

Ca²⁺ 이온으로 완전히 치환된 제올라이트 X, Ca₄₆-X와 Ca²⁺ 이온과 K⁺ 이온으로 치환된 제올라이트 X, Ca₃₂K₂₈-X를 완전히 진공 탈수한 결정구조

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Crystal Structures of Fully Dehydrated Ca²⁺-Exchanged Zeolite X, Ca₄₆-X, and Ca²⁺ and K⁺-Exchanged Zeolite X, Ca₃₂K₂₈-X

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요 약. Ca²⁺ 이온으로 완전히 치환된 제올라이트 X(Ca₄₆Al₉₂Si₁₀₀O₃₈₄)와 Ca²⁺ 이온과 K⁺ 이온으로 치환된 제올라이트 X(Ca₃₂K₂₈Al₉₂Si₁₀₀O₃₈₄)를 360 °C 에서 2 × 10⁻⁶ Torr의 진공하에서 탈수한 구조를 21 °C 에서 입방 공간군 *Fd* $\bar{3}$ 을 사용하여 단결정 X-선 회절법으로 해석하고 구조를 정밀화하였다. 탈수한 Ca₄₆-X의 구조는 Full-matrix 최소자승법 정밀화 계산에서 $I > 3\sigma(I)$ 인 166개의 독립반사를 사용하여 최종오차인자를 $R_1 = 0.096$, $R_2 = 0.068$ 까지 정밀화 계산하였고, Ca₃₂K₂₈-X의 구조는 130개의 독립반사를 사용하여 $R_1 = 0.078$, $R_2 = 0.056$ 까지 정밀화시켰다. 탈수된 Ca₄₆-X에서 Ca²⁺ 이온은 점유율이 높은 서로 다른 두개의 자리에 위치하고 있었다. 16개의 Ca²⁺ 이온은 이중 6-산소고리(D6R)의 중심에 위치하였고(자리 I; Ca(1)-O(3) = 2.51(2) Å), 30개의 Ca²⁺ 이온은 큰 동공에 있는 자리 II에 위치하고 있었다. 뒤에 있는 30개의 Ca²⁺ 이온은 O(2)의 평면에서 큰 동공쪽으로 약 0.44 Å 들어간 자리에 위치하고 있다(Ca(2)-O(2) = 2.24(2) Å, O(2)-Ca(2)-O(2) = 119(1)°). 탈수한 Ca₃₂K₂₈-X의 구조에서 모든 Ca²⁺ 이온과 K⁺ 이온은 4개의 서로 다른 결정학적 자리에 위치하고 있었다: 16개의 Ca²⁺ 이온은 D6R의 중심에 위치하였고, 다른 16개의 Ca²⁺ 이온과 16개의 K⁺ 이온은 큰 동공에 있는 자리 II에 각각 위치하고 있었다. 이러한 Ca²⁺ 이온과 K⁺ 이온은 O(2)의 평면에서 큰 동공쪽으로 약 0.56 Å과 1.54 Å 들어간 자리에 각각 위치하고 있었다(Ca(2)-O(2) = 2.29(2) Å, O(2)-Ca(2)-O(2) = 119(1)°, K(1)-O(2) = 2.59(2) Å, O(2)-K(1)-O(2) = 99.2(8)°). 12개의 K⁺ 이온은 큰 동공에 있는 자리 III에 위치하고 있었다(K(2)-O(4) = 3.11 Å, O(1)-K(2)-O(1) = 128(2)°).

ABSTRACT. The crystal structures of Ca₄₆-X (Ca₄₆Al₉₂Si₁₀₀O₃₈₄) and Ca₃₂K₂₈-X (Ca₃₂K₂₈Al₉₂Si₁₀₀O₃₈₄) dehydrated at 360 °C and 2 × 10⁻⁶ Torr have been determined by single-crystal X-ray diffraction techniques in the cubic space group *Fd* $\bar{3}$ at 21(1) °C. Their structures were refined to the final error indices, $R_1 = 0.096$ and $R_w = 0.068$ with 166 reflections, and $R_1 = 0.078$ and $R_w = 0.056$ with 130 reflections, respectively, for which $I > 3\sigma(I)$. In dehydrated Ca₄₆-X, Ca²⁺ ions are located at two different sites of high occupancies. Sixteen Ca²⁺ ions are located at site I, the centers of the double six rings (Ca(1)-O(3) = 2.51(2) Å and thirty Ca²⁺ ions are located at site II, the six-membered ring faces of sodalite units in the supercage. Latter Ca²⁺ ions are recessed 0.44 Å into the supercage from the three O(2) oxygen plane (Ca(2)-O(2) = 2.24(2) Å and O(2)-Ca(2)-O(2) = 119(1)°). In the structure of Ca₃₂K₂₈-X, all Ca²⁺ ions and K⁺ ions are

