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Application of a New Method for the Determination of Accurate Intensities from Powder Diffraction Data. Crystal Structure Determination of Fibrillar Silver Trimolybdate

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A new approach for the determination of accurate intensities from powder diffraction data has been successfully applied to a sample of fibrillar silver trimolybdate $Ag_2O \cdot 3MoO_3 \cdot 1.8H_2O$. At the beginning the pattern decomposition program could find only 30 nonoverlapping reflections, but after a few cycles of the "intensity estimating" procedure a set of 130 "unique" intensities was obtained. This set was sufficient to solve the phase problem both by the direct method and Patterson programs. The final Rietveld method refined to R_f = 14.1% and R_{wp} = 20.4%. Space group *Pnma*; a = 13.201(10), b = 7.577(6), c = 9.757(7) Å, Z = 4. © 1994 Academic Press, Inc.

INTRODUCTION

The most important step in ab initio crystal structure determination from powder diffraction data consists of the deconvolution of the intensities from the measured powder data. Since accurate integrated intensities are needed for the structure determination, this separation should lead to as many reflection as possible. According to the literature the best technique for this aim is the Whole Pattern Fitting procedure. Several programs have been developed to perform this refinement (1, 2). However, even the best fitting procedure cannot retrieve accurate intensities for highly overlapping reflections whose diffraction angles differ less than some critical value. In that case only the total integrated intensity of each cluster of overlapping peaks will be accurately available.

Recently a few procedures in which the intensities of these reflections can be predicted have been presented. One of them has been proposed by David (3). His estimations are based on the entropy maximization of the $|F|^2$ Patterson function. Another approach is based on the triplet and quartet relations from direct methods and the theory of the Patterson function (4). The last method was used for the ab initio crystal structure determination of fibrillar silver trimolybdate. Only powder diffraction data are available for this compound due to the small diameter of the fibers (about 0.1–1 μm). The results of crystal structure determination and the description of the applied procedure are presented below.

INTENSITY ESTIMATION AND THE STRUCTURE SOLUTION

Synthesis, chemical analysis results, and lattice parameters for the silver trimolybdate were presented in a previous paper (5). The sample was ground thoroughly under ethanol and after drying pressed into a holder according to the so-called "back-packed technique," to avoid texture. Based on the powder diffraction data the space group was found to be *Pnma*. The details of the data collection are presented in Table 1. Even though powder data were collected in the range of 10–100° 2θ, a smaller range of the X-ray pattern from 10 to 65° was considered for structure determination purposes. The number of possible reflections in this range was 200. The small size of the fibrillar crystals caused peak broadening and low intensities for the reflections. The pattern decomposition was performed by LSQPROF program (2) with R = 3.8%. Only 30 nonoverlapping unique "single" peaks, with distances larger than half of their halfwidth to their next-neighbors, were found by the pattern decomposition program. These 30 intensities were used as a starting point for five cycles of calculations with the program DOREES, which uses direct and Patterson methods to estimate the intensities of strongly overlapping reflections (4). In this iterative procedure weights for all five contributions (four from direct methods and one from the Patterson function) were set equal to 1. In each cycle 5 and 10 reflections with the greatest probability of being strong and weak, respectively, were added to the file of unique reflections, ending with the number of uniquely determined reflections increased to 130.

At this stage both the direct method program SIM-

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TABLE 1

Crystallographic and Rietveld Refinement Data for $Ag_2O \cdot 3MoO_3 \cdot 1.8H_2O$

Diffractometer	PW1710
Radiation	Cu$K\alpha$, filtered
2θ range [°]	10–100
Step scan increment [°2θ]	0.02
Count time [sec/step]	10
Standard peak: *hkl*, [2θ], *R*	111, 16.14, 11%
Peak shape	learned
Background	substracted
Space group	*Pnma* (62)
a [Å]	13.201(10)
b [Å]	7.577(6)
c [Å]	9.757(6)
Number of observations	4500
Number of reflections	507
Number of refined structural parameters	33
Number of profile parameters	10
Preferred orientation vector and factor	010, 0.15(3)
Preferred orientation function	$\exp(p \cos(2\alpha))$
R_f	14.1
R_{wp}	20.4
R_{exp}	13.0
Max shift/error	0.4

