Experimental report

11/12/2025

Proposal: 5-21-1206 **Council:** 10/2024

Title: KNb2O5F: A TETRAGONAL TUNGSTEN BRONZE FRAMEWORK AS POTENTIAL ANODE FOR RECHARGEABLE K-ION BATTERIES

Research area: Materials

This proposal is a new proposal

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Samples: KNb2O5F
KxWO3
KxNbyW1-yO3-d

Instrument	Requested days	Allocated days	From	To
D2B	1	2	14/05/2025	15/05/2025
			28/05/2025	29/05/2025

Abstract:

This proposal aims to determine the crystal structure and composition of a tetragonal tungsten bronze-type material with the nominal composition KNb¿O¿F, which may be used as an electrode material in rechargeable K-ion batteries (KIBs). The primary objective of this work is to accurately establish the position and occupancy of oxygen/fluorine and potassium atoms, as well as to identify the presence of water molecules or other species within the structural tunnels. Additionally, we intend to examine whether modifications in the synthesis method lead to compositional or structural differences that could explain the variations in the electrochemical performance of the samples. For this study, we request 12 hours of beam time on the D2B diffractometer.

KNb_2O_5F: a tetragonal tungsten bronze framework as potential anode for rechargeable K-ion batteries

Tungsten bronzes are non-stoichiometric compounds with the general formula M_xWO3, where M is typically an alkali metal (e.g., Ba, Pb, Cu, Ag) or a rare-earth element, and x typically lies within $0 < x < 1$[1]. These materials crystallize in several structure types, including hexagonal (HTB), tetragonal I (TTB-I), perovskite-related tetragonal (TTB-II), and cubic (CTB)[2]. The TTB framework features three-, four-, and five-sided tunnels, with metallic ions preferentially occupying the four- and five-sided channels along the *c*-axis to preserve charge neutrality[3]. The mobility of ions through these cavities confers the material high electrical conductivity[1].

The tetragonal tungsten bronze (TTB) unit cell ($a = b = 12.6$ Å, $c = 3.8$ Å) consists of WO_6 octahedra arranged in (001) layers that stack to form a structure with *P4/mbm* symmetry[4]. KNb_2O_5F adopts this TTB-type structure (space group *P4/mbm*), where Nb is octahedrally coordinated by five O atoms and one F atom (Figure 1). The resulting $Nb(O_5F)$ octahedra connect via corner sharing to create a three-dimensional network containing pentagonal, tetragonal, and triangular channels along [001]. Because the triangular channels are too small for cation insertion, K-ions accommodate only in the tetragonal and pentagonal tunnels, ensuring overall electroneutrality[3].

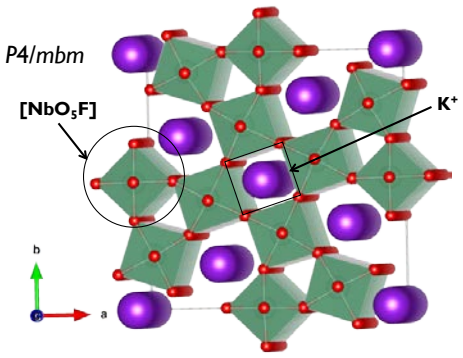

Figure 1. Tetragonal tungsten bronze (TTB) structure, where purple spheres represent K-ions, while the red spheres correspond to oxygen (O) atoms in octahedral arrangement around the W atoms (green).

This material was synthesized following the same procedure, but with variations in the inert atmosphere used during the synthesis steps (Figure 2). Due to this reason, we performed Neutron Powder Diffraction to these compounds in order to see differences in the atomic contents of the samples.

