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결정성 아날심($|Na_{0.94}(H_2O)|[Si_{2.06}Al_{0.94}O_6]$-ANA)의 합성 및 단결정구조: 양이온 및 물 분자의 위치, Si/Al 비의 결정

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Synthesis of Single Crystalline Analcime and Its Single-crystal Structure, $|Na_{0.94}(H_2O)|[Si_{2.06}Al_{0.94}O_6]$-ANA: Determination of Cation Sites, Water Positions, and Si/Al Ratios

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요 약. 최대 0.20 mm 크기를 가진 아날심 단결정은 $3.00SiO_2 : 1.50NaAlO_2 : 8.02NaOH : 454H_2O : 5.00TEA$의 겔 조성으로부터 합성되어졌다. Na^+ 이온으로 완전히 이온교환 된 아날심은 0.1 M 농도의 NaCl 수용액으로부터 준비하였다(이온교환용액의 pH는 NaOH 용액을 첨가하여 6에서 11로 맞추었다). $|Na_{0.94}(H_2O)|[Si_{2.06}Al_{0.94}O_6]$-ANA($a$=13.703(3) Å)의 분자식을 가지는 수화된 아날심 단결정의 구조는 294 K에서 *Ibca*의 orthorhombic 공간군으로 단결정 X-선 회절기법에 의해 결정되었다. 결정 구조의 최종 에러값은 R_1/wR_2 = 0.054/0.143에 수렴되었다. 약 15개의 Na^+ 이온이 팔면체 배위로 3군데의 비동등한 위치에서 발견되었다. 합성된 아날심의 화학적 조성은 $Na_{0.94}(H_2O)Si_{2.06}Al_{0.94}O_6$ 확인되었으며, Si/Al 비는 단결정 구조 정밀화를 통하여 찾은 양이온의 점유수인 14.79개에 의해 2.19로 결정되었다.
주제어: 아날심, 제올라이트, 구조, 단결정, Si/Al 비

ABSTRACT. Large colorless single crystals of analcime with diameters up to 0.20 mm have been synthesized from gels with the composition of $3.00SiO_2 : 1.50NaAlO_2 : 8.02NaOH : 454H_2O : 5.00TEA$. The fully Na^+-exchanged analcime have been prepared with aqueous 0.1 M NaCl (pH adjusted from 6 to 11 by dropwise addition of NaOH). The single-crystal structure of hydrated $|Na_{0.94}(H_2O)|[Si_{2.06}Al_{0.94}O_6]$-ANA per unit cell, a=13.703(3) Å, has been determined by single-crystal X-ray diffraction technique in the orthorhombic space group *Ibca* at 294 K. The structure was refined using all intenties to the final error indices (using only the 1,446 reflections for which $F_o > 4\sigma(F_o)$) R_1/wR_2 = 0.054/0.143. About 15 Na^+ ions are located at three nonequivalent positions and octahedrally coordinated. The chemical composition is $Na_{0.94}(H_2O)Si_{2.06}Al_{0.94}O_6$. The Si/Al ratio of synthetic analcime is 2.19 determined by the occupations of cations, 14.79, in the single-crystal determination work.
Keywords: Analcime, Zeolite, Structure, Single-crystal, Si/Al ratio

Zeolites are today being used in diverse industrial applications such as an ion exchanger, a sorption agent, a molecular sieve, and a catalyst due primarily to its excellent structural stability, large and accessible pore volume, high activity, high resistance to nitrogen compounds, and high regenerability.[1,2] The Si/Al ratio of zeolite is very important factor in their applications because the chemical/physical properties of zeolites and the Si-Al ordering at the tetrahedral sites are quite different depending on their differing Si/Al ratios. The ion-exchanging and adsorptive properties of zeolites also depend heavily on the Si/Al ratios of zeolite frameworks.

