

탈수한 Ag^+ 이온과 Ca^{2+} 이온으로 치환한 제올라이트 A, $\text{Ag}_{12-2x}\text{Ca}_x\text{-A}$ ($x=2$ and 3)를 Cs 증기로 처리한 결정구조

宋承煥 · 金 洋[†]

동서공과대학교 화학공학과

[†]부산대학교 자연과학대학 화학과

(1994. 4. 28 접수)

Two Crystal Structures of Dehydrated Ag^+ - and Ca^{2+} -Exchanged Zeolite A, $\text{Ag}_{12-2x}\text{Ca}_x\text{-A}$ ($x=2$ and 3) Treated with Cesium Vapor

Seong Hwan Song and Yang Kim[†]

Department of Chemical Engineering, Dongseo University, Pusan 612-012, Korea

[†]Chemistry Department, Pusan National University, Pusan 609-735, Korea

(Received April 28, 1994)

요 약. Ag^+ 이온과 Ca^{2+} 이온으로 치환된 제올라이트 A($\text{Ag}_{12-2x}\text{Ca}_x\text{-A}$, $x=2$ 및 3)를 탈수하고 250°C , 0.15 torr 의 Cs 증기로 처리한 결정구조를 X-선 단결정 회절법으로 입방공간군 $Pm\bar{3}m$ ($a=12.344(2)$ Å과 12.304(2) Å)을 사용하여 해석하였다. 이들 구조에서 최종 오차인자 값 R_w 는 $I>3\sigma(I)$ 인 180 및 179개의 반사를 이용하여 0.091 및 0.093까지 정밀화시켰다. 이들 구조에서 Cs종은 네 개의 서로 다른 결정학적 자리에 위치하였다. 단위세포당 세 개의 Cs^+ 이온은 8-링 중심에 위치하며, 6.81~7.14개의 Cs^+ 이온은 큰 동공내의 3회 회전축상 6-링상에 위치하고, 1.83~2.03개의 Cs^+ 이온은 소다라이트 동공내의 3회 회전축상에 위치하고, 0.66~0.71개의 Cs^+ 이온은 4-링에 위치하였다. 또한 4.12~4.27개의 Ag 원자는 큰 동공 중심 가까이에 위치하였다. 이들 구조에서 단위세포내에 과잉으로 흡착된 Cs 원자들은 3회 회전축상 위에 놓여 있는 Cs^+ 이온과 결합하여 선형의 $(\text{Cs}_4)^{3+}$ 클러스터를 형성하고 있었다. 또 Cs^+ 이온이 8-링을 차지하고 있어서 은 원자가 구조 밖으로 나오지 못하게 막고 있었다. 이들 원자는 큰 동공 중심에서 hexasilver 클러스터를 형성하고 있었으며, 14개의 Cs^+ 이온과 배위하여 안정화되어 있었다.

ABSTRACT. Two crystal structures of dehydrated, Ag^+ and Ca^{2+} -exchanged zeolite A treated at 250°C with 0.15 torr of Cs vapor have been determined by single-crystal X-ray diffraction technique in the cubic space group $Pm\bar{3}m$ at $21(1)^\circ\text{C}$ ($a=12.344(2)$ Å and $12.304(2)$ Å). Their structures were refined to the final error indices, R (weighted), of 0.091 with 180 reflections, and 0.093 with 179 reflections, respectively, for which $I>3\sigma(I)$. In each structure, Cs species are found at four different crystallographic sites: 3 Cs^+ ions per unit cell are located at 8-ring centers, ca. 6.81~7.14 Cs^+ ions are found on opposite 6-rings on threefold axes in the large cavity, ca. 1.93~2.03 Cs^+ ions are found on threefold axes in the sodalite unit, and 0.53~0.66 Cs^+ ions lie on opposite 4-rings. Also, ca. 4.12~4.27 Ag atoms are located near the center of the large cavity. In these structures, excess cesium atoms in a unit cell are associated with other Cs^+ ions on a single threefold axis to form the linear cationic cluster $(\text{Cs}_4)^{3+}$. By blocking 8-rings, the Cs^+ ions may have prevented silver atoms from migrating out of the structure. The Ag atoms are likely to have formed hexasilver clusters at the centers of the large cavities. Each hexasilver cluster is stabilized by coordination to 14 Cs^+ ions.