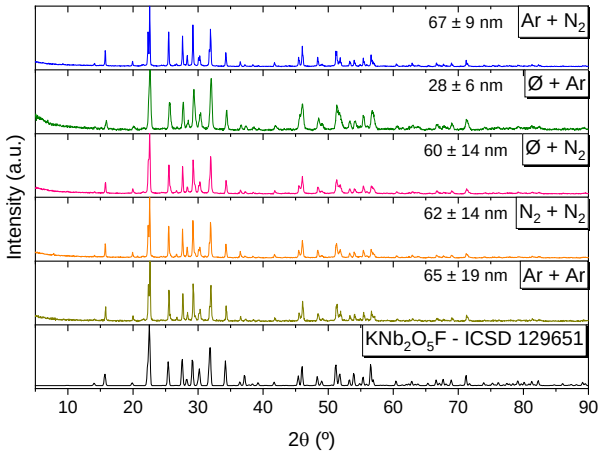

Figure 2. XRD patterns of the different samples of KNb_2O_5F and their comparison to the bibliographic sample from ICSD. Blue, orange and yellow samples were synthesized in two steps under Ar + N_2, N_2 + N_2 and Ar + Ar, respectively. Green and pink samples were synthesized in only one step under Ar and N_2, respectively.

Room temperature Neutron Powder Diffraction (NPD) patterns for KNb_2O_5F samples collected at Institut Laue Langevin (ILL) using a High-Resolution Two-Axis Diffractometer (D2B) with $\lambda = 1.594$ Å are shown in Figure 3. These compounds' structure was refined in the tetragonal *P4/mbm* (#127) space group.

In Table 1 it is shown the refined structural parameters obtained from NPD for all samples.

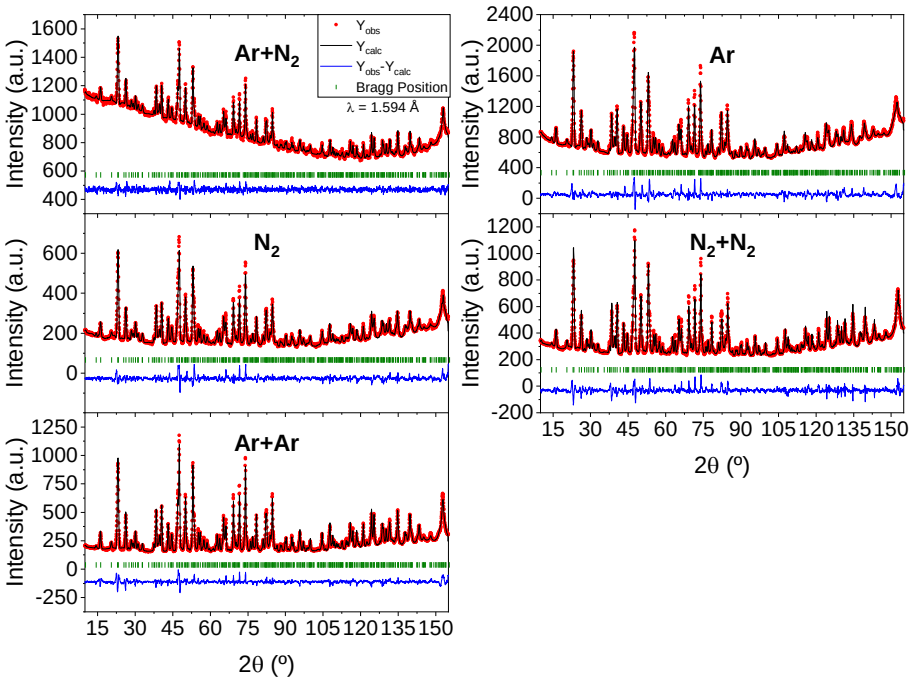

Figure 3. Observed (red dots), calculated (black, full line) and difference (blue line) neutron powder diffraction profile for KNb_2O_5F samples. The vertical green bars correspond to the allowed Bragg reflections.

Table 1. Refined structural parameters obtained from NPD for KNb_2O_5F samples at room temperature.