One of the most importantly applied and informative technique for characterization of exchangeable cations, adsorbates, and framework in zeolites is single-crystal X-ray diffraction. So many attempts have been made to synthesize the large single crystals of various zeolites and then determine those structures by single-crystal X-ray diffraction technique. The first analysis of the crystal structure of a zeolite, analcime, was reported by Taylor in 1930.[3] The X-ray diffraction analysis was performed on a single crystal of natural analcime, $|Na_{0.96}K_{0.06}Ca_{0.06}$

$(H_2O)_{1.12}$|[$Si_{2.05}Al_{0.95}Fe_{0.02}Ti_{0.01}O_6$]-ANA, by Pechar.[4] Recently, Seryotkin studied the crystal structure of Ag-exchanged natural analcime, |$Ag_{1.88}(H_2O)_2$|[$Si_{4.12}Al_{1.88}O_{12}$]-ANA, by single-crystal X-ray diffraction technique and then compared the framework structure with the original Na-analcime.[5] Despite these extensive attempts at structural refinement of natural anacime, considerable detail cation sites, water positions, and ordering is still unknown. This work was thus made to investigate the sites of Na^+ and H_2O in analcime and determine the exact Si/Al ratio of framework of synthetic analcime by single-crystal Synchrotron X-ray diffraction technique. It is impossible to determine the Si/Al ratio of synthetic analcime by using ICP and Si NMR with the products of zeolite mixture.

For the experiments, we synthesized colorless single crystals of sodium Analcime, stoichiometry $NaSi_2AlO_6$, with diameters up to 0.20 mm from a gel prepared using fumed silica (99.8%, Sigma), sodium aluminate (technical, Wako), sodium hydroxide (96%, Wako), triethanolamine (TEA, 99+%, Acros), and distilled water (resistivity > 18.4 MΩ-cm). Its composition was $3.00SiO_2 : 1.50NaAlO_2 : 8.02NaOH : 454H_2O : 5.00$TEA. First, a silica slurry was prepared by placing 0.90 g of fumed silica in 18.57 g of distilled water in a 30-ml PTFE beaker. A suspension was prepared by shaking in an orbital shaker at 200 rpm for 10 min. In a 250-ml PTFE beaker, 1.60 g of sodium hydroxide was dissolved in 22.30 g of distilled water, and 0.62 g of sodium aluminate was added. The resulting solution was filtered through a 0.2-μm membrane filter (PTFE syringe, Whatman). After adding 3.73 g of TEA to the filtered sodium aluminate solution, it was filtered two times through 0.2-μm membrane filters. Finally, the latter solution was added to the former slowly; the mixture was a very viscous gel. These steps were all done at 294 K. This gel was put in a 30-ml PTFE bottle which was placed in a convection oven at 373 K for 14 days. The product was filtered, washed with distilled water 10 times, and dried at 323 K for 24 hr.

The product was characterized by optical microscopy and SEM (JSM-300, Jeol) analysis. SEM showed that the cubo-octahedral products were large Analcime single crystals with diameters up to 0.02 to 0.20 mm and that the octahedral and polycrystalline spherical impurities were faujasite and gismondine, respectively. Microscopic examination showed that the single crystals of analcime were transparent and colorless.

Hydrated and sodium saturated Analcime single crystals were prepared by static ion-exchanging method of the products with aqueous 0.1 M NaCl (Aldrich, 99.99%) (pH adjusted from 6 to 11 by dropwise addition of NaOH (Aldrich, 99.998%)). The ion-exchange procedure was repeated 5 times with the fresh solution. The product was then washed each time with 300-mL distilled water followed by filtration and oven-dried at 323 K for 1 day. One of these, a clear and colorless cubo-octahedron about 0.10 mm in cross-section, hydrated Na^+-saturated Analcime single crystal was lodged in a fine Pyrex capillary and then sealed in it by torch.

