Intergrowths of Cubic and Hexagonal Polytypes of Faujasitic Zeolites

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Intergrowths of hexagonal and cubic phases of faujasitic structure have been synthesised using crown ether templates and the phase integrity monitored by high-resolution electron microscopy.

Zeolite Y is an important material finding uses for a wide range of applications. The large pore sizes and three-dimensional access to the interior of the crystals mean that large molecules can diffuse more easily than in many other zeolites. A number of related zeolites have been reported such as CSZ-1,[1–4] ECR-30,[5] CSZ-3,[6] ZSM-3[7] and ZSM-20.[8–12] These zeolites are all intergrowths of zeolite Y (cubic symmetry, known as FAU) with a hexagonal polytype sometimes

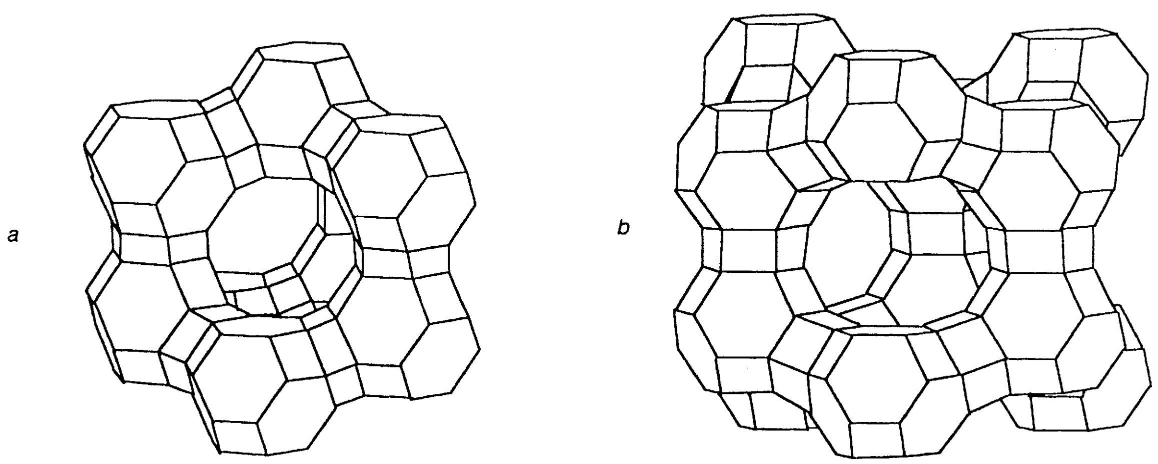

Fig. 1 Representations of the structure the two polymorphs (*a*) FAU and (*b*) BSS. In both structures sodalite cages are linked together through double six-rings.

