

[s10.m1.p19.1a] Powder Solve – a complete package for structure determination from powder diffraction data.

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Increasingly powerful methods have been developed recently to facilitate the crystal structure determination from powder data. Based on earlier work at Molecular Simulations¹, we have developed a fast and efficient indirect structure solution package, called POWDER SOLVE², which is fully integrated into MSI's modelling environment.

Positions and orientations of structural fragments within the unit cell are modified to obtain optimal agreement between experimental and simulated powder patterns. An efficient global optimisation algorithm allows the method to be applied to organic and inorganic systems. Validation work shows that the method can be applied successfully to systems with up to 18 degrees of freedom with moderate computational effort. At the same time, the package can also be used as a stable and powerful tool for rigid-body Rietveld refinement.

As for related techniques³, the experimental powder pattern (not necessarily from a synchrotron source) must be successfully indexed prior to structure solution, and peak shapes and background parameters must be determined. For this purpose, we have implemented a modification to the Pawley method⁴, which avoids the instabilities inherent to the original algorithm.

[s11.m1.p18.1a] Site occupancies of spinel solid solutions.

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A large number of cations can enter the spinel structure, and several can enter both T and M sites, in relative amounts which are very sensitive to the equilibrium temperature. Cation distribution cannot always be determined unambiguously. For instance, concerning a widely investigated spinel like MgAl₂O₄, extremely scattered data are reported, with differences of the inversion degree measured at the same temperature of up to 15%.

Spinel structure is described by only two parameters, oxygen coordinate *u* and cell edge *a*₀, related by simple equations to the tetrahedral and octahedral bond distances. If these distances can be reproduced accurately by means of a set of crystal radii, and if the site mean atomic numbers are known, a good estimate of the distribution can be obtained.

Until now, calculation of bond distances has been performed without taking into account the mutual influence of the two sites, but recently this influence has been evidenced by several authors. An accurate inspection of all published data containing accurate cation distribution reveals that this influence is appreciable only as regards the T-O distance when Fe³⁺ and/or Ni²⁺ are present in M site. Optimisation of both bond distances and cation distributions were therefore performed, and the bond distances were calculated according to:

$$T-O = \sum_i X_{Ti} * D_{Ti} + k_1 * Fe^3+_M + k_2 * Ni_M$$

$$M-O = \sum_j X_{Mj} * D_{Mj}$$

where *k*₁ and *k*₂ are adjustable parameters.

A computing system was prepared based on a modified version of the MINUIT program. A main routine controls *D* and minimises the function:

$$G(D) = (1/N) \sum F(X_i)$$

where *F*(*X*_{*i*}) is a function minimised for each sample of the database by a subroutine controlled by the main program, and *N* is the number of samples. *F*(*X*_{*i*}) is defined as follows:

$$F(X_i) = \sum_{j=1-n} ((O_j - C_j(X_i) / \sigma_j)^2) / n$$

where *O*_{*j*} is a quantity observed, *C*_{*j*}(*X*_{*i*}) the same quantity calculated by means of variable cation fraction *X*_{*i*}, and *σ*_{*j*} is the standard deviation of the observed quantity. Residuals *n* refer to the observed parameters (T-O and M-O bond distances, m.a.n. of T and M sites, atomic proportions from chemical analysis) and to three constraints: occupancy of T and M sites (1 and 2 respectively) and formal valences.

This procedure gave a set of bond distances – with maximum changes of 0.03Å with respect to Shannon's value - which allows reproduction of cell parameters *a*₀ and *u* within 1σ, and within 2σ of all reliable distributions. Some examples about testing the reliability of experimental data and the dependence of physical properties on cation distribution will be supplied.

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