located at the four different crystallographic sites: 16 Ca^{2+} ions are located in the centers of the double six rings, another sixteen Ca^{2+} ions and sixteen K^+ ions are located at the site II in the supercage. These Ca^{2+} ions and K^+ ions are recessed 0.56 Å and 1.54 Å, respectively, into the supercage from their three O(2) oxygen planes ($\text{Ca}(2)\text{-O}(2)=2.29(2)$ Å, $\text{O}(2)\text{-Ca}(2)\text{-O}(2)=119(1)^\circ$, $\text{K}(1)\text{-O}(2)=2.59(2)$ Å, and $\text{O}(2)\text{-K}(1)\text{-O}(2)=99.2(8)^\circ$). Twelve K^+ ions lie at the site III, twofold axis of edge of the four-membered ring ladders inside the supercage ($\text{K}(2)\text{-O}(4)=3.11(6)$ Å and $\text{O}(1)\text{-K}(2)\text{-O}(1)=123(2)^\circ$).

INTRODUCTION

The synthetic zeolite X has a framework with a structure similar to that of the natural mineral faujasite¹. The chemical composition can vary, according to the silicon and aluminium content, from a Si/Al ratio of ca. 1.0~1.5. The increase of the aluminium content increases the number of exchangeable cations and influences their distribution in the different possible sites of the lattice. The knowledge of the three-dimensional structure is quite important for understanding their properties, such as absorption and catalysis, which are sensitive to the nature of the cations, their number and distribution in the framework cavities.

Cation substitution is one of the methods of modification of their physical and chemical properties. So the problem of reactivity and location of multivalent-exchanged ions is of interest from both theoretical and practical points of view. The distribution and coordination of various cations in the framework of faujasite-type zeolites have been widely investigated and reviewed. Most of these studies have been summarized by Mortier². The cations and water molecules are usually distributed in zeolite X over the sites I, I', II, II', and III. The site I lies in the center of the double six ring. The site II lies at the six-membered ring face of sodalite unit in the supercage side. The site I' and II' lie inside the sodalite unit and on the opposite sides of the six-membered rings as compared with sites I and II. The site III lies at the twofold axis of the edge of the four-membered ring ladder inside the supercage. Alkali-metal cations other than sodium are of interest for use in catalysis and sorption. Li-exchanged zeolites X and Y were studied using powder³ and single-crystal⁴ diffraction data. Pluth and Showmaker investigated a single-crystal of the dehydrated K-ex-

changed natural faujasite (Si/Al=2.3)⁵. The structures of four K-exchanged Y and X zeolites with various Si/Al ratio were also studied in the hydrated⁶ and dehydrated⁷ states using X-ray powder data. Anderson, Shepelev and Smolin studied the structures of Mg^{2+} -exchanged Na-X and Ca-X⁸. They found that Mg^{2+} ions are located in three sites, I', II, and III in hydrated MgNa-X, and I and II' in hydrated CaMg-X. In the dehydrated forms, the sites of Mg^{2+} ions are I, I', and II in dehydrated MgNa-X, and II II' in dehydrated CaMg-X. They also found that Ca^{2+} ions in dehydrate CaNa-X are located in sites I, I', and II.

Calligaris *et al.* have studied hydrated and dehydrated structures of some monovalent and divalent cation exchanged chabazite^{9,10} and heulandite¹¹, by single crystal X-ray techniques. They have shown that the extra-framework structure can be explained in terms of the sizes, charges and electronic structures of the exchanged cations. In addition, they have also shown that the comparison of the electron density maps of the same zeolite, exchanged with different cations, may be useful in determining site locations and possibly the approximate ratio of two different cations at the same site¹¹.

