

## Ca<sup>2+</sup> 이온과 Cs<sup>+</sup> 이온으로 치환되고 탈수된 두개의 제올라이트 X Ca<sub>35</sub>Cs<sub>22</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>와 Ca<sub>29</sub>Cs<sub>34</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>의 결정구조

張世福 · 宋承煥<sup>†</sup> · 金 洋

부산대학교 화학과

<sup>†</sup> 동서대학교 화학공학과

(1996. 4. 1 접수)

### Crystal Structures of Full Dehydrated Ca<sub>35</sub>Cs<sub>22</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub> and Ca<sub>29</sub>Cs<sub>34</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>

Se Bok Jang, Seong Hwan Song<sup>†</sup>, and Yang Kim

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

<sup>†</sup>Department of Chemical Engineering, Dongseo University, Pusan 612-012, Korea

(Received April 1, 1996)

**요 약.** Ca<sup>2+</sup> 이온과 Cs<sup>+</sup> 이온으로 치환되고 완전히 탈수된 제올라이트 X, Ca<sub>35</sub>Cs<sub>22</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>(Ca<sub>35</sub>Cs<sub>22</sub>-X;  $a=25.071(1)$  Å)와 Ca<sub>29</sub>Cs<sub>34</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>(Ca<sub>29</sub>Cs<sub>34</sub>-X;  $a=24.949(1)$  Å)의 두 개의 결정 구조를 21 °C에서 입방 공간군  $Fd\bar{3}$ 을 사용하여 단결정 X-선 회절법으로 해석하고 구조를 정밀화하였다. 탈수한 Ca<sub>35</sub>Cs<sub>22</sub>-X의 구조를 Full-matrix 최소자승법 정밀화 계산에서  $I>3\sigma(I)$ 인 322개의 독립 반사를 사용하여 최종 오차 인자를  $R_1=0.051$ ,  $R_2=0.044$ 까지 정밀화 계산하였고, 탈수한 Ca<sub>35</sub>Cs<sub>22</sub>-X의 구조는 260개의 독립 반사를 사용하여  $R_1=0.058$ ,  $R_2=0.055$ 까지 정밀화시켰다. 이들 구조에서 Ca<sup>2+</sup> 이온과 Cs<sup>+</sup> 이온은 서로 다른 5개의 결정학적 자리에 위치하고 있다. 탈수한 Ca<sub>35</sub>Cs<sub>22</sub>-X 구조에서는 16개의 Ca<sup>2+</sup> 이온은 D6R의 중심, 자리 I에 모두 채워져 있다(Ca-O=2.41(1) Å, O-Ca-O=93.4(3)°). 다른 19개의 Ca<sup>2+</sup> 이온은 자리 II에(Ca-O=2.29(1) Å, O-Ca-O=118.7(4)°), 10개의 Cs<sup>+</sup> 이온은 큰 공동에서 6-링 맞은편 II에 채워져 있고, 각각 3개의 산소로 만들어지는 산소 평면으로부터 1.95 Å 들어가 위치하고 있다(Cs-O=2.99(1) Å, O-Cs-O=82.3(3)°). 3개의 Cs<sup>+</sup> 이온은 산소 평면에서 소다라이트 공동쪽으로 2.27 Å 들어간 자리 II'에서 위치하고 있다(Cs-O=3.23 Å, O-Cs-O=75.2(3)°). 나머지 9개의 Cs<sup>+</sup> 이온은 각각 큰 공동내 2회 회전축을 가지고 있는 48(f) 위치인 자리 III에 통계학적으로 분포하고 있다(Cs-O=3.25(1) Å, Cs-O=3.49(1) Å). 탈수한 Ca<sub>29</sub>Cs<sub>34</sub>-X에서 16개의 Ca<sup>2+</sup> 이온은 자리 I에 채워지고(Ca-O=2.38(1) Å, O-Ca-O=94.1(4)°) 13개의 Ca<sup>2+</sup> 이온은 자리 II에 채워져 있다(Ca-O=2.32(2) Å, O-Ca-O=119.7(6)°). 다른 12개의 Cs<sup>+</sup> 이온은 자리 II에 채워져 있고, 이들은 산소 평면으로부터 각각 1.93 Å 들어가 위치하고 있다(Cs-O=3.02(1) Å, O-Cs-O=83.1(4)°). 7개의 Cs<sup>+</sup> 이온은 각각 자리 II'에 위치하고 있고, 산소 평면으로부터 소다라이트 공동으로 2.22 Å 들어가 위치하고 있다(Cs-O=3.21(2) Å, O-Cs-O=77.2(4)°). 나머지 16개의 Cs<sup>+</sup> 이온은 큰 공동내의 자리 III에 있다(Cs-O=3.11(1) Å, Cs-O=3.46(2) Å). Ca<sup>2+</sup> 이온은 자리 I과 II에 우선적으로 위치하고 Cs<sup>+</sup> 이온은 너무 커서 자리 I에 채워질 수 없으며 나머지 자리에 채워진다.

**ABSTRACT.** The structures of fully dehydrated Ca<sup>2+</sup>- and Cs<sup>+</sup>-exchanged zeolite X, Ca<sub>35</sub>Cs<sub>22</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>(Ca<sub>35</sub>Cs<sub>22</sub>-X;  $a=25.071(1)$  Å) and Ca<sub>29</sub>Cs<sub>34</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>(Ca<sub>29</sub>Cs<sub>34</sub>-X;  $a=24.949(1)$  Å), have been determined by single-crystal X-ray diffraction methods in the cubic space group  $Fd\bar{3}$  at 21(1) °C. Their structures were refined to the final error indices  $R_1=0.051$  and  $R_2=0.044$  with 322 reflections for Ca<sub>35</sub>Cs<sub>22</sub>-X, and

