

Synthesis of Fully Dehydrated Partially Cs⁺-exchanged Zeolite Y (FAU, Si/Al = 1.56), [Cs₄₅Na₃₀][Si₁₁₇Al₇₅O₃₈₄]-FAU and Its Single-crystal Structure

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Large single crystals of zeolite, [Na₇₅][Si₁₁₇Al₇₅O₃₈₄]-FAU (Na-Y, Si/Al = 1.56), were synthesized from gels with composition of 3.58SiO₂ : 2.08NaAlO₂ : 7.59NaOH : 455H₂O : 5.06TEA : 2.23TCl. One of these, a colorless single-crystal was ion exchanged by allowing aqueous 0.02 M CsOH to flow past the crystal at 293 K for 3 days, followed by dehydration at 673 K and 1 × 10⁻⁶ Torr for 2 days. The crystal structure of fully dehydrated partially Cs⁺-exchanged zeolite Y, [Cs₄₅Na₃₀][Si₁₁₇Al₇₅O₃₈₄]-FAU per unit cell (*a* = 24.9080(10) Å) was determined by single-crystal X-ray diffraction technique in the cubic space group *Fd* $\bar{3}$ *m* at 294(1) K. The structure was refined using all intensities to the final error indices (using only the 877 reflections with *F*_o > 4σ(*F*_o)) *R*₁ = 0.0966 (Based on *F*) and *R*₂ = 0.2641 (Based on *F*²). About forty-five Cs⁺ ions per unit cell are found at six different crystallographic sites. The 2 Cs⁺ ions occupied at site I, at the centers of double 6-ring (D6Rs, Cs-O = 2.774(10) Å and O-Cs-O = 88.9(3) and 91.1(3)^o). Two Cs⁺ ions are found at site I' in the sodalite cavity; the Cs⁺ ions were recessed 2.05 Å into the sodalite cavity from their 3-oxygen plane (Cs-O = 3.05(3) Å and O-Cs-O = 77.4(13)^o). Site-II' positions (opposite single 6-rings in the sodalite cage) are occupied by 7 Cs⁺ ions, each of which extends 2.04 Å into the sodalite cage from its 3-oxygen plane (Cs-O = 3.067(11) Å and O-Cs-O = 80.1(3)^o). The 26 Cs⁺ ions are nearly three-quarters filled at site II in the supercage, being recessed 2.34 Å into the supercage (Cs-O = 3.273(8) Å and O-Cs-O = 74.3(3)^o). The 4 Cs⁺ ions are found at site III deep in the supercage (Cs-O = 3.321(19) and 3.08(3) Å), and 4 Cs⁺ ions at another site III' (Cs-O = 2.87(4) and 3.38(4) Å). About 30 Na⁺ ions per unit cell are found at one crystallographic site; The Na⁺ ions are located at site I' in the sodalite cavity opposite double 6-rings (Na-O = 2.578(11) Å and O-Na-O = 97.8(4)^o).

Key Words: Faujasite-type zeolite, Na-Y, Single-crystal structure, Cesium, Sodium

Introduction

Faujasite-type zeolites (FAU) have been found in the range of applications from catalysts, adsorbents, and ion exchangers to quantum-confined semiconductors, materials for gas storage and catalysts capable of size and shape.^{1,2} Synthetic faujasite-type zeolites (FAU) with Si/Al ratios of 1.0 ~ 1.5 and 1.5 ~ 3.0 are called X and Y, respectively. Zeolites X and Y have topologically similar aluminosilicate extra-framework structures, although they are distinguished on the basis of cation composition and distribution, the Si/Al ratio and possible Si-Al ordering in tetrahedral sites.³

Cs⁺-exchanged zeolite is useful as microporous catalysts for industrially important reactions such as dehydrogenation of alcohols, isomerization of olefins, side-chain alkylation of toluene and the synthesis of 4-methylthiazole.⁴⁻⁶ In addition, Cs⁺-exchanged faujasite-type zeolites are used in fuel/gasoline desulphurization processes.⁷

The crystal structures of Cs⁺-exchanged faujasite-type zeolites have been reported by several scientists.⁸⁻¹² Smolin *et al.* investigated hydrated and dehydrated partially Cs⁺-exchanged zeolite X (Si/Al = 1.11(2)) with an exchanged level of 0.48(4) by using the single-crystal X-ray diffraction technique.⁸ They suggested Cs⁺ ions were located only in the supercage by the analysis of the cation distribution in the hydrated forms. Cs⁺ ions, however, had been observed in the sodalite and double

