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

Understanding the Sodium Ion Transport Properties，Deintercalation Mechanism, Phase Evolution of $Na_2Mn_2Si_2O_7$ Cathode by Atomistic Simulation

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Tab. S1 Interatomic potentials used for the $Na_2Mn_2Si_2O_7$ cathode material

interation	Dij/eV	Aij/Å^{-2}	r/ Å	Cij /eV ·Å^{12}
$O^{1.2-}$-- $O^{1.2-}$	0.042395	1.379316	3.618701	22.0[1]
$Si^{2.4+}$-- $O^{1.2-}$	0.340554	2.0067	2.1	1[1]
$Mn^{1.8+}$-- $O^{1.2-}$	0.818169	1.743523	2.216688	3
$Mn^{1.2+}$-- $O^{1.2-}$	0.029658	1.997543	2.852075	3[1]
$Na^{0.6+}$-- $O^{1.2-}$	0.02336	1.76387	3.00631	5[1]

Tab. S2 Input Fractional Coordinates of $Na_2Mn_2Si_2O_7$ (P21/c) structural parameters for calculation

ion	x	y	z	Occ.	site
Na1	0.17725	0.00175	0.03425	1	4e
Na2	0.029	0.0205	0.0845	1	4e
Mn1	0.2425	0.0295	0.20475	1	4e
Mn2	0.1125	0.0415	0.046	1	4e
Si1	0.07625	0.06125	0.18025	1	4e
Si2	0.154	0.04025	0.16775	1	4e
O1	0.23925	0.05225	0.15525	1	4e
O2	0.022	0.0095	0.17475	1	4e
O3	0.15425	0.03325	0.06675	1	4e
O4	0.006	0.04125	0.0175	1	4e
O5	0.07975	0.03875	0.093	1	4e
O6	0.20325	0.01375	0.20725	1	4e
O7	0.10375	0.0285	0.23375	1	4e

Tab. S3 Deviation (Δ) between calculated and experimental structures of the $Na_2Mn_2Si_2O_7$ cathode material from Pedone potential model used in MD calculations

parameter	calcd	exptl	Deviation Δ%
a	8.8566	8.757	1.14
b	13.4453	13.294	1.14
c	5.8074	5.744	1.10
α=β(deg)	90	90	--
γ	90.17	90.17	--

Tab. S4 Calculated and experimental bond lengths

ion pair	calcd (Å)	exptl (Å)	Δ /%
Na1-O4	2.48763	2.4231	2.66312
Na1-O7	2.38527	2.3377	2.03491
Na1-O5	2.39549	2.3381	2.45456
Na1-O3	2.37101	2.3266	1.90879
average Na1-O	2.4099	2.3564	2.27041
Na2-O6	2.43855	2.4034	1.46251
Na2-O3	2.36414	2.3503	0.58886
Na2-O4	2.61347	2.5167	3.84511
Na2-O7	2.45826	2.4091	2.0406
average Na2-O	2.4686	2.4199	2.01248
Mn1-O3	2.05745	2.0040	2.66717
Mn1-O7	2.05039	1.9837	3.3619
Mn1-O6	2.10279	2.0919	0.52058
Mn1-O2	2.13520	2.0965	1.84593
average Mn1-O	2.0865	2.0440	2.07926
Mn2-O5	2.08829	2.0342	2.65903
Mn2-O2	2.20287	2.1691	1.55687
Mn2-O4	2.14652	2.0564	4.38242
Mn2-O6	2.23579	2.1511	3.93706
Mn2-O2	2.44901	2.4040	1.8723
average Mn2-O	2.2245	2.1630	2.84327
Si1-O4	1.60220	1.6397	2.287
Si1-O2	1.58642	1.6365	3.06019
Si1-O1	1.63119	1.6641	1.97765
Si1-O6	1.57145	1.6110	2.455
average Si1-O	1.5978	1.6378	2.4423
Si2-O3	1.57471	1.5982	1.46978
Si2-O5	1.57872	1.5846	0.37107
Si2-O1	1.67100	1.7018	1.80985
Si2-O7	1.58439	1.6170	2.0167
average Si2-O	1.6022	1.6254	1.42734

