Synthesis, Characterization and Structure Solution of ULS-1 $[\text{ETMA}_8(\text{H}_2\text{O})_{20}][\text{Si}_{24}\text{O}_{48}(\text{OH})_8]$, a layered silicate composed of half-sodalite cages

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Abstract

UOP Layered Silicate – 1 (ULS-1), a highly siliceous layered silicate composed of $[4^26^2]$ half sodalite cages, has been synthesized hydrothermally at 100°C from solutions containing ethyltrimethylammonium hydroxide and silica or aluminosilicate sources and the structure solved from powder XRD data in the Ibam spacegroup with $a = 28.909 \text{ \AA}$, $b = 8.380 \text{ \AA}$, $c = 11.569 \text{ \AA}$ at room temperature. TGA/MS and NMR, Raman and IR spectroscopic characterization were utilized to examine the properties of ULS-1 and provide information for structure solution. ULS-1 contains the same silicate layer structure and stacking as that found in RUB-15 and DLM-2, but with ethyltrimethylammonium (ETMA) cations in place of tetramethylammonium stabilizing the half sodalite cages. The presence of ETMA increases the interlayer spacing to $\sim 8.3 \text{ \AA}$ from the previously observed $8 \text{ \AA}$, but also slightly increases the c unit cell constant in the layer direction.

Keywords

Ethyltrimethylammonium, sodalite, charge-density mismatch, layered silicate

1. Introduction

Layered silicates are an important class of materials which have been used as ion-exchange adsorbents, catalysts and scaffolds for biocomposites.[1,2,3] These materials tend to exist as thin silicate sheets of SiO_4 tetrahedral units extending in two dimensions with a surface comprising SiOH / SiO^- groups, thereby generating an interlayer space of charge balancing cations and hydrogen bonded water which determine the layer spacing. Typically, these layers are impermeable; a rare example of a layered silicate containing pores through the layer is that of AMH-3. [4] Many groups have used the exchangeability of the cations between the impenetrable layers to layer expand, exfoliate and otherwise chemically modify the silicate layers giving multiple new materials and uses from a single layered silicate starting material.[1] Both natural and synthetic layered silicates are known with the minerals magadiite [5,6],

kenyaite [7,8], kanemite [9,10,11] and makatite [12] among the most well studied. Marler and Gies have recently written an excellent review and classification of the hydrous layer silicate field [13] and an entire issue of Dalton Transactions was devoted to layered inorganic solids and their uses. [14]

A class of the large number of layered silicate materials is that comprising layers cut from the SOD zeolite structure. Both β -HLS [15] and HUS-1 [16] are made from layers cut from the [100] direction of SOD, albeit with different layer stackings, *ABAB* for β -HLS and *AA* for HUS-1. While these layers are cut from the SOD structure, condensation of the layers would lead to the AST structure, so they should be referred to as ast layers. [13] Interestingly, the precursor to HUS-1, HUS-5, has *ABAB* stacking of ast layers as does β -HLS, and is converted to the *AA* stacking of HUS-1 through no more than washing with H₂O. [17] Conversely, slicing along the [110] direction of SOD leads to sod layers composed of halved sodalite cages. [16] Multiple materials with this motif have been made from many different synthetic approaches, but which typically have tetramethylammonium (TMA⁺) cations stabilizing the half sodalite cages, balancing the charge from the SiO⁻ groups and separating the silicate layers. RUB-15 [18] was synthesized from silicate solutions containing TMA hydroxide after a month at 120°-140°C while DLM-2 [19] crystallized after a failed synthesis starting from TMA⁺ silsesquioxane (the well-known D4R zeolite building block), yet both preparations yielded the same TMA⁺ stabilized half sodalite cage material. Recently, Gies and coworkers have shown in the preparation of RUB-51 the same sod layer structure, but with benzyltrimethylammonium (BzTMA⁺) cations as the interlayer species.[20] In RUB-51, the layer stacking is *AA* rather than the *ABAB* observed for RUB-15 and DLM-2.

