X-ray Diffuse Scattering Study of Framework Faulting in Mordenite

B.J. Campbell,[1] T.R. Welberry,[2] R.W. Broach,[3] H. Hong,[4] A.K. Cheetham[5]
[1]Department of Physics & Astronomy, Brigham Young University, Provo, UT, U.S.A.
[2]Research School of Chemistry, Australian National University, Canberra, Australia
[3]UOP Research Center, Des Plaines, IL, U.S.A.
[4]Materials Research Laboratory, University of Illinois at Urbana-Champaign (UIUC), Urbana, IL, U.S.A.
[5]Materials Research Laboratory, University of California, Santa Barbara, CA, U.S.A.

Introduction

Zeolite mordenite is a widely used industrial catalyst that has long been suspected of framework variability. Zeolites exhibit absorptive and catalytic properties that are fundamentally shape-selective. The specificity of a given application, such as methanol-to-gasoline conversion or air separation, depends strongly on the local environment of the active sites, as well as the sizes and shapes of the micropores that permit guest molecules to access them. Framework defects, such as metal-substituted tetrahedral sites, intergrowths, faults, and hydroxide nests, greatly complicate zeolite characterization. Even in very small concentrations, framework defects locally reshape the pore structure, creating a variety of new potential active sites that may significantly alter the useful material properties.

Early single-crystal x-ray diffraction studies of natural mordenite samples have reported evidence of a dilute concentration of tetrahedral sites that appeared to be shifted by ½[001] relative to their expected locations [1]. More recent work on synthetic mordenites has shown that it is sometimes possible to improve Rietveld fits to x-ray powder diffraction data by assuming the presence of ½[001]-shifted framework material [2]. Electron diffraction patterns from mordenite [3] have shown diffuse scattering within the $l = 2n+1$ planes of reciprocal space, suggesting the presence of linear fault defects [4]. This observation was recently explained by Campbell and Cheetham [5], who found that the presence of long *c*-axis columns of material that have been fault-shifted by ½[001] transfer intensity uniformly out of the $l = 2n+1$ Bragg reflections and into diffuse sheets within the $l = 2n+1$ planes. The present work [6] provides a gigapixel x-ray diffuse scattering survey of intensity variations within these sheets that establishes the structure of mordenite's columnar framework defects and yields surprising evidence for correlated columnar defects that form a block-mosaic network of planar stacking faults.

Methods and Materials

Synchrotron x-ray diffuse scattering measurements were carried out at UNI-CAT beamline 33-ID at the APS by using a photon energy of 20 keV. The natural single-crystal mordenite sample from Challis Valley, Idaho, exhibited a typical needle-shaped habit, with the needle axis parallel to [001] and with lateral dimensions of 40 × 40 μm. The needle was oriented parallel to the omega axis of the goniometer, which was perpendicular to the 200-μm x-ray beam. The use of a charge-coupled device (CCD) x-ray detector (Bruker APEX) permitted the rapid acquisition of a large 3-D volume of reciprocal space. At each crystal position, a curved 2-D section of reciprocal space was projected onto the CCD detector. By rotating the crystal about the omega axis in 0.1° increments and collecting one CCD frame (approximately 10 s) at each position, a large, approximately cylindrical volume with an outer diameter $q = 9.5$ Å^{-1} was mapped out in just a few hours.