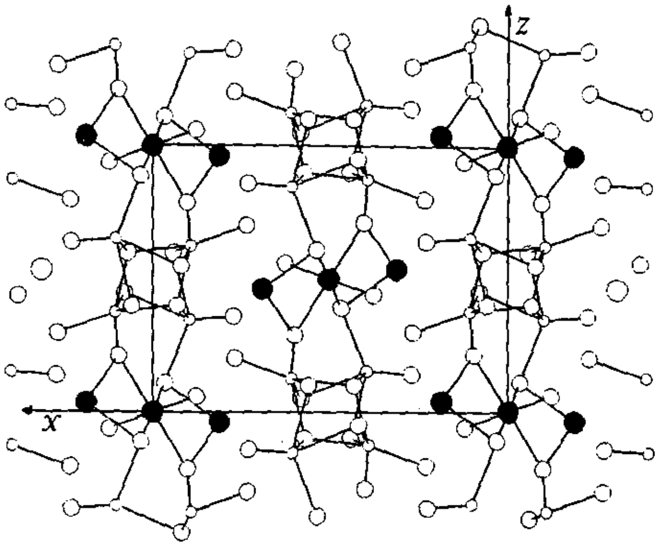

FIG. 2. The plot of the elementary cell along the *b* axis. The black and white circles denote silver and oxygen atoms, small circles represent molybdenum.

PEL88 (6), as optimized for powder diffraction (7), and the Patterson procedures of SHELXS86 (8) were successfully used to find the heavy atoms. Next, the programs of XTAL (9) were used to refine the heavy atom positions and to locate the oxygen atoms. Since only some of the oxygen atoms could be found, the RSCAN program of the XTAL system was used to test for possible sources of errors. The most interesting results of the RSCAN program are as follows:

—There exists no correlation between *h, k, l* values in

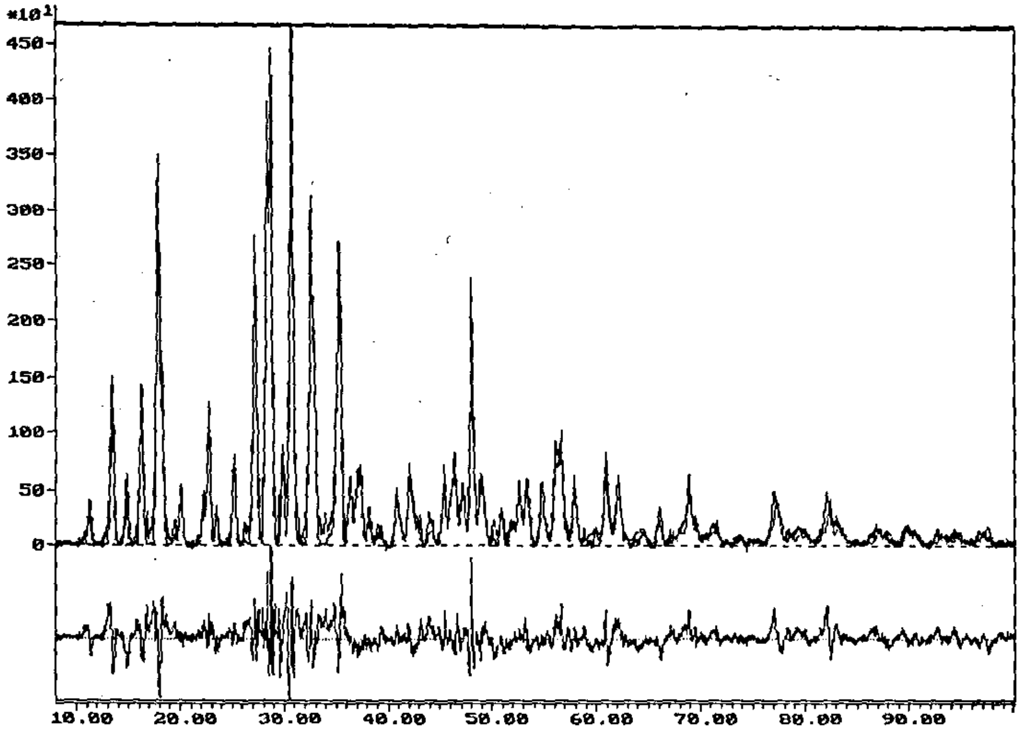

FIG. 1. Observed and calculated diffraction pattern for $Ag_2O \cdot 3MoO_3 \cdot 1.8H_2O$ with a difference plot indicated at the base of the figure.

