Experimental report

28/12/2023

Proposal: **5-21-1178** **Council:** 10/2022

Title: Impact of the composition on the electrochemical performance of KyVxTi8-xO16 (0 ¿ x ¿ 2)

Research area: Materials

This proposal is a new proposal

Main proposer: **Jesus PRADO GONJAL**

Experimental team: Marta GONZALEZ-BARRIOS
Juan Andres NIETO SIMON
Jesus PRADO GONJAL

Local contacts: Maria Teresa FERNANDEZ DIAZ

Samples: KyVxTi8-xO16 (x=0.25,0.5,0.75,1,1.25,1.75,2)

Instrument	Requested days	Allocated days	From	To
D2B	1	1	17/04/2023	18/04/2023

Abstract:

This proposal focuses on the determination of the crystal structure and composition of 7 hollandite-type compositions with the general formula KyVxTi8-xO16 (0 ¿ x ¿ 2), which might be employed as electrode materials in rechargeable K-ion batteries. The main goal of this work is to accurately determine the position and occupancy of oxygen and potassium atoms as well as the likely presence of water molecules or other species in the structural tunnels. Furthermore, this neutron diffraction experiment would aid in determining the samples' relative titanium and vanadium contents (by difference) or any possible V-Ti ordering. For these tasks we ask for 1 days at D2B diffractometer

Hollandite-type compounds, with *I4/m* space group, have the chemical composition $A_yB_xTi_{8-x}O_{16}$, where the species A corresponds to a mono or divalent cation (in this case K) and B refers to a trivalent metal[2] (in this case V, Al). The unit cell consists of doble chains of stacked, shared edges $(V\text{-}Al/Ti)O_6$ octahedra that form one-dimensional tunnels with square cross-section (2x2) propagating along the c axis, where the cations can be accommodated (Figure 1). Also, these cations are needed to function as template for the hollandite structure. The larger tunnels can be occupied by A^{n+} cations up to a maximum of x = 2 in the case of K and for more in the case of Li, this depends on the size of the cation. This compositional versatility gives hollandite-type materials interesting physical and chemical properties related to electrical, magnetic, optical, etc. applications.

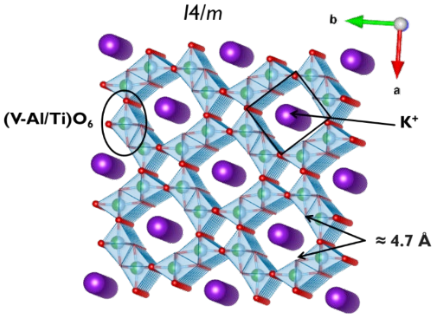

Figure 1. *Hollandite-type structure (2x2) where (V-Al/Ti)O6 coordination octahedra is in blue and tunnels of varied sizes are shown. The oxygen atoms are shown in red. The smaller tunnels include no cations in them while the larger ones contain K-ions (in purple) along [001] direction[3].*

Room temperature Neutron Powder Diffraction (NPD) patterns for $K_y(V/Al)_xTi_{8-x}O_{16}$ ($0 \leq x \leq 2$) samples collected at Institut Laue Langevin (ILL) using a High-Resolution Two-Axis Diffractometer (D2B) with λ = 1.594 Å are shown in Figures 2 and 3. These compounds' structures were refined in the tetragonal *I4/m* (#87) space group. Figure 2 shows a comparison among six different hollandite-type nominal compositions doped with V in the B site, while Figure 3 shows a comparison between two different hollandite-type nominal compositions doped with Al in the B site.