At UOP, we have been working with ethyltrimethylammonium (ETMA) because it is a simple and readily available tetraalkylammonium available for use as a structure directing agent in zeolite synthesis. It is available as a solution in hydroxide form, allowing use as the hydroxide source to replace some or all of the traditionally utilized sodium in synthesis. While ETMA⁺ has not been used with nearly the same frequency as TMA⁺, the effect of ETMA⁺ on zeolite crystallization has been extensively studied [21] by Lewis and coworkers. They have shown that while the structure directing effects of ETMA⁺ tend to be similar to those of TMA⁺ due to the structural similarity between them, unique products are obtained in syntheses using ETMA⁺. In this manner, products such as the layered material UZM-17 [22,23], which condenses to UZM-25 (CDO framework) upon calcination, UZM-8 [24], and PKU-9 [25] are seen in syntheses where ETMA⁺ has been used as a structure directing agent.

ETMA is of particular interest while using the charge density mismatch (CDM) synthesis technique. As shown by Lewis and Hong, CDM uses clear solutions containing silicon, aluminum and a large, low charge density tetraalkylammonium hydroxide [26]. These solutions are stable

and do not crystallize. To crystallize a zeolite product, a solution containing a small, high charge density ion such as lithium, sodium or magnesium is introduced. The method has been successful in yielding microporous materials such as UZM-4 (BPH) [27], UZM-5 (UFI) [28], UZM-9 (LTA) [29], UZM-12(ERI) [30,31] and UZM-35 (MSE) [32]. Starting from either CDM-aluminosilicate solutions or all-silica solutions while using ETMA hydroxide as the structure directing agent, we have synthesized a novel layered silicate composed of $[4^2 6^2]$ half sodalite cages, named ULS-1, and report its structural characterization here.

2. Experimental

2.1 Synthesis

CDM preps were performed by making an aluminosilicate solution by dissolving $\text{Al}(\text{OH})_3$ in ETMAOH. 1,4-bismethylpyrrolidinium butane dibromide (C4P2 Br) and Ludox AS-40 were then added. To this solution, a solution of $\text{Mg}(\text{OH})_2$ or LiOH was then added to form a solution of composition 100 Si : 5 $\text{Al}(\text{OH})_3$: 80 ETMAOH : 15 C4P2 Br: 1.25 $\text{Mg}(\text{OH})_2$: 3566 H_2O or 100 Si : 5 $\text{Al}(\text{OH})_3$: 60 ETMAOH : 7.5 C4P2 Br: 2.5 LiOH : 2632 H_2O .

The resulting solution was then put into a Teflon bottle and kept at 100°C statically for 5-7 months. By this time, white solid formed. The chunks of white solid were separated from any clear gel remaining and were worked up by washing and filtration followed by drying at 100°C to yield a white powder. Other preps were loaded into 45mL Teflon lined Parr bombs and kept in 125°C to 175°C ovens statically for times listed in Table 1.

Syntheses from all silica solutions were performed by combining solutions of ETMAOH and Ludox to yield solutions of composition 1 SiO_2 : 0.8 ETMAOH : 28.7 H_2O . To these, $\text{Mg}(\text{OH})_2$ or LiCl was sometimes added at 0.0125 mole ratio. These solutions were loaded into Teflon bottles and kept at 100°C for 6 weeks to 3.5 months before workup by washing and filtration to yield a papery, white product.

Additionally, a preparation at 1 SiO_2 : 0.8 ETMAOH : 18.7 H_2O : 4 EtOH was performed by combining ETMA hydroxide and TEOS, mixing well and then loading into a Teflon bottle for 4 months at 100°C.

2.2 Structure Solution

The structure solution used x-ray diffraction data collected from laboratory and synchrotron radiation sources. Initial data were collected for samples packed in flat plates using Bragg-Brentano geometry on a Rigaku Ultima IV diffractometer equipped with a scintillation detector and diffracted beam monochromator or with a Detex silicon strip linear detector and a nickel filter. Materials were also packed into a 0.5mm glass capillary and mounted on a Rigaku Ultima

IV in parallel beam mode. The capillary was rotated at 60rpm to obtain scans with minimal preferred orientation. Prior to several capillary experiments, the ULS-1 was dehydrated in-situ as described below. High resolution synchrotron powder diffraction data were collected at a temperature of 100K using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average wavelength of 0.413296 Å. Discrete detectors covering an angular range from -6 to 16 ° 2θ are scanned over a 34° 2θ range, with data points collected every 0.001° 2θ and scan speed of 0.01°/s.

