

Three Crystal Structures of Dehydrated Cd^{2+} and Rb^+ Exchanged Zeolite A, $\text{Cd}_x\text{Rb}_{12-2x}\text{-A}$, $x = 4.0, 5.0$ and 5.95

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Three crystal structures of dehydrated Cd(II) and Rb(I) exchanged zeolite A, $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$ ($a = 12.204(3)$ Å), $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ ($a = 12.202(1)$ Å), and $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$ ($a = 12.250(2)$ Å), have been determined by single-crystal X-ray diffraction techniques. Their structures were solved and refined in the cubic space group $Pm\bar{3}m$ at 21(1) °C. All crystals were ion exchanged in flowing streams of mixed $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and RbNO_3 aqueous solution with total concentration of 0.05 M. All crystals were dehydrated at ca. 450 °C and 2×10^{-6} Torr for 2 days. In all of these structures, Cd^{2+} ions are found on threefold axes, each nearly at the center of a 6-oxygen ring. The first three Rb^+ ions per unit cell preferentially associate with 8-oxygen rings, and additional Rb^+ ions, if present, are found on threefold axes in the large cavity. The final R_1 and R_2 values for the three structures are 0.087 and 0.079, 0.059 and 0.067, and 0.079 and 0.095, respectively.

Introduction

The exchangeable cations in zeolite A associate themselves in various ways, depending primarily on their size, with 8-rings, 6-rings or 4-rings.^{1,2} The 4-ring site has the weakest affinity for all cations. The pore size and sorption properties of zeolite A molecular sieve all usually controlled by the number and the ionic radii of the 8-ring cations. In the commercial molecular sieves 3A and 4A, the 8-ring windows are blocked or hindered by potassium and sodium ions, respectively.¹ The crystal structure of fully Cd(II) exchanged Zeolite A has been determined crystallographically by McCusker and Seff.³⁻⁶ All six Cd^{2+} ions per unit cell are associated with 6-oxygen rings of the aluminosilicate framework. The structures of dehydrated partially rubidium exchanged crystals of zeolite A were also determined previously.^{7,8} Three equivalent Rb^+ ions lie at the centers of the 8-rings, while five equivalent Rb^+ ions lie on threefold axes opposite 6-rings in the large cavity. The three remaining Rb^+ ions were found to be nonequivalent and to lie on a unique threefold axis.

This work was undertaken with the hope of establishing some points on the ion exchange isotherm of Cd^{2+} and Rb^+ and to determine the cation positions in the crystal structures of variously Cd^{2+} and Rb^+ exchanged zeolite A. It would be interesting to learn how different numbers of exchanged Cd^{2+} ions (divalent cation) and Rb^+ ions (monovalent cation) arrange themselves in the zeolite framework. In addition, the relative preference of the cations for the coordination sites available within the zeolite would be seen. Because Cd^{2+} ions and Rb^+ ions are relatively strong X-ray scatterers and because their ionic radii are quite different, reliable and precise structures of Cd(II) and Rb(I) exchanged zeolite A can be determined by X-ray crystallography.

Experimental

Crystals of zeolite 4A were prepared by Charnell's method.⁹ A single crystal about 0.08 mm on an edge was lodged

in a fine glass capillary. To prepare Cd^{2+} and Rb^+ ion exchanged solutions of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, 99.999%) and RbNO_3 (Aldrich, 99.999%) with a total concentration of 0.05 M were used. The crystals of approximate composition $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$, $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$ ¹⁰ were prepared by flow methods using exchange solutions in which mole ratios of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and RbNO_3 were 1:100, 1:10 and 1000:1, respectively.

For all crystals, the solution was allowed to flow past the crystal at a velocity of approximately 1.0 cm/sec for 4 days. The crystals were then washed by continuing this procedure using distilled water at 80 °C for 2 hours. Each crystal of $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$, $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$ ¹⁰ was dehydrated at ca. 450 °C and 2×10^{-6} Torr for 2 days.

The cubic space group $Pm\bar{3}m$ (no systematic absences) was used for reasons discussed previously.¹¹⁻¹³ Preliminary crystallographic experiments and subsequent data collections were performed with an automated, four circle Enraf-Nonius CAD-4 diffractometer, equipped with a graphite monochromator. Mo K_α radiation was used for all experiments. ($K_{\alpha 1}$, $\lambda = 0.70930$ Å; $K_{\alpha 2}$, $\lambda = 0.71359$ Å).