The present study has been initiated to investigate the cation positions in zeolite X. Because the ionic radii of Ca^{2+} and K^+ ion are quite different, precise and reliable crystallographic determination should be easy to achieve. The present work is preliminary to later studies of crystal structures of $\text{Ca}_{46-x}\text{K}_x\text{-X}$ absorbed with other guest molecules.

EXPERIMENTAL SECTION

Large single crystals of sodium zeolite X, having stoichiometry of $\text{Na}_{92}\text{Al}_{92}\text{Si}_{100}\text{O}_{384}$, were prepared

in St. Petersburg, Russia¹². Each of two single crystals, a colorless octahedron about 0.2 mm in cross-section was lodged in a fine Pyrex capillary.

An exchange solution of 0.04325 M $\text{Ca}(\text{NO}_3)_2$ and 0.00675 M CaO with a total concentration of 0.05 M was filtered through a membrane filter for crystal 1. Crystal 2 of composition $\text{Ca}_{32}\text{K}_{28}\text{-X}$ was prepared using an exchange solution whose $\text{Ca}(\text{NO}_3)_2$: KNO_3 mole ratio was 1 : 1 with total concentration 0.05 M. Ion exchange was accomplished by flow methods; the solution was allowed to flow past each crystal at a velocity of approximately 1.5 cm/s for 5 day at 24(1) °C. Each crystal was dehydrated at 360 °C and 2×10^{-6} Torr for 2 days.

After cooling to room temperature, each crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal 1 has remained colorless. However, crystal 2 has become red.

The cubic space group $Fd\bar{3}$ was used throughout this work. Diffraction data were collected with an automated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using $\text{Mo K}\alpha$ radiation ($K\alpha_1$, $\lambda = 0.70930$ Å, $K\alpha_2$, $\lambda = 0.71359$ Å). The unit cell constants at 21(1) °C determined by least-squares refinement of 25 intense reflections for which $14^\circ < 2\theta < 24^\circ$ are $a = 25.046(1)$ Å for crystal 1 and $a = 25.002(1)$ Å for crystal 2, respectively.

For each crystal, the θ - 2θ scan technique was used. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.24 deg and 0.33 deg min^{-1} in ω . The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and X-ray source stability. Only small random fluctuations of these check reflections were noted during the course of data collection. The intensities of all lattice points for which $2\theta < 60^\circ$ were recorded. Only those of which $I > 3\sigma(I)$ were used for structure solution and refinement. This amounted to 166 of the 1200 reflections examined for crystal 1, and 130 of the 1151 reflections for crystal 2.

The intensities were corrected for Lorentz and

polarization effects; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs, BEGIN and WEIGH¹³.

For the first crystal, $\mu R = 0.077$, $\rho_{\text{cal}} = 1.405$ g/cm³ and $F(000) = 6542$; for the second the corresponding values are 0.078, 1.468 g/cm³ and 6794, respectively. An absorption correction was made empirically using a ψ scan for both crystals¹⁴. The calculated transmission coefficients ranged from 0.975 to 0.999. This correction had little effect on the final R indices.

STRUCTURE DETERMINATION

Dehydrated $\text{Ca}_{46}\text{-X}$. Full-matrix least-squares refinement was initiated with fixed thermal parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] of dehydrated Na-X treated with Rb(g)¹⁵. Isotropic refinement of the framework atoms converged to an R_1 index, $(\sum |F_o - |F_c||) / \sum F_o$ of 0.36 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2 / \sum w F_o^2)^{1/2}$ of 0.35.

The initial difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.222, 0.222, 0.222) with heights of 10.0 and 6.49 eÅ⁻³, respectively. These two peaks were stable in least-squares refinement. Anisotropic refinement including these Ca^{2+} ions at Ca(1) and Ca(2) positions converged to $R_1 = 0.092$ and $R_2 = 0.070$.

Occupancy refinement converged at 16.3(5) and 31.3(7), respectively. These values were reset and fixed at 16.0 and 30.0 Ca^{2+} ions at Ca(1) and Ca(2), respectively, because the cationic charge should not be exceeded +92 per $Fd\bar{3}$ unit cell. Anisotropic refinement of the framework atoms and cations at Ca(1) and Ca(2) converged to $R_2 = 0.096$ and $R_2 = 0.068$ (see Table 1).