The 11-BM instrument uses x-ray optics with two platinum-stripped mirrors and a double-crystal Si(111) monochromator, where the second crystal has an adjustable sagittal bend.[33] Ion chambers monitor incident flux. A vertical Huber 480 goniometer, equipped with a Heidenhain encoder, positions an analyzer system comprised of twelve perfect Si(111) analyzers and twelve Oxford-Danfysik LaCl₃ scintillators, with a spacing of 2° 2θ.[34] Analyzer orientation can be adjusted individually on two axes. A three-axis translation stage holds the sample mounting and allows it to be spun, typically at ~5400 RPM (90 Hz). A Mitsubishi robotic arm is used to mount and dismount samples on the diffractometer.[35] An Oxford Cryosystems Cryostream Plus device allows sample temperatures to be controlled over the range -193-227°C when the robot is used.

The diffractometer is controlled via EPICS.[36] Data are collected while continually scanning the diffractometer 2θ arm. A mixture of NIST standard reference materials, Si (SRM 640c) and Al₂O₃ (SRM 676) is used to calibrate the instrument, where the Si lattice constant determines the wavelength for each detector. Corrections are applied for detector sensitivity, 2θ offset, small differences in wavelength between detectors, and the source intensity, as noted by the ion chamber before merging the data into a single set of intensities evenly spaced in 2θ.

Following XRD experiments, the extraction of the peak positions for structure solution and indexing was performed using the WinPLOTR program suite. Pattern indexing was carried out using DICVOL04 from twenty lines, with an absolute error on peak positions of 0.05° 2θ. The structure solution then followed from direct methods as described below.

2.3 Additional Characterization

²⁹Si and ¹³C MAS NMR were carried out at a frequency of 39.7491 and 50.3096 MHz (4.7 T), respectively. Samples were packed in zirconia rotors (7 mm o.d.) and spun at a frequency of 5 kHz. ²⁹Si CP MAS experiments were carried out using 3 msec contact time with a delay of 5 sec. Quantitative ²⁹Si NMR experiments with TPPI proton decoupling were carried out using 5μs pulses with delay between pulses of 120 sec. ¹³C NMR spectra were referenced using an external standard of glycine (CO peak set to 176 ppm) and ²⁹Si NMR spectra were referenced using an external standard of Q₈M₈. Typical number of scans for the ¹³C and ²⁹Si CP MAS NMR

were 6144 and 24, 576, respectively. The number of scans for the quantitative ^{29}Si MAS NMR is 512. ^1H NMR spectra were collected at nominal frequency of 400.134 MHz. A 90° degree pulse of $2\mu\text{s}$ duration, and a pulse delay of 10s were applied. The number of accumulations was 256, and the spinning speed was 14.5 kHz. The spectra were referenced with respect to external TMS.

Raman analysis was carried out with a Kaiser Holoprobe Raman system with 25.6 mW 532 nm excitation and a 10X objective. Spectra were recorded at 90 s total exposure time. The layered material was ground and loaded in a 5 mm glass capillary tube. We then heated the capillary tube to 90°C under evacuation for 2 h before sealing. The dehydrated sample was then put onto the instrument and spun at 1000 rpm. This sample was photobleached by exposure to the laser beam for 5 minutes prior to recording the spectrum to greatly reduce fluorescence from the sample. Ethyltrimethylammonium chloride (as a 55 wt% solution in water) was loaded into a 5 mm glass NMR tube and the spectrum acquired during rotation without the need for the photobleaching step. Spectra were then processed using GRAMS/AI 7 software.

IR spectroscopy was performed in a diffuse reflectance IR (DRIFTS) cell in the region of $4000\text{--}400\text{ cm}^{-1}$. Following the initial scan, the material was dehydrated in-situ by heating in a stream of helium for either 100°C for 1h or 125°C for 2h. The sample was then cooled down to room temperature and an IR spectrum collected.

Thermogravimetric analysis (TGA) of the samples was performed on a TA Q5000 V3.15 with a heating rate of 2°C min^{-1} from 25 to 900°C under an air flow. This instrument is coupled with a mass-spectrometric detector for identification of desorbed species.

3. Results and Discussion

3.1 ULS-1 Synthesis and Characterization

We performed initial zeolite synthesis investigations of the ETMA system in an aluminosilicate system using a temperature scan ranging from 100°C to 175°C as shown in Table 1. In general, product formation in the Mg system was slower than in the Li containing system. In addition to the layered ULS-1 phase of interest here, we saw the formation of UZM-15 [37] at 150°C after 14 days and products of the RUT or RTH family at 160 and 175°C at times ranging from 5 days to 2 weeks from the lithium containing gel. UZM-15 has previously been shown to form from charge-density mismatch gels of intermediate Si/Al ratio (10-50) containing ETMA^+ at temperatures including 150°C [21]. RUT has been shown to form in ETMA^+ containing gels at 150°C , [21] therefore, it is relatively unsurprising to form this type of clathrasil. Products from the magnesium gels were amorphous at the end of the time scan of 2 weeks and for the most part were not run at longer times.

