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완전히 탈수되고 부분적으로 칼슘 이온으로 교환된 제올라이트 A의 셀레늄 수착 화합물의 구조 연구

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Structural Study of Selenium Sorption Complex of Fully Dehydrated, Partially Ca^{2+}-exchanged Zeolite A

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요 약: Ca^{2+} 이온으로 부분적으로 치환된 제올라이트 A ($|Ca_4Na_4|[Si_{12}Al_{12}O_{48}]$-LTA) 단결정과 Se을 가는 모세관에 넣은 후 523 K 에서 5일동안 반응을 시켜 Se이 흡착된 제올라이트 A 단결정을 합성 하였다. 이 결정의 구조는 294 K 에서 단결정 X-선 회절 기술을 이용하여 $Pm\bar{3}m$ ($a = 12.2787(13)$ Å) 입방 공간군에 속함을 확인 하였고, $F_o > 4s(F_o)$를 사용하여 최종 오차 인자를 $R_1/wR_2 = 0.0960/0.3483$로 정밀화 하였다. 이 구조에서는 4개의 Na^+와 4개의 Ca^{2+} 이온이 모든 6-ring 자리에 채워져 있었으며, 이들 이온들은 모두 6-ring 맞은편의 3-fold 축 상의 결정학적 위치에서 발견되었다. Se 원자들은 뚜렷하게 서로 다른 3개의 결정학적 위치에서 발견되었다. 단위 세포당 2개의 Se(1) 원자는 sodalite cavity 내 6-ring 맞은편 (Se(1)-Na(1) = 2.53(5) Å), 1개의 Se(2) 원자는 4-ring 맞은편 (Se(2)-O(1) = 2.76(10) Å), 그리고 1개의 Se(3) 원자는 large cavity 내 6-ring 맞은편 (Se(3)-Na(1) = 2.48(5) Å)에 각각 위치하고 있었다. 2가지 형태의 Se_2 분자 (Se(1)-Se(1) = 2.37(7) or 2.90(8) Å and Se(2)-Se(3) = 2.91(5)) Å)가 sodalite cavity와 large cavity 내에서 발견되었으며, Se_4와 Se_8과 같은 형태의 클러스터가 large cavity 내에 존재할 수 있었다. 이들 클러스터내 Se 원자들 사이의 거리는 기체상태의 Se_2 분자내 Se 원자 사이의 거리보다 더 길게 나타났다.

핵심어: 제올라이트 A, 셀레늄, 구조, 칼슘

Abstract: Single crystal of fully dehydrated and partially Ca^{2+}-exchanged zeolites A ($|Ca_4Na_4|[Si_{12}Al_{12}O_{48}]$-LTA) was brought into contact with Se in fine pyrex capillary at 523 K for 5 days. Crystal structure of Se-sorbed $|Ca_4Na_4|[Si_{12}Al_{12}O_{48}]$-LTA has been determined by single-crystal X-ray diffraction techniques at 294 K in the cubic space group $Pm\bar{3}m$ ($a = 12.2787(13)$ Å). The crystal structure of yellow $|Ca_4Na_4Se_4|[Si_{12}Al_{12}O_{48}]$-LTA has been refined to the final error indices of $R_1/wR_2 = 0.0960/0.3483$ with 327 reflections for which $F_o > 4s(F_o)$. In this structure, 4 Na^+ and 4 Ca^{2+} ions fill every 6-ring site: These ions are all found at three crystallographic positions, on 3-fold axes equipoints of opposite 6-rings. Selenium atoms are found at three crystallographically distinct positions: 2 Se atoms per unit cell at Se(1) are located opposite 6-rings in the sodalite cavity (Se(1)-Na(1) = 2.53(5) Å) and 1 at Se(2) opposite 4-rings (Se(2)-O(1) = 2.76(10) Å) and 1 at Se(3) opposite 6-rings in the large cavity (Se(3)-Na(1) = 2.48(5) Å). Two molecular of Se_2 (Se(1)-Se(1) = 2.37(7) or 2.90(8) Å and Se(2)-Se(3) = 2.91(5)) Å) are found in all sodalite cavity and large cavity. Other clusters such as Se_4 and Se_8 could be existed in large cavity. The inter-selenium distances turned out to be longer that of gases Se_2 molecule.

