

## Crystal Structures of Dehydrated Partially Sr<sup>2+</sup>-Exchanged Zeolite X, Sr<sub>31</sub>K<sub>30</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub> and Sr<sub>8.5</sub>Tl<sub>75</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>

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### 부분적으로 스트론튬이온으로 교환되고 탈수된 제올라이트 X의 결정구조

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#### Abstract

The crystal structures of Sr<sub>31</sub>K<sub>30</sub>-X (Sr<sub>31</sub>K<sub>30</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>; a=25.169(5) Å) and Sr<sub>8.5</sub>Tl<sub>75</sub>-X (Sr<sub>8.5</sub>Tl<sub>75</sub>Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>; a=25.041(5) Å) have been determined by single-crystal X-ray diffraction techniques in the cubic space group *Fd* $\bar{3}$  at 21(1)°C. Each crystal was prepared by ion exchange in a flowing stream of aqueous Sr(ClO<sub>4</sub>)<sub>2</sub> and (K or Tl)NO<sub>3</sub> whose mole ratio was 1:5 for five days. Vacuum dehydration was done at 360°C for 2d. Their structures were refined to the final error indices R<sub>1</sub>=0.072 and R<sub>w</sub>=0.057 with 293 reflections, and R<sub>1</sub>=0.058 and R<sub>w</sub>=0.044 with 351 reflections, for which  $I > 2\sigma(I)$ , respectively. In dehydrated Sr<sub>31</sub>K<sub>30</sub>-X, all Sr<sup>2+</sup> ions and K<sup>+</sup> ions are located at five different crystallographic sites. Sixteen Sr<sup>2+</sup> ions per unit cell are at the centers of the double six-rings (site I), filling that position. The remaining 15 Sr<sup>2+</sup> ions and 17 K<sup>+</sup> ions fill site II in the supercage. These Sr<sup>2+</sup> and K<sup>+</sup> ions are recessed *ca* 0.45 Å and 1.06 Å into the supercage, respectively, from the plane of three oxygens to which each is bound. (Sr-O=2.45(1) Å and K-O=2.64(1) Å). Eight K<sup>+</sup> ions occupy site III' (K-O=3.09(7) Å and 3.11(10) Å) and the remaining five K<sup>+</sup> ions occupy another site III' (K-O=2.88(7) Å and 2.76(7) Å). In Sr<sub>8.5</sub>Tl<sub>75</sub>-X, Sr<sup>2+</sup> and Tl<sup>+</sup> ions also occupy five different crystallographic sites. About 8.5 Sr<sup>2+</sup> ions are at site I. Fifteen Tl<sup>+</sup> ions are at site I' in the sodalite cavities on threefold axes opposite double six-rings; each is 1.68 Å from the plane of its three oxygens (Tl-O=2.70(2) Å). Together these fill the double six-rings. Another 32 Tl<sup>+</sup> ions fill site II opposite single six-rings in the supercage, each being 1.48 Å from the plane of three oxygens (Tl-O=2.70(1) Å). About 18 Tl<sup>+</sup> ions occupy site III in the supercage (Tl-O=2.86(2) Å), and the remaining 10 are found at site III' in the supercage (Tl-O=2.96(4) Å).

#### 요 약

제올라이트 X에 Sr<sup>2+</sup>와 K<sup>+</sup> 이온이 교환된 Sr<sub>31</sub>K<sub>30</sub>-X와 Sr<sup>2+</sup>와 Tl<sup>+</sup> 이온이 교환된 Sr<sub>8.5</sub>Tl<sub>75</sub>의 결정구조를 공간군 *Fd* $\bar{3}$ 로 21(1)°C에서 단결정 X선 결정학적 방법으로 해석하였다. 각각의 결정은 Sr(ClO<sub>4</sub>)<sub>2</sub>와 (K 혹은 Tl)NO<sub>3</sub>의 몰 비가 1:5인 용액을 사용해서 흐름 법으로 5일 동안 이온 교환시키고 360°C에서 진공탈수시켜 두 결정을 얻었다. 이들 결정은 회절강도가  $I > 2\sigma(I)$ 인 293개와 351개의 회절반사를 사용하여 최종오차인자가 R<sub>1</sub>=0.072, R<sub>w</sub>=0.057과 R<sub>1</sub>=0.058, R<sub>w</sub>=0.044까지 각각 정밀화 하였다. Sr<sub>31</sub>K<sub>30</sub>-X결정에서 Sr<sup>2+</sup> 이온과 K<sup>+</sup> 이온은 모두 다섯 개의 서로 다른 결정학적 자리에 존재하였다 단위세포당 16개의 Sr<sup>2+</sup> 이온은 결정학적 자리 I인 D6R의 중심에 각각 위

