

SOLVING ZEOLITE-LIKE CRYSTAL STRUCTURES BY POWDER DIFFRACTION

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ABSTRACT

Methods of structure determination from powder diffraction data (SDPD) have progressed a lot in the past decades. Nevertheless, crystal structure determination of complex microcrystalline materials, like zeolites, still remains a challenge. On the other hand, zeolite-like materials have some *a-priori* known structural characteristics that can be efficiently used for solving their crystal structures. The general procedure of the SDPD is briefly presented, showing its basic steps and various methods of accomplishing them. Special attention is paid to the methods of the structure solution step, where the specific features of zeolite-like structures can be used to achieve the goal.

Keywords: zeolite-like materials, crystal structure solution, powder diffraction.

INTRODUCTION

Knowledge about crystal structure of a material is crucial for understanding its properties and crystal structure determination is one of the first tasks when a novel material is synthesized. If the material is available in the form of large enough and well-crystallized single crystals, this task is more or less a routine, while it remains a serious challenge in the cases of microcrystalline materials. As it is well known, this is due to the overlap of the Bragg reflections of the polycrystalline sample, resulting in the significant loss of information, as the three-dimensional diffraction pattern is reduced into one-dimensional only. Consequently, the individual reflection intensities cannot be resolved.

Methods of structure determination of polycrystalline materials that, one or another way, overcome the overlap problem progressed significantly in the past decades. Nowadays successful structure determinations from powder diffraction data of rather complex structures, containing more than 20 atoms in the asymmetric unit, are quite common [1-3]. The structures can be of any kind from pure inorganic-ionic through metal-organic, organometallic and coordination compounds to organic-molecular ones.

Zeolite-like materials are often available only in the microcrystalline-polycrystalline form and their peculiar structure characteristics, especially nanoporosity, causing large unit cells, present a difficulty for the structure analysis on one hand and an opportunity on the other – i.e. there exists a lot of prior knowledge on the coordination and bond lengths and angles. These facts had been efficiently utilized by zeolite powder crystallographers, who many times pushed the frontiers of the SDPD and made significant contribution in the development of the methodology in this field.

In the following sections a short overview of the general steps and methods of the SDPD is given, with a special emphasis on the methods of structure solution, where the specific structural characteristics of zeolite-like materials play an important role.

STEPS OF THE SDPD

In general, SDPD can be divided into the following seven steps, but not all of them are applied in all cases [4]: 1) data collection, 2) indexing, 3) space group determination, 4)

pattern decomposition (not in all cases), 5) structure solution, 6) completion of the structure (if the initial model is incomplete), 7) final refinement. The procedure, showing various possibilities of accomplishing individual steps is outlined in Figure 1 [5]. It is necessary to stress that the decisions in all steps can be rather ambiguous and the confirmation that all are correct is only the final successful refinement.