6-rings with minor amounts by the migration of cations in the dehydrated Cs⁺-exchanged zeolite X. Seff *et al.* synthesized a single-crystal of [Cs₁₂₈][Si₁₀₀Al₉₂O₃₈₄]-FAU by reaction [Na₉₂][Si₁₀₀Al₉₂O₃₈₄]-FAU with cesium vapor at 723 K this resulted that all sodalite and supercage were full of cesium atoms and ions in its structure.⁹ They observed that not only had all 92 Na⁺ ions been replaced with Cs⁺ by redox reaction, but an additional 36 atoms of Cs were sorbed to give [Cs₁₂₈][Si₁₀₀Al₉₂O₃₈₄]-FAU. Also, 6 Cs⁺ ions were found at the centers of double 6-rings. Kim *et al.*¹⁰ and Bae¹¹ reported that fully dehydrated partially Cs⁺-exchanged zeolite X (Si/Al = 1.09) were determined by single-crystal X-ray diffraction techniques in the space group *Fd* $\bar{3}$ at 294 K. Kim *et al.*¹⁰ prepared single crystal of [Cs₄₅Na₄₇][Si₁₀₀Al₉₂O₃₈₄]-FAU by the flow method using 0.02 M CsOH at 294 K for 100 hrs Bae¹¹ prepared single crystal of [Cs₅₂Na₄₀][Si₁₀₀Al₉₂O₃₈₄]-FAU by the flow method using exchange solution in which the molar ratio of CsOH and CsNO₃ was 1:1 with total concentration of 0.05 M. Bae¹¹ tried to prepare a fully Cs⁺-exchanged zeolite X from the conventional ion exchange method using different solution from Kim *et al.*'s,¹⁰ but failed. Koller *et al.* studied the structure of a 72% Cs⁺-exchanged zeolite Y (Si/Al = 2.49) dehydrated in vacuum at 623 K by ²³Na and ¹³³Cs magic-angle spinning NMR with combination of Rietveld refinement.¹² They observed that calcinations and rehydration of a 72% Cs⁺-exchanged zeolite Y led to a partial migration of Na⁺ ions from the sodalite units

into the supercages making them accessible to further ion exchange. They could obtain a 90% Cs⁺-exchanged zeolite Y by a three-fold exchange-calcination cycle of the 72% Cs⁺-exchanged sample without damage to the zeolite structure.

Some scientists suggested that a Cs⁺ ion passed through the 6-ring window to enter sodalite cavities and D6Rs even though a Cs⁺ ion (ionic diameter *ca.* 3.38 Å) is much larger than the size of 6-ring windows (van der Waals diameter (aperture) *ca.* 2.2 Å).^{10-12,14-17} In addition, they reported that the highest exchange level of Cs⁺ ions per unit cell was about 70% in faujasite-type zeolites by the conventional aqueous solution method at room temperature.¹³ Incomplete exchange with cesium may be the reason for the large cation size relative to zeolite aperture diameters.

This work was carried out to investigate the precise cation position of Cs⁺ and Na⁺ ions in fully dehydrated partially Cs⁺-exchanged zeolite Y with Si/Al = 1.56 by single-crystal X-ray diffraction technique, confirming the cation-site selectivity for Cs⁺ ions in Si-Al ordering at the tetrahedral site of zeolite framework. Previous reports for the structures of Cs⁺-exchanged faujasite-type zeolites will be compared with that from our results.

Experimental Section

Synthesis of Large Single Crystals of Zeolite Y (FAU). Colorless large single-crystals of zeolite Na-Y, stoichiometry of [Na₇₅][Si₁₁₇Al₇₅O₃₈₄]-FAU, with diameters up to *ca.* 280 μm were synthesized from gels with the composition of 3.58SiO₂ : 2.08NaAlO₂ : 7.59NaOH : 455H₂O : 5.06TEA : 2.23TCl.¹⁸ The starting gel was prepared from fumed silica (99.8%, Sigma), sodium aluminate (technical, Wako), sodium hydroxide (98%, Aldrich), triethanolamine (TEA, 99+%, Acros), bis(2-hydroxyethyl)-dimethylammonium chloride (TCl, 99%, Acros), and distilled water (resistivity > 18.4 MΩ-cm). Further description on the synthetic procedure is available in reference.¹⁹

The product was characterized by optical microscopy, SEM, and single-crystal X-ray technique analysis. Microscopic examination showed that the single crystals were colorless and transparent. SEM showed that the octahedral products were large faujasite-type single crystals with diameters up to *ca.* 280 μm (see Figure 1). The Si/Al ratio of faujasite-type single crystals was determined by a crystallographic-method using a fully Tl⁺-exchanged single crystal. The number of Tl⁺ ions per unit cell in this structure was 75.3(4), indicating the Si/Al ratio is equal to 1.56.²⁰ This was confirmed again by nine more single-crystal structure determinations of Tl⁺-exchanged zeolites Y. Tl⁺ ion was selected to determine the Si/Al ratio because of its powerful scattering factor for X-rays, facileness of quantitative ion exchange into zeolites, and easy distinguishableness from sodium ions, 80e⁻ and 10e⁻ for Tl⁺ and Na⁺ ion, respectively.

Ion-exchange of Single Crystal of Zeolite Y (FAU). One of synthetic zeolite [Na₇₅][Si₁₁₇Al₇₅O₃₈₄]-FAU, a clear colorless octahedron about 280 μm in cross-section was lodged in a Pyrex capillary. Ion exchange was accomplished by the dynamic method. 0.02 M aqueous CsOH (Aldrich, 99%, Na 192.0

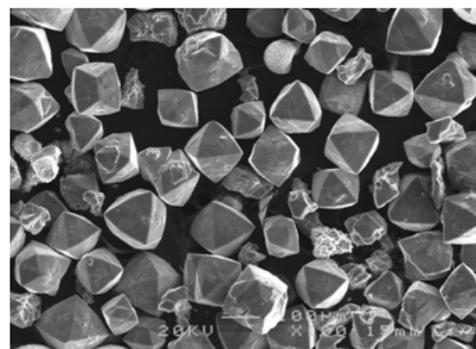


Figure 1. SEM image magnified 100× of the large single crystals of zeolite Y used in this work.

