FullProf Tutorial

How to extract structure factors from X-ray powder diffraction and solve the structure using direct space methods. A *trivial* example: Y_2O_3

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We provide in this document an introduction to the use of the program **FullProf** for extracting integrated intensities from powder diffraction data using the Le Bail method, as well as preparing a file with overlapped reflections to be used in simulated annealing work. The preparation of the PCR file for simulated annealing and the complete determination and refinement of the structure is also illustrated step by step. This document is written just to provide tricks and hints for running the program. Knowledge of basic crystallography and the basis of the powder method is a pre-requisite for following the tutorial.

Extracting integrated intensities using the Le Bail Method.

The first step in structure determination using strictly powder diffraction data is the indexing stage. For this step we shall use as an interface, **WinPLOTR** or **WinPLOTR-2006**. The first program works only in Windows and the second one is multi-platform (Windwos, Linux and MacOS). We distribute two programs because **WinPLOTR-2006** has features lacking in **WinPLOTR** and it has not all the possibilities of **WinPLOTR**. We intend to implement all the features of **WinPLOTR** within WinPLOTR-**2006** progressively. These programs are accessible from the **FullProf Suite** (FPS) Toolbar by clicking on the icons:

WinPLOTR  **or** **WinPLOTR-2006** 

Extracting integrated intensities or structure factors from powder diffraction data once we know the unit cell parameters is straightforward in well crystallised samples; however there are cases where the tasks may be complicated due to the presence of broadening due to micro-structural effects. To avoid, from the beginning, pitfalls due to the handling of full width at half maximum it is convenient to work with instrumental resolution function files. This has as an additional advantage the production of micro-structural files containing information about the size and strain effects of your sample.

The procedure used for extracting the integrated intensities within **FullProf** (profile matching) is currently known as Le Bail fitting [A. LeBail, H. Duroy and J.L. Fourquet, *Mat. Res. Bull.* **23**, 447(1988)]. It does not require any structural information except approximate unit cell and resolution parameters. A similar method developed by Pawley uses traditional least squares with constraints [G.S. Pawley, *J. Applied Cryst*. **14**, 357 (1981)]. A discussion about the profile matching algorithm involved in this kind of refinement may be found in [J. Rodríguez-Carvajal, *Physica B* **192**, 55 (1993)]. This method makes the data input much simpler and enlarges considerably the field of application of powder pattern profile refinement. However the constraints applied to the refinement are far less severe than for Rietveld refinement and

profile matching is thereby more prone to instabilities if profile shape parameters or micro-structural parameters are refined. In **FullProf** this refinement mode can be used in two ways:

1. *Profile Matching with constant scale factor* (`Jbt=2`). In this mode the scale factor is not allowed to vary and integrated intensities are refined individually using iteratively the Rietveld formula for obtaining the integrated *observed* intensity. The recommended procedure is as follows:
   - For the first refinement, set `IRF(n)` of the phase *n* undergoing profile matching to 0 and the number of refined parameters (`MAXS` on **line 13**) to zero. Set to 0 the flag controlling the automatic assignment of refinement codes (`Aut=0`). Run **FullProf** for a few cycles (say 10). This will set up the *hkl* 's and intensity file **CODFILn.hkl**.
   - If the result of the above step is satisfactory (see plot!), rename the file **CODFIL.new** to **CODFIL.pcr**, or use directly **CODFIL.pcr** if it was automatically updated. Edit the new **CODFIL.pcr** file to select the parameters to refine. The progression of the refinement is very similar to that used for Rietveld refinement: zero point of detector, background parameters and lattice constants.

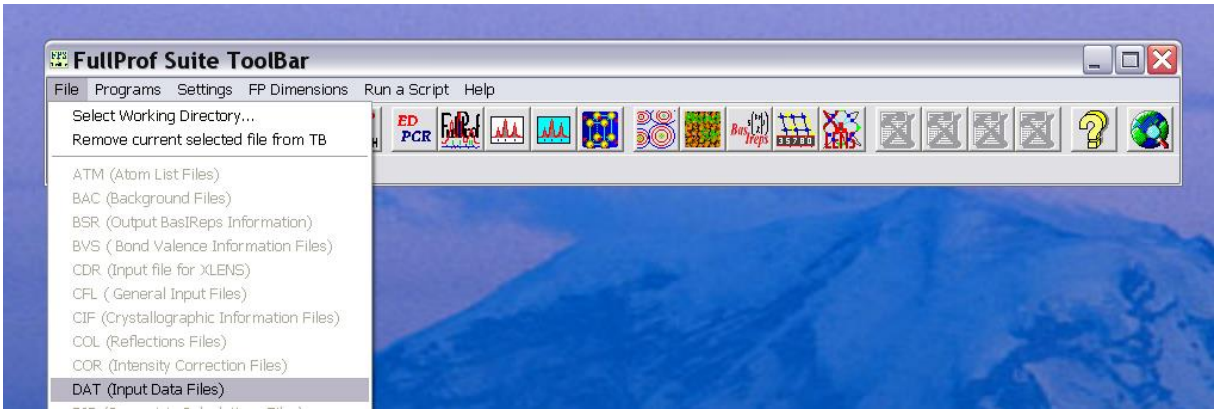
   In this mode of refinement **FullProf** cannot calculate *theoretical* line intensities and all *hkl* values permitted by the space group are considered and included in the refinement, which sometimes means a lot of reflections! Using this type of refinement one has to bear in mind that the starting cell parameters and resolution function determines to a large extend the obtained intensity parameters. One cannot expect to refine properly the cell parameters of a compound with a severe overlap of reflections if the starting parameters are of poor reliability. It is wise to start with low angle reflections (without refining the FWHM parameters) and progressively increase the angular domain.

2. *Profile Matching with constant relative intensities* (`Jbt=3`). In this mode the intensities are held fixed and only the scale factor is varied. Since profile matching does not require the calculation of the structure factors it runs faster than Rietveld refinement.

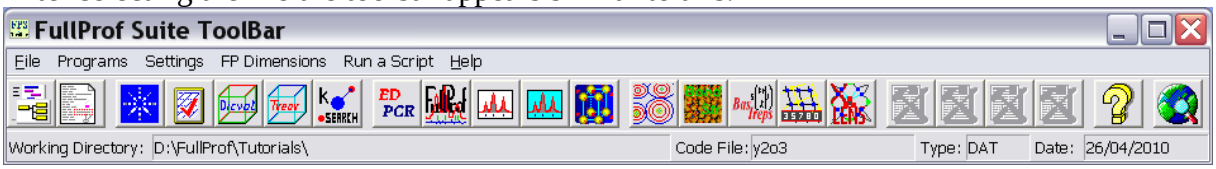
3. *Profile Matching with biased intensities* (`Nat≠0`). In the normal Le Bail fit the intensity of overlapped reflections that are very close are taken equal. This may be quite wrong for solving a crystal structure. When one knows a significant part of the structure it is possible to biased the partitioning of overlapped reflections according to the structure factors of the partial structure. For doing that one has to put a list of atoms. The program takes as starting intensities (when `Irf=0`) those calculated using the provided structure and then applies the algorithm that maintains as much as possible the partitioning imposed by the structure.

Extracting integrated intensities from the diffraction pattern of Y_2O_3 taken in a conventional diffractometer.

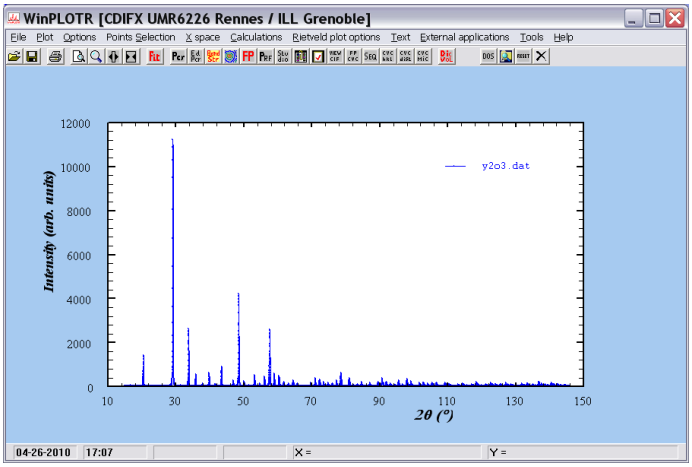
Use **WinPLOTR** to visualise the diffraction pattern of Y_2O_3 (file `y2o3.dat`, `Ins=0`). For indexing that we shall use only the **DICVOL06** program (Treor90 is also perfectly working). For starting, the user should open the **FullProf Suite** Toolbar by clicking on its icon. In the File menu select: Select Working Directory and then load the data file `y2o3.dat` into the toolbar.

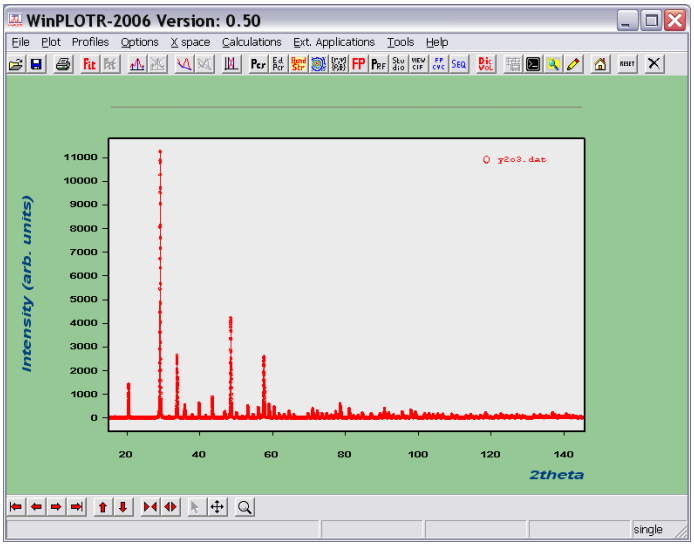


After selecting the file the toolbar appears similar to this:



Clicking on the **WinPLOTR** (or **WinPLOTR-2006**) icons of the toolbar we obtain a plot of the data.