The cubic unit cell constants, as determined by a least-squares refinement of 25 intense reflections for which $18^\circ < 2\theta < 24^\circ$, are 12.204(3) Å for $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$, 12.202(1) Å for $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and 12.250(2) Å for $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$, respectively. Reflections from two intensity-equivalent regions of reciprocal space (hkl , $h \leq k \leq l$ and lkh , $l \leq h \leq k$) were examined using the ω - 2θ scan technique.

The data were collected using variable scan speeds. The most reflections were collected at the slow speed, ranging between 0.119° and 0.384° in ω/min . 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 fluctuation of these check reflections were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70^\circ$ were collected. The raw data for each region were corrected for Lorentz and polarization effects, including that due to incident beam monochro-

Table 1. Positional, Thermal^a, and Occupancy Parameters(a) Crystal 1, $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$

Atom	Wyc. Posi.	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^b	
											varied	fixed
(Si,Al)	24(<i>k</i>)	0	1837(5)	3724(5)	39(4)	23(4)	18(4)	0	0	17(9)		24.0
O(1)	12(<i>h</i>)	0	2190(20)	5000	90(20)	70(20)	50(20)	0	0	0		12.0
O(2)	12(<i>i</i>)	0	2950(10)	2950(10)	60(20)	30(10)	30(10)	0	0	40(30)		12.0
O(3)	24(<i>m</i>)	1133(8)	1133(8)	3380(10)	51(7)	51(7)	70(10)	50(20)	-40(20)	-40(20)		24.0
Cd(1)	8(<i>g</i>)	1889(5)	1889(5)	1889(5)	122(3)	122(3)	122(3)	188(7)	188(7)	188(7)	4.25(4)	4.0
Rb(1)	3(<i>i</i>)	0	5000	5000	210(20)	200(10)	200(10)	0	0	0	2.95(5)	3.0
Rb(2)	8(<i>g</i>)	2560(20)	2560(20)	2560(20)	40(10)	40(10)	40(10)	20(30)	20(30)	20(30)	0.92(4)	1.0

(b) Crystal 2, $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$

Atom	Wyc. Posi.	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^b	
											varied	fixed
(Si,Al)	24(<i>k</i>)	0	1838(5)	3702(4)	28(3)	34(3)	20(3)	0	0	7(7)		24.0
O(1)	12(<i>h</i>)	0	2150(20)	5000	60(20)	80(20)	70(20)	0	0	0		12.0
O(2)	12(<i>i</i>)	0	2955(9)	2955(9)	30(10)	43(8)	43(8)	0	0	50(20)		12.0
O(3)	24(<i>m</i>)	1112(7)	1112(7)	3320(10)	58(6)	58(6)	70(10)	60(20)	-30(10)	-30(10)		24.0
Cd(1)	8(<i>g</i>)	1888(4)	1888(4)	1888(4)	105(2)	105(2)	105(2)	161(5)	161(5)	161(5)	3.94(4)	4.0
Cd(2)	8(<i>g</i>)	1473(9)	1473(9)	1473(9)	33(6)	33(6)	33(6)	-0(1)	-0(1)	-0(1)	1.08(3)	1.0
Rb(1)	3(<i>i</i>)	0	5000	5000	130(20)	190(10)	190(10)	0	0	0	2.10(4)	2.0

(c) Crystal 3, $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$

Atom	Wyc. Posi.	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^b	
											varied	fixed
(Si,Al)	24(<i>k</i>)	0	1825(3)	3684(2)	23(2)	23(2)	20(2)	0	0	5(3)		24.0
O(1)	12(<i>h</i>)	0	2020(10)	5000	60(10)	70(10)	27(8)	0	0	0		12.0
O(2)	12(<i>i</i>)	0	2944(7)	2944(7)	44(8)	45(5)	45(5)	0	0	60(10)		12.0
O(3)	24(<i>m</i>)	1109(5)	1109(5)	3250(6)	44(4)	44(4)	41(6)	20(10)	4(8)	4(8)		24.0
Cd(1)	8(<i>g</i>)	1915(3)	1915(3)	1915(3)	59(1)	59(1)	59(1)	62(3)	62(3)	62(3)	3.12(3)	2.97
Cd(2)	8(<i>g</i>)	1554(2)	1554(2)	1554(2)	32(1)	32(1)	32(1)	19(3)	19(3)	19(3)	3.28(3)	2.98
Rb(1)	3(<i>i</i>)	0	5000	5000	100(100)	100(80)	100(80)	0	0	0	0.12(3)	0.10

^aPositional and Isotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^bOccupancy factors are given as the number of atoms or ions per unit cell. ^cOccupancy for (Si) = 12; occupancy for (Al) = 12.

matization; the reduced intensities were merged by the computer program, PAINT.¹⁴ An absorption correction was judged to be unimportant because the crystals used were very small cubes, and was not applied ($\mu = 4.59 \text{ mm}^{-1}$ for $\text{Cd}_4\text{Rb}_4\text{-A}$, $\mu = 3.27 \text{ mm}^{-1}$ for $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and $\mu = 2.17 \text{ mm}^{-1}$ for $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$). Only the observed reflections, those whose net counts exceeded three times their corresponding esd's, were used in structure solution and refinement. Only the 862 pairs of reflections for $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$, 859 for $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and 874 for $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$, reciprocal, 162, 174 and 414 pairs for which $I > 3\sigma(I)$, respectively, were used in subsequent structural determinations.

