IMPROVING THE ACCURACY OF RIETVELD-DERIVED LATTICE PARAMETERS BY AN ORDER OF MAGNITUDE

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ABSTRACT

This is the fourth in a series of papers on Rietveld materials characterisation metrology presented at recent Denver X-ray Conferences [refs 1-3]. Reference 3 examined the management of the zero-point and specimen displacement corrections in extracting lattice parameters from Bragg-Brentano x-ray diffraction data by Rietveld analysis. This paper emphasises the importance of pre-determining the zero-point of the 2θ-scale, $2\theta_o$, prior to, and independently of, the Rietveld calculations. In addition, the specimen displacement correction must be refined in the Rietveld computations with Bragg-Brentano data to minimise systematic errors in the lattice parameters.

A zero-point determination procedure is described using line-position standard reference materials (SRMs) to extrapolate a plot of $2\theta_{bias}$ versus $cos\,\theta_{obs}$ to θ = 90°, with $2\theta_{bias} = 2\theta_{true} - 2\theta_{obs}$ for $2\theta_{true}$ calculated with the known lattice parameters and $2\theta_{obs}$ being the measured value. Excellent agreement was obtained for $2\theta_o$ values determined with NIST SRM 660a LaB_6 and NIST Si 640 standards. The effectiveness of this approach when used with the co-refinement of the lattice parameters and specimen displacement refinement is demonstrated with data sets for CeO_2, Al_2O_3 and TiO_2 (rutile) powders from the NIST SRM 674a set. The accuracy of lattice parameters determined by this Rietveld approach is approximately 1 part in 50,000.

INTRODUCTION

The Curtin University Materials Research Group has gained extensive experience in the use of Rietveld analysis of advanced ceramics characterisation with particular reference to 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 on Rietveld analysis metrology [1-3]. This latest 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 had 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 [4].

Reference 3 considers the impact on Rietveld lattice parameter determinations of the heavy Rietveld parameter correlations between the lattice parameters, the specimen displacement (SD), and the instrument zero-point of the 2θ measurement scale ($2\theta_o$). These correlations cause the propagation of bias between these parameters.

DETERMINING THE ZERO-POINT INDEPENDENTLY OF THE RIETVELD CALCULATIONS USING SRMs

The zero-point, $2\theta_o$, for a single Bragg peak is one of the systematic errors contributing to the quantity θ_{bias} in:

$$\lambda = 2d\ sin(\theta_{obs} + \theta_{bias}) \quad (1)$$

where θ_{obs} is the measured Bragg angle. If θ_{bias} is dominated by the specimen displacement and zero-point errors, the peaks are biased by:

$$2\theta_{bias} = 2\theta_o + 2[\Delta_R / R]\ cos\theta \quad (2)$$

for specimen displacement Δ_R and goniometer radius R.

The zero-point may be determined as follows: (1) measure the $2\theta_{obs}$ using a line-position standard reference material (SRM), with high-angle data only being acquired; (2) for each of these reflections, the bias is determined as $2\theta_{bias} = 2\theta_{true} - 2\theta_{obs}$, where the values $2\theta_{true}$ are calculated with the certified lattice parameters for the SRM; and then (3) a plot of $2\theta_{bias}$ versus $cos\theta_{obs}$ is prepared and the line-of-best-fit extrapolated to $\theta_{obs} = 90°$. The intercept on the $2\theta_{bias}$ axis gives $2\theta_o$.

It is noted that specimen transparency causes an additional SD contribution according to the information depth for symmetric optics,

$$ID = sin\theta / 2\mu \quad (3)$$

where μ is the linear attenuation coefficient. This effect should be included in the extrapolation procedure and the Rietveld algorithm when working with x-ray transparent materials. In that case, equation 2 becomes

$$2\theta_{bias} = 2\theta_o + 2\ [(\Delta_R + sin\theta / 2\mu)/ R]\ cos\theta \quad (4)$$

EXPERIMENTAL

The materials employed for the study were (i) NIST SRM 660a LaB_6 and SRM 640 Si powders for constructing $2\theta_o$ calibrations, and (ii) the set of NIST SRM 674a powders for CeO_2, α-Al_2O_3 and TiO_2 (rutile) for acquiring whole-pattern data for the Rietveld determinations of lattice parameters.

The 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 (Kα wavelengths: 1.54060, 1.54439 Å); fixed slit optics with incident beam divergence = 1°, receiving slit = 0.15°, post-diffraction graphite analyser; and NaI detector with pulse discrimination. In collecting data sets, the 2θ step size was 0.02°; the counting time per step was 2s; and the 2θ range = 20 - 150°.

