

## 12.3-2 INDEXING OF ORTHORHOMBIC POWDER PATTERNS WITH THE OPTIMIZATION METHOD.

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The optimization technique consists in the numerical search for the extremum of a suitable function. Such a method may be applied to find the solution of the indexing problem, i.e. to determine unknown lattice constants by search of the minimum of some "indexing function". The definition of the function being analyzed together with an application to the polyphase specimens were reported recently (Paszkowicz and Rozbiewska, Proc. 8-th European Crystallographic Meeting, Liege 1983).

On account of the promising results obtained with the early versions of the FORTRAN program using the concept of optimization indexing, the new version has been written and tested. The procedure applied in the algorithm is divided into three main steps:

1. systematic search in the space of direct cell dimensions,
2. refinement of the solution by Monte Carlo method,
3. least squares refinement of as obtained unit cell constants.

The results yielded by the third step allow to choose the best solution of the indexing problem.

The features of the described program are:

- application to single phase specimens of orthorhombic or higher symmetry,
- lack of severe requirements concerning the accuracy of diffraction data,
- short computing time.

12.5-1 ON THE LOCATION OF ALUMINIUM IN THE UNIT CELL OF ZSM-5. By S.G. Hill and D. Seddon, The Broken Hill Proprietary Co. Ltd., Melbourne Research Laboratories, 245 Wellington Road, Mulgrave, Victoria, Australia 3170.

The proximity of aluminium atoms (aluminate moieties) substituting for silicon in the framework lattice of zeolites is predicted by Löwenstein's rule which favours aluminate tetrahedra being adjacent to silica rather than other aluminate moieties. Thus, zeolite A (Si/Al = 1) has an ordered alternating distribution of aluminate and silica.

Silicious zeolites, such as the ten ring pentasil zeolites of the ZSM-5 family (Si/Al > 10) can have aluminate moieties in very remote positions relative to one another. Work by Ballmoos and Meier (R. von Ballmoos and W.M. Meier, Nature (1981) 289, 782) has indicated that aluminate may not be evenly distributed across crystals, but may be preferentially sited in surface positions. It may also be the case that the aluminate has preferred sites within the unit cell. Work on  $^{29}\text{Si}$ ,  $^{27}\text{Al}$  NMR has attempted to resolve this problem (J.M. Thomas, J. Klinowski, C.A. Fyfe, G.C. Gobbi, S. Ramdas, and M.W. Anderson, in Intrazeolite Chemistry, G.D. Stucky and F.G. Dwyer, ACS 218 (1983) Washington, D.C.), but has not as yet been successful.

We are performing X-ray powder pattern simulations, using a Rietveld type program, of the ZSM-5 structure in the space group Pnma (after the single crystal structure refinement of Olson *et al.* (D.H. Olson, G.J. Kokotaillo, S.L. Lawton and W.M. Meier, J. Phys. Chem. (1981) 85, 2238 - 2243) and Price *et al.* (G.D. Price, J.J. Pluth, J.V. Smith, I. Araki, J.M. Bennett, Nature (1981) 292, 818-819)) in which the aluminium is progressively placed

at one of twelve crystallographically distinct positions of an asymmetric secondary building unit, eight of which, as four pairs related by a 2 fold screw axis, constitute a unit cell. Atomic coordinates, and hence lattice parameters, were not changed during the analysis, so d-spacings remained unchanged. The changes in structure factors, brought about by the systematic change in aluminium position, even at such low aluminium concentration (Si/Al = 12) does change absolute and relative intensities of some peaks in the calculated XRD patterns.

Our analysis is continuing by studying the effects of other elements, such as iron and gallium, in place of aluminium.

## 12.5-2 RIETVELD REFINEMENT OF THE CRYSTAL STRUCTURE OF THE NEW ZEOLITE MINERAL GOBBINSITE.

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The crystal structure of gobbinsite (approx. composition  $\text{Ca}_{0.6}\text{Na}_{2.6}\text{K}_{2.2}\text{Al}_6\text{Si}_{10}\text{O}_{32}\cdot 12\text{H}_2\text{O}$ ), a new zeolite mineral from Co. Antrim, N. Ireland, has been determined by x-ray powder diffraction techniques in the space group  $Pmn2_1$  with  $a = 10.108(1)$ ,  $b = 9.766(1)$  and  $c = 10.171(1)$  Å.

The gismondine-type structure was refined with the XRS-82 system of programs for whole-pattern refinement of x-ray powder data, and converged with  $R_F = 0.131$  and  $R_{wp} = 0.138$  (statistically expected  $R_{wp} = 0.121$ ). Fifty geometric restrictions on the bond distances and angles of the framework atoms were included in the least-squares refinement as additional observations. This facilitated the location of the non-framework cations and water molecules, and improved the stability of the refinement. Although these restrictions were given less and less weight as structure solution progressed, they could not be removed completely.

$Pmn2_1$  is a subgroup of  $I4_1/amd$ , the ideal space group for the gismondine framework structure type. It was expected that the pseudo-tetragonal axis in gobbinsite would be parallel to the short unit cell dimension, but such was not the case. As in the closely-related synthetic zeolite Na-P2, which was solved by single-crystal methods in the space group  $P2_12_12_1$  (Lars Fålh, Univ. Lund), the pseudo-tetragonal axis is parallel to one of the two near-equivalent cell constants. The arrangement of cations within the zeolitic channels suggests an explanation for this distortion of the ideally tetragonal framework.