

QUESTIONNAIRE FOR the  
STRUCTURE DETERMINATION BY POWDER DIFFRACTOMETRY ROUND ROBIN - 3

Please answer all questions as completely as possible. Provide one filled questionnaire for each data (samples 1 and 2).

Preferably, attach the results as one PDF file or as a MS Word document compressed by Winzip.

It is advised to complete the form as the structure determination progress.

0.0 Precise date of  
- data download : 2 Feb 2008  
- results submission : 21 Apr 2008

0.1 Is the first sample structure solvable with this quality of data ? Yes [] No []  
0.2 Is the second sample structure solvable with this quality of data ? Yes [] No []  
0.3 If not, what data would be required ?

Then, for each sample :

## sample 2

### 1. Preliminary work

1.1 Did you obtained additional informations ? Yes from ICSD  
(for instance from CSD or ICSD or ICDD databases)

1.2 Did you obtained additional informations from the powder pattern ? If yes, how and what information ? NO  
(for instance using the JCPDS-ICDD database)

1.3 Did you extract the structure factors ? Yes [] No []

1.3.1 If yes, which program(s) did you use ?

1.3.2 Give the angular range:

1.3.3 Give the number of extracted structure factors:

1.3.4 Give the Rp and Rwp (conventional Rietveld, background subtracted):

1.3.5 Give the Rp and Rwp (background not subtracted):

1.3.6 If not, did you use the whole pattern ? Yes/no

1.3.7 Or a partial pattern (if yes, give the angular range):

Neutron data: the whole pattern was used.

X-ray data: for the refinement the whole pattern was used  
for the structure solution: 1-25°

1.3.8 If you use the whole or a partial pattern, did you keep fixed the profile parameters, and if yes, how did you obtained them ?

In FOX: fixed profile parameters obtained by the lebail module  
In GSAS: refined profile parameters

## 2- Structure solution

2.1 Did you use direct methods ? Yes [ ] No [X]

- 2.1.1 If yes, was it on the whole dataset ?
- 2.1.2 Or on a partial dataset ?
- 2.1.3 Give the number of reflections:
- 2.1.4 Which program(s) did you use ?
- 2.1.5 Did you modified intensities of closely neighbouring reflections ? If yes, explain how.

2.2 Did you use Patterson methods ? Yes [ ] No [X]

- 2.2.1 If yes, was it on the whole dataset ?
- 2.2.2 Or on a partial dataset ?
- 2.2.3 Give the number of reflections:
- 2.2.4 Which program(s) did you use ?
- 2.2.5 Did you modified intensities of closely neighbouring reflections ? If yes, explain how.

2.3 Did you use another method ? Yes [X] No [ ]

- 2.3.1 If yes, which method(s) (give details : molecule location by direct space - genetic algorithm, Monte Carlo, Simulated annealing, scratch, charge flipping, other) ? Parallel tempering
- 2.3.2 Which program(s) did you use (name and reference) ? FOX
- 2.3.3 If you used direct space methods, how many independent molecules did you use (give details on these molecules)? How many degrees of freedom (total) ? How many torsion angles ?

Started with set of La atoms and W06 octahedrons.  
FOX fourier map shows missing heavy atoms. FOX merges atoms when too many atoms have been entered. Sometimes La atoms and W-octahedra had to be interchanged.  
Initially only the X-ray pattern was used to find heavy atom positions. Later on the neutron pattern was added to position O atoms.  
The final FOX solution had 11 La atoms and 5 W-octahedra

2.4 Did you first locate the whole structure ? Yes [x] No [ ]

- 2.4.1 If not, how many atoms did you locate ?
  - 2.4.2 Give their name and initial atomic coordinates
- | Atom  | x     | y       | z     |
|-------|-------|---------|-------|
| ..... | see   | fox.cif | ..... |
| ..... | ..... | .....   | ..... |
| ..... | ..... | .....   | ..... |

2.4.3 Were the initial atomic coordinates taken from a known structure ? Yes [ ] No [X]  
If yes, which one (give reference) ?

### 3- Structure completion

3.1 Did you performed Fourier difference syntheses before refining the structure by the Rietveld method ? Yes [X] No [ ]

3.2 If yes, with what program ? FOX

3.3 If yes, how many additional atoms did you obtained from Fourier difference syntheses ? don't know, see above

3.4 Give their name and atomic coordinates as they were obtained

Atom	x	y	z
.....			
.....			
.....			

3.5 Did you made first Rietveld refinements without preliminary Fourier difference syntheses ? Yes [ ] No [x]

3.5.1 If yes, with what program ?

3.5.2 What were the Rp and Rwp (background subtracted AND not subtracted) and RB and RF that you obtained at the first Rietveld application ?

3.5.3 Did you get the structure factors from this result and performed a Fourier difference synthesis ?

3.5.4 Did you locate additional atoms at this stage ?

3.5.5 And which one ?

Atom	x	y	z
.....			
.....			
.....			

3.5.6 If you repeated Rietveld refinements and Fourier synthese several times before to complete the model, give the number of times and which atoms you locate and the Rp, Rwp RB, RF at each times.

Atom	x	y	z
Lal2: See comment below; no R values available			
.....			
.....			

### 4- Final refinement: GSAS

- Give the final atomic coordinates, thermal parameters, standard deviations, Reliability factors:

Atom	x	y	z	B
.....see enclosed CIF file.....				
.....				
.....				

- Give details about constraints, restraints: see below

- 5- Feel free to add any intermediate results (list of extracted structure factors, software decisive input and output data...) or comments you might consider as essential (details on hardware, time for solving the structure, number of moves by Monte Carlo or molecule position trial, any picture...).

It was initially tried to solve the structure in P -62c, but due to symmetry violation of the O atoms of one of the W-octahedra and a badly fitting neutron trace the symmetry, and in no other hexagonal space group a solution was found, the symmetry was lowered to orthorhombic. In the final stage of the structure solution in C 2cm a residue was found in the X-ray difference Fourier. As only the presence of 3 atom types was mentioned in the RR description an La atom was inserted in the structure at the position indicated in the difference Fourier. It refined well with frac=0.5. Whether this atom is really La or something else should be examined by other techniques, for example elemental analyses and/or NMR, or maybe sample history may give an answer on this question.

Resolution of Neutron data was not good enough for reliable refinement of Uiso: Cross correlation between badly defined background and Uiso. Refining Uiso's by constraining it to be equal for all atoms was stable as long as neutron background and Uiso was not refined in parallel. Absorption correction of X-ray data was done on a trail and error basis. Preferred orientation correction of X-ray data improved the R value. Based on the residual peaks in the difference trace the 110 was chosen as PO direction, but a change to 100 hardly influenced the PO parameter and the R value.

Distance restraints applied to all W-O bonds (1.95Å) and angle restraints to O-W-O (90° or 180°). The weight of the angle restraints was decreased soon to allow for distorted octahedra.

Solving the structure of sample 2 was clearly much more time consuming and for someone with a normal fulltime job not easy to do without coming into trouble with what the daily business that has be done with more priority like the RR.