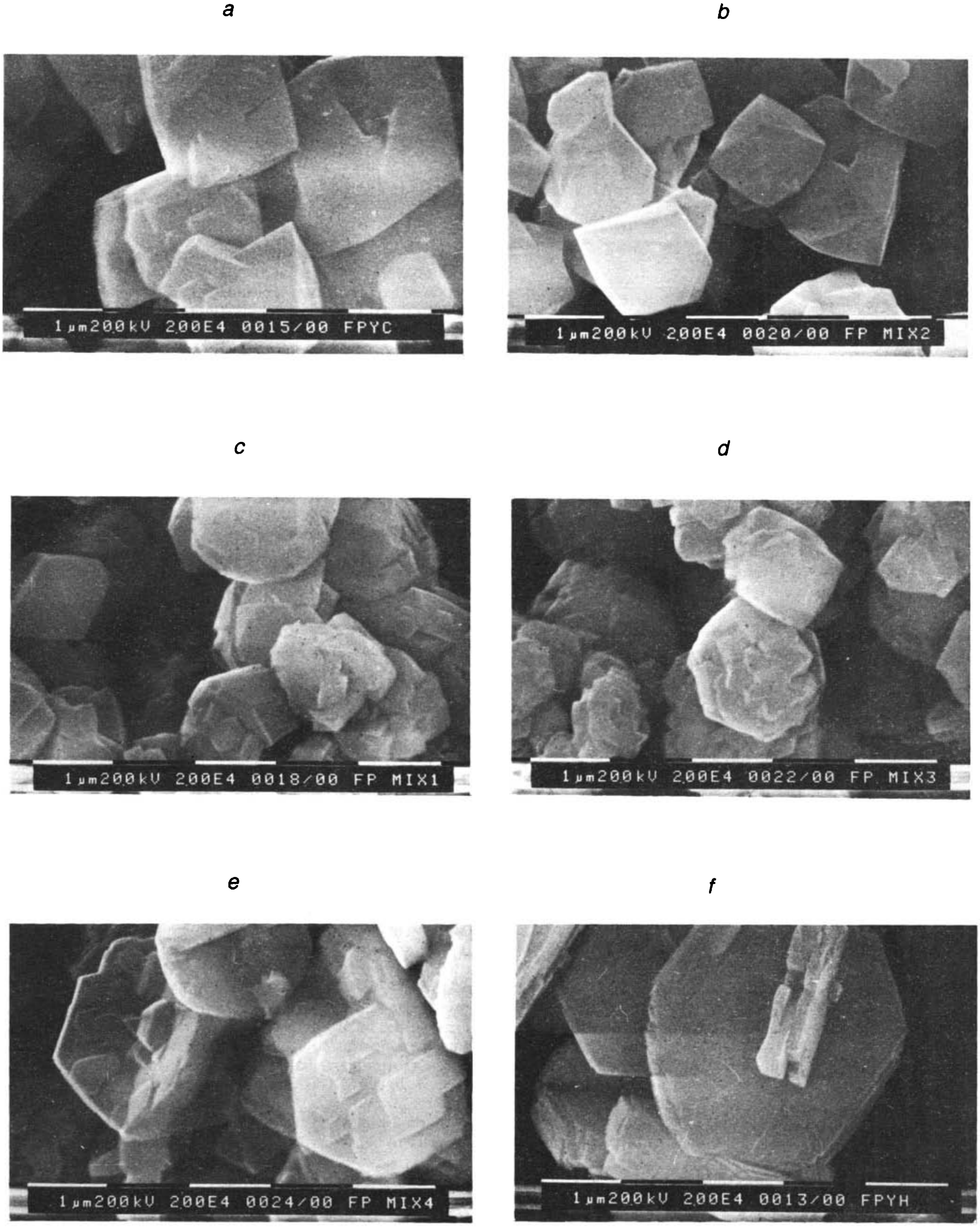

Fig. 2 Scanning electron micrographs showing faujasite polytypes synthesized with: (*a*) 100% 15-crown-5; (*b*) 80% 15-crown-5, 20% 18-crown-6; (*c*) 50% 15-crown-5, 50% 18-crown-6; (*d*) 40% 15-crown-5, 60% 18-crown-6; (*e*) 15% 15-crown-5, 84% 18-crown-6; (*f*) 100% 18-crown-6