Steps of the procedure

- Use the mouse to select an area up to 80 degrees in 2θ in order to be sure of getting at least 25 visible peaks.

In **WinPLOTR**

- Select from the Point Selection menu the item: Automatic peak search

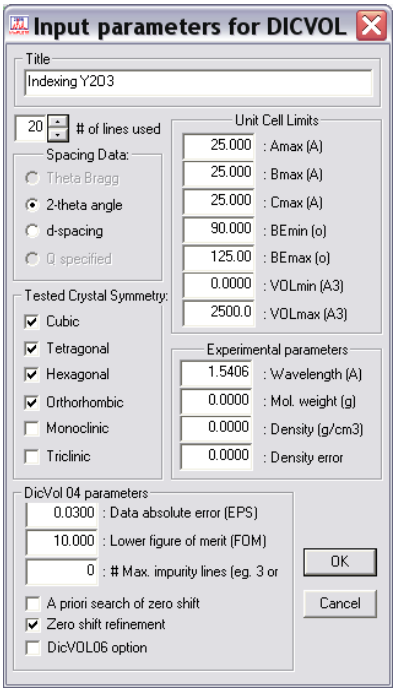
In **WinPLOTR-2006**

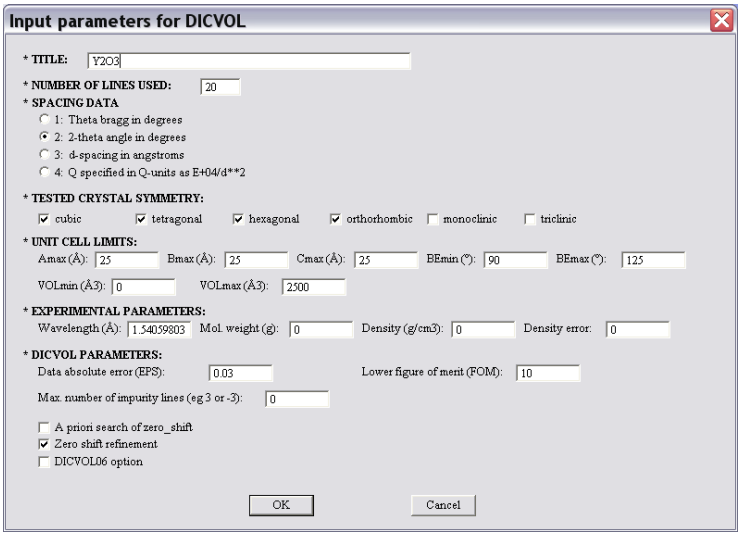
- Select from the Calculations menu the item: Peak Detection → Enable and then repeat the selections but now with Calculations→ Peak Detection→ Auto detection

For both

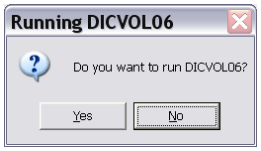
- Adjust the value of Peak threshold to 0.01 and eventually the Background threshold to a lower value than the default. Do not forget to select Cu-kα doublets! Click OK and run the procedure. The positions of the automatically detected peaks are shown in the screen as vertical bars.

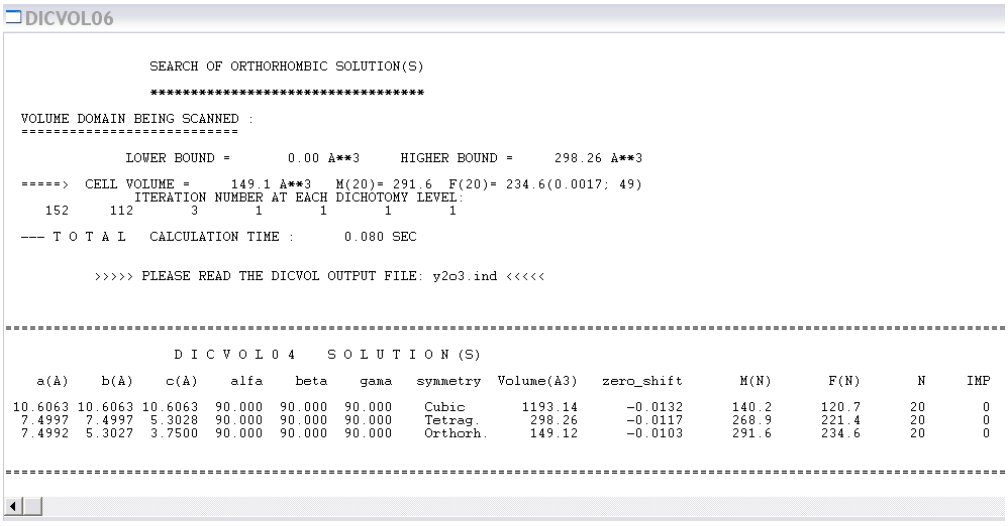
- In **WinPLOTR** go to the Point Selection→ Save as → Save points for DICVOL items and complete the items "Title" (give just the name of the compound: Y2O3) and activate the boxes containing the crystal systems to be tested. For instance activate the boxes "cubic", "tetragonal", "hexagonal" and "orthorhombic". Click on OK when finished. In **WinPLOTR-2006** the sequence is: Calculations→ Peak Detection→ Save Peaks→ DICVOL format. The dialogs for the two programs are as below.



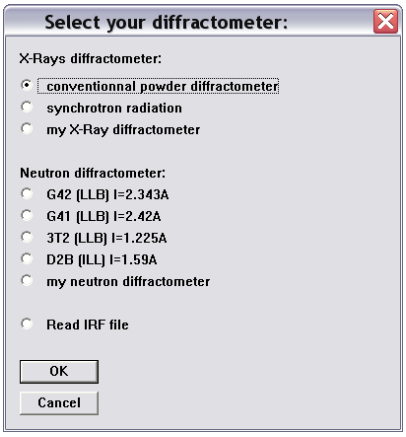


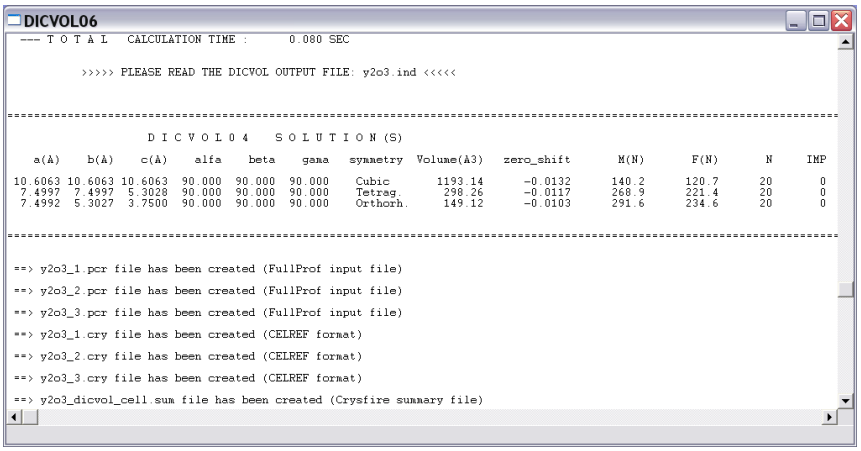
- The program responds with an information box telling that the desired file has been created. Clicking on OK the program proposes to edit the file. Do that only if you want to modify something. After that the program proposes to run automatically **DICVOL**. Select yes!

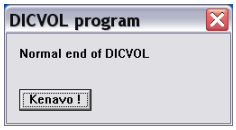




- After running **DICVOL**, if a solution has been found the program proposes to select the type of diffractometer you have in order to select approximate FWHM (`U,V,W`) parameters or to read an instrumental resolution function file. In this case just select Conventional Powder Diffractometer. A message signalling the end of the run appears on the screen. Look at the list of files created by **DICVOL**. Depending on the number of solutions various PCR files for running the Le Bail algorithm by **FullProf** are created.

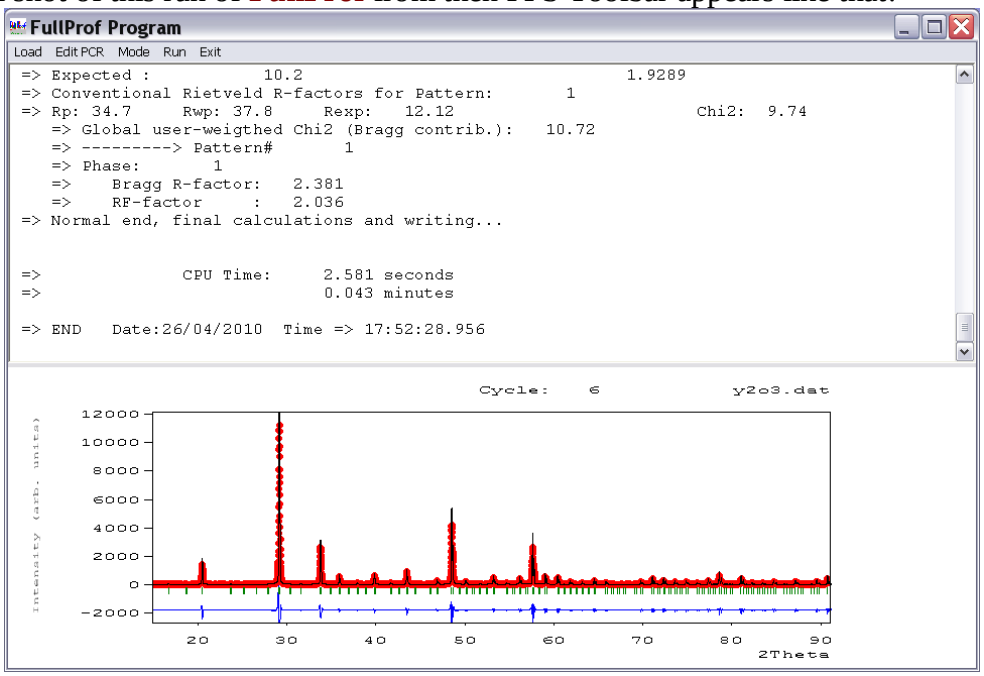






- Edit one of these files. In particular the first one that is called `y2o3_1.pcr`. Notice that only the wavelength of Cu-Kα_1 is given. Change this by putting `Lambda2`=1.5444 and `Ratio`=0.5. Read the warning messages written in the PCR file. The data have been taken with a graphite monochromator, so $\cos^2(2\theta_M)$= $\cos^2(26.5545)$= `Cthm`=0.8001. This number should be written by hand in the file.
- The space group attributed by **DICVOL** (or **TREOR**) is the holohedral group of the crystal system. In our case this group is *P m 3 m*. The determination of the real space group is done in a further step (see below).
- Run **FullProf** from **WinPLOTR** by clicking on the button `FP` (or from the FPS Toolbar, clicking on ). Select the PCR file `y2o3_1.pcr` and then the data file: `y2o3.dat`.