Structure Determination

All structure calculation were done using the Structure Determination Package (SDP)¹⁴ programs supplied by Enraf-Nonius.

Crystal 1($\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$). Full matrix least-square refinement was initiated using the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] and of the Cd^{2+} ions at Cd(1) in $\text{Cd}_6\text{-A}$.⁶ Anisotropic refinement of the framework atoms and Cd(1) converged to and R_1 Anisotropic refinement of the framework atoms and Cd(1) converged to an unweighted R_1 index, $(\sum |F_o - F_c| / \sum F_o)$ of 0.266 and a weighted R_2 index, $(\sum w(F_o - F_c)^2 / \sum wF_o^2)^{1/2}$, of 0.346. A different Fourier synthesis revealed large and distinct peaks at (0.0, 0.5, 0.5) with a height of $7.9(28)\text{e}\text{\AA}^{-3}$ and (0.25, 0.25, 0.25) with a height of $2.6(17)\text{e}\text{\AA}^{-3}$. Anisotropic refinement including these Rb(1) and Rb(2) positions, respectively, converged to $R_1 = 0.087$ and $R_2 = 0.079$ (see Table 1).

It is easy to distinguish Cd^{2+} from Rb^+ ions for several reasons. First, their atomic scattering factors are quite different, $46e^-$ for Cd^{2+} vs $36e^-$ for Rb^+ . Secondly, their ionic radii are different, $\text{Cd}^{2+} = 0.97 \text{ \AA}$ and $\text{Rb}^+ = 1.48 \text{ \AA}$.¹⁵ Also, the approach distances between those ions and zeolite oxy-

Table 2. Selected Interatomic Distance(Å) and Angles(deg)

	Crystal 1	Crystal 2	Crystal 3
(Si,Al)-O(1)	1.616(9)	1.629(6)	1.630(4)
(Si,Al)-O(2)	1.65(1)	1.639(8)	1.643(9)
(Si,Al)-O(3)	1.682(9)	1.637(8)	1.702(6)
Cd(1)-O(3)	2.24(1)	2.20(2)	2.15(1)
Cd(2)-O(3)		2.34(1)	2.22(1)
Rb(1)-O(1)	3.43(2)	3.48(2)	3.65(1)
Rb(1)-O(2)	3.55(1)	3.53(1)	3.56(1)
Rb(2)-O(3)	2.66(2)		
O(1)-(Si,Al)-O(2)	109.8(9)	110.2(8)	115.1(5)
O(1)-(Si,Al)-O(3)	112.1(7)	113.1(5)	112.6(4)
O(2)-(Si,Al)-O(3)	106.0(4)	106.4(3)	104.9(2)
O(3)-(Si,Al)-O(3)	110.7(5)	107.2(4)	105.9(3)
O(3)-Cd(1)-O(3)	120.0(3)	119.9(2)	119.2(2)
O(3)-Cd(2)-O(3)		109.2(3)	113.6(2)
O(1)-Rb(1)-O(1)	180.1(4)	180.1(2)	90.1(2)
O(2)-Rb(1)-O(2)	90.1(2)	90.1(2)	90.1(2)
O(3)-Rb(2)-O(3)	93.4(3)		

Table 3. Deviation of atoms(Å) from the (111) plane at O(3)

	Crystal 1	Crystal 2	Crystal 3
O(2)	0.17	-0.26	-0.30
Cd(1)	0.01	-0.09	-0.20
Cd(2)		0.79	0.57
Rb(2)	1.44		

A positive deviation indicates that the atom lies on the same side of the plane as the origin.

gens in dehydrated $\text{Cd}_6\text{-A}^6$ and $\text{Rb}_{11}\text{Na}_1\text{-A}^7$ have been determined and are indicative.

The largest peak on the final difference Fourier function whose estimated standard deviation is $0.62 \text{ e}\text{\AA}^{-3}$, was $1.64 \text{ e}\text{\AA}^{-3}$ in height and was located just at Cd(1). Final positional, thermal, and occupancy parameters are presented in Table 1(a), bond lengths and bond angles are given in Table 2. All shifts in the final cycles of least-squares refinement were less than 0.5% of their corresponding esd's.

