

Ag⁺이온과 Rb⁺이온으로 치환된 제올라이트A (Ag_{12-x}Rb_x-A, x=2 및 3)를 탈수한 결정구조

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Two Crystal Structures of Dehydrated Ag⁺ and Rb⁺ Exchanged Zeolite A, Ag_{12-x}Rb_x-A, x=2 and 3

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요 약. X-선 단결정법으로 탈수한 Ag₉Rb₃-A (a=12.278(2)Å) 와 Ag₁₀Rb₂-A (a=12.286(2)Å)의 구조를 입방공간군 Pm3m을 써서 해석하였다. Ag₉Rb₃-A의 구조는 I>3σ(I)인 회절반점291개를 이용하여 R₁=0.064, R₂=0.060까지 정밀화 시켰으며 Ag₁₀Rb₂-A의 구조는 416개의 회절반점을 이용하여 R₁=0.063, R₂=0.080까지 정밀화 시켰다. 두 구조 모두 단위세포당 하나의 환원된 은 원자가 소다라이트 동공 내에 있으며 이 환원된 은 원자는 소다라이트 동공 1/6개 마다 Ag₆로 존재하거나 혹은 모든 소다라이트 동공마다 4mm 대칭성을 가지는 (Ag₆)⁴⁺ 클러스터로 존재한다. 그 밖에 탈수한 Ag₉Rb₃-A에서는 8개의 Ag⁺이온은 6-링 중심 3회 회전축 상에 있으며 3개의 Rb⁺이온은 8-링 중심 D_{4h} 대칭성을 가지고서 위치하고 있다. 또 탈수한 Ag₁₀Rb₂-A 구조에서는 2개의 다른 6-링 Ag⁺ 이온 즉 7개의 Ag⁺ 이온은 6-링 평면상에 위치하고 1개의 Ag⁺이온은 소다라이트 동공 내에 위치한다. 두 개의 서로 다른 8-링 양이온이 있으며 두 개의 Rb⁺이온은 8-링 중심에 위치하였고 1개의 Ag⁺이온은 8-링에서 0.1Å 만큼 큰 동공 쪽으로 이동하여 위치한다. 두 구조에서 보면 Ag⁺이온은 6-링 위치에 Rb⁺이온은 8-링 위치에 우선적으로 위치한다.

ABSTRACT. Two crystal structures of dehydrated Ag⁺ and Rb⁺ exchanged zeolite A, stoichiometries of Ag₉Rb₃-A(a=12.278(2)Å) and Ag₁₀Rb₂-A(a=12.286(2) Å) per unit cell, have been determined by single crystal x-ray diffraction techniques. Their structures were solved and refined in the cubic space group Pm3m at 21(1)°C. The crystals of Ag₁₀Rb₂-A and Ag₉Rb₃-A were prepared by flow methods using exchanged solution in which mole ratios of AgNO₃ and RbNO₃ were 1:5 and 1:50, respectively, with the total concentration of 0.05 M. The structures of the dehydrated Ag₉Rb₃-A and the Ag₁₀Rb₂-A were refined to the final error indices, R₁=0.064 and R₂=0.060 with 291 reflections, and R₁=0.063 and R₂=0.080 with 416 reflections respectively, for which I>3σ(I). In both structures, one reduced silver atom per unit cell was found inside the sodalite cavity. It may be present as a hexasilver cluster in 1/6 of the sodalite units or as an isolated Ag atom coordinated to 4 Ag⁺ ions in each sodalite unit to give (Ag₆)⁴⁺, symmetry 4mm. In the structure of dehydrated Ag₉Rb₃-A, 8 Ag⁺ ions lie on the threefold axis and each is nearly at the center of the 8-rings at the sites of D_{4h} symmetry. In the structure of dehydrated Ag₁₀Rb₂-A, two crystallographically different eight 6-ring Ag⁺ ions were found; 7Ag⁺ ions in the (111) planes of their O(3) framework oxygens and one Ag⁺ ion inside of sodalite cavity. Two crystallog-

raphically different 8-ring cations were also found; two Rb⁺ ions at the centers of the 8-oxygen rings and one Ag⁺ ion into the large cavity. Both structures indicate that Rb⁺ ions prefer to occupy the 8-ring sites, while Ag⁺ ions prefer to occupy the 6-ring sites.

