Li⁺-exchanged Zeolites X and Y (FAU) from Undried Formamide Solution

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Two single-crystals of fully dehydrated, partially Li⁺-exchanged zeolites X (Si/Al = 1.09, crystal 1) and Y (Si/Al = 1.56, crystal 2), were prepared by flow method using 0.1 M LiNO₃ at 393 K for 48 h, respectively, followed by vacuum dehydration at 673 K and 1×10^{-6} Torr. Their structures were determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ and $Fd\bar{3}m$ at 100(1) K for crystals 1 and 2, respectively. They were refined to the final error indices $R_1/wR_2 = 0.065/0.211$ and $0.043/0.169$ for crystals 1 and 2, respectively. In crystal 1, about 53 Li⁺ ions per unit cell are found at three distinct positions; 9 at site I', 19 at another site I', and the remaining 25 at site II. The residual 25 Na⁺ ions occupy three equipoints; 2 are at site I, 7 at site II, and 16 at site III'. In crystal 2, about 31 Li⁺ ions per unit cell occupy sites I' and II with occupancies at 22 and 9, respectively; 3, 4, 23, and 3 Na⁺ ions are found at sites I, I', II, and III', respectively. The extent of Li⁺ ion exchange into zeolite X (crystal 1) is higher than that of zeolite Y (crystal 2), *ca.* 73% and 56% in crystals 1 and 2, respectively.

Key words: Lithium, Zeolite, Structure, Ion exchange, Formamide

Stereoviews of representative sodalite units in crystals 1 and 2; (a) crystal 1 and (b) crystal 2.

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Introduction

Zeolites have been used in various industrial applications such as catalysis, gas separation, and sorption (Gaffney, 1996; Feuerstein and Lobo, 1998; Kim et al., 2012b). Their characteristic properties depend on partly the nature of the exchangeable cations (Moreno-Gutierrez and Olguin, 2003; Herden et al., 1982). The cation exchange behavior of zeolite depends on (1) the nature of the exchangeable cations, (2) the temperature, (3) the solvent, and (4) the structural properties dictated by the zeolite framework (Moreno-Gutierrez and Olguin, 2003). When the exchangeable cations are relatively large and have small charges, they can better balance the local anionic charges of the zeolite framework (Seff, 1996; Kim et al., 2012a). The zeolite framework experience less strain from the diffuse positive charges at the surfaces of monovalent cations and is less distorted (Seff, 1996; Kim et al., 2012a). Similarly these cations are less able to attract, polarize, and sorb guest molecules, so sorption and catalysis processes are discouraged (Kim et al., 2012a). However, Li^+ ion is an exception. It is small and its positive charge is not distributed over a large surface area. Its concentrated charge can interact strongly with the dipoles or quadrupoles of sorbed molecules (Kim et al., 2012a). In gas separation, for example, Li^+ -exchanged low silica zeolite X (LSX) shows a strong affinity for N_2 over O_2 because the quadrupole moment of N_2 is larger than that of O_2 (Gaffney, 1996; Feuerstein et al., 2000). The capacity of nitrogen adsorption correlates with the amount of Li^+ ion and distribution in zeolites (Feuerstein and Lobo, 1998).

Nearly always, when ion-exchange is done from solution, the solvent is water. Unfortunately, the result of ion-exchange experiment from aqueous solution is usually not simple (Seff, 2010; Kim et al., 2012b). The following problems are usually associated with the ion exchange of zeolites. Ion exchange is often incomplete (Ho et al., 1995). Often H^+ , OH^- , or both, arising from the hydrolysis of the incoming cation, generally enhanced by the zeolite, are accepted into zeolite (Ho et al., 1995; Seff, 2010).

The complete exchange of Li^+ for Na^+ has been achieved for LSX from aqueous solution (Plevart et al., 1997; Feuerstein and Lobo, 1998), but it has not yet been achieved for zeolite Y. It was attempted using NH_4^+ -exchanged zeolite Y ($\text{Si}/\text{Al} = 2.36$), but both Na^+ and H^+ ions were found in the products (Forano et al., 1989). To achieve

completely Li^+ -exchanged zeolite Y, Li^+ exchange was attempted using methanol-water mixed solvents (These solvents ranging in composition from purchased (undried) methanol (water concentration 0.02 M) to pure water were used) at 333 K (Kim et al., 2012a). However, the complete Li^+ exchange did not occur in any solvent composition; the highest degree of Li^+ exchange, 96%, was achieved from methanol solution containing *ca.* 0.02 M H_2O , and the degree of exchange from pure water solution is the least (Kim et al., 2012a). These results show that complete Li^+ exchange into zeolite is not simple and ion exchange with Li^+ using undried methanol (water concentration 0.02 M) is more efficient than traditional aqueous exchange when Si/Al ratio is higher than 1.0 (Kim et al., 2012a).