X-ray diffraction data for two single crystals were collected at 294(1) K using an ADSC Quantum210 detector at Beamline 4A MXW at the Pohang Light Source. Crystal evaluation and data collection were done using λ = 0.76999Å radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell constants and an orientation matrix were determined from 36 sets of frames collected at scan intervals of 5° with an exposure time of 1 second per frame. The basic scale file was prepared using the program HKL2000.[6] The reflections were successfully indexed by the automated indexing routine of the DENZO program.[6] The 30,025 reflections (see *Table* 1) were har-

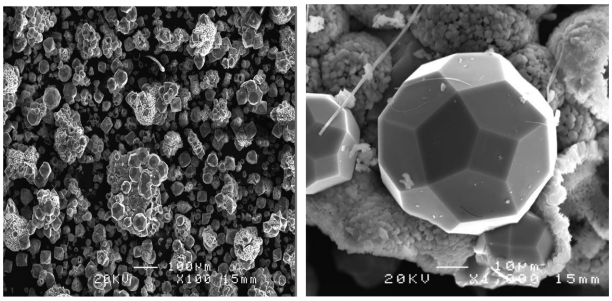
***Table* 1.** Summary of experimental and crystallographic data

	|$Na_{0.94}(H_2O)$|[$Si_{2.06}Al_{0.94}O_6$]-ANA
Crystal cross-section (mm)	0.10
Crystal color	transparent
Data collection T (K)	294(2)
Crystal System, Space group, *Z*	Orthorhombic, *Ibca,* 16
X-ray source	Beamline 4A MXW (PAL)
Wavelength (Å)	0.76999
Unit cell constant, *a* (Å)	13.703(3)
b (Å)	13.704(3)
c (Å)	13.703(3)
2θ range in data collection (deg)	60.56
Total reflections harvested	30,025
No. of unique reflections, *m*	1,512
No. of reflections with $F_o > 4\sigma(F_o)$	1,446
No. of variables, *s*	107
Data/parameter ratio, *m*/*s*	14.1
Weighting parameters, *a*/*b*	0.039/27.9
Final error indices	
R_1/wR_2 ($F_o > 4\sigma(F_o)$)[a]	0.054/0.143
R_1/wR_2 (all intensities)[b]	0.055/0.145
Goodness-of-fit[c]	1.32

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma F_o$ and $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; R_1 and wR_2 are calculated using only the 1,446 reflections for which $F_o > 4\sigma(F_o)$. [b]R_1 and wR_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.

vested for each crystal by collecting 72 sets of frames with 5° scans and an exposure time of 1 second per frame. These highly redundant data sets were corrected for Lorentz and polarization effects; negligible corrections for crystal decay were also applied. The space group *Ibca* was determined by the program XPREP.[7] A summary of the experimental and crystallographic data is presented in *Table* 1.

Full-matrix least-squares refinement using SHELXL97[8] was done on F_o^2 using all data for each crystal. A Fourier function revealed three large peaks at (0.6625, 0.0871, 0.1249), (0.6241, 0.1624, -0.0871), and (0.5859, -0.1246, 0.1626) with heights 2.54, 3.31, and 3.25 eÅ^{-3}, respectively. Isotropic refinement including them as Si,Al(1), Si,Al(2), and Si,Al(3) converged to $R_1 = 0.386$ and $wR_2 = 0.795$. From a subsequent difference Fourier function, peaks of heights 8.83, 9.11, 8.41, 9.14, 8.59, and 8.03 eÅ^{-3} were found at (0.6173, 0.1489, 0.0306), (0.7805, 0.1011, 0.1326), (0.6499, -0.0301, 0.1165), (0.5999, 0.1308, 0.2811), (0.6329, 0.2817, -0.1002), and (0.4705, 0.1492, -0.1186) which were refined as O(1), O(2), O(3), O(4), O(5), and O(6), respectively. Isotropic refinement including these peaks as framework oxygens converged to $R_1 = 0.319$ and $wR_2 = 0.735$. On an ensuing difference Fourier function, three peaks of heights 13.96, 14.49, and 12.70 eÅ^{-3} appeared



(a) (b)

