Supporting information

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Solid state NMR of α_1-$VOPO_4$

Table S1. Atomic parameters of the α_1-$VOPO_4$ unit-cell used for DIFFaX+ refinement with the space-group *P1*. Bold numbers are the refined parameters.

Table S2. Information of the different stacking faults and their probabilities refined by DIFFaX+ code.

Table S3. Atomic positions of α_1-$VOPO_4$ in the monoclinic model before Rietveld refinement (*C2/m*, a = 8.69 Å, b = c = 6.18 Å, β = 104.32°).

Table S4. Crystal data and summary of data collection, structure solution and refinement for α_2-$VOPO_4$ considering disordered oxygen positions or twinning crystals.

Figure S1. Representation of α_1-$VOPO_4$ layer isolated in a supercell. Blue square pyramids and green tetrahedra represent VO_5 and PO_4 units, respectively.

Figure S2. Williamson-Hall plot for α_1-$VOPO_4$.

Figure S3. ^{31}P NMR spectra in MAS conditions recorded at 17.6T (a) and ^{51}V NMR spectra in MAS conditions recorded at 7.1T and 17.6T (b).

Figure S4. ^{51}V-decoupled ^{31}P NMR spectra recorded in MAS conditions at 7.1T.

Figure S5. Representation of α_2-$VOPO_4$ layer isolated in a supercell. Blue square pyramids and green tetrahedra represent VO_5 and PO_4 units, respectively.

Solid state NMR of α_1-$VOPO_4$

In order to validate the α_1-$VOPO_4$ model, ^{31}P and ^{51}V solid-state NMR have been performed (Figure S3). ^{31}P NMR spectra recorded in 30 kHz MAS conditions show a main peak at 2.6 ppm in agreement with the value reported by Aït-Lachgar *et al.*[1] (3.6 ppm). For both magnetic fields, a shoulder at ca 7 ppm is also visible. ^{51}V NMR spectra in MAS conditions exhibit one line at -690 ppm in good agreement with Lapina *et al.* reported value[2] (-691 ppm). At 17.6 T, it is possible to observe a shoulder at ca -680 ppm. The shoulders in ^{31}P and ^{51}V spectra could be attributed to the presence of $VOPO_4.2H_2O$. Indeed, α_1-$VOPO_4$ is an hygroscopic phase whose rehydration product is the dihydrate $VOPO_4.2H_2O$. Moreover, Aït-Lachgar *et al.*[1] reported a ^{31}P signal at 7.6 ppm and Zhu *et al.*[3] reported a ^{51}V signal at -685 ppm for the $VOPO_4.2H_2O$ compound.

Atoms	x	y	z
O1	0	0.5	0.22
O2	0.5	0	0.78
O3	0.038	0.183	0.715
O4	0.183	0.962	0.285
O5	0.683	0.462	0.715
O6	0.538	0.683	0.285
O7	0.462	0.317	0.285
O8	0.317	0.538	0.715
O9	0.962	0.817	0.715
O10	0.817	0.038	0.285
P1	0	0	0.5
P2	0.5	0.5	0.5
V1	0	0.5	**0.6419(1)** / 0.6176
V2	0.5	0	**0.3461(1)** / 0.3824

Table S1. Atomic parameters of the α_1-$VOPO_4$ unit-cell used for DIFFaX+ refinement with the space-group *P1*. Bold numbers are the refined parameters.

Transition description	Stacking vectors	Refined probabilities
1 to 1	(0; 0)	0.001
1 to 2	(0.5; 0.1724)	0.000
1 to 3	(0.5; 0.8276)	0.999
1 to 4	(0.1724; 0.5)	0.000
1 to 5	(0.8276; 0.5)	0.000
2 to 1	(0; 0)	0.000
2 to 2	(0.5; 0.1724)	0.000
2 to 3	(0.5; 0.8276)	0.000
2 to 4	(0.1724; 0.5)	1.000
2 to 5	(0.8276; 0.5)	0.000
3 to 1	(0; 0)	0.000
3 to 2	(0.5; 0.1724)	0.000
3 to 3	(0.5; 0.8276)	0.939
3 to 4	(0.1724; 0.5)	0.026
3 to 5	(0.8276; 0.5)	0.035
4 to 1	(0; 0)	0.000
4 to 2	(0.5; 0.1724)	0.017
4 to 3	(0.5; 0.8276)	0.029
4 to 4	(0.1724; 0.5)	0.917
4 to 5	(0.8276; 0.5)	0.037
5 to 1	(0; 0)	0.000
5 to 2	(0.5; 0.1724)	0.000
5 to 3	(0.5; 0.8276)	0.000
5 to 4	(0.1724; 0.5)	0.142
5 to 5	(0.8276; 0.5)	0.858

Table S2. Information of the different stacking faults and their probabilities refined by DIFFaX+ code.

