Crystal structure of Ba^{2+}-exchanged zeolite Y (FAU), $|Ba_{35.5}|[Si_{121}Al_{71}O_{384}]$ (Si/Al = 1.70)

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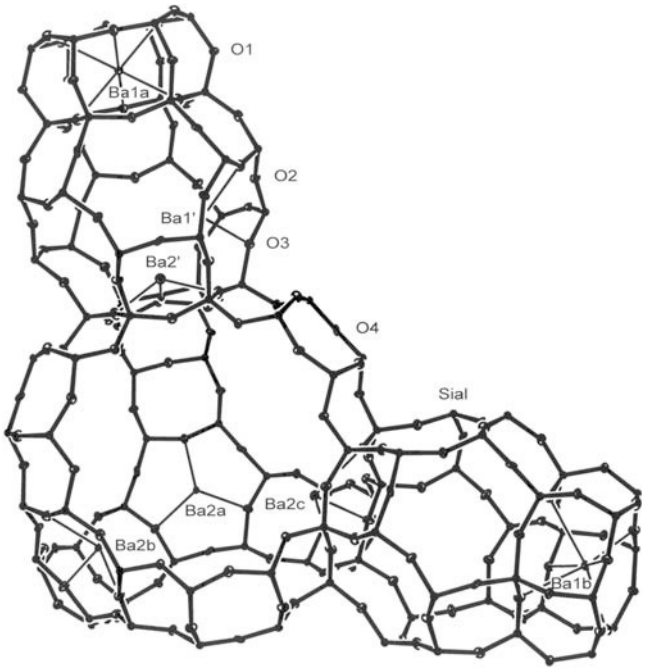

Abstract

$Al_{71}Ba_{35.5}O_{384}Si_{121}$, cubic, $Fd\bar{3}m$ (no. 227), a = 25.096(3) Å, V = 15806 Å^3, Z = 1, $R_{gf}(F)$ = 0.070, $wR_{ref}(F^2)$ = 0.203, T = 293 K.

Source of material

Large single crystals of sodium zeolite Y (FAU), stoichiometry $Na_{71}Si_{121}Al_{71}O_{384}$ per unit cell, were prepared by Lim *et al.* [1]. One of these, a clear colorless octahedron about 0.22 mm in cross-section was lodged in a Pyrex capillary. Crystal of $[Ba_{35.5}][Si_{121}Al_{71}O_{384}]$ was prepared by dynamic ion exchange with 0.05 M aqueous $Ba(OH)_2$ solution. The solution was allowed to flow fast the crystal at 294 K for 2 days. The resulting clear colorless crystal was dehydrated at 673 K and a dynamic vacuum of 1×10^{-6} Torr for 2 days.

Experimental details

Single crystal X-ray diffraction data were collected at Beamline 4A MXW of Pohang Light Source. The crystal evaluation and data collection were done using λ = 0.76999 Å radiation with a detector-to-crystal distance of 6.0 cm. Preliminary cell parameters 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 [2]. The reflections were successfully indexed by the automated indexing routine of the DENZO program. The final reflections set was obtained from 72 sets of frames with 5° scans and an exposure time of 1 second per frame.

Discussion

Zeolites are inorganic crystalline and nanoporous solids with well-defined crystal structures. They have been widely studied and used as ion exchangers, adsorbents and catalysts in industrial processes, because of the properties originated from the unique crystal structure containing large pore size and void volume [1].