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 1.24 eÅ⁻³ at (0.250, 0.999, 0.750). This peak was not refined at the least-squares refinement.

Dehydrated $\text{Ca}_{32}\text{K}_{28}\text{-X}$. Full-matrix least-

Table 1. Positional, thermal, and occupancy parameters^a(a) Crystal 1. Dehydrated Ca₄₆-X

Atom	Wyc. Pos.	x	y	z	β_{11}^b B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^c	
											varied	fixed
Si	96(g)	-559(5)	334(4)	1215(5)	5(2)	-0(2) ^f	-1(2) ^f	3(4)	6(5)	3(4)		96
Al	96(g)	-549(5)	1220(6)	365(4)	6(2)	5(2)	-2(2) ^f	22(5)	-6(4)	-13(4)		96
O(1)	96(g)	-1116(8)	30(20)	1109(8)	-6(4) ^f	12(5) ^f	-2(5)	5(8)	-9(6)	-1(8)		96
O(2)	96(g)	-30(10)	-30(10)	1445(8)	-12(3) ^f	8(5)	9(5)	-5(8)	-2(7)	15(8)		96
O(3)	96(g)	-342(8)	646(9)	680(10)	2(5)	-2(4) ^f	13(5)	2(8)	15(9)	-18(8)		96
O(4)	96(g)	-551(8)	766(9)	1720(10)	5(4)	-6(3) ^f	25(6)	-25(6)	-10(10)	-28(8)		96
Ca(1)	16(c)	0	0	0	6(2)	6(2)	6(2)	2(4)	2(4)	2(4)	16.3(5)	16
Ca(2)	32(e)	2228(5)	2228(5)	2228(5)	10(1)	10(1)	10(1)	17(4)	17(4)	17(4)	31.3(7)	30

(b) Crystal 2. Dehydrated Ca₃₂K₂₈-X

Atom	Wyc. Pos.	x	y	z	β_{11}^b B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^c	
											varied	fixed
Si	96(g)	-526(5)	329(6)	1220(8)	0(2)	4(2)	9(2)	4(4)	1(6)	12(6)		96
Al	96(g)	-565(5)	1218(7)	370(4)	5(2)	3(2)	-5(2) ^f	12(7)	3(4)	8(5)		96
O(1)	96(g)	-1076(8)	30(10)	1125(7)	5(5)	-8(4)	-10(4) ^f	-4(7)	-13(5)	-3(7)		96
O(2)	96(g)	-50(10)	-52(9)	1435(8)	16(6)	-5(4) ^f	-1(5) ^f	-31(8)	-17(7)	20(6)		96
O(3)	96(g)	-366(6)	609(9)	643(7)	-5(3) ^f	-4(3) ^f	-15(2) ^f	15(5)	12(5)	4(5)		96
O(4)	96(g)	-612(9)	780(10)	1677(19)	0(5)	16(7) ^f	-11(4) ^f	-8(9)	-10(10)	-9(6)		96
Ca(1)	16(c)	0	0	0	0.1(4) ^d						16.1(6)	16
Ca(2)	32(e)	2239(8)	2239(8)	2239(8)	2.0(9)						16.3(9)	16
K(1)	32(e)	2465(8)	2465(8)	2465(8)	0.3(6)						16.7(7)	16
K(2)	48(f)	4180(30)	1250	1250	6(2)						12.7(13)	12

^aPositional 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. ^bThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^cOccupancy factors are given as the number of atoms or ions per unit cell. ^dIsotropic thermal parameter in units of \AA^2 . ^eSome of physically unacceptable values of anisotropic thermal parameters were increased by 1σ to 3σ in the preparation of Fig. 1, 2, and 3.

squares refinement was initiated by using the atomic parameters of framework atoms for the previous crystal of Ca₄₆-X. Isotropic refinement of the framework atoms converged to an R_1 index of 0.30 and a weighted R_2 index of 0.33, respectively.

