Supporting Information

for

Compositionally Enhanced Flexibility in a Ga-Rich Zeolite Affords Unusual Structural Changes via Alkali Ion Exchange

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Structural Analysis

To determine the crystal structures of various alkali ion-exchanged PST-1 samples in both hydrated and dehydrated states, synchrotron powder XRD data were collected on the 9B beamline equipped with a ceramic furnace of the Pohang Acceleration Laboratory (Pohang, Korea) using monochromated X-rays. The detector arm of the vertical scan diffractometer consists of seven sets of Soller slits, flat Ge(111) crystal analyzers, antiscatter baffles, and scintillation detectors, with each set separated by 20°. Data were obtained on the sample at room temperature and 100 °C for hydrated (and partially dehydrated) and dehydrated samples, respectively, in flat plate mode, with a step size of 0.01° and overlaps of 1° to the next detector bank over the 2θ range 10°-131°.

The framework structure and extraframework cation positions were determined by direct methods using the program EXPO2009.[1] The structural refinements were performed by Rietveld method[2] using the GSAS suite of programs[3] and EXPGUI graphical interface.[4] The background was refined using the Chebyschev polynomial function, and the pseudo-Voigt profile function was used to fit the observe peaks.[5] Geometrical soft-restraints on the T-O (T = Si, Ga) and O-O bond distances of the tetrahedral were applied: the distances between (Si,Ga)-O were restrained to target value of (mean) 1.712 ± 0.002 Å and the O-O distances to (mean) 2.789 ± 0.005 Å for the (Si,Ga) tetrahedral. These mean values were used by assuming that all T-sites are disordered such that contain about 44% Ga and 56% Si. The additional extraframework cations and water molecules were located along the elliptical channels from Fourier difference maps. Difference Fourier peaks located at reasonable distances from the framework atoms were investigated as possible sites by refinement of occupancy and position. The total extraframework cation concentration was constrained to its chemically determined value. In the final stage of the refinements, the weight of the soft-restrain was reduced, which did not lead to any significant changes for the interatomic distances. The isotropic displacement factors were refined by grouping the framework tetrahedral atoms, the framework oxygen atoms, the non-framework cations, and water oxygen atoms, respectively. The convergence was achieved by refining simultaneously profile parameters, scale factor, lattice constants, 2θ zero, the atomic positional, thermal displacement parameters, and occupancy factors for the extraframework cations and water oxygen atoms. A summary of the crystallographic data is presented in Table S1. The final refined structural parameters are given in Tables S2-S5, and selected interatomic distances

and angles can be found in Table S6. Their final Rietveld plots are displayed in Figures S1-S4, providing a good agreement of the observed and simulated powder diffraction patterns.

Analytical methods

Crystal morphology was determined by a Hitachi S-4700 scanning electron microscope (SEM). Thermogravimetric and differential thermal analyses (TGA/DTA) were performed in air on an SII EXSTAR 6000 thermal analyzer as a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (XRD) patterns were recorded on a PANalytical X´Pert diffractometer (Cu Kα radiation) with an X´Celerator detector. In situ variable-temperature XRD experiments were performed in Bragg-Brentano geometry using the same diffractometer equipped with an Edmund Bühler HDK 1.4 high-temperature attachment.

Table S1. Crystallographic Data for Various Alkali Ion-Exchanged PST-1 Zeolites in Hydrated and (Partially) Dehydrated States

material	hydrated Na-PST-1	partially dehydrated Na-PST-1	as-made hydrated K-PST-1	dehydrated K-PST-1	hydrated Rb-PST-1	dehydrated Rb-PST-1	hydrated Cs-PST-1
unit cell composition[a]	$\|Na_{8.0}(H_2O)_{12.7}\|$-$[Ga_{8.8}Si_{11.2}O_{40}]$	$\|Na_{8.0}(H_2O)_{11.1}\|$-$[Ga_{8.8}Si_{11.2}O_{40}]$	$\|K_{16.0}(H_2O)_{22.1}\|$-$[Ga_{17.5}Si_{22.5}O_{80}]$	$\|K_{8.0}\|$-$[Ga_{8.8}Si_{11.2}O_{40}]$	$\|Rb_{8.0}(H_2O)_{11.2}\|$-$[Ga_{8.8}Si_{11.2}O_{40}]$	$\|Rb_{8.0}\|$-$[Ga_{8.8}Si_{11.2}O_{40}]$	$\|Cs_{16.0}\|$-$[Ga_{17.5}Si_{22.5}O_{80}]$
symmetry	monoclinic	tetragonal	orthorhombic	tetragonal	tetragonal	tetragonal	orthorhombic
space group (No.)	*Cc* (9)	$I\bar{4}2d$ (122)	*Fdd*2 (43)	$I\bar{4}2d$ (122)	$I\bar{4}2d$ (122)	$I\bar{4}2d$ (122)	*Fdd*2 (43)
a, Å	6.65531(21)	13.18696(4)	19.23393(12)	12.4864(3)	13.87867(3)	12.68344(13)	18.6217(6)
b, Å	19.2867(3)	13.18696(4)	19.30226(11)	12.4864(3)	13.87867(3)	12.68344(13)	18.7021(5)
c, Å	10.09792(17)	6.72418(3)	6.528780(24)	6.52359(9)	6.61213(4)	6.61739(9)	6.63975(8)
β, °	71.7769(20)	90	90	90	90	90	90
unit cell volume, Å^3	1231.2	1169.3	1211.9 (×2)	1017.1	1273.6	1064.5	1156.2 (×2)
X-ray source	Beamline 9B, Pohang Accelerator Laboratory (PAL)						
wavelength, Å	1.5490	1.5472	1.5406	1.5406	1.5494	1.5494	1.5494
no. of observation	627	297	574	268	324	273	538
no. of parameters	120	61	93	65	52	66	48
no. of restraints	50	18	29	19	20	19	28
R_p, %	9.61	7.86	9.56	10.72	8.29	8.11	6.53
R_{wp}, %	12.48	11.01	12.89	13.84	10.61	11.62	9.09
R_F^2, %	8.18	11.29	8.20	12.01	13.19	11.71	8.33
χ^2	9.890	8.859	1.756	3.857	2.763	11.35	5.597
goodness of fit	3.14	2.98	1.66	1.96	1.66	3.37	2.37

[a]Determined by refinement of powder diffraction data.

