

# Crystal Structure of Dehydrated $\text{Ag}_{7.5}\text{Ti}_{4.5}-\text{A}$

*Kim Duk-soo\* and Han Sung-bin\*\**

탈수된  $\text{Ag}_{7.5}\text{Ti}_{4.5}-\text{A}$ 의 결정 구조

金德洙\* · 韓性彬\*\*

## Summary

The crystal structure of dehydrated  $\text{Ag}_{7.5}\text{Ti}_{4.5}-\text{A}$  has been determined by single-crystal X-ray diffraction techniques. This structure was solved and refined in the cubic space group  $Pm\bar{3}m$  at 21(1) °C. The crystal was ion exchanged in flowing streams of mixed  $\text{AgNO}_3$  and  $\text{TINO}_3$  aqueous solution, followed by dehydration at 360°C and  $2 \times 10^{-4}$  Torr for 2 days. In this structure, one-sixth of the sodalite units contain octahedral hexasilver clusters at their centers and eight  $\text{Ag}^+$  ions are found on threefold axes, each nearly at the center of a 6-oxygen ring. The hexasilver cluster is stabilized by coordination to eight  $\text{Ag}^+$  ions. The  $\text{Ag}-\text{Ag}$  distance in the cluster, 2.82(2) Å is near the 2.89 Å bond length in silver metal. The remaining five-sixths of the sodalite units are empty of silver species. The first three  $\text{Ti}^{IV}$  ions per unit cell preferentially associate with 8-oxygen rings.

---

\* 自然科學大學 專任講師

\*\* 自然科學大學 副教授

\*\*\* 본 연구는 1988년도 학술연구비 지원에 의해 수행되었음.

## Introduction

The open framework of crystalline molecular sieve zeolites allow ready exchange of numerous cations and the sorption of variety of small molecules. The catalytic and selective sorptive properties of zeolites rely upon the structures of these molecular sieves. These structures are variously changed by exchanged cations. A knowledge of the position of these cations within a zeolite framework can provide a structural basis for understanding those properties. Thus far, the structures of various cation exchanged zeolite A have been determined crystallographically.

Numerous investigation have been reported that various types of silver clusters are located in dehydrated fully and partially silver ion exchanged zeolite A, Y, mordenite, and chabazite.  $\text{Ag}^+$  ions can be reduced by heating (Kim and Seff, 1978, Kim et al, 1988), by reaction with reducing agents such as  $\text{H}_2$ , alcohol, and alkylbenzenes, or by the sorption of metal atoms. The existence of these silver clusters was identified and reconfirmed by many workers.

This work has been initiated to investigate the cation positions in the crystal structure of  $\text{Ag}^+$  and  $\text{Tl}^+$  exchanged zeolite A. It would be interesting to learn how different numbers of exchanged  $\text{Tl}^+$  ions arrange themselves in the zeolite framework. This work is preliminary to later studies of the crystal structure of  $\text{Ag}_{12-x}\text{Tl}_x\text{-A}$  treated with  $\text{H}_2$  or other guest molecules.

## Experimental

Crystals of zeolite 4A were prepared by Charnell's method (Charnell, 1971). A single crystal (0.08mm on an edge) was lodged in a fine glass capillary.

Crystal of  $\text{Ag}_{7.5}\text{Tl}_{4.5}\text{-A}$  were prepared using exchange solution in which mole ratio of  $\text{AgNO}_3$  and  $\text{TlNO}_3$  was 1 : 2.6 with a total concentration of 0.05M.

Ion exchange was accomplished allowing the solution to flow past crystal at a velocity of approximately 1.0cm/sec for 2 days at 23(1) °C. The crystal was evacuated at 360°C and  $P = 2 \times 10^{-4}$  torr for 2 days. After cooling to room temperature, the crystal, still under vacuum was sealed in its capillary by a torch.

