

## Materials Science 142

Laboratory Exercises 7

Assigned: 5/24/06

Due: 6/01/06

### Rietveld Refinement: Complete Analysis of X-ray Powder Diffraction Data

**Goal:** Extract crystallographic data from X-ray powder diffraction data.

You are provided with diffraction data for a sample that contains a mixture of  $\text{SrPrO}_3$  and  $\text{SrPr}_2\text{O}_4$ , SrPr03\_riet.xy. Data were collected using the Siemens D-500,  $\text{Cu K}\alpha$  radiation, in  $0.01^\circ$  steps, with a dwell time of 15 s/step. You are to perform refinement of the preliminary structural data to obtain relevant crystallographic data (e.g. lattice parameters, atomic coordinates, atomic displacement factors, and phase fractions). If you have a material relevant to your own research, you are highly encouraged to collect diffraction data from that material instead.

For performing the refinement, you can choose to use the XPert Pro software, or a freeware program entitled Rietica and available from ANSTO (Australian Nuclear Science and Technology Organization). Detailed instructions for using Rietica are provided below. For instructions on using XPert Pro for Rietveld refinement see your TA, Mikhail Kislitsyn.

Starting atomic coordinates for  $\text{SrPrO}_3$  are given in the cif file, SrPrO3.cif. Starting atomic coordinates for  $\text{SrPr}_2\text{O}_4$  are given in a paper by Fiscus and zur Loye. The 'cif' file is an ascii file with crystallographic data compiled in a standard format that many programs can import.

- 1) If using your own sample, collect diffraction data over an appropriate  $2\theta$  range. Record the instrument settings.
- 2) Input the data for analysis into the program you are using (again, see below for detailed instructions for Rietica) and also enter the crystallographic data for the two phases using the information provided. The cif file can be imported to provide the crystallographic data for  $\text{SrPrO}_3$ , whereas the data for  $\text{SrPr}_2\text{O}_4$  will have to be entered manually.
- 3) Sequentially turn on parameters for refinement. Do not use the automatic sequence option offered by XPert Pro.

In general, you will have to use your judgment as to whether to keep a parameter turned on for refinement as you proceed to turn on the following parameters, or to turn it off to prevent the refinement from 'blowing up.' Simultaneous refinement of highly correlated parameters causes this problem and must be avoided. For example, occupancies and displacements parameters should not be simultaneously refined. Similarly, the overall scale factor should not be refined at the same time as the occupancy factors of all of the atoms. One amongst these parameters must be fixed. Also, it is important to refine the parameters most uncorrelated with other parameters first. The refinement strategy suggested in Young's "Rietveld Method" (p. 35) is

1. Scale factor — stable
2. Specimen displacement — stable
3. Flat background — stable
4. Lattice parameters — stable
5. More background — stable
6.  $W$ , in the Caglioti function for peak widths—poorly stable
7.  $x, y, z$  (atomic coordinates) — fairly stable
8. Occupancies and isotropic (thermal) displacement parameters — not generally stable
9.  $U, V$ , (in the Caglioti function) and other profile parameters — not generally stable
10. Anisotropic (thermal) displacement parameters — not generally stable
11. Zero point — stable

In most cases it is not very meaningful to refine anisotropic displacement parameters using conventional X-ray diffraction data. If you must limit the refinement to isotropic parameters in order to prevent the displacements of the atoms from becoming 'non-positive definite' then do so.

As you proceed with the refinement, you must periodically examine the difference plot (plot of  $I_{\text{calc}} - I_{\text{obs}}$ ). This will provide you with insight as to what parameters might be misbehaving and whether you have selected the appropriate peak profile function. If appropriate, you may choose to change the values of parameters such as the scale factor and flat background to more closely match the data and get the refinement 'jump-started.'

Report:

- Derived Bragg R-factor, goodness-of-fit (GOF),  $R_p$ , and  $R_{wp}$
- Plot of calculated and measured  $I(2\theta)$ , as well as difference plot
- Molar and weight percentages of phases with standard deviations
- Space group and cell parameters of both phases with standard deviations
- Indexed  $2\theta$ ,  $I_{\text{calc}}$ ,  $I_{\text{obs}}$  (integrated intensities)
- Wyckoff positions, site multiplicities, atomic coordinates and displacement parameters for atoms in  $\text{SrPrO}_3$  with standard deviations. For coordinates fixed by the Wyckoff position, standard deviations are meaningless and not reported.
- Bond distances and angles in  $\text{SrPrO}_3$  with standard deviations
- Total number of refined parameters and their roles (e.g. 4 background parameters, 6 profile parameters, etc.)
- Statement as to which profile function was selected.

## Instructions for Rietica

1. Open data file
  - LFile
    - LOpen
      - change file type to \*.xy
      - open file SrPr03\_riet.xy
    - LPreferences
      - LMemory
        - Set the "Number of Data Points Per Histogram" to 20,000

At this point you should have a graph of the data. Do not be concerned if the graph only goes up to  $50^\circ$  in  $2\theta$ , it is a glitch in the program. You can zoom in on the graph using the mouse to click and drag over the region of interest. If you left click and drag you can scroll across the graph. Double clicking on the magnifying glass icon returns the graph to full range.

## 2. Create input files

- LFile
  - LNew
    - LOK
      - Create an input file name
- LModels
  - LGeneral
    - Make sure "Read data format" is set to "x,y"
    - Click desired "Output File Options" such as "Obs. & Calc. Intensities" and set "Bond Distances and Angles"
  - LPhase
    - Left click on "Phase 1" title
      - LRead Phase from CIF File
        - open the SrPrO3.cif file
    - Under "Phase 2," the CIF file will be loaded, however the file does not load perfectly so you need to delete atom 5. Left click on atom #5, and from the menu choose "Delete atom." Also, under "Type," you need to go through and select the appropriate ions.
    - There is no ICSD file for the second phase in this material ( $\text{Sr}_2\text{PrO}_4$ ), so we must load it by hand. From the paper given (Fiscus, zur Loye, *J. Alloys and Compounds*, **306** (2000) 141-145) use the given data to fill in Phase 1 for  $\text{Sr}_2\text{PrO}_4$ .
    - Set "B" thermal parameters, to "0.6" as an appropriate starting point.
    - Left click on # to "Add atom"
    - Left click on # and "Set all atoms to full occupancies", this sets "n" such the position has full occupancy, where  $n = \text{site mult} / \text{gen mult}$ .
- LHistograms
  - Set "Data min-max:" to 3 and 100
  - Set "Data step" to 0.005
- LSample
  - Start with "Pseudo-Voigt" for "Peak Shape"

- Under “Instrument PeakShape,” set  $w = 0.03$ ,  $ASY1 = 0.02$ ,  $\text{Gam}0 = 0.1$ , and  $u, v, \text{Gam}1, \text{Gam}2 = 0$  as generic start values
- “Plot FWHM” to get an idea of what kind of peaks these values produce

↳File

↳Save

### 3. Refine data

Indicate the number of refinement cycles and the specific parameters that will be refined. For example, to refine the “scale factor/phase scale.”

↳Models

↳Phase

For each phase, checkmark next to the “Phase scale:” box. This tells the program that this is a parameter to refine.

↳Rietveld

↳Refine

In the “Refine” dialogue box, click “Dynamic Plotting” and “Watch Values” to see how the selected parameters are refining. Click “Start” and a starting graph will appear. Then click “Step” and a first iteration will be carried out. Continue to click on “Step” until the parameter being refined is stable. To update these values into your input file, check the “Update” box, and click “Finish.”