Table S2. Atomic Coordinates and Displacement and Population Parameters for Hydrated and Partially Dehydrated Na-PST-1 Zeolites

atom	*x*	*y*	*z*	U_{iso}, $10^2 \times Å^2$	multi.	occupancy
	hydrated Na-PST-1 (space group *Cc*)					
Si1	0.4557(7)	0.12527(19)	0.1521(4)	1.902(21)	4	0.5614
Si2	0.2470(6)	0.33329(18)	0.83964(29)	1.902(21)	4	0.5614
Si3	0.4073(6)	0.41597(18)	0.47993(27)	1.902(21)	4	0.5614
Si4	0.0344(6)	0.03710(17)	0.24353(29)	1.902(21)	4	0.5614
Si5	0.1130(6)	0.21415(17)	0.07192(31)	1.902(21)	4	0.5614
Ga1	0.4557(7)	0.12527(19)	0.1521(4)	1.902(21)	4	0.4386
Ga2	0.2470(6)	0.33329(18)	0.8396(3)	1.902(21)	4	0.4386
Ga3	0.4073(6)	0.41597(18)	0.4799(3)	1.902(21)	4	0.4386
Ga4	0.0344(6)	0.03710(17)	0.2435(3)	1.902(21)	4	0.4386
Ga5	0.1130(6)	0.21415(17)	0.0719(3)	1.902(21)	4	0.4386
O1	0.4194(10)	0.4638(4)	0.6167(4)	2.77(11)	4	1.0
O2	0.4916(19)	0.45735(26)	0.3235(5)	2.77(11)	4	1.0
O3	0.0684(10)	0.15349(25)	0.9689(6)	2.77(11)	4	1.0
O4	0.3274(7)	0.19719(29)	0.1247(6)	2.77(11)	4	1.0
O5	0.1489(19)	0.29555(25)	0.9994(5)	2.77(11)	4	1.0
O6	0.8949(10)	0.22216(34)	0.2184(5)	2.77(11)	4	1.0
O7	0.5554(7)	0.1336(5)	0.2824(4)	2.77(11)	4	1.0
O8	0.9095(10)	0.09989(25)	0.3616(6)	2.77(11)	4	1.0
O9	0.6498(7)	0.1065(5)	0.9989(6)	2.77(11)	4	1.0
O10	0.2979(7)	0.05319(29)	0.1824(9)	2.77(11)	4	1.0
Na1	0.3761(18)	0.4109(5)	0.0970(6)	2.13(15)	4	1.0
Na2	0.8071(20)	0.3482(5)	0.2142(7)	2.13(15)	4	1.0
OW1	0.610(6)	0.3198(11)	1.0643(19)	6.46(33)	4	0.660(12)
OW2	0.311(4)	0.2908(9)	0.2738(13)	6.46(33)	4	0.848(14)
OW3	0.0439(34)	0.4303(8)	0.2845(12)	6.46(33)	4	1.0
OW4	0.316(4)	0.0850(11)	0.5369(17)	6.46(33)	4	0.659(14)
	partially dehydrated Na-PST-1 (space group $I\bar{4}2d$)					
Si1	0	0	0	0.831(14)	4	0.5614
Si2	0.05799(8)	0.63144(7)	0.62755(21)	0.831(14)	16	0.5614
Ga1	0	0	0	0.831(14)	4	0.4386
Ga2	0.05799(8)	0.63144(7)	0.62755(21)	0.831(14)	16	0.4386
O1	0.11457(31)	0.75	0.625	1.36(7)	8	1.0
O2	0.05399(22)	0.59246(17)	0.3899(4)	1.36(7)	16	1.0
O3	0.94189(21)	0.63908(21)	0.7313(6)	1.36(7)	16	1.0
Na1	0.30641(22)	0.2454(12)	0.1153(32)	1.86(10)	16	0.5
OW1	0.87450(34)	0.251(6)	0.134(8)	10.00(24)	16	0.699(4)

Table S3. Atomic Coordinates and Displacement and Population Parameters for Hydrated (As-Made) and Dehydrated K-PST-1 Zeolites

