A New Layered Silicate with Structural Motives of Silicate Zeolites: Synthesis, Crystals Structure, and Properties

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A new layered silicate, RUB-51, $[Si_{12}O_{24}(OH)_4][C_6H_5CH_2N(CH_3)_3]_4$, was synthesized from hydrothermal experiments using benzyl trimethylammonium hydroxide as the structure-directing agent (SDA) in the $SiO_2-H_3BO_3-SDA-H_2O$ system. Its crystal structure was refined from X-ray powder diffraction data collected at both room temperature and 180 °C. It crystallizes in the orthorhombic space group $Pca2_1$ (No. 29) with $a = 8.3855(2)$ Å, $b = 14.4122(5)$ Å, $c = 11.7246(4)$ Å and $a = 8.4047$ (1) Å, $b = 14.5238$ (2) Å, $c = 11.7705$ (2) Å at room temperature and 180 °C, respectively. RUB-51 has the same silicate layer as RUB-15, another layered silicate that was first described in 1996, but with a different stacking sequence and intercalate SDA. The stacking sequence of the silicate layers in RUB-51, a segment of the structure of zeolite sodalite, is *AA* rather than *ABAB* as in RUB-15. Other characterization experiments using techniques like SEM, DTA-TG, and solid-state NMR complement and confirm the diffraction study.

Introduction

Zeolites and microporous materials are still most attractive as research topics due to their unique and interesting physical and chemical properties concerning catalysis, molecular sieving, adsorption, and ion exchange.[1,2] There is especially a demand for large pore materials, which are needed for new catalytic applications involving bulky reactant molecules. Considerable effort has been paid in developing the synthesis strategy based on structure-directing agents (SDA) for making new large pore materials.[3–6] Classically, high silica zeolites are prepared in direct synthesis runs using hydrothermal techniques from reaction mixtures containing organic molecules as SDA where they act as templates for pore space within the inorganic tetrahedral framework. However, new synthesis procedures are explored in addition, e.g., the use of ionic liquids as reactant media and the dry gel or quasi dry gel conversion technique, respectively.[7–9]

Recently, layered silicates have been introduced as catalytically active materials after delamination[10] or as precursors for the preparation of new mesoporous[11] and crystalline, microporous materials.[12] In a "two-step synthesis method" the first step comprises the synthesis of the layered silicates. Subsequently, these layered precursors are either delaminated or transformed in a topotactic solid state dehydration−condensation reaction into mesoporous or microporous framework materials.

Corma et al. successfully showed that the delamination method utilizing layered silicates produces structures with zeolitic surface-structural features such as semi pores which are highly active as acid catalysts.[13] In a first step, they synthesized layered precursors, swelled the layers with micellar *n*-alkyl, trimethyl-ammonium cations, and then subject the intermediate to ultrasound treatment to complete the delaminating process.

In addition, several laboratories started to explore new synthesis strategies in the search for new microporous materials. For example, layered silicate materials possessing layers with terminal Si−OH groups have been converted in a topotactic reaction into new framework structures upon calcination.[14–19] Similar to what was already known for MCM-22 and PREFER, the thermal process leads to two Si−OH groups of neighboring silicate layers to approach

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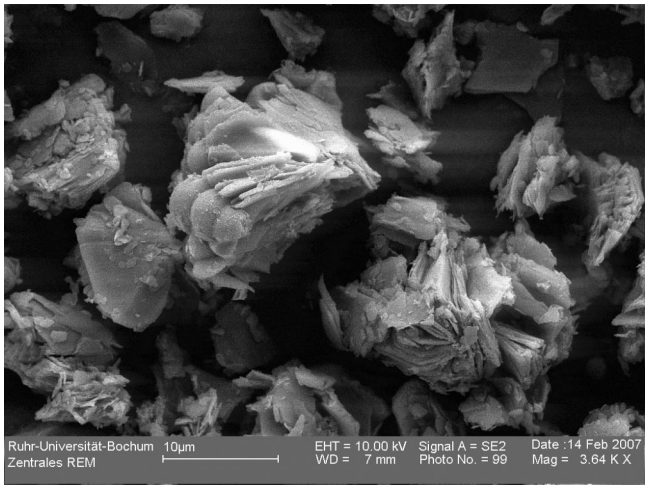

Figure 1. SEM image of the layered silicate RUB-51.