Diffraction intensities were subsequently collected at 21(1)°C. The space group  $Pm\bar{3}m$  (no systematic absences) was used throughout this work for reasons discussed previously. An Enraf-Nonius 4-circle computer controlled CAD-4 diffractometer, equipped with scintillation counter, pulse-height analyzer, a PDP micro 11/73 computer, and a graphite monochromator was used. Molybdenum radiation ( $K_{\alpha 1}$ ,  $\lambda = 0.70930 \text{ \AA}$ ;  $K_{\alpha 2}$ ,  $\lambda = 0.71359 \text{ \AA}$ ) was used for experiment. The unit cell constant as determined by a least-squares refinement of 2 $\theta$  intense reflections for which  $18^\circ < 2\theta < 24^\circ$ , are 12,256(2) Å

Reflections from two intensity-equivalent regions of reciprocal space ( $hk\ell$ ,  $h\leq k \leq \ell$ , and  $\ell hk$ ,  $\ell \leq h \leq k$ ) were examined using the  $\omega$ -2 $\theta$  scan technique. The data were collected using variable scan speeds. The maximum final scan speed was 5 minutes per one reflection. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 100 reflections to mon-

itor crystal and instrument stability. 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 deviation were assigned to each average reflection by the computer programs, PAINT and WEIGHT (SDP, 1987). Of the 714 pairs of reflections, only 314 pairs, for which  $I > 3\sigma(I)$ , were used in subsequent structure determinations.

## Structure Determination

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

The initial structural parameters used in least-squares refinement were the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] in  $\text{Ag}_x\text{Na}_y\text{-A}$ . Anisotropic refinement of the framework atoms averaged to an  $R_1$  index,  $(\sum |F_o - |F_c|| / \sum F_o)$ , of 0.426 and a weighted  $R_2$  index,  $(\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2}$  of 0.483. A difference Fourier synthesis revealed large and distinct peaks at (0.1934, 0.1934, 0.1934) with a height of  $14.35(3)\text{e}\text{\AA}^{-3}$ , (0, 0, 0.4434, 0.4709) with a height of  $9.13(2)\text{e}\text{\AA}^{-3}$ , and (0.01, 0.0, 0.166) with a height of  $4.52(3)\text{e}\text{\AA}^{-3}$ . Anisotropic refinement including these Ag(1), Ti(2), and Ag(3) positions, respectively, converged to  $R_1=0.201$  and  $R_2=0.253$ . A subsequent difference synthesis revealed two peaks at (0.25, 0.25, 0.25) and (0.1387, 0.1387, 0.1387) with heights of  $9.03(3)\text{e}\text{\AA}^{-3}$  and  $3.87(2)\text{e}\text{\AA}^{-3}$ , respectively. These were stable in least-squares refinement and anisotropic refinement including these

positions, as Ti(1) and Ag(2), respectively, converged to  $R_1=0.053$  and  $R_2=0.074$ .

It is easy to distinguish  $\text{Ag}^+$  from  $\text{Ti}^+$  ions for several reasons. First, their atomic scattering factors are quite different,  $46e^-$  for  $\text{Ag}^+$  vs  $80e^-$   $\text{Ti}^+$ . Secondly, their ionic radii are different,  $\text{Ag}^+=1.26\text{\AA}$  and  $\text{Ti}^+=1.47\text{\AA}$  (Chemical Rubber Co., 1974). Also, the approach distances between those ions and zeolite oxygens in dehydrated  $\text{Ti}_{12}\text{-A}$  and partially decomposed  $\text{Ag}_{12}\text{-A}$  have been determined and are indicative. Finally, the requirement that 12 metal atoms or ions be found limits the assignment of ionic identities.

The occupancies of these ions per unit cell refined to  $\text{Ag}(1)=5.7(1)$ ,  $\text{Ag}(2)=1.1(1)$ ,  $\text{Ag}(3)=0.7(1)$ ,  $\text{Ti}(1)=1.4(1)$ , and  $\text{Ti}(2)=2.9(2)$ . 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 three 8-ring sites are also filled when cations are found more than 11 per unit cell.

The ions at the Ag(1), Ag(2), and Ti(1) sites are associated with 6-rings and lie on threefold-axes and their occupancy have been fixed as 5.5, 1, and 1.5, respectively. The maximum number of ions per unit cell at those positions is 8. The ions at Ti(2) are associated with 8-rings and their occupancies have been fixed as 3.0 because these 8-ring can accommodate no more than three  $\text{Ti}^+$  ions per unit cell. To allow the occupancies to sum to 12, the occupancy, at Ag(3) was fixed as 1. The final refinement using anisotropic thermal parameters for all atoms yield  $R_1=0.057$  and  $R_2=0.080$ .

