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Extraction of Crystal structural data of a number of chromate use complexes by of Rietveld equation and WinPLOTR program from powder diffraction patterns

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ABSTRACT

Tetraalkylammonium salts produced micro crystals that are not suitable for x-ray single crystal diffractions. Structural data can be extracted from powder diffraction patterns and by use of mathematical methods. The method used for this research based on Rietveld method to perform full matrix least-squares refinement of unit parameters from powder diffraction patterns. Powder Diffraction pattern of a number of chromate complexes were successfully analyzed by mathematical equations. The use of pattern-fitting techniques for the characterization of the microstructure is discussed through applications to nanocrystalline materials. We used direct space that need no powder pattern analysis and is based on global optimization of a structural model to improve agreement between the observed and calculated diffraction patterns. The extracted data compared with single crystal X-ray data and found good agreement between two kinds of data.

Keywords: Crystal structural data, WinPLOTR program, Rietveld equation, Chromate complexes, Powder diffraction patterns.

INTRODUCTION

Tetraalkylammonium and phosphonium salts produced micro crystals that are not suitable for x-ray single crystal diffractions. Figures 1 and 2 show the micro crystals of these type complexes that are not suitable for single crystal x-ray diffraction. Structure determination from powder diffraction (SDPD) is more difficult than structure determination on single crystals, because the available data are a projection of a three-dimensional diffraction pattern on to one dimension (radial distance from the reciprocal space origin), and consequently the diffraction peaks are overlapped [1-3]. The pattern matching was performed with Fullprof 2k using the WinPLOTR. Powder diffraction using X-rays and neutrons plays a major role in the search for new materials that are not available in the form of single crystals. On the other hand, X-rays or neutron data recorded with Position-Sensitive-Detectors as a function of a

variable physical parameter (temperature, pressure,) are leading to analyses simultaneously many different patterns with a relatively small number of points per diagrams.

WinPLOTR has been written in Fortran 90, using the new syntax and features of this language. It has been developed for the Windows 9x/2k/NT operating system and it takes advantage of this graphical environment to provide a friendly tool to the user. The WinPLOTR kit consists of a compacted ('winplotr.zip') file containing all the files needed to run and install automatically the program WinPLOTR and the Windows versions of the Rietveld-type program FullProf (single and multiple patterns versions), Dicvol91 (WINDIC), Treor90 (WTREOR90), automatic indexing of powder diffraction patterns- and others tools as for example a neutron periodic table (MENDEL) or SUPERCELL. Furthermore, the visualisation of the agreement between experimental data and those calculated from a physical model implemented in particular software (for instance a Rietveld-type program) is of primary necessity to validate the interpretation of the experiment on the sample under study [4]. The structures of a number of chromate complexes were refined using Fullprof.

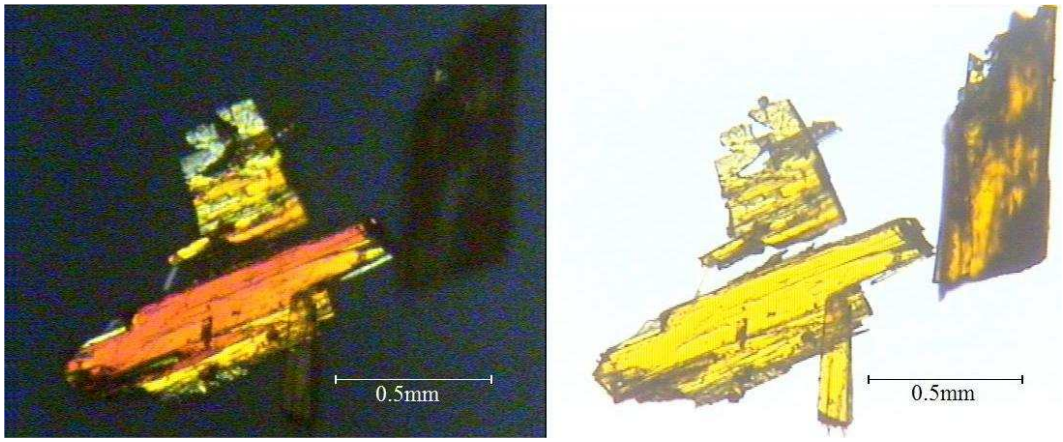

Figure 1. The polarimetric (a) and non-polarimetric (b) images of $Ph_4P[CrO_3Cl]$, method: slow evaporation, solvent: MeCN, Room temperature.

