Supporting information for

"Mapping Sodium Intercalation Mechanism, Electrochemical Properties and Structural Evolution in Non-stoichiometric Alluaudite $Na_{2+2\delta}Fe_{2-\delta}(SO_4)_3$ Cathode Materials"

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Figures and Tables

Table S1 Fractional atomic coordinates and occupancies for the fully-desodiated $Fe_2(SO_4)_3$ structure with *C2/c* symmetry in which a = 17.27 Å, b = 6.41 Å, c = 9.57 Å, and β = 119.08°

Site	Wyckoff	*x*	*y*	*z*	Occu.
Fe1	8*f*	0.1387	0.1313	0.1199	1.0
S1	4*e*	0.0000	0.0017	0.2500	1.0
S2	8*f*	0.3114	0.1297	0.3230	1.0
O11	8*f*	0.0467	0.1384	0.1911	1.0
O12	8*f*	0.4367	0.3631	0.1188	1.0
O21	8*f*	0.3689	0.3152	0.3905	1.0
O22	8*f*	0.2355	0.1295	0.3580	1.0
O23	8*f*	0.2634	0.1289	0.1423	1.0
O24	8*f*	0.1299	0.4451	0.1076	1.0

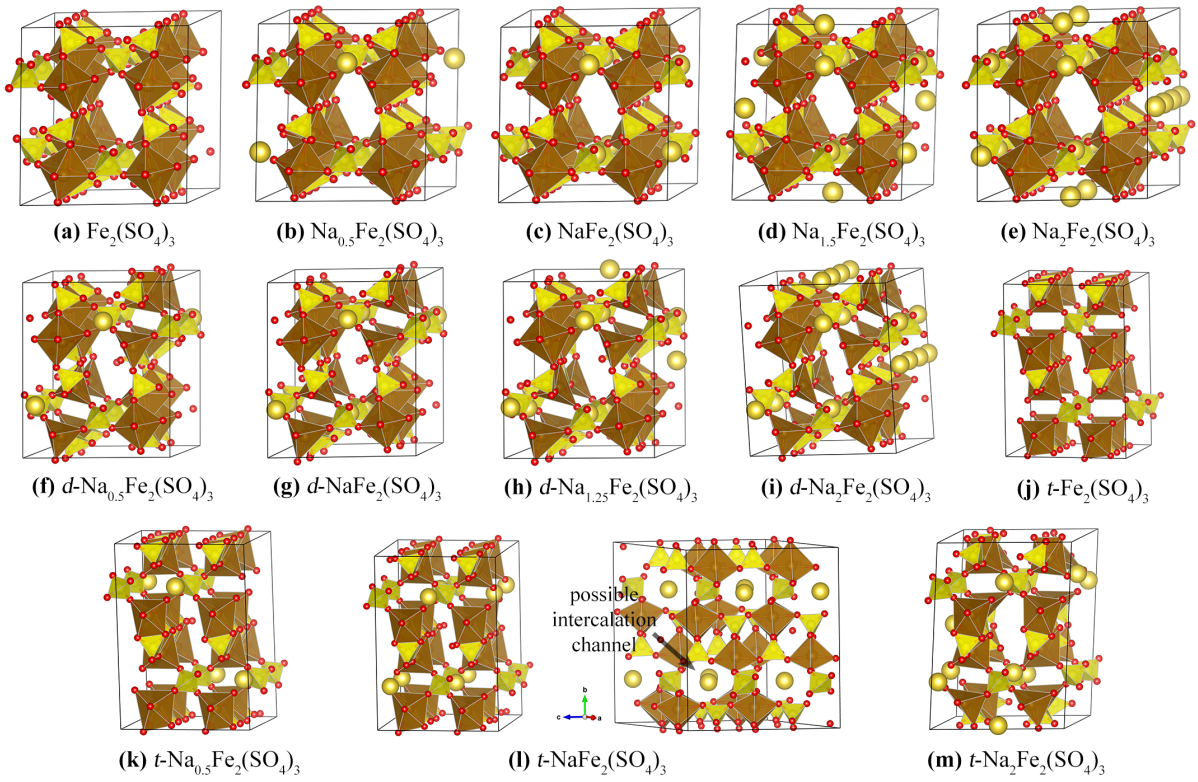

Figure S1 Minimum energy configurations of $Na_xFe_2(SO_4)_3$ illustrated in (a-e) pristine, (f-i) *d*-phase and (j-m) *t*-phase.

