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## Crystal Structure of $\text{Na}_2\text{V}_2(\text{PO}_4)(3)$ , an Intriguing Phase Spotted in the $\text{Na}_3\text{V}_2(\text{PO}_4)(3)$ - $\text{Na}_1\text{V}_2(\text{PO}_4)(3)$ System

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# Crystal Structure of $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , an Intriguing Phase Spotted in the $\text{Na}_3\text{V}_2(\text{PO}_4)_3 - \text{Na}_1\text{V}_2(\text{PO}_4)_3$ System

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## Abstract

The Na-superionic-conductor (NASICON)  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  is an important positive electrode material for Na-ion batteries. Here, we investigate the mechanisms of phase transition in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  ( $1 \leq x \leq 4$ ) upon a non-equilibrium battery cycling. Unlike the widely believed two-phase reaction in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3 - \text{Na}_1\text{V}_2(\text{PO}_4)_3$  system, we determine, for the first time, the structure of a recently reported intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase using operando synchrotron X-ray diffraction. Density functional theory calculations further support the existence of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase. We propose two possible crystal structures of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  analyzed by Rietveld refinement. The two structure models with the space groups  $P2_1/c$  or  $P2/c$  for the new intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase show similar unit cell parameters but different atomic arrangements, including a vanadium charge ordering. As the appearance of the intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase is accompanied by symmetry reduction, Na(1) and Na(2) sites split into several positions in  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , in which one of the splitting Na(2) position is found to be a vacancy whereas the Na(1) positions are almost fully filled. The intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase reduces the lattice mismatch between  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  phases facilitating a fast phase transition. This work paves the way for a better understanding of great rate capabilities of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ .

## Introduction

Na-superionic-conductor (NASICON) structured materials are considered as promising electrodes for sodium-ion batteries because of their 3D open-framework crystal structure, resulting in high cyclability and fast rate capability.<sup>1-5</sup> Among them,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  has been extensively studied, showing satisfactory energy density and rate performance as well as good thermal stability.<sup>6-13</sup> The crystal structure of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  is composed of repeating units called lanterns, into which two  $\text{VO}_6$  octahedra are joined together through three corner-sharing  $\text{PO}_4$  tetrahedra. Within the 3D framework generated by these lanterns, two crystallographic sodium sites, labeled Na(1) and Na(2), are usually reported. The Na(1) site is located between the lantern units along the  $[001]_{\text{hexagonal}}$  direction and is surrounded by six oxygen atoms in its first coordination sphere and by six Na(2) atoms in its second one. At maximum, the Na(1) and Na(2) sites (of different multiplicities) can respectively generate one and three Na positions per formula unit, thus leading to the final stoichiometry  $\text{Na}_4\text{V}_2(\text{PO}_4)_3$ . During electrochemical reactions, although the Na(1) site is involved in the global Na-ion transport mechanism (Na(2) – Na(1) – Na(2) pathways), it tends to be almost fully occupied regardless of the total Na content into the material, whereas the Na(2) site is partially/fully emptied or filled depending on the compositions.<sup>8,9,14-16</sup>

It is well known that two  $\text{Na}^+$  ions can be reversibly electrochemically extracted from a  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  electrode, through a voltage-composition “plateau” at  $\sim 3.4$  V (vs.  $\text{Na}^+/\text{Na}$ ) utilizing the  $\text{V}^{4+/3+}$  redox couple (with a theoretical capacity of 117.6 mAh/g).<sup>13,17-22</sup> The reaction has been described by many authors as a mechanism of two-phase reaction between  $\text{Na}_3\text{V}_2^{3+}(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2^{4+}(\text{PO}_4)_3$ .<sup>13,17-22</sup> Additionally, one  $\text{Na}^+$  ion can be inserted into  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  at  $\sim 1.6$  V (vs.  $\text{Na}^+/\text{Na}$ ) through the  $\text{V}^{3+/2+}$  redox couple towards the  $\text{Na}_4\text{V}_2(\text{PO}_4)_3$  composition (theoretical capacity of 58.8 mAh/g).<sup>18,19,22-27</sup> Recently, Zakharkin et al.<sup>20</sup> noticed the signature of an intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase, which involves the  $\text{V}^{4+/3+}$  redox couple. Nevertheless, no structural information on the intermediate phase was provided. Other previous reports also suggested the existence of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , but the authors barely contemplated the existence of a new intermediate phase.<sup>18,19</sup> This suggests that the widely

believed two-phase reaction between  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  needs to be reinvestigated, in particular, providing structural information and the origin of the appearance of the intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase.

Here, we elucidate the mechanisms of phase transition of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3 - \text{Na}_1\text{V}_2(\text{PO}_4)_3$  system including the intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase, utilizing  $\text{V}^{4+/3+}$  redox couple. We also investigate the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3 - \text{Na}_4\text{V}_2(\text{PO}_4)_3$  system involving the  $\text{V}^{3+/2+}$  redox couple. The intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase was detected by *operando* X-ray synchrotron diffraction as well as predicted by theoretical calculations. Here, we report for the first time on the crystal structure of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase, compared in detail with those of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  ( $x = 1, 3, 4$ ). The intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase appears as reducing the lattice mismatch between  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  phases, and as the Na(1) and Na(2) sites split into several positions with different  $\text{Na}^+$  distributions, including vacancies. This study is highly relevant to better understand the behavior of fast-rate electrode materials that display transient phases, such as the intermediate  $\text{Li}_x\text{FePO}_4$  phases ( $x = 0.6-0.75$ ) detected during non-equilibrium battery operations.<sup>28-36</sup>

## Experimental

**Synthesis:** The carbon-coated  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was prepared by a sol-gel-assisted solid-state reaction.  $\text{Na}_2\text{CO}_3$  (Sigma-Aldrich, 99.5 %),  $\text{C}_{10}\text{H}_{14}\text{O}_5\text{V}$  (Sigma-Aldrich, 97 %),  $\text{NH}_4\text{H}_2\text{PO}_4$  (Sigma-Aldrich, 98.5 %), and citric acid (Alfa Aesar, 99 %) in a molar ratio of 1.5:2:3:2, were dissolved in deionized water and ethanol (50/50 by volume). The solution was stirred overnight at 80 °C in an oil bath before being dried in oven. The obtained powder was ground and pre-heated at 400 °C for 4 h in Ar. The resulting powder was then mixed in a mortar and annealed at 700 °C for 10 h under Ar/ $\text{H}_2$  (95/5) atmosphere.

**Material Characterization:** The chemical composition of the synthesized material was quantified using inductively coupled plasma-optical emission spectroscopy (ICP-OES) with a Varian Model 720-ES spectrometer. The standard solutions of Na (Agilent, 1001±2 mg/L), V

(SCP Science, 1004±5 mg/L), and P (SCP Science, 1003±5 mg/L) were used for calibrations. The amount of carbon coating on the synthesized material was measured by thermogravimetric analyses (TGA) with a NETZSCH STA 449C. The morphology of the powder was examined by scanning electron microscopy (SEM) with a Hitachi Model S-4500 microscope.

**Operando Synchrotron X-ray Diffraction:** Operando synchrotron X-ray powder diffraction (SXRPD) measurements were performed on the MSPD beamline of the ALBA synchrotron in Spain<sup>37</sup> with Debye–Scherrer geometry ( $\lambda=0.8266$  Å) using an *in situ* coin cell with glass windows. Prior to the *operando* measurements, the SXRPD pattern of the pristine  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was collected with a 0.3 mm diameter capillary. Two *in situ* cells containing  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  electrodes were measured at the same time thanks to the eight-cells holder with an automatic positioning system available at the MSPD beamline.<sup>38</sup> Each SXRPD pattern was collected every 30 minutes with an acquisition time of ~3.5 minutes in the  $2\theta$  angular range of 2–40°, with a  $2\theta$  step size of 0.006° using a MYTHEN detector for rapid pattern collection. The working electrodes were composed of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  powder and carbon black (80/20 in wt%), and Na metal was used as counter/reference electrode. The mass loadings of the active material in the electrodes were 5.33 and 6.12 mg, respectively. One sheet of Whatman glass fiber (GF/D) was used as a separator and the electrolyte was composed of 1 M  $\text{NaPF}_6$  in ethylene carbonate (EC) / dimethyl carbonate (DMC) (1:1, w/w) with 2 wt.% of fluoroethylene carbonate (FEC). The first cell was measured for one cycle with a slow electrochemical reaction rate of 0.11 C (1 C = 58.2 mA/g, or about 9 h for the exchange of  $1\text{Na}^+ / 1\text{e}^-$ ) with a voltage window of 1 –3.75 V versus  $\text{Na}^+/\text{Na}$ . The second cell was measured for six cycles with higher C-rates (i.e., 0.37-0.77-0.77-0.77-0.37-0.77 C). A large overpotential was observed during the measurements of the second cell, hence the voltage windows were adjusted with the respected C-rates (detailed cycling conditions can be found in Table S1 in the supporting information section).

**Density Functional Theory Calculations:** To assess the thermodynamic stability of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  with distinct Na-vacancy orderings at 0 K, we used the spin-polarized density functional theory (DFT), as implemented in VASP.<sup>39,40</sup> The exchange-correlation was approximated by

the strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation functional,<sup>41</sup> with a  $U$  correction of 1.0 eV on all vanadium atoms to improve the localization of  $3d$  electrons.<sup>42</sup> The total energies were converged to within  $10^{-5}$  eV/cell, atomic forces (stresses) within  $10^{-2}$  eV/Å (0.29 GPa). The 1<sup>st</sup> Brillouin zone was integrated over a  $\Gamma$ -centered  $k$ -point grid of  $3 \times 3 \times 3$  for all primitive structures containing 2 formula units (f.u.) with 42 atoms, a  $1 \times 3 \times 3$   $k$ -point mesh for all supercells with 4 f.u. (84 atoms), and a  $1 \times 1 \times 3$  mesh for 8 f.u. (168 atoms). The valence electrons were treated in terms of plane-waves up to an energy cutoff of 520 eV, while projector augmented wave potentials were used to describe the core electrons,<sup>43</sup> with Na  $3s^1$ , V\_pv  $3p^6 3d^4 4s^1$ , P  $2s^2 3p^3$ , O  $2s^2 2p^4$ .