Samples from both the Li and Mg aluminosilicate systems were amorphous at 100°C for quite some time. Every few days, the Teflon bottle was removed from the 100°C oven and checked for solids formation. Finally, at 5 months, white solids had formed in both the Li and Mg systems. A better sample was synthesized in the Mg system by waiting for 7 months.

The ULS-1 materials crystallized from these solutions have the XRD pattern shown in Figure 1. The pattern is dominated by the large peak at low angle and was readily indexable to unit cells of approximate 1bam symmetry with cell parameters of approximately 29, 8.4 and 11. 6Å.

The material crystallizes in thin sheets of 100nm or less thickness and multiple microns across the larger dimensions which agglomerate to form stacks of plates as shown in the SEM photos in Figures 2 and 3 of the product from the Li system. It is possible that growth in the system occurs in a layer-by-layer fashion in the thin direction as seen by the apparent layers in the high magnification image in Figure 3. Slightly smaller, not as well defined plates were observed in the Mg system [Figure S1]. As is typical for layered silicates, electron diffraction using TEM shows that the sod layers are parallel to the large plates. Elemental analysis of the aluminosilicate products showed that the material is close to a silicate, having a Si/Al ratio of 105 in the Li system and 207 for the Mg system. Cations present give a M/Al ratio of around 0.25 on a charge basis, being 0.31 for the Li system and 0.22 for the Mg system. CHN analysis shows that the material contains 20.6%C and a C/N ratio of 5.1, essentially equivalent to that of ETMA.

Upon seeing the Si/Al ratio of the ETMA silicate product, we also tried syntheses in the absence of Al at temperatures of 100°C and 150°C (taken from DLM-2 work). Results at 100°C yielded ULS-1 after times ranging from 6 weeks to 4 months. Syntheses both in the presence of or absence of Li or Mg were successful, with syntheses in the absence of cation crystallizing slightly quicker while crystallization at 150°C in the presence of Li led to formation of Li_2SiO_3 and hydrated lithium silicates at 5-14 days [Figure S2] with amorphous product at earlier times. A sample without added cation provided one of the most crystalline samples after 3.5 months at 100°C. Products other than ULS-1 were not observed from these all-silica solutions at 100°C. Additionally, control experiments performed in the absence of ETMA^+ yielded amorphous products.

As the product is a silicate, we were hopeful the material was thermally stable. Unfortunately, the material is unstable to elevated temperature, yielding an XRD pattern consisting of an amorphous hump and a peak around $9.5^\circ 2\theta$ upon calcination at 550°C [Figure S3]. TGA analysis of the material in air shows that decomposition of the framework is complete far before 550°C as shown in Figure S4. Two distinct weight losses comprising almost 15% of the sample occur prior to 100°C and have been identified by mass-spec analysis as water. A large mass loss then occurs, centered around 215°C, giving a total loss on ignition of 50%. This mass

loss coincides with loss of crystallinity, indicating that template decomposition causes framework destruction. Mass-spec analysis shows that the template decomposition is occurring at this point, with ethylene, trimethylamine (the decomposition products of ETMA) and CO₂ as major products. Analysis in N₂ atmosphere gave similar results, though with a slightly higher template decomposition temperature and slightly less CO₂ evolved.