$R_1=0.058$  and  $R_2=0.055$  with 260 reflections for  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ ;  $I>3\sigma(I)$ . In both structures,  $\text{Ca}^{2+}$  and  $\text{Cs}^+$  ions are located at five different crystallographic sites. In dehydrated  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$ , sixteen  $\text{Ca}^{2+}$  ions fill site I, at the centers of the double 6-rings ( $\text{Ca-O}=2.41(1)$  Å and  $\text{O-Ca-O}=93.4(3)^\circ$ ). Another nineteen  $\text{Ca}^{2+}$  ions occupy site II ( $\text{Ca-O}=2.29(1)$  Å,  $\text{O-Ca-O}=118.7(4)^\circ$ ) and ten  $\text{Cs}^+$  ions occupy site II opposite single six-rings in the supercage; each is 1.95 Å from the plane of three oxygens ( $\text{Cs-O}=2.99(1)$  and  $\text{O-Cs-O}=82.3(3)^\circ$ ). About three  $\text{Cs}^+$  ions are found at site II', 2.27 Å into sodalite cavity from their three-oxygen plane ( $\text{Cs-O}=3.23(1)$  Å and  $\text{O-Cs-O}=75.2(3)^\circ$ ). The remaining nine  $\text{Cs}^+$  ions are statistically distributed over site III, a 48-fold equipoint in the supercages on twofold axes ( $\text{Cs-O}=3.25(1)$  Å and  $\text{Cs-O}=3.49(1)$  Å). In dehydrated  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ , sixteen  $\text{Ca}^{2+}$  ions fill site I ( $\text{Ca-O}=2.38(1)$  Å and  $\text{O-Ca-O}=94.1(4)^\circ$ ) and thirteen  $\text{Ca}^{2+}$  ions occupy site II ( $\text{Ca-O}=2.32(2)$  Å,  $\text{O-Ca-O}=119.7(6)^\circ$ ). Another twelve  $\text{Cs}^+$  ions occupy site II; each is 1.93 Å from the plane of three oxygens ( $\text{Cs-O}=3.02(1)$  and  $\text{O-Cs-O}=83.1(4)^\circ$ ) and seven  $\text{Cs}^+$  ions occupy site II'; each is 2.22 Å into sodalite cavity from their three-oxygen plane ( $\text{Cs-O}=3.21(2)$  and  $\text{O-Cs-O}=77.2(4)^\circ$ ). The remaining sixteen  $\text{Cs}^+$  ions are found at III site in the supercage ( $\text{Cs-O}=3.11(1)$  Å and  $\text{Cs-O}=3.46(2)$  Å). It appears that  $\text{Ca}^{2+}$  ions prefer sites I and II in that order, and that  $\text{Cs}^+$  ions occupy the remaining sites, except that they are too large to be stable at site I.

## INTRODUCTION

The crystal structure of zeolite X in its hydrated form was determined by Broussard and Shoemaker<sup>1</sup> using powder diffraction techniques. The crystal structure of hydrated Na-X has been reinvestigated using single crystal X-ray techniques.<sup>2</sup> The distribution and coordination of various cations in the framework of faujasite-type zeolites have been widely investigated and reviewed.<sup>3</sup>

The exchangeable cations in zeolites have received a great deal of attention in the scientific literature. The thermal stability, sorption parameters, and catalytic properties of zeolites are all determined by the type and number of exchangeable cations and their distribution over the available sites. Cation distributions in faujasite-type zeolites have been widely studied by X-ray diffraction methods.<sup>3-5</sup> Zeolite X has a wide range of industrial applications<sup>6</sup> primarily due to the excellent stability of the crystal structure and a large available pore volume and surface area. In addition to the accessible pore volume, the adsorptive properties of zeolites heavily depend on the size, charge density, and distribution of cations in the porous, and structure.

Only few studies of dehydrated divalent cation-exchanged zeolite X are reported in the literature.<sup>7,8</sup> Anderson *et al.*<sup>7</sup> determined the crystal structures

of partially and fully dehydrated  $\text{Mg}_{31}\text{Na}_{30}\text{-X}$  and  $\text{Ca}_{23}\text{Mg}_{23}\text{-X}$ . They found that  $\text{Mg}^{2+}$  ions are located at three sites I', II', and III in hydrated Mg, Na-X, and II and II' in dehydrated Ca, Mg-X. They also found that  $\text{Ca}^{2+}$  ions in dehydrated Ca, Mg-X are located in site I, I', and II'. Smolin *et al.*<sup>8</sup> determined the crystal structures of Ca-X at various dehydration temperatures. In the partially dehydrated form,  $\text{Ca}^{2+}$  ions are located in sites I, I', II and III.

Single crystals of  $\text{K}_{92}\text{-X}\cdot 50\text{K}^9$  and  $\text{Cs}_{92}\text{-X}\cdot 36\text{Cs}^{10}$  were synthesized by exposing Na-X to potassium metal vapor, and their structures were determined by X-ray diffraction methods. At high potassium loadings, all potassium clusters in the sodalite cavities of zeolite X were linked by potassiums at the centers of double six-oxygen rings (D6R's) to form rings or chains (one-dimensional continua: zig-zag strands). In  $\text{Cs}_{92}\text{-X}\cdot 36\text{Cs}$ , it can be seen that all sodalite and supercage cavities are "full" of cesium in this structure. Each sodalite cavity contains two cesiums which attach as a linear appendix, one per supercage. A three-dimensional potassium continuum, similar to that found in  $\text{Cs}_{92}\text{-X}\cdot 36\text{Cs}$ , formed in  $\text{K}_{92}\text{-X}\cdot 50\text{K}$ .<sup>9</sup> A cationic cesium continuum was found to be present in  $\text{Cs}_{92}\text{-X}\cdot 36\text{Cs}$ .<sup>10</sup> This superlattice cluster fills all of the channels and cavities of the zeolite framework to

form an interpenetrating structure. Pseudo-icosahedral clusters, each with a cesium atom at its center, in the supercages of zeolite X are arranged as the carbon atoms in diamond, tetrahedrally connected to form the continuum.

Recently our work, the crystal structure of dehydrated  $\text{Ca}^{2+}$  and  $\text{K}^+$ -exchanged zeolite X,  $\text{Ca}_{32}\text{K}_{28}\text{-X}$ , has been determined by single-crystal X-ray diffraction methods.<sup>11</sup> In this structure, the principle positions of  $\text{Ca}^{2+}$  ion are Ca(1) position at site I, the center of the double six-oxygen ring (symmetry of  $\bar{3}$ ) and the Ca(2) position in the supercage at site II, symmetry of 3. Because the ionic radius of  $\text{K}^+$  ion is larger than that of  $\text{Ca}^{2+}$  ion, large  $\text{K}^+$  ions (sites II and III) preferentially occupy deep in the large supercage. Smaller  $\text{Ca}^{2+}$  ions occupy smaller pore sites such as the centers of the double 6-rings and the positions near the centers of single 6-ring planes in the supercage.