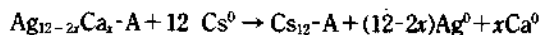
INTRODUCTION

The structures of metal clusters are of great interest because of their pronounced catalytic activity. Ag^+ ions in zeolite A can be reduced by heating,^{1,2} treating with reducing agents,³ or sorbing metal vapors.⁴ Kim and Seff reported earlier that the hexasilver molecule in the sodalite unit of zeolite A is stabilized by coordination to eight silver ions in vacuum-dehydrated fully Ag^+ -exchanged zeolite A.² They also reported that an $(\text{Ag}^+)_6(\text{Ag}_6)$ cluster was found in the sodalite cavity of an ethylene sorption complex of partially decomposed fully Ag^+ -exchanged zeolite.⁵ In the structure of $\text{Ag}_{4.6}\text{Na}_{7.4}\text{-A}$, vacuum dehydrated and treated with H_2 at 350°C , $(\text{Ag}_6)^{3+}$ clusters of low symmetry were found in a large cavity.⁶

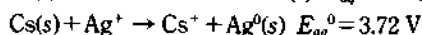
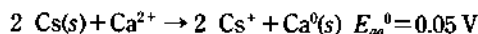
Heo *et al.* studied the crystal structures of fully dehydrated, fully Cs^+ -exchanged zeolite A prepared by the reactions of dehydrated $\text{Ca}_6\text{-A}$, $\text{Co}_4\text{Na}_4\text{-A}$, $\text{Na}_{12}\text{-A}$ and $\text{K}_{12}\text{-A}$ with cesium vapor.^{7,8} They reported that Cs^+ ions were distributed over four crystallographically distinct sites and excess cesium atoms in the unit cell are associated with other Cs^+ ions on a single threefold axis to form the linear cationic cluster $(\text{Cs}_4)^{3+}$. They also found that the reaction of $\text{Ag}_{12}\text{-A}$ treated with 1.0×10^{-4} torr of cesium vapor at 100°C resulted in crystal damage and that some Ag^+ ions were partially reduced by Cs .⁹

Recently, we reported the synthesis of fully Rb^+ -exchanged zeolite A by the reduction of all Na^+ ions of $\text{Na}_{12}\text{-A}$ by rubidium vapor.⁹ This redox reaction goes to completion at 250°C with ca. 0.1 torr of Rb^0 . In this structure, extra Rb atoms are sorbed and associate with Rb^+ ions to form $(\text{Rb}_6)^{4+}$, cationic clusters of symmetry $3mm$ (C_{3v}). We also reported that in the crystal structure of dehydrated $\text{Ag}_2\text{Ca}_5\text{-A}$ ¹⁰ and $\text{Ag}_{3.2}\text{Na}_{3.8}\text{-A}$ ¹¹ treated with 0.1 torr of Cs vapor at 250°C , all the Ca^{2+} and Na^+ ions were reduced by Cs vapor and replaced by Cs^+ ions, but the Ag^+ ions were not.

This work was initiated with the expectation that the intrazeolitic redox potential for the reaction would be positive enough at the conditions employed to result in complete exchange.



The E^0 values, which are not involved with the zeolite, are easily calculated.¹²



The resulting reaction product would be of interest because the volume of exchangeable Cs^+ ions would be large and some extra Cs^0 atoms forming Cs clusters might be present. However, in this experiment, the reduced silver may not be able to diffuse to the surface of the zeolite because of the blockage of the 8-windows by the large Cs^+ ions. By such trapping, some new, perhaps larger clusters might be formed and identified. If hexasilver were to form, its occupancy might be full, which would allow its existence to be confirmed crystallographically. Furthermore, because of the atomic sizes and the high scattering powers of Cs^+ and Ag^+ , precise and reliable crystallographic determinations of structure should be achieved easily.