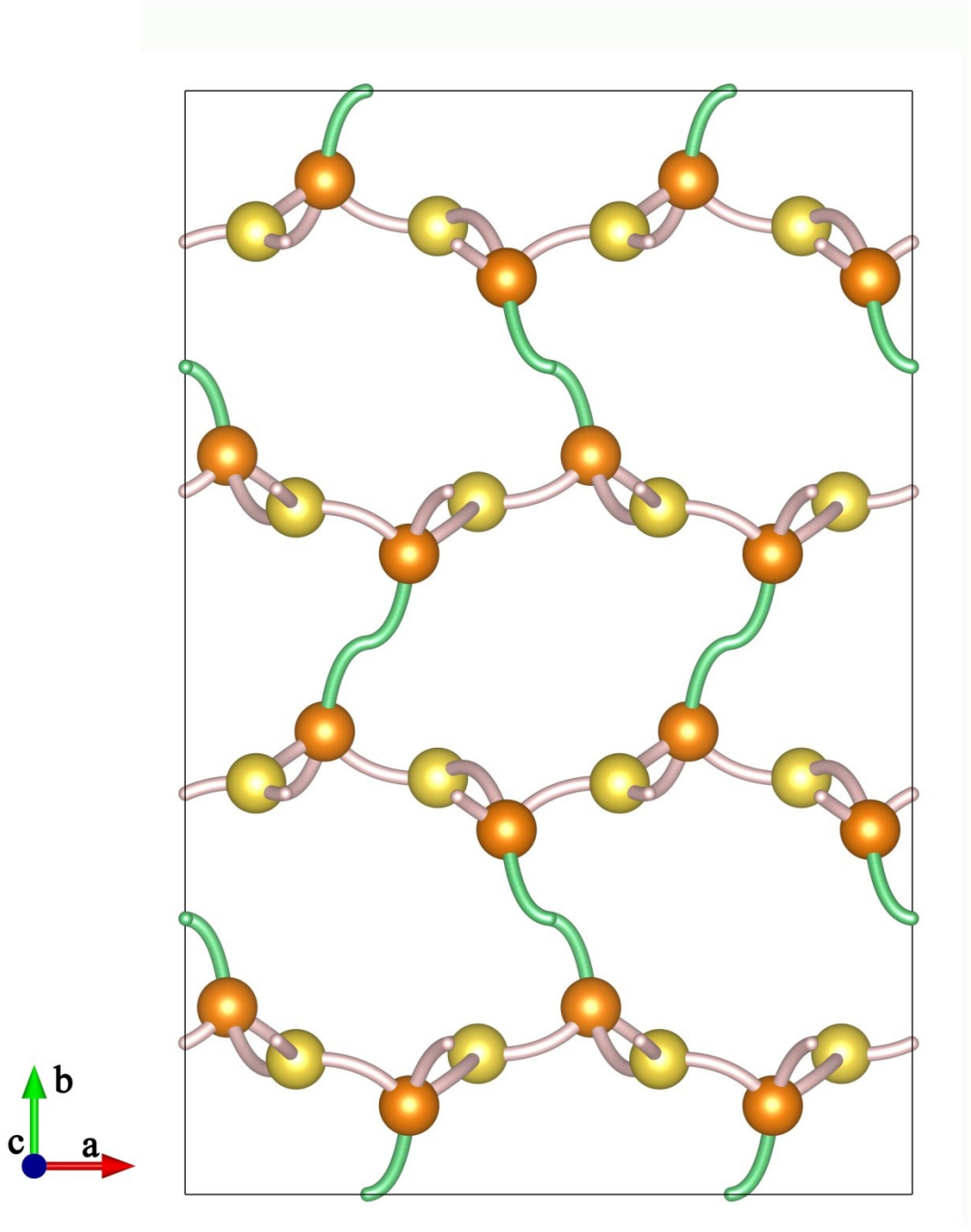

Fig. S1 c view of the panorama of the possible diffusion paths inside a 3×3×3 super cell