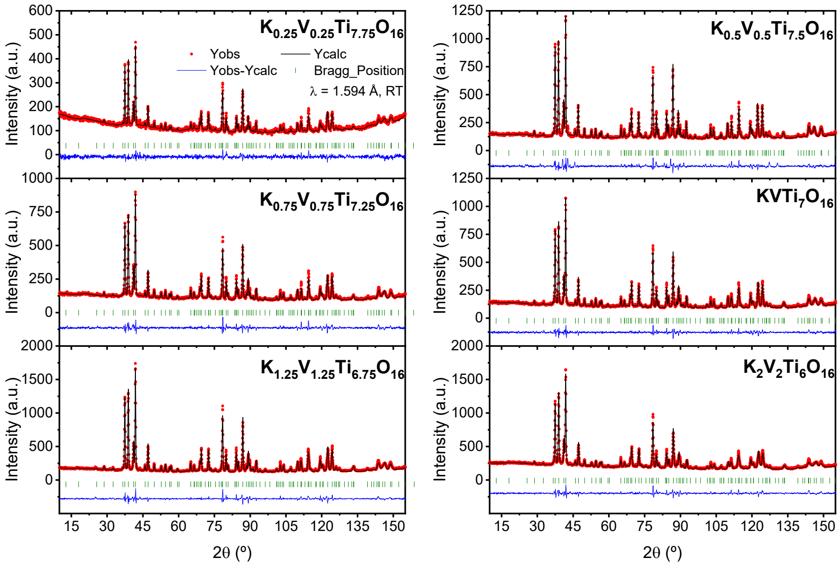

Figure 2. *Observed (red dots), calculated (black, full line) and difference (blue line) neutron powder diffraction profile for nominal compositions:* $K_{0.25}V_{0.25}Ti_{7.75}O_{16}$, $K_{0.5}V_{0.5}Ti_{7.5}O_{16}$, $K_{0.75}V_{0.75}Ti_{7.25}O_{16}$, $KVTi_7O_{16}$, $K_{1.25}V_{1.25}Ti_{6.75}O_{16}$ *and* $K_2V_2Ti_6O_{16}$. *The vertical green bars correspond to the allowed Bragg reflections.*

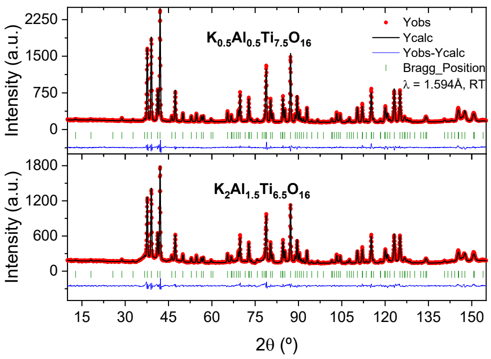

Figure 3*. Observed (red dots), calculated (black, full line) and difference (blue line) neutron powder diffraction profile for nominal composition:* $K_{0.5}Al_{0.5}Ti_{7.5}O_{16}$ *and* $K_2Al_{1.5}Ti_{6.5}O_{16}$. *The vertical green bars correspond to the allowed Bragg reflections.*

In Tables 1 and 2, it is shown the refined structural parameters obtained from NPD for all vanadium and aluminium nominal compositions, respectively.

Table 1. *Refined structural parameters obtained from NPD for nominal compositions: $K_{0.25}V_{0.25}Ti_{7.75}O_{16}$, $K_{0.5}V_{0.5}Ti_{7.5}O_{16}$, $K_{0.75}V_{0.75}Ti_{7.25}O_{16}$, $KVTi_7O_{16}$, $K_{1.25}V_{1.25}Ti_{6.75}O_{16}$ and $K_2V_2Ti_6O_{16}$ at room temperature.*