In this report, the occupancy numbers and locations of cations in the structure of dehydrated  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$  are compared with those in dehydrated  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ . This study was done to learn the selective positions of  $\text{Ca}^{2+}$  and  $\text{Cs}^+$  ions within zeolite X and to investigate the geometry of the both structures. It is easy to distinguish  $\text{Cs}^+$  from  $\text{Ca}^{2+}$  because of the large difference in their atomic scattering factors ( $54 e^-$  for  $\text{Cs}^+$  vs.  $18 e^-$  for  $\text{Ca}^{2+}$ ) and ionic radii ( $\text{Cs}^+ = 1.67 \text{ \AA}$  vs.  $\text{Ca}^{2+} = 0.99 \text{ \AA}$ ).<sup>12</sup>

## EXPERIMENTAL SECTION

Large colorless crystals of Na-X (stoichiometry;  $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ ) were prepared in St. Petersburg, Russia.<sup>13</sup> Each of two single crystals, octahedra ca. 0.20 mm in diameter, was lodged in a fine Pyrex capillary.

$\text{Ca}_{35}\text{Cs}_{22}\text{-X}$  (crystal 1) and  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$  (crystal 2) were prepared using an exchange solutions whose  $\text{Ca}(\text{NO}_3)_2 : \text{CsNO}_3$  mole ratio was 1 : 1 and 1 : 100, respectively, with a total concentration of 0.05 M. Ion exchange was accomplished by flow methods: each aqueous solution was allowed to flow past each crystal at a velocity of approximately 1.5 cm/s for three days at 24(1) °C. Each capillary with its crystal was then connected to a vacuum line. Each

crystal was cautiously dehydrated under vacuum by gradually increasing its temperature (ca. 20 °C/h) to 380 °C at a constant pressure of  $2 \times 10^{-6}$  torr. These conditions were maintained for 48 h. After each crystal had cooled to room temperature, it was sealed under vacuum in its capillary by torch. Each crystal remained red.

## X-RAY DATA COLLECTION

Preliminary crystallographic experiments and subsequent data collection were performed with an automated four-circle Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator, a pulse-height analyzer and a micro-Vax 3100 computer. Mo  $K\alpha_1$  radiation ( $K\alpha_1$ ,  $\lambda = 0.70930 \text{ \AA}$ ;  $K\alpha_2$ ,  $\lambda = 0.71359 \text{ \AA}$ ) was used for all experiments. The cubic unit cell constants determined by a least-squares refinement of 25 intense reflections for which  $14^\circ < 2\theta < 26^\circ$  are 25.071(1) Å for  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$  and 24.949(1) Å for  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ .

For each crystal, the  $\omega$ - $2\theta$  scan technique was used. The data were collected at variable scan speeds. Most reflections were observed at slow speeds from 0.24 to 0.34 degree/min in  $\omega$ . The intensities of three reflections in diverse regions of reciprocal space were recorded every three hours to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were noted during the course of data collection. All unique reflections for an F-centered unit cell for which  $2\theta < 60^\circ$  for each crystal was examined by counter methods.

The raw data were corrected for Lorentz and polarization effects including incident beam monochromatization, and the resultant estimated standard deviations were assigned to each reflection by the computer programs GENESIS and BEGIN.<sup>14</sup> Of the 1196 unique reflections measured for  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$  and 1187 for  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ , only the 322 and 260 reflections, respectively, for which  $I > 3\sigma(I)$  were used in subsequent structure determinations.

## STRUCTURE DETERMINATION

The crystal structures were solved in the cubic

space group  $Fd\bar{3}$ . This is established for zeolite X, and is consistent with the systematic absences observed.

**Ca<sub>35</sub>Cs<sub>22</sub>-X (crystal 1).** Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] of dehydrated Rb<sub>78</sub>Na<sub>26</sub>-X.<sup>15</sup> Anisotropic refinement of the framework atoms converged to an unweighted  $R_1$  index,  $(\sum w(F_o - |F_c|))/\sum F_o$ , of 0.34 and a weighted  $R_2$  index,  $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$ , of 0.42. The initial difference Fourier function revealed two large peaks: at (0.0, 0.0, 0.0) with peak height 13.8 eÅ<sup>-3</sup>, and at (0.261, 0.261, 0.261) with peak height 9.8 eÅ<sup>-3</sup>. These two positions were stable in least-squares refinement. Anisotropic refinement including these peaks as Ca<sup>2+</sup> ions and Cs<sup>+</sup> ions converged to  $R_1=0.203$  and  $R_2=0.235$  with occupancies Ca(1)=13.2(8) and Cs(2)=10.5(5).

A subsequent difference Fourier function revealed two additional peaks: at (0.22, 0.22, 0.22) with height 6.3 eÅ<sup>-3</sup>, and at (0.427, 0.125, 0.125) with height 4.2 eÅ<sup>-3</sup>. Inclusion of these peaks as Ca<sup>2+</sup> ions at Ca(2) and Cs(3) lowered the error indices to  $R_1=0.069$  and  $R_2=0.070$ . The occupancy numbers at Ca(2) and Cs(3) refined to 21.0(6) and 11.6(2), respectively. From an ensuing Fourier function, the third Cs<sup>+</sup> ion position was found at (0.166, 0.166, 0.166) with height 1.9 eÅ<sup>-3</sup>. Anisotropic refinement of framework atoms and all the cations converged to  $R_1=0.050$  and  $R_2=0.040$ . The occupancies of Ca(1), Ca(2), Cs(1), Cs(2), and Cs(3) were fixed at the values shown in Table 1 considering the cationic charge per unit cell, +92 per unit cell. The final error indices were  $R_1=0.051$  and  $R_2=0.044$ .

