Single-Crystal–Like Diffraction Data from Polycrystalline Materials

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A method for solving structures from powder diffraction data was developed, and its validity was demonstrated on three complex structures. The method uses a textured sample and exploits the high intensity and parallel nature of synchrotron radiation. In principle, crystal structures as complex as those routinely solved by single-crystal methods can be determined with this approach. For example, the as-synthesized form of the zeolite UTD-1, with 69 nonhydrogen atoms in the asymmetric unit, could be solved directly. With this method, a larger range of structural complexity becomes accessible to scientists interested in the structures of polycrystalline materials that cannot be grown as single crystals.

Many industrially important materials, ranging from ceramics to catalysts to pharmaceuticals, are polycrystalline and cannot be grown as single crystals. To understand the properties of these materials, structural information on an atomic level is essential. However, if an approximate structure is not known, one has to be determined, and that is not a trivial matter if only powder diffraction data are available.

In principle, the diffraction pattern from a polycrystalline material is simply a superposition of millions of single-crystal diffraction patterns oriented randomly. Unfortunately, reflections with similar diffraction angles, which are well separated in the single-crystal pattern, lie on top of one another in the powder pattern, and their individual intensities cannot be determined. If there are too many of these overlapping reflections, conventional approaches to structure solution will fail.

Attempts to overcome this problem have become increasingly innovative and successful in recent years, and now structures of moderate complexity can usually be solved. Synchrotron radiation and increased computing power have been particularly important to the realization of some of these exciting new approaches. Single-crystal methods have been adapted to deal with the special problems posed by powder diffraction data (*1*), chemical information has been integrated into the structure solution process (*2*), and clever methods of data analysis have been developed to obtain better estimates of the relative intensities of overlapping reflections (*3*, *4*). However, all of these methods have their limitations. The structural complexity that can be handled falls well below that which could be tackled with single-crystal data. This is not surprising: A one-dimensional powder diffraction pattern necessarily contains less information than does its three-dimensional single-crystal counterpart.

Two experimental approaches to recovering this "lost" data have been described in the literature. In both cases, several different, but related, powder diffraction patterns are collected on the same sample. Such a set of patterns contains more information than does any individual pattern, and by extracting a single set of reflection intensities from all of the patterns simultaneously, the additional information can be harvested and a more single-crystal–like data set obtained.

One way of producing such diffraction patterns is to exploit differential thermal expansion (*5*). If the lattice parameters exhibit an appreciable and anisotropic change as a function of temperature and the compound does not undergo a phase transition, the intensities of the reflections will remain approximately constant, but their relative positions will change slightly. Lines that are superimposed at one temperature will be separated at another.

The second possibility is to collect data from a sample with a preferential orientation of the crystallites (textured sample), and this is the subject of this report. Lasocha and Schenk (*4*) described a related approach in 1997. Using a conventional laboratory instrument, they measured diffraction patterns of several samples of the same compound, each prepared with a different texture. The texture for each specimen was estimated from a statistical analysis of the diffracted intensities (*6*) and then described with a simple function. From these data, a somewhat better partitioning of the overlapping reflections could be obtained. Although this method has the advantage of simplicity, that is also its drawback. Its applicability is limited to cases in which several samples with different, strong, and simple textures can be prepared. The approach described here, on the other hand, involves a full quantitative texture analysis of a single sample, so almost any texture can be described, and that is the key to the success and broad applicability of the method. It is based on an approach first described and simulated by Hedel *et al.* (*7*) for conventional laboratory diffractometers, but the experimental setup and data analysis were modified considerably. In particular, the high intensity and parallel nature of a synchrotron beam were exploited.

A textured powder sample can be regarded as being something between an "ideal" powder (randomly oriented crystallites) and a single crystal and can, therefore, provide more diffraction intensity information than an "ideal" powder can. The three-dimensional intensity distribution of two reflections with the same d (interplanar) spacing (and therefore the same diffraction angle 2θ) is shown schematically for the three cases in Fig. 1. For the single crystal, there is only a single orientation of the diffracting planes for each reflection, so diffraction occurs at only those two orientations and the result is two separated reflections. For the "ideal" powder, all orientations of the diffraction planes occur with equal frequency, so both reflections are present at all orientations and the intensity is constant over the entire hemisphere. For the textured sample, the crystallites are oriented preferentially, so the orientations of the diffracting planes do not occur with equal frequency but are concentrated in a certain direction. Thus, the two reflections are separated in space but not as sharply as for the single crystal.