Keywords: Zeolite A, Selenium, Structure, Calcium

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INTRODUCTION

Zeolites are three dimensional crystalline solids with well defined structures that contain aluminum, silicon, and oxygen in their regular framework, can confine molecules or clusters in their void space in a controlled fashion (Heron, 1995). The confined materials to the nanometer scale can have dramatic effects on the optical, electronic, vibrational, and thermodynamic properties of condensed matter (Armand *et al*., 1997; Kim *et al*., 2006). Chalcogen elements such as S, Se, and Te can be confined within cavities or channels of different zeolites so a number of recent papers deal with the introduction of chalcogen elements into those of zeolites (Bogomolov *et al*., 1983; Bogomolov *et al*., 1985; Tamura *et al*., 1986; Parise *et al*., 1988; Goldbach *et al*., 1996).

Tamura *et al.* extensively studied Se chains confined in the channels of synthetic mordenite by the measurement of the extended X-ray absorption fine structure and the photoacoustic spectroscopy and then found that the isolated Se chains in the mordenite channels were strongly photo-sensitive (Tamura *et al*., 1986). Bogomolov *et al.* investigated single Se chains stabilized in the regular system of parallel channels of a mordenite dielectric matrix and reported that the interchain interaction in trigonal Se crystals weakens significantly the intrachain bonding (Bogomolov *et al*., 1985). Parise *et al.* successfully loaded selenium into zeolites A, X, Y, AlPO-5, and mordenite and then characterized those products by EXAFS, solid-state NMR, and diffuse-reflectance techniques (Parise *et al*., 1988). Their study revealed selenium was predominantly of the trigonal (helical chains) form in all but zeolite A, where only the Se_8-crown ring form was found. Goldbach *et al.* studied selenium incorporated in Nd-Y zeolite by Raman spectroscopy and suggested the formation of the Se_2^- radical anion (Goldbach *et al*., 1996).

In this work, we synthesized partially Ca^{2+}-exchanged zeolite A ($|Ca_4Na_4|[Si_{12}Al_{12}O_{48}]$-LTA) which had the pore opening of the 8-ring and then treated this with selenium in an attempt to synthesize nanoclusters of selenium within the zeolite A. The single-crystal structure of the resulting product was determined to learn the positions, size, and geometry of the loaded selenium nanoclusters, and to observe their interactions with the zeolite framework and Ca^{2+} cations.

EXPERIMENTAL SECTION

Preparation of Partially Ca^{2+}-exchanged Zeolite A

Large colorless single crystals of zeolite 4A (LTA), $Na_{12}Si_{12}Al_{12}O_{48}\cdot 27H_2O$ (Na_{12}-A$\cdot 27H_2O$ or Na-A), were synthesized by Kokotailo and Charnell. A single crystal about 85 μm on edge was selected and lodged in a fine quartz capillary. A partially Ca^{2+}-exchanged zeolite A ($Ca_4Na_4Si_{12}Al_{12}O_{48}\cdot xH_2O$) was prepared by the dynamic (flow) ion-exchange of Na-A using exchange solution in which molar ratio of $Ca(NO_3)_2$ (Aldrich 99.997%) and NaOH (99%) was 100 : 1, with a total concentration 0.05 M. The resulting colorless $|Ca_4Na_4|[Si_{12}Al_{12}O_{48}]$-LTA crystal in its own fine Pyrex capillary was completely dehydrated by gradually increasing its temperature (*ca.* 20 °C/h) to 623 K at a constant pressure of 1×10^{-6} Torr.

Synthesis of Selenium Sorption Complex in Partially Ca^{2+}-exchanged Zeolite A

The crystal of fully dehydrated $|Ca_4Na_4|[Si_{12}Al_{12}O_{48}]$-LTA was brought into contact with Se (Aldrich Chem. Co., 99.999%) under vacuum in fine Pyrex capillary at 523 K for 5 days. This was achieved by condensing Se on and near the crystal, whose temperature (523 K) was lower than that of the metal (623 K), in coaxially connected heating ovens. Although the vapor pressure of Se(*l*) is reported to be somewhat low at 523 K (3.54×10^{-2} Torr) (Kwon *et al*., 1998), droplets of Se were seen to form very close to the zeolite crystal. Except for this reversed temperature gradient during the reaction period, other experimental procedures for the reaction were similar in detail to those previously described for solvent-free ion exchange (Heo *et al*., 1997). After cooling to room temperature, the crystal, still under vacuum, was then sealed in its capillary with a small flame. The color of the resulting crystal, still under vacuum in its capillary, was yellow.

X-ray Data Collection

The structure of the resulting crystal was determined by single-crystal X-ray diffraction techniques at 294(1) K using a Bruker SMART CCD diffractometer. The crystal evaluation and data collection were done using Mo Kα radiation with a sealed-tube X-ray source operating at 1.5 kW with a detector-to-crystal distance of 4.8 cm.

