

완전히 탈수한 $Ag_{12-2x}Co_x-A(x=3$ 및 $4.5)$ 의 결정구조

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Two Crystal Structures of Fully Dehydrated $Ag_{12-2x}Co_x-A(x=3$ and $4.5)$

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요 약. Co^{2+} 이온과 Ag^+ 이온으로 교환된 제올라이트 A 즉, $Ag_6Co_3-A(a=12.131(5)\text{\AA})$ 과 $Ag_3Co_{4.5}-A(a=12.145(1)\text{\AA})$ 의 결정구조를 X-선 단결정회절법으로 입방공간군 $Pm3m$ 을 사용하여 해석하였다. $I)3\sigma(I)$ 인 189개의 회절반점을 써서 Ag_6Co_3-A 구조에 대해서는 $R_1=0.066$, $R_2=0.076$ 까지 정밀화시켰으며 $Ag_3Co_{4.5}-A$ 구조에 대해서는 $I)3\sigma(I)$ 인 258개의 회절반점을 써서 $R_1=0.045$, $R_2=0.041$ 까지 정밀화시켰다. 두 구조 모두 $Co(II)$ 이온은 골조의 3개의 산소와 배위하고 있었고 $Co(II)-O(3)$ 거리는 $Ag_3Co_{4.5}-A$ 에서는 $2.118(4)\text{\AA}$ 이었고 Ag_6Co_3-A 에서는 $2.106(1)\text{\AA}$ 이었다. 또 두 구조 모두 $O(3)-Co(II)-O(3)$ 각도는 약 120° 로서 $Co(II)$ 와 3개의 $O(3)$ 는 거의 이상적인 삼각 평면형의 배열을 갖고 있었다. 단위포당 양이온의 총수가 8개 이상이면 Ag^+ 이온은 8-링 위치에 Co^{2+} 이온은 6-링 위치의 골조산소와 우선적으로 결합한다. $Co(II)$ 이온의 수가 단위포당 4.5개 이상이 되면 $Ag_{12-2x}Co_x-A(x > 4.5)$ 결정은 X-선 회절패턴이 없었고, 이것은 Co^{2+} 이온이 H_2O 분자를 가수분해하여 생성되는 H^+ 이온 농도가 축적되어 제올라이트 골조를 파괴시켰을 것으로 생각된다.

ABSTRACT. The Crystal structures of Co^{2+} and Ag^+ exchanged zeolite A, $Ag_6Co_3-A(a=12.131(5)\text{\AA})$ and $Ag_3Co_{4.5}-A(a=12.145(1)\text{\AA})$, have been determined by single crystal X-ray diffraction techniques. Both structures were solved and refined in the cubic space group $Pm3m$ at $21(1)^\circ C$. Full-matrix least-squares refinement converged to the final error indices of $R_1=0.045$ and $R_2=0.041$ for $Ag_3Co_{4.5}-A$, and $R_1=0.066$ and $R_2=0.076$ for Ag_6Co_3-A using the 258 and 189 reflections, respectively, for which $I)3\sigma(I)$. Both structures indicate that $Co(II)$ ions are coordinated by three framework oxygens; the $Co(II)$ to $O(3)$ distances are $2.118(4)\text{\AA}$ for $Ag_3Co_{4.5}-A$ and $2.106(1)\text{\AA}$ for Ag_6Co_3-A , respectively. In each structure, the angle subtended at $Co(II)$, $O(3)-Co(II)-O(3)$ is *ca* 120° , close to the idealized trigonal-planar value. Co^{2+} ions prefer to 6-ring sites and Ag^+ ions prefer to 8-ring site when total number of cations is more than 8. The crystals of hydrated and dehydrated $Ag_{12-2x}Co_x-A(x > 4.5)$ had no crystal-line diffraction pattern, indicating the apparent exchange limit of Co^{2+} into $Ag_{12}-A$ is 4.5 Co^{2+} ions per unit cell. Co^{2+} ions hydrolyze H_2O molecules and H_3O^+ concentration is accumulating. These H_3O^+ ions destroy the zeolite structures.