EXPERIMENTAL

Crystals of sodium zeolite 4A (stoichiometry: $\text{Na}_{12}\text{Si}_{12}\text{Al}_{12}\text{O}_{48} \cdot 27\text{H}_2\text{O}$) were prepared by Charnell's method.¹³ Two crystals of composition $\text{Ag}_6\text{Ca}_2\text{-A}$ (crystal 1) and $\text{Ag}_6\text{Ca}_3\text{-A}$ (crystal 2) were prepared. To do this, exchange solutions of AgNO_3 and $\text{Ca}(\text{NO}_3)_2$ in the mole ratios of 1:35 and 1:75, respectively, with a total concentration of 0.05 M, were used. These ratios were obtained from a previous study of the crystal structures of dehydrated $\text{Ag}_2\text{Ca}_5\text{-A}$ and $\text{Ag}_7\text{Ca}_{2.5}\text{-A}$ which were prepared using exchange solutions in which $\text{AgNO}_3/\text{Ca}(\text{NO}_3)_2$ 1:1000 and 1:50, respectively.¹⁴

Ion exchange was accomplished by allowing the solutions to flow past each crystal at a velocity of approximately 0.5 cm/sec for 4 days. The crystals remained colorless.

Each crystal was placed in a fine Pyrex capillary of 0.08 mm (diameter) on a vacuum line. After complete dehydration at 350°C and 5×10^{-6} torr for 2 days, cesium vapor was introduced to the Pyrex

tube extension of the crystal-containing capillary from a side-arm break-seal ampule. The glass reaction vessel was then sealed off under vacuum and placed in a pair of cylindrical horizontal ovens, axes collinear. The oven around the crystal was always maintained at a higher temperature than that around the cesium metal so that cesium vapor was not distilled onto the crystal.

Each crystal was allowed to react with 0.15 torr of $\text{Cs}(g)$ (the vapor pressure of $\text{Cs}(l)$ at 220°C) at 250°C for 12 hrs, after which it was sealed off from the reaction vessel by using a torch after cooling to room temperature. Microscopic examination showed that all crystals became black.

The space group $Pm\bar{3}m$ (no systematic absences) was used throughout this work for reasons discussed previously.^{15,16} Preliminary crystallographic experiments and subsequent data collection were performed with an Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer, equipped with a graphite monochromator, a pulse-height analyzer, and a PDP micro 11/73 computer. Molybdenum radiation ($K_{\alpha 1}$; $\lambda = 0.70930 \text{ \AA}$, $K_{\alpha 2}$, $\lambda = 0.71359 \text{ \AA}$) was used for all experiments. In each case, the cell constant, $a = 12.344(2) \text{ \AA}$; and $12.303(3) \text{ \AA}$ for crystals 1 and 2, respectively, were determined by a least-squares treatment of 25 intense reflections for which $20^\circ < 2\theta < 30^\circ$. Reflections from two intensity-equivalent regions of reciprocal space (hkl , $0 \leq h \leq k \leq l$; $h\bar{l}k$, $0 \leq h \leq l \leq k$) were examined by using the ω - 2θ scan technique. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, from 0.25 to 0.32 deg min^{-1} in ω . The intensities of three reflections in diverse regions of reciprocal space were recorded after every 3 h to monitor the stability of crystal and X-ray source. Only small random fluctuations of three 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 recorded. The raw data from each region were corrected for Lorentz and polarization effects 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.¹⁷ An absorption correction ($\mu_R = \text{ca. } 0.38 \sim 0.40$) was judged to be negligible.¹⁸ Of the 891 and 881 pairs of reflections for crystals 1 and 2, respectively, only the 180 and 179 pairs, respectively, for which $I > 3\sigma(I)$, were used in subsequent structure determinations.

STRUCTURE DETERMINATION

Dehydrated $\text{Ag}_6\text{Ca}_2\text{-A}$ treated with $\text{Cs}(g)$. Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [$(\text{Si}, \text{Al}), \text{O}(1), \text{O}(2), \text{O}(3)$] and Cs^+ ions at $\text{Cs}(1), \text{Cs}(2),$ and $\text{Cs}(3)$ of $\text{Ag}_2\text{Ca}_5\text{-A}$ ¹⁰ treated with Cs vapor. Anisotropic refinement of the framework atoms and $\text{Cs}(i)$ species, $i = 1-3$, converged to an unweighted R_1 index, $(\sum |F_o - |F_c||) / \sum F_o$, of 0.13 and a weighted R_2 index, $(\sum W(F_o - |F_c|)^2 / \sum W F_o^2)^{1/2}$, of 0.16. Subsequently, the occupancies at $\text{Cs}(1), \text{Cs}(2),$ and $\text{Cs}(3)$ refined to 3.1(1), 7.3(1), and 2.1(1), respectively. A difference Fourier synthesis revealed the positions of Cs^+ ions at $\text{Cs}(4), (0.254, 0.254, 0.5)$, with peak height $3.1(3) \text{ e\AA}^{-3}$, and Ag species at $\text{Ag}(1), (0.332, 0.5, 0.5)$, with peak height $8.7(3) \text{ e\AA}^{-3}$. $\text{Cs}(4)$ was refined with an unusually large isotropic thermal parameter, so it was fixed at the more reasonable value shown in Table 1.