The data sets were collected with a 40-position sample holder. The influence of re-mounting the powder in the holder and also of changing the position of the sample were also investigated.

Rietveld modelling was performed using the *Rietica* program [5]. Crystal structure data (atom coordinates) were fixed at values from the Inorganic Crystal Structure Data Base (FachInformationsZentrum and Gmelin Institut, Germany) - ICSD 72155 from reference [6] for CeO_2, ICSD 73724 for α-Al_2O_3 [7] and ICSD 64987 for TiO2 (rutile) [8]. The refinements involved adjusting the pattern-background polynomial parameters (4 terms), the SD, the lattice parameters, the phase scale and peak profile functions (pseudo-Voigt with asymmetry). The values of $2\theta_o$ and SD were fixed in some refinements and relaxed in others. Transparency corrections were not applied (see following section).

ZERO-POINT CALIBRATION RESULTS

Figure 1 shows the plots for determining $2\theta_o$ by extrapolation. The excellent linearity is indicated by the regression R^2 values. The agreement between the two independent determinations of $2\theta_o$, 0.0410° for LaB_6 and 0.0418° for Si, respectively, is sound. The difference in the slopes of the 2 powders corresponds to differences in SD, with the effective SD values being 236 μm for LaB_6 and 197 μm for Si, respectively (goniometer radius R = 200.5 mm). It is noted that the corresponding *ID*s for x-ray attenuation at $2\theta_o = 0°$, 5 μm for LaB_6 and 36 μm for Si, are substantially less than the values derived by extrapolation, indicating that transparency is not dominant.

Based on the 2 calibrations, the value of $2\theta_o$ was set at the mean value for the Rietveld refinements, 0.0414° ± 0.0004°.

RIETVELD REFINMENT TRIALS FOR LATTICE PARAMETERS

Figure 2a shows the CeO_2 lattice parameter Rietveld refinement results obtained by fixing the SD at zero and refining $2\theta_o$. The figure shows the influence of (i) repeating the data collection without removing the specimen from the holder, (ii) re-packing the powder into the same holder before recollecting the data, and (iii) recollecting the data by moving the specimen holder to another position for the 40-sample holder.

The serious mis-match between the values obtained here and the NIST certificate value is evident. The systematic difference between the values obtained and the NIST value is approximately 0.003Å or 1 in 2000. Clearly the high correlation between $2\theta_o$ and the lattice parameter forces the latter to a biased value if the SD is not refined. Figure 2b shows the dramatic improvement realised when $2\theta_o$ value is fixed at the calibration value and the SD is refined. By inspection, the Rietveld results now agree with the NIST value within the stated limits of uncertainty. It is evident that the true accuracy of the Rietveld lattice parameters is approximately 0.0005 Å or 1 part in 50,000.

