

# Supporting Information

## Stability in water and electrochemical properties of the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3 - \text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$ solid solution

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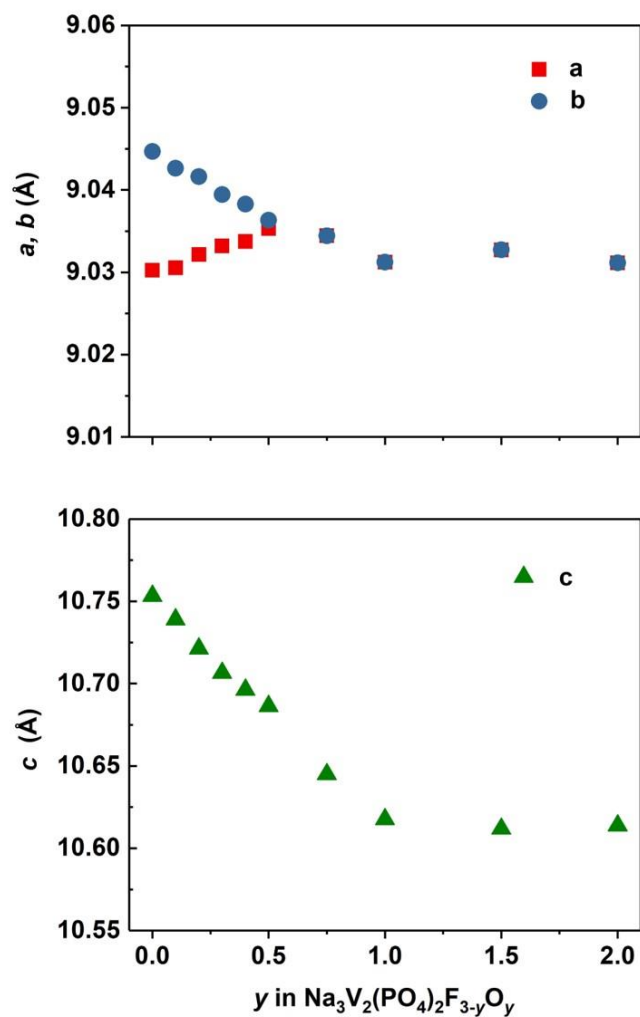
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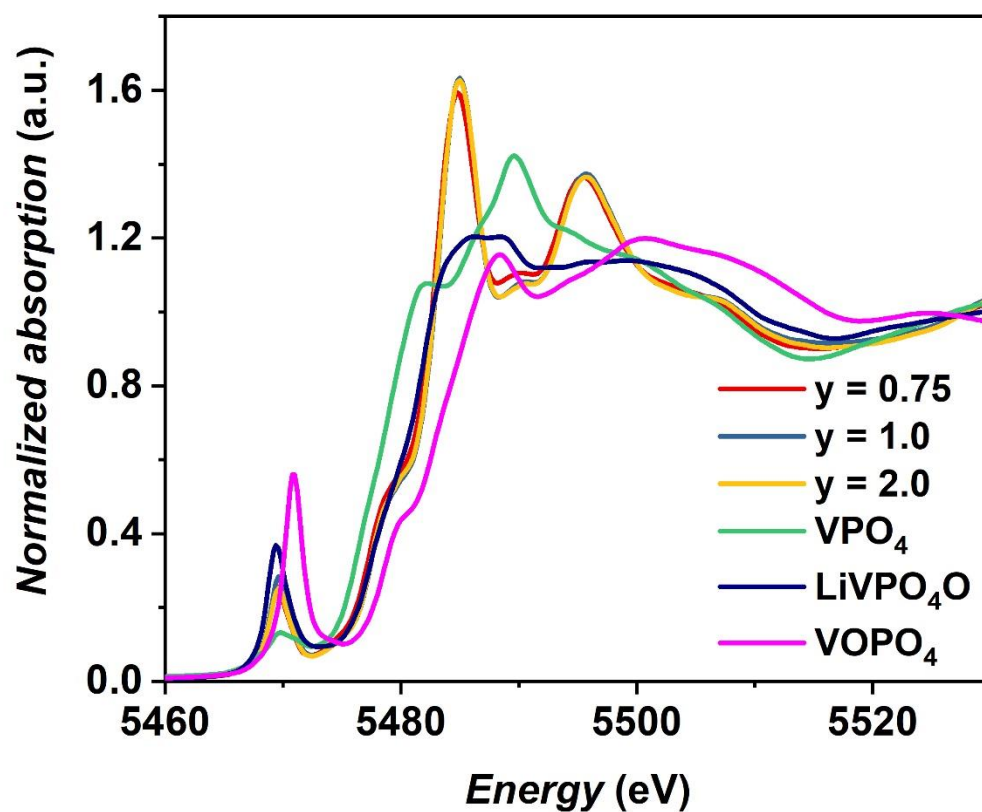
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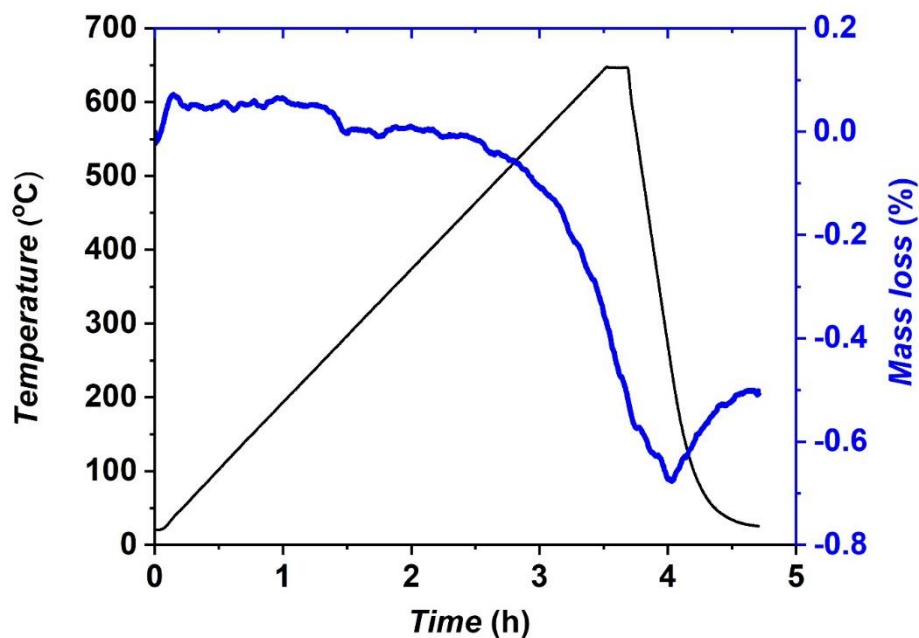
**Figure S1:** The evolution of the unit cell parameters of the materials synthesized by using Equation (1) in the range of  $0 \leq y \leq 2.0$ . A linear evolution of the cell parameters was observed for  $0 \leq y \leq 1.0$ . When  $y > 1.0$ , there was no further change in the cell parameters.



