

# Supporting information

## Thermally and Electrochemically Driven Topotactical Transformations in Sodium Layered Oxides $\text{Na}_x\text{VO}_2$

*Christophe Didier<sup>1,2</sup>, Marie Guignard<sup>1,2\*</sup>, Matthew R. Suchome<sup>3 †</sup>, Dany Carlier<sup>1,2</sup>, Jacques Darriet<sup>1,2</sup>, Claude Delmas<sup>1,2</sup>*

<sup>1</sup> CNRS, ICMCB, 87 avenue du Dr A. Schweitzer, 33608 Pessac Cedex, France, <sup>2</sup> Université de Bordeaux, ICMCB, 87 avenue du Dr A. Schweitzer, 33608 Pessac Cedex, France. <sup>3</sup>

Argonne National Laboratory, Advanced Photon Source, Lemont, Illinois 60439, USA

The structure of sodium layered oxides  $\text{Na}_x\text{MO}_2$  is generally described as a stack of different layers: one layer  $(\text{MO}_2)_n$ , formed by edge-sharing  $\text{MO}_6$  octahedra, alternates with one layer of sodium ions. Whereas the environment of the transition metal within  $(\text{MO}_2)_n$  layers is nearly always octahedral, the stacking of the  $(\text{MO}_2)_n$  layers imposes an environment for the sodium ions which is either octahedral or prismatic. A nomenclature is commonly used to describe the different structure types found in these materials: an initial letter describes the environment of the sodium ions (O for octahedral and P for prismatic) and is followed by a number which indicates the number of different  $(\text{MO}_2)_n$  layers, formed by edge-sharing  $\text{MO}_6$  octahedra,

needed to describe the structure. O3-type structure corresponds to  $\alpha$ -NaFeO<sub>2</sub> structure and its structure is described in a hexagonal cell with the translation vectors  $\vec{a}_h, \vec{b}_h$  and  $\vec{c}_h$  (space group:  $R\bar{3}m$ ). However it can also be described in a monoclinic cell with the translation vectors  $\vec{a}_m, \vec{b}_m$  and  $\vec{c}_m$  (space group:  $C2/m$ ). The transformation from the hexagonal cell to the monoclinic one is possible using the following relationships:

$$\begin{pmatrix} \vec{a}_m \\ \vec{b}_m \\ \vec{c}_m \end{pmatrix} = \begin{pmatrix} 2 & 1 & 0 \\ 0 & 1 & 0 \\ -4/3 & -2/3 & 1/3 \end{pmatrix} \begin{pmatrix} \vec{a}_h \\ \vec{b}_h \\ \vec{c}_h \end{pmatrix}$$

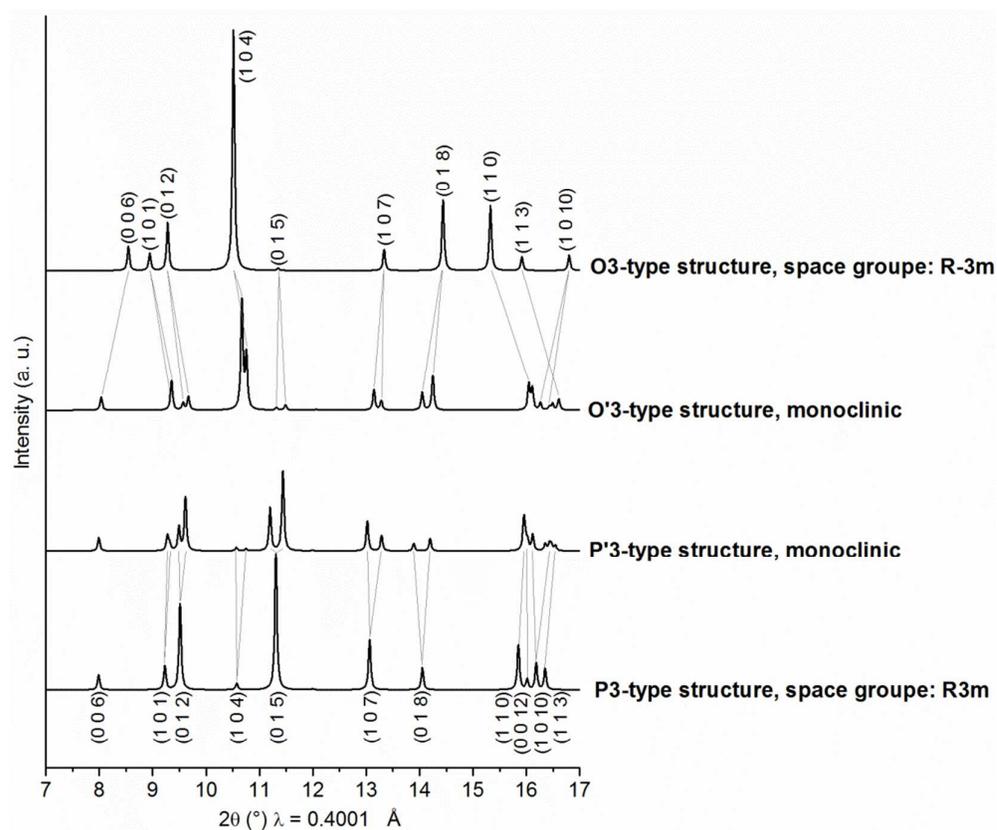
Sometimes, the structure of sodium layered oxides is slightly distorted and it cannot be described with the hexagonal cell anymore, but only with the monoclinic one. The structure is called O'3-type structure.