A screen shot of this run of **FullProf** from then FPS Toolbar appears like that:

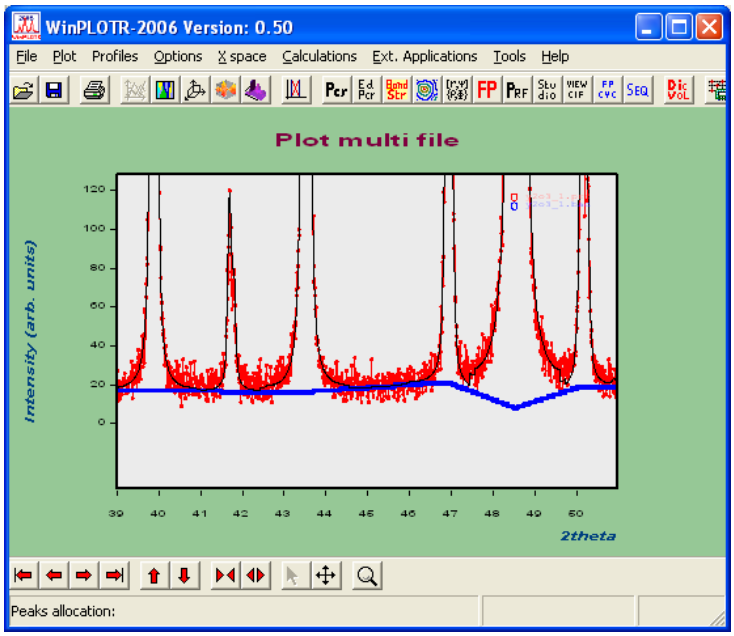


- Re-start now using the full range and put `Irf=0` in order to generate all reflections in the new range. Run **FullProf** from **WinPLOTR** by clicking on the button `FP`. You can follow directly in the screen the progress on the refinement.

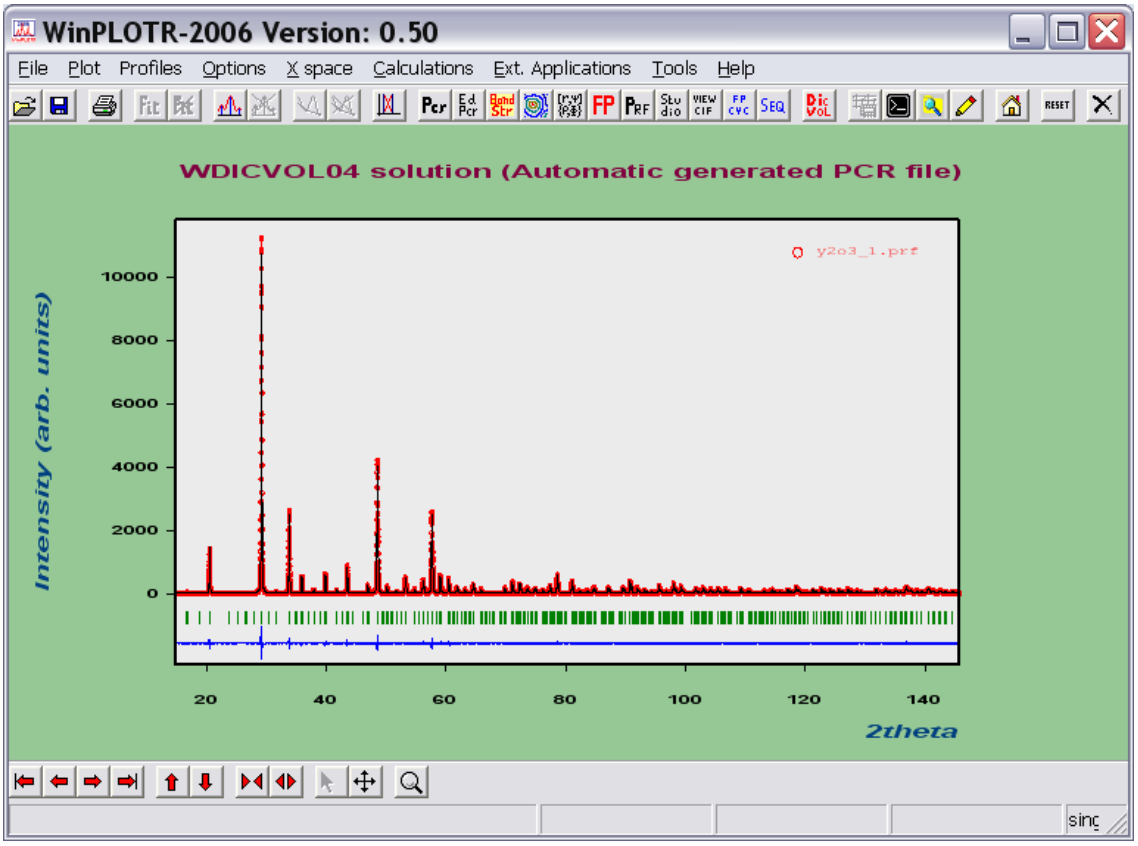
- Now put `Aut=1` and refine the cell parameters, the zero point and the `U`, `V` and `W` parameters, some background intensities, as well as the `eta0` and `X` parameters of the pseudo-Voigt function. When the refinement converges the procedure is finished and a series of output files have been generated depending on the values of some control parameters.

  Be careful with the automatic linear background selected by **WinPLOTR** when looking for peaks. This has to be submitted to inspection by an option of **FullProf** (`Ppl=2`) allowing saving the background separately and then it can be superimposed

to the diffraction pattern. It is easy to see if there is some mistake of some points that are too close to peak positions and then have to be changed and repeat the refinement. A situation similar to that described above is provided in the following picture in which we have represented also the background together with the normal representation of the plot.



The noticeable background point should be removed from the file!
A final refinement appears as below in **WinPLOTR-2006**:



Notice that there are many more tick markers that experimental peaks in the diffraction pattern. This is because we have used the space group *P m 3 m* without systematic extinctions

The output file after running a Le Bail fit

Primary integrated intensity file: **CODFILn.hkl**

The format of this file depends on the value of the indicator `Jbt`. For `Jbt=2` the header of the file is similar to the following:

```
Pattern# 1 Phase No: 1 Y2O3 Lambda:  1.540600 CELL:  10.6046 10.6046 10.6046   90.0 90.0 90.0
     576       0    0.00  SPGr: P m 3 m  <-- The number of effective reflections may be lower
   2   0   0    6          3.783          0.346      16.7066       0.1023
   2   1   0   24          0.233          0.174      18.6953       0.1022
   2   1   1   24        153.099          1.179      20.4980       0.1022
   2   2   0   12          0.981          0.233      23.7119       0.1022
   2   2   1   24          0.263          0.099      25.1732       0.1023
   3   0   0    6          0.263          0.099      25.1732       0.1023
   3   1   0   24          2.121          0.271      26.5591       0.1024
   3   1   1   24          5.644          0.339      27.8810       0.1025
   2   2   2    8       1282.459          3.065      29.1476       0.1027
   3   2   0   24          4.518          0.283      30.3658       0.1028
   3   2   1   48          9.059          0.436      31.5413       0.1030
.........
```

Notice that the wavelength, cell parameters and space group symbol are provided in order to be used by other programs. The first three items in the second line are: Number of lines, "numor" (number related to the use of ILL database, which is of no interest here) and temperature of the sample.

The items of the rest of lines are:

```
 h, k, l, mult, Intensity, Pseudo-sigma, 2theta/T.O.F./Energy, FWHM
```

Here the intensity contains all geometrical and physical factors multiplying the square of the structure factors. The units are counts × degrees or counts × micro-seconds or counts × keV, depending of the scattering variable units.

In the case of `Jbt=-2` the header of the file is as before except that in the place of the integrated intensity the structure factors are written. Of course they are not in absolute units when no information about the structure has been provided.

