Quantitative High-Resolution TEM/STEM and Diffraction

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Structural analysis of ETS-10 with 3D electron diffraction tomography and electron microscopy observations

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The microporous titanosilicate, ETS-10, composes of tetrahedral SiO_4^{4-} and TiO_6^{8-} units, which form layers of –Ti-O-Ti-O- chains and three dimensional 12-ring pore systems. Previous study suggests that ETS-10 can be constructed on basis of layers parallel to main channels. Each layer contains two sets of mutually orthogonal $[(TiSi_5O_{13})^{2-}]_n$ columns. The packing of layers along *c* direction is achieved by shifting ±1/4*a* and ±1/4*b* with respect to its former layer, which produce various stacking arrangements, as well as two kinds of defects, layer stacking defect and defect in one layer. The high degree of defects existed in ETS-10 introduce the complexity and variety of its crystal structure, which are close related to its perspective catalytic and photoelectric properties. [1-3]

In this work, structural study of ETS-10 was investigated by combination of the recently developed three dimensional electron diffraction tomography (3D EDT) method [4] and electron microscopy (EM) observations. Sweeping reciprocal space is conducted by using electron beam tilt in an available angular range with a designated step. The total tilting angles covered was from –62.7° to +68.9° (~132° in total) with a step size of 0.15°. From the reconstructed 3D reciprocal space, strong diffusion scattering was observed in ED pattern frames due to extensive defects present in crystal. The diffuse streaks appear only in the direction of *c** axis, which is the orientation of layer packing. According to layer shifting rules, stacking defects will affect those reflections which satisfy *h*=2n+1 or *k*=2n+1, which are consistent with (1-10) slice in Figure 2a.

Even in the presence of strong diffuse scattering , the *ab* initio structure can still be solved based on extracted reflections using charge flipping method in Jana2006 (Figure 1b,c). [5] The structure solution gives a rather reasonable model of polymorph B (s.g. *C*2/*c*, *a*=*b*=21Å, *c*=14.5 Å and β=111.12°). Only three O atoms are missing in comparison with the model reported before with *R* factor equal to 38.9%. This structure is consistent with the projection along [1-10] zone axis in HRTEM image (Figure 2d).

Figure 2a, b show SEM images of ETS-10 along different viewpoint, which present a point groups of 4/mmm. The 4-fold symmetry along *z* axis can be explained by the existence of twins in 110 planes, which also show the evidence in ED pattern along [1-10] in Figure 1a. The main stacking sequence of layers is *ABCDABCD*…, consistent with polymorph B structure (Figure 2b). This might be the reason that *ab* initio structure solution gives a model of polymorph B.

Besides, layer stacking defects can be clearly seen in EM image as shown in Figure 2. Stacking sequence was marked by yellow line with the notation of *A* (*B, C* or *D*) layer in Figure 2d. Different packing styles might form other possible polymorph, like polymorph A (s.g. $P4_1$, *a*=*b*=14.8Å, *c*=27.0Å) with *ABAB*… stacking. The other type of defects appears in the same layer, which might form a large pore or block the straight pores along [1-10] direction as shown red square marked areas in Figure 2d.

In conclusion, structure of ETS-10 has been solved using 3D EDT method and EM observations. Defects in the structure have been discussed briefly.