치고 D6R 모두를 채우고 있다. 나머지 15개의  $\text{Sr}^{2+}$  이온과 17개의  $\text{K}^+$  이온은 큰 동공 속에 있는 결정학적 자리 II에 위치하고 세 개의 산소이온이 이루는 평면에서 각각  $0.45\text{\AA}$ ,  $1.06\text{\AA}$  큰 동공 속으로 이동하여 위치하고 골조산소와 결합거리는 각각  $2.45(1)\text{\AA}$ ,  $2.64(1)\text{\AA}$ 이다. 13개의  $\text{K}^+$  이온은 두 개의 다른 결정학적 자리 III'에 위치하며 인접한 산소와의 결합거리는 각각  $2.88(7)\text{\AA}$ 와  $3.11(10)\text{\AA}$ 이다.  $\text{Sr}_{8.5}\text{Ti}_{75}\text{-X}$ 에서는  $\text{Sr}^{2+}$  이온과  $\text{Ti}^+$  이온이 역시 다섯 개의 서로 다른 결정학적 자리에 위치한다. 약 8.5개의  $\text{Sr}^{2+}$  이온은 결정학적 자리 I에 있으며, 15개의  $\text{Ti}^+$  이온은 D6R의 3회 회전축상의 소다라이트내에 있는 결정학적 자리 I'에 있다. 이  $\text{Ti}^+$  이온은 골조산소와의 결합거리가  $2.70(2)\text{\AA}$ 이며 세 개의 산소가 이루는 평면에서  $1.68\text{\AA}$  소다라이트내로 이동하여 위치한다. 32개의  $\text{Ti}^+$  이온은 결정학적 자리 II에 존재하고 있으며 산소와의 결합거리를  $2.70(1)\text{\AA}$ 을 유지하면서 큰 동공속으로  $1.48\text{\AA}$  이동하여 위치한다. 약 18개의  $\text{Ti}^+$  이온은 결정학적 자리 III에, 또 다른 10개의  $\text{Ti}^+$  이온은 결정학적 자리 III'에 존재하고 골조 산소와 각각  $2.86(2)\text{\AA}$ ,  $2.96(4)\text{\AA}$ 의 결합거리를 이룬다.

## 1. Introduction

Synthetic zeolite X has the same framework structure as the natural mineral faujasite.<sup>1)</sup> Its Si/Al ratio can vary from 1.0 to 1.5. An increase in the aluminium content leads to the increase in the number of exchangeable cations and affects their distribution in the different possible sites in the zeolite.

Zeolite X has a wide range of industrial applications primarily due to the excellent stability of the crystal structure and the large available pore volume and surface area.<sup>2)</sup> In addition to the accessible pore volume, the sorptive and catalytic properties of zeolites heavily depend on the size, charge density, and distribution of cations in the lattice. Alkali-metal cation exchanged zeolites have been the subject of numerous investigations because of their importance in adsorption and catalysis. Li-exchanged zeolites X and Y were studied using powder<sup>3)</sup> and single-crystal diffraction data.<sup>4)</sup> Smith *et al.* investigated a single-crystal of dehydrated  $\text{K}^+$ -exchanged natural faujasite (Si/Al=2.3).<sup>5)</sup> The structures of four hydrated<sup>6)</sup> and dehydrated,<sup>7)</sup> partially  $\text{K}^+$ -exchanged X and Y zeolites with various Si/Al ratios were also studied using X-ray powder data. Recently Smolin *et al.* investigated the structures of the partially  $\text{K}^+$ ,  $\text{Rb}^+$ , and  $\text{Cs}^+$ -exchanged forms of NaX zeolites and the structures of Mg-exchanged NaX and CaX zeolites in both the hydrated and the dehydrated states by

single X-ray diffraction method.<sup>8,9)</sup>

Also a variety of reactions have been studied over transition-metal exchanged zeolites. The hydrogenation of methyl acetoacetate<sup>10)</sup> and the gas-phase decomposition of nitromethane<sup>11)</sup> have been conducted over X- and Y-type zeolites containing Ni(II), U(VI) or Zn(II) ions.

Recently, the structure of fully dehydrated  $\text{Ti}_{92}\text{-X}$  was determined.<sup>12)</sup> In the structure, all 92  $\text{Ti}^+$  ions were located at four crystallographically non-equivalent sites as described in Table 1.

This work was initiated to investigate further the cation positions in zeolite X. Because the ionic radius of  $\text{Sr}^{2+}$  is somewhat different from that of  $\text{Ti}^+$  or  $\text{K}^+$ , precise and reliable crystallographic determination should be easy to achieve.

## 2. Experimental Section

Large single crystals of sodium zeolite X, stoichiometry  $\text{Na}_{92}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$  per unit cell, were prepared in St. Petersburg, Russia.<sup>13)</sup> Each of two crystals, octahedra ca. 0.2 mm in cross-section, was lodged in a fine Pyrex capillary.

