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.

O.0 Precise date of
- data download : Sat, 2 Feb 2008 19:56:00
- results submission : Tue, 29 Apr 2008 20:00:00

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

Then, for each sample :

La2WO6

1. Preliminary work

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

Yes, from ICSD and then from the journals.

1.2 Did you obtained additional informations from the powder pattern ? If yes, how and what information ?
(for instance using the JCPDS-ICDD database)

Yes, the indexing and extinction conditions were checked.

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

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

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

Yes, the profile parameters were refined by LeBail refinement with FullProf.

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) ?

Yes, direct space method with Simulated annealing in Parallel tempering mode.

2.3.2 Which program(s) did you use (name and reference) ?

Fox: Favre-Nicolin, V.; Cerny, R.: FOX, J. Appl. Crystallography 35 (2002) 734-743.
See also http://objcryst.sourceforge.net/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 ?

Space group P31c.

6 free atoms of La
9 free atoms of W
18 free atoms of O
1 octahedron WO6
In total 105 DoF.

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

2.4.1 If not, how many atoms did you locate ?
35

2.4.2 Give their name and initial atomic coordinates

Atom	x	y	z	occ	Biso
La1	0.2597	0.2553	0.1682,	Occup=1.0000 ,	Biso= 1.0000
La2	0.9632	0.7241	0.3341,	Occup=1.0000 ,	Biso= 1.0000
La3	0.5798	0.6071	0.5829,	Occup=1.0000 ,	Biso= 1.0000
La4	0.4331	0.0520	0.7519,	Occup=1.0000 ,	Biso= 1.0000
La5	0.5748	0.6292	0.4166,	Occup=1.0000 ,	Biso= 1.0000
La6	0.7260	0.9661	0.9997,	Occup=1.0000 ,	Biso= 1.0000
W1	0.0000	0.0000	0.0849,	Occup=1.0000 ,	Biso= 1.0000
W2	0.3333	0.6667	0.1699,	Occup=1.0000 ,	Biso= 1.0000
W3	0.3333	0.6667	0.5000,	Occup=1.0000 ,	Biso= 1.0000
W4	0.3333	0.6667	0.6625,	Occup=1.0000 ,	Biso= 1.0000
W5	0.0000	0.0000	0.9188,	Occup=1.0000 ,	Biso= 1.0000

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W6          0.0000 0.0000 0.2516, Occup=1.0000  , Biso=    1.0000
W7          0.6667 0.3333 0.5271, Occup=1.0000  , Biso=    1.0000
W8          0.6667 0.3333 0.8344, Occup=1.0000  , Biso=    1.0000
W9          0.6667 0.3333 0.3837, Occup=1.0000  , Biso=    1.0000
W10         0.6667 0.3333 0.2483, Occup=1.0000  , Biso=    1.0000
O1          0.8509 0.3659 0.3352, Occup=1.0000  , Biso=    1.0000
O2          0.5339 0.3872 0.6269, Occup=1.0000  , Biso=    1.0000
O3          0.1837 0.7010 0.4591, Occup=1.0000  , Biso=    1.0000
O4          0.3984 0.8514 0.9847, Occup=1.0000  , Biso=    1.0000
O5          0.2762 0.4819 0.2243, Occup=1.0000  , Biso=    1.0000
O6          0.5364 0.1329 0.1834, Occup=1.0000  , Biso=    1.0000
O7          0.2889 0.4744 0.0489, Occup=1.0000  , Biso=    1.0000
O8          0.9628 0.1326 0.9479, Occup=1.0000  , Biso=    1.0000
O9          0.8141 0.8506 0.5439, Occup=1.0000  , Biso=    1.0000
O10         0.3120 0.4891 0.2978, Occup=1.0000  , Biso=    1.0000
O11         0.3147 0.4997 0.5371, Occup=1.0000  , Biso=    1.0000
O12         0.3269 0.4708 0.9167, Occup=1.0000  , Biso=    1.0000
O13         0.4771 0.2916 0.1194, Occup=1.0000  , Biso=    1.0000
O14         0.8336 0.8229 0.2084, Occup=1.0000  , Biso=    1.0000
O15         0.3084 0.4788 0.3775, Occup=1.0000  , Biso=    1.0000
O16         0.9766 0.1593 0.7939, Occup=1.0000  , Biso=    1.0000
O17         0.1374 0.9841 0.3829, Occup=1.0000  , Biso=    1.0000
O18         0.1803 0.0094 0.6137, Occup=1.0000  , Biso=    1.0000
O19         0.8112 0.4950 0.2905, Occup=1.0000  , Biso=    1.0000
```

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 [ ] No [x]
3.2 If yes, with what program ?
3.3 If yes, how many additional atoms did you obtained from Fourier difference syntheses ?
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 [x] No [ ]

3.5.1 If yes, with what program ?

Topas.

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 ?

No

3.5.4 Did you locate additional atoms at this stage ?

No

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
.....			
.....			
.....			

4- Final refinement

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

