SSZ-35 and SSZ-44: Two Related Zeolites Containing Pores Circumscribed by Ten- and Eighteen-Membered Rings**

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Large and extra-large pore high-silica microporous materials are in demand as catalysts in the petrochemical and pharmaceutical industries because of their combined properties of shape selectivity, acid strength, and high thermal stability.[1–3] Important insights into the catalytic properties of microporous materials are gained through a knowledge of their crystal structures, and these insights can, in turn, lead to the design of new materials with desirable properties.

Here we present the structure solution of two related high-silica molecular sieves, SSZ-44[4, 5] and SSZ-35,[4, 6] with unusual one-dimensional straight channels which contain pore openings that alternate between rings of ten and eighteen tetrahedral atoms (ten- and eighteen-membered rings, 10MR and 18MR). SSZ-35 and SSZ-44 are the first high-silica zeolites that possess pores with rings larger than 14MR (during the review of this paper the structure of a clathrasil, that is a nonporous silicate, was reported[7] that is composed of cages that also contain 18MR). The experimental micropore volumes obtained for SSZ-44 (0.185 $cm^3 g^{-1}$)[5] and SSZ-35 (0.197 $cm^3 g^{-1}$)[6] are significantly larger than any other known one-dimensional high-silica zeolite including the 14MR zeolites UTD-1[2] and CIT-5[3] that both have micropore volumes less than 0.14 $cm^3 g^{-1}$. SSZ-35 and SSZ-44 demonstrate the potential for a dramatic increase in the pore size of thermally stable high-silica zeolites beyond the currently available 14MR materials. These extra-large pore zeolites are highly desired because they permit catalysis and adsorption to be carried out on large molecules (greater than 8 Å) that are of interest to the pharmaceutical and fine chemicals industries, as well as the petrochemical industry. In addition to possessing unique, large pores, SSZ-35 and SSZ-44 are also the pure end-member polymorphs of a new fault series and allow the complex relationship between the organic structure-directing agent (SDA) and the stacking-fault probability of the zeolite framework to be investigated.

The structure of SSZ-44 (Figure 1 a) was solved by the application of the FOCUS[8] Fourier recycling algorithm to the synchrotron powder X-ray data (SPXRD) and confirmed from the Rietveld refinement[9] of the SPXRD (Figure 2). The SSZ-44 structure is seen to possess mirror plane symmetries parallel to the pore direction [001] that separate two layerlike units related by AB stacking. These layer units are composed of basic building units (BBU) that contain five-membered rings (Figure 1 b). The BBUs are stacked along the [001] pore direction and offset to form staircase-like columns (Figure 1 c). These columns are then interconnected to create the layerlike unit (Figure 1 d).