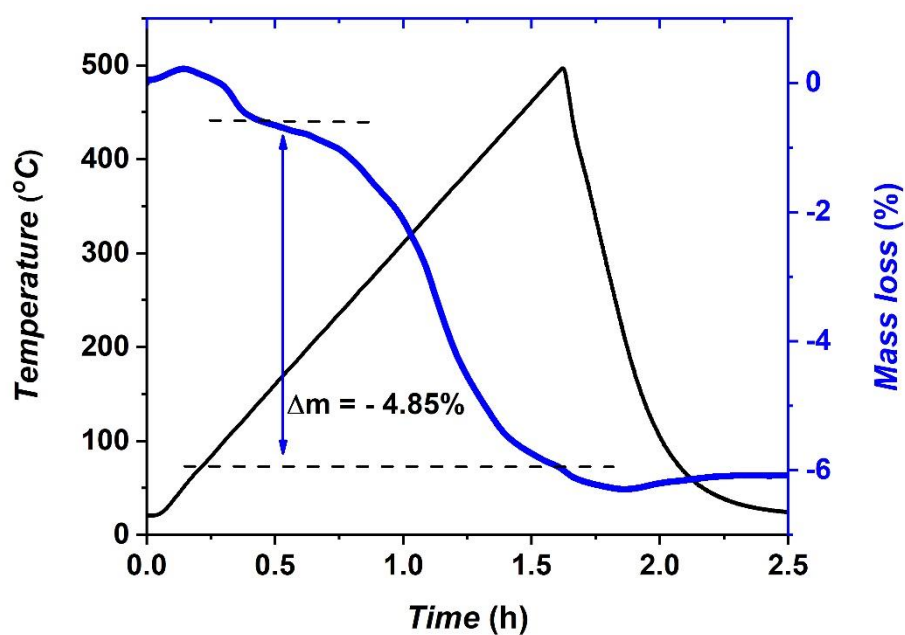
**Figure S2:** XANES at Vanadium *K* edge of the materials synthesized according to Equation (1) with  $y = 0.75$ ,  $y = 1.0$  and  $y = 2.0$ . The XANES spectra of  $V^{3+}PO_4$ ,  $LiV^{4+}PO_4O$ , and  $V^{5+}PO_4O$  are used as external references to determine the oxidation state of Vanadium in the concerning materials. No difference is observed between the spectra recorded for  $y = 1.0$  and  $y = 2.0$ . The position of the absorption edge reveals that both materials contain only  $V^{4+}$ .



**Figure S3a:** The thermal gravimetric analysis (TGA) curve of a mixture of (2 VPO<sub>4</sub> + 3 NaF) recorded from ambient temperature to 650°C with a heating rate of 5°C.min<sup>-1</sup>. The minor mass loss (~ -0.5 wt.%) recorded in this temperature range is due to the release of F (m/z = 19).



**Figure S3b:** The thermal gravimetric analysis (TGA) curve of a mixture of (VPO<sub>4</sub> + VOPO<sub>4</sub> + 2 NaF + ½ Na<sub>2</sub>CO<sub>3</sub>) recorded from ambient temperature to 500°C with a heating rate of 5°C.min<sup>-1</sup>. The mass loss (~ -4.85 wt.%) recorded in this temperature range is due to the release of CO<sub>2</sub>.

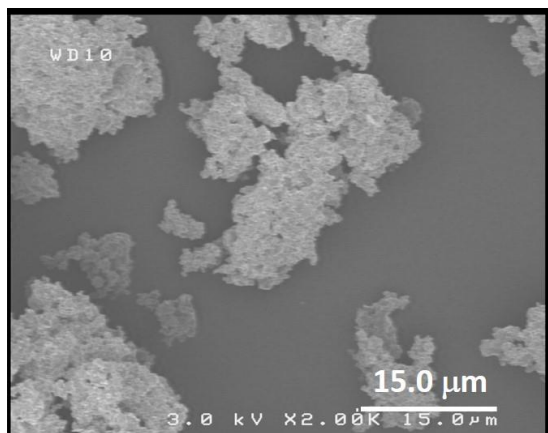


**Table S1:** Comparison of the cell parameters obtained from Cu  $K_\alpha$  diffractometer for  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$ , before and after washing in water.

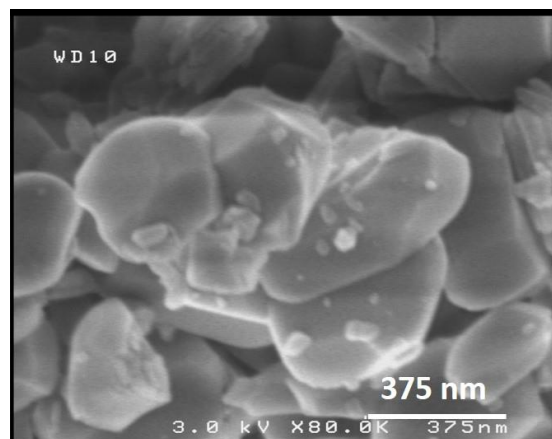
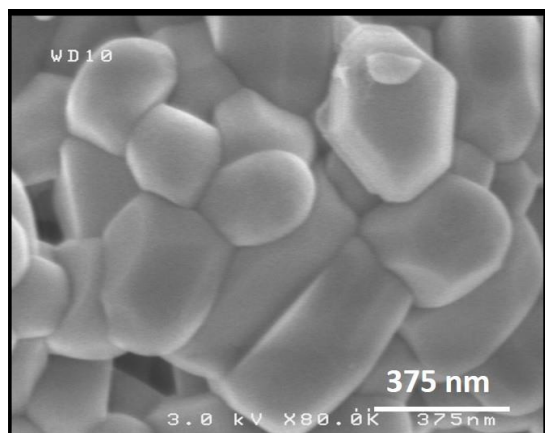
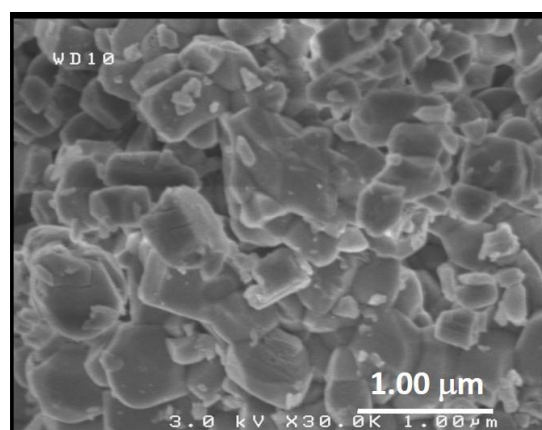
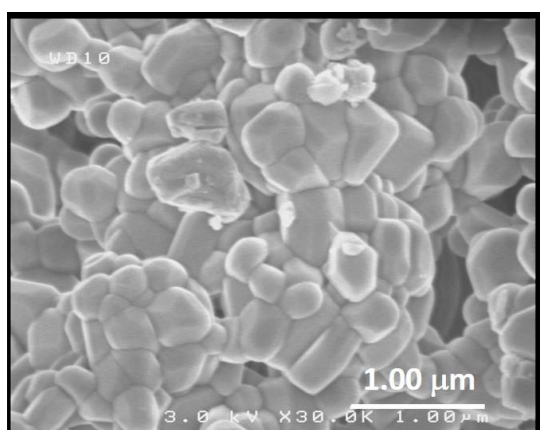
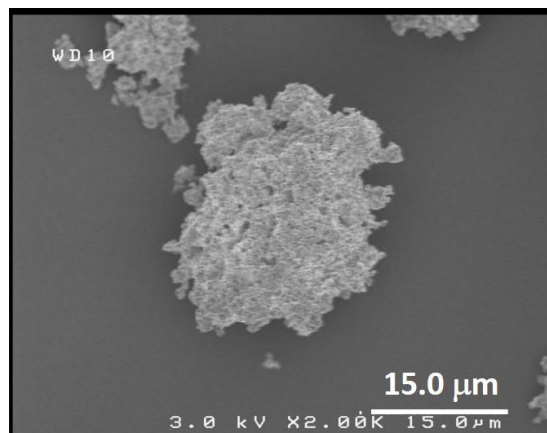
	<b>S.G.</b>	<b>a (Å)</b>	<b>b (Å)</b>	<b>c (Å)</b>	<b>V/Z (Å<sup>3</sup>)</b>
<b>Before washing</b>	<i>P4<sub>2</sub>/mnm</i>	9.0317(2)	9.0317(2)	10.622(5)	216.63(2)
<b>After washing</b>	<i>P4<sub>2</sub>/mnm</i>	9.0324(1)	9.0324(1)	10.6173(2)	216.55(1)

