

Determination of Si/Al Ratio of Faujasite-type Zeolite by Single-crystal X-ray Diffraction Technique. Single-crystal Structures of Fully Tl⁺- and Partially K⁺-exchanged Zeolites Y (FAU), [Tl₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU and [K₅₃Na₁₈][Si₁₂₁Al₇₁O₃₈₄]-FAU

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Large colorless single crystals of faujasite-type zeolite with diameters up to 200 μm have been synthesized from gels with the composition of 3.58SiO₂:2.08NaAlO₂:7.59NaOH:455H₂O:5.06TEA:1.23TCl. Two of these, colorless octahedron about 200 μm in cross-section have been treated with aqueous 0.1 M TIC₂H₃O₂ and KNO₃ in order to prepare Tl⁺- and K⁺-exchanged faujasite-type zeolites, respectively, and then determined the Si/Al ratio of the zeolite framework. The crystal structures of [Tl₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU and [K₅₃Na₁₈][Si₁₂₁Al₇₁O₃₈₄]-FAU per unit cell, $a = 24.9463(2)$ and $24.9211(16)$ Å, respectively, dehydrated at 673 K and 1×10^{-6} Torr, have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}m$ at 294 K. The two single-crystal structures were refined using all intensities to the final error indices (using only the 905 and 429 reflections for which $F_o > 4\sigma(F_o)$) $R_1/R_2 = 0.059/0.153$ and $0.066/0.290$, respectively. In the structure of fully Tl⁺-exchanged faujasite-type zeolite, 71 Tl⁺ ions per unit cell are located at four different crystallographic sites. Twenty-nine Tl⁺ ions fill site I' in the sodalite cavities on 3-fold axes opposite double 6-rings (Tl-O = 2.631(12) Å and O-Tl-O = 93.8(4)°). Another 31 Tl⁺ ions fill site II opposite single 6-rings in the supercage (Tl-O = 2.782(12) Å and O-Tl-O = 87.9(4)°). About 3 Tl⁺ ions are found at site III in the supercage (Tl-O = 2.91(6) and 3.44(3) Å), and the remaining 8 occupy another site III' (Tl-O = 2.49(5) and 3.06(3) Å). In the structure of partially K⁺-exchanged faujasite-type zeolite, 53 K⁺ ions per unit cell are found at five different crystallographic sites and 18 Na⁺ ions per unit cell are found at two different crystallographic sites. The 4 K⁺ ions are located at site I, the center of the hexagonal prism (K-O = 2.796(8) Å and O-K-O = 89.0(3)°). The 10 K⁺ ions are found at site I' in the sodalite cavity (K-O = 2.570(19) Å and O-K-O = 99.4(9)°). Twenty-two K⁺ ions are found at site II in the supercage (K-O = 2.711(9) Å and O-K-O = 94.7(3)°). The 5 K⁺ ions are found at site III deep in the supercage (K-O = 2.90(5) and 3.36(3) Å), and 12 K⁺ ions are found at another site III' (K-O = 2.55(3) and 2.968(18) Å). Twelve Na⁺ ions also lie at site I' (Na-O = 2.292(10) and O-Na-O = 117.5(5)°). The 6 Na⁺ ions are found at site II in the supercage (Na-O = 2.390(17) Å and O-Na-O = 113.1(11)°). The Si/Al ratio of synthetic faujasite-type zeolite is 1.70 determined by the occupations of cations, 71, in two single-crystal structures.

Key Words : Faujasite-type zeolite, Si/Al ratio, Crystal structure, Thallium, Potassium

Introduction

Single-crystal X-ray diffraction is one of the most frequently used and informative techniques for the characterization of solid materials. The single crystals of solid material should be grown to minimum of 80 μm to be examined in the conventional single-crystal X-ray diffractometer. Because of this reason, the growth of large single crystals of zeolite is of interest in order to obtain the 3-dimensional structural parameters of the framework, and the information on the exchangeable cations and the adsorbates.

The large single crystals of zeolites have been synthesized by numerous scientists. After first reporting the method of preparing the large single crystals of synthetic zeolites by Ciric,¹ Charnell reported the growing method of appreciable quantities of large crystals of Na-A and Na-X zeolites.² He suggested that the synthesized single crystals were suitable

for single-crystal X-ray diffraction studies and for diffusion measurements. Sacco *et al.*³⁻⁵ synthesized the large single crystals of faujasite-type zeolites (Si/Al = 1.35-1.45, 1.71, and 1.90) with diameters of 95 to 340 μm from a reaction mixture composed of Na₂O, Al₂O₃, SiO₂, H₂O, triethanolamine (TEA), bis(2-hydroxyethyl)dimethylammonium chloride (TCl). Especially, Sacco and co-workers made several attempts to grow large, perfect crystals of zeolite on the space shuttle.^{6,7} Zeolite A, X, mordenite, Beta, and silicate crystals grown on the USML-1 and USML-2 missions in 1992 and 1997, respectively, had exhibited substantial increase in size over those grown on the ground.

Synthetic faujasite (FAU) with $1.5 \leq \text{Si/Al} \leq 3.0$ is called zeolite Y. Zeolite Y has a wide range of industrial applications as an ion exchanger, a sorption agent, a molecular sieve, and a catalyst because of its structural stability, large and accessible pore volume, high activity, and high regener-

ability.⁸ So we have synthesized the large single crystals of zeolite Y diameters up to 200 μm were synthesized from gels with the composition $3.58\text{SiO}_2:2.08\text{NaAlO}_2:7.59\text{NaOH}:455\text{H}_2\text{O}:5.06\text{TEA}:1.23\text{TCl}$ in order to study those chemical properties. However, the products were mixtures of large faujasite-type zeolites and of polycrystalline spherical impurities. It is difficult or impossible to determine the Si/Al ratio of faujasite-type zeolites by using ICP and Si NMR with the products of zeolite mixture.