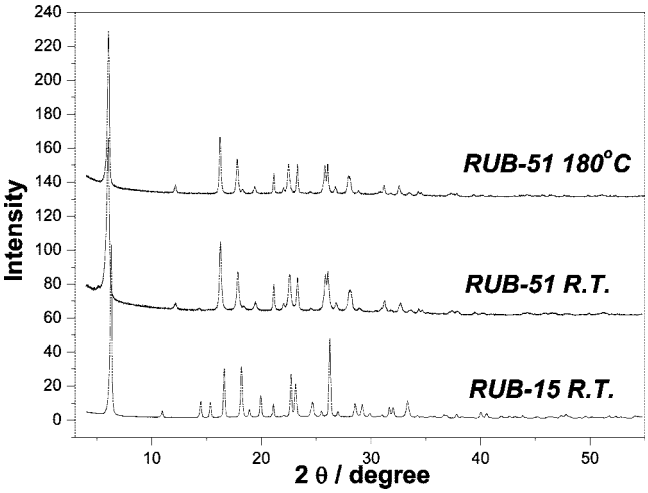

Figure 2. Powder X-ray diffraction patterns of RUB-15 and RUB-51 at room temperature and of RUB-51 at 180 °C.

each other and condensate, forming a Si−O−Si bond. As a consequence, all Q^3−Si units change to Q^4−Si units, i.e., a three-dimensional, four-connected silicate framework is formed during the condensation process. One of the most interesting examples is the transformation of RUB-39 to RUB-41,[20] in which a zeolite with a new framework structure type, RTT, was obtained via topotactic condensation reaction. This new zeolite can not be obtained otherwise so far. Similarly, the zeolite framework structure types of CDO and RTW are produced. The condensation reaction, at the same time, produces the empty, porous framework structure and, thus, is equivalent to the calcination step in the preparation of classical zeolite catalysts. As already mentioned, there are two more examples, PREFER, which condenses to FER-type material,[21] and MCM-22, which condenses to MWW type material.[12,22] However, both materials can also be obtained in a single-step synthesis.