INTRODUCTION

The unit cell of molecular sieve zeolite A has three eight-membered oxygen rings, eight six-membered ones, and twelve four-membered ones. The exchangeable cations in zeolite A can occupy a site near the center of the 8-ring (called α site), 6-ring (β site), or 4-ring (γ site). The γ site has weak affinities for all cations. The β site is favorable for most cations because its coordination environments afford the cations to form the symmetrical tricoordinated bonds with three oxygen ions of zeolite framework.¹²

The pore size and sorption properties of molecular sieves are usually controlled by the contents and the identities of α -site cations. In commercial molecular sieves 3A and 4A, the 8-ring windows are blocked by potassium and sodium ions, respectively. These ions are located so as to directly contact oxygen ions of the window framework.¹

Thus far, no structural study of mixed cation system of Ag⁺ and Rb⁺ ion exchanged zeolite A has been reported. The structures of Ag_{12-x}Rb_x-A (x=2 and 3) were determined as a preliminary work for later studies of the crystal structure of Ag_{12-x}Rb_x-A (1 < x < 12) treatment with H₂. In the future experiments, treatment with H₂ might lead to Ag cluster formation, and Rb⁺ ions, by blocking 8-ring windows, might prevent these clusters from migrating out of the structure.

EXPERIMENTAL

Crystals of zeolite 4A were prepared by Char-

nell's method.³ Each of two single crystals about 0.08 mm on edge was lodged in a fine capillary. Crystals of Ag₁₀Rb₂-A and Ag₉Rb₃-A were prepared using exchange solutions in which mole ratios of AgNO₃ and RbNO₃ were 1:5 and 1:50, respectively, and the total cationic concentration were kept at 0.05M.

Ion exchange was accomplished allowing the solution to flow past each crystal at a velocity of approximately 1.0 cm/sec for 3 days at 21(1) °C. Both crystals were dehydrated at 370°C and p=2×10⁻⁶ Torr for 2 days. Microscopic examination indicated that no crystal damage resulted from dehydrated procedures and both crystals became red.

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously.^{2,4} Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four circle Enraf Nonius CAD4 diffractometer. Molybdenum radiation was used for all experiments (K_{α1}, λ=0.70930Å; K_{α2}, λ=0.71359Å). The unit cell constants, as determined by a least-squares refinement of 25 intense reflections for which 10° < θ < 15°, are 12.286(2) Å for Ag₁₀Rb₂-A and 12.278(2) Å for Ag₉Rb₃-A, respectively.

For each crystal, reflections from intensity-equivalent regions of reciprocal space (hkl, h≤k≤l and hlk, h≤l≤k) were examined using the ω-2θ scan techniques. The data were collected using variable scan speed. The maximum final scan time was 5 minutes per one reflection. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 3 hours to monitor crystal and instru-

ment stability.

The raw data for each crystal were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard deviation were assigned to each average reflection by the computer programs, PAINT and WEIGHT.⁵ Of the 880 pairs of reflections for the dehydrated $\text{Ag}_9\text{Rb}_2\text{-A}$ and 878 for the dehydrated $\text{Ag}_5\text{Rb}_3\text{-A}$, only 416 and 291 pairs, for which $I > 3\sigma(I)$ respectively, were used in subsequent structure determinations.

STRUCTURE DETERMINATION

Dehydrated $\text{Ag}_9\text{Rb}_2\text{-A}$. Full-matrix least-squares refinement of the structure was performed using the atomic parameters of the dehydrated and partially decomposed $\text{Ag}_x\text{-A}$ for the atoms of the aluminosilicate framework ((Si, Al), O(1), O(2), and O(3)).^{6,7} Anisotropic refinement of framework atoms converged to $R_1 = (\sum(F_o - |F_c|) / \sum F_o) = 0.412$ and $R_2 = (\sum w(F_o - |F_c|)^2 / \sum w F_o^2)^{1/2} = 0.471$. A subsequent difference Fourier synthesis showed one large threefold axis peak at $x=y=z=0.1934$ (peak height = $14.8(5) \text{ eA}^{-3}$). This peak was stable at least-squares refinement. Simultaneous refinement of occupancy, positional, and anisotropic thermal parameters converged to $R_1=0.193$ and $R_2=0.260$. From a subsequent difference Fourier synthesis, the Rb(1) position was located at (0.0, 0.5, 0.5) and refined to $3.2(1) \text{ Rb}^+$ ions with $R_1=0.112$ and $R_2=0.127$. A third difference Fourier synthesis was generated to locate a Ag species at (0.0, 0.0, 0.166) with a peak of $11.3(10) \text{ eA}^{-3}$. Simultaneous occupancy, positional and anisotropic thermal parameter refinement of the framework and of the Ag(1), Ag(2), and Rb(1) positions converged to the error indices of $R_1=0.016$ and $R_2=0.057$.