Table 1. Summary of experimental and crystallographic data

Crystal cross section (μm)	280
Ion exchange T (K)	293
Ion exchange for Cs ⁺ (days, mL)	3, 15.0
Dehydration T (K)	673
Data collection T (K)	294(1)
Space group, <i>Z</i>	<i>Fd</i> $\bar{3}m$, 1
X-ray source	PLS (4A MXW BL)
Wavelength (Å)	0.76999
Unit cell constant, <i>a</i> (Å)	24.9080(10)
2θ range in data collection (deg)	54.80
No. of unique reflections, <i>m</i>	922
No. of reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	877
No. of variables, <i>s</i>	57
Data/parameter ratio, <i>m/s</i>	16.2
Weighting parameters, <i>a/b</i>	0.120/1483.7
Final error indices	
<i>R</i> ₁ / <i>R</i> ₂ (<i>F</i> _o > 4σ(<i>F</i> _o)) ^a	0.0966/0.2641
<i>R</i> ₁ / <i>R</i> ₂ (all intensities) ^b	0.0987/0.2644
Goodness-of-fit ^c	1.142

^a*R*₁ = Σ|*F*_o - |*F*_c||/Σ*F*_o and *R*₂ = [Σ*w*(*F*_o² - *F*_c²)²/Σ*w*(*F*_o²)²]^{1/2}; *R*₁ and *R*₂ are calculated using only the 877 reflections for which *F*_o > 4σ(*F*_o). ^b*R*₁ and *R*₂ are calculated using all unique reflections measured. ^cGoodness-of-fit = (Σ*w*(*F*_o² - *F*_c²)²/(*m-s*))^{1/2}, where *m* and *s* are the number of unique reflections and variables, respectively.

ppm, Rb 154.9 ppm, K 8.80 ppm) was allowed to flow past the crystal at 294(1) K for 3 days.¹⁰ The resulting clear colorless crystal was dehydrated at 673 K under a dynamic vacuum of 1 × 10⁻⁶ Torr for 2 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. Still under a vacuum in capillary, the crystal was cooled down to room temperature and sealed in its capillary by torch. Microscopic examination showed that the crystal was turned to pale yellow.

X-ray Diffraction Work. X-ray diffraction data for the crystal dehydrated at 673 K were collected at 294(1) K using an ADSC Quantum 210 detector at Beamline 4A MXW at The Pohang Light Source. Crystal evaluation and data collection were done using λ = 0.76999 Å radiation with a detector-to-crystal distance of 60 mm. Preliminary cell constants and an

orientation matrix were determined from 36 sets of frames collected at scan intervals of 5° with an exposure time of 1 second per frame. The basic scale file was prepared using the program HKL2000.²¹ The reflections were successfully indexed by the automated indexing routine of the DENZO program.²¹ A total of 88,841 reflections were harvested for the crystal by collecting 72 sets of frames with 5° scans and an exposure time of 1 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects; negligible corrections for crystal decay were also applied. The space group $Fd\bar{3}m$ was determined by the program XPREP.²² A summary of the experimental and crystallographic data is presented in Table 1.

Structure Determination

Full-matrix least-squares refinement (SHELXL97)²³ was done on F_o^2 using all data. Refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), O(4)] in dehydrated $[K_{71}][Si_{121}Al_{71}O_{384}]$ -FAU.²⁴ The initial refinement using anisotropic thermal parameters

for (Si,Al) and framework oxygens converged to the error indices (defined in footnotes of Table 1) R_1 and R_2 of 0.5138 and 0.8637, respectively. See Table 2 for the steps of structure determination and refinement as new atomic position were found on successive difference Fourier electron-density functions.

The final cycles of refinement were done with anisotropic temperature factors at Cs(I), Cs(II') and Cs(II), and with the final refined weighting-scheme parameters (see Table 1). The final error indices R_1 and R_2 are given in Table 1. The largest peaks on the final difference-Fourier function (0.125, 0.125, 0.125) were not included in the final model either because they were too far from framework oxygen atoms to be cations, or because their peak heights were negligible. All shifts in the final cycles of refinement were less than of 0.1% of their corresponding estimated standard deviations. The final structural parameters are given in Table 3. Selected interatomic distances and angles are given in Table 4.

Fixed weights were used initially; the final weights were assigned using the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$; a and b were refined parameters.

Table 2. Initial steps of structure refinement^a

Step	Occupancy ^b at							R_1	R_2
	Cs(I)	Cs(I')	Cs(II')	Cs(II)	Cs(III)	Cs(III')	Na(I')		
1 ^c								0.5138	0.8637
2				14.6(6)				0.2852	0.7217
3			4.5(4)	22.2(7)				0.2190	0.6450
4			7.2(4)	27.9(6)			37.2(18)	0.1539	0.5342
5	1.6(2)		7.0(3)	25.9(5)			38.6(16)	0.1271	0.4843
6	1.8(2)	2.1(5)	7.1(3)	26.3(5)			32.0(22)	0.1229	0.4766
7	2.1(2)	1.8(2)	7.2(3)	25.5(4)	4.2(3)		28.5(14)	0.1038	0.2932
8	2.2(2)	1.9(2)	7.2(3)	25.8(3)	4.4(3)	4.2(4)	28.7(13)	0.0986	0.2661
9	2.2(2)	1.9(2)	7.2(3)	25.7(3)	4.4(3)	4.2(4)	28.6(13)	0.0966	0.2641

^aIsotropic temperature factors were used for all Cs⁺ and Na⁺ positions except for the last step. ^bThe occupancy is given as the number of ions per unit cell at each position. ^cOnly the atoms of zeolite framework were included in the initial structure model.