atom	*x*	*y*	*z*	U_{iso}, $10^2 \times Å^2$	multi.	occupancy
	hydrated (as-made) K-PST-1 (space group *Fdd*2)					
Si1	0	0	-0.0098(4)	2.530(16)	8	0.5614
Si2	0.08246(9)	0.55097(9)	0.10607(25)	2.530(16)	16	0.5614
Si3	0.19838(9)	0.16716(8)	0.61907(25)	2.530(16)	16	0.5614
Ga1	0	0	-0.0098(4)	2.530(16)	8	0.4386
Ga2	0.08246(9)	0.55097(9)	0.10607(25)	2.530(16)	16	0.4386
Ga3	0.19838(9)	0.16716(8)	0.61907(25)	2.530(16)	16	0.4386
O1	0.19159(13)	0.20494(14)	0.38439(34)	2.65(7)	16	1.0
O2	0.16405(13)	0.58600(13)	0.1117(10)	2.65(7)	16	1.0
O3	0.40692(21)	0.03370(12)	0.0455(5)	2.65(7)	16	1.0
O4	0.03384(12)	0.09408(19)	0.4300(5)	2.65(7)	16	1.0
O5	0.29514(15)	0.19202(13)	0.09242(34)	2.65(7)	16	1.0
K1	0.1178(4)	0.1335(4)	0.1032(20)	3.06(8)	16	0.3359(3)
K2	0.0857(5)	0.1642(4)	0.1017(20)	3.06(8)	16	0.2882(4)
K3	0.1461(4)	0.10308(33)	0.1105(19)	3.06(8)	16	0.3761(3)
OW1	0.7310(8)	-0.0109(6)	-0.1637(26)	10.522	16	0.683(7)
OW2	0.2207(7)	0.0270(6)	0.2002(17)	10.522	16	0.699(7)
	dehydrated K-PST-1 (space group $I\bar{4}2d$)					
Si1	0	0	0	2.823(34)	4	0.5614
Si2	0.13200(15)	0.07317(17)	0.38480(26)	2.823(34)	16	0.5614
Ga1	0	0	0	2.823(34)	4	0.4386
Ga2	0.13200(15)	0.07317(17)	0.38480(26)	2.823(34)	16	0.4386
O1	0.6447(5)	0.25	0.125	11.13(26)	8	1.0
O2	0.08724(22)	0.04819(33)	0.16380(31)	11.13(26)	16	1.0
O3	0.45427(24)	0.16337(31)	0.2536(6)	11.13(26)	16	1.0
K1	0.8789(4)	0.25	0.125	5.90(14)	8	1.0

Table S4. Atomic Coordinates and Displacement and Population Parameters for Hydrated and Dehydrated Rb-PST-1 Zeolites

atom	*x*	*y*	*z*	U_{iso}, $10^2 \times Å^2$	multi.	occupancy
	hydrated Rb-PST-1 (space group $I\bar{4}2d$)					
Si1	0	0	0	1.453(13)	4	0.5614
Si2	0.47743(6)	0.13128(6)	0.13063(19)	1.453(13)	16	0.5614
Ga1	0	0	0	1.453(13)	4	0.4386
Ga2	0.47743(6)	0.13128(6)	0.13063(19)	1.453(13)	16	0.4386
O1	0.43710(24)	0.25	0.125	1.54(6)	8	1.0
O2	0.10152(10)	0.01298(18)	0.14465(25)	1.54(6)	16	1.0
O3	0.37963(16)	0.06157(14)	0.1913(4)	1.54(6)	16	1.0
Rb1	0.05310(11)	0.25	0.125	7.22(5)	8	0.6018(3)
Rb2	0.97763(30)	0.25	0.125	7.22(5)	8	0.2266(7)
Rb3	0.8588(4)	0.25	0.125	7.22(5)	8	0.1653(8)
OW1	0.7300(4)	0.22032(32)	0.0002(8)	9.87(25)	16	0.7017(24)
	dehydrated Rb-PST-1 (space group $I\bar{4}2d$)					
Si1	0	0	0	2.236(31)	4	0.5614
Si2	0.06946(13)	0.63041(12)	0.6270(4)	2.236(31)	16	0.5614
Ga1	0	0	0	2.236(31)	4	0.4386
Ga2	0.06946(13)	0.63041(12)	0.6270(4)	2.236(31)	16	0.4386
O1	0.1339(6)	0.75	0.625	8.15(20)	8	1.0
O2	0.0556(4)	0.59002(31)	0.3956(7)	8.15(20)	16	1.0
O3	0.9474(4)	0.6460(4)	0.7268(9)	8.15(20)	16	1.0
Rb1	0.86482(11)	0.25	0.125	2.774(28)	8	1.0

Table S5. Atomic Coordinates and Displacement and Population Parameters for Dehydrated Cs-PST-1 Zeolite

atom	*x*	*y*	*z*	U_{iso}, $10^2 \times Å^2$	multi.	occupancy
	dehydrated Cs-PST-1 (space group *Fdd*2)					
Si1	0	0	0.0077(6)	0.476(25)	8	0.5614
Si2	0.15588(16)	0.21335(16)	0.6355(5)	0.476(25)	16	0.5614
Si3	0.54029(15)	0.09470(16)	0.1252(5)	0.476(25)	16	0.5614
Ga1	0	0	0.0115(7)	0.476(25)	8	0.4386
Ga2	0.15588(16)	0.21335(16)	0.6355(5)	0.476(25)	16	0.4386
Ga3	0.54029(15)	0.09470(16)	0.1252(5)	0.476(25)	16	0.4386
O1	0.28357(30)	0.18351(18)	0.1141(5)	3.54(17)	16	1.0
O2	0.56829(21)	0.18216(21)	0.1312(18)	3.54(17)	16	1.0
O3	0.09995(28)	0.04444(20)	0.4967(8)	3.54(17)	16	1.0
O4	0.04211(20)	0.40671(30)	0.0184(8)	3.54(17)	16	1.0
O5	0.18058(18)	0.22025(33)	0.3957(5)	3.54(17)	16	1.0
Cs1	0.04905(9)	0.19705(11)	0.1337(25)	5.510(32)	16	1.0