In this work, large single crystals of faujasite-type zeolite was synthesized and then the Si/Al ratio of faujasite-type zeolite framework was determined crystallographically using fully Ti^+ and partially K^+ -exchanged single crystals. Ti^+ and K^+ were selected for this work because of their large scattering factors for X-rays (80, 18, and 10 e^- for Ti^+ , K^+ , and Na^+ , respectively), their large difference in ionic radii (1.47, 1.33, and 0.97 \AA for Ti^+ , K^+ , and Na^+ , respectively), their ease of quantitative ion exchange into zeolites, and their easy distinguishability from Na^+ . It was also done as a test of the suitability of these faujasite-type zeolite crystals for further work.

Experimental Section

Synthesis of the Large Single Crystals of Faujasite-type Zeolite. Colorless single crystals of faujasite-type zeolite with diameters up to *ca.* 200 μm were synthesized from gels of composition $3.58\text{SiO}_2:2.08\text{NaAlO}_2:7.59\text{NaOH}:455\text{H}_2\text{O}:5.06\text{TEA}:1.23\text{TCl}$. A starting gel was prepared from fumed silica (99.8%, Sigma), sodium aluminate (technical, Wako), sodium hydroxide (96%, Wako), triethanolamine (TEA, 99+%, Acros), bis(2-hydroxyethyl)dimethylammonium chloride (TCl, 99%, Acros), and distilled water.

First, a silica slurry was prepared by placing 0.58 g of fumed silica in 10 g of distilled water in a 30-mL PTFE beaker. A suspension was prepared by shaking in an orbital shaker at 200 rpm for 10 min. In a 250-mL PTFE beaker, 11.51 g of sodium hydroxide was dissolved in 170.4 g of distilled water, and 6.47 g of sodium aluminate was added. The resulting solution was filtered through a 0.2- μm membrane filter (PTFE syringe, Whatman). After adding 15.19 g of TEA and 4.19 g of TCl to the filtered sodium aluminate solution, it was filtered two times through 0.2- μm membrane filters. Finally, the latter solution was added to the former slowly; the mixture was a very viscous gel. These steps were all done at 294 K. This gel was put in a 30-mL PTFE bottle which was placed in a convection oven at 368 K for 18 days. The product was filtered, washed with distilled water 10 times, and dried at 323 K for 2 days.

The product was characterized by optical microscopy, powder XRD (D/max 2000, Rigaku), and SEM-EDS (JSM-300, Jeol) analysis. SEM and powder XRD showed that the octahedral products were large faujasite-type single crystals with diameters up to 100 to 200 μm and that the polycrystalline spherical impurities were gismondine. Microscopic examination showed that the single crystals were transparent and colorless.

Ion-exchange of Faujasite-type Zeolites. Two of crystals, colorless octahedron about 200 μm in cross-section were lodged in each fine Pyrex capillary. Crystals of hydrated $[\text{Ti}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU (crystal 1) and $[\text{K}_{53}\text{Na}_{18}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU (crystal 2) were prepared by the dynamic (flow) ion-exchange of $[\text{Na}_{71}][\text{Si}_{121}\text{Al}_{71}\text{O}_{384}]$ -FAU with aqueous 0.1 M $\text{TiCl}_2\text{H}_3\text{O}_2$ (Alfa Aesar, 99.999%) and KNO_3 (Aldrich, 99.999%), respectively.^{9,10} The pH values were 6.4 and 5.9 for each solution. The solution was allowed to flow past the crystal at a velocity of approximately 1.5 cm/s for 5 days at 294(1) K. The resulting clear, colorless, hydrated Ti^+ and K^+ -exchanged faujasite-type zeolite crystals were dehydrated at 673 K and 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 cooled to ambient temperature to prevent the movement of water molecules from more distant parts of the vacuum system to the crystal. Still under vacuum in their capillaries, the crystals were then allowed to cool and were sealed in their capillaries and removed from the vacuum lines by torch. Microscopic examinations showed that the crystals had become black and pale yellow for Ti^+ and K^+ -exchanged crystals, respectively.

X-ray Data Collection. X-ray diffraction data for the two single crystals dehydrated at 673 K were collected at 294(1) K using an ADSC Quantum210 detector at Beamline 4A MXW at The Pohang Light Source. Crystal evaluation and data collection were done using $\lambda = 0.76999$ \AA radiation with a detector-to-crystal distance of 6.0 cm. 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 HKL2000.¹¹ The reflections were successfully indexed by the automated indexing routine of the DENZO program.¹¹ The total of 85,711 and 109,522 reflections were harvested for each 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.¹² A summary of the experimental and crystallographic data is presented in Table 1.

Analysis for Ti^+ , Na^+ , and K^+ . Later in this work, to test the crystallographic indications that Ti^+ , Na^+ , and K^+ are present in the crystals studied, each single crystal after X-ray data collections were intentionally broken to expose fresh surfaces, and were attached to carbon-attach tape for analysis (see Figure 1). SEM images were taken using a JSM-6300 scanning electron microscope and atomic concentrations were measured with an energy dispersive X-ray spectrometer (EDS), both at 294 K and 1×10^{-7} Torr (see Figure 1).