According to the previous studies of Li^+ -exchanged zeolites (Forano et al., 1989; Plevart et al., 1997; Feuerstein and Lobo, 1998; Feuerstein et al., 2000; Wozniak et al., 2008; Kim et al., 2012a; Kim et al., 2012b), the sites I' and II are preferentially occupied with Li^+ ions and the remaining Li^+ ions are located at sites III or III' in the supercage. However, it is difficult to determine the distribution of Li^+ ions at sites III or III' in the supercage due to the high mobility and low occupancy of Li^+ ion (Kim et al., 2012b). Sometimes, some Li^+ ions at sites III or III' for charge balance of the zeolite framework are not found, crystallographically (Feuerstein and Lobo, 1998; Kim et al., 2012a; Kim et al., 2012b).

In this work, Li^+ -exchange into zeolites X ($\text{Si}/\text{Al} = 1.09$) and Y ($\text{Si}/\text{Al} = 1.56$) was attempted from formamide solution at an elevated temperature, 393 K, to study the ion exchange behavior of Li^+ ion in zeolites X and Y and to investigate the distribution and coordination geometry of cations in the framework.

Materials and Methods

Preparation of Partially Li^+ -exchanged zeolites X and Y

Large single crystals of zeolite X and Y (FAU), stoichiometry $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ and $\text{Na}_{75}\text{Si}_{117}\text{Al}_{75}\text{O}_{384}$ per unit cell, respectively, were synthesized by Petranovskii et al. (Bogomolov et al., 1986) and Lim et al. (Lim et al., 2010). Each of two single-crystals, colorless octahedra about 0.20 mm in cross-section, was lodged in its own fine Pyrex capillary. Ion exchange was accomplished by dynamic (flow) method in these capillaries using 0.1 M LiNO_3 solution (Aldrich, 99.99%, Ca 4.82 mg L^{-1} , Na 1.91 mg L^{-1} , Sc 0.48

Table 1. Summary of experimental and crystallographic data.

	Crystal 1	Crystal 2
Si/Al ratio	1.09	1.56
Crystal cross-section (mm)	0.19	0.20
Ion exchange t(h), T(K)	48, 393	48, 393
[H ₂ O] ^a	0.06	0.06
Crystal color after dehydration	colorless	colorless
Dehydration T(K)	673	673
Data collection T (K)	100(1)	100(1)
Space group, Z	<i>Fd</i> $\bar{3}$, 1	<i>Fd</i> $\bar{3}m$, 1
X-ray source	Pohang Light Source (PLS) (Beamline 6B MXI)	
Wavelength (Å)	0.90000	0.90000
Unit cell constant, <i>a</i> (Å)	24.7409(4)	24.8106(1)
2 θ range in data collection (deg)	60.71	70.44
No. of unique reflections, <i>m</i>	940	854
No. of reflections with <i>F</i> _o > 4(<i>F</i> _o)	919	820
No. of variables, <i>s</i>	84	57
Data/parameters, <i>m/s</i>	11.3	15.0
Weighting parameters, <i>a/b</i>	0.095/219.2	0.059/160.4
Final error indices		
<i>R</i> ₁ / <i>wR</i> ₂ (<i>F</i> _o > 4(<i>F</i> _o)) ^b	0.065/0.211	0.043/0.169
<i>R</i> ₁ / <i>wR</i> ₂ (all intensities) ^c	0.066/0.214	0.049/0.196
Goodness-of-fit ^d	1.26	1.52

^aWater concentration (mol/l) in the exchange solution. ^b*R*₁ = $|F_o - F_c|/F_o$ and *wR*₂ = $[w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$. *R*₁ and *wR*₂ are calculated using only the reflections for which *F*_o > 4(*F*_o). ^c*R*₁ and *wR*₂ are calculated using all unique reflections measured. ^dGoodness-of-fit = $(w(F_o^2 - F_c^2)^2/(m-s))^{1/2}$, where *m* is the number of unique reflections and *s* is the number of variables, respectively.

