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Powder X-ray Structure Refinement Applying a Theory for Particle Statistics

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Abstract. A new method for analysis of powder diffraction intensity data recently developed by the author has been modified to include the effects of possible statistical errors in the goniometer angle 2Θ. The analytical method is based on the maximum-likelihood estimation. Structure parameters refined by the method for fluorapatite $Ca_5(PO_4)_3F$, anglesite $PbSO_4$ and barite $BaSO_4$ have become closer to those obtained by single-crystal structure analyses than the results obtained by applications of a conventional Rietveld refinement to the same powder diffraction data, similarly to the previous analyses, where the errors in 2Θ are not included. The statistical errors about 2Θ are estimated at $\Delta 2\Theta = 0.0030^{\circ}$, 0.00099° and 0.0036° from the powder diffraction data sets of fluoroapatite, anglesite and barite, respectively.

Introduction

The Rietveld analysis is an application of the least-squares method to powder diffraction intensity data based on a crystallographic structure model. In principle, errors in optimized crystallographic parameters, such as lattice constants, atomic coordinates, site occupancy, atomic displacement parameters *etc* could be evaluated by the method, provided that the experimental errors are known quantities.

However, we often encounter too small errors in the parameters optimized by the Rietveld analysis on powder X-ray diffraction data, particularly in the cases: strong x-ray source, long measurement time, high-resolution optics, high-sensitivity detectors, samples with high crystallinity and large scattering cross section. This problem is simply ascribed to the under-estimation of the experimental errors, and the solution should simply be the use of appropriate values for the assumptions of the statistical errors as the input to Rietveld programs.

It is well known that the statistical errors in the observed powder diffraction intensity data are caused by counting statistics and particle statistics [1,2]. Recently, the author has developed a new analytical method based on the maximum-likelihood estimation (MLE) method [3], where a model for statistical errors including counting, particle and proportional uncertainties is optimized. In this study, the author has extended the new methodology to examine the effects of possible errors in the goniometer angle 2Θ.

Theory

Powder X-ray diffraction intensities $\{Y_j\}$ observed at diffraction (goniometer) angles $\{2\Theta_j\}$ are supposed to be normally distributed around the values calculated by an appropriate model $y(2\Theta_j)$ with statistical errors $\{\sigma_j\}$. Then the probability that this data set should be realized is given by

$$P = \prod_{j=1}^{N} \frac{1}{\sqrt{2\pi}\sigma_j} \exp\left(-\frac{\Delta_j^2}{2\sigma_j^2} \right), \tag{1}$$

where $\Delta_j \equiv Y_j - y(2\Theta_j)$ is the deviation of the observed intensity from the caluculated value. Maximum-likelihood estimation (MLE), which means the maximization of the probability *P*, is exactly equivalent to the minimization of the unlikelihood estimator *U*, defined by

$$U \equiv -2\ln P - N\ln(2\pi) = \sum_{j=1}^{N} \left(\frac{\Delta_j^2}{\sigma_j^2} + \ln\sigma_j^2 \right), \tag{2}$$

The total statistical variance σ_j^2 is modeled by the sum of the variance caused by counting statistics $(\sigma_{\mathrm{c}})_j^2$ and particle statistics $(\sigma_{\mathrm{p}})_j^2$ in powder diffractometry [1,2], and the term for errors proportional to the observed intensity $(\sigma_{\mathrm{r}})_j^2$ suggested by Toraya [4,5], and another term propagated from statistical variance about 2Θ angle $(\sigma_{2\Theta})_j^2$, that is,

$$\sigma_j^2 = (\sigma_{\mathrm{c}})_j^2 + (\sigma_{\mathrm{p}})_j^2 + (\sigma_{\mathrm{r}})_j^2 + (\sigma_{2\Theta})_j^2 . \tag{3}$$

The variance caused by counting statistics $(\sigma_{\mathrm{c}})_j^2$ is approximated by the expected value of the number of observed X-ray photons,

$$(\sigma_{\mathrm{c}})_j^2 = y(2\Theta_j) . \tag{4}$$

The variance caused by particle statistics $(\sigma_{\mathrm{p}})_j^2$ at the diffraction angle $2\Theta_j$ for the symmetric reflection (Bragg-Brentano) geometry is formulated by [1,3]

$$(\sigma_{\mathrm{p}})_j^2 = \frac{C_{\mathrm{p}}[y(2\Theta_j) - b_j]^2 \sin\Theta_j}{(m_{\mathrm{eff}})_j} , \tag{5}$$

where C_{p} is an unknown proportionality factor and b_j is the background intensity. The effective multiplicity $(m_{\mathrm{eff}})_j$ is defined for overlapped reflections with the component intensity $y_k(2\Theta_j)$ by the following equation [6]:

$$(m_{\mathrm{eff}})_j \equiv \frac{[y_1(2\Theta_j) + \cdots + y_m(2\Theta_j)]^2}{[y_1(2\Theta_j)]^2 + \cdots + [y_m(2\Theta_j)]^2} . \tag{6}$$

