

The First Zeolite with Three-Dimensional Intersecting Straight-Channel System of 12-Membered Rings

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Received March 26, 2001

Zeolite Beta is the first synthetic large pore zeolite with a three-dimensional channel system and a high Si/Al ratio.¹ Zeolite Beta has attracted much interest for its potential applications in a number of acid-catalyzed reactions, such as the alkylation² and acylation of aromatics.^{3,4} However, most interest on this zeolite came after the framework structure was independently solved by J. M. Newsam et al.⁵ and J. B. Higgins et al.⁶ a long time after the first report on Beta in 1967.¹ They found that the structure of Beta contained disorderings in the stacking sequence which do not significantly affect the accessible pore volume but influence the tortuosity of the pore connectivity along the *z*-direction and the models were described by polytypic series of a layer. Two different ordered series, polytype A (space group *P4₁22* or *P4₃-22*) and B (space group *C2/c*) were proposed on the basis of high-resolution electron microscopy (HREM) images and electron diffraction (ED) patterns. A hypothetical polytype C (space group *P4₂/mmc*) was also suggested as a hypothetical structure.⁵ However, up until now, there was no experimental evidence such as electron micrographs and powder X-ray diffraction data for the occurrence of polytype C. Beta was difficult to synthesize in high silica form, but recently pure SiO₂ Beta was synthesized in fluoride media. The existence of double four-ring (D4R) has been suggested recently from ¹⁹F MAS NMR in ITQ-14,⁷ but structural details have been left unsolved.

In general, crystal structures can be determined by X-ray diffraction methods; however, ordinary X-ray methods are not applicable for multiphase materials or crystallites with many planar defects. Electron crystallography is sometimes available to determine such crystal structures, because it is easy to take ED patterns and HREM images from a single crystalline region.

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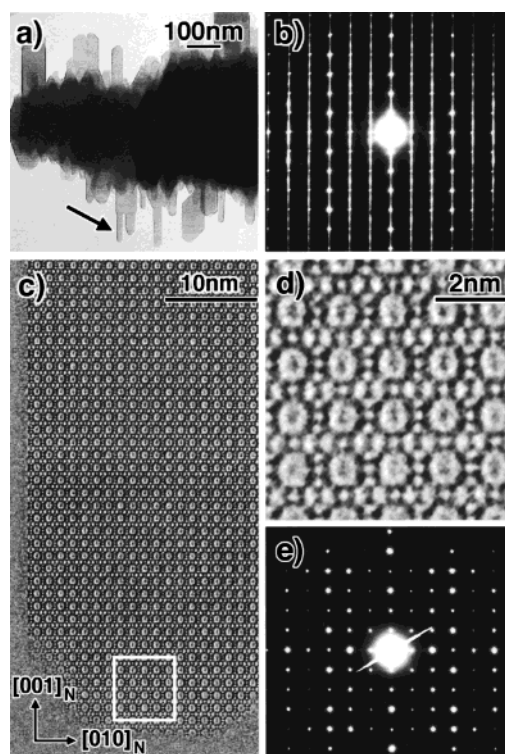


Figure 1. (a) Low-magnification TEM image, (b) electron diffraction pattern (showing very strong diffuse line corresponding to the coexistence of polytypes A and B), (c) HREM image of the overgrown crystal along $[100]_N$, (d) an enlarged image of a part of (c), and (e) ED pattern of the overgrown crystal.

In the present case, a new structure in the multiphase crystallites is solved by a new electron crystallography which will be reported separately. Furthermore, we obtained a surface structure which may be an important structure unit in the crystal growth process by comparing observed images of the fine termination structure at the surfaces with simulated ones based on the structure solution.