The SEM-EDS experiments showed that the relative intensity of Si was larger than that of Al. The lines of Ti in spectrum (a) in Figure 1 indicate that the replacement of Na^+

Table 1. Summary of experimental and crystallographic data

	Crystal 1	Crystal 2
Formula	Tl ₇₁ Si ₁₂₁ Al ₇₁ O ₃₈₄	K ₅₃ Na ₁₈ Si ₁₂₁ Al ₇₁ O ₃₈₄
Crystal cross-section (mm)	0.20	0.20
Ion exchange T (K)	294	294
Ion exchange for Tl ⁺ (day, mL)	5, 10	–
Ion exchange for K ⁺ (day, mL)	–	5, 15
Dehydration T (K)	673	673
Crystal color	black	pale brown
Data collection T (K)	294(1)	294(1)
Space group, Z	<i>Fd</i> $\bar{3}$ <i>m</i> , 1	<i>Fd</i> $\bar{3}$ <i>m</i> , 1
X-ray source	PLS (4A MXW BL)	PLS (4A MXW BL)
Wavelength (Å)	0.76999	0.76999
Unit cell constant, a (Å)	24.946(3)	24.921(3)
2θ range in data collection (deg)	60.70	60.61
No. of unique reflections, <i>m</i>	923	845
No. of reflections with <i>F</i> _o > 4σ(<i>F</i> _o)	905	429
No. of variables, <i>s</i>	54	58
Data/parameter ratio, <i>m/s</i>	17.1	14.6
Weighting parameters, <i>a/b</i>	0.037/3917.6	0.116/197.3
Final error indices		
<i>R</i> ₁ / <i>R</i> ₂ (<i>F</i> _o > 4σ(<i>F</i> _o)) ^a	0.0589/0.1530	0.0663/0.2898
<i>R</i> ₁ / <i>R</i> ₂ (all intensities) ^b	0.0594/0.1535	0.1541/0.2850
Goodness-of-fit ^c	1.212	1.301

^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 905 and 429 reflections for which *F*_o > 4σ(*F*_o) for crystal 1 and 2, respectively. ^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.

by Tl⁺ was fully completed. Surprisingly, SEM-EDS of K⁺-exchanged zeolite showed that the lines of K and Na in spectrum as shown in Figure 1(b), indicating ion-exchanging of K⁺ was not completed in this work. These measurements are in reasonable agreement with the crystallographic results.

The Na⁺ content of these crystals was something we had sought to avoid, and their presence is a surprise. It is due either to incomplete K⁺ exchange, perhaps due to the presence of the template cation (bis(2-hydroxyethyl)dimethylammonium), or to exchange of Na⁺ into the crystals from the potassium nitrate solution (99.999% KNO₃, 10.2 ppm Na, 0.6 ppm B, 0.2 ppm Ca).

Structure Determination

Full-matrix least-squares refinement (SHELXL97)¹³ was done on *F*_o² using all data. Refinement was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), O(3), and O(4)] in dehydrated [Tl₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU.⁹ The initial refinements of crystal 1 and 2 using anisotropic thermal parameters for all positions converged to the error indices (defined in Table 1, footnote a) *R*₁/*R*₂ = 0.59/0.86 and 0.29/0.71, respectively.

See Table 2 for the steps of structure determination and refinement as new atomic positions were found on successive difference Fourier electron-density functions.

The final cycles of anisotropic refinement, done with the

occupancies at the framework atoms and Tl⁺, K⁺, and Na⁺ ions fixed at their nearest integral values to facilitate the discussion (see Table 3) and with the final weighting-scheme parameters, converged to *R*₁/*R*₂ = 0.059/0.153 and 0.066/0.290 in crystals 1 and 2, respectively. On the final difference Fourier function for each crystal, the largest peak appeared at (0.089, 0.089, 0.589) and (0.125, 0.125, 0.125). They were not included in the final models because they were too far from framework oxygen atoms to be a cation.

All shifts in the final cycles of refinement were less than 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/[σ²(*F*_o²) + (*aP*)² + *bP*] where *P* = [Max(*F*_o², 0) + 2*F*_c²]/3, with *a/b* = 0.037/3917.6 and *a/b* = 0.116/197.3 as refined parameters in crystals 1 and 2, respectively (see Table 1). Atomic scattering factors for Tl⁺, K⁺, Na⁺, O[–], and (Si,Al)^{1.82+} were used.^{14,15} The function describing (Si,Al)^{1.82+} is the weighted mean of the Si⁴⁺, Si⁰, Al³⁺, and Al⁰ functions. All scattering factors were modified to account for anomalous dispersion.^{16,17}

Results and Discussion

Synthesis of the Large Single Crystals of Faujasite-type Zeolite. Large colorless single crystals of faujasite-type zeolite with diameters up to ca. 200 μm have been