Preliminary cell constants and an orientation matrix were determined from three series of scans at different starting angles. Each series consisted of 20 frames collected at scan intervals of 0.3° with an exposure time of 10 seconds per frame. The reflections were successfully indexed by the automated indexing routine of the SMART program (Bruker SMART, 1999). A total of 11,959 reflections for $|Ca_4Na_4Se_4|[Si_{12}Al_{12}O_{48}]$-LTA, was harvested by collecting four sets of frames with 0.3° scans with an exposure time of 10 seconds per frame. The highly redundant data sets were corrected for Lorentz and polarization effects, and a (negligible) correction for crystal decay was also applied. The space group $Pm\bar{3}m$ was determined by the program SAINT-plus (Bruker SMART, 1999). A summary of the experimental and crystallographic data is presented in Table 1.

Table 1. Summary of experimental and crystallographic data

Crystal cross-section (mm)	0.15
Ion exchange T (K)	294
Ion exchange for Ca^{2+} (days, mL)	4, 16.0
Data collection T (K)	294(1)
Scan technique	ω-scans
Radiation (Mo Kα) λ_1 (Å)	0.70930
λ_2 (Å)	0.71359
Unit cell constant, a (Å)	12.2787(13)
2θ range in data collection (deg)	2.82<2θ<56.6
No. of unique reflections, m	512
No. of reflections with $F_o > 4\sigma(F_o)$	327
No. of variables, s	41
Data/parameter ratio, m/s	12.5
Weighting parameters, a/b	0.183/21.6
Final error indices	
$R_1/wR_2\,(F_o > 4\sigma(F_o))^a$	0.0960/0.3483
R_1/wR_2 (all intensities)^b	0.1573/0.4149
Goodness-of-fit^c	1.232

[a] $R_1 = \Sigma|F_o-|F_c||/\Sigma F_o$ *and* $R_2 = [\Sigma w(F_o^2-F_c^2)2/Sw(F_o^2)^2]^{1/2}$; R_1 and R_2 are calculated using only the 327 reflections for which $F_o > 4\sigma(F_o)$, where F_o and F_c are observed and calculated structure factors, respectively. [b] R_1 and R_2 are calculated using all unique reflections measured. [c] Goodness-of-fit $= (\Sigma w(F_o^2-F_c^2)^2/(m-s))^{1/2}$, where m and s are the number of unique reflections and variables, respectively.

Structure Determination

Full-matrix least-squares refinement (SHELXL97) (Sheldrick, 1997) was initiated with the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), and O(3)] in dehydrated $|Na_{12}|[Si_{12}Al_{12}O_{48}]$-LTA (Firor and Seff, 1978). The initial refinement using isotropic thermal parameters for all positions converged to the error indices $R_1 = 0.2613$ and $R_2 = 0.6433$. (See Table 2, footnotes.) Refinement including the Na(1) position at a peak (0.1879, 0.1879, 0.1879, opposite a 6-ring) from the initial difference Fourier function led to convergence with $R_1 = 0.1817$ and $R_2 = 0.4979$ and an occupancy of 7.1(4) Na^+ ions. The next difference Fourier function (based on this model) revealed a peak at (0.2209, 0.2209, 0.2209), opposite a 6-ring in the large cavity. Refinement including this peak as Ca(1) converged to $R_1 = 0.1545$ and $R_2 = 0.4184$, with occupancies of 4.4(6) and 1.8(3) for Na(1) and Ca(1), respectively. The addition of another peak at Se(3) (0.3002, 0.3002, 0.3002, inside the large cavity) reduced the error indices to $R_1 = 0.1465$ and $R_2 = 0.3860$, with occupancies of 4.6(5), 2.2(3), and 1.91(3) for Na(1), Ca(1), and Se(3), respectively. A subsequent refinement included Se(1), a peak found opposite a 6-ring in the sodalite cavity at (0.0710, 0.0710, 0.0710), led to $R_1 = 0.1211$ and $R_2 = 0.3423$, with occupancies of 4.5(4), 1.96(23), 1.60(16), and 1.91(14) for isotropically refined Na(1), Ca(1), Se(3), and Se(1), respectively. Successive Fourier functions revealed two peaks of height 2.30 eÅ^{-3} and 0.87 eÅ^{-3} at (0.1423, 0.1423, 0.1423) and (0.1927, 0.3622, 0.5). Simultaneous positional, thermal, and occupancy refinement including