In the final cycle of least-squares refinement, all shifts in atomic parameters were less than 0.1% of their corresponding standard deviations. The final difference function was featureless except for a peak of height 0.59 eÅ<sup>-3</sup> at (0.055, 0.055, 0.196). This peak was not stable in least-squares refinement. An absorption correction ( $\mu R=0.216$ ,  $\rho_{cal}=1.672$  g/cm<sup>3</sup>, and  $F(000)=7532$ )<sup>15</sup> was made empirically using a  $\psi$  scan. The adjusted transmission coefficients ranged from 0.995 to 0.999. This corre-

ction had little effect on the final R values. The final structure parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

**Ca<sub>26</sub>Cs<sub>34</sub>-X (crystal 2).** Full-matrix least-squares refinement was initiated by using the atomic parameters of framework atoms for the previous crystal of Ca<sub>35</sub>Cs<sub>22</sub>-X. Anisotropic refinement of the framework atoms converged to  $R_1=0.37$  and  $R_2=0.44$ . A subsequent Fourier synthesis revealed two large peaks: at (0.0, 0.0, 0.0) with height 13.2 eÅ<sup>-3</sup> and (0.26, 0.26, 0.26) with height 9.8 eÅ<sup>-3</sup>. Anisotropic refinement of the framework atoms, Ca<sup>2+</sup> at Ca(1), and Cs<sup>+</sup> at Cs(2) converged to  $R_1=0.26$  and  $R_2=0.28$  with occupancies of 10.7(11) at Ca(1) and 10.2(7) at Cs(2).

A subsequent difference Fourier function revealed two additional peaks: at (0.425, 0.125, 0.125) with height 6.0 eÅ<sup>-3</sup>, and at (0.22, 0.22, 0.22) with height 2.3 eÅ<sup>-3</sup>. Inclusion of these peaks as ions at Cs(3) and Ca(2) lowered the error indices to  $R_1=0.095$  and  $R_2=0.103$ . The occupancy numbers at Cs(3) and Ca(2) refined to 18.4(4) and 17.8(10), respectively. The third Cs<sup>+</sup> ion position was found on an ensuing Fourier function at (0.167, 0.167, 0.167) with height 3.5 eÅ<sup>-3</sup>. Anisotropic refinement of framework atoms and all the cations converged to  $R_1=0.054$  and  $R_2=0.050$ . The occupancies of Ca(1), Ca(2), Cs(1), Cs(2), and Cs(3) were fixed at the values shown in Table 1 considering the cationic charge per unit cell. The final error indices were  $R_1=0.058$  and  $R_2=0.055$ . The shifts in the final cycle of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final difference function was featureless except for a peak of height 0.85 eÅ<sup>-3</sup> at (0.125, 0.125, 0.625). This peak was not stable in least-squares refinement.

An absorption correction ( $\mu R=0.295$ ,  $\rho_{cal}=1.831$  g/cm<sup>3</sup>,  $F(000)=8072$ )<sup>16</sup> was made empirically using a  $\psi$  scan. The adjusted transmission coefficients ranged from 0.964 to 0.998. This correction had no effect on the final R indices.

All crystallographic calculations were done using MoIEN<sup>14</sup> (a structure determination program package supplied by Enraf-Nonius). The full-matrix

Table 1. Positional, thermal,<sup>a</sup> and occupancy parameters  
a. dehydrated Ca<sub>35</sub>CS<sub>22</sub>-X

Atom	Wyc. Pos.	x	y	z	$\beta_{11}^b$ B <sub>100</sub>	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy <sup>c</sup>	
											varied	fixed
Si	96(g)	-540(1)	336(1)	1230(2)	3(1)	3(1)	3(1)	1(1)	1(1)	-1(1)		96
Al	96(g)	-563(2)	1219(2)	363(2)	4(1)	2(1)	3(1)	-1(1)	1(1)	-4(2)		96
O(1)	96(g)	-1071(3)	-14(4)	1131(4)	8(2)	10(2)	4(2)	-5(3)	-1(3)	-5(3)		96
O(2)	96(g)	-42(4)	-41(4)	1429(3)	5(1)	4(1)	4(2)	7(3)	0(3)	-4(3)		96
O(3)	96(g)	-358(3)	605(3)	658(3)	7(2)	0(1)	4(2)	-2(3)	2(3)	-1(2)		96
O(4)	96(g)	-630(3)	770(4)	1699(4)	10(2)	6(2)	4(1)	-2(4)	10(3)	-6(3)		96
Ca(1)	16(c)	0	0	0	4(1)	4(1)	4(1)	1(1)	1(1)	1(1)	16.5(4)	16
Ca(2)	32(e)	2231(3)	2231(3)	2231(3)	15(1)	15(1)	15(1)	25(2)	25(2)	25(2)	19.8(6)	19
Cs(1)	32(e)	1642(6)	1642(6)	1642(6)	25(3)	25(3)	25(3)	-2(6)	-2(6)	-2(6)	3.5(3)	3
Cs(2)	32(e)	2620(1)	2620(1)	2620(1)	10(1)	10(1)	10(1)	-1(1)	-1(1)	-1(1)	10.1(3)	10
Cs(3)	48(f)	4250(3)	1250	1250	3(1)	26(2)	19(2)	0	0	1(4)	10.1(3)	9

b. dehydrated Ca<sub>29</sub>CS<sub>34</sub>-X

Atom	Wyc. Pos.	x	y	z	$\beta_{11}^b$ B <sub>100</sub>	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy <sup>c</sup>	
											varied	fixed
Si	96(g)	-537(2)	335(2)	1229(3)	3(1)	2(1)	2(1)	0(2)	-3(2)	-2(2)		96
Al	96(g)	-555(2)	1219(3)	363(2)	6(1)	2(1)	3(1)	-1(3)	1(2)	-4(3)		96
O(1)	96(g)	-1072(5)	-16(7)	1120(5)	7(3)	11(3)	1(3)	4(5)	1(4)	-7(5)		96
O(2)	96(g)	-55(6)	-46(7)	1414(5)	6(3)	9(3)	8(2)	6(5)	1(5)	-10(5)		96
O(3)	96(g)	-362(5)	595(6)	650(5)	6(2)	2(2)	0(2)	4(5)	11(5)	4(4)		96
O(4)	96(g)	-659(5)	777(6)	1676(5)	8(3)	10(3)	-5(2)	-5(6)	13(5)	-2(4)		96
Ca(1)	16(c)	0	0	0	2(1)	2(1)	2(1)	1(2)	1(2)	1(2)	16.4(2)	16
Ca(2)	32(e)	2202(7)	2202(7)	2202(7)	13(2)	13(2)	13(2)	21(5)	21(5)	21(5)	12.8(4)	13
Cs(1)	32(e)	1656(5)	1656(5)	1656(5)	36(3)	36(3)	36(3)	-10(5)	-10(5)	-10(5)	5.7(3)	7
Cs(2)	32(e)	2622(2)	2622(2)	2622(2)	17(1)	17(1)	17(1)	-2(2)	-2(2)	-2(2)	11.5(3)	12
Cs(3)	48(f)	4229(3)	1250	1250	1(1)	23(2)	19(1)	0	0	-12(4)	16.4(3)	15