Atoms	x	y	z
O1	0.11	0.5	0.2013
O2	0.3575	0.5	0.6043
O3	0.1425	0.317	0.7126
O4	0.1425	0	0.0296
P1	0.25	0.5	0.75
V1	0.3088	0.5	0.2704

Table S3. Atomic positions of α_1-$VOPO_4$ in the monoclinic model before Rietveld refinement (*C2/m*, a = 8.69 Å, b = c = 6.18 Å, β = 104.32°).

Chemical formula	VPO_5 Crystal 1	VPO_5 Crystal 2	VPO_5 Crystal 3
Crystal system	Tetragonal	Tetragonal	Tetragonal
Space group	*P4/n*	*P4/n*	*P4/n*
a (Å)	6.014(5)	6.024(5)	6.019(5)
c (Å)	4.438(5)	4.440(5)	4.441(5)
V ($Å^3$)	160.5(3)	161.1(3)	160.9(3)
T (°K)	293(2)	293(2)	293(2)
Z	2	2	2
Maximum 2θ	54.96°	69.96°	54.96°
Data collected	h: -7, 7	h: -9, 9	h: -7, 7
	k: -7, 7	k: -9, 9	k: -7, 7
	l: -5, 5	l: -7, 6	l: -5, 5
Unique data after merging	188	358	188
Observed data ($>2.0\sigma(F^2)$)	188	328	186
Chemical formula weight ($g.mol^{-1}$)	40.48	40.48	40.48
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
Absorption coefficient	3.455 cm^{-1}	3.442 cm^{-1}	3.446 cm^{-1}
$\rho_{calc.}$ ($g.cm^{-3}$)	3.350	3.337	3.342
Disordered oxygen positions			
Free parameters	28	29	29
R_{int}	0.0464	0.0551	0.0291
R_1	0.0836	0.0393	0.0620
wR_2	0.2793	0.1702	0.1776
Goodness-of-fit	1.298	1.322	1.437
Min, Max (e/ $Å^3$)	-1.363, +1.580	-1.291, +1.540	-0.877, 0.254
Disorder occupancy	0.16(6)	0.18(3)	0.25(13)
Twinning crystals			
Free parameters	19	19	19
R_{int}	0.0208	0.0323	0.0293
R_1	0.0146	0.0279	0.0172
wR_2	0.0375	0.0720	0.0440
Goodness-of-fit	1.199	1.138	1.202
Min, Max (e/ $Å^3$)	-0.299, +0.220	-0.719, +0.947	-0.525, 0.250
Twinning rate	0.460	0.256	0.384

Table S4. Summary of data collection, structure solution and refinement for α_2-$VOPO_4$ considering disordered oxygen positions or twinning crystals.

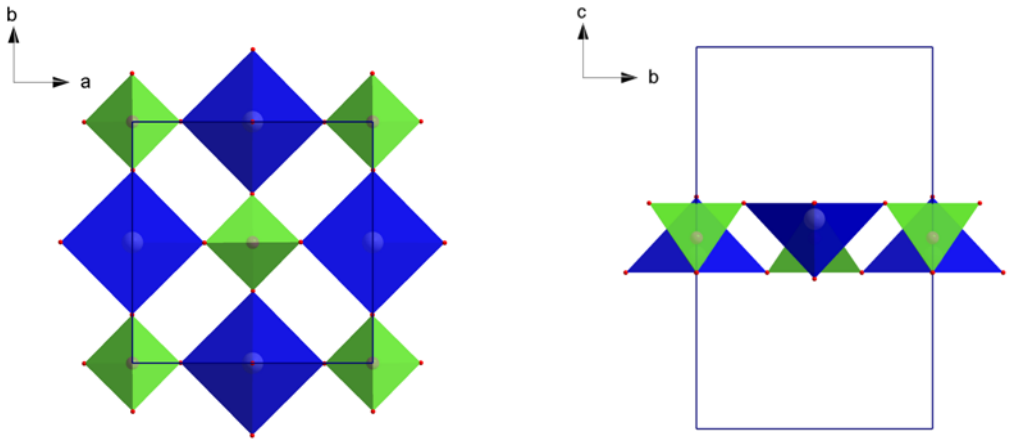

Figure S1. Representation of α_1-$VOPO_4$ layer isolated in a supercell. Blue square pyramids and green tetrahedra represent VO_5 and PO_4 units, respectively.