A difference Fourier function showed the positions of Ca²⁺ ions at Ca(1), (0.0, 0.0, 0.0), with peak height $7.92 \text{ e}\text{\AA}^{-3}$; K⁺ ions at K(1), (0.249, 0.249, 0.249), with peak height $5.10 \text{ e}\text{\AA}^{-3}$; and Ca²⁺ ions at Ca(2), (0.222, 0.222, 0.222), with peak height $3.18 \text{ e}\text{\AA}^{-3}$. These were stable in least-squares refinement, and anisotropic refinement of framework atoms and isotropic refinement of Ca(1), K(1) and Ca(2) converged to $R_1=0.092$ and $R_2=0.078$ with occupancies of 16.1(6), 16.7(7), and 16.3(9), respec-

tively (see Table 1).

It is not so difficult to distinguish Ca²⁺ from K⁺ ions for several reasons. First, their ionic radii are different, $\text{Ca}^{2+}=0.99 \text{ \AA}$ and $\text{K}^+=1.33 \text{ \AA}$ ¹⁶. Secondly, the approach distances between those ions and zeolite oxide ions in the previous Ca₄₆-X (see Table 1 and 2) and K₃₂-X¹⁷ have been determined and are indicative. Finally, the requirement that 92 monovalent metal ions (or 46 divalent metal ions) per unit cell be found do not allow the major positions to refine to acceptable occupancies with the alternative assignment of ionic identities.

From successive difference Fouriers, one peak was found at (0.42, 0.125, 0.125), height = $2.09 \text{ e}\text{\AA}^{-3}$, which refined as K(2). Simultaneous positional iso-

Table 2. Selected interatomic distances (Å) and angles (deg)

	Crystal 1	Crystal 2
Si-O(1)	1.61(3)	1.58(3)
Si-O(2)	1.70(3)	1.61(3)
Si-O(3)	1.64(3)	1.65(3)
Si-O(4)	1.67(3)	1.61(3)
Al-O(1)	1.73(3)	1.76(3)
Al-O(2)	1.73(3)	1.75(3)
Al-O(3)	1.72(3)	1.74(3)
Al-O(4)	1.65(3)	1.70(3)
Ca(1)-O(3)	2.51(2)	2.40(2)
Ca(2)-O(2)	2.24(2)	2.29(2)
K(1)-O(2)		2.59(2)
K(2)-O(1)		3.42(4)
K(2)-O(4)		3.11(6)
O(1)-Si-O(2)	118(2)	114(2)
O(1)-Si-O(3)	112(1)	106(1)
O(1)-Si-O(4)	116(1)	109(1)
O(2)-Si-O(3)	106(1)	111(1)
O(2)-Si-O(4)	94(1)	106(2)
O(3)-Si-O(4)	108(1)	111(1)
O(1)-Al-O(2)	109(2)	108(1)
O(1)-Al-O(3)	112(1)	106(1)
O(1)-Al-O(4)	118(1)	117(1)
O(2)-Al-O(3)	108(1)	107(1)
O(2)-Al-O(4)	96(1)	103(1)
O(3)-Al-O(4)	111(1)	114(1)
Si-O(1)-Al	122(1)	124(1)
Si-O(2)-Al	137(1)	141(2)
Si-O(3)-Al	132(1)	130(1)
Si-O(4)-Al	169(2)	168(2)
O(3)-Ca(1)-O(3)	180(0)	180(0)
O(2)-Ca(2)-O(2)	119(1)	119(1)
O(2)-K(1)-O(2)		99.2(8)
O(3)-K(2)-O(3)		104.8(6)
O(1)-K(2)-O(1)		128(2)

Numbers in parentheses are estimated standard deviations in the least significant digit given for the corresponding value.

tropic thermal parameter refinement with varied occupancy numbers converged to the error indices $R_1=0.078$ and $R_2=0.055$.

Allowing all occupancies of K(1), Ca(2), and K(2) to vary except that of Ca(1) which was not permitted to exceed 16.0 (its maximum occupancy), led to $R_1=0.078$ and $R_2=0.056$. The occupancy numbers of Ca(1), Ca(2), K(1), and K(2) were reset

Table 3. Deviations of atoms (Å) from the plane of three 6-ring oxygens at O(2)

	Crystal 1	Crystal 2
Ca(2)	0.44(1)	0.56(1)
K(1)		1.54(1)

A positive deviation indicates that the atom lies in the supercage.

and fixed as in the last column of Table 1.