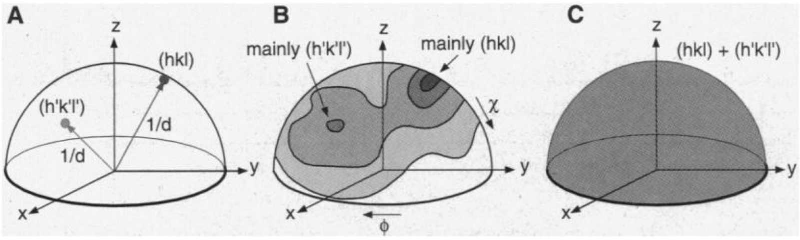

Fig. 1. Three-dimensional distribution of diffracted intensity for two reflections with the same d value for (**A**) a single crystal, (**B**) a textured sample, and (**C**) an "ideal" powder sample.

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The intensity fluctuation on a hemisphere reflects the distribution of crystallite orientations in the sample. If only a single reflection is present, the projection of the (normalized) density distribution is called a pole figure (*8*). Given a sufficient number of such pole figures, the orientation distribution function can be determined and the intensity variations then calculated for all reflections. Thus, the two reflections in Fig. 1B can be deconvoluted with only a limited number of data points on the hemisphere. In contrast to the method based on differential thermal expansion, systematically overlapping reflections can also be separated.

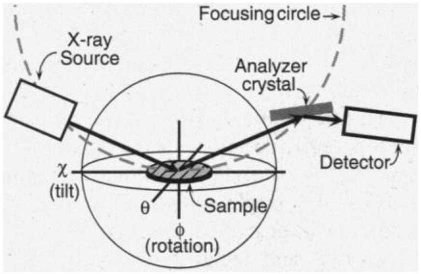

Fig. 2. Schematic design of the experimental setup showing the tilt (χ) and rotation (ϕ) circles and the predetector analyzer crystal.

As is apparent in Fig. 1B, the diffracted intensities from a textured polycrystalline sample depend very much on the orientation of the sample with respect to the x-ray beam, so a controlled way of tilting and rotating the sample is necessary. Therefore, two additional circles are attached to the powder diffractometer (Fig. 2) to produce an experimental setup very similar to that of a standard four-circle single-crystal diffractometer.

In a conventional laboratory setup, tilting leads to a violation of the focusing condition (parts of the sample are moved away from the focusing circle), so line broadening occurs. However, Hastings *et al.* (*9*) showed that by combining a highly collimated parallel beam (for example, at a synchrotron source) with a crystal analyzer, all sample displacement aberrations are eliminated. All x-rays that are diffracted from the sample and fulfill the Bragg condition at the analyzer are recorded simultaneously by the detector, independent of their point of origin in the sample. Thus, the whole pattern can be measured at any tilt angle without any additional line broadening.

Data collection entails (i) the measurement of an untextured sample of a standard material to calibrate the instrument, (ii) the measurement of pole-figure data for several single reflections of the textured sample, from which the orientation of the crystallites is determined, and (iii) the measurement of complete diffraction patterns for several sample orientations. The diffracted intensity of a textured sample, $y(2\theta, \chi, \phi)$, at step 2θ, can be expressed as a function of the sample orientation (tilt χ and rotation ϕ) in the form

$$y(2\theta,\chi,\phi) = \sum_{hkl} I_{hkl}P_{hkl}(\chi,\phi)G(2\theta - 2\theta_{hkl}) \qquad (1)$$

where the summation is over all reflections contributing to the intensity at that step, I_{hkl} is the true integrated intensity of the reflection *hkl* (single-crystal value), $G(2\theta - 2\theta_{hkl})$ is the peak-profile function, and $P_{hkl}(\chi, \phi)$ is the pole-density distribution function. The quantities $P_{hkl}(\chi, \phi)$ are determined from the measured pole figures, and then the I_{hkl} values can be derived from the full diffraction patterns. Model calculations show that if the texture $P_{hkl}(\chi, \phi)$ is known, extremely good intensity values for overlapping reflections can be derived.

