Observation of Spatially Correlated Intergrowths of Faujastic Polytypes and the Pure End Members by High-Resolution Electron Microscopy

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Controlled intergrowths of cubic and hexagonal phases of faujasitic materials have been synthesized, using mixtures of crown ethers, and studied by high-resolution electron microscopy. The results reveal that the end-member materials are pure phases, nearly free of defects and intergrowths such as those observed without the use of crown ethers. Mixed phases form intergrowths, rather than overgrowths, consisting of short blocks of up to 10 unit cells. In intergrowths with greater than 50% hexagonal phase there is a spatial correlation between these intergrowing blocks. The growth mechanism for the formation of these crystals and the role of the crown ethers as structure directing agents is discussed.

Zeolite Y is a wide-pore zeolite consisting of supercages of 12-Å diameter which are accessed via 12-ring windows. These are connected to give a three-dimensional pore system which permits unrestricted diffusion of certain adsorbates through the material. This pore network and its high hydrothermal stability give zeolite Y a range of important applications. It has also received attention as a suitable matrix for growing quantum confined semiconductor dots and wires. Recently, a synthesis of the hexagonal polymorph of zeolite Y[1], EMT structure (sometimes referred to as BSS, Breck's structure six[21]), was reported.[2,3] This material was originally postulated by D. W. Breck. Cubic zeolite Y (FAU structure) consists of sodalite cages (truncated octahedra) connected via double-six rings to give a zinc-blende arrangement of sodalite cages. The stacking sequence of the repeat layers in the 111_{CUBIC} direction is then ABCABC.... The EMT structure on the other hand consists of a wurtzite arrangement of sodalite cages whereby the stacking of the repeat layers, now along the 001_{HEX} direction of this hexagonal material, is ABABAB....[22] This difference in the arrangement of the building units leads to different pore dimensions and cage connectivities. In the FAU structure there is only one large cage type, the so-called supercage with ca. 13-Å diameter. In the EMT structure there are two large cage types: supercages connected in a linear fashion to produce a one dimensional channel with window diameter ca. 7.4 Å; a smaller oblate cage with access through a 12-ring aperture with dimension 6.9 Å × 7.4 Å (see Figure 1).[4] There are a number of related zeolites such as CSZ-1,[5-8] ECR-30,[9] CSZ-1,[10] ZSM-3,[11] and ZSM-20[12-16] which are

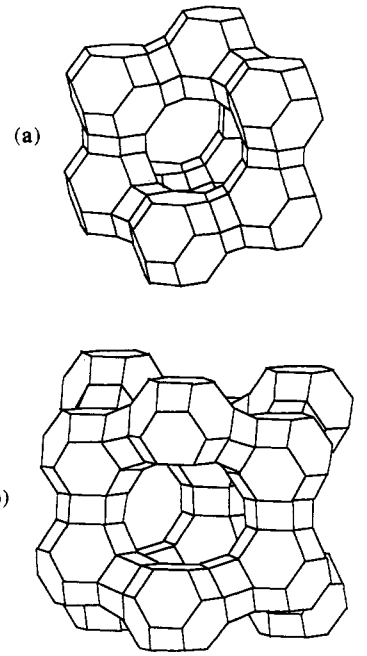

Figure 1. Representations of the structure the two polymorphs (a) FAU and (b) EMT. In both structures sodalite cages are linked together through double 6-rings.

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all believed to be EMT/FAU intergrowths. In these materials it is not possible to control the degree of intergrowth.

The EMT structure can be synthesized by incorporating the crown ether 18-crown-6 into a synthesis gel of overall molar composition 10 SiO_2:1.0 Al_2O_3:2.4 Na_2O:140 H_2O:1.0 crown ether. The sources of materials were 30 wt % colloidal silica (Ludox), 40 wt % sodium aluminate solution, and 18-crown-6 as supplied by Aldrich. The exact synthesis conditions were described previously.[17] On the other hand if a gel of identical composition is used but incorporating 15-crown-5 instead of 18-crown-6 the FAU structure is produced. Gels containing a mixture of crown ethers produce materials which contain intergrowths.