***Fig.* 1.** The SEM images magnified 100 (a) and 1000 (b) of the Na^+-Analcime.

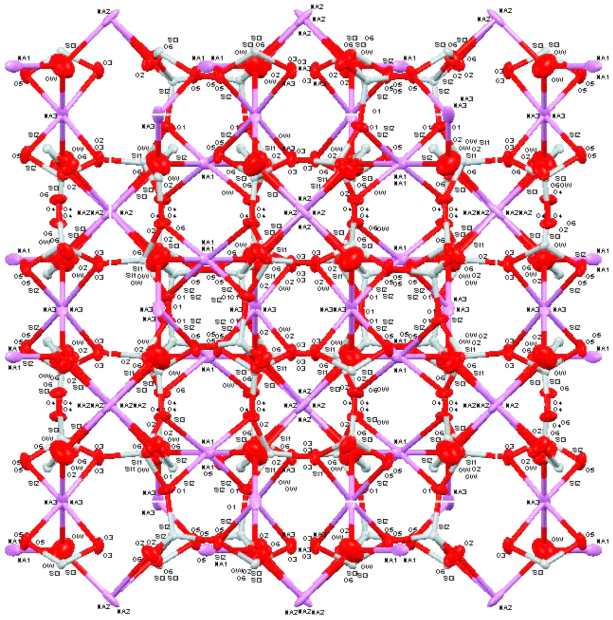


***Fig.* 2.** Stereoview of an analcime. The analcime framework is drawn with heavy bonds. The coordinations of the exchangeable cations to oxygens of the zeolite framework are indicated by light bonds. Ellipsoids of 25% probability are shown.

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

atom	Wyckoff position	x	y	z	[b]U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	[c]Occupancy	
											varied	fixed
Si,Al(1)	16(*f*)	66227(8)	8768(8)	12508(9)	139(6)	138(6)	139(6)	38(4)	37(4)	4(4)		16
Si,Al(2)	16(*f*)	62502(9)	16229(8)	-8771(8)	138(6)	139(6)	139(6)	-4(4)	-38(4)	35(4)		16
Si,Al(3)	16(*f*)	58772(8)	-12494(9)	16232(8)	139(6)	136(6)	140(6)	-34(4)	3(4)	-38(4)		16
O(1)	16(*f*)	61482(31)	14652(31)	3073(27)	416(22)	447(23)	184(17)	91(15)	35(15)	150(19)		16
O(2)	16(*f*)	78057(27)	10373(31)	13503(31)	187(17)	444(23)	424(23)	160(19)	-36(15)	-81(15)		16
O(3)	16(*f*)	64632(31)	-3069(26)	11456(31)	452(24)	173(17)	414(22)	-22(15)	149(19)	-98(15)		16
O(4)	16(*f*)	60376(31)	13488(31)	21931(27)	451(24)	432(23)	179(17)	37(15)	91(15)	170(19)		16
O(5)	16(*f*)	63497(31)	28068(26)	-10360(31)	425(23)	182(17)	447(24)	77(15)	-166(19)	-45(15)		16
O(6)	16(*f*)	53057(27)	11484(31)	-14636(31)	189(17)	418(22)	451(24)	-160(19)	-88(15)	36(15)		16
Na(1)	8(*d*)	50000	25000	12563(38)	456(29)	214(22)	0	0	357(25)	357(25)	4.90(12)	5
Na(2)	8(*c*)	87465(39)	0	25000	221(22)	451(29)	455(29)	354(25)	0	0	5.00(11)	5
Na(3)	8(*d*)	75000	-12423(38)	0	448(28)	211(22)	454(29)	0	350(25)	0	4.89(12)	5
O_w	16(*f*)	62573(59)	-12448(58)	-12586(59)	842(47)	857(47)	873(48)	251(38)	-233(38)	-225(38)	16.0(4)	16

[a]Positional parameters × 10^5 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. [b]The anisotropic temperature factor is $\exp[-2\pi^2 a^{-2}(U_{11}h^2 + U_{22}k^2 + U_{33}l^2 + 2U_{23}kl + 2U_{13}hl + 2U_{12}hk)]$. [c]Occupancy factors are given as the number of atoms or ions per unit cell.

