

## Quantitative Three-Dimensional Modeling of Zeotile Through Discrete Electron Tomography

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**Abstract:** Discrete electron tomography is a new approach for three-dimensional reconstruction of nanoscale objects. The technique exploits prior knowledge of the object to be reconstructed, which results in an improvement of the quality of the reconstructions. Through the combination of conventional transmission electron microscopy and discrete electron tomography with a model-based approach, quantitative structure determination becomes possible. In the present work, this approach is used to unravel the building scheme of Zeotile-4, a silica material with two levels of structural order. The layer sequence of slab-shaped building units could be identified. Successive layers were found to be related by a rotation of 120°, resulting in a hexagonal space group. The Zeotile-4 material is a demonstration of the concept of successive structuring of silica at two levels. At the first level, the colloid chemical properties of Silicalite-1 precursors are exploited to create building units with a slablike geometry. At the second level, the slablike units are tiled using a triblock copolymer to serve as a mesoscale structuring agent.

### Introduction

Discrete tomography is a new reconstruction technique that has recently been applied to electron tomography for the first time.<sup>1,2</sup> It can be used to reconstruct three-dimensional (3D) grayscale volumes that contain only a small number of gray levels, typically corresponding to the different materials in the sample. Exploiting the discreteness of the set of admissible gray levels in the reconstruction algorithm can reduce reconstruction artifacts, improve the correspondence between the reconstruction and the measured physical object, and, in some cases, result in a substantial reduction in the required number of experimental projection images. The latter benefit is especially useful when investigating beam- or contamination-sensitive materials. Another major advantage of discrete tomography is that segmentation, which is required for a (quantitative) interpretation of a 3D reconstruction, is done automatically during the reconstruction. Recently, a new robust and efficient discrete reconstruction algorithm called the discrete algebraic reconstruction technique (DART) was developed and shown to be useful when reconstructing for large 3D data sets.<sup>2</sup>

Ordered mesoporous silica materials are ideal research objects for discrete reconstructions. Experimentally, the possibility of limiting the number of projections to be recorded on these beam-

sensitive materials is very attractive. Ordered mesoporous silica materials with amorphous walls are obtained using structure-directing surfactants or triblock copolymers.<sup>3,4</sup> In these syntheses, the trend of the amphiphilic structure-directing agent to form an ordered mesophase in an aqueous environment is exploited, and a malleable silicate source is cast into the ordered surfactant- or polymer-water structure.<sup>5</sup> Silica condensation occurs in the hydrophilic regions, and after removal of structure-directing agents and solvents, a silica negative of the mesostructure with controlled porosity is obtained. The resulting mesoporous silica adopts a high degree of uniformity and ordering of its mesopores, but the silica pore walls themselves are internally unstructured. The mesopore geometry is entirely defined by the surfactant or polymer. Structural variation is expected to occur when larger preshaped building units are used instead of monomeric silicate precursors. The mesoscale structure of the material then results from a compromise between polymer or surfactant supramolecular chemistry and the possibilities for arranging the building units. *Zeotiles* were claimed to be such 3D mosaic structures built from silica nanoslabs with discrete nanoscale dimensions and geometry.<sup>6,7</sup> Identification of the detailed tiling patterns of Zeotiles hitherto was not possible, and structure solving was limited to two dimensions, as accessible with transmission electron microscopy (TEM). A material designated as Zeotile-4 (ZT-4) is a representative example.<sup>6</sup> Here we report the use of discrete electron

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tomography in combination with a model-based approach to reveal the exact tiling scheme of the slablike subunits in the ZT-4 material.