Crystal 1 was prepared using an aqueous exchange solution of  $\text{Sr}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Johnson Matthey, 99.9%) and  $\text{KNO}_3$  (Aldrich Chem. Co. 99.999%) with a 1:5 mole ratio and a total concentration of 0.05 M. Crystal 2 was prepared identically instead of  $\text{KNO}_3$  using  $\text{TINO}_3$ . For each crystal, ion exchange was accomplished by

**Table 1. Distribution of Cations over Sites in Fully Dehydrated Zeolite X<sup>a</sup>**

Site	I	I'	II	II'	III	III'
Maximum Occup. <sup>b</sup>	16	32	32	32	48	96
Structure						
K <sub>92</sub> -X <sup>c</sup>	15.3(5)	12.5(8)	29.1(7)		21.2(10)	8.6(18)
Tl <sub>92</sub> -X <sup>d</sup>		31.8(4)	32.1(4)			16.3(5) 10.6(6)
Mg <sub>46</sub> -X <sup>e</sup>	14.7(7)	4.2(11)	28.2(11)			
Ca <sub>46</sub> -X <sup>e</sup>	16.3(5)		31.3(7)			
Ba <sub>46</sub> -X <sup>e</sup>	13.6(1)	1.6(2)	28.9(2)			
Cd <sub>46</sub> -X <sup>f</sup>	16.6(2)		29.5(2)			
Cd <sub>24.5</sub> Tl <sub>43</sub> -X <sup>f</sup>	14.6(7) Cd <sup>2+</sup>		10.8(9) Cd <sup>2+</sup> 21.1(4) Tl <sup>+</sup>		18.1(4) Tl <sup>+</sup>	
Sr <sub>8.5</sub> Tl <sub>75</sub> -X <sup>g</sup>	8.5(2) Sr <sup>2+</sup>	14.9(1) Tl <sup>+</sup>	30.9(8) Tl <sup>+</sup>		18.3(1) Tl <sup>+</sup>	10.1(3) Tl <sup>+</sup>
Sr <sub>31</sub> K <sub>30</sub> -X <sup>g</sup>	16.4(2) Sr <sup>2+</sup>		15.6(3) Sr <sup>2+</sup> 17.5(5) K <sup>+</sup>			5.9(7) K <sup>+</sup> 10.6(11) K <sup>+</sup>
Ca <sub>32</sub> K <sub>28</sub> -X <sup>h</sup>	16.1(6) Ca <sup>2+</sup>		16.3(9) Ca <sup>2+</sup> 16.7(7) K <sup>+</sup>		12.7(13) K <sup>+</sup>	

<sup>a</sup>These are all single-crystal diffraction results using crystals of framework composition (Si<sub>100</sub>Al<sub>92</sub>O<sub>384</sub>)<sup>92-</sup> per unit cell prepared by V. P. Petranovskii. Reference 11. <sup>b</sup>Ions per unit cell. <sup>c</sup>Reference 24. <sup>d</sup>Reference 12. <sup>e</sup>Reference 23. <sup>f</sup>Reference 22. <sup>g</sup>this work. <sup>h</sup>Reference 16.

flow methods: the exchange solution was allowed to flow past each crystal at a velocity of approximately 1.5 cm/s for 5 d at 21(1)°C. Each crystal was dehydrated at 360°C and 2×10<sup>-6</sup> Torr for 2 d. After cooling to room temperature, each crystal was sealed in its Pyrex capillary under vacuum. Crystal 1 was pale light brown and crystal 2 was pale yellow.

### 3. Data Collection

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 Mo radiation ( $K\alpha_1$ ,  $\lambda=0.70930$  Å;  $K\alpha_2$ ,  $\lambda=0.71359$  Å). The unit cell constants at 21(1) °C, each determined by least-squares refinement of 25 intense reflections within  $14^\circ < 2\theta < 240^\circ$ , are  $a=25.169(5)$  Å for crystal 1 and  $25.041(5)$  Å for crystal 2.

The  $\omega$ - $2\theta$  scan technique was used. The intensities of all lattice points for which  $2\theta < 60^\circ$  were recorded. Of the 1266 and 1251 unique reflections measured for crystal 1 and crystal 2, only the 293 and 351, respectively, for which  $I > 2\sigma(I)$ , were used in subsequent structure determinations.

### 4. Structure Determination

The crystal structures were solved in the cubic space group  $Fd\bar{3}$  which is established for zeolite X.<sup>15)</sup>

#### 4-1. Crystal 1

Full-matrix least-squares refinement was initiated using the atomic positions of the framework atoms [Si, Al, O(1), O(2), O(3), O(4)] of dehydrated Ca<sub>32</sub>K<sub>28</sub>-X.<sup>16)</sup> Isotropic refinement converged to an R<sub>1</sub> index,  $(\Sigma(|F_o| - |F_c|))/\Sigma F_o$  of 0.35 and a weighted R<sub>2</sub> index,  $(\Sigma w(F_o - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$  of 0.38.

A difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.22, 0.22, 0.22) with peak height of  $13.2$  and  $6.5 \text{ e}\text{\AA}^{-3}$ , respectively. Isotropic refinement including these peaks as  $\text{Sr}^{2+}$  ions at Sr(1) and Sr(2) converged to  $R_1=0.20$  and  $R_2=0.22$  with occupancies of 16.4(2) and 15.6(3), respectively (see Table 2).