To probe the viability of this approach to structure solution for real polycrystalline materials, we modified the powder diffractometer on

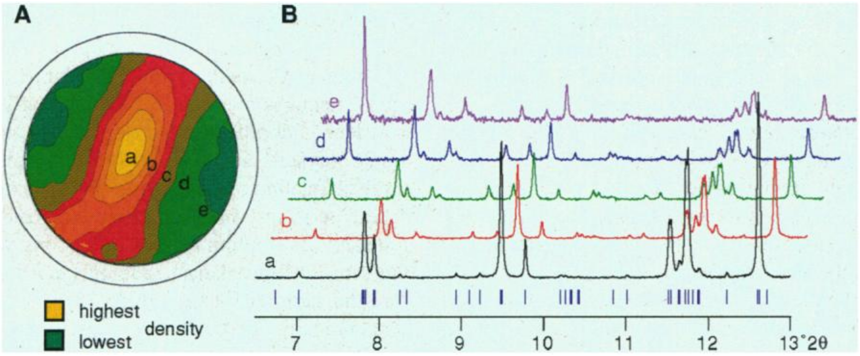

Fig. 3. As-synthesized UTD-1. (**A**) Pole figure for the 10$\bar{2}$ reflection, and (**B**) small sections of the five diffracted patterns (wavelength λ = 0.99747 Å) collected at the sample orientations indicated in the pole figure.

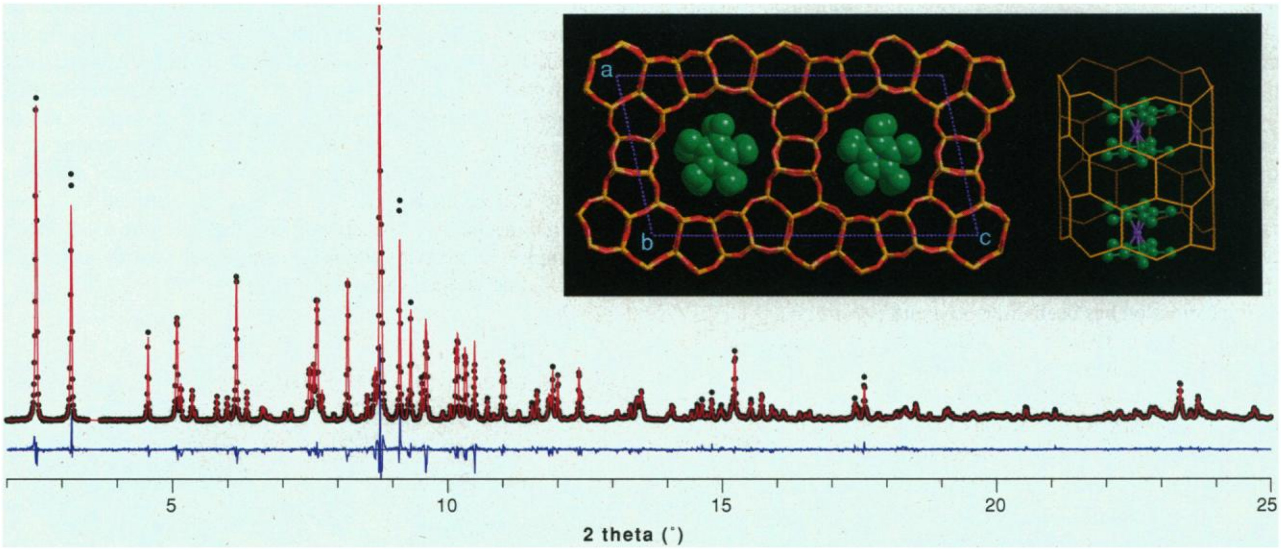

Fig. 4. Structure of UTD-1 in space group *Pc* (*a*, *b*, and *c* axes of the unit cell indicated) and observed (black dots), calculated (red), and difference (blue) profiles for a section of the data used for the Rietveld refinement (λ = 0.6480 Å; *R* values: structure factor R_F = 0.041, weighted profile R_{wp} = 0.134, and statistically expected R_{exp} = 0.101).

the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility in Grenoble according to Fig. 2. The method was first tested on a textured sample of the zeolite ZSM-5 ($[\mathrm{Si}_{96}\mathrm{O}_{192}]\cdot 4(\mathrm{C}_3\mathrm{H}_7)_4\mathrm{NOH}$, space group *Pnma*, a = 20.049 Å, b = 19.933 Å, c = 13.390 Å) with 38 framework atoms in the asymmetric unit. Pole-figure data for eight single reflections and full diffraction patterns at four sample orientations were measured. As predicted, all four patterns displayed the same very high resolution independent of the tilt angle. A single set of reflection intensities was extracted from the four patterns with a modified Le Bail algorithm (*10*) and was used as input into a standard direct methods program. With default settings, all 12 Si positions and 19 of the 26 O positions were found in the top 40 peaks of the sharpened electron density map (E-map). With the improved reflection intensity data, this very complex structure could be solved in a routine manner.