Table S6. Selected Interatomic Distances (Å) and Angles (°) for Various Alkali Ion-Exchanged PST-1 Zeolites in Hydrated and (Partially) Dehydrated States[a]

	hydrated Na-PST-1	partially dehydrated Na-PST-1	hydrated K-PST-1	dehydrated K-PST-1	hydrated Rb-PST-1	dehydrated Rb-PST-1	dehydrated Cs-PST-1
(Si,Ga)1-O1	-	-	1.705(3) ×2	-	-	-	1.687(4) ×2
(Si,Ga)1-O2	-	1.697(3) ×4	-	1.63985(4) ×4	1.7124(15) ×4	1.652(4) ×4	-
(Si,Ga)1-O4	1.69680(2)	-	-	-	-	-	-
(Si,Ga)1-O5	-	-	1.714(3) ×2	-	-	-	1.679(4) ×2
(Si,Ga)1-O7	1.65585(3)	-	-	-	-	-	-
(Si,Ga)1-O9	1.71574(5)	-	-	-	-	-	-
(Si,Ga)1-O10	1.71117(3)	-	-	-	-	-	-
(Si,Ga)1-O (mean)	1.69489(2)	1.697(3)	1.710(2)	1.63985(4)	1.7124(15)	1.652(4)	1.683(3)
(Si,Ga)2-O1	-	1.7322(20)	-	1.72471(6)	1.7405(14)	1.723(4)	-
(Si,Ga)2-O2	-	1.680(3)	1.709(3)	1.57806(3)	1.688(2)	1.624(5)	1.732(5)
(Si,Ga)2-O3	-	1.685(3), 1.727(3)	1.694(3)	1.72019(5), 1.72090(5)	1.665(2), 1.714(2)	1.689(5), 1.695(5)	1.690(5)
(Si,Ga)2-O4	-	-	1.700(3)	-	-	-	1.685(6)
(Si,Ga)2-O5	1.70304(3)	-	1.707(3)	-	-	-	1.662(5)
(Si,Ga)2-O6	1.69021(3)	-	-	-	-	-	-
(Si,Ga)2-O7	1.68194(4)	-	-	-	-	-	-
(Si,Ga)2-O8	1.74076(3)	-	-	-	-	-	-
(Si,Ga)2-O (mean)	1.70444(2)	1.706(1)	1.703(2)	1.68597(2)	1.700(1)	1.683(2)	1.692(3)
(Si,Ga)3-O1	1.68325(2)	-	1.702(3)	-	-	-	1.676(5)
(Si,Ga)3-O2	1.70094(3)	-	1.701(3)	-	-	-	1.717(5)
(Si,Ga)3-O3	1.69762(3)	-	1.692(3)	-	-	-	1.687(6)
(Si,Ga)3-O4	-	-	1.705(3)	-	-	-	1.691(5)
(Si,Ga)3-O9	1.71921(5)	-	-	-	-	-	-
(Si,Ga)3-O (mean)	1.70505(2)	-	1.700(2)	-	-	-	1.693(3)
(Si,Ga)4-O1	1.68480(3)	-	-	-	-	-	-
(Si,Ga)4-O2	1.71890(2)	-	-	-	-	-	-
(Si,Ga)4-O8	1.72035(3)	-	-	-	-	-	-
(Si,Ga)4-O10	1.69615(6)	-	-	-	-	-	-
(Si,Ga)4-O (mean)	1.70505(2)	-	-	-	-	-	-
(Si,Ga)5-O3	1.65267(2)	-	-	-	-	-	-
(Si,Ga)5-O4	1.70362(5)	-	-	-	-	-	-
(Si,Ga)5-O5	1.71713(2)	-	-	-	-	-	-
(Si,Ga)5-O6	1.72521(5)	-	-	-	-	-	-

(Si,Ga)5-O (mean)	1.69966(2)	-	-	-	-	-	-
M1-O1	2.44921(4)	2.565(17) ×2	2.699(11)	2.92519(11), 3.27536(7) ×2	3.30886(15) ×2	2.928(8), 3.30873(6) ×2	3.041(11)
M1-O2	2.77895(4)	-	-	2.91345(7) ×2	2.8751(17) ×2	2.888(4) ×2	3.143(4), 3.33(2), 3.37(2)
M1-O3	-	2.402(12), 2.438(11)	2.675(11)	3.37132(7) ×2	3.185(2) ×2	-	-
M1-O4	-	-	2.782(11)	-	-	-	-
M1-O5	3.02342(4)	-	2.642(10)	-	-	-	3.036(10)
M1-O8	2.32593(4)	-	-	-	-	-	-
M1-OW1	2.30379(4)	2.3(18), 2.4(18), 2.5(18), 2.6(18)	-	-	2.480(5) ×2	-	-
M1-OW2	2.87353(3)	-	2.924(14)	-	-	-	-
M1-OW3	2.44861(8)	-	-	-	-	-	-
M1-OW4	2.79669(9)	-	-	-	-	-	-
M2-O1	-	-	2.859(11)	-	3.5115(18) ×2	-	-
M2-O2	2.93374(5)	-	-	-	2.7281(16) ×2	-	-
M2-O3	2.56565(7)	-	2.624(12)	-	2.812(3) ×2	-	-
M2-O4	-	-	2.724(12)	-	-	-	-
M2-O5	2.79757(7)	-	2.771(11)	-	-	-	-
M2-O6	2.50396(4)	-	-	-	-	-	-
M2-OW1	2.35547(5)	-	2.749(16)	-	3.480(6) ×2	-	-
M2-OW2	-	-	2.675(15)	-	-	-	-
M2-OW3	2.48871(4)	-	-	-	-	-	-
M2-OW4	2.19225(3)	-	-	-	-	-	-
M3-O1	-	-	2.798(10)	-	3.429(4) ×2	-	-
M3-O2	-	-	-	-	3.254(4) ×2	-	-
M3-O3	-	-	3.008(10)	-	2.972(3) ×2	-	-
M3-O4	-	-	3.008(10)	-	-	-	-
M3-O5	-	-	2.755(10)	-	-	-	-
M3-OW1	-	-	3.111(17)	-	2.801(6) ×2	-	-
M3-OW2	-	-	2.136(14)	-	-	-	-
(Si,Ga)1-O1-(Si,Ga)3	-	-	131.71(17)	-	-	-	142.6(3)
(Si,Ga)2-O1-(Si,Ga)2	-	129.0(3)	-	117.6(4)	142.5(2)	123.3(5)	-
(Si,Ga)3-O1-(Si,Ga)4	140.162(1)	-	-	-	-	-	-
(Si,Ga)1-O2-(Si,Ga)2	-	139.47(17)	-	154.59(18)	133.39(12)	144.5(3)	-
(Si,Ga)2-O2-(Si,Ga)3	-	-	136.18(18)	-	-	-	127.4(3)
(Si,Ga)3-O2-(Si,Ga)4	144.500(1)	-	-	-	-	-	-