Allowing all occupancies of $\text{Cs}(i), i = 1-4$ and $\text{Ag}(1)$, except that of $\text{Cs}(1)$ which was not permitted to exceed 3.0 (its maximum occupancy by symmetry), and allowing all anisotropic thermal parameters to vary, except for that of $\text{Cs}(4)$ which was refined isotropically, led to $R_1 = 0.101$ and $R_2 = 0.091$ (see Table 1).

The final difference function was featureless except for some residual density ($2.4(6) \text{ e\AA}^{-3}$) at $(0.4434, 0.5, 0.5)$, near $\text{Ag}(1)$, deep in the large cavity.

Dehydrated $\text{Ag}_6\text{Ca}_3\text{-A}$ treated with $\text{Cs}(g)$. Full-matrix least-squares refinement was initiated with the atomic parameters for all atoms and ions in crystal 1. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement, except for that of $\text{Cs}(4)$, which was refined isotropically,

Table 1. Positional, thermal,^a and occupancy parameters of Crystal 1,^b Crystal 2.^c

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	Biso ^d β ₁₁ ^e	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃	Occupancy ^f
Crystal 1											
(Si, Al)	24(<i>k</i>)	0	1839(7)	3720(7)	34(6)	20(6)	5(6)	0	0	0(10)	24 ^g
O(1)	12(<i>h</i>)	0	2240(30)	5000	160(40)	20(20)	30(30)	0	0	0	12
O(2)	12(<i>i</i>)	0	2920(20)	2920(20)	50(30)	30(10)	30(10)	0	0	10(50)	12
O(3)	24(<i>m</i>)	1130(10)	1130(10)	3440(10)	40(10)	40(10)	50(20)	10(30)	10(20)	10(20)	24
Cs(1)	3(<i>c</i>)	0	5000	5000	210(20)	77(6)	77(6)	0	0	0	3
Cs(2)	8(<i>g</i>)	2804(3)	2804(3)	2804(3)	85(2)	85(2)	85(2)	21(6)	21(6)	21(6)	7.14(7)
Cs(3)	8(<i>g</i>)	1044(9)	1044(9)	1044(9)	68(8)	68(8)	68(8)	-20(20)	-20(20)	-20(20)	2.03(7)
Cs(4)	12(<i>j</i>)	2480(60)	2480(60)	5000	8(fixed)						0.50(11)
Ag(1)	6(<i>f</i>)	3460(30)	5000	5000	310(40)	460(30)	460(30)	0	0	0	4.27(11)
Crystal 2											
(Si, Al)	24(<i>k</i>)	0	1832(7)	3723(7)	29(6)	29(6)	14(6)	0	0	20(10)	24
O(1)	12(<i>h</i>)	0	2280(30)	5000	140(40)	60(30)	0(30)	0	0	0	12
O(2)	12(<i>i</i>)	0	2930(20)	2930(20)	20(30)	50(10)	50(10)	0	0	20(50)	12
O(3)	24(<i>m</i>)	1110(10)	1110(10)	3450(20)	50(10)	50(10)	40(20)	0(30)	10(20)	10(20)	24
Cs(1)	3(<i>c</i>)	0	5000	5000	210(20)	75(5)	75(5)	0	0	0	3
Cs(2)	8(<i>g</i>)	2806(3)	2806(3)	2806(3)	81(2)	81(2)	81(2)	21(6)	21(6)	21(6)	6.81(6)
Cs(3)	8(<i>g</i>)	1020(10)	1020(10)	1020(10)	73(9)	73(9)	73(9)	0(20)	0(20)	0(20)	1.93(6)
Cs(4)	12(<i>j</i>)	2700(60)	2700(60)	5000	8(fixed)						0.66(9)
Ag(1)	6(<i>f</i>)	3440(30)	5000	5000	380(50)	510(30)	510(30)	0	0	0	4.12(9)

