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4.3 (12:15-12:40)

Application of Maximum Likelihood Method to Powder Structure Refinement

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Motivation

Errors in Optimized Parameters (Lattice Const., Atomic Positions, etc) ?

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Too Small Errors in Optimized Parameters in the Output of Rietveld Analysis, particularly in the cases :

- Strong X-ray Source (Rotating Anode, Synchrotron)
- Long Measurement Time
- High-Resolution Optics (Crystal Analyzer or Monochromator)
- High-Seinsitivity Detectors (1-D, 2-D)
- Samples with Good Crystallinity and/or Heavy Elements

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Experimental Errors are Under-Estimated !

→ Use Appropriate Values for Experimental Errors !

Background/Theory (1/2)

Assumption about statistical errors on Rietveld analysis

$$\sigma_j^2 = \left(\sigma_c\right)_j^2$$

(1) σ_c : Error caused by counting (Poisson) statistics for count-loss negligible case

= square root of count $\sigma_c = \sqrt{y_{calc}}$

Background/Theory (1/2)

A theoretical model for statistical errors

$$\sigma_j^2 \approx (\sigma_c)_j^2 + (\sigma_p)_j^2$$

(1) σ_c : Error caused by counting (Poisson) statistics for count-loss negligible case

= square root of count $\sigma_c = \sqrt{y_{calc}}$

(2) σ_p : Error caused by particle (sampling) statistics (Alexander *et al.* 1948)

$$\sigma_p^2 \approx C_p (y_{calc} - b)^2 \sin\theta / m_{eff}$$

$(y_{calc} - b)$: peak intensity, m_{eff} : effective multiplicity

Dependence on (y_{calc} - b), 2θ and m_{eff} (for symmetric relection, stationary specimen) is acceptable.

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Proportionality factor C_p , determined by crystallite size, absorption factors of the sample and geometry of the diffractometer,

can experimentally be evaluated for stationary specimens,

in symmetric-reflection mode, if a standard powder and a sample-spinning attachment are used (Ida *et al.*, 2009).

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Background/Theory (1/2)

A theoretical model for statistical errors

$$\sigma_j^2 = (\sigma_c)_j^2 + (\sigma_p)_j^2 + (\sigma_r)_j^2$$

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$$\sigma_p^2 = C_p (y_{calc} - b)^2 \sin\theta / m_{eff}$$

$(y_{calc} - b)$: peak intensity, m_{eff} : effective multiplicity

Proportionality factor C_p is unknown

(3) σ_r : Error proportional to intensity (Toraya 1998, 2000)

Incompleteness of count-loss correction (?) and/or peak profile model (?)

$$\sigma_r^2 = C_r y_{calc}^2$$

Proportionality factor C_r is unknown

Background/Theory (1/2)

A theoretical model for statistical errors

$$\sigma_j^2 = (\sigma_c)_j^2 + (\sigma_p)_j^2 + (\sigma_r)_j^2$$

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$$\sigma_r^2 = C_r y_{calc}^2$$

Proportionality factor C_r is unknown

How can we optimize the statistical model including two unknowns C_p & C_r in variance to fit experimental data ?

Background/Theory (2/2)

Maximum likelihood estimation (MLE)

Maximization of the probability that the observed data should appear

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

Deviation of the observed value from calculated value : $\Delta_j = \left(Y_{\text{obs}}\right)_j - \left(y_{\text{calc}}\right)_j$

MLE can optimize not only $\left(y_{\text{calc}}\right)_j$, but also the error σ_j

Background/Theory (2/2)

Maximum likelihood estimation (MLE)

Maximization of the probability that the observed data should appear

= Minimization of $\sum_{j=1}^{N}\left(\frac{\Delta_j^2}{\sigma_j^2}+\ln\sigma_j^2\right)$ $\Leftrightarrow$ Maximization of $\prod_{j=1}^{N}\frac{1}{\sqrt{2\pi}\sigma_j}\exp\left(-\frac{\Delta_j^2}{2\sigma_j^2}\right)$