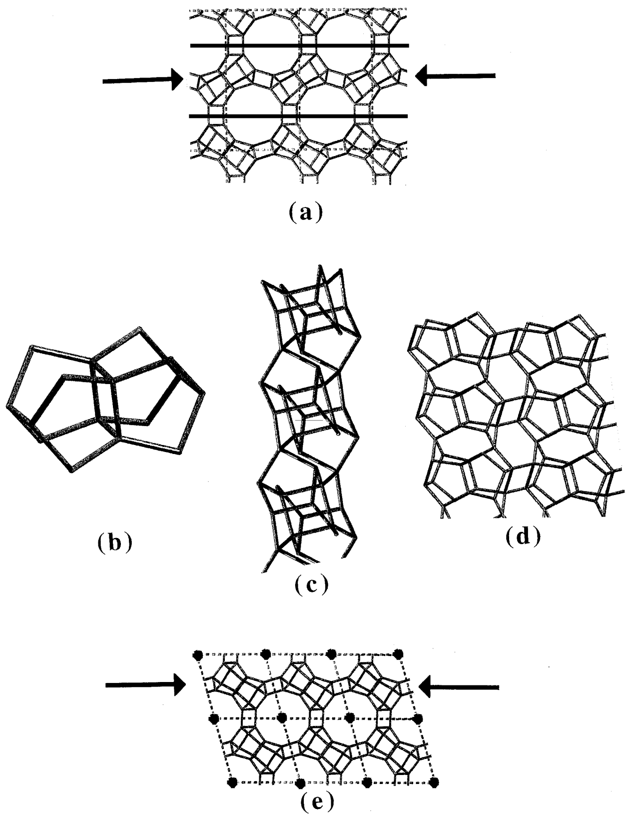

Figure 1. a) Framework topology of SSZ-44 viewed down the pores ([001] direction). The oxygen atoms have been omitted for clarity. Mirror planes are represented by solid lines separating layerlike building units. Arrows indicate the layer-like unit common to both SSZ-44 and SSZ-35. b) Basic building unit (BBU) of SSZ-35 and SSZ-44. c) Interconnection of BBUs along pore direction ([001] direction) to form stacked columns. d) Interconnection of stacked columns to form layer-like unit common to both SSZ-35 and SSZ-44. e) Framework topology of SSZ-35 viewed down the pores ([001] direction). Inversion centers are represented by black dots separating layerlike building units.

Replacement of the mirror plane symmetries possessed by the SSZ-44 structure with inversion centers generates a new topology composed of the same layerlike units found in SSZ-44. This new topology involves ABC stacking of the layers but still contains a one-dimensional pore system similar to that found in SSZ-44. The distance-least-squares (DLS[10]) refinement indicated reasonable structural parameters for this ABC stacking topology.

Similarities between the catalytic activity of SSZ-35 and SSZ-44 led to the identification of SSZ-35 as a potential candidate for the ABC stacking polymorph of SSZ-44. Comparison of the simulated powder X-ray data[11] for the ABC stacking polymorph to the experimental SPXRD for SSZ-35 and the subsequent Rietveld refinement (Figure 3) confirmed that SSZ-35 (Figure 1 e) is the ABC stacking polymorph of SSZ-44.[12]

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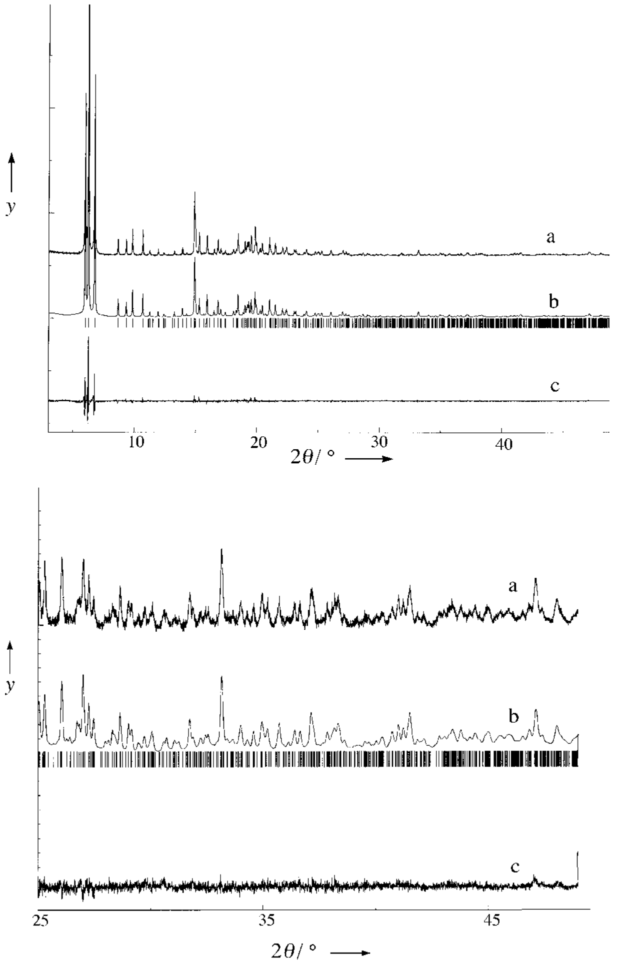

Figure 2. Synchrotron powder X-ray Rietveld refinement of SSZ-44: a) experimental, b) simulated, c) difference plots (plotted vs. relative intensity y). The lower data set shows an expansion of the 2θ range between 25 and 50° (multiplication factor × 10 relative to upper data set).