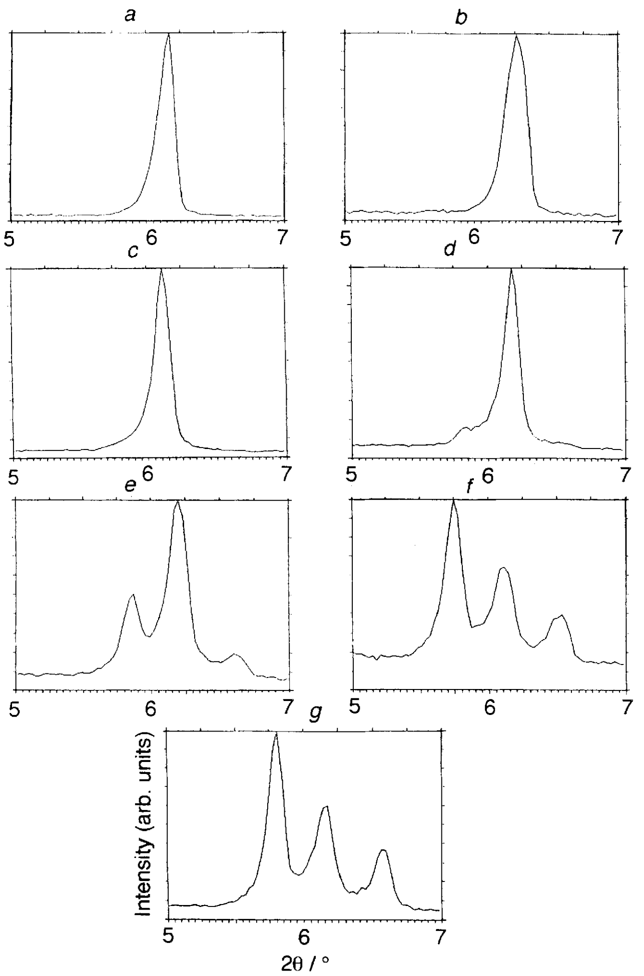

Fig. 3 X-Ray diffractograms of intergrowths of FAU and BSS synthesized with: (*a*) 100% 15-crown-5; (*b*) 80% 15-crown-5, 20% 18-crown-6; (*c*) 50% 15-crown-5, 50% 18-crown-6; (*d*) 40% 15-crown-5, 60% 18-crown-6; (*e*) 15% 15-crown-5, 84% 18-crown-6; (*f*) 10% 15-crown-5, 90% 18-crown-6; (*g*) 100% 18-crown-6

referred to as Breck's structure six (BSS).[13,14] These two structures are shown in Fig. 1. The essential difference between these structures is that in FAU, the truncated octahedra, or sodalite cages, are connected through double six-rings (the zinc blend structure) while in BSS they are arranged as in the wurtzite structure. This difference in the arrangement of zeolite building units leads to different pore dimensions and cage connectivities. In the FAU structure there is only one cage type, the so-called supercage with *ca.* 13 Å diameter. In the BSS structure there are two cage types: similar supercages which are connected in a linear fashion to produce a one-dimensional tunnel with window diameter *ca.* 7.4 Å; and a smaller oblate cage with access through a 12-ring aperture with dimension *ca.* 6.9 × 7.4 Å.[15,16] Consequently, both the FAU and the BSS structures have three-dimensional pore systems with large cages and tunnels but with potentially different shape-selective properties.

The discovery by Delprato *et al.*[17] that the end member hexagonal and cubic polytypes of faujasite can be synthesized using the crown ethers 18-crown-6 and 15-crown-5, respectively, as structure directing agents has prompted us to attempt to synthesize controlled intergrowths of the two phases using mixtures of crown ethers. The zeolites were crystallized in the system $10SiO_2 : 1.0Al_2O_3 : 2.4Na_2O : 140H_2O : 1.0$ crown ether. The sources of materials were: 30wt% colloidal silica, (Ludox); 40wt% sodium aluminate solution; 15-crown-5 and 18-crown-6 as supplied by Aldrich. Intermediate syntheses were made by combining the two crown ethers and adding to the sodium aluminate solution before combining with the silica source to form the synthesis gel. The gels were aged for two days at room temperature followed by crystallization in Teflon bottles for 7–10 days at 95 °C. Six intermediate samples were prepared using 80, 66, 50, 40, 33 and 15 mol% of 15-crown-5, respectively. Using this method a series of highly crystallize zeolite samples were obtained which were characterised as per below. For the electron microscopy studies it was necessary to stabilise the zeolites against beam damage by the following dealumination procedure. The method chosen to dealuminate the zeolites (ammonium hexafluorosilicate method[18]) was that least likely to alter the nature of the framework of the zeolites. The zeolites were first calcined to remove the crown ether template followed by ammonium ion exchange. 6 g of zeolite was placed in 450 ml of 0.8 mol dm^{-3} ammonium acetate. To this solution 15.6 ml of 0.5 mol dm^{-3} ammonium hexafluorosilicate was added slowly. The mixture was stirred at 75 °C for 3 h, then the zeolite was filtered off and washed. The degree of dealumination of the samples was monitored by high-resolution solid-state ^{29}Si nuclear magnetic resonance with magic angle spinnning (MAS–NMR).[19] It was found that in most cases the Si : Al ratio of the framework increased from *ca.* 3.5 to *ca.* 5.5. This corresponds to a reduction in the framework aluminium content by about 30%. However, Si : Al ratios of *ca.* 9.5, a 57% reduction in aluminium content could be achieved with longer treatment times.