The average intercalation voltage was derived using **Eq. 1**.

$$V = -\frac{\Delta G^0}{yF} \approx -\frac{E(\text{Na}_{x+y}\text{V}_2(\text{PO}_4)_3) - [E(\text{Na}_x\text{V}_2(\text{PO}_4)_3) + y\mu_{\text{Na}}]}{yF} \quad (1)$$

where  $\Delta G^0$  is the change of Gibbs free energy, as approximated from our DFT total energies, which ignore the zero-point energy correction, the  $pV$  term, and entropic effects. Thus,  $E(\text{Na}_{x+y}\text{V}_2(\text{PO}_4)_3)$ ,  $E(\text{Na}_x\text{V}_2(\text{PO}_4)_3)$  and  $\mu_{\text{Na}}$  are the DFT total energies of stable Na-vacancy orderings at compositions  $x$  and  $x + y$ , and the Na chemical potential of Na metal, *respectively*.  $F$  is the Faraday constant. Mixing enthalpies ( $H_{\text{mixing}}$ ) at different Na compositions, to construct the 0 K phase diagram were defined in **Eq. 2**.

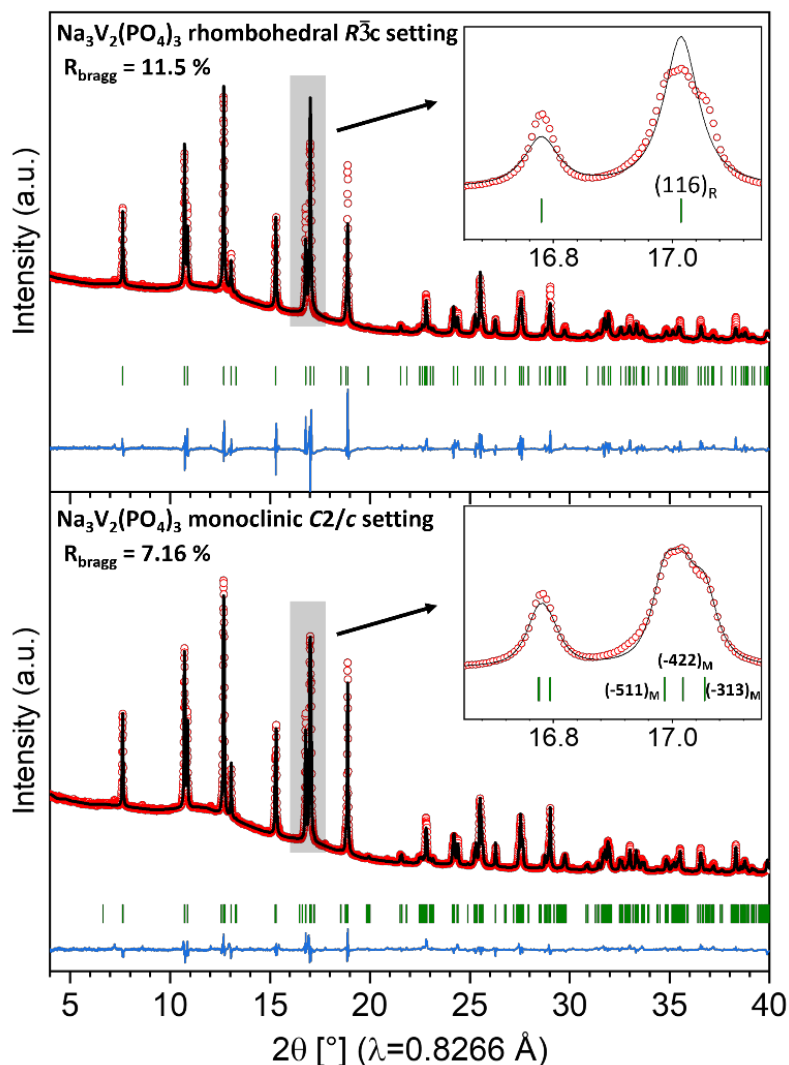
$$H_{\text{mixing}}(x) \approx E[\text{Na}_x\text{V}_2(\text{PO}_4)_3] - \left(\frac{4-x}{3}\right) E[\text{Na}_1\text{V}_2(\text{PO}_4)_3] - \left(\frac{x-1}{3}\right) E[\text{Na}_4\text{V}_2(\text{PO}_4)_3] \quad (2)$$

## Results and Discussion

The composition of the as-synthesized  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  powder was determined by elemental analysis using ICP-OES. The Na/V/P ratio was found to be 3.03(2):1.97(3):2.99(6), suggesting that the target composition  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was achieved through the sol-gel-assisted solid-state reaction. SEM images of the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  powder (**Figure S1**) show that the particles have no particular shapes as similar to other studies.<sup>11–13,17–22</sup> However, relatively large agglomerates ranging from few microns to several tenths of microns were found with the primary particles in the size of a few hundreds of nanometers. The powder is carbon-coated on the surface, *ca.* 9 wt% of carbon as determined by TGA measurements in air, shown in **Figure S2**.

The SXRPD pattern of the as-synthesized  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  powder is shown in **Figure 1**. No impurity phases were detected based on the XRD analysis. As previously reported,<sup>44</sup> at room temperature the crystal structure of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cannot be indexed using a rhombohedral ( $R\bar{3}c$ ) cell, but a monoclinic distortion must be considered. This is illustrated by the splitting of the  $(116)_{\text{rhombohedral}}$  reflection at  $d_{\text{hkl}} \sim 2.8 \text{ \AA}$  into  $(-511)_{\text{monoclinic}}$ ,  $(-422)_{\text{monoclinic}}$ , and  $(-313)_{\text{monoclinic}}$ , which are signatures of the monoclinic distortion (inset images of **Figure 1**). Depending on the thermal history of the sample,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  can crystallize either in the monoclinic  $\alpha$  or  $\beta$  form at room temperature (the reversible phase transition occurring very close to room temperature with about  $10^\circ$  of hysteresis).<sup>44</sup> In the present study, the crystal structure was refined with the monoclinic  $\beta$  phase since the  $(111)$  reflection at  $6.74^\circ$  ( $\lambda=0.8266 \text{ \AA}$ ) was not observed, while it is allowed in the  $\alpha$  (i.e.,  $\text{Na}^+$  ordered) phase, as shown in **Figure S3**. The refined cell parameters using the Rietveld method are  $a=15.4104(4) \text{ \AA}$ ,  $b=8.7288(2) \text{ \AA}$ ,  $c=8.8257(2) \text{ \AA}$ ,  $\beta=126.1202(17)^\circ$ , and  $V/Z=239.75(2) \text{ \AA}^3$  with the space group  $C2/c$ . The weak unindexed satellite reflections at low angles are attributed to an incommensurate modulated structure. These modulations originate both from the occupancies and the positions of  $\text{Na}^+$  ions in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ . No detailed structural study of the incommensurate  $\beta$  phase has been reported yet and thus the SXRPD pattern was refined without modulation vectors.

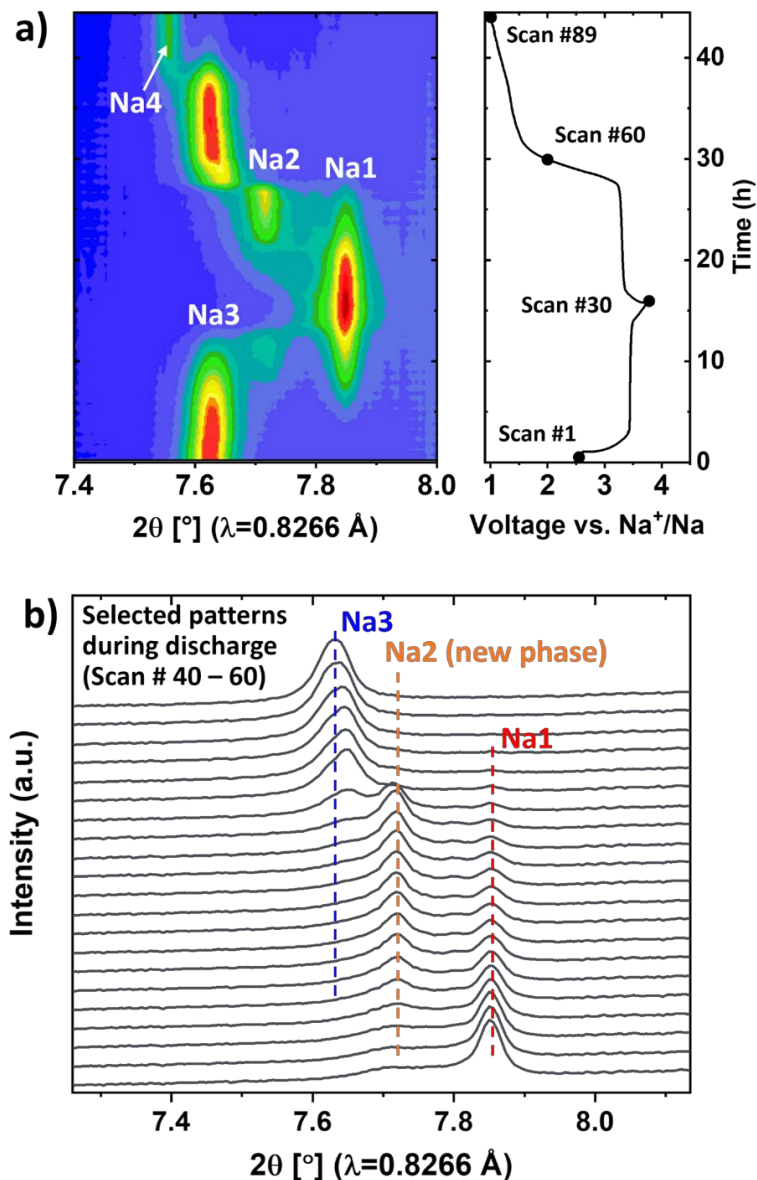




**Figure 1.** Rietveld refinement results of the as-synthesized  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  powder with (top) the space group  $R\bar{3}c$  and (bottom) the space group  $C2/c$ . The corresponding SXRPD pattern was collected at 298 K. It clearly shows that the structure of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  contains a monoclinic distortion as, for instance,  $(116)_R$  reflection splits into  $(-511)_M$ ,  $(-422)_M$ , and  $(-313)_M$  (R and M here stand for rhombohedral and monoclinic, respectively).