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

Si,Al(1)-O(1)	1.656(4)	O(6)-Si,Al(3)-O(4)	105.7(2)
Si,Al(1)-O(2)	1.641(4)	O(6)-Si,Al(2)-O(5)	112.8(2)
Si,Al(1)-O(3)	1.643(4)	O(4)-Si,Al(2)-O(5)	111.2(2)
Si,Al(1)-O(4)	1.652(4)	O(6)-Si,Al(2)-O(3)	111.2(2)
		O(4)-Si,Al(2)-O(3)	112.9(2)
Si,Al(2)-O(1)	1.644(4)		
Si,Al(2)-O(2)	1.655(4)	Si,Al(2)-O(1)-Si,Al(1)	143.3(3)
Si,Al(2)-O(5)	1.643(4)	Si,Al(1)-O(2)-Si,Al(2)	143.6(3)
Si,Al(2)-O(6)	1.656(4)	Si,Al(1)-O(3)-Si,Al(3)	143.2(3)
		Si,Al(3)-O(4)-Si,Al(1)	143.5(3)
Si,Al(3)-O(3)	1.656(4)	Si,Al(2)-O(5)-Si,Al(3)	143.5(3)
Si,Al(3)-O(4)	1.642(4)	Si,Al(3)-O(6)-Si,Al(2)	143.4(3)
Si,Al(3)-O(5)	1.655(4)		
Si,Al(3)-O(6)	1.642(4)	O_w-Na(1)-O_w	179.8(4)
		O_w-Na(1)-O(4)	87.5(2),92.4(2)
Na(1)-O(1)	2.486(4)	O(4)-Na(1)-O(4)	117.7(2)
Na(1)-O(4)	2.482(4)	O_w-Na(1)-O(1)	87.4(2),92.7(2)
Na(2)-O(2)	2.482(4)	O(4)-Na(1)-O(1)	62.94(11),174.9(2)
Na(2)-O(6)	2.486(5)	O(1)-Na(1)-O(1)	116.9(2)
Na(3)-O(3)	2.476(4)		
Na(3)-O(5)	2.489(4)	O_w-Na(2)-O_w	179.7(4)
		O_w-Na(2)-O(6)	87.5(2),92.7(2)
Na(1)-O_w	2.435(7)	O(6)-Na(2)-O(6)	117.0(2)
Na(2)-O_w	2.409(7)	O_w-Na(2)-O(2)	87.5(2),92.3(2)
Na(3)-O_w	2.423(7)	O(6)-Na(2)-O(2)	63.02(11),174.97(14)
		O(2)-Na(2)-O(2)	117.4(2)
O(2)-Si,Al(1)-O(3)	105.7(2)		
O(2)-Si,Al(1)-O(4)	111.2(2)	O_w-Na(3)-O_w	179.8(4)
O(3)-Si,Al(1)-O(4)	113.0(2)	O_w-Na(3)-O(5)	87.8(2),92.1(2)
O(2)-Si,Al(1)-O(1)	112.8(2	O(5)-Na(3)-O(5)	116.9(2)
O(3)-Si,Al(1)-O(1)	111.1(2)	O_w-Na(3)-O(3)	87.2 (2),92.9(2)
O(4)-Si,Al(1)-O(1)	103.2(2)	O(5)-Na(3)-O(3)	63.01(11),175.00(14)
		O(3)-Na(3)-O(3)	117.6(2)
O(5)-Si,Al(2)-O(1)	105.5(2)		
O(5)-Si,Al(2)-O(2)	111.2(2)		
O(1)-Si,Al(2)-O(2)	112.9(2)		
O(5)-Si,Al(2)-O(6)	112.8(2)		
O(1)-Si,Al(2)-O(6)	111.2(2)		
O(2)-Si,Al(2)-O(6)	103.3(2)		

[a]The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

at (0.5, 0.25, 0.1248), (0.8759, 0.0, 0.2500), and (0.75, -0.1229, 0.0), respectively. Least-squares refinement including these peaks isotropically as Na(1), Na(2), and Na(3) converged to $R_1 = 0.266$ and $wR_2 = 0.682$. The next difference Fourier function showed the oxygen atoms of the water molecules at (0.6250, -0.1245, -0.1255) with a peak height of 6.28 eÅ^{-3}, which was refined as O_w. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement for all atoms converged to the error indexes $R_1 = 0.055$ and $wR_2 = 0.146$. The occupancy refinement of Na^+ ions at Na(1), Na(2), and Na(3) converged to 4.90(12), 5.00(11), and 4.89(12), respectively.