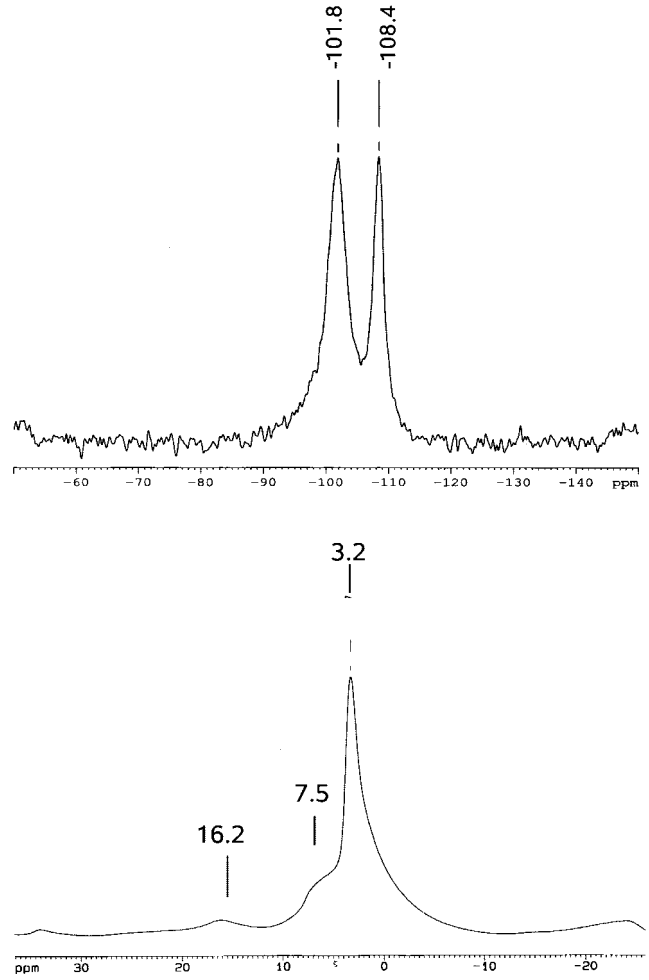

Figure 3. ^{29}Si and ^{1}H solid-state MAS NMR spectra of RUB-51.

In this study, our investigation was aimed at the synthesis of new layered silicate precursors that then might be converted to porous framework materials. It is known that the tetramethylammonium cation is a very powerful and versatile SDA for the synthesis of layered or framework silicates. In addition to several layered silicates and zeolites described in literature,[23] we were able to produce RUB-10,[24] RUB-15,[25] RUB-20 (isostructural to PLS-1[14] and ERS-12[26]),

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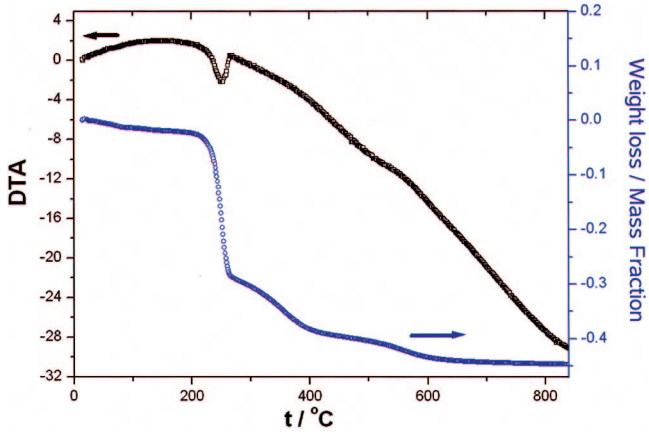

Figure 4. TG-DTA measurement of RUB-51.

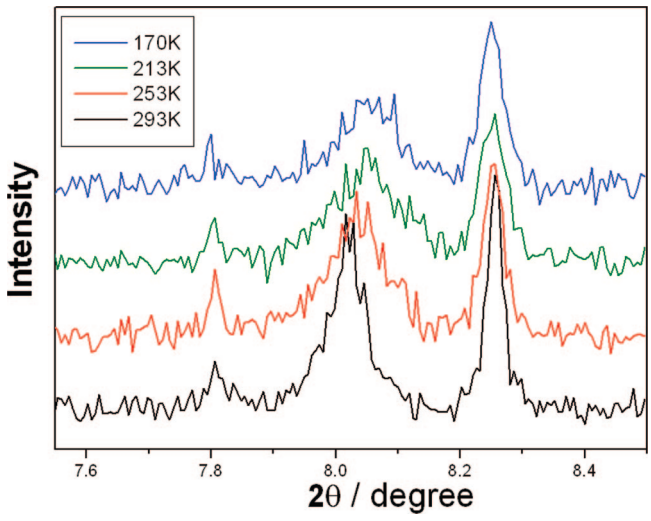

Figure 5. In situ synchrotron XRD patterns of RUB-51 at low temperatures with $\lambda = 0.54641$Å.

and RUB-22[27] by using this SDA. Thereon, we modified the simple tetramethyl ammonium cation in a systematic way by substituting one or more methyl groups by, for example, ethyl-, propyl-, phenyl-, or other groups.

In this paper, we present the synthesis and structure analysis of a new layered silicate precursor, RUB-51, synthesized with benzyl trimethylammonium hydroxide.