To study the (de-)intercalated phases and the  $\text{Na}^+$  insertion/extraction mechanisms in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , *operando* SXRPD measurements were performed. **Figure 2a** displays a 2D view of the SXRPD of a selected  $2\theta$  range during the first electrochemical charge-discharge cycle together with the corresponding galvanostatic data measured within a voltage window of 1.0 – 3.75 V (vs.  $\text{Na}^+/\text{Na}$ ) at a C-rate of  $\sim 0.11$  C (for wider  $2\theta$  range, see **Figure S4**). A total number of 89 scans were recorded during the first cycle. From scan number 1 to 30,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  is first oxidized up to 3.75 V vs.  $\text{Na}^+/\text{Na}$ . During the charge process, two  $\text{Na}^+$

cations are extracted leading to the composition  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ . Close to the mid-charge (i.e., after approximately 10h of cycling) a weak reflection at  $2\theta \approx 7.7^\circ$  starts to appear together with the presence of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (corresponding reflection at  $2\theta \approx 7.63^\circ$ ) and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  (corresponding reflection at  $2\theta \approx 7.85^\circ$ ).  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  is then reduced back to  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (scan number 60) and further to  $\text{Na}_4\text{V}_2(\text{PO}_4)_3$  (scan number 89) at a potential of  $\sim 1$  V vs.  $\text{Na}^+/\text{Na}$ . During the discharge process, the very same peak at  $2\theta \approx 7.7^\circ$  re-appears with an increased intensity. This new reflection that is attributed to the new intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase can be more clearly seen in the selected SXRPD patterns (scan number 40-60) of **Figure 2b**. As previously reported by Zakharkin *et al.*<sup>20</sup> the appearance of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase indicates that the electrochemical mechanisms of  $\text{Na}^+$  insertion/extraction in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , involving the  $\text{V}^{4+/3+}$  redox couple at  $\sim 3.4$  V (vs.  $\text{Na}^+/\text{Na}$ ), are different from most of the existing reports.<sup>13,17-22</sup>

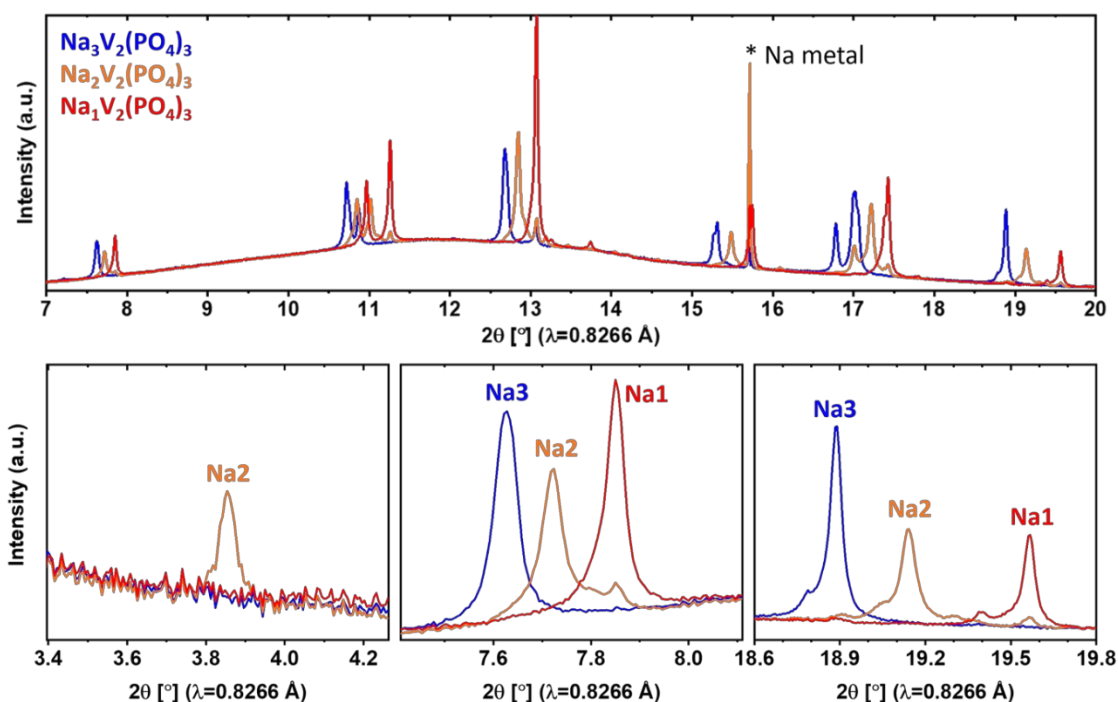


**Figure 2.** a) *Operando* SXRPD patterns using  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  as positive electrode material in a half cell versus Na metal upon charge and discharge, with a voltage window of 1.0 – 3.75 V vs.  $\text{Na}^+/\text{Na}$  at a C-rate of 0.11 C ( $\approx 1 \text{ Na}^+$  in 9 h). b) Selected SXRPD patterns (from scan number 40-60 during discharge), where the intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase appears more clearly.  $\text{Na}_x$  ( $x = 1, 2,$  and  $3$ ) refers to  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ .

The intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase tended to coexist with the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  phases at low C-rate (0.11 C). However, when a higher current density was applied (i.e., towards a non-equilibrium state), the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase became more isolated. Similarly, in the operando study of  $\text{LiFePO}_4$ , a higher C-rate (1 C to 10 C) allowed a more intense appearance of the intermediate  $\text{Li}_x\text{FePO}_4$  phase.<sup>30</sup> Even though the C-rates used in this study

were relatively low, the battery cells already reached a non-equilibrium condition. This is probably because (i) the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  powder contains relatively large particles (see **Figure S1**); and (ii) the electrodes without binder can induce a higher overpotential.<sup>45</sup> This is further confirmed by the observation of the large polarization of  $\sim 150$  mV using the *in situ* cell compared to a low polarization of 30 mV observed using a normal coin cell, cycled at the same C-rate of 0.11 C (**Figure S5**). **Figure S6** shows *operando* SXRPD data collected during six cycles with the C-rates of 0.37-0.77-0.77-0.77-0.37-0.77 C (which are about three to seven times higher current densities than 0.11 C). To increase the chance of isolating a 'pure'  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase, multiple cycles were measured. The SXRPD pattern which appears mostly composed by the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase was obtained during the last cycle (see **Figure S6** for more details).

**Figure 3** shows a comparison of the SXRPD patterns among the  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  ( $x = 1, 2, \text{ and } 3$ ) compositions. The strong background in the SXRPD patterns originates from the cell components, such as the electrolyte and the glass windows.<sup>45</sup> Importantly, a careful evaluation of the SXRPD pattern of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  reveals the appearance of weak Bragg peak at a very low  $2\theta$  angle ( $\sim 3.85^\circ$ ,  $d_{hkl} = 12.29 \text{ \AA}$ ). Through a *operando* technique, this weak Bragg peak at such a low angle (equivalent to  $\sim 7.2^\circ$  in  $\text{Cu}_{K\alpha}$  radiation) may be missed with a standard laboratory X-ray equipment, while we clearly observed it with a synchrotron X-ray source. This provides critical information to solve the crystal structure of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ .

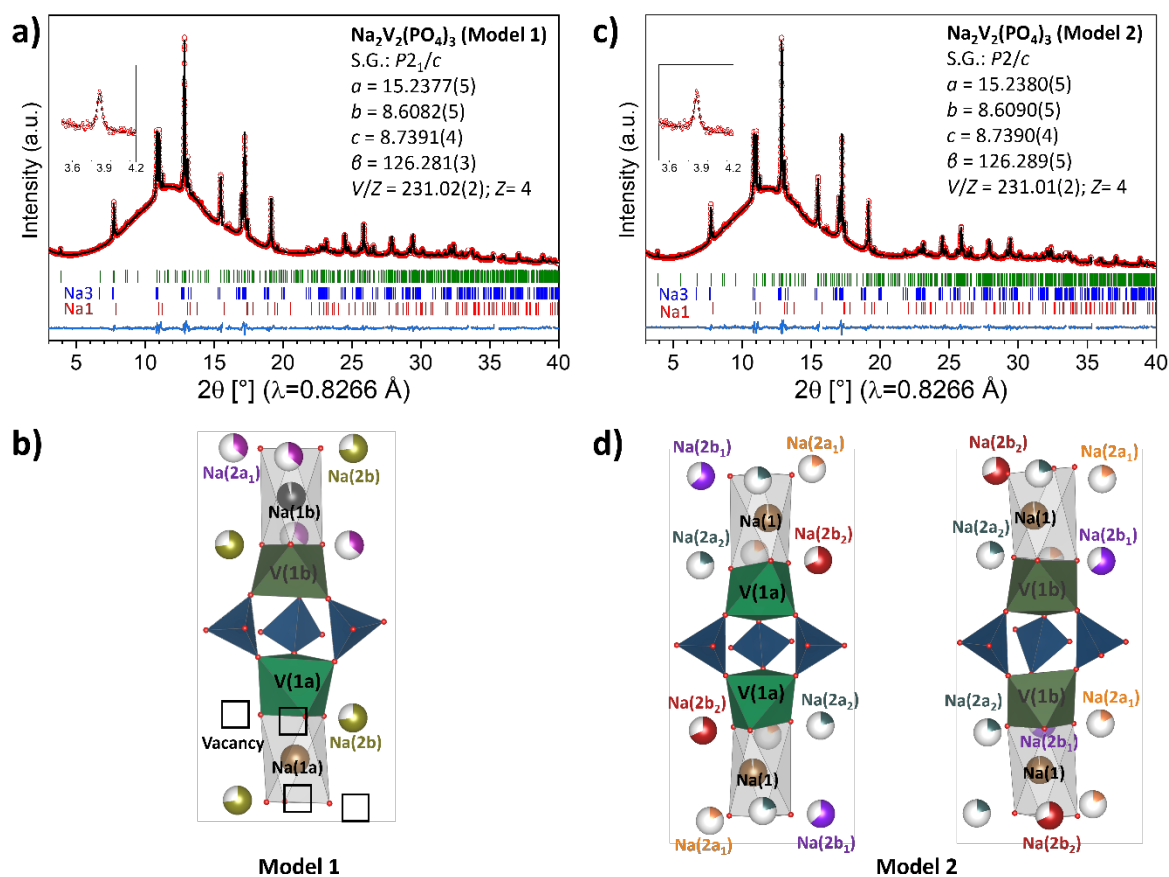


**Figure 3.** The SXRPD patterns of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (blue),  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  (orange), and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  (red) with different angular domains. The Bragg peak at  $3.85^\circ$  is only observed for the new  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase. The overall positions of the Bragg peaks manifest the appearance of the intermediate phase which can be differentiated from  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  phases.

The powder pattern of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  presented in **Figure 3** was then used to solve its crystal structure. The indexing of the powder pattern, the space group determination, and the cell transformation with group-subgroup relationships were carried out using Dicvol,<sup>46</sup> Chekcell,<sup>47</sup> and POWDERCELL<sup>48</sup> software, to fully resolve the crystal structure of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ . During the steps of indexing and space group determination, it was found that the reflection at  $2\theta = 3.85^\circ$  excludes the rhombohedral lattices (**Figure S7**) as well as *C*-centered monoclinic-type cells (**Figure S8**). Possible space groups are then primitive, and thus several structure models with different space groups were examined to solve the structure. The initial atomic positions of each model were deduced from the group-subgroup relationships starting from the  $R\bar{3}c$  rhombohedral cell. The highest to lowest symmetry of the examined space groups are  $P2_1/c$ ,  $P2/c$ ,  $P2_1/m$ , and  $P/m$  (corresponding to 22, 23, 42, and 46 independent atoms per cell, respectively). We attempted unsuccessfully to solve the structure using the two space groups ( $P2_1/m$ , and  $P/m$ ). The structure model, namely “Model 1”, using the  $P2_1/c$  space group

showed slightly better results than that using a  $P2_1/c$  space group (i.e., Model 2). The detailed comparisons between Models 1 and 2 are discussed later in this paper.

For the structure of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  using the space group  $P2_1/c$  (Model 1), the refined cell parameters are:  $a = 15.2377(5) \text{ \AA}$ ,  $b = 8.6082(5) \text{ \AA}$ ,  $c = 8.7391(4) \text{ \AA}$ ,  $\beta = 126.281(3)$ ,  $V/Z = 231.02(2) \text{ \AA}^3$ . The results of Rietveld refinement are presented in **Figure 4a**, illustrating that the reflection at  $2\theta = 3.85^\circ$  can be fully explained. The final refinement was performed using  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  as secondary phases with final weight fractions of 8.4(5) and 7.1(3) %, respectively. The global structural information, including atomic coordinates, atomic displacement parameters, and occupancy factors, are listed in **Table 1**. The crystal structure of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  contains two different vanadium Wyckoff positions, V(1a) and V(1b), involved in the same lantern unit as illustrated in **Figure 4b**. From the examination of the V-O bond distances (**Table S2**), it appears that the environment of both V(1a) and V(1b) are similar with an average V-O bond distance of  $1.99(9) \text{ \AA}$ , which suggests that  $\text{V}^{3+}$  and  $\text{V}^{4+}$  are randomly distributed over the V(1a) and V(1b) positions. For the Na crystallographic sites, the Na(1) and Na(2) sites split into two Na(1) (labeled Na(1a) and Na(1b)) and three Na(2) positions (labeled Na(2a<sub>1</sub>), Na(2a<sub>2</sub>), and Na(2b)) in the space group  $P2_1/c$ . The refined occupancy factor for Na(2a<sub>2</sub>) position was 0.08(7), which can be considered as fully empty. The refined occupancy factors for Na(1a), Na(1b), Na(2a<sub>1</sub>), and Na(2b) are 1, 0.98(8), 0.36(7), and 0.73(10), respectively, yielding a composition  $\text{Na}_{2.1(3)}\text{V}_2(\text{PO}_4)_3$ .



**Figure 4.** Rietveld refinement results of the intermediate phase  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  using **a)** the space group  $P2_1/c$  (Model 1) and **b)** the space group  $P2/c$  (Model 2). **c)** Lantern unit with adjacent  $\text{Na}^+$  ions in the crystal structure of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , refined with the space group  $P2_1/c$ . V(1a) and V(1b) atoms are involved in a single lantern unit. Vacant  $\text{Na}^+$  positions are shown as empty squares. **d)** Lantern units with adjacent  $\text{Na}^+$  ions in the crystal structure of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , refined with the space group  $P2/c$ . Two different lantern units exist in the structure: each vanadium position forms a distinct lantern unit.

We tested another structural model for  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  using the space group  $P2/c$  (Model 2), which showed similar agreement factors with the following cell parameters:  $a = 15.2380(5) \text{ \AA}$ ;  $b = 8.6090(5) \text{ \AA}$ ;  $c = 8.7390(4) \text{ \AA}$ ;  $\beta = 126.289(5)^\circ$ ,  $V/Z = 231.01(2) \text{ \AA}^3$  (**Figure 4c**). Model 2 also contains two vanadium positions, but it generates two distinct lantern units in the structure: one with two V(1a) atoms and the other one with two V(1b) atoms (**Figure 4d**). Furthermore, the average V-O distances in V(1a)O<sub>6</sub> and V(1b)O<sub>6</sub> octahedra are 1.92(8) Å and 2.04(8) Å, respectively, suggesting a possible charge ordering of the V<sup>4+</sup> and V<sup>3+</sup> in the crystal structure (see the details of V-O distances in **Table S2**). In terms of V charge ordering, Model 2 compares well with the DFT data discussed below. Finally, the Na(1) site is unique, while the Na(2) site splits into four distinct Wyckoff positions, i.e., Na(2a<sub>1</sub>), Na(2a<sub>2</sub>), Na(2b<sub>1</sub>), and Na(2b<sub>2</sub>). The

refined occupancy factors for Na(1), Na(2a<sub>1</sub>), Na(2a<sub>2</sub>), Na(2b<sub>1</sub>), and Na(2b<sub>2</sub>) are 0.98(3), 0.17(7), 0.21(7), 0.63(11), and 0.68(11), respectively, yielding a composition Na<sub>2.0(3)</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. Detailed structural information is listed in **Table S3**.

**Table 1.** Refined structural parameters of the intermediate phase Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> using the space group *P2<sub>1</sub>/c* (Model 1). <sup>a</sup>Refined and fixed at the last stages of refinement.

<b>Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub></b>						
Space group: <i>P2<sub>1</sub>/c</i> (#14); <i>Z</i> = 4						
<i>a</i> = 15.2377(5) Å; <i>b</i> = 8.6082(5) Å; <i>c</i> = 8.7391(4) Å; <i>β</i> = 126.281(3);						
<i>V</i> = 924.069(8) Å <sup>3</sup> ; <i>V/Z</i> = 231.02(2) Å <sup>3</sup>						
<i>R</i> <sub>wp</sub> = 13.3 %; <i>R</i> <sub>p</sub> = 19.5 %; <i>R</i> <sub>bragg</sub> = 6.21 %						
Atom	Wyckoff position	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Uiso, Å <sup>2</sup>	Occ.
V(1a)	4e	0.848(2)	0.492(5)	0.630(4)	0.026(3)	1
V(1b)	4e	0.640(2)	0.493(5)	0.834(4)	0.026(3)	1
P(1a)	4e	0.1047(10)	0.3521(17)	0.958(2)	0.033(4)	1
P(1b)	4e	0.3965(10)	0.3581(17)	0.564(2)	0.033(4)	1
P(2)	4e	0.2572(10)	0.7725(14)	0.262(2)	0.033(4)	1
O(1b)	4e	0.397(7)	0.372(10)	0.389(7)	0.012(3)	1
O(1d)	4e	0.094(7)	0.423(7)	0.107(10)	0.012(3)	1
O(1e)	4e	0.338(5)	0.700(10)	0.230(10)	0.012(3)	1
O(2b)	4e	0.208(6)	0.637(5)	0.303(10)	0.012(3)	1
O(2c)	4e	0.706(5)	0.916(10)	0.960(14)	0.012(3)	1
O(2f)	4e	0.805(5)	0.926(10)	0.547(14)	0.012(3)	1
O(1a)	4e	0.398(7)	0.319(2)	0.081(14)	0.012(3)	1
O(1c)	4e	0.104(7)	0.325(2)	0.478(10)	0.012(3)	1
O(1f)	4e	0.004(5)	0.085(10)	0.270(7)	0.012(3)	1
O(2a)	4e	0.506(5)	0.083(10)	0.240(7)	0.012(3)	1
O(2d)	4e	0.331(7)	0.614(10)	0.927(10)	0.012(3)	1
O(2e)	4e	0.167(6)	0.639(10)	0.582(7)	0.012(3)	1
Na(1a)	2a	0	0	0	0.090(13)	1 <sup>a</sup>
Na(1b)	2d	0.5	0	0.5	0.090(13)	0.98(8)
Na(2a <sub>1</sub> )	4e	0.557 <sup>a</sup>	0.168 <sup>a</sup>	0.908 <sup>a</sup>	0.090(13)	0.36(7)
Na(2a <sub>2</sub> )	4e	0.936	0.169	0.565	0.090(13)	0 <sup>a</sup>
Na(2b)	4e	0.232(7)	0.140(14)	0.243(14)	0.090(13)	0.73(10)