mg L⁻¹, Mg 0.42 mg L⁻¹, Ba 0.41 mg L⁻¹, Zr 0.31 mg L⁻¹, Cu 0.21 mg L⁻¹, Al 0.07 mg L⁻¹, La 0.05 mg L⁻¹, Sr 0.04 mg L⁻¹), with solvent formamide (Aldrich, assay 99.5%, HCOOH 0.02%, Water content 0.1% (0.06 M), Ca 5 mg L⁻¹, Cd 1 mg L⁻¹, Co 1 mg L⁻¹, Cr 1 mg L⁻¹, Cu 1 mg L⁻¹, Fe 1 mg L⁻¹, K 20 mg L⁻¹, Mg 1 mg L⁻¹, Mn 1 mg L⁻¹, Na 20 mg L⁻¹, Ni 1 mg L⁻¹, Pb 1 mg L⁻¹, Zn 1 mg L⁻¹), at 393 K. Although a previously unopened bottle of formamide was used, the water content of solution could have increased significantly during its preparation by sorption of moisture from the LiNO₃(s) and from the atmosphere.

Each of the resulting clear colorless single crystals was slowly heated under dynamic vacuum to 673 K and dehydrated at 1×10^{-6} Torr for two days. While these conditions were maintained, the hot contiguous downstream lengths of the vacuum system, including a sequential 17-cm U-tube of zeolite 5A beads fully activated in situ, were allowed

to cool to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to each crystal. While still under vacuum, each crystal was allowed to cool to room temperature and was sealed in its capillary by torch. Microscopic examination showed them all to be colorless.

Single-crystal X-ray Diffraction Synchrotron X-ray diffraction data for two crystals were collected at 100(1) K using an ADSC Quantum210 detector at Beamline 6B MXI at the Pohang Light Source. Crystal evaluation and data collection were done with a detector-to-crystal distance of 60 mm. Preliminary cell constants and an orientation matrix were determined from 72 sets of frames collected at scan intervals of 5° with an exposure time of 1 s per frame. The basic scale file was prepared using the HKL2000 program (Otwinowski and Minor, 1997). The reflections were successfully indexed by the automated indexing routine of the DENZO program (Otwinowski

and Minor, 1997). The diffraction data were harvested by collecting 72 sets of frames with 5° scans with an exposure time of 1 s per frame. These highly redundant data sets were corrected for Lorentz and polarization effects, and a very small correction for crystal decay was applied. The space group $Fd\bar{3}$ conventional for zeolite X and $Fd\bar{3}m$ for zeolite Y, were determined by the program XPREP, respectively (Bruker-AXS, 2001). A summary of the experimental and crystallographic data is presented in Table 1.

Structure Determination Full-matrix least-squares refinement using SHELXL97 (Sheldrick, 1997) was done on F^2 using all data for each crystal. The refinement was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in dehydrated $[\text{Rb}_{71}\text{Na}_{21}][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]$ -FAU (Lee et al., 1998) and $[\text{K}_{71}]$

$[\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU (Lim et al., 2006) for crystals 1 and 2, respectively. Initial refinement used anisotropic thermal parameters and converged to the error indices given in steps 1 of Table 2. The detailed progress of structure determination as subsequent peaks were found on difference Fourier functions and identified as nonframework atoms is provided in Table 2. The final cycles of refinement were done with anisotropic temperature factors for all positions except those that were not stable in anisotropic refinement: Na(I'a) in crystal 1 and Na(III') in crystal 2. The final error indices, R_1 and R_2 , are given in Table 1. The final structural parameters are given in Table 3, and selected interatomic distances and angles are given in Table 4. All shifts in the final cycles of refinements were less than 0.1% of their corresponding estimated standard deviations (esds). Atomic scattering factors for Li^+ , Na^+ ,

Table 2. Steps of structure refinement^a.