INTRODUCTION

Successful exploitation of the catalytic and selective sorptive properties of zeolites rely upon an appreciation of the structural features of these molecular sieves; *i.e.*, the dimensions of zeolitic channels and cages, the nature of the active sites, and the locations of the exchangeable cations and their interactions with the zeolitic framework oxygens.¹ To this purpose a number of first row transition-metal exchanged zeolite A system of $\text{M}_x\text{Na}_{12-2x}\text{-A}$,² where $\text{M} = \text{Mn(II)}$,³ Fe(II) ,⁴ Co(II) ,⁵ Ni(II) ,⁶ Cu(II) ⁷ or Zn(II) ,^{8,9} and $2.5 < x < 6$ have been examined by single crystal X-ray diffraction techniques.

Transition metal ions in zeolite structures are generally unusually coordinated or coordinately unsaturated.⁶ The zeolite framework, in contrast to conventional complexing ligands, does not conform to the geometrical requirements of the metal ions to form stable complexes. Rather metal ions must situate to themselves in the most suitable of the various unsuitable sites available, using water or guest molecule, if available, to achieve a relatively stable coordination environment. Upon dehydration, coordinative unsaturation appears or is very much enhanced.

Previous attempts to ion exchange Co^{2+} ions into zeolite A ($\text{Na}_{12}\text{-A}$) by flow method resulted in crystal damage,⁶ yet, static exchange produced good $\text{Na}_x\text{Co}_x\text{-A}$ crystals.

It was hoped initially that, by flow methods, the number of Co^{2+} ions in Ag^+ -exchanged zeolite A could be maximized without incurring crystal damage. If this could be accomplished, crystallographic analysis could provide a more detailed and reliable description of the structure for comparison with the crystal structure of $\text{Na}_x\text{Co}_x\text{-A}$, because Ag^+ ions have higher scattering power than Na^+ ions; $46 e^-$ for Ag^+

vs. $10 e^-$ for Na^+ ions. It would also be interesting to learn how different numbers of exchanged Co^{2+} ions and Ag^+ ions arrange themselves in the zeolite framework.

EXPERIMENTAL

Crystals of zeolite 4A were prepared by Charnell's method.¹⁰ Two single crystals, 0.08 mm on an edge were lodged in fine glass capillaries. Each crystal was first exchanged with 0.05M AgNO_3 (Mallinckrodt, analytic reagent, impurities: Pb, 0.001%; Fe, 0.0002%; all other cation, less than 0.002%) by flow methods—a continuous stream of fresh solution flowed past the crystal at a velocity of approximately 0.5 cm/sec for a period of 2 days at 22 (1)°C. Next the crystals were similarly exchanged with 0.05M $\text{Co(NO}_3)_2$ solution for 72h and 120h, respectively. Each crystal was then dehydrated at 370°C and 2×10^{-6} torr for 2 days. After cooling to room temperature, the crystal was sealed in its capillary, while still under vacuum, by torch (See Table 1). Microscopic examination showed that the crystal had become dark pink.

The space group $Pm\bar{3}m$ (no systematic absences) was used throughout this work for reasons discussed previously.¹¹ Preliminary crystallographic experiments and subsequent data collection were performed with an automated Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator, and a MICRO PDP 11/73 computer. Molybdenum K_α radiation ($K_{\alpha 1}$, $\lambda = 0.70930 \text{ \AA}$; $K_{\alpha 2}$, $\lambda = 0.71359 \text{ \AA}$) was used. The unit cell constants and orientation matrices at 21(1)°C, as determined by least-squares refinement of 25 intense reflections ($20^\circ > 2\theta > 30^\circ$ in each case) are 12.145 Å and 12.131 Å for $\text{Ag}_3\text{Co}_{4.5}\text{-A}$ and $\text{Ag}_6\text{Co}_3\text{-A}$, respectively.

