$TiOSO_4.2H_2O$, why the structure solution failed from synchrotron powder diffraction data ?

Negative Results · May 2025

DOI: 10.13140/RG.2.2.31641.12648

1 author:

Armel Le Bail
Le Mans University
488 PUBLICATIONS **10,432** CITATIONS

SEE PROFILE

$TiOSO_4.2H_2O$, why the structure solution failed from synchrotron powder diffraction data ?

Armel Le Bail

In 2010, August 06, Phillip English asked for help through the SDPD mailing list :

[sdpd] General questions/stuck

Dear SDPD group,

I stumbled onto this group from the back of the SDPD book by David et al. and I was wondering if some of you might be able to help me some difficulties I've been having completing a structural determination. I'm going to try to give as much detailed info as possible to give some context to my question, so I hope you'll forgive me if I bang on a bit. Also, this is the first time for me posting to a mailing group, so I hope I get the protocol right!

* I'm looking at the structure of $TiOSO_4.2H_2O$, the dihydrate in the series of $TiOSO_4$ and $TiOSO_4.H_2O$ whose structures have been well known for some time now. My supervisors and I are reasonably sure that the $TiOSO_4.2H_2O$ will contain the same motifs of Ti-O octahedra shared with SO_4 tetrahedra as seen in the rest of the series and in analogues of Zr and Hf (so that's our 'chemical information').

* I've collected two sets of laboratory X-ray diffraction patterns (an old Siemens and a newer machine installed last year at my university), two sets of synchrotron X-ray diffraction (from the APS and the Australian Synchrotron) and a relatively poor, but still possibly useful neutron diffraction pattern (deuterated). We are very confident that we have single-phase diffraction patterns.

* Following the general recipe/method for SDPD, I've obtained a unit cell that has been indexed using multiple programs and has been verified by the beamline scientists at the two synchrotron institutions.

* Using the 'space group explorer' in the program FOX, I've generated a list of possible spacegroups.

* In both the FOX and JANA2006 programs, I've used the Le Bail method to generate a list of integrated intensities to be used in the FOX, superflip and EXPO2004 routines.

Now, at this stage I fall down a bit. Looking at other papers of (relatively) similar structures, such as those in

http://scripts.iucr.org/cgi-bin/paper?la0055 and

http://pubs.acs.org/doi/abs/10.1021/ic00268a025

It seems they generated a Patterson map in order to determine the positions of heavy atoms. Now, I'm a bit of a newbie and I cannot for the life of me figure out how they did this. So the most basic of my questions is: how can I generate a Patterson map in either FOX or JANA2006? JANA2006 has the option of producing a Fourier map, but in order to do so I need to add atoms, which seems counter-intuitive. Quite confused on this issue :

Detouring from Patterson maps a bit, I've also tried invoking the FOX reverse Monte Carlo technique and the JANA2006 Superflip method, but I've received nothing but nonsense answers thus far from them. My first thought was that the unit cell might be incorrect, and so I checked into ways in which indexing from a synchrotron can go wrong, and noticed a quote in the David SDPD book about there being issues if two of the lattice constants are very long and one is short, and the peak that has been used to determine that short lattice constant is spurious. I have a similar situation with my indexed unit cell, (a ~ 18Ang, b~16Ang, c~5Ang) and so was wondering how I might check for this?

If anyone is interested enough in this problem to want to lend a helping hand in a more direct way, feel free to contact me at and I can provide any data files/extra info you might need. I am entering the final stages of my Ph.D., and while I would love to have the time to puzzle all these problems out myself and learn from them, I'm spending more time banging my head against walls than is useful at this point. That said, I am well aware that all of you are professionals with your own challenges to overcome, and demands on your time.