SSZ-44 and SSZ-35 both possess an unusual one-dimensional straight channel system with a pore diameter that alternates between a 10MR and a contorted 18MR (Figure 4). This alternating pore diameter of the straight channels can also be viewed as a consequence of the stacking of cages with 10 MR portals at the top and bottom. The cage structures of the two related materials SSZ-44 and SSZ-35 differ from each other in their unique arrangements of the four-, five-, and six-membered rings that circumscribe the internal walls of the cage (Figure 4). The 10MR of the SSZ-35 material has a free diameter of 5.5 × 6.1 Å, while the 18MR has a free diameter of 12.5 × 9 Å. The 10MRs in the SSZ-44 material are nearly circular (free diameter of 5.8 Å), while the 18MRs possess a slightly larger free diameter (12.9 × 9 Å) than those in the SSZ-35 material. For comparison, the only two known extra-large pore 14MR zeolites, UTD-1 and CIT-5, contain pores with free diameters of 10 × 7.5 Å and 7.4 Å, respectively.

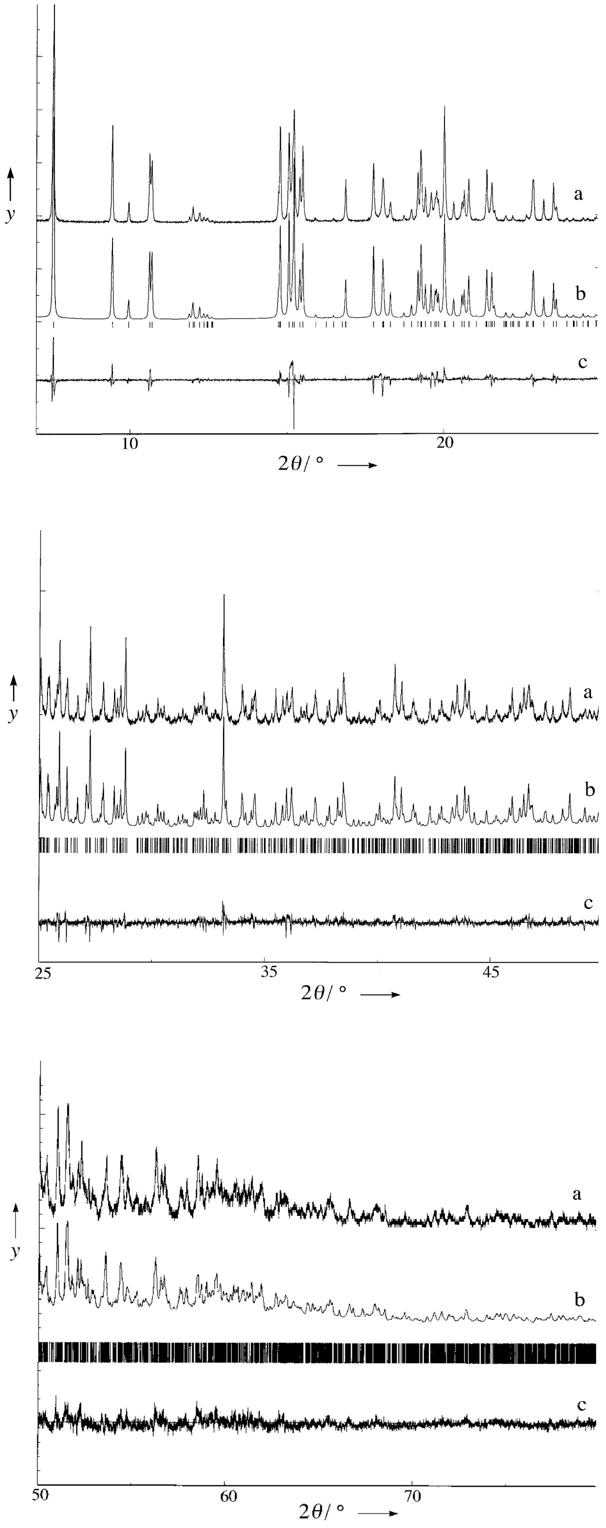

Figure 3. Synchrotron powder X-ray Rietveld refinement of SSZ-35: a) experimental, b) simulated, c) difference plots (plotted vs. relative intensity y). The middle data set shows an expansion of the 2θ range between 25–50° (multiplication factor × 8 relative to upper data set), the lower data set shows an expansion of the 2θ range between 50–80° (multiplication factor × 32 relative to upper data set).

As previously observed, SSZ-35 and SSZ-44 are related to each other through the orientation of the successively stacked layerlike unit that is contained in both structures (Figure 1 d). The SSZ-44 topology results if the layers are related through mirror planes and the SSZ-35 topology results if these layers are related through inversion centers (Figures 1 a and e). However, Rietveld refinement indicates that these materials are the pure end-member polymorphs which means they are neither faulted or intergrown. This is surprising since there

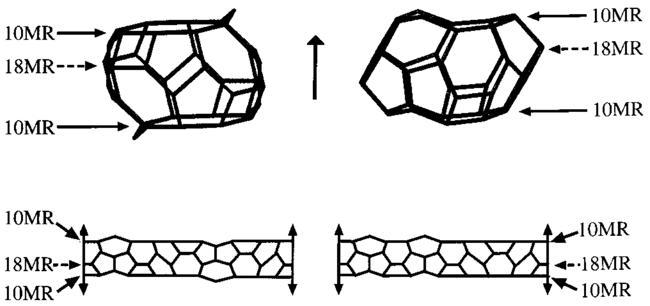

Figure 4. Illustration of the alternating 10 MR – 18 MR pore diameter for the SSZ-35 (left) and SSZ-44 (right) structures. Pore direction ([001] direction) is parallel to central vertical arrow (top half of the Figure). Arrangement of the ring system which circumscribes the internal pore surface is depicted in the bottom half of the Figure.

