THE IMPORTANCE OF THE SPECIMEN DISPLACEMENT CORRECTION IN RIETVELD PATTERN FITTING WITH SYMMETRIC REFLECTION-OPTICS DIFFRACTION DATA

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ABSTRACT

Displacement of the specimen surface from the instrument rotation axis in reflection optics diffractometry introduces bias into the measured Bragg peak positions thereby causing systematic shifts in the 2θ-dependent Rietveld parameters. Specimen transparency also results in 2θ-bias, which tends to mimic that from specimen displacement. The authors have investigated the influence of specimen displacement bias on Rietveld lattice parameters when Bragg-Brentano XRD optics are employed. A strategy is recommended for refining lattice parameters using a specimen displacement correction and with the zero-point correction being determined independently of the Rietveld zero-point correction to cope with the strong correlations between lattice parameters, zero-point and specimen displacement.

INTRODUCTION

The Curtin University Materials Research Group has gained extensive experience in the use of Rietveld analysis for material characterisation with particular reference to advanced ceramics characterisation of phase composition, linear strain (lattice parameter changes), non-linear strain and crystallite size (line broadening), and texture. The present study is the latest in a series of Advances in X-ray Analysis publications by authors B O’Connor and D Li on Rietveld analysis methodology [1,2]. This particular study was conducted in view of their experience in various studies of linear strain by Rietveld analysis with Bragg-Brentano XRD data that the lattice parameters have poor reproducibility. This experience is consistent with the IUCr Rietveld round robin study on m-ZrO2 data which found that the accuracy of lattice parameters was x16 worse than the esd estimates from Rietveld refinements [3].

SPECIMEN DISPLACEMENT BIAS

A specimen displacement (subsequently designated SD) ΔR of the specimen surface from the instrument rotation axis for Bragg-Brentano optics results in the bias of peak positions by -

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\[ \delta(2\theta) = 2 \left( \frac{\Delta R}{R} \right) \cos \theta \]  

(1)

where \( R \) is the distance between the specimen and the detector aperture assuming that the diffracted photons derive from the surface. It is noted that specimen transparency also causes an effective SD according to the information depth in symmetric optics,

\[ \text{ID} = \frac{\sin \theta}{2\mu} \]  

(2)

where \( \mu \) is the linear attenuation coefficient.

There are pronounced Rietveld parameter correlations between the SD, the instrument zero-point of the \( 2\theta \) measurement scale (designated ZP) and the lattice parameters (Table 1). These correlations cause the propagation of bias between these parameters. The table also includes coefficients involving the Rietveld asymmetry factor to illustrate how the three parameters may cause bias in the peak profile model.

<table>
<thead>
<tr>
<th>Zero-point (2( \theta_0 ))</th>
<th>Lattice Param (( a_0 ))</th>
<th>Asymmetry (As)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen Disp.</td>
<td>(-91%)</td>
<td>(-47%)</td>
</tr>
<tr>
<td>Zero-point (2( \theta_0 ))</td>
<td>100%</td>
<td>(-50%)</td>
</tr>
<tr>
<td>Lattice Param (( a_0 ))</td>
<td>(-91%)</td>
<td>20%</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

The material employed for the study was the \( \alpha \)-Al\(_2\)O\(_3\) polishing compound supplied by Praxair Surface Technologies Inc. The material was micronised for 15 minutes to give a median particle size less than 5\( \mu \)m. Powders were mounted for XRD by lightly front-pressing.

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\( ^\circ \), receiving slit = 0.15\( ^\circ \), post-diffraction graphite analyser; and NaI detector with pulse discrimination. In collecting data sets, the \( 2\theta \) step size was 0.02\( ^\circ \); the counting time per step was 2s; and \( 2\theta \) range covered 20\( ^\circ \) to 150\( ^\circ \). The maximum peak count rate recorded for the most intense Bragg line was 4,500 counts per second.
Data sets were collected in 2 experiments. First, a standard specimen holder (specimen displacement = 0 µm) and special specimen holders produced for the study to provide SDs of +500, -500 and –1000 µm were used to measure XRD data (sign convention provides a positive value for SDs in front of the rotation axis of the instrument). Second, the standard specimen holder was used to collect four data sets under the same conditions, with the powder being removed and then re-packed after each data collection.

Rietveld modelling was performed using the Rietica-LHPM Microsoft Windows 95 program [4] which derives from the Hill-Howard-Hunter LHPM program [5]. Crystal structure data (atom coordinates and unit cell parameters) were fixed at values from the Inorganic Crystal Structure Data Base (FachInformationsZentrum and Gmelin Institut, Germany) - ICSD 73725 from reference [6] for $\alpha$-Al$_2$O$_3$. The refinements involved adjustment of the ZP, SD, pattern-background polynomial parameters (4 terms), phase scale, lattice parameters and peak profile functions (pseudo-Voigt with asymmetry).

RESULTS FOR DATA SETS COLLECTED WITH SPECIMEN DISPLACEMENT

Figure 1 shows the Rietveld-derived SD parameters versus the physical values. Two features are noted – (i) the substantial relative errors in the Rietveld SDs, indicating that derivation of the SD in this way is poorly determined; and (ii) the shift of the plot from the origin along the horizontal axis which is attributed to the departure of the true ZP, $2\theta_0 = -0.038^\circ$, from the value set for these calculations, 0.000$^\circ$.

