칼슘 및 탈륨 이온으로 치환된 제올라이트 A, Ca_xTl_{12-2x}-A ($x=1.4$ 및 5.6)를 탈수한 결정구조

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Two Crystal Structures of Dehydrated Ca^{2+}- and Tl^+-Exchanged Zeolite A, Ca_xTl_{12-2x}-A ($x=1.4$ and 5.6)

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요 약. Ca(II)와 Tl(I)으로 교환되고 완전히 진공 탈수된 2개의 제올라이트 A 결정 즉, $Ca_{5.6}Tl_{0.8}$-A($a=$ 12.242(2) Å)와 $Ca_{1.4}Tl_{9.2}$-A($a=12.191(1)$ Å)의 구조를 21(1) ℃에서 입방공간군 $Pm3m$을 사용하여 X-선 단결정 회절법으로 해석하였다. 이들 두 결정은 총농도를 $0.05M$로 한 $Ca(NO_3)_2$와 $TlNO_3$ 혼합용액을 사용하여 흐름법으로 이온교환하여 만들었고 탈수는 360℃ 및 $2×10^{-6}$torr에서 2일간 행하였다. $Ca_{5.6}Tl_{0.8}$-A 구조에서는 $I>3\sigma(I)$인 회절점 179개를 사용하여 $R_1=0.072$와 $R_2=0.076$까지, $Ca_{1.4}Tl_{9.2}$-A 구조에서는 $I>3\sigma(I)$인 회절점 226개를 사용하여 $R_1=0.048$와 $R_2=0.043$까지 정밀화시켰다. 두 구조에서 Ca(II) 이온은 3개의 6-링 산소와 결합하면서 3회 회전축 상에 위치하였다. 단위세포당 교환된 양이온의 총수가 8개 이상이면 Ca^{2+} 이온은 6-링 자리에, Tl^+ 이온은 8-링 자리에 우선적으로 위치한다.

ABSTRACT. Two crystal structures of fully dehydrated Ca(II) and Tl(I) exchanged zeolite A, $Ca_{5.6}Tl_{0.8}$-A ($a=12.242(2)$ Å) and $Ca_{1.4}Tl_{9.2}$-A ($a=12.191(1)$ Å), have been determined by single-crystal X-ray diffraction methods in the cubic space group $Pm3m$ at 21(1)°C. All crystals were ion exchanged in flowing streams of mixed $Ca(NO_3)_2$ and $TlNO_3$ aqueous solution with total concentration of $0.05M$. All crystals were dehydrated at 360°C under $2×10^{-6}$ torr for two days. The structures of the dehydrated $Ca_{5.6}Tl_{0.8}$-A and $Ca_{1.4}Tl_{9.2}$-A were refined to the final error indicies, $R_1=0.072$ and $R_2=0.076$ with 179 reflections for $I>3\sigma(I)$, and $R_1=0.048$ and $R_2=0.043$ with 226 reflections for $I>3\sigma(I)$, respectively. In each structure, Ca(II) ions are located on threefold axes associated with three 6-ring oxygens. Ca^{2-} ions prefer to 6-ring sites and Tl^+ ions prefer to 8-ring sites when total number of exchanged cations per unit cell is more than 8.

INTRODUCTION

The selective sorption and catalytic properties of zeolites rely heavily upon the kinds of cations, their numbers, and their positions within the lattice. A knowledge about siting of these cations within zeolite framework can provide a structural basis for understanding these properties.

12 Na^+ ions of zeolite 4A with stoichiometry

of $Na_{12}Al_{12}Si_{12}O_{48} \cdot 27H_2O$ per unit cell may be easily exchanged. The exchangeable cations in zeolite A can occupy a site near the center of the 6-ring (β-site), that of the 8-ring (α-site), and that of the 4-ring (γ-site)[1,2]. The site selectivities of various cations have been extensively studied[3~10].

In the crystal structure of dehydrated fully Ca (II)-exchanged zeolite A[2], Ca_6-A[11,12], six Ca^{2+} ions occupy 6-ring sites; the 8-ring and 4-ring sites are empty. This occurs because the ionic radius of Ca^{2-} is relatively small and the 6-ring sites are the most stable positions.