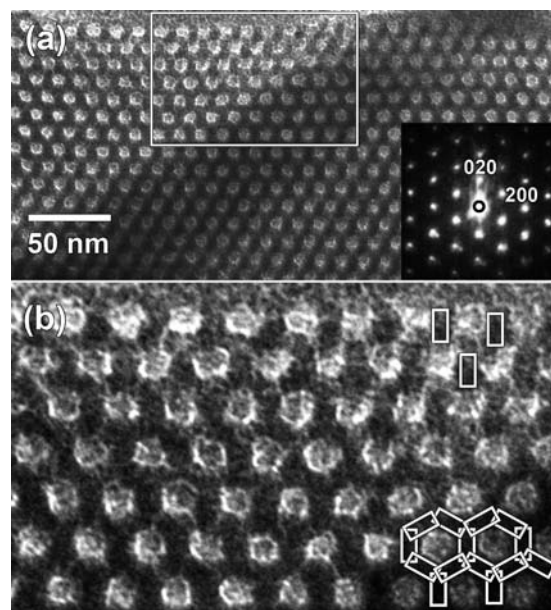
## Experimental Section

**Synthesis.** A 10 g sample of BASF Pluronic P123 ethylene oxide (EO)–propylene oxide (PO) triblock copolymer ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) was dissolved in 90 g of water under stirring, after which 24 g of this secondary template solution was combined with 8 g of 5 M HCl aqueous solution. A clear Silicalite-1 synthesis suspension of colloidal zeolite precursors was prepared from 37.32 g of tetraethylorthosilicate (TEOS, Acros, 98%) hydrolyzed in 32.13 g of a 40 wt % aqueous primary template solution of tetrapropylammonium hydroxide (TPAOH, Alfa) under stirring. After hydrolysis, 30.55 g of water was added, and stirring was continued for 24 h. Next, 18 g of this suspension was mixed with 9 g of 5 M HCl solution under vigorous stirring, and the mixture was then combined with the acidic triblock copolymer solution. The mixture was heated and kept at 90 °C under quiescent conditions for 4 days. A solid product was formed and separated from the liquid by centrifugation at 12 000 rpm. The product was washed with water until the pH exceeded 3. The sample was dried at 60 °C and finally calcined at 350 °C with a temperature ramping of 0.5 °C/min.

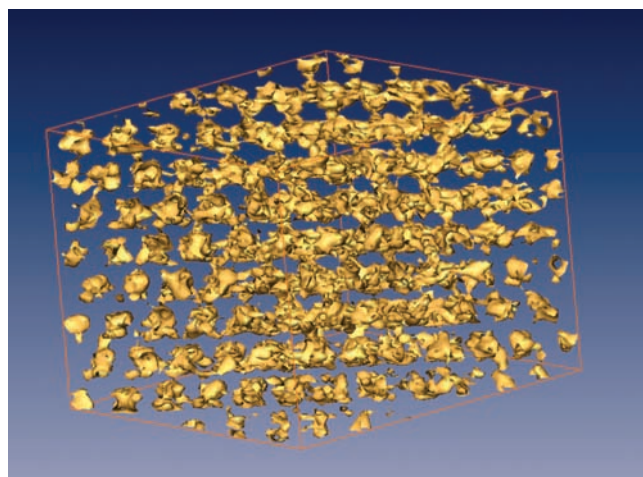
**TEM Investigation.** To obtain 3D information, a bright-field TEM (BF-TEM) tilt series of a ZT-4 crystal was recorded on a JEOL 3000F microscope at negative focus. The use of BF-TEM was motivated by the fact that the wall structures can be regarded as low-contrast materials. Diffraction contrast therefore does not hamper the projection requirement. The use of a Fischione ultrahigh-tilt tomography holder (model 2020) during acquisition resulted in an angular range of  $-48$  to  $+66^\circ$ , with projections taken every  $2^\circ$ . The angular range of the tilt series was limited by contamination of the sample induced by the electron beam as well as by shadowing by the amorphous carbon layer on which the ZT-4 crystals were deposited. The FEI software-packet Inspec3D was used to align these 2D projections prior to 3D reconstruction. This 3D reconstruction was carried out using the conventional simultaneous iterative reconstruction technique (SIRT) as well as DART for discrete reconstruction.<sup>2,8,9</sup> For the discrete reconstruction of ZT-4, the only prior knowledge used was that a pixel in the 2D projection obtained by BF-TEM represents either part of the wall structure, part of a pore, or part of a thin transition zone between the solid wall and an empty pore, accounting for slight misalignments of the building units. After reconstruction, the reconstructed volume was visualized using isosurface rendering.