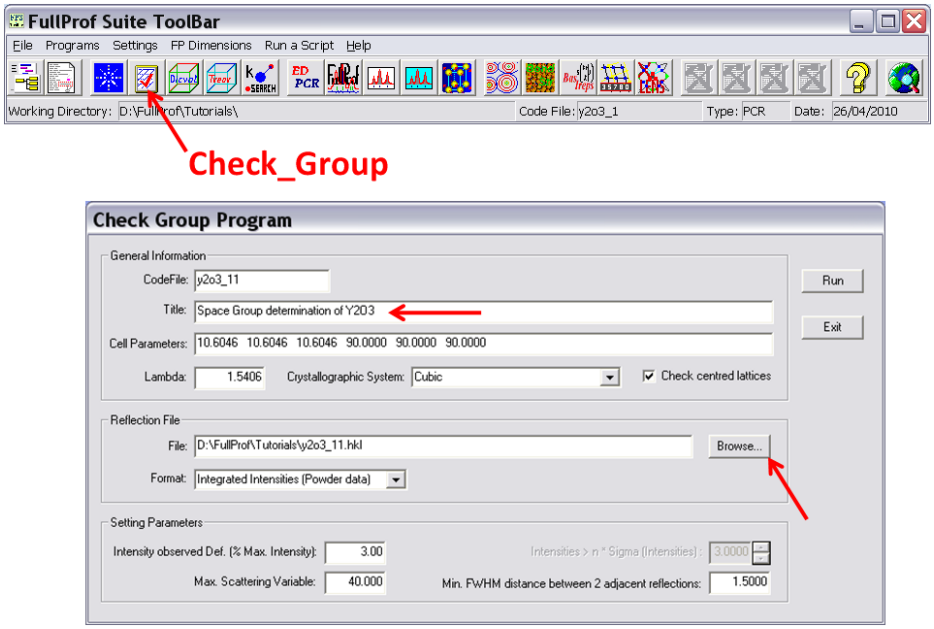
Exercise: Modify `Jbt` and put `Irf=0` in the previous PCR files to see what happens.

Determining the space group from powder patterns

The determination of the space group form powder patterns is much more difficult than with single crystals. In some cases it is nearly impossible and one has to use other techniques, like electron diffraction, to select a space group for solving the structure. However there are several programs trying to provide some hints about the possible space group. In the **FullProf Suite** there is a small utility for helping to find the space group. This is a program called

Check_Group that reads the primary hkl-file coming from the Le Bail fit (described in the previous paragraph) and some indications from the user to classify the possible space groups in terms of a merit figure.

The program can be invoked by clicking on the toolbar as indicated in the following panel:



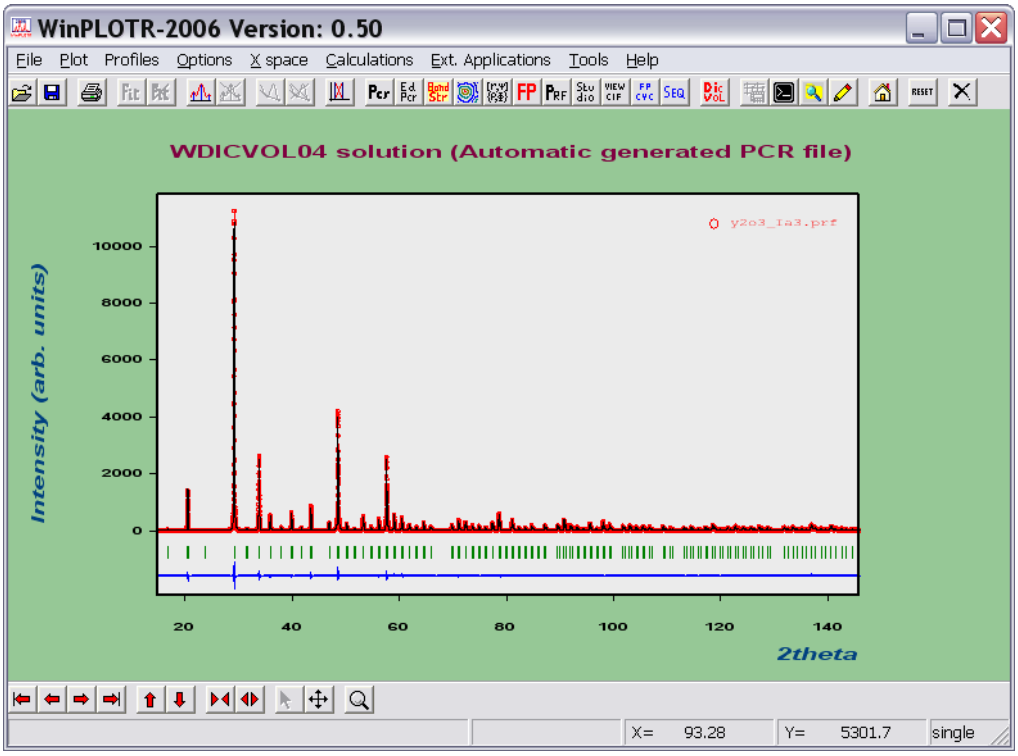
When the dialog opens the first thing to do is to click on the Browse button in order to select the file generated by **FullProf** that has the name `y2o3_11.hkl`. This is the file that is updated for each run of a Le Bail fit and contains all the information needed for running **Check_Group**. After selecting the file all the appropriate boxes of the dialog are filled with the stored information except the Title that should be introduced by the user if needed.
Once the information has been checked for correctness the used may play with the setting parameters in the bottom part of the dialog. It is important not to go to very high angle in order to avoid overlap as much as possible. If we let the default values (as shown in the panel) and we click on the Run button, the program runs and shows the results that may also be seen in the output file: `y2o3_11.spg`. The important part of this file is for our case:

```
 => LIST OF POSSIBLE SPACE GROUPS, a total of 23 groups are possible
    ------------------------------------------------------------------
    Number(IT)      Hermann-Mauguin Symbol     Hall Symbol         Merit
    ------------------------------------------------------------------
      206                   I a -3                -I 2b 2c 3         2.22
      214                   I 41 3 2              I 4bd 2c 3         2.00
      211                   I 4 3 2               I 4 2 3            1.82
      217                   I -4 3 m              I -4 2 3           1.82
      197                   I 2 3                 I 2 2 3            1.82
      229                   I m -3 m              -I 4 2 3           1.82
      204                   I m -3                -I 2 2 3           1.82
      199                   I 21 3                I 2b 2c 3          1.82
      222                   P n -3 n:1            P 4 2 3 -1n        1.67
      223                   P m -3 n              -P 4n 2 3          1.33
      218                   P -4 3 n              P -4n 2 3          1.33
      201                   P n -3:1              P 2 2 3 -1n        1.18
      224                   P n -3 m:1            P 4n 2 3 -1n       1.18
      205                   P a -3                -P 2ac 2ab 3       1.18
      213                   P 41 3 2              P 4bd 2ab 3        1.11
```

. . . . . .

This gives the ordered list of possible space groups.

One has to check properly the provided result because the final assignment is only possible after solving and refining the crystal structure. In our case the first space group is the correct one. The whole process of refining the profile with the Le Bail fit should now be repeated starting with `Irf=0` and putting the space group *I a -3* in the PCR file (let us suppose that we have copied the file `y2o3_1.pcr` into `y2o3_Ia3.pcr`). After doing that the final refinement looks like the following panel:



The tick marks correspond only to the allowed Bragg reflections of the space group *I a -3*. Notice that the density of tick marks is much lower than that corresponding to the holohedral space group *P m 3 m*.

Other output files after running a Le Bail fit

Apart from the primary hkl-file used in Le Bail fits one can generate other files by putting the items `Hkl` and/or `Fou` with values different from zero. An interesting option is putting `Fou=4`, the program then generates output files for **GFourier** to calculate a Patterson map.
Exercise: Put `Fou=4` in the previous PCR files and run **FullProf** from **WinPLOTR-2006**. Use the program **GFourier**, by clicking on its corresponding icon in the FPS toolbar  to calculate and visualise the Patterson map.

Here we reproduce a corrected part of the manual of **FullProf** for the different `Hkl` options. The name of the generated file is **CODFIL.hkl** and contains the complete list of reflections of each phase. This file can be used as a **CODFILn.hkl** files for new runs.

- **Hkl=1**
  - If **Job < 2**

Code, h,k,l , $mult, d_{hkl}, 2\theta$, FWHM, I_{obs} , I_{calc} , $I_{obs} - I_{calc}$

➢ If **Job > 1**

h,k,l , $mult, I_{calc}, 2\theta, d_{hkl}$

- **Hkl =2,-2**

  Output for EXPO

  h,k,l , $mult, \sin\theta/\lambda, 2\theta, FWHM, F^2, \sigma(F^2)$

- **Hkl =3,-3**

  Output of real and imaginary part of structure factors (only for crystal structures)

  h,k,l , $mult, F_{real}, F_{imag}, 2\theta, Intensity$

If Hkl is negative the structure factors are given for the conventional cell, otherwise the structure factor corresponds to the non-centrosymmetric part of the primitive cell.

- **Hkl =4**

  Output of: $h,k,l,F^2,\sigma(F^2)$.

  Where the quantity F^2 is the *observed* structure factor squared. The file may be used as an input for a *pseudo-single crystal* integrated intensity file using `Cry=1` and `Irf=4`.

- **Hkl =5**

  Output of: $h,k,l,mult,F_{calc},T_{hkl},d_{hkl},Q_{hkl}$

  Where the quantity F_{calc} is the module of the calculated structure factor. This file can be used as an input for `Jbt=-3 Irf=2` in order to perform quantitative analysis without re-calculating the structure factors for each cycle. The F_{calc} values are given in absolute units for the conventional unit cell.