We previously reported[17] the high-resolution electron microscopy (HREM) of intergrowths cubic and hexagonal faujasite synthesized using crown ether templates. In this article we extend this study and discuss in more detail the role of the templating agent and the mechanism of crystal growth. We also report the observation, for the first time, of spatially correlated intergrowths of cubic and hexagonal faujasite. In our previous paper[17] the zeolite materials were partially dealuminated using ammonium hexafluorosilicate to improve the stability of the materials in the electron microscope. The materials synthesized with crown ethers are stable enough to be imaged in their as-prepared forms without any postsynthesis modification or calcination which might alter the microscopic nature of the material. Here the materials were imaged with the crown ethers intact.

Results

Figure 2 shows the high-resolution electron micrograph of a material prepared with 18-crown-6 imaged down the 100_{HEX} direction. To determine the structure purity of such materials, it is important to image down this direction. Although the 100_{HEX} image shows the perfection of one layer (as described previously), it does not reveal the presence of cubic intergrowths in the hexagonal structure. The consistent ABABAB... stacking of the layers is clearly portrayed in Figure 2 revealing the almost perfect nature of these crystals. The micrograph in Figure 2 shows 108 stacking layers (A, B, or C) along the (120) direction. The complete stacking sequence for this particular micrograph is

BCB|CACA|CBCBC|BABABABABABABABABA
BABAB|CBCBCBCBCBCBCBCBCBCBCBCB
CBCBCBCBCBCBCBCBCBCBCBCB|ABABA
BABABABAB|CBCBCBC

It can be seen from this sequence that there are six stacking sequence defects in this nearly perfectly ordered hexagonal system. This represents ca. 6% probability of a stacking sequence defect. Three of these defects occur near the surface of the material, but it is not clear whether this is representative of the whole sample. Therefore, near the surface of this crystal, in this micrograph, there is a 23% probability of a stacking defect but in the bulk there is only a 3% probability of a stacking defect. The only regions of FAU structure in this material are the planes of FAU supercages created at the stacking defects. These images obtained on the as-prepared materials show that the channels extend right to the edge of the crystal with no evidence of an amorphous outer layer. This allows the detailed observation of the growing faces of the zeolite. There are clear steps along the 001_{HEX} face which are one layer thick (14.2 Å) and represent partially grown 001 faces (see later).

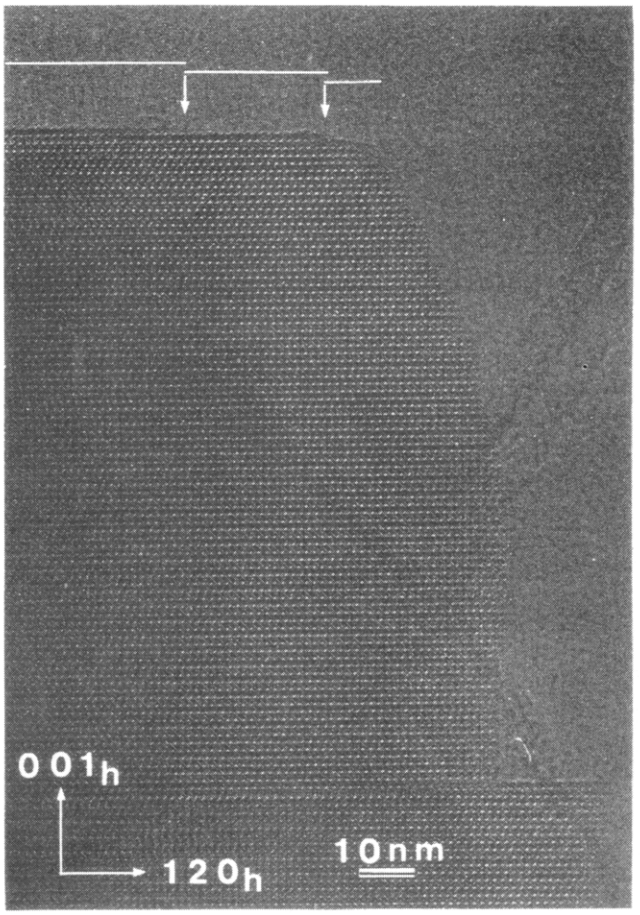

Figure 2. High-resolution electron micrograph of EMT structure synthesized using 18-crown-6 imaged down the 100_h direction. The image reveals the near perfect nature of the crystal. Also revealed are growing steps at the top of the image and a macroscopic defect step caused by a raft of ABABAB... stacking meeting a raft of BCBCBC... stacking.