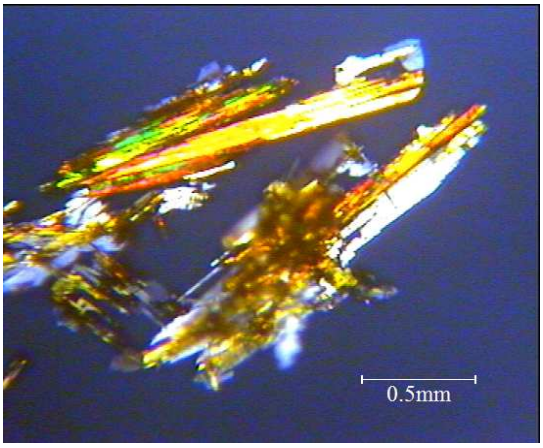

Figure 2. The polarimetric images of $Ph_4P[CrO_3Cl]$, method: slow evaporation, solvent: CH_2Cl_2, Temperature:0°C.

Mathematical Information

The Rietveld Method. Calculated profile

A powder diffraction pattern can be recorded in numerical form for a discrete set of scattering angles, times of flight or energies. We will refer to this scattering variable as *T*. Then, the experimental powder diffraction pattern is usually given as two arrays $\{T_i , y_i \}_{i=1,2,...,n}$ .Where δ is the standard deviation of the profile intensity y_i are needed in order to properly weight the residuals in the least squares procedure. The profile can be modeled using the calculated counts Yci at the ith step by summing the contribution from neighboring Bragg reflections plus the background:

$$y_{c,i} = \sum_{\Phi} S_{\Phi} \sum_{h} I_{\Phi,h} \Omega(T_i - T_{\Phi,h}) + b_i \qquad (1)$$

In the following sections we discussed the different terms in more detail. The Rietveld Method consist of refining a crystal (and/or magnetic) structure by minimising the weighted squared difference between the observed $\{y_i\}_{=1,2,...,n}$ and the calculated (1) pattern $\{ y_{c,i} , (\alpha)\}_{i=1,2,...,n}$ against the parameter vector $\boldsymbol{\alpha}=(\alpha_1, \alpha_2, \alpha_3, ... ,\alpha_p)$.

Several calculations capabilities are available in the 'Calculations' menu: background subtraction, data files difference, centroid determination, integration... The result of these operations is automatically displayed as a superimposed file and data can be saved as an ASCII file. An interactive profile fitting procedure using the no-linear least-squares Marquard algorithm has been implemented [5-7]. This process uses independent pseudo-Voigt functions with a global FWHM (full width at half maximum) and a global η (Lorentzian component), and a linear background. Each peak is characterized by its position, intensity and the shifts of FWHM and η with respect to the global parents. The function that is minimised is the chi-square χ^2:

$$\chi^2 = \frac{\sum_i w_i^* \left| Y_{obs}^i - Y_{calc.}^i \right|^2}{N - P} \qquad (2)$$

where $\sum I$; is summation over the *N* points of the fitted region, *Wi* ; weighting factor; Yobs; observed counts, Ycalc; calculated counts, P; number of refined parameters.

The analysis of the grain size (L_{hkl}) of the sulfate has been done to all samples using the Scherrer´s equation:

$$L_{hkl} = \frac{k\lambda}{\beta \cos\theta} \qquad (3)$$

Where k is the shape coefficient (values between 0.9 and 1.0), λ is the wavelength of the radiation, β is the full width at half maximum (FWHM) of the peaks of each phase and θ is the diffraction angle. For this purpose the β parameter has been corrected in order to represent only the effect of the grain size in the FWHM [7-13].

RESULTS AND DISCUSSION

A powder X-ray diffraction pattern of this compound was recorded at room temperature. To determine the lattice parameters of the phases, the profiles with a 2θ angle lower than 55° were refined with the program Winplotr. It has been found that one of these compounds has: a monoclinic symmetry, a space group C2 (#5), Z=4 and lattice parameters. The SDPD methods can be divided into two groups according to the working space, as found in David and references therein: (i) Reciprocal space methods (ii) Direct space methods. Three direct method programs were optimized for working with data from powder diffraction: WINPLOTR, FULLPROF, EXPO and a program based on the modulus sum function. This was the main idea behind WINPLOTR which has become a friendly tool for solving molecular structures from powder diffraction data. (By Rietveld method).

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