exist numerous examples of faulted or intergrown zeolites that are also composed of similarly related layers with varying stacking probabilities (e.g. FAU/EMT,[14] CON/SSZ-33/SSZ-26,[15] and zeolite beta[16]). These faulted intermediates are encountered frequently as a result of the poor specificity of the structure-directing agent for a particular end-member polymorph.

Often the pure end-member polymorphs are highly desired for properties that are unique from the faulted intermediates. One notable example is that of the chiral end-member of the zeolite beta fault series that could have tremendous utility in the catalysis and separation of chiral molecules. However, the designed synthesis of pure end-member zeolite polymorphs from the observed faulted intermediates has met with only limited success due to the poor understanding between the properties of the organic structure-directing agent or template and the stacking probability of the resulting zeolite framework. Although studies of the EMT/FAU fault series with crown ether SDAs have provided some insight into the effects of the SDA on the FAU/EMT fault probability,[17, 18] a greater understanding of the factors that influence zeolite faulting is needed.

The SSZ-35 and SSZ-44 materials allow the complex relationship between the SDA and resulting inorganic framework to be investigated by probing the synthetic and structural parameters that determine the stacking probabilities between these end-members.[19] Determination of the pertinent factors that govern zeolite faulting will open the possibility of eventually designing fault- and intergrowth-free microporous materials that are of great industrial and academic interest such as chiral zeolite beta.

In addition to being the pure end-member polymorphs of a new fault series, these materials are also the first high-silica zeolites found to possess 18MR-containing pores and illustrate the potential for the synthesis of thermally stable zeolites with pores larger than 14MR. Such extra-large pore zeolites are in great demand industrially for catalytic applications on large molecules.