In the crystal structure of $|Ba35.5|[Si_{121}Al_{71}O_{384}]$-FAU, about 35.5 Ba^{2+} ions per unit cell are found at seven different crystallographic sites. The 12.5 Ba^{2+} ions are on 3-fold axes in the double 6-rings (D6Rs) at site 1 and near site 1. The 6.5 Ba^{2+} ions at Ba1A are exactly at the centers of their D6Rs, and six Ba^{2+} ions at Ba1B are off center in the D6Rs. Of the 12.5 Ba^{2+} ions inside D6Rs, the 6.5 Ba^{2+} ions at Ba1A coordinate six framework O3 atoms at 2.809(7) Å. The six Ba^{2+} ions at Ba1B coordinate six framework O3 atoms at 2.639(8) and 3.008(9) Å, respectively. The 1.5 Ba^{2+} ion at Ba1' is located at site 1' in the sodalite cavities opposite D6Rs; the Ba^{2+} ion was recessed by 1.32 Å into the sodalite cavity from their 3-oygen plane. The Ba1'-O3 distance is 2.69(1) Å, which is almost same with the sum of the radii of Ba^{2+} and O^{2-}, 1.34 + 1.32 = 2.66 Å [3]. Site 2' position (opposite single 6-rings in the sodalite cage) are occupied by 0.5 Ba^{2+} ion. The Ba^{2+} ion is shifted by 0.88 Å in to the sodalite cage from its 3-oxygen plane (d(Ba2'—O2) = 2.58(2) Å and ∠O2–Ba2'–O2 = 109(2)°). The remaining 21 Ba^{2+} ions are located at three nonequivalent sites 2 (opposite single 6-rings in the supercage) with occupancies of 1, 13, and 7 per unit cell, respectively. One Ba^{2+} ion at Ba2A is strongly bonded to three O2 atoms at 2.47(1) Å, which is a little shorter than the sum of the radii of $Ba^{2+} + O^{2-}$. The O2–Ba2A–O2 angle is 116.2(7)°. The 13 and 7 Ba^{2+} ions at Ba2B and Ba2C position bond three O2 at 2.693(8) and 2.860(9) Å, respectively. When the fully dehydrated structure of $|Ba_{46}|[Si_{100}Al_{92}O_{384}]$-FAU and $|Ba_{35.5}|[Si_{121}Al_{71}O_{384}]$-FAU are compared [4], it can be seen that Ba^{2+} ions have various distributions in $|Ba_{35.5}|[Si_{121}Al_{71}O_{384}]$-FAU: Sites 1 and 2 split in two and three positions, respectively. It may due to the Si/Al ordering in the tetrahedral site with the increased Si/Al ratio.

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Table 1. Data collection and handling.

Crystal:	colorless block, size 0.22 × 0.22 × 0.22 mm
Wavelength:	0.76999 Å
μ:	31.14 cm^{-1}
Diffractometer, scan mode:	ADSC Quantum 210, φ/ω with 2° steps
$2\theta_{max}$:	60.64°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1574, 940
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 919
$N(param)_{refined}$:	61
Programs:	HKL2000 [2], DENZO [2], SHELXL-97 [5], ORTEP-III [6]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
Ba(1A)	16*c*	0.41(6)	0	0	0	0.018(2)
Ba(1B)	32*e*	0.19(3)	0.0077(2)	*x*	*x*	0.016(2)
Ba(1')	32*e*	0.05(1)	0.0659(5)	*x*	*x*	0.026(4)
Ba(2')	32*e*	0.02(1)	0.195(2)	*x*	*x*	0.03(1)
Ba(2A)	32*e*	0.03(1)	0.227(1)	*x*	*x*	0.026(7)
Ba(2B)	32*e*	0.41(3)	0.2423(1)	*x*	*x*	0.0102(7)
Ba(2C)	32*e*	0.22(3)	0.2502(2)	*x*	*x*	0.015(2)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Si/Al	192*i*	$^{0.63}/_{0.37}$	–0.05691(6)	0.12536(6)	0.03513(6)	0.0138(8)	0.0110(8)	0.0099(8)	–0.0022(5)	0.0009(5)	–0.0036(5)
O(1)	96*h*		–0.1102(2)	0	–*x*	0.020(2)	0.026(3)	U_{11}	–0.006(2)	–0.003(2)	U_{12}
O(2)	96*g*		–0.0048(2)	–*x*	0.1364(3)	0.022(2)	U_{11}	0.042(4)	0.008(3)	–0.007(2)	U_{13}
O(3)	96*g*		–0.0406(3)	0.0738(2)	*y*	0.030(4)	0.027(2)	U_{22}	–0.001(2)	U_{12}	0.008(3)
O(4)	96*g*		–0.0646(3)	0.0685(2)	¼–*y*	0.030(3)	0.020(2)	U_{22}	–0.002(2)	–U_{12}	–0.011(2)

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