Pair Distribution Function Analysis of Zeolite Beta

M.M. Martínez-Iñesta,[1] I. Peral,[2] T. Proffen,[3] R.F. Lobo[1]

[1]University of Delaware, Newark, DE, U.S.A.
[2]National Institute of Standards and Technology, Gaithersburg, MD, U.S.A.
[3]Los Alamos National Laboratory, Los Alamos, NM, U.S.A.

Introduction

The pair distribution function (PDF), $G(r)$, describes the distribution of the atomic distances of a material. It is defined as follows:

$$G(r) = 4\pi r[\rho(r) - \rho_o], \qquad (1)$$

where $\rho(r)$ is the microscopic pair density and ρ_o is the average atomic density of the material. The PDF is obtained experimentally by the sine Fourier transform of the total scattering structure function $S(Q)$, which is determined from the powder diffraction pattern of the material [1] as follows:

$$G(r) = 2/\pi \int_0^\infty Q[S(Q) - 1]\sin Qr \, dQ, \qquad (2)$$

where $Q = 4\pi\sin\theta/\lambda$. It can be simulated from a structural model [2] by using the following:

$$G(r) = 1/r \sum_{i,j} b_i b_j/\langle b\rangle^2 \delta(r - r_{ij}) - 4\pi r\rho_o, \qquad (3)$$

where the sum is taken over all the atoms in the structure, and r_{ij} is the distance separating atoms i and j. Thus, the PDF is characterized by peaks centered at the characteristic distances r_{ij} that separate the pairs of atoms. The integrated intensity of each peak is proportional to the number of pairs of atoms separated by that distance and the scattering lengths, b_i and b_j, of the atoms involved. (The compositional average scattering length of the material is $\langle b\rangle$.) When neutrons are used, b_i is the coherent scattering length of atom i, and when x-rays are used, b_i is usually the form factor of atom i at $Q = 0$ Å^{-1} (although other values such as the average Q value of the data set are also used).

Zeolite beta can be conceived as an intergrowth of two crystalline (hypothetical) polytypes A and B. They are depicted in projection in the top section of Fig. 1 [3]. In this drawing (the oxygen atoms have been omitted for clarity), the pores in polytype A are arranged in an ABABAB…-type configuration, and the pores in polytype B are arranged in an ABCABC…-type configuration. Because of its stacking faults, the structure of zeolite beta has not been able to be refined by using conventional methods.

An inspection of polytypes A and B in Fig. 1 shows
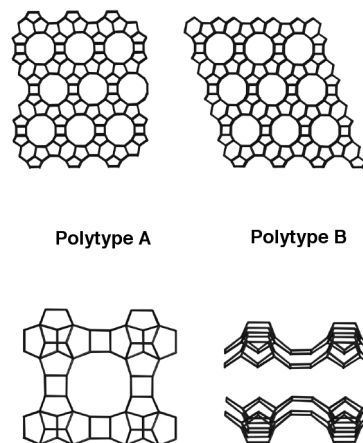

Polytype A   Polytype B

FIG. 1. Structures of polytype A and B.

that each layer of pores that forms each polytype is topologically identical. We thus surmise that despite the fact that actual samples of zeolite beta do not have the long-range order of either polytype, we can refine the local structure of the disordered zeolite by using either of the end-member polytypes as the model of the local structure. Magic-angle spinning nuclear magnetic resonance (MAS-NMR) ^{29}Si spectra of siliceous and defect-free samples of zeolite beta support this premise [4]. We are therefore confident that the local structure of zeolite beta can, in principle, be refined by using the PDF method, with the main difficulty being the complexity of the structure.

In this work, we were able to refine the structure of both polytypes of zeolite beta by using a combination of neutron and synchrotron PDFs.

Methods and Materials

A defect-free Si beta was made via acetic acid treatment of CIT-6 by using the protocol described in Ref. 5. The sample was characterized by using solid-state ^{29}Si MAS-NMR measurements, in-house x-ray powder diffraction (XRD), and thermogravimetric analyzer (TGA) experiments.