Up to present, no structural studies of mixed cation system of Ca^{2+} and Tl^+ ion exchanged zeolite A have been reported. The site selectivities for these two ions of substantially different size and charge would be studied. Zeolite A containing relatively small and highly charged cations such as Ca^{2+}, and with 8-rings blocked by Tl^- ions, might be useful for the storage of small molecules such as H_2.[13] A detail knowledge of the structure of Ca^{2+} and Tl^+ exchanged zeolite A could be more interesting because this can provide information on the pore size of 8-ring and sorption properties of guest molecules. The present work is preliminary to later studies of the crystal structures of Ca_xTl_{12-2x}-A ($0<x<6$) treated with H_2 or other guest molecules.

EXPERIMENTAL

Crystals of zeolite 4A were prepared by Charnell's method[14]. Two single crystals, about 0.08 mm on an edge were lodged in fine capillaries. To prepare Ca^{2-} and Tl^+ ion exchanged zeolite A crystals, mixed exchange solutions of $Ca(NO_3)_2$ and $TlNO_3$ with a total cocentration of $0.05\,M$ were used. The exchange was then performed by flow methods using exchange solutions in which mole ratios of $TlNO_3$ and $Ca(NO_3)_2$ were $1:100$ and $1:1$, respectively.

For all crystals, the solution was allowed to flow past the crystal at a velocity of approximately 1.0 cm/sec for two days at 24(1)°C. Each crystal was evacuated at 360°C under 2×10^{-6} torr for 48 hours. After cooling to room temperature, each

crystal, still under vacuum, was sealed in its capillary by torch. Subsequent diffraction experiments were performed at 21(1)°C. The cubic space group $Pm3m$ (no systematic absences) was used for reasons discussed previously[15~17]. Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four circle Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Mo $K\alpha$ 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 $18°<2\theta<24°$ are 12.242(2) Å and 12.191(1) Å for $Ca_{5.6}Tl_{0.8}$-A and $Ca_{1.4}Tl_{9.2}$-A, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h\leq k\leq l$ and lkh, $l\leq k\leq h$) were examined using the ω-2θ scan technique. The data were collected by using variable scan speeds. 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 fluctuations of these check reflections were noted during the course of data collection. For eah region of reciprocal space, the intensities of all lattice points for which $2\theta<70°$ were collected.

The raw data for each crystal were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization; the resultant estimated standard deviations were assinged to each reflection by the computer program WEIGHT[28]. An absorption correction ($\mu R=0.11$ and $\rho_{cal}=1.644$ g/cm^3 for the crystal of $Ca_{5.6}Tl_{0.8}$-A and $\mu R=0.89$ and $\rho_{cal}=3.084$ g/cm^3 for the crystal for $Ca_{1.4}Tl_{9.2}$-A) was judged to be unimportant[19], and was not applied. Of the 621 pairs of reflections, only 179 pairs for the crystal of $Ca_{5.6}Tl_{0.8}$-A and 226 pairs for the crystal of $Ca_{1.4}Tl_{9.2}$-A for which $I>3\sigma(I)$, respectively, were used in subsequent structure determination.

STRUCTURE DETERMINATION

Crystal 1 ($Ca_{5.6}Tl_{0.8}$-A). Full-matrix least-squares refinement was initiated using the atomic pa-