Similar micrographs were recorded of materials synthesized with 15-crown-5. In the previous communication[17] it was demonstrated that these materials consist of pure FAU phase.

Figure 3 shows the high-resolution electron micrograph imaged along the $100_{HEX}/1\bar{1}0_{CUBIC}$ direction of a material prepared from a gel containing 33.3 mol % 15-crown-5 and 66.7 mol % 18-crown-6. These materials synthesized with mixtures of crown ethers are clearly intergrown and not overgrown. Each stacking layer in Figure 3 is complete. There are very few stacking defects along the length of

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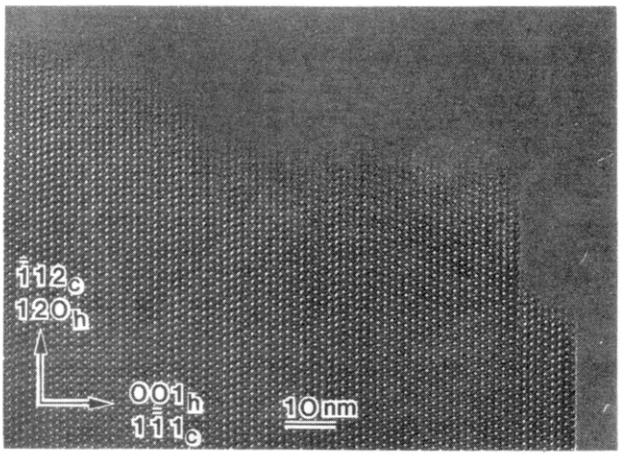

Figure 3. High-resolution electron micrograph of intergrowth sample synthesized with 67% 18-crown-6 and 33% 15-crown-5. The image is viewed down the $100_h1\bar{1}0_c$ direction.

each stacking layer. The sequence of these stacking layers can be determined from the micrograph and is

$$\begin{array}{l} \overset{\text{CUB}}{\text{BC}}|\text{BA}\overset{\text{CUB}}{\text{C}}|\text{ACBA}\overset{\text{CUB}}{\text{C}}\text{BAC}|\text{ACA}\overset{\text{HEX}}{\text{C}}\text{A}\overset{\text{CUB}}{\text{C}}\text{A}|\text{BC}\overset{\text{CUB}}{\text{A}}\text{BCA}| \\ \text{CACA}\overset{\text{HEX}}{\text{C}}\text{A}\overset{\text{HEX}}{\text{C}}\text{A}\overset{\text{HEX}}{\text{C}}\text{AC}|\text{BC}\overset{\text{HEX}}{\text{B}}\text{C}|\text{AC}\overset{\text{HEX}}{\text{A}}\text{C}\overset{\text{HEX}}{\text{A}}\text{C}|\text{BC}\overset{\text{CUB}}{\text{A}}\text{B}|\text{AB}\overset{\text{HEX}}{\text{A}}\text{BAB}| \\ \overset{\text{HEX}}{\text{A}}\text{CAC}|\text{BA}\overset{\text{HEX}}{\text{B}}|\text{CB}\overset{\text{CUB}}{\text{A}}|\text{BACBACBAC}\overset{\text{CUB}}{\text{B}}\text{ACBACBACBA} \end{array}$$

It is apparent from such a sequence that the layers are not stacked at random. There is a preference for blocks of hexagonal EMT structure or cubic FAU structure. At first sight these blocks would appear to be randomly stacked. The scanning electron micrographs, as shown in the previous paper,[17] give the appearance that at high relative 18-crown-6 proportions there are small triangles of FAU structure growing on top of hexagonal plates of EMT structure. The data presented above suggest that the external morphology of crystals (as determined by SEM) is not a good guide to the nature of the EMT/FAU intergrowths.[18] Figure 3 also shows that the EMT structure is only growing on one of the four possible crystallographically equivalent faces of FAU structure. The 001_{HEX} plane can intergrow with the four {111} planes of the cubic structure. This occurs readily in ZSM-20 (prepared using tetraethylammonium cation as structure directing agent) and results in a highly disrupted structure with a large number of defects. Such intergrowths growing on all the available cubic planes do not mesh on a macroscopic scale. The use of crown ether structure directing agents gives the macroscopic crystals with a near perfect intergrowth structure. The implication of this with respect to the mechanism of crystal growth is discussed later.