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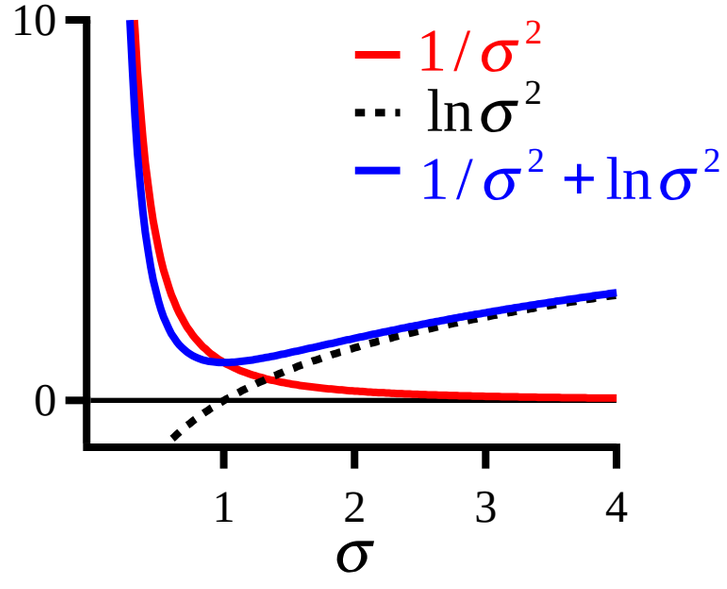
Least-squares method (LSQ)

= Minimization of $\sum_{j=1}^{N} \frac{\Delta_j^2}{\sigma_j^2}$ (σ_j : known error)

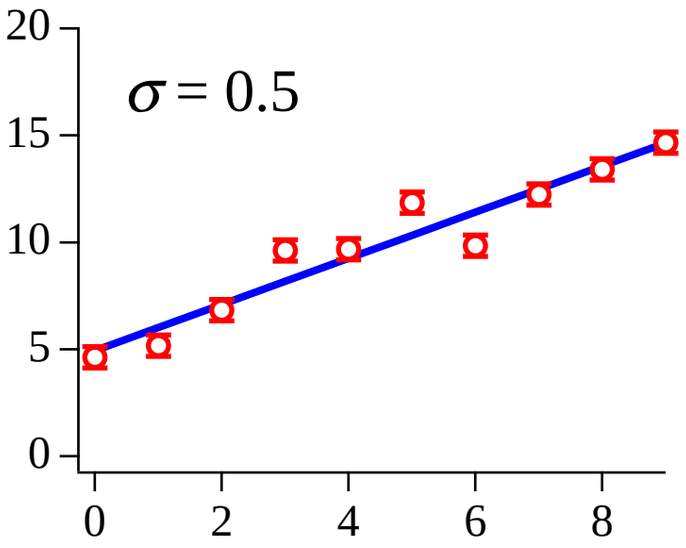
Weighted Sum of Squared Deviations

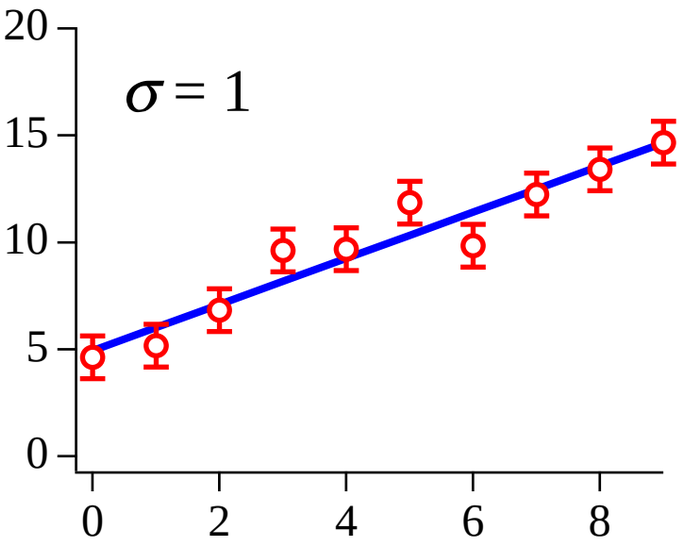


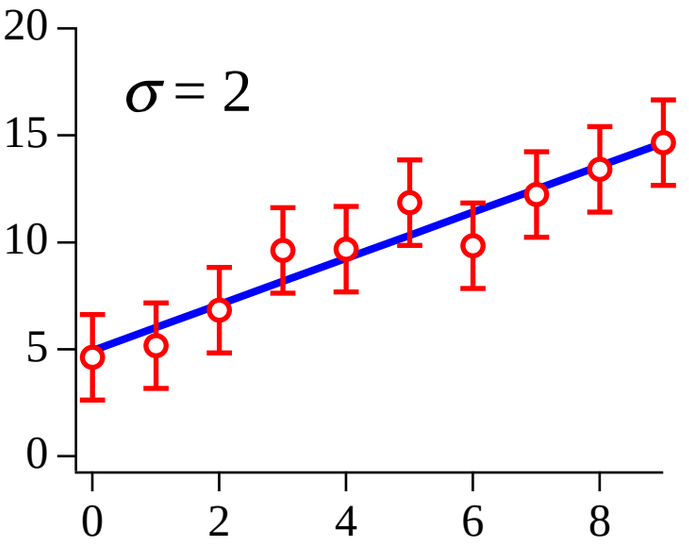
Background/Theory (2/2)