The term for errors proportional to the intensities are formulated by

$$(\sigma_{\mathrm{r}})_j^2 = C_{\mathrm{r}}[y(2\Theta_j)]^2 , \tag{7}$$

where C_{r} is another unknown proportionality factor. Finally, the term propagated from statistical variance about 2Θ angle $(\sigma_{2\Theta})_j^2$ is given by

$$(\sigma_{2\Theta})_j^2 = \left[\frac{\partial y(2\Theta_j)}{\partial(2\Theta_j)} \Delta 2\Theta \right]^2 , \tag{8}$$

where $\Delta 2\Theta$ is the statistical error about the goniometer angle 2Θ, and the derivative is approximated by the finite difference:

$$\frac{\partial y(2\Theta_j)}{\partial(2\Theta_j)} \approx \frac{y(2\Theta_{j+1}) - y(2\Theta_{j-1})}{2\Theta_{j+1} - 2\Theta_{j-1}}, \tag{9}$$

in this study.

Analytical procedures

The following procedures are applied to structure refinement, similarly to the procedures the author has already reported [3], except that another unknown parameter $\Delta 2\Theta$ is additionally included in this study.

(i) A conventional Rietveld refinement is applied to powder diffraction data, with initial statistical errors of $\sigma_j = Y_j^{1/2}$.

(ii) An individual diffraction peak profile $y_k(2\Theta_j)$ is extracted on the final calculation of the optimized diffraction intensity in the Rietveld analysis. Then the effective multiplicity at each data point is calculated by Eq. 6.

(iii) The three-dimensional unlikelihood function $U(C_p, C_r, \Delta 2\Theta)$ is minimized by a downhill simplex (Nelder-Mead) algorithm [7].

(iv) A further Rietveld refinement is carried out with the statistical error σ_j calculated by Eq. 3 at each data point, and then steps (ii)–(iv) are repeated until convergence.

Applications to X-ray powder diffraction data

The results of Rietveld analysis and the new analytical method based on the maximum likelihood estimation upon fluorapatite $Ca_5(PO_4)_3F$, anglesite $PbSO_4$ and barite $BaSO_4$, measured with Bragg-Brentano diffractometers, are demonstrated in this section. The Rietveld analysis program *RIETAN-FP* (version 2.13) developed by Izumi and Momma [8] was used for all the Rietveld refinements. The scale factor, a constant peak-shift parameter, a ninth-order polynomial for the background intensity, and the profile parameters of a split pseudo-Voigt function [9] were optimized during the structure refinements. The peak profile cut-off range was extended to 28 times of the full-width at half maximum (FWHM), while it was 14 times of the FWHM in the previous analyses [3]. Correction for preferred orientation or surface roughness was not applied.

Fluorapatite, $Ca_5(PO_4)_3F$. Cu$K\alpha$ X-ray powder diffraction data of fluorapatite, $Ca_5(PO_4)_3F$, were originally attached to the *DBWS* Rietveld program package [10], and are currently available as an example data set in the *RIETAN-FP* package [8]. The space group of fluorapatite is $P6_3/m$ (No. 176). The statistical error in the goniometer angle was estimated at $\Delta 2\Theta = 0.0030°$ at the final refinement, which causes considerable contribution of $(\sigma_{2\Theta})_j$ as shown in Fig. 1. Figure 2 plots the difference in atomic coordinates between the structure refinements from the powder and single-crystal diffraction data [3,11]. The optimized atomic coordinates are almost unchanged from the previous results without the term $(\sigma_{2\Theta})_j^2$ [3], and show better coincidence with the single crystal data than the results of the Rietveld method.

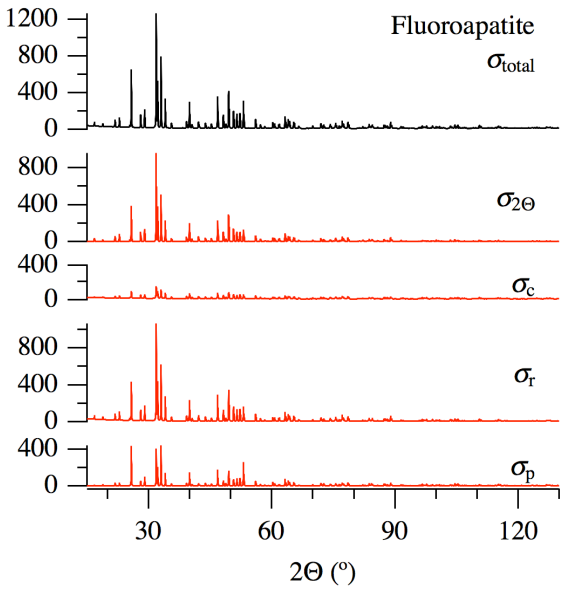

Fig. 1 Total statistical errors σ_{total} and component errors $\sigma_{2\Theta}$, σ_c, σ_r and σ_p, estimated for a data set of fluorapatite by the maximum likelihood estimation.