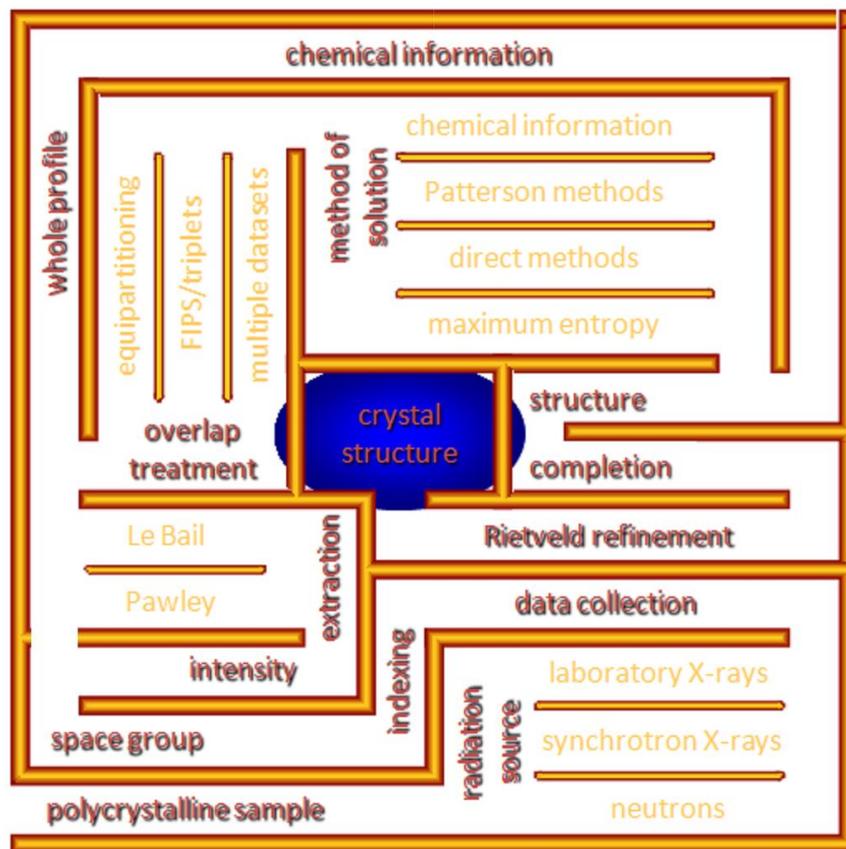


Figure 1. Procedure of structure determination from powder diffraction data (courtesy of L.B. McCusker).

STRUCTURE SOLUTION

As seen in Fig. 1, there are several possibilities to solve the crystal structure (obtain initial, close-to-correct, structural model), using powder data. They can be divided into two groups: the first working in the reciprocal space, using modified tools, known from single crystals and thus requiring extraction of reflection intensities out of the overlapping peaks in the diffraction pattern. This group includes for example direct methods and Patterson method as the two most known. The other group of methods works in the direct (real) space and use the unit cell and symmetry, together with chemical information to position structural fragments into the unit cell so that the calculated powder pattern of the trial structure matches best to the observed one, while the chemical restraints are respected, resulting in a reasonable structure. Chemical information here is used in a broad sense and can mean any information that is known before the structure is solved, i.e. chemical composition, coordination, connectivity, expected bond-lengths and angles, pore-size etc., that can be obtained by chemical analysis, crystal-chemical knowledge, sorption experiments etc. Many methods of global optimization are used in this group, including Monte Carlo, simulated annealing, genetic algorithms etc.

There are some approaches that combine both types of methods, i.e. switch between reciprocal and direct space, trying to use as much of the *a-priori* chemical knowledge as

possible. For example, using a difference Fourier map to locate the missing fragments in the trial structure, obtained by direct-space methods. However, these combinations should not be mixed up with so-called “dual space methods”, like charge-flipping, which do not use the chemical information. They try to improve the reflection phases (reciprocal space) by posing constraints on and modifying the calculated electron densities (real space). Figure 2 shows how the new zeolite-like structures were solved in fifteen-years period from 1996-2011 [6].

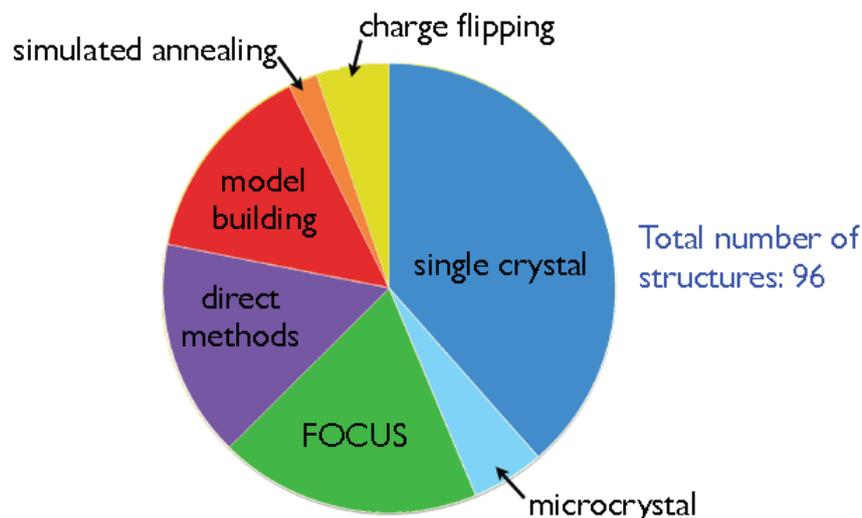


Figure 2. Methods used to solve new zeolite-like structures between 1996-2011 (courtesy of Ch. Baerlocher).