The morphology of the crystals was determined by scanning electron microscopy (SEM). Fig. 2 shows the change in the morphology as the nature of the crown ether composition is altered. The morphology of the end members is the same as that reported by Delprato *et al.*[17] *i.e.* typical cubic morphology for FAU using 15-crown-5 and hexagonal platelets for BSS using 18-crown-6. The intermediate samples show first severe distortions of the octahedral crystals at low 18-crown-6 concentrations to essentially hexagonal plates with small octahedra growing from the surface at high 18-crown-6 concentrations. At concentrations approaching 50 mole% 15-crown-5–50 mole% 18-crown-6 the crystals exhibit a high degree of twinning and consequently a very distorted particle morphology. The morphology of the mixed samples is somewhat different to that of ZSM-20 which exhibits interpenetrating twinned platelets.[10]

The progression from the cubic FAU structure to the hexagonal BSS structure can also be monitored by powder X-ray diffraction. Fig. 3 shows the distinctive region $2\theta = 5$–7° which for FAU shows one line corresponding to the 111 reflection and for BSS shows three lines corresponding to the 100 002 and 101 reflections. From these diffractograms the lattice parameter for FAU was calculated to be $a = 24.61$ Å and for BSS were $a = 17.39$, $b = 28.42$Å. It appears that the onset of the hexagonal phase is not realised until about 60% 18-crown-6 is incorporated into the synthesis mixture. This is somewhat inconsistent with the SEM work which indicate particle morphology changes at lower 18-crown-6 concentrations, *ca.* 20–50%. This suggests that any intergrowths of BSS structure formed at these low 18-crown-6 concentrations only exist for a few unit cells. There is no long range order which is necessary to be observed by X-ray diffraction.

Fig. 4 shows the high-resolution electron micrographs (HREM) of the two end member FAU and BSS structures and that of an intermediate structure synthesized with 33 mole% 15-crown-5, 67 mole% 18 crown-6. The two end member samples both have almost fault-free structures. In the case of FAU this is to be compared with a conventional synthesis using no organic structure directing agent which Audier *et al.*[16] showed to contain a considerable degree of twinning. This indicates that the structure directing power of both 15-crown-5