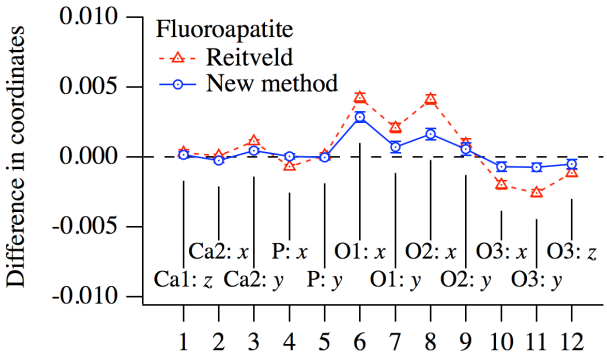

Fig. 2 Difference in atomic coordinates of fluorapatite optimized by the Rietveld method (triangles) and the new analytical method based on the maximum-likelihood estimation (circles).

Anglesite, $PbSO_4$. Cu$K\alpha$ X-ray powder diffraction data of anglesite, $PbSO_4$, supplied for a Rietveld refinement round robin [12], were reanalyzed in this study. The data are available as an example file in the *FullProf* package developed by Rodríguez-Carvajal [13]. The space group of anglesite is *Pnma* (No. 62). The statistical error in the goniometer angle was estimated at $\Delta 2\Theta$ = 0.0099º at the final refinement. The estimated total and component errors are shown in Fig. 3. The difference in atomic coordinates between the structure refinements from the powder and single-crystal diffraction data reported by Miyake *et al.* [14] are plotted in Fig. 4. The structure optimized by the Rietveld method is well coincided with the single-crystal data, and almost unchanged by the new analytical method.

Barite, $BaSO_4$. Cu$K\alpha_1$ X-ray powder diffraction data of barite, $BaSO_4$, are available as an example data set in the *RIETAN-FP* package [8]. The space group of barite is *Pnma* (No. 62) and isostructural to anglesite. The statistical error in the goniometer angle was estimated at $\Delta 2\Theta$ = 0.0036º at the final refinement. The estimated total and component errors are shown in Fig. 5. It is suggested that the effect of particle statistics is dominant on the statistical properties of this observed diffraction intensity data set. It is possibly caused by the lower probability to satisfy the diffraction condition by the use of monochromated X-ray source. The difference in atomic coordinates between the structure refinements from the powder and single-crystal diffraction data reported by Miyake *et al.* [14] are plotted in Fig. 6. Coincidence with the single crystal data is significantly improved by application of the MLE method based on the statistical model including particle statistics.

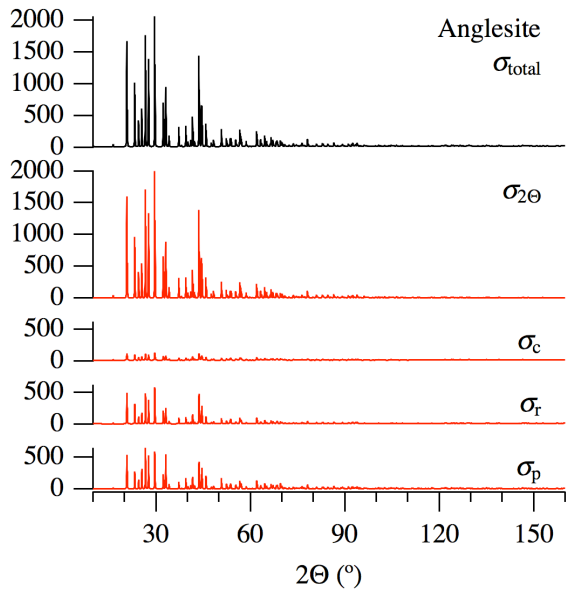

Fig. 3 Total statistical errors σ_{total} and component errors $\sigma_{2\Theta}$, σ_c, σ_r and σ_p, estimated for a data set of anglesite by the maximum likelihood estimation.