Table 1. Positional, thermal[a], and occupancy parameters

(a) Crystal 1, Ca$_{5.6}$Tl$_{0.8}$-A

Atom	Wyc. Posi.	x	y	z	β$_{11}$ or β$_{iso}$	β$_{22}$	β$_{33}$	β$_{12}$	β$_{13}$	β$_{23}$	Occupancy[c] varied	Occupancy[c] fixed
(Si, Al)	24(k)	0	1832(4)	3710(4)	34(3)	27(3)	22(3)	0	0	11(7)		24.0[d]
O(1)	12(h)	0	2180(10)	5000	60(20)	60(20)	50(10)	0	0	0		12.0
O(2)	12(i)	0	2866(9)	1866(9)	100(20)	40(9)	40(9)	0	0	50(30)		12.0
O(3)	24(m)	1103(6)	1103(6)	3352(9)	69(6)	69(6)	40(10)	40(20)	0(1)	0(1)		24.0
Tl(1)	8(g)	2622(5)	2622(5)	2622(5)	22(4)	22(4)	22(4)	-11(9)	-11(9)	-11(9)	0.79(2)	0.8
Ca(1)	8(g)	1410(30)	1410(30)	1410(30)	6(2)[b]					0.99(9)	1.2	
Ca(2)	8(g)	1985(9)	1985(9)	1985(9)	110(6)	110(6)	110(6)	140(10)	140(10)	140(10)	4.20(10)	4.4

(b) Crystal 2, Ca$_{4.4}$Tl$_{1.4}$-A

Atom	Wyc. Posi.	x	y	z	β$_{11}$ or β$_{iso}$	β$_{22}$	β$_{33}$	β$_{12}$	β$_{13}$	β$_{23}$	Occupancy[c] varied	Occupancy[c] fixed
(Si, Al)	24(k)	0	183(4)	3687(3)	22(2)	21(3)	19(3)	0	0	7(5)		24.0[d]
O(1)	12(h)	0	2130(10)	5000	60(10)	70(10)	20(10)	0	0	0		12.0
O(2)	12(i)	0	3000(10)	3000(10)	70(10)	48(8)	48(8)	0	0	50(20)		12.0
O(3)	24(m)	1122(5)	1122(5)	3313(8)	47(5)	47(5)	38(8)	10(20)	20(10)	20(10)		24.0
Tl(1)	8(g)	2580(1)	2580(1)	2580(1)	40(1)	40(1)	40(1)	-3(2)	-3(2)	-3(2)	4.84(2)	4.8
Tl(2)	8(g)	1048(3)	1048(3)	1048(3)	47(2)	47(2)	47(2)	8(6)	8(6)	8(6)	1.43(2)	1.4
Ca(1)	8(g)	1580(30)	1580(30)	1580(30)	7(1)[b]					0.92(9)	1.4	
Tl(3)	12(i)	0	4562(3)	4562(3)	216(8)	144(4)	144(4)	0	0	-214(8)	2.92(5)	3.0

[a] Positional and anisotropic thermal parameters are given ×10⁴. Numbers in parentheses are the esd's in units of least significant digit given for the corresponding parameter. The anisotropic temperature factor = exp$[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Isotropic thermal parameters in units of Å². [c] Occupancy factors are given as the number of atoms or ions per unit cell. [d] Occupancy for (Si) =12 and occupancy for (Al)=12.

rameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)] and a Tl^+ ion at Tl(1) in Ag_7Tl_5-A^{20} and of the Ca^{2+} ion at the Ca(1) in Ca(II) and Cs(I) exchanged zeolite A^{21}. Anisotropic refinement of the framewok atoms and isotropic refinement of Tl^+ at Tl(1) and Ca^{2+} ion at Ca(2) converged to $R_1=\Sigma F_o-F_c/\Sigma F_o=0.106$ and $R_2=(\Sigma w (F_o-F_c)^2/\Sigma wF_o^2)^{1/2}=0.103$. A subsequent difference Fourier function revealed a three fold axis peak at P(0.1387, 0.1387, 0.1387) with a height of 2.7(2) $e\text{Å}^{-3}$. This peak was stable at least-squares refinement. Simultaneous positional, thermal, and occupancy refinement including this position as Ca(1) converged $R_1=0.071$ and $R_2=0.075$.

It is easy to distinguish Ca^{2+} from Tl^+ ion for several reasons. First, their atomic scattering factors are quite different, 19 e^- for Ca^{2+} vs 80 e^- for Tl^+. Secondely, their ionic radii are different, $Ca^{2+}=0.99$ Å and $Tl^+=1.47$ Å^{22}. Also, the approach distances between those ions and zeolite oxygens in dehydrated Tl_{12}-A^7 and Ca_6-A^{12} have been determined and are indicative.