Experimental Section

Synthesis. Appropriate amounts of amorphous SiO_2, H_3BO_3, and aqueous benzyltrimethylammonium hydroxide solution (40% weight percentage) were mixed and stirred until a uniform gel was obtained. Water content was then controlled by evaporation at 60 °C in an oven to reach the starting gel composition of SiO_2:H_3BO_3:SDA:H_2O = 0.9:0.1:0.5:3–4. The mixture was then transferred into a Teflon-lined stainless steel autoclave and kept at 120 °C for 21 to 30 days. The autoclave was quenched in cold water to room temperature after reaction. The solid product, laboratory-code RUB-51, was separated by centrifugation, washed with distilled water and ethanol, and finally dried in the oven at 70 °C.

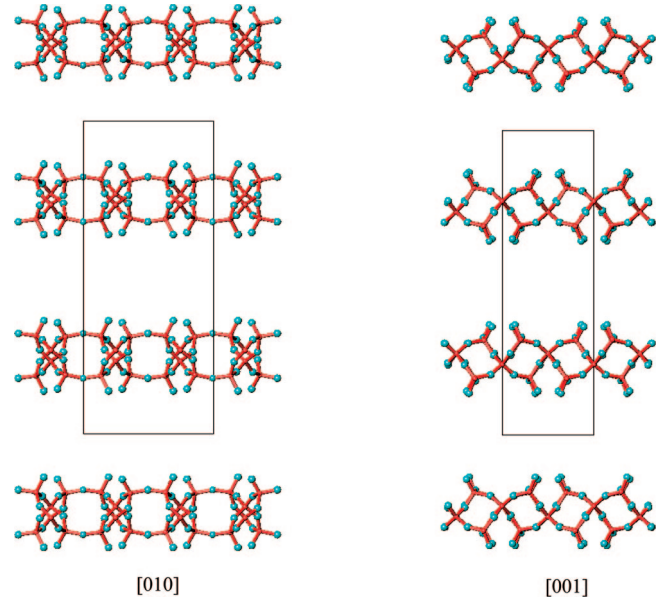

Figure 6. Crystal structure of RUB-15, projections along [010] and [001] (SDA and H_2O are omitted for clarity).

Characterizations. TG-DTA analysis experiments were carried out on a Bähr STA 503 thermal analyzer with heating rate of 1 °C/min, and kept for 2 h at 800 °C. Powder X-ray diffraction (PXRD) was performed at both room temperature and 180 °C on a Siemens D-5000 diffractometer with monochromatized Cu Kα_1 radiation in a rotating capillary (φ = 0.3 mm) to prevent preferred orientation. The diffraction data were collected with a Braun position sensitive detector in the range from 4 to 95° 2θ and step width of 0.0079° 2θ. In addition, synchrotron diffraction powder data at lower temperatures (170 to 293 K) were collected at Beamline B2 at HASYLAB, DESY Hamburg with λ = 0. 54641 Å.

Indexing of the powder pattern was carried out with the program Dicvol implemented in the FULLPROF 2K suite.[28] The structure of RUB-51 was solved from model building and subsequently refined with FULLPROF 2K.

^{29}Si, and ^{1}H solid-state MAS NMR spectroscopy were performed at RT on a Bruker ASX 400 using 7- and 4-mm Bruker probes.

Results and Discussion

Synthesis. According to our previous experience, layered silicates emerge preferentially at synthesis temperatures lower than 150 °C. In this study, RUB-51 was obtained at 120 °C as small, colorless crystals. As shown in Figure 1, plate like morphology, typical for layer silicates, is formed for this newly synthesized material. The size of the crystals is about 5 × 5 μm and submicrometer (ca. 0.1 μm) in thickness.