Pure silica ITQ-14 zeolite was prepared using tetramethylene bisquinuclidinium diquaternary cation (M_4BQ^{2+}). This organic cation was prepared at room temperature by reaction of 1,4-dibromobutane (4 mol, Aldrich) with quinuclidine (9 mol, Aldrich) using ethanol as a solvent. The mixture was stirred for 3 days before the solvent was evaporated under vacuum, and the resultant solid was washed with ethyl acetate and diethyl ether. The obtained dibromide dihydrated salt was then exchanged to the dihydroxide form by anion-exchange with Dowex-1 strongly alkaline resin (around 95% exchange).

For the zeolite synthesis tetraethyl orthosilicate (TEOS, Merck) was added to an aqueous solution of $M_4BQ(OH)_2$, and then the mixture was stirred at room temperature for an extended period of time to allow complete evaporation of the ethanol produced plus the water needed to reach the desired final composition. Then, the required amount of HF (aqueous solution recently titrated, typically 45–48 wt %) was added, and the mixture was homogenized by hand stirring. The mixture was poured into a Teflon-lined stainless steel autoclave and was then heated at 175 °C for 12 days while being tumbled (60 rpm). The gel composition was



After cooling the autoclaves, the contents were filtered, and the recovered solid was washed with water and dried. According to chemical analysis, the material contains 3.5 F⁻ per 64 SiO₂. Recently, the existence of D4R in pure ITQ-10 and ITQ-14 was

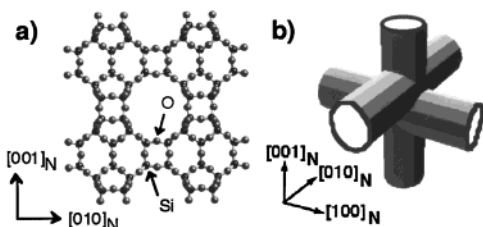


Figure 2. (a) A schematic drawing of new structure projected along $[100]_N$ direction. 12-MR is surrounded by 6-, 5-, and 4-MRs, (b) three-dimensional intersecting straight-channel system of 12-MRs.

Table 1: Atom Coordinates, Lattice Parameters, Mean Bond Lengths, and Mean Bond Angles of the New Phase in Beta

atom	Wyckoff notation	x	y	z
Si1	16r	0.120	0.377	0.116
Si2	8p	0.5	0.378	0.115
Si3	8n	0.312	0.312	0.25
O4	16r	0.401	0.328	0.170
O5	16r	0.204	0.325	0.190
O6	8q	0.141	0.354	0
O7	8p	0.5	0.132	0.629
O8	8o	0	0.351	0.139
O9	4k	0.5	0.352	0
O10	4h	0.5	0.5	0.129

^a Lattice parameters $a = b = 1.31$ nm, $c = 1.38$ nm. Mean bond length $\langle \text{Si-O} \rangle = 0.164$ nm. Mean bond angle $\langle \text{O-Si-O} \rangle = 109.4^\circ$, $\langle \text{Si-O-Si} \rangle = 157.0^\circ$.

claimed from the chemical shifts in ^{19}F MAS NMR of -38.5 and -39.3 ppm which were assigned to F located in D4R.⁷

High-resolution electron microscopy (HREM) observations were performed with a 400 kV electron microscope (JEM-4000EX). Some images and ED patterns were recorded with a slow-scan CCD camera.

Figure 1a shows a low-magnification TEM image of the as-made ITQ-14 sample. Many small pillars grown from the typical truncated square bipiramidal-shaped Beta crystals can be seen in the image. Figure 1b shows an ED pattern obtained from a large region including the pillars and Beta matrixes along $[010]_A$. [All indices are shown with a reference to the crystal structure type: A, B, and N for polytypes A, B, and new overgrown crystal, respectively.] Besides the many streaks which come from the Beta matrixes, mixture of polytypes A and B, there are also new spots just lying on the streaks with a nearly square mesh. The quantities of pillars are so small compared to the Beta matrix that the crystal structure of the pillars could hardly be determined from the X-ray diffraction patterns.

