The Crystal Structure of Fully Dehydrated Fully Ba^{2+}-Exchanged Zeolite X

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Received November 29, 1994

The crystal structure of Ba$_{46}$-X, Ba$_{46}$Al$_{92}$Si$_{100}$O$_{384}$ [$a = 25.297(1)$ Å], has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\overline{3}$ at 21(1) °C. The crystal was prepared by ion exchange in flowing stream of 0.05 M Ba(OH)$_2$ aqueous solution for 5 days. The crystal was then dehydrated at 380 °C and 2×10^{-6} Torr for 2 days. The structure was refined to the final error indices $R_1 = 0.051$ and $R_u = 0.054$ with 369 reflections for which $I > 3\sigma(I)$. In this structure, all Ba^{2+} ions are located at the three different crystallographic sites: fourteen Ba^{2+} ions are located at site I, the centers of the double six rings, two Ba^{2+} ions lie at site I', in the sodalite cavity opposite double six rings (D6R's) and another thirty Ba^{2+} ions are located at site II in the supercage. Two Ba^{2+} ions are recessed *ca.* 0.27 Å into the sodalite cavity from their three O(3) oxygen plane and thirty Ba^{2+} ions are recessed *ca.* 1.11 Å into the supercage from their three O(2) oxygen planes, respectively (Ba(1)-O(3) = 2.76(1) Å, O(3)-Ba(1)-O(3) = 180(0)°, Ba(2)-O(3) = 2.45(1) Å, O(3)-Ba(2)-O(3) = 108(1)°, Ba(3)-O(2) = 2.65(1) Å, and O(2)-Ba(3)-O(2) = 103.9 (4)°).

Introduction

Most zeolites contain exchangeable cations in their channels and cavities, as needed to balance the anionic charge of their frameworks. Thermal stability, sorptive and catalytic properties are determined by the types and numbers of exchanged cations and their distributions over available sites. Therefore, it is very important to know the positions and populations of cations in zeolite cavities.

Sherry *et al.*[1] showed that Ba^{2+}-exchange into zeolite A could be carried to near completion at room temperature, but zeolite structure was lost when evacuation at higher temperature was attempted. Similar instability was not noted with Ca^{2+} and Sr^{2+}, and indeed the crystal structures of fully dehydrated Ca$_6$-A and Sr$_6$-A were determined.[2] Kim *et al.* determined the crystal structures of hydrated and partially dehydrated fully Ba^{2+}-exchanged zeolite A and partially Ba^{2+}-exchanged dehydrated Na$_5$Ba$_{3.5}$-A and Na$_{10}$Ba$_1$-A.[3] They found that the relatively large Ba^{2+} ions cannot approach oxide ions as closely as smaller cations can. As a result, Ba^{2+} ions do not fit into conventional sites near 6-ring centers, and 8-ring sites are occupied more than in those corresponding structures involving smaller cations such as Ca^{2+} and Sr^{2+} ions. Low coordinate Ba^{2+} ions at the 8-ring sites, which appear to form the three coordination upon dehydration, may seek to increase its coordinate number by disrupting the zeolite framework.

Barrer *et al.* reported that the barium ion ($r = 1.34$ Å)[4] was not exchanged completely at room temperature and did not occupy site I in zeolite X.[5] Complete exchange was obtained with calcium and strontium but exchange with barium was limited to 80 percentage at 25 °C.[5,6] For divalent ions, the enthalpy of exchange is either small negative or small positive. The selectivity shown for the calcium and strontium ions is primarily due to the positive entropy. The dependence of the selectivity coefficients on the zeolite composition indicates that some calcium and barium ions are located in the supercages of zeolite X.[5,6]

In Ba-faujasite,[7] Ba^{2+} ions occupy sites I, I', and II and in Ba$_{18}$Na$_{16}$-Y, Ba^{2+} is found to be the most highly populated at site II.[8] Ca^{2+} ions principally occupy site I and II in zeolite X[9] and I in zeolite Y.[10] Sr^{2+}-exchanged zeolites, on the other hand, display a different distribution. In zeolite Y, site I' is the most populated, while in zeolite X, Sr^{2+} is observed in site II and II'.[11]

Up to the present, there is no structural study of the fully dehydrated Ba^{2+}-exchanged zeolite X. This work was performed to learn whether fully dehydrated, fully Ba^{2+}-exchanged zeolite X could be prepared and, if so, its structure could be determined.