Experimental Section

Synthesis of the organic structure-directing agent (SDA): The quaternary ammonium compound for use in the SSZ-44 reaction, *N,N*-diethyl 2,6-*cis*-dimethylpiperidinium (SDA I), is prepared by exhaustive ethylation of 2,6-*cis*-dimethylpiperidine by ethyl iodide in the presence of potassium bicarbonate in methanol. A more detailed procedure can be found in the analogous description for the 3,5-dimethylpiperdine derivative published by Nakagawa.[20]

N-ethyl, *N*-methyl 2,6-*cis*-dimethylpiperidinium (SDA II), used to synthesize SSZ-35, is prepared by a sequential alkylation of the 2,6-*cis*-dimethylpiperidine with ethyl iodide in methanol, removal of HI with potassium bicarbonate, and subsequent reaction of the tertiary base product with methyl iodide, again with methanol as solvent. Note that a large number of other organic SDAs can also be used to crystallize SSZ-35.[21]

Both SDAs are converted to their OH^- forms from the iodide salts by treatment with AG1-X8 hydroxide ion-exchange resin from BioRad. The exchange can be carried out by running the compound through the resin in a column, or by simply stirring the components overnight. The molarity of the SDA solution is determined by titration.

Zeolite synthesis: Either zeolite can be synthesized from the appropriate SDA by use of the following reaction quantities. SDA (5.1 g of a 0.58 M solution) (SDA I is employed to crystallize SSZ-44 or SDA II for SSZ-35) was measured into the Teflon cup of a Parr 23 mL reactor bomb. KOH (1.5 g of a 1.0 N solution) and water (4.4 g) were also added. Reheis F-2000 (hydrated alumina, ~53 wt% Al_2O_3) (0.04 g) was dissolved in the solution. Finally Cabosil-M5 (97% fumed SiO_2) (0.90 g) was added to the synthesis mixture and the mixture was stirred. The Teflon cup with the synthesis mixture was closed and sealed in a Parr autoclave. The autoclave was rotated at 43 rpm, while heated to 160 °C. The crystalline zeolite product was obtained after the mixture had been heated for 6 – 11 days. The solids were filtered, washed with approximately 100 times the water volume of the reaction, and air-dried.

The high-silica materials were prepared for synchrotron powder X-ray data (SPXRD) collection by calcination at 550 °C, then the sample was heated under vacuum in a capillary tube to 350 °C and the capillary tube was sealed under vacuum. The data were collected at the X7A beamline at the National Synchrotron Light Source at Brookhaven Laboratory (Upton, NY).

For the Rietveld refinements of SSZ-35 and SSZ-44 from the SPXRD, the background parameters (shifted Chebyshev function), the scale factor, and the zero shift were first refined, followed by the refinement of the lattice parameters and the profile parameters (Simpson's rule integration of the pseudovoight function), and finally the atomic positions and the isotropic temperature factors were refined.

Structure and refinement details for SSZ-44: The initial unit cell parameters for the calcined SSZ-44 material were obtained from the indexation of the SPXRD and refined to $a = 11.48534(26)$, $b = 21.94579(49)$, $c = 7.38811(14)$ Å and $\beta = 94.7016(3)^\circ$ ($V = 1855.9$ Å^3). Analysis of the systematic absences indicated symmetry consistent with space group $P2_1/m$ (no. 11). The observed structure factors were extracted by the LeBail extraction technique[22] and normalized by use of the scale factor obtained from the Wilson plot of the data. Reflections with d spacings larger than 1.3 Å were used as a pseudo single-crystal data set for input into the Fourier recycling algorithm, FOCUS,[8] for structure solution. At the 1.3 Å resolution limit employed, the reflection overlap (defined here as $\theta_1 - \theta_2 < [\mathrm{FWHM}_1 + \mathrm{FWHM}_2)/2]0.15$) (FWHM = full width at half maximum) is approximately 80%.