To obtain further information to help in the structure solution, we carried out NMR, Raman and IR spectroscopic characterization. CPMAS ¹³C NMR showed peaks at 7.6ppm, 49.4ppm, 51.2ppm and 60.3ppm, consistent with pore-filling by ETMA and its decomposition product trimethylamine as shown in Figure 4. Integration of the trimethylamine peak at 49.4ppm versus the ETMA peak at 51.2ppm or 7.6ppm gives a ratio of about 85/15 for ETMA/trimethylamine. The presence of trimethylamine as a pore-filling agent is likely due to slow decomposition of ETMA over the long synthesis period via Hoffman elimination of ethylene. Trimethylamine has been noted as a pore-filling agent in other syntheses where it was derived from template decomposition. [38,39] ¹H NMR of the as-synthesized ULS-1 is shown in Figure 5. Peaks at 1.4 and 3.2 ppm are due to the methyl protons on the ethyl and methyl groups of ETMA⁺, respectively, while the shoulder at 5.4ppm and the relatively sharp feature at 16.2ppm are due to hydrogen bonded water. Using the equation $\delta \text{ (ppm)} = 90.3 - 30.4 \cdot d(\text{O-H}\cdots\text{O})$, where d is the distance in Å between H and two O centers in a hydrogen bond, [40] we calculate that the distance is 2.79Å for the feature at 5.4ppm, typically assigned as water molecules interacting with another water or with layer silanols, and 2.44Å for the feature at 16.2ppm, typically, for a sod layer, protons involved in hydrogen bonds between adjacent surface silanols. Thus we observe, as is typical for layered silicates, the interlayer space contains hydrogen bonds, some of which are quite strong. [11,16]

Raman analysis of ULS-1 initially showed a broad band with several tiny peaks due to a significant amount of fluorescence. Photobleaching the sample was quite effective and gives the spectrum shown in red in Figure 6. A complication of Raman analysis of zeolitic materials still containing organic SDAs is that the scattering cross-section of the organic is many times higher than that of the framework. [41] With this in mind, to help determine which Raman peaks are due to the framework and which to the ETMA, we ran a spectrum of ETMA chloride in water. As shown in blue in Figure 6, essentially all the peaks in the spectrum of ULS-1 are due to the ETMA cation, again confirming the presence of ETMA in the product. There are two bands present due to the framework, one at 510cm⁻¹ which has been previously assigned as due to bending vibration of 4MR rings [41,42] and a second at about 1050 cm⁻¹, most likely due to Si-O-Si asymmetric stretching. [41] Turning to the strong peaks due to ETMA, the peak at 721cm⁻¹ is the C-N symmetric stretch of the ν_1 mode, 880cm⁻¹ is a symmetric stretching from the ν_2 mode, and 961cm⁻¹ is the asymmetric C-N stretch of the ν_3 and ν_4 modes [43] while the feature at 1450 cm⁻¹ is due to C-H bending vibrations.

IR analysis of the hydroxyl region of the as-synthesized product shows a large broad band peaking around 3400 cm^{-1} as well as a sharper band at $\sim 1650\text{ cm}^{-1}$ due to water. We then performed the hydroxyl IR analysis in a DRIFTS cell, heating the cell to either 100°C for 1 hour or 125°C for 2 hours in a flow of He before cooling to room temp in He to perform the hydroxyl region analysis. Figure 7 shows that the water has been removed by the heat treatment and that the template is intact, with regions due to C-H stretches and bends both visible, confirming the TGA-MS results. Looking to the framework region of the IR, the T-O-T stretch is apparent at 1046.6 cm^{-1} [Figure S5] and confirms the band observed in the Raman spectrum. A zeolitic all- SiO_2 material has a T-O-T stretch of nearly 1100 cm^{-1} . According to Flanigen, a stretch of 1046 cm^{-1} would correspond to a material of Si/Al around 3 to 5 [44] if the material were zeolitic. From the low frequency exhibited in the framework IR region and the Si/Al ratio reported by ICP-MS along with the absence of hydroxyl bands, we understood that the material was layered rather than zeolitic and contained 4-rings; we sought structure solutions using this information.

3.2 XRD Structure Solution

The extraction of the peak positions for indexing was performed from multiple samples using the WinPLOTR program suite, but primarily from samples obtained by packing a capillary and dehydrating the ULS-1 in-situ at 90°C before sealing the capillary and mounting in a goniometer. Samples not dehydrated prior to XRD data collection exhibit significantly higher amounts of diffuse scattering due to the almost 15% water removed during the dehydration. Pattern indexing was carried out using DICVOL04 from twenty lines, with an absolute error on peak positions of $0.05^\circ 2\theta$. An orthorhombic solution was found with satisfactory figures of merit. Systematic absences were consistent with several spacegroups. The spacegroups in which fewer symmetry operators were present were chosen as a starting point after the positions and intensities were extracted using the Fullprof program suite [45] and subsequent structure solution calculations were performed with ShelX97. We compiled a list of 220 reflections extracted in the angular range $5\text{--}90^\circ 2\theta$.