Figure 4 shows the powder X-ray diffraction pattern of this same material. The diffraction pattern was simulated using the DIFFaX routine devised by Treacy et al.[19] This routine permits a description of materials in terms of clustered faults whereby the twin faults are uncorrelated within the structure but appear with a given probability. In other words the structure is described in terms of blocks of FAU and EMT structure randomly interspersed but with a predetermined mean length for each block. The

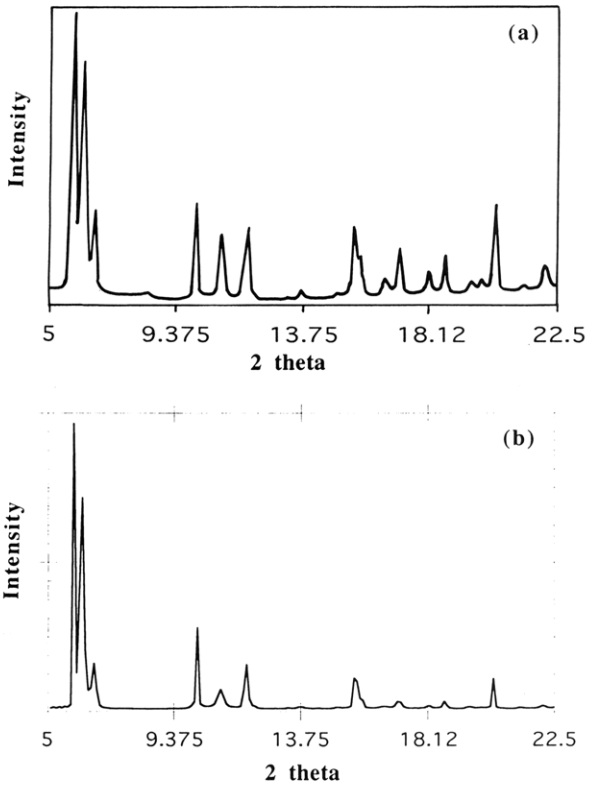

Figure 4. Powder X-ray diffraction pattern of intergrowth sample synthesized with 67% 18-crown-6 and 33% 15-crown-5: (a) experimental; (b) simulation using DIFFaX routine.[19]

best fit for the diffraction data is also shown in Figure 4. The fitting parameters are consistent with a material which is 38% FAU and 62% EMT structure and where the average length of the FAU structure is 11.5 stacking units and that of EMT 19 stacking units. Each stacking unit consists of one A, B, or C layer (i.e., a 001_{HEX} plane or a 111_{CUBIC} plane). The calculated degree of intergrowth correlates well with that observed from the HREM image. This suggests that the image shown in Figure 3 is representative of the sample. For this particular intergrowth material the ratio of FAU/EMT structure (32%/68%) is similar to that of 15-crown-5/18-crown-6 (33%/67%) used in the synthesis. Studies on a range of 18-crown-6/15-crown-5, however, shows that there is not a linear relationship. At 50% 18-crown-6 no EMT structure is observed by X-ray diffraction.

Figure 5 shows the optical diffraction pattern of the selected-area HREM image of Figure 3. This diffraction pattern has a number of different features: (i) the sharp spots are consistent with the large regions of FAU and EMT structure, greater than ca. five unit cells; (ii) diffuse streaking which is either due to the very narrow regions of FAU and EMT structure, less than ca. 5 unit cells, or the presence of position disorder in the crystal; (iii) sharp spots due to twinning of FAU and EMT structure; (iv) extra sharp spots. All the expected reflections are present, however, these additional sharp spots (iv) must be due to a spatial correlation between the FAU and EMT regions. In other words, the regions of FAU and EMT structure do not occur with a random frequency. Conversely the probability of FAU changing to EMT increases after certain thicknesses of crystal have grown. This diffraction