If the user wants **FullProf** to use integrated intensities for making a simulated annealing work for solving or completing the structure, the indicator `Jvi`, appearing when `More=1` in the line containing the number of atoms, that follows immediately after the mentioned line should be put equal to 11 (`Jvi=11`). For doing that, the user may open the PCR file used for the Le Bail fit within **EdPCR**, then click in the button and tabs: Output→ Phases Output Information→ Overlapped Peaks List (INT) and then tick the Overlapped Peaks check box. After saving, the PCR file will contain the value `Jvi=11`. In such a case the program generates an additional file called **CODFILn_cltr.int** in which the integrated intensities of overlapped clusters of reflections are written. The header of this file (in our case `y2o3_Ia31_cltr.int`) is like:

```
! Phase No:   1  Y2O3           Overlapped reflections re-grouped  -> Obs = j LP F^2
(3i4,2f16.5,i4,3f14.4)
  1.54060    0   2    0.0000
    0.8001    0.0000
   2   0   0         3.91339         0.33413   1        0.0000        0.0000       16.7060
   2   1   1       146.11604         1.14988   1        0.0000        0.0000       20.4973
   2   2   0         1.50771         0.24188   1        0.0000        0.0000       23.7111
   3   1   0         0.51602         0.21285   1        0.0000        0.0000       26.5582
   2   2   2      1243.60303         3.06322   1        0.0000        0.0000       29.1465
   3   2   1         6.71182         0.41137   1        0.0000        0.0000       31.5402
   4   0   0       295.82135         1.61802   1        0.0000        0.0000       33.7809
   3   3   0        -1.00000         0.42124   1        0.0000        0.0000       35.8976
   4   1   1        67.20276         0.59575   1        0.0000        0.0000       35.8976
   4   2   0        13.68797         0.52158   1        0.0000        0.0000       37.9114
   3   3   2        76.81688         0.91308   1        0.0000        0.0000       39.8381
   4   2   2        12.02710         0.50658   1        0.0000        0.0000       41.6900
   4   3   1        -1.00000         0.52226   1        0.0000        0.0000       43.4770
   5   1   0       105.58928         0.73859   1        0.0000        0.0000       43.4770
```

```
......
  11    6    3        33.77916         0.38284    1        0.0000        0.0000      138.7305
  10    8    2        69.84793         0.91119    1        0.0000        0.0000      140.5987
   9    8    5        -1.00000         0.18286    1        0.0000        0.0000      142.5442
  11    7    0        -1.00000         0.18284    1        0.0000        0.0000      142.5442
  12    5    1        -1.00000         0.18286    1        0.0000        0.0000      142.5442
  13    1    0        39.44728         0.36570    1        0.0000        0.0000      142.5442
......
```

A negative value of the intensity means that the corresponding reflection contributes to the first positive reflection following in the list. For instance the reflections (9 8 5), (11 7 0), (12 5 1) and (13 1 0) contribute altogether with an intensity of 39.44 to a single observation. The degree of overlap can be controlled by the user modifying the parameters `RMub` and `RMuc` (see the **FullProf** manual).

Solving the structure of Y_2O_3. Illustration of the use of simulated annealing with FullProf

Let us assume that the space group of Y_2O_3 is *I a -3* which is the one having the highest figure of merit after running the program **Check_Group**. Let us also suppose that we have determined the density and, knowing the cell parameters and the molecular weight we have obtained that Z=16, so there are 16 formula units per unit cell. Using **WinPLOTR**, or looking into the International Tables, we obtain the following set of Wyckoff positions (other than the general position of multiplicity 48):

```
=> Special Wyckoff Positions for I a -3

    Multp      Site        Representative Coordinates (centring translations excluded)
     24        d              x,0,1/4              -x,1/2,1/4           0,1/4,x
                              1/2,1/4,-x           1/4,x,0              1/4,-x,1/2
                              -x,0,3/4             x,1/2,3/4            0,3/4,-x
                              1/2,3/4,x            3/4,-x,0             3/4,x,1/2

     16        c              x,x,x                x+1/2,-x+1/2,-x      -x,x+1/2,-x+1/2
                              -x+1/2,-x,x+1/2      -x,-x,-x             -x+1/2,x+1/2,x
                              x,-x+1/2,x+1/2       x+1/2,x,-x+1/2

      8        b              1/4,1/4,1/4          3/4,1/4,3/4          3/4,3/4,1/4
                              1/4,3/4,3/4

      8        a              0,0,0                1/2,1/2,0            0,1/2,1/2
                              1/2,0,1/2
```

We have 2×16=32 Y atoms and 3×16=48 O atoms. They can be distributed in a number of ways.

It is clear that Y atoms should be in special positions and the total multiplicity should be 32, so we are faced to three possible options:
a-Y: Three Y sites in the positions 8a, 8b and 16c
b-Y: Two Y sites in the positions 24d and 8a
c-Y: Two Y sites in the positions 24d and 8b
d-Y: Two Y sites in the positions 16c, 16c'

For oxygen atoms, total multiplicity equal to 48, we have the following options:
a-O: A single atom in general positions 48e (compatible with all Y distributions)
b-O: Two O sites in the positions 24d, 24d' (compatible with all Y distributions)

c-O: Three O sites in the positions 24d, 16c, 8a (incompatible with a-Y and b-Y)
d-O: Three O sites in the positions 24d, 16c, 8b (incompatible with a-Y and c-Y)
e-O: Three O sites in the positions 16c, 16c', 16c" (compatible with all Y distributions)
f-O: Four O sites in the positions 8a, 8b, 16c and 16c' (only compatible with option d-Y)

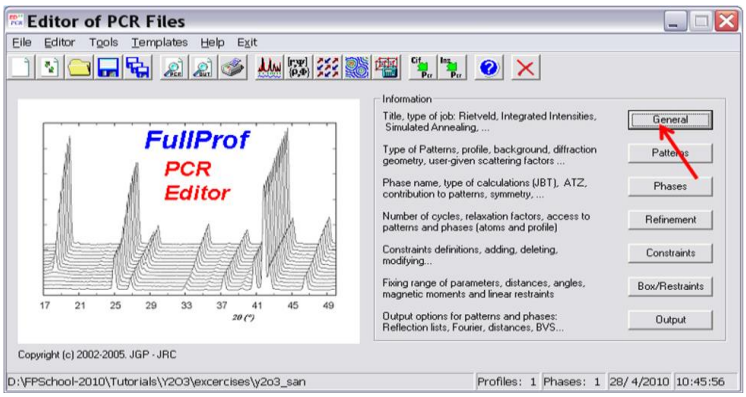
We have only 17 possible combinations of the two types of atoms that can be summarized as:
1:(a-Y, a-O) with 4 free parameters; 2:(a-Y, b-O) with 3 free parameters; 3:(a-Y, e-O) with 4 free parameters.
4:(b-Y, a-O) with 4 free parameters; 5:(b-Y, b-O) with 3 free parameters; 6:(b-Y,d-O) with 3 free parameters; 7:(b-Y, e-O) with 4 free parameters.
8:(c-Y, a-O) with 4 free parameters; 9:(c-Y, b-O) with 3 free parameters; 10:(c-Y,c-O) with 3 free parameters; 11:(c-Y, e-O) with 4 free parameters.
12:(d-Y, a-O) with 5 free parameters; 13:(d-Y, b-O) with 4 free parameters; 14:(d-Y,c-O) with 4 free parameters; 15:(d-Y, d-O) with 4 free parameters; 16:(d-Y, e-O) with 5 free parameters and 17:(d-Y,f-O) with 4 free parameters.

We can test all the configurations trying to determine the free parameters using simulated annealing within **FullProf**, but, from the beginning we can consider the less reliable configurations as those having three O sites on the ternary axes (those containing e-O), or two Y sites on the ternary axes (those containing d-Y)

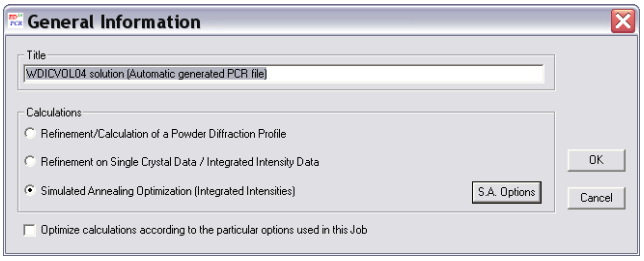
For the purposes of this tutorial we will use only two options, the options 1:(a-Y, a-O) and the option 8:(c-Y, a-O) which is the good one.
For using simulated annealing we have to transform the PCR file `y2o3_Ia3.pcr` used for the Le Bail fit into another one including atoms and able to work with the regrouped integrated intensities stored in the file `y2o3_Ia31_cltr.int`. We will use the program **EdPCR** (together with some manual editing) to modify `y2o3_Ia3.pcr` . First we copy this file into another with the name `y2o3_san.pcr`. Now we should follow strictly the steps below for transforming the PCR file in order to include atoms and make it adapted to simulated annealing.

Steps for transforming a PCR file to another appropriate for simulated annealing

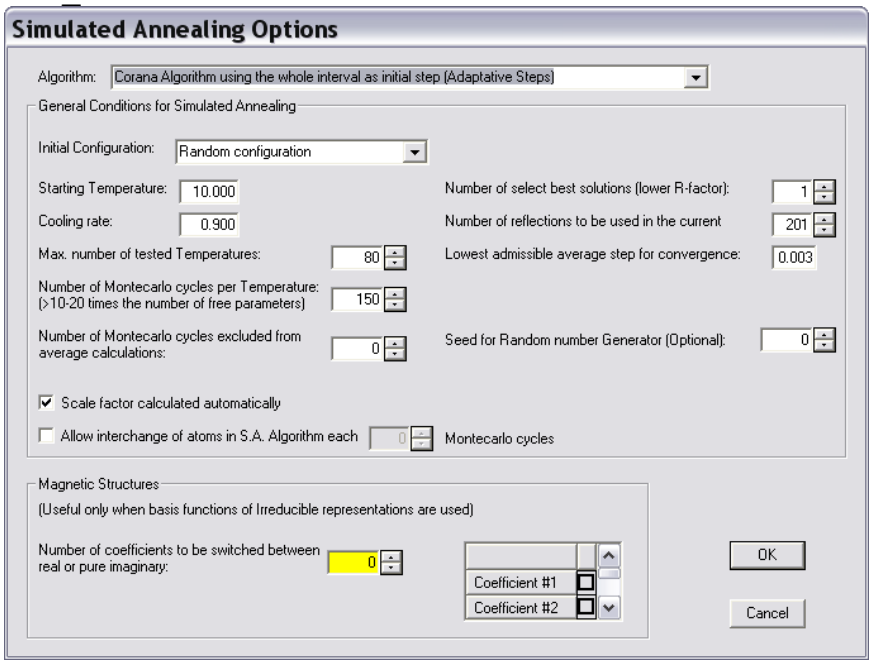
Step 1: Charge `y2o3_san.pcr` into the Toolbar and open **EdPCR** by clicking in the corresponding icon.
Step 2: Click on the General button



Step 3: Select Simulated Annealing Optimization (Integrated Intensities) and click on the button S.A. Options. If you wish, you may change also the content of the Title box.