(Si,Ga)2-O3-(Si,Ga)2	-	134.39(18)	-	125.6(3)	129.28(15)	133.6(3)	-
(Si,Ga)2-O3-(Si,Ga)3	-	-	130.01(22)	-	-	-	132.7(3)
(Si,Ga)3-O3-(Si,Ga)5	138.700(1)	-	-	-	-	-	-
(Si,Ga)1-O4-(Si,Ga)5	136.214(1)	-	-	-	-	-	-
(Si,Ga)2-O4-(Si,Ga)3	-	-	128.75(22)	-	-	-	138.7(4)
(Si,Ga)1-O5-(Si,Ga)2	-	-	132.06(17)	-	-	-	139.6(3)
(Si,Ga)2-O5-(Si,Ga)5	139.084(1)	-	-	-	-	-	-
(Si,Ga)2-O6-(Si,Ga)5	135.037(1)	-	-	-	-	-	-
(Si,Ga)1-O7-(Si,Ga)2	147.653(1)	-	-	-	-	-	-
(Si,Ga)2-O8-(Si,Ga)4	128.122(1)	-	-	-	-	-	-
(Si,Ga)1-O9-(Si,Ga)3	126.655(2)	-	-	-	-	-	-
(Si,Ga)1-O10-(Si,Ga)4	136.113(1)	-	-	-	-	-	-
average chain rotation angle of T_5O_{10} unit, ψ	19.41	24.61	17.34	30.08	14.12	28.18	24.50

[a]The numbers in parentheses are the estimated standard deviations (esd's) in the units of the least significant digit given for the corresponding parameter.

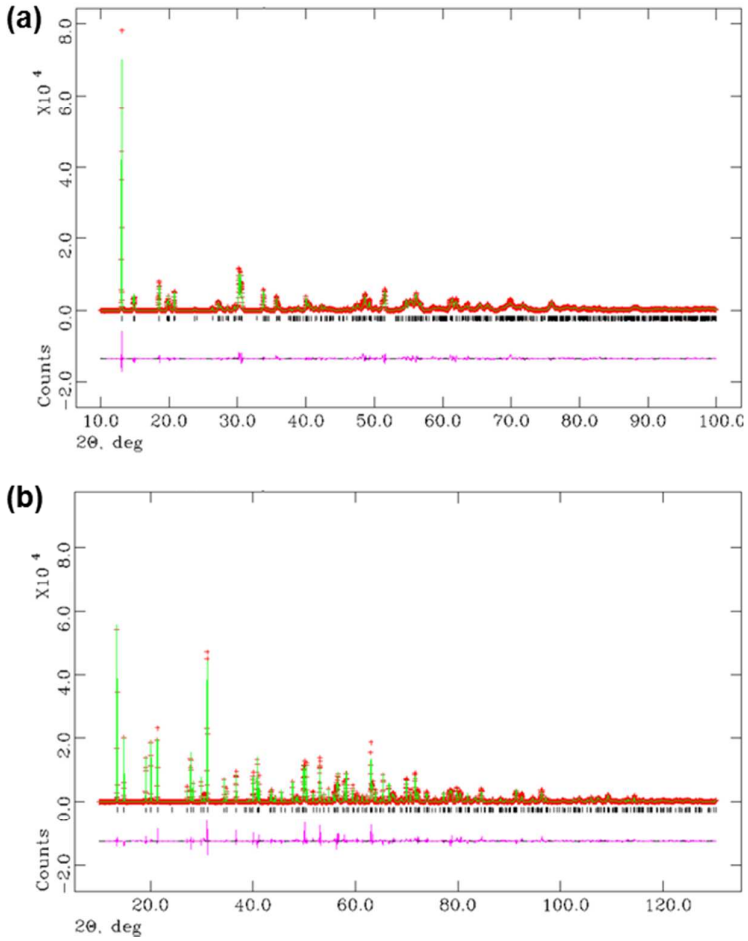

Figure S1. Rietveld plots for (a) hydrated and (b) partially dehydrated Na-PST-1 samples: observed data (crosses), calculated fit (solid line), and difference plot (lower trace). The tick marks indicate the positions of allowed reflections. The 2θ range higher than 40° has been scaled up by a factor of 3 to show more detail.