Thank you for your time and I hope to hear from some of you soon,

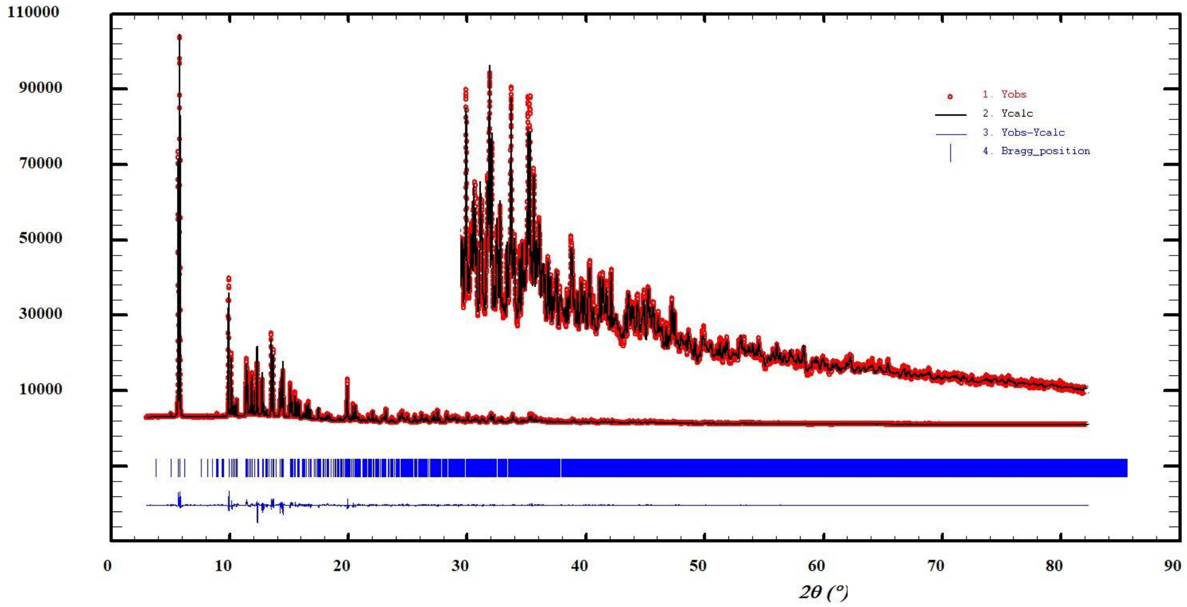
Phillip English

In June 2011, the thesis was published, entitled :“Structural Studies of Titanyl and Zirconyl Sulphate Hydrates”.

https://core.ac.uk/download/pdf/195631652.pdf

And the text shows that several scientists offered their help (including me) but all failed in solving the structure of $TiOSO_4.2H_2O$ from the synchrotron powder data.

In 2025, having time, being retired, I decided to look again at this problem and could find in the literature that the structure was solved finally by electron diffraction tomography (Klementová et al., 2017). I compared the calculated powder pattern to the original observed one and obtained a quite nice fit without any atomic coordinate refinement by the Rietveld method (Fig. 1).



So why the previous failure ?

Well, electron diffraction tomography is a fantastic technique providing single-crystal equivalent data from very small particles. And if the cell parameters of the thesis were confirmed, the final space group retained is Pn, acentric. Most attempts in the thesis were done in the $P2_1/n$ space group (for this set of monoclinic cell parameters). Indeed, the powder pattern does not show any exception to the 0k0, k = 2n extinction rule. However, the pattern starts at 3°(2θ) and the 010 should be at 2.837°(2θ)... One of the first thing I do, after having obtained the CIF from CCDC, was to see if the calculated intensity of the 010 was important. It is not, so close to zero that it could not be clearly observed. Extinction test with the Platon software provides, from the calculated intensities :

```
Analysis of Systematic Absences

=============================================================

Nr    Ex. Condition    Aver(I/sig(I)) Number of Refl  I/sigI     False? .T/F.

                 .True. .False. .True. .False. Max.False. H  K  L Ratio

=============================================================
12 E  ny H0L:H+L=2N     161.10    0.00    118      0      0.00      0  0  0 999.0
16 E 21x H00:H=2N       77.45    0.00      6      0      0.00    0  0  0 999.0
17 ? 21y 0K0:K=2N      276.84   19.01     20     20    39.13     0 15  0  14.6
18 E 21z 00L:L=2N      255.04    0.00     11      0      0.00    0  0  0 999.0
=============================================================
```

Of course, the 0,15,0 reflection is not detectable without overlapping, nor the 090 which is another 0k0 with k odd having high enough calculable intensity.

Another thing crystallographers do is a laser frequency doubling test which can be realized on powders, possibly establishing acentricity. But this had not been done, otherwise, if the compound had been positively confirmed as acentric, more efforts would have been done in the Pn space group for which there was no experimental evidence. Without such evidence the Pn choice was instinctively refused because it multiplies the difficulty by two, two more atoms to locate, 54 non-H independent atoms instead of 27 in $P2_1/n$. Moreover the density was not measured and Z could be either 12 or 16 (it is finally 12). Most searches were made for Z = 16, corresponding to 36 independent non-H atoms in $P2_1/n$ compared to 72 in Pn.

Today, knowing the solution, this is too late, but would it have been possible to solve the structure if more effort had been made in the Pn space group ? Probably yes.