<sup>a</sup>Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>b</sup>The anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>c</sup>Occupancy factors are given as the number of atoms or ions per unit cell.

least-squares program used minimized  $\sum w(F_o - |F_c|)^2$ ; the weight ( $w$ ) of an observation was the reciprocal square of  $\sigma(F_o)$ , its standard deviation. Atomic scattering factors<sup>17,18</sup> for Si, Al, O<sup>-</sup>, Ca<sup>2+</sup> and Cs<sup>+</sup> were used. All scattering factors were modified to account for anomalous dispersion.<sup>19</sup> The final structural parameters are listed in Table 1, and selected interatomic distances and angles are given in Table 2.

## DISCUSSION

Zeolite X, a synthetic version of the mineral fauja-

site, has an open, negatively charged framework.<sup>20</sup> See Fig. 1. Its framework structure is composed of 192 corner-shared SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra per cubic unit cell;  $a \cong 25.0 \text{ \AA}$ .<sup>20</sup> If the number of Al ions = number of Si ions = 96, and Loewenstein's rule<sup>21</sup> is obeyed, the space group of the framework alone is precisely  $Fd\bar{3}$ .

The basic building unit of zeolite X can be considered to be the sodalite cavity, a truncated octahedron (cubooctahedron) of composition Si<sub>12</sub>Al<sub>12</sub>O<sub>36</sub>. Its faces are eight 6-rings (12-membered Si<sub>3</sub>Al<sub>3</sub>O<sub>6</sub> rings whose apertures are defined by the six large

Table 2. Selected interatomic distances(Å) and angles (deg)<sup>a</sup>

Framework	Ca <sub>35</sub> Cs <sub>22</sub> -X	Ca <sub>29</sub> Cs <sub>34</sub> -X
Si-O(1)	1.61(1)	1.62(1)
Si-O(2)	1.64(1)	1.60(2)
Si-O(3)	1.65(1)	1.64(1)
Si-O(4)	1.61(1)	1.60(2)
Average	1.63(1)	1.62(1)
Al-O(1)	1.71(1)	1.69(1)
Al-O(2)	1.73(1)	1.71(2)
Al-O(3)	1.78(1)	1.78(2)
Al-O(4)	1.69(1)	1.72(2)
Average	1.73(1)	1.73(1)
Ca(1)-O(3)	2.41(1)	2.38(1)
Ca(2)-O(2)	2.29(1)	2.32(2)
Cs(1)-O(2)	3.23(1)	3.21(2)
Cs(2)-O(2)	2.99(1)	3.02(1)
Cs(3)-O(1)	3.49(1)	3.46(2)
Cs(3)-O(4)	3.25(1)	3.11(1)
O(1)-Si-O(2)	111.1(5)	110.3(9)
O(1)-Si-O(3)	109.0(5)	106.5(7)
O(1)-Si-O(4)	111.2(5)	109.5(8)
O(2)-Si-O(3)	106.8(4)	106.8(7)
O(2)-Si-O(4)	105.8(5)	110.5(8)
O(3)-Si-O(4)	113.3(5)	113.1(8)
O(1)-Al-O(2)	113.1(5)	111.6(8)
O(1)-Al-O(3)	105.3(5)	104.0(7)
O(1)-Al-O(4)	114.4(5)	110.6(6)
O(2)-Al-O(3)	106.7(4)	107.1(7)
O(2)-Al-O(4)	103.0(4)	108.0(7)
O(3)-Al-O(4)	114.4(5)	114.2(7)
Si-O(1)-Al	125.7(6)	126.5(9)
Si-O(2)-Al	141.8(5)	144.5(9)
Si-O(3)-Al	129.4(5)	128.9(8)
Si-O(4)-Al	164.8(6)	160.2(9)
O(3)-Ca(1)-O(3)	93.4(3)	94.1(4)
O(2)-Ca(2)-O(2)	118.7(4)	119.7(6)
O(2)-Cs(1)-O(2)	75.2(3)	77.2(4)
O(2)-Cs(2)-O(2)	82.3(3)	83.1(4)
O(1)-Cs(3)-O(1)	127.3(3)	127.9(4)
O(4)-Cs(3)-O(4)	60.8(3)	61.5(4)

<sup>a</sup>Numbers in parentheses are estimated standard deviations in units of the least significant digit given for the corresponding value.

oxygens) and six 4-rings (8-membered Si<sub>2</sub>Al<sub>2</sub>O<sub>4</sub> rings). The sodalite units are arranged tetrahedrally in space like the carbon atoms in diamond. Each bonded pair of sodalite units is joined at

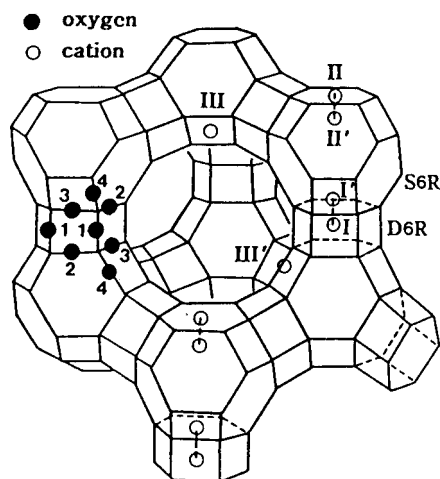


Fig. 1. A stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen atoms are indicated by the numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals.