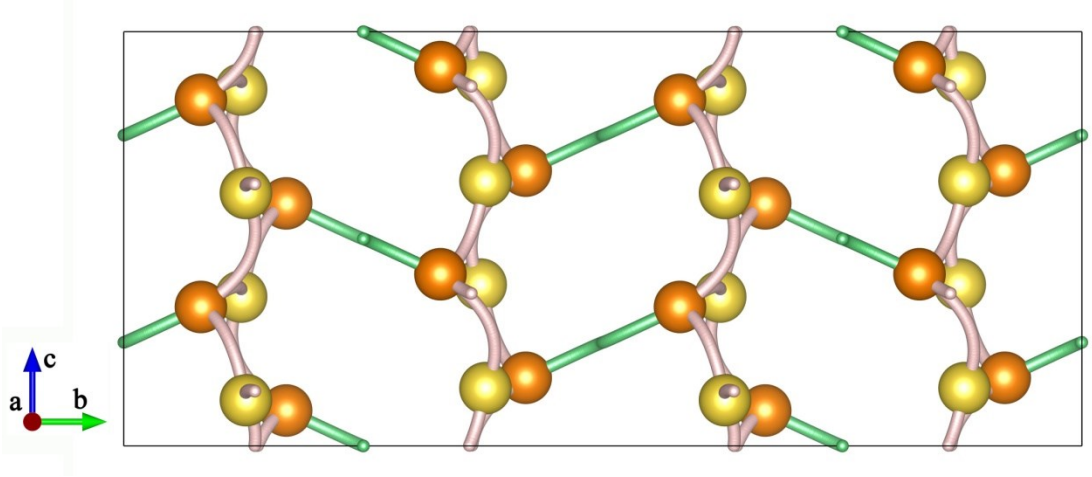

Fig. S2 a view of the panorama of the possible diffusion paths inside a 3×3×3 super cell