X-ray Diffraction. The XRD powder pattern of RUB-51 is displayed in Figure 3. This material has only moderate crystallinity showing peak half-width of ca. 0.20° 2θ at low diffraction angles and a sharp decrease in intensity at angles higher than ca. 35° 2θ. This led to a low-resolution data set with severe overlap of reflections at already medium 2θ ranges. Therefore, the atomicity criterion in resolution of the data set can not be met (Sheldrick's rule) which prevented

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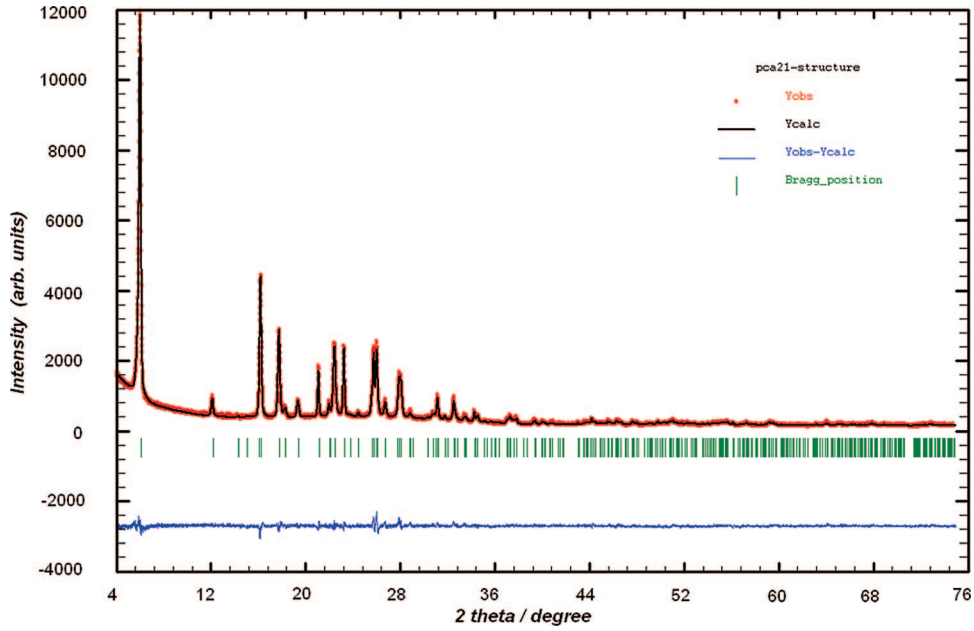

Figure 7. Rietveld refinement of the structure of RUB-51 from powder diffraction data collected at 180 °C using Fullprof.

Table 1. Experimental Parameters Used for the Structure Refinement of RUB-51 at 180 °C

diffractometer	Siemens D 5000
sample holder	capillary
wavelength (Å)	1.54056
2θ range (deg)	4.0−75.0
step size (° 2θ)	0.0079
no. of points	8988
Total no. of reflections	405
fwhm ($2\theta = 6.03°$)	0.18
fwhm ($2\theta = 17.9°$)	0.19
peak profile	pseudovoigt
no. of restraints	64
space group	$Pca2_1$ (29)
lattice parameter	
a (Å)	8.4047 (1)
b (Å)	14.5238 (1)
c (Å)	11.7705 (2)
unit-cell volume (Å^3)	
R_p	14.9
R_{wp}	14.3
R_{exp}	10.85
χ^2	1.73
R_{Bragg}	4.76

from solving the structure using direct methods. Attempts to improve crystallinity significantly by optimizing the synthesis condition such as increasing the synthesis time failed; the improvement was very minor. We also tried direct space structure solution, however, without success.

Using DICVOL, the pattern of RUB-51 was readily indexed with an orthorhombic cell of $a = 14.42$ Å, $b = 8.38$ Å, and $c = 11.72$ Å. Analysis of systematically extinct reflections led to space group symmetries $Pbc2_1$ (No. 29, acentric) and *Pbam* (No. 55, centrosymmetric).