KNb_2O_5F		**Ar + N_2**	**Ar**	**N_2**	**N_2 + N_2**	**Ar + Ar**
Temperature (K)		298.15	298.15	298.15	298.15	298.15
Space group		*P4/mbm*	*P4/mbm*	*P4/mbm*	*P4/mbm*	*P4/mbm*
***a* = *b* (Å)**		12.6172(4)	12.6298(12)	12.6154(8)	12.6207(5)	12.6196(5)
***c* (Å)**		3.94537(18)	3.9574(5)	3.9484(3)	3.9468(2)	3.94669(22)
Volume (Å^3)		628.07(4)	631.24(12)	628.38(8)	628.65(5)	628.53(5)
K1 (*2a*) (0 0 0)	B_{iso} (Å^2)	3(2)	2(2)	7(3)	1(1)	3(2)
	Occ	0.078(13)	0.090(15)	0.086(18)	0.06(1)	0.063(11)
K2 (*4g*) (x y 0)	x	0.1714(19)	0.1684(24)	0.1692(23)	0.171(2)	0.1722(15)
	y	0.6714(19)	0.6684(24)	0.6692(23)	0.671(2)	0.6722(15)
	B_{iso} (Å^2)	4.0(8)	4(1)	4(1)	4.6(9)	4.1(7)
	Occ	0.288(16)	0.292(24)	0.285(21)	0.33(2)	0.276(14)
Nb1 (*8j*) (x y 1/2)	x	0.0696(9)	0.0716(13)	0.0701(11)	0.071(1)	0.0707(8)
	y	0.2150(9)	0.2153(12)	0.2134(10)	0.2142(9)	0.2129(8)
	B_{iso} (Å^2)	1.35(23)	0.7(3)	0.8(3)	0.6(2)	1.28(18)
	Occ	0.438(13)	0.422(18)	0.413(16)	0.42(1)	0.426(11)
Nb2 (*2c*) (0 1/2 1/2)	B_{iso} (Å^2)	1.3(4)	0.4(7)	1.1(5)	0.8(4)	0.9(3)
	Occ	0.125(5)	0.117(6)	0.125(5)	0.119(5)	0.113(3)
O1/F1 (*2d*) (0 1/2 0)	B_{iso} (Å^2)	0.9(3)	1.5(0.7)	0.9(5)	1.745	1.5(3)
	Occ O1	0.09434	0.09434	0.09434	0.057	0.09434
	Occ F1	0.01887	0.01887	0.01887	0.068	0.01887
O2/F2 (*8j*) (x y 1/2)	x	0.1449(8)	0.1432(11)	0.1416(9)	0.1429(9)	0.1430(6)
	y	0.0705(9)	0.0703(13)	0.0704(11)	0.071(1)	0.0703(8)
	B_{iso} (Å^2)	0.48(19)	0.0(3)	0.31(23)	1.25	0.55(15)
	Occ O2	0.37736	0.37736	0.37736	0.4	0.37736
	Occ F2	0.07547	0.07547	0.07547	0.4	0.07547
O3/F3 (*8j*) (x y 1/2)	x	0.3464(9)	0.3479(12)	0.3482(9)	0.3462(9)	0.3461(7)
	y	0.0017(9)	0.0012(12)	0.0012(10)	0.001(1)	0.0023(6)
	B_{iso} (Å^2)	0.50(18)	0.2(3)	0.02(20)	1.165	0.48(15)
	Occ O3	0.37736	0.37736	0.37736	0.4	0.37736
	Occ F3	0.07547	0.07547	0.07547	0.4	0.07547
O4/F4 (*8i*) (x y 0)	x	0.0787(9)	0.0767(13)	0.0771(10)	0.077(1)	0.0779(7)
	y	0.2061(9)	0.2039(12)	0.2049(11)	0.207(19	0.2069(8)
	B_{iso} (Å^2)	0.53(17)	0.2(3)	0.31(22)	1.072	0.50(15)
	Occ O4	0.37736	0.37736	0.37736	0.4	0.37736

