Supporting Information

Topotactic Ion Exchange in a Three-Dimensional Close-Packed Trirutile Structure with an Octahedral Network

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EXPERIMENTAL

Synthesis

The white colored $\alpha$-LiNbWO$_6$ was synthesized by a solid-state reaction as reported in the literature.$^{37}$ For this purpose, stoichiometric quantities of Li$_2$CO$_3$ (Sigma Aldrich, $\geq 98.0\%$), Nb$_2$O$_5$ (Sigma Aldrich, $\geq 99.9\%$) and WO$_3$ (Sigma Aldrich, $\geq 99.0\%$) were first weighed along with 10 mole % of Li$_2$CO$_3$ and 20 mole % of WO$_3$ in excess (to compensate the loss due to volatilization of the components at higher temperatures). The constituents were then ground thoroughly in an agate mortar for 1 h and calcined at 780 °C for 24 h in a high quality ($\geq 99.8\%$ Al$_2$O$_3$) alumina boat.

The ion exchange reaction was performed by taking 1 g of $\alpha$-LiNbWO$_6$ powder in 100 mL of 0.2 M aqueous solution of FeCl$_2$.4H$_2$O (Sigma Aldrich, $\geq 99.0\%$) and stirring at 60 °C in Argon
atmosphere for 4 days. During the ion exchange, the aged aqueous FeCl$_2$.4H$_2$O solution was replaced with a fresh solution intermittently after 2 days. Finally, the product was washed with distilled water for several times and dried at room temperature in a desiccator. The dried sample after ion exchange was mustard-yellow in color.

Characterization

*Powder X-ray diffraction (P-XRD)*

P-XRD measurements were carried out using a Bruker AXS D8 Advance diffractometer operating at 40 kV and 30 mA with graphite monochromatized CuK$_a$ (1.5406 Å) radiation in the angular range of 5–90°. Indexing of the P-XRD pattern and least-square refinement of lattice parameters were carried out using PROSZKI program. Rietveld refinement of the P-XRD data for Li$_{0.1}$Fe$_{0.45}$NbWO$_6$ was carried out using the FULLPROF program suite. For refinement, the P-XRD data was collected in the 2θ range 15–90° with a step size of 0.018°. In the initial refinement runs, the background coefficients along with zero-shift and cell parameters were refined. In the successive runs, the profile and shape parameters were refined step by step to avert any divergence. The presence of light atoms (Li and O) together with the heavier elements (Nb and W) made the structure refinement rather challenging due to poor scattering of Li and O by the X-rays. Thus, in the refinement runs heavy element positions (Nb, W) and their thermal parameters were refined first, keeping the light atom positions (Li, O) fixed. Subsequently, the position and thermal parameters of Li/Fe were refined keeping the oxygen coordinates fixed to those of the model structure (from neutron data). Finally, the oxygen thermal parameters were refined by restricting to one at a time.

*Field-Emission Scanning Electron Microscopy (FE-SEM)*
Microstructural studies of the samples were investigated with the aid of an FE-SEM (Zeiss, Ultra plus55), operating at an accelerating voltage of 20 kV. The samples were smeared on a carbon tape pasted on an Aluminium stub and sputter coated with a thin layer of Au for electrical conductivity. The elemental compositions of all the compounds were determined by energy dispersive X-ray (EDX) spectroscopy. Spot and area analyses were carried out to determine the elemental compositions in several regions of the sample.

*Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES)*

The ICP-OES analysis was carried out on an Agilent 720ICP-OES instrument. For this, samples were dissolved in concentrated hydrofluoric acid. Calibration solutions in concentration ranges of 200 ppb, 400 ppb and 600 ppb were prepared from 1000 ppm standard lithium nitrate solution (purchased from SRL chemicals). The amount of Li in the compound was determined and accordingly the composition was determined. The composition of the final product corresponded to the general formula \( \text{Li}_{(1-2x)}\text{Fe}_x\text{NbWO}_6 \), with \( x = 0.45 \).

*High-Resolution Transmission Electron Microscopy (HR-TEM)*

Transmission electron microscopic (TEM) images and selective area electron diffraction (SAED) patterns were recorded with JEM-3200FS electron microscope, operating at an acceleration voltage of 300 kV. For the TEM analysis, fine powder of \( \text{Li}_{0.1}\text{Fe}_{0.45}\text{NbWO}_6 \) was dispersed in ethanol and ground for 10 min. Then, one drop of the suspension was put on carbon coated copper grid and allowed to dry in air overnight.

*Solid State Nuclear Magnetic Resonance (ssNMR)*

\(^7\text{Li}\) solid state nuclear magnetic resonance spectra (ssNMR) were recorded on a JEOL MHz NMR spectrometer (model ECX 400 II) using a 4mm rotor as sample holder. \(^7\text{Li}\) spectra were averaged
for 32 scans using a 90° pulse length of 3.7 μs and a recycle delay of 8s. The $^7$Li spectra were referenced to aq. 1M LiCl at 0 ppm.