A subsequent difference Fourier synthesis showed the positions of K(2) at (0.25, 0.25, 0.25) with height  $2.1 \text{ e}\text{\AA}^{-3}$ , K(3) at (0.109, 0.129, 0.418) with height  $2.0 \text{ e}\text{\AA}^{-3}$  and K(4) at (0.06, 0.06, 0.4) with height of  $1.4 \text{ e}\text{\AA}^{-3}$ . Simultaneous positional parameter refinement with occupancy numbers varying converged to the indices  $R_1=0.070$  and  $R_2=0.055$ . The occupancy numbers at Sr(1), Sr(2), K(2), K(3), and K(4) were refined to 16.4(2), 15.6(3), 17.5(5), 5.9(7) and 10.6(11) per unit cell, respectively. These were fixed at 16, 15, 17, 5 and 8, respectively, because site I cannot hold more than 16 ions and because the cationic charge should not exceed 92+. All shifts in the final cycle of least-squares were less than 0.01% of their corresponding standard deviations. Anisotropic refinement of Sr(1), Sr(2) and K(2), and isotropic refinement of framework atoms, K(3) and K(4) converged to  $R_1=0.072$  and  $R_2=0.057$ . The final difference function was featureless except for the peak at (0.125, 0.125, 0.125) of height  $1.4 \text{ e}\text{\AA}^{-3}$ . This peak is far away from the framework oxygens: it was not refined and was not considered further.

The final structural parameters and selected interatomic distances and angles are presented in Tables 2 and 3, respectively.

#### 4-2. Crystal 2

Full-matrix least-squares refinement was initiated with the positional and thermal parameters of the framework atoms in crystal 1. Isotropic refinement converged to  $R_1=0.52$  and  $R_2=0.56$ .

A difference Fourier function showed the positions of  $\text{Sr}^{2+}$  ions at Sr(1), (0.0, 0.0, 0.0), with peak height  $5.0 \text{ e}\text{\AA}^{-3}$ ; the  $\text{Ti}^+$  ions at Ti(2),

(0.25, 0.25, 0.25) with peak height  $6.0 \text{ e}\text{\AA}^{-3}$ ; and the  $\text{Ti}^+$  ions at Ti(1), (0.07, 0.07, 0.07) with height  $3.2 \text{ e}\text{\AA}^{-3}$ . Each peak was identified by its distance to the framework oxygen. Isotropic refinement of the framework atoms and anisotropic refinement of Sr(1), Ti(1), and Ti(2) converged to  $R_1=0.15$  and  $R_2=0.19$ .

A subsequent difference Fourier synthesis revealed two peaks: at Ti(3), (0.125, 0.125, 0.41), with peak height  $8.0 \text{ e}\text{\AA}^{-3}$ , and at Ti(4), (0.06, 0.06, 0.4), of height  $4.9 \text{ e}\text{\AA}^{-3}$ . These peaks were stable in least-squares refinement. Isotropic refinement of the framework atoms and anisotropic refinement of Sr(1), Ti(1), Ti(2), Ti(3), and Ti(4) converged to  $R_1=0.056$  and  $R_2=0.041$ . The occupancy numbers at Sr(1), Ti(1), Ti(2), Ti(3), and Ti(4) were refined to 8.5(2), 14.9(1), 30.9(8), 18.3(1) and 10.1(3), respectively, per unit cell. These were fixed at 8.5, 15, 32, 18 and 10, respectively (see Table 2), because site II can hold 32 ions and because the cationic charge should not exceed 92+ per unit cell. All shifts in the final cycle of least-squares refinement were less than 0.01% of their corresponding standard deviations. The final error indices converged to  $R_1=0.058$  and  $R_2=0.044$ . The final difference function was featureless except for a peak at (0.00, 0.00, 0.74) of height  $1.3 \text{ e}\text{\AA}^{-3}$ . This peak was not stable in least-squares refinement..

All crystallographic calculations were done using MolEN.<sup>14)</sup> The full-matrix 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 for Si, Al, O,  $\text{Sr}^{2+}$ ,  $\text{K}^+$  and  $\text{Ti}^+$  were used. All scattering factors<sup>17)</sup> were modified to account for anomalous dispersion.<sup>18)</sup> The final structural parameters and selected interatomic distances and angles are presented in Tables 2 and 3, respectively.