All shifts in the final cycles of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final error indices converged to $R_1=0.078$ and $R_2=0.057$. The final difference function was featureless except for a peak at (-0.06, 0.0, 0.0) of height 0.69 eÅ^{-3} . This peak was not within bonding distance of any other atom, and was not considered further.

All crystallographic calculations were done using the MolEN (a structure determination package programs, supplied by Enraf-Nonius). The full-matrix least-squares program used minimized $\Sigma (F_o - |F_c|)^2$; the weight (W) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors^{18,19} for Si, Al, O⁻, Ca²⁺, and K⁺ were used. All scattering factors were modified to account for anomalous dispersion²⁰. The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

DISCUSSION

In the crystal structure of vacuum-dehydrated $\text{Ca}_{46}\text{-X}$, all Ca²⁺ ions are located at the two different sites of high occupancy. The Ca²⁺ ions at Ca(1) lie at site I in the center of a double six-oxygen ring (D6R). This 16-fold position is fully occupied. The Ca(1)-O(3) distance, 2.51 Å, is longer than a Ca²⁺-O²⁻ the sum of the ionic radii, $0.99 + 1.32 = 2.31 \text{ Å}$ ¹⁶. The Ca²⁺ ions at Ca(2) are located at site II, in the supercage. Thirty of 32-fold position may be occupied. Each Ca²⁺ ion coordinates at 2.24(2) Å to three O(2) framework oxygens, and is recessed ca. 0.44 Å into the supercage from its nearer 6-ring plane. The O(2)-Ca(2)-O(2) bond angle is 119(1)°, close to near trigonal planar.

Smolin, Shepeler, and Anderson studied the crystal structure of the hydrated and dehydrated Ca^{2+} -exchanged zeolite X²¹. They also investigated the migration of cations during the dehydration by heating under a stream of hot N_2 gas. In the initial hydrated form, Ca^{2+} ions are located in the sodalite cavities and supercages. Upon dehydration the Ca^{2+} ions migrate in the direction of the hexagonal prism and sit on the single six oxygen ring faces on the supercage sites. Recently, the crystal structures of fully dehydrated $\text{Co}_{46}\text{-X}$, $\text{Cd}_{46}\text{-X}$, and $\text{Mn}_{46}\text{-X}$ have been determined by single crystal X-ray diffraction methods¹⁷. In these structures, all divalent cations are located at the site I and II. In present work, all Ca^{2+} ions are located in the centers of double six ring (site I) and near the plane of single six oxygen rings inside the supercage (site II). Therefore, the present structure is in good agreement with the other works^{17,21}.

In dehydrated $\text{Ca}_{32}\text{K}_{28}\text{-X}$, thirty two Ca^{2+} ions occupy two crystallographic sites and about twenty eight K^+ ions to O(3) distance are found at four such sites. The Ca^{2+} ions at Ca(1) lie at site I, in the centers of the double six-oxygen rings (D6R's). The distance between Ca(1) and O(3) is long, 2.40(2) Å (see Table 2). It is shorter than those distances of the previous Ca^{2+} ions at Ca(1) in the structure of $\text{Ca}_{46}\text{-X}$. Such long interaction dis-

tances have been observed previously in the center of a D6R in the zeolite X structures²¹.

The 16 Ca^{2+} ions at Ca(2) are on the threefold axis in the supercage, 0.56 Å from the plane of the single 6-ring at site II. Each Ca^{2+} ion is coordinated to their three oxygens, O(2) with Ca(2)-O(2) distances of 2.29 Å. The O(2)-Ca(2)-O(2) angle of 119(1)° also indicates that Ca(2) has achieved near trigonal-planar coordination (see Table 2). A plausible atomic arrangement in a particular unit cell is shown in Fig. 1 and 2. Also 16 K^+ ions at K(1) lie at site II and are recessed 1.54 Å into the supercage from the single 6-oxygen ring plane at O(2). Each of these K^+ ions coordinates to three O(2) oxygens at 2.59(2) Å, somewhat less than the sum of K^+ and O^{2-} radii, 2.65 Å¹⁶.