Crystal 2($\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$). Least-squares refinement began using the framework position and the Cd(1) position found in the structure of crystal 1. Refinement with anisotropic thermal parameters converged to $R_1 = 0.184$ and $R_2 = 0.265$. A difference Fourier synthesis revealed a large and distinct peak at (0.0, 0.5, 0.5) with a height of $5.7(20) \text{ e}\text{\AA}^{-3}$. Anisotropic refinement including this position, Rb(1), converged to $R_1 = 0.091$ and $R_2 = 0.107$. A subsequent difference synthesis revealed a peak at (0.147, 0.147, 0.147) with heights of $1.0(6) \text{ e}\text{\AA}^{-3}$. This was stable in least-squares refinement and anisotropic refinement including this position as Cd(2) converged to $R_1 = 0.059$ and $R_2 = 0.067$. The largest peak on the final difference Fourier function whose estimated standard deviation is $1.2 \text{ e}\text{\AA}^{-3}$, was $2.8 \text{ e}\text{\AA}^{-3}$ in height and was located at (0.0, 0.0, 0.0). The final structural parameters are presented in Table 1(b).

Crystal 3($\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$). Using the atomic parameters of the framework atoms, Cd(2) in the structure of crystal 2,

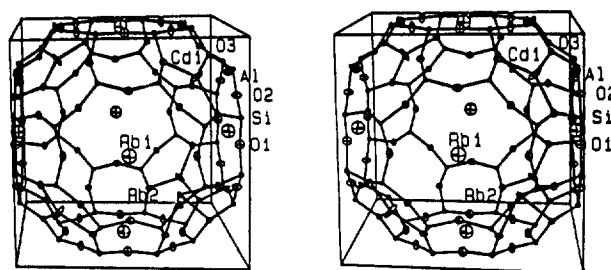


Figure 1. A stereoview of a large cavity of the dehydrated $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$. 4 Cd^{2+} ions at Cd(1), 3 Rb^{+} ions at Rb(1) and 1 Rb^{+} ions at Rb(2) are shown. Ellipsoids of 20% probability are used.

least-squares refinement was initiated. Anisotropic refinement of the framework atoms and Cd(2) converged to $R_1 = 0.323$ and $R_2 = 0.354$. A difference Fourier synthesis revealed a peak at (0.192, 0.192, 0.192) with height of $10.5(17) \text{ e}\text{\AA}^{-3}$. Anisotropic refinement including these positions, Cd(1) and Cd(2), converged to $R_1 = 0.079$ and $R_2 = 0.096$. A subsequent difference synthesis revealed a peak (0.0, 0.5, 0.5) with height of $1.4(10) \text{ e}\text{\AA}^{-3}$. This was stable in least-square refinement and anisotropic refinement including this position as Rb(1) converged to $R_1 = 0.079$ and $R_2 = 0.095$. The final difference map was featureless. The final results are shown in Table 1, 2 and 3.

The full-matrix least-squares program used in all structure determinations 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^{16,17} for Cd^{2+} , Rb^{+} , O^{-1} , and $(\text{Si}, \text{Al})^{1.75+}$ were used. The function describing $(\text{Si}, \text{Al})^{1.75+}$ is the mean of the Si^0 , Si^{4+} , Al^0 , and Al^{3+} functions. All scattering factors were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction.¹⁸ See Table 1, 2 and 3 for additional information.

Discussion

Zeolite A has generally been shown to bind stoichiometrically with 12 cation charges per unit cell needed for balancing the anionic charge of the aluminosilicate framework. All of the three crystal structures studied in this work have 12 cationic charges per unit cell.

The Cd^{2+} ions at Cd(1) in all three structures are located on threefold axes of the unit cell. These Cd^{2+} ions lie almost on the center of 6-rings. These cations approach the three zeolite framework oxygens at O(3) at a distances of *ca.* 2.20 Å. The Cd(1)-O(3) distances agree relatively well with the sum of ionic radii of Cd^{2+} and O^{-2} , 2.29 Å. The angle subtended at Cd(1), O(3)-Cd(1)-O(3) is *ca.* 120°, the idealised trigonal planar angle (Table 2).

The Cd^{2+} ions at Cd(2) in the crystal structures of the dehydrated $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$ lie relatively deep in the sodalite cavity. These Cd^{2+} ions extend 0.79 Å for $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and 0.57 Å for $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$ into the sodalite cavity. These cations are trigonally coordinated to their respectively set of three O(3) framework oxygens at 2.34(1) Å for $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$ and 2.22(1) Å for $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$, respectively.