Results and Discussion

The detailed atomic structure of mordenite's columnar defects is a challenging problem that may have important consequences for its catalytic properties. The normal mordenite framework structure can be assembled from a smaller motif consisting of a four-membered ring (4MR) of $(Si,Al)O_4$ tetrahedra and eight tetrahedral legs attached to the outer vertices. The 4MR motifs stack in columns parallel to the [001] channel axis. A logical model for an isolated columnar defect can be constructed by displacing a single column of 4MR motifs by half a unit cell along [001], which preserves stoichiometry and tetrahedral coordination and also allows for reasonable Si-O bond lengths [4]. Experimental verification of such a model requires mapping out the 3-D diffuse scattering distribution in detail. The CCD detector image contained in Fig. 1 is representative of the x-ray diffuse scattering patterns obtained from mordenite in the present study. Diffuse streaks of intensity are evident in the data, each spanning roughly the width of the frame from left to right. The positions of these streaks remain constant as the crystal is rotated through 100°, revealing the streaks to be the cross sections of large sheets of diffuse intensity in the reciprocal lattice planes normal to (001). Because the sheets of diffuse scattering are observed to be very tightly compressed at integer values of *l*, we assume that the columnar defects effectively span the entire crystal along [001].

The experimental $l = 2n+1$ reciprocal lattice planes (from $l = -5$ to $+5$) were reconstructed by combining portions of each of the 2-D CCD images collected. The

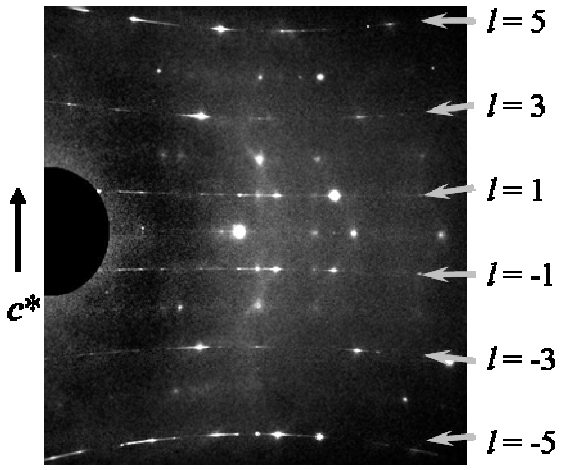

FIG. 1. CCD camera image of high-energy (20-keV) x-ray diffuse scattering from mordenite. The circular shadow of the beam stop has been blackened out on the left-hand side of the image. The needle-shaped crystal was oriented with its [001] axis parallel to the left-hand edge and mounted 5 cm in front of the center of the detector.

intersection of a reciprocal lattice plane with the Ewald sphere is a circle, which then projects outward as a cone into the laboratory space. The intersection of this cone with the flat detector plane then forms a general conic section, explaining the hyperbolic shape of the diffuse streaks in Fig. 1. To reconstruct a given plane, the relevant conic section must be calculated and extracted from each CCD frame. These 1-D slices are then placed side by side to form an image of the whole plane, as shown in Fig. 2(a) for the *hk*5 plane. This image reveals a wealth of structure and contains at least three distinct types of diffuse features: (1) broad features that span the space around several Bragg reflections, (2) star-shaped intensity distributions centered around certain Bragg reflections, and (3) narrow streaks of intensity along lines for which $h \pm k$ = integer. The linear streaks appear to join together to form diamonds at some positions, while the broad features give the appearance of filling in the interior of some of the diamonds.

Computer simulations of the diffuse scattering distribution, based on computer-generated mordenite models incorporating a random spatial distribution of defects, were used to verify the defect structure. Figure 2(b) contains the simulated pattern obtained from the final model described below. This diffuse scattering simulation utilized a mordenite crystal model containing $256 \times 256 \times 16 = 2^{10}$ unit cells, thus spanning 512 columnar motifs along both the [100] and [010]