12 K^+ ions at K(2) lie in the supercage (at site III). This is 48-fold position, but this is occupied by only 12 ions (see Fig. (a) and 2). The K^+ ions at K(2) are loosely held to framework oxygens K(2)-O(1)=3.42(4) Å and K(2)-O(4)=3.11(6) Å. For comparison the sum of the corresponding ionic radii is 1.33+1.32=2.65 Å¹⁶. These distances are substantially longer than the sum of the ionic radii. Such long interaction distances have been observed previously in supercage in other X structures²².

The mean values of the Si-O and Al-O bond lengths are 1.63(3) Å and 1.72(3) Å, respectively. The individual bond lengths show marked varia-

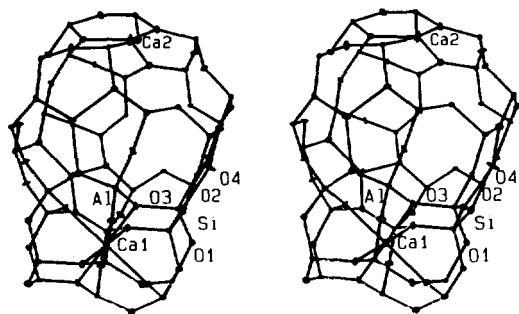


Fig. 1. A stereoview of sodalite cavity of dehydrated $\text{Ca}_{46}\text{-X}$. One Ca^{2+} ion at Ca(1) lies at site I and four Ca^{2+} ions at Ca(2) lie at site II. All double six-rings have this arrangement. About 75% of the sodalite cavities may have this arrangement. Remaining 25% may have only three Ca^{2+} ions at Ca(1). Ellipsoids of 20% probability are shown.

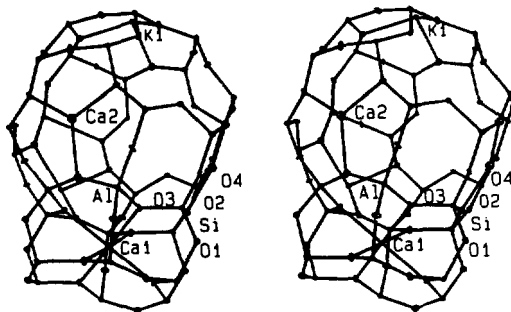


Fig. 2. A stereoview of sodalite cavity of dehydrated $\text{Ca}_{32}\text{K}_{28}\text{-X}$. Two Ca^{2+} ions at Ca(2), two K^+ ions at K(1), and one Ca^{2+} ion at Ca(1) are shown. All the double 6-rings and sodalite cavities have this arrangement. Ellipsoids of 20% probability are shown.

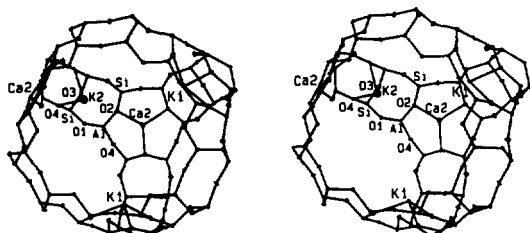


Fig. 3. A stereoview of supercage of dehydrated $\text{Ca}_{32}\text{K}_{28}\text{-X}$. Two Ca^{2+} ion at Ca(2), two K^{+} ions at K(1), and one K^{+} ion at K(2) are shown. About 50% of the supercages have this arrangement. Remaining 50% of supercages may have two Ca^{2+} ions at Ca(2), two K^{+} ions at K(1) and two K^{+} ions at K(2). Ellipsoids of 20% probability are shown.

tions: Si-O from 1.58(3) to 1.70(3) Å and Al-O from 1.65(3) to 1.76(3) Å. The Si-O-Al bond angles range from 122° to 169°. The framework geometries of the zeolites presented here are not sensitive to ion exchange and dehydration as in other zeolite X structures^{4,8,22}. Therefore, our discussion have been focused mainly on the distribution of cations in the zeolite framework.

In summary, the principal positions of Ca^{2+} ion are Ca(1) position (site I), the center of the double six-oxygen ring (symmetry of $\bar{3}$) and the Ca(2) position in supercage (site II and symmetry of 3). Because the ionic radius of K^{+} ion is larger than that of Ca^{2+} ion, larger K^{+} ions preferentially occupy deep in the large supercage (site II and III). Smaller 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.

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