Rb^{+} ions at Rb(1) in all three structures lie at the centers of the 8-oxygen rings, a site of $C_{4v}(D_{4h}$ in $Pm3m$) symmetry (See Figure 1). Each such ion is *ca.* 3.5 Å from four O(1) oxy-

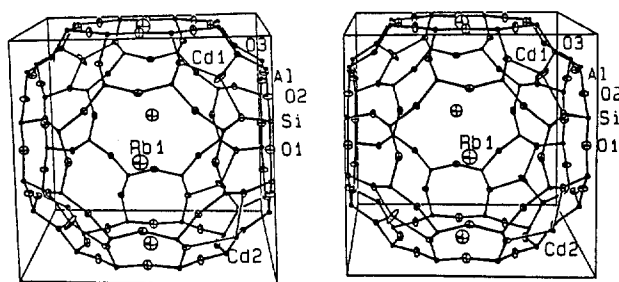


Figure 2. A stereoview of a large cavity of the dehydrated $\text{Cd}_{5.0}\text{Rb}_{2.0}\text{-A}$. 4 Cd^{2+} ions at Cd(1), 1 Cd^{2+} ions at Cd(2) and 2 Rb^{+} ions at Rb(1) are shown. Ellipsoids of 20% probability are used.

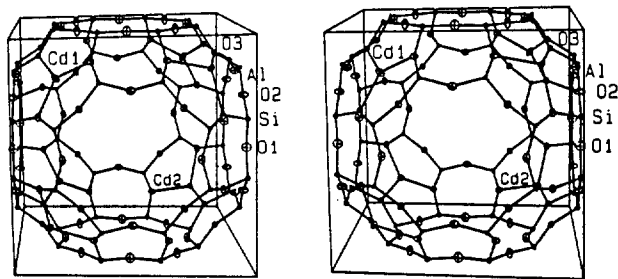


Figure 3. A stereoview of a large cavity of the dehydrated $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$. 3 Cd^{2+} ions are Cd(1), 3 Cd^{2+} ions at Cd(2) are shown. About 95% of unit cell have this stoichiometry.

gens and ca. 3.55 Å from four O(2) (See Table 2). These distances are substantially longer than the sum of the ionic radii, 2.79 Å.¹⁵ Such long interaction distances have been observed previously in other zeolite A structures.^{7,19} This indicates that these Rb^{+} ions are loosely bound to the framework oxygens. Such loosely bound Rb^{+} ions have been also observed spectroscopically by Maxwell and Baks.²⁰ The large thermal ellipsoids also indicated these bonding characters.

The Rb^{+} ions at Rb(1) in $\text{Cd}_{4.0}\text{Rb}_{4.0}\text{-A}$ are located in the large cavity and lie one threefold axis of unit cell. Each Rb^{+} ion at Rb(2) is coordinated to three O(3) framework oxygen at 2.66(2) Å. The distance is a shorter than the sum of ionic radii, 2.79 Å.¹⁵ The angle subtended at Rb(2), O(3)-Rb(2)-O(3) is 93.4(3)°.

For $\text{Cd}_{5.95}\text{Rb}_{0.1}\text{-A}$ crystal, 2.97 of the 5.95 Cd^{2+} ions are located at Cd(1), and the remaining Cd^{2+} ions are located at Cd(2). 0.1 Rb^{+} ions lie at the center of the 8-oxygen rings. This indicates that 95% of the unit cells have 3 Cd^{2+} at Cd(1) ions and 3 Cd^{2+} ions at Cd(2), 3% of the unit cells have 2 Cd^{2+} ions at Cd(1), 3 Cd^{2+} ions at Cd(2) and 2 Rb^{+} ions at Rb(1) and the remaining 2% of the unit cells may have 3 Cd^{2+} ions at Cd(1), 2 Cd^{2+} ions at Cd(2) and 2 Rb^{+} ions at Rb(1).

The comparison of three crystal structures led as the the following conclusion. Firstly, the first three Rb^{+} ions per unit cell preferentially located at the center of 8-oxygen ring and additional Rb^{+} ions, if presented, are found on the threefold axes, deep in the large cavity. Because the ionic radius of

Rb^{+} ion is larger than that of Cd^{2+} ion, Rb^{+} ions are preferentially occupy the larger 8-ring sites. Secondly, the principal position of Cd^{2+} ion is Cd(1) position near the centers of oxygen 6-rings and the next favorable Cd^{2+} position is the Cd(2) position deep in the sodalite cavity. Thirdly, Cd^{2+} ions have greater selectivity of ion exchange into zeolite A than Rb^{+} ions.

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