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

atom	Wyckoff position	Cation site	x	y	z	^b U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	^c Occupancy		
												initial	varied	fixed
Si,Al	192(i)		-548(1)	1252(1)	358(1)	145(10)	129(10)	112(10)	-35(6)	3(6)	-37(6)	192		
O(1)	96(h)		-1084(2)	0	1084(2)	243(25)	295(42)	243(25)	-67(23)	-23(32)	-67(23)	96		
O(3)	96(g)		-357(4)	746(3)	746(3)	312(47)	305(29)	305(29)	69(36)	-9(27)	-9(27)	96		
O(4)	96(g)		-710(4)	710(3)	1794(3)	313(46)	276(28)	276(28)	-157(34)	12(27)	-12(27)	96		
Cs(I)	16(c)	I	0	0	0	289(48)	289(48)	289(48)	97(35)	97(35)	97(35)		2.2(2)	2
Cs(I')	32(e)	I'	857(9)	857(9)	857(9)	500 ^d							1.9(2)	2
Cs(II')	32(e)	II'	1681(2)	1681(2)	1681(2)	523(31)	523(31)	523(31)	-85(19)	-85(19)	-85(19)		7.2(3)	7
Cs(II)	32(e)	II	2699(1)	2699(1)	2699(1)	427(9)	427(9)	427(9)	-2(5)	-2(5)	-2(5)		25.7(3)	26
Cs(III)	48(f)	III	492(7)	492(7)	4410(10)	500 ^d							4.4(3)	4
Cs(III')	96(g)	III'	437(15)	1131(15)	4613(15)	500 ^d							4.2(4)	4
Na(I')	32(e)	I'	673(2)	673(2)	673(2)	500 ^d							28.6(13)	30
												(Cs ⁺ + Na ⁺) = 74.2(4)		

^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. ^dTo achieve convergence, the isotropic thermal parameters at Cs(I'), Cs(III), Cs(III'), and Na(I') were fixed.

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

Distances		Angles	
(Si,Al)-O(1)	1.659(4)	O(1)-(Si,Al)-O(2)	111.8(3)
(Si,Al)-O(2)	1.659(3)	O(1)-(Si,Al)-O(3)	110.6(4)
(Si,Al)-O(3)	1.659(4)	O(1)-(Si,Al)-O(4)	107.0(4)
(Si,Al)-O(4)	1.653(3)	O(2)-(Si,Al)-O(3)	107.0(4)
Mean (Si,Al)	1.658(4)	O(2)-(Si,Al)-O(4)	107.7(4)
		O(3)-(Si,Al)-O(4)	112.7(5)
Cs(I)-O(3)	2.774(10)		
Cs(I')-O(3)	3.05(3)	(Si,Al)-O(1)-(Si,Al)	134.1(6)
Cs(II')-O(2)	3.067(11)	(Si,Al)-O(2)-(Si,Al)	148.6(6)
Cs(II)-O(2)	3.273(8)	(Si,Al)-O(3)-(Si,Al)	143.4(6)
Cs(III)-O(1)	3.321(19)	(Si,Al)-O(4)-(Si,Al)	142.8(6)
Cs(III)-O(4)	3.08(3)		
Cs(III')-O(1)	2.87(4)	O(3)-Cs(I)-O(3)	88.9(3), 91.1(3)
Cs(III')-O(4)	3.38(4)	O(3)-Cs(I')-O(3)	77.4(13)
Na(I')-O(3)	2.578(11)	O(2)-Cs(II')-O(2)	80.1(3)
Cs(I)···Na(I')	2.904(10)	O(2)-Cs(II)-O(2)	74.3(3)
		O(1)-Cs(III)-O(4)	49.0(3)
		O(1)-Cs(III')-O(4)	45.7(8), 47.9(9)
		O(3)-Na(I')-O(3)	97.8(4)

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

Table 5. Deviations (Å) of cations from 6-ring planes

	Position	Cation site	Displacement
At O(3) ^a	Cs(I)	I	-1.63
	Cs(I')	I'	2.05
	Na(I')	I'	1.26
At O(2) ^b	Cs(II')	II'	-2.04
	Cs(II)	II	2.34

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

Additional refinement data are given in Table 1. Atomic scattering factors^{25,26} for (Si,Al), O⁻, Na⁺ and Cs⁺ were used. All scattering factors were modified to account for anomalous dispersion.^{27,28}

Result and Discussion

The framework structure of faujasite is characterized by the double 6-ring (D6R, hexagonal prism), the sodalite cavity (a cubooctahedron) and the supercage (see Figure 2). Each unit cell has 8 supercages, 8 sodalite cavities, 16 D6Rs, 16 12-rings, and 32 single 6-rings (S6Rs).