For instance using the direct space software ESPOIR on the 1000 first extracted intensities with a model of 6 Ti, 6 S and 42 O atoms in scratch mode (all atoms moving free), a R=0.094 value is obtained at test 5 (4 hours per test, 8 millions moves and permutations per test) :

```
Test number :   5

 18-May-2025     8 hour 52 min  5 Sec

  ISEED =    117677727

  Object number  1 at test  5.  Previous minimum R=0.102 at test  2
     0 moves acc.      0 tested; Chi**2=0.464    , R=0.464
     0 perm. acc.      0 tested
     0 events did not improve the fit, DAMP = 1.000000


  Object number  1 at test  5.  Previous minimum R=0.102 at test  2

  43802 moves acc.  720018 tested; Chi**2=0.211    , R=0.211

   2191 perm. acc.   80001 tested

  26152 events did not improve the fit, DAMP = 0.853812


  Object number  1 at test  5.  Previous minimum R=0.102 at test  2

  61227 moves acc. 1441041 tested; Chi**2=0.172    , R=0.172

   2832 perm. acc.  160115 tested
```

```
36559 events did not improve the fit, DAMP = 0.715348

Object number  1 at test  5.  Previous minimum R=0.102 at test  2
65858 moves acc. 2160405 tested; Chi**2=0.173    , R=0.173
 2968 perm. acc.  240044 tested
39343 events did not improve the fit, DAMP = 0.585592

Object number  1 at test  5.  Previous minimum R=0.102 at test  2
66842 moves acc. 2887130 tested; Chi**2=0.149    , R=0.149
 2977 perm. acc.  320792 tested
39911 events did not improve the fit, DAMP = 0.463608

Object number  1 at test  5.  Previous minimum R=0.102 at test  2
67004 moves acc. 3603550 tested; Chi**2=0.140    , R=0.140
 2986 perm. acc.  400394 tested
39999 events did not improve the fit, DAMP = 0.353031

Object number  1 at test  5.  Previous minimum R=0.102 at test  2
67077 moves acc. 4321086 tested; Chi**2=0.130    , R=0.130
 2992 perm. acc.  480120 tested
40037 events did not improve the fit, DAMP = 0.252839

Object number  1 at test  5.  Previous minimum R=0.102 at test  2
67128 moves acc. 5056621 tested; Chi**2=0.125    , R=0.125
 2992 perm. acc.  561846 tested
40062 events did not improve the fit, DAMP = 0.162424

Object number  1 at test  5.  Previous minimum R=0.102 at test  2
```

```
 67232 moves acc. 5762705 tested; Chi**2=0.117    , R=0.117

  2992 perm. acc.  640300 tested

 40104 events did not improve the fit, DAMP = 0.089191


 Object number  1 at test  5.  Previous minimum R=0.102 at test  2

 67509 moves acc. 6482001 tested; Chi**2=0.105    , R=0.105

  2992 perm. acc.  720222 tested

 40224 events did not improve the fit, DAMP = 0.031491


 Object number  1 at test  5.  Previous minimum R=0.094 at test  5

 68259 moves acc. 7200000 tested; Chi**2=0.104    , R=0.094

  2992 perm. acc.  799999 tested

 40525 events did not improve the fit, DAMP = 0.010000


Final coordinates x,y,z and occupation numbers


Ti1    0.55437    0.40426    0.16027     1.000

Ti2    0.45376    0.99088    0.53909     1.000

Ti3    0.33490    0.09870    0.24589     1.000

Ti4    0.55613    0.59345    0.82824     1.000

Ti5    0.80126    0.08853    0.43717     1.000

Ti6    0.18898    0.50231    0.91788     1.000

S1     0.93255    0.16876    0.66779     1.000

S2     0.69337    0.65789    0.16318     1.000

S3     0.17894    0.65900    0.30072     1.000

S4     0.95432    0.83682    0.46716     1.000

S5     0.93656    0.48930    0.91650     1.000

S6     0.69482    0.99557    0.03239     1.000
```