Occupancy ^b at									
Step	Na(I)	Li(I'a)	Li(I'b)	Na(I')	Li(II)	Na(II)	Na(III')	R ₁	R ₂
[Li ₆₇ Na ₂₅][Si ₁₀₀ Al ₉₂ O ₃₈₄]-FAU, crystal 1									
1 ^c								0.1564	0.5886
2					40(3)			0.1410	0.5557
3			42.1(4)		61(3)			0.1337	0.5093
4			41(3)		58(3)		15.1(8)	0.0751	0.2493
5	1.5(3)		42(3)		60(3)		16.5(3)	0.0717	0.2269
6	1.6(3)		43(3)		34(5)	5.8(11)	16.4(8)	0.0661	0.2192
7	1.6(3)	27(8)	16(8)		35(5)	5.8(11)	16.4(8)	0.0658	0.2164
8 ^d	1.8(4)	5.6(4)	23.2(4)		32(5)	5.8(11)	15.8(8)	0.0655	0.2128
9 ^e	1.8(4)	7.2(4)	21.7(4)		25.0(3)	7.0(3)	15.7(8)	0.0653	0.2126
10 ^f	1.9(4)	8.9(4)	19.8(4)		24.6(3)	7.4(3)	15.7(8)	0.0653	0.2110
[Li ₄₂ Na ₃₃][Si ₁₁₇ Al ₇₅ O ₃₈₄]-FAU, crystal 2									
1 ^c								0.1857	0.4813
2						23.9(6)		0.0784	0.2393
3		37(3)				24.1(5)		0.0623	0.2011
4	2.2(3)	37.1(24)				24.0(4)		0.0551	0.1878
5	2.4(3)	23(3)		3.6(6)		24.2(4)		0.0481	0.1776
6	2.5(3)	23.1(24)		3.6(5)	11(4)	22.0(9)		0.0438	0.1726
7	2.7(3)	23.4(24)		3.6(5)	12(4)	21.9(9)	2.7(7)	0.0425	0.1693
8 ^d	2.7(3)	22.9(3)		3.7(3)	12(4)	22.0(9)	2.6(7)	0.0426	0.1694
9 ^e	2.7(3)	22.9(4)		3.7(4)	9.6(4)	22.4(4)	2.5(6)	0.0426	0.1694
10 ^f	2.7(3)	22.7(4)		3.9(5)	9.3(4)	22.7(4)	2.6(7)	0.0425	0.1690

^aIsotropic temperature factors were used for all Li^+ and Na^+ positions except for the last step. ^bThe occupancy is given as the number of Li^+ and Na^+ ions per unit cell. ^cOnly the atoms of zeolite framework were included in the initial structure model. ^dOccupancies at sites I and I' constrained so that $n_I + n_{I'}/2 \leq 16$. ^eConstrained to sum to 32, the maximum occupancy at site II. ^f Li^+ and Na^+ ions were refined anisotropically, except Na(I'a) in crystal 1 and Na(III') in crystal 2.

Table 3. Positional, thermal, and occupancy parameters^a.

atom	Wyckoff position	Cation site	x	y	z	^b <i>U</i> ₁₁ or <i>U</i> _{iso}	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	°Occupancy		
												initial	varied	fixed
[Li ₆₇ Na ₂₅][Si ₁₀₀ Al ₉₂ O ₃₈₄]-FAU, crystal 1														
Si	96(<i>g</i>)		-511(1)	1231(1)	374(1)	373(11)	338(10)	341(10)	-18(6)	-2(7)	-6(7)	96		
Al	96(<i>g</i>)		-501(1)	362(1)	1244(1)	268(10)	256(10)	254(10)	-16(6)	-7(6)	2(6)	96		
O(1)	96(<i>g</i>)		-997(2)	-4(2)	1039(2)	433(25)	538(28)	428(25)	-100(20)	6(20)	-105(21)	96		
O(2)	96(<i>g</i>)		-12(2)	4(2)	1511(2)	346(22)	361(22)	392(23)	41(17)	10(17)	71(17)	96		
O(3)	96(<i>g</i>)		-683(2)	-724(2)	231(2)	368(22)	351(22)	436(24)	44(18)	42(18)	67(17)	96		
O(4)	96(<i>g</i>)		-721(2)	783(2)	1689(2)	375(23)	345(22)	330(22)	-70(17)	7(16)	-3(16)	96		
Na(I)	16(<i>c</i>)	I	0	0	0	458(190)	458(190)	458(190)	-120(120)	-120(120)	-120(120)	1.9(4)	2	
Li(I'a)	32(<i>e</i>)	I'	411(20)	411(20)	411(20)	117(240)						8.9(4)	9	
Li(I'b)	32(<i>e</i>)	I'	501(14)	501(14)	501(14)	278(100)	278(100)	278(100)	121(140)	121(140)	121(140)	19.8(4)	19	
Li(II)	32(<i>e</i>)	II	2226(11)	2226(11)	2226(11)	554(136)	554(136)	554(136)	41(119)	41(119)	41(119)	24.6(3)	25	
Na(II)	32(<i>e</i>)	II	2360(8)	2360(8)	2360(8)	409(83)	409(83)	409(83)	129(91)	129(91)	129(91)	7.4(3)	7	
Na(III')	96(<i>g</i>)	III'	1027(5)	1472(5)	3945(5)	222(68)	360(76)	300(72)	-12(54)	50(50)	-37(51)	15.7(8)	16	
[Li ₄₂ Na ₃₃][Si ₁₁₇ Al ₇₅ O ₃₈₄]-FAU, crystal 2														
Si,Al	192(<i>i</i>)		-508(1)	1234(1)	366(1)	115(4)	95(4)	98(4)	-15(2)	1(2)	-5(2)	192		
O(1)	96(<i>h</i>)		-1035(1)	0(0)	1035(1)	213(9)	201(14)	213(9)	-48(8)	-24(11)	-48(8)	96		
O(2)	96(<i>g</i>)		-17(1)	-17(1)	1471(1)	185(9)	185(9)	173(14)	27(8)	27(8)	67(11)	96		
O(3)	96(<i>g</i>)		-263(1)	707(1)	707(1)	247(15)	166(8)	166(8)	34(10)	39(8)	39(8)	96		
O(4)	96(<i>g</i>)		773(1)	773(1)	3196(1)	182(9)	182(9)	199(14)	29(8)	29(8)	55(11)	96		
Na(I)	16(<i>c</i>)	I	0	0	0	180(75)	180(75)	180(75)	-13(51)	-13(51)	-13(51)	2.7(3)	3	
Li(I'a)	32(<i>e</i>)	I'	434(7)	434(7)	434(7)	167(37)	167(37)	167(37)	44(46)	44(46)	44(46)	22.7(5)	22	
Na(I')	32(<i>e</i>)	I'	604(10)	604(10)	604(10)	274(91)	274(91)	274(91)	93(90)	93(90)	93(90)	3.9(5)	4	
Li(II)	32(<i>e</i>)	II	2225(17)	2225(17)	2225(17)	137(126)	137(126)	137(126)	106(155)	106(155)	106(155)	9.3(4)	9	
Na(II)	32(<i>e</i>)	II	2348(2)	2348(2)	2348(2)	179(17)	179(17)	179(17)	18(13)	18(13)	18(13)	22.7(4)	23	
Na(III')	192(<i>i</i>)	III'	1009(20)	1491(20)	3934(29)	333(220)						2.6(7)	3	