The occupancies of these ions per unit cell

refined to Ag(1)=7.8(1), Ag(2)=1.08(3), and Rb(1)=3.16(5). In zeolite A structures, 12 monovalent cations, or in this case 12 cations or Ag atoms should be found per unit cell. Furthermore 6-ring sites are usually favored and all eight 6-ring sites are usually filled. Also all 3 8-ring sites are also filled when cations are found more than 11 per unit cell.

The ions at the Ag(1) sites are associated with 6-rings and lie on threefold-axes and their occupancies have been fixed as 8, the maximum number of ions per unit cell at that position. The ions at Rb(1) are associated with 8-rings and their occupancies have been fixed as 3.0 because these 8-ring can accommodate no more than three Rb^+ ions per unit cell. To allow the occupancies to sum to 12, the occupancy, at Ag(2) was fixed as 1. The final refinement using anisotropic thermal parameters for all atoms yield $R_1=0.064$ and $R_2=0.060$.

A final difference Fourier synthesis was featureless except one small peak with height of 3.9 eA^{-3} at the origin of the unit cell ($\text{esd}=0.26 \text{ eA}^{-3}$ at general position and therefore $\text{esd}=0.26(48)^{1/2}=1.8 \text{ eA}^{-3}$ at that position).⁸ The final structural parameters are presented in Table 1. Interatomic distances and angles are given in Table 3.

Dehydrated $\text{Ag}_{10}\text{Rb}_2\text{-A}$. Full-matrix least-squares refinement of the structure was performed using the atomic parameters obtained from a study of the dehydrated $\text{Ag}_5\text{Rb}_3\text{-A}$. Anisotropic refinement of framework atoms converged to $R_1=0.499$ and $R_2=0.549$. An examination of a difference Fourier map revealed two large peaks, one along the threefold axis at $x=y=z=0.1934$ with height of $22.1(10) \text{ eA}^{-3}$ and the other in sodalite cavity opposite 4-ring at (0.0, 0.0, 0.160) with height of $19.2(13) \text{ eA}^{-3}$. Both peaks were stable at least-squares refinement (see Table 1) and lowered error indices to

Table 1. Positional, Thermal^a, and Occupancy parameters of dehydrated Ag₁₀Rb₂-A

Atom	Wyc. Pos.	x	y	z	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	Occupancy Varied fixed	
(Si,Al)	24(k)	0	1830(2)	3700(2)	23(1)	24(1)	13(1)	0	0	5(2)	24.0	
O(1)	12(h)	0	2173(7)	5000	49(6)	52(7)	30(5)	0	0	0	12.0	
O(2)	12(i)	0	2960(5)	2960(5)	25(5)	36(3)	36(3)	0	0	29(9)	12.0	
O(3)	24(m)	1106(4)	1106(4)	3378(5)	41(2)	41(2)	47(4)	3(7)	26(5)	26(5)	24.0	
Ag(1)	8(g)	1894(1)	1894(1)	1894(1)	67(1)	67(1)	67(1)	87(1)	87(1)	87(1)	6.8(1)	7.0
Ag(2)	6(e)	0	0	1725(9)	67(5)	67(5)	62(8)	0	0	0	0.8(1)	1.0
Ag(3)	8(g)	1400(10)	1400(10)	1400(10)	108(6)	108(6)	108(6)	60(20)	60(20)	60(20)	0.8(1)	1.0
Ag(4)	24(l)	1020(30)	3780(30)	5000	170(40)	50(20)	220(40)	-10(50)	0	0	1.1(1)	1.0
Rb(1)	3(c)	0	5000	5000	79(6)	290(10)	290(10)	0	0	0	2.0(1)	2.0

^aPositional and isotropic thermal parameters are given × 10⁴. Numbers in parentheses are the esd's in units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor = exp[-(β₁₁h² + β₂₂k² + β₃₃l² + β₁₂hk + β₁₃hl + β₂₃kl)]. ^bOccupancy factors given as the number of atoms or ions per unit cell. Occupancy for (Si)=12; occupancy for (Al)=12.

