

Synthesis, characterization and control of faulting in STF/SFF topologies, a new family of intergrowth zeolites.

Luis A. Villaescusa, Wuzong Zhou, Russell E. Morris and Philip A. Barrett

1. X-ray diffraction powder pattern simulations of the disordered intergrowths in the family STF/SFF.

The powder XRD patterns were simulated using the DIFFaX program of Treacy et al.¹ A 16 T-atom periodic building unit (including oxygens) was taken from the structure of SSZ-44 using the structural parameters derived by Wagner et al. The b and c axes and atomic coordinates were interchanged to make the layers stack along the c direction, a requirement for DIFFaX. A second layer was generated from the first by symmetry (see IZA website for details of the structures of STF and SFF including the relationship between the periodic building units). Appropriate translations are applied to each layer to complete the connectivity in accordance with the unit cell parameters and symmetry. In this model SSZ-35 is represented by an AAAA or stacking of the layers and SSZ-44 by an ABAB sequence². The powder XRD patterns of the end members were simulated firstly as a check on the validity of the model at the Cu K α wavelength using a Pseudo-Voigt function to represent the shape of the peaks. A good agreement was found between the simulation and experimental diffraction patterns for both structures. Calculations were then performed spanning a range of compositions from one structure type to the other. We have considered both random sequences of layers (see figure 1) as well as ordered domains each rich in one of the end members (figure 2 and 3).

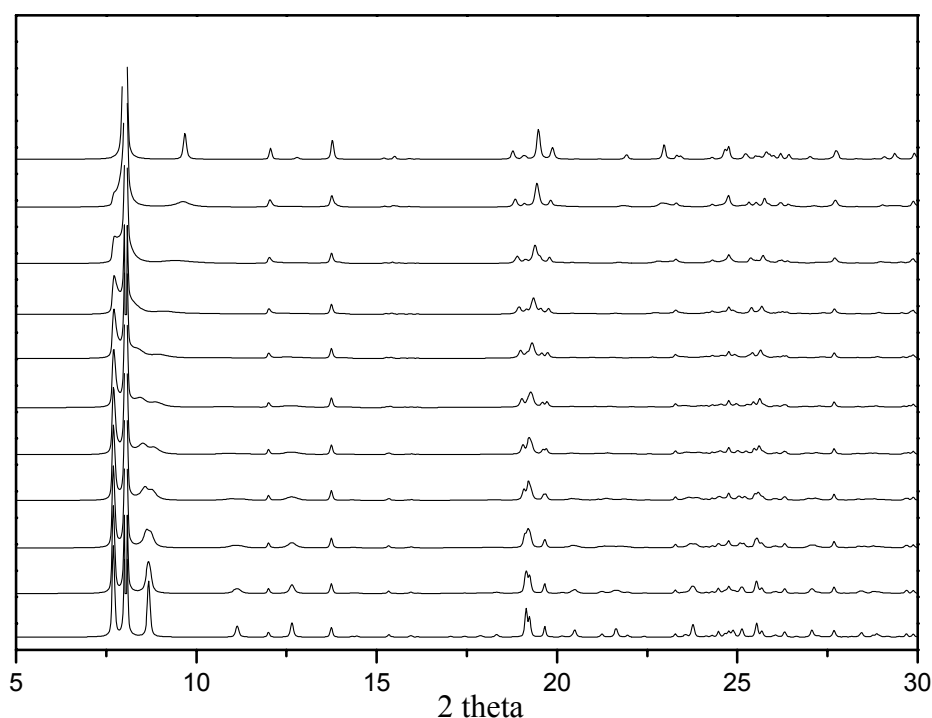


Figure 1. Simulated XRD patterns using DIFFaX of materials consisting of random intergrowths of STF and SFF for different stacking probabilities (shown in increments of 10% from one end member to the other. Lower trace, SFF, Upper trace, STF).