TABLE 2

Final Positional and Thermal parameters with Their esd for $Ag_2O \cdot 3MoO_3 \cdot 1.8H_2O$

ATOM	X	Y	Z	U	sof[a]
Ag1	0.5000	0	0.5000	0.05(1)	0.92(3)
Ag2	0.312(1)	−0.2500	0.536(2)	0.06(1)	1.00(4)
Mo1	0.393(1)	−0.003(2)	0.875(1)	0.009(4)	
Mo2	0.396(2)	−0.2500	0.153(3)	0.04(1)[b]	
O1	0.069(4)	0.02(2)	0.599(8)	−0.008(3)	
O2	0.267(8)	0.091(3)	0.298(9)		
O3	0.403(7)	0.02(1)	0.712(9)		
O4	0.058(9)	0.2500	0.40(1)		
O5	0.229(1)	0.2500	0.64(2)		
O6	0.42(1)	0.2500	0.95(1)		
O7	0.034(9)	0.2500	0.890(9)		
O8 (H_2O)	0.377(1)	0.2500	0.44(1)		

[a] Occupancy factor equals 1 unless specified.

[b] Temperature factors for oxygen were constrained to be equal to each other, refined to small values oscilating around 0.0.

any reflection groups and in the discrepancy factor R calculated for these groups.

—There is no correlation between R and 2θ in the range from 10 to 65°.

—R factors are smaller for the strong reflections than for weak and very weak reflections.

—even though estimates are usually correct, differences between estimated and calculated intensities can be high for a few reflections.

The results of the RSCAN program suggest that:

—The preferred orientation in the sample is rather small.

—For "weak reflections" and for reflection with the highest $|F_{\mathrm{est}} - F_{\mathrm{cal}}|$ some threshold value could be applied during the crystal structure refinement or Fourier calculations.

—Many "ghost" peaks can be expected in the Fourier maps due to the errors in estimates.

Taking into account the results of the RSCAN program, we decided to finish the structure solution using the Rietveld method. After refinement of the heavy atom positions by the Rietveld method, subsequent Fourier calculations permitted the location of all but one oxygen atom. Fourier calculations and the Rietveld refinement of the structure was performed using programs of the XRS-82 system (10). The final R factors in the full range of diffraction data are as follows: $R_{\mathrm{f}} = 14.1\%$, $R_{\mathrm{wp}} = 20.4\%$. Some details about the refinement procedure are presented in Table 1. The plot of observed and calculated powder pattern is presented in Fig. 1.

STRUCTURE DESCRIPTION AND DISCUSSION

The XRS-82 system allows known interatomic distances or angles to be used as constraints in the refinement procedure. In this paper, however, only results of unconstrained refinement are given in Tables 1 and 2. A view of the elementary cell along the b axis is presented in Fig. 2. The structure consists of infinite chains built up of edge-shared distorted MoO_6 octahedra, running in the b axis direction. The distortions present in the MoO_6 octahedra are reflected by the Mo–O distances that vary from 1.63 to 2.65 Å. The molybdenum–oxygen chains are very similar to those found in rubidium trimolybdate (11) and in both ammonium trimolybdates (12, 13). The Mo–O distances in rubidium and ammonium trimolybdate (11, 13) range from 1.68 to 2.82 Å and from 1.714 to 2.319 Å, respectively. The Ag–O distances range from 2.23 to 2.91 Å. Ammonium trimolybdate, obtained at high pressure and temperature (13), has the same space group and very similar lattice parameters. However, intensity calculations indicate that these two structures are not isomorphous. It was found that in the present structure the silver cations occupy quite different positions than the NH_4^+ cations in the ammonium salt, though position and orientation of the molybdenum–oxygen chains are similar.

It was found that the site occupation factor for one of the silver cation positions is considerably less than 1 (see Table 2). To avoid positive charge deficiency some oxygen atoms in the infinite molybdenum–oxygen chains can be protonated forming OH groups. By bond distances and chemical analysis such groups were detected in a number of molybdates (14). The presence of the OH groups in this structure is consistent with the high contribution of OH groups observed by solid state ^{1}H NMR in the magnetic resonance spectrum recorded at 77 K (5).

One water molecule could be easily located on the Fourier difference maps, and its distances to silver cations are in the range of the Ag–O bonds in similar compounds. The other water molecule cannot be located using the Fourier method, it is probable that it is zeolite water occupying some positions with a site occupancy factor less than 1. Its zeolite character is indicated by the chemical formula of the investigated compound: $Ag_2O \cdot 3MoO_3 \cdot 1.8H_2O$ and is based on results of DTA measurements (5).

It is significant to note that even with less than optimum X-ray data (small fibrillar crystals, standard power diffractometer) applied methods allow a structural solution to be achieved.

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