^aPositional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parenthesis are the esds in the units of the least significant digit given for the corresponding parameter. ^bAg₈Ca₂-A treated with 0.15 torr of Cs vapor at 250°C for 12 hrs. ^cAg₆Ca₃-A treated with 0.15 torr of Cs vapor at 250°C for 12 hrs. ^dIsotropic thermal parameters in units of Å². ^eThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^fOccupancy factors are given as the number of atoms or ions per unit cell. ^gOccupancy for (Si)=12; occupancy for (Al)=12.

converged to $R_1=0.10$ and $R_2=0.10$. Subsequently, the occupancies at Cs(1), Cs(2), Cs(3), Cs(4), and Ag(1) refined to 3.0(1), 6.9(1), 1.8(1), 0.6(1), and 4.1(1), ions or atoms per unit cell, respectively. The occupancy of Cs(1) was fixed at 3.0, its maximum occupancy by symmetry. The final R values converged to $R_1=0.098$ and $R_2=0.093$. The final difference function was featureless except for some residual density (2.8(7) eÅ⁻³) at (0.332, 0.5, 0.5), near Ag(1), deep in the large cavity.

For all structures, 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 $\sigma(F)$, its standard deviation. Atomic scattering factors for Cs⁺, Ag⁻, Ag⁰, O⁻ and (Si, Al)^{1.75+} were used.^{19,20} The function describing (Si, Al)^{1.75+} is the mean of the Si⁰, Si⁴⁺, Al⁰ and Al⁺³ functions. All scattering factors were modified to account for

anomalous dispersion.^{21,22} The final structure parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

DISCUSSION

In the structure of crystals 1 and 2, Cs⁺ ions are found at four different crystallographic sites and Ag species are found at one site. The two structures are similar except for the occupancies at the Cs(2), Cs(3), Cs(4), and Ag(1) positions.

In both structures, three Cs⁺ ions at Cs(1) fill the equipoints of symmetry C_{3h} (D_{3h} in $Pm3m$) at the centers of 8-rings (see Fig. 1). Each Cs(1) ion is ca. 3.37 Å from four O(1) oxygens and ca. 3.62 Å from four O(2)'s (see interatomic distances in Table 2). These distances are substantially longer

Table 2. Selected interatomic distances (Å) and angles (deg) of $\text{Ag}_{12-2x}\text{Ca}_x\text{-A}$ ($x=2$ and 3) treated with Cs vapor

	Crystal 1	Crystal 2
(Si, Al)-O(1)	1.65(1)	1.66(1)
(Si, Al)-O(2)	1.66(2)	1.67(2)
(Si, Al)-O(3)	1.68(1)	1.66(1)
Cs(1)-O(1)	3.41(3)	3.34(3)
Cs(1)-O(2)	3.64(2)	3.60(2)
Cs(2)-O(2)	3.46(1)	3.45(1)
Cs(2)-O(3)	3.03(1)	3.05(2)
Cs(3)-O(2)	3.51(2)	3.56(2)
Cs(3)-O(3)	2.97(2)	3.00(2)
Cs(4)-O(1)	3.08(7)	3.36(7)
Cs(4)-O(3)	3.08(7)	3.36(4)
Ag(1)-O(1)	5.46(4)	5.40(4)
Ag(1)-O(2)	5.61(3)	5.56(3)
Cs(1)-Cs(2)	5.16(1)	5.15(1)
Cs(1)-Cs(4)	4.36(5)	4.36(5)
Cs(1)-Ag(1)	4.27(4)	4.24(4)
Cs(2)-Cs(2)	5.43(1)	5.40(1)
Cs(2)-Cs(3)	3.76(1)	3.81(1)
Cs(2)-Ag(1)	3.91(1)	3.89(1)
Cs(3)-Cs(3)	4.46(1)	4.33(2)
Ag(1)-Ag(1)	2.69(4)	2.71(4)
O(1)-(Si, Al)-O(2)	109(1)	106(1)
O(1)-(Si, Al)-O(3)	110(2)	112(1)
O(2)-(Si, Al)-O(3)	107.5(8)	108.4(7)
O(3)-(Si, Al)-O(3)	111.6(7)	110.6(8)
(Si, Al)-O(1)-(Si, Al)	146(2)	141(2)
(Si, Al)-O(2)-(Si, Al)	163(1)	161(1)
(Si, Al)-O(3)-(Si, Al)	146(1)	147(1)
O(3)-Cs(2)-O(3)	83.6(5)	83.6(5)
O(3)-Cs(3)-O(3)	86.0(3)	85.4(3)
Cs(2)-Cs(3)-Cs(3)	180	180
Ag(1)-Cs(1)-Ag(1)	180	180