The exchangeable cations, which balance the negative charge of the faujasite framework, usually occupy some or all of the sites shown with Roman numerals in Figure 2. The maximum occupancies at the cation sites I, I', II, II', III, and III' in faujasite are 16, 32, 32, 32, 48 and (in *Fd3m*) 192, respectively. Further description is available.²⁹⁻³¹

In this structure, the total number of Cs⁺ and Na⁺ ions per unit cell is 74.2(4), which is approximately equal to the sum of

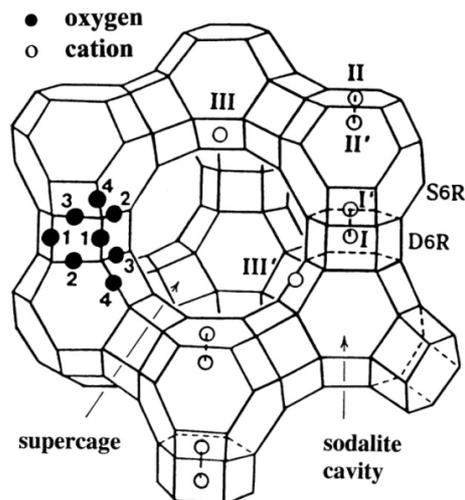


Figure 2. Stylized drawing of the framework structure of zeolite Y. Near the center of the each line segment is an oxygen atom. The nonequivalent oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Loewenstein's rule (ref. 32) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

occupancy number of TI⁺ ions in reference 20. This indicates that the product synthesized at this work has 1.56 of Si/Al ratio and is classified as zeolite Y.

Forty-five Cs⁺ ions are found at six different crystallographic sites and twenty-nine Na⁺ ions at one crystallographic site (see Table 3). Two Cs⁺ ions per unit cell are exactly at the centers of their D6Rs, at site I (see figure 3(a)). Notably, no Na⁺ ions are found at site I even though Na⁺ ions were found at this site in the other structures of partially Cs⁺-exchanged zeolites X.^{8,10,11} Each Cs⁺ ion at Cs(I) is coordinated by six O(3) oxygen atoms of hexagonal prism at distance of 2.774(10) Å, a little shorter than the sum of the conventional ionic radii of Cs⁺ and O²⁻, 1.67 + 1.32 (respectively) = 2.99 Å,¹⁴ indicative of a good fit (see Table 4). The Cs⁺ ions are octahedral. Each Cs⁺ ion at Cs(I) is recessed *ca.* 1.63 Å into the D6R from its 6-ring plane (see Table 5).

Two Cs⁺ and thirty Na⁺ ions at Cs(I') and Na(I'), respectively, occupy site I' in the sodalite cavity opposite D6Rs (see Figures 3(b), 3(c), and 4). These 32-fold positions are fully occupied indicating that Cs⁺ and Na⁺ ions at Cs(I') and Na(I'), respectively, are present at the every opposite D6Rs in the sodalite unit. Each ion at Cs(I') and Na(I') lies inside the sodalite cavity, 2.05 and 1.26 Å, respectively, from the plane of three O(3) framework oxygen of the D6Rs to which each is bound (see Table 5). The Cs⁺ and Na⁺ ions at Cs(I') and Na(I'), respectively, are coordinated by three O(3) oxygen atoms of their D6R at distances of 3.05(3) and 2.578(11) Å, respectively, which are almost the same as the sum of the ionic radii of Cs⁺ and O²⁻, 1.67 + 1.32 (respectively) = 2.99 Å and much longer than the sum of the ionic radii of Na⁺ and O²⁻, 0.97 + 1.32 (respectively) = 2.29 Å (see Table 4 and Figure 4).¹⁴ The actual O(3) coordinates in a Cs⁺-containing sodalite cavity must be somewhat different from those in a Na⁺-containing sodalite cavity and this must lead to inaccuracies in