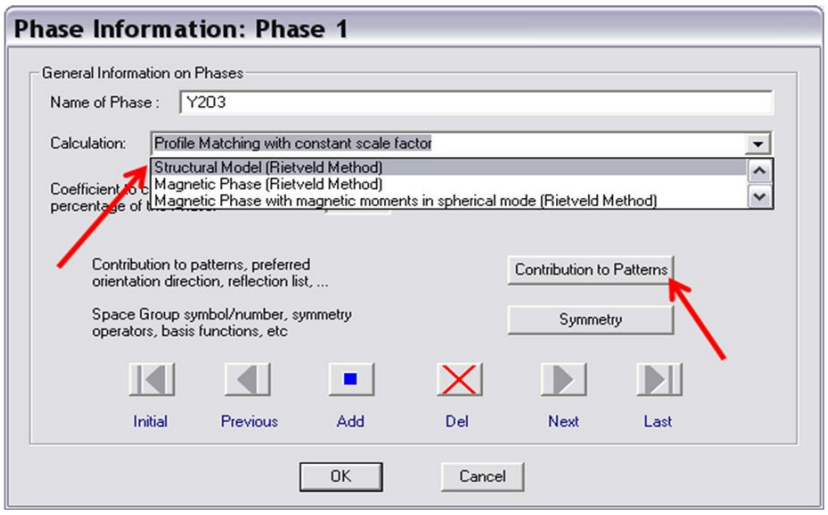


Step 4: In the Simulated Annealing Options (Integrated Intensities) dialog (shown below) change the Starting Temperature, the Cooling rate, etc, as shown below (do not forget ticking the Scale factor calculated automatically checkbox). If we leave the Number of reflections to be used in the current job equal to zero, the program will use all reflections existing in the file `y2o3_Ia31_cltr.int`.

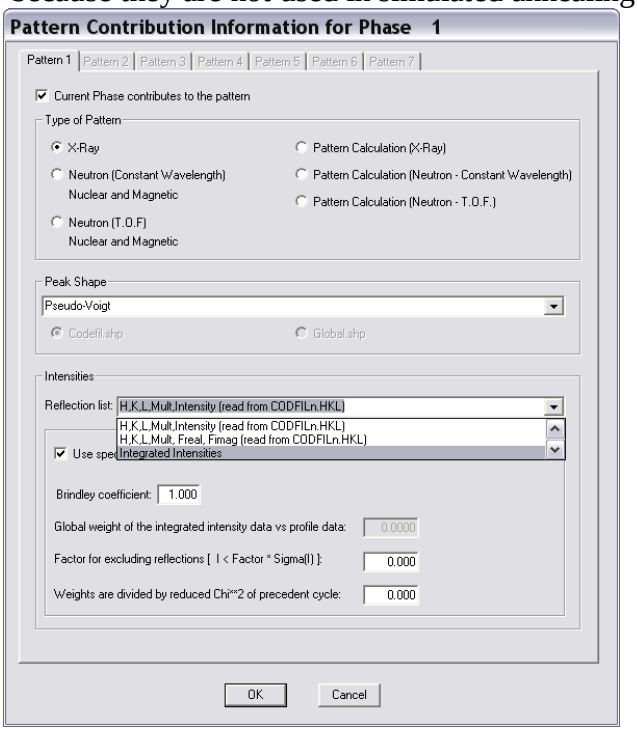


Click on OK buttons to accept the changes in the current dialog and in the previous one for coming to the general interface of **EdPCR**.

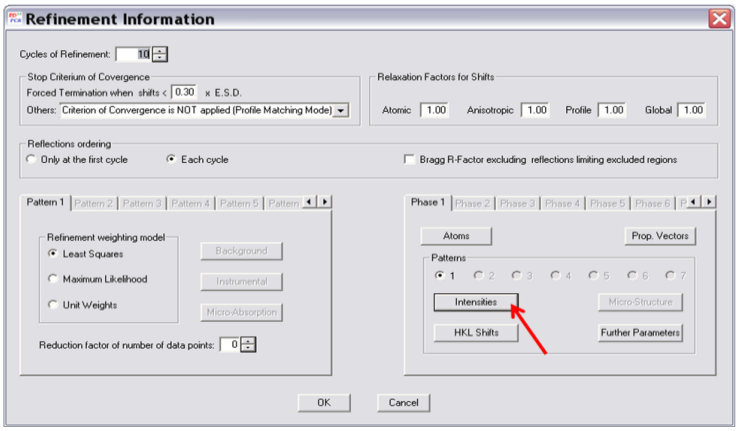
Step 5: Click on the Phases button and change the content of the Calculation box in the Phase Information dialog to Structural Model (Rietveld Method), and then click on the Contributions to pattern button.



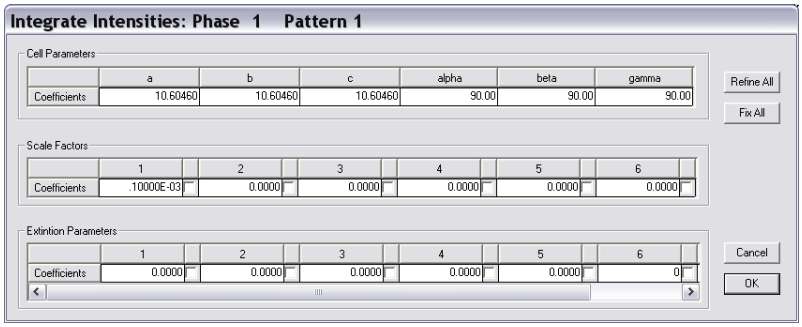
Step 6: Change the content of the Reflection list box to Integrated Intensities, and then click on the OK buttons to accept the changes in the current and previous dialogs. We can leave the other default values because they are not used in simulated annealing work.



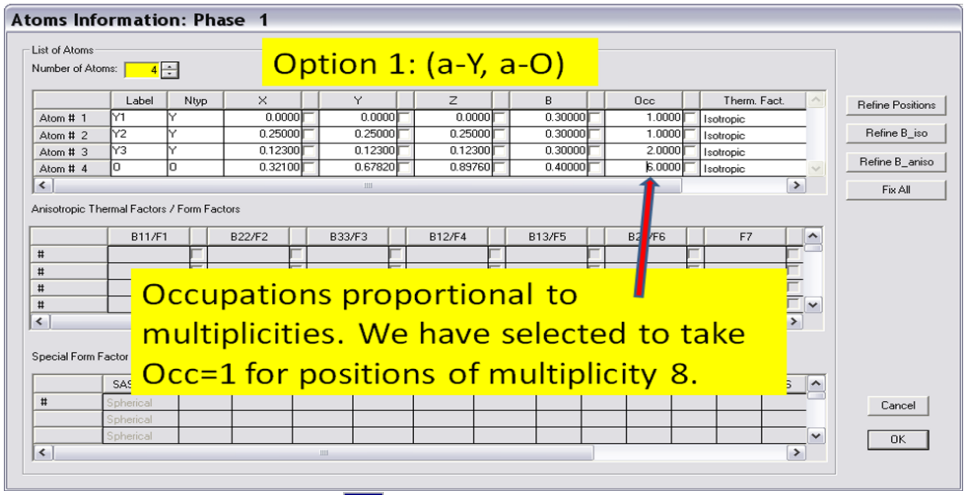
Step 7: In the general interface of **EdPCR** click on the Refinement button and in the new open dialog (Refinement Information) click on the Intensities button.



Step 8: In the new open dialog click on the Fix All button and put to zero all Scale factors except the first one and all the Extinction Parameters coefficients. Click on OK button to accept the changes.



Step 9: In the Refinement Information dialog click on the Atom button and add the appropriate number of atoms (in our case 4 atoms: 3 Y and 1 O). Fill the boxes with the atom information with arbitrary values of the coordinates except for those that are in special positions. One can use isotropic B equal to 0.3 for Y and 0.4 for O atoms. The occupation factors should be proportional to the multiplicities of the sites. Click on OK button to accept the changes in the current dialog and in the Refinement Information dialog for coming back to the general interface of **EdPCR**.