## 5. Discussion

Zeolite X is a synthetic counterpart of the na-

Table 2. Positional, Thermal, and Occupancy Parameters<sup>a</sup>

Atom	Wyc. Pos.	Site	x	y	z	U <sup>b</sup>		U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>	Occupancy <sup>c</sup>	
						U <sub>11</sub> <sup>d</sup>	U <sub>33</sub> <sup>d</sup>					varied	fixed
Si	96(g)		-561(2)	1238(4)	342(2)	127(13)						varied	96
Al	96(g)		-565(3)	350(2)	1236(4)	76(13)						varied	96
O(1)	96(g)		-1108(6)	5(7)	1105(4)	203(38)						varied	96
O(2)	96(g)		-50(5)	-51(5)	1378(4)	101(38)						varied	96
O(3)	96(g)		-395(5)	665(6)	653(6)	127(38)						varied	96
O(4)	96(g)		-609(6)	752(6)	1747(6)	164(38)						varied	96
Sr(1)	16(c)	I	0	0	0	207(17)	207(17)	207(17)	112(22)	112(22)	112(22)	varied	16
Sr(2)	32(e)	II	2255(2)	2262(2)	2262(2)	203(26)	203(26)	203(26)	159(30)	159(30)	159(30)	varied	15
K(2)	32(e)	II	2423(4)	2408(48)	2408(48)	435(48)	435(48)	435(48)	438(61)	438(61)	438(61)	varied	17
K(3)	48(f)	III'	1094(35)	1289(56)	4181(32)	291(210)						varied	5
K(4)	96(g)	III'	621(29)	604(29)	4194(26)	367(202)						varied	8

(b) Sr<sub>0.5</sub>Tl<sub>1.5</sub>X

Atom	Wyc. Pos.	Site	x	y	z	U <sup>b</sup>		U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>	Occupancy <sup>c</sup>	
						U <sub>11</sub> <sup>d</sup>	U <sub>33</sub> <sup>d</sup>					varied	fixed
Si	96(g)		-537(3)	1241(4)	349(3)	63(13)						varied	96
Al	96(g)		-544(3)	367(3)	1232(4)	63(13)						varied	96
O(1)	96(g)		-1080(6)	8(8)	1045(6)	215(38)						varied	96
O(2)	96(g)		-33(9)	-53(8)	1436(5)	139(38)						varied	96
O(3)	96(g)		-325(7)	729(7)	686(7)	114(38)						varied	96
O(4)	96(g)		-704(6)	759(7)	1777(7)	114(38)						varied	96
Sr(1)	16(c)	I	0	0	0	177(25)						varied	8.5
Tl(1)	32(e)	I'	751(1)	751(1)	751(1)	286(13)	286(13)	286(13)	-5(16)	-5(16)	-5(16)	varied	15
Tl(2)	32(e)	II	2515(1)	2515(1)	2515(1)	311(3)	311(3)	311(3)	-7(12)	-7(12)	-7(12)	varied	32
Tl(3)	48(f)	III	1250	1250	4091(3)	2027(100)	2442(113)	203(39)	-1126(66)	0	0	varied	18
Tl(4)	96(g)	III'	731(14)	734(14)	4159(9)	2429(223)	2475(227)	492(125)	1611(148)	-346(191)	-339(191)	varied	10

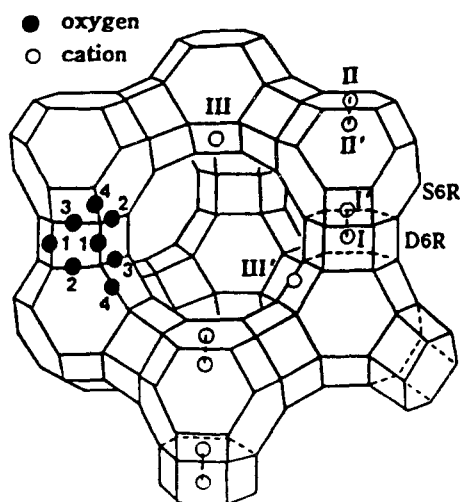
<sup>a</sup>Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>b</sup>The anisotropic temperature factor =  $\exp[-2\pi^2/a^2(h^2U_{11} + k^2U_{22} + l^2U_{33}) + 2hkU_{12} + 2hlU_{13} + 2klU_{23}]$ . <sup>c</sup>Occupancy factors are given as the number of atoms or ions per unit cell. <sup>d</sup> $U_{iso} = (B_{110}/8\pi^2)$ .