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

than the sum of the ionic radii of O^{2-} and Cs^+ , 2.99 Å.²³ Cs^+ ions were observed at this site in all previous studies of Cs^+ in zeolite A, with the similar length of contact distances.^{7,10}

In the large cavity, ca. 6.81~7.14 Cs^+ ions are found opposite 6-rings at Cs(2) (see Table 1 and Fig. 1). In the sodalite unit, ca. 1.93~2.03 Cs's are found opposite 6-rings at Cs(3) (see Fig. 2). The sum of these occupancies on the threefold axes

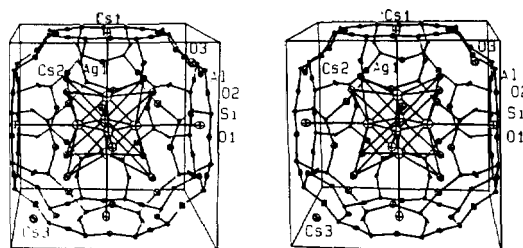


Fig. 1. Stereoview of the large cavity containing an Ag_6 molecule. The octahedral Ag_6 molecule is stabilized by coordination to 6 Cs^+ ions at Cs(1) and 8 Cs^+ ions at Cs(2). Ellipsoids of 20% probability are used.

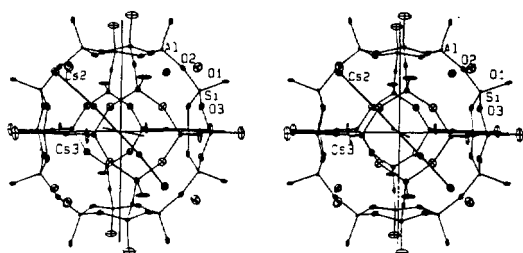


Fig. 2. Stereoview of the sodalite cavity. A $(\text{Cs}_4)^{3+}$ cluster is shown. Ellipsoids of 20% probability are used.

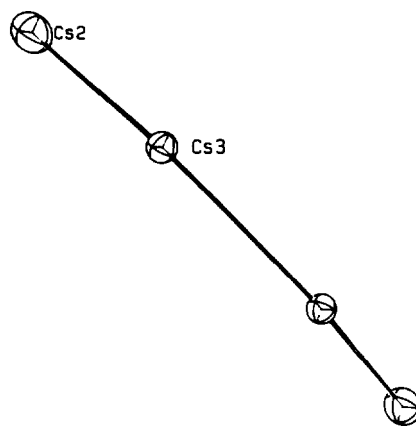


Fig. 3. The $(\text{Cs}_4)^{3+}$ cluster using ellipsoids of 20% probability.

at Cs(2) and Cs(3) are 8.74~9.17. This indicates that more than the usual limit of eight 6-ring cations per unit cell are found. If the Cs species at Cs(2) and Cs(3) are all ions, this sum should not exceed eight; otherwise an unacceptably short

Table 3. Deviations of atoms (Å) from (111) Plane at O(3) of $\text{Ag}_{12-2x}\text{Ca}_x\text{-A}$ ($x=2$ and 3) treated with Cs vapor^a

	Crystal 1	Crystal 2
Cs(2)	1.937(2)	1.949(2)
Cs(3)	-1.828(7)	-1.865(7)
Cs(4)	3.043(42)	3.360(41)
Ag(1)	5.531(21)	5.521(21)

^aA negative deviation indicates that the atom lies on the same side of the plane as the origin.