Step 10: Click on the save button (or select File → Save in the menu) of **EdPCR** in order to save all changes. Now we have a template file that should be completed by editing with a

text editor. We can use the integrated editor within **EdPCR**, for that we select in the menu Editor→ Input Control File (.PCR) and then a new window opens with the content of the saved file `y2o3_san.pcr`. The following changes have to be done:

1: Change the value of `Nre` to `4` (four free parameters, and four relations to be written below)

2: Put `More = 0` and remove the two lines below

3: Put codes to the free position parameters as written below (remember we are with the option (a-Y, a-O):

```
I a -3                    <--Space group symbol
!Atom   Typ       X         Y         Z      Biso       Occ     In Fin N_t Spc /Codes
Y1      Y       0.00000   0.00000   0.00000  0.30000   1.00000   0   0   0    0
                  0.00      0.00      0.00     0.00      0.00
Y2      Y       0.25000   0.25000   0.25000  0.30000   1.00000   0   0   0    0
                  0.00      0.00      0.00     0.00      0.00
Y3      Y       0.12300   0.12300   0.12300  0.30000   2.00000   0   0   0    0
                 11.00     11.00     11.00     0.00      0.00
O       O       0.32100   0.67820   0.89760  0.40000   6.00000   0   0   0    0
                 21.00     31.00     41.00     0.00      0.00
```

4: Remove the refinement codes that may be still present for the cell parameters

5: Add four lines, just before the line with: `! T_ini` …, containing the number of the parameter (n), the range of variation (0 to 1), the step (put zero, the program will determine that dynamically) and the value 1 for telling that we are dealing with periodic boundary conditions in the value of the parameters (atom positions). The four lines should appear like:

```
...
! x-Lambda/2  +          Not yet used parameters
     0.00000     0.00000     0.00000     0.00000     0.00000
        0.00        0.00        0.00        0.00        0.00
1 0 1 0 1
2 0 1 0 1
3 0 1 0 1
4 0 1 0 1
! T_ini   Anneal  Accept NumTemps NumThCyc InitConf
  10.000   0.900   0.003       80        0        0
```

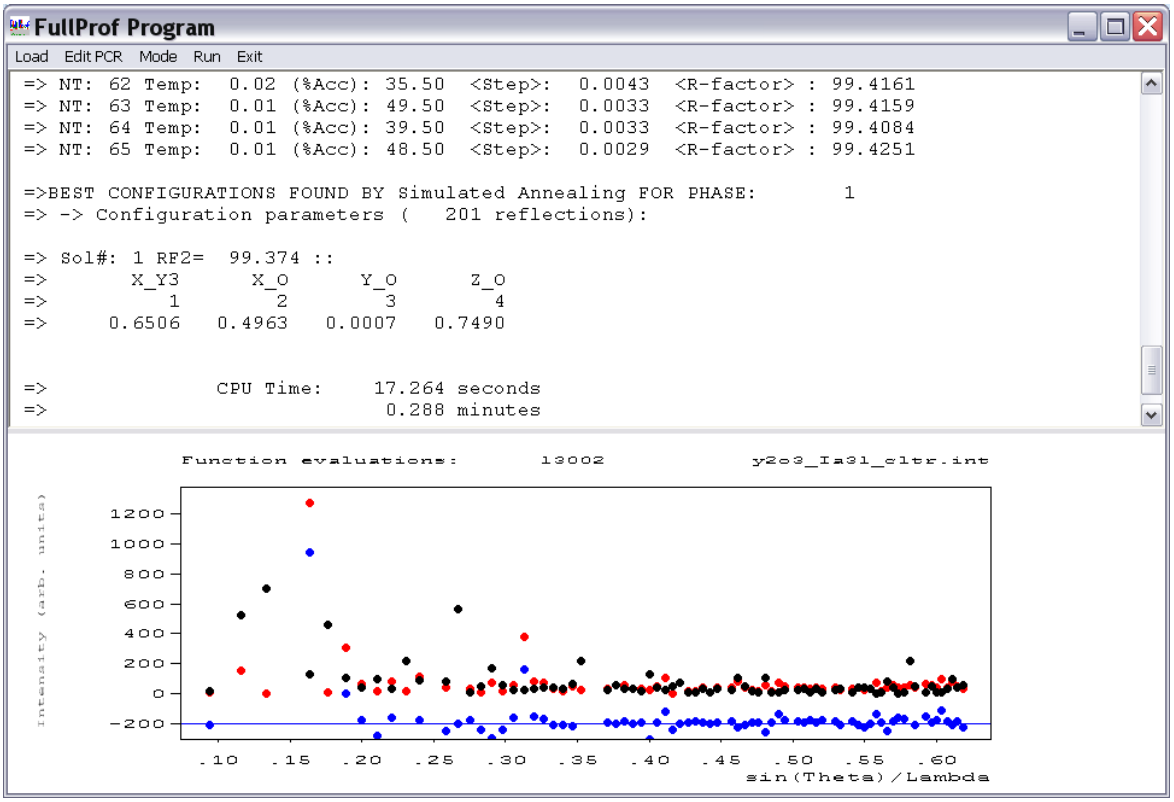
After the changes have been performed, save the edited file and close the editor. The **EdPCR** program will ask for re-loading the PCR file, click on OK button to accept re-loading the file.

Click on the save button  (or select File → Save in the menu) of **EdPCR** in order to save all changes and get the file prepared for running **FullProf**.

Running the simulated annealing job

If we run **FullProf** from the toolbar, it will take automatically the charged PCR file `y2o3_san.pcr` as input and the toolbar will ask immediately for the intensity file. One should select the file `y2o3_Ia31_cltr.int`.

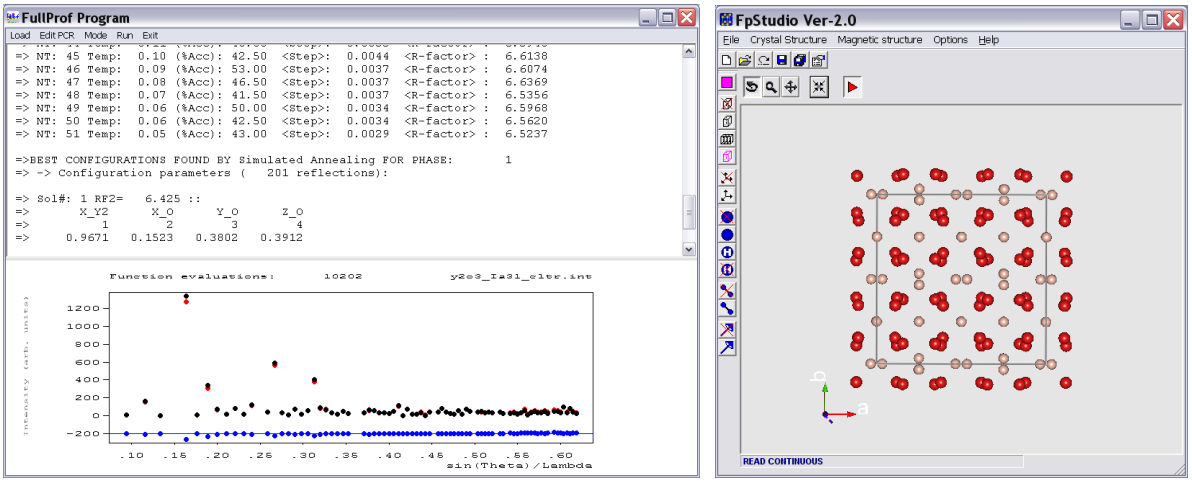
The program runs and it can be easily verified that the R-factors of this possible solution stays quite high (more than 99 %!):



Now we can change the PCR file introducing the option 8:(c-Y, a-O) in which we have only three atoms in the asymmetric unit. For doing that we can make a copy of the previous `y2o3_san.pcr` file to `y2o3_san_Option1.pcr` for saving our first trial and now we modify again the PCR file using whatever editor or directly **EdPCR**. The relevant part should appear like:

```
!
I a -3                    <--Space group symbol
!Atom Typ       X         Y         Z      Biso       Occ     In Fin N_t Spc /Codes
Y1    Y       0.25000   0.25000   0.25000  0.30000   1.00000   0   0   0     0
                0.00      0.00      0.00     0.00      0.00
Y2    Y       0.91341   0.00000   0.25000  0.30000   3.00000   0   0   0     0
               11.00      0.00      0.00     0.00      0.00
O     O       0.11111   0.34444   0.88333  0.40000   6.00000   0   0   0     0
               21.00     31.00     41.00     0.00      0.00
```

Before running **FullProf** with the new atom positions it is interesting to know that each time you run a simulated annealing job, there is a generated file, called `simann.fst` that is periodically updated in the course of the optimisation process. You can open this file using **FullProf Studio** clicking in the corresponding button of the toolbar  and click on the continuous reading button  for updating the picture of the current crystal structure being optimised by **FullProf**. Running now **FullProf** from the toolbar, we can see simultaneously the evolution of the optimisation and the image with the evolving crystal structure.



The result obtained with the trial of the option 8:(c-Y, a-O), is directly the good one. You can see that in the particular run shown in the above panel, the best RF2-factor is 6.4%! This may change for different runs because we have selected a random seed depending on the clock of the system. In any case the solution is easily found by simulated annealing. The final PCR file `y2o3_san.pcr` is updated with the best solution found.

After solving the structure with the simulated annealing algorithm, one has just to copy and paste the part of the PCR file containing the structural information into the PCR file prepared for performing a Rietveld refinement. For doing that you just have to copy the file `y2o3_Ia31.pcr` into the file `y2o3_Rietveld.pcr`, edit this new file and do the following changes:

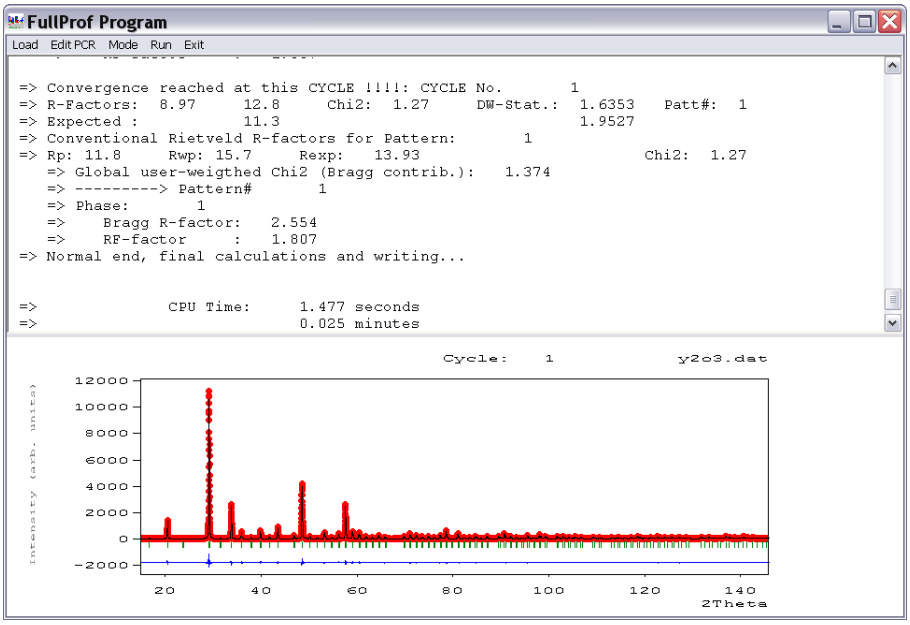
1: In the line just below `!Nat Dis Ang Pr1 Pr2 Pr3 ...` put `Nat=3`, `Jbt=0` and `Irf=0`. You may leave `More=1` for later use.