Table 1. A summary of experimental results

Crystal	Ion exchange		Dehydration			No. of observed reflection $I > 3\sigma(I)$	Unit cell constant (Å)	Final error index	
	Solution	Period flow rate (day) (cm/sec)	Temp. (°C)	period (day)	press. (Torr)			R_1	R_2
Ag ₁₂ -A	0.05N AgNO ₃	2 1.0							
Ag ₆ Co ₃ -A	0.05N Co(NO ₃) ₂	3 1.0	370	2	2 × 10 ⁻⁶	189	12.131(5)	0.045	0.041
Ag ₃ Co _{4.5} -A	0.05N Co(NO ₃) ₂	5 1.0	370	2	2 × 10 ⁻⁶	258	12.145(1)	0.066	0.076
Ag _{12-2z} Co _z -A ($z > 4.5$)	0.05N Co(NO ₃) ₂	7 1.0	370	2	2 × 10 ⁻⁶	No diffraction pattern			

Reflections from two intensity-equivalent regions of reciprocal space (hkl , $h\bar{k}l$, and lhk , $l\bar{h}k$) were examined w - 2θ scan technique. The data was collected by variable scan speeds. The maximum final scan time was 300 seconds per one reflection. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 3 hours to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

All unique reciprocal lattice points for which $2\theta < 70^\circ$ were examined. The raw data from each region were corrected for Lorentz and polarization effect, including that due to incident beam monochromatization; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs, PAINT and WEIGHT.¹²

Of the 886 unique pairs of reflections examined for the crystals of Ag₃Co_{4.5}-A and Ag₆Co₃-A, only the 258 and 189 reflections, respectively, for which $I > 3\sigma(I)$ were used in structure solution and refinement.

STRUCTURE DETERMINATION

Ag₃Co_{4.5}-A. Full-matrix least-squares refinement of the structure was initiated using the atomic parameters of Ag₁₂-A¹³ for the atoms of the aluminosilicate framework ((Si, Al), O(1),

O(2) and O(3)). Anisotropic refinement of framework atoms converged to $R_1 = (\sigma F | F_c | / \sigma F_0) = 0.414$ and $R_2 = (\sigma w(F_0 | F_c |)^2 / \sigma w F_0^2)^{1/2} = 0.490$.

A subsequent difference Fourier map showed two three-fold axis peaks, one inside the sodalite unit at $x=y=z=0.1460$ (peak height = $3.90(7) \text{ e}\ddot{\text{A}}^{-3}$) and another on the 6-ring plane at $x=y=z=0.1934$ (peak height = $5.81(6) \text{ e}\ddot{\text{A}}^{-3}$). These two peaks were stable at least-squares refinement. Simultaneous refinement of occupancy, positional, and anisotropic thermal parameters converged to $R_1 = 0.045$ and $R_2 = 0.050$. The occupancy of Co²⁺ ions at Co(1) was refined to 8.2(1) and the occupancy of Ag⁺ ions at Ag(1) was refined to 1.1(2). However, the sum of these two ions cannot exceed 8.0. The thermal ellipsoid of Co(1) became elongated in subsequent refinements indicating the presence of two nonequivalent ions at this position. Attempts to refine two nonequivalent cations at three-fold axes (x, x, x) were preformed by using following criteria: (1) the bond length of Ag⁺ ion to framework oxygens may be longer than that of Co²⁺ ion to framework oxygens (ionic radius of Ag = 1.26 \AA and that of Co²⁺ ion = 0.74 \AA); (2) total number of charges per unit cell should be 12.0; and (3) total number of ions on 3-fold axes cannot exceed 8.0 (otherwise unacceptable close interionic distances would occur). The occupancy numbers of these ions per unit cell refined to Ag(1) = 1.1

Table 2. ^aPositional, thermal, and occupancy parameters of dehydrated $\text{Ag}_5\text{Co}_{4.5}\text{-A}$