A final difference Fourier synthesis was

Table 1. <sup>a</sup>Positional, Thermal, and Occupancy Parameters of Dehydrated Ag<sub>7.5</sub>Tl<sub>4.5</sub>-A

Atom	Wyc. Posi.	x	y	z	<sup>b</sup> $\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	<sup>c</sup> Occupancy varied fixed	
(Si, Al)	24(k)	0	1830(2)	2689(2)	16(2)	21(2)	15(2)	0	0	4(3)		24.0
O(1)	12(h)	0	2120(10)	0.5	40(8)	90(10)	11(7)	0	0	0		12.0
O(2)	12(i)	0	2971(6)	2971(6)	41(8)	23(4)	23(4)	0	0	10(10)		12.0
O(3)	24(m)	1112(5)	1112(5)	3331(6)	37(4)	37(4)	37(6)	0(1)	15(7)	15(7)		24.0
Ag(1)	8(g)	1904(2)	1904(2)	1904(2)	57(1)	57(1)	57(1)	77(2)	77(2)	77(2)	5.7(1)	5.5
Ag(2)	8(g)	1370(30)	1370(30)	1370(30)	302(7)	302(7)	302(7)	550(20)	550(20)	550(20)	1.1(1)	1.0
Ag(3)	6(e)	0	0	1630(10)	97(9)	97(9)	50(10)	0	0	0	0.6(1)	1.0
Tl(1)	8(g)	2580(3)	2580(3)	2580(3)	60(2)	60(2)	60(2)	9(4)	9(4)	9(4)	1.4(1)	1.5
Tl(2)		0	4387(3)	4711(3)	137(4)	39(3)	58(5)	0	0	-13(5)	2.9(2)	3.0

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

Table 2. Selected interatomic distances (Å) and angles (deg)

(Si, Al)-O(1)	1.646(5)	O(1)-(Si, Al)-O(3)	111.6(4)
(Si, Al)-O(2)	1.653(5)	O(2)-(Si, Al)-O(3)	107.8(2)
(Si, Al)-O(3)	1.681(5)	O(3)-(Si, Al)-O(3)	108.3(3)
Ag(1)-O(3)	2.223(7)	(Si, Al)-O(1)-(Si, Al)	154.9(9)
Ag(2)-O(3)	2.441(9)	(Si, Al)-O(2)-(Si, Al)	154.3(4)
Tl(1)-O(3)	2.706(5)	(Si, Al)-O(3)-(Si, Al)	141.3(4)
Ag(3)-O(3)	2.84(1)	O(3)-Ag(1)-O(3)	119.8(2)
Tl(2)-O(1)	2.80(1)	O(3)-Ag(3)-O(3)	57.3(3)
Tl(2)-O(2)	2.75(7)	O(1)-Tl(2)-O(1)	110.6(1)
Ag(1)-Ag(3)	3.317(2)	O(1)-Tl(2)-O(2)	52.4(2)
Ag(3)-Ag(3)	2.82(2)	O(3)-Ag(2)-O(3)	104.0(9)
		O(3)-Tl(1)-O(3)	90.6(2)
		Ag(1)-Ag(3)-Ag(1)	89.40(6)
		O(1)-(Si, Al)-O(2)	109.6(6)

Numbers in parentheses are estimated standard deviations in the units of the last significant digit given for the corresponding value.

Table 3. Deviations of atoms ( $\text{\AA}$ ) from the (111) plane at 0(3)

Ag (1)	0.11(1)
Ag (2)	-1.014(19)

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

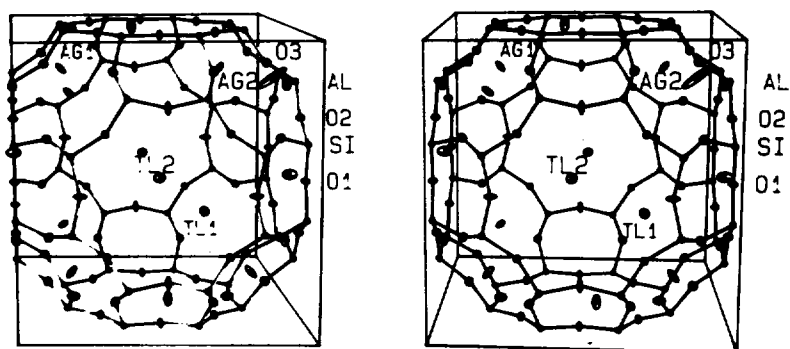


Figure 1. A stereoview of the large cavity of dehydrated  $\text{Ag}_{7.5}\text{Ti}_{4.5}-\text{A}$  is shown with ellipsoids of 20% probability.

