
Using the parallel tempering algorithm to overcome complex problems in structure determination of inorganic materials with laboratory X-rays

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Abstract. The crystal structures of two inorganic compounds, $\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ and $\text{YK}(\text{C}_4\text{O}_4)_2$, have been solved *ab initio* from laboratory X-ray powder diffraction data using the parallel tempering algorithm. It is assumed that one reason of the failure of the direct methods in structure determination is the noticeable diffraction line overlap displayed by the powder patterns. Then, we discuss the influence of line broadening on the efficiency of the direct methods and the parallel tempering algorithm to solve back the crystal structure of $\gamma\text{-Zn}_2\text{P}_2\text{O}_7$ from powder diffraction patterns simulated for several crystallite sizes.

Introduction

Ab initio structure determination from powder laboratory X-ray diffraction data remains a challenge in many cases. One of the major problems is the lack of accurate structure factor amplitudes, due to the projection of the three-dimensional reciprocal lattice onto the one-dimensional 2θ space. This feature is dramatically exacerbated by diffraction line broadening observed when using laboratory X-rays instead of synchrotron X-rays and in case of samples with a microstructure, i.e. small diffracting domains and/or structural imperfections. If the degree of diffraction line overlap is severe, the extraction of integrated intensities cannot provide enough Bragg reflections to solve the crystal structure. Few years ago, direct space approaches, such as Monte-Carlo simulated annealing (MC-SA) method [1] or genetic algorithm [2,3], were successfully applied to solve *ab initio* the crystal structure and molecular packing of organic molecules. These methods become undoubtedly efficient with the fast development of computer technology, provided that (i) powder data are accurately collected

(with negligible preferred orientation), (ii) diffraction line profiles are correctly modelled, (iii) Bragg peaks have been properly indexed and (iv) the chemical formula and molecular diagram are known. However, the application of direct space methods for solving crystal structures of inorganic and mineral compounds remains often tricky. Indeed, data collection using rotating capillaries is often unreliable, at least when conventional X-ray sources are used due to the X-ray absorption of heavy atoms, and the crystal structures of these compounds generally result from the assembly of isolated atoms rather than large molecules. Procedures to circumvent these problems have been elaborated, e.g. the introduction of a partial model obtained from the direct methods into a MC-SA algorithm, using coordination polyhedra [4] or the potential energy minimisation combined with the MC-SA optimisation [5]. Recently, the parallel tempering algorithm [6] has been used in the program FOX [7]. The software also proposes the introduction of coordination polyhedra and molecules in the starting model, as well as a variation of a preferred orientation parameter.

In the present study, we describe the successful application of the parallel tempering approach to solve the crystal structure of two inorganic materials, namely $\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$ and $\text{YK}(\text{C}_4\text{O}_4)_2$, for which the structure determination failed when using the direct methods. Additionally, we discuss the influence of line broadening on the efficiency of the direct methods and the parallel tempering algorithm to solve back the crystal structure of $\gamma\text{-Zn}_2\text{P}_2\text{O}_7$ [8] from powder diffraction patterns simulated for several crystallite sizes.

Collection of high-resolution powder X-ray diffraction data

High quality powder data were obtained with a Siemens D500 diffractometer, with the Bragg-Brentano optics, using monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) selected with an incident beam curved-crystal germanium monochromator. The patterns of $\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}/\text{YK}(\text{C}_4\text{O}_4)_2$ were scanned at room temperature, over the angular range $10\text{-}120/10\text{-}150^\circ$ (2θ), with step lengths of $0.02/0.03^\circ$ (2θ) and counting times of $71/66 \text{ s step}^{-1}$. Powder pattern indexing was performed with the program DICVOL04 [9]. Structure determination was carried out using the direct methods program EXPO [10] including a whole-pattern decomposition iterative algorithm [11], and with the parallel tempering algorithm available in the global optimization program FOX [7]. Structure refinement was achieved with the program FULLPROF [12] available in the software package WINPLOTR [13]. The Rietveld refinement was carried out with a pseudo-Voigt function to describe the individual line profiles. The background was modelled with a linear interpolation between refined intensity points. The program DIAMOND (version 2.1e), supplied by Crystal Impact, was used for structure drawing.