**Table 3. Selected Interatomic Distances (Å) and Angles (deg)<sup>o</sup>**

Crystal 1, Sr <sub>31</sub> K <sub>30</sub> -K		Crystal 2, Sr <sub>8.5</sub> Tl <sub>75</sub> -X	
Si-O(1)	1.65(2)		1.61(2)
Si-O(2)	1.65(2)		1.62(2)
Si-O(3)	1.68(2)		1.63(2)
Si-O(4)	1.65(2)		1.62(2)
ave.	1.66		1.62
Al-O(1)	1.65(2)		1.68(2)
Al-O(2)	1.68(2)		1.73(2)
Al-O(3)	1.72(2)		1.73(2)
Al-O(4)	1.65(2)		1.73(2)
ave.	1.68		1.72
Sr(1)-O(3)	2.55(1)	Sr(1)-O(3)	2.64(2)
Sr(2)-O(2)	2.45(1)	Tl(1)-O(3)	2.70(2)
K(2)-O(2)	2.64(1)	Tl(2)-O(2)	2.70(1)
K(3)-O(1)	3.09(9)	Tl(3)-O(1)	3.40(3)
K(3)-O(4)	3.11(10)	Tl(3)-O(4)	2.86(2)
K(4)-O(1)	2.88(7)	Tl(4)-O(4)	2.38(3)
K(4)-O(4)	2.76(7)	Tl(4)-O(1)	2.96(4)
O(1)-Si-O(2)	111.5(8)		110.3(12)
O(1)-Si-O(3)	106.4(8)		110.6(10)
O(1)-Si-O(4)	114.3(8)		108.6(10)
O(2)-Si-O(3)	106.4(8)		107.5(9)
O(2)-Si-O(4)	105.3(8)		107.6(9)
O(3)-Si-O(4)	113.6(8)		112.6(10)
O(1)-Al-O(2)	111.5(8)		110.3(11)
O(1)-Al-O(3)	106.1(8)		108.7(10)
O(1)-Al-O(4)	114.6(8)		109.9(9)
O(2)-Al-O(3)	105.4(7)		108.4(9)
O(2)-Al-O(4)	104.8(8)		106.5(8)
O(3)-Al-O(4)	114.1(8)		113.5(9)
Si-O(1)-Al	127.2(9)		135.9(11)
Si-O(2)-Al	151.7(9)		143.2(10)
Si-O(3)-Al	136.8(9)		136.1(11)
Si-O(4)-Al	164(1)		147.2(11)
O(3)-Sr(1)-O(3)	94.9(4)	O(3)-Sr(1)-O(3)	92.1(5)
O(2)-Sr(2)-O(2)	117.2(5)	O(3)-Tl(1)-O(3)	85.3(5)
O(2)-K(2)-O(2)	102.9(5)	O(2)-Tl(2)-O(2)	93.0(6)
O(1)-K(3)-O(1)	131(2)	O(1)-Tl(3)-O(1)	133.4(4)
O(4)-K(3)-O(4)	67(2)	O(4)-Tl(3)-O(4)	78.2(5)
O(1)-K(4)-O(1)	116(2)	O(1)-Tl(4)-O(1)	119.2(9)
O(1)-K(4)-O(4)	58(1)	O(1)-Tl(4)-O(4)	62.1(8)

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

turally occurring mineral faujasite. The polyhedron with 14 vertices known as the sodalite cavity or  $\beta$  cage may be viewed as the principal building block of the aluminosilicate framework of the zeolite (see Fig. 1). These  $\beta$  cages are



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

connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6R's, hexagonal prisms), and, concomitantly, an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately half-way between each pair of Si and Al atoms, but are displaced from those points to give near tetrahedral angles about Si and Al.

The nomenclature of the cation sites is as follows: site I at the center of a D6R; II at the center of a single six-ring (S6R, shared by a  $\beta$  and a supercage), or displaced from this point into a supercage; I' and II' lie in the sodalite cavity, on opposite sides of the corresponding six-rings from sites I and II, respectively; III on a twofold axis opposite a four-ring inside the supercage; and III' near III but off the twofold axis.

### 5-1. Crystal 1, Sr<sub>31</sub>K<sub>30</sub>-X

In this structure, 31  $\text{Sr}^{2+}$  ions occupy two crystallographic sites and 30  $\text{K}^+$  ions occupy three sites.

The  $\text{Sr}^{2+}$  ions at Sr(1) fill the 16-fold site I, at the centers of the D6R's. The distance between Sr(1) and O(3), 2.55(1) Å (see Table 3), is just a little longer than the sum of the corresponding ionic radii,  $1.12+1.32=2.44$  Å.<sup>19</sup>

The  $\text{Sr}^{2+}$  ions at Sr(2) are at site II in the supercage; each is recessed ca. 0.45 Å into the supercage from the plane of the three oxygens to which it coordinates at 2.45(1) Å. The O(2)-Sr(2)-O(2) bond angle,  $117.2(5)^\circ$ , is near trigonal planar. A plausible atomic arrangement in a particular supercage is shown in Fig. 2.

The 17  $\text{K}^+$  ions at K(2) also lie in the supercage at site II; each is recessed ca. 1.06 Å into the supercage from the plane of the three oxygens to which it coordinates at 2.64(1) Å. Five  $\text{K}^+$  ions at K(3) lie at site III'. The  $\text{K}^+$  ions at K(3) are very loosely held by the framework oxygens: K(3)-O(1)=3.09(9) and K(3)-O(4)=3.11(10) Å. These are substantially longer than the sum of the corresponding ionic radii,  $1.33+1.32=2.65$  Å (see Fig. 2). Such a long interaction distance has been observed previously in other X structures.<sup>8)</sup> The eight  $\text{K}^+$  ions at K(4) lie in the supercage at site III'. Each of these  $\text{K}^+$  coordinates to the framework oxygens, O(1) and O(4), at 2.88(7) and 2.76(7) Å, respectively, a little longer than the sum of the cor-

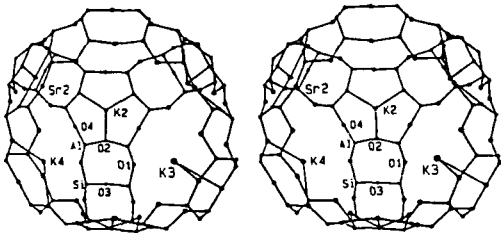


Fig. 2. A stereoview of the supercage of dehydrated  $\text{Sr}_{31}\text{K}_{30}\text{-X}$ . Two  $\text{Sr}^{2+}$  ions at Sr(2) (site II), two  $\text{K}^+$  ions at K(2) (site II), one  $\text{K}^+$  ion at K(3) (site III) and one  $\text{K}^+$  ion at K(4) (site III') are shown. About 62.5% of the supercages may have this arrangement. Ellipsoids of 20% probability are shown.