2: Insert after the line containing the space group symbol, the block from `y2o3_san.pcr` containing the list of atoms, and replace the scale factor for that of `y2o3_san.pcr`. In order to avoid conflicts with previous refinement codes existing in the original PCR file it is recommended to put all of them equal to zero in the structural part for a first run.

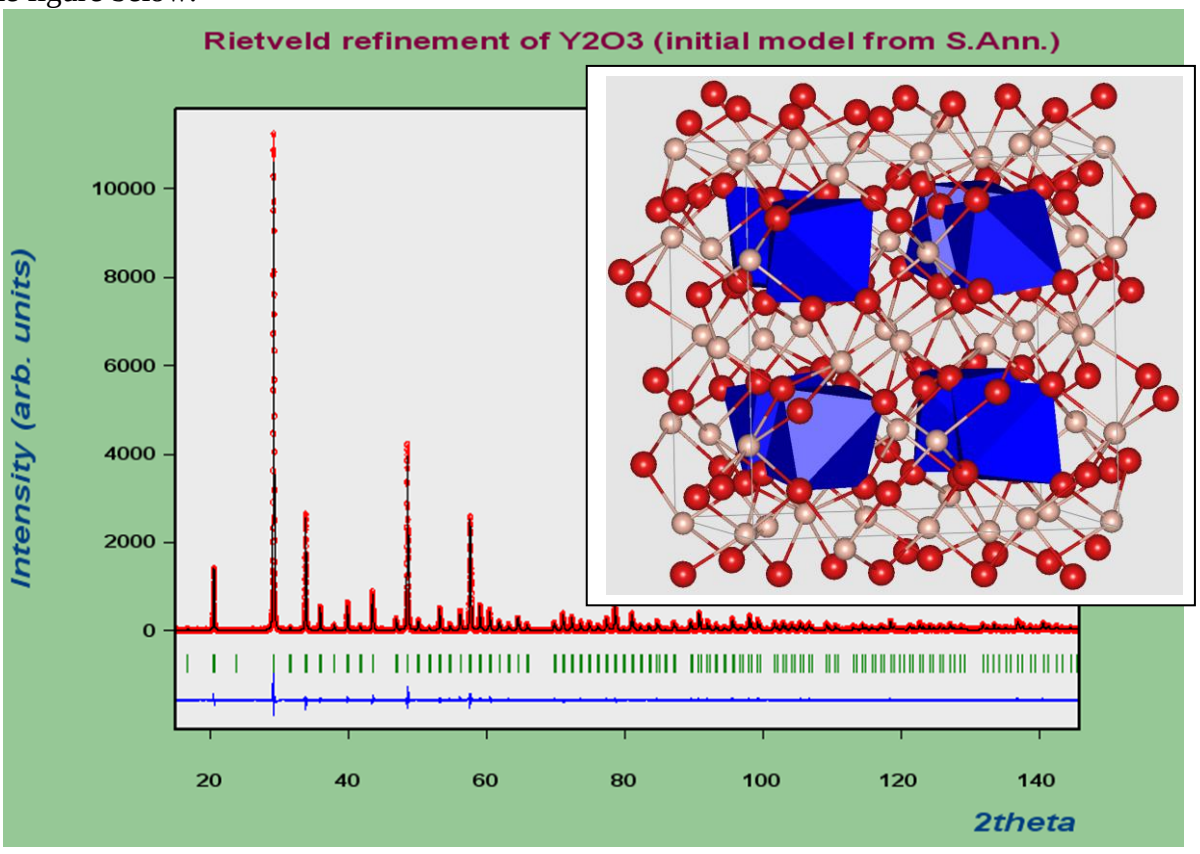
This part of the PCR file should be similar to this one:

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ     Nvk Npr More
   3   0   0 0.0 0.0 1.0   0   0   0   0    0     130066.562   0   5   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift N_Domains
  11   0   0   0   0   0  1.0000  0.0000  0.0000  0.0000    0       0       0       0
!
I a -3                    <--Space group symbol
!Atom   Typ       X         Y         Z      Biso       Occ      In Fin N_t Spc /Codes
Y1      Y       0.25000   0.25000   0.25000  0.30000   1.00000    0   0   0     0
                  0.00      0.00      0.00     0.00      0.00
Y2      Y       0.96711   0.00000   0.25000  0.30000   3.00000    0   0   0     0
                  0.00      0.00      0.00     0.00      0.00
O       O       0.15226   0.38021   0.39123  0.40000   6.00000    0   0   0     0
                  0.00      0.00      0.00     0.00      0.00
```

Running **FullProf** in Rietveld mode immediately converges without problems. Now we can refine the atom positions and the thermal parameters together with all background and profile parameters. A panel with the final refinement is shown below



A picture of the crystal structure and the final refined powder diffraction pattern is shown in the figure below.



One can modify the PCR file in order to make additional calculations, for instance, interatomic distances, angles and bond valence sums. Add some information for **FullProf Studio** in order to obtain a more appealing picture of the crystal structure, etc. We provide the relevant part of the PCR file with additional items.

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     2.55
!-------------------------------------------------------------------------------
 Y2O3                      VARY xyz b
!
```

```
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   3   0   0 0.0 0.0 1.0   0   0   0   0   0     130066.562   0   5   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift N_Domains
   0   3   0   0   0   0  1.0000  0.0000  0.0000  0.0000    0       0       0       0
!
! Max_dst(dist) (angles)  Bond-Valence Calc.
      3.5000      2.5000        BVS
!  N_cations   N_anions     Tolerance(%) / Name or cations/ and Anions
       1           1               0.00
Y+3
O-2
!
I a -3                   <--Space group symbol
!Atom   Typ       X        Y        Z     Biso       Occ    In Fin N_t Spc /Codes
Y1     Y       0.25000  0.25000  0.25000  0.45776   1.00000  0  0 0  1  #conn Y O 0 2.4
                 0.00     0.00     0.00    91.00      0.00
Y2     Y       0.96759  0.00000  0.25000  0.37000   3.00000  0  0 0  1  #poly Y1 color 0 0 1 1
                121.00     0.00     0.00   101.00      0.00
O      O       0.15175  0.38035  0.39107  0.30789   6.00000  0  0 0  2  #
                151.00   141.00   131.00   111.00      0.00
!-------> Profile Parameters for Pattern #  1
!  Scale        Shape1       Bov      Str1      Str2      Str3   Strain-Model
 0.36438E-06   0.52211   0.00000   0.00000   0.00000   0.00000       0
    11.00000    71.000     0.000     0.000     0.000     0.000
!       U          V          W          X          Y        GauSiz   LorSiz Size-Model
   0.013715  -0.003012   0.010487   0.002738   0.000000   0.000000   0.000000    0
     31.000     41.000     51.000     61.000      0.000      0.000      0.000
!     a          b          c        alpha      beta       gamma      #Cell Info
  10.604637  10.604637  10.604637  90.000000  90.000000  90.000000
   81.00000   81.00000   81.00000    0.00000    0.00000    0.00000
```

The above part of the PCR file allows the calculation of bond valence sums and distances as well as a picture of the structure like that of the final panel. Moreover summaries of the structural parameters and bond valence calculations are provided in files `y2o3_Rietveld_1.cfl` and `y2o3_Rietveld_1_sum.bvs` part of which are shown below.

y2o3_Rietveld_1.cfl

```
Title  CFL-file generated from FullProf for phase:  Y2O3
Cell    10.604637(4)  10.604637(4)  10.604637(4)  90.0  90.0  90.0
SpGR  I a -3
!  Atom-strings in the order: Label, Species, x, y, z, Biso, Occ [,2*Spin, charge]
Atom Y1   Y+3    0.25000       0.25000       0.25000       0.46(2)       1.00000
Atom Y2   Y+3    0.96759(4)    0.00000       0.25000       0.370(14)     3.00000
Atom O    O-2    0.1518(3)     0.3803(3)     0.3911(3)     0.31(6)       6.00000
```

y2o3_Rietveld_1_sum.bvs

```
Title: Summary of Bond-Valence calculations for file: y2o3_Rietveld_1.cfl
   Atom      Coord  D_aver Sigm   Distort(x10-4)    Valence    BVSum(Sigma)
    Y1        6.00  2.2875(  13)         0.000       3.000       2.904( 10)
    Y2        6.00  2.2824(  13)         2.985       3.000       2.961( 10)
    O         4.00  2.2836(  16)         2.245      -2.000       1.965(  8)
 =>  Old Global Instability Index (  GII=SQRT{SUM{|BVS-abs(q)|^2}/Num_Atoms} ) =   6.33 /100
 =>  Normalized   GII(a)=       SUM {|BVS-abs(q)|  *mult}       /N_Atoms_UCell =   4.25 /100
 =>  Normalized   GII(b)=       SUM {|BVS-abs(q)|  *mult/abs(q)}/N_Atoms_UCell =   1.77 %
 =>  Normalized   GII(c)= SQRT{ SUM {|BVS-abs(q)|^2*mult}       /N_Atoms_UCell}=   4.62 /100
```