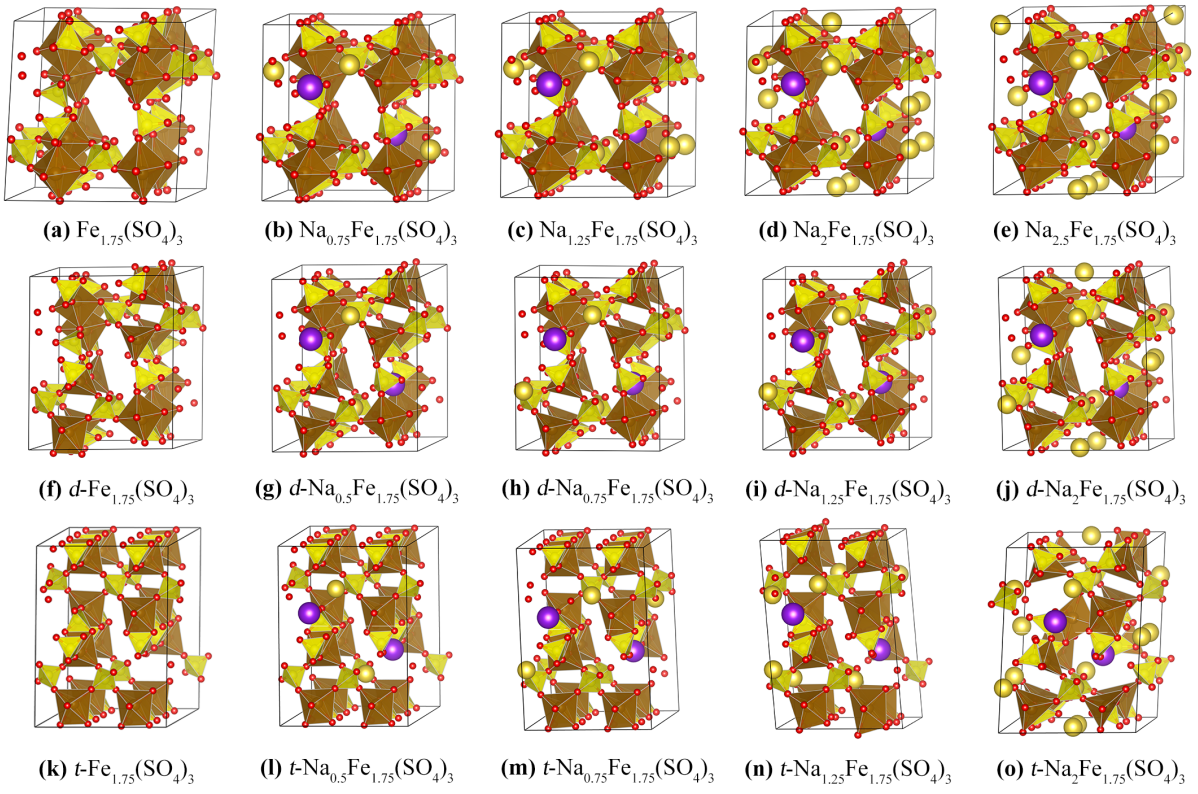

Figure S2 Minimum energy configurations of $Na_xFe_{1.75}(SO_4)_3$ illustrated in (a-e) pristine, (f-j) *d*-phase and (k-o) *t*-phase.

