Electronic Supplementary Information for

Structures, formation mechanisms, and ion-exchange properties of *α*-, *β*-, and *γ*-Na_2TiO_3

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S1. Supplementary Figures

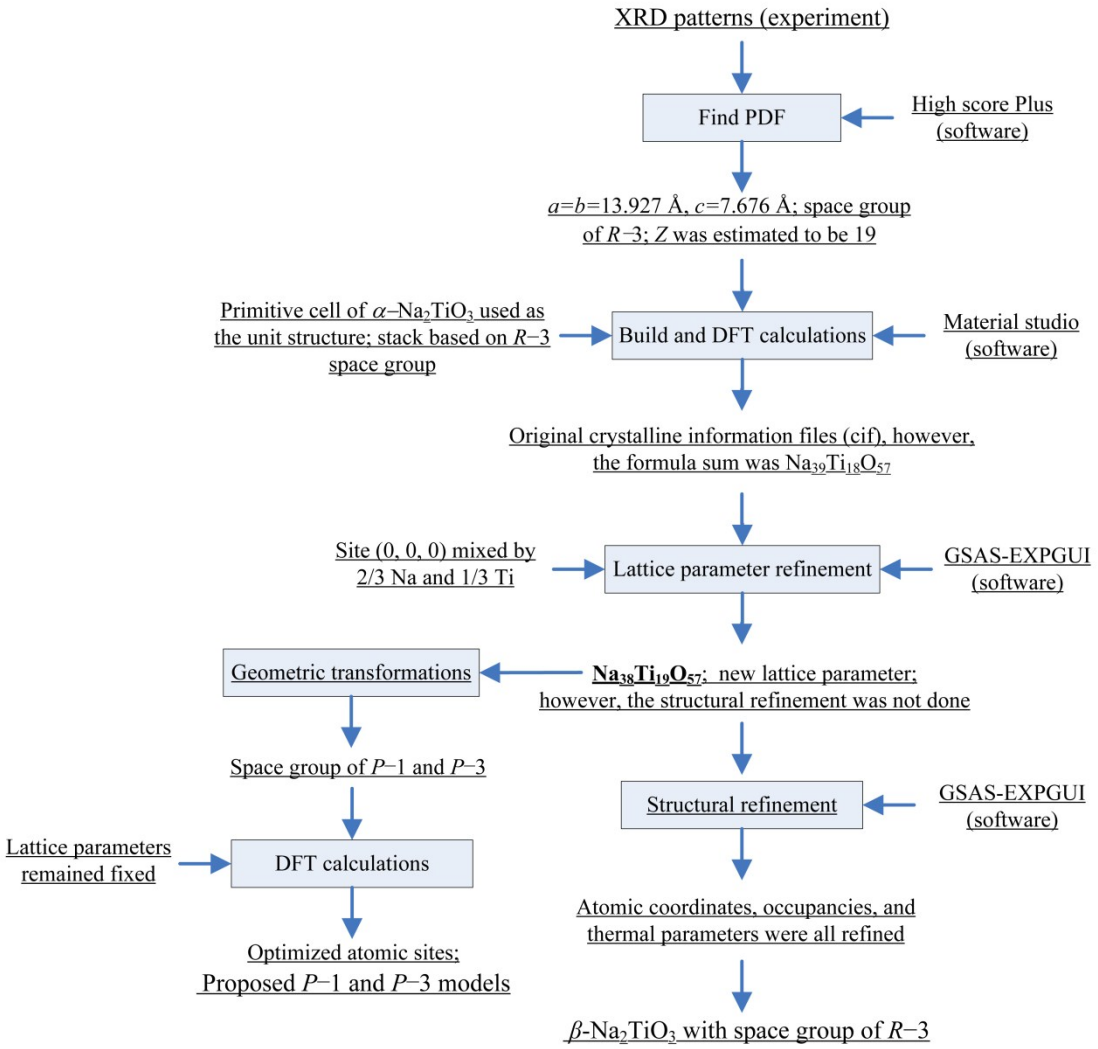

Fig. S1 The procedure of obtaining the crystal structures of β-Na_2TiO_3

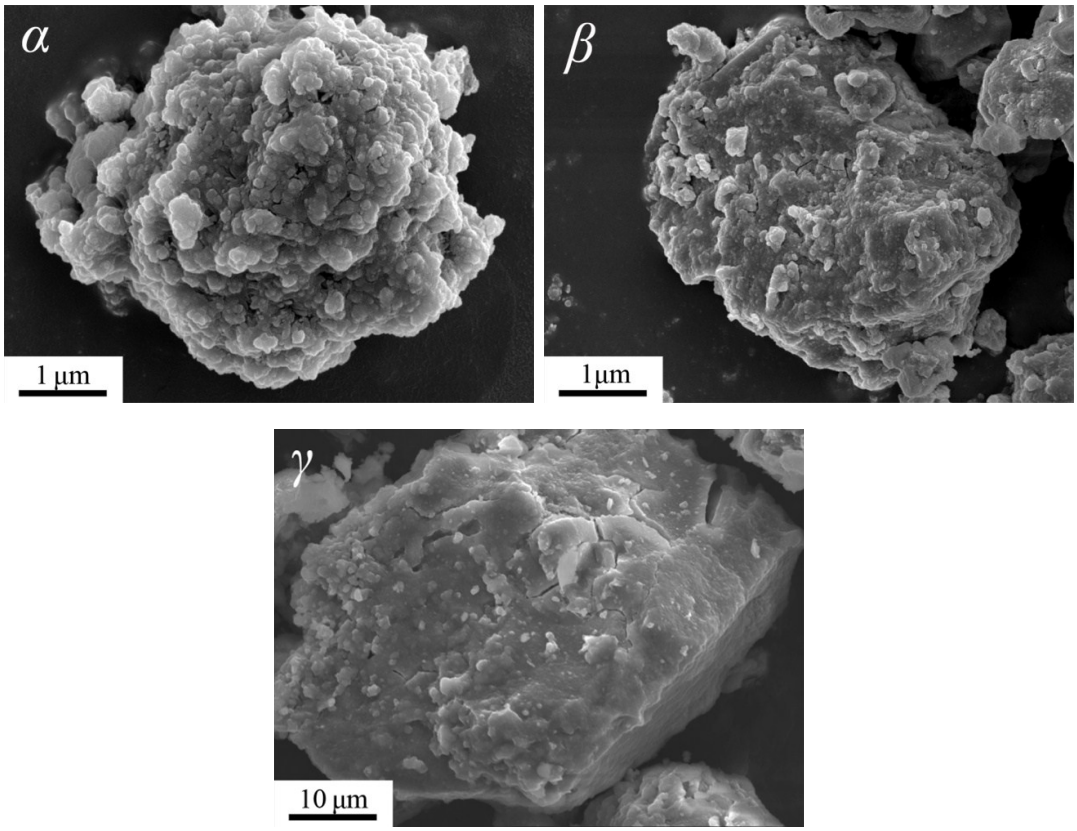

Fig. S2. SEM of the prepared α-, β- and γ-Na_2TiO_3.