6-rings by six additional oxygen atoms, each of which bridges from an Al of one sodalite unit to a Si of the other; only alternating (tetrahedrally arranged) 6-rings of each sodalite unit are used. This leads to the existence of small double 6-ring (D6R) cavities, single 6-rings (S6R's) which were not used in joining, and large supercages. Each supercage has access to four other supercages through near-circular 12-rings (24-membered Si<sub>6</sub>Al<sub>6</sub>O<sub>12</sub> rings) and to four sodalite units through 6-rings. Each unit cell contains eight supercages, eight sodalite units, and sixteen D6R's.

Exchangeable cations, which balance the negative charge of the aluminosilicate framework, are found within the zeolite's cavities. They are usually found at the following sites, shown in Fig. 1: site I at the center of a D6R (alternatively called the hexagonal prism), site I' in the sodalite (β) cavity on the opposite side of one of the D6R's 6-rings from site I, site II' inside the sodalite cavity near the S6R entrance to the supercage, site II in the supercage opposite the S6R from site I', site III in the supercage on a twofold axis

Table 3. Deviations ( $\text{\AA}$ ) of cations from 6-ring planes

	$\text{Ca}_{35}\text{Cs}_{22}\text{-X}$	$\text{Ca}_{29}\text{Cs}_{34}\text{-X}$
at O(3) <sup>a</sup>		
Ca(1)	-1.31(1)	-1.27(1)
at O(2) <sup>b</sup>		
Ca(2)	0.27(1)	0.12(1)
Cs(1)	-2.27(1)	-2.22(1)
Cs(2)	1.95(1)	1.93(1)

<sup>a</sup>A negative deviation indicates that the atom lies in the sodalite unit. <sup>b</sup>A positive deviation indicates that the atom lies in the supercage.

Table 4. Distribution of nonframework atoms over sites

Sites	Crystals	
	$\text{Ca}_{35}\text{Cs}_{22}\text{-X}$	$\text{Ca}_{29}\text{Cs}_{34}\text{-X}$
I	16 Ca(1)	16 Ca(1)
II'	3 Cs(1)	7 Cs(1)
II	19 Ca(2)	13 Ca(2)
	10 Cs(2)	12 Cs(2)
III	9 Cs(3)	15 Cs(3)

opposite a 4-ring between two 12-rings, and site III' somewhat off III (off the twofold axis).<sup>22</sup>

$\text{Ca}_{35}\text{Cs}_{22}\text{-X}$  (crystal 1). The  $\text{Ca}^{2+}$  ions at Ca(1) fill the 16-fold site I ( $\text{Ca}(1)\text{-O}(3) = 2.41(1) \text{\AA}$ ,  $\text{O}(3)\text{-Ca}(1)\text{-O}(3)$  angle =  $93.4(3)^\circ$ ) (see Fig. 2). About 19.0  $\text{Ca}^{2+}$  ions at Ca(2) occupy the 32-fold site II in the supercage. The  $\text{Ca}(2)\text{-O}(2)$  distance, 2.29  $\text{\AA}$ , is shorter than the sum of the conventional radii<sup>12</sup> of  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$ ,  $0.99 \text{\AA} + 1.32 \text{\AA} = 2.31 \text{\AA}$ , presumably because Ca(2) is only three-coordinate. These  $\text{Ca}^{2+}$  ions are slightly recessed, 0.27 (1)  $\text{\AA}$ , into the supercage from the plane of the three O(2) oxygens (see Tables 2 and 3). The O(2)-Ca(2)-O(2) bond angle,  $118.7(4)^\circ$ , is nearly trigonal planar.

Recently the crystal structures of  $\text{Ba}_{46}\text{-X}$ ,<sup>23</sup>  $\text{Ca}_{46}\text{-X}$ ,<sup>11</sup>  $\text{Mg}_{46}\text{-X}^{24}$ , and  $\text{Sr}_{46}\text{-X}^{24}$  were determined (see Table 4). From these it appears that site I (at the center of the D6R) is generally the lowest energy cation site, unless the cation is simply too large or too small.  $\text{Ca}^{2+}$  ions in  $\text{Ca}_{46}\text{-X}^{11}$  and  $\text{Sr}^{2+}$  ions in  $\text{Sr}_{46}\text{-X}^{24}$  fill the site I position, with the remain-

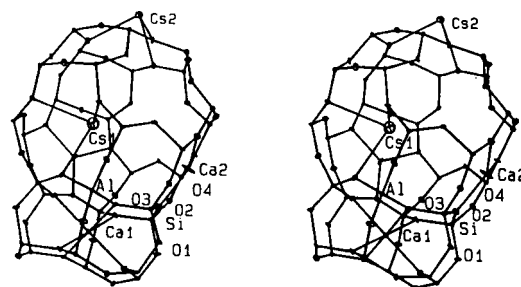


Fig. 2. Stereoview of a representative sodalite cavity and D6R in dehydrated  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$ . All D6R's are filled as shown with  $\text{Ca}^{2+}$  ions at Ca(1). Two  $\text{Ca}^{2+}$  ions at Ca(2), one  $\text{Cs}^+$  ion at Cs(1) and one  $\text{Cs}^+$  ion at Cs(2); the remainder may have two  $\text{Ca}^{2+}$  ions at Ca(2) are shown. Ellipsoids of 20% probability are shown.

der going to site II in the supercage, nearly filling it as in  $\text{Cd}_{46}\text{-X}$ . About thirteen  $\text{Ba}^{2+}$  ions (relatively large) in  $\text{Ba}_{46}\text{-X}^{23}$  and fourteen  $\text{Mg}^{2+}$  (relatively small) in  $\text{Mg}_{46}\text{-X}^{24}$  occupy the 16-fold site I positions.

The Cs(1) position is at site II', on a threefold axis inside the sodalite unit at the single six-oxygen ring (see Fig. 2). This is 32-fold position, but it is occupied by only 3  $\text{Cs}^+$  ions. Each  $\text{Cs}^+$  ion lies relatively far inside the sodalite cavity, 2.27  $\text{\AA}$  from the plane of the three O(2) framework oxygens. The  $\text{Cs}(1)\text{-O}(2)$  distances are 3.23(1)  $\text{\AA}$ , longer than the sum of the corresponding ionic radii,  $1.67 + 1.32 = 2.99 \text{\AA}$ .<sup>12</sup> This indicates that each  $\text{Cs}^+$  ion at Cs(1) coordinates weakly to its three O(2) oxygens.