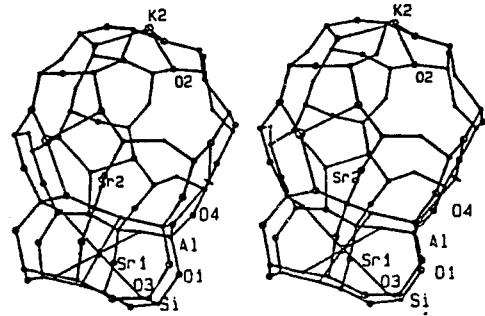


Fig. 3. A stereoview of the sodalite cavity with an attached D6R in dehydrated  $\text{Sr}_{31}\text{K}_{30}\text{-X}$ . Two  $\text{Sr}^{2+}$  ions at Sr(2) (site II), two  $\text{K}^+$  ions at K(2) (site II) and one  $\text{Sr}^{2+}$  at Sr(1) (site I). About 87.5% of the sodalite unit may have this arrangement. Ellipsoids of 20% probability are shown.

responding ionic radii.

## 5-2. Crystal 2, $\text{Sr}_{8.5}\text{Tl}_{7.5}\text{-X}$

In this structure, about 8.5  $\text{Sr}^{2+}$  ions at Sr(1) are at site I. The octahedral Sr(1)-O(3) distances are 2.64(2) Å, longer than the sum of the corresponding ionic radii,  $1.12+1.32=2.44$  Å.<sup>19</sup>

75  $\text{Tl}^+$  ions are found at four different crystallographic sites. 15  $\text{Tl}^+$  ions finish filling the D 6R's by occupying site I'. 32  $\text{Tl}^+$  ions completely fill site II. Eighteen  $\text{Tl}^+$  ions occupy site III and the remaining ten  $\text{Tl}^+$  ions are found at site III'.

The Tl(1) position is at site I' on threefold axes in the sodalite cavity. Each  $\text{Tl}^+$  ion lies re-

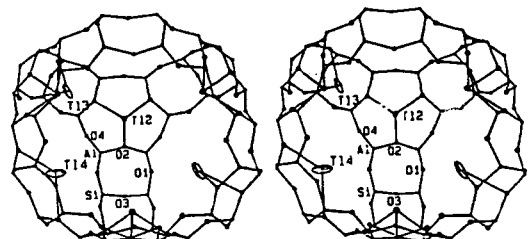


Fig. 4. A stereoview of the supercage of dehydrated  $\text{Sr}_{8.5}\text{Tl}_{7.5}\text{-X}$ . Four  $\text{Tl}^+$  ions at Tl(2) (site II), two  $\text{Tl}^+$  ions at Tl(3) (site III) and one at Tl(4) (site III') are shown. About 75% of the supercage may have this arrangement. The remaining 25% of the supercage have three  $\text{Tl}^+$  ions at Tl(3) and two at Tl(4). Ellipsoids of 20% probability are shown.

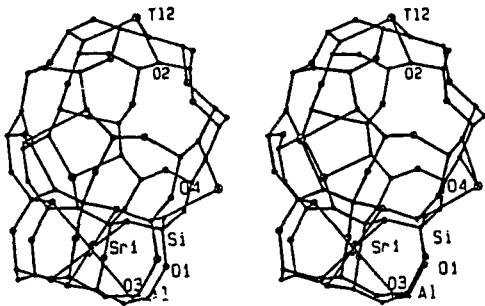


Fig. 5. A stereoview of the sodalite cavity with an attached D6R in dehydrated  $\text{Sr}_{8.5}\text{Ti}_{75}\text{-X}$ . Four  $\text{Ti}^+$  ions at TI(2) (site II) and one  $\text{Sr}^{2+}$  ion at Sr(1) (site I) are shown. Ellipsoids of 20% probability are shown.

