Influence of Refinement Strategies on Rietveld Phase Composition Determinations

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Abstract

Refinement strategy may profoundly influence phase composition (PC) results due to various parameter correlations if the measured data are biased in some way and/or if the refinement model is inadequate. The principal issues considered in this paper are (i) the influence of preferred orientation (PO) on the refinement PC results and (ii) the need to refine individual-atom thermal parameters with particular reference to parameter correlations.

The paper examines these questions by examining a powder x-ray diffraction data set for a 4-phase mixture comprising - (i) α-Al₂O₃ (corundum), ZnO (zincite) and TiO₂ (rutile), all with minimal preferred orientation; and (ii) CaCO₃ (calcite) which introduced substantial preferred orientation into the mixture. The quality of the phase composition results is assessed according to their disagreement with the known values; the phase composition precision estimates; and the refinement figures-of-merit.

Introduction

The authors have more than 10 years experience in obtaining Rietveld PC analysis (PCA) results in their own materials research projects, and also in providing Rietveld PCA services to minerals-oriented clients. Additionally, they have extensive experience in teaching Rietveld analysis to undergraduate and postgraduate students some having weak mathematical backgrounds and also minimal crystallography and diffraction science knowledge. It is evident in teaching Rietveld principles and practice that practitioners without an adequate appreciation of the underlying principles, who adopt a 'black box' approach, are likely to obtain severely erroneous phase composition results. Aspects of the method which must be appreciated by 'beginners' include parameter correlations and the associated influence of bias on the validity of the results.

The study reported here was designed to consider the extent to which parameters correlating with the phase scale factors (notably the thermal and PO parameters) will influence PCA results. Two specific questions were considered:
1. The influence of thermal parameter refinement strategy on the quality of the PCA estimates.
2. The extent to which neglect of PO biases the PCs.
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Procedures

The powders selected to make up the mixture for the study were designed to provide a multi-phase specimen with one component having substantial PO. Three of the four components were regarded as likely to provide minimal PO - $\alpha$-$\text{Al}_2\text{O}_3$ [corundum], $\text{ZnO}$ [zincite]; and $\text{TiO}_2$ [rutile]. The fourth component $\text{CaCO}_3$ [calcite] was included to provide PO. The $\alpha$-$\text{Al}_2\text{O}_3$ was type 1000SG supplied by Alcoa of America, and the $\text{ZnO}$, $\text{TiO}_2$ and $\text{CaCO}_3$ were all Univar grade powders from AJAX Chemicals. The PCs-by-weight in the specimen were 40% for $\alpha$-$\text{Al}_2\text{O}_3$ and 20% for each of the other phases.

The volumetric median sizes for the four phases were reduced below 5$\mu$m with a micronising mill to reduce microabsorption bias, and reasonable comminution was then achieved by briefly micronising the components together. Samples were mounted for XRD by lightly front-pressing to minimise PO.

XRD data were measured with a Siemens D500 Bragg-Brentano diffractometer configured as follows - Cu tube [type Fk60-04 CU] operating at 40 kV and 30 mA (K$\alpha$ wavelengths: 1.54060, 1.54439 Å); fixed slit optics with incident beam divergence = 1°, receiving slit = 0.15°, post-diffraction graphite analyser; NaI detector with pulse discrimination; 2$\theta$ step size = 0.04°, counting time = 1 s/step, 2$\theta$ range = 5-100°.

PCA was performed by the Rietveld method using the Rietica-LHPM Microsoft Windows 95 program [1] which derives from the Hill-Howard-Hunter LHPM program [2]. Crystal structure data (atom coordinates and unit cell parameters) were taken from the Inorganic Crystal Structure Data Base (FachInformationsZentrum and Gmelin Institut, Germany) - ICSD (see Table 1). These structural parameters were fixed during the refinements.

The computations involved adjustment of the scale factors, pattern-background polynomial parameters, $2\theta$-scale offset and peak profile functions (pseudo-Voigt with asymmetry). Refinement trials of two types were conducted - the first with random orientation (RO) assumed for all phases, and second with the March-Dollase PO model [3] being employed for calcite.

Table 1. Crystal Structure Models Used in Rietveld Refinements

<table>
<thead>
<tr>
<th>Structural Models</th>
<th>ICSD Number</th>
<th>Authors/Data*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-$\text{Al}_2\text{O}_3$</td>
<td>73725</td>
<td>Maslen et al - ref 4: SC-XRD</td>
</tr>
<tr>
<td>$\text{ZnO}$</td>
<td>65119</td>
<td>Albertson et al - ref 5: SC-XRD</td>
</tr>
<tr>
<td>$\text{TiO}_2$, rutile</td>
<td>63710</td>
<td>Howard et al - ref 6: PWD-ND</td>
</tr>
<tr>
<td>$\text{CaCO}_3$, calcite</td>
<td>73446</td>
<td>Maslen et al - ref 7: SC-XRD</td>
</tr>
</tbody>
</table>