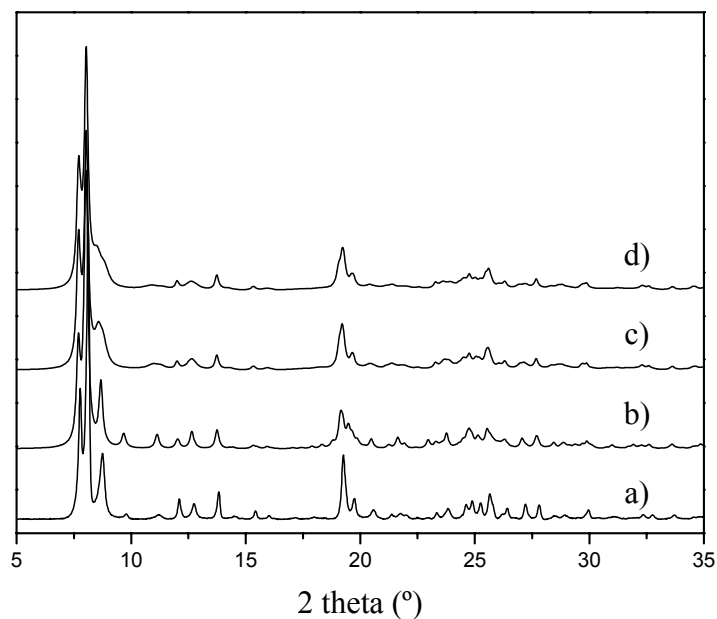


Figure 2. Simulated XRD patterns using DIFFaX for a non random stacking sequence (i.e. domains rich in one end member) compared to the experimental sample (STF:SFF 33:67) and random stacking model. a) Experimental sample. b) Domains 33:66. c) Random 30:70. d) Random 40:60.

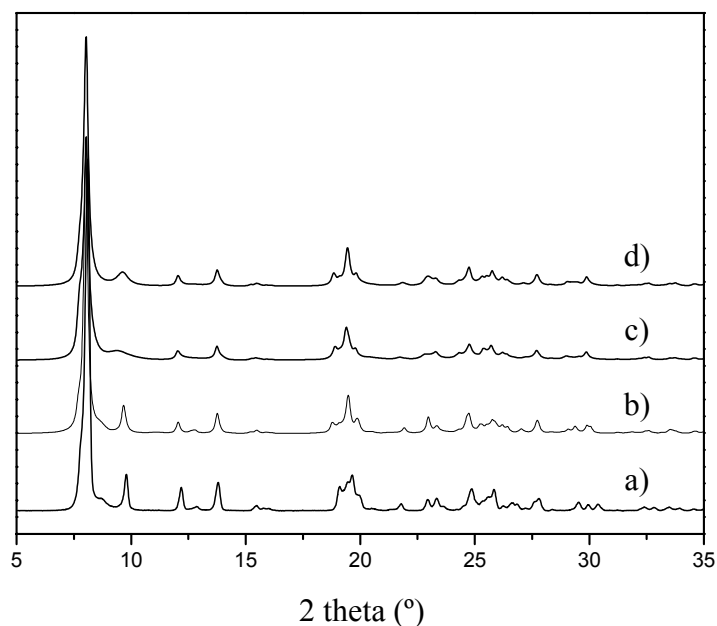


Figure 3. Simulated XRD patterns using DIFFaX for a non random stacking sequence (i.e. domains rich in one end member) compared to the experimental sample (STF:SFF 85:15). a) Experimental sample. b) Domains 28:5. c) Random 20:80. d) Random 90:10.

Looking at figure 1 calculated assuming that the intergrowths are random in nature, some reflections can be observed to split and shift. At the same time other peaks are observed to appear or disappear as we move across the sequence from one end member

to the other. On the contrary, the sequence of the XRD patterns shown by the zeolites synthesised in this work (figure 3 in the paper) show only changes in intensity as they get broader and no shift in peak position is found in these synthetic samples. It is clear that a model based on a random sequence of intergrowths doesn't reproduce the features of the XRD patterns observed experimentally.

In an attempt to produce a more realistic situation according to both, the XRD patterns and the homogeneity of the crystal morphology observed experimentally, we have performed some calculations using a domain approach. We have modelled a situation where large domains of each phase alternate along the crystal. We have simulated the XRD patterns of the intermediate experimental faulted zeolites (samples B and C (see paper), STF:SFF 85:15 and 33:67 respectively) by using the observed faulting ratio extracted from the ^{29}Si solid state MAS NMR spectra. This simulation can be carried out by directly specifying the number of layers of each type and their stacking order. Several possibilities for the size of the domains representing each experimental sample were considered. The best results are depicted in figures 2 and 3 together with the corresponding XRD pattern of experimental sample as well as the analogous results from simulations where a random stacking was enforced.

The XRD patterns simulated using the domain based approach shows an improved agreement with the experimental data compared to the random intergrowths in figure 1. The positions of the peaks and the broadness are reasonably well reproduced by the simulations. We can't rule out the possibility that the domains of variable thickness exist in the experimental samples and therefore our simulations in using DIFFaX represent a more idealised scenario. However, these calculations support the conclusions from other characterisation (see paper) which implied some level of ordering of each end member in the intergrown materials, synthesised in this work.

¹ Treacy, M.M.J; Newsam, J.M.; Deem, M.W. A General Recursion Method for Calculating Diffracted Intensities From Crystals Containing Planar Faults. Proceedings of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences 1991, vol 433, iss 1889, pp 499-520.

² Wagner, P.A. ; Zones, S.I. ; Davis, M.E.L; Medrud, R.C.; SSZ-35 and SSZ-44: Two Related Zeolites Containing Pores Circumscribed by ten and eighteen Membered Rings. Angew. Chem. Int. Ed. 1999, vol 38, pp. 1269-1272.