$K_yV_xTi_{8-x}O_{16}$		**x = y = 0.25**	**x = y = 0.50**	**x = y = 0.75**	**x = y = 1.00**	**x = y = 1.25**	**x = y = 2.00**
Temperature (K)		298.15	298.15	298.15	298.15	298.15	298.15
Space group		*I4/m*	*I4/m*	*I4/m*	*I4/m*	*I4/m*	*I4/m*
***a = b* (Å)**		10.1573(3)	10.1610(2)	10.1565(2)	10.1488(2)	10.1509(4)	10.1370(5)
***c* (Å)**		2.9625(1)	2.96196(7)	2.96264(8)	2.96379(7)	2.9650(2)	2.9659(2)
Volume (Å^3)		305.65(2)	305.81(5)	305.61(1)	305.26(1)	305.51(2)	304.77(3)
Ti1/V1 (*8h*) (x y 0)	x	0.3514(7)	0.3514(4)	0.3510(5)	0.3493(4)	0.3500(9)	0.350(1)
	y	0.1672(8)	0.1679(5)	0.1675(6)	0.1664(5)	0.167(1)	0.166(1)
	B_{iso} (Å^2)	0.6(1)	0.86(9)	0.8(1)	0.92(9)	0.8(2)	0.7(3)
	Occ Ti1	0.48(1)	0.493(9)	0.454(9)	0.449(7)	0.45(2)	0.42(2)
	Occ V1	0.02(1)	0.007(9)	0.046(9)	0.051(7)	0.05(2)	0.08(2)
K1 (*2b*) (0 0 1/2)	B_{iso} (Å^2)	3(1)	4(1)	3.0(9)	1.3(6)	1(1)	1(1)
	Occ	0.06(1)	0.059(7)	0.057(6)	0.049(4)	0.047(7)	0.054(9)
K2 (*4e*) (0 0 z)	z	0.75(3)	0.77(4)	0.78(2)	0.75(1)	0.79(3)	0.80(3)
	B_{iso} (Å^2)	3(1)	4(1)	3.0(9)	1.3(6)	1(1)	1(1)
	Occ	0.044(9)	0.026(5)	0.040(5)	0.050(4)	0.042(7)	0.045(9)
O1 (*8h*) (x y 0)	x	0.1559(6)	0.1557(3)	0.1561(4)	0.1561(3)	0.1554(6)	0.1555(8)
	y	0.2033(4)	0.2049(2)	0.2047(2)	0.2043(2)	0.2041(4)	0.2030(5)
	B_{iso} (Å^2)	0.39(8)	0.54(5)	0.49(6)	0.46(5)	0.5(1)	0.3(1)
	Occ	0.5	0.5	0.5	0.5	0.5	0.5
O2 (*8h*) (x y 0)	x	0.5412(4)	0.5400(2)	0.5402(3)	0.5409(2)	0.5402(5)	0.5407(6)
	y	0.1641(8)	0.1652(4)	0.1655(5)	0.1659(4)	0.1666(8)	0.166(1)
	B_{iso} (Å^2)	0.39(8)	0.54(5)	0.49(6)	0.46(5)	0.5(1)	0.3(1)
	Occ	0.5	0.5	0.5	0.5	0.5	0.5
R factors							
R_p		3.01	3.91	3.51	3.47	3.69	2.95
R_{wp}		3.91	5.63	4.87	4.62	5.12	4.14
R_{exp}		1.31	1.18	1.28	1.26	1.08	0.95
R_{Bragg}		9.67	5.98	5.39	3.08	4.01	3.98

Table 2. Refined structural parameters obtained from NPD for nominal compositions: $K_{0.5}Al_{0.5}Ti_{7.5}O_{16}$ and $K_2Al_{1.5}Ti_{6.5}O_{16}$ at room temperature.

$K_yAl_xTi_{8-x}O_{16}$		**x = y = 0.50**	**x = 1.5; y = 2.00**
Temperature (K)		298.15	298.15
Space group		*I4/m*	*I4/m*
***a = b* (Å)**		10.12251(9)	10.1224(1)
***c* (Å)**		2.94974(3)	2.94972(4)
Volume (Å^3)		302.246(5)	302.237(7)
Ti1/Al1 (*8h*) (x y 0)	x	0.3509(2)	0.3514(3)
	y	0.1675(3)	0.1672(4)
	B_{iso} (Å^2)	0.61(5)	0.33(7)
	Occ Ti1	0.453(1)	0.450(2)
	Occ Al1	0.047(1)	0.050(2)
K1 (*2b*) (0 0 0.5)	B_{iso} (Å^2)	2.9(4)	0.9(4)
	Occ	0.032(2)	0.038(2)
K2 (*4e*) (0 0 z)	z	0.718(7)	0.768(8)
	B_{iso} (Å^2)	2.9(4)	0.9(4)
	Occ	0.060(3)	0.044(3)

O1 (*8h*) (x y 0)	x	0.1555(1)	0.1560(2)
	y	0.2052(1)	0.2053(2)
	B_{iso} (Å^2)	0.58(2)	0.40(4)
	Occ	0.5	0.5
O2 (*8h*) (x y 0)	x	0.5400(2)	0.5401(2)
	y	0.1655(2)	0.1667(3)
	B_{iso} (Å^2)	0.58(2)	0.40(4)
	Occ	0.5	0.5
R factors			
R_p		3.05	3.37
R_{wp}		4.02	4.31
R_{exp}		0.97	1.04
R_{Bragg}		3.91	4.56

In all cases good fittings were achieved with single hollandite tetragonal phase. After Rietveld refinement, it is observed that the experimental content of K and V of all the samples is different than the nominal expected as shown in Table 3.

