

FullProf Suite Tutorial using a perovskite example.

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The session is intended for an audience of post-graduates and thesis students in the field of Solid State Chemistry and Physics. A basic knowledge of Crystallography and the Rietveld method is a pre-requisite for following properly the lecture.

Tutorial: Crystal and magnetic structure determination of the oxygen deficient perovskite $\text{YBa}_2\text{Mn}_2\text{O}_{5.5}$.

In this tutorial session we shall perform a complete analysis of X-ray and neutron diffraction data of the title compound, using the programs of the FullProf Suite. All the results have been recently published in the article:

“Crystal and magnetic structures of the Mn^{3+} orbital ordered manganite $\text{YBaMn}_2\text{O}_{5.5}$ ”
C. Perca, L. Pinsard-Gaudart, A. Daoud-Aladine, M.T. Fernández-Díaz and J. Rodríguez-Carvajal.
Chemistry of Materials **17**, 1835-1843 (2005)

The data files, at room temperature, corresponding to a laboratory X-ray diffraction pattern and two neutron diffraction patterns of different instruments and wavelengths will be used in the final refinement. The content of this part of the tutorial is in the file *RT_RX+Neutrons.ZIP*. There are three data files and three IRF files containing the characteristics of the instruments. There are also three individual PCR files that are appropriate for refining individually the three diffraction patterns and another file called *Multi-Pattern.PCR* that allow a combined refinement of all patterns simultaneously. The ZIP file must be decompressed in a directory (named, for instance, “YbaMn_RT”).

Another set of files, corresponding to neutron diffraction data taken on G4.1 (LLB), will be used to determine the magnetic structure of $\text{YBaMn}_2\text{O}_{5.5}$ as a function of temperature. The use of FullProf in cyclic/sequential mode to treat a large number of diffraction patterns will be shown. There are 59 data files (lg34783.dat up to lg34841.dat) corresponding to different temperatures and two PCR files adequate for refining the magnetic structure in two different temperature ranges. All these files are contained in the ZIP file called *data_G41.zip* that must be unzipped in a separated directory (named, for instance, “YbaMn_LT”).

Exercise number 1

After installing the FullProf Suite and configuring the file *winplotr.set*, open the file *YBaMn2O55_RX.dat* selecting the instrument format INSTRM=0. Play with the zoom option and select an angular region up to 60-70 degrees on 2θ . Make an automatic peak selection, save the peaks as DICVOL04 file. Run DICVOL04 and determine the unit cell. The wavelength is $\text{CuK}_{\alpha 1}=1.5406\text{\AA}$

Exercise number 2

Import the CIF file, using EdPCR, corresponding to the data of the Karppinen's article and calculate the powder diffraction pattern for $\text{CuK}_{\alpha 1}$ using the instrumental resolution function file: *rx.irf*. Compare with the experimental data in the file *YBaMn2O55_RX.dat*. Convert the PCR for refining (the provided *rx_Ammm.pcr* file does the work) and try to refine the crystal structure using the Karppinen's model. Notice that many small peaks are unindexed.

Exercise number 3

Determine the possible space groups of $\text{YBaMn}_2\text{O}_{5.5}$ after indexing the powder diffraction pattern. Verify that *Icma*, after re-arranging the ordering of cell parameters (exchange the *a* and *b* cell parameters with respect to those given in the Karppinen's article), is one of the most symmetric ones. (This exercise can be done individually at home!). Try to prepare by hand (using eventually EdPCR) an input file for the *Icma* space group taking into account that a translation of the origin, with respect to *Ammm*, is necessary. The provided file `sp_rx_RT.pcr` corresponds to the final refinement in *Icma*.

Exercise number 4

Convert the PCR file for X-ray diffraction for neutron diffraction and refine the data for 3T2 and D1A. The files `sp_D1A_RT.pcr` and `sp_3T2_RT.pcr` correspond to the final refinements for both instruments. The characteristics of these two neutron diffractometers can be read in the content of the instrumental resolution files: `3t2.irf` and `d1a.irf`.

Exercise number 5

Combine all refinement PCR files into a single multi-pattern refinement file and perform a final refinement using all the collected data at room temperature. You may try to construct the multiple pattern file using EdPCR and a copy of one of the single pattern files. The details can be finished by hand. The file `Multi-Pattern.pcr` does the final work.

Exercise number 6

Perform a sequential refinement of the cell parameters as a function of temperature.

Step 1: For doing that you must prepare a file doing a Le Bail fit with the file `lg34783.dat`, with a format corresponding to INSTRM=5, and then use the facilities already incorporated within WinPLOTTR. The input PCR file already prepared is called `YBaMn_Cell.pcr`. Remember to put the variable `Rpa=-2` in order to generate a file with extension “`.seq`” (SEQ file) where all the refined parameters are written at the end of refinement. The SEQ file has an “append” attribute, so new refinements are added at the end of the file, so before running the sequential refinement with all data files remember to delete the SEQ file if the starting PCR file has the same name as that you used for preparing the sequential refinement. Let us suppose that you have called this PCR file `ybacell.pcr`. Once you have this starting PCR file, which runs properly with the initial data file, you can go to the following step.

Step 2: You must select the button FP-CYC in the buttons' bar of WinPLOTTR, select a starting PCR file (`ybacell.pcr`) and then fill the fields of the window that opens after selecting the PCR file. You must give a code for the files and starting and finishing number of the files. In our case we can give as codes for the data files “lg34”, the starting number should be “783” and the final number “841”. You can click on the boxes: “Save PRF files”, “Save HKL files” and “Plot cyclic FullProf results”. As variable external parameter you can enter: “Temperature”. After clicking on OK button, WinPLOTTR launch FullProf in console mode and it will plot the variable parameters at the end. If something is going wrong you can consult the file `ybacell.log`, where the normal FullProf screen output has been re-directed.

Exercise number 7

Determine the magnetic structure at low temperature of $\text{YBaMn}_2\text{O}_{5.5}$ using the data from G41. For that the data file to be used is called `lg34783.dat`, with a format corresponding to INSTRM=5. Use `BasIreps` for symmetry analysis. The file `ybamag.pcr` does the final work.

Exercise number 8

Perform a sequential refinement of the magnetic structure of $\text{YBaMn}_2\text{O}_{5.5}$ using the facilities already incorporated within WinPLOTR. For doing that you must prepare a copy of the PCR file corresponding to the previous exercise to be used as starting PCR file. You must follow the steps already explained for exercise number 6.

You must take into account that the refinement of the magnetic structure becomes unstable as soon as the paramagnetic state is reached. In order to avoid divergence or instabilities in running the program you can make box constraints for the value of the magnetic moments. The file `ybamag.pcr` already contains these constraints.

You can verify that a blind refinement is unable to detect the presence of a spin reorientation. Looking into the PRF files `lg34808.prf` up to `lg34815.prf` it is easy to see that the magnetic structure just before the paramagnetic state cannot be described with the low temperature phase.