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry Na$_{92}$Al$_{92}$Si$_{100}$O$_{384}$, were prepared in St. Petersburg, Russia.[12] One of these, a colorless octahedron about 0.23 mm in cross-section was lodged in a fine Pyrex capillary.

To prepare fully Ba^{2+}-exchanged zeolite X, an exchange solution of Ba(OH)$_2$ with total concentration of 0.05 M was used. 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 days at 24(1) °C. The clear, colorless, hydrated Ba^{2+}-exchanged zeolite X was dehydrated at 380 °C and 2×10^{-6} Torr for 2 days.

After cooling to room temperature, the crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal has become yellow.

The cubic space group $Fd\overline{3}$ 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 Kα radiation (Kα_1, $\lambda = 0.70930$ Å; Kα_2, $\lambda = 0.71359$ Å). The unit cell constant at 21(1) °C determined by least-squares refinement of 25 intense reflections for which $14° < 2\theta < 24°$ is $a = 25.297(1)$ Å for dehydrated Ba$_{46}$-X.

Table 1. [a]Positional, Thermal, and Occupancy Parameters for Dehydrated Ba46-X

Atom	Wyc. Pos.	x	y	z	[b]β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
Si	96(g)	−560(2)	338(2)	1253(3)	3(1)	7(1)	1(1)	0(2)	1(2)	1(2)		96
Al	96(g)	−576(2)	1247(3)	364(2)	2(1)	0(1)	0(1)	3(2)	3(2)	−2(2)		96
O(1)	96(g)	−1070(5)	−11(6)	1114(5)	6(3)	0(2)	3(3)	−5(4)	−3(4)	−3(4)		96
O(2)	96(g)	−44(5)	−45(6)	1376(4)	3(2)	4(2)	1(2)	−0(4)	−2(4)	−1(4)		96
O(3)	96(g)	−387(5)	687(6)	735(6)	4(2)	2(2)	3(3)	0(4)	2(5)	−4(4)		96
O(4)	96(g)	−624(5)	665(6)	1793(5)	3(2)	7(3)	−0(2)	−2(5)	1(4)	−4(4)		96
Ba(1)	16(c)	0	0	0	7(0)	7(0)	7(0)	4(1)	4(1)	4(1)	13.6(1)	14
Ba(2)	32(e)	550(20)	550(20)	550(20)	30(6)	30(6)	30(6)	30(20)	30(20)	30(20)	1.6(2)	2
Ba(3)	32(e)	2408(1)	2408(1)	2408(1)	6(0)	6(0)	6(0)	6(1)	6(1)	6(1)	28.9(2)	30

[a]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. [b]The anisotropic temperature factor $= \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [c]Occupancy factors are given as the number of atoms or ions per unit cell.

The ω-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 and 0.34 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 $2\theta < 60°$ were recorded. Of the 1236 reflections examined, only the 369 whose net counts exceeded three times their corresponding estimated standard deviations were used in structure solution and refinement.

The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant esd's were assigned to each reflection by the computer programs, GENESIS, BEGIN, and WEIGHT.[13]

An absorption correction ($\mu R = 3.222$, $\rho_{cal} = 1.822$ g/cm^3 and $F(000) = 8198$)[14] was made empirically using a ψ scan. The calculated transmission coefficients ranged from 0.975 to 0.995. This correction had little effect on the final R indices.

Structure Determination

Full-matrix least-squares refinement was initiated with atomic thermal parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in dehydrated Ca46-X.[15] Anisotropic refinement of the framework atoms converged to an R_1 index, $(\Sigma|F_o - |F_c||)/\Sigma F_o)$ of 0.57 and a weighted R_2 index, $(\Sigma w (F_o - |F_c|)^2/\Sigma w F_o^2)^{1/2}$ of 0.64.