## Results and Discussion

High-resolution 2D TEM (HRTEM) images acquired in thin regions of ZT-4 crystals, as presented in previous work,<sup>6</sup> revealed that the building units in the ZT-4 structure appear as rectangular units with dimensions of 4 nm  $\times$  8 nm. This is also illustrated in Figure 1, which shows that the building units are arranged in a layer with rectangular planar tiling. However, electron diffraction (ED) clearly indicated that the pore symmetry in the material is hexagonal, with the hexagonal axis perpendicular to the individual layers and a lattice constant of 11.3 nm. The number of models in which a stacking of rectangular units leads to a hexagonal ordering of the pores is



**Figure 1.** (a) [001] HRTEM image of ZT-4 and (inset) the corresponding ED pattern. It should be noted that the ED pattern is indexed with respect to the orthorhombic structure. (b) Enlargement of the area marked by white rectangle in (a). The 2D orthogonal arrangement of the nanoslabs within a single layer is marked by the white rectangles, which have a fixed size of 4 nm  $\times$  8 nm. A 3D structural model of ZT-4 is overlaid on the HRTEM image.



**Figure 2.** Isosurface rendering of the 3D reconstruction of ZT-4 based on SIRT. Rectangular building units cannot be observed.

limited. Nevertheless, it was impossible to experimentally determine the assembly on the basis of independent 2D projections. Therefore, 3D analysis by electron tomography was necessary to reveal the thickness of the building units and the sequence of the layers.

A series of TEM images with a fixed tilt increment was acquired, and an initial 3D reconstruction was computed using the SIRT algorithm (Figure 2), a common procedure during electron tomography in materials science.<sup>8,9</sup> Although the hexagonal ordering of pores could be observed, individual rectangular building units, which were clearly observed in the HRTEM study,<sup>6</sup> could not be discerned in the 3D reconstruction (Figure 2). The limited angular range of the acquisition and the small number of projection images caused artifacts to appear in the reconstruction. This hampered a straightforward inter-

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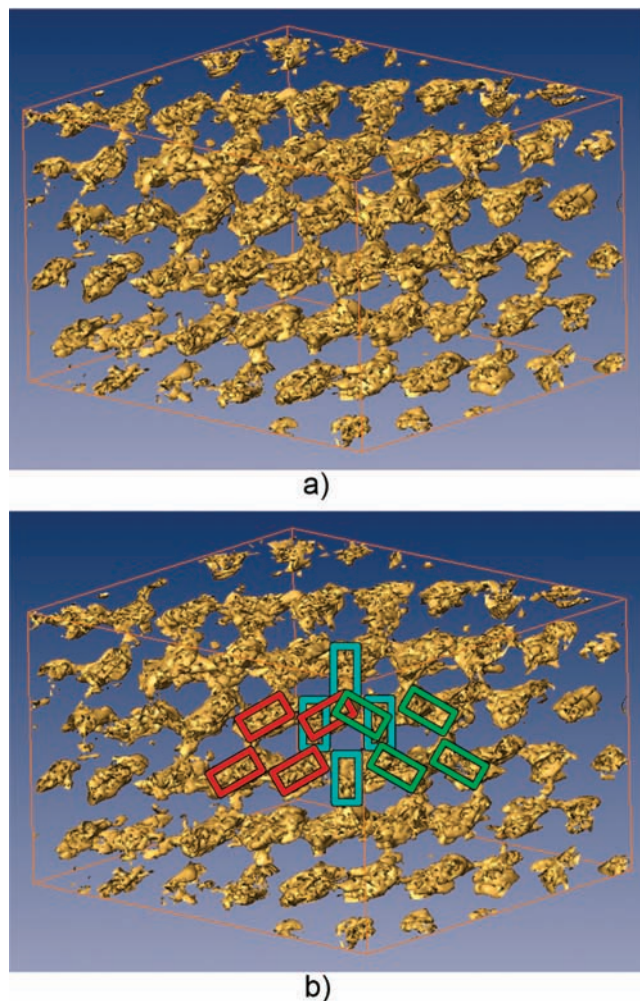
pretation of the SIRT reconstruction. Even if a full range of angles would have been available, several other artifacts would have obstructed a (quantitative) interpretation of the SIRT reconstruction because an additional segmentation step is required for the determination of the correspondence between different gray scales in the reconstruction and different compositions in the original structure.