R₁=0.071 and R₂=0.270. A difference Fourier synthesis revealed two peaks at (0, 0, 0.5, 0.5) with electron density of 13.8(27) eÅ⁻³ and (0, 138, 0.138, 0.138) with electron density of 8.4 (9) eÅ⁻³. Both peaks were stable in least-squares refinement. First peak were refined as two Rb⁺ ions and second peak as one Ag⁺ ion. The R values converged to R₁=0.084 and R₂=0.123. A subsequent difference Fourier synthesis revealed a possible Ag⁺ ion at (0.09, 0.38, 0.5). This peak was refined as one Ag⁺ ion. Anisotropic and occupancy refinement of all positions in the structure converged with the final error indices. of R₁=0.061 and R₂=0.076.

The occupancy numbers of these ions per unit cell were refined to Ag(1)=6.8(1), Ag(2)=0.8(1), Ag(3)=0.8(1), Ag(4)=1.1(1) and Rb(1)=2.0(1). The ions at Rb(1) and Ag(4) are associated with 8-rings. As mentioned at the previous structure, the occupancy of Rb(1) and that of Ag(4) were therefore held fixed as 2 and 1, respectively. The ions at Ag(1) and Ag(3) are associated with 6-rings and lie on threefold axes. Therefore the occupancy of Ag(1) and that of Ag(3) were fixed as 7 and 1, res-

pectively. The occupancy of Ag(2) was refined to 0.8(1) and fixed as 1. The final R values with the fixed occupancy factors are R₁=0.063 and R₂=0.080.

The largest peak on the final difference Fourier function was at (0, 0, 0, 0) with a peak height of 6.2(18) eÅ⁻³. This position was not stable at the least-square refinement.

The full-matrix least-squares used in all structure determinations minimized Σω|ΔF|², the weight (ω) of an observation was the reciprocal squares of σ, its standard deviation. Atomic scattering factors for O⁻, (Si, Al)^{1.75+} (the average of Si⁰, Si⁴⁺, Al³⁺, and Al³⁺), Rb⁺, Ag⁰, and Ag⁺, all properly modified to include the real components (f') of anomalous dispersion corrections, were used.^{9,10}

The final structure parameters are presented in Table 2. Interatomic distances and angles are given in Table 3.

DISCUSSION

Every 8-oxygen rings for the structure of the dehydrated Ag₆Rb₃-A (or two-thirds of 8-oxygen

Table 2. Positional, thermal^a, and occupancy parameters of dehydrated Ag₅Rb₃-A

Atom	Wyc. Pos.	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	^b Occupancy Varied fixed
(Si,Al)	24(k)	0	1841(3)	3701(2)	18(2)	11(2)	7(2)	0	0	2(4)	24.0
O(1)	12(h)	0	2180(10)	5000	40(10)	40(10)	25(9)	0	0	0	12.0
O(2)	12(i)	0	2964(7)	2964(7)	19(8)	23(5)	23(5)	0	0	10(10)	12.0
O(3)	24(m)	1107(5)	1107(5)	3361(7)	28(4)	28(4)	25(7)	0(1)	11(8)	11(8)	24.0
Ag(1)	8(g)	1869(2)	1869(2)	1869(2)	72(1)	72(1)	72(1)	104(2)	104(2)	104(2)	7.8(1) 8.0
Ag(2)	6(e)	0	0	1700(10)	48(7)	48(7)	50(10)	0	0	0	1.1(1) 1.0
Rb(1)	3(c)	0	5000	5000	106(9)	247(9)	247(9)	0	0	0	3.2(1) 3.0

^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 given as the number of atoms or ions per unit cell. Occupancy for (Si)=12; occupancy for (Al)=12.

Table 3. Selected interatomic distances(Å) and angles(deg) of dehydrated Ag₁₂Rb₃-A (X=2 and 3).