Ab initio structure determination

$\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4)\cdot 2\text{H}_2\text{O}$

The title compound was hydrothermally prepared in powder form in the course of the investigation of open-framework mixed vanado-phosphato-oxalate materials. The first twenty lines of the pattern were indexed on the basis of a monoclinic solution and the complete review and least-squares refinement of the thirty-two diffraction lines led to the unit cell

dimensions $a = 6.349(1) \text{ \AA}$, $b = 17.144(3) \text{ \AA}$, $c = 6.557(1) \text{ \AA}$, $\beta = 106.59(2)^\circ$, $V = 684.0 \text{ \AA}^3$ [refined zero-shift 0.011° (2θ), $M_{20} = 48$, $F_{32} = 79(0.007,56)$]. The extinction conditions were consistent with space group $P2_1/m$. The direct methods were firstly used in order to locate the heaviest atoms, V, P and Na. Since the expected O atoms were not found from subsequent difference Fourier syntheses, the heavy atoms could not be properly attributed to the electron density positions on the lone basis of peaks height. Then, the absence of significant preferred orientation allowed starting the structure solution using the parallel tempering algorithm available in FOX. The initial model consisted in one PO_4 tetrahedron, one rigid C_2O_4 group, two Na atoms and two water O atoms. The V atom was assumed to be at the centre of an octahedron, according to common results reported in the literature. A reasonable model was found after 4.4 million moves (110 minutes), with a PC equipped with two AMD Athlon 1.7GHz processors. At the end, one sodium atom needed to be replaced by one water molecule, while the other water molecule was removed from the structure model. The final Rietveld refinement led to satisfactory R values. Figure 1a shows the best agreement obtained between observed and calculated patterns. Results of the refinement are given in Table 1.

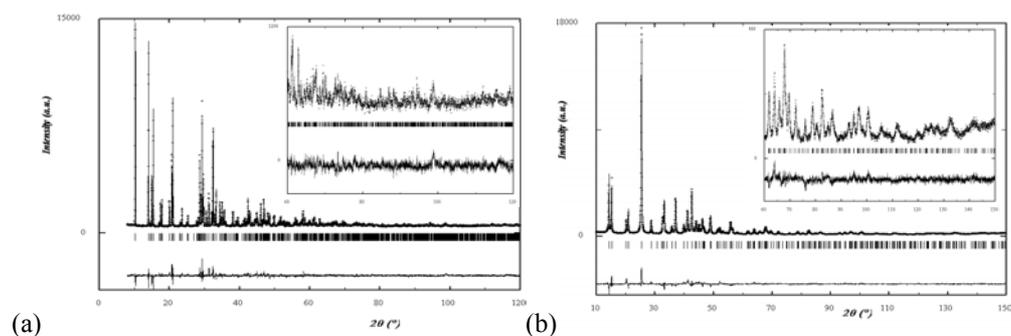


Figure 1. Final Rietveld plots for (a) $\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ and (b) $\text{YK}(\text{C}_4\text{O}_4)_2$. The experimental data are represented by crosses, while the calculated pattern is shown by the solid line. The lower trace corresponds to the difference curve between observed and calculated patterns. The Bragg reflections are shown by the vertical bars.

Table 1. Details of the Rietveld refinements for $\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ and $\text{YK}(\text{C}_4\text{O}_4)_2$.