A difference Fourier function showed the positions of Ba^{2+} ions at Ba(1), (0.0, 0.0, 0.0) with peak height 8.94 e$\mathring{A}^{-3}$ and Ba^{2+} ions at Ba(3), (0.242, 0.242, 0.242) with peak height 8.66 e$\mathring{A}^{-3}$. These were stable in least-squares refinement. Anisotropic refinement of framework atoms and isotropic refinement of Ba(1) and Ba(3) converged to $R_1 = 0.070$ and $R_2 = 0.070$ with occupancies of 13.6(1) and 28.9(2), respectively (see Table 1).

From a successive difference Fourier, one peak was found at (0.055, 0.055, 0.055), height $= 1.14$ e$\mathring{A}^{-3}$, which refined as Ba(2). Simultaneous positional occupancy, and isotropic thermal parameter refinement converged to the error indices

$R_1 = 0.048$ and $R_2 = 0.052$ with occupancy of 1.6(2). The occupancy numbers of Ba(1), Ba(2), and Ba(3) were reset and fixed as in the last column of Table 1. The final error indices converged to $R_1 = 0.051$ and $R_2 = 0.054$.

All shifts in the final cycles of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final difference function was featureless except for a peak at (0.299, 0.950, 0.799) of height 0.76 e$\mathring{A}^{-3}$. This peak was not within bonding distance of any other atom, and was not considered further.

All crystallographic calculations were done using the MolEN[13] (a structure determination package programs supplied by Enraf-Nonius). The full-matrix least-squares program used minimized $\Sigma w (F_o - |F_c|)^2$; the weight (w) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors[16,17] for Si, Al, O$^-$, and Ba^{2+} were used. All scattering factors were modified to account for anomalous dispersion.[18] The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

Discussion

Zeoite X has an aluminosilicate framework that may be viewed as an assemblage of sodalite cavities, cubo-octahedral of composition $(Si_{12}Al_{12}O_{48})^{12-}$, which are arranged in space like the carbon atoms in diamond. They are joined at alternating 6-oxygen rings by six bridging oxygen atoms, one bound to each vertex to complete a tetrahedron. This leads to the existence of small double 6-ring and large supercage. The extra-framework cations that compensate for the negative charge of the framework occupy the various positions, called the sites I, I′, II, II′, III, and III′ (see Figure 1). The site I is in the center of hexagonal prism. The site II is at the six-membered ring face of the sodalite cavity in supercage side. The site I′ and II′ lie on the opposite sides of the six-membered ring in sodalite cavities as compared with the sites I and II. The site III lies at the twofold axis of the edge of the four-membered ring ladders inside the supercage.[19,20]

In this structure, the mean values of the Si-O and Al-O

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Dehydrated Ba_{46}-X

Si-O(1)	1.60(2)
Si-O(2)	1.66(1)
Si-O(3)	1.60(2)
Si-O(4)	1.61(2)
Al-O(1)	1.69(2)
Al-O(2)	1.72(1)
Al-O(3)	1.79(2)
Al-O(4)	1.73(2)
Ba(1)-O(3)	2.76(1)
Ba(2)-O(3)	2.45(1)
Ba(3)-O(2)	2.65(1)
O(1)-Si-O(2)	110.7(8)
O(1)-Si-O(3)	110.5(8)
O(1)-Si-O(4)	112.9(8)
O(2)-Si-O(3)	104.9(7)
O(2)-Si-O(4)	102.7(7)
O(3)-Si-O(4)	114.5(8)
O(1)-Al-O(2)	111.2(8)
O(1)-Al-O(3)	107.2(7)
O(1)-Al-O(4)	116.1(7)
O(2)-Al-O(3)	105.8(7)
O(2)-Al-O(4)	101.1(7)
O(3)-Al-O(4)	115.0(7)
Si-O(1)-Al	133.0(9)
Si-O(2)-Al	153.1(8)
Si-O(3)-Al	142.9(9)
Si-O(4)-Al	150(1)
O(3)-Ba(1)-O(3)	180(0)
O(3)-Ba(2)-O(3)	108(1)
O(2)-Ba(3)-O(2)	103.9(4)