Discrete tomography can overcome these limitations<sup>1,2</sup> by exploiting prior knowledge of the studied materials, leading to better reconstructions with fewer artifacts. As explained in the Experimental Section, this prior knowledge was based on the fact that the studied structure was consistently composed of regions with homogeneous density, resulting in well-defined local contrast. It must be noted that no assumptions were made concerning a possible lattice structure of the material. With discrete tomography, (missing wedge) artifacts are strongly reduced. Furthermore, segmentation is performed automatically during the reconstruction procedure, which results in a straightforward interpretation.<sup>1,2</sup> The same set of 2D images previously used for the SIRT reconstruction served as input for the DART algorithm. The material was assumed to be built from wall structures with one average density and separated by empty pores. The DART algorithm for discrete tomography could then be used to compute a new 3D reconstruction. The result of this procedure is shown in Figure 3a, which presents an isosurface rendering of the reconstructed volume along the pore direction.

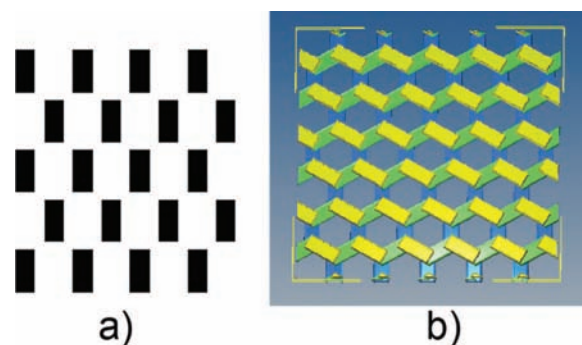
In this figure, the hexagonal arrangement of the pores can be clearly recognized. Moreover, rectangular building units now are clearly visible, confirming that the ZT-4 structure is indeed made up of 3D slablike species. This was suggested before and is consistent with the previous HRTEM study.<sup>6,7,10</sup> It must be noted that the figure shows a cubic subsection of the reconstruction volume. As the thickness of this subsection in the viewing direction varies throughout the figure, the visual impression of the pore shape also varies slightly. The pore shape appears rectangular in the lower area of Figure 3, corresponding to a region of the 3D reconstruction that contains fewer layers along the viewing direction, and more hexagonal in the middle of the image, where the reconstruction contains successive layers along the pore axis.

From this reconstruction, a model for the stacking of the building units could be derived. In Figure 3b and in the movies available at the authors' websites,<sup>11</sup> it is shown that the slab units are present in different layers along the direction of the main pore. Neighboring layers are related by a rotation of 120° with respect to the hexagonal axis. The structural model of ZT-4 deduced from our 3D reconstruction is illustrated in Figure 4. A single layer of the structure can be seen in Figure 4a, and the 3D stacking is illustrated in Figure 4b.

To ascertain the validity of our model, the experimental results were compared to a simulation study. The proposed tiling model was used to create a digital model of the structure. This computer model was used to generate projection data along the same projection angles as used in the TEM experiment. To make the simulation more realistic, Gaussian noise was added to each of the projection images and each of the projection images was



**Figure 3.** (a) Isosurface rendering of the 3D reconstruction of ZT-4 based on DART. (b) Rectangular nanoslabs indicating the rotation over 120° are overlaid on the image from (a).