Table 3. Comparison between nominal composition and NPD composition

$K_y(V/Al)_xTi_{8-x}O_{16}$	
Nominal Composition	*NPD Composition*
$K_{0.25}V_{0.25}Ti_{7.75}O_{16}$	$K_{1.59}V_{0.32}Ti_{7.68}O_{16}$
$K_{0.5}V_{0.5}Ti_{7.5}O_{16}$	$K_{1.36}V_{0.12}Ti_{7.88}O_{16}$
$K_{0.75}V_{0.75}Ti_{7.25}O_{16}$	$K_{1.54}V_{0.73}Ti_{7.27}O_{16}$
$KVTi_7O_{16}$	$K_{1.44}V_{0.82}Ti_{7.18}O_{16}$
$K_{1.25}V_{1.25}Ti_{6.75}O_{16}$	$K_{1.41}V_{0.90}Ti_{7.10}O_{16}$
$K_2V_2Ti_6O_{16}$	$K_{1.60}V_{1.29}Ti_{6.71}O_{16}$
$K_{0.5}Al_{0.5}Ti_{7.5}O_{16}$	$K_{1.49}Al_{0.76}Ti_{7.24}O_{16}$
$K_2Al_{1.5}Ti_{6.5}O_{16}$	$K_{1.32}Al_{0.79}Ti_{7.21}O_{16}$

In Figure 4a, it is shown that the longest distances of the octahedra, Ti-O1 (blue), follow a similar trend to the average distances Ti-O2 (purple) of the octahedra, while the shortest distances of the octahedra, Ti-O2 (orange) follow a similar trend to the average distances Ti-O1 (red) of the octahedra. Figure 4b, exhibits a trend in Ti-O2-Ti angles, where the highest Ti-O2-Ti angle in b axis for $K_{0.5}V_{0.5}Ti_{7.5}O_{16}$ corresponds to the lowest Ti-O2-Ti angle in c axis for that composition. The trend between Ti-O2-Ti angles in c and b axis are opposite, while the trend observed between Ti-O1-Ti angles in c axis and diagonal are similar. Figure 4c shows the octahedra $(V/Ti)O_6$ where it is shown the name of the atoms that were considered when calculating the Ti-O1 and Ti-O2 distances and the Ti-O1-Ti and Ti-O2-Ti angles. As an example, Figure 4d shows the trend of the K (K1=K2) B_{iso} versus the nominal V content and the experimental K content. It is observed that this trend does not follow any particular order: nominal composition $K_{0.5}V_{0.5}Ti_{7.5}O_{16}$ exhibits the potassium's B_{iso} highest value, but the lowest NPD K content, while nominal composition $K_2V_2Ti_6O_{16}$ exhibits the lowest value of potassium B_{iso} but the highest NPD K content.

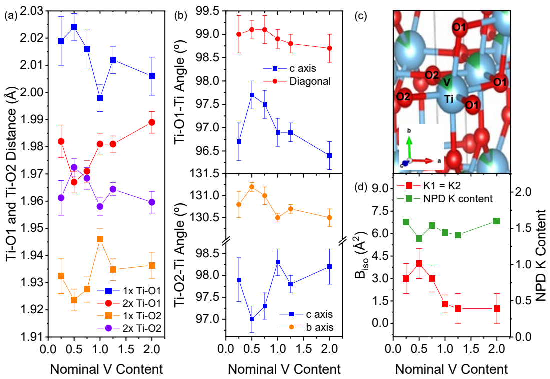

Figure 4. *(a) Ti-O1 and Ti-O2 distances vs. Nominal V content. (b) Ti-O1-Ti and Ti-O2-Ti angles vs. Nominal V content. (c) Octahedra of $(V/Ti)O_6$ where blue spheres are Ti, green spheres are V and red spheres are O. (d) B_{iso} of K vs. Nominal V content and NPD K content.*