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Using the Battery to Synthesize New Vanadium Oxides

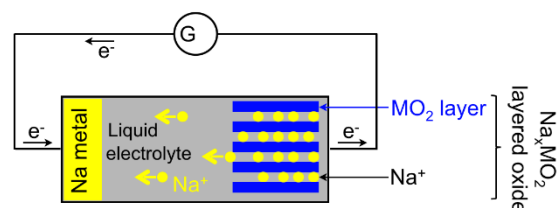
Marie Guignard^{*[a]} and Claude Delmas^[a]

Abstract: Sodium electrochemical deintercalation in a battery was used as a route to synthesize new vanadium oxides. Sodium layered oxides were used as positive electrode materials in batteries and sodium was electrochemically deintercalated up to a precise composition resulting in the discovery of a new phase $\text{Na}_{1/2}\text{VO}_2$. As for many vanadium oxides, this compound presents a magnetic transition, slightly above room temperature, around 325 K, as well as a structural transition involving displacements of vanadium ions. The discovery of this new vanadium oxide and the study of its unique electronic properties have only been possible because the battery permits the synthesis of this new phase at room temperature. This shows that many more new systems could be explored using electrochemical (de)intercalation in a battery and new materials that would be impossible to synthesize by classical solid state reaction could be obtained.

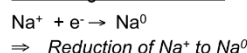
Introduction

New inorganic solid-state materials with unique physical properties have been continuously discovered and renewed by chemists over the last century. Increasingly however, most solid-state chemistry research today focuses on existing materials to improve their properties for applications. Research for new materials capable of introducing novel electronic states and exceptional physical properties has decreased significantly in recent years. However, there is still a paramount need to discover new materials, especially in the area of strongly correlated electron systems. The periodic table contains a limited number of available, affordable and non-dangerous elements. Within this limited sub-set of the periodic table, many new systems were discovered by developing diverse techniques of synthesis such as high temperature, high pressure, hydrothermal or supercritical methods. However, all these approaches require a heat treatment step; even "chimie douce" synthesis routes usually include a heat treatment at a moderate temperature of at least 500 K. Therefore, the final products obtained from these routes are usually the most thermodynamically stable phases at the synthesis temperature. By contrast, deintercalation/intercalation chemistry does not require any heat treatment. Until the beginning of the 1960's intercalation chemistry was essentially the chemistry of graphite intercalation compounds.[1] In subsequent years, alkali (de)intercalation was further studied in layered sulphides and new metastable phases were synthesized at room temperature by alkali deintercalation using iodine or bromine as an oxidizing agent,[2] or by lithium intercalation using n-butyllithium as a reducing agent.[3] However these chemical routes present some disadvantages: it is difficult to monitor the reaction progress and side reactions are often observed. Moreover, the control of

stoichiometry achieved by this technique is poor. Compared to chemical (de)intercalation, an electrochemical approach in a battery cell affords very precise control of the amount of (de)intercalated ions by control of the current, i.e. the number of electrons exchanged in the system.



At the negative electrode:



At the positive electrode:

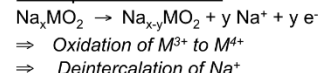


Figure 1. Schematic representation of the sodium electrochemical deintercalation of a Na_xMO_2 phase in a sodium battery.

Sodium layered oxides with the general formula Na_xMO_2 (where x is comprised between 0 and 1 and M is transition metal) are particularly well adapted to this technique as they have been studied for 30 years for use as positive electrode in sodium batteries (Figure 1). Moreover, some of these phases exhibit fascinating physical properties such as superconductivity, high thermoelectric power, and metal-insulator transitions.[4][5][6] Therefore sodium electrochemical deintercalation/intercalation appears as an excellent candidate to explore new strongly electron correlated systems in sodium layered oxides.