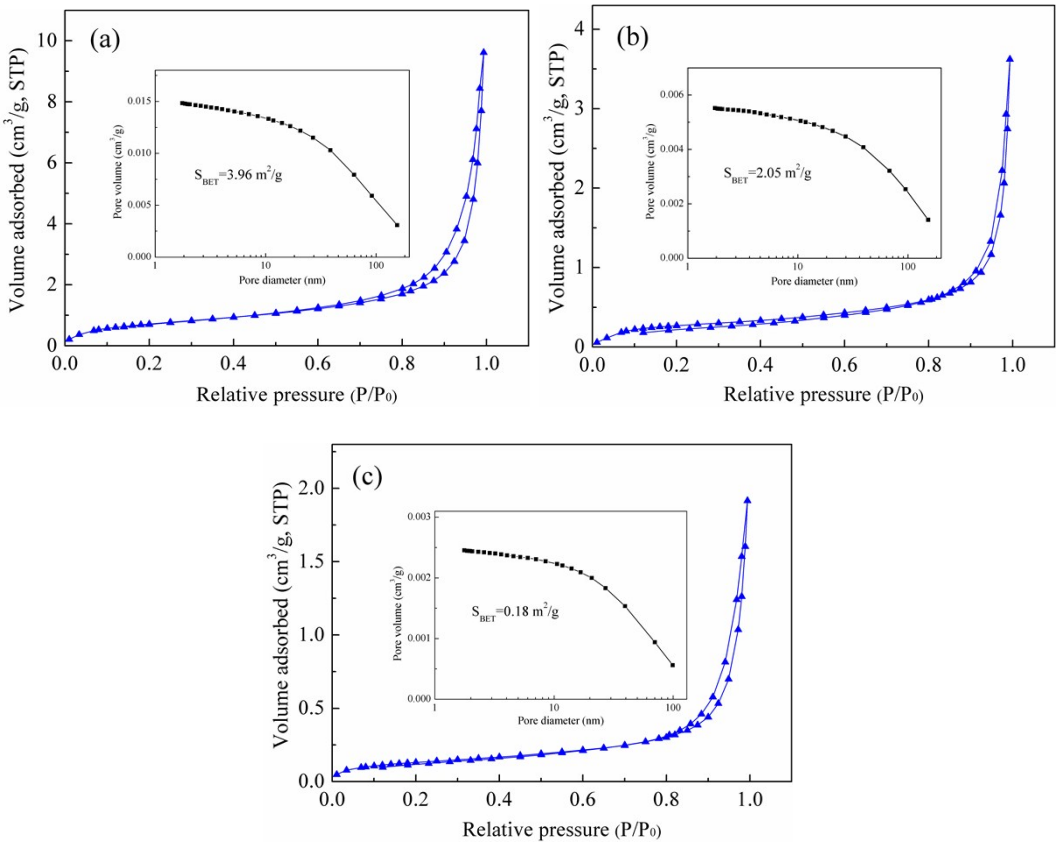

Fig. S3 N_2 adsorption–desorption isotherms and pore size distribution of the prepared of α-Na_2TiO_3 (a), β-Na_2TiO_3 (b), and γ-Na_2TiO_3 (c).

S2. Bond valence calculations of β-Na_2TiO_3 with space group $R\bar{3}$ with 2/3 Na and 1/3 Ti at site (0, 0, 0)

By revising the atomic site of Na (0, 0, 0) by both Na and Ti atoms (a Na/Ti mixing site), Na and Ti atoms occupy this site with 2/3 and 1/3 probability, respectively. The lattice parameters were refined by GSAS-EXPGUI software, $a = b = 13.9252$ Å, $c = 7.7024$ Å. The atomic sites were optimized from DFT calculations, as shown in see Table S1.

Table S1 Atomic sites of β-Na_2TiO_3 with the space group $R\bar{3}$ with 2/3 Na and 1/3 Ti at site (0, 0, 0)

Atoms	site	*x/a*	*y/b*	*z/c*	occupancy
O1	18f	0.6828	0.4557	0.5444	1.0000
O2	18f	0.0893	0.8607	0.5008	1.0000
O3	18f	0.2207	0.9681	0.8003	1.0000
O4	3b	2/3	1/3	1/6	1.0000
Na1	18f	0.1077	0.8451	0.0048	1.0000
Na2	18f	0.4191	0.3708	0.0093	1.0000
Ti1	18f	0.1412	0.1222	0.3336	1.0000
Na3	3a	0.0000	0.0000	0.0000	2/3
Ti2	3a	0.0000	0.0000	0.0000	1/3

Bond valence calculations were performed by Bond_Str program[1] with the obtained R−3 model, using the Brown-Altermatt empirical expression: Valence = $\Sigma\exp(R_o - d)/B$ with B = 0.37 Å.[2] The R_o values for Ti(+4)–O(−2) and Na(+1)–O(−2) were 1.803 and 1.81 Å，respectively.[3] For Na and Ti at (0, 0, 0), they are treated as one “new” atom named as M with the theoretical valence of +2. Considering the occupancies of Na and Ti at this site, the R_o value was estimated to be 1.808 Å while B = 0.37 Å. The bond valence sums (BVS) for the atoms and bond length between cations and anions in β-Na_2TiO_3 are presented in Tables S2 and S3, respectively. In Table S2, the discrepancies between calculated BVS and the theoretical values (O, −2; Ti, +4; Na, +1; M, +2) do not exceed 25%, and the maximum found for Na2. The equivalent M atom also gives an acceptable result.