**Figure S4:** SEM images of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$  powder before and after washing

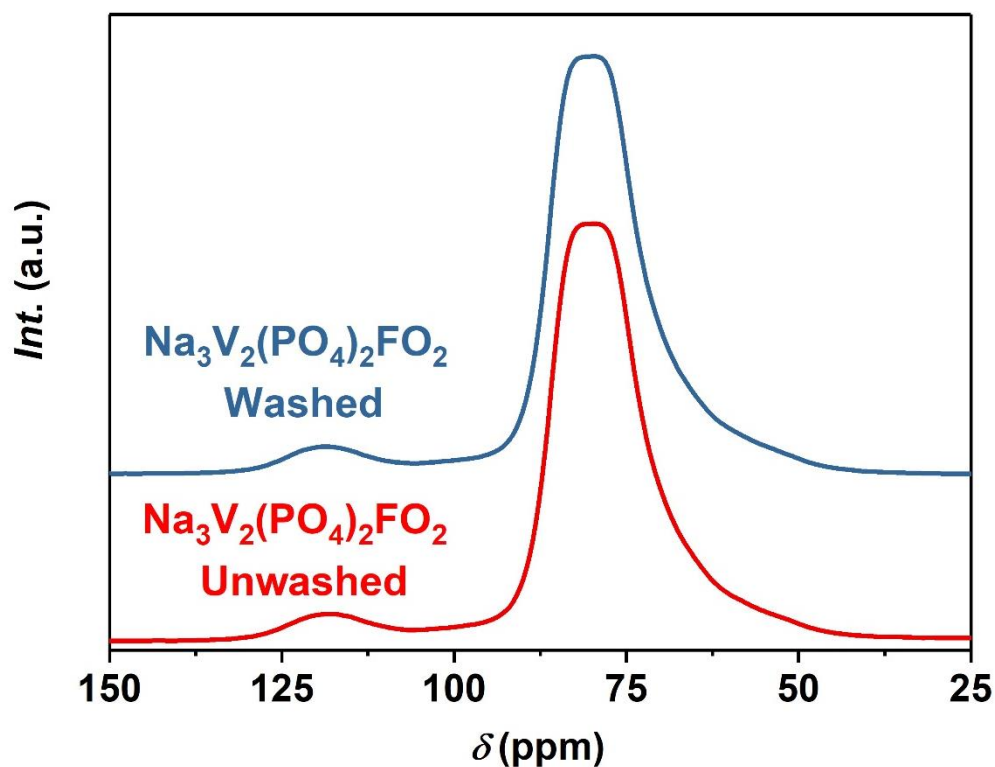
**Before washing**



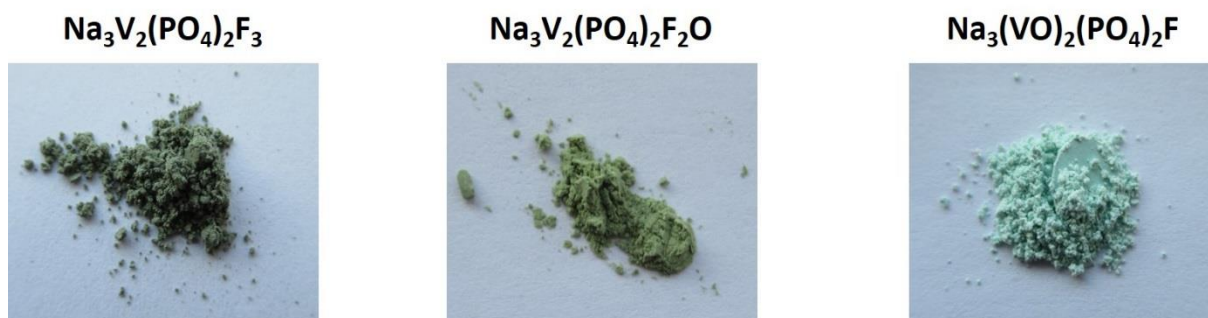
**After washing**



**Figure S5a:**  $^{23}\text{Na}$  ss-NMR spectra collected for  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$  before and after washing. The spectra were recorded at 500 MHz (MAS = 30 kHz).