Compound	$\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$	$\text{YK}(\text{C}_4\text{O}_4)_2$
Z	4	2
No. of atoms	13	4
No. of reflections	1110	269
No. of structural parameters	51	11
No. of profile parameters	25	22
R_F	0.071	0.035
R_B	0.092	0.071
R_D	0.052	0.077
R_{wp}	0.067	0.098
R_{exp}	0.038	0.053

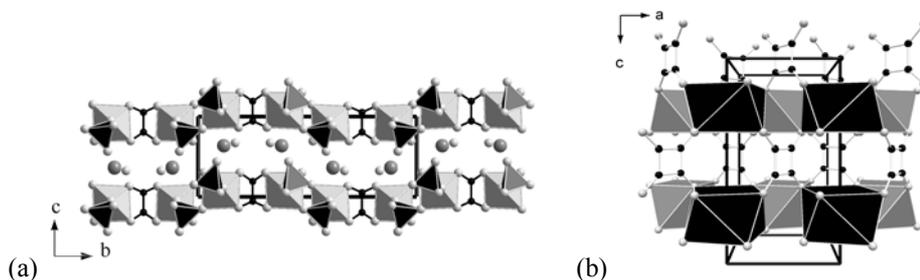


Figure 2. Projection of the structures of (a) $\text{Na}_2[\text{VO}(\text{HPO}_4)]_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ along the a axis and (b) $\text{YK}(\text{C}_4\text{O}_4)_2$ along the b axis (medium grey polyhedron: VO_6/YO_8 , black polyhedron: PO_4/KO_8 , black sphere: C, pale grey sphere: O, medium grey sphere: Na).

The structure (Figure 2a) consists of anionic layers of oxalato-phosphate of vanadium between which are located Na^+ and water molecules. One layer is made of double-chains of corner-sharing PO_4 and VO_6 polyhedra, connected by the oxalate groups.

$\text{YK}(\text{C}_4\text{O}_4)_2$

The squarate compound was obtained at 240 °C during the thermal decomposition of the precursor $[\text{Y}(\text{H}_2\text{O})_6]\text{K}(\text{C}_4\text{O}_4)_2(\text{H}_2\text{C}_4\text{O}_4)$ [14]. As for a majority of decomposition products, its powder pattern exhibits a significant diffraction line broadening, i.e. five times larger than the instrumental resolution function of the Siemens D500 diffractometer. The first 20 lines were indexed with DICVOL04 on the basis of a tetragonal symmetry, with unit cell dimensions $a = 6.2011(5)$ Å, $c = 11.639(1)$ Å, $V = 447.6$ Å³ [refined zero-shift 0.007° (2θ), $M_{20} = 57$, $F_{20} = 71(0.006,44)$]. Due to the high crystal symmetry and the small volume, a few number of Bragg positions were available in the whole pattern. In addition to the broadened lines, the amount of reflections only allowed to find the extinction condition of reflections $0kl$, $l = 2n + 1$. Thus, eleven space groups were retained in this symmetry. Structure determinations using the direct methods and difference Fourier calculations were attempted for each selected space group, leading to unreliable models. Consequently, a structure solution was carried out in the triclinic space group $P1$ with the program FOX, in order to avoid symmetry errors. The starting model consisted of two Y and two K atoms and four squarate groups. The solution was found after 6.3 million trials (10 hours, AMD Athlon XP 3000+ processor). From the positions of atoms of the same species displayed by the program, symmetry elements were retrieved leading to the correct space group $P4/mcc$. The final Rietveld refinement led to satisfactory R factors and a chemically plausible structure model. Figure 1b shows the best agreement obtained between observed and calculated patterns. Results of the refinement are given in Table 1. The pillared structure, displayed in Figure 2b, consists of layers of Y and K atoms connected by pendant squarate groups. A layer is built from alternating edge-sharing yttrium and potassium antiprisms.

