Supplementary Information for

Crystal structure and migration paths of alkaline ions in $NaVPO_4F$

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Table S1. Bond lengths (Å) and angles (°) in the coordination polyhedra of P^{5+} and V^{3+} in $NaVPO_4F$ (Sample 1) within the *C*2/*c* S.G.

PO_4				
P	O1	O1	O2	O2
O1	**1.53972(5)**	115.81°	109.46°	109.25°
O1		**1.53972(5)**	109.25°	109.46°
O2			**1.56312(5)**	102.80°
O2				**1.56312(5)**
Average bond length P-O = 1.5514			Distortion index Δ = 0.0075	

VO_4F_2						
V	O1	O1	O2	O2	F1	F1
O1	**2.05915(9)**	180°	90.63°	89.37°	88.51°	91.49°
O1		**2.05915(9)**	89.37°	90.63°	91.49°	88.51°
O2			**1.96545(8)**	180°	88.89°	91.11°
O2				**1.96545(8)**	91.11°	88.89°
F1					**1.93647(8)**	180°
F1						**1.93647(8)**
Average bond length V-O(F) = 1.987				Distortion index Δ = 0.0242		

The distortion index was calculated as follows:

$$\Delta = \frac{1}{2}\sum_{1}^{n}\frac{|d_n - \langle d\rangle|}{\langle d\rangle}, \quad (1)$$

where d_n – a bond length, n – a bond number, <d> - an average bond length.

Table S2. Bond lengths (Å) and angles (°) in the coordination polyhedra of P^{5+} and V^{3+} in $Na_3V_2(PO_4)_2F_3$ (Sample 1) within the *Amam* (a) and $P4_2/mnm$ (b) S.G.

(a)		**PO_4** *Amam* S.G.		
P	O1	O1	O2	O2
O1	**1.471(1)**	117.78°	111.78°	110.39°
O1		**1.471(1)**	110.39°	111.78°
O2			**1.644(1)**	91.76°
O2				**1.644(1)**
Average bond length P-O = 1.5576		Distortion index Δ = 0.05576		

	VO_4F_2 *Amam* S.G.					
V	O1	O1	O2	O2	F1	F2
O1	**1.895(1)**	92.39°	89.87°	165.5°	87.5°	96.9°
O1		**1.895(1)**	165.5°	89.87°	87.5°	96.9°
O2			**2.0915(1)**	84.49°	78.3°	97.1°
O2				**2.0915(1)**	78.3°	97.1°
F1					**1.9883(1)**	173.7°
F2						**1.9502(1)**
Average bond length V-O(F) = 1.9852			Distortion index Δ = 0.03619			

(b)		**$P1O_4$** $P4_2/mnm$ S.G.		
P1	O1	O1	O1	O1
O1	**1.5564(1)**	111.16°	106.15°	111.16°
O1		**1.5564(1)**	111.16°	106.15°
O1			**1.5564(1)**	111.16°
O1				**1.5564(1)**
Average bond length P-O = 1.5564		Distortion index Δ = 0		

	$P2O_4$ $P4_2/mnm$ S.G.			
P2	O2	O2	O3	O3
O2	**1.5724(1)**	99.58°	113.7°	113.7°
O2		**1.5724(1)**	113.7°	113.7°
O3			**1.5186(1)**	102.9°
O3				**1.5186(1)**
Average bond length P-O = 1.5455		Distortion index Δ = 0.01741		

	VO_4F_2 $P4_2/mnm$ S.G.					
V	O1	O1	O2	O3	F1	F2
O1	**1.96476(5)**	166.5°	89.5°	88.7°	83.3°	96.7°
O1		**1.96476(5)**	89.5°	88.7°	83.3°	96.7°
O2			**2.01750(5)**	164.3°	83.4°	90.4°
O3				**2.02647(5)**	80.9°	105.4°
F1					**1.9852(1)**	173.8°
F2						**1.9681(1)**
Average bond length V-O(F) = 1.9878			Distortion index Δ = 0.0115			

Table S3. Bond lengths (Å) and angles (°) in the coordination polyhedra of P^{5+} and V^{3+} in $Na_3V_2(PO_4)_2F_3$ (Sample 2) within the *Amam* (a) and $P4_2/mnm$ (b) S.G.