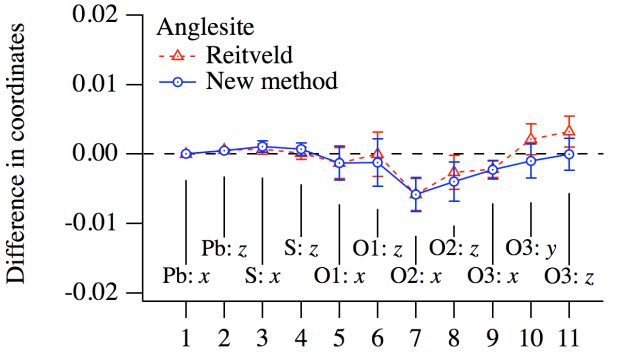

Fig. 4 Difference in atomic coordinates of anglesite optimized by the Rietveld method (triangles) and the new analytical method based on the maximum-likelihood estimation (circles).

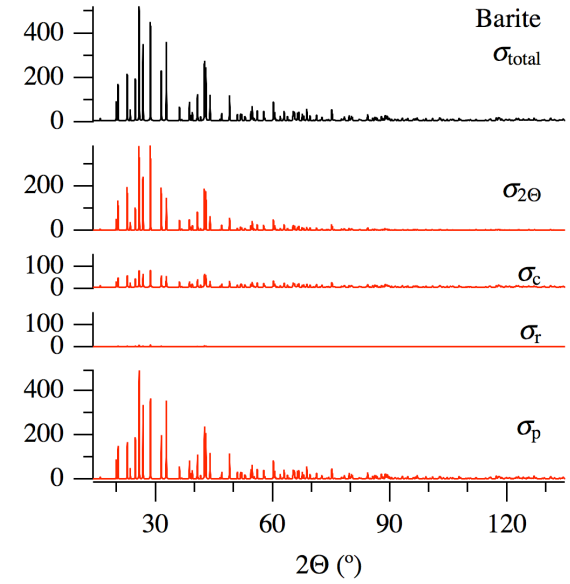

Fig. 5 Total statistical errors σ_{total} and component errors $\sigma_{2\Theta}$, σ_c, σ_r and σ_p, estimated for a data set of barite by the maximum likelihood estimation.

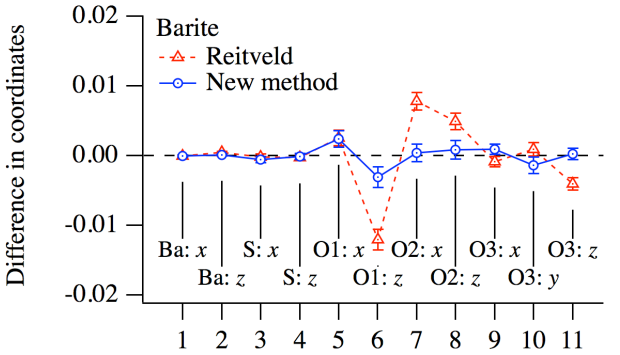

Fig. 6 Difference in atomic coordinates of barite optimized by the Rietveld method (triangles) and the new analytical method based on the maximum-likelihood estimation (circles)

Conclusions

A new methodology for structure refinement from powder X-ray diffraction data based on the maximum-likelihood estimation, recently developed by the author, has been extended to examine the possible contribution of the errors in the goniometer angle 2Θ. The errors in the goniometer angles are estimated at $\Delta 2\Theta = 0.0030$, 0.0099 and 0.0036º from the powder X-ray diffraction data sets of fluorapatite, anglesite and barite, respectively.

References

[1] L. Alexander, H. P. Klug and E. Kummer: J. Appl. Phys. Vol. 19 (1948), p. 742

[2] P. M. de Wolff: Appl. Sci. Res. Vol. 7 (1958), p. 102

[3] T. Ida and F. Izumi: J. Appl. Cryst. Vol. 44 (2011), p. 921

[4] H. Toraya: J. Appl. Cryst. Vol. 31 (1998), p. 333

[5] H. Toraya: J. Appl. Cryst. Vol. 33 (2000), p. 95

[6] T. Ida, T. Goto and H. Hibino: J. Appl. Cryst. Vol. 42 (2009), p. 597

[7] W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vettering: *Numerical Recipes: the Art of Scientific Computing, 3rd ed.* (Cambridge University Press 2007)

[8] F. Izumi and K. Momma: Solid State Phenom. Vol. 130 (2007), p. 15

[9] H. Toraya: J. Appl. Cryst. Vol. 23 (1990), p. 485

[10] R. A. Young, A. Sakthivel, T. S. Moss and C. O. Paiva-Santos: J. Appl. Cryst. Vol. 28 (1995), p. 366

[11] K. Sudarsanan, P. E. Mackie and R. A. Young: Mater. Res. Bull. Vol. 7 (1972), p. 1331

[12] R. J. Hill: J. Appl. Cryst. Vol. 25 (1992), p. 589

[13] J. Rodríguez-Carvajal: Phisica B Vol. 192 (1993), p. 55

[14] M. Miyake, I. Minato, H. Morikawa and S. Iwai: Am. Mineral. Vol. 63 (1978), p. 503