The Ca(2), Cs(1), and Cs(2) ions occupy sites II, II', and II, respectively, with occupancies of 19, 3, and 10, respectively, nearly filling this 32-fold equipoint.  $\text{Ca}(2)\text{-O}(2)$  is 2.29(1)  $\text{\AA}$  and  $\text{O}(2)\text{-Ca}(2)\text{-O}(2) = 118.7(4)^\circ$ ;  $\text{Cs}(1)\text{-O}(2) = 3.23(1) \text{\AA}$  and  $\text{O}(2)\text{-Cs}(1)\text{-O}(2) = 75.2(3)^\circ$ ;  $\text{Cs}(2)\text{-O}(2)$  is 2.99(1)  $\text{\AA}$  and  $\text{O}(2)\text{-Cs}(2)\text{-O}(2)$  is  $82.3(3)^\circ$ . The nineteen  $\text{Ca}^{2+}$  ions at Ca(2) are only 0.27  $\text{\AA}$  from the plane of the single 6-ring; the ten  $\text{Cs}^+$  ions at Cs(2) are much further, 1.95  $\text{\AA}$ , from the corresponding plane. Plausible ionic arrangements for a sodalite unit and a supercage are shown in Fig. 2 and 3, respectively.

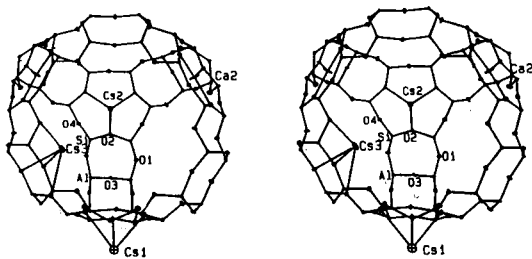


Fig. 3. A stereoview of the large cavity of dehydrated  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$ . Two  $\text{Ca}^{2+}$  ion at Ca(2), one  $\text{Cs}^+$  ion at Cs(1) and one  $\text{Cs}^+$  ions at Cs(3) are shown. Ellipsoids of 20% probability are shown.

$\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ (crystal 2). About 16.0  $\text{Ca}^{2+}$  ions at Ca(1) fill the 16-fold site I. Cations with Pauling radii much greater than 1.25 Å should not be able to replace the  $\text{Na}^+$  ions in the D6R's.<sup>25</sup> The radii of the  $\text{Ca}^{2+}$  and  $\text{Cs}^+$  ions are 0.99 Å and 1.67 Å, respectively,<sup>12</sup> so site I should be accessible only to  $\text{Ca}^{2+}$ . Proof of this comes from the crystal structure of the partially  $\text{Cs}^+$ -exchanged zeolite X in which site I remains entirely unoccupied.<sup>26</sup> Each Ca(1) is octahedrally coordinated by O(3) framework oxygens at 2.38(1) Å (see Fig. 3).

The Cs(1) position is at site II', on a threefold axis inside the sodalite unit at the single six-oxygen ring. (see Fig. 4). This is 32-fold position, but it is occupied by only 7  $\text{Cs}^+$  ions. Each  $\text{Cs}^+$  ion lies relatively far inside the sodalite cavity, 2.22 Å from the plane of the three O(2) framework oxygens. The Cs(1)-O(2) distances are 3.21(2) Å, longer than the sum of the corresponding ionic radii, 1.67+1.32=2.99 Å.<sup>12</sup> This indicates that each  $\text{Cs}^+$  ion coordinates weakly to its three O(2) oxygens. Its structure is similar to the structure of dehydrated  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$  discussed in the previous section.

The Ca(2), Cs(1), and Cs(2) ions occupy sites II, II', and II, respectively, with occupancies of 13, 7, and 12, respectively, nearly filling this 32-fold equipoint. Ca(2)-O(2) is 2.32(1) Å and O(2)-Ca(2)-O(2)=119.7(6)°; Cs(1)-O(2)=3.21(2) Å and O(2)-Cs(1)-O(2)=77.2(4)°; Cs(2)-O(2) is 3.02(1) Å and O(2)-Cs(2)-O(2) is 83.1(4)°. The fourteen  $\text{Ca}^{2+}$  ions at Ca(2) are only 0.12 Å from the plane of the single 6-ring; the ten  $\text{Cs}^+$  ions at Cs(2)

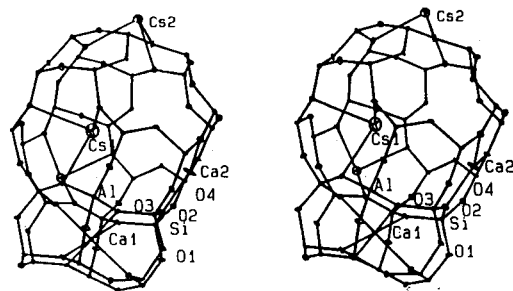


Fig. 4. Stereoview of a representative sodalite cavity and D6R in dehydrated  $\text{Ca}_{29}\text{Cs}_{34}\text{-X}$ . All D6R's are filled as shown with  $\text{Ca}^{2+}$  ions at Ca(1). Two  $\text{Ca}^{2+}$  ions at Ca(2), one  $\text{Cs}^+$  ion at Cs(1) and one  $\text{Cs}^+$  ion at Cs(2) are shown. Ellipsoids of 20% probability are shown.

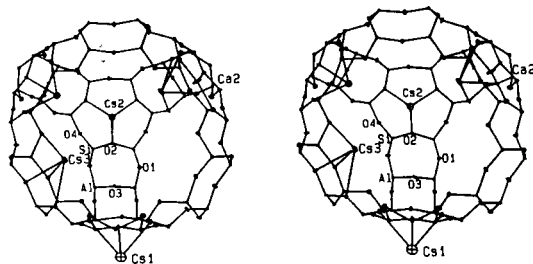


Fig. 5. A stereoview of the large cavity of dehydrated  $\text{Ca}_{35}\text{Cs}_{22}\text{-X}$ . Two  $\text{Ca}^{2+}$  ion at Ca(2), one  $\text{Cs}^+$  ion at Cs(1) and one  $\text{Cs}^+$  ions at Cs(3) are shown. Ellipsoids of 20% probability are shown.

are much further, 1.93 Å, from the corresponding plane. Plausible ionic arrangements for a sodalite unit and a supercage are shown in Fig. 4 and 5, respectively.