The data for the x-ray PDF were obtained at SRI-CAT beamline 1-ID at the APS. The measurements were done in symmetric transmission geometry at room temperature. A Si(111) crystal monochromator was collected with an intrinsic germanium detector

connected to a multichannel analyzer. Several diffraction runs were conducted with the sample at room temperature, and the intensities were averaged to get better statistics. The data treatment was done with the program PDFgetX [5].

The data for the neutron pair distribution function was obtained in the time-of-flight spectrometer GLAD (glass, liquids, and amorphous materials diffractometer) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. The scattering data were obtained with adequate statistics up to 20 Å^{-1}. The data reduction was performed by using the ATLAS package.

To improve the refinement, the structures of polytypes A and B, as reported by Newsam et al. [3], were optimized by using GULP [6]. The energy minimization was carried out by letting all the atoms move while the original crystal system and space group of the respective unit cell were kept.

Results and Discussion

The powder XRD patterns of the as-made, treated, and calcined samples were typical of zeolite beta [3]. The ^{29}Si MAS-NMR spectrum is very similar to the one reported by Camblor [4] for Si beta prepared by using the fluoride method, although with somewhat less resolution. The high resolution of the NMR is indicative of a zeolite with a framework containing very few tetrahedra [7].

Figure 2 compares the experimental PDF obtained from the XRD data measured at the APS to the calculated data based on Ref. 3 and to the structures optimized by GULP. The first three peaks correspond to the Si-O, O-O, and Si-Si nearest distances (at approximately 1.6, 2.8, and 3.1 Å, respectively), which are very characteristic of siliceous zeolites. The oscillations before the Si-O peak are termination ripples, common in PDFs, that are a consequence of having a limited Q range to integrate Eq. (2). The two small peaks between the Si-O and O-O peaks are artifacts of the data at low r, also a consequence of the limited Q range of the Fourier transform as well as instrumental contributions (they can be partially described with the refinement) [8, 9].

The peak positions in the neutron PDF are similar to those obtained from synchrotron experiments. They differ mainly because of the large difference in the Si and O neutron scattering lengths between the two radiation sources.

The refinement of the data was done by using the program PDFfit [10], which does real-space refinement of structural models by least square error minimization of the PDF. Refinement from a PDF is, however, different from refinements done in reciprocal space with regard to the number and nature of the parameters to be refined and the number of significant peaks and also with regard to the fact that we are refining only the
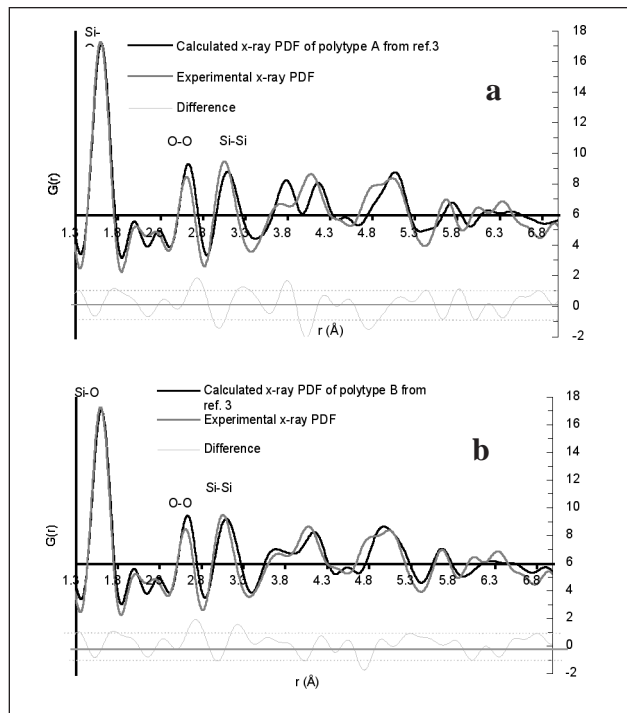

FIG. 2. Comparison of the experimental and calculated x-ray PDFs of the hypothetical structures of (a) polytype A and (b) polytype B.

local structure. Another practical difference is that we do not have the capability to apply soft constraints. These differences forced a meticulous refinement approach that was suitable for beta, since its structure is more complicated than the materials for which PDF is usually used. The best structural model for a system with stacking faults like zeolite beta should be able to account for all the possible stackings of layers in the sample. However, it is important to note that in the experimental PDF, we have useful data only from 1.3 to ~10 Å. (The PDF signal is very noisy and weak for higher values of interatomic distances.) Also, the length of the periodic building unit (PerBU) along the faulting direction is ~7 Å. Therefore, our PDF information is basically confined to the PerBU, and the data were refined in the range between 1.3 and 7 Å. Because of this refinement range, the refinement of the cell parameters (on the order of 10-20 Å) was set on the basis of in-house diffraction patterns.