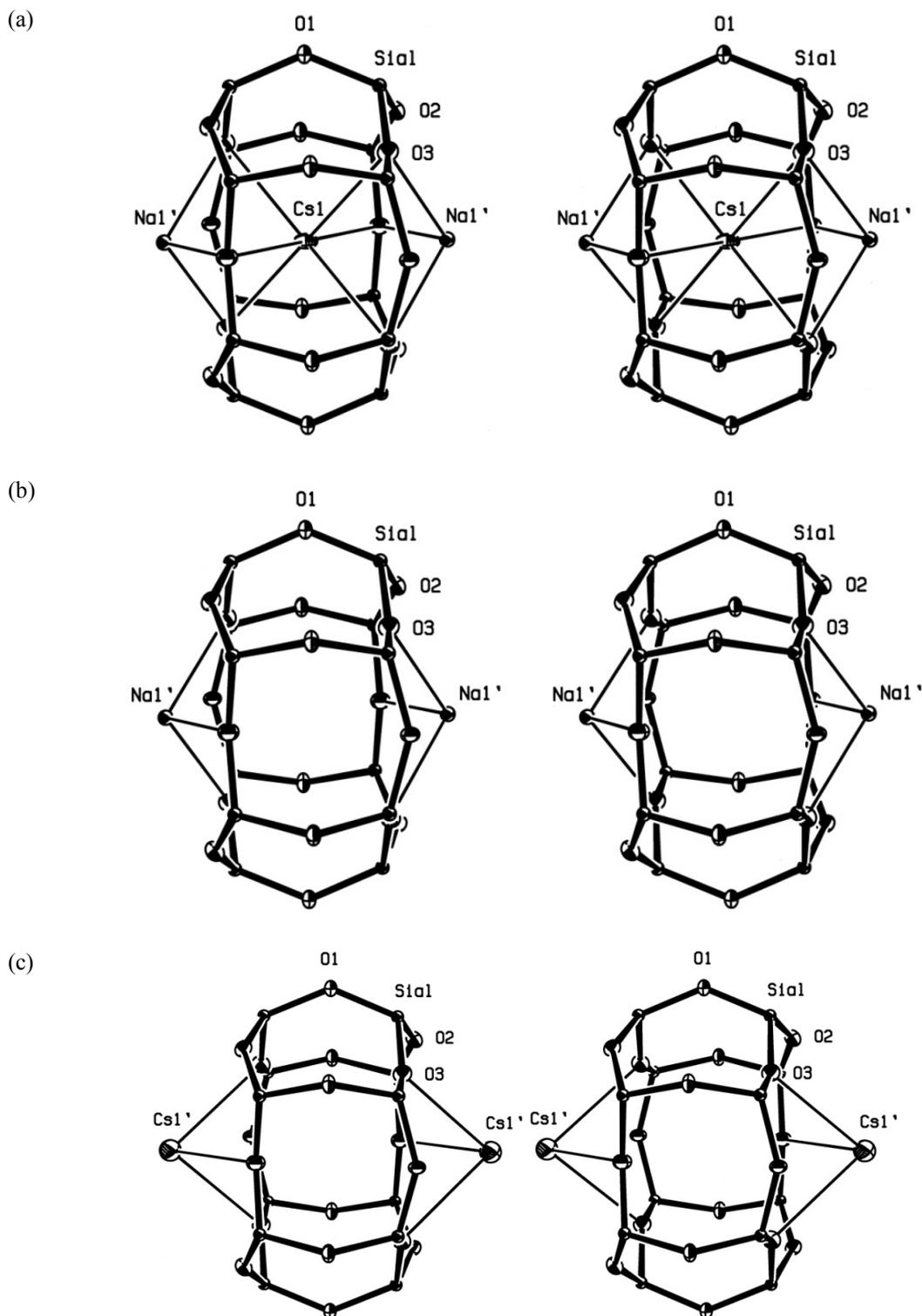


Figure 3. Stereoviews of the three ways that cations occupy double 6-rings (D6Rs) in dehydrated $[\text{Cs}_{45}\text{Na}_{30}][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]$ -FAU. Of the 16 D6Rs per unit cell in dehydrated $[\text{Cs}_{45}\text{Na}_{30}][\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]$ -FAU, two are occupied as shown in (a), one as shown in (b), and about thirteen as shown in (c). The zeolite Y framework is 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.

both Cs(I')-O(3) and Na(I')-O(3) bond lengths.

Seven Cs⁺ ions and twenty-six Cs⁺ ions are located at Cs(II') and Cs(II), respectively; site II' is opposite S6Rs in the sodalite while site II is opposite S6Rs in the supercage (see Figures 4 and 5). The Cs⁺ ions at site II' do not fill the 32-fold

site-II' position perhaps because some S6Rs are deficient in Al atoms. Similarly, the Cs⁺ ions at site II do not fill the 32-fold site-II position. Each Cs⁺ ion at Cs(II') and Cs(II) lies inside the sodalite and supercage, 2.04 and 2.34 Å, respectively, from the plane of three O(2) framework oxygens of the

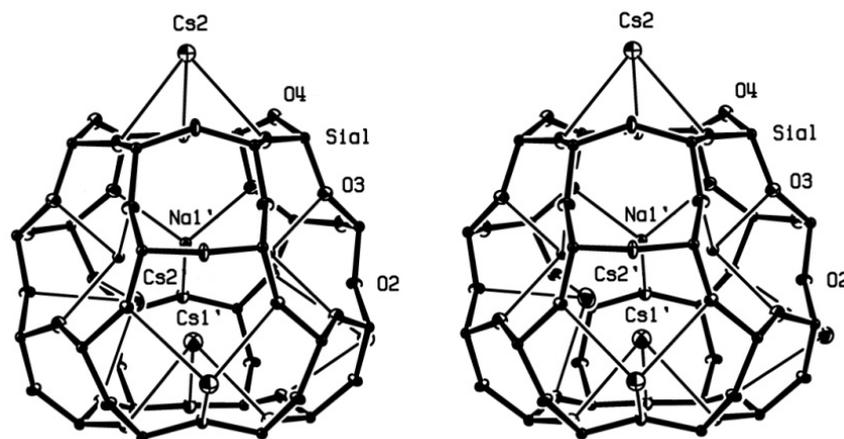


Figure 4. A stereoview of a representative sodalite unit in dehydrated $|\text{Cs}_{45}\text{Na}_{30}|[\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$. See the caption to Fig. 3 for other details.