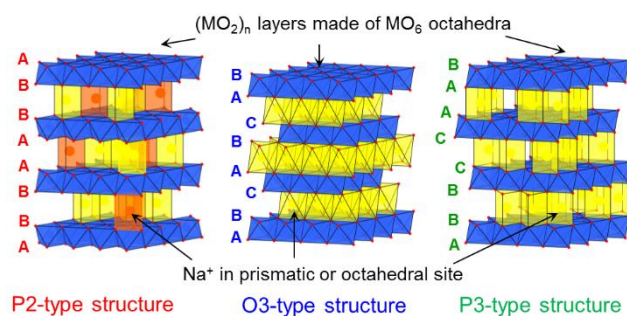


Figure 2. Common structure types of sodium-based layered oxides.

The structure of these materials is generally described as a stack of different layers: one layer $(\text{MO}_2)_n$, formed by edge-sharing MO_6 octahedra, alternates with one layer of sodium ions. Whereas the environment of the transition metal within $(\text{MO}_2)_n$ layers is always octahedral except for niobium, the stacking of the $(\text{MO}_2)_n$ layers imposes an environment for the sodium ions which is either octahedral or trigonal prismatic. Depending on the sodium amount, x , and the synthesis conditions, the sodium layered oxides crystallize with different oxygen arrangements which give

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rise to the different environments for sodium ions. 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 needed to describe the structure. Figure 2 shows the most common structure types that are found in sodium layered oxides.

We initiated an exploration of Na_xVO_2 systems based on sodium electrochemical deintercalation. Vanadium oxides are known to present unusual electronic properties and the possibility to introduce vanadium ions into the layered oxide structure was therefore expected to lead to a new family of materials with highly correlated electrons. In vanadium oxides, structural transitions are generally intimately connected to their electronic properties. A metal-insulator transition (MIT) occurring at approximately 340 K in vanadium dioxide VO_2 has been known for more than 50 years.[7] Above 340 K, the VO_2 structure is tetragonal with equivalent vanadium-vanadium nearest-neighbor distances of 2.851 Å.[8] Below 340 K, its structure is monoclinic and is characterized by the existence of vanadium-vanadium bonds with V-V distances as short as 2.619 Å.[9] However, the primary mechanism of the MIT in VO_2 is still under debate. Questions remain concerning the relative importance of electron-lattice interactions and electron-electron correlations in the transition.

Whereas VO_2 is still a topic of interest for many researchers, our approach consists in proposing new strongly correlated materials. The sodium electrochemical (de)intercalation offered us new systems to explore to discover new electronic phases that would not be possible to synthesize by classical solid state reaction.

As a first step, we have discovered two new metastable phases in the Na_xVO_2 system for $x = 1/2$ and $x = 2/3$ by the use of electrochemical deintercalation from the parent O3-NaVO_2 compound in a battery cell.[10] Both new phases possess an O'3 structure type, which differs from the O3 type due to a monoclinic distortion (denoted by the apostrophe) of the hexagonal cell usually used to describe layered oxides with the $\alpha\text{-NaFeO}_2$ structure. The structure of $\text{O}'3\text{-Na}_{1/2}\text{VO}_2$ was solved using the Rietveld method and X-ray powder diffraction data.[11] In the monoclinic cell, sodium ions occupy half the octahedral sites available between the $(\text{VO}_2)_n$ layers in a perfectly ordered way to form zigzag chains. Vanadium ions also rearrange and shift from the center of the VO_6 octahedra to give rise of vanadium-vanadium distances of 2.64 Å. These short V-V distances shown in red in Figure 4 lead to what we call "dimers".

As a second step, our interest was focused on the $\text{P2-Na}_x\text{VO}_2$ system. Among the new metastable phases discovered in this system, a new polymorph $\text{P2-Na}_{1/2}\text{VO}_2$ was obtained using sodium electrochemical deintercalation from the precursor $\text{Na}_{0.73}\text{VO}_2$ which is the only composition that can be synthesized by solid state chemistry. Its ambient temperature structure was determined from high resolution X-ray powder diffraction (HRXRPD) and it is distinguished not only by sodium ordering (sodium ions occupy trigonal prismatic sites), but also by the existence of vanadium pseudo-trimers in the triangular lattice formed by the vanadium ions.[12] More recently, we have found that these pseudo-trimers disappear above 322 K as a structural transition is observed at this temperature accompanied by an increase of two orders of magnitude in the electronic conductivity.[13]