Atom	Wyc. Pos.	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	^b Occupancy	
											Varied	Fixed
(Si, Al)	24(<i>k</i>)	0	1826(2)	3675(2)	42(1)	31(1)	27(1)	0	0	5(2)		24.0
O(1)	12(<i>h</i>)	0	1987(6)	5000	103(7)	64(6)	42(5)	0	0	0		12.0
O(2)	12(<i>i</i>)	0	2979(4)	2979(4)	94(7)	39(3)	39(3)	0	0	34(9)		12.0
O(3)	24(<i>m</i>)	1117(3)	1117(3)	3243(4)	81(3)	81(3)	60(4)	79(7)	-42(6)	-42(6)		24.0
Ag(1)	8(<i>g</i>)	1462(5)	1462(5)	1462(5)	80(3)	80(3)	80(3)	69(8)	69(8)	69(8)	1.1(2)	1.0
Ag(2)	8(<i>g</i>)	1957(3)	1957(3)	1957(3)	95(2)	95(2)	95(2)	24(5)	24(5)	24(5)	1.9(1)	2.0
Co(1)	8(<i>g</i>)	1922(2)	1922(2)	1922(2)	59(4)	59(4)	59(4)	108(2)	108(2)	108(2)	4.6(2)	4.5

^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 = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{33}hl + \beta_{23}kl)]$. ^bOccupancy factors given as the number of atoms or ions per unit cell. Occupancy for (Si)=12; occupancy for (Al)=12.

Table 3. ^aPositional, thermal, and occupancy parameters of dehydrated $\text{Ag}_6\text{Co}_3\text{-A}$

Atom	Wyc. Pos.	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	^b Occupancy	
											Varied	Fixed
(Si, Al)	24(<i>k</i>)	0	1827(5)	3670(4)	45(3)	33(3)	29(3)	0	0	5(6)		24.0
O(1)	12(<i>h</i>)	0	2001(2)	5000	100(2)	90(2)	20(1)	0	0	0		12.0
O(2)	12(<i>i</i>)	0	3000(1)	3000(1)	70(1)	35(8)	35(8)	0	0	50(2)		12.0
O(3)	24(<i>m</i>)	1131(9)	1131(9)	3250(1)	86(7)	86(7)	70(1)	100(2)	-40(2)	-40(2)		24.0
Ag(1)	8(<i>g</i>)	1453(6)	1453(6)	1453(6)	118(3)	118(3)	118(3)	145(8)	145(8)	145(8)	2.8(3)	3.0
Ag(2)	8(<i>g</i>)	2134(9)	2134(9)	2134(9)	68(5)	68(5)	68(5)	70(1)	70(1)	70(1)	1.9(1)	2.0
Ag(3)	24(<i>l</i>)	570(5)	3950(3)	5000	330(9)	0	270(8)	-200(6)	0	0	0.6(1)	0.5
Ag(4)	12(<i>i</i>)	0	4380(4)	4380(4)	400(2)	30(2)	30(2)	0	0	100(6)	0.5(2)	0.5
Co(1)	8(<i>g</i>)	1910(4)	1910(4)	1910(4)	66(5)	66(5)	66(5)	40(1)	40(1)	40(1)	3.2(2)	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 = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{33}hl + \beta_{23}kl)]$. ^bOccupancy factors given as the number of atoms or ions per unit cell. Occupancy for (Si)=12; occupancy for (Al)=12.

(2), $\text{Ag}(2)=1.9(1)$ and $\text{Co}(1)=4.6(2)$. These were fixed at $\text{Ag}(1)=1.0$, $\text{Ag}(2)=2.0$ and $\text{Co}(1)=4.5$. The final *R* values are $R_1=0.041$ and $R_2=0.045$.

The largest peak on the final difference Fourier map whose estimated standard deviation was $0.07 \text{ e}\text{\AA}^{-3}$ at a general position, was $2.59 \text{ e}\text{\AA}^{-3}$ in height and was at origin, where the esd was approximately $3.36 \text{ e}\text{\AA}^{-3}$. There was no peak on 8-ring sites, indicating cations were only existed on three-fold axis sites and asso-

ciated with 6-ring oxygens. The final structural parameters are presented in Table 2.