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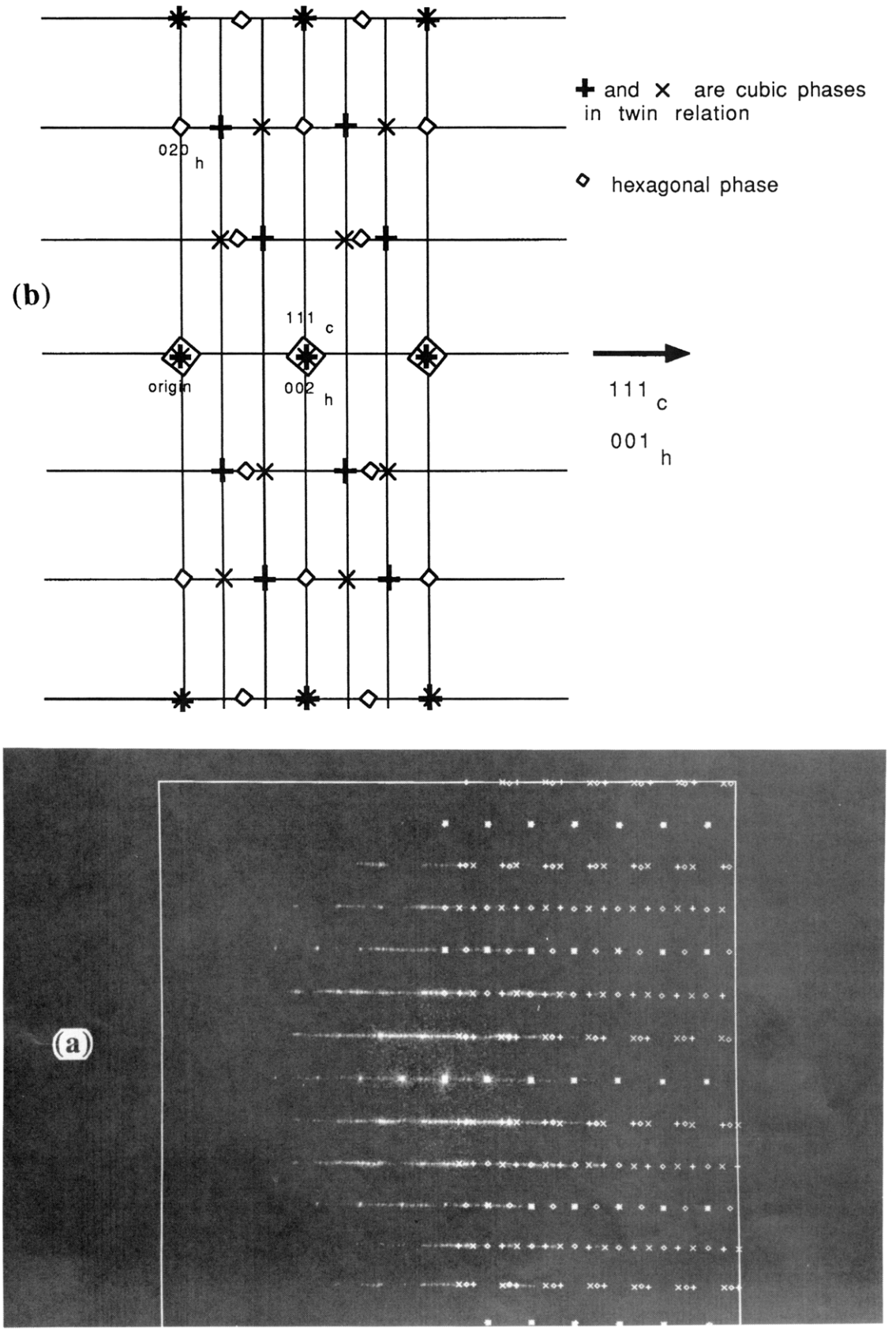

Figure 5. Selected area optical diffraction pattern[20] taken from image in Figure 3 of intergrowth sample synthesized with 67% 18-crown-6 and 33% 15-crown-5: (a) experimental data; (b) explanation of observed reflections.

pattern only relates to a selected area of the crystal; however, we believe this phenomenon to be generally true at high concentrations of 18-crown-6 in the synthesis gel and consequently at high proportions of EMT structure.