Results and Discussion

In this paper, we report on the synthesis and on the structure of a third new polymorph: $\text{P}'3\text{-Na}_{1/2}\text{VO}_2$. As for $\text{O}'3\text{-Na}_{1/2}\text{VO}_2$, the apostrophe indicates that the structure is slightly distorted compared to the ideal P3-type structure presented in Figure 2. Its synthesis is more complex than that of the two first polymorphs. It needs two successive sodium electrochemical deintercalations and a heat treatment: the first step of the synthesis is the electrochemical deintercalation in a battery at ambient temperature from the parent O3-NaVO_2 to obtain $\text{O}'3\text{-Na}_{-0.55}\text{VO}_2$, then the second step consists in a heat treatment for 15 hours at 200°C that transforms irreversibly this $\text{O}'3\text{-Na}_{-0.55}\text{VO}_2$ phase into a new phase $\text{P}'3\text{-Na}_{-0.55}\text{VO}_2$. Finally, the third step consists in a new sodium electrochemical deintercalation in a battery from $\text{P}'3\text{-Na}_{-0.55}\text{VO}_2$ to $\text{P}'3\text{-Na}_{1/2}\text{VO}_2$.

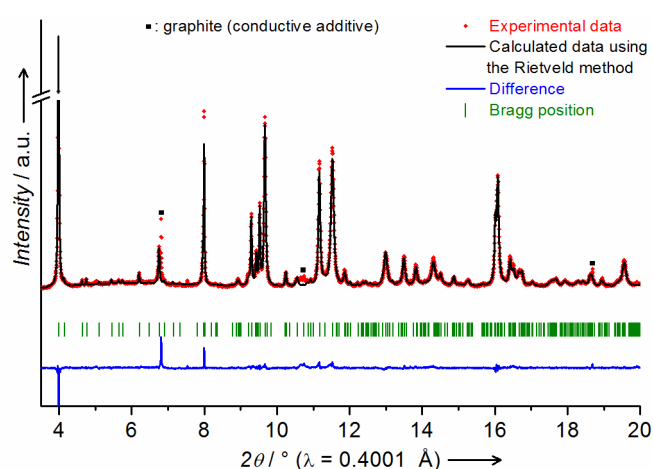


Figure 3. High resolution X-ray powder diffraction of $\text{P}'3\text{-Na}_{1/2}\text{VO}_2$ at 300 K.

Table 1. Refined atomic positions and atomic displacement parameters (Biso) in $\text{P}'3\text{-Na}_{1/2}\text{VO}_2$ at 300 K in the monoclinic unit cell $a=9.8919(2)$ Å, $b=5.7391(1)$ Å, $c=5.8864(2)$ Å, $\beta=103.505(2)^\circ$ and the space-group $P2_1/m$.

Atom	x	y	z	Biso (Å ²) ^[a]
V(1)	0.7521(4)	0.0169(4)	0.9861(6)	0.33(3)
V(2)	0.9784(4)	1/4	0.9844(8)	0.33(3)
V(3)	0.4833(4)	1/4	0.9846(9)	0.33(3)
Na(1)	0.1124(7)	1/4	0.4992(14)	0.79(8)
Na(2)	0.5850(7)	1/4	0.5110 (15)	0.79(8)
O(1)	0.052(1)	0.001(1)	0.794(1)	0.59(4)
O(2)	0.442(1)	0.006(1)	0.195(1)	0.59(4)
O(3)	0.297(1)	1/4	0.817(2)	0.59(4)
O(4)	0.809(1)	1/4	0.769(2)	0.59(4)
O(5)	0.178(1)	1/4	0.184(2)	0.59(4)
O(6)	0.694(1)	1/4	0.154(2)	0.59(4)

[a] The atomic displacement parameters were constrained to be equal for each element.