**UV-Visible Diffuse Reflectance Spectra (UV- vis DRS)**

The optical properties of the compounds were recorded using a Shimadzu UV-2450 UV-vis spectrophotometer in the 200-800 nm wavelength range using BaSO$_4$ as a reference material. The acquired reflectance data were converted to absorption term using the Kubleka-Munk (K-M) theory.

$$F (R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$ (1)

where, $R_{\infty}$ is the reflectance of the sample and $F (R_{\infty})$ is the K-M function. The band gap of the samples was determined from the Tauc plots using the following equation.$^{38}$

$$(\alpha h\nu)^{1/n} = A (h\nu - E_g)$$ (2)

where, $\alpha$, $h\nu$, $A$, and $E_g$ are the absorption coefficient, incident energy, proportionality constant and band gap, respectively. The value of exponent, $n$ determines the nature of electronic transition; for assigning direct transition, $n = \frac{1}{2}$ and for indirect transition, $n = 2$ were used. The linear extrapolation of $(\alpha h\nu)^{1/n}$ to zero gave the band gap energies of the samples. The value of $E_g$ calculated for the exponent, $n = \frac{1}{2}$, i. e., for an indirect transition was reasonably close to the value of $E_g$ estimated from the corresponding absorption edge.

**X-ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Physical Electronics PHI 5000 VersaProbe III spectrometer using Al Kα radiation ($\lambda = 1486.6$ eV).

**Magnetic Measurements**

Magnetization (zero field cooled and field cooled) data of Li$_{0.1}$Fe$_{0.45}$NbWO$_6$ (~ 54 mg) were performed on a superconducting quantum interference device (SQUID) magnetometer (Quantum
Design MPMS XL Ever Cool) in the temperature range of 4 – 300 K in a magnetic field of 1000 Oe.

**Figure S1.** FE-SEM and corresponding EDX data of Li$_{0.1}$Fe$_{0.45}$NbWO$_6$ (a) after 24 h of ion exchange and (b) after 48 h of ion exchange.

**Figure S2.** P-XRD patterns of LiNbWO$_6$ and Li$_{0.1}$Fe$_{0.45}$NbWO$_6$. 

| Element | LiNbWO$_6$ | Li$_{0.1}$Fe$_{0.45}$NbWO$_6$ |
|---------|------------|-------------------------------|
| Fe      | 7.40       | 12.06                         |
| Nb      | 47.50      | 44.25                         |
| W       | 45.09      | 43.69                         |
**Figure S3.** FE-SEM and corresponding EDX data of (a) $\alpha$-LiNbWO$_6$ and (b) Li$_{0.1}$Fe$_{0.45}$NbWO$_6$. EDX elemental mapping of Fe, Nb and W for Li$_{0.1}$Fe$_{0.45}$NbWO$_6$ along with the corresponding bright field SEM image.
Table S1. Atomic Positions, Site Occupancy and Thermal Parameters of Li$_{0.1}$Fe$_{0.45}$NbWO$_6$.

| atom  | $x$    | $y$    | $z$     | $B_{iso}$   | occ. |
|-------|--------|--------|---------|-------------|------|
| Li    | 0.000  | 0.5    | 0.4159  | 2.70(1)     | 0.10 |
| Fe    | 0.000  | 0.5    | 0.4159  | 2.70(1)     | 0.45 |
| Nb    | 0.000  | 0.5    | 0.0893  | 0.24(1)     | 1    |
| W     | 0.000  | 0.5    | 0.7305  | 3.23(1)     | 1    |
| O1    | 0.291  | 0.791  | 0.7712  | 2.55(1)     | 2    |
| O2    | 0.3032 | 0.8032 | 0.0809  | 2.16(1)     | 2    |
| O3    | 0.2993 | 0.7993 | 0.3939  | 3.49(1)     | 2    |

| parameter       | value         |
|-----------------|---------------|
| space group     | $P-42_{1}m$   |
| $a$             | 4.6737(1) Å   |
| $c$             | 9.2411 (3) Å  |
| $V$             | 201.87(1) Å$^3$ |
| $R_{Bragg}$ (%) | 4.1           |
| $R_F$ (%)       | 2.5           |
| $R_p$ (%)       | 4.8           |
| $R_{wp}$ (%)    | 6.1           |
| $\chi^2$       | 6.8           |
Table S2. Selected Bond Lengths (Å) in Li$_{10.1}$Fe$_{0.45}$NbWO$_6$

| Bond          | Length (Å) |
|---------------|------------|
| Fe – O1 (×2)  | 2.213(6)   |
| Fe – O3 (×2)  | 2.201(6)   |
| Fe – O3 (×2)  | 1.988(6)   |
| < Fe – O >    | 2.130      |
| Nb – O1 (×2)  | 1.889(5)   |
| Nb – O2 (×2)  | 2.005(6)   |
| Nb – O2 (×2)  | 2.041(5)   |
| <Nb – O >     | 1.970      |
| W – O1 (×2)   | 1.959(6)   |
| W – O3 (×2)   | 2.174(6)   |
| W – O2 (×2)   | 1.755(4)   |
| < W – O >     | 1.960      |
Figure S4. P-XRD patterns of Li$_{0.1}$Fe$_{0.45}$NbWO$_6$ after heating at 350 (in air), 550 and 800°C (in argon atmosphere).