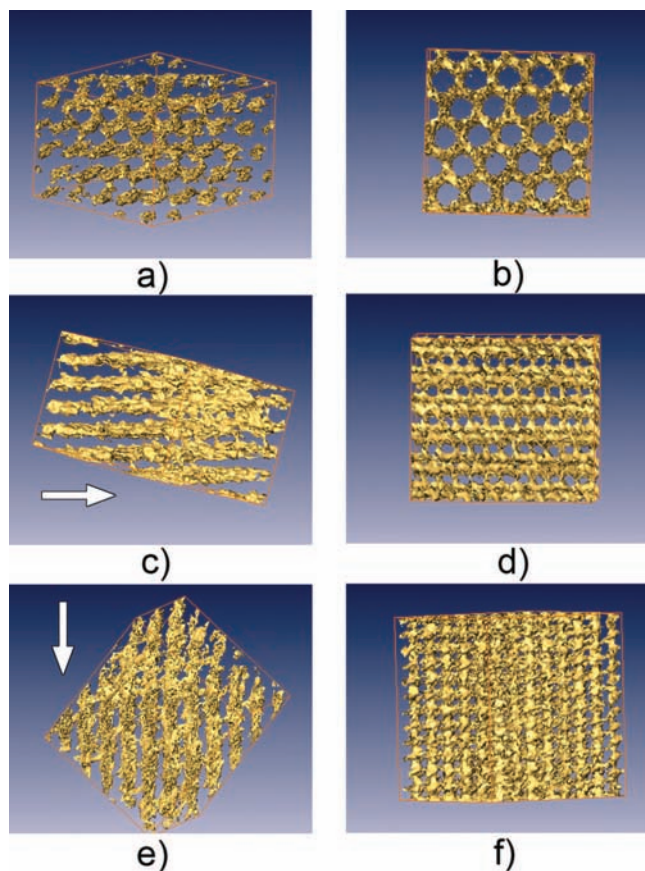
**Figure 4.** (a) Binary model of the nanoslabs in a single layer. (b) 3D stacking in the model structure.

misaligned by a small, random amount of at most one detector pixel. The projections obtained in this manner served as an input for a new DART reconstruction. The result of this procedure can be seen in Figure 5, where the experimental 3D reconstruction (Figure 5a,c,e) is compared to the simulated reconstruction (Figure 5b,d,f). For each of these directions, a reasonable match between the experimental and simulated reconstructions was found, confirming the validity of our 3D model.

The arrangement of the slabs as proposed in the idealized model corresponds to the chiral space groups  $P6_2$  and  $P6_4$ ,

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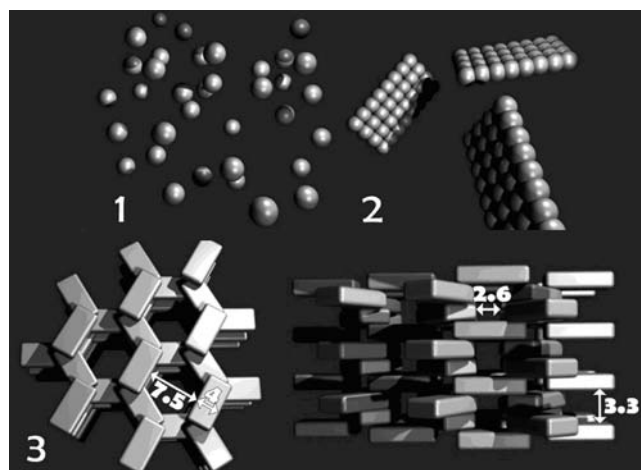


**Figure 5.** Comparison between the experimental 3D reconstruction (a, c, e) and the simulated reconstruction along the same viewing directions (b, d, f). The hexagonal axis in (a) is along the viewing direction. In (c) and (e), the hexagonal axis is indicated by the white arrow.

depending on the direction of the rotation of the layers. The lattice constants  $a$  and  $b$  could be derived directly from the high-resolution 2D images (Figure 1), but the height  $c$  of the unit cell, corresponding to 3 times the thickness of the slabs according to the space group, could not be obtained so easily from the 2D projections.