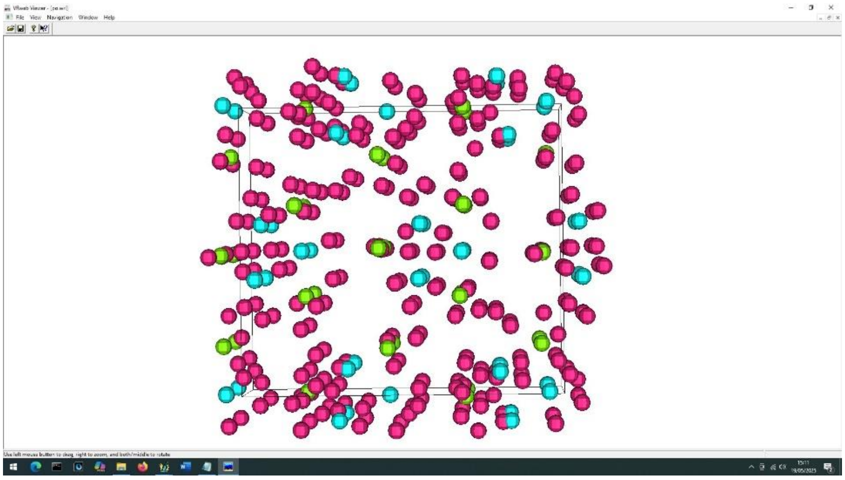
O1	0.16192	0.73343	0.06622	1.000
O2	0.83489	0.23774	0.05914	1.000
O3	0.36762	0.89865	0.13267	1.000
O4	0.93918	0.49371	0.57334	1.000
O5	0.54536	0.20119	0.24797	1.000
O6	0.05404	0.96616	0.89756	1.000
O7	0.04565	0.03709	0.48040	1.000
O8	0.46896	0.09510	0.74673	1.000
O9	0.86952	0.05178	0.20448	1.000
O10	0.73024	0.85781	0.45768	1.000
O11	0.18447	0.98195	0.86856	1.000
O12	0.44147	0.72653	0.95736	1.000
O13	0.07039	0.26840	0.08609	1.000
O14	0.10096	0.50811	0.11259	1.000
O15	0.70116	0.35997	0.56165	1.000
O16	0.50825	0.56635	0.51726	1.000
O17	0.30921	0.10272	0.22643	1.000
O18	0.24088	0.92988	0.68148	1.000
O19	0.62419	0.55991	0.57342	1.000
O20	0.19265	0.89355	0.33904	1.000
O21	0.68041	0.93394	0.27707	1.000
O22	0.79053	0.28715	0.16316	1.000
O23	0.74533	0.68388	0.91549	1.000
O24	0.51551	0.68861	0.60310	1.000
O25	0.23771	0.71006	0.38128	1.000
O26	0.48366	0.88880	0.33912	1.000
O27	0.66427	0.01854	0.76043	1.000
O28	0.94873	0.81535	0.16431	1.000

O29	0.78997	0.06164	0.12660	1.000
O30	0.02018	0.50402	0.42881	1.000
O31	0.77879	0.59796	0.13894	1.000
O32	0.41062	0.51525	0.70267	1.000
O33	0.98412	0.60916	0.83248	1.000
O34	0.52969	0.31122	0.33810	1.000
O35	0.60256	0.37078	0.86323	1.000
O36	0.73962	0.95588	0.83803	1.000
O37	0.77233	0.46202	0.30486	1.000
O38	0.17999	0.22784	0.77463	1.000
O39	0.77946	0.98381	0.46121	1.000
O40	0.51455	0.92824	0.71279	1.000
O41	0.16031	0.31606	0.50358	1.000
O42	0.98533	0.19817	0.54405	1.000