(a)			**PO_4** *Amam* S.G.			
P1	O1		O1	O2		O2
O1	**1.548(9)**		107.3°	112.4°		110.7°
O1			**1.548(9)**	110.7°		112.4°
O2				**1.522(10)**		103.5°
O2						**1.522(10)**
Average bond length P-O = 1.535			Distortion index Δ = 0.0083			
			VO_4F_2 *Amam* S.G.			
V	O1	O1	O2	O2	F1	F2
O1	**1.991(8)**	87.5°	88.73°	167.1°	80.8°	97.0°
O1		**1.991(8)**	167.1°	88.73°	80.8°	97.0°°
O2			**1.985(10)**	92.2°	86.4°	95.8°
O2				**1.985(10)**	86.4°	95.8°
F1					**1.9810(18)**	176.8°
F2						**1.961(5)**
Average bond length V-O(F) = 1.9824			Distortion index Δ = 0.0038			
(b)			**$P1O_4$** $P4_2/mnm$ S.G.			
P1	O1		O1	O1		O1
O1	**1.5561(1)**		111.5°	105.4°		111.5°
O1			**1.5561(1)**	111.5°		105.4°
O1				**1.5561(1)**		111.5°
O1						**1.5561(1)**
Average bond length P-O = 1.5561			Distortion index Δ = 0			
			$P2O_4$ $P4_2/mnm$ S.G.			
P2	O2		O2	O3		O3
O2	**1.5241(1)**		102.9°	110.9°		110.9°
O2			**1.5241(1)**	110.9°		110.9°
O3				**1.5206(1)**		110.1°
O3						**1.5206(1)**
Average bond length P-O = 1.5224			Distortion index Δ = 0.0011			
			VO_4F_2 $P4_2/mnm$ S.G.			
P	O1	O1	O2	O3	F1	F2
O1	**1.97595(3)**	165.5°	92.1°	86.5°	83.2°	96.9°
O1		**1.97595(3)**	92.1°	86.5°	83.2°	96.9°
O2			**1.99064(3)**	168.4°	86.7°	91.4°
O3				**1.98571(3)**	81.6°	100.2°
F1					**1.97874(5)**	178.2°
F2						**1.98073(5)**
Average bond length V-O(F) = 1.9813			Distortion index Δ = 0.0023			

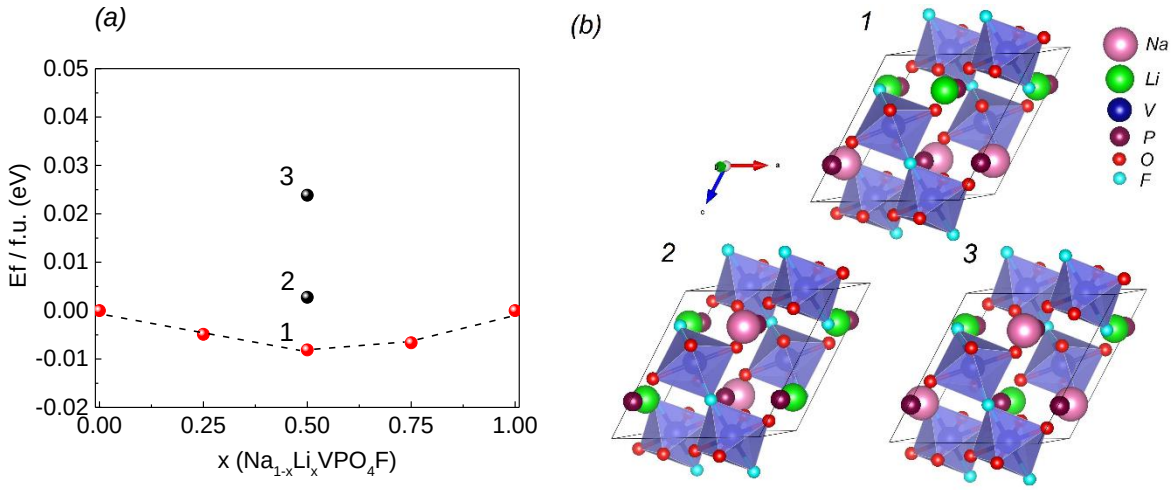

Fig. S1. (a) Thermodynamic convex hull of the $Na_{1-x}Li_xVPO_4F$(*C*2/*c*) system, red balls denote stable configurations; and (b) three possible configurations for the $Na_{0.5}Li_{0.5}VPO_4F$ composition.

The convex hull (Fig S1(a)) was obtained by calculating the formation energy E_f of $Na_{1-x}Li_xVPO_4F$ (*C*2/*c* S.G., $0 \leq x \leq 1$) using the following equation:

$$E_f(Na_{1-x}Li_xVPO_4F) = E_o(Na_{1-x}Li_xVPO_4F) - (1-x)E_o(NaVPO_4F) - xE_o(LiVPO_4F)$$

The negative formation energy indicates the $Na_{1-x}Li_xVPO_4F$ intermediate derivatives are stable though the energy value is comparable with thermal energy at room temperature, this hints at the low stability.

All possible configurations were determined by using the Supercell package [Ref.1]. For the $Na_{0.5}Li_{0.5}VPO_4F$ composition there is three possible configurations #1-3 (Fig. S1(b)) that differ in the distribution of Na^+ and Li^+ sites and correspond to black balls in Fig. S1(a). The only stable configuration #1 corresponds to the most symmetrical distribution of Na^+ and Li^+ ions where the ions of each type are located in different layers alternating along *c* direction.

[Ref.1] K. Okhotnikov, T. Charpentier, and S. Cadars, *J. Cheminformatics*, 2016, **8**, 1-15.