ESI: Electronic Supplementary Information

Methods and Potentials

In this study, the atomistic simulations are based on *interatomic potentials* methods, which rest upon the specification of an effective potential function, which expresses the total energy of the system as a function of the nuclear coordinates. Short range interactions are modeled using a Buckingham potential which is defined as follows:

$$V_{ij}(r_{ij}) = A\exp^{-\frac{r_{ij}}{\rho}} - \frac{C}{r_{ij}^6}$$

A, ρ and C are ion-ion parameters and r is the inter-atomic distance. A three body term has been used to take in to account for the angle dependent nature of the PO_4 tetrahedral units. This is defined in terms of a force constant and equilibrium bond angle as follows:

$$V = k(\theta - \theta_0)^2$$

where k is the force constant and θ_o is the equilibrium bond angle. Since charged defects will polarise other ions in the lattice, electronic polarisation must be incorporated into the potential model. The shell model provides a simple description of such effects (particularly for the polarisable oxygen) and has proven to be effective in simulating the dielectric properties of a range of oxides and fluorides.

Geometry optimisation provides the lowest energy configuration of a given structure through a search of the potential energy surface using efficient minimisation routines. Here, energy minimisation of the crystal lattice is carried out using Newton-Raphson (second derivative) methods using symmetry in the optimisation procedures. For bulk systems, three-dimensional

periodic boundary conditions are normally applied to the simulation box, in effect making the structure infinite in extent.

Table S1. Short-range potential parameters for Na[Fe,Mn]PO_4 and Na_2FePO_4F (*-indicates the value for the Na_2FePO_4F only).

a)

Two-body			
Bond	A (eV)	ρ(Å)	C(eV·Å^6)
Na-O	560	0.32	0
Na-O*	1497.830598	0.287483	0
Na-F*	2810.326262	0.246520	0
Fe-O	1105.2409	0.3106	0
Fe-F*	5609.2542	0.227	0
Mn-O	1305.25	0.31	0
P-O	897.2648	0.3577	0
O-O	22764.3	0.149	44.53
O-F*	11000.389	0.244179	41.18
F-F*	1153	0.1365	0

Three-body		
Bond type	k (eV·rad^{-2})	Θ_0 (deg)
O-P-O	1.3226	109.47

b)

Species	Y (e)	K(eV·Å-2)
Na	1	99999.0
Fe	2.997	19.26
P	5	99999.0
O	-2.96	65.0
F	-2.321	63.57