Table S2 BVS of β-Na_2TiO_3 with the space group $R\bar{3}$ with 2/3 Na and 1/3 Ti at site (0, 0, 0)

	Na1	Na2	Ti1	M	Sum
O1	0.148 0.118	0.259	0.635 0.650	0.276 (×6)	2.087
O2	0.134	0.162 0.218 0.235	0.652 0.662		2.063
O3	0.276 0.269 0.238	0.100 0.268	1.054		2.205
O4			0.309(×6)		1.854
Sum	1.184	1.242	3.962	1.656	

Note: M is equivalent to 2/3 Na and 1/3 Ti at (0, 0, 0).

Table S3 Bond lengths (Å) in β-Na_2TiO_3 with space group of $R\bar{3}$ with 2/3 Na and 1/3 Ti at site (0, 0, 0) in comparison with the prediction from Bond Valence Model.

	Na1	Na2	Ti1	M	Average	Predicted
O1(b)	2.509 2.593	2.303	1.983 1.975	2.284	2.274	2.215
O2(b)	2.545	2.477 2.366 2.339	1.974 1.968		2.278	2.222
O3(t)	2.279 2.288 2.335	2.655 2.291	1.795		2.274	2.222
O4(c)			2.249		2.249	2.222
Average	2.425	2.405	1.991	2.284		
Predicted	2.466	2.466	1.965	2.215		

Note: (b) the bridged O atoms; (t) the terminal O atoms; (c) the central O atom. M is equivalent to 2/3 Na and 1/3 Ti at (0, 0, 0).

The ionic radii sums of six-coordination Na(+) and O(−2), Ti(+4) and O(−2) are 2.42 and 2.005 Å, respectively.[4] There are three kinds of O atoms in a Ti_6O_{19} cluster: the central O atoms linked by six Ti atoms, the bridged O atoms linked with two adjacent Ti atoms, and the terminal O atoms linked with one Ti atom. Tables S2 and S3 indicates that O(c) distribute its valence for its six neighboured Ti atoms, and gives Ti–O bond length of 2.249 Å, which is very close to the

prediction of 2.221 Å from the Bond Valence Model. There are very short bond related to Ti–O(t) of 1.795 Å in the trans-position of the TiO_6 octahedron. The average Ti1–O bond length is 1.991 Å, and the Na–O bond lengths corresponding to Na1 and Na2 are about 2.41 Å, which were all close the predictions of Bond Valence Model and their ionic radii sums. For the equivalent M atom, its bond length of 2.284 Å falls between the ionic radii sums, and is also close to the predicted value 2.215 Å.

β-Na_2TiO_3 supposedly contains the Ti_6O_{19} clusters. In β-Na_2TiO_3 with space group of $R\bar{3}$ with 2/3 Na and 1/3 Ti at site (0, 0, 0), one third of Ti_6O_{19} clusters are isolated and the rest 2/3 dimerized into $Ti_{13}O_{38}$ clusters by linking with an isolated octahedral Ti atom under the assumption of the uniform distribution of this bridging octahedra.

Reference

1. J. Rodriguez-Carvajal, *BONDSTR-Program for Distance, Angle and Bond Strength Calculations*, Laboratoire Leon Brillouin, Centre d'Etudes de Saclay, France, 1995.
2. I. D. Brown, *The Chemical Bond in Inorganic Chemistry. The Bond Valence Model*, 2002.
3. I. D. Brown and D. Altermatt, *Acta Crystallographica*, 1985, **41**, 244-247.
4. R. D. Shannon, *Acta Crystallographica*, 1976, **32**, 751–767.