$\text{Ag}_6\text{Co}_3\text{-A}$. Least-squares refinement began using the same framework position and $\text{Ag}(1)$ coordinates found in the structure of dehydrated $\text{Ag}_5\text{Co}_{4.5}\text{-A}$. Anisotropic refinement of all these positions converged quickly to $R_1=0.22$ and $R_2=0.24$. A difference Fourier map revealed possible cation position on three-fold axes at $x=0.20$. The occupancy number of this position as Co^{2+} ions ($\text{Co}(1)$) refined to 5.8 and

the thermal ellipsoids of Co(1) became elongated in subsequent refinements indicating the presence of two nonequivalent cations at that position. These were refined at (0.2134, 0.2134, 0.2134) and (0.191°, 0.191°, 0.191°) (See Table 3). The occupancies of these ions per unit cell were refined to Ag(2)=1.9(1), Co(1)=3.2(2), and Ag(1)=2.8(3).

A subsequent difference Fourier map based on this eight-cation model revealed two peaks at (0, 0, 0.4380, 0.4380) with electron density of 1.15 eÅ⁻³ and (0.057, 0.395, 0.57) with electron density of 1.08 eÅ⁻³. Both peaks are stable in least-squares refinement and refined well as each 1/2 Ag⁺ ion (See Table 3). The final *R* values converged to *R*₁=0.076 and *R*₂=0.066.

The final difference Fourier map show no significant peaks; one at the origin (0, 0, 0) with electron density of 3.6(7)eÅ⁻³. This peak was not refined in least-squares refinement.

The quantity minimized in the least-squares treatment was $\sum (F_o - |F_c|)^2$ where the weight (*w*) are the reciprocal squares of $\sigma(I)$, the standard deviation of each observation. Atomic scattering factors for Ag⁺, Co²⁺, (Si, Al)^{1.75+} and O were used.¹⁴ The function describing (Si, Al)^{1.75+} is the mean of Si⁰, Si⁴⁺, Al⁰, and Al³⁺ functions. All scattering factors were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction.¹⁵ The final structural parameters are presented in Table 3. Interatomic distances and angles are given in Table 4.

DISCUSSION

Dehydrated Ag₃Co_{4.5}-A. In dehydrated Ag₃Co_{4.5}-A, 4.5 Co²⁺ ions at Co(1) are located on threefold axes and recessed 0.203(2)Å into the large cavity (See Table 5). These positions are familiar, having been found in previous work.⁵

Table 4. Selected interatomic distances(Å) and angles(deg) of dehydrated Ag_{12-2x}Co_x-A(x=3 and 4.5)

	Ag ₃ Co _{4.5} -A	Ag ₆ Co ₃ -A
(Si, Al)-O(1)	1.621(2)	1.627(5)
(Si, Al)-O(2)	1.635(4)	1.640(1)
(Si, Al)-O(3)	1.690(4)	1.690(7)
Ag(1)-O(3)	2.243(4)	2.25(1)
Ag(2)-O(3)	2.126(5)	2.19(1)
Ag(3)-O(1)		2.463(3)
Ag(3)-O(2)		2.78(2)
Ag(4)-O(1)		2.98(2)
Ag(4)-O(2)		2.367(5)
Co(1)-O(3)	2.118(4)	2.106(1)
Ag(1)-Ag(1)		4.98(2)
O(1)-(Si, Al)-O(2)	114.2(3)	112.5(9)
O(1)-(Si, Al)-O(3)	111.7(2)	111.4(7)
O(2)-(Si, Al)-O(3)	106.0(1)	106.4(4)
O(3)-(Si, Al)-O(3)	106.8(2)	108.7(5)
(Si, Al)-O(1)-(Si, Al)	166.2(6)	165.0(2)
(Si, Al)-O(2)-(Si, Al)	152.3(2)	150.0(6)
(Si, Al)-O(3)-(Si, Al)	136.2(3)	136.0(8)
O(3)-Ag(1)-O(3)	108.9(2)	107.9(3)
O(3)-Ag(2)-O(3)	120.0(2)	112.2(3)
O(3)-Co(1)-O(3)	119.1(1)	119.5(3)
O(1)-Ag(3)-O(2)		60.0(2)
O(1)-Ag(4)-O(2)		61.9(7)

Table 5. Deviation of atoms (Å) from the (111) plane at O(3) of dehydrated Ag_{12-2x}Co_x-A(x=3 and 4.5).