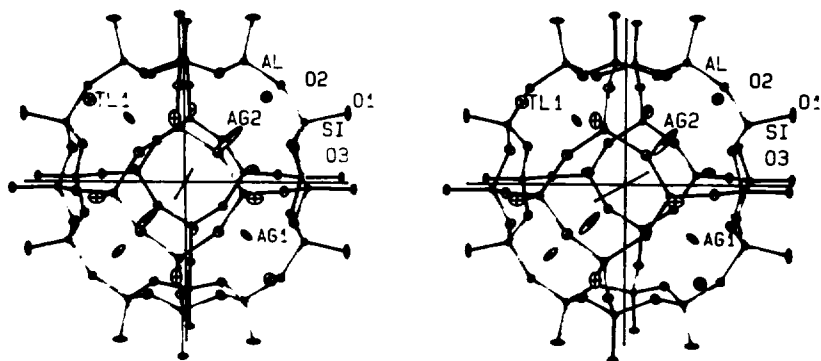


Figure 2. A stereoview of the sodalite unit of the dehydrated  $\text{Ag}_{7.5}\text{Ti}_{4.5}-\text{A}$  is shown 50% of unit cells may have this arrangements.

featureless except one small peak with height of  $1.12(2)e\text{\AA}^{-3}$  at (0.5, 0.5, 0.5). The final structural parameters are presented in Table 1. Interatomic distances and angles are given in Table 2.

The full-matrix least-squares program used in all structure determination minimized  $\sum w(F_o - F_c)^2$ ; the weight ( $w$ ) of an observation was the reciprocal square of  $\sigma(F_o)$  its standard deviation. Atomic scattering factors (Kynoch Press, 1974) for  $\text{Ag}^+$ ,  $\text{Ag}^0$ ,  $\text{O}^-$ ,  $\text{Tl}^+$ , and  $(\text{Si}, \text{Al})^{1.75+}$  were used. The function describing  $(\text{Si}, \text{Al})^{1.75+}$  is the mean of the  $\text{Si}^+$ ,  $\text{Si}^0$ ,  $\text{Al}^+$ , and  $\text{Al}^0$  functions. All scattering factors were modified to account for the real component ( $\Delta f'$ ) of the anomalous dispersion correction.

See Table 1, 2, and 3 for additional information.

## Discussion

$\text{Tl}^+$  ions are found at two crystallographic sites, as presented in Table 1. In this structure, three  $\text{Tl}^+$  ions at Tl(2) are associated with 8-oxygen rings, but not at their centers in order to make favorable approaches to the framework oxygens. The Tl(2)-O(2) distance is 2.75(7) Å and Tl(2)-O(1) is 2.80(1) Å (see Table 2).

The  $\text{Tl}^+$  ions at Tl(1) occupy threefold-axis positions near 6-rings and the Tl(1)-O(3) distance is 2.706(5) Å (see Table 2 and Fig. 1).

The silver species at Ag(1) are located near framework oxygens and may be considered to be  $\text{Ag}^+$  ions. All Ag(1) is associated with a six-ring and approaches three O(3) oxygens at 2.223(7) Å. As

compared to the sum of the  $\text{Ag}^+$  and  $\text{O}^-$  radii is 2.58 Å, this bond is quite short and therefore quite covalent. Each  $\text{Ag}^+$  ion at Ag(1) is trigonally coordinated to its respective set of three O(3) framework oxygens.

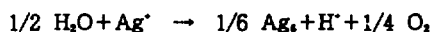
The silver species at Ag(2) are also located on threefold axes. These ions lie relatively far inside the sodalite cavity from the (111) plane at O(3) (see Table 3) and are also trigonally coordinated to their respective sets of three O(3) framework oxygens. The distance between Ag(2) and the nearest framework oxygens at O(3), 2.441(9) Å (see Table 2), indicates that the species at Ag(2) are ions,  $\text{Ag}^+$ .