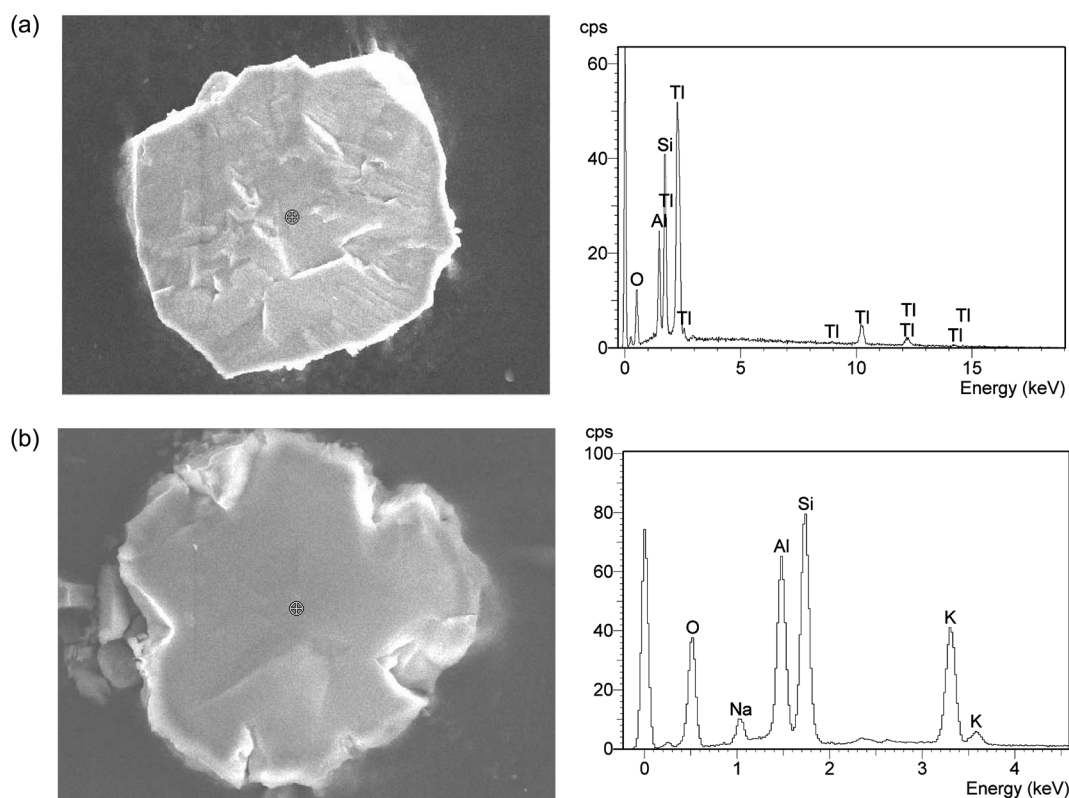


Figure 1. The SEM images magnified 750, intentionally broken for EDS analysis and EDS spectra of the fully Tl^+ -exchanged zeolite Y (a) and of the partially K^+ -exchanged zeolite Y (b).

synthesized from gels with the composition of $3.58\text{SiO}_2:2.08\text{NaAlO}_2:7.59\text{NaOH}:455\text{H}_2\text{O}:5.06\text{TEA}:1.23\text{TCl}$. The products contained the aggregated octahedral crystals and the polycrystalline spherical impurities. The optical microscopy, XRD, and SEM showed that the aggregated octahedral products were large transparent crystals of faujasite-type zeolite with diameters up to *ca.* $200\ \mu\text{m}$ and that the translucent polycrystalline spheres were gismondine. Large, uniform, and well shaped octahedral single crystals of faujasite-type zeolite, in this work, are suitable for single-crystal X-ray diffraction experiments.

Further EDS experiment using the fresh surface of an intentionally broken large single crystal of faujasite-type zeolite confirmed the present of Si, Al, O, and Tl (see Figure 1(a)). This indicates faujasite-type zeolite (crystal 1) was exchanged fully with Tl^+ ions. Otherwise, EDS experiment of crystal 2 showed that the spectrum of Si, Al, O, Na, and K. This means that it was not fully exchanged with K^+ ions in crystal 2 (see Figure 1(b)). These results are consistent with the later more precise crystallographic determinations.

Brief Description of FAU. 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 S6Rs (single 6-rings).

The exchangeable cations, which balance the negative charge of the faujasite framework, usually occupy some or

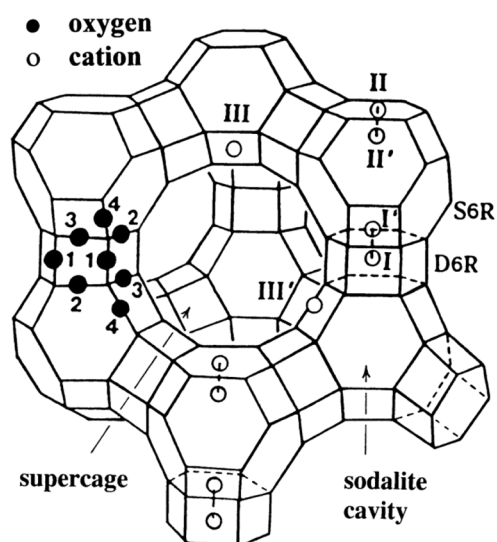


Figure 2. Stylized drawing of the framework structure of zeolite Y. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. There is no evidence in this work of any ordering of the silicon and aluminum atoms among the tetrahedral positions, although it is expected that Loewenstein's rule (ref. 18) would be obeyed. Extraframework cation positions are labeled with Roman numerals.

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 96, respectively.