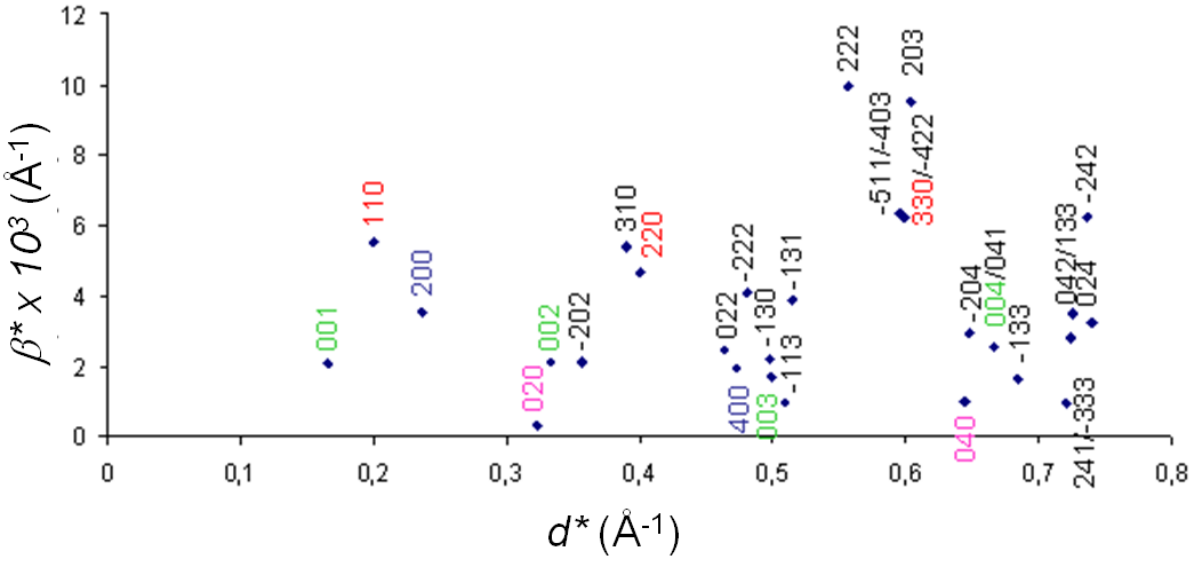

Figure S2. Williamson-Hall plot for α_1-$VOPO_4$.

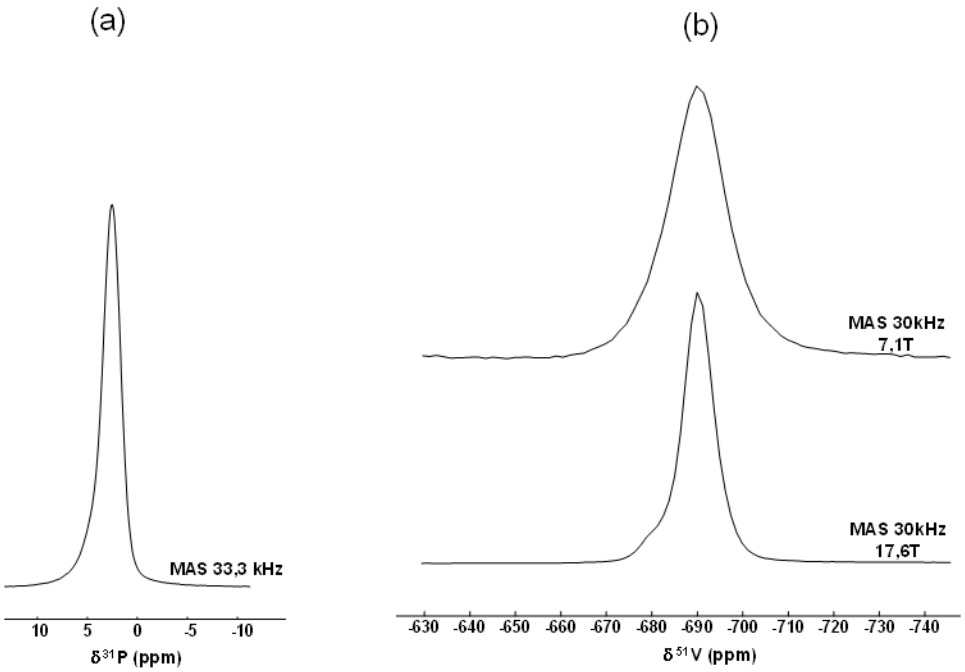

Figure S3. ^{31}P NMR spectra in MAS conditions recorded at 17.6T (a) and ^{51}V NMR spectra in MAS conditions recorded at 7.1T and 17.6T (b) for α_1-$VOPO_4$