	Ag ₃ Co _{4.5} -A	Ag ₆ Co ₃ -A
Ag(1)	0.768(1)	0.806(4)
Ag(2)	-0.277(2)	-0.624(6)
Co(1)	-0.203(2)	-0.157(0)

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

Each of these Co²⁺ ions is coordinated to three O(3) framework oxide ions at 2.118(4) Å. The corresponding Co-O distance in dihydrated Co₄Na₄-A is 2.077(18) Å. The O(3)-Co(1)-O(3) angle is 119.1(1)°-near the idealized trigonal-planar angle; each Co²⁺ ion lies somewhat

"above" (by 0.023 \AA ; see Table 5) its plane of O(3) atoms.

The fractional occupancy observed at Co^{2+} ions at Co(1) indicate that about 50% of unit cells many have 5 Co^{2+} ions and the remaining 50% of unit cell many have 4 Co^{2+} ions.

To distribute positive charge more uniformly so as to minimize cation-cation interaction as well as to neutralize the negative charge of the zeolite framework, three Ag^+ ions adopt two nonequivalent crystallographic sites at Ag(1) and Ag(2). One Ag^+ ion at Ag(1) lies relatively far inside the sodalite cavity, $0.768(1) \text{ \AA}$ from (111) plane at O(3). However, two Ag^+ ions at Ag(2) are in the large cavity, 0.769 \AA from (111) plane at O(3). Each Ag^+ ion is coordinated to three framework oxygens at O(3), i.e. those not bound to a Co^{2+} ion. The Ag(1) to O(3) distance is $2.243(5) \text{ \AA}$ and the Ag(2) to O(3) distance is $2.126(5) \text{ \AA}$. For comparison, the sum of the Ag^+ and O^{2-} radii is 2.58 \AA .¹⁶

The crystal structures of several oxygen containing silver salts have been determined. Some of Ag-O distances found are 2.05 \AA in Ag_2O , 2.34 \AA in Ag_3PO_4 , 2.48 \AA in $AgNO_3$,¹⁷ and 2.21 \AA in dehydrated and partially decomposed $Ag_{12}A$.¹³ It appears that the relatively short, ca $2.24 \sim 2.13 \text{ \AA}$ bonds between Ag^+ ions at Ag(1) and Ag(2), and oxide ions of the zeolite framework are quite covalent.¹⁸ See Fig. 1 and 2 for a probable large cavity and a sodalite unit of $Ag_3Co_{4.5}A$.

Ag_6Co_3A . The principal positions of Ag^+ ions, Ag(1), Ag(2), and Co(1) position are nearly same as those determined previously in the structure of $Ag_3Co_{4.5}A$ (See Table 2 and 3). The three Ag^+ ions at Ag(1) lie relatively far inside the sodalite cavity. They have been arranged in triangular fashion within their low occupancy equipoint in order to maximize their

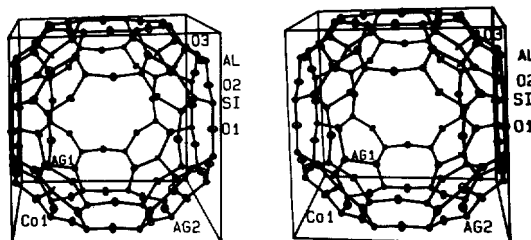


Fig. 1. A stereoview of a large cavity of dehydrated $Ag_3Co_{4.5}A$ is shown using ellipsoids of 20% probability.

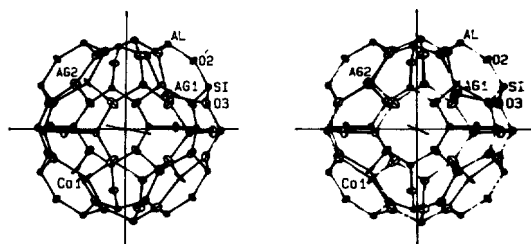


Fig. 2. A stereoview of a sodalite unit of dehydrated $Ag_3Co_{4.5}A$ is shown using ellipsoids of 20% probability.