^aPositional parameters $\times 10^4$ and thermal parameters $\times 10^4$ are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. ^bThe anisotropic temperature factor is $\exp[-2\pi^2 a^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{23}kl + 2U_{13}hl + 2U_{12}hk)]$. ^cOccupancy factors are given as the number of atoms or ions per unit cell.

O', and (Si,Al) were used (Doyle and Turner, 1968; Ibers and Hamilton, 1974). All scattering factors were modified to account for anomalous dispersion (Cromer, 1965).

Results and Discussion

The framework structure of zeolites X and Y (FAU) are characterized by the double 6-ring (D6R, hexagonal prism), sodalite cavity (a cubooctahedron), and supercage (see Fig. 1). Each unit cell has 8 supercage, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 S6Rs (single 6-rings). The exchangeable cations, which balance the negative charge of the zeolites X and Y framework, usually occupy some or all of the sites shown with Roman numerals in Fig. 1. The maximum occupancies at the cation sites I, I', II, II', and III are 16, 32, 32, 32, and 48, respectively. Site III' in zeolites X and Y is 96 and 192, respectively. Further description is available (Breck, 1974; Van Bekkum et al., 2001).

Fig. 1. Stylized drawing of the framework structures of zeolites X and Y. Near the center of each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Loewenstein's rule (Loewenstein, 1954) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

Fig. 2. Stereoviews of the two and three possible ways that cations occupy double 6-rins (D6Rs) in crystals 1 and 2. Of the 16 D6Rs per unit cell in crystal 1, the arrangements of Li^+ and Na^+ ions are possible as shown in (a) and (b). For crystal 2, Li^+ and Na^+ ions are occupied as shown in (c), (d), (e), and (f). The zeolites X and Y framework are drawn with heavy bonds. The coordination of the exchangeable cations to oxygens of the zeolite framework is indicated by light bonds. Ellipsoids of 25% probability are shown.

Crystal Structure of $[\text{Li}_{67}\text{Na}_{25}][\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}$ (Crystal 1)

At three crystallographic sites, 53 Li^+ ions are found per unit cell (see Table 3). The 9 and 19 Li^+ ions are found at two different site I' positions, 25 occupy site II. About 25 Na^+ ions are found at three different crystallographic sites I, II, and III' with occupancies of 2, 7, and 16, respectively (see Table 3). Only 78^+ cations are found, where 92 are needed per unit cell to balance the negative charge of the zeolite framework. Because Na^+ ion scatters X-rays much better than Li^+ ion, and should therefore have all

been found, and because sites I' and II are all full, it is assumed that the 14 Li^+ ions, not located in this work, are present at III or III' sites, as seen in previous reports (Kim et al., 2012b). Thus the degree of Li^+ ion exchange is taken to be $67/92$, about 73%. Some or all of these missing ions may be H^+ , the result of H_3O^+ exchange; if so, the degree of exchange would be less (Kim et al., 2012a, Kim et al., 2012b).

