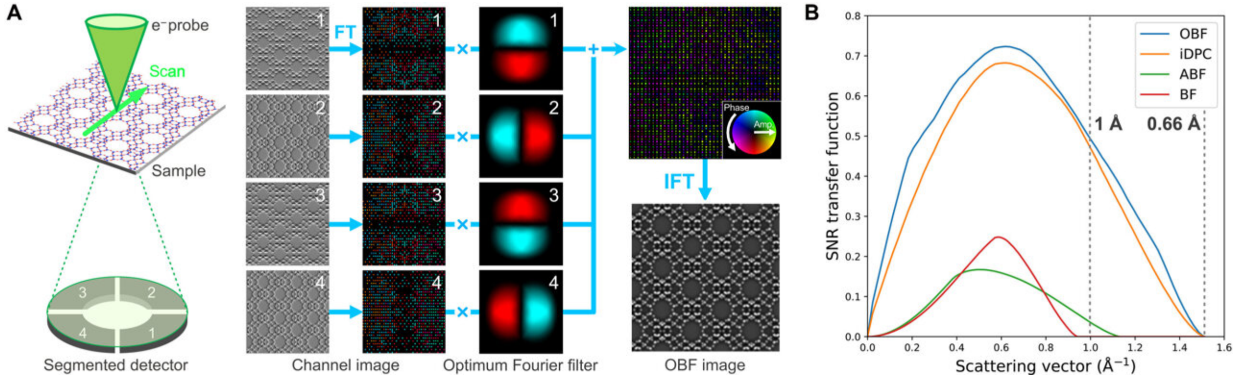
PHYS.ORG

Uncovering the local atomic structure of zeolite using optimum bright-field scanning transmission electron microscopy

August 14 2023, by Thamarasee Jeewandara



Reconstruction scheme of OBF STEM and dose-efficiency comparison based on SNR transfer functions for different STEM imaging techniques. (A) Schematic illustration of OBF STEM image processing workflow. In OBF STEM, a segmented detector is located on the diffraction plane that collects the intensity of transmitted/diffracted electrons at each probe position. The STEM images acquired by each segment are then processed with frequency filters to extract the phase-contrast component. The frequency filters are derived via STEM CTF, which are of a complex value. Subsequently, the filters are also complex-valued and visualized as a color map representing the phase and amplitude. After filtering, all the images are summed, and the OBF image is synthesized. As the filter is calculated via microscope optical information such as accelerating voltage and convergence angle of the probe as well as the CTF, OBF reconstruction does not need a priori knowledge of the sample. (B) SNR transfer functions of OBF and various phase-contrast imaging techniques. CTFs show the window of contrast transfer from samples as a function of spatial frequency. SNR transfer function is calculated by normalizing CTFs based on the noise level at each spatial frequency within the Poisson statistics, which shows a proportionality factor for the sample potential and electron dose to determine the SNR at each Fourier component. Here, the SNR transfer functions are calculated at an accelerating voltage of 300 kV, a convergence semi-angle of 15 mrad, and a sample thickness of 10 nm, the same conditions as those of the experiments conducted in this study. These transfer functions are shown as radially averaged values, and the OBF technique shows a higher SNR transfer than both the conventional methods (BF and ABF) and iDPC, the recently developed phase imaging technique. Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adf6865

Zeolites have unique porous atomic structures and are useful as catalysts, ion exchangers and molecular sieves. It is difficult to directly observe the local atomic structures of the material via electron microscopy due to low electron irradiation resistance. As a result, the fundamental property-structure relationships of the constructs remain unclear.

Recent developments of a low-electron dose imaging method known as optimum bright-field scanning transmission electron microscopy (OBF STEM) offers a method to reconstruct images with a high signal-to-noise ratio with high dose efficiency.

In this study, Kousuke Ooe and a team of scientists in engineering and nanoscience at the University of Tokyo and the Japan Fine Ceramics Center performed low-dose atomic resolution observations with the method to visualize atomic sites and their frameworks between two types of zeolites. The scientists observed the complex atomic structure of the twin-boundaries in a faujasite-type (FAU) zeolite to facilitate the characterization of local atomic structures across many electron beam-sensitive materials.

Analyzing zeolites in the materials lab

Zeolites are porous materials that are regularly arranged in nanosized pores suited for a variety of applications during catalysis, gas separation and ion exchange. The material properties are closely related to the pore geometry allowing subsequent interactions with adsorbed guest molecules and ions. Researchers have thus far used diffractometric methods to analyze the structure of zeolites.