Note that both monoclinic structural models for  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  ( $P2/c$  and  $P2_1/c$ ) have very similar cell parameters and can fully account for the existence of the (100) reflection at  $2\theta = 3.85^\circ$ . However, subtle differences to distinguish between the two space groups are convoluted in the possible existence of  $[(0k0), k=2n+1]$  reflections for  $P2/c$  while they are forbidden for  $P2_1/c$ . A very low-intensity peak at  $\sim 5.5^\circ$  (of the SXRPD pattern) could be assigned to the (010) reflection in the space group  $P2/c$ , although the same was also observed in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  phases with the same intensity. This evidence suggests this peak may not originate from the phase reflection of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  but it is rather a noisy background (**Figure S9**). For this reason, we believe that the  $P2_1/c$  model (Model 1) is more suitable, although the  $P2/c$  one (Model 2) cannot be completely excluded.

To shed light on the thermodynamic stability of the intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase, detected with our SXRPD diffraction, we performed dedicated DFT calculations. **Figure 5** shows the thermodynamic properties of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  in the region of  $x = 1 - 3$  at 0 K, as computed by DFT. **Figure 5a** shows the DFT mixing enthalpies ( $H_{\text{mixing}}$  in **eq. 2**) for all Na/vacancy orderings of the  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  compositions. Using a convex hull minimization algorithm, all the ground-state configurations were obtained. It can be concluded that besides the end-members  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , which are assigned to rhombohedral and monoclinic symmetry, respectively, the new  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase appears as a stable configuration. However,  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  shows a relatively low mixing enthalpy (*ca.* -23 meV/f.u.) with respect to  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , and this suggests that the intermediate phase may be metastable at room temperature.

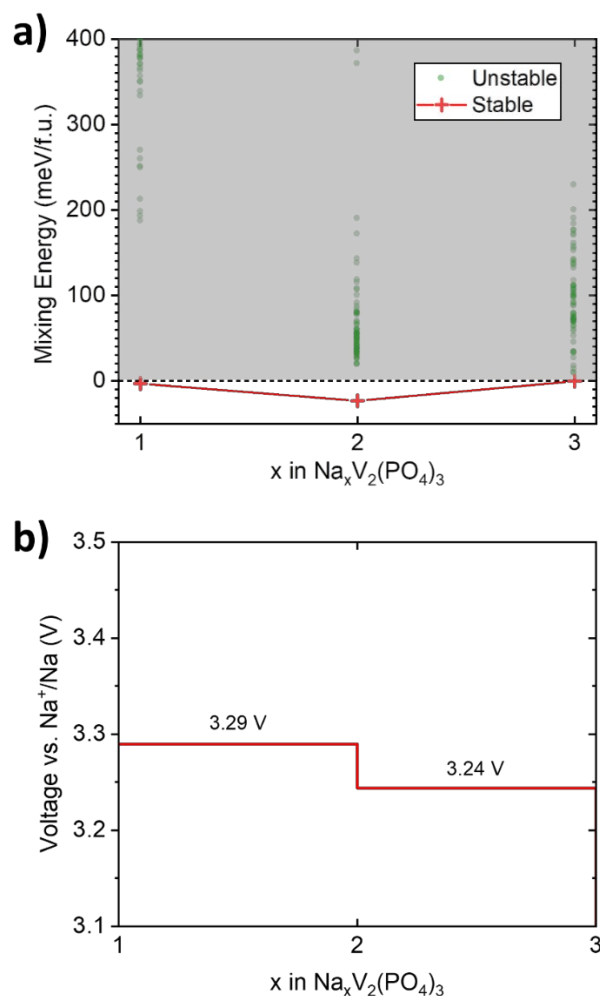
**Table 2.** Unit cell parameters, Na occupancy factors, and average of V-O distances of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  obtained by DFT calculations.

	S.G.	<i>a</i>	<i>b</i>	<i>c</i>	$\alpha$	$\beta$	$\gamma$	<i>V</i> / <i>Z</i>	Na(1) /f.u.	Na(2) /f.u.	Total Na /f.u.	Avg. V-O (Å)
$\text{Na}_2\text{V}_2(\text{PO}_4)_3$	$P\bar{1}$	8.712	8.667	8.629	59.729	58.858	59.602	227.159	1	1	2	1.964

**Table 2** presents unit cell parameters, sodium occupancy factors, and the average of V-O distances of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  structure obtained by DFT calculations. The computed structure

of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  shows a similar cell volume with the experimentally observed one, and this calculated phase is assigned to a triclinic symmetry  $P\bar{1}$  with distinguished  $\text{V}^{4+}$  and  $\text{V}^{3+}$  states, and with fully ordered Na(1) and Na(2) sites. Higher temperatures will enable other Na-vacancy ordering to be stable, with intrinsic symmetries maybe similar to what was found experimentally. Therefore, the structures extracted from the synchrotron measurements can be assumed with a superposition of several Na-vacancy orderings. A closer look to the local arrangement of Na ions in the DFT structure of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  shows that fully occupied Na(1) site is surrounded by two fully occupied Na(2) sites and four vacancies.<sup>49</sup> Consequently, we could observe unique  $\text{Na}^+$  sites of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  ground-state predicted by DFT split into a larger number of distinct Wyckoff positions compared to what elaborated by our experimental Model 1 and 2. However, our room-temperature synchrotron data of the intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  structure detected under non-equilibrium conditions will likely incorporate several possible Na-vacancy configurations, averaging out the Na ions among the available Na(1) and Na(2) sites, which can be the origin of the observed fractional occupancies from SXRPD.<sup>44,50</sup> Furthermore, our DFT calculations suggest a specific vanadium charge orderings within the ground-state  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , which may be disrupted by temperature effects. Ongoing synthesis efforts to obtain  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  chemically as a pure phase will further clarify the discrepancies between the DFT data and our experimental models.

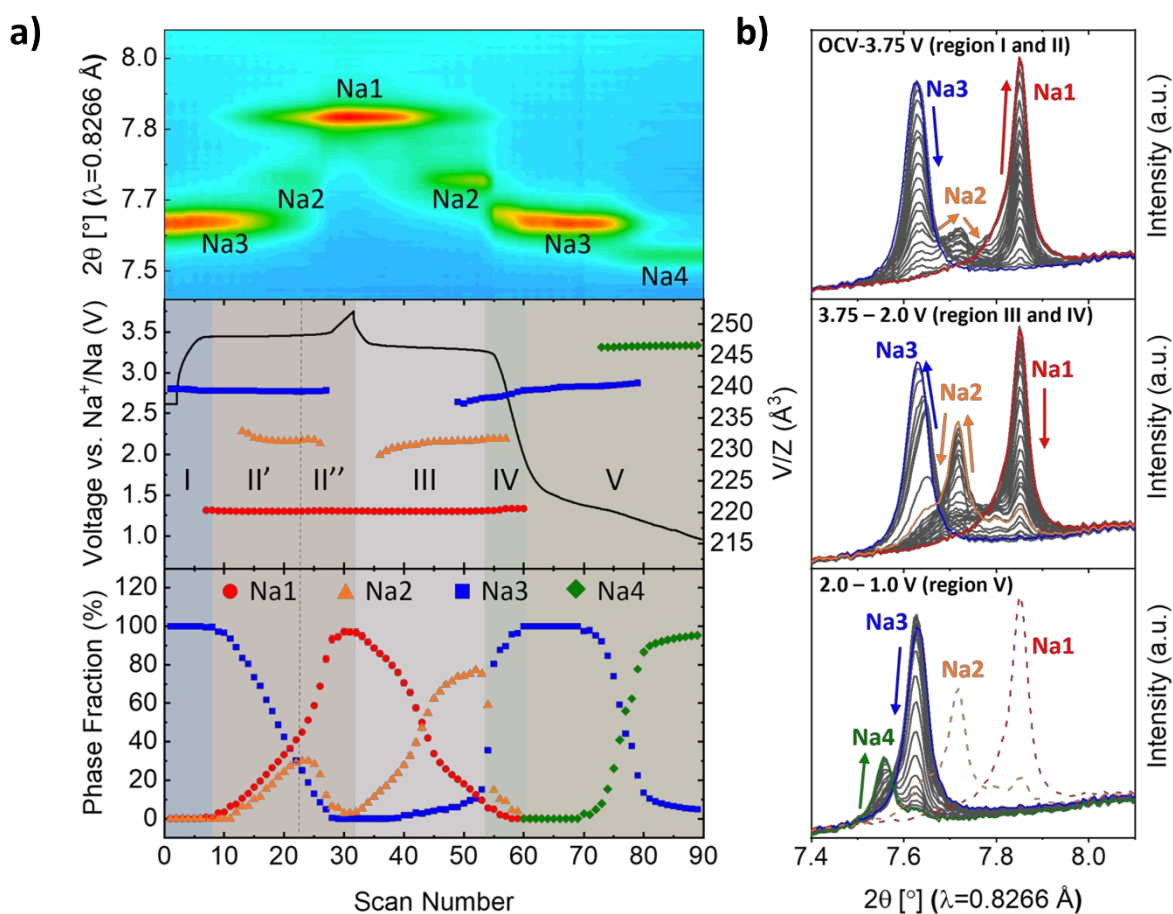
**Figure 5b** depicts the DFT-derived voltage profile in the region of  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  to  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ . By identifying the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase, we could realize two voltage plateaus while  $\text{Na}^+$  intercalation via biphasic reaction mechanisms, namely 3.29 V vs.  $\text{Na}^+/\text{Na}$  between  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , and 3.24 V vs.  $\text{Na}^+/\text{Na}$  between  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ . Notably, the Na ordering of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  give rise to a small voltage step (~50 mV).