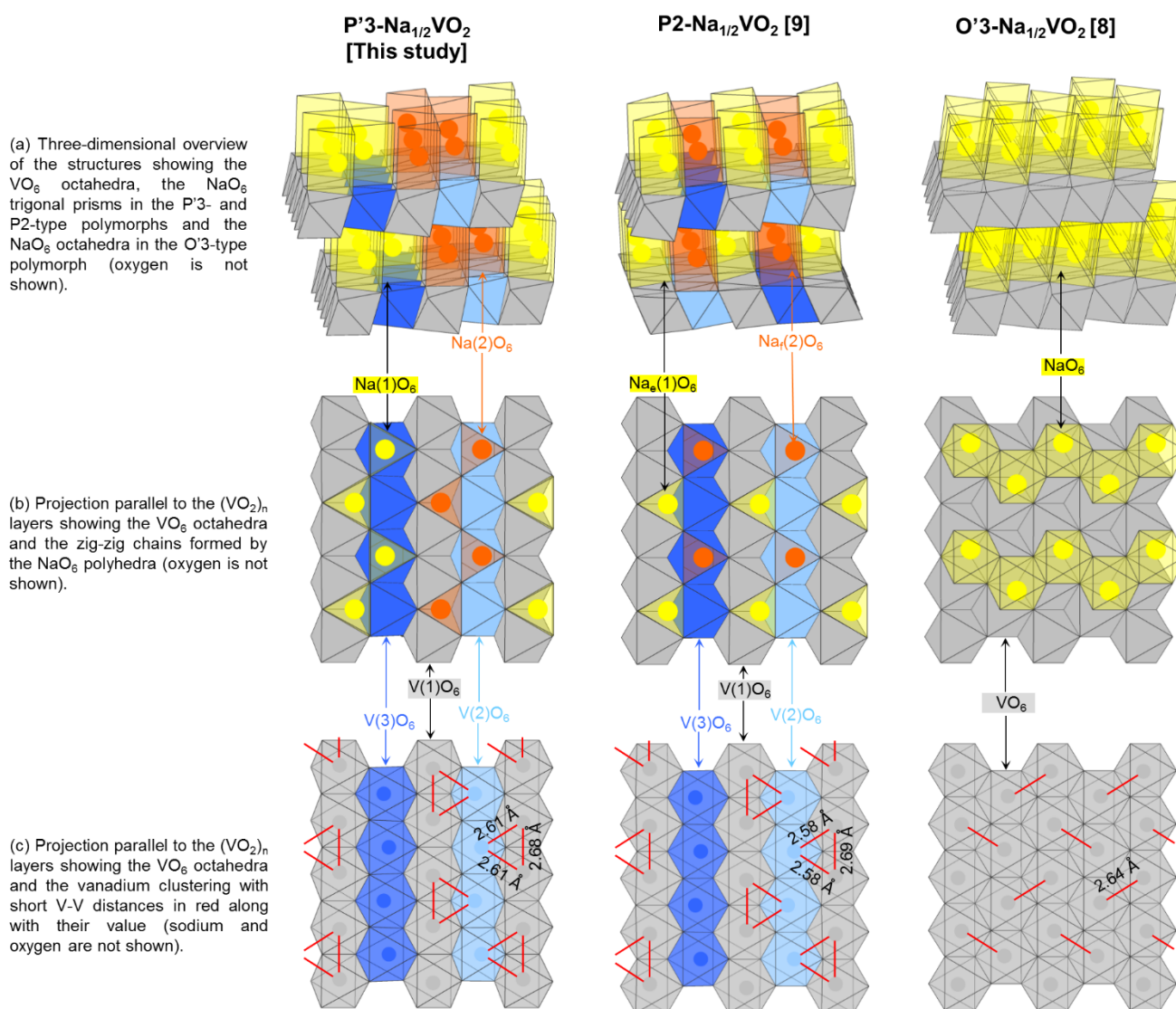


Figure 4. Structures of the three polymorphs Na_{1/2}VO₂. (a) 3D-structures. (b) and (c) Projection parallel to the (VO₂)_n layers.