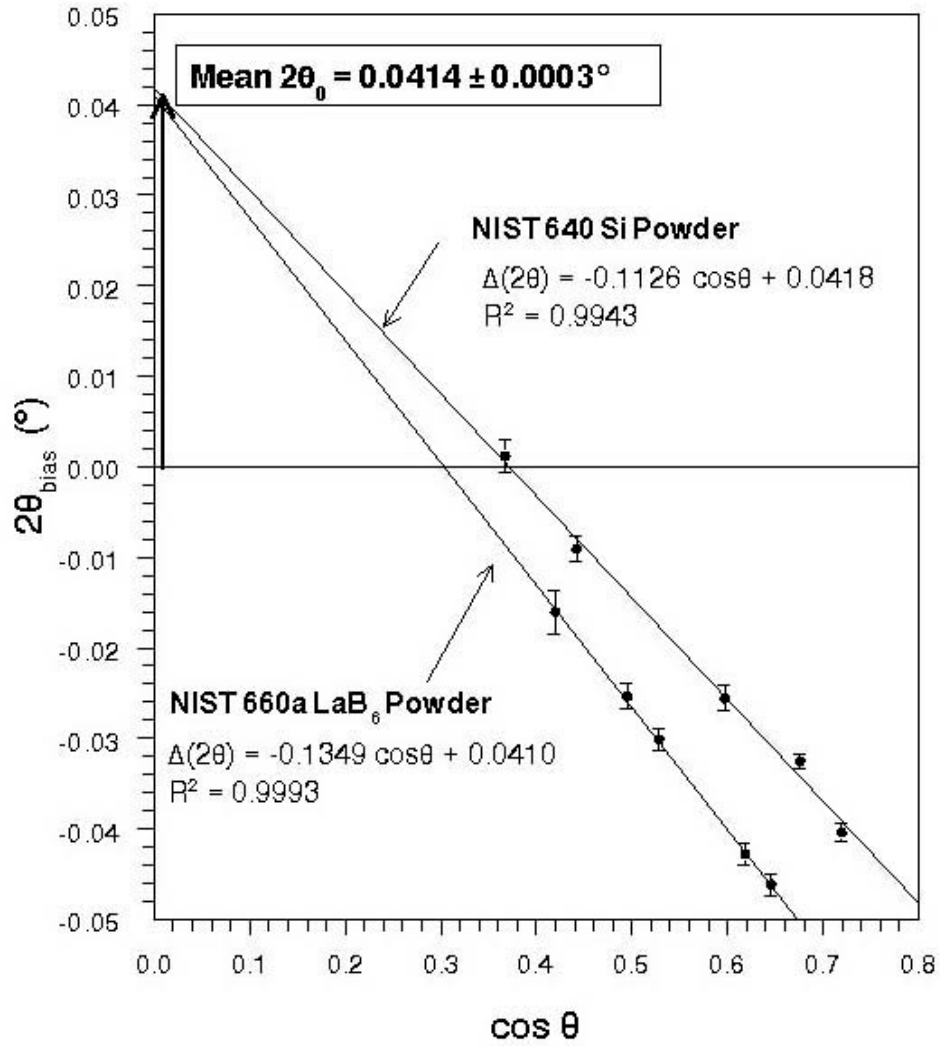

Figure 1. Calibration plots to determine the $2\theta_o$ value with SRM data. The error bars indicate ± 1 standard deviation.