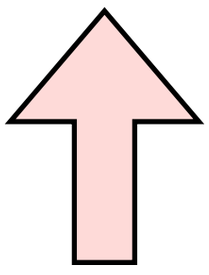
Ability of Maximum Likelihood Method

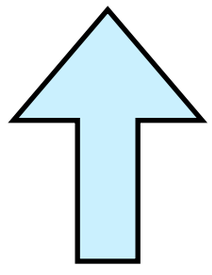
(= Minimum Unlikelihood Optimization)

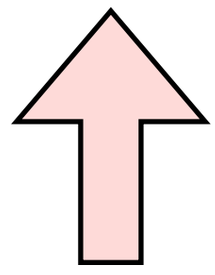












Unlikely

Likely

Unlikely

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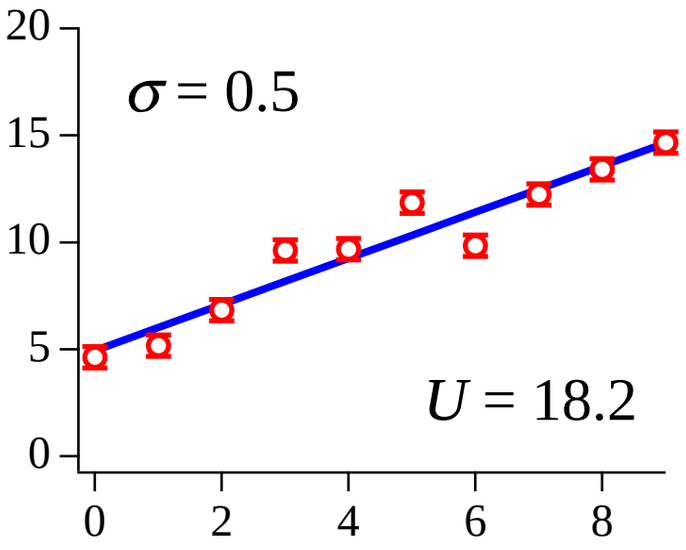