For the Rietveld refinement of SSZ-44, 136 variables were refined over a profile range of $3.0 - 50^\circ 2\theta$ ($\lambda = 1.20106$ Å, step size $= 0.005^\circ 2\theta$ which resulted in 9400 observables) and contained 731 reflections. A total of 82 soft constraints were employed (32: $d(\mathrm{Si{-}O}) = 1.61(01)$ Å, 50: $d(\mathrm{O{-}O}) = 2.61(01)$ Å) which resulted in $\bar{d}(\mathrm{Si{-}O})$ of 1.597(15) Å (max 1.627, min 1.568 Å). The average O-Si-O angle was 109.47° (max 112.4°, min 106.2°), and the average Si-O-Si angle was 151.4° (max 165.5°, min 133.0°). The weighting for the soft constraints was reduced but elimination of the constraints caused slight bond angle and distance distortions. The final residual values were $wR_p = 0.1058$ and an $R_p = 0.0892$. The Fourier difference map showed maximum peaks heights all less than 0.5 e^- Å^{-1}. The atomic positions together with the isotropic temperature factors are presented in Table 1.

Structure and refinement details for SSZ-35: The highest maximal topology of the pure-silica SSZ-35 framework and the symmetry of the as-made

Table 1. Fractional atomic coordinates for SSZ-44, esds in parentheses, (monoclinic, $P2_1/m$, $a = 11.48534(26)$, $b = 21.94579(49)$, $c = 7.38811(14)$ Å, $\beta = 94.7016(3)°$).[a]

Atom	x	y	z	U(iso)
Si	0.27227(57)	0.97791(29)	0.93601(92)	– 0.0044
Si	0.13548(63)	0.62930(29)	0.10193(97)	– 0.0023
Si	0.23886(57)	0.67904(28)	0.47825(90)	0.0142
Si	0.39323(60)	0.56890(30)	0.59794(84)	0.0019
Si	0.03652(58)	0.68184(27)	0.74254(92)	0.0161
Si	0.05149(61)	0.04087(32)	0.76211(88)	0.0115
Si	0.11053(58)	0.06798(30)	0.36508(91)	– 0.0059
Si	0.35948(58)	0.02838(31)	0.29204(89)	0.0039
O	0.22578(82)	0.91806(33)	0.02742(13)	0.0110
O	0.32885(84)	0.96241(46)	0.75474(103)	0.0330
O	0.36382(71)	0.01059(45)	0.08089(86)	0.0365
O	0.16115(66)	0.02349(41)	0.89856(12)	0.0162
O	0.02146(73)	0.59436(39)	0.15514(13)	– 0.0042
O	0.19913(84)	0.66360(45)	0.27348(97)	0.0097
O	0.09682(88)	0.67737(39)	0.94529(100)	0.0453
O	0.27877(107)	0.7500	0.49498(185)	0.0128
O	0.34544(77)	0.63729(30)	0.55819(136)	0.0259
O	0.13244(80)	0.66902(52)	0.60239(139)	0.0218
O	0.36967(107)	0.53179(37)	0.41218(103)	0.0088
O	0.53084(53)	0.57271(41)	0.65389(140)	0.0194
O	0.93509(70)	0.63319(30)	0.70903(128)	0.0258
O	0.98407(103)	0.7500	0.71105(177)	0.0303
O	0.96479(79)	0.98471(36)	0.73380(146)	0.0147
O	0.09791(92)	0.06329(49)	0.57827(89)	0.0087
O	0.24371(53)	0.06267(46)	0.32726(144)	0.0365

[a] This structure solution has been accepted by the International Zeolite Association Structure Committee and the code SFF has been assigned for SSZ-44.