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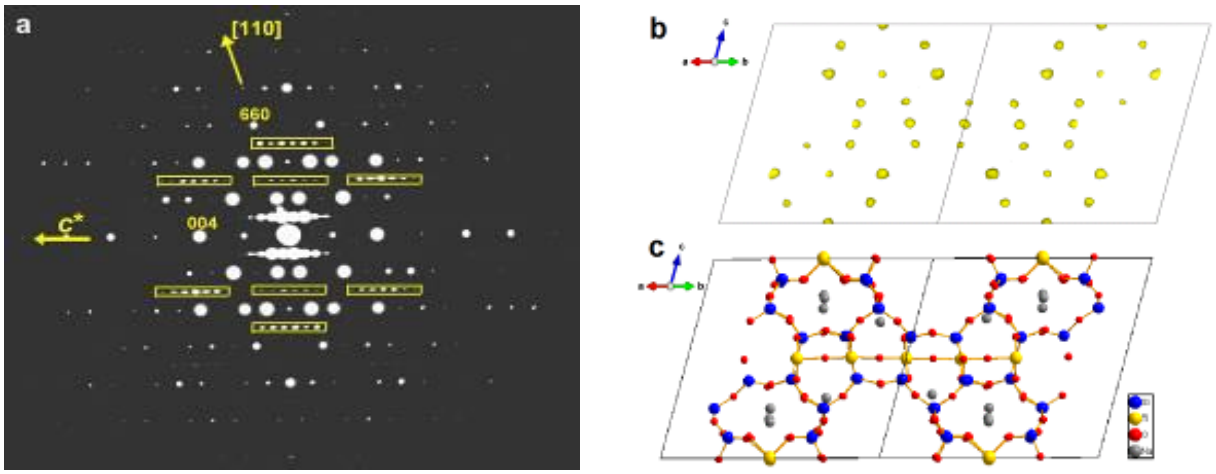

Figure 1. (a) One (1-10) slice of reconstructed 3D reciprocal space from 3D EDT data, (b) electrostatic potential map and structural model obtained using charge flipping method in Jana2006. The yellow rectangle marked diffuse streaks with intensity maxima along *c** axis.

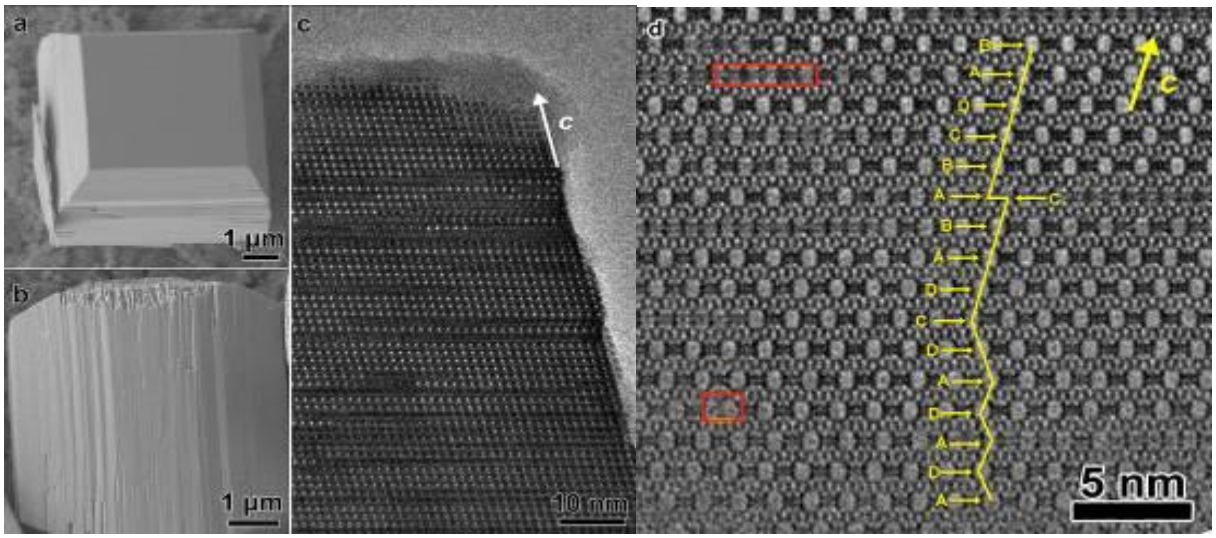

Figure 2. (a), (b) SEM image of ETS-10 viewed along different directions, (c) low-mag HRTEM image and (d) high-mag HRTEM images along [1-10] (or [110]) direction. The yellow line in Figure 2d traced layer stacking sequence along *c* axis, and red rectangle marked defects in one layer introduced by different stacking style in the same layer.