distance (3.78 Å) between Cs(2) and Cs(3) would exist. By difference, therefore, at least 0.64~1.71 of these very close Cs(2)-Cs(3) contact distances must exist per unit cell (see Fig. 3). The fractional occupancies observed at Cs(2), Cs(3), and Cs(4) are explained by proposing that 2 types of unit cells exist in the case of crystal 1. About 60% of unit cells in the crystal may have 8 ions at Cs(2) and 2 ions at Cs(3). All eight threefold-axis sites in the large cavity are occupied Cs⁻ ions at Cs(2). About 40% of unit cells may have 6 ions at Cs(2) and 2 ions at Cs(3), and 1 ions at Cs(4). The fractional occupancies observed at Cs(2), Cs(3), and Cs(4) in crystal 2 also indicate the presence of two types of "unit cells" with respect to the cations (see Table 4).

In crystal 1, the eight Cs⁺ ions at Cs(2) in about 60% of the unit cells are better associated with sodalite units containing the Cs(3), to allow further electron delocalization. It follows that this sodalite unit has, associated with its 6-ring, ten (2+8) Cs species, nine of which may be counted as Cs⁺ (to balance framework charge) and one as Cs⁰. An electrons from one Cs⁰s per sodalite unit must be delocalized over the shortest Cs-Cs contacts in the structure, those among the two Cs(3)'s in the sodalite cavity and the two Cs(2)'s nearest to these Cs(3)'s, to give the (Cs₄)³⁺ cluster shown in Fig. 3 and 4. The intercesium distances for the (Cs₄)³⁺ cluster are ca. 3.78 Å, 4.39 Å, and 3.78 Å for Cs(2)-Cs(3), Cs(3)-Cs(3), and Cs(3)-Cs(2), respectively, which are similar to the corresponding distances obtained from previous studies (see Fig. 3).^{7,10}

Each ion at Cs(2) is ca. 3.04 Å from the three

Table 4. Inferred unit cell compositions for Crystals 1 and 2

Positions of cations and atoms	Crystal 1		Crystal 2	
	60%	40%	40%	60%
8-ring, Cs(1)	3	3	3	3
6-ring, Cs(2)	8	6	8	6
6-ring, Cs(3)	2	2	2	2
Opposite 4-rings, Cs(4)	0	1	0	1

O(3) oxygens of its 6-ring and ca. 1.93 Å from the (111) plane at O(3). Each partially reduced ion at Cs(3) is somewhat further recessed inside the sodalite unit, ca. 2.99 Å from three O(3) oxygens and ca. 1.86 Å from its (111) plane (see Table 3).

The sums of the Cs(*i*), *i*=1~4, and Ag(1) occupancies in crystals 1 and 2 (see Table 1) are 16.94 and 16.52, respectively. The unit cells clearly contain more metal species than the approximately 12 monovalent cations which are required to balance the anionic charge of the zeolite framework, which are variously estimated to be -11.75²⁴ to -12¹⁶ per 12.248 Å unit cell. Therefore, about five metal atoms must exist per unit cell. These may be present as isolated atoms or neutral clusters, or they may associate with cations to form cationic clusters.

About 4.2 Ag atoms at Ag(1), the products of the reduction of Ag⁺ by Cs⁰, are located near the center of the large cavity. The distance between Ag(1) and its nearest framework oxygens, four at O(1), is very much longer (Ag(1)-O(1)=ca. 5.43 Å) than the sum of the corresponding ionic radii, 2.58 Å.²³ This indicates that the species at Ag(1) must be not Ag⁺ but Ag⁰. The shortest Ag(1)-Ag(1) distance, ca. 2.70(6) Å, is far too short to be an unmoderated Ag⁺-Ag⁺ contact distance. This Ag(1)-Ag(1) distance is close to the Ag-Ag distance in silver metal, 2.89 Å.²⁵ This short distance was also found in previous work on the crystal structures of dehydrated Ag⁺- and Ca²⁺-exchanged zeolite A treated with Rb vapor.²⁶ Ag species at Ag(1) are likely to have formed hexasilver clusters at the centers of the large cavity as seen in the previous work.¹⁰ If the Ag(1) equipoint is filled in a fraction of the

large cavities, as is sensible to infer but not proven solely by these crystallographic results, closest-packed clusters of six silver atoms would exist at the centers of about 70% of the large cavities. The hexasilver molecule would be octahedral and would show the full symmetry of its site, O_h , at the center of the large cavity (Fig. 1). The relatively large thermal ellipsoids of the atoms at Ag(1) indicate that the hexasilver cluster is loosely held. It is stabilized by association with 8 Cs^+ ions at Cs(2) and 6 Cs^+ ions at Cs(1) $\text{Cs(1)-Ag(1)}=4.25(4)$ Å and $\text{Cs(2)-Ag(1)}=3.90(1)$ Å (see Fig. 2).