The cupancy numbers of ions per unit cell were refined to Tl(1)=0.79(2), Ca(1)=0.99(9), and Ca(2)=4.20(10). These were fixed at Tl(1)=0.8, Ca(1)=1.2, and Ca(2)=4.4, respectively, because the charges of the exchangeable cations should sum to 12 per unit cell and the number of ions on three-fold axes per unit cell cannot sum to more than 8. The final R values were $R_1=0.072$ and $R_2=0.076$.

The largest peak on the final difference Fourier function whose estimated standard deviation is 0.6 $e\text{Å}^{-3}$, was 3.3 $e\text{Å}^{-3}$ in height and was at origin. There was no peak on 8-ring sites, indicating cations were only existed on threefold axis sites and associated with 6-ring oxygens. Final positional, thermal, and occupancy parameters are presented in Table 1, bond lengths and bond angles are given in Table 2. All shifts in the final cycles of least-squares refinement were less than 3% of their corresponding esd's.

Crystal 2 ($Ca_{1.4}Tl_{9.2}$-A). Initial full-matrix least-squares refinement began using the framework position and the Tl(1) position found in the structure of crystal 1. Anisotropic refinement of the

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

	Crystal 1	Crystal 2
(Si, Al)-O(1)	1.635(6)	1.641(5)
(Si, Al)-O(2)	1.63(1)	1.65(2)
(Si, Al)-O(3)	1.677(7)	1.680(5)
Tl(1)-O(3)	2.778(7)	2.669(5)
Tl(2)-O(3)		2.764(9)
Tl(3)-O(1)		3.02(1)
Tl(3)-O(2)		2.696(9)
Ca(1)-O(3)	2.43(4)	2.26(1)
Ca(2)-O(3)	2.27(2)	
O(1)-(Si, Al)-O(2)	114.3(7)	107.8(7)
O(1)-(Si, Al)-O(3)	112.9(5)	112.2(4)
O(2)-(Si, Al)-O(3)	104.4(4)	107.7(3)
O(3)-(Si, Al)-O(3)	107.3(4)	108.9(3)
(Si, Al)-O(1)-(Si, Al)	150(1)	155(2)
(Si, Al)-O(2)-(Si, Al)	168.6(7)	151.1(6)
(Si, Al)-O(3)-(Si, Al)	142.2(6)	139.7(5)
O(3)-Tl(1)-O(3)	89.0(3)	90.1(2)
O(3)-Tl(2)-O(3)		86.2(2)
O(3)-Ca(1)-O(3)	106.2(4)	113.6(9)
O(3)-Ca(2)-O(3)	118.5(2)	
O(1)-Tl(3)-O(2)		55.3(2)

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

framework atoms and isotropic refinement of Tl^+ at Tl(1) converged to $R_1=0.261$ and $R_2=0.294$. A difference Fourier synthesis revealed large and distinct peaks at P(0.109, 0.109, 0.109) with a height of 12.16(34) $e\text{Å}^{-3}$, and P(0.0, 0.443, 0.443) with a height of 11.30(28) $e\text{Å}^{-3}$. Isotropic refinement including these Tl(2) and Tl(3) positions, respectively, converged to $R_1=0.141$ and $R_2=0.173$. A subsequent difference synthesis revealed a peak at P(0.166, 0.166, 0.166) with a height of 1.51(33) $e\text{Å}^{-3}$. This was stable in least-squares refinement and simultaneous positional, thermal, and occupancy refinement including this position as Ca(1) converged to $R_1=0.048$ and $R_2=0.043$.

The final difference Fourier map was featureless except an insignificant one at P(0.5, 0.5, 0.5) with a height of 0.74(29) $e\text{Å}^{-3}$. The final results are shown in Table 1 and 2.

The full-matrix least-squares program used in

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

	Crystal 1	Crystal 2
O(2)	0.122(7)	0.130(7)
Ca(1)	−0.933(22)	−0.583(19)
Ca(2)	0.281(6)	
Tl(1)	1.632(4)	1.537(1)
Tl(2)		−1.698(19)

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

all structure determinations minimized $\Sigma w(F_0 - F_c)^2$; the weight(w) of an observation was the reciprocal square of $\sigma(F_o)$ its standard deviation. Atomic scattering factors[23,24] for Ca^{2+}, Tl^+, O^- and $(Si, Al)^{1.75+}$ were used. The function describing $(Si, Al)^{1.75+}$ 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[25].