	Ag ₁₀ Rb ₂ -A	Ag ₅ Rb ₃ -A
(Si, Al)-O(1)	1.651(3)	1.648(4)
(Si, Al)-O(2)	1.659(4)	1.651(9)
(Si, Al)-O(3)	1.670(3)	1.685(7)
Ag(1)-O(3)	2.279(5)	2.261(7)
Ag(2)-O(3)	2.793(9)	2.80(1)
Ag(3)-O(2)	2.486(6)	
Ag(4)-O(1)	3.98(1)	
Ag(4)-O(2)	2.98(2)	
Rb(1)-O(1)	3.471(9)	3.48(1)
Rb(1)-O(2)	3.542(6)	3.538(6)
Ag(1)-Ag(2)	3.296(1)	3.255(2)
Ag(2)-Ag(2)	3.00(1)	2.96(2)
O(1)-(Si,Al)-O(2)	108.4(3)	108.9(5)
O(1)-(Si,Al)-O(3)	111.4(3)	112.0(4)
O(2)-(Si,Al)-O(3)	108.4(2)	108.1(2)
O(3)-(Si,Al)-O(3)	108.8(3)	107.7(3)
(Si,Al)-O(1)-(Si,Al)	150.4(6)	151.1(9)
(Si,Al)-O(2)-(Si,Al)	156.4(4)	156.6(4)
(Si,Al)-O(3)-(Si,Al)	144.1(4)	143.3(5)
O(3)-Ag(1)-O(3)	119.9(1)	120.0(2)
O(3)-Ag(2)-O(3)	58.2(2)	58.1(4)
O(3)-Ag(3)-O(3)	105.1(3)	
O(1)-Ag(4)-O(2)	59.3(6)	
O(1)-Rb(1)-O(2)	45.1(1)	45.1(1)
Ag(1)-Ag(2)-Ag(1)	89.77(3)	89.77(6)

rings for the structure of the dehydrated Ag₁₀Rb₂-A contains a Rb⁺ ion at its center, a site of C_{4v} (D_{4h} in Pm3m) symmetry (see Fig. 1). Each such ion is 3.48 Å from 4 O(1) oxygens and 3.54 Å from 4 O(2)'s (see Table 3). These distances are substantially longer than the sum

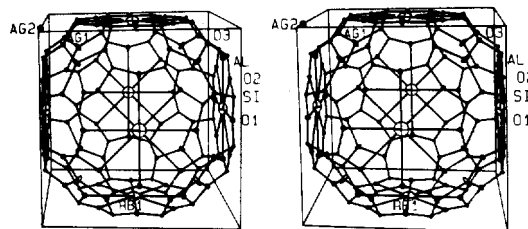


Fig. 1. A stereoview of the large cavity of dehydrated Ag₅Rb₃-A is shown with ellipsoids of 20% probability.

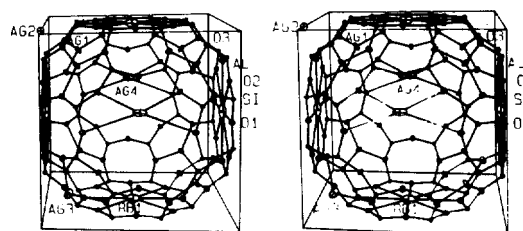


Fig. 2. A stereoview of the large cavity of dehydrated Ag₁₀Rb₂-A is shown with ellipsoids of 20% probability.

Table 4. Deviation of atoms(A) from the (111) plane at O(3) of dehydrated Ag_{12-x}Rb_x-A (x=2 and 3)

	Ag ₁₀ Rb ₂ -A	Ag ₉ Rb ₃ -A
O(2)	-0.234(3)	-0.249(5)
Ag(1)	-0.066(1)	-0.024(1)
Ag(2)	2.740(10)	2.748(10)
Ag(3)	0.994(7)	

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

of the ionic radii, 2.79 Å¹¹. Similar long interatomic distances have also been observed previously in other zeolite A structures.¹²⁻¹⁴

The remaining one-thirds of 8-oxygen rings for structure of the dehydrated Ag₁₀Rb₂-A contain one Ag⁺ ion at Ag(4) (see Fig. 2). This Ag⁺ ion is moved ca. 0.1 Å into the large cavity from the 8-oxygen ring plane. It is also located off the center of the 8-oxygen and approaches zeolite framework oxygens at equal distances of 2.98(1) Å, to O(1) and O(2). One Ag⁺ ion at Ag(4) lies at this position to minimize the cation (Ag⁺)-cation (Rb⁺) repulsive force.