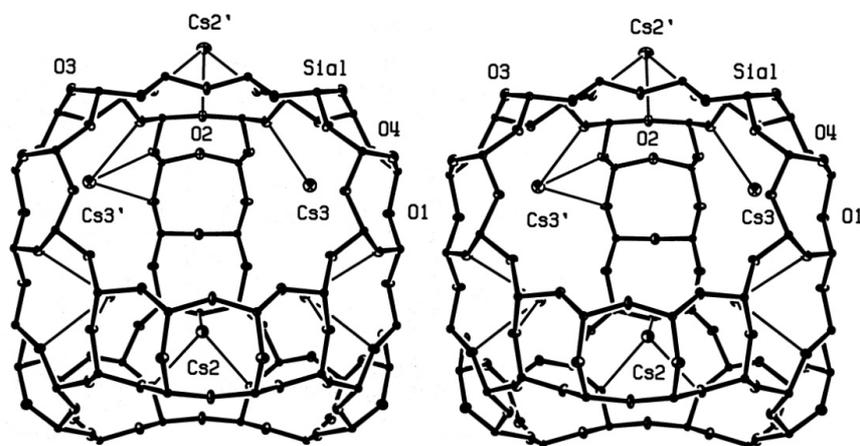


Figure 5. A stereoview of a representative supercage in dehydrated $|\text{Cs}_{45}\text{Na}_{30}|[\text{Si}_{117}\text{Al}_{75}\text{O}_{384}]\text{-FAU}$. See the caption to Fig. 3 for other details.

Table 6. Distribution of Cs^+ and Na^+ cations of fully dehydrated partially Cs^+ -exchanged faujasite-type zeolites

Crystal	Site Si/Al	I		I'		II'		II		III		III'		Extent of Cs^+ ion exchange (%)
		Cs^+	Na^+											
$\text{Cs}_{45}\text{Na}_{47}\text{-X}^a$	1.09	1.8	14.2	2.0	-	5.0	-	5.0	27.0	30.0	1.5	5.5	48.9	
$\text{Cs}_{52}\text{Na}_{40}\text{-X}^b$	1.09	1.0	14.0	2.0	-	6.0	-	6.0	26.0	36.0	1.0	-	56.5	
$\text{Cs}_{44}\text{Na}_{47}\text{-X}^c$	1.11	1.0	12.5	5.6	5.0	1.6	-	-	32.0	37.9	-	-	48.4	
$\text{Cs}_{45}\text{Na}_{29}\text{-Y}^d$	1.56	2.2	-	1.9	28.6	7.2	-	25.7	-	4.4	4.2	-	60.0	

^aReference 10. ^bReference 11. ^cReference 8. ^dThis work.

S6Rs to which each is bound (see Table 5). Seven and twenty-six Cs^+ ions at Cs(II') and Cs(II) bond to three O(2)s at 3.067(11) and 3.273(8) Å, respectively, are almost identical with the sum and are longer than the corresponding conventional ionic radii of Cs^+ and O^{2-} , $1.67 + 1.32 = 2.99$ Å,¹⁴ respectively (see Table 4).

The remaining Cs^+ ions at Cs(III) and Cs(III') occupy in the supercage at sites III and III', respectively. These positions are 92-fold and 192-fold positions, respectively. The Cs(III)-O(4) and Cs(III')-O(4) distances are 3.08(3) and 3.38(4) Å, respectively.

In this crystal structure, an interesting feature of the hexa-

gonal prism is that Cs^+ ions are occupied without Na^+ ions at site I. Site I' is filled with 30 Na^+ and 2 Cs^+ ions (see Table 3). These results are quite different from previous reports (see Table 6).^{8,10,11} Among three single-crystal structures of fully dehydrated partially Cs^+ -exchanged zeolites X,^{8,10,11} Smolin *et al.* reported that 12.5 Na^+ and 1.0 Cs^+ ions were found at site I in dehydrated zeolite X ($|\text{Cs}_{44}\text{Na}_{47}|[\text{Si}_{101}\text{Al}_{91}\text{O}_{384}]\text{-FAU}$, Si/Al = 1.11) and established a small content of cesium in the double 6-ring which could not cause crystallinity loss.⁸ Kim *et al.* and Bae also elucidated that both Na^+ and Cs^+ ions were observed at hexagonal prism of fully dehydrated partially Cs^+ -exchanged zeolites X ($|\text{Cs}_{45}\text{Na}_{47}|[\text{Si}_{100}\text{Al}_{92}\text{O}_{384}]\text{-FAU}$ and

[Cs₅₂Na₄₀][Si₁₀₀Al₉₂O₃₈₄]-FAU, Si/Al = 1.09).^{10,11} There are quite similarities in their cation distribution and occupancy at site I between structures from Kim *et al.*¹⁰ and Bae.¹¹ Kim *et al.* refined the structure with both Cs(I) and Na(I) at site I, with their thermal parameters constrained to be equal and their occupancies constrained to sum 16.0, converged with 14.2(2) Na⁺ and 1.8(2) Cs⁺ cations; Because *U* value of the Na(I) positions is somewhat too small and the occupancy is more than the maximum occupancy at that position, sixteen.¹⁰ For the same reason, Bae refined it Kim *et al.*'s method.¹¹

Hexagonal prism is not especially favorable to alkali-metal cations, from Na⁺ to Cs⁺, being independent of cation size. Low D6R occupancies of Cs⁺ ions in this work were seen for K⁺ and Rb⁺ ions in the structures of [K₁₄₂][Si₁₀₀Al₉₂O₃₈₄]-FAU³³ and [Rb₇₁Na₂₁][Si₁₀₀Al₉₂O₃₈₄]-FAU,³⁴ respectively, which were prepared by the reaction sodium-type zeolite X single-crystals with K and Rb vapor, respectively. Furthermore, five Na⁺ ions were found at the center of D6R in the structure of [Na₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU³⁵ which was prepared by conventional aqueous solution method at room temperature even though D6R is entirely empty in the structure of [Na₉₂][Si₁₀₀Al₉₂O₃₈₄]-FAU.³⁶

In this work, only Cs⁺ ions were found without Na⁺ ions at site II. This result is the same with Koller *et al.*'s structure.¹² Koller *et al.* studied the location of Na⁺ and Cs⁺ cations in dehydrated zeolite Y (Si/Al = 2.49) by Rietveld method and ²³Na and ¹³³Cs magic-angle spinning (MAS) NMR spectra and reported that the Na⁺ cations at site I' and site II were exchanged first for Cs⁺ ions with increasing Cs⁺ ions content.

Considering previous works by Smolin *et al.*,⁸ Kim *et al.*,¹⁰ and Bae,¹¹ we made an attempt to prepare fully dehydrated fully Cs⁺-exchanged faujasite-type zeolite but the conventional method of ionic exchange solution was not successful in this work. However, the highest Cs⁺-exchanged level (60%) in the single-crystal structure of faujasite-type zeolite was achieved by the conventional aqueous solution method at room temperature (see Table 6). In addition, differences are found in the cation distributions between previously reported structures of fully dehydrated partially Cs⁺-exchanged zeolites^{8,10-12} and that of this work. With an increasing Si/Al ratio, the population of Na⁺ ions at site I are decreased. On the other hand, the occupancies of Na⁺ and Cs⁺ ions at site I' and II, respectively, are dramatically increased (see Table 6). It seems due to the Si-Al ordering in tetrahedral site by the increased Si/Al ratio. In addition, Na⁺ ions at site I are replaced by Cs⁺ ions at the increased Cs⁺-exchanged level. Na⁺ ions at site II' are not found at all the structures of the fully dehydrated partially Cs⁺-exchanged faujasite-type zeolites.^{8,10,11}

Summary

Large single crystals of zeolite Y (FAU) were prepared from gels of composition 3.58SiO₂: 2.08NaAlO₂: 7.59NaOH : 455H₂O : 5.06TEA : 2.23TCl and the synthetic single crystals had octahedron shape, colorless, and *ca.* 280 μm.

The single crystal structure of fully dehydrated partially Cs⁺-exchanged zeolite Y (Si/Al = 1.56) was determined by X-ray diffraction techniques in the cubic space group *Fd* $\bar{3}$ *m* (*a* = 24.9080(10) Å) at 294 K. In the crystal-structure of [Cs₄₅

Na₃₀][Si₁₁₇Al₇₅O₃₈₄]-FAU, about forty-five Cs⁺ ions per unit cell are found at six different crystallographic sites. The 2 Cs⁺ ions are occupied at site I, at the centers of double 6-ring (Cs(I)-O(3) = 2.774(10) Å and O(3)-Cs(I)-O(3) = 88.9(3) and 91.1(3)^o). Two Cs⁺ ions are found at site I' in the sodalite cavity; the Cs⁺ ions are recessed 2.05 Å into the sodalite cavity from their 3-oxygen plane (Cs(I')-O(3) = 3.05(3) Å and O(3)-Cs(I')-O(3) = 77.4(13)^o). Site-II' positions (opposite S6Rs in the sodalite cage) are filled 7 Cs⁺ ions, each of which extends 2.04 Å into the sodalite cage from its 3-oxygen plane (Cs(III')-O(2) = 3.067(11) Å and O(2)-Cs(III')-O(2) = 80.1(3)^o). The 26 Cs⁺ ions are nearly three-quarters filled at site II in the supercage, being recessed 2.34 Å into the supercage (Cs(II)O(2) = 3.273(8) Å and O(2)-Cs(II)-O(2) = 74.3(3)^o). The 4 Cs⁺ ions are found at site III deep in the supercage (Cs(III)-O(1) = 3.321(19) Å and Cs(III)-O(4) = 3.08(3) Å), and 4 Cs⁺ ions are found at another site III' (Cs(III')-O(1) = 2.87(4) Å and Cs(III')-O(4) = 3.38(4) Å). About 30 Na⁺ ions per unit cell are found at one crystallographic site, locating at site I' in the sodalite (Na(I')-O(3) = 2.578(11) Å and O(3)-Na(I')-O(3) = 97.8(4)^o). Fully Cs⁺-exchanged zeolite Y was not achieved because Cs⁺ ions are too large to enter the 6-ring windows. However, this work achieved the highest Cs⁺-exchanged level (60%) in the single-crystal structure of zeolite Y by conventional aqueous solution method at room temperature. The distributions of Cs⁺ and Na⁺ ions in our result, as compared to fully dehydrated partially Cs⁺-exchanged zeolites X, may be due to the local Si/Al order among the T atoms in zeolite Y.

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Supporting Information. Tables of calculated and observed structure factors (11 pages). The supporting materials are available via the Internet <http://www.kcsnet.or.kr/bkcs>.

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