Table 2. Initial steps of structure refinements^a(a) Crystal 1, [Ti₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU

Step	Occupancy ^b at				R ₁	R ₂
	Ti(I')	Ti(II)	Ti(III)	Ti(III')		
1 ^c					0.5920	0.8624
2	30.7(36)				0.4686	0.7929
3	31.5(19)	29.8(18)			0.3332	0.5724
4	32.3(20)	43.1(28)		13.2(19)	0.3065	0.5508
5	28.6(5)	30.9(5)	2.6(5)	8.5(10)	0.0891	0.1806
6	28.9(4)	31.2(5)	2.7(5)	8.3(8)	0.0589	0.1530
7	29.0 ^d	31.0 ^d	3.0 ^d	8.0 ^d	0.0589	0.1530

(b) Crystal 2, [K₅₃Na₁₈][Si₁₂₁Al₇₁O₃₈₄]-FAU

Step	Occupancy ^b at						R ₁	R ₂	
	K(I)	K(I')	K(II)	K(III)	K(III')	Na(I')			Na(II)
1 ^c								0.2898	0.7123
2			24.1(14)					0.1761	0.5664
3			24.3(11)			24.5(23)		0.1301	0.4799
4	4.6(8)		22.9(9)			22.2(20)		0.1195	0.4608
5	4.5(7)		21.0(10)			24.9(22)	3.9(13)	0.1107	0.4501
6	4.0(6)	7.1(11)	20.7(10)			15.0(18)	6.0(14)	0.0916	0.4250
7	4.0 ^d	8.7(12)	21.4(7)	4.5(10)		15.4(18)	6.0 ^d	0.0823	0.3468
8		8.3(10)	22.5(6)	5.4(9)	12.3(19)	15.2(15)		0.0711	0.2928
9		8.2(10)	22.0 ^d	5.0 ^d	12.0 ^d	15.1(15)		0.0715	0.2974
10		10.3(38)				11.8(60)		0.0687	0.2884
11		10.0 ^d				12.0 ^d		0.0663	0.2898

^aIsotropic temperature factors were used for all Na⁺ positions except for the last step. ^bThe occupancy is given as the number of Ti⁺, K⁺, and Na⁺ ions per unit cell. ^cOnly the atoms of zeolite framework were included in the initial structure model. ^dThe occupancy was fixed at its nearest integral value.

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
Crystal 1, [Ti ₇₁][Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU														
Si, Al	192(<i>i</i>)		-539(1)	1254(1)	362(1)	153(15)	131(15)	132(15)	-18(10)	18(10)	-21(10)	192		
O(1)	96(<i>h</i>)		-1046(3)	0	1046(3)	223(37)	242(60)	223(37)	-70(33)	-20(46)	70(33)	96		
O(2)	96(<i>g</i>)		-16(4)	-16(4)	1421(5)	258(38)	258(38)	260(65)	-37(37)	37(37)	91(52)	96		
O(3)	96(<i>g</i>)		-322(5)	767(3)	767(3)	211(59)	203(35)	203(35)	14(45)	0(33)	0(33)	96		
O(4)	96(<i>g</i>)		-712(5)	708(4)	1792(4)	219(60)	228(38)	228(38)	-56(48)	71(35)	-71(35)	96		
Ti(I')	32(<i>e</i>)	I'	732(1)	723(1)	723(1)	274(5)	274(5)	274(5)	-54(3)	-54(3)	54(3)		28.9(4)	29
Ti(II)	32(<i>e</i>)	II	2536(1)	2536(1)	2536(1)	311(6)	311(6)	311(6)	-48(3)	-48(3)	-48(3)		31.2(5)	31
Ti(III)	96(<i>g</i>)	III	1250	1250	4089(33)	2813(85)	2813(85)	282(203)	0	0	1781(866)		2.7(5)	3
Ti(III')	192(<i>g</i>)	III'	671(14)	671(14)	4208(19)	3359(535)	3359(535)	561(143)	-215(196)	-215(196)	890(531)		8.3(8)	8
												ΣTi ⁺ = 71.1(6)		
Crystal 2, [K ₅₃ Na ₁₈][Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU														
Si, Al	192(<i>i</i>)		-552(1)	1254(1)	355(1)	458(13)	425(14)	402(12)	-46(10)	1(8)	-33(11)	192		
O(1)	96(<i>h</i>)		-1078(2)	0	1078(2)	516(30)	647(50)	516(30)	-88(28)	-9(35)	88(28)	96		
O(2)	96(<i>g</i>)		-32(3)	-32(3)	1400(3)	621(33)	621(33)	622(49)	-98(31)	98(31)	175(43)	96		
O(3)	96(<i>g</i>)		-361(3)	751(2)	751(2)	674(56)	523(32)	523(32)	145(39)	9(31)	9(31)	96		
O(4)	96(<i>g</i>)		-692(3)	698(2)	1802(2)	583(51)	550(32)	550(32)	-132(39)	14(28)	-14(28)	96		
K(I)	16(<i>c</i>)	I	0	0	0	746(89)	746(89)	746(89)	278(117)	278(117)	278(117)		4.0(6)	4
K(I')	32(<i>e</i>)	I'	663(8)	663(8)	663(8)	931(92)	931(92)	931(92)	395(115)	395(115)	395(115)		10.3(38)	10
K(II)	32(<i>e</i>)	II	2486(2)	2486(2)	2486(2)	529(22)	529(22)	529(22)	39(25)	39(25)	39(25)		22.5(6)	22
K(III)	96(<i>g</i>)	III	1250	1250	4053(29)	1253(315)	1253(315)	1413(554)	0	0	-496(411)		5.0(9)	5
K(III')	192(<i>g</i>)	III'	1808(22)	1808(22)	4215(13)	3120(523)	3120(523)	378(172)	-344(249)	-344(249)	1372(645)		11.9(19)	12
Na(I')	32(<i>e</i>)	I'	465(8)	465(8)	465(8)	722(99)	722(99)	722(99)	26(92)	26(92)	26(92)		11.8(60)	12
Na(II)	32(<i>e</i>)	II	2303(13)	2303(13)	2303(13)	395(126)	395(126)	395(126)	263(158)	263(158)	263(158)		6.0(14)	6
												ΣK ⁺ (53.7(16)) + ΣNa ⁺ (17.8(37)) = 71.5(27)		

^aPositional parameters × 10⁴ and thermal parameters × 10⁴ 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[-2π²a⁻²(U₁₁h² + U₂₂k² + U₃₃l² + 2U₂₃kl + 2U₁₃hl + 2U₁₂hk)]. ^cOccupancy factors are given as the number of atoms or ions per unit cell.