	Occ F4	0.07547	0.07547	0.07547	0.4	0.07547
O5/F5 (*4h*) (x y 1/2)	x	0.2844(9)	0.2825(14)	0.2834(10)	0.2843(9)	0.2847(7)
	y	0.7843(9)	0.7825(14)	0.7834(10)	0.7843(9)	0.7847(7)
	B_{iso} (Å^2)	0.6(3)	1.3(6)	0.7(5)	1.118	0.8(3)
	Occ O5	0.18867	0.18867	0.18867	0.2	0.18867
	Occ F5	0.03774	0.03774	0.03774	0.2	0.03774
R factors						
R_p		1.11	2.75	3.36	3.39	3.72
R_{wp}		1.43	3.82	4.59	4.60	4.96
R_{exp}		1.28	1.31	2.32	2.08	2.28
R_{Bragg}		13.0	15.7	9.97	6.82	6.37

After Rietveld refinement, it is observed that the experimental contents of K and Nb of all the samples are lower than the nominal ones as shown in Table 2.

Table 2. Comparison between nominal composition and NPD composition

Nominal Composition	*NPD Composition*				
	Ar + N_2	**Ar**	**N_2**	**N_2 + N_2**	**Ar + Ar**
KNb_2O_5F	$K_{0.65}Nb_{1.88}O_5F$	$K_{0.67}Nb_{1.81}O_5F$	$K_{0.66}Nb_{1.78}O_5F$	$K_{0.72}Nb_{1.81}O_{5.26}F_{1.37}$	$K_{0.62}Nb_{1.82}O_5F$

Regarding electrochemistry performances, Figure 4 shows the capacity obtained during galvanostatic charge-discharge of every cycle of the different samples when cycled at different C-rates in a potential window of 0.1 – 3.0 V using 2.5 M KFSI (TEP) as electrolyte. It seems the sample with the lowest K content, the one synthesized using two steps (Ar + Ar), reaches the higher capacities compared to the others. However, the sample with the highest K content, the one synthesized using two steps (N_2 + N_2), reaches the lower capacities and the reversibility is worse compared to the other samples.

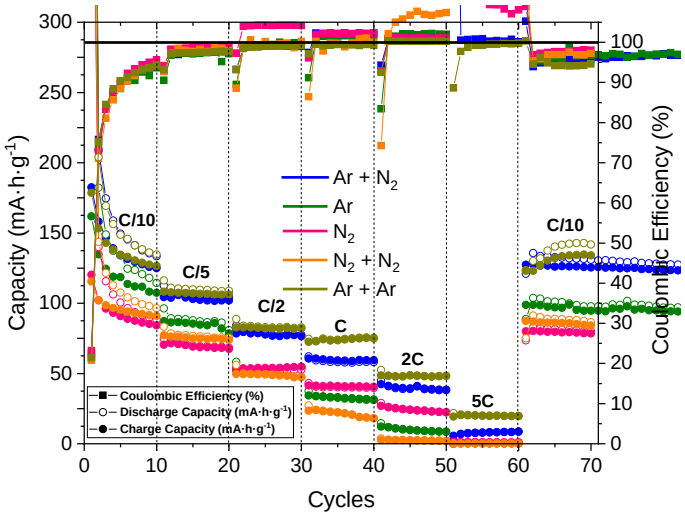

Figure 4. Capacities reached during galvanostatic charge-discharge (70 cycles) of the different samples when cycled at different C-Rates. The graph also shows the Coulombic Efficiency.

References:

(1) Wold, A.; Dwight, K. *Solid state chemistry: synthesis, structure, and properties of selected oxides and sulfides*; Chapman & Hall, Inc., **1993**. (2) Haldolaarachchige, N.; Gibson, Q.; Krizan, J.; Cava, R. Superconducting properties of the K*x*WO_3 tetragonal tungsten bronze and the superconducting phase diagram of the tungsten bronze family. *Physical review B* **2014**, *89* (10), 104520. (3) Han, Y.; Yang, M.; Zhang, Y.; Xie, J.; Yin, D.; Li, C. Tetragonal tungsten bronze framework as potential anode for Na-ion batteries. *Chemistry of Materials* **2016**, *28* (9), 3139-3147. (4) Labbe, P. Tungsten oxides, tungsten bronzes and tungsten bronze-type structures. *Key Engineering Materials* **1992**, *68*, 293.