The Ag⁺ ions at Ag(1) are at the same positions as found in dehydrated and partially decomposed Ag₁₂-A.^{6,7} Each Ag⁺ ion lies on a threefold axis and is almost nearly the center of a 6-ring. The local symmetry of this position is close to D_{3h}. Each Ag⁺ ion is trigonally coordinated at ca. 2.27 Å to 3 O(3) framework oxygens. As compared to the sum of the Ag⁺ and O⁻ radii, 2.58 Å, these bonds are quite short and therefore quite covalent.¹⁵ On the surface of each sodalite unit, and consistent with its high symmetry, O_h, eight Ag⁺ ions at Ag(1) for the dehydrated Ag₉Rb₃-A lie at the corner of a cube 4.54 Å on an edge. However, in the structure of dehydrated Ag₁₀Rb₂-A, 7 Ag⁺ ions at Ag(1) and one Ag⁺ ion at Ag(3) lie on the

threefold axis of unit cell.

The Ag⁺ ion at Ag(3) lies relatively far inside the sodalite cavity, ca. 0.99 Å from (111) plane of O(3). The distance between Ag(3) and its nearest framework oxygens at O(3) is 2.486 (6) Å.

The Ag(2) position is very similar to that of the neutral silver atom in the structure of dehydrated partially decomposed Ag₁₂-A. The distance between Ag(2) and the nearest oxygen at O(3) is quite long, ca. 2.80 Å, as compared to the corresponding ion to ion distances observed, and about the same as was found between a neutral silver atom and framework oxygens. The shortest available Ag(2)-Ag(2) distances, 3.00(1) Å for Ag₁₀Rb₂-A and 2.96(2) Å for Ag₉Rb₃-A, respectively, may be considered slightly longer than the Ag(2)-Ag(2) bond in silver metal, 2.89 Å.¹⁶

One may conclude that an average of one reduced silver per unit cell has formed inside the sodalite unit presumably by the reaction of a Ag⁺ ion with half of an oxygen atom (oxide ion) of the framework of with half of a residual water molecule. The cation which has been reduced is the one which is most easily reduced Ag⁺, and the cation site which is no longer occupied is the least favorable, the one opposite 4-ring in the large cavity. This position is the least favorable because the approach of the Ag⁺ ion to framework oxygens has been the longest and the most one-sided in previous studies.^{6,7}

It may be that a neutral hexasilver cluster has formed in one-sixth of the sodalite cavity. As an other alternative, it is also possible that an isolated Ag atom exists in each sodalite unit coordinated to 4 Ag⁺ ions. The local symmetry of Ag⁺ cluster has 4mm (C_{4v}) near D_{3h} symmetry. The neutral silver atom was also seen in other structures such as Ag_{12-x}Tl_x-A(x=2,3,4 and

5)¹⁷. $\text{Ag}_{12x}\text{K}_x\text{-A}$ ($x=1.2$ and 2.7)¹⁸, $\text{Ag}_{12}\text{-A}$ treated first with H_2 and then with O_2 , both at 330°C ,¹⁹ and $\text{Ag}_{7.6}\text{Na}_{4.6}\text{-A}$ ²⁰.

In summary, in the structure of dehydrated $\text{Ag}_8\text{Rb}_3\text{-A}$ 8 Ag^+ ions per unit cell lie on the threefold axes and each Ag^+ is nearly at the center of one of the eight 6-rings. Three Rb^+ ions lie at the centers of the 8-rings at sites of D_{4h} symmetry. One reduced silver atom per unit cell was found inside the sodalite unit.

The reduced Ag atom may exist as a hexasilver cluster in one-sixth of the sodalite units or as an other alternative, the reduced Ag atom may coordinate to four Ag^+ ion in sodalite unit to give $(\text{Ag}_5)^{4+}$, symmetry $4mm$. In the structure of dehydrated $\text{Ag}_{10}\text{Rb}_2\text{-A}$, two different 8 6-ring Ag^+ ions were found; 7 Ag^+ ions in the (111) planes of its 3 O(3) framework oxygens and one Ag^+ ion inside of sodalite cavity. Two different 8-ring cations were found; each of two Rb^+ ions at the center of a 8-oxygen ring and one Ag^+ ion into the large cavity off the 8-ring plane. One reduced Ag atom per unit cell was also found inside the sodalite cavity, as in the structure of dehydrated $\text{Ag}_6\text{Cs}_3\text{-A}$.²¹ Both crystal structures indicates that Rb^+ ions prefer to occupy the 8-ring sites and Ag^+ ions prefer to occupy the 6-ring sites (see Fig. 1 and 2).

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