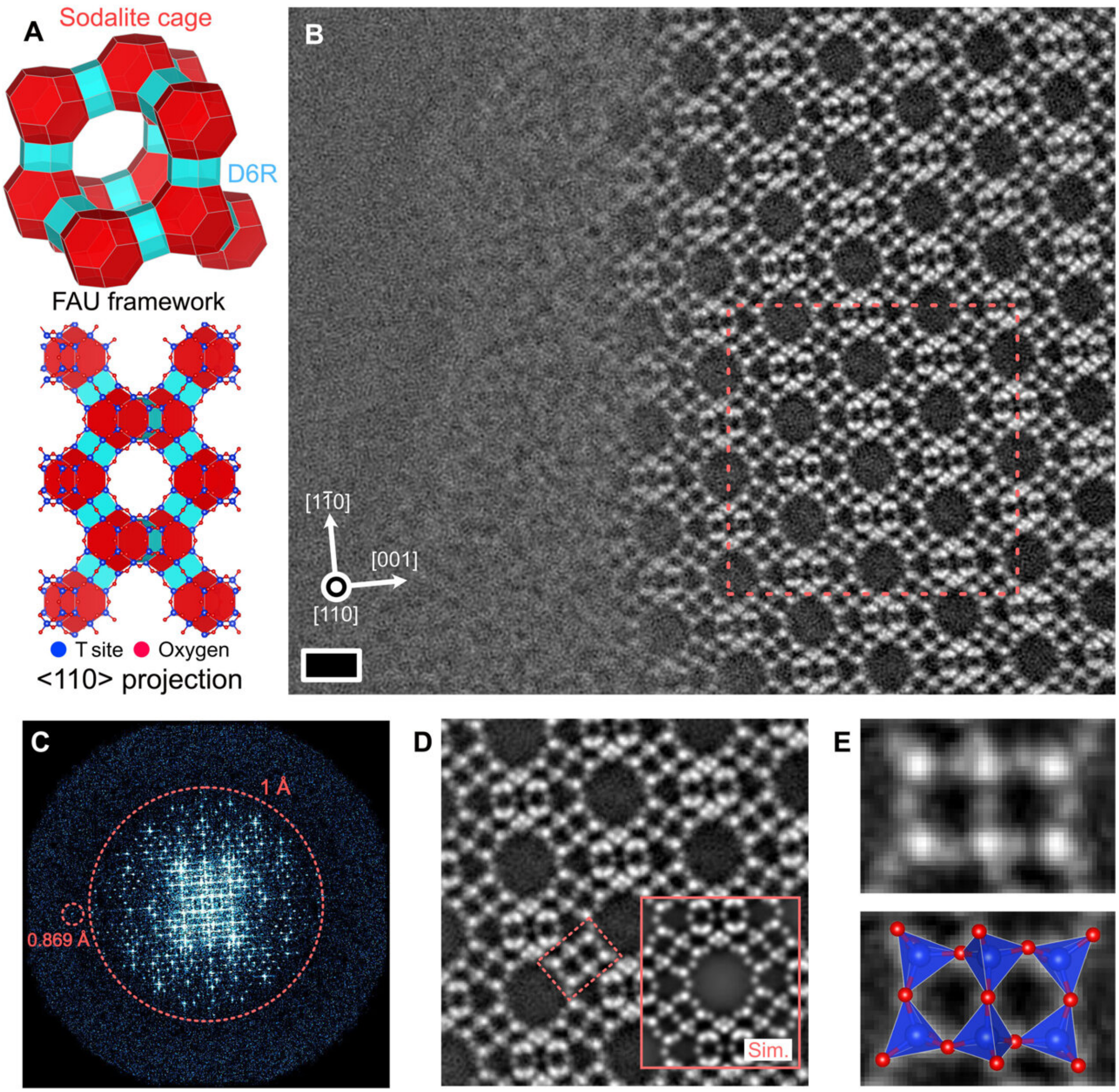
For example, materials scientists have demonstrated scanning electron microscopy to be a powerful method to analyze local structures to observe the atomic arrangement of electron-resistant materials at the sub-angstrom level. Zeolites are, however, more electron-beam sensitive when compared to other organic materials thereby limiting electron microscopy-based observations due to electron irradiation.

Optimum bright-field scanning transmission electron microscopy (OBF/STEM)

In 1958, materials scientist J. W. Menter observed zeolites using a high-resolution transmission electron microscope to report a lattice resolution of 14 Angstrom. Images of the zeolite framework substantially improved via advanced imaging in the 1990s, although it remained challenging to observe the atomic sites in the materials.