* Codes: SC = single crystal, PWD = powder diffraction
XRD = x-ray diffraction, ND = neutron diffraction
The final Rietveld scale factors were converted to PCs-by-weight using the 'ZMV' expressions,

**Relative Phase Compositions:**

\[
\text{wt \% (analyte phase) = } \frac{[s \ (ZMV)]_{\text{analyte phase}}}{\sum [s \ (ZMV)]_{\text{all phases}}} \quad (1)
\]

**Absolute Phase Compositions with Internal Standard (\(\alpha\)-Al\(_2\)O\(_3\)):**

\[
\text{wt \% (analyte phase) = } \frac{[s \ (ZMV)]_{\text{analyte phase}}}{[s \ (ZMV)]_{\text{int std}}} \times \text{wt \% (analyte phase)} \quad (2)
\]

where \(s\), \(Z\), \(M\) and \(V\) signify the phase scale factors; number of formula units/cell; formula weights and unit cell volumes, respectively. These two measures of PC were examined in view of the authors' experience that constraining the aggregate of the PCs to 100\% may substantially bias the final results. The \(\alpha\)-Al\(_2\)O\(_3\) component was designated the internal standard for "absolute" determination with equation (2).

Four refinement trials were conducted, as summarised in Table 2. Trial 1 was intended to examine the impact of ignoring preferred orientation. In this initial trial, thermal parameters were set using a guideline generally followed by the authors in setting initial thermal values for inorganic phases - we have little confidence in published thermal parameters, particularly those from XRD studies.

Table 2. Rietveld Refinement Trials

<table>
<thead>
<tr>
<th>Trial</th>
<th>Model</th>
</tr>
</thead>
</table>
| #1    | • No preferred orientation  
       | • Thermal parameters fixed: \(B = 0.5 \ \text{Å}^2\) for first atom, 1.0 for second atom, 1.5 for third atom, e.g. CaCO\(_3\): 0.5 for Ca, 1.0 for C, 1.5 for O. |
| #2    | • Preferred orientation for CaCO\(_3\)  
       | • Thermal parameters fixed at trial 1 values. |
| #3    | • Preferred orientation for CaCO\(_3\)  
       | • Phase thermal parameters refined. |
| #4    | • Preferred orientation for CaCO\(_3\)  
       | • Atom thermal parameters refined. |

In the second trial, PO was introduced for calcite and thermal parameters remained fixed at their assigned values. Next, in trial 3, the phase thermal parameters were refined. Then, finally, the individual atom isotropic thermal parameters were relaxed in trial 4.
Results and Discussion

The results were examined in terms of (1) comparison of the PCA results with the known values - Figures 1 and 2; (2) the refinement figures-of-merit - Table 3; (3) the PC esds; and (4) the refinement correlation coefficients - see Table 4 for selected coefficients cross-linking the scale factors, the atom thermal parameters and the calcite PO parameter. These correlation coefficients provide indications of likely bias in the PC results. Other coefficients linked to the scale factors were all small, the largest of these being < 0.2. It is noted also that the inter-phase correlations are very small, and therefore bias in the scale factor for one phase will not translate to bias in the scale factors of other phases.

Table 3. Figures-of-merit for the Refinements

<table>
<thead>
<tr>
<th>Ref</th>
<th>Rexp</th>
<th>Rp</th>
<th>Rwp</th>
<th>χ²</th>
<th>Bragg R-factors (R_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>1</td>
<td>8.1</td>
<td>16.0</td>
<td>22.0</td>
<td>8.1</td>
<td>6.3</td>
</tr>
<tr>
<td>2</td>
<td>12.0</td>
<td>15.4</td>
<td>3.7</td>
<td></td>
<td>7.4</td>
</tr>
<tr>
<td>3</td>
<td>11.8</td>
<td>15.2</td>
<td>3.6</td>
<td></td>
<td>6.8</td>
</tr>
<tr>
<td>4</td>
<td>11.4</td>
<td>14.8</td>
<td>3.4</td>
<td></td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 4. Selected Correlation Coefficients for Refinement 4

Correlations linking the four scale factors and the PO parameter for calcite with the thermal parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ scale factor:</td>
<td>( Al₂O₃ \text{ parameters} )</td>
</tr>
<tr>
<td></td>
<td>( B_{Al} = 0.79, B_{O} = 0.61 )</td>
</tr>
<tr>
<td>ZnO scale factor:</td>
<td>( ZnO \text{ parameters} )</td>
</tr>
<tr>
<td></td>
<td>( B_{Zn} = 0.81, B_{O} = 0.16 )</td>
</tr>
<tr>
<td>TiO₂ scale factor:</td>
<td>( TiO₂ \text{ parameters} )</td>
</tr>
<tr>
<td></td>
<td>( B_{Ti} = 0.76, B_{O} = 0.44 )</td>
</tr>
<tr>
<td>CaCO₃ scale factor:</td>
<td>( CaCO₃ \text{ parameters} )</td>
</tr>
<tr>
<td></td>
<td>( B_{Ca} = 0.70, B_{C} = -0.01, B_{O} = 0.65 )</td>
</tr>
<tr>
<td>CaCO₃ PO parameter:</td>
<td>( CaCO₃ \text{ parameters} )</td>
</tr>
<tr>
<td></td>
<td>( D_{Ca} = 0.56, B_{C} = -0.06, B_{O} = 0.56, )</td>
</tr>
<tr>
<td></td>
<td>scale factor = 0.95</td>
</tr>
</tbody>
</table>