Another hexagonal structure, less common, can be found in sodium layered oxides: the P3-type structure (space group:  $R3m$ ). As in the O3-type structure, transition metal ions occupy octahedral sites, but sodium ions occupy trigonal prismatic sites. Also, as for the O3-type structure, the P3-type structure can be described with a monoclinic cell (space group:  $C2/m$ ) with the translation vectors  $\vec{a}_{m'}, \vec{b}_{m'}$  and  $\vec{c}_{m'}$  that can be written as a function of the translation vectors  $\vec{a}_{h'}, \vec{b}_{h'}$  and  $\vec{c}_{h'}$  of the hexagonal cell used to describe the P3-type structure:

$$\begin{pmatrix} \vec{a}_{m'} \\ \vec{b}_{m'} \\ \vec{c}_{m'} \end{pmatrix} = \begin{pmatrix} 2 & 1 & 0 \\ 0 & 1 & 0 \\ -2/3 & -1/3 & 1/3 \end{pmatrix} \begin{pmatrix} \vec{a}_{h'} \\ \vec{b}_{h'} \\ \vec{c}_{h'} \end{pmatrix}$$

As for the O3-type structure, the P3-type structure can be slightly distorted and it cannot be described with the hexagonal cell anymore, but only with the monoclinic one. The structure is called P'3-type structure.

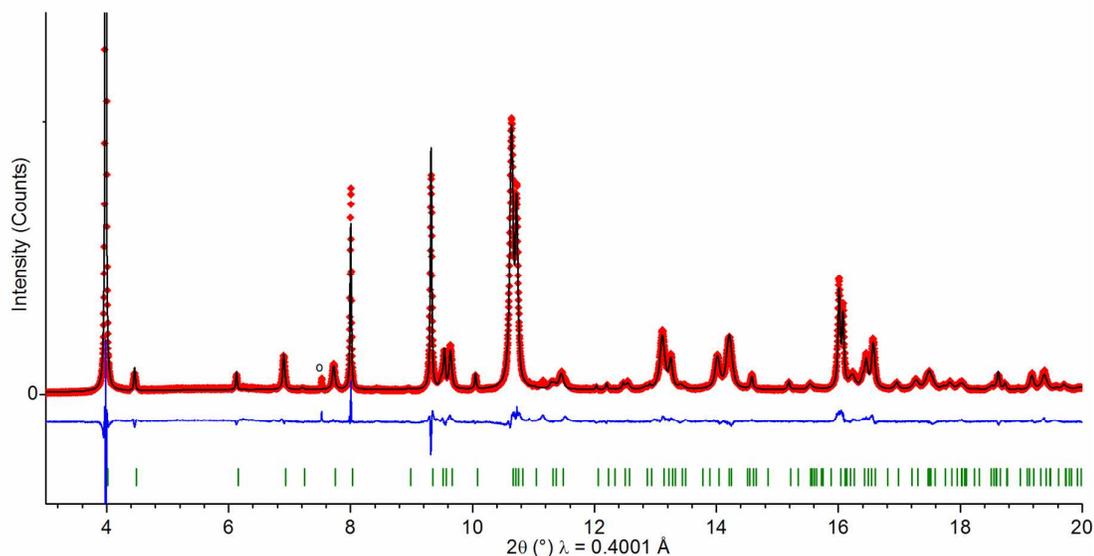
The distortion of the both hexagonal cells induces changes in the diffraction patterns of the sodium layered oxides with the splitting of most of the reflections. Calculated X-ray diffraction patterns for the four structure types (O3, O'3, P'3 and P3) are presented in Figure S1 to highlight the differences between these structure types. The diagrams were calculated using the wavelength used at the ID31 beamline for the experiments presented in this article ( $\lambda$  0.4001 Å).



**Figure S1.** Calculated synchrotron diffraction patterns for the four structure types (O3, O'3, P'3 and P3). For O3-type structure, the composition used was  $\text{NaVO}_2$ , whereas for the three other structure types, a more realistic composition  $\text{Na}_{0.55}\text{VO}_2$  was chosen.

A structural refinement was obtained for O'3- $\text{Na}_{1/2}\text{VO}_2$  using the Rietveld method and high-resolution powder diffraction data recorded at beamline ID31 at the ESRF. The good

agreement between the calculated diffraction diagram and the experimental one is shown in Figure S2 and the atomic positions determined from the Rietveld refinement are given in Table S1.



**Figure S2.** Experimental high resolution X-ray powder diffraction pattern of O'3-Na<sub>1/2</sub>VO<sub>2</sub> recorded at 25 °C (red diamonds), calculated pattern obtained from the Rietveld refinement (black line) and difference line (blue line). The most intense peak of an unknown impurity is topped by an open circle.

**Table S1.** Refined atomic positions and atomic displacement parameters ( $B_{\text{iso}}$ ) in O'3-Na<sub>1/2</sub>VO<sub>2</sub> at 25°C in the monoclinic unit cell with  $a = 13.2993(2)$  Å,  $b = 5.7098(1)$  Å,  $c = 4.9713(1)$  Å,  $\beta = 120.845(1)$  ° and the space-group  $C2/c$ .

	x	y	z	$B_{\text{iso}}$ (Å <sup>2</sup> )
V	0.2475(1)	0.3664(2)	0.2269(2)	0.13(1)
Na	0	0.3050(3)	1/4	0.58(5)
O(1)	0.3557(2)	0.1272(5)	0.2316(5)	0.40(5)
O(2)	0.1611(2)	0.1272(4)	0.2897(5)	0.36(5)