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(21) Recently the IZA Structure Commission has given the hexagonal framework structure the designation EMT.

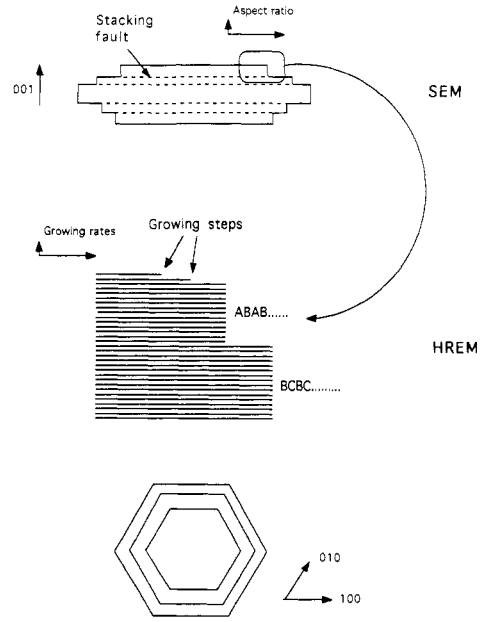

Figure 6. Schematic representation of features observed in high-resolution electron micrograph of EMT structure synthesized using 18-crown-6 imaged down the 100_h direction shown in Figure 2.

Mechanisms of Crystal Growth (Structure-Directing Properties of 18-Crown-6)

Figure 2 illustrates the anisotropy of the crystal growth rates in the EMT structure on the microscopic scale. The steps at the top edge of the crystal are the final growing faces of the crystal when the crystallization was stopped. These steps are illustrated schematically in Figure 6 and indicate that the growth rate in the 001_{HEX} direction is ca. 15 times faster than growth in the 010_{HEX} and 100_{HEX} directions. These growth rates as seen on the microscopic scale are in exact agreement with the overall aspect ratio of the crystals as observed by scanning electron microscopy previously. The growth pattern of these crystals seems to be fully explained by 001_{HEX} planes each half unit cell thick, growing one at a time beginning near the central axis of the crystal. Subsequent faces begin to grow when ca. 30 unit cells of these planes are complete in the 010_{HEX}/100_{HEX} directions.

Figure 2 shows the larger steps in the EMT crystals which are easily observed by scanning electron microscopy and reported previously. These macroscopic steps always occur at a fault plane. The crystals are composed of rafts of EMT structure displaced by one stacking fault, e.g., an ABABAB... raft growing on a BCBCBC... raft. However, the converse is not always true—i.e., a stacking fault in the crystal is not always manifested as a macroscopic step in the crystal.

Figure 3 provides further evidence of the role of the crown ether structure directing agents in the formation of EMT/FAU structures. We have already noted that EMT/FAU intergrowths prepared using crown ethers show highly directional growth. This clearly suggests that the EMT polymorph controls the nature of these intergrowths. There is only one face which FAU can nucleate on the EMT structure, and as a consequence directed intergrowths occur. In the case of ZSM-20 a disordered intergrowth is observed; this strongly suggests that EMT is nucleated on the FAU polymorph as there is a choice of faces on which EMT can growth on FAU. Hence, it is resonable to suppose that the crown ether templates play a role different from that of tetraethylammonium ion in the nucleated growth of intergrowths. Experiments conducted with different ratios of 18-crown-6/15-crown-5 indicate that a proportion of greater than 50% 18-crown-6 is required to observe the presence of small amounts of EMT (by powder X-ray diffraction). It is also possible to produce intergrown structures with 18-crown-6 as the only organic in the mixture. It is well-known that the FAU structure can readily be prepared without 15-crown-5 template. We postulate that 18-crown-6 has a very specific role in the nucleation of the EMT structure whereas the 15-crown-5 plays little role in the preparation of these materials. It is postulated that the 18-crown-6 is adsorbed onto the growing surface in such a way as to modify the growing surface. (The 18-crown-6 will contain a Na^+ cation at its center and so can be considered to be a macrocation. The interaction with the surface will therefore be partially electrostatic.) Figure 7 illustrates the growing surface of either the EMT or the FAU structure. The surface is characterized by surface pockets into which 18-crown-6 fits extremely snuggly. For the FAU case the next layer is added in such a way that the new layer is related by a screw axis and a supercage is generated on addition of each layer. However, in the case of EMT the layers build up of alternating layers related by a mirror plane to generate large tunnels and oblate side cages. The 18-crown-6 itself contains a mirror plane which if now adsorbed in the surface pockets is oriented in the 001_{HEX} plane. We suggest that this mirror symmetry is now completed by the favored growth of the mirror surface resulting in the EMT structure. As a result the 18-crown-6 will become clathrated within the small oblate cages of the EMT structure and thus acts as a template for their formation. Excess Na^+ may stabilize a center of inversion about the double-six ring (D6R) as the Na^+ cation fits very closely into the octahedral positions created at the center of the D6R. We are currently performing theoretical calculations to determine the modification of surface energies by the deposition of 18-crown-6 on the growing surface. Such a positioning of 18-crown-6 in the oblate side-cages is different from that suggested by Delprato et al.[1] They suggested that the crown ether was clathrated in the larger one-dimensional tunnels.