Table 2. Positional, thermal, and occupancy parameters[a]

Atom	Wyckoff position	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	[b]Occupancy	
											Varied	Fixed
Si,Al	24(*k*)	0	1841(2)	3735(2)	130(17)	104(15)	90(17)	34(10)	0	0		24[c]
O(1)	12(*h*)	0	2327(10)	5000[d]	464(82)	322(69)	218(59)	0	0	0		12
O(2)	12(*i*)	0	2842(8)	2842(8)	633(95)	228(42)	228(42)	198(53)	0	0		12
O(3)	24(*m*)	1111(6)	1111(6)	3477(8)	364(39)	364(39)	399(59)	67(36)	67(36)	239(45)		24
Na(1)	8(*g*)	1874(8)	1874(8)	1874(8)	76(28)						3.6(5)	4
Ca(1)	8(*g*)	2173(12)	2173(12)	2173(12)	323(44)						2.05(24)	2
Ca(2)	8(*g*)	1501(29)	1501(29)	1501(29)	1270(172)						1.6(3)	2
Se(1)	8(*g*)	682(20)	682(20)	682(20)	2178(173)						2.33(16)	2
Se(2)	24(*l*)	1843(78)	3620(72)	5000[d]	1666(557)						1.3(4)	1
Se(3)	8(*g*)	3038(23)	3038(23)	3038(23)	1667(257)						1.39(14)	1

[a] Positional parameters × 10^4 and thermal parameters × 10^4 are given. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. The anisotropic temperature factor is $\exp[-2\pi^2a^2(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{23}kl + 2U_{13}hl + 2U_{12}hk)]$. [b] Occupancy factors are given as the number of atoms or ions per unit cell. [c] Occupancy for (Si) = 12, occupancy for (Al) = 12. [d] Exactly 0.5 by

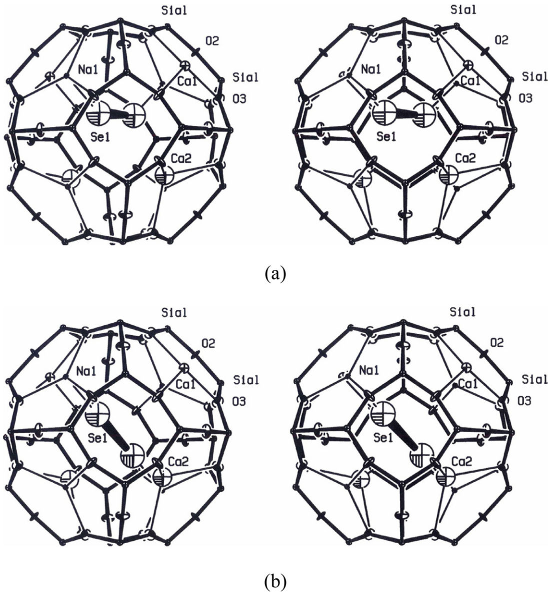
these positions converged at $R_1 = 0.0968$ and $R_2 = 0.3544$ with occupancies of 3.6(5), 2.05(24), 1.6(3), 2.33(16), 1.6(3), and 1.1(3) for Na(1), Ca(1), Se(3), Se(1), Ca(2), and Se(2), respectively. A subsequent refinement with fixed occupancies of 4.0, 2.0, and 2.0 at Na(1), Ca(1), and Ca(2) because the cationic charge should not be exceeded +12 per $Pm\bar{3}m$ unit cell (Jang *et al.*, 1995) converged to $R_1 = 0.0960$ and $R_2 = 0.3483$ with occupancies of 2.33(16), 1.3(4), and 1.39(14) for Se(1), Se(2), and Se(3). The final cycles of refinement with occupancies of 4.0, 2.0, 2.0, 2.0, 1.0, and 1.0 at Na(1), Ca(1), Ca(2), Se(1), Se(2), and Se(3), respectively, as shown in Table 2 converged to $R_1 = 0.0968$ and $R_2 = 0.3485$ with anisotropic thermal parameters for all framework. It is easy to distinguish Ca^{2+} from Na^+ ions because (1) the atomic scattering factors are largely different, 18e$^-$ for Ca^{2+} *vs*. 10e$^-$ for Na^+ and (2) If Ca^{2+} ions were Na^+ ions on the 3-fold axis, the sum of Na^+ ions on the 3-fold axes were about twelve but the maximum number of ions per unit cell at these positions cannot sum to more than eight (Jang *et al.*, 1995).