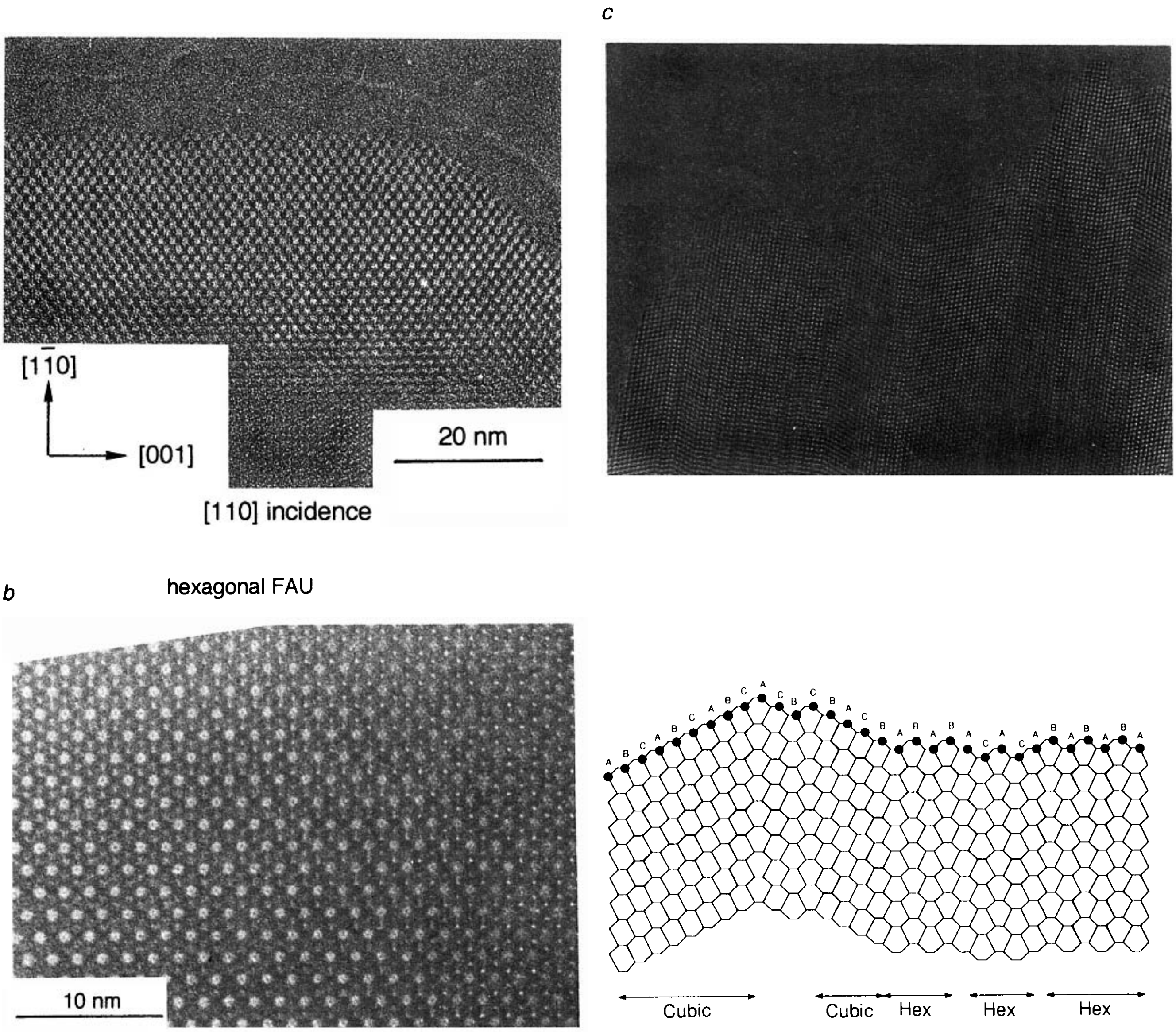

Fig. 4 High-resolution electron micrographs of (*a*) FAU, (*b*) BSS and (*c*) integrowth structure synthesized with 33% 15-crown-5 and 67% 18-crown-6

and 18-crown-6 is quite formidable, stabilising the FAU and BSS structure, respectively. The HRER of the intergrowth sample shows a number of interesting features. First, the structure contains mainly blocks of FAU structure and blocks of BSS structure (these pertain to an ABCABC..... and an ABABAB..... stacking of faujasitic sheets respectively). These structures are only the end members of an infinite series of structures formed by changing the stacking sequences of the faujasitic sheets. An area of the diffractogram has been drawn pictorially to show that the details of the stacking sequences can be discerned for the whole micrograph. A random stacking of A, B and C layers is not observed which is consistent with the fact that both 15-crown-5- and 18-crown-6 preferentially stabilise the FAU and BSS structures and not necessarily the intergrowth regions. This block structure is also consistent with the X-ray diffraction pattern which is indicative of two overlapping powder patterns from FAU and BSS structures. A random intergrowth of A, B and C layers would result in only two peaks in the region $2\theta = 5$–$7°$ at low incorporation of the BSS structure[20] whereas we always observe three peaks. Such a formation of blocks of FAU and blocks of BSS structure has been observed before for zeolite ZSM-20[12] which is synthesized using tetraethylammonium hydroxide as the structure-directing agent. Indeed it would appear that the intergrowth structure produced by using mixtures of crown ethers is identical in many respects to ZSM-20.

The micrograph, Fig. 4(*c*), also displays defect regions and in particular a large region on the right exhibits two cubic regions intergrowing at 38.8° with a corresponding defect region in between., To our knowledge such a defect has not been observed before in zeolite Y and requires considerable disruption of the zeolite structure. Normally an intergrowth of FAU with BSS will produce a perfect structure with no mismatch of bonds as the 001 face of BSS matches the 111 face of FAU. However, the BSS structure can also grow on the $\bar{1}11$ and $1\bar{1}1$ face of the FAU structure. If this happens then the independently growing BSS structures will not match at their interface. The incorporation of units of BSS structure growing on different faces of the FAU structure cannot, however, be the mechanism for the observed 38.8° intergrowth of FAU structure. It would appear that the integrowths are mirror images about the 111 direction as shown in Fig. 5. The disrupted region seems to eminate from a point defect which

