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Supporting information - Atomistic modeling of site exchange defects in lithium iron phosphate and iron phosphate

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Table S1. Mechanical properties, dielectric constants and heat capacities of $LiFePO_4$ and $FePO_4$ from atomistic calculations.

	$LiFePO_4$	$FePO_4$
Bulk moduli		
K_{Reuss}	117.3 GPa	63.9 GPa
K_{Voigt}	118.0 GPa	64.4 GPa
K_{Hill}	117.6 GPa	64.1 GPa
Shear moduli		
G_{Reuss}	56.8 GPa	36.9 GPa
G_{Voigt}	59.6 GPa	42.5 GPa
G_{Hill}	58.2 GPa	39.7 GPa
Youngs moduli		
E_a	142.9 GPa	111.0 GPa
E_b	179.6 GPa	179.5 GPa
E_c	151.0 GPa	97.2 GPa
Dielectric constants		
ε_0	19.8	17.5
ε_{hf}	3.77	5.19
Heat capacities		
$C_{p,\ 100K}$	43.5 J/(K.mol)	35.1 J/(K.mol)
$C_{p,\ 200K}$	87.8 J/(K.mol)	70.3 J/(K.mol)
$C_{p,\ 300K}$	113.6 J/(K.mol)	92.5 J/(K.mol)
$C_{p,\ 400K}$	129.7 J/(K.mol)	107.1 J/(K.mol)
$C_{p,\ 500K}$	140.2 J/(K.mol)	116.8 J/(K.mol)
$C_{p,\ 600K}$	147.1 J/(K.mol)	123.3 J/(K.mol)

To assess the transferability of the set of potentials, we calculated the optimized crystal structures of γ-Li_3PO_4 and the Nasicon analogue $Li_3Fe_2(PO_4)_3$:

Table S2. Comparison of calculated and experimental crystal structure parameters of γ-Li_3PO_4.

Li_3PO_4	Experimental[1]	Calculated	Rel. error / %
a / Å	6.12	6.03	1.5
b / Å	10.53	10.27	2.5
c / Å	4.93	4.87	1.2
$Li_3Fe_2(PO_4)_3$	Experimental[2]	Calculated	Rel. error / %
a / Å	8.32	8.20	1.4
c / Å	22.46	21.63	3.7

It can be seen, that the potentials are valid with restrictions also for other compounds of the lithium and iron phosphate system. Note: This potential set should only be used for structures where oxygen is covalently bonded to phosphor in phosphate groups.

For calculations of defect correlation, we determined a quantity of charge localization on the unit cell scale. This quantity was determined from the relaxed structures by integrating all charges within the volume of one unit cell. This volume was then moved across the complete super cell by ¼ unit cell steps in each crystallographic direction to obtain an average of charge localization in the super cell.

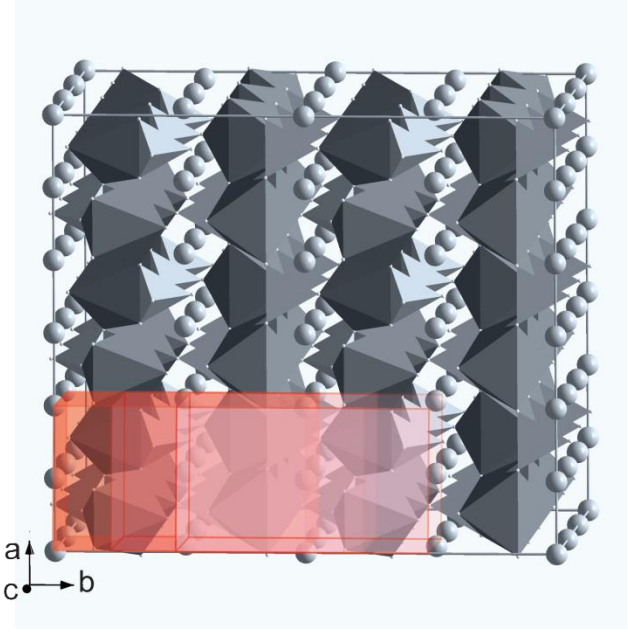

Figure S1. Illustration of iterative charge integration to obtain the value termed average localized charge. The red cuboids correspond to the volume of one unit cell each. The left cuboid determines the integration boundaries for the first integration step. The other cuboids illustrate the movement of the integration boundaries during the iterative integration over the whole super cell. An average of integrated charge per unit cell is then determined for the complete super cell.

References

1. J. Zemann, *Acta Crystallographica*, 1960, **13**, 863-867.
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