S3. Supplementary Tables

Table S4 Atomic sites of β-Na_2TiO_3 with space group $P\bar{1}$ obtained from DFT calculations

Atoms	site	*x/a*	*y/b*	*z/c*	occupancy
O1	2i	0.5672	0.3407	0.2005	1.0000
Na2	2i	0.1950	0.1759	0.2197	1.0000
Na3	2i	0.2980	0.1752	0.3882	1.0000
Ti4	2i	0.6546	0.5052	0.2392	1.0000
O5	2i	0.9846	0.3383	0.3866	1.0000
O6	2i	0.8403	0.6412	0.4460	1.0000
O7	2i	0.8145	0.0475	0.2762	1.0000
Na8	2i	0.2101	0.8392	0.4141	1.0000
Na9	2i	0.0461	0.1739	0.4905	1.0000
Ti10	2i	0.5639	0.1724	0.2730	1.0000
O11	2i	0.4138	0.6356	0.2623	1.0000
O12	2i	0.1651	0.6430	0.3489	1.0000
O13	2i	0.8902	0.3382	0.2460	1.0000
Na14	2i	0.7465	0.8482	0.2013	1.0000
Na15	2i	0.4722	0.8509	0.3124	1.0000
Ti16	2i	0.9365	0.1681	0.3261	1.0000
O17	2i	0.5816	0.0492	0.3687	1.0000
O18	2i	0.6832	0.0274	0.5092	1.0000
O19	2i	0.7368	0.3512	0.4838	1.0000
Na20	2i	0.1287	0.4987	0.4471	1.0000
Na21	2i	0.0265	0.5016	0.2887	1.0000
Ti22	2i	0.6776	0.1589	0.4316	1.0000
O23	2i	0.3365	0.3404	0.2922	1.0000
O24	2i	0.4889	0.0371	0.2253	1.0000
O25	2i	0.5002	0.6313	0.4104	1.0000
Na26	2i	0.1121	0.8417	0.2514	1.0000
Na27	2i	0.2762	0.5012	0.1779	1.0000
Ti28	2i	0.7669	0.5056	0.3967	1.0000
O29	2i	0.9087	0.0448	0.4151	1.0000
O30	2i	0.1550	0.0380	0.3205	1.0000
O31	2i	0.4285	0.3537	0.4394	1.0000
Na32	2i	0.5829	0.8371	0.4621	1.0000
Na33	2i	0.8516	0.8252	0.3558	1.0000
Ti34	2i	0.3816	0.5105	0.3406	1.0000

O35	2i	0.7361	0.6321	0.3091	1.0000
O36	2i	0.6469	0.6391	0.1641	1.0000
O37	2i	0.6595	0.3411	0.3422	1.0000
O38	2i	0.0888	0.0014	0.1406	1.0000
Na39	2i	0.4704	0.1535	0.1133	1.0000
Na40	2i	0.3725	0.1546	0.9561	1.0000
Ti41	2i	0.0031	0.8339	0.0970	1.0000
O42	2i	0.6752	0.0058	0.9507	1.0000
O43	2i	0.8252	0.6982	0.8877	1.0000
O44	2i	0.8437	0.2971	0.0614	1.0000
Na45	2i	0.4502	0.4998	0.9206	1.0000
Na46	2i	0.6266	0.1727	0.8454	1.0000
Ti47	2i	0.0992	0.1654	0.0626	1.0000
O48	2i	0.2441	0.7046	0.0780	1.0000
O49	2i	0.4933	0.6956	0.9839	1.0000
O50	2i	0.7644	0.0043	0.0928	1.0000
Na51	2i	0.9129	0.5072	0.1271	1.0000
Na52	2i	0.1898	0.4890	0.0270	1.0000
Ti53	2i	0.7261	0.1740	0.0079	1.0000
O54	2i	0.0834	0.2881	0.9693	1.0000
O55	2i	0.9900	0.3005	0.8238	1.0000
Na56	2i	0.1735	0.8254	0.8339	1.0000
Ti57	1h	1/2	1/2	1/2	1.0000
O58	1a	0	1	1	1.0000

Table S5 Atomic sites of β-Na_2TiO_3 with space group $P\bar{3}$ obtained from DFT calculations