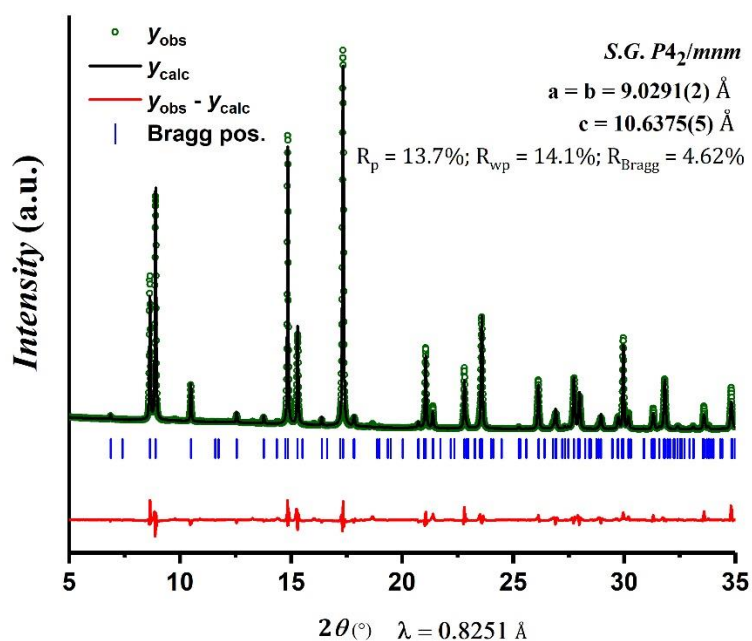
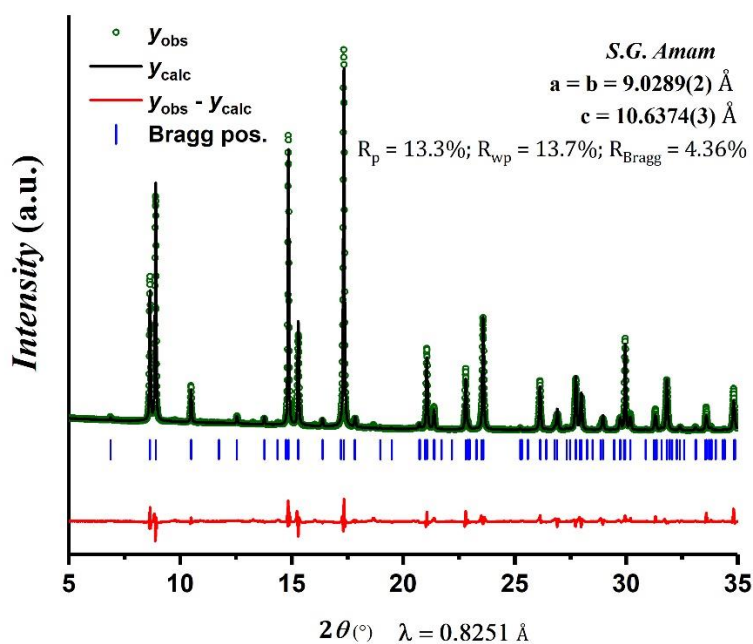


**Figure S5b:** The colors of three samples:  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ,  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_2\text{O}$ , and  $\text{Na}_3(\text{VO})_2(\text{PO}_4)_2\text{F}$  obtained after washing.



**Figure S6 and Table S2 - Comparison of the structural description of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{1.5}\text{O}_{1.5}$  in the  $Amam$  and  $P4_2/mnm$  space groups**

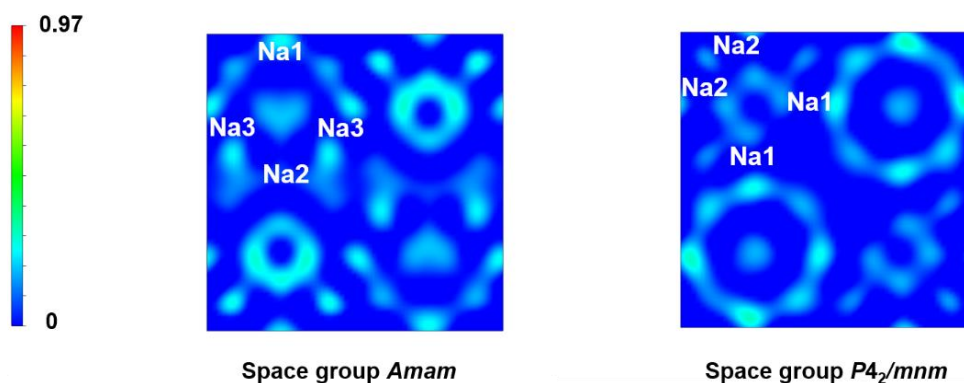
The comparison of the **Rietveld refinements** of synchrotron powder X-ray diffraction data of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{1.5}\text{O}_{1.5}$  recorded at  $\lambda = 0.8251 \text{ \AA}$ , considering the description of the structure in the  $Amam$  (top) and  $P4_2/mnm$  (bottom) space groups shows a rather good minimization of the difference ( $I_{\text{obs.}} - I_{\text{calc.}}$ ) for the two hypotheses. The reliability factors are in fact very similar.





The corresponding **Fourier difference maps** and the associated sodium distributions are compared hereafter showing very similar residual charge densities observed for the two structural models.

Residual charge density



It appears that the residues observed in the Fourier difference maps are small around the Na<sup>+</sup> ions and around the anions. In *Amam*, small residues (concentrated rings) are observed around the fluorine anions, whereas in *P4<sub>2</sub>/mnm*, they (rings of larger diameters) are observed at the oxygen anions corresponding to the square plane around the transition metal ions.

The three tables given hereafter compare the **structural parameters** obtained from these Rietveld refinements. In the *Amam* model, heterogeneous thermal displacement parameters (Biso) are obtained for the three different Na crystallographic sites (from 0.54 to 4.5), the same observation can be done for the oxygen atoms O(1) and O(2) from the square plane of the VO<sub>4</sub>(O,F)<sub>2</sub> octahedra.. In the *P4<sub>2</sub>/mnm* model, the heterogeneities just mentioned are not observed, but heterogeneous thermal displacement parameters (Biso) are obtained for the two different P crystallographic sites (from 0.6 to 1.2). The comparison of the interatomic distances in Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>1.5</sub>O<sub>1.5</sub> obtained from Rietveld refinement considering the two structural descriptions in the *Amam* and *P4<sub>2</sub>/mnm* space groups reveals that the vanadium octahedral environments calculated in both cases are very similar. The main differences are observed for the PO<sub>4</sub><sup>3-</sup> anionic groups, with a single one in *Amam* (2 x 1.56 Å + 2 x 1.50 Å) and two in *P4<sub>2</sub>/mnm* (a symmetric one 4 x 1.49 Å, and another one 2 x 1.54 Å + 2 x 1.60 Å).