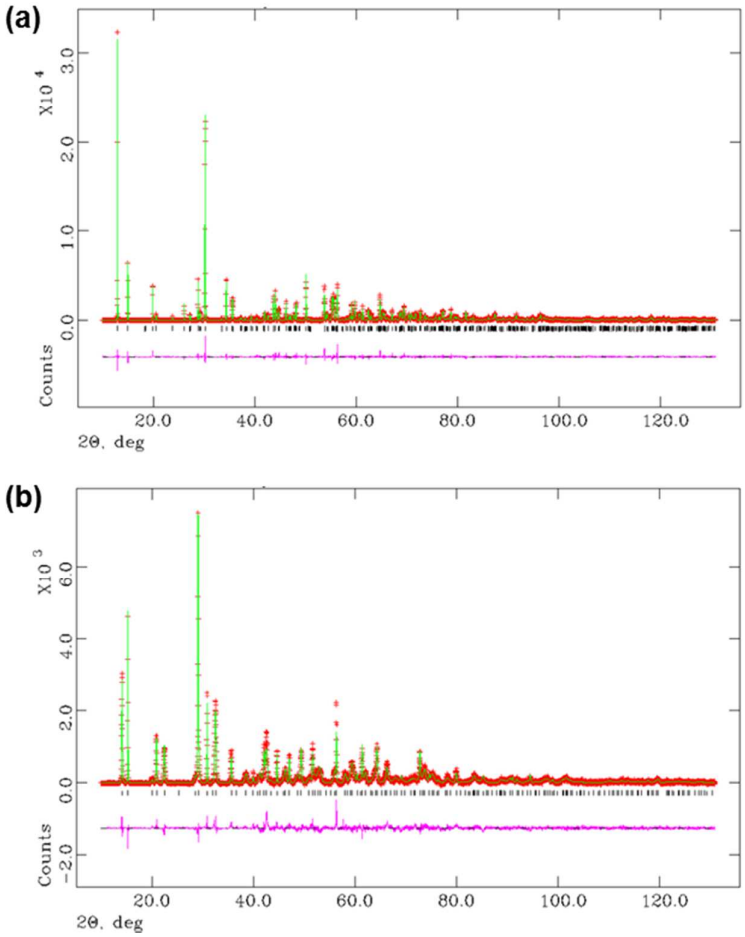

Figure S2. Rietveld plots for (a) hydrated and (b) dehydrated K-PST-1 samples: observed data (crosses), calculated fit (solid line), and difference plot (lower trace). The tick marks indicate the positions of allowed reflections. The 2θ range higher than 40° has been scaled up by a factor of 3 to show more detail.

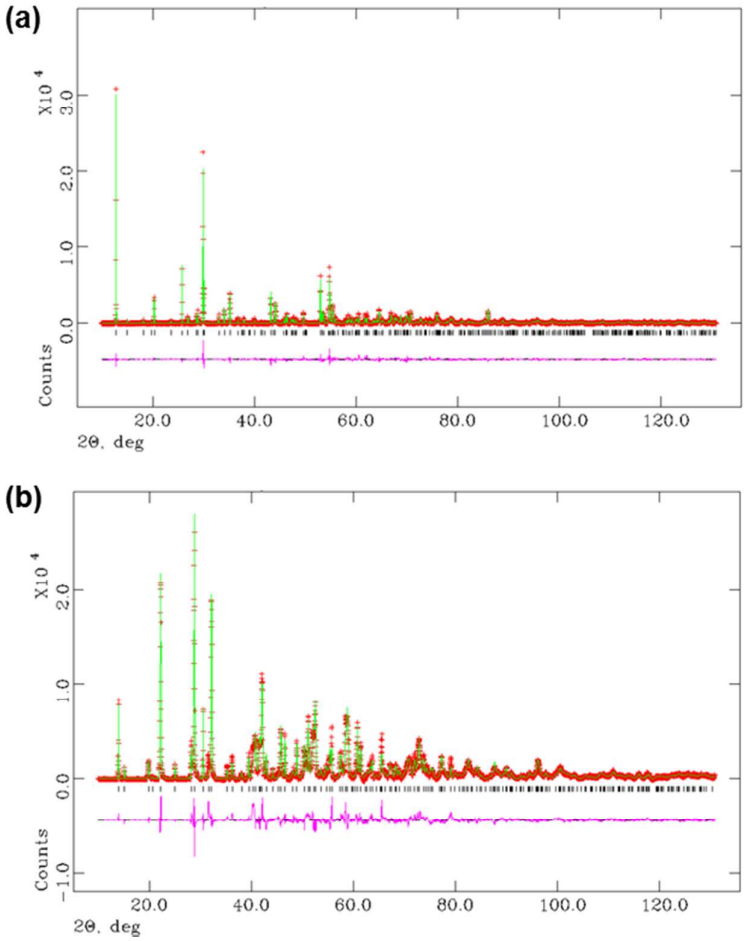

Figure S3. Rietveld plots for (a) hydrated and (b) dehydrated Rb-PST-1 samples: observed data (crosses), calculated fit (solid line), and difference plot (lower trace). The tick marks indicate the positions of allowed reflections. The 2θ range higher than 40° has been scaled up by a factor of 3 to show more detail.