Table 2. Fractional atomic coordinates for SSZ-35, esds in parentheses, (triclinic, $P\bar{1}$, $a = 11.411404(137)$ Å, $b = 11.526825(136)$ Å, $c = 7.376957(74)$ Å, $\alpha = 94.6607(7)°$, $\beta = 96.2055(8)°$, $\gamma = 104.8919(6)°$).[a]

Atom	x	y	z	U(iso)
Si	0.36019(35)	0.35630(33)	0.61106(50)	0.01319
Si	0.41221(34)	0.42852(33)	0.21918(49)	0.01888
Si	0.14209(37)	0.64205(36)	0.40966(53)	0.02179
Si	0.36181(37)	0.85678(37)	0.57148(54)	0.02607
Si	0.13396(37)	0.44151(35)	0.67151(54)	0.01930
Si	0.23859(38)	0.56731(36)	0.04636(53)	0.02242
Si	0.46001(38)	0.75796(38)	0.92351(53)	0.02925
Si	0.55968(37)	0.87468(35)	0.30376(52)	0.02226
O	0.36502(60)	0.37709(37)	0.40067(83)	0.02369
O	0.23168(48)	0.36461(47)	0.67114(77)	0.01125
O	0.47018(43)	0.45770(45)	0.73017(88)	0.03990
O	0.37472(50)	0.22510(37)	0.64375(83)	0.02625
O	0.30673(48)	0.47043(48)	0.10734(76)	0.03288
O	0.44890(49)	0.32523(47)	0.09908(72)	0.03153
O	0.22725(38)	0.77005(38)	0.50790(72)	0.02335
O	0.16588(60)	0.54074(44)	0.53230(76)	0.02545
O	0.17639(55)	0.61558(53)	0.20899(78)	0.03111
O	0.00178(28)	0.64477(50)	0.39598(79)	0.01427
O	0.43707(44)	0.85788(66)	0.39827(68)	0.03808
O	0.35217(52)	0.99191(30)	0.62479(81)	0.02041
O	0.43055(53)	0.81119(54)	0.73707(58)	0.02927
O	0.13629(45)	0.50548(50)	0.87315(54)	0.01517
O	0.33382(44)	0.67945(46)	0.98040(85)	0.03128
O	0.52218(51)	0.86584(43)	0.08546(49)	0.02315

[a] This structure solution has been accepted by the International Zeolite Association Structure Committee and the code STF has been assigned for SSZ-35.

SSZ-35 material is monoclinic ($C2/m$) with unit cell parameters of $a = 13.9$, $b = 18.2$, $c = 7.4$ Å and $\beta = 99.4°$. However, upon calcination the interaxial angles of the monoclinic cell relax to $\alpha = 90.924°$, $\beta = 98.920°$, and $\gamma = 89.437°$ which lowers the symmetry to triclinic (space group symmetry to $P\bar{1}$). The refined unit cell parameters for the SSZ-35 reduced cell are $a = 11.411404(137)$, $b = 11.526825(136)$, $c = 7.376957(74)$ Å, $\alpha = 94.6607(7)$, $\beta = 96.2055(8)$, and $\gamma = 104.8919(6)°$ ($V = 926.244$ Å^3).

For the Rietveld refinement of SSZ-35, 123 parameters were refined over the profile range 7–80° 2θ ($\lambda = 1.20106$ Å, step size $= 0.005° 2\theta$ which resulted in 14600 observables). 80 soft constraints were employed (32: $d(\text{Si–O}) = 1.61(01)$ Å, 48: $d(\text{O–O}) = 2.61(01)$ Å) which resulted in $\bar{d}(\text{Si–O}) = 1.599(11)$ Å (max 1.6165, min 1.5765 Å), an average O-Si-O angle of 109.466° (max 111.77°, min 107.52°), and an average Si-O-Si bond angle of 152.33° (max 162.62°, min 136.618°). The weighting for the soft constraints was reduced but elimination of the constraints caused slight bond angle and distance distortions. The final refinement resulted in $wR_p = 0.1188$ and $R_p = 0.0995$. The Fourier difference map showed maximum peaks heights less than 0.6 e$^-$ Å^{-1}. The atomic positions together with the isotropic temperature factors are presented in Table 2.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-410595 (SSZ-35) and CSD-410596 (SSZ-44).

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