Numbers in parentheses are estimated standard deviations in the least significant digit given for the corresponding value.
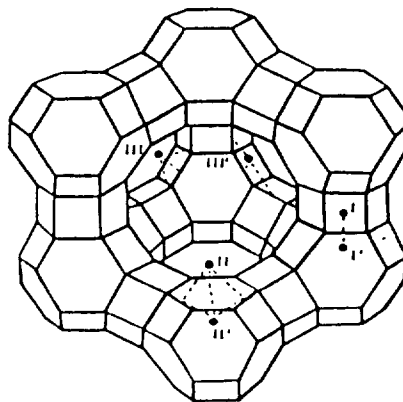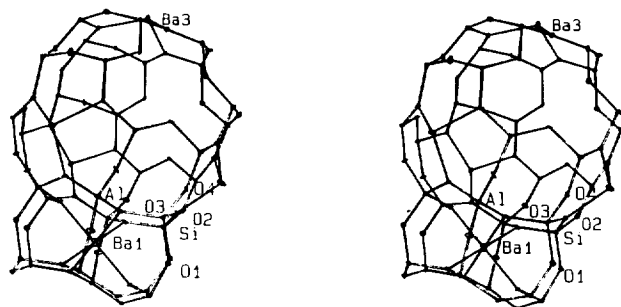
Table 3. Deviations of atoms (Å) from the plane of 6-ring oxygens at O(2)

O(3)	0.34(1)
Ba(3)	1.11(1)

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

Figure 1. Framework structure of zeolite X. Extraframework cation positions are labeled with Roman numerals.

Figure 2. A stereoview of sodalite cavity of dehydrated Ba_{46}-X. One Ba^{2+} ion at Ba(1) lies at site I and four Ba^{2+} ions at Ba(3) lie at site II. All double six-rings have this arrangement. About 75% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.

bond lengths are 1.62(2) Å and 1.73(2) Å, respectively. The individual bond lengths show marked variations: Si-O from 1.60(2) Å to 1.66(1) Å and Al-O from 1.69(2) Å to 1.79(2) Å. The Si-O-Al bond angles range from 133° to 153°. In this structure, the Si-O distances are all shorter than the Al-O distances. The framework geometries of the zeolites presented here are not sensitive to ion exchange and dehydration as in other zeolite X structures.[9,21,22] Therefore, our discussion will be focussed mainly on the distribution of cations in the zeolite framework.

All Ba^{2+} ions in this structure are found at three different crystallographic sites. Fourteen Ba^{2+} ions at Ba(1) lie at site I in the center of a double six-oxygen ring (D6R). This is

sixteenfold position, but this is occupied by only 14 ions. The Ba(1)-O(3) distance, 2.76(1) Å, is longer than the sum of the ionic radii of Ba^{2+} and O^{2-}, $1.34+1.32=2.65$ Å.[4] Therefore, Ba^{2+} ions are loosely held by six framework oxygens at O(3). This site is apparently not quite suited to large alkaline earth metal cation like Ba^{2+} ($r=1.34$ Å)[4] because other smaller divalent cations such as Ca^{2+} ($r=0.99$ Å),[15] Mn^{2+} ($r=0.80$ Å),[23] Co^{2+} ($r=0.74$ Å)[23] and Zn^{2+} ($r=0.74$ Å)[24] ions are fully occupied at this sixteenfold position.

The Ba(2) position is on a threefold axis in the sodalite unit (see Figure 2) opposite a double six-ring (D6R's), at site I'. This is thirty-two-fold position, but it is occupied by only 2 Ba^{2+} ions. Each Ba^{2+} ion coordinates at 2.45(1) Å to three O(3) framework oxygens, and is recessed ca. 0.27 Å into the sodalite cavity from their plane. The positions of Ba^{2+} ions at Ba(2) are close to site I (distance between site I and Ba^{2+} at Ba(2) is 2.41 Å). Therefore, if site I is occupied by a Ba^{2+} ion at Ba(1), the two adjacent site I', the position of Ba^{2+} ion at Ba(2), are unoccupied because of electrostatic repulsive force of cations. Each of two Ba^{2+} ions at Ba(2) occupies the site I' which does not have any adjacent Ba^{2+} ions at site I (see Figure 3).