As shown in Figure 3, the powder X-ray diffraction pattern of this newly synthesized material has some similarity to the layer silicate RUB-15.[25] The unit-cell dimensions of RUB-51 are closely related to those of RUB-15 ($a = 27.92$ Å, $b = 8.41$ Å, and $c = 11.52$ Å). Assuming that RUB-51 is a layered material and knowing about the modular character of silicate subunits it was concluded that RUB-51 and RUB-15 should have almost the same silicate layer (extending in the $b-c$-plane), with stacking periodicity in RUB-51 of about half that of RUB-15.

For the Rietveld refinement of RUB-51 (see below), we used the standard setting in the space group ($Pca2_1$, No. 29) which is derived by exchanging the a and b axes. Please note that in the following, the unit cell $a = 8.38$ Å, $b = 14.42$ Å, and $c = 11.72$ Å will be used for RUB-51.

^{29}Si solid-state NMR spectra also supported the proposed structure. The ^{29}Si NMR spectrum (Figure 4) showed that there exist two types of Si environment in RUB-51. The signals were assigned to Q^3-silicon for the peak at δ −101.8 and Q^4-silicon at δ −108.4. The intensity ratio is Q^3:Q^4 = 2: 1 as it was observed for RUB-15 (Q^3, δ −101; Q^4, δ −108). The chemical shift values of the corresponding signals were also very close. The ^{1}H NMR spectra showed that the SDA protons gave very broad signals at 3.2 and 7.5 ppm, which could be attributed to protons in the alkyl groups and aromatic group, respectively. A broad signal at δ 16.2 was also observed, similar to other layered silicates like RUB-39[17] and RUB-18,[29] which indicated strongly H-bonded Si−OH groups involving the silanol groups of the silicate layer. This unusual proton chemical shift is different from defect silanol groups in as synthesized high-silica zeolites, at ∼10 ppm, indicating stronger and more linear H-bonds for the former environment.[30] Our previous careful studies on RUB-18[31,32] revealed that two neighboring silanol groups in the silicate layer shared one hydrogen atom and carried one negative charge. This structural feature gave rise to the high-field-shifted ^{1}H signal, so it is likely that there exist similar structural units in the silicate layer of RUB-51.

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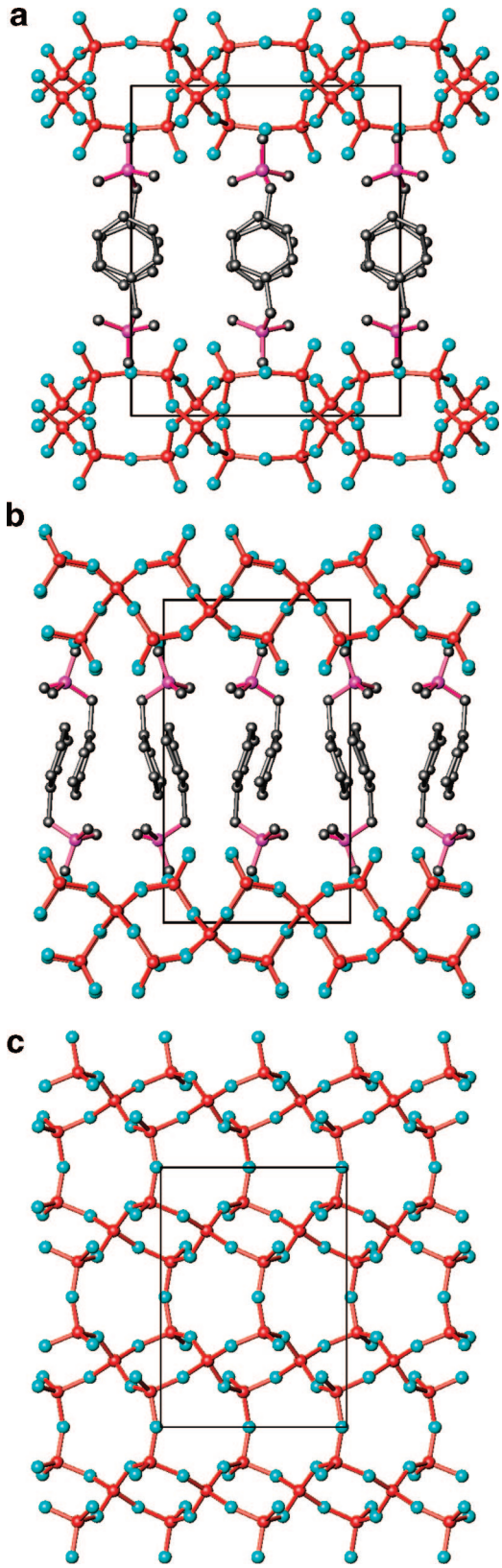