The method was then applied to two materials with unknown structures. The first of these materials was the aluminophosphate molecular sieve Mu-9 (*11*). Like many materials, Mu-9 contained an unidentified impurity. This impurity not only made an accurate chemical analysis impossible but also created serious problems with the indexing of the powder pattern. However, the texture measurement allowed the peaks belonging to Mu-9 to be identified unambiguously and the pattern to be indexed satisfactorily (space group $R\bar{3}c$, a = 14.057 Å and c = 42.295 Å). Intensity extraction (six pole figures and five full patterns) followed by the application of direct methods then revealed an unexpected framework composition ($[\mathrm{Al}_{66}\mathrm{P}_{72}\mathrm{O}_{288}]^{18-}$) and an unusual structure with 13 framework atoms in the asymmetric unit. One of the three Al atoms proved to be (unexpectedly) six- rather than four-connected to framework P atoms.

The second material of unknown structure was the zeolite UTD-1 (*12*) prepared with a modification of the published synthesis procedure (*13*). In contrast to the body-centered orthorhombic unit cell reported for calcined UTD-1 (a = 18.98 Å, b = 8.41 Å, c = 23.04 Å) (*14*), the diffraction pattern of this as-synthesized material could only be indexed with a primitive monoclinic cell (a = 14.9633 Å, b = 8.4704 Å, c = 30.0098 Å, β = 102.667°). Furthermore, no evidence of faulting, which was reported for the calcined form, could be discerned. These observations indicated that the material might be substantially different from that of Lobo and coworkers (*14*), and further investigation seemed to be warranted.

The needle-like crystals were aligned with shear forces in a polystyrene matrix. Pole-figure data for seven reflections and full diffraction patterns at five sample orientations were measured (Fig. 3). Application of direct methods to the reflection intensities extracted assuming the space group $P2_1/c$ produced an E-map with 16 Si atoms, which described a complete three-dimensional, four-connected framework with 14-ring pores [related to polymorph C in (*14*)]. Seventeen of the bridging O atoms were also found on that initial E-map. Difference electron density maps allowed the remaining 15 O atoms, the (nonframework) Co, and the pentamethylcyclopentadienyl rings to be located. Subsequent Rietveld refinement showed the correct space group to be noncentrosymmetric (Pc) with 117 atoms in the asymmetric unit (Fig. 4). The Co complex is fully ordered in the 14-ring channels.

The determination of such a complex structure (69 non-H atoms in the asymmetric unit in $P2_1/c$) from powder diffraction data with standard crystallographic methods provides a clear demonstration of the power of the texture approach. The method can be applied to any class of compounds, and the only requirement is that a sample with preferred orientation can be prepared. This is generally possible with one of the many known techniques. A larger range of structural complexity hereby becomes accessible to scientists interested in the structures of polycrystalline materials that cannot be grown as single crystals.

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Synergistic Signaling in Fetal Brain by STAT3-Smad1 Complex Bridged by p300

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The cytokines LIF (leukemia inhibitory factor) and BMP2 (bone morphogenetic protein–2) signal through different receptors and transcription factors, namely STATs (signal transducers and activators of transcription) and Smads. LIF and BMP2 were found to act in synergy on primary fetal neural progenitor cells to induce astrocytes. The transcriptional coactivator p300 interacts physically with STAT3 at its amino terminus in a cytokine stimulation–independent manner, and with Smad1 at its carboxyl terminus in a cytokine stimulation–dependent manner. The formation of a complex between STAT3 and Smad1, bridged by p300, is involved in the cooperative signaling of LIF and BMP2 and the subsequent induction of astrocytes from neural progenitors.

Interleukin (IL)–6 and the five related cytokines IL-11, LIF, ciliary neurotrophic factor, oncostatin M, and cardiotrophin-1 share the membrane glycoprotein gp130 as a receptor component critical for signal transduction (*1*). These six IL-6–type cytokines trigger the dimerization of gp130, activating associated cytoplasmic tyrosine kinases in the Janus ki-