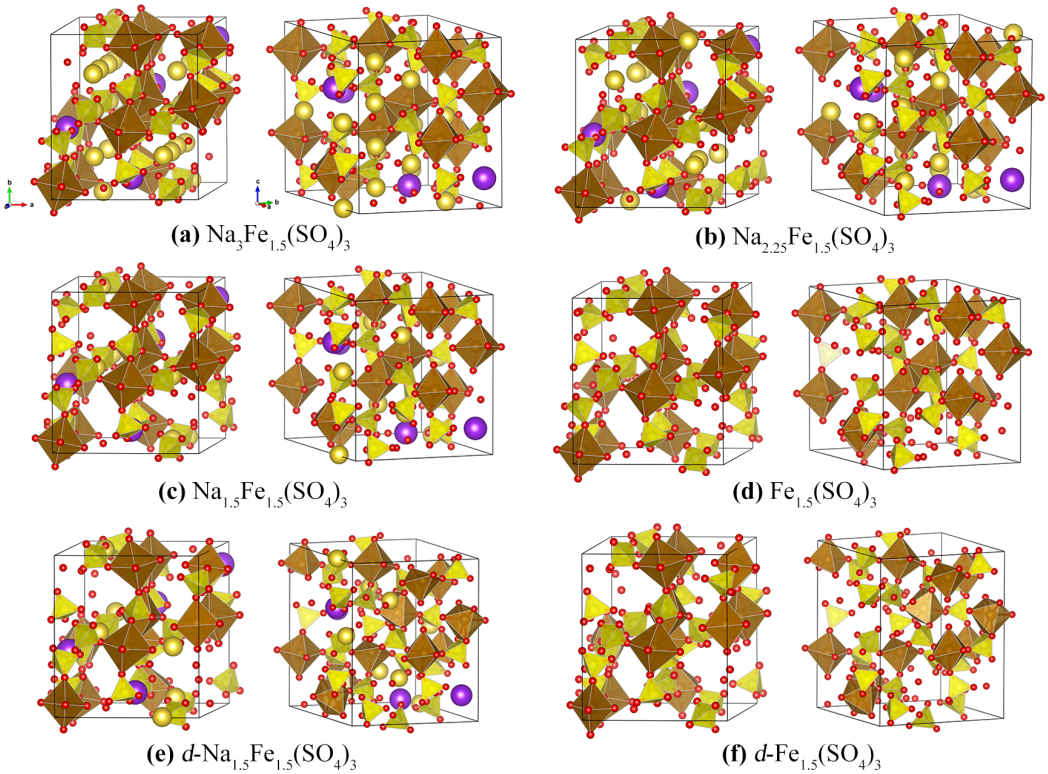

Figure S3 Minimum energy configurations of $Na_xFe_{1.5}(SO_4)_3$ illustrated in (a-d) pristine and (e-f) *d*-phase.

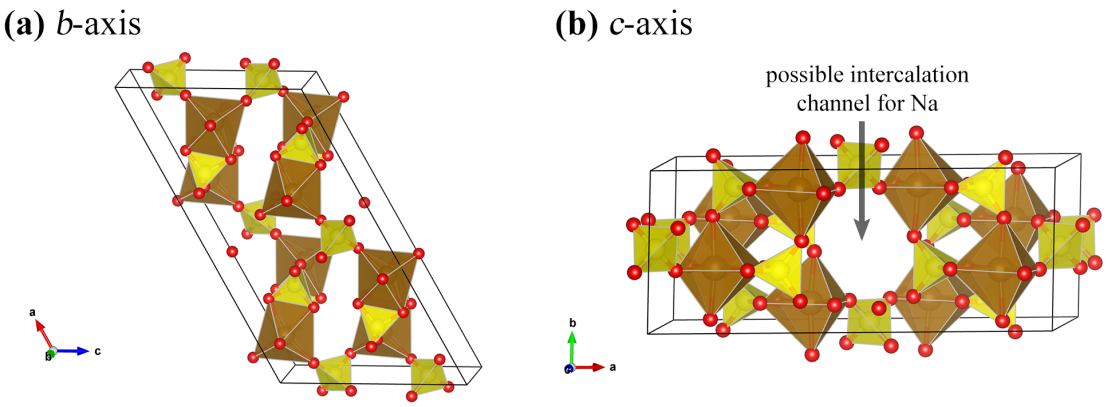

Figure S4 The primitive crystal structure of $Fe_2(SO_4)_3$ in *C2/c* space group (*t*-phase) illustrated along (a) *b*-direction and (b) *c*-direction. Possible intercalation channel for Na^+ ion in *t*-phase is emerged as shown in (b).