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

Crystal 1		Crystal 2	
[Ti ₇₁][Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU		[K ₅₃ Na ₁₈][Si ₁₂₁ Al ₇₁ O ₃₈₄]-FAU	
(Si,Al)-O(1)	1.639(5)	(Si,Al)-O(1)	1.641(3)
(Si,Al)-O(2)	1.663(5)	(Si,Al)-O(2)	1.657(3)
(Si,Al)-O(3)	1.671(5)	(Si,Al)-O(3)	1.665(3)
(Si,Al)-O(4)	1.652(5)	(Si,Al)-O(4)	1.648(3)
Mean (Si,Al)-O	1.656(5)	Mean (Si,Al)-O	1.653(3)
Ti(I')-O(3)	2.631(12)	K(I)-O(3)	2.796(8)
Ti(I')-O(2)	3.148(13)	K(I')-O(3)	2.570(19)
Ti(II)-O(2)	2.782(12)	K(II)-O(2)	3.062(13)
Ti(II)-O(4)	3.120(13)	K(II)-O(2)	2.711(9)
Ti(III)-O(4)	2.91(6)	K(II)-O(4)	2.984(9)
Ti(III)-O(1)	3.44(3)	K(III)-O(4)	2.90(5)
Ti(III')-O(4)	2.49(5)	K(III)-O(1)	3.36(3)
Ti(III')-O(1)	3.06(3)	K(III')-O(4)	2.55(3)
		K(III')-O(1)	2.968(18)
		Na(I')-O(3)	2.292(10)
		Na(I')-O(2)	2.916(9)
		Na(II)-O(2)	2.390(17)
		Na(II)-O(4)	2.832(9)
O(1)-(Si,Al)-O(2)	111.9(5)	O(1)-(Si,Al)-O(2)	111.6(3)
O(1)-(Si,Al)-O(3)	110.7(5)	O(1)-(Si,Al)-O(3)	110.3(4)
O(1)-(Si,Al)-O(4)	110.1(6)	O(1)-(Si,Al)-O(4)	109.5(4)
O(2)-(Si,Al)-O(3)	105.7(6)	O(2)-(Si,Al)-O(3)	106.7(4)
O(2)-(Si,Al)-O(4)	107.4(6)	O(2)-(Si,Al)-O(4)	106.5(4)
O(3)-(Si,Al)-O(4)	111.0(6)	O(3)-(Si,Al)-O(4)	112.2(4)
(Si,Al)-O(1)-(Si,Al)	142.5(8)	(Si,Al)-O(1)-(Si,Al)	136.0(5)
(Si,Al)-O(2)-(Si,Al)	145.8(9)	(Si,Al)-O(2)-(Si,Al)	149.7(5)
(Si,Al)-O(3)-(Si,Al)	140.7(8)	(Si,Al)-O(3)-(Si,Al)	144.1(6)
(Si,Al)-O(4)-(Si,Al)	141.3(8)	(Si,Al)-O(4)-(Si,Al)	144.5(5)
O(3)-Ti(I')-O(3)	93.8(4)	O(3)-K(I)-O(3)	89.0(3), 91.0(3)
O(2)-Ti(II)-O(2)	87.9(4)	O(3)-K(I')-O(3)	99.4(9)
O(1)-Ti(III)-O(4)	49.5(7)	O(2)-K(II)-O(2)	94.7(3)
O(1)-Ti(III)-O(1)	64.9(8)	O(1)-K(III)-O(4)	50.2(6), 96.8(16)
O(1)-Ti(III')-O(4)	57.1(8)	O(4)-K(III)-O(4)	84.4(19)
		O(1)-K(III')-O(1)	115.2(11)
		O(1)-K(III')-O(4)	57.6(5)
		O(3)-Na(I')-O(3)	117.5(5)
		O(2)-Na(II)-O(2)	113.1(11)

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

Further description is available.¹⁹⁻²¹

Consideration of Space Group. The crystals of [Ti₇₁]-[Si₁₂₁Al₇₁O₃₈₄]-FAU and [K₅₃Na₁₈][Si₁₂₁Al₇₁O₃₈₄]-FAU were refined using the space group *Fd3m* because they showed Si-O and Al-O bond length did not differ significantly and clearly showed mirror symmetry at (110) from the X-ray diffraction intensities, indicating that the Si and Al positions were not distinguishable. Other details are the same as previously reported.^{9,10}

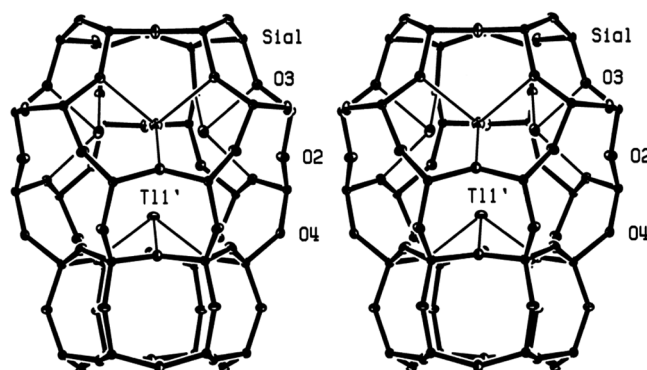


Figure 3. A stereoview of a representative double 6-ring (D6R) and sodalite unit in dehydrated [Ti₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU. The Ti⁺ ion at Ti(I') is shown at site I'. The zeolite Y framework is drawn with heavy bonds. The coordination of Ti⁺ ions to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.