The final difference Fourier function was featureless; the notation $|Ca_4Na_4Se_4|[Si_{12}Al_{12}O_{48}]$-LTA will be used for this crystal. All shifts in the final cycles of refinement were less than 0.1% for the corresponding estimated standard deviations. The final structural parameters are given in Table 2. Selected interatomic distances and angles are given in Table 3. Fixed weights were used initially; the final weights were assigned using the formula $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$, with $a = 0.183$ and $b = 21.6$ as refined parameters (see Table 1). Atomic scattering factors for Ca^{2+}, Se, and $(Si,Al)^{1.75+}$ were used (Doyle and Turner., 1968; Ibers and Hamilton., 1974a). The function describing $(Si,Al)^{1.75+}$ is the mean of the Si^{4+}, Si^0, Al^{3+}, and Al^0 functions. All scattering factors were modified to account for anomalous dispersion (Cromer, 1965; Ibers and Hamilton., 1974b).

RESULTS AND DISCUSSION

Overview of Crystal Structure

In the crystal structure of Se-sorbed partially Ca^{2+}-exchanged zeolite A ($|Ca_4Na_4Se_4|[Si_{12}Al_{12}O_{48}]$-LTA), all Na^+ and Ca^{2+} ions are found on three distinguished 3-fold axis (see Table 2 and Figure 1 and 2). About 4 Na^+ ions at Na(1) are recessed 0.06 Å into the large cavity from the O(3) planes of the 6-ring. Each of these Na^+ ions at Na(1) is coordinated to three O(3)



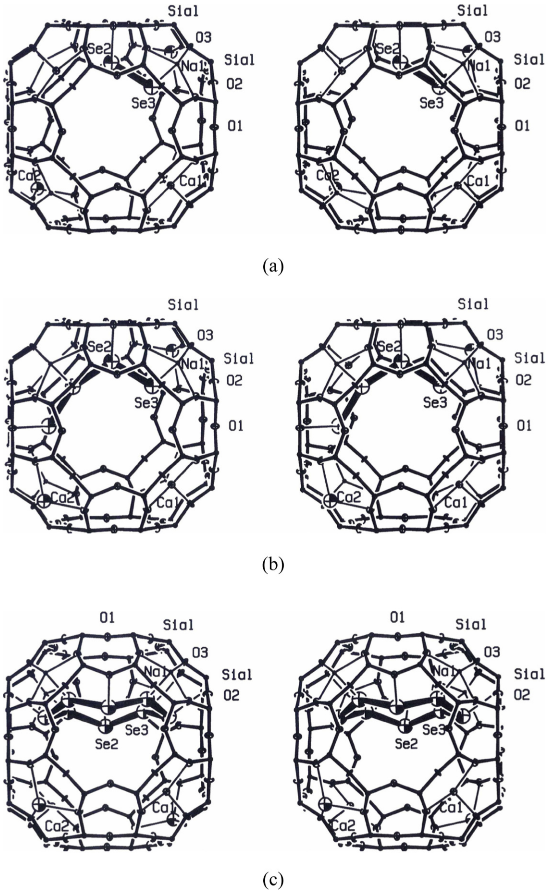
(a)

(b)

Fig. 1. **A stereoview of a sodalite cavity in |$Ca_4Na_4Se_4$||[$Si_{12}Al_{92}O_{48}$]-LTA (inter-Se distance is 2.37(7) Å (a), 2.90(8) Å (b)). The zeolite A framework is drawn with light bonds between oxygens and tetrahedrally coordinated (Si,Al) atoms. Ellipsoids of 20% probability are shown.**

framework oxygens at 2.373(9) Å (see Table 3 and 4). Considering that the sum of ionic radii of Na^+ and O^{2-} is 0.97 + 1.32 = 2.29 Å (Weast, 1989), the Na(1)-O(3) approach distances, 2.373(9) Å, are very reasonable. The O(3)-Na(1)-O(3) angles are close to 120° (119.95(4)°), so the Ca^{2+} ions are nearly trigonal-planar (see Table 3). About 2 Ca^{2+} ions at Ca(1) and 2 at Ca(2) extend 0.58 and 0.85 Å into the large cavity and sodalite cavity, respectively, from the (111) plane at O(3). These are coordinated to three O(3) oxygens at 2.44(11) and 2.519(23) Å, respectively, in a distorted trigonal planar arrangement (O(3)-Ca(1)-O(3) = 114.5(5)° and O(3)-Ca(2)-O(3) = 109.3(13)°). Considering that the sum of ionic radii of Ca^{2+} and O^{2-} is 0.99 + 1.32 = 2.31 Å (Weast, 1989), the Ca(1)-O(3) approach distances, 2.44(11) and 2.519(23) Å, are somewhat longer than that, 2.31 Å.