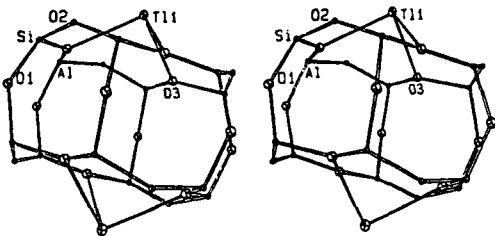


Fig. 6. A stereoview of the less common D6R in dehydrated  $\text{Sr}_{8.5}\text{Ti}_{75}\text{-X}$ . If Sr(1) is not occupied by a  $\text{Sr}^{2+}$  ion, then the two adjacent sites I' at TI(1) are occupied as shown. About 47% of the double six-rings may have this arrangement. Ellipsoids of 20% probability are shown.

latively far inside the sodalite cavity, 1.68 Å from the plane of the three O(3) framework oxygens of the D6R to which it is bound. The TI(1)-O(3) distances are 2.70(2) Å, shorter than the sum of the corresponding ionic radii, 1.47+1.32=2.79 Å. This indicates that each  $\text{Ti}^+$  ion coordinates strongly to its three O(3) oxygens as would be expected by the low coordination number.

The TI(2) position is at site II, far inside the supercage. Each TI(2) ion is 1.48 Å from the plane of the three O(2) framework oxygens of the S6R to which it is bound. The TI(2)-O(2) distances are 2.70(1) Å. Because all site II's are filled, four  $\text{Ti}^+$  ions at TI(2) must be arranged tetrahedrally within each supercage. In dehydrated  $\text{Sr}_{1.6}\text{Ti}_{8.8}\text{-A}$ <sup>20)</sup> and  $\text{Ti}_{12}\text{-A}$ ,<sup>21)</sup> similar TI-O distances (2.66(1) Å and 2.62(1) Å) and  $\text{Ti}^+$  dis-

Table 4. Deviations (Å) of Cations from Six-Ring Planes

	Crystal 1, $\text{Sr}_{31}\text{K}_{30}\text{-X}$	Crystal 2, $\text{Sr}_{8.5}\text{Ti}_{75}\text{-X}$
at O(3) <sup>a</sup>		
Sr(1)	-1.34	-1.58
Ti(1)		1.68
at O(2) <sup>b</sup>		
Sr(2)	0.45	
K(2)	1.06	
Ti(2)		1.48

<sup>a</sup>A positive deviation indicates that the atoms lie in the sodalite unit; negative, in the D6R. <sup>b</sup>A positive deviation indicates that the atoms lie in the supercage.

placements from six-ring planes (1.51 Å and 1.56 Å) were also observed.

The  $\text{Ti}^+$  ions at TI(3) lie in the supercage at site III. Eighteen  $\text{Ti}^+$  ions occupy the 48-fold TI(3) position (TI(3)-O(4)=2.86(2) Å). The 10  $\text{Ti}^+$  ions at TI(4) lie in the supercage at site III'.

The mean values of Si-O and Al-O bond lengths are 1.62(2) and 1.72(2) Å, respectively. The individual bond lengths show marked variations: Si-O from 1.61(2) to 1.63(2) Å and Al-O from 1.68(2) to 1.73(3) Å.

Recently the structures of  $\text{Cd}_{46}\text{-X}$ ,<sup>22)</sup>  $\text{Ca}_{46}\text{-X}$ ,<sup>23)</sup>  $\text{Ba}_{46}\text{-X}$ ,<sup>23)</sup>  $\text{Mg}_{46}\text{-X}$ ,<sup>23)</sup>  $\text{K}_{92}\text{-X}$ ,<sup>23)</sup>  $\text{Cd}_{24.5}\text{Ti}_{43}\text{-X}$ ,<sup>22)</sup> and  $\text{Ca}_{32}\text{K}_{28}\text{-X}$ <sup>16)</sup> were determined (see Table 1). From these it appears that site I is the lowest energy site for most cations, except for the largest and the smallest.  $\text{Ca}^{2+}$  ions in  $\text{Ca}_{46}\text{-X}$  and  $\text{Cd}^{2+}$  ions in  $\text{Cd}_{46}\text{-X}$  fill site I, with the remainder going to site II in the supercage, nearly filling it. About 13  $\text{Ba}^{2+}$  ions in  $\text{Ba}_{46}\text{-X}$  and 14  $\text{Mg}^{2+}$  ions  $\text{Mg-X}$  occupy D6R centers. Considerations of ionic size and charge govern the competition for sites in  $\text{Cd}_{24.5}\text{Ti}_{43}\text{-X}$ <sup>22)</sup> and  $\text{Ca}_{32}\text{K}_{28}\text{-X}$ .<sup>16)</sup> The smaller and more highly charged  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$  ions select their sites "first" because they can approach the anionic oxygens of the zeolite framework more closely. They nearly fill site I, with the remainder going to site II as in  $\text{Cd}_{46}\text{-X}$  and  $\text{Ca}_{46}\text{-X}$ . The  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$  ions have selected their sites and the  $\text{Ti}^+$  and  $\text{K}^+$  ions finish filling site II, with the remainder occupying the least



suitable cation site in the structure, site III.

In summary, the smaller and more highly charged  $\text{Sr}^{2+}$  ions preferentially occupy sites I (D6R), and thereafter the site II (near S6R centers). Because the ionic radii of  $\text{K}^+$  or  $\text{Tl}^+$  ions are larger than that of  $\text{Sr}^{2+}$ , and their charge smaller, these ions occupy the remaining sites II, III, or III' in the supercage.

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