To summarize, cesium vapor reacted with dehydrated $\text{Ag}_{12-2x}\text{Ca}_x\text{-A}$ ($x=2$ and 3) to performed solvent-free redox ion exchange. Hexasilver clusters stabilized by coordination to Cs^+ ions formed in the large cavity. Excess Cs atoms are sorbed to form clusters such as $(\text{Cs}_6)^{3+}$. It appears that zeolites exposed to Cs metal vapor readily absorb extra metal atoms into their cavities to form cationic Cs clusters.

Recently the crystal structure of dehydrated $\text{Ag}_2\text{Ca}_5\text{-A}^{10}$ and $\text{Ag}_{32}\text{Na}_{88}\text{-A}^{11}$ zeolite A treated with 0.1 torr of cesium vapor at 250°C was studied. In this crystal, the Ag^+ ions were not reduced by Cs vapor; only Ca^{2+} and Na^+ ions were reacted and reduced. However, in the present work, the redox reaction was conducted under higher Cs vapor pressure (0.15 torr) than in previous work (0.1 torr). All Ag^+ ions and Ca^{2+} ions were reduced and replaced by Cs^+ ions. The Ca metal produced was only on the single crystal surface, not within the crystal structures. This suggests that the previously incomplete reactions may have resulted from the very low vapor pressure of cesium metal.

ACKNOWLEDGMENT

This paper was supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1993.

REFERENCES

- Kim, Y.; Seff, K. *J. Am. Chem. Soc.* **1977**, *99*, 7055.
- Kim, Y.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 6989.
- Kim, Y.; Seff, K. *Bull. Korean Chem. Soc.* **1984**, *5*, 135.
- McCusker, L. B. Ph. D. Thesis, University of Hawaii, 1990.
- Kim, Y.; Seff, K. *J. Am. Chem. Soc.* **1978**, *100*, 175.
- Kim, Y.; Seff, K. *J. Phys. Chem.* **1987**, *91*, 668.
- Heo, N. H.; Seff, K. *J. Am. Chem. Soc.* **1987**, *109*, 7986.
- Heo, N. H. Ph. D. Thesis, University of Hawaii, 1987.
- Song, S. H.; Kim, Y.; Seff, K. *J. Phys. Chem.* **1992**, *96*, 10937.
- Song, S. H.; Kim, Y.; Seff, K. *J. Phys. Chem.* **1990**, *94*, 5959.
- Kim, D. S.; Song, S. H.; Kim, Y. *Bull. Korean Chem. Soc.* **1989**, *10*, 234.
- Handbook of Chemistry and Physics*, 70th Ed.; The Chemical Rubber Co.: Cleveland, 1989/1990, p D 157-158.
- Charnell, J. F. *J. Cryst. Growth* **1971**, *8*, 192.
- Song, S. H.; Park, J. Y.; Kim, U. S.; Kim, Y. *J. Korean Chem. Soc.* **1989**, *33*, 452.
- Seff, K. *Acc. Chem. Res.* **1978**, *9*, 121.
- Seff, K.; Mellum, M. D. *J. Phys. Chem.* **1984**, *88*, 3560.
- Principal computer programs used in this study were "Structure Determination Package Programs" written by Frentz, B. A.; Okaya, Y. These programs were supplied by Enraf-Nonius, Netherlands, 1987.
- International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. II, p 132.
- Doyle, P. A.; Turner, P. S. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 390.
- Reference 18, Vol. IV, p 73-87.
- Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
- Reference 18, Vol. IV, p 149-150.
- Reference 12, p F187.
- Blackwell, C. S.; Pluth, J. J.; Smith, J. V. *J. Phys. Chem.* **1985**, *89*, 4420.
- Reference 12, p F189.
- Song, S. H.; Kim, Y.; Seff, K. *J. Phys. Chem.* **1991**, *95*, 9919.