Recent advances of scanning transmission electron microscopy (STEM) electron detectors have led to more advanced imaging methods such as the optimum bright-field (OBF) STEM method to observe atomic structures at the highest signal-to-noise ratio to obtain atomic-resolution images in real-time.

In this work, Ooe and colleagues used real-time OBF imaging to determine the architecture of zeolites at subangstrom resolution. The outcomes emphasized the capacity of advanced electron microscopy to characterize the local structure of beam-sensitive materials.



Atomic-resolution OBF STEM observation of an FAU zeolite along zone axis. (A) Schematic of the FAU zeolite framework structure and projected atomic structure model along zone axis. Red and blue polygons represent the building units (sodalite cages and D6Rs, respectively). (B) OBF STEM image of FAU zeolite observed at the edge of the sample. Bright spots indicate T and oxygen sites. Scale bar, 1 nm. The dashed rectangular indicates the repeat unit structure used for the averaging process shown in (D). (C) Fourier transform spectrum of (B), wherein the spots are seen up to 0.869 Å resolution in real space. (D) Repeat-unit-cell–averaged OBF image, which is obtained by cropping and averaging the multiple subimages obtained from the raw image shown in (B), offering a higher SNR. The inset is a simulated OBF image calculated with the same observation condition as that in the experiment. The location of the D6R structure, which is shown in (E), is highlighted by a dashed rectangular. (E) Magnified OBF image of the rectangular region indicated by the red dashed line in (D). The atomic structure models are drawn using visualization for electronic and structural analysis software. Credit: *Science Advances* (2023). DOI: 10.1126/sciadv.adf6865

Direct imaging of atomic structures in zeolites: Real-time OBF imaging vs. STEM imaging

The zeolite framework consisted of two building blocks—sodalite cages and double 6-membered rings. Using real-time optimum bright-field (OBF) imaging, the team detected the framework of the material and used an electron probe current of 0.5 pico-angstrom to prevent any beam-related damage in order to analyze the typical inorganic materials. They then compared the OBF images with other scanning transmission electron microscopy images obtained under similar dose conditions.

The existing STEM methods showed a basic structure of the material framework; however, atomic structure analysis with this method was challenging due to a low current dosage. In contrast, the OBF images offered a more reliable and interpretable image contrast with higher dose efficiency.

Direct observation of the twin boundary

The research team used the optimum bright-field method to examine the atomic structure of a twin boundary in the zeolite structure. The framework was made by cubic stacking a layered structure unit known as a "faujasite sheet." The outcomes of imaging with OBF showed a power spectrum of the image with an information transfer beyond 1 Angstrom. The low-dose light-element imaging with OBF STEM offered a better alternative to analyze the structure of zeolites including the local change of symmetry.

Ooe and colleagues conducted density functional theory calculations to examine the stability of the twin boundary structure where the experimental image agreed with its simulated counterpart.

The team applied the method to a different type of zeolite sample to show how the typical silicon aluminum ratio of these samples are crucial to the material properties to influence the adherence of ions and molecules. When they applied the method to a sodium-based zeolite sample for atomic observations, the outcomes facilitated the conception of extra cation sites with low occupancy in the zeolitic framework.

Outlook

In this way, Kousuke Ooe and colleagues devised a dose-efficient scanning transmission electron microscopy imaging method known as "optimum bright field scanning transmission electron microscopy" (OBF-STEM) for low-dose atomic resolution imaging. The team showed how the method directly revealed the atomic structures of all elements in a faujasite-type zeolite material—a known beam-sensitive material with subangstrom space resolution.

The method can be used to detect lattice defects in the material framework. They visualized the atomic sites in the framework alongside its captured cations to obtain results that were in quantitative agreement with image simulations. The method is applicable across beam-sensitive materials beyond zeolites to characterize the local atomic structure and study the structure-property relationships of sensitive materials.

More information: Kousuke Ooe et al, Direct imaging of local atomic structures in zeolite using optimum bright-field scanning transmission electron microscopy, *Science Advances* (2023). DOI: 10.1126/sciadv.adf6865

L. A. Bursill et al, Zeolitic structures as revealed by high-resolution electron microscopy, *Nature* (2004). DOI: 10.1038/286111a0

Citation: Uncovering the local atomic structure of zeolite using optimum bright-field scanning transmission electron microscopy (2023, August 14) retrieved 29 April 2024 from https://phys.org/news/2023-08-uncovering-local-atomic-zeolite-optimum.html