We refined the polytype structures by using the neutron and synchrotron data independently. However, we found some inconsistencies in the structures. Mainly, they were that the higher coordinate Si-O distances could not be refined by using only the x-ray PDF and that the Si-Si distance was very distorted when it was refined only with the neutron PDF. We thus decided to refine the structure by using both PDFs
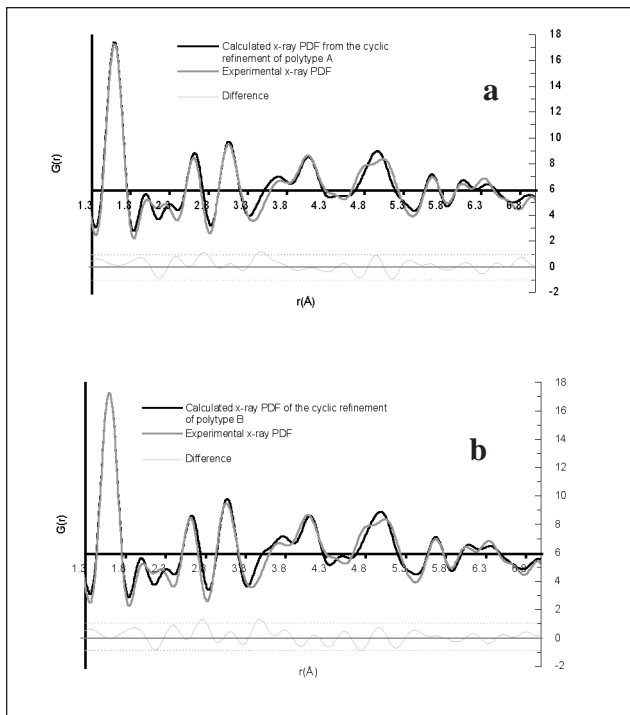
FIG. 3. Experimental and calculated x-ray PDFs from the structures obtained by the cyclic refinement of (a) polytype A and (b) polytype B.

simultaneously. However, different displacement parameters were needed for the two radiation sources to describe the two PDFs well. This is because specific systematic errors occur when the data are treated by using different sources, and they contribute differently to the width of the peaks. At this time, PDFfit cannot incorporate this factor. We were thus unable to refine both data sets simultaneously.

As an alternate approach, "cyclic refinement" was done by first refining our models with the synchrotron data and then using the refined model as input for refining with the neutron data. Note that during the neutron refinement, the Si atomic positions can change significantly because of their low contribution to G(r). Therefore, we did not refine the silicon positions with the neutron data.

By comparing the calculated x-ray PDFs in Figs. 2 and 3, we can see that there is an overall improvement in the fitting of the x-ray PDF with the cyclic model, as seen in the difference curves. The peak positions are better described, and the peak at 3.7 Å now follows the right functionality for polytype A. Still, however, the peak at 5 Å is not fitted quantitatively by the model. Overall, it can be seen that refinement with the neutron data improves the overall agreement of the PDFs by shifting the oxygen positions, and that refinement with the x-ray data readjusts the atomic positions to improve

the geometry of the tetrahedra (with its more equal atomic scattering contribution giving an overall better model).

In summary, we have shown that it is possible to use the PDF method to refine the local structure of disordered zeolites, even in the case of structures as complex as zeolite beta. However, it is also evident that neither x-ray nor neutron PDFs, on their own, are sufficient to obtain reliable refinements. It is necessary to refine both PDFs sequentially to obtain reasonable models of the zeolite structures.

Zeolite beta is an example of many materials that lack long-range periodic order in three dimensions. The strategy of refining the local structure of this material, as shown here, demonstrates a promising route for tackling such problems.

Acknowledgments

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