The direct synthesis of P'3-Na_{1/2}VO₂ by the heat treatment at 200°C of O'3-Na_{1/2}VO₂ was not possible: a mixture of phases was always obtained and P'3-Na_{1/2}VO₂ was never obtained as a pure phase. Despite it has been used several times in the battery, the powder obtained after the second electrochemical deintercalation was still very well crystallized and the structure of this new polymorph was determined from HXRPD data.

Usually, the P'3-type structure of Na_xMO₂ layered oxides is described using a unit cell with the space group *C2/m* and a number of formula units per unit cell *Z* = 2 [14]. However, for P'3-Na_{1/2}VO₂, several weak diffraction peaks were not indexed using this unit cell. From our experience with sodium layered oxides, we assumed that these peaks could come from the existence of a superstructure that would allow to describe a sodium/vacancies ordering and/or a vanadium clustering. Initially, we found that the cell parameters *a* and *b* needed to be doubled to index all the superstructures peaks. Then, from the observation of the

extinction conditions, we found the space group *P2₁/m* with a number of formula units per unit cell *Z* = 8. To build the structural model for P'3-Na_{1/2}VO₂, we started from the atomic positions for vanadium and oxygen atoms in the known P'3-type structure adapted to the new supercell [14]. Atomic positions for sodium ions were found by the Fourier difference technique. Finally, the structural model was refined from the HRXRPD data using the Rietveld method. The final refined atomic parameters are given in Table 1 and Figure 3 shows the good agreement between experimental diffraction data and the calculated ones using this model. Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository number CSD-432720).