Atoms	site	*x/a*	*y/b*	*z/c*	occupancy
O1	6g	0.3469	0.7895	0.1225	1.0000
Na2	6g	0.7769	0.1769	0.9485	1.0000
Na3	6g	0.0841	0.7055	0.9459	1.0000
Ti4	6g	0.8095	0.4548	0.0596	1.0000
O5	6g	0.7538	0.1888	0.1198	1.0000
O6	6g	0.8918	0.2974	0.2142	1.0000
O7	6g	0.0138	0.1233	0.9003	1.0000
Na8	6g	0.4381	0.5155	0.0569	1.0000
Na9	6g	0.7506	0.0317	0.0578	1.0000
Ti10	6g	0.4753	0.7885	0.1650	1.0000
O11	6g	0.4264	0.5292	0.2223	1.0000
O12	6g	0.5557	0.6356	0.3242	1.0000
O13	6g	0.6834	0.4571	0.0201	1.0000
Na14	6g	0.1099	0.8437	0.1695	1.0000
Na15	6g	0.4213	0.3754	0.1768	1.0000
Ti16	6g	0.1427	0.1209	0.9432	1.0000
O17	6g	0.0935	0.8613	0.9998	1.0000
O18	6g	0.2216	0.9685	0.1022	1.0000
Na19	6g	0.5527	0.4894	0.2754	1.0000
Na20	6g	0.2503	0.9667	0.2762	1.0000
Ti21	6g	0.5165	0.2069	0.1696	1.0000
O22	6g	0.5785	0.4740	0.1181	1.0000
O23	6g	0.4482	0.3665	0.0138	1.0000
O24	6g	0.6522	0.2160	0.2247	1.0000
Ti25	6g	0.1916	0.5447	0.2784	1.0000
O26	6g	0.2403	0.8042	0.2226	1.0000
O27	6g	0.1098	0.6979	0.1213	1.0000
O28	6g	0.3193	0.5433	0.3221	1.0000
Na29	6g	0.8903	0.1425	0.1648	1.0000
Na30	6g	0.5862	0.6383	0.1649	1.0000
O31	6g	0.3478	0.7891	0.4606	1.0000
Na32	6g	0.7784	0.1766	0.2823	1.0000
Na33	6g	0.0908	0.7042	0.2807	1.0000
Ti34	6g	0.8136	0.4600	0.3891	1.0000
O35	6g	0.7601	0.1965	0.4406	1.0000
O36	6g	0.8880	0.3026	0.5436	1.0000

O37	6g	0.0150	0.1227	0.2407	1.0000
Na38	6g	0.4371	0.5149	0.3904	1.0000
Na39	6g	0.7528	0.0362	0.3928	1.0000
Ti40	6g	0.4737	0.7890	0.5004	1.0000
O41	6g	0.4264	0.5285	0.5579	1.0000
O42	6g	0.5585	0.6339	0.6548	1.0000
O43	6g	0.6792	0.4498	0.3355	1.0000
Na44	6g	0.1107	0.8427	0.5025	1.0000
Na45	6g	0.4165	0.3661	0.5033	1.0000
Ti46	6g	0.1394	0.1225	0.2809	1.0000
O47	6g	0.0908	0.8606	0.3407	1.0000
O48	6g	0.2254	0.9666	0.4363	1.0000
O49	6g	0.9860	0.8832	0.4447	1.0000
Na50	6g	0.2271	0.8162	0.3857	1.0000
Na51	6g	0.9170	0.3030	0.3853	1.0000
Ti52	6g	0.8523	0.8720	0.3914	1.0000
O53	6g	0.9089	0.1388	0.3391	1.0000
O54	6g	0.7774	0.0281	0.2376	1.0000
Na55	2d	2/3	1/3	0.9484	1.0000
O56	2d	2/3	1/3	0.1221	1.0000
Ti57	2d	2/3	1/3	0.2780	1.0000
O58	2d	2/3	1/3	0.4398	1.0000
Na59	2c	1	1	0.1680	1.0000
O60	2c	1	1	0.3414	1.0000
O61	2d	1/3	2/3	0.2236	1.0000
Na62	2d	1/3	2/3	0.3871	1.0000
O63	1a	1	1	0	1.0000
Ti64	1b	1	1	1/2	1.0000