**These results do not allow to choose between the two models as no obvious added value is obtained by choosing one versus the other, except considering that in *Amam* the XRD pattern is calculated with a smaller number of diffraction lines. Indeed, in *P4<sub>2</sub>/mnm*, a lot of diffraction lines are calculated and show null intensities. Furthermore, in *Amam*, the Na<sup>+</sup>-Na<sup>+</sup> distances are longer, allowing a minimization of the electrostatic repulsions within the diffusion channels.**

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**Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>1.5</sub>O<sub>1.5</sub>**

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*S.G. Amam**Z = 4**a = 9.0289(2) Å**b = 9.0288(2) Å**c = 10.6374(3) Å**V = 867.186 Å<sup>3</sup>**R<sub>Bragg</sub> = 4.36%**R<sub>p</sub> = 13.3%**R<sub>wp</sub> = 13.7%*

<b>Atoms</b>	<b>Wyckoff positions</b>	<b>x</b>	<b>y</b>	<b>z</b>	<b>Occupancy</b>	<b>B<sub>iso</sub></b>
<b>V (1)</b>	8g	¾	0.249(2)	0.1962(3)	1	1.16(4)
<b>P (1)</b>	8e	½	0	0.255(2)	1	0.83(6)
<b>O (1)</b>	16h	0.589(3)	0.096(2)	0.159(2)	1	0.3(1)
<b>O (2)</b>	16h	0.596(3)	0.399(3)	0.169(2)	1	1.0(1)
<b>F (1)</b>	4c	¾	0.242(4)	0	1	0.6(1)
<b>F(2)/O(3)</b>	8g	¾	0.252(4)	0.357(1)	¼ ¾	0.4(1)
<b>Na (1)</b>	4c	¼	0.492(6)	0	0.756(2)	1.3(3)
<b>Na (2)</b>	8f	0.027(3)	0.210(2)	0	0.846(5)	4.5(2)
<b>Na (3)</b>	4c	¼	0.02(3)	0	0.480(2)	0.54(2)

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**Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>1.5</sub>O<sub>1.5</sub>**

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*S.G. P4<sub>2</sub>/mnm**Z = 4**a = b = 9.0291(2) Å**c = 10.6375(5) Å**V = 867.212(2) Å<sup>3</sup>**R<sub>Bragg</sub> = 4.62%**R<sub>p</sub> = 13.7%**R<sub>wp</sub> = 14.1%*

<b>Atoms</b>	<b>Wyckoff positions</b>	<b>x</b>	<b>y</b>	<b>z</b>	<b>Occupancy</b>	<b>B<sub>iso</sub></b>
<b>V (1)</b>	8j	0.249(1)	0.249(1)	0.1952(3)	1	1.07(3)
<b>P (1)</b>	4d	½	0	¼	1	0.6(3)
<b>P (2)</b>	4e	0	0	0.257(1)	1	1.2(4)
<b>O (1)</b>	16k	0.406(3)	0.095(3)	0.167(2)	1	0.4(1)
<b>O (2)</b>	8j	0.094(3)	0.094(3)	0.158(3)	1	0.4(1)
<b>O (3)</b>	8j	0.402(3)	0.402(3)	0.159(3)	1	0.3(1)
<b>F (1)</b>	4f	0.247(3)	0.247(3)	0	1	1.1(1)
<b>F(2)/O(4)</b>	8j	0.251(2)	0.251(2)	0.3583(9)	¼ ¾	1.1(1)
<b>Na (1)</b>	8i	0.780(5)	0.026(3)	0	1	3.5(3)
<b>Na (2)</b>	8i	0.514(5)	0.229(3)	0	½	4.9(1)

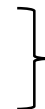
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<i>Amam</i>		<i>P4<sub>2</sub>/mnm</i>	
Interatomic distances (Å)		Interatomic distances (Å)	
P(1)—O(1)	1.557(9) x 2	P(1)—O(1)	1.495(6) x 4
P(1)—O(2)	1.50(1) x 2	P(2)—O(2)	1.599(9) x 2
		P(2)—O(3)	1.536(9) x 2
V(1)—O(1)	2.048(9) x 2	V(1)—O(1)	2.007(7) x 2
V(1)—O(2)	1.96(1) x 2	V(1)—O(2)	2.004(8)
		V(1)—O(3)	1.994(7)
V(1)—F(1)	2.089(1)	V(1)—F(1)	2.0830(9)
V(1)—F(2)/O(3)	1.706(5)	V(1)—F(2)/O(4)	1.729(4)
Na(1)-Na(1)	4.518(1)	Na(1)-Na(1)	3.282(1)
Na(1)-Na(2)	3.234(1)	Na(1)-Na(2)	3.015 (1)
Na(2)-Na(3)	2.646(1)	Na(2)-Na(2)	2.482 (1)

Describe all PO<sub>4</sub>



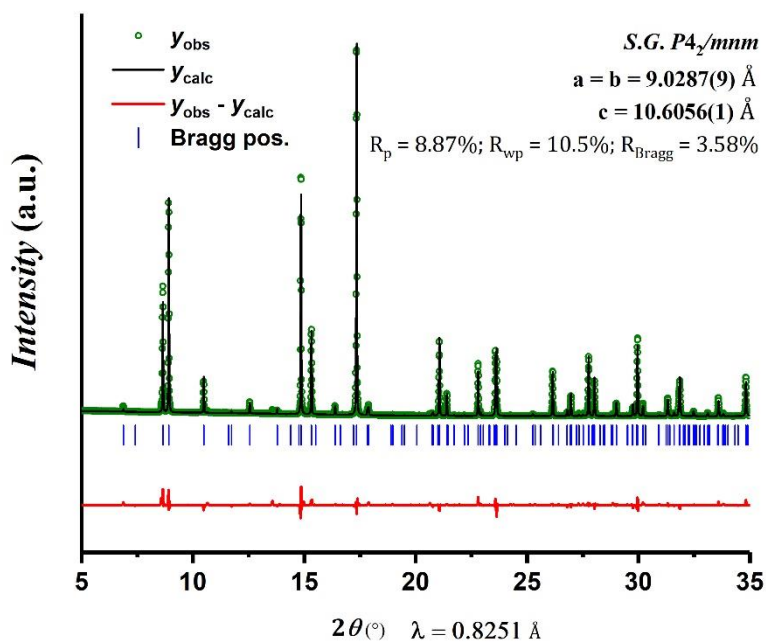
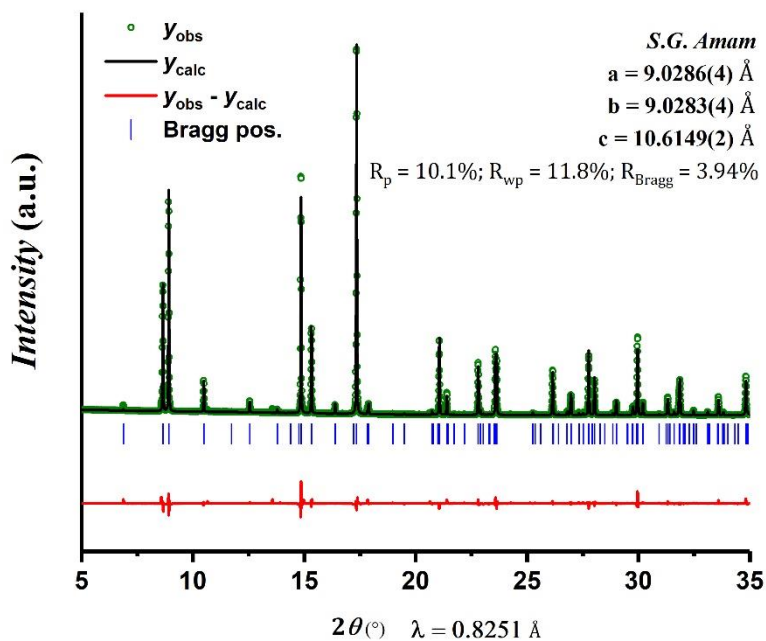
Describe 1 PO<sub>4</sub>