The Ag(3) position is very similar to that of the neutral silver atoms in the structure of dehydrated  $\text{Ag}_{12}\text{-A}$ . The distance between Ag(3) and its nearest framework oxygens, again O(3), is much longer, 2.84(1) Å (see Table 2). This indicates that the silver species at Ag(3) are reduced silver atoms,  $\text{Ag}^0$ .

The Ag(1)-Ag(3) distance is 3.317(2) Å and this distance is too short to be an unmoderated  $\text{Ag}^+ - \text{Ag}^+$  contact, and too long to be a  $\text{Ag}^+ - \text{Ag}^0$  bond. This is consistent with conclusion that Ag(1) contains silver ions and Ag(3) silver atoms.

The distance between Ag(3) and Ag(3), 2.82(2) Å (see Table 2), is nearly equal to the  $\text{Ag}^0 - \text{Ag}^0$  distance, 2.89 Å, found in silver metal, and in the  $(\text{Ag}^+)_6(\text{Ag}^0)_6$  cluster. Accordingly and consistent with previous conclusion, the silver species at Ag(3) is a neutral silver atom,  $\text{Ag}^0$ .

The reduction of  $\text{Ag}^+$  to  $\text{Ag}^0$  per unit cell proceeds by following reaction:



This reduced Ag atom would have formed by

autoreduction during the dehydration process. It is likely that a neutral  $Ag_6$  cluster has formed in 1/6 of the sodalite units; the remaining 5/6 are empty of silver species. This six atom cluster, subsequently verified by esr work is stabilized by coordination to 8  $Ag^+$  ions near the centers of 6-rings, and may therefore be viewed as a  $(Ag_6)_8^+$  cluster.

The ionic radius of  $Ti^{IV}$ , 1.47 Å, is larger

than that of  $Ag^+$ , 1.26 Å. From a consideration of ionic radii, one would expect the larger  $Ti^{IV}$  ions to associate with the larger rings, the 8-ring. This consideration is affirmed by the present study.

Only the one  $Ag^+$  ion per unit cell which is located at the least favorable position is reduced. The neutral silver atoms produce probably from an  $Ag$  cluster in a fraction of the sodalite cages.

## References

- Charnell, J. F. 1971. Gel Growth of Large Crystals of Sodium A and Sodium X Zeolites, *J. Cryst. Growth*, 8, 291-294.
- Chemical Rubber Co., 1974. Handbook of Chemistry and Physics, 55th ed. pF-198. Cleveland, Ohio.
- Kim, D. S., Song, S. H., and Kim, Y. 1988. Four Crystal Structures of Dehydrated  $Ag^+$  and  $Ti^{IV}$  Exchanged Zeolite A,  $Ag_{12-x}Ti_x-A$ ,  $x=2, 3, 4$ , and 5, *Bull. Korean Chem. Soc.*, 9, 303-308.
- Kim, Y., Seff, K. 1978. The Octahedral Hexasilver Molecule. Seven Crystal Structures of Various Vacuum-Dehydrated Fully  $Ag^+$ -Exchanged Zeolite A, *J. Am. Soc.*, 100, 6989-6997.
- Kynoch Press, 1974. International Tables for X-ray Crystallography, Vol. IV, 73-87, Birmingham, England.
- Principal computer programs used in this study was "Structure Determination Package" supplied from the Enraf-Nonius, Netherland, 1987.

### <摘要>

### 탈수된 $Ag_{7.5}Ti_{4.5}-A$ 의 결정 구조

X-선 단결정법으로 탈수된  $Ag_{7.5}Ti_{4.5}-A$  ( $a=12.252(2)$  Å)의 구조를 입방공간군  $pm3m$ 을 사용하여 해석하였으며  $D_{3h}(I)$ 인 최결반점 314개를 이용하여  $R_1=0.053$ ,  $R_2=0.074$ 까지 정밀화시켰다. 이 구조에서 단위세포당 하나의 은 원자가 소다라이트 동공내에 있으며 이 환원된 은 원자는 소다라이트 동공 1/6개 마다  $Ag_6$ 로 존재하며 8개의  $Ag^+$  이온에 의해 배위되어 안정화되었다. 나머지 5/6개의 소다라이트 동공에는 환원된 은이 존재하지 않았다. 이온의 크기가 큰  $Ti^{IV}$  이온은 크기가 더 큰 8-링에 우선적으로 위치한다.