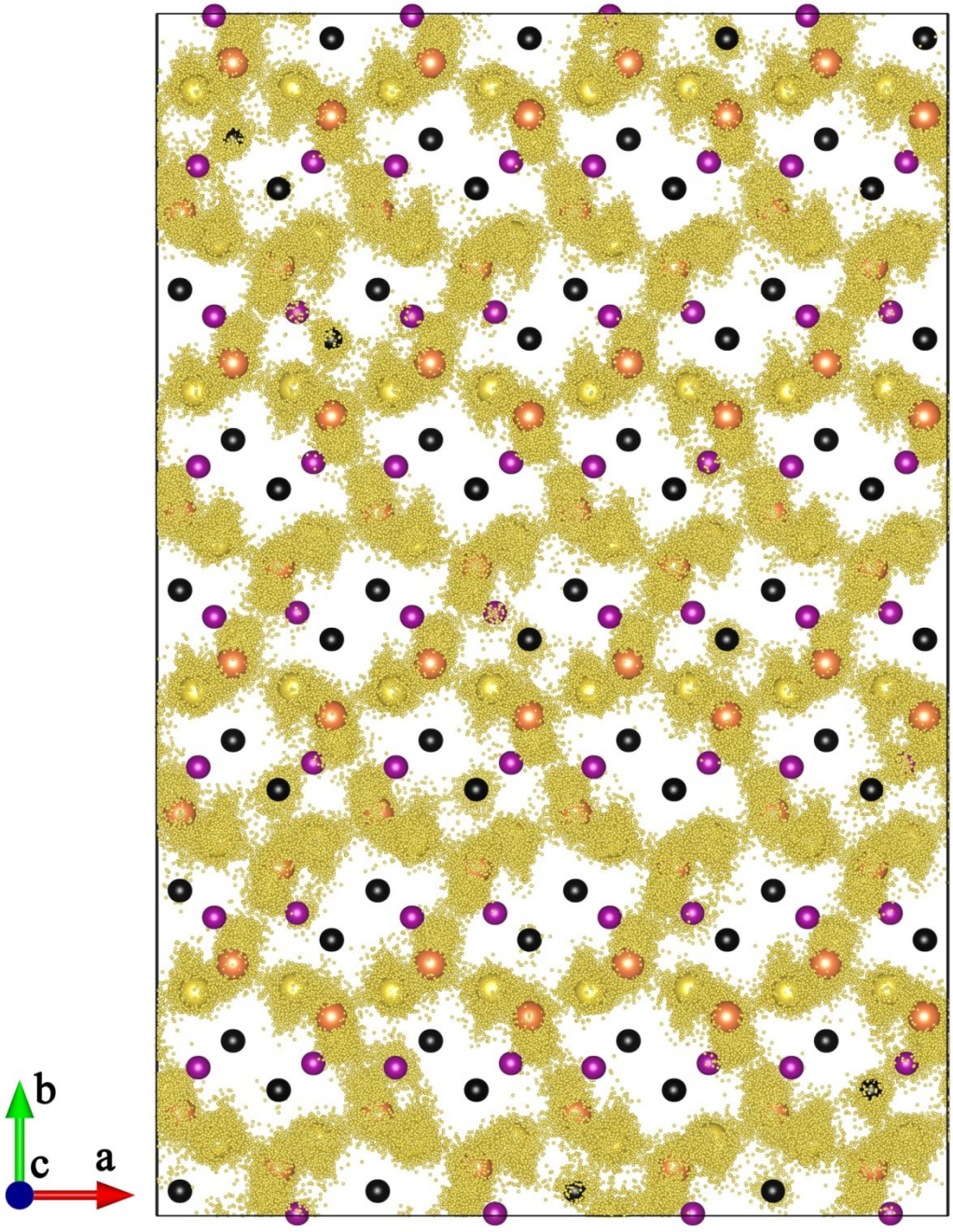

Fig. S3 c view image of the superimposed Na^+ trajectories combined with the positions of Na and Mn atoms at the simulation temperature of 1200 K

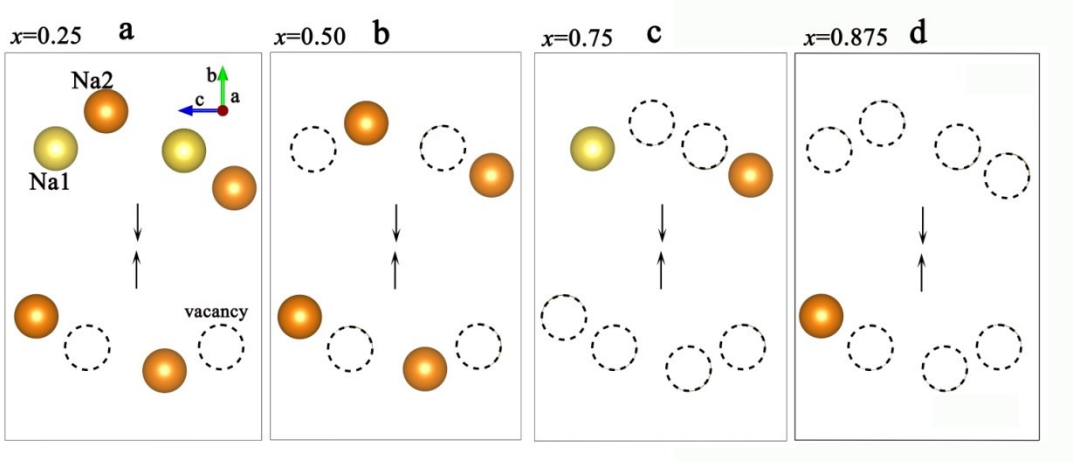

Fig. S4 The relaxed structure of the four intermediate phases at their base ground at deintercalation level x=0.25, 0.50, 0.75 and 0.875, respectively. The dash line circles indicate the vacancy realized by the deintercalation of the sodium ions; A pair of solid arrow lines suggests the inward movement of the left sodium ions with the deintercalation of the sodium ions;