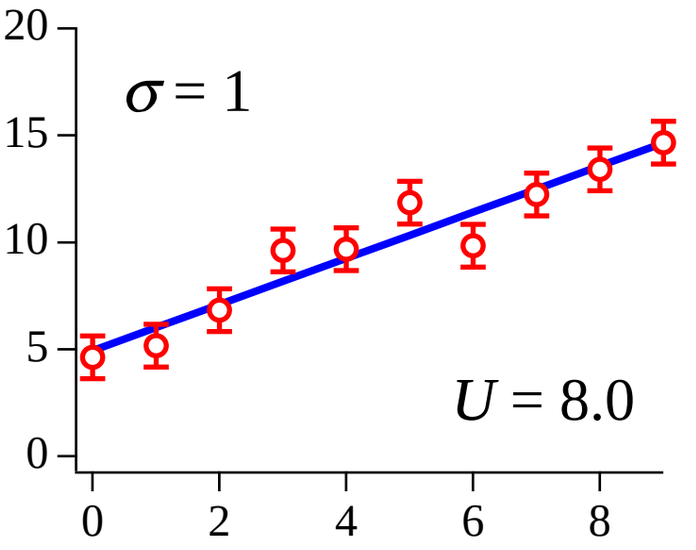

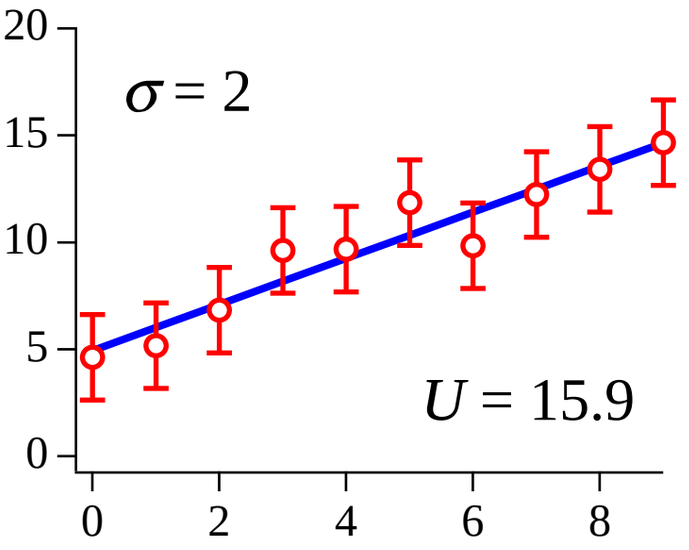

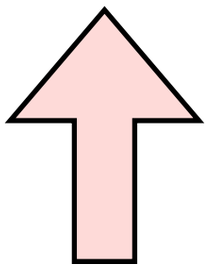

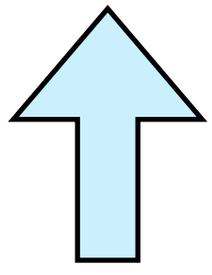

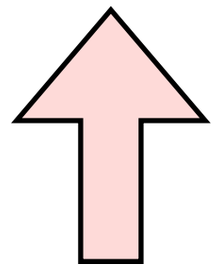

U = 18.2

U = 8.0

U = 15.9

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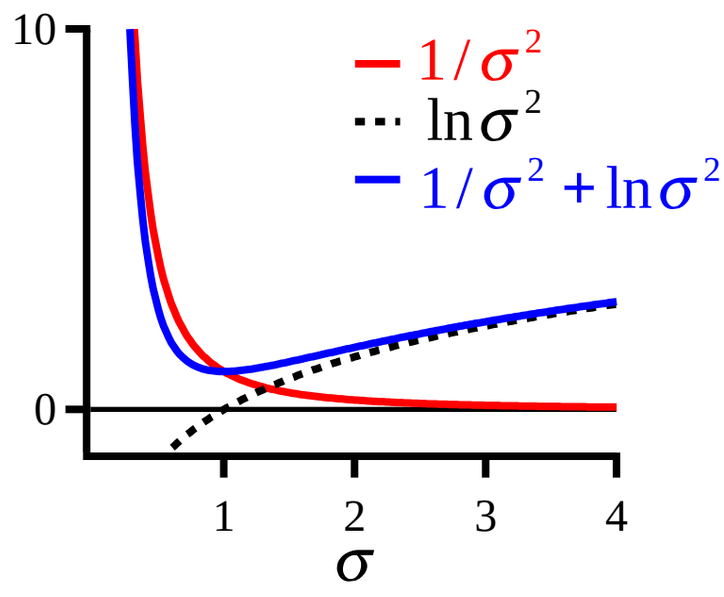

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Weighted Sum of Squared Deviations

Method of MLE Calculation

Step (1) : Structure refinement by the Rietveld method

Optimization of structure and profile models

(with *RIETAN-FP ver. 2.x*)

$\Delta, \{y_1, ..., y_M\}$

σ

Step (2) : Error estimation by MLE method

Evaluation of effective multiplicity at each data point

Optimization of error model by downhill simplex method

Calculation of statistical errors

(coded with a graphing software *Igor Pro ver. 6.2* macro language)

Iterations of steps (1) & (2)

Maximum-likelihood solution of structure, profile and error models will be obtained, when no change is observed on further iteration (typically 2~3 iterations are needed).