See *Table* 1, 2 and 3 for additional informations.

DISCUSSION

Crystal 1 (Ca$_{5.6}$Tl$_{0.8}$-A). In this structure, 5.6 Ca^{2+} ions at Ca(1) and Ca(2) occupy 6-ring sites on the threefold axes of the unit cell as shown in *Fig.* 1 and *Table* 1. The Ca^{2+} ions at Ca(1) and Ca(2) are 2.43(4) Å and 2.27(2) Å from their nearest framework oxygens at O(3), respectively (see *Table* 2). The corresponding Ca-O distances in dehydrated Ca$_6$-A[12] are 2.64(2) Å and 2.28(1) Å, respectively. For comparison, the sum of the conventional radii of Ca^{2+} and O^{2-} is 2.31 Å[22].

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, 5.6 Ca^{2+} ions adopt two nonequivalent crystallographic sites at Ca(1) and Ca(2). 1.2 Ca^{2+} ions at Ca(1) are recessed 0.933(2) Å into the sodalite cavity from the (111) plane at O(3). 4.4 Ca^{2+} ions at Ca(2) are correspondingly recessed 0.28(6) Å into the large cavity (see *Table* 3).

0.8 Tl^+ ions at Tl(1) lie on the threefold axes of the unit cell (see *Fig.* 1 and *Table* 1), recessed 1.632(4) Å (see *Table* 3) into the large cavity from
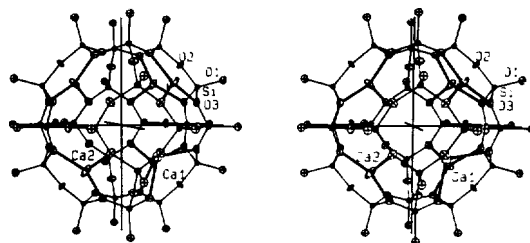

Fig. 1. A stereoview of the sodalite unit of dehydrated Ca$_{5.6}$Tl$_{0.8}$-A. About 40% of the sodalite units have this arrangement. Ellipsoids of 20% probability are used.

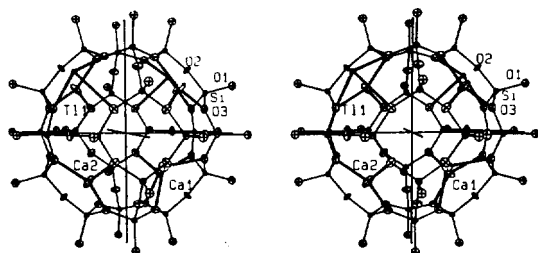*Fig.* 2. A stereoview of the sodalite unit of dehydrated Ca$_{5.6}$Tl$_{0.8}$-A. Another about 40% of the sodalite units have this arrangement. Ellipsoids of 20% probability are used.

the (111) plane at O(3). This position is familiar, having been found in previous work[20]. The Tl(1)-O(3) distance is 2.778(7) Å (see *Table* 2). In this structure, cations occupy only 6-ring sites; the 8-ring and 4-ring sites are empty.

Considering fractional occupancies, this crystal can perhaps have three types of unit cells. About 40% of unit cells have 1 Ca^{2+} ions at Ca(1) and 5 Ca^{2+} ion at Ca(2). Another 40% of unit cells have 1 Ca^{2+} ions at Ca(1), 4 Ca^{2+} ion at Ca(2), and 2 Tl^+ ions at Tl^+(1). The remainder have 2 Ca^{2+} ions at Ca(1) and 4 Ca^{2+} ions at Ca(2). A plausible and unique relative arrangement of the threefold-axis cations is presented in *Fig.* 1 and 2.