Influence of diffraction line overlap on structure determination

The diffraction line overlap, observed in the powder diffraction patterns of the two compounds, is generally the major restraint in structure determination using the direct methods. On the contrary, it is expected that the direct space approach should be less sensitive to this feature. In order to verify this assumption, powder diffraction patterns were simulated for

nanocrystalline powders. The structure model of the inorganic decomposition product γ - $\text{Zn}_2\text{P}_2\text{O}_7$, whose structure was determined *ab initio* from powder diffraction data [8] [S. G. *Pbcm*, $a = 4.9504(5)$ Å, $b = 13.335(2)$ Å, $c = 16.482(3)$ Å, $V = 1088.1(2)$ Å³], was used to generate calculated patterns [15]. Samples were assumed to be strain-free, with isotropic and monodisperse crystallites. Various crystallite diameters D were selected in the range 80-1200 Å. The apparent sizes ε_β ($= 3D/4$) were transformed into integral breadths β^* ($= \varepsilon_\beta^{-1}$) and, then, expressed in 2θ units $\beta_{2\theta}$ ($= \lambda\beta^*/\cos\theta$) for selected diffraction lines within the angular range 9-80° (2θ). To avoid unnecessary truncation errors with Lorentzian profiles [16], a Gaussian function was preferred to describe individual reflections. The angular dependence of FWHM was modelled with the usual quadratic function in $\tan\theta$ from the FWHM values of the Gaussian reflections calculated from the relation $\text{FWHM} = 0.9394\beta_{2\theta}$ [17].

Using the simulated patterns, the crystal structure of γ - $\text{Zn}_2\text{P}_2\text{O}_7$ was solved back using the programs EXPO and FOX. The efficiency of the direct methods was estimated by the number of correct electron peak positions found. Using the parallel tempering algorithm, it was pointed out that both the calculation time per trial and the number of trials increased when crystallite diameter decreased. A penalty factor E [$= (N_t/D)^{1/2}$], combining the number of trials N_t required to find the structure model and the crystallite diameter D (in Å), was then calculated. This result deserves the following comments:

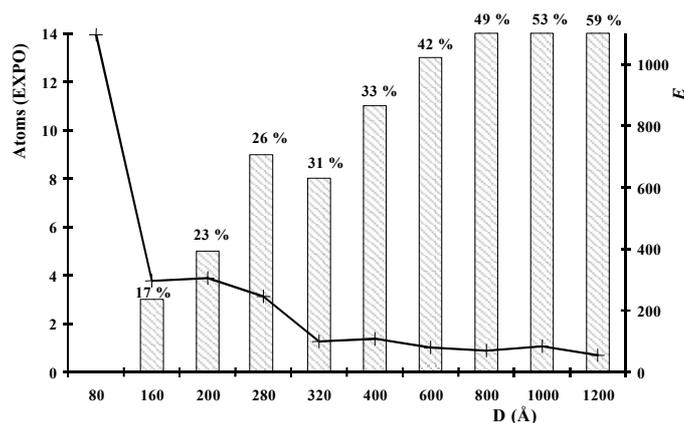


Figure 3. Comparison of the efficiency of direct methods and parallel tempering algorithm applied to powder patterns simulated for various spherical crystallite diameters D (Å) from the crystal structure of γ - $\text{Zn}_2\text{P}_2\text{O}_7$. The number of atoms (on 14 independent atoms) found by EXPO is shown by the histogram, together with the percentage of statistically independent reflections (%) [10 and refs therein], the penalty factor E related to the direct space method is represented by the solid line.

- $D \geq 400$ Å: the crystal structure could be solved easily by the two approaches. The direct methods required a few minutes only, while the parallel tempering needed a few hours.
- $160 \text{ Å} \leq D \leq 320 \text{ Å}$: the structure was also solved by the two approaches. While the parallel tempering algorithm was moderately affected by line broadening, the direct methods provided only half atoms. Subsequent different Fourier calculations were thus time-consuming.
- $D = 80$ Å: the extraction of integrated intensities was not possible, due to the excessive diffraction line broadening. The structure model was found by FOX after longer time.

Concluding remarks

This study demonstrates the efficiency of a direct space approach to solve the crystal structure of inorganic compounds when the direct methods fail, especially in the case of noticeable diffraction line overlap. However, it is also shown, through the structure determination of γ -Zn₂P₂O₇, that some atoms are usually found using the direct methods. Then, it is useful to consider this partial model for structure completion using a global optimisation approach.

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