Figure 2 indicates the influence of SD bias on the ZP and lattice parameters. When the SD is not refined, the bias in both the ZP and lattice parameters is substantial and consistent with the parameter correlations. When the SD is refined the bias in the ZP and LP is reduced, but some bias is still evident indicating that it is undesirable to permit the Rietveld correction to correct for heavy bias in the SD.

RESULTS FOR DATA SETS COLLECTED WITH NO SPECIMEN DISPLACEMENT

Table 2 shows the lattice parameter estimates of precision for the reproducibility tests using the four data sets. The preferred value of ZP in the FIXED ZP refinements, 0.038$^\circ$, was determined independently of the Rietveld calculation – see below. The results for the FIXED ZP/ REFINED SD calculations are clearly superior in quality compared with those for the FIXED ZP/ FIXED SD and REFINED ZP/ REFINED SD calculations. The REFINED ZP/ REFINED SD results are very poor, as expected from the Figure 1, due to the influence of the ZP correlations. The mean SD for FIXED ZP/ REFINED ZP, 66 µm, is consistent with the estimated ID for these samples whereas the values from the REFINED ZP/ REFINED SD are highly scattered. The superior quality of the lattice parameters from the FIXED ZP/ REFINED SD calculations is highlighted in Figure 3. These indicate that the precision for these refinements is approximately 1 in $10^5$. 
DETERMINING THE ZERO-POINT INDEPENDENTLY OF THE RIETVELD CALCULATIONS

In view of the desirability of determining the ZP independently of the Rietveld calculations, a procedure is now described. The ZP, $2\theta_0$, for a single Bragg peak is one of the systematics errors contributing to the term $\theta_{\text{bias}}$ in:

$$\lambda = 2d \sin(\theta_{\text{obs}} + \theta_{\text{bias}})$$  \hspace{1cm} (3)

If the term $\theta_{\text{bias}}$ is dominated by the specimen displacement and zero-point errors, the peaks are biased by:

$$2\theta_{\text{bias}} = 2\theta_0 + 2 \left( \frac{\Delta R}{R} \right) \cos \theta$$  \hspace{1cm} (4)

The ZP may be determined as follows: (1) measure the $2\theta_{\text{obs}}$ using a line-position SRM such as NIST 640b Si, with high-angle data only being acquired; (2) For each of these reflections, the bias is determined as $2\theta_{\text{bias}} = 2\theta_{\text{true}} - 2\theta_{\text{obs}}$, where the values $2\theta_{\text{true}}$ are calculated using the certified lattice parameters for the SRM; and then (3) plots of $2\theta_{\text{bias}}$ versus $\cos \theta_{\text{obs}}$ are prepared and the plot extrapolated to $2\theta_{\text{obs}} = 180^\circ$. The plot will be linear if the SD and the ZP dominate the errors. The intercept of $2\theta_{\text{bias}}$ on the $\cos \theta_{\text{obs}}$ axis at $\theta_{\text{obs}} = 180^\circ$ gives the ZP.
Figure 2. Influence of specimen displacement on the Rietveld-determined zero-point ($2\theta_0$) and lattice parameter, $a_0$. Errors bars are $\pm 2\sigma$. 
Table 2. Lattice parameter reproducibility tests. Rietveld results for data sets collected with standard specimen holder. Specimen re-packed in holder for each data acquisition. Numbers in parentheses are the most significant figures of the Rietveld esd estimate. See Figure 3 for the lattice parameter values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Data Set</th>
<th>ZP Fixed SD Refined</th>
<th>ZP Fixed SD Fixed</th>
<th>ZP Refined SD Refined</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZP (2θ) - degrees</td>
<td>1</td>
<td>-0.038 (fixed)</td>
<td>-0.038 (fixed)</td>
<td>-0.074(34)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td></td>
<td></td>
<td>-0.059(34)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td></td>
<td></td>
<td>-0.067(34)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td></td>
<td></td>
<td>-0.056(35)</td>
</tr>
<tr>
<td>SD - µm</td>
<td>1</td>
<td>87.8 (2.0)</td>
<td>0.0 (fixed)</td>
<td>11.0(67.9)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>69.1 (2.0)</td>
<td></td>
<td>36.7(69.3)</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>41.8 (2.0)</td>
<td></td>
<td>-17.9(68.0)</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>67.0 (1.9)</td>
<td></td>
<td>28.8(71.3)</td>
</tr>
</tbody>
</table>

Figure 3. Analysis of precision for the reproducibility tests with a standard specimen holder. Error bars are ± 2σ.
CONCLUSION

It has been demonstrated that:
1. The strong parameter correlations linking the specimen displacement, the $2\theta$-scale zero-point and the lattice parameters should be addressed in Rietveld analysis when $2\theta$-dependent parameters are being refined.
2. Analysis of the reproducibility of lattice parameters has shown that the zero-point should be determined independently of the Rietveld calculations using a procedure which involves use of an SRM.
3. Small values of specimen displacement may be reliably determined by Rietveld analysis if the zero-point is fixed at a well-determined value.
4. Pre-determining the zero-point in this way should give a precision in the vicinity of 1 part in $10^5$.

REFERENCES