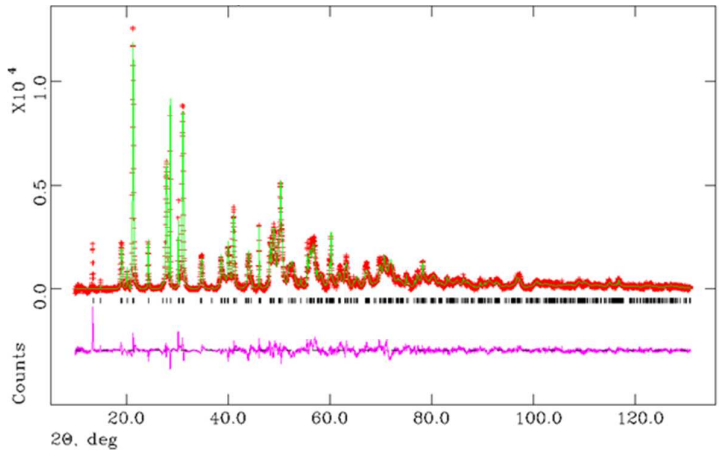

Figure S4. Rietveld plot for dehydrated Cs-PST-1: observed data (crosses), calculated fit (solid line), and difference plot (lower trace). The tick marks indicate the positions of allowed reflections. The 2θ range higher than 40° has been scaled up by a factor of 3 to show more detail.

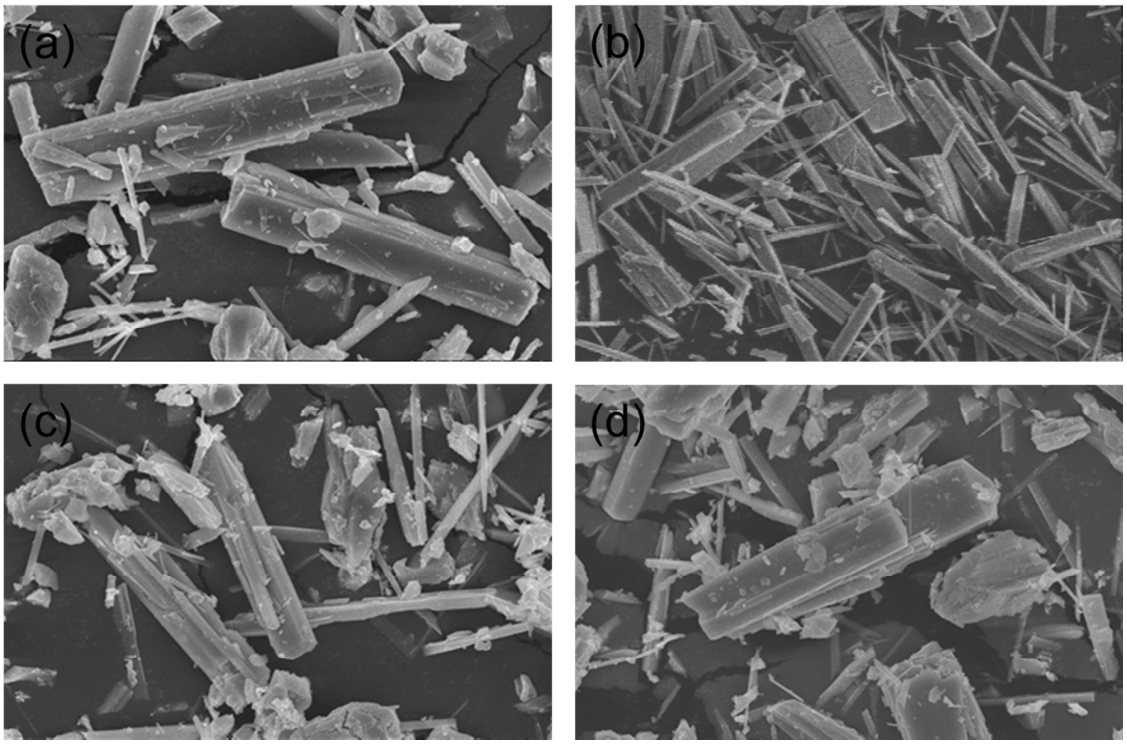

Figure S5. SEM images of the (a) Na^+, (b) K^+, (c) Rb^+, and (d) Cs^+ forms of PST-1.