The remaining sixteen  $\text{Cs}^+$  ions occupy the 48-fold Cs(3) position at site III (see Fig. 5). The Cs(3)-O(4) approach distance, 3.11(1) Å, a little longer than the sum of ionic radii of  $\text{Cs}^+$  and  $\text{O}^{2-}$ , 1.69 Å+1.32 Å=3.01 Å.<sup>12</sup>

Shepelev, Butikova and Smolin<sup>26</sup> studied the crystal structures of the partially  $\text{K}^+$ -,  $\text{Rb}^+$ -, and  $\text{Cs}^+$ -exchanged forms of NaX zeolite in both the hydrated and the dehydrated (400 °C) states. They investigated the migration of cations during the dehydration. Analysis of the cation distribution in the hydrated forms shows that  $\text{K}^+$  ions penetrate into all zeolite cavities, whereas  $\text{Rb}^+$  ions diffuse



into the sodalite cage, but not into the hexagonal prism, and  $\text{Cs}^+$  ions are located only in the supercage. Dehydration of the zeolites is accompanied by a migration of unexchanged sodium cations into the hexagonal prism. Destruction of the dehydrated  $\text{Rb}^+$ -exchanged crystal after the 6 hour-long exposure at  $400^\circ\text{C}$  seems to be caused by a slow migration of the  $\text{Rb}^+$  ions into the hexagonal prism. In present work, all  $\text{Cs}^+$  ions are located at the site II', II and III. Therefore, the present structure is in good agreement with the previous work.<sup>26</sup>

**Conclusions.** This work indicates that all of the  $\text{Na}^+$  ions in zeolite X can readily be replaced by  $\text{Ca}^{2+}$  and  $\text{Cs}^+$  ions.  $\text{Ca}^{2+}$  ions in both structures fill the apparently most favorable site I position (at the D6R centers), with the remainder going to site II in the supercage. Considerations of ionic size and charge govern the competition for sites in both structures. The smaller and more highly charged  $\text{Ca}^{2+}$  ions nearly fill site I, with the remainder going to site II as in  $\text{Ca}_{46}\text{-X}$ ,<sup>11</sup> affirming that  $\text{Ca}^{2+}$  ions prefer site I. The larger  $\text{Cs}^+$  ions, which are less able to balance the anionic charge of the zeolite framework because of their size, finish satisfying the sodalite cavity with some occupancy at II' and finish filling site II, with the remainder going to the least suitable cation site in the structure, site III.

**Acknowledgement.** This work was supported in part by the Basic Research Institute Program, Ministry of Education, Korea, 1995, Project No. BSRI-95-3409.

#### REFERENCES

1. Broussard, L.; Shoemaker, D. P. *J. Am. Chem. Soc.* **1960**, *82*, 1041.
2. Olson, D. H. *J. Phys. Chem.* **1970**, *74*, 14.
3. Mortier, W. J. *Compilation of Extra-framework Sites in Zeolites*; Butterworth Scientific Ltd.: Guildford, U. K., 1982.
4. Schollner, R.; Broddack, R.; Kuhlmann, B.; Nozel, P.; Herden, H. Z. *Phys. Chem. (Leipzig)* **1981**, *262*, 17.
5. Egerton, T. S.; Stone, F. S. *J. Chem. Soc., Faraday Trans. I* **1970**, *66*, 2364.
6. Flanigen, E. M. *Zeolites, Science and Technology*; Nijhoff, M., Ed.; The Hague, 1984.
7. Anderson, A. A.; Shepelev, Y. F.; Smolin, Y. I. *Zeolites* **1990**, *10*, 32.
8. Smolin, Y. I.; Shepelev, Y. F.; Anderson, A. A. *Acta Crystallogr., Sect B* **1989**, *45*, 124.
9. Sun, T.; Seff, K. *J. Phys. Chem.* **1993**, *97*, 5213.
10. Sun, T.; Seff, K.; Heo, N. H.; Petranovskii, V. P. *Science* **1993**, *259*, 495.
11. Jang, S. B.; Song, S. H.; Kim, Y. J. *Korean Chem. Soc.* **1995**, *39*, 7.
12. *Handbook of Chemistry and Physics*, 70th Ed.; The Chemical Rubber Co., Cleveland, Ohio, 1989/1990; p F-187.
13. Bogomolov, V. N.; Petranovskii, V. P. *Zeolites* **1986**, *6*, 418.
14. Calculations were performed with Structure Determination Package Programs, MolEN, Enraf-Nonius, Netherlands, 1990.
15. Kim, Y.; Han, Y. W.; Seff, K. *J. Phys. Chem.* **1993**, *97*, 12663.
16. International Tables for X-ray Crystallography. Vol. II, Kynoch Press: Birmingham, England, 1974; p 302.
17. Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
18. International Tables for X-ray Crystallography, Vol. IV, Kynoch Press: Birmingham, England, 1974; pp 73~87.
19. Reference 18, pp 149~150.
20. Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.
21. Loewenstein, W. *Am. Mineral.* **1954**, *39*, 92.
22. Smith, J. V. *Molecular Sieve Zeolites-I*; Flanigen, E. M.; Sand, L. B., Ed.; Adv. Chem. Series, No. 101, American Chemical Society, Washington, D. C., 1971; pp 171~200.
23. Jang, S. B.; Kim, Y. *Bull. Korean Chem. Soc.* **1995**, *16*, 248~251.
24. Yeom, Y. H.; Jang, S. B.; Kim, M. J.; Han, Y. W.; Kim, Y.; Seff, K. submitted to the *J. Phys. Chem.*
25. Sherry, H. S. *J. Phys. Chem.* **1968**, *72*, 12.
26. Shepelev, Y. F.; Butikova, I. K.; Smolin, Yu. I. K.; Smolin, Yu. I. *Zeolites* **1991**, *11*, 287.