According to the degree of diffraction overlap, 35.51% of these reflections were statistically considered as independent. The Si and O atoms were found from the E-map with the highest figure of merit. Consequent Fourier maps aided the location of the organic moiety, and the corresponding atomic co-ordinates were used as the starting model for Rietveld refinement using the GSAS program suite. Atomic positions in the ETMA cations were allowed to refine but with soft constraints on the first and second nearest neighbor distances. A satisfactory solution with 2 crystallographically independent T sites was obtained in the spacegroup $Ibam$, the results of which are shown in Table 2. Atomic coordinates and isotropic displacement parameters are shown in Table 3. Water sites (O atoms 5 and 6) appear to be partially occupied. C4, the CH_3 carbon from the ethyl group of ETMA^+ is disordered over two crystallographically

related sites. Interatomic distances are shown in Table 4 and bond angles in Table S1. The interatomic distances in the ETMA cation are heavily influenced by the soft constraints.

In order to ensure that the space group selection was correct, the atomic coordinates were input into the PLATON program suite, and additional symmetry sought. The symmetry remained unchanged however, suggesting that the structure is in the correct space group. From the ^{29}Si NMR spectrum, we see that Q3 Si (Si1) and Q4 Si (Si2) are present in a 2:1 ratio as required by the structure solution. However, the material is likely somewhat disordered in the interlayer space as the ^{29}Si NMR usually contains a small side peak on the Q3 signal [Figure S6] which integrates to between 12.5% and 25% of the total spectral intensity depending on the sample examined. We sought to lower the symmetry to one of the monoclinic subgroups of *Ibam*, but were unable to find an improved space group of lower symmetry, even from the higher resolution data acquired at the synchrotron.

With the structure solved, we can then see that the ULS-1 structure contains the same layer structure as that reported in the materials DLM-2 [19], RUB-15 [18], and RUB-51 [20]. As noted previously, the layer stacking for the materials synthesized using TMA^+ is *ABAB*, while that for the material synthesized using BzTMA^+ is *AA*. As can be seen from the *ab* plane shown in Figure 8, the layer stacking for ULS-1 is *ABAB*, the same as that observed in RUB-15, synthesized with TMA^+ as the cation. In ULS-1, the unit cell volume is larger than DLM-2 and RUB-15 to accommodate the larger ETMA cation between the layers, but smaller than RUB-51, synthesized with BzTMA^+ . In particular, note the expansion of the long axis compared to the TMA^+ forms as shown in Table 5. Measuring from the closest approach of two polyhedra, the interlayer spacing between the silicate layers is determined by the size of the organic SDA as the layer spacing increases from 8.0 Å in RUB-15 / DLM-2 to 8.3 Å in ULS-1 to 8.8 Å for RUB-51. The difference in unit cell size between ULS-1 and RUB-51 is largely due to the expansion of the *c* axis in RUB-51. One layer of the ULS-1 structure is shown in two orientations in Figure 9 as a polyhedral representation. The situation observed here for layered silicates with sod layers is similar to that observed for those containing fer layers; varying the organic SDA utilized in the synthesis gives rise to different layer spacings and stacking sequences. [46]

In the ULS-1 structure, one methyl group of the ETMA^+ is directed into each halved sodalite cage of the layer with the ethyl group (disordered over two positions) directed into the interlayer space. This is shown in the plot shown in Figure 10. On opposite sides of the layer are alternate halved sodalite cages, each with an ETMA^+ . The relationship of the halved sodalite cages are shown in the tiled representation of Figure 11. As observed previously in other zeolite syntheses, ETMA^+ acts similarly to TMA^+ , in this case templating the same layer structure in the same fashion, but yielding a new material due to the ethyl group on the SDA.

Okubo and coworkers have repeated the DLM-2 synthesis and shown how to acid treat the layers to allow condensation to the SOD structure.[47] We have attempted to pillar the layers of ULS-1 using TEOS; these experiments failed to yield a different XRD pattern than that obtained by simply calcining the material (Figure S7). Likewise, ion-exchanging the ETMA⁺ for Sr²⁺ did not yield a stable material (Figure S8). Individual halved sodalite cages are not located directly opposite each other, but are instead shifted by a half cage. It may be due to the fact that the layer needs to shift in order to condense that these pillaring and condensation experiments were not successful.

4. Conclusions

With ETMA⁺ as the structure directing agent, the novel layered silicate ULS-1 crystallizes. The layer spacing and one of the unit cell constants for ULS-1 expands versus the related TMA⁺ directed materials RUB-15 and DLM-2. However, these values are smaller than those exhibited by RUB-51, templated by the even larger cation BzTMA⁺. We have explored the synthesis space and characteristics of ULS-1 and used the information obtained to seed the structure solution, resulting in the orthorhombic Ibam solution with a=28.909, b=8.380, c=11.569 at room temperature.