**Figure 5. a)** DFT-derived phase diagram in the composition range ( $1 \leq x \leq 3$ ) for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  at 0 K, in terms of Na mixing enthalpies. The stable ground-state configurations, namely  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ ,  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ , and the unstable configurations are represented by red cross and green dots, respectively. **b)** The computed voltage profile from  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  to  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ .

Having the crystal structures of the new  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase determined (with the space group  $P2_1/c$ ), the *operando* SXRPD data collected upon cycling at a C-rate of 0.11 C (shown in **Figure 2**) were analyzed by Rietveld refinements including the evolutions of phase transitions, cell volumes, and phase weights as shown in **Figure 6**. Five different regions can be distinguished during the charge and discharge processes (labeled from I to V) in **Figure 6**. In region I (solid solution part), only  $\text{Na}_{3-\delta}\text{V}_2(\text{PO}_4)_3$  is present and its unit cell volume ( $V/Z$ ) slightly decreases from  $239.687(6) \text{ \AA}^3$  to  $239.384(8) \text{ \AA}^3$  whereas the voltage increases from 2.61 to 3.44 V vs.  $\text{Na}^+/\text{Na}$ . Region II (plateau at 3.4 V vs.  $\text{Na}^+/\text{Na}$ ) can be divided into two sub-regions (II' and II''). The  $\text{Na}^+$  extraction mechanism occurs first through an out-of-equilibrium “three-phase”

reaction, where the amount of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  phase decreases while those of  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phases increase concomitantly up to mid-charge (region II'). This can be rationalized as the overlap of two biphasic reactions of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3 - \text{Na}_2\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{V}_2(\text{PO}_4)_3 - \text{Na}_1\text{V}_2(\text{PO}_4)_3$ . We note that the two reactions tend to separate more when higher current densities are furnished (**Figure S6**). After that (in region II'' of **Figure 6**), the quantities of  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  phases diminish, while the  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  content keeps increasing until the end of charge at  $\sim 3.75$  V vs.  $\text{Na}^+/\text{Na}$ . The discharge process down to  $\sim 2$  V vs.  $\text{Na}^+/\text{Na}$  appears rather different (region III). On the plateau, the main reaction seems to occur between  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  via a two-phase reaction. At this stage, the amount of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  remains low ( $< 10$  wt%). Afterwards, in region IV, the phase transition from  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  to  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  occurred rapidly. Even though the voltage plateau at around 1.6 V vs.  $\text{Na}^+/\text{Na}$  accompanies a slight sloping profile, in region V (reduction down to 1 V vs.  $\text{Na}^+/\text{Na}$ ), a biphasic reaction between  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_4\text{V}_2(\text{PO}_4)_3$  is observed. When the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  phase re-appears during discharge, the reaction mainly occurs through a two-phase reaction mechanism. However, the slight peak-shift to lower angles and the increase of  $V/Z$  observed in **Figures 6b** and **6a** indicates that a partial solid solution mechanism is also involved. This behavior is typically observed in  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ,<sup>17-22</sup> but also in other electrode materials, such as  $\text{Na}_3\text{Al}_{0.5}\text{V}_{1.5}(\text{PO}_4)_3$ ,<sup>51</sup>  $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$ ,<sup>52</sup>  $\text{Na}_2\text{TlV}(\text{PO}_4)_3$ <sup>53</sup> and  $\text{LiVOPO}_4$ ,<sup>54</sup> all including a two-phase reaction mechanism upon cycling. A major change in lattice parameters between the two end-members of a two-phase reaction induces strains at the boundaries between these two different domains and results in small changes of the cell parameters of the two end-members as if a solid solution occurs.<sup>51,53,54</sup> Nevertheless, the SXRPD pattern of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  is recovered after the re-sodiation, showing the high reversibility of the electrochemical reaction.



**Figure 6.** **a)** Counter plot of *operando* SXRPD patterns in the 7.46-8.03° angular range (top). Voltage profile of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  during the first cycle, in a voltage window of 1.0 - 3.75 V vs.  $\text{Na}^+/\text{Na}$  at a C-rate of 0.11 C and V/Z evolution of the  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  ( $x = 1, 2, 3,$  and  $4$ ) phases (middle). The corresponding phase weights (bottom). **b)** Details of the SXRPD patterns, upon  $\text{Na}^+$  extraction from  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  to  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ , upon  $\text{Na}^+$  re-insertion from  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  to  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (middle), and upon one additional  $\text{Na}^+$  insertion from  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  to  $\text{Na}_4\text{V}_2(\text{PO}_4)_3$  (bottom).  $\text{Na}_x$  ( $x = 1, 2, 3,$  and  $4$ ) refers to  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ .

From the phase fraction analysis, it is clear that the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase could not be observed as completely isolated but rather coexisting together with the  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  ones. The maximum phase fraction of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase observed during charge was of 30.1(8) wt% while it reached 77(1) wt% during discharge. The asymmetric behaviors in the appearance of the intermediate phase during charge and discharge were also observed in other studies of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ <sup>18-20</sup> and of  $\text{LiFePO}_4$ <sup>30,32,35,36</sup>. The intermediate phases of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  and  $\text{Li}_x\text{FePO}_4$  are more visible during charge in some cases<sup>18-20,30,36</sup> and during discharge in other cases<sup>20,32,35</sup>. Zakharkin *et al.* investigated three different synthesis routes for preparing  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  with different precursors resulting in different intensities of the

XRD reflections of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  intermediate phase.<sup>20</sup> Depending on the synthesis procedures, the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  phase was either not observed, or observed only during charge, or observed during both charge and discharge.<sup>20</sup> These observations may suggest that the intermediate phase could be metastable/transient. Further investigations are required to understand the origin of the asymmetric behavior of the  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  intermediate phase in the  $\text{Na}_3\text{V}_2(\text{PO}_4)_3 - \text{Na}_1\text{V}_2(\text{PO}_4)_3$  system.

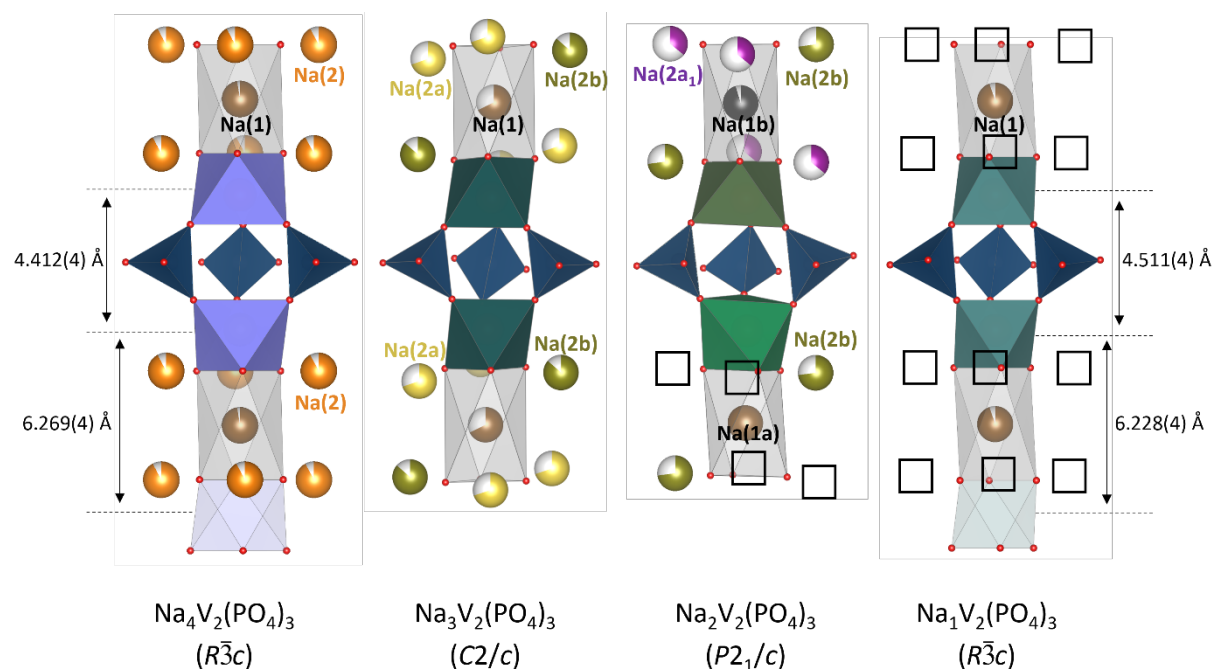
A global overview of cell parameters, Na site occupancies, and average of V-O bond lengths of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  ( $x = 1, 2, 3,$  and  $4$ ) is summarized in **Table 3**. For the monoclinic phases,  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$ , the  $a$ ,  $b$ , and  $c$  parameters decrease by  $\sim 1.1, 1.38,$  and  $0.97\%$ , respectively, and a slight increase in the  $\beta$  angle ( $0.14\%$ ) is noticed from  $x = 3$  to  $2$  in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ . The two end-members ( $\text{Na}_4\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ ) crystallize in the same space group  $R\bar{3}c$ . From the Na-rich phase,  $\text{Na}_4\text{V}_2(\text{PO}_4)_3$ , to the Na-poor one,  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$ , the  $a$  parameter dramatically decreases from  $8.94302(10)$  to  $8.42631(12)$  Å ( $\Delta a/a = -5.81\%$ ) while the  $c$  parameter slightly increases from  $21.3609(4)$  to  $21.4772(6)$  Å ( $\Delta c/c = 0.54\%$ ). This noticeable anisotropy in the change of cell parameters is closely linked to the occupancies of the Na(1) and Na(2) sites.