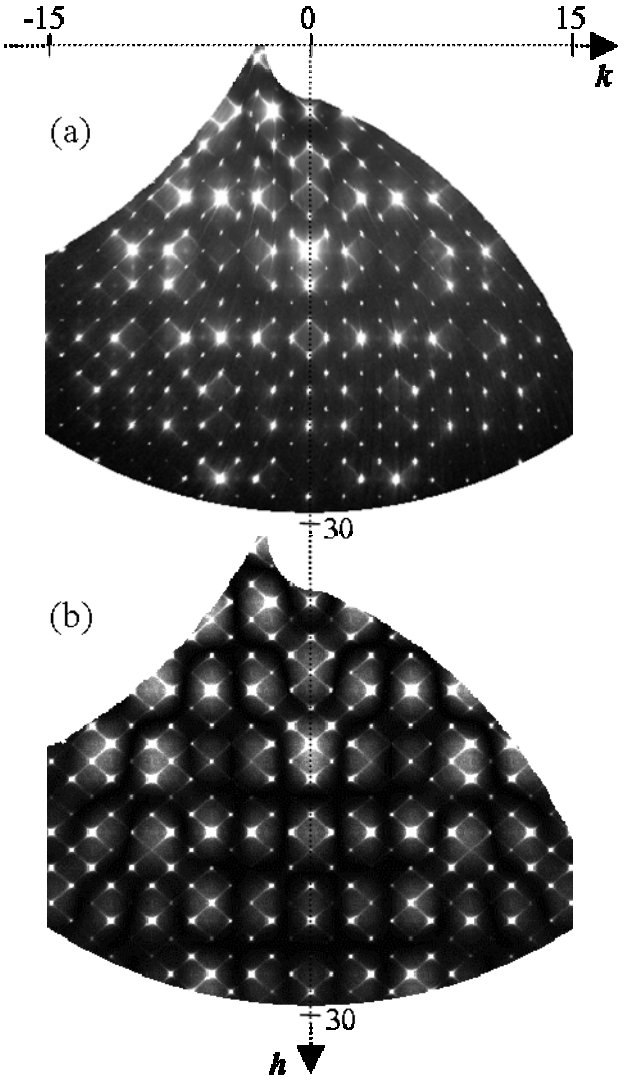

FIG. 2. (a) Reconstructed image of the hk5 reciprocal lattice plane obtained by extracting the hyperbolic l = 5 streak from each CCD frame as the crystal was rotated about the [001] axis in increments of Δω = 0.1°. (b) Simulated diffuse scattering pattern of the same reciprocal space region based on the final columnar defect model represented in Fig. 3.

directions. The sharp experimental features indicate fairly long-range defect structures that required this extraordinarily large real-space model. Defects were injected into the model by using a 2-D array of random variables $X_{i,j}$, where the i and j indices each run from 1 to 512. A value of $X_{i,j} = 0$ indicates that the columnar motif labeled (i,j) is in its normal position, whereas a value of $X_{i,j} = 1$ indicates that the motif has been displaced by ½[001]. The resulting defect fraction p is simply the

probability of obtaining a value of $X_{i,j}$ = 1. The simulations were performed by using the program DIFFUSE [7], which calculates the diffraction pattern by using the method of lots. Because the columnar defects traverse the structure along [001], their actual length has no effect on the structure of the diffuse scattering within planes normal to [001]. Therefore, we found it practical to reduce the lot size considerably along this direction. After preliminary testing, a lot size of $14 \times 14 \times 2$ unit cells was chosen, and the number of lots was selected to be 100, so that about 3.7% of the model crystal was sampled in one simulation.

The final structural model is represented in Fig. 3, which reproduces each of the essential diffuse scattering feature types observed experimentally. The broad peaks and nodes in Fig. 2 are the Fourier transform of an isolated columnar defect. The good match between the calculated and experimental patterns verifies the 4MR columnar motifs as the defect-shifted blocks of material in real mordenite. The narrow streaks and star-shaped scattering features, on the other hand, arise as a result of longer-range intercolumnar correlations along the <110> crystal directions. These features are strong evidence of ½[001] stacking faults, as illustrated in Fig. 3(a). One such fault plane comprises a sheet of columnar motifs that become cooperatively displaced relative to their normal positions. The best match to the experimental data in Fig. 2(a) was achieved by creating a block-mosaic pattern of stacking faults superimposed on a random distribution of isolated columnar defects. The pixel map representation of the final structural model in Fig. 3(b) was used to produce the simulated diffuse scattering pattern in Fig. 2(b).