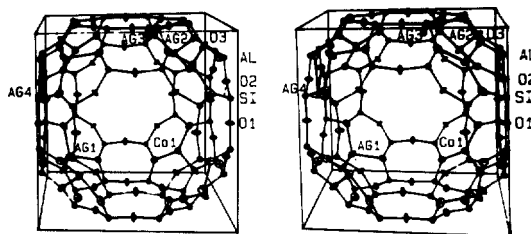


Fig. 3. A stereoview of a large cavity of dehydrated Ag_6Co_3A is shown using ellipsoids of 20% probability.

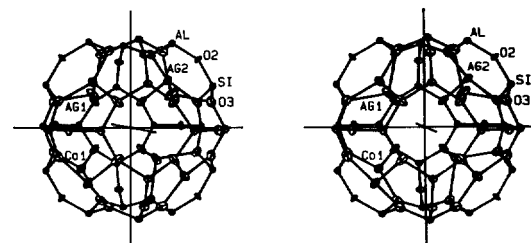


Fig. 4. A stereoview of a large cavity of dehydrated Ag_6Co_3A is shown using ellipsoids of 20% probability.

interatomic distance: $\text{Ag}(1)-\text{Ag}(1)=4.98 \text{ \AA}$. A plausible and unique relative arrangement of the eight threefold-axis cation is presented in Fig. 3 and 4. The Ag^+ ions and Co^{2+} ions in Fig. 4 have been placed within their partially occupied equipoints so as to maximize the distribution of positive charge (to balance most evenly the anionic charge of the framework) and to minimize their electrostatic repulsion (by maximizing the shorter of their intercationic approaches). To minimize electrostatic repulsion, the Ag^+ ions at $\text{Ag}(1)$ and Co^{2+} ions at $\text{Co}(1)$ are placed each three of four tetrahedrally placed 6-rings and two Ag^+ ions at $\text{Ag}(2)$ are placed on opposite sides of the origin.

0.5 Ag^+ ion at $\text{Ag}(3)$ and 0.5 Ag^+ ion at $\text{Ag}(4)$ are associated with 8-ring oxygens (See Fig. 3). The fractional occupancies of these Ag^+ ions indicate that the 50% of the unit cells have only one Ag^+ ion at $\text{Ag}(3)$ and the remaining 50% of the unit cells have one Ag^+ ion at $\text{Ag}(4)$. The Ag^+ ion at $\text{Ag}(3)$ approaches to the zeolite framework oxide ions at $2.463(3) \text{ \AA}$ to one ion at $\text{O}(1)$ and $2.78(4) \text{ \AA}$ to one $\text{O}(2)$. The Ag^+ ion at $\text{Ag}(4)$ is coordinated to two $\text{O}(1)$ framework oxygens at $2.98(2) \text{ \AA}$ and also coordinated one $\text{O}(2)$ framework oxygen at $2.367(5) \text{ \AA}$. These bonding distances are longer than the distances between Ag^+ ions at 6-ring sites and their three nearest 6-ring oxygen neighbors (2.25 and 2.19 \AA , see Table 4). Also the thermal parameters of $\text{Ag}(3)$ and $\text{Ag}(4)$ are larger than those of $\text{Ag}(1)$ and $\text{Ag}(2)$. This indicates that Ag^+ ions at 8-ring site have weak interaction with zeolite framework.

The ionic radius of Ag^+ , 1.26 \AA is much larger than that of Co^{2+} , 0.72 \AA . Smaller Co^{2+} ions prefer 6-ring sites and larger Ag^+ ions prefer 8-ring sites when number of ions per unit cell is more than 8.

During this work, many other Co^{2+} exchanged zeolite A crystals were prepared by the dynamic flow method for more than 7 days. These Co^{2+} ion exchanged crystals do not give any single crystal diffraction pattern. It appears that the exchange limit for $\text{Co}(\text{II})$ into zeolite A is 4.5 bivalent ion per unit cell. If zeolite A has more than 4.5 $\text{Co}(\text{II})$ ions per unit cell, bivalent cation hydrolyze H_2O and the resulted H_3O^+ concentration is accumulating and destroying zeolite structure.

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