Two Na^+ ions per unit cell at Na(I) occupy site I (at the center of the D6Rs, see Fig. 2(a)). Each coordinates

to six O(3) framework oxygens of its D6R at distance of 2.529(4) Å, which is somewhat longer than the sum of the corresponding ionic radii, $0.97 + 1.32 = 2.29$ Å (Weast

et al., 1989). This distance is likely to be virtual; only two of the 16 D6Rs contain Na⁺ ions; the actual distance is likely to be substantially shorter (Kim et al., 2012a).

Table 4. Selected interatomic distances (Å) and angles (deg)^a.

Crystal 1			Crystal 2		
Si-O(1)	1.699(4)	-	O(1)-Al-O(2)	112.70(23)	-
Si-O(2)	1.736(4)	-	O(1)-Al-O(3)	109.56(22)	-
Si-O(3)	1.751(4)	-	O(1)-Al-O(4)	108.77(22)	-
Si-O(4)	1.670(4)	-	O(2)-Al-O(3)	106.00(20)	-
Mean Si-O	1.714	-	O(2)-Al-O(4)	108.85(20)	-
Al-O(1)	1.607(4)	-	O(3)-Al-O(4)	110.96(21)	-
Al-O(2)	1.639(4)	-	O(1)-(Si,Al)-O(2)	-	111.77(11)
Al-O(3)	1.652(4)	-	O(1)-(Si,Al)-O(3)	-	109.35(12)
Al-O(4)	1.609(4)	-	O(1)-(Si,Al)-O(4)	-	110.77(13)
Mean Al-O	1.627	-	O(2)-(Si,Al)-O(3)	-	106.10(13)
(Si,Al)-O(1)	-	1.649(1)	O(2)-(Si,Al)-O(4)	-	106.98(13)
(Si,Al)-O(2)	-	1.670(1)	O(3)-(Si,Al)-O(4)	-	111.77(14)
(Si,Al)-O(3)	-	1.687(1)	Si-O(1)-Al	143.8(3)	-
(Si,Al)-O(4)	-	1.641(1)	Si-O(2)-Al	129.9(3)	-
Mean(Si,Al)	-	1.662	Si-O(3)-Al	126.7(3)	-
Na(I)-O(3)	2.529(4)	2.565(3)	Si-O(4)-Al	142.2(3)	-
Li(I'a)-O(3)	1.891(5)	1.977(4)	(Si,Al)-O(1)-(Si,Al)	-	140.82(19)
Li(I'b)-O(3)	1.946(15)	-	(Si,Al)-O(2)-(Si,Al)	-	136.88(18)
Na(I')-O(3)	-	2.182(20)	(Si,Al)-O(3)-(Si,Al)	-	129.84(17)
Li(II)-O(2)	2.018(7)	2.133(9)	(Si,Al)-O(4)-(Si,Al)	-	147.09(19)
Na(II)-O(2)	2.159(13)	2.256(4)	O(3)-Na(I)-O(3)	80.65(14), 99.35(14)	83.14(10), 96.86(10)
Na(III')-O(1)	2.724(13), 2.785(13)	2.69(5), 2.69(5)	O(3)-Li(I'a)-O(3)	119.8(4)	118.8(3)
Na(III')-O(4)	2.502(13), 2.531(12)	2.62(5), 2.62(5)	O(3)-Li(I'b)-O(3)	114.5(13)	-
O(1)-Si-O(2)	113.91(22)	-	O(3)-Na(I')-O(3)	-	102.5(13)
O(1)-Si-O(3)	107.83(21)	-	O(2)-Li(II)-O(2)	118.8(5)	118.7(8)
O(1)-Si-O(4)	110.43(20)	-	O(2)-Na(II)-O(2)	107.1(9)	108.93(17)
O(2)-Si-O(3)	106.92(19)	-	O(4)-Na(III')-O(4)	78.1(4)	79.4(20)
O(2)-Si-O(4)	106.98(19)	-			
O(3)-Si-O(4)	110.73(20)	-			

^aThe numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Table 5. Displacements of atoms (Å) from 6-ring planes.