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7. Tables

7.1 Table 1. Aluminosilicate synthesis conditions and products found

CDM / Temp.	100°C	125°C	150°C	160°C	175°C
Li	150 days ULS-1	Not performed	14 days UZM-15	6-11 days RUT / RTH	5 days RUT / RTH
Mg	150-210 days ULS-1	32 days amorph.	Up to 14 days largely amorph.	Up to 14 days largely amorph.	4 days largely amorph.

7.3 Table 2

Table 2. Crystallographic data from the Rietveld refinement of ULS-1.

Space group	Ibam
a (Å)	28.909(7)
b (Å)	8.380(2)
c (Å)	11.569(3)
V (Å ³)	2803(2)
R(F ²)	0.061
R _p	0.038
R _{wp}	0.054
R _{exp}	0.016
χ ²	11.834
Largest diffraction hole and peak (e/Å ³)	-0.24, 0.30
No. of observations	11701
No. of reflections	804
No. of parameters	93
No. of geometrical restraints	46
λ (Å)	CuKα
Refined pattern 2θ range (°)	3-100
Refined composition	[(ETMA)(O) _{2.15}][Si ₃ O ₇]
Z	8

7.3 Table 3

Table 3. Fractional atomic coordinates and isotropic displacement parameters ($\text{\AA}^2$) for ULS-1.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}	Occ. (<1)
Si1	0.69115 (16)	0.2015 (6)	0.1351 (3)	0.0430 (11)	
Si2	0.7329 (2)	0.5	0.25	0.0430 (11)	
O1	0.6990 (3)	0.3789 (10)	0.1829 (6)	0.0524 (13)	
O2	0.7390 (3)	0.0947 (9)	0.1563 (6)	0.0524 (13)	
O3	0.6476 (2)	0.1334 (7)	0.1956 (6)	0.0524 (13)	
O4	0.6830 (3)	0.2205 (12)	0	0.0524 (13)	
O5	0	0.5	0.25	0.014 (8)	0.816 (15)
O6	0.0589 (2)	0.2865 (9)	0.1240 (5)	0.051 (4)	0.873 (8)
N1	0.1170 (3)	0.8173 (16)	0	0.110 (3)	
C1	0.0791 (4)	0.6972 (15)	0	0.110 (3)	
C2	0.6665 (3)	0.7344 (17)	0	0.110 (3)	
C3	0.1015 (3)	-0.0920 (8)	0.1045 (6)	0.110 (3)	
C4	0.0491 (4)	0.949 (2)	0.1086 (11)	0.110 (3)	0.5
H1A	0.0492 (4)	0.752 (2)	0	0.165 (4)	
H1B	0.0817 (6)	0.6303 (15)	0.0692 (3)	0.165 (4)	
H2A	0.1864 (5)	0.860 (3)	0	0.165 (4)	
H2B	0.1725 (5)	0.702 (2)	0.0691 (3)	0.165 (4)	
H3A	0.1192 (6)	0.0082 (16)	0.108 (2)	0.165 (4)	
H3B	0.1093 (7)	0.845 (2)	0.1736 (4)	0.165 (4)	
H3C	0.0685 (4)	-0.0713 (19)	0.1000 (12)	0.165 (4)	0.5
H4A	0.0437 (12)	0.054 (11)	0.074 (15)	0.165 (4)	0.5
H4B	0.0381 (16)	0.95 (2)	0.1888 (16)	0.165 (4)	0.5
H4C	0.0316 (7)	0.869 (14)	0.065 (14)	0.165 (4)	0.5

7.4 Table 4.

Table 4. Interatomic distances (Å) for ULS-1.			
Si1—O1	1.603 (7)	C1—H1A	0.980 (3)
Si1—O2	1.665 (7)	C1—H1B	0.979 (2)
Si1—O3	1.549 (6)	C1—H1B ^v	0.979 (2)
Si1—O4	1.588 (3)	C2—H2A ^{ix}	0.979 (3)
Si2—O1	1.610 (8)	C2—H2B ^{ix}	0.979 (2)
Si2—O1 ⁱ	1.610 (8)	C2—H2B ^x	0.979 (2)
Si2—O2 ⁱⁱ	1.570 (7)	C3—H3A ^{xi}	0.984 (3)
Si2—O2 ⁱⁱⁱ	1.570 (7)	C3—H3B ^{xi}	0.983 (3)
N1—C1	1.490 (3)	C3—H3C	0.973 (3)
N1—C2 ^{vi}	1.493 (3)	C4—H4A	0.981 (3)
N1—C3 ^{vii}	1.497 (2)	C4—H4B	0.981 (3)
N1—C3 ^{viii}	1.497 (2)	C4—H4C	0.981 (3)
C3—C4 ^{xi}	1.554 (3)		