Figure 8. Crystal structure of RUB-51, projections along [100], [001], and [010].

Thermoanalysis. The DTA-TG measurement of RUB-51 (Figure 5) shows quite different curves compared to RUB-15. In contrast to RUB-15, RUB-51 contains very little H_2O. There is only a very slight weight loss from room temperature to 200 °C. This is attributed to physically absorbed water. A strong weight loss of about 28% is visible around 250 °C followed by an additional weight loss of ca. 15% which occurs in two steps between ca. 270° and 600 °C. This decrease in weight is due to the removal of organic species and to the expulsion of water, which is generated by the condensation of neighboring silanol groups. The total weight loss is about 44.7%; however, the final product is colorless, amorphous silica.

Because we observed no differences in peak intensity or position when conducting X-ray diffraction experiments with RUB-51 at room temperature and 180 °C (see Figure 3), we concluded that there is no structural water present in RUB-51.

Variable-Temperature XRD. On the basis of the analysis of the peak half-width, we drew the conclusion that RUB-51 has a higher degree of structural order at higher temperature. After careful comparison of the two XRD patterns recorded at RT and 180 °C we observed narrower fwhm values at 180 °C indicating improved crystallinity. Also, when we compared the synchrotron diffraction pattern collected at low temperature, we noticed that the peaks became considerably broader with lower intensity as we decreased the temperature. Figure 6 shows a section of the synchrotron diffraction patterns of RUB-51 at temperatures between 170K and 293K. This indicates a significant decrease in structural order with decreasing temperature.

The reason for disorder has not been analyzed yet. Additional investigations on the nature of disorder are in progress that apply structure simulations of stacking disordered materials generated by the program DIFFAX.

Structure Analysis. For the structure refinement a starting model for RUB-51 was built on the basis of the known structure of RUB-15.[25]

In RUB-15, there exist 20 H_2O molecules in the unit cell that form strong hydrogen bonds in the crystal structure and are almost a mirror image of the silicate layer in the unit cell. The hydrogen-bond network plays an important role for the stability of the crystal structure. RUB-15 can be viewed as a microporous 3-dimensional bond network built from silicate layers interstratified with an ordered water network. In its pores, tetramethylammonium cations are occluded which compensate the negative charge of the silicate layer. The silicate layers alone stack in an *ABABAB* sequence along the *a* axis. Figure 6 shows the projections of the RUB-15 structure along the [010] and [001] directions. Neighboring silicate layers seem to be identical in the [010] projection; in the [001] projection, however, a displacement of *b*/2 between neigboring layers is realized, leading to an *ABABAB* stacking sequence. Considering the fact that in RUB-51 the unit-cell dimension perpendicular to the layers is only half of that of RUB-15, the stacking sequence in RUB-51 should be AAA and, thus, the positions of the layers should be exactly the same.

Now, assuming the topology of the silicate layer and not knowing the molecular arrangement of the organic cations located between the layers, we generated a first rough model of the structure of RUB-15 to start the Rietveld refinement. Because the position and the orientation of the tetramethylammonium group and the phenyl ring of the organic cation were unknown, these two groups were in the beginning

simulated by two C atoms. They were placed between the silicate layers at random and were given a suitable occupation factor and displacement parameter to cover the overall scattering power of the intercalated SDA molecule.