In this work, a total of 4 sorbed Se atoms per unit cell are found at two different 3-fold axes and at 24-fold axes. The 2 Se atoms per unit cell are found at Se(1) and 1 at Se(3) on the 3-fold axes in deep sodalite cavity and in the large cavity, respectively, while additional 1 Se atom per unit cell is located at Se(2) opposite 4-ring in the large cavity.



(a)

(b)

(c)

Fig. 2. **A stereoview of large cavity in |$Ca_4Na_4Se_4$||[$Si_{12}Al_{92}O_{48}$]-LTA (100% (a), 50% (b), and 25% (c) of large cavity). See the caption to Figure 1 for other details.**

Selenium in the Sodalite Cavity

The 2 Se atoms per unit cell at Se(1) are found on the 3-fold axis in each sodalite cavity (see Figure 1). The location of Se at Se(1), opposite 6-ring in the sodalite cavity, is unambiguous, because no other chemically possible atoms or ions. The approach distances of these Se atoms to 6-ring Na^+ cations of the same 3-fold axis is 2.54(5) Å (see Table 3). Considering the radii of Na^+ (r_{Na^+} = 0.97 Å) and Se atom (1.20 Å)

Table 3. Selected interatomic distances (Å) and angles (deg)[a]

	Distances		Angles
(Si,Al)-O(1)	1.664(5)	O(1)-(Si,Al)-O(2)	110.8(7)
(Si,Al)-O(2)	1.646(3)	O(1)-(Si,Al)-O(3)	111.8(4)
(Si,Al)-O(3)	1.663(3)	O(2)-(Si,Al)-O(3)	106.0(4)
		O(3)-(Si,Al)-O(3)	110.3(7)
Na(I)-O(3)	2.373(9)		
Na(1)-Se(1)	2.54(5)	(Si,Al)-O(1)-(Si,Al)	138.0(8)
Na(1)-Se(3)	2.48(5)	(Si,Al)-O(2)-(Si,Al)	173.5(10)
Ca(1)-O(3)	2.44(11)	(Si,Al)-O(3)-(Si,Al)	148.1(6)
Ca(2)-O(3)	2.519(23)		
		O(3)-Na(I)-O(3)	119.95(4)
Se(1)-Se(1)	2.37(7), 2.90(8)	O(3)-Ca(1)-O(3)	114.5(5)
Se(2)-Se(3)	2.91(5)	O(3)-Ca(2)-O(3)	109.3(13)
Se(2)-O(1)	2.76(10)		
		Na(1)-Se(1)-Se(1)	144.7(4), 180[b]
		Se(1)-Se(1)-Se(1)	60[c]
		Na(1)-Se(3)-Se(2)	109.2(21)
		Se(3)-Se(2)-O(1)	105.8(24)
		Se(2)-Se(3)-Se(2)	109.8(22)

[a] The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. [b] Exactly 180° by symmetry. [c] Exactly 60° by symmetry.

Table 4. Deviations of Atoms (Å) from (111) Plane at O(3)

Ions or Atoms	Charge	Distance
at O(3)[a]		
Na(1)	+1	0.06
Ca(1)	+2	0.58
Ca(2)	+2	-0.85
Se(1)	0	-2.59
Se(3)	0	2.42

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin, *i.e.*, inside the sodalite cavity of zeolite A

(Slater., 1964; Weast, 1989), the Se atoms have a little bit long approach distance to their neighbors to be considered as having relatively weak interactions. The 2 Se atoms at Se(1) on the inner surface of the sodalite cavity may be placed within their partially occupied equipoints in various ways. Provided that Se atoms are sorbed in 100% of all of sodalite cavities, then linear Se_2 clusters may exist. The shortest possible inter-Se distance, Se(1)-Se(1) = 1.67(5) Å, is impossibly short and is dismissed. Other inter-Se distances, 2.37(7) or 2.90(8) Å, suggest the possibility of an Se(2)-Se(2) interactions. A stereoview of Se_2 cluster in the sodalite cavity is shown in Figure 1(a and b).

Selenium in the Large Cavity

The 2 atoms of Se in the large cavity are found at two crystallographically distinct positions. That there are two kinds of positions indicates that the Se atoms are not arranging themselves by simple packing within the highly symmetric zeolites. It is attributed to dipolar interactions among the sorbed Se (*vide infra*). One Se atom at Se(2) lies opposite a 4-ring and another Se atom at Se(3) lies on a 3-fold axis opposite a 6-ring (see Figure 2(a)).