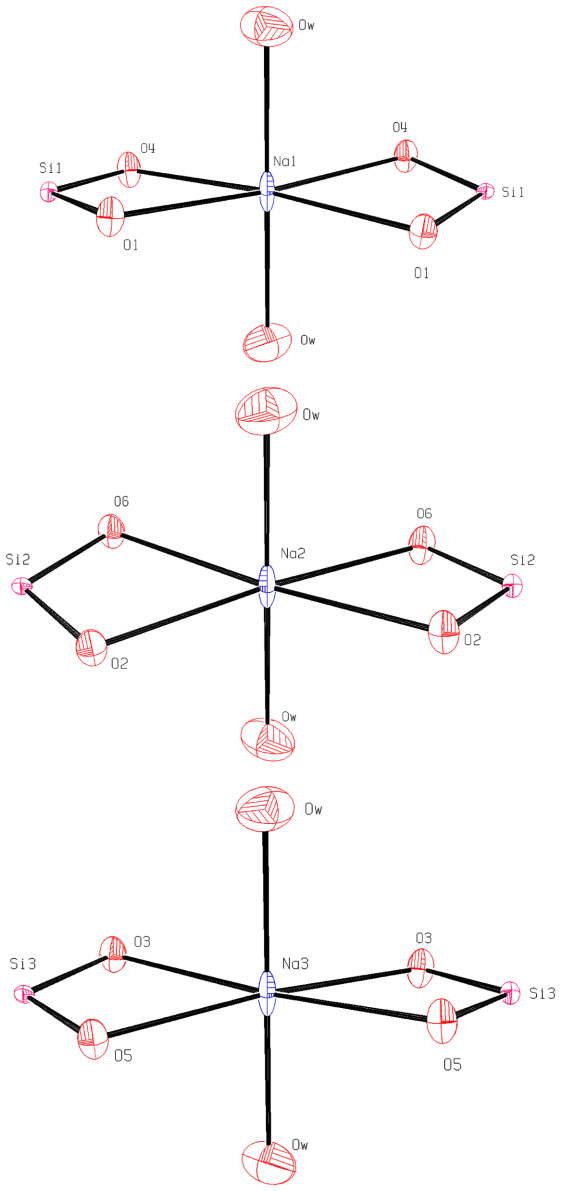


***Fig*. 3.** Images of the coordinations among Na^+ ion, framework oxygens, and water molecules as Ow.

Crystallographic data, atomic coordinates, thermal parameters, bonding distances and angles are presented in *Tables* 1~3. The tetrahedral sites by Si and Al were estimated by means of the average Si,Al-O distances. *Table* 3 lists the bonding distances and angles between tetrahedral Si,Al and framework oxygens. About 15 Na^+ ions per unit cell have been found at three nonequivalent positions (see *Table* 2). Each Na^+ ion has bonding distance of 2.476(4) ~ 2.489(4) Å with framework oxygens which is a little longer than the sum of the traditional ionic radii of Na^+ and O^{2-}, 0.97 + 1.32 = 2.29 Å[9] indicative of a good fit. These Na^+ ions are surrounded by four framework oxygens and water molecules which are characterized by the distorted octahedron of oxygen atoms. The 16 water molecules have been found at axial positions of octahedral Na^+ ions. The bonding distances of Na^+ ions with water molecules, 2.409(7)~2.435(7) Å, are smaller than with framework oxygens 2.476(4)~2.489(4) Å (see *Table* 3). The chemical composition of synthetic analcime in this work is $Na_{0.94}(H_2O)Si_{2.06}Al_{0.94}O_6$. It is concluded that the synthetic analcime had 2.19 of Si/Al ratio.

Supporting information available. Tables of calculated and observed structure factors (17 pages). The supporting materials are available *via* the Internet http://www.kcsnet.or.kr/bkcs.

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