

m30.o02**Deciphering the structural information in a zeolite powder diffraction pattern**

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The fascinating properties and diverse applications of zeolites and their analogs are a direct result of their unusual microporous structures. Consequently, structure analysis is central to the understanding of their chemistry. However, these materials tend to be produced and used in polycrystalline rather than single-crystal form, so powder diffraction is often the only option available for such investigations.

In principle, a powder diffraction pattern contains all the structural information of a single-crystal diffraction pattern. It is just that some of that information is obscured by reflection overlap. Over the years, zeolite crystallographers have devised different ways of dealing with this problem in their attempts to elucidate the crystal structures of zeolitic materials, and as a result a colorful palette of deciphering techniques has emerged.

Sometimes the framework type is known, and further structural details, such as the location of the structure directing agent in the pores, the arrangement of cations after ion exchange, or the effect of calcination on the framework geometry, are of interest. In this case, the framework structure can be used as a starting point for phasing, and difference Fourier analysis combined with Rietveld refinement to complete and refine the structure. With the quality of the data that can now be measured, surprisingly detailed structural information can be determined in this way, if care is taken.

If, however, the framework structure is not known, it must first be determined, and this presents a different challenge to the zeolite crystallographer. The unit cell dimensions, and some symmetry information can usually be gleaned from the powder diffraction pattern, but direct extraction of reliable reflection intensities suitable for standard structure solution programs is difficult if the degree of reflection overlap is high. To overcome this problem, methods to estimate the relative intensities of overlapping reflections based on information from the non-overlapping reflections have been developed, two experimental methods involving the collection of multiple datasets on perturbed samples have been devised, and direct methods programs have been adapted to deal with the intensity ambiguity.

In the past, novel zeolite framework structures were solved primarily by building a physical model consistent with all available information (not just the powder pattern), and comparing the powder pattern calculated for the model with the experimentally measured one. In this way, the problem of reflection overlap could be circumvented. Despite the amazing advances that have been made in computing power and instrumentation, this method remains the most powerful one available to us. When all other methods fail, this one still might work. However, success is heavily dependent upon the skill and experience of the model builder. Fortunately, some of the ideas used in model building have now been successfully incorporated into automated structure determination algorithms.

Thus, a zeolite crystallographer has a rich array of decoding methods at his disposal. The question is, which should he use?

m30.o03**Analysis of structure factors of zeolitic materials**Jordi Rius, Inmaculada Peral^a, Carlos Miravittles*Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, 08193 Bellaterra, Spain. ^apresent address: Departament de Física. Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain. E-mail: jordi.rius@icmab.es***Keywords: structure factors, zeolites, powder diffraction**

The solution of complex inorganic structures from powder diffraction data is much easier when dominant scatterers are present. Due to the relatively low X-ray scattering contrast between Si and O, solution of complex zeolitic materials is still difficult. One approach is to take advantage of the characteristics specific to them, for example, the 3D connectivity and the known tetrahedral coordination, which means that once the positions of the Si are located, the positions of the O can be estimated from the Si positions. The ideal situation for solving crystal structures from powder data at moderate resolution ($d > 2 \text{ \AA}$) by direct methods would be to have at one's disposal structure factor moduli with the contributions of the O removed [1,2]. We have further analyzed the possibility of obtaining structure factors with the contribution of the O atoms removed. The study shows that for diffraction data at moderate resolution ($d > 2.2 \text{ \AA}$) the average effect of the O on the experimental structure factors can be described by a simple empirical mathematical expression that seems to be general for zeolites. This expression could then be used to subtract the O contribution, thus producing approximate normalized structure factors moduli of the Si partial structure.

[1] Rius J.: Derivation of a new Tangent Formula from Patterson-Function Arguments. *Acta Cryst. A* 49 (1993) 406-409.

[2] Rius J.: Advances and some recent applications of the origin-free modulus sum function. *Z. Kristallogr.* 219 (2004), 826-832.