Crystal 2 (Ca$_{1.4}$Tl$_{9.2}$-A). In this structure, 1.4 Ca^{2+} ions at Ca(1) are located on threefold axes and recessed 0.583(19) Å into the sodalite cavity from the (111) plane at O(3) (*Table* 3 and *Fig.* 3). Each of these Ca^{2+} ions is coordinated to three O(3) framework oxide ions at 2.26(1) Å.
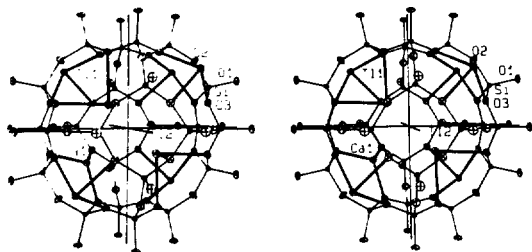
Fig. 3. A stereoview of the sodalite unit of dehydrated $Ca_{1.4}Tl_{9.2}$-A. About 60% of the sodalite units have this arrangement. Ellipsoids of 20% probability are used.

Fig. 4. A stereoview of the large cavity of dehydrated $Ca_{1.4}Tl_{9.2}$-A is shown using ellipsoids of 20% probability.

Tl^+ ions are found at three crystallographic sites, as presented in *Table* 1. The three Tl^+ ions at Tl(3) are associated with 8-ring oxygens. These ions are located in the planes of the 8-oxygen rings, but not at their centers in order to make favorable approaches to the framework oxygens (see *Table* 1 and *Fig.* 4). This position is almost identical with the corresponding one in dehydrated Tl_{12}-A[7], Ag_9Tl_3-A, and Ag_8Tl_4-A[20]. The Tl(3)-O(2) distance is 2.696(9) Å (see *Table* 2).

6.2 Tl^+ ions are distributed over two nonequivalent threefold axis equipoints. 4.8 Tl^+ ions at Tl(1) are recessed 1.537(1) Å into the large cavity from the O(3) planes of the 6-rings. 1.4 Tl^+ ions at Tl(2) are recessed into the sodalite cavity from the (111) plane at O(3) (see *Table* 1 and 3). The Tl(1)-O(3) and Tl(2)-O(3) distances are 2.669(5) Å and 2.764(9) Å, respectively (see *Table* 2). For comparison, the sum of the conventional Tl^+ and O^{2-} radii is 2.79 Å[22].

The fractional occupancies observed at Tl(1), Tl(2), and Ca(1) indicate the existence of approximately three types of unit cell. For example, about 60% of the unit cells have 5 Tl^+ ions at Tl(1), 2 Tl^+ ions at Tl(2), and 1 Ca^{2+} ion at Ca(1). About 20% of unit cells have 5 Tl^+ ions at Tl(1) and 2 Ca^{2+} ion at Ca(1). The remaining 20% of unit cells have 4 Tl^+ ions at Tl(1), 1 Tl^- ion at Tl(2), and 2 Ca^{2+} ions at Ca(1). All unit cells have 3 Tl^+ ions at Tl(3).

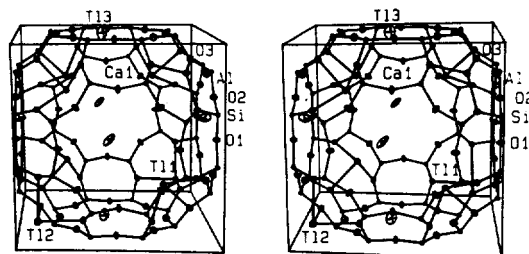A comparison of two crystal structures determined in this work shows that, Ca^{2+} ions prefer 6-ring sites and Tl^+ ions prefer 8-ring sites when number of ions per unit cell is more than 8. This result is reasonable considering ionic radii of Tl^+ ion (1.47 Å) and that of Ca^{2+} ion (0.99 Å). Larger Tl^+ ion will better fit to larger 8-ring site over small 6-ring site. But Tl^+ ions prefer 6-ring sites when number of ions per unit cell is less than 8. In crystal structures of Cd_xRb_{12-2x}-A, $x=4.0$, 5.0, and 5.95, Rb^+ ions prefer 8-ring sites when number of ions per unit cell is less than 8[19]. Tl^+ ions have greater selectivity of ion exchange into zeolite A than Ca^{2+} ions.

ACKNOWLEDGEMENT

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