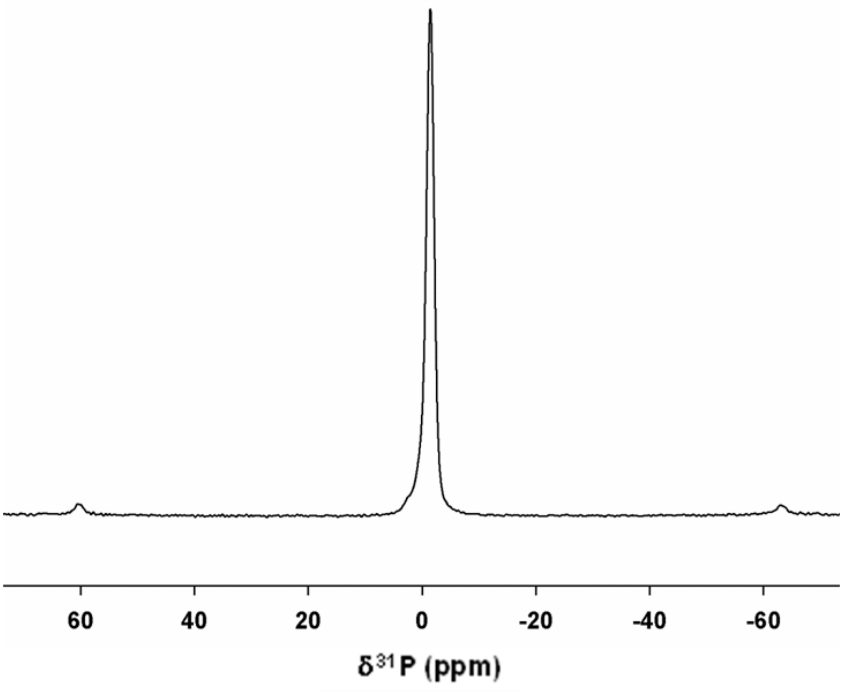

Figure S4. ^{51}V-decoupled ^{31}P NMR spectra recorded in MAS conditions at 7.1T for α_1-$VOPO_4$

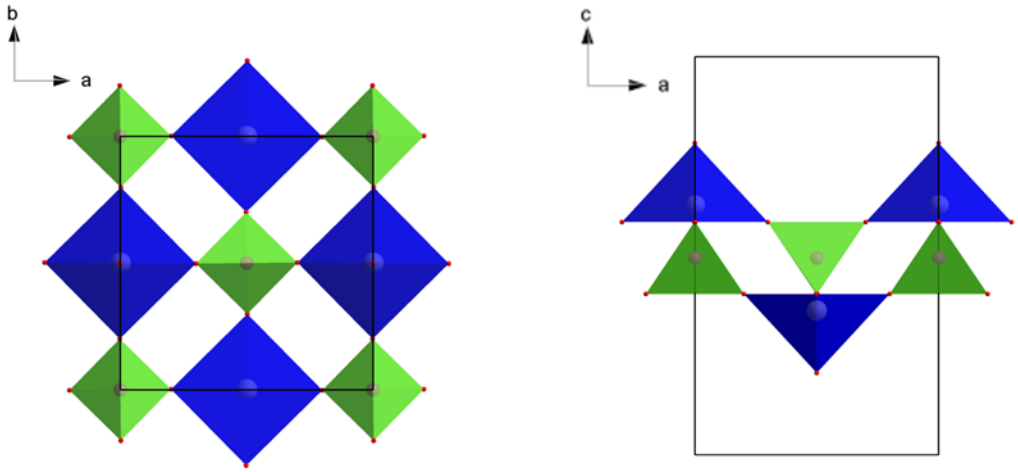

Figure S5. Representation of α_2-$VOPO_4$ layer isolated in a supercell. Blue square pyramids and green tetrahedra represent VO_5 and PO_4 units, respectively.

References

(1) Aït-Lachgar, K.; Tuel, A.; Brun, M.; Herrmann, J. M.; Krafft, J. M.; Martin, J. R.; Volta, J. C.; Abon, M. *J. Catal.* **1998**, *177*, 224-230.

(2) Lapina, O. B.; Khabibulin, D. F.; Shubin, A. A.; Bondareva, V. M. *J. Mol. Catal. A Chem.* **2000**, *162*, 381-390.

(3) Zhu, J.; Huang, Y. *Langmuir* **2010**, *26*, 10115-10121