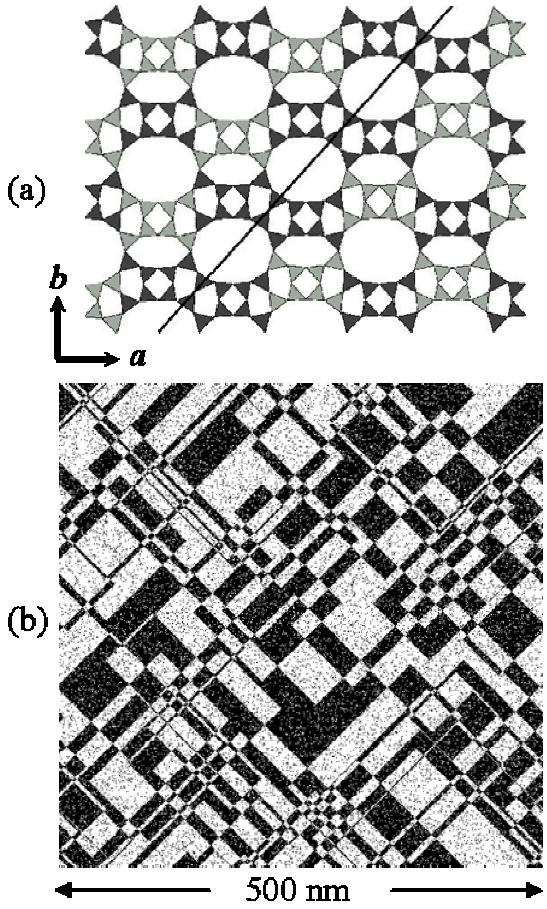

FIG. 3. (a) Illustration of a ½[001] stacking fault in the (110) plane. The fault plane is indicated by a solid line. Darkly shaded columns are translated by ½[001] relative to the lightly shaded columns. Normally, a columnar motif is translated relative to each of its nearest neighbors, a pattern that the anti-phase boundary clearly disrupts. (b) Pixel map representation of the final defect correlation model. Black pixels represent columnar motifs that are shifted by ½[001] relative to their normal positions. © 2004 by The International Union of Crystallography, http://journals. iucr.org/.

Acknowledgments

We acknowledge J.J. Pluth for providing natural mordenite single-crystals. UNI-CAT is supported by the UIUC Materials Research Laboratory (U.S. Department of Energy [DOE] State of Illinois Board of Higher Education, Higher Education Cooperation Act; and National Science Foundation); Oak Ridge National Laboratory (DOE) under contract with UT-Battelle, LLC); National Institute of Standards and Technology (U.S. Department of Commerce); and UOR LLC. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under contract No. W-31-109-ENG-38. This work was also supported by an award from the Merit Allocation Scheme on the National Facility of the Australian Partnership for Advanced Computing.

References

[1] W.J. Mortier, J.J. Pluth, and J.V. Smith, Mater. Res. Bull. **10**, 1319 (1975); J.L. Schlenker, J.J. Pluth, and J.V. Smith, Mater. Res. Bull. **14**, 849 (1979).

[2] P.R. Rudolf and J.M. Garcés, Zeolites **14**, 137 (1994).

[3] J.V. Sanders, Zeolites **5**, 81 (1985).

[4] J.D. Sherman and J.M. Bennett, in *Molecular Sieves*, edited by M.W. Meier and J.B. Uytterhoeven (American Chemical Society, Washington, DC, 1973), pp. 53-65.

[5] B.J. Campbell and A.K. Cheetham, J. Phys. Chem. B **106**, 52 (2002).

[6] B.J. Campbell, T.R. Welberry, R.W. Broach, H. Hong, and A.K. Cheetham, J. Appl. Crystallogr. **37**, 187-192 (2004).

[7] B.D. Butler and T.R. Welberry, J. Appl. Crystallogr. **33**, 1046 (1992).