**Table 3.** Unit cell parameters, Na occupancy factors, and average V-O distances for the compositions  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , ( $x = 1, 2, 3,$  and  $4$ ) obtained by Rietveld refinement. See the profiles of the Rietveld refinements for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  ( $x = 1, 3,$  and  $4$ ) in **Figures S10-S12**, and the details of their structural information in **Table S4-S6**.

S.G.	$a$	$B$	$c$	$\beta$	$V/Z$	Na(1) /f.u.	Na(2) /f.u.	Total Na /f.u.	Avg. V-O (Å)
$\text{Na}_4\text{V}_2(\text{PO}_4)_3$ $R\bar{3}c$	8.94302(10)	8.94302(10)	21.3609(4)	120	246.585(7)	0.97(4)	2.77(7)	3.74(11)	2.078(14)
$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ $C2/c$	15.4065(3)	8.7288(2)	8.8243(2)	126.1091(16)	239.682(10)	0.679(14)	2.27(8)	2.9(1)	2.02(4)
$\text{Na}_2\text{V}_2(\text{PO}_4)_3$ $P2_1/c$	15.2377(5)	8.6082(5)	8.7391(4)	126.281(3)	231.02(2)	0.98(4)	1.2(3)	2.2(3)	1.99(9)
$\text{Na}_1\text{V}_2(\text{PO}_4)_3$ $R\bar{3}c$	8.42631(12)	8.42631(12)	21.4772(6)	120	220.105(8)	0.96(4)	0	0.96(4)	1.91(2)

Generally,  $\text{Na}^+$  insertion in the NASICON structure increases the  $a$  parameter and decreases the  $c$  parameter (in hexagonal axes). When the Na(1) site is depopulated, the  $c$  parameter

increases mainly due to an increasing repulsion between parallel  $O_3$  triangular faces of the  $MO_6$  octahedra through the Na(1) site, as less screened by the  $Na^+$  ions.<sup>15,52,55–57</sup>



**Figure 7.** Illustration of the lantern units with adjacent Na ions of the compositions  $Na_xV_2(PO_4)_3$  ( $x = 1, 2, 3,$  and  $4$ ). Black squares represent Na vacancies. The distances shown in  $Na_4V_2(PO_4)_3$  and  $Na_1V_2(PO_4)_3$  indicate V–V distances either through the Na(1) site or within the lantern unit.

In the case of  $Na_xV_2(PO_4)_3$ , the distances between adjacent  $VO_6$  octahedra through the Na(1) site along  $[001]_{\text{hexagonal}}$  remain nearly constant,  $6.269(4) \text{ \AA}$  in  $Na_4V_2(PO_4)_3$  and  $6.228(4) \text{ \AA}$  in  $Na_1V_2(PO_4)_3$ , (**Figure 7**), as the Na(1) site stays fully occupied ( $0.96(4) \rightarrow 0.97(4)$ ) when  $x$  varies from 4 to 1 in  $Na_xV_2(PO_4)_3$ . As a consequence, the  $c$  parameter undergoes no significant variation. The main reason for the slight increase in the  $c$  parameter may be the stronger repulsion of neighboring between  $VO_6$  octahedra within the lantern unit when vanadium is oxidized from  $V^{2.5+}$  to  $V^{4+}$ . Therefore, the V–V distances within the lantern unit themselves increase from  $4.412(4)$  to  $4.511(4) \text{ \AA}$  (**Figure 7**). Similar evolutions of the  $a$  and  $c$  cell parameters were found in other NASICON positive electrode materials but with a more pronounced increase of the  $c$  parameter:  $\Delta a/a = -6.1 \%$  and  $\Delta c/c = 2.4 \%$  in  $Na_xMnV(PO_4)_3$ ,<sup>15</sup> and  $\Delta a/a = -4.9 \%$  and  $\Delta c/c = 2.2 \%$  in  $Na_xMnCr(PO_4)_3$ ,<sup>52</sup> when  $x$  varies from 4 to 1. Unlike the

case of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , a much depopulated Na(1) site is observed in  $\text{Na}_x\text{MnV}(\text{PO}_4)_3$  (from 1 to 0.49(1) when  $x$  varies from 4 to 1) inducing stronger repulsions between the  $(\text{Mn},\text{V})\text{O}_6$  octahedra through the Na(1) site, and thus a remarkable increase of the  $c$  parameter.<sup>15,55</sup>

Overall, the value of  $V/Z$  gradually decreases with a decreasing number of  $\text{Na}^+$  ions in the structure (driving a progressive oxidation of vanadium), from 246.585(7), 239.682(10), 231.02(2), and to 220.105(8)  $\text{\AA}^3$  when  $x$  varies from 4 to 1 in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ . The lattice mismatch in the phase transition between  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  ( $\Delta V/V = 8.2\%$ ) is noticeably reduced when  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  is invoked ( $\Delta V/V = 3.6$ , and  $4.7\%$ , for  $\text{Na}_3\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Na}_2\text{V}_2(\text{PO}_4)_3$ , and  $\text{Na}_2\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Na}_1\text{V}_2(\text{PO}_4)_3$ , respectively). The reduced lattice mismatch enables a rapid phase transition between  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{Na}_1\text{V}_2(\text{PO}_4)_3$  via  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  by lowering their nucleation energies.<sup>30</sup>

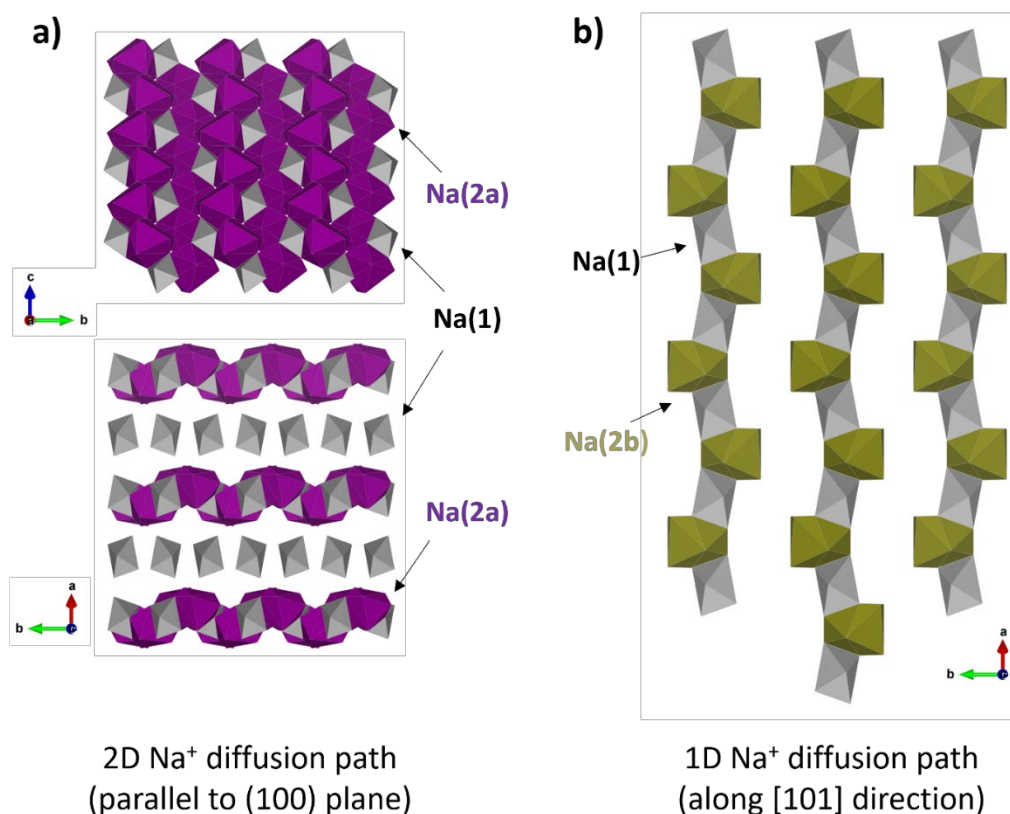
The average V-O bond distances consequently show a gradual decrease from 2.076(14), to 2.02(4), to 1.99(9), and to 1.91(2)  $\text{\AA}$  when  $x$  in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  changes from 4 to 1. The details of (not average but individual) V-O bond distances in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  are shown in **Table S2**. Also, the volumes of the  $\text{VO}_6$  octahedra decrease in parallel from 11.69, to 10.73, to 10.16, and to 9.15  $\text{\AA}^3$ , respectively ( $\Delta V_{\text{oct}}/V_{\text{oct}} = 21.7\%$ ). As a comparison, the volume of the  $(\text{Mn},\text{V})\text{O}_6$  octahedra decreases about 23.8% when  $x$  varies from 4 to 1 in  $\text{Na}_x\text{MnV}(\text{PO}_4)_3$ .<sup>15</sup> Furthermore, as  $x$  in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  decreases from 4 to 1, the average oxidation states of vanadium obtained by BVS calculation are 2.44(4), 2.92(11), 3.3(3) and 3.87(8), respectively, showing a good agreement with the average vanadium oxidation states expected for each composition (i.e., 2.5, 3, 3.5, and 4, respectively).