It can be seen that more than half of the structures were solved using powder diffraction data and more than half of those by two methods that use the crystal-chemical information of zeolites extensively – model building and FOCUS. These facts clearly show that the known structural information plays an important role in structure solution of zeolite-like materials from powder data.

Zeolite-like materials are built from corner-sharing tetrahedra, forming four-connected three-dimensional frameworks with relatively lot of empty space (sometimes filled by water or template molecules). The bond lengths and angles within the framework are rather well known in advance from numerous well-defined crystal structures, solved so far. If the framework connectivity is known, it is even possible to refine the structure only with respect to known bond lengths and angles – there are more geometrical restraints than atomic coordinates. It is thus natural that many zeolite structures were, and still are, solved by model building, which means manual building of a tetrahedral framework that fits into the unit cell and has the symmetry, both obtained from powder data. The model is then tested against the observed powder pattern. The logic of manual model building was also transferred to computers, which are much faster in producing and testing the trial frameworks.

The development in this direction led to FOCUS algorithm [7] that can be regarded as a structure solution method, dedicated to zeolite-like materials. Its algorithm is presented in Figure 3 and its essential part is finding possible tetrahedral frameworks among the peaks in the electron density maps that are produced from integrated intensities and starting phases, which can be obtained in different ways.

The starting phases in FOCUS are the point where this algorithm is open for alternative methods, which can either improve the phase set, for example preferred orientation [1], electron diffraction [2], charge flipping [3] or limit the space where the framework is searched for, like structure envelopes [8]. These combinations, that exploit the synergy between the knowledge of structural features of zeolite-like materials with the information from other sources, proved to be very powerful.

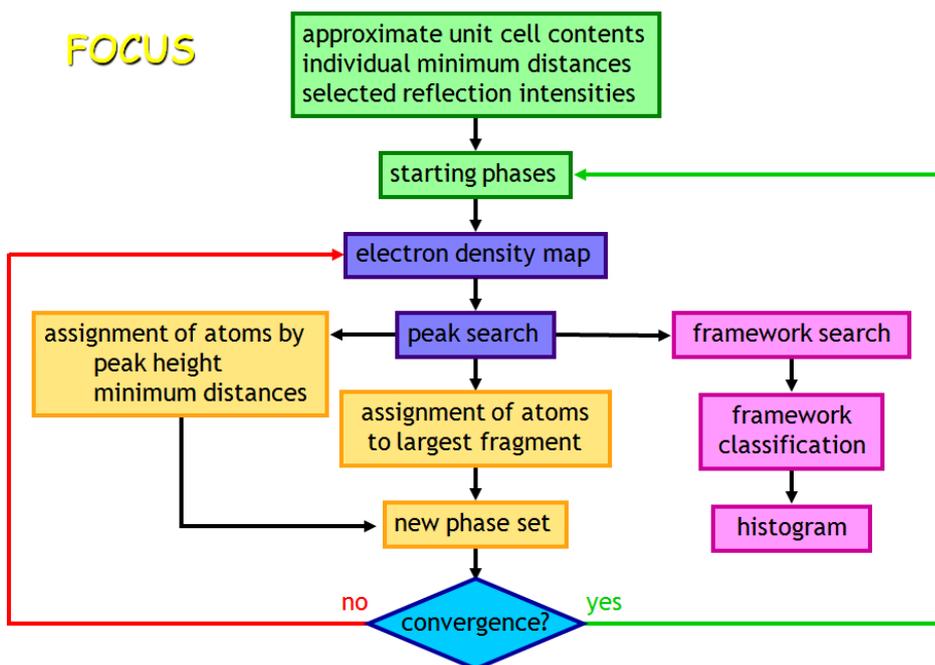


Figure 3. Focus algorithm (courtesy of L.B. McCusker).

CONCLUSION

Several methods are available to solve a crystal structure of a novel zeolite-like material. If it cannot be prepared in a form of large enough single crystal, it is rather likely that the structure can be solved from powder diffraction data, using one of the available methods, among which the ones, applying the *a-priori* known structural information, are very powerful. However, structure determination of complex materials from powder diffraction is still far from being routine. It remains a challenge and further development is in progress.

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