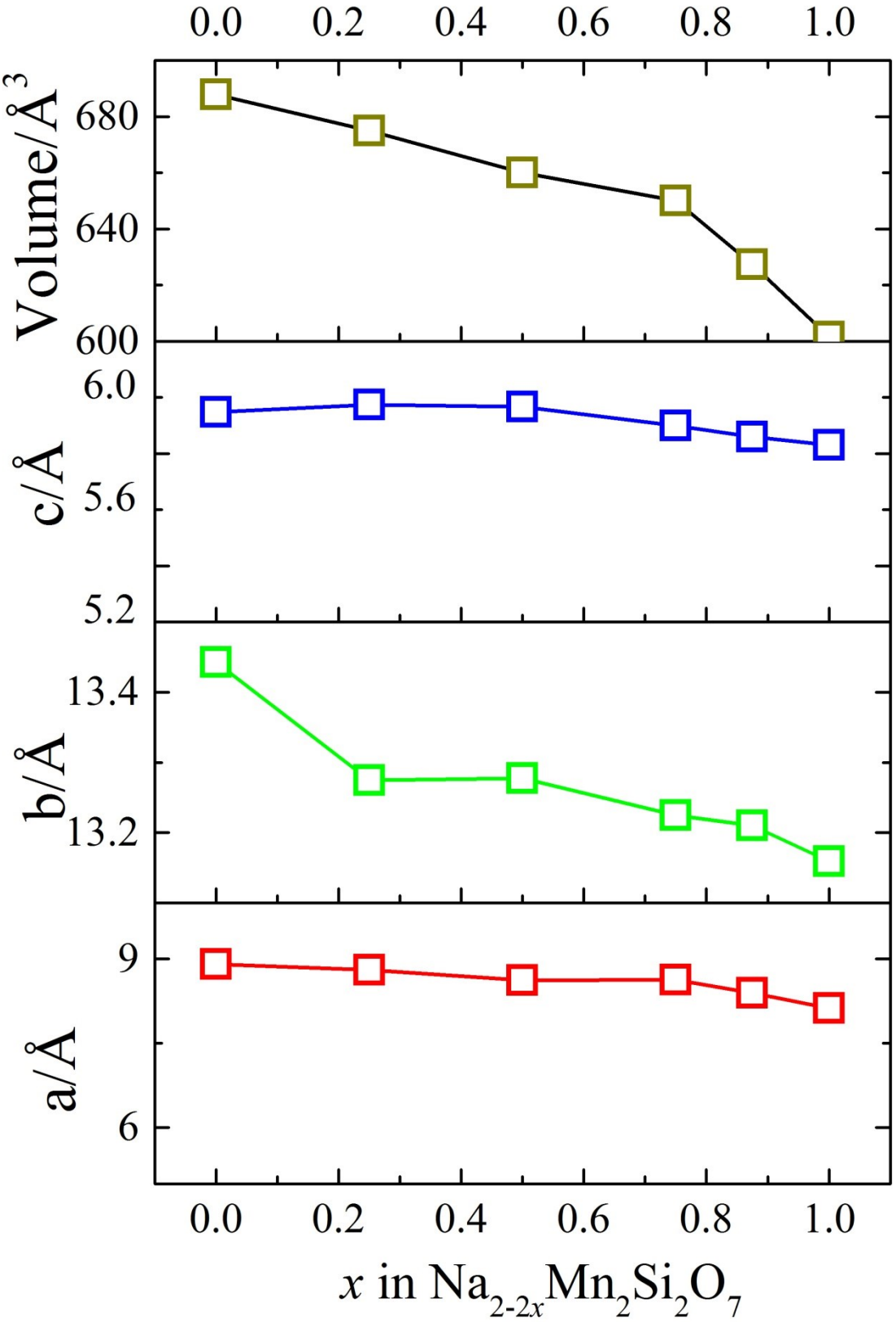

Fig. S5 The relationship between lattice parameter a, b, c and the cell volume and the deintercalation level *x*.

References

[1]Alfonso Pedone, Gianluca Malavasi, M. Cristina Menziani, Alastair N. Cormack and Ulderico Segre, *J. Phys. Chem. B*, 2016,**110**, 11780-11795.