When it comes to the number of  $\text{Na}^+$  in the Na(1) and Na(2) sites per formula unit (**Table 3**), our findings establish that the Na(1) site is almost fully occupied in all compositions except for  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  as the occupancy factor of Na(1) site is 0.679(14). For the Na(2) site, when the  $\text{Na}^+$  content changes from  $x=4$  to 1 in  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ , the occupancy factor gradually decreases from almost 100% down to  $\sim 0\%$ . This evidence appears in good agreement with the computational analysis on Na(1) and Na(2) sites at room temperature.<sup>49</sup> Other NASICON-type



materials also show similar trends, i.e. the Na(1) site tends to keep its high occupancies while the Na(2) site is populated or depopulated depending on the compositions.<sup>8,9,14-16</sup> Overall, the refined total number of Na<sup>+</sup> per formula unit shows very good agreement with the expected compositions.

The detailed evolution on the Na<sup>+</sup> distributions around the lantern units of the four compositions (Na<sub>x</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, with x=1, 2, 3, and 4) is illustrated in **Figure 7**. The Na(2) site in Na<sub>4</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (*R* $\bar{3}$ *c*) splits into the two Na(2) positions, Na(2a) and Na(2b), in Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (*C*2/*c*). Then, from Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> to Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (*P*2<sub>1</sub>/*c*), the Na(1) site splits into the Na(1a) and Na(1b) positions that are almost fully occupied in Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The Na(2a) position also further splits into Na(2a<sub>1</sub>) and Na(2a<sub>2</sub>) in Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, but the Na(2a<sub>2</sub>) is found to be empty. Finally, from Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> to Na<sub>1</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, the structure is back to rhombohedral unit cell (*R* $\bar{3}$ *c*), having the Na(2) site fully emptied. It is interesting that from Na<sub>4</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> to Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, the Na(2b) position tends to be more occupied than the Na(2a) positions. This may be related to different connectivities of Na(2a) and Na(2b) with the Na(1) site. **Figure 8** shows the polyhedra constructed from Na and O atoms in Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> or Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The connectivity between Na(2a) and Na(1) forms distinct 2D Na<sup>+</sup> diffusion paths parallel to the (100) plane, while the connectivity between Na(2b) and Na(1) results in 1D Na<sup>+</sup> diffusion chains along the [101] direction. Although a computational assessment of the migration barriers of Na-ions in the Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> or Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> phases can support our structural analysis, we hypothesize that Na<sup>+</sup> ions in Na(2a) position may show easier migration than those in Na(2b) position, and therefore explaining the lower occupancy factor observed for Na(2a) than Na(2b).



**Figure 8.** Different connectivities of (a) Na(2a) with Na(1), and (b) Na(2b) with Na(1) in Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> or Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>. The polyhedra are constructed from Na and O atoms.

## Conclusions

In this study, we report for the first time the crystal chemistry of the new intermediate Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> composition as well as the electrochemical reaction mechanisms of Na<sub>x</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> ( $1 \leq x \leq 4$ ) including the intermediate phase. The appearance of the Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> phase occurs in a non-equilibrium battery operation and it is better observed with a higher current density (i.e., non-equilibrium state). The results of Rietveld refinement suggest that the crystal structure of Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> crystallizes in a primitive (monoclinic) cell with the possible space groups of  $P2_1/c$  (Model 1) or  $P2/c$  (Model 2) rather than rhombohedral ( $R\bar{3}c$ ) or monoclinic ( $C2/c$ ) cells of other Na<sub>x</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> ( $x = 1, 3, \text{ and } 4$ ) compositions. The main difference between the two structure models proposed for Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> is ascribed to different vanadium environments. As the symmetry is reduced in the Na<sub>2</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, the vanadium site splits into two Wyckoff positions. The structure with the space group  $P2_1/c$  (Model 1) contains a single

lantern unit with a random distribution of  $V^{3+}$  and  $V^{4+}$  types over two vanadium positions. The structure with the space group  $P2/c$  (Model 2) contains two different lantern units, each vanadium position forming its own lantern unit, with a possible charge ordering between  $V^{3+}$  and  $V^{4+}$ . For the sodium sites, the Na(1) site is almost fully occupied for both structure models. The Na(2) site splits into several positions, in which one of the splitting Na(2) position [Na(2a<sub>2</sub>)] is found to be a vacancy in the structure Model 1 whereas the four splitting Na(2) positions are all partially filled in the structure Model 2. The structure independently predicted by our DFT simulations at 0 K also shows a vanadium charge ordering as well as a full  $Na^+$ /vacancy ordering. A fully ordered  $Na^+$  at 0 K becomes partially ordered at room temperature. These different  $Na^+$  distributions suggest that the  $Na_2V_2(PO_4)_3$  phase can have possible phase transitions versus temperature due to  $Na^+$  order/disorder phenomena. Furthermore,  $Na^+$  ions in Na(2a) position may diffuse more easily than those in Na(2b) position due to different connectivities with Na(1) site. The intermediate  $Na_2V_2(PO_4)_3$  phase appears by reducing the lattice mismatch between  $Na_3V_2(PO_4)_3$  and  $Na_1V_2(PO_4)_3$  phases lowering their nucleation energy thus beneficial for a high-rate performance. This study opens the door to a better understanding of the behavior of  $Na_3V_2(PO_4)_3$  electrode upon cycling when the intermediate phase is involved. We believe our findings in this work will encourage researchers to further investigate the nature of the new  $Na_2V_2(PO_4)_3$  phase.

### **Supporting Information**

SEM images, TGA, synchrotron powder XRD patterns, *operando* XRD data, and detailed crystallographic information

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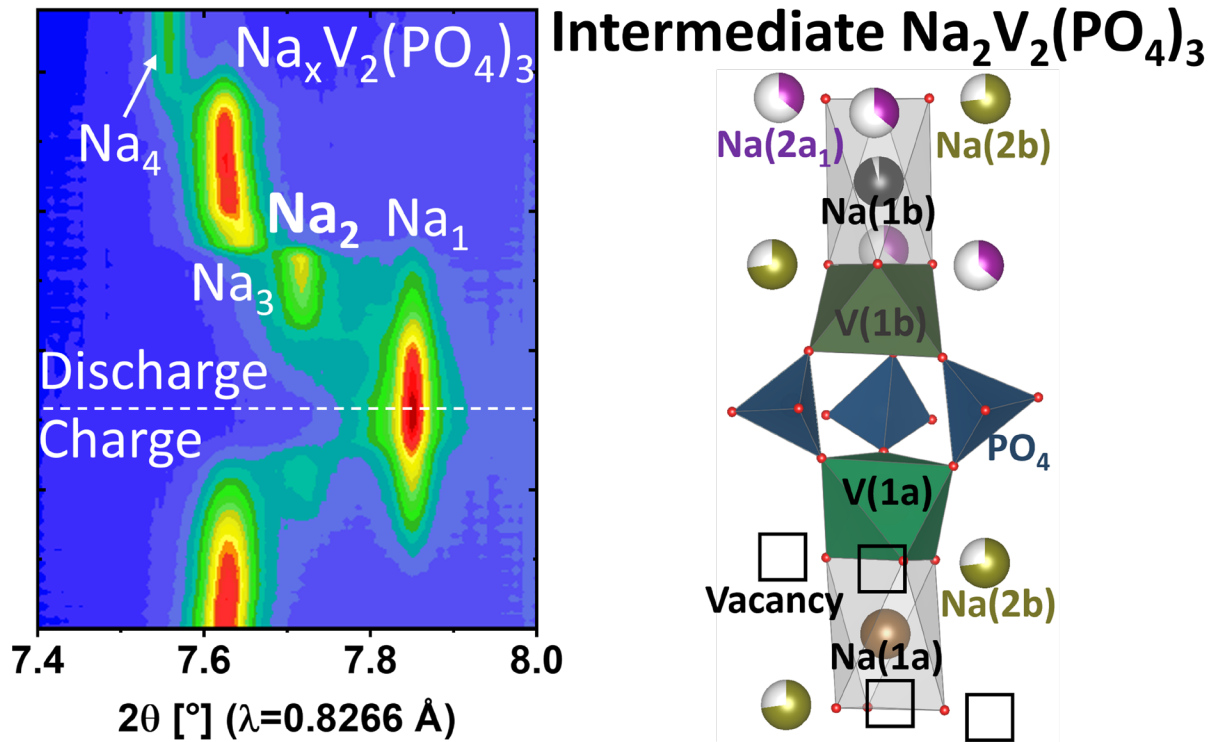


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TOC



**TOC:** Counter plot of *operando* SXRPD patterns in the 7.46-8.03° angular range of  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$  during charge ( $x=3$  to  $x=1$ ) and during discharge ( $x=1$  to  $x=4$ ). During Discharge, the intermediate  $\text{Na}_2\text{V}_2(\text{PO}_4)_3$  can be isolated and its corresponding crystal structure was solved. Vacancies are found to be ordered on the Na(2) sites while Na(1) are almost fully occupied.