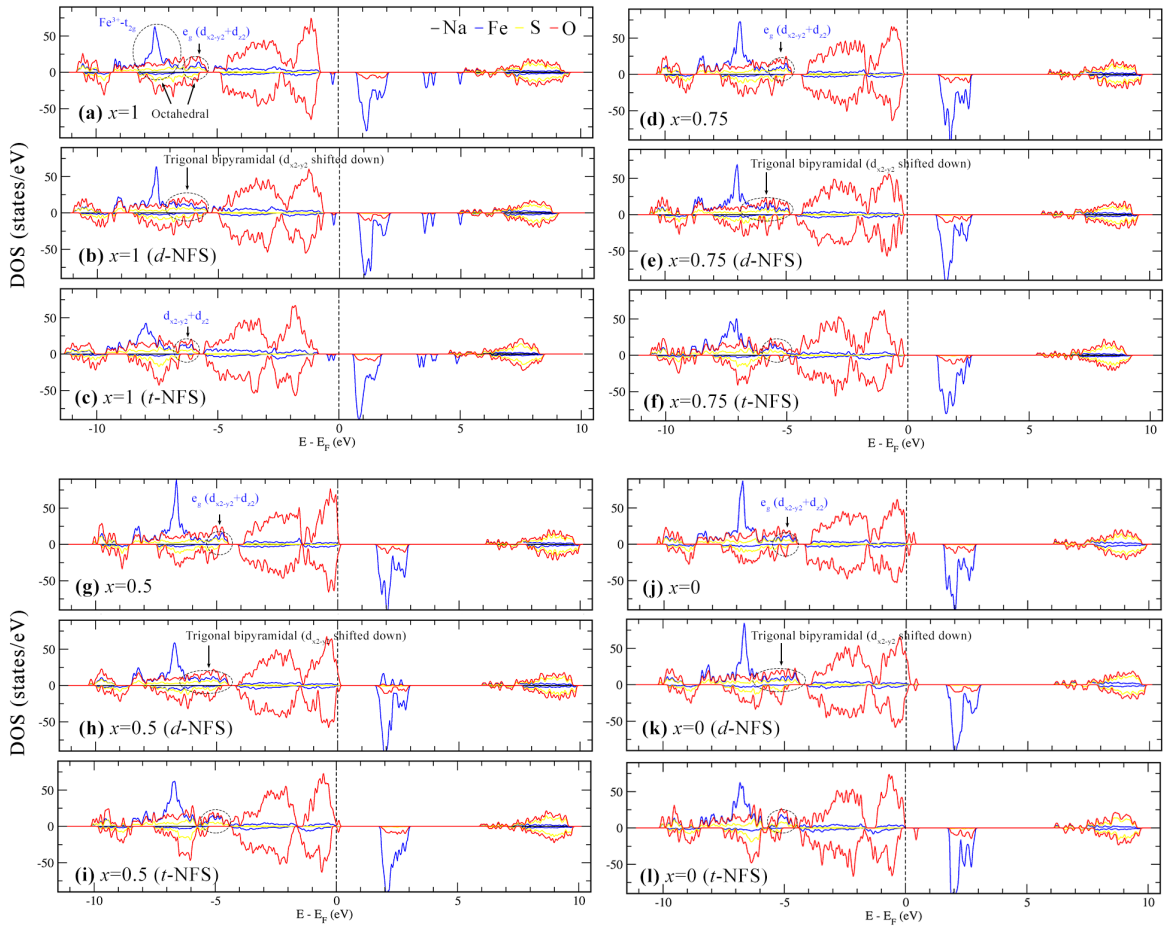

Figure S5 Density of states of desodiated $Na_xFe_{1.75}(SO_4)_3$ cathodes with (a-c) x = 1, (d-f) x = 0.75, (g-i) x = 0.5 and (j-l) x = 0 in three different phases; the original, *d*- and *t*-phases, respectively. The Fermi levels are set to zero and are represented by the dashed lines. Dashed-circles indicate the change in electronic state for each phase due to the different crystal field splitting around Fe, where the doubly degenerate state (e_g orbital; d_{x2-y2} and d_{z2}) is appeared due to FeO_6 octahedral field in the original and *t*-phase, and the lowering d_{x2-y2} orbital is preset due to FeO_5 trigonal bipyramidal field in *d*-phase.