(22) The FAU or EMT family of framework structures are defined by a total of six layer types—each layer comprising a sheet of puckered 6-rings of sodalite cages. There are a number of different ways to define these different layers. One way is to describe the three possible displaced sheets as A, B, and C and their mirror images by A′, B′, and C′. The problem with this nomenclature is that the A and A′ sheets never occur at the same displacement (the symbol A usually being reversed to represent one such displacement). The six sheets can also be fully described by their displacement with a subscript to determine which layer will follow, i.e., A_B, $A_{C'}$, B_A, $B_{C'}$, C_A and C_B. The relationship between these two sets of nomenclature is as follows: A_B = A; B_A = A′; $B_{C'}$ = B; C_B = B′; C_A = C; $A_{C'}$ = C′. The usefulness of this latter set of nomenclature is that for a series of stacked sheets the subscript becomes redundant, e.g., A_BB_C $C_AA_{C'}C_BB_A$ is the same as ABCACB. The precise layer type can be read from this sequence by noting the layer displacement and the following layer type and is used throughout the text. The FAU framework then becomes ABCABC... or ACBACB... (in the other terminology these are equivalent to ABCABC... and A′B′C′A′B′C′...) and the EMT framework becomes ABABAB... or ACACAC... or BCBCBC... (in the other terminology these are equivalent to AA′AA′AA... or CC′CC′CC′... or BB′-BB′BB′...). The rules for stacking in integrowth structures are followed much more simply with the terminology used here. Using this nomenclature the minimum number of layers to define the FAU framework containing at least one supercage is three in the correct sequence, e.g., ABC. (In the other nomenclature only two sheets related by an inversion, e.g., AB are required to define a supercage but because of the rules for stacking such layers in this nomenclature the third layer by definition has a predetermined displacement). Similarly three layers in the correct sequence are required to define the EMT structure, e.g., ABA.