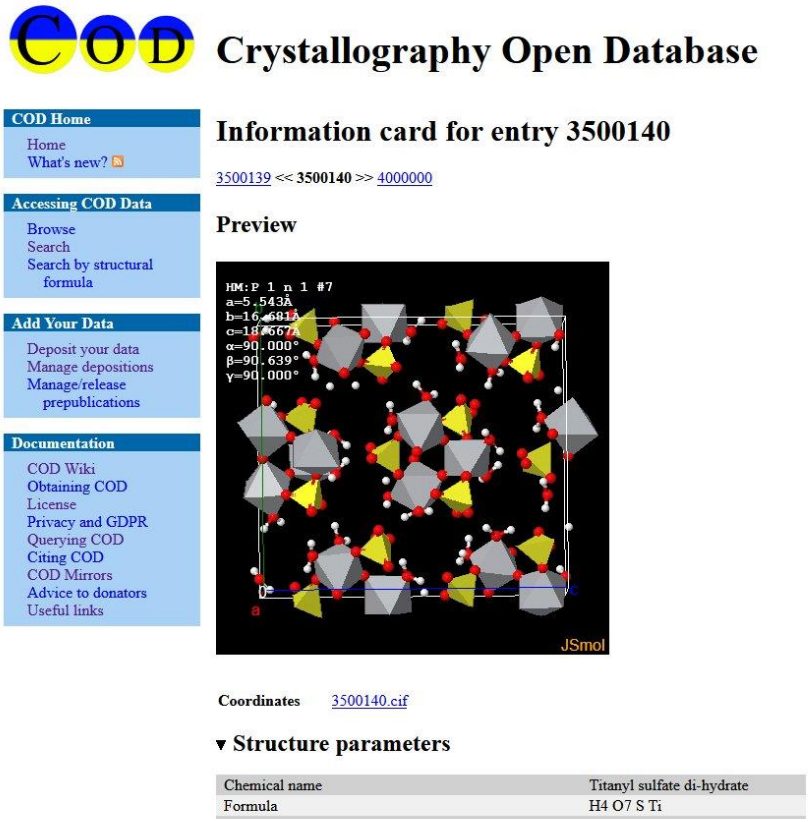
18-May-2025 12 hour 48 min 38 Sec

End of this test

And the plot of the positions allow for recognizing the motif of 3 Ti (blue) and 3 S (green) atoms aggregated in TiO6 octahedra and SO4 tetrahedra forming spirals along the short c axis :



The synchrotron file corresponding to these figures is now available from the CIF deposited at the Crystallography Open Database, after Rietveld-refined atomic coordinates. COD number :
https://www.crystallography.net/cod/3500140.html



Crystallography Open Database

COD Home
Home
What's new?

Accessing COD Data
Browse
Search
Search by structural formula

Add Your Data
Deposit your data
Manage depositions
Manage/release prepublications

Documentation
COD Wiki
Obtaining COD
License
Privacy and GDPR
Querying COD
Citing COD
COD Mirrors
Advice to donators
Useful links

Information card for entry 3500140

3500139 << **3500140** >> 4000000

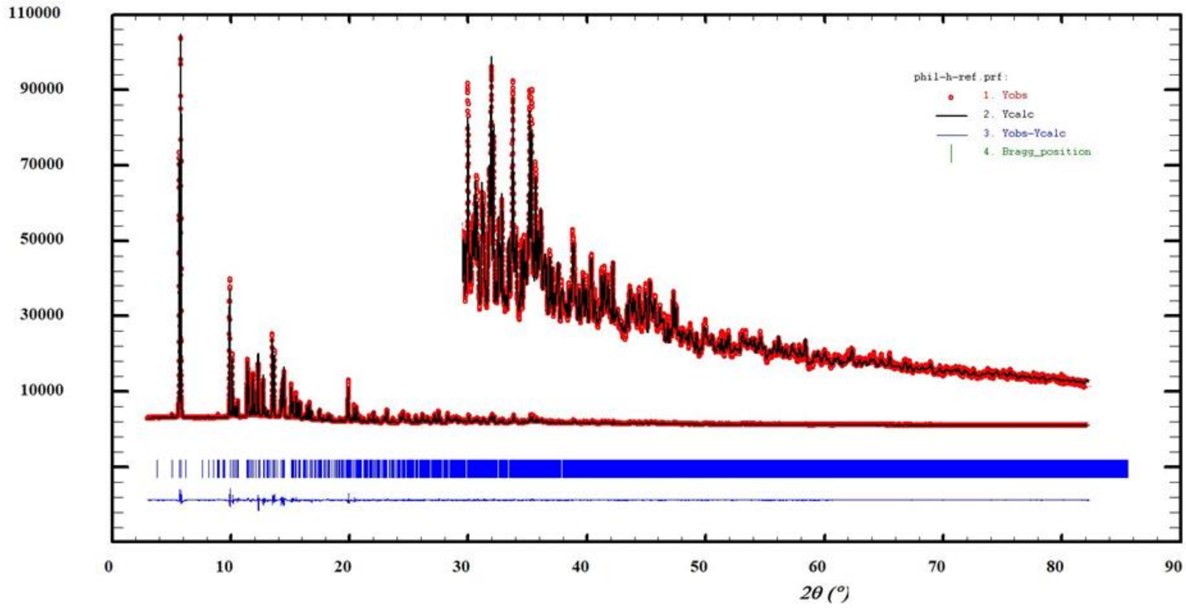
Preview

Coordinates 3500140.cif

▾ Structure parameters

Chemical name	Titanyl sulfate di-hydrate
Formula	H4 O7 S Ti

Fit after refinement of the coordinates (using restraints on H atoms) :



At least, the cell parameters accuracy from synchrotron powder data is much better than from electron diffraction tomography.

References

English, P. M. (2011). Thesis “Structural Studies of Titanyl and Zirconyl Sulphate Hydrates”. https://core.ac.uk/download/pdf/195631652.pdf

Klementová, M., Motlochová, M., Boháček, J., Kupčík, J., Palatinus, L., Pližingrová, E., Szatmáry, L. & Šubrt, J. (2017). Cryst. Growth Des. 17, 6762−6769.