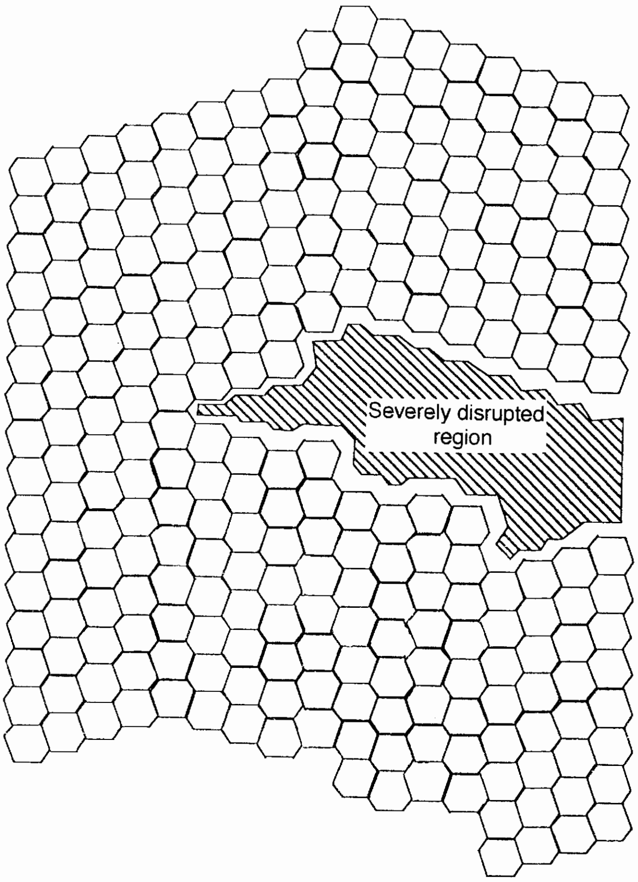

Fig. 5 Schematic representation of the severely disrupted region in the integrowth structure synthesized with 33% 15-crown-5 and 67% 18-crown-6

then precipitates into a massive extended defect structure. Incorporation of large amounts of such defects could severly restrict the intrazeolitic void space. Also observed in Fig. 4(*c*) is a line defect whereby the conversion from an ABABABAB..... stacking to ABABCBAB..... occurs over *ca*. 6 unit cells.

Synthesis of faujasite-type integrowths using crown-ethers produces novel structures with mainly intergrown blocks of BSS and FAU structure. Extended defects are observed which distinguishes the material from ZSM-20. However, in other respects the intergrowth materials strongly resemble ZSM-20.

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References

1 M. G. Barret and D. E. W. Vaughan, US Pat. 4 309 313, 1982.
2 M. M. J. Treacy, J. M. Newsam, R. A. Beyerlein, M. E. Leonowicz and D. E. W. Vaughan, *J. Chem. Soc., Chem. Commun.*, 1986, 1211.
3 J. A. Martens, P. A. Jacobs and S. Cartilidge, *Zeolites*, 1989, **9**, 423.
4 M. M. J. Treacy, J. M. Newsam, D. E. W. Vaughan, R. A. Beyerlein, S. B. Rice and C. B. deGruyter, *MRS Symp. Proc.*, 1988, **111**, 177.
5 D. E. W. Vaughan, Eur. Pat. Appl. 315 461, 1988.
6 D. E. W. Vaughan and M. G. Barret, US Pat. 4 333 859, 1982.
7 G. T. Kokotailo and J. Cinc, *Adv. Chem. Ser.*, 1971, **101**, 109.
8 J. Ciric, US Pat. 3 972 983, 1976.
9 J. Ciric, US Pat. 4 021 331, 1977.
10 S. Ernst, G. T. Kokotailo and J. Weitkamp, *Zeolites*, 1987, **7**, 180.
11 V. Fülöp, G. Borbély, H. K. Beyer, S. Ernst, and J. Weitkamp, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 2139.
12 J. M. Newsam, M. M. J. Treacy, D. E. W. Vaughan, K. G. Stohmaier and W. J. Mortier, *J. Chem. Soc., Chem. Commun.*, 1989, 493.
13 D. W. Breck, *Zeolite Molecular Sieves*, Wiley, New York and London, 1974, 56.
14 P. B. Moore and J. V. Smith, *Miner. Mag.*, 1964, **34**, 1008.
15 J. M. Thomas, M. Audier and J. Klinowski, *J. Chem. Soc., Chem. Commun.*, 1981, 1221.
16 M. Audier, J. M. Thomas, J. Klinowski, D. A. Jefferson and L. A. Bursill, *J. Phys. Chem.*, 1982, **86**, 581.
17 F. Delprato, L. Delmotte, J. L. Guth and L. Huve, *Zeolites*, 1990, **10**, 546.
18 Q. L. Wang, G. Giannetto and M. Guisnet, *Zeolites*, 1990, **10**, 301.
19 G. Engelhardt, U. Lohse, E. Lippmaa, M. Tarmak and M. Mägi, *Z. Annorg. Allg. Chem.*, 1981, **482**, 49.
20 M. M. J. Treacy, personal communication.