A direct, quantitative measurement of the slab thickness in the 3D reconstruction was not straightforward because of geometric distortions caused by the limited tilt range (missing wedge) during acquisition as well as other reconstruction artifacts. Accurate determination of the slab thickness from the 3D reconstruction had to account for the missing wedge artifacts. This was achieved using a model-based approach: the thickness of the building units in the digital model was adjusted to obtain the same height/thickness ratio of the slabs in the experimental and simulated reconstructions. Since the same missing wedge was used in both the simulation and the experiment, it could be safely assumed that the two reconstructions were affected by the same distortions. Furthermore, the face of the slabs could be determined from the 2D projections. Once the optimized reconstruction was obtained, the thickness of the slabs, which was used as an input for the simulations, served as an estimate of the actual thickness of the slabs. This procedure resulted in a thickness of  $1.65 \pm 0.25$  nm. The estimated error was determined by the sampling of the slice thickness in the reconstructions.

The discrete tomography analysis of ZT-4 revealed that this material indeed involves a unique stacking of slablike silica units to create a 3D mesoporous network. Neighboring hexagonal



**Figure 6.** Concept of tile formation and ZT-4 structure viewed along the hexagonal channel and from the side. Dimensions are given in nanometers.

channels with a free diameter of  $\sim 7.5$  nm, which is typical for many mesoporous materials, are systematically interconnected in this structure. These openings are situated between equivalent slabs recurring every fourth layer. The height of the openings ( $\sim 3.3$  nm) is twice the slab thickness, and the openings are narrowed toward the middle to a width of 2.3 nm (Figure 6). The arrangement of these openings follows the screw axis of the space group around the hexagonal channels, so four sides of each hexagonal pore are always connected to neighboring channels.

The synthesis of ZT-4 made use of intimate knowledge of the species present in the colloidal zeolite synthesis (Figure 6).<sup>12</sup> The clear solutions used for syntheses of siliceous zeolite Silicalite-1 were obtained using a molecular level template, TPAOH, in combination with a monomeric silica source, TEOS, in basic aqueous solution. In these mixtures, species with sizes of a few nanometers are formed wherein silica is enclosed by a shell of TPA cations.<sup>12–14</sup>

Over time or while the mixture is being heated, the interaction between the template and the enclosed silica causes self-organization, eventually leading to precursors that upon aggregation form the microporous zeolite framework.<sup>15–17</sup> The ready availability of these uniformly sized colloidal zeolite precursor species was exploited to restructure silica into novel mesoporous structures. The clear solution used for ZT-4 synthesis contained zeolite precursors with a size of  $\sim 2$  nm.<sup>13</sup> The pH of this solution was rapidly changed from 13 to 1. After acidification, the size of the colloidal particles was retained, as confirmed by dynamic light scattering (DLS). To this suspension, the triblock copolymer was added as structuring agent,

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and an immediate increase of particle size was observed with DLS, indicating spontaneous aggregation. The sudden changes in the colloidal environment resulted in the formation of specifically sized and shaped silica units, the previously proposed and now observed  $4\text{ nm} \times 8\text{ nm}$  slabs with a thickness of  $\sim 2\text{ nm}$ . The secondary structure-directing agent leading to mesoporous structures then had to contend with these preshaped building units (Figure 4). The Zeotile concept led to new structures with two levels of structural order. It opens the way to a much broader structural variety of ordered mesoporous materials. The applicability of this strategy was proven through this 3D structural analysis of Zeotile-4.

## Conclusions

Discrete electron tomography was combined with a model-based approach in order to unravel the 3D structure of Zeotile-4. Only by revealing the 3D stacking sequence of the previously observed orthorhombic 2D layers of rectangular building units could the truly multilevel organization within Zeotile-4 be disentangled. Furthermore, the thickness of the building units could be determined from the 3D reconstruction in a quantitative

manner. Formation of this new structure can occur only if the concept of successive assembly of anisotropic building units first into slablike structures and then into the hierarchical superstructure is applicable. Finally, this paper proves that the combination of conventional TEM, discrete electron tomography, and a model-based approach is a very powerful method for quantitative structure determination of a broad range of materials.

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