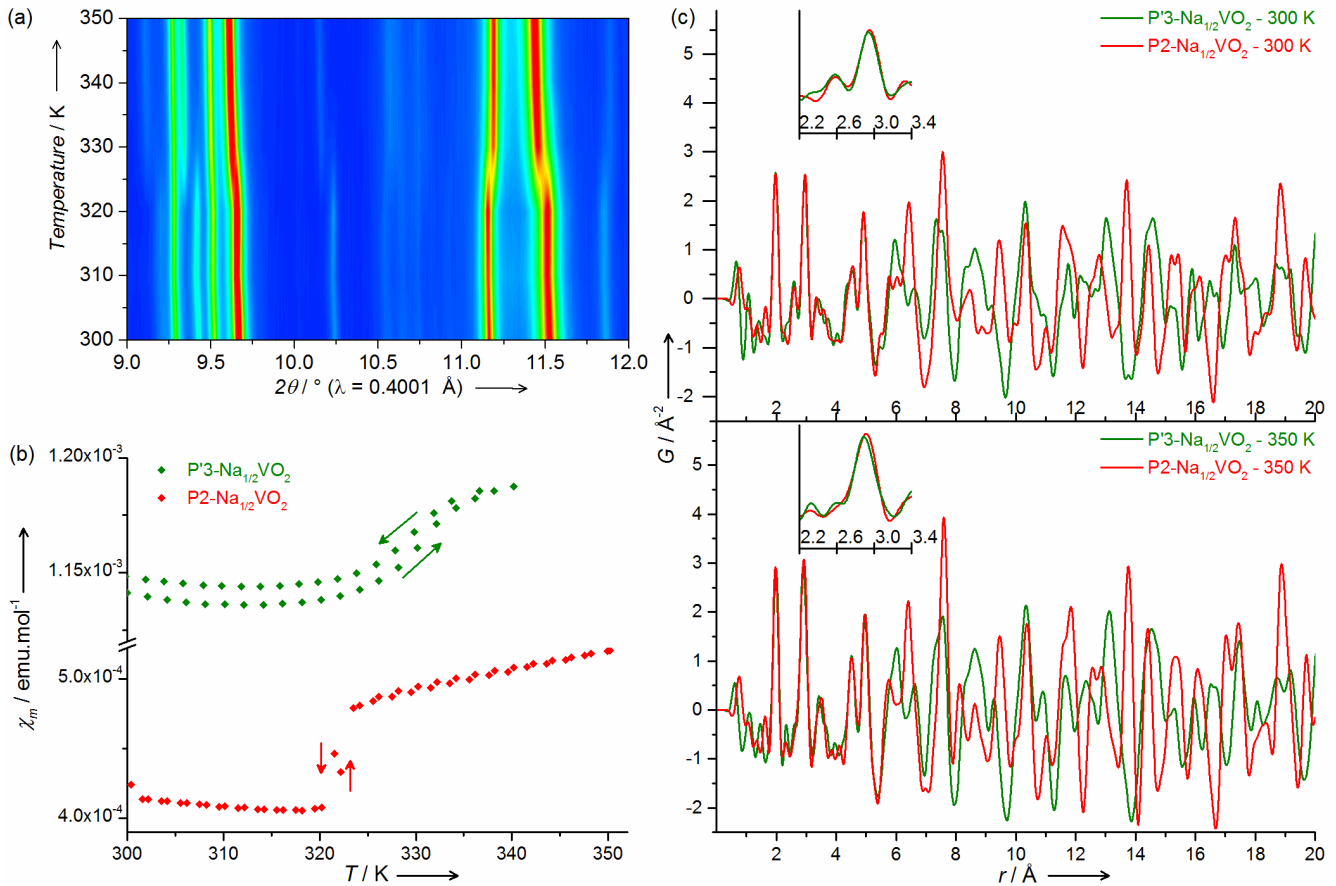


Figure 5. (a) Molar magnetic susceptibility, χ_m , of P'3-Na_{1/2}VO₂ and of P2-Na_{1/2}VO₂. (b) Experimental reduced pair distribution functions (PDFs), $G(r)$, at 300 K and 350 K of P'3-Na_{1/2}VO₂ and of P2-Na_{1/2}VO₂.

Figure 4 shows different representations of the structure of P'3-Na_{1/2}VO₂ at 300 K, along with those of P2- and O'3-Na_{1/2}VO₂. The structure of P'3-Na_{1/2}VO₂ is very similar to that of P2-Na_{1/2}VO₂: sodium ions are located in 2 prismatic sites, ordered to form zigzag chains, and vanadium ions rearrange to form pseudo-trimers with short V-V distances.

The main difference comes from the sodium environment. In both polymorphs, sodium ions occupy two distinct crystallographic sites. However, whereas they are different by nature in P2-Na_{1/2}VO₂ (one shares faces with VO₆ octahedra, the other one shares edges), they are very similar in P'3-Na_{1/2}VO₂ (they both share one face with one VO₆ octahedron on one side and edges with three VO₆ octahedra on the other side).

In P2-Na_{1/2}VO₂, we found that the vanadium trimers were involved in the electronic transition occurring at 322 K. Therefore, we studied the evolution of the structure P'3-Na_{1/2}VO₂ as a function of temperature: HRXRPD data were recorded from 300 K to 350 K (Figure 5(a)). We found that a reversible phase transition occurred around 325 K. A smooth anomaly in the magnetic susceptibility was also observed within the same temperature range (Figure 5(b)). The structure of P'3-Na_{1/2}VO₂ at 350 K was determined from HRXRPD data using the Rietveld method. The final refined atomic parameters are given in Table 2. As for P2-

type polymorph, the pseudo-trimers disappear above the transition temperature whereas the sodium ordering remains. This could explain the anomaly in the magnetic susceptibility thermal evolution as the same phenomenon was observed for the P2-type polymorph. Unfortunately we could not perform electronic transport measurements on P'3-Na_{1/2}VO₂ as we were not able to obtain a sintered pellet without any conductive additive. However, we can reasonably think that an increase of the electronic conductivity should be observed above the transition temperature as it was observed in P2-Na_{1/2}VO₂.