Position	Sites	Crystal 1		Crystal 2	
		at O(3) ^a	at O(2) ^b	at O(3) ^a	at O(2) ^b
Na(I)	I	-1.68		-1.66	
Li(I'a)	I'	0.09		0.21	
Li(I'b)	I'	0.46			
Na(II)	II		0.80		0.77

^aA positive displacement indicates that the cation lies in a sodalite cavity; a negative deviation indicates that the cation lies in a D6R. (Na(I) lies at the center of D6Rs) ^bA positive displacement indicates that the cation lies in a supercage.

Fig. 3. Stereoviews of representative sodalite units in crystals 1 and 2; (a) crystal 1 and (b) crystal 2. See the caption to Fig. 2 for other details.

The O(3)-Na(I)-O(3) bond angles are $80.65(14)^\circ$ and $99.35(14)^\circ$ (see Table 4), nearly perfectly octahedral.

At two site-I' positions, 9 and 19 Li^+ ions occupy the $\text{Li}(\text{I}'\text{a})$ and $\text{Li}(\text{I}'\text{b})$ positions (see Fig. 2(b)), respectively. These 32-fold positions are not fully occupied because of intercationic electrostatic repulsion for Na^+ and Li^+ ion at distances of $\text{Na}(\text{I})-\text{Li}(\text{I}') = 1.78$ and 2.14 Å, respectively. The observed occupancies indicate that it is being avoided. If a site I is occupied, the two I' positions of that same D6Rs should not be. Accordingly, only $(16-2) \times 2 = 28$ site I' positions should be available for cations per unit cell which are in agreeable with the number found at site I'.

Each Li^+ ion at $\text{Li}(\text{I}'\text{a})$ and $\text{Li}(\text{I}'\text{b})$ coordinates to three O(3) oxygen atoms of the D6R at $1.891(5)$ and $1.946(15)$ Å, respectively, which is very close to the sum of the conventional ionic radii of Li^+ and O^{2-} , 1.91 Å (Lide et al., 1996b; Wozniak et al., 2008). This indicates that Li^+ ions coordinate tightly to their three O(3) oxygens. Each Li^+ ion extends inside the sodalite cavity 0.09 and 0.46 Å from its three O(3) plane, respectively (see Fig. 3(a) and Table 5).

At site-II positions (opposite S6Rs in the supercage), 25 Li^+ and 7 Na^+ ions are found at $\text{Li}(\text{II})$ and $\text{Na}(\text{II})$, respectively (see Fig. 3(a)). These 32-fold positions are fully occupied by the Li^+ and Na^+ ions. The Li^+ and Na^+ ions at $\text{Li}(\text{II})$ and $\text{Na}(\text{II})$, respectively, are coordinated by three O(2) oxygen atoms of the S6Rs at distances of

Fig. 4. Stereoviews of representative supercages in crystals 1 and 2; (a) crystal 1 and (b) crystal 2. See the caption to Fig. 2 for other details.

$2.018(7)$ and $2.159(13)$ Å, respectively, which are in close agreement with the sum of the ionic radii of Li^+ and O^{2-} , 1.91 Å and Na^+ and O^{2-} , 2.29 Å (Lide et al., 1996b; Wozniak et al., 2008; Weast et al., 1989). While $\text{Li}(\text{II})$ extends 0.22 Å into supercage from its three O(2) plane, $\text{Na}(\text{II})$ extends, 0.80 Å, which is 0.58 Å much further than $\text{Li}(\text{II})$ (see Fig. 4(a) and Table 5).

The remaining 16 Na^+ ions in the supercage at site III' are 4-coordinated by framework oxygen atoms, two O(1) atoms at $2.724(13)$ and $2.785(13)$ Å, and two O(4) atoms at $2.502(12)$ and $2.531(12)$ Å (see Fig. 4(a) and Table 4). These distances are much longer than the sum of the Na^+ and O^{2-} radii, 2.29 Å (Weast et al., 1989). However, these long interaction distances were also observed in the structures of fully dehydrated $\text{Na}_{92}\text{-X}$, $\text{Li}_{86}\text{Na}_6\text{-Y}$, and $\text{Li}_{87}\text{Na}_5\text{-X}$ (Zhu et al., 1999; Kim et al., 2012a; Kim et al., 2012b).

Crystal Structure of $[\text{Li}_{42}\text{Na}_{33}][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$ (Crystal 2)

About 31 Li^+ ions are found at sites I' and II, and 33 Na^+ ions at sites I, I', II, and III' (see Table 3). Only 64^+ cations are found, where 75 are needed per unit cell to balance the negative charge of the zeolite framework. As in crystal 1, it is assumed that the 11 Li^+ ions were not found at sites III or III', so the extent of Li^+ exchange is 56%, less if H^+ ions were present.