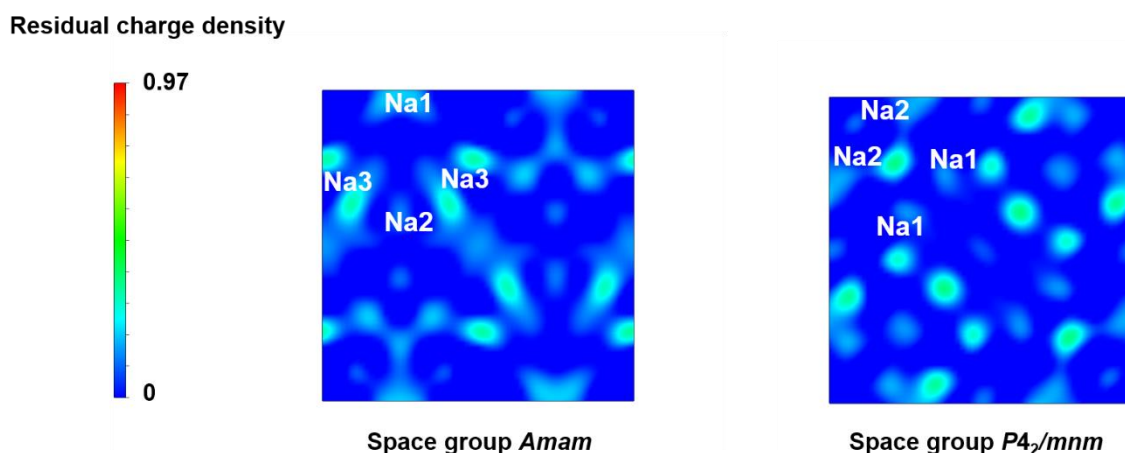
Describe 1 PO<sub>4</sub>

**Figure S7 and Table S3 - Comparison of the structural description of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$  in the  $Amam$  and  $P4_2/mnm$  space groups**

As detailed hereafter, as for  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{1.5}\text{O}_{1.5}$ , it is difficult to discriminate between the two structural models. A rather good minimization of the difference ( $I_{\text{obs.}} - I_{\text{calc.}}$ ) is obtained for the two hypotheses and the reliability factors are in fact very similar.



The corresponding **Fourier difference maps** and the associated sodium distributions are compared hereafter showing very similar residual charge densities observed for the two structural models.



It appears that the residues observed in the Fourier difference maps are slightly higher (despite small) in *P4<sub>2</sub>/mnm*, with residues localized at the Na<sup>+</sup> sites and at the oxygen sites corresponding to the square plane around the transition metal ions. A better minimization seems to be obtained for the *Amam* model.

The three tables given hereafter compare the **structural parameters** obtained from these Rietveld refinements. In the *Amam* model, heterogeneous thermal displacement parameters (Biso) are obtained for the three different Na crystallographic sites (from 0.7 to 3.1). Furthermore, the Biso associated to O(3) (i.e. to the vanadyl-type bond V=O) is surprisingly higher than that of F(1) (i.e. to the opposite V-F bond). In the *P4<sub>2</sub>/mnm* model: (i) heterogeneous thermal displacement parameters (Biso) are obtained for the two different P crystallographic sites (from 0.7 to 1.3), (ii) a huge heterogeneity of the Biso associated to the oxygen atoms (O(1), O(2) and O(3)) from the square planes of the VO<sub>4</sub>FO octahedra is observed, and (iii) the Biso associated to O(4) (i.e. to the vanadyl-type bond V=O) is surprisingly higher than that of F(1) (i.e. to the opposite V-F bond).

The comparison of the interatomic distances in Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>FO<sub>2</sub> obtained from Rietveld refinement considering the two structural descriptions in the *Amam* and *P4<sub>2</sub>/mnm* space groups reveals that the vanadium octahedral environments calculated in both cases are very similar, with a short V=O vanadyl-type bond of 1.62 Å and a long V-F bond of 2.11 Å. The PO<sub>4</sub><sup>3-</sup> anionic groups are also very similar, with a single one in *Amam* (2 x 1.50 Å + 2 x 1.56 Å) and two in *P4<sub>2</sub>/mnm* (a symmetric one 4 x 1.54 Å, and another one 2 x 1.54 Å + 2 x 1.50 Å). The main difference is observed for the Na<sup>+</sup>-Na<sup>+</sup> distances.

**These results suggest that the *Amam* description is the most appropriate, indeed: (i) a slightly better minimization of the Fourier difference map is obtained; (ii) the XRD pattern is calculated with a smaller number of diffraction lines. Indeed, in *P4<sub>2</sub>/mnm*, a lot of diffraction lines are calculated and show null intensities; and (iii) the Na<sup>+</sup>-Na<sup>+</sup> distances are longer, allowing a minimization of the electrostatic repulsions within the diffusion channels.**

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**Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>FO<sub>2</sub>**

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<i>S.G. Amam</i>	$a = 9.0286(4) \text{ \AA}$	$R_{\text{Bragg}} = 3.94\%$
$Z = 4$	$b = 9.0283(4) \text{ \AA}$	$R_{\text{p}} = 10.1\%$
	$c = 10.6149(2) \text{ \AA}$	$R_{\text{wp}} = 11.8\%$
	$V = 865.25(2) \text{ \AA}^3$	

Atoms	Wyckoff positions	$x$	$y$	$z$	Occupancy	$B_{\text{iso}}$
V (1)	8g	$\frac{3}{4}$	0.247(2)	0.1984(3)	1	0.86(4)
P (1)	8e	$\frac{1}{2}$	0	0.253(2)	1	0.91(4)
O (1)	16h	0.587(3)	0.098(2)	0.156(2)	1	0.4(1)
O (2)	16h	0.594(3)	0.398(3)	0.169(2)	1	0.5(1)
F (1)	4c	$\frac{3}{4}$	0.245(4)	0	1	0.4(1)
O(3)	8g	$\frac{3}{4}$	0.250(4)	0.352(1)	1	1.0(1)
Na (1)	4c	$\frac{1}{4}$	0.491(6)	0	0.808(2)	0.7(3)
Na (2)	8f	0.017(3)	0.208(2)	0	0.846(5)	3.1(2)
Na (3)	4c	$\frac{1}{4}$	0.03(3)	0	0.424(2)	1.4(3)