These similarities between the P'3- and P2-type polymorphs indicate that their electronic properties are mostly related to the atomic arrangement within the VO₂ layers and that they are minimally impacted by the 3D long range order. More precisely, the short-range order is very similar in both polymorphs up to 5 Å as it is shown by the Pair Distribution Function (PDF) analysis (Figure 5(b)), both below and above the transition temperature, showing that similar structural modifications are involved at the electronic transition. It is surprising that dimers are found in the O'3-type polymorph instead of trimers. This indicates that its electronic structure is different that of the P2 and P'3-type ones: whereas the formation of pseudo-trimers may lead to a band gap opening in the electronic band structure of the P2 and P'3-type

polymorphs to lower the energy of the system, this is not the case in O'3- Na_{1/2}VO₂ and no electronic transition is observed in this compound. The electronic structure does not simply derive from the absolute number of electrons in the system as this number is the same in all the three polymorphs. Instead, the environment of the sodium ions, either octahedral in O'3- Na_{1/2}VO₂ or prismatic P2- and P'3- Na_{1/2}VO₂, also influences the electronic charge carried by oxygen anions, giving rise to different electronic properties in these three polymorphs. Electronic structure calculations are currently under progress to understand better the difference in these properties.

Table 2. Refined atomic positions and atomic displacement parameters (Biso) in P'3-Na_{1/2}VO₂ at 350 K in the monoclinic unit cell $a=4.9806(2)$ Å, $b=5.7457(2)$ Å, $c=5.9279(2)$ Å, $\beta=104.547(2)^\circ$ and the space-group $P2_1/m$.

Atom	x	y	z	Biso (Å ²) ^[b]
V(1)	0	0	1/2	0.48(5)
V(2)	0.5184(4)	1/4	0.5116(8)	0.48(5)
Na	0.2975(12)	1/4	0.9878(13)	1.28(11)
O(1)	0.605(1)	0.005(1)	0.297(1)	0.81(7)
O(2)	0.896(2)	1/4	0.699(1)	0.81(7)
O(3)	0.111(1)	1/4	0.314(2)	0.81(7)

[b] The atomic displacement parameters were constrained to be equal for each element.

Conclusions

A new layered vanadium oxide with the chemical composition Na_{1/2}VO₂ was obtained by sodium electrochemical deintercalation in a sodium battery. This was the third polymorph with a layered structure that could be synthesized using this technique. As in the polymorph with a P2-type structure, vanadium ions rearranged within the (VO₂)_n layers formed by edge-sharing VO₆ octahedra in the P'3-Na_{1/2}VO₂ phase to form vanadium pseudo-trimers with very short V-V distances. A reversible magnetic and structural transition was observed in this new oxide around 325 K. It was associated with the disappearance of vanadium pseudo-trimers in the triangular

lattice formed by the vanadium ions. The discovery of this new vanadium oxide and the study of its unique electronic properties have only been possible because the battery allows to synthesize new oxides at room temperature that would be impossible to synthesize by classical solid state reaction.

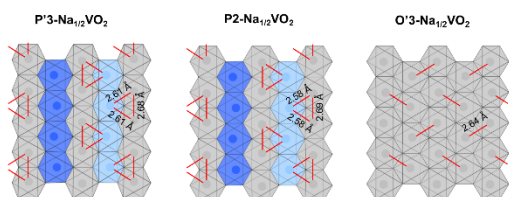
Supporting Information Summary

The description of the sample preparation is shown in the Supporting Information. In this part the different characterization techniques are also described.

Keywords: Layered compounds • Sodium battery • Solid-state structures

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Entry for the Table of Contents



Vanadium clustering in three polymorphs $\text{Na}_{1/2}\text{VO}_2$: Projection parallel to the $(\text{VO}_2)_n$ layers showing the VO_6 octahedra and the vanadium clustering in three polymorphs $\text{Na}_{1/2}\text{VO}_2$. Short V-V distances are shown in red along with their value (Na and O atoms are not shown). Whereas a similar vanadium arrangement is observed in the P'3- and P2- type polymorphs (pseudo-trimers), dimers are formed in O'3- $\text{Na}_{1/2}\text{VO}_2$.