Symmetry codes: (i) $x-1, -y, -z-1/2$; (ii) $-x+3/2, y+1/2, z$; (iii) $-x+1/2, -y-1/2, -z-1/2$; (iv) $-x+3/2, y-1/2, z$; (v) $x, y, -z$; (vi) $x-1/2, -y+3/2, z$; (vii) $x, y+1, z$; (viii) $x, y+1, -z$; (ix) $x+1/2, -y+3/2, z$; (x) $x+1/2, -y+3/2, -z$; (xi) $x, y-1, z$; (xii) $x-1, -y+1, -z-1/2$; (xiii) $x+3/2, -y+5/2, -z$.

7.5 Table 5 – unit cell parameters for the related layered materials

Sample	Space Group	a	b	c	V	Composition
ULS-1 at 100K	Ibam	28.697	8.430	11.486	2779	ETMA ₈ (H ₂ O) ₂₀ [Si ₂₄ O ₄₈ (OH) ₈]
ULS-1 at RT	Ibam	28.909	8.380	11.569	2802	ETMA ₈ (H ₂ O) ₂₀ [Si ₂₄ O ₄₈ (OH) ₈]
DLM-2	Ima2	11.524	8.414	27.908	2706	TMA ₈ (H ₂ O) ₂₀ [Si ₂₄ O ₄₈ (OH) ₈]
RUB-15	Iba2	27.905	8.408	11.518	2702	TMA ₈ (H ₂ O) ₂₀ [Si ₂₄ O ₅₂ (OH) ₄]
RUB-51 at RT	Pca2 ₁	8.3855	14.412	11.725	1417	BzTMA ₄ (H ₂ O) ₁₀ [Si ₁₂ O ₂₄ (OH) ₄]

8. Figures

8.1 Figure 1 – X-Ray diffraction pattern for ULS-1 obtained using a Cu source at $1.54\text{\AA}$ with the line pattern calculated from the ULS-1 structure solution displayed in purple.

8.2 Figure 2 – High resolution SEM photos of the thin plates in ULS-1

8.3 Figure 3 – High resolution SEM of ULS-1 showing platelet size and shape

8.4 Figure 4 – ^{13}C CPMAS NMR analysis of the as-synthesized ULS-1

8.5 Figure 5 – ^1H MAS NMR of ULS-1. Inset shows the vertical expansion of the same spectrum. Only the isotropic region is shown. Chemical shifts of the distinct peaks are marked on the spectrum.

8.6 Figure 6 – Raman analysis of ULS-1 (red spectrum) in comparison with ETMA chloride (blue pattern). Peaks due to ETMA+ are marked in black, those due to ULS-1 framework in green.

8.7 Figure 7 – Hydroxyl IR region of ULS-1 showing a) the as-synthesized ULS-1, b) the material after 125°C dehydration, c) the material after 100°C dehydration.

8.8 Figure 8 – View of the ULS-1 a-b plane showing the layer structure. The sod silicate layer is shown in yellow tetrahedra, N of the ETMA⁺ in blue, C atoms of ETMA⁺ in gray and O of water atoms in red.

8.9 Figure 9 – Polyhedral representations of one layer in ULS-1. (a) The (010) projection shows one layer in the same orientation as in Figure 7. (b) The (100) projection of this same fragment shows the $[4^26^2]$ half sodalite cages within the layer.

8.10 Figure 10 – Plot showing how a methyl group from ETMA^+ is directed into the halved sodalite cages. Si are indicated in blue, O as red, the N atom of ETMA^+ in light blue, C atoms of ETMA^+ in black and H atoms in gray. The crystallographically disordered ethyl group is shown in both positions it occupies.

8.11 Figure 11 – Tiled representation of $[4^2 6^2]$ half sodalite cages within the sod layer. 6 rings are colored in blue and 4 rings in yellow.