Figure 1c shows a high-resolution image taken from $[100]_N$ direction of the overgrown pillar indicated by the arrow in Figure 1a. An enlargement of a part indicated by a rectangle is shown in Figure 1d. The corresponding diffraction pattern is shown in Figure 1e. It can be seen that the diffraction spots in Figure 1e are just the new spots lying on the streaks in Figure 1b. This indicates that there is a certain geometrical relation among polytypes A, B, and this new phase. Obtained conditions from ED patterns for the observation of reflections are: (i) for hkl ; no conditions, (ii) for hhl ; $l = \text{even}$, and (iii) for $0k0$; no conditions. It is concluded from these that the crystal structure of pillars is tetragonal with space group $P4_2/mmc$. The lattice parameters are determined to be $a = 1.31$ nm, $c = 1.38$ nm from HREM images and ED patterns.

Much electron crystallography for solving crystal structures has been reported in the latest 20 years.⁸⁻¹⁴ Previously, we

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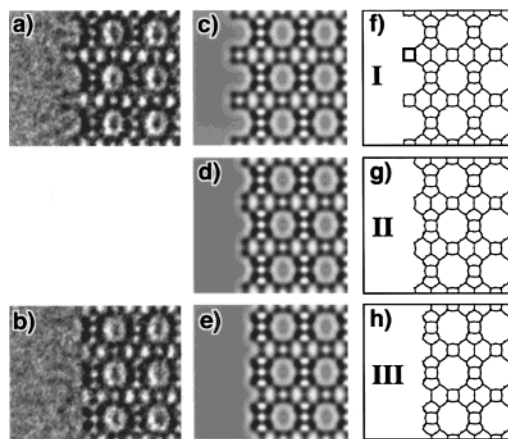


Figure 3. Enlarged HREM images of Figure 1c at two different surfaces (a, b), three different surface structures of types I, II and III (f, g, h), simulated images for the three different surfaces (c, d, e). The square drawn by thick lines in (f) shows D4R.

succeeded in solving unknown structures by using ED patterns¹⁵ or HREM images.^{16,17} However, for this present problem, the crystal structure could not be solved by these methods. Therefore, we took a new approach which consists of a combination of a HREM image and a Patterson map for retrieving three-dimensional framework topology, and refinement of Si and O atom positions using a way similar to that in the DLS program.¹⁸ Details of the procedure will be reported elsewhere. Figure 2a shows a schematic drawing of the resultant framework projected along the $[100]_N$ direction. One can see 4-, 5-, 6-, and 12-membered rings which correspond to the bright contrast dots with different sizes in the HREM image shown in Figure 1d. The framework has three straight channels with 12-MRs window along $[100]_N$, $[010]_N$ and $[001]_N$ directions as shown in Figure 2b. Atom coordinates, lattice parameters, mean bond lengths, and mean bond angles are listed in Table 1. It turns out that the structure solution is the same as that of the hypothetical polytype C proposed by Newsam et al.⁵ and that the atom coordinates are almost the same as those proposed by them by shifting the origin to the same position. This is the first experimental demonstration of the real existence of polytype C, and it is a beautiful single-crystal pillar overgrown on ordinary Beta.

Figure 3a,b shows enlarged HREM images from two different surface areas of the observed image taken from the $[100]_N$ direction of the overgrown crystal (Figure 1c). The observation of the type in Figure 3b is much more frequent than that of Figure 3a. Three different kinds of termination at the surface (Type I, II, and III) are possible based on our structure solution, and they are shown in Figure 3f,g,h. Corresponding image simulations are shown in Figure 3c,d,e. By comparison of the observed images with the simulated ones, it is clear that the image of Figure 3b fits well to type III and Figure 3a to type I. Type III corresponds to type I after removing D4Rs on the surface. The surface framework either ended with or without D4Rs suggests that D4R is the key growth unit during the crystal growth process.

Acknowledgment. This work was supported by CREST, Japan Science and Technology Cooperation.

JA0107778

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