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**Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>FO<sub>2</sub>**

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<i>S.G. P4<sub>2</sub>/mnm</i>	$a = b = 9.0287(9) \text{ \AA}$	$R_{\text{Bragg}} = 3.58\%$
$Z = 4$	$c = 10.6056(1) \text{ \AA}$	$R_{\text{p}} = 8.87\%$
	$V = 864.53(2) \text{ \AA}^3$	$R_{\text{wp}} = 10.5\%$

Atoms	Wyckoff positions	$x$	$y$	$z$	Occupancy	$B_{\text{iso}}$
V (1)	8j	0.751(1)	0.249(1)	0.1952(3)	1	1.09(2)
P (1)	4d	$\frac{1}{2}$	0	$\frac{1}{4}$	1	0.7(2)
P (2)	4e	0	0	0.257(1)	1	1.3(2)
O (1)	16k	0.594(3)	0.095(3)	0.159(2)	1	1.1(2)
O (2)	8j	0.904(3)	0.096(3)	0.169(3)	1	0.3(2)
O (3)	8j	0.598(3)	0.402(3)	0.164(3)	1	1.0(2)
F (1)	4f	0.247(3)	0.247(3)	0	1	0.79(8)
O(4)	8j	0.751(2)	0.249(2)	0.3518(9)	1	1.20(7)
Na (1)	8i	0.780(5)	0.026(3)	0	1	3.5(3)
Na (2)	8i	0.514(5)	0.229(3)	0	$\frac{1}{2}$	4.9(1)

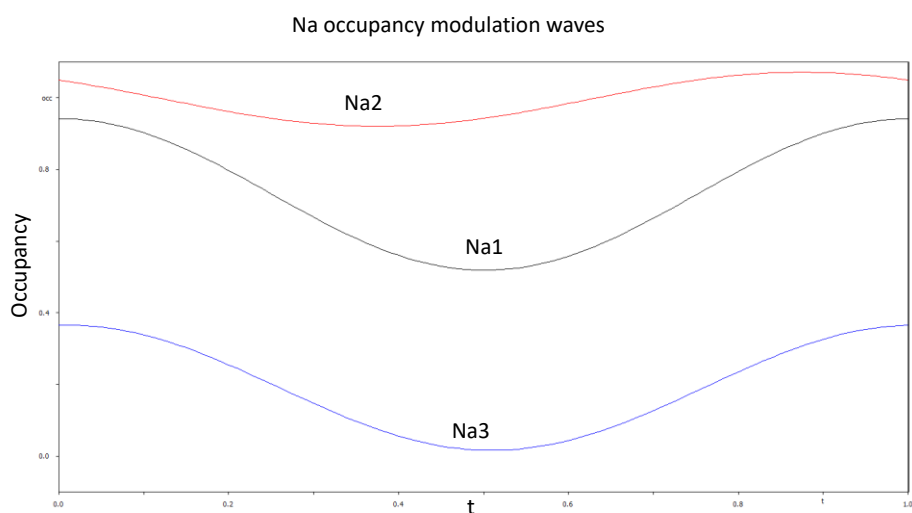
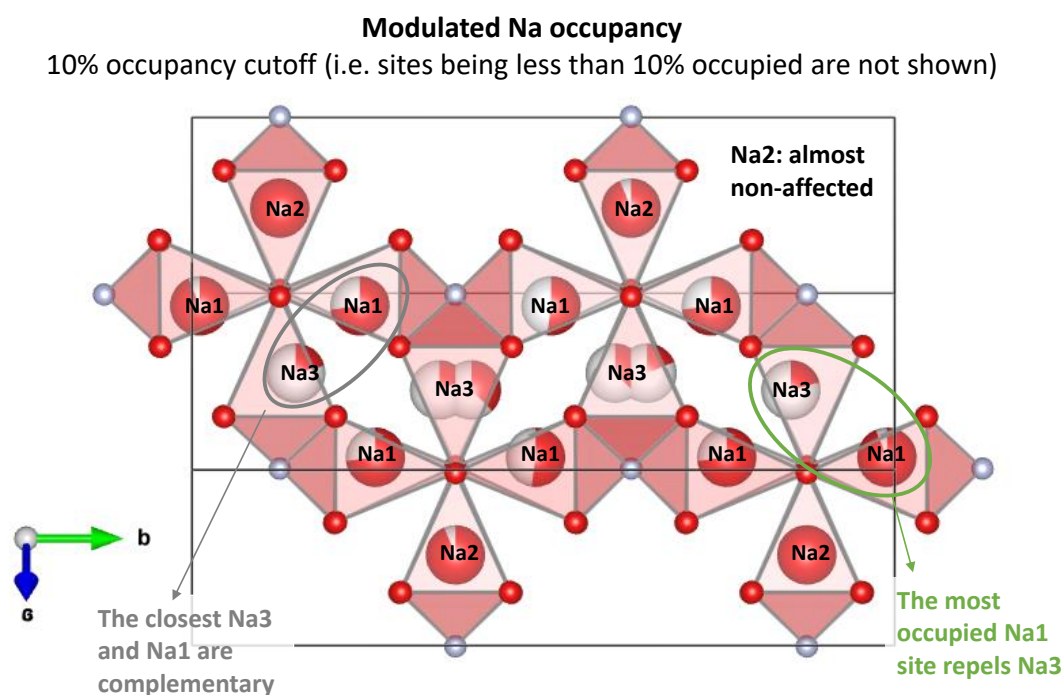
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	<i>Amam</i>	<i>P4<sub>2</sub>/mnm</i>		
	Interatomic distances (Å)	Interatomic distances (Å)		
Describe 1 PO <sub>4</sub>	P(1)–O(1)	1.564(3) x 2	Describe 1 PO <sub>4</sub>	
	P(1)–O(2)	1.499(1) x 2		
		P(1)–O(1)	1.545(3) x 4	
		P(2)–O(2)	1.537(3) x 2	
		P(2)–O(3)	1.503(3) x 2	
	V(1)–O(1)	2.045(1) x 2	V(1)–O(1)	2.027(2) x 2
	V(1)–O(2)	1.988(1) x 2	V(1)–O(2)	1.974(2)
			V(1)–O(3)	2.000(2)
	V(1)–F(1)	2.1064(9)	V(1)–F(1)	2.1101(8)
	V(1)–O(3)	1.6255(9)	V(1)–O(4)	1.6208(8)
	Na(1)-Na(1)	4.517(1)	Na(1)-Na(1)	3.172(1)
	Na(1)-Na(2)	3.306(1)	Na(1)-Na(2)	3.206(1)
	Na(2)-Na(3)	2.670(1)	Na(2)-Na(2)	2.374(1)

Nevertheless, it is important to mention that additional tiny diffraction lines observed in the diffraction pattern of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>FO<sub>2</sub> cannot be taken into account without considering the doubling of all the unit cell parameters (see Figure S8 in the following).

