Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Stabilizing the crystal structures of $NaFePO_4$ with Li substitutions

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Supporting Information

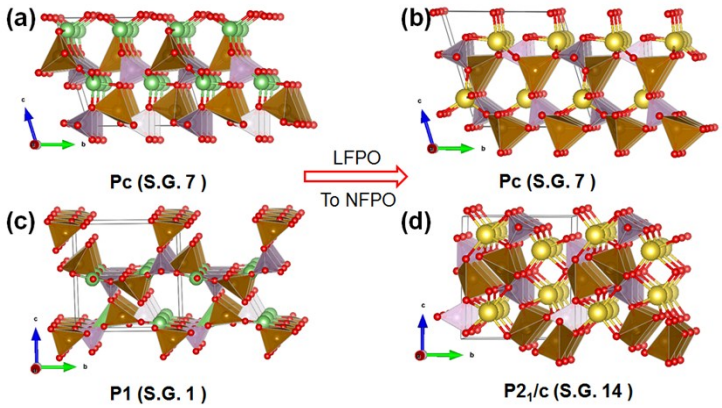

Figure S1 Lowest two FeO4 type NFPOs and corresponding LFPOs.

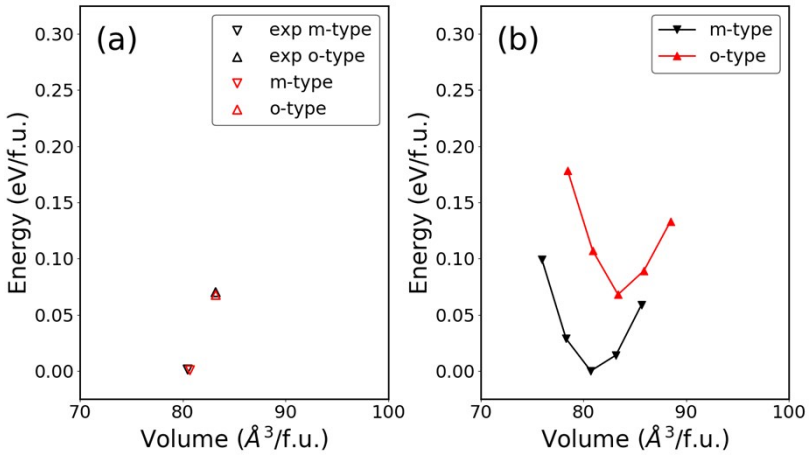

FIG. S2. Energy vs. volume plot of m-type and o-type structures. (a) The m-type and o-type structures in our database get from $LiFePO_4$, and two experimental structures after DFT relaxation. (b) The plot of total energies by varying the volume of the unit cells for m-type and o-type structures. The two lowest black and red points in (b) are the equilibrium states of the m-type and o-type structures, which are consistent with the two points in (a).

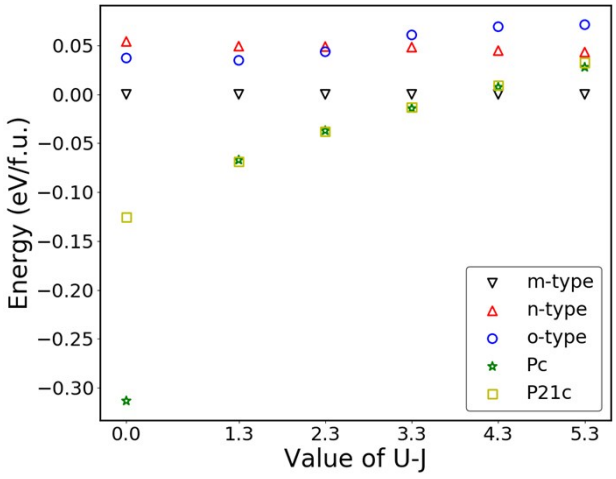

FIG. S3. Energy vs. value of U-J plot of five different types (m-type, o-type n-type, Pc and P21c) of NFPOs. In the energy, the value is relative to the ground state of m-$NaFePO_4$ in different value of U-J.

Table S1. Crystallographic data of m-type $NaFePO_4$.

Phase	Space group	Lattice param.	Wyckoff site	Atom	x	y	z
m-type	*Pnma*		4c	Na1	0.34861	0.25000	0.46888
		a=9.113	4b	Fe1	0.00000	0.00000	0.50000
		b=6.934	4c	P1	0.17481	0.25000	-0.03621
		c=5.108	4c	O1	0.34717	0.25000	-0.04585
		α=β=γ=90°	8d	O2	0.87981	-0.06788	0.18174
			4c	O3	0.11555	0.25000	0.25008

Table S2. Crystallographic data of o-type $NaFePO_4$.

Phase	Space group	Lattice param.	Wyckoff site	Atom	x	y	z
o-type	*Pnma*		4a	Na1	0.00000	0.00000	0.50000
		a=10.551	4c	Fe1	0.78710	0.25000	0.48682
		b=6.321	4c	P1	0.60976	0.25000	-0.05871
		c=4.999	4c	O1	0.61433	0.25000	0.25165
		α=β=γ=90°	4c	O2	0.46755	0.25000	0.84350
			8d	O3	0.32403	-0.05482	0.18739

Table S3. Crystallographic data of n-type $NaFePO_4$.

Phase	Space group	Lattice param.	Wyckoff site	Atom	x	y	z
n-type	*Cmcm*		4c	Na1	0.00000	0.18425	0.25000
		a=5.488	4b	Fe1	0.00000	0.50000	0.00000
		b=8.521	4c	P1	0.00000	0.83590	0.25000
		c=6.898	8g	O1	0.26704	0.44285	0.25000
		α=β=γ=90°	8f	O2	0.00000	0.73066	0.43203

Table S4. Crystallographic data of Pc type $NaFePO_4$.

Phase	Space group	Lattice param.	Wyckoff site	Atom	x	y	z
Pc-type	*Pc*		2a	Na1	0.25194	0.18275	0.82220
			2a	Na2	0.75298	0.70170	-0.09271
			2a	Fe1	0.50122	0.69346	0.14417
			2a	Fe2	0.00218	0.19946	0.06710
		a=9.230	2a	P1	0.62689	0.78784	0.51304
		b=5.300	2a	P2	0.13125	0.70550	-0.04971
		c=9.062	2a	O1	0.78051	0.73313	0.48169
		α=γ=90°	2a	O2	0.61526	0.63551	0.65571
		β=107.2°	2a	O3	0.61408	0.07491	0.53993
			2a	O4	0.49916	0.69651	0.36935
			2a	O5	0.00016	0.82793	0.00021
			2a	O6	0.11490	0.41438	-0.04905
			2a	O7	0.13075	0.79492	0.78676
			2a	O8	0.28244	0.79514	0.06674

Table S5. Crystallographic data of $P2_1/c$ type $NaFePO_4$.

Phase	Space group	Lattice param.	Wyckoff site	Atom	x	y	z
$P2_1/c$ - type	*P2₁/c*		4e	Na1	0.48075	-0.02418	0.81565
		a= 5.0370	4e	Fe1	0.77552	0.35511	0.04688
		b= 8.375	4e	P1	0.80899	0.71648	0.13605
		c= 10.111	4e	O1	0.67409	-0.04854	0.64228
		α=γ=90°	4e	O2	0.57049	0.69268	0.50967
		β=113.3°	4e	O3	0.86070	0.69285	0.77713
			4e	O4	0.09524	0.80521	0.61519