The closest approach of the Se atom to framework oxygen (Se(2)-O(1)) is 2.76(10) Å, while that to extra-framework cation is 2.48(5) Å for Na(1)-Se(3) (see Table 3). Considering the radii of the cations (r_{Na^+} =

0.97 Å), framework oxygens (1.32 Å), and Se atoms (1.20 Å) (Slater., 1964; Weast, 1989), the Se atoms have a little bit long approach distances to their neighbors to be considered as having relatively weak interactions. In particular, when the distances are compared to the sum of the above radii for Na^+ and Se, 0.97 + 1.20 = 2.17 Å (Slater., 1964; Weast, 1989), the approach distance of the 3-fold axis Se atom, Se(3), to the 6-ring Na^+ ion (2.48(5) Å) indicates relatively weak Na^+-Se interaction. This interaction between Se atom at Se(3) in the large cavity and 6-ring Na^+ ion is very similar with the interaction between Se at Se(1) in the sodalite cavity and 6-ring Na^+ (Na(1)-Se(1) = 2.53(5) Å).

The 2 Se atoms at Se(2) and Se(3) on the inner surface of the large cavity may be placed within their partially occupied equipoints in various ways. The shortest inter-Se distance, Se(2)-Se(3) = 2.91(5) Å, is possible and suggests the possibility of an Se(2)-Se(3) interaction with favorably oriented induced dipoles (see Figure 2(a)). In this linear Se_2 cluster, Se atoms alternatively approach Na^+ ion and 4-oxygen ring and are polarized oppositely, allowing their inter-Se approaches to be attractive, like $O(1)^{d-}$-$Se(2)^{d-}$-$Se(3)^{d+}$-$Na(1)^{d+}$.

Provided that Se atoms are sorbed in only 50% of all large cavities, then bent linear Se_4 clusters may exist. The 4 Se atoms at Se(2) and Se(3) on the inner surface of the large cavity may be placed in similar way to above. A distance found between Se(2) and Se(3), 2.91(5) Å, is also possible and suggests the possibility of an Se(2)-Se(3)-Se(2)-Se(3) interaction with favorably oriented induced dipoles (see Figure 2(b)). In this bent linear Se_4 cluster, Se atoms alternatively approach 2 Na^+ ions and 2 4-oxygen rings; they are therefore polarized oppositely, allowing their inter-Se approaches to be attractive, like $O(1)^{d-}$-$Se(2)^{d+}$-$Se(3)^{d-}$-$Se(2)^{d+}$-$Se(3)^{d-}$-$Na(1)^{d+}$.

If 25% of the large cavity is sorbed by Se atoms, the most favorable arrangement of 8 Se atoms is a butterfly-shape, [-Se(2)-Se(3)-Se(2)-Se(3)-Se(2)-Se(3)-Se(2)-Se(3)-], Se(2)-Se(3) = 2.91(5) Å, and Se(2)-Se(3)-Se(2) = 109.8(22)°, because of its higher symmetry and the considerations regarding alternating polarizations of Se atoms as seen in Figure 2(c).

SUMMARY

Single crystal of fully dehydrated and partially Ca^{2+}-exchanged zeolite A ($|Ca_4Na_4|[Si_{12}Al_{12}O_{48}]$-LTA) was reacted with Se at 523 K for 5 days. Crystal structure of Se-sorbed partially Ca^{2+}-exchanged zeolite A ($|Ca_4Na_4Se_4|[Si_{12}Al_{12}O_{48}]$-LTA) has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$. The crystal structure of $|Ca_4Na_4Se_4|[Si_{12}Al_{12}O_{48}]$-LTA has been refined to the final error indices of $R_1/wR_2 = 0.0960/0.3483$ with 327 reflections for which $F_o > 4s(F_o)$. In the crystal structure of Se-sorbed partially Ca^{2+}-exchanged zolite A ($|Ca_4Na_4Se_4|[Si_{12}Al_{12}O_{48}]$-LTA), a total of 4 sorbed Se atoms per unit cell found at two different 3-fold axes and at 24-fold axes. The 2 Se atoms per unit cell are found at Se(1) on the 3-fold axis in the sodalite cavity and another Se atom at Se(3) is located on the 3-fold axis in deep large cavity. Additional one Se atom per unit cell is found at Se(2) opposite 4-ring in the large cavity.

