Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Defect and dopant properties of the α- and β-polymorphs of the Li_3FeF_6 lithium battery material

Supporting information

Table S1. Calculated and Experimental Mean Bond Distances for Monoclinic and Orthorhombic Li_3FeF_6.

a) Monoclinic (C2/c)

Parameter	*Calc*	*Expt*	Δ (Å)
Fe1-F4	2.067	1.944	0.123
Fe1-F6	2.055	1.894	0.160
Fe1-F8	2.081	1.927	0.154
Fe2-F1	2.049	1.952	0.098
Fe2-F2	2.057	1.895	0.161
Fe2-F3	2.058	1.929	0.128
Fe2-F5	2.052	1.921	0.131
Fe2-F7	2.088	1.954	0.134
Fe2-F9	2.079	1.967	0.112
Li1-Fe1	2.892	2.964	-0.072
Li1-F1	2.012	1.971	0.041
Li1-F6	1.946	2.062	-0.116
Li1-F8	1.975	2.009	-0.034
Li2-F1	1.861	1.984	-0.123
Li2-F2	1.859	1.849	0.009
Li2-F4	1.910	1.929	-0.018
Li2-F5	2.274	2.553	-0.279
Li2-F6	2.939	2.963	-0.024
Li2-F7	2.267	2.419	-0.151

b) Orthorhombic $Pna2_1$

Parameter	*Calc*	*Expt*	Δ (Å)
Fe1-F1	2.081	2.022	0.059
Fe1-F2	2.065	1.992	0.073
Fe1-F3	2.063	1.919	0.144
Fe1-F4	2.058	1.806	0.252
Fe1-F5	2.058	2.046	0.012
Fe1-F6	2.096	1.865	0.231
Fe2-F5	2.052	1.921	0.131
Fe2-F7	2.088	1.954	0.134

Fe2-F9	2.079	1.967	0.112
Li1-Fe1	2.892	2.964	-0.072
Li1-F1	2.011	1.971	0.040

Table S2. .Interatomic Potential Parameters for the monovalent and divalent dopants.

Interaction	*A* (eV)	*ρ* (Å)	*C* (eV· Å^6)	Lattice energy (eV)
Na^+- F^-	1497.45	0.2589	0.00	-11.13
K^+- F^-	1701.31	0.2963	13.70	-9.72
Ni^{2+}- F^-	907.90	0.2816	0.00	-29.95
Mg^{2+}- F^-	841.30	0.2831	0.00	-30.12
Co^{2+}- F^-	917.20	0.2856	0.00	-29.47
Mn^{2+}- F^-	1000.70	0.2926	0.00	-28.34
Cd^{2+}- F^-	1057.60	0.3059	10.00	-27.35
Ca^{2+}- F^-	1.00	1534.3	0.29	-27.09
Sr^{2+}- F^-	3400.00	0.2906	0.00	-24.47
Ba^{2+}- F^-	1746.90	0.3237	16.70	-23.94

Table S3. Solution Energies of monovalent and divalent dopants on Li and Fe Sites as a function of ion size in monoclinic and orthorhombic Li_3FeF_6.

Dopant		Energy (eV)			
		Li site		Fe site	
	Radii(Å)	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Na^+	1.02	-0.54	0.34	0.50	2.19
K^+	1.38	0.79	1.19	1.01	2.88
Ni^{2+}	0.69	0.55	1.32	-0.62	-0.21
Mg^{2+}	0.72	0.55	1.34	-0.78	-0.25
Co^{2+}	0.74	0.61	1.42	-0.53	-0.14
Mn^{2+}	0.83	0.54	1.53	-0.18	0.07
Cd^{2+}	0.95	0.95	1.72	-0.29	0.38
Ca^{2+}	1.00	1.09	1.93	-0.09	0.60
Sr^{2+}	1.2	2.08	3.00	0.72	1.69
Ba^{2+}	1.35	2.34	3.16	0.94	1.89