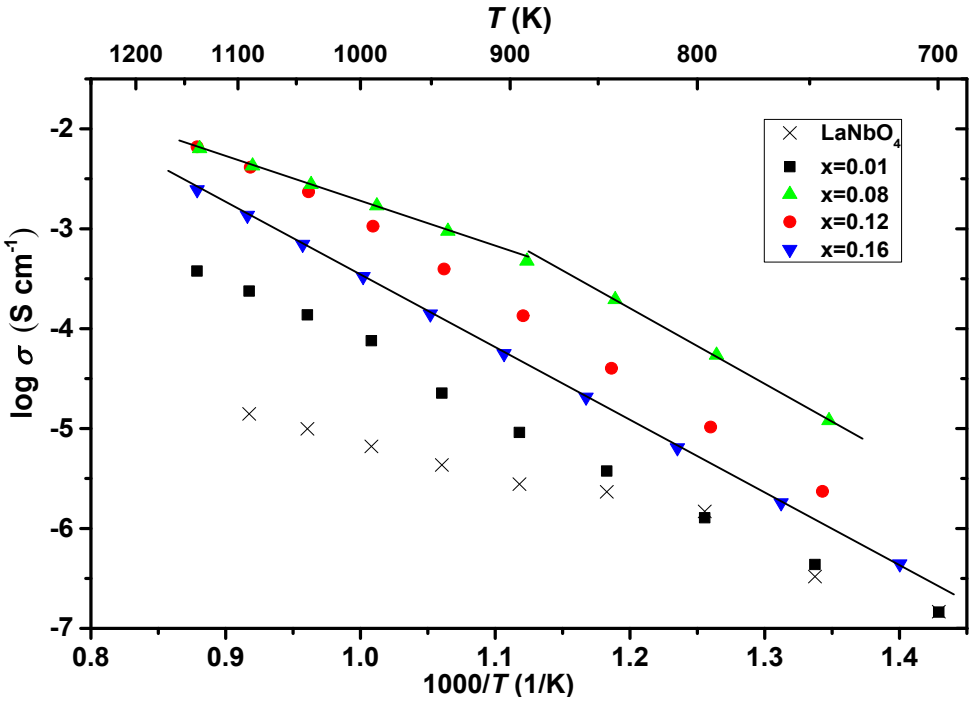

Figure S3: Total conductivity of $LaNb_{1-x}W_xO_{4+d}$ phases in comparison with the $LaNbO_4$ reference measured under static air. The solid lines highlight the different behaviour between $LaNb_{0.92}W_{0.08}O_{4+d}$ and $LaNb_{0.84}W_{0.16}O_{4+d}$ compositions: the former has two distinctive regions with different E_a whereas the latter has a fixed E_a.