Thirty Ba^{2+} ions at Ba(3) lie at site II and are recessed 1.11 Å into the supercage from the single 6-ring plane at O(2) (see Figure 4). Each of these Ba^{2+} ions coordinates

The Crystal Structure of Ba₄₆-X

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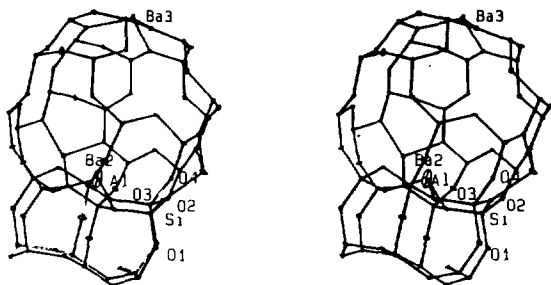
Figure 3. A stereoview of sodalite cavity of dehydrated Ba₄₆-X. One Ba²⁺ ion at Ba(2) lies at site I and three Ba²⁺ ions at Ba(3) lie at site II. About 25% of the sodalite cavities may have this arrangement. Ellipsoids of 20% probability are shown.
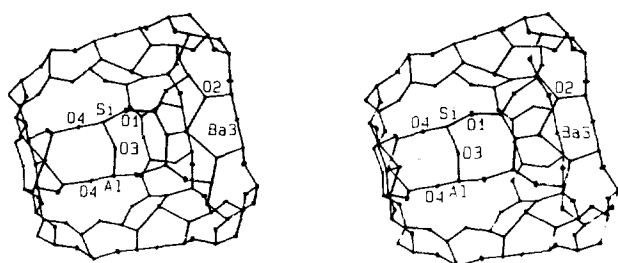
Figure 4. A stereoview of supercage of dehydrated Ba₄₆-X. Four Ba²⁺ ions at Ba(3) are shown. About 75% of the supercages have this arrangement. Ellipsoids of 20% probability are shown.

to three O(2) oxygens at 2.65(1) Å, which is the same distance as the sum of the ionic radii, of Ba²⁺ and O²⁻. The angle subtended at Ba(3), O(2)-Ba(3)-O(2) is 103.9(4)°.

Ba²⁺ ion is the largest dipositive ion except for Ra²⁺ ion.[4] However, the ionic radius of Ba²⁺ ($r=1.34$ Å)[4] are small compared to, for example, Rb⁺ ($r=1.47$ Å)[4] and Cs⁺ ($r=1.67$ Å).[4] As a result, smaller Ba²⁺ ions are found to occupy the sodalite cages and hexagonal prism sites to a much larger extent than Rb⁺ and Cs⁺.[21,25] In Ba faujasite, all Ba²⁺ ions are located in three sites I, I' and II.[7,26] In the present work, all the Ba²⁺ ions are also located at the site I, I', and II.

Anderson *et al.*[9] studied the structures of Mg²⁺-exchanged Na-X and Ca-X.[9] They found that Mg²⁺ ions are located in three sites, I' II, and III in hydrated MgNa-X, and in two sites I and II' in hydrated CaMg-X. In the dehydrated forms, the sites of Mg²⁺ ions are I, I', and II in dehydrated MgNa-X, and II and II' in dehydrated CaMg-X. They also found that Ca²⁺ ions in dehydrated CaNa-X are located in sites I, I' and II.[9]

In summary, fully Ba²⁺-exchanged zeolite X was successfully synthesized and its structure was determined by X-ray diffraction methods. In this structure all Ba²⁺ ions are located in the sites I, I', and II. The Ba²⁺ ions are not found inside the supercage (sites III and III'). Therefore the occupation of sites III and III' by divalent cations is rare. In

addition, this work showed that Ba²⁺-exchanged zeolite X is stable and can be fully dehydrated at high temperature (*ca.* 380 °C).

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