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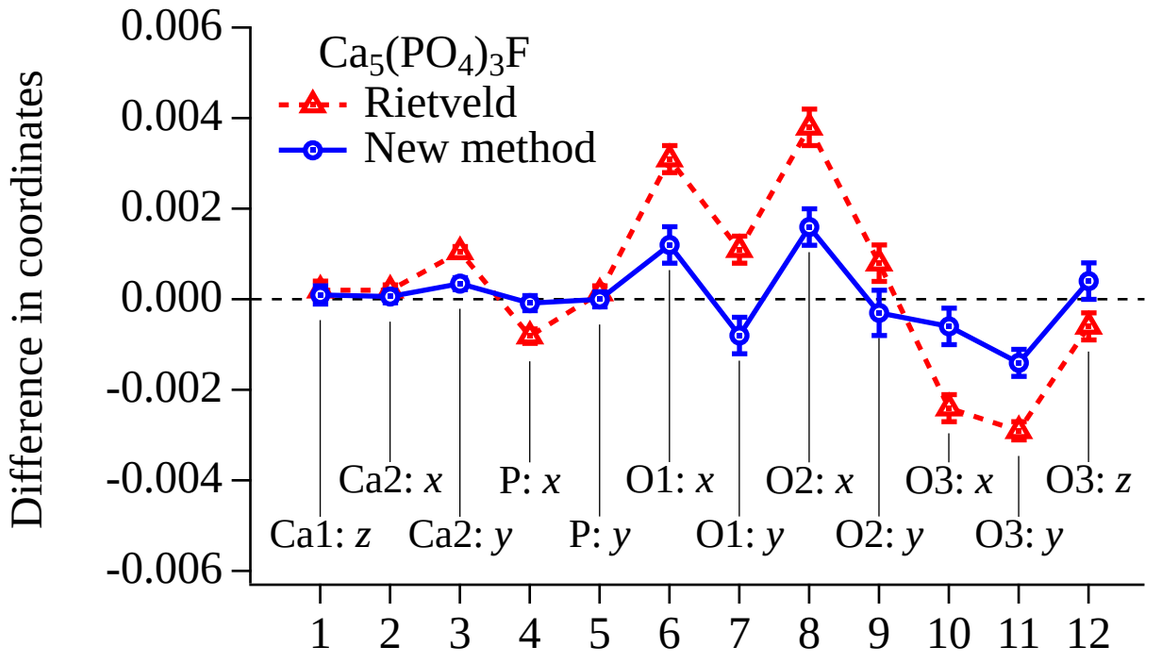
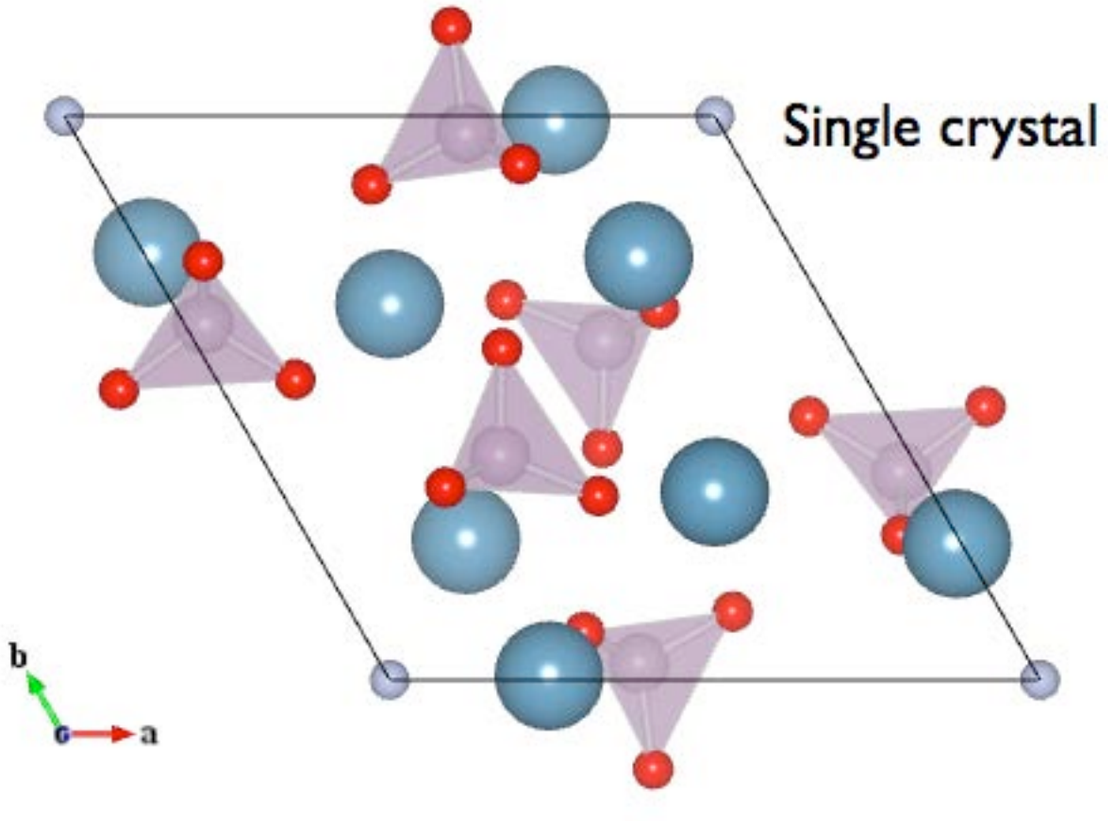
Results (1/4) $Ca_5(PO_4)_3F$ (open powder data attached to *RIETAN-FP*)

Comparison with single-crystal data

Synthetic (Sudarsanan *et al.* 1972)



Difference in atomic coordinates
(from synthetic single crystal)



$P6_3/m$

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