Three Na⁺ ions per unit cell at Na(I) occupy site I (see Fig. 2(c)). The octahedral Na(I)-O(3) distance, 2.565(3) Å, is about the same as that seen in crystal 1. As discussed above, it is long and likely to be virtual.

The 22 Li⁺ ions at Li(I'a) lie at two site I' positions (see Fig. 2(d) and 2(e)). The distances of Li (I'a) to the framework oxygens at O(3), 1.977 (4) Å, are almost the same as in crystal 1 (see Table 4). Unlike crystal 1, Na⁺ ions occupy site I' in this structure. Na(I') is 0.95 Å from the plane of the three O(3) oxygen atoms to which it bonds (see Fig. 3(b) and Table 5). The Na(I'a)-O(3) distance is 2.182(20) Å, a little shorter than sum of the ionic radii, 2.29 Å (Weast et al., 1989). However, this distance was also seen in fully dehydrated partially Li⁺-exchanged zeolites Y (Kim et al., 2012a).

About 9 Li⁺ and 23 Na⁺ ions per unit cell at Li(II) and Na(II), respectively, are located at site II position, complete the filling of the 6-rings. Each of these ions lie inside the supercage, 0.25 and 0.77 Å, respectively, from the plane of their three O(2) framework oxygen atoms (see Fig. 4(b) and Table 5). The Li(II)-O(2) and Na(II)-O(2) bond lengths are 2.133(9) and 2.256(4) Å, respectively, which are in close agreement with the sum of the ionic radii, 1.91 and 2.29 Å (Lide et al., 1996b; Wozniak et al., 2008; Weast et al., 1989).

The remaining three Na⁺ ions are found at site III' in the supercages (see Fig. 4(b)). These Na⁺ ions bind to two framework oxygen atoms, O(1) at 2.69 (5) Å and O(4) at 2.62 Å. These positions and long distances are similar to those found in previous results in fully dehydrated partially Li⁺-exchanged zeolites Y (Kim et al., 2012a).

The complete exchange of Li⁺ ion into zeolites X and Y are not achieved in any crystal. In both structures, Li⁺ and Na⁺ ions fill sites I, I', II, and III'. The number of Na⁺ ions at sites I, I', and II decreased with increasing Li⁺ exchanged level in both structures. The site preference for Li⁺ over Na⁺ ion is approximately I' > II > III or III'. This is in agreement with previous results (Forano et al., 1989; Plevart et al., 1997; Feuerstein and Lobo, 1998; Feuerstein et al., 2000; Wozniak et al., 2008; Kim et al., 2012a; Kim et al., 2012b).

The extent of Li⁺ ions exchange into zeolite X (Si/Al = 1.09, crystal 1) is higher than that of zeolite Y (Si/Al = 1.56, crystal 2) at given ion-exchange temperature, *ca.* 73% in Li-X and 56% in Li-Y, respectively, at 393 K. A similar trend is seen when Li⁺-exchanged zeolites X and Y from aqueous solution are compared: Li⁺ exchange

level is 95 and 72% for zeolites X and Y, respectively (Kim et al., 2012a; Kim et al., 2012b). This can be attributed to the difference of the composition of the zeolite framework (Si/Al = 1.09 and 1.56). Considering Al content in zeolites X and Y, the negative charge of the zeolite framework oxygen and the resulting electric fields in zeolites X are higher than in zeolite Y, thus, encouraging the entry of Li⁺ ions into zeolite X.

In this work, the T-O-T angles at O(2) and O(3) are 129.9(3)° / 126.7(3)° and 133.66(18)° / 129.84(17)° for crystal 1 and crystal 2, respectively. These angles are much smaller than that in fully dehydrated Na-X (Olson, 1995, Si/Al = 1.09) and Na-Y (Su et al., 2012, Si/Al = 1.56), 145.6(3)° / 141.2(4)° and 145.3(2)° / 140.4(2)°, respectively. This observation is an excellent agreement with the results of previous works (Kim et al., 2012a; Kim et al., 2012b). It indicates that zeolite framework is under some strain as a result of much smaller size and higher interaction of Li⁺ ion than Na⁺ ion: it strongly pulls the oxygen atoms of its 6-rings toward the 6-ring centers as the bond strengths indicate (Li-O, 333.5 kJ/mol, Na-O, 256.1 kJ/mol) (Lide et al., 1996a; Kim et al., 2012a).

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