**Figure S8 and Table S4 - Description of the modulated structure proposed for  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$**

The modulated structure proposed for  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$  is shown hereafter and described in a monoclinic unit cell with the space group  $P2_1/m$  and a vector of modulation  $q = \frac{1}{2} b^* + \frac{1}{2} c^*$ : (i) the distribution of the  $\text{Na}^+$  ions within the diffusion channels and (ii) the modulation waves associated to each  $\text{Na}^+$  site. Note that the thermal displacement parameters (Biso) associated to the different atoms Na, V, P and O/F are homogeneous from one site to another for a given atom, and in good agreement with the values expected: 1, 0.11, 0.08 and 0.10 respectively. The single  $\text{PO}_4^{3-}$  anionic group is such that the P-O bonds vary between 1.48 and 1.59 Å, whereas two vanadium sites are observed, one with a short V=O vanadyl type bond at 1.53 Å and the other one with a longer V=O vanadyl type bond at 1.71 Å.





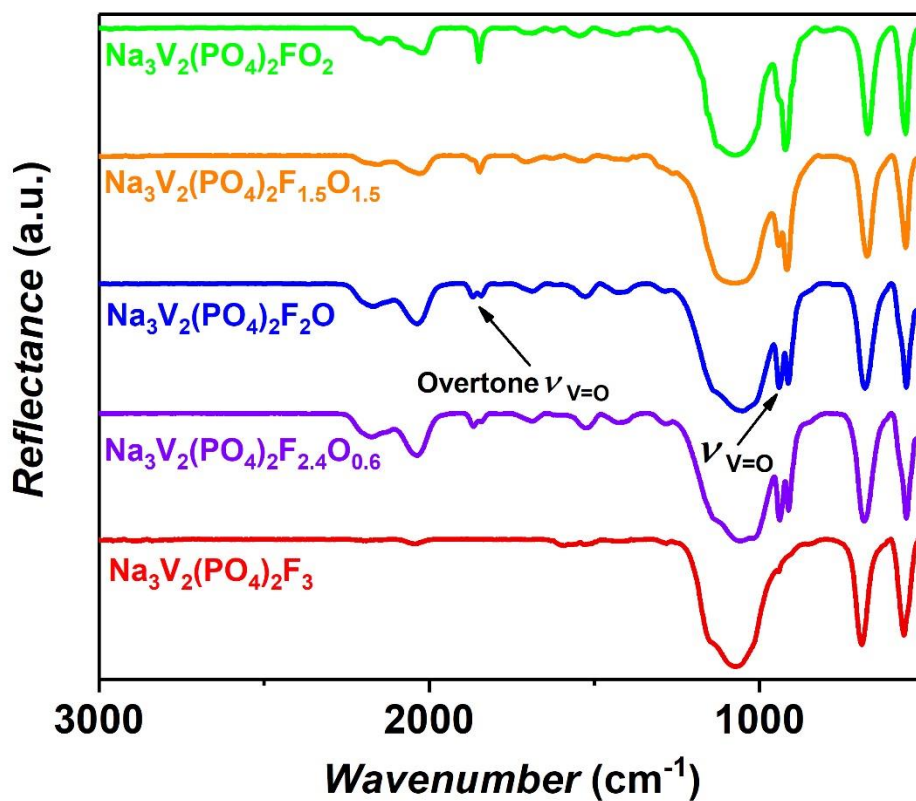
**Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>FO<sub>2</sub>**

<i>S.G. P2<sub>1</sub>/m</i>		<i>a</i> = 6.9688(1) <i>b</i> = 9.0298(1) Å <i>c</i> = 6.9686(1) Å <i>β</i> = 99.24(1)			<i>R</i> <sub>Bragg</sub> = 3.87% <i>R</i> <sub>p</sub> = 3.59% <i>R</i> <sub>wp</sub> = 5.20%	
Atoms	Wyckoff positions	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	Biso
V (1)		0.0496(1)	<b>0.25</b>	0.9473(3)	1	0.11(1)
V (2)		0.4474(2)	<b>0.25</b>	0.5487(2)	1	0.11(1)
P (2)		0.2544(4)	0.0028(3)	0.2460(5)	1	0.08(1)
O (1)		0.2375(3)	0.0948(4)	0.0667(2)	1	0.10(1)
O (2)		0.0594(4)	0.5898(3)	0.2426(2)	1	0.10(1)
O (3)		0.4464(3)	0.5902(4)	0.2553(5)	1	0.10(1)
O (4)		0.2731(4)	0.0915(3)	0.4269(5)	1	0.10(1)
O (5)		0.6010(4)	<b>0.25</b>	0.3807(5)	1	0.10(1)
O (6)		0.9160(5)	<b>0.25</b>	0.1022(3)	1	0.10(1)
F (1)		0.2474(3)	<b>0.25</b>	0.7473(3)	1	0.10(1)
Na (1)		0.7833(4)	0.0224(3)	0.2882(3)	0.73	1.0(1)
Na (2)		0.5046(2)	<b>0.25</b>	0.0128(2)	0.99	1.0(1)
Na (3)		0.0195(3)	0.7008(2)	0.5351(3)	0.19	1.0(1)

***P2<sub>1</sub>/m***

<b>Interatomic distances (Å)</b>	
P(1)—O(1)	1.490(1)
P(1)—O(2)	1.592(1)
P(1)—O(3)	1.572(1)
P(1)—O(4)	1.482(1)
V(1)—O(1)	2.005(1) x 2
V(1)—O(2)	2.024(1) x 2
V(1)—O(6)	1.534(1)
V(1)—F(1)	2.112(1)
V(2)—O(3)	2.041(1) x 2
V(2)—O(4)	1.977(1) x 2
V(2)—O(5)	1.707(1)
V(2)—F(1)	2.115(1)
Na(1)-Na(2)	3.243(1)
Na(1)-Na(3)	2.389(1)

**Figure S9:** The IR spectra of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ ,  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{2.4}\text{O}_{0.6}$ ,  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_2\text{O}$ ,  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{1.5}\text{O}_{1.5}$ , and  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$  powders recovered after washing in the wavenumber range of  $400 - 3000 \text{ cm}^{-1}$ . No vibrational frequency of V=O bond was detected in  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ , while the characteristic stretching modes of V=O bond at  $\sim 900 \text{ cm}^{-1}$ , and  $\sim 1800 \text{ cm}^{-1}$  (overtone) were observed in other compounds.



**Figure S10:** The evolution of the energy of the absorption edge (taken at normalized intensity = 1.0) of *operando* Vanadium K edge XANES spectra recorded for a Na//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>3</sub> half-cell and a Na//Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>1.5</sub>O<sub>1.5</sub> half-cell.