```
Atom      x                   y                   z             Occupancy              Biso        synchrotron    neutrons
La1     0.25446`_0.00077   0.25879`_0.00077   0.16620`_0.00032 occ La+3  1             beq bLa   0.7711`_0.0219 0.8905`_0.0402
La2     0.96440`_0.00090   0.72271`_0.00088   0.33571`_0.00021 occ La+3  1             beq =  bLa;
La3     0.57949`_0.00088   0.61477`_0.00091   0.58486`_0.00030 occ La+3  1             beq =  bLa;
La4     0.42860`_0.00097   0.04596`_0.00089   0.75254`_0.00028 occ La+3  1             beq =  bLa;
La5     0.57205`_0.00060   0.62934`_0.00051   0.41897`_0.00031 occ La+3  1             beq =  bLa;
La6     0.72590`_0.00094   0.96654`_0.00089   0.0000           occ La+3  1             beq =  bLa;
W1      0;                 0;                 0.08344`_0.00032 occ W+6   1             beq    bW 0.5139`_0.0180 0.8638`_0.0762
W2      1/3;               2/3;               0.17275`_0.00030 occ W+6   1             beq  = bW;
W3      1/3;               2/3;               0.50261`_0.00029 occ W+6   1             beq  = bW;
W4      1/3;               2/3;               0.66640`_0.00029 occ W+6   1             beq  = bW;
W5      0;                 0;                 0.91805`_0.00035 occ W+6   1             beq  = bW;
W6      0;                 0;                 0.25243`_0.00034 occ W+6   1             beq  = bW;
W7      2/3;               1/3;               0.52658`_0.00030 occ W+6   1             beq  = bW;
W8      2/3;               1/3;               0.83552`_0.00029 occ W+6   1             beq  = bW;
W9      2/3;               1/3;               0.38559`_0.00029 occ W+6   0.8785`_0.0118 beq  = bW;
W10     2/3;               1/3;               0.29917`_0.00030 occ W+6   0.7589`_0.0130 beq  = bW;
O1      0.84828`_0.00179   0.36191`_0.00178   0.35304`_0.00042 occ O-2   1             beq    bO 0.1908`_0.1312 0.3765`_0.0343
O2      0.61099`_0.00160   0.46803`_0.00152   0.65151`_0.00042 occ O-2   1             beq  = bO;
O3      0.17731`_0.00187   0.68466`_0.00178   0.46282`_0.00047 occ O-2   1             beq  = bO;
O4      0.37199`_0.00149   0.85840`_0.00164   0.99738`_0.00045 occ O-2   1             beq  = bO;
O5      0.28968`_0.00198   0.48780`_0.00203   0.21730`_0.00045 occ O-2   1             beq  = bO;
O6      0.55184`_0.00160   0.14427`_0.00165   0.19919`_0.00043 occ O-2   1             beq  = bO;
O7      0.28230`_0.00215   0.47256`_0.00198   0.06290`_0.00044 occ O-2   1             beq  = bO;
O8      0.98169`_0.00187   0.13972`_0.00182   0.95019`_0.00046 occ O-2   1             beq  = bO;
O9      0.82144`_0.00191   0.84972`_0.00211   0.54224`_0.00045 occ O-2   1             beq  = bO;
O10     0.31890`_0.00175   0.49309`_0.00196   0.29704`_0.00046 occ O-2   1             beq  = bO;
O11     0.33133`_0.00184   0.50384`_0.00197   0.53715`_0.00048 occ O-2   1             beq  = bO;
O12     0.28648`_0.00144   0.46606`_0.00146   0.91291`_0.00043 occ O-2 = ocW9;         beq  = bO;
O13     0.48161`_0.00182   0.29460`_0.00186   0.12691`_0.00044 occ O-2   1             beq  = bO;
O14     0.84724`_0.00213   0.81048`_0.00192   0.21296`_0.00045 occ O-2   1             beq  = bO;
O15     0.29708`_0.00205   0.48493`_0.00221   0.37513`_0.00046 occ O-2   1             beq  = bO;
O16     0.98421`_0.00207   0.15265`_0.00206   0.79046`_0.00047 occ O-2   1             beq  = bO;
O17     0.16281`_0.00214   0.98895`_0.00173   0.37957`_0.00048 occ O-2   1             beq  = bO;
O18     0.17424`_0.00188   0.01967`_0.00169   0.62005`_0.00049 occ O-2   1             beq  = bO;
O19     0.83122`_0.00224   0.53586`_0.00261   0.27692`_0.00053 occ O-2 = ocW10;        beq  = bO;
```

Space group P31c.

```
Synchrotron: r_exp  8.823 r_wp  9.483 r_p_dash  20.404 gof  1.075     r_bragg  4.02
Neutrons:    r_exp  3.434 r_wp  8.377 r_p_dash  11.452 gof  2.439     r_bragg  2.89
```

- Give details about constraints, restraints

Both data sets used jointly for structure solution and refinement.

z-coordinate of La6 fixed to 0 due to polar space group
Occupancy of O12 constrained to occupancy of W9.
Occupancy of O19 constrained to occupancy of W10.
Three Biso parameters for synchrotron data and three Biso parameters for neutron data.

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...).

According to [Yanovskii and Voronkova, 1975] who synthesized the single crystals of the compound the composition variation of La2W1+xO6+3x is between x=0-0.25, Laue class is 6/mmm, the crystals show no piezoelectric effect and extinction symbol is P — - c. The fact that having the single crystals they were not able to solve the structure has signalized that the structure was probably of the lower symmetry and twinned by merohedry. We have not obtained any solution in the hexagonal space groups P63/mmc, P63mc or P-62c. The trigonal space groups were therefore tried and the solution was found in P31c. It means that the crystal can be piezoelectric, but if it is composed from twinned microdomains of equal volume the piezoelectric effect cannot be observed.

Yanovskii V.K. and Voronkova V.I. Sov. Phys. Crystallogr. 20 (1975) no. 3 354-355