

Supporting information

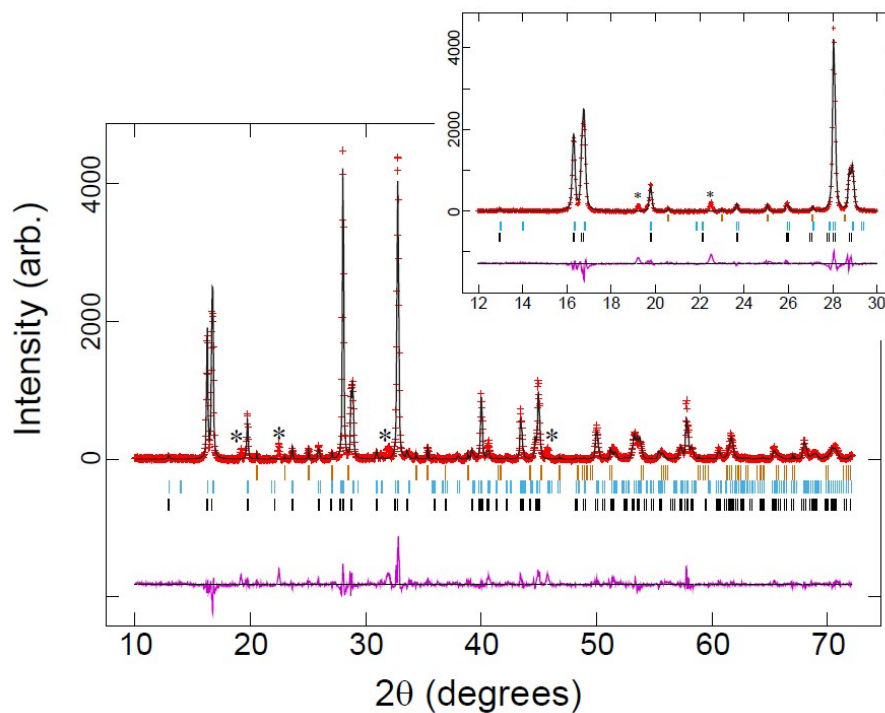


Figure S1. Rietveld refined fit of the *Amam* and *P4₂/mnm* $\text{Na}_3\text{V}_2\text{O}_{2x}(\text{PO}_4)_2\text{F}_{3-2x}$ and VPO_4 models to laboratory XRD data. Data are shown as crosses, the calculated Rietveld model as a line through the data, and the difference between the data and the model as the line below the data. The vertical reflection markers are for the phases present with *Amam* in black, *P4₂/mnm* in blue and VPO_4 in brown. The asterisk show reflections from the unidentified impurity phase.

Table S1. Crystallographic details of the models used.

Name	x	y	z	U _{iso} (x100)
<i>Amam</i> - a = 9.033(2), b = 9.045(2), c = 10.7208(9) Å				
Na(1)	0.75	0.023	0	2.5
Na(2)	0.536	0.283	0	2.5
Na(3)	0.593	0.364	0	2.5
V(1)	0.25	0.251(3)	0.187(1)	1.5
P(1)	0	0	0.243(4)	2.2
O(1)	0.090(6)	0.101(6)	0.167(4)	4.3
O(2)	0.091(5)	0.407(6)	0.154(4)	4.3
F(1)	0.25	0.250(10)	0	4.3
F(2)	0.25	0.754(9)	0.138(2)	4.3
<i>P4₂/mnm</i> - a = 9.0379(6), c = 10.6509(9) Å				
Na(1)	0.519(9)	0.264(8)	0	2.5
Na(2)	0.732(4)	0.022(6)	0	2.5
V(1)	0.251(2)	0.251(2)	0.194(1)	4.4
P(1)	0	0.5	0.25	3.2
P(2)	0	0	0.241(4)	4.3
O(1)	0.104(3)	0.400(3)	0.162(2)	0.14
O(2)	0.090(5)	0.090(5)	0.129(4)	19.5
O(3)	0.413(3)	0.413(3)	0.161(4)	2.4
F(1)	0.259(7)	0.259(7)	0	9.1
F(2)	0.243(4)	0.243(4)	0.370(2)	7.2

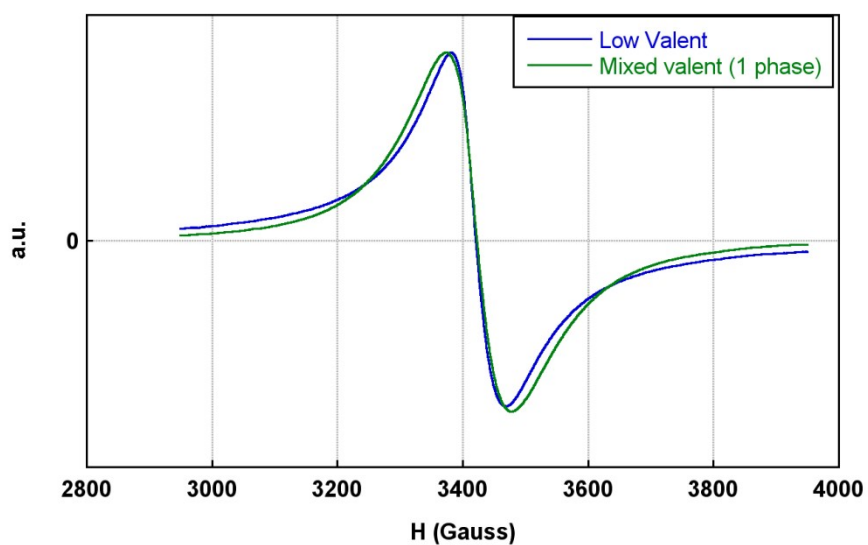


Figure S2. EPR spectra of the studied material (Low Valent sample) and a one-phase sodium vanadium fluorophosphate sample with mixed valent vanadium that was prepared in our laboratory to compare the EPR signals. As it can be seen, the signal of the Mixed valent sample goes to 0 intensity values in the extremes, whereas the signal of the Low valent material does not, which indicates the presence of a secondary phase as a very wide signal in the spectrum.