Structure refinement was first based on the room-temperature data set. The successful refinement of silicon and oxygen positions of the RUB-51 layer proved the model right. Thereafter, we searched for the organic cation by difference fourier synthesis, ρ(obsd) − ρ(calcd, silicate layer). The aromatic group showed up clearly and was easily located, and so were the bridging CH_2 group, the N atom, and two of the three methyl groups. The search for the remaining methyl group proved to be very difficult. Nearly no localized electron density from the contour map was observed at the expected methyl position; however, some residual, diffuse density was detected. This fact was attributed to the intrinsic poor crystallinity of the sample. For the final refinement procedure, a carbon atom with a appropriate occupation factor and a very high displacement parameter was used to represent the complete tetramethylammonium group. The results of the RT structure refinement are supplied as Supporting Information (Table 3 and Figure 1).

From Figure 5, it is obvious that the crystallinity of RUB-51 became worse as temperature was lowered. So it is not surprising that the synchrotron diffraction data set recorded at 170 K was useless for structure refinement due to very low diffracted intensity leading to an atomic resolution of only about 2.5 Å in the diffraction pattern. Finally, we refined the data set collected at 180 °C. The profile parameters were first refined with a Le Bail fit. This time, we started the refinement with the complete structure model as obtained from the refinement of the room temperature data set. Now, the organic cation including both, the aromatic group and the nitrogen atom together with all three methyl groups, were easily located in the unit cell from the contour map. The positions of the hydrogen atoms could not be located. As shown in Figure 7, the agreement between experimental data and the structure model after the refinement is very good. The details are listed in Table 1. A list of atomic parameters and selected interatomic distances and bond angles are deposited as Supporting Information (Tables 1 and 2).

Although boron was present in the reaction mixture, we did not observe any evidence of boron substituting Si in the structure during the refinement. Elemental analysis also confirmed that there is no boron in this compound. However, synthesis experiments without H_3BO_3 led only to an amorphous product. So far, the function of the H_3BO_3 during the synthesis is not clear. Most likely, the influence on the pH of the synthesis solution is important.

Figure 8 shows the crystal structure projections of RUB-51 along [100], [001] and [010] directions. RUB-51 is built of silicate layers similar to those which had already been observed for RUB-15. Layers of benzyl trimethylammonium cations as SDAs are intercalated between neighboring silicate layers. The stacking sequence of the silicate layers is *AAAA*.

The layers are made up by 4- and 6-rings forming a puckered sheet of interconnected cups which point alternatively up and down (see Figure 8c). The cups can be described as one-half of a sodalite cage. Thus, the layers represent a section through the framework structure of sodalite. Two out of three Si atoms are 3-connected to other silicon atoms (Q^3-units), the third Si atom is 4-connected (Q^4-unit).

Between the silicate layers, the benzyl trimethylammonium cations are arranged such that their C_6H_5-groups are approximately parallel to each other along the [100] direction. The distance between neighboring groups is about 4.2Å, which is a typical distance between aromatic groups with van der Waals' interactions between each other.[33]

The positively charged trimethylammonium groups of the cations point toward the anionic silicate layers. The particular arrangement of the tetramethylammonium groups which form ionic bonds with the terminal $Si-O^-$ groups of the silicate layers are responsible for the generation of an *AAA* stacking sequence of the silicate layers. This is in contrast to the structure of RUB-15[25] where the interconnection between water network and silicate layer leads to an *ABABAB* stacking.

So far, all attempts to condensate the silicate layers of RUB-51 by heating failed. Formally, the layers can be condensated if the organic cations are removed and neighboring layers are shifted half-the unit cell along the *a*-axis. If neighboring layers are then shifted toward each other along the b direction until the oxygen atoms of the terminal SiO^-/SiOH groups coincide, the framework structure of silica−sodalite would form.

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Supporting Information Available: Crystallographic information in CIF format; four additional tables and one additional figure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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