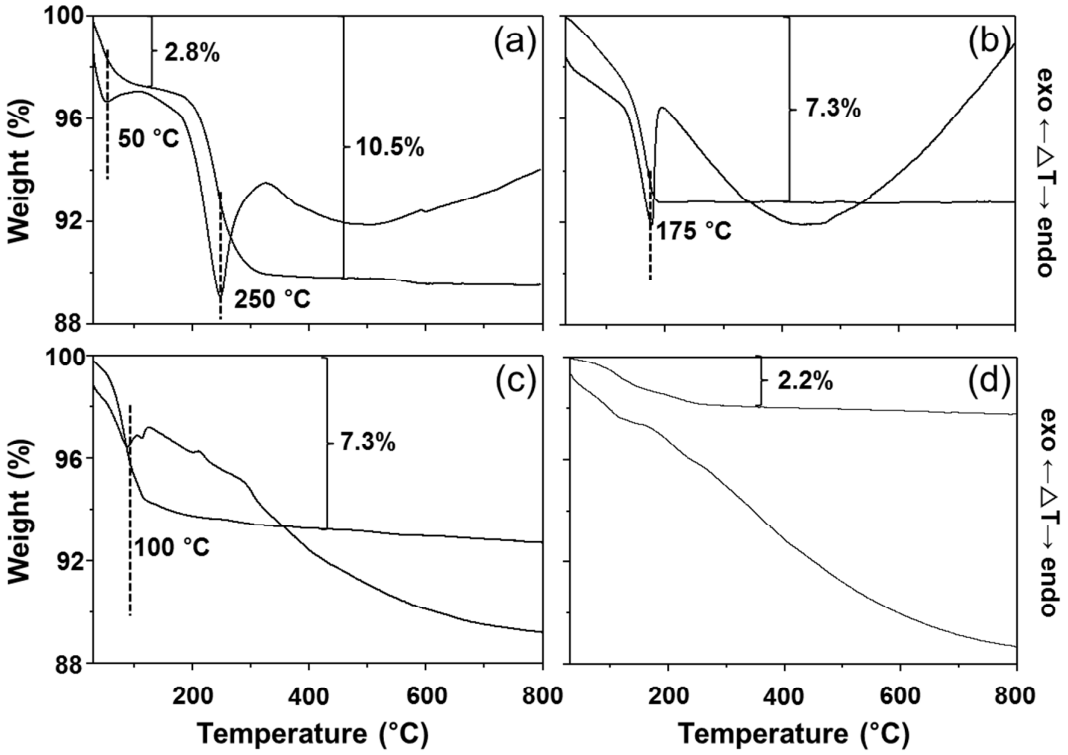

Figure S6. TGA/DTA curves for the (a) Na^+, (b) K^+, (c) Rb^+, and (d) Cs^+ forms of PST-1. All samples were dried overnight at room temperature after the crystallization or ion exchange process.

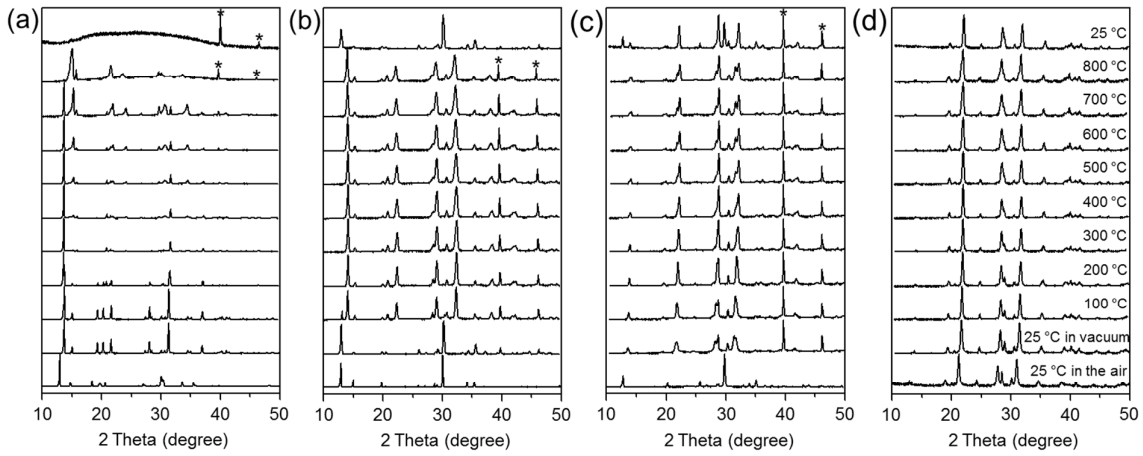

Figure S7. Powder XRD patterns of (a) Na-, (b) K-, (c) Rb-, and (d) Cs-PST-1 zeolites measured during *in situ* heating under vacuum to a residual pressure of 5×10^{-3} Torr. The top trace is the pattern measured at room temperature after temperature-programmed XRD experiments up to 800 °C followed by exposure to ambient air for 0.5 h. The asterisk denotes an X-ray peak from the Pt sample holder.

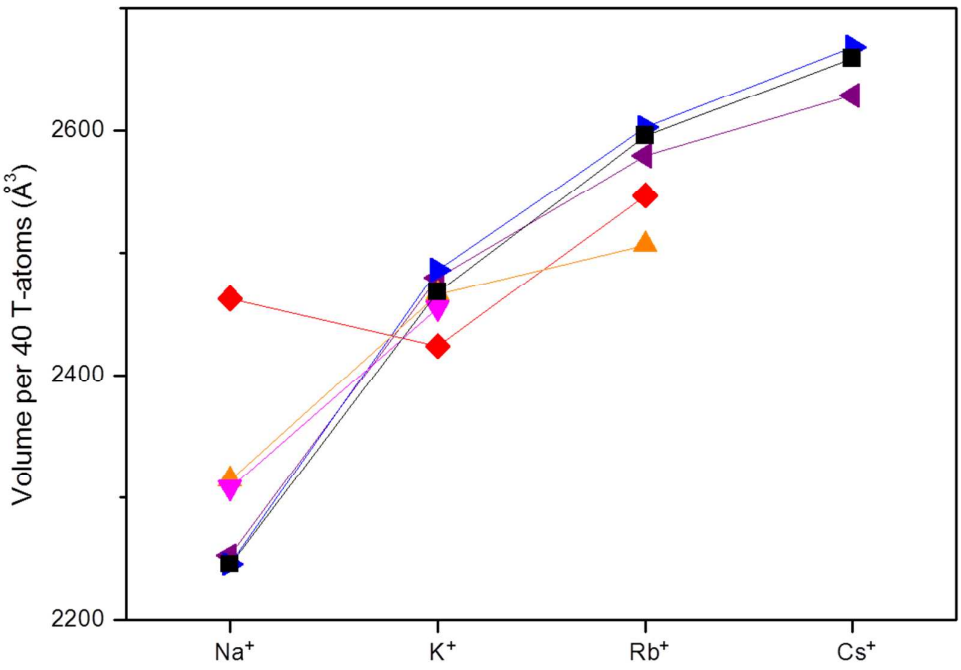

Figure S8. Changes in volume per 40 T-atoms of the Na^+, K^+, Rb^+, and Cs^+ forms of natrolite zeolites with different compositions and T-atom distributions in hydrate state. PST-1, red diamond; PST-3, violet left triangle; PST-4, blue right triangle; TNU-3, orange up triangle; TNU-4, pink down triangle; natural natrolite with complete Si-Al order, black square.

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