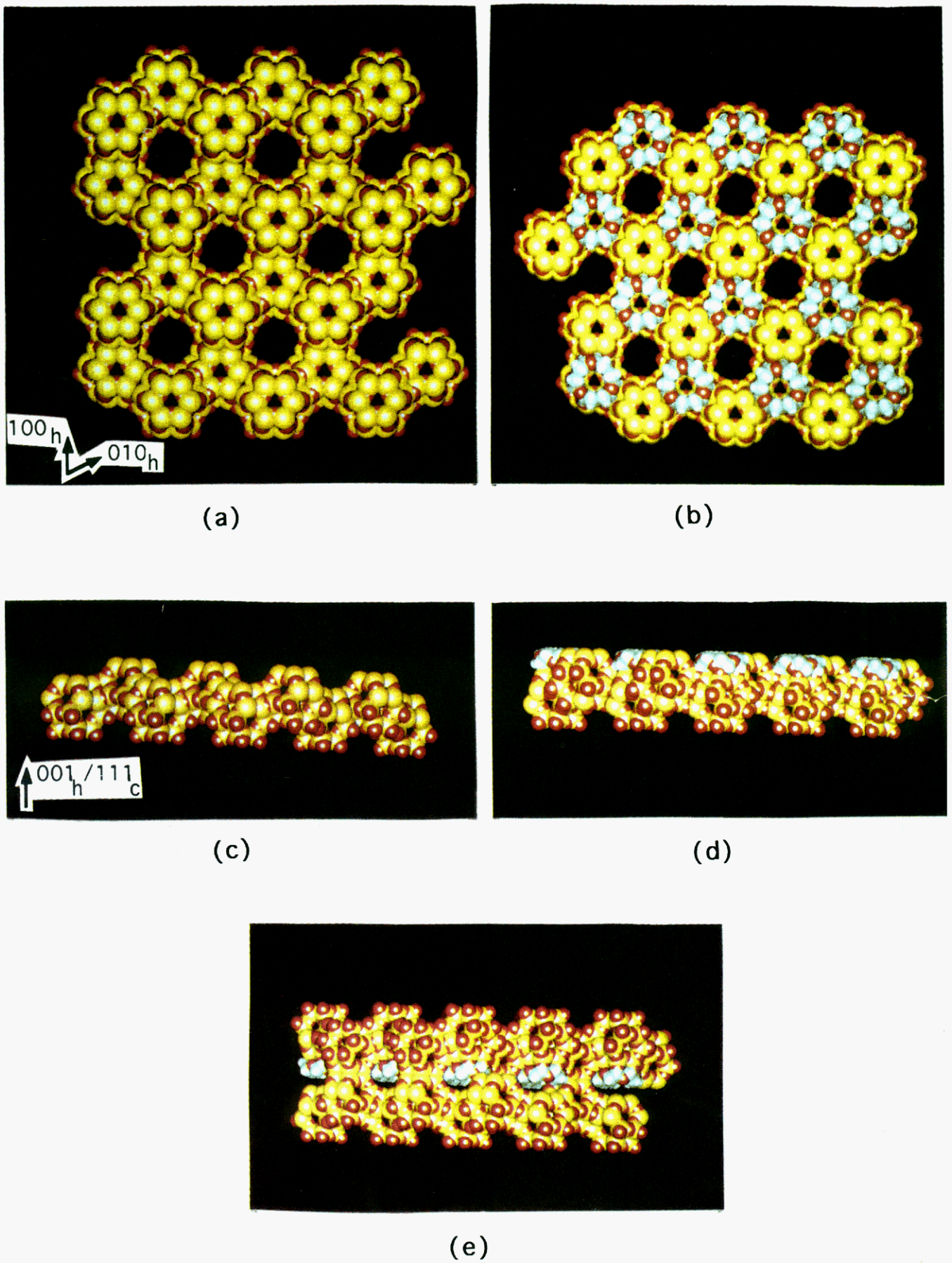

Figure 7. Computer graphic representation of the influence of 18-crown-6 for directing growth to EMT structure: (a) 001_h or 111_c growing surface; (b) surface modified by adsorption of 18-crown-6/Na^+ complexes in half-pockets on surface; (c) as in (a) but viewed along 100_h or $1\bar{1}0_c$; (d) as in (b) but viewed along 100_h or $1\bar{1}0_c$; (e) next growing surface complete with clathration of 18-crown-6/Na^+ complex in oblate side-pockets exhibiting mirror symmetry.

The presence of blocks of FAU and EMT structure in the intergrowth materials is probably a result of diffusion-limited transport of 18-crown-6 to the growing surface. As a block of EMT structure grows so the concentration of 18-crown-6 in the region of the growing surface is depleted. Below a certain critical concentration (probably ca. 50% in light of the requirement of at least 50% 18-crown-6 in the synthesis gel for EMT structure to form) the FAU structure is favoured until sufficient 18-crown-6 diffuses once again to the growing surface. It is probable that 18-crown-6 is only required to nucleate each growing surface which will continue to grow with or without 18-crown-6. A neutron diffraction study of these materials, currently underway, should reveal the occupancy of various sites for 18-crown-6.

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