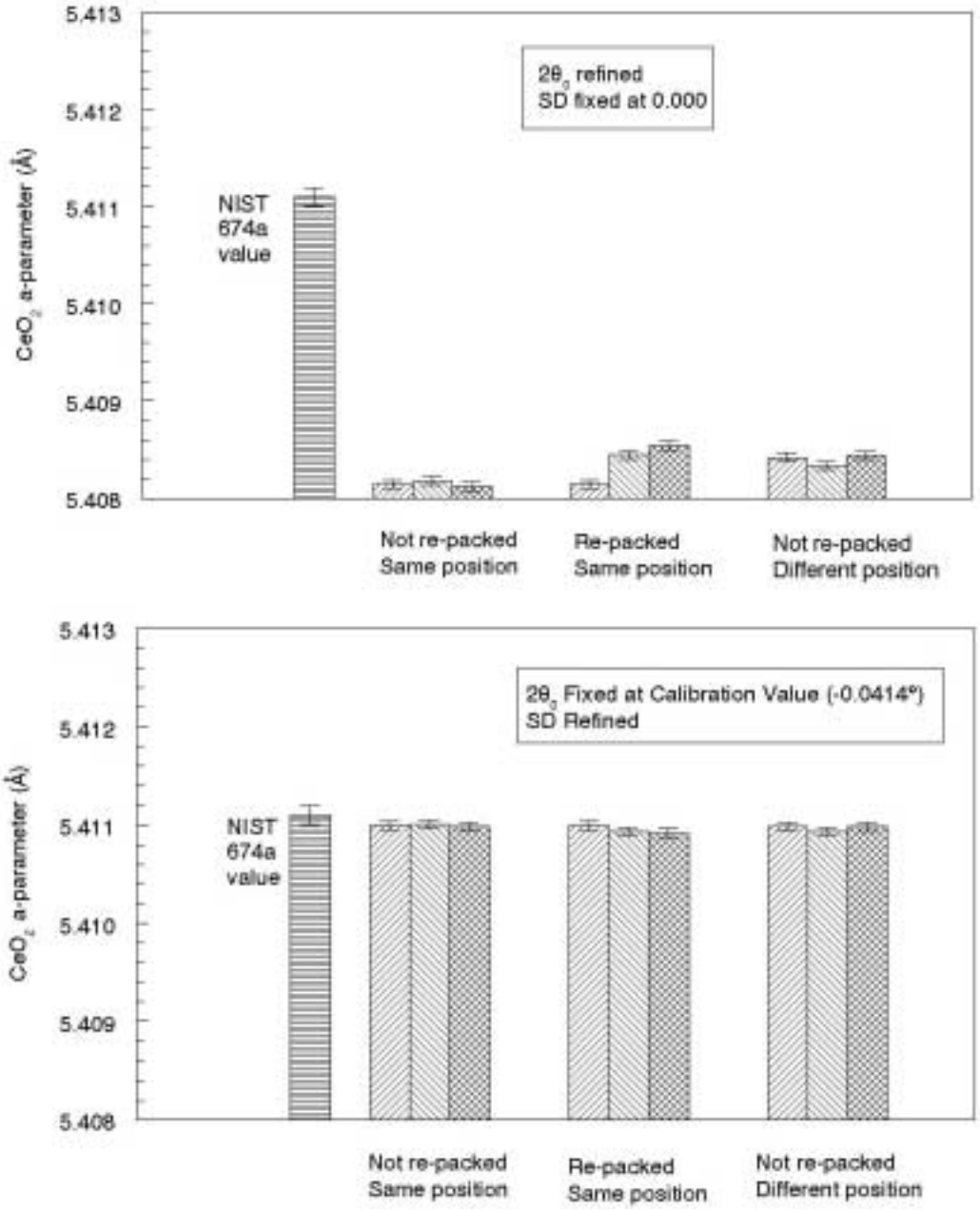

Figure 2. CeO_2 lattice parameters obtained with the $2\theta_o$ value (a - above) not fixed at the calibration value and (b - below) fixed at the calibration value. The error bars indicate ± 1 standard deviation.

Table 1. Analysis of Rietveld precision in the lattice parameters for CeO_2 repeat analyses with data collected after re-packing the powder into the holder. The $2\theta_o$ value was fixed at the calibration value, 0.0414 °, and the SD was refined.

Refinement	Lattice parameter (Å)	Rietveld esd (Å)
1	5.410991	0.000043
2	5.410929	0.000042
3	5.410916	0.000043
4	5.410987	0.000043
5	5.410981	0.000048
6	5.410975	0.000049
7	5.411004	0.000045
8	5.410978	0.000045
Mean values	5.410970	0.00045
	Esd (pop stats)*	0.000031

$$^{*}Esd\,(pop\ stats) = \sqrt{\frac{\sum\left(\bar{x} - x\right)^2}{(n-1)}}$$

Table 1 provides a comparison of a population statistics analysis of the uncertainty in CeO_2 lattice parameter with the estimated standard deviations provided by the Rietveld program. The Rietveld repeat values were obtained by fixing the $2\theta_o$ at 0.0414º. The esd from population statistics, 0.000031 Å, is comparable with, but less than the average value from the Rietveld program which is expected. These results indicate that the accuracy of determining the CeO_2 lattice parameter by this method is better than 1 part in 50,000, taking the accuracy to be ± 2 standard deviations as given by the Rietveld program.

Table 2 confirms the accuracy estimate of approximately 1 part in 50,000 from an examination of the Rietveld lattice parameters for the NIST 674a powders for CeO_2, Al_2O_3 and TiO_2 (rutile), again using the $2\theta_o$ calibration value of 0.0414º and with the SD refined. The agreement between the Rietveld values from this study and the NIST certificate value are all less than 3 standard deviations of the difference. Taking the accuracy to be ± 2 standard deviations, the values for CeO_2 and α-Al_2O_3 are better than 1 in 50,000 whereas those for rutile are marginally less.

Table 2. Lattice parameters from the Rietveld refinement trials for the NIST 674a powders, compared with the NIST certificate values. The final column gives the 'accuracy', defined as the ratio of the parameter and the esd for the difference between the Rietveld and certificate values.

SRM	Parameter	This Study	NIST Certificate	Δ/σ	Accuracy = parameter/σ
CeO_2	a	5.410991	5.411102	1.1	1:130,000
	σ	0.000043	0.000097		
α-Al_2O_3	a	4.759208	4.759397	2.2	1: 180,000
	σ	0.000026	0.000080		
	c	12.99202	12.99237	1.4	1: 120,000
	σ	0.00011	0.00022		
TiO_2, rutile	a	4.593867	4.593939	0.9	1: 74,000
	σ	0.000051	0.000062		
	b	2.958941	2.958862	-1.0	1: 90,000
	σ	0.000048	0.000063		

CONCLUSION

The authors recommend the following strategies for Rietveld lattice parameter determinations with Bragg-Brentano diffractometer data:

- Determining the zero-point ($2\theta_o$) independently of the Rietveld analysis, using SRM line position standards. The SRM should have minimal x-ray transparency.
- The specimen displacement error must be included in the Rietveld refinement model when extracting lattice parameters, and the zero-point should be constrained at the calibration value.
- Only small displacements should modelled (*ca*. several hundred μm).

Accuracy in the vicinity of 1:50,000 is achievable. Co-refinement of the lattice parameters with $2\theta_o$, and no SD refinement, is likely to result in an accuracy of 1 part in several thousand only.

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