The Se clusters in zeolite A are stabilized by interaction with cations and framework oxygen. In sodalite cavity, Se-Se distance of 2.37(7) Å exhibit strong covalent property due to their interaction with Na^+ ions. Inter-Se distance, 2.90(8) Å, in sodalite cavity could be also possible. On the other hand, in large cavity, that of 2.91(5) Å in zeolite framework shows ionic property because alternative ionic interaction was formed through framework oxygen at one end and Na^+ ions at the other end.

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REFERENCES

Armand, P., Saboungi, M.L., Price, D.L., Iton, L., Cramer, C. and Grimsditch, M., 1997. Nanoclusters in zeolite. Physical Review Letters, 79, 2061-2064.

Bogomolov, V.N., Kholodkevich, S.V., Romanov, S.G. and Agroskin. L.S., 1983. The absorption spectra of single selenium and tellurium chains in dielectric matrix channels. Solid State Communications, 47, 181-182.

Bogomolov, V.N., Poborchy, V.V., Romanov, S.G. and Shagin, S.I., 1985. Raman spectra of chalcogen chains isolated in zeolite matrixes. Journal of the Physical Chemistry C: Solid State Physics, 18, L313-L317.

Bruker SMART (version 5.0) and SAINT-plus (version 6.0)., 1999, Bruker AXS Inc., Madison, Wisconsin, USA.

Cromer, D.T., 1965. Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. Acta Crystallogrphy. 18, 17-23.

Doyle, P.A. and Turner, P.S., 1968, Crystal physics, diffraction, theoretical and general crystallography. Acta Crystallographica A. 24, 390-397.

Firor, R.L. and Seff. K., 1978. Near zero coordinate Ca^{2+} and Sr^{2+} in zeolite A. Crystal structures of dehydrated Ca_6-A and Sr_6-A. Journal of the American Chemical Society, 100, 3091-3096.

Goldbach, A., Iton, L., Grimsditch, M. and Saboungi. M.L., 1996. The formation of Se_2^-: a new resonace Raman feature in the photochemistry of zeolite-encapsulated selenium. Journal of the American Chemical Society, 118, 2004-2007.

Heo, N.H., Choi, H.C., Jung, S.W., Park, M. and Seff, K., 1997. Complete redox exchange of indium for Tl^+ in zeolite A. Crystal structure of anhydrous Tl_{12}-A and In_{10}-A·In. Indium appears as In^{2+}, In^+, and In^0. The clusters $(In_5)^{8+}$ and $(In_3)^{2+}$ are proposed. Journal of the Physical Chemistry B, 101, 5531-5539.

Herron, N., 1995, Zeolites as Hosts for novel optical and electronic materials. Journal of Inclusion Phenomena and Molecular Recognition in Chemistry, 21, 283-298.

Ibers, J. A. and Hamilton, W.C., 1974a, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, 71-98.

Ibers, J. A. and Hamilton, W.C., 1974b, International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, 148-150.

Jang, S.B., Song, S.H. and Kim, Y., 1995, Crystal Structures of bromine sorption complexes of Ca^{2+}-exchanged zeolite A. Bulletin of the Korean Chemical Society, 16, 1163-1167.

Kim, S.H., Lim, W.T., Kim, G.H., Lee, H.S. and Heo. N.H., 2006, Synthesis and crystal structure of lead iodide in the sodalite cavities of zeolite A (LTA). Bulletin of the Korean Chemical Society, 27, 679-686.

Kwon, K.R., 1998. Crystal structure of selenium sorption complex of Ca^{2+}-exchanged zeolite A, Korea, ME thesis, Kyungpook National University, 54p.

Parise, J.B., MacDougall, J.E., Herron, N., Farlee, R., Sleight, A.W., Wang, Y., Bein, T., Moller, K. and Moroney, L.M., 1988, Characterization of Se-loaded molecular sieves A, X, Y, AlPO-5, and mordenite. Inorganic Chemistry, 27, 221-228.

Sheldrick, G.M., 1997, SHELXL97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany.

Slater, J.C., 1964, Atomic Radii in crystals. Journal of Chemical Physics, 41, 3199-3205.

Tamura, K., Hosokawa, S., Endo, H., Yamasaki, S. and Oyanagi, H., 1986, The isolated Se chains in the channels of mordenite crystal. Journal of the Physical Society of Japan, 55, 528-533.

Weast, R.C., 1989/1990, Handbook of Chemistry and Physics, 70th ed., The chemical Rubber Co.: Cleveland, OH, F-18.

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