The Refinement 1 results in Figures 1 and 2 show severe bias due to the neglect of PO. The absolute PCs give a value of 35.2 (0.7)* for the calcite level compared with

* Value in parentheses is the PC esd derived from the Rietveld scale factor esds.
Figure 1. Plots of relative Rietveld phase composition results for each of the four refinement procedures. The numbers alongside each point give the PC value and, in parentheses, the PC esd. Error bars represent ±2 esds. The broken lines indicate the known values of PC.
Figure 2. Plots of absolute Rietveld phase composition results for each of the four refinement procedures. The numbers alongside each point give the PC value and, in parentheses, the PC esd. Error bars represent ±2 esds. The broken lines indicate the known values of PC. The PC value for Al₂O₃ was fixed.
the expected 20.0. Clearly, constraining the relative concentration sum to 100% biases
the estimates of PC for other three phases - note especially, the pronounced bias in the
$\alpha$-$\text{Al}_2\text{O}_3$ value, 33.8 (0.8) rather then 40.0. Also, constraining the PCs has biased the
$\text{ZnO}$ and $\text{TiO}_2$ concentrations below their actual values.

Relaxation of the March r-parameter in Refinement 2, with non-optimum thermal parameters still in use, results in the calcite concentration being biased "low", due presumably to the influence of bias in the declared thermal parameters. It is noted for this refinement that the esd estimates are substantially lower than those obtained when thermal parameters were relaxed (lower than the Refinement 4 esds by more than x 0.5). The generation of diminished PC esds for Refinement 2 shows the serious underestimates in the esds caused by neglecting parameters which correlate with the phase scale factors.

The calcite PC estimates improve in Refinement 3 through the adjustment of phase thermal parameters, and again in Refinement 4 when atom thermal parameters are relaxed. The ‘best’ results (Refinement 4, Figure 2) give a calcite PC which agrees with the expected 20.0 value within 1.6 $\sigma$. It is evident from these results that it is important to refine the individual thermal parameters for PCA.

The corresponding final PCs for $\text{ZnO}$ and $\text{TiO}_2$ [23.5 (0.5) and 22.8 (0.6), respectively] both deviate from the true value by more than 3$\sigma$. Examination of the mass attenuation coefficients for the phases (30.4, 47.3, 127.5 and 69.8 cm$^2$/g for $\text{Al}_2\text{O}_3$, $\text{ZnO}$, $\text{TiO}_2$ and $\text{CaCO}_3$, respectively) indicate that the $\text{ZnO}$ and $\text{TiO}_2$ PCs may be biased low by microabsorption.

It is instructive to examine the atom thermal parameters obtained in Refinement 4 (Table 5). First, the atom thermal parameters for $\text{Al}_2\text{O}_3$, $\text{ZnO}$ and $\text{TiO}_2$ all satisfy $B_{\text{cation}} > B_O$ and, second, the thermal parameters for $\text{CaCO}_3$ appear to be suffer from serious bias. The latter observation may be attributed to inadequacies in the March model for $\text{CaCO}_3$ (ref. 8).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Values (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>$B_{\text{Al}} = 0.34(16)$, $B_O = -0.09(20)$</td>
</tr>
<tr>
<td>$\text{ZnO}$</td>
<td>$B_{\text{Zn}} = 0.97(12)$, $B_O = 0.10(39)$</td>
</tr>
<tr>
<td>$\text{TiO}_2$</td>
<td>$B_{\text{Ti}} = 0.78(16)$, $B_O = 0.49(31)$</td>
</tr>
<tr>
<td>$\text{CaCO}_3$</td>
<td>$B_{\text{Ca}} = 3.56(31)$, $B_C = -3.15(39)$, $B_O = 2.24(42)$</td>
</tr>
</tbody>
</table>

**Conclusions**

The specific conclusions drawn from this study are:

- The study has underlined the importance of refining individual thermal parameters in Rietveld PCA.
Neglect of PO may seriously bias the PC value for that phase due to the substantial scale-PO correlation coefficient.

Inter-phase correlations are sufficiently small that an error in the scale factor of one phase will have minimal influence on the PC estimates of other phases.

Constraining the sum of the PCs to 100% by weight tends to mask the presence of systematic errors in the PCs.

The PC esds are artificially reduced when the model is inadequate.

Acknowledgement

The authors wish to acknowledge the supply of the Rietveld program Rietica-LHPM by Dr Brett Hunter of the Australian Nuclear Science and Technology Organisation.

References