Crystal Structure of [Ti₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU (Crystal 1). In structure of [Ti₇₁][Si₁₂₁Al₇₁O₃₈₄]-FAU, the total number of Ti⁺ ions found per unit cell, 71.1(6). About 71 Ti⁺ ions have been found at four equipoints. Twenty-nine Ti⁺ ions at Ti(I') per unit cell are located at site I' in the sodalite cavity opposite D6Rs (see Figure 3). Each Ti⁺ ions at Ti(I') is recessed *ca.* 1.42 Å into the sodalite cavity opposite D6Rs (see Figure 3). This 32-fold position is almost fully occupied. The distance between Ti(I') and its nearest framework oxide ions, at O(3), is 2.631(12) Å, which is a little shorter than the sum of the conventional ionic radii of Ti⁺ and O²⁻, 1.47 + 1.32 (respectively) = 2.79 Å.²² This indicates that each Ti⁺ ions coordinates strongly to its three O(3) oxygens, as would be expected by the low coordination number.

About 31 Ti⁺ ions are located at site II positions opposite S6Rs in the supercage (see Figure 4). These Ti⁺ ions at site II also almost fully occupied the 32-fold site-II position. Each ions at Ti(II) lies inside the supercage, 1.66 Å, from the plane of three O(2) framework oxygens of the S6R to which each is bound. The Ti⁺ ions at site II bond to three O(2)s at 2.782(12) Å, which is almost same with the sum of the conventional ionic radii of Ti⁺ and O²⁻, 1.47 + 1.32 (respectively) = 2.79 Å,²² indicative of a good fit (see Table 4 and Figure 4).

Three Ti⁺ ions at Ti(III) per unit cell occupy the 96-fold position at site III in the supercages (see Figure 4). The Ti(III)-O(4) distance is 2.91(6) Å. The remaining 8 Ti⁺ ions at Ti(III') occupy sites-III' positions near triple 4-rings in the supercage (see Figure 4). The site-III' cations at Ti(III') are 2.49(5) and 3.06(3) Å from the framework oxygens at O(4) and O(1), respectively (see Table 4 and Figure 4).

There is no indication that the structure contains the template cation, bis(2-hydroxyethyl)dimethylammonium, used in its synthesis. If it was present in the starting crystal, it was washed away by the intensive Ti⁺-exchange process.

Crystal Structure of [K₅₃Na₁₈][Si₁₂₁Al₇₁O₃₈₄]-FAU (Crystal 2). In the structure of [K₅₃Na₁₈][Si₁₂₁Al₇₁O₃₈₄]-FAU, the total number of K⁺ and Na⁺ ions found per unit cell, 71.5(27),

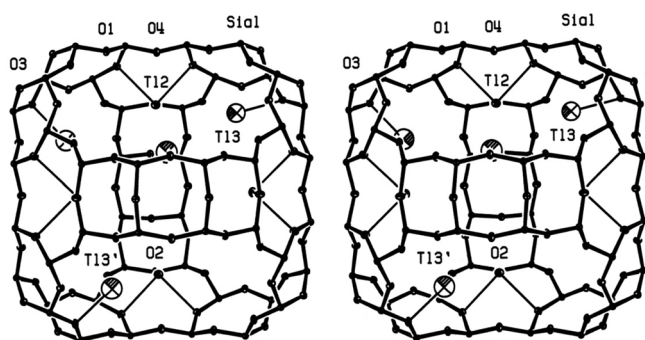


Figure 4. A stereoview of a representative supercage in dehydrated $[Tl_{71}][Si_{121}Al_{71}O_{384}]$ -FAU. See the caption to Figure 3 for other details.

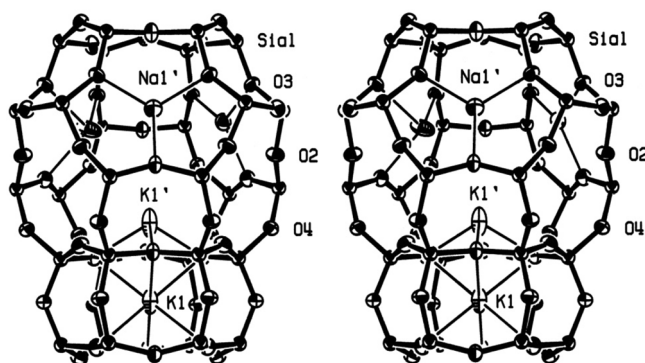


Figure 5. A stereoview of a representative double 6-ring (D6R) and sodalite unit in dehydrated $[K_{53}Na_{18}][Si_{121}Al_{71}O_{384}]$ -FAU. The K^+ ion at K(I) and K(I'), and Na^+ ion at Na(I') are shown at site I and I'. The zeolite Y framework is drawn with heavy bonds. The coordination of K^+ and Na^+ ions to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.

which is approximately equal to the sum of occupancy number of Tl^+ ions in crystal 1.

Fifty-three K^+ ions are found at five different crystallographic sites and eighteen Na^+ ions are found at two different crystallographic sites. Four K^+ ions per unit cell are exactly at the centers of their D6Rs, at site I (see Figure 5). This 16-fold positions in not fully occupied. Each K^+ ion at K(I) is coordinated by six O(3) oxygen atoms of hexagonal prism at distance of 2.796(8) Å, slightly longer than the sum of the conventional ionic radii of K^+ and O^{2-} , 1.33 + 1.32 (respectively) = 2.65 Å,²² indicative of a good fit. The K^+ ions are octahedral.

Ten K^+ ions at K(I') and twelve Na^+ ions at Na(I') lie at site I' in the sodalite cavity opposite D6Rs (see Figure 5). This is 32-fold position, but it is occupied by only twenty-two cations (This indicates that K^+ and Na^+ ions at K(I') and Na(I'), respectively, are not present at the every opposite D6Rs in the sodalite unit). Each ions at K(I') and Na(I') lies inside the sodalite cavity, 1.15 and 0.32 Å, respectively, from the plane of three O(3) framework oxygen of the D6Rs to which each is bound. The K^+ ions at K(I') and Na^+ ions at Na(I') are coordinated by the six O(3) oxygen atoms of their D6R at distances of 2.570(19) and 2.292(10) Å, respectively,

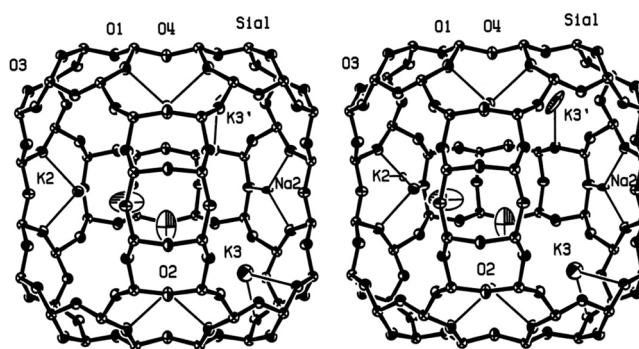


Figure 6. A stereoview of a representative supercage in dehydrated $[K_{53}Na_{18}][Si_{121}Al_{71}O_{384}]$ -FAU. See the caption to Figure 5 for other details.

which are shorter than the sum of the ionic radii of K^+ and O^{2-} , 1.33 + 1.32 (respectively) = 2.65 Å²² and almost same with the sum of the ionic radii of Na^+ and O^{2-} , 0.97 + 1.32 (respectively) = 2.29 Å,²² indicative of good fits.

Twenty-two K^+ ions at K(II) and six Na^+ ions are located at site II positions opposite S6Rs in the supercage (see Figure 6). These K^+ and Na^+ ions at site II do not fill the 32-fold site-II position perhaps because some S6Rs are deficient in Al atoms. Each these ions at K(II) and Na(II) lies inside the supercage, 1.43 and 0.60 Å, respectively, from the plane of three O(2) framework oxygens of the S6R to which each is bound. The twenty-two K(II) ions and six Na(II) ions bond to three O(2)s at 2.711(9) and 2.390(17) Å, respectively, are slightly longer than the sum of the corresponding conventional ionic radii, 2.65 Å (γ_{K^+} (1.33 Å) + $\gamma_{O^{2-}}$ (1.32 Å)) and 2.29 Å (γ_{Na^+} (0.97 Å) + $\gamma_{O^{2-}}$ (1.32 Å)).²²

The remaining K^+ ions at K(III) and K(III') lie in the supercage at two different III and III' sites, respectively. These positions are 96-fold and 192-fold positions, respectively. The K(III)-O(4) and K(III')-O(4) distances are 2.90(5) and 2.55(3) Å, respectively (see Table 4 and Figure 6).

There is no indication that the structure contains the template cation, bis(2-hydroxyethyl)dimethylammonium, used in its synthesis. If it was present in the starting crystal, it was washed away by the intensive K^+ -exchange process.

Summary

Large single crystals of faujasite-type zeolite were successfully prepared from gels with the composition 3.58SiO₂:2.08NaAlO₂:7.59NaOH:455H₂O:5.06TEA:1.23TCl and the single-crystal structures of fully Tl^+ -exchanged and partially K^+ -exchanged faujasite-type zeolites were determined by single-crystal X-ray diffraction methods. The synthetic single crystals had the size of ca. 200 μm.

In the crystallographic studies of fully Tl^+ -exchanged faujasite-type zeolite, 71.1(6) Tl^+ ions are distributed over four sites like those in $[Tl_{71}][Si_{121}Al_{71}O_{384}]$ -FAU.^{9,23} In the structure of partially K^+ -exchanged faujasite-type zeolite, 53.7(16) K^+ and 17.8(37) Na^+ ions are distributed over five and two sites, respectively. The total occupancies of cations in two crystals are almost same each other. The occupation

of 71 cations in two single-crystals structures is meaning that the Si/Al ratio of synthetic large single crystals is 1.70. It is concluded that the synthetic faujasite-type zeolite had 1.70 of Si/Al ratio and was zeolite Y.

The deficiency of occupation at each site, in two single-crystal structures, may be due to the local Si/Al order among the T atoms.

Supporting Information: Tables of calculated and observed structure factors (19 pages). The supporting materials will be given upon your request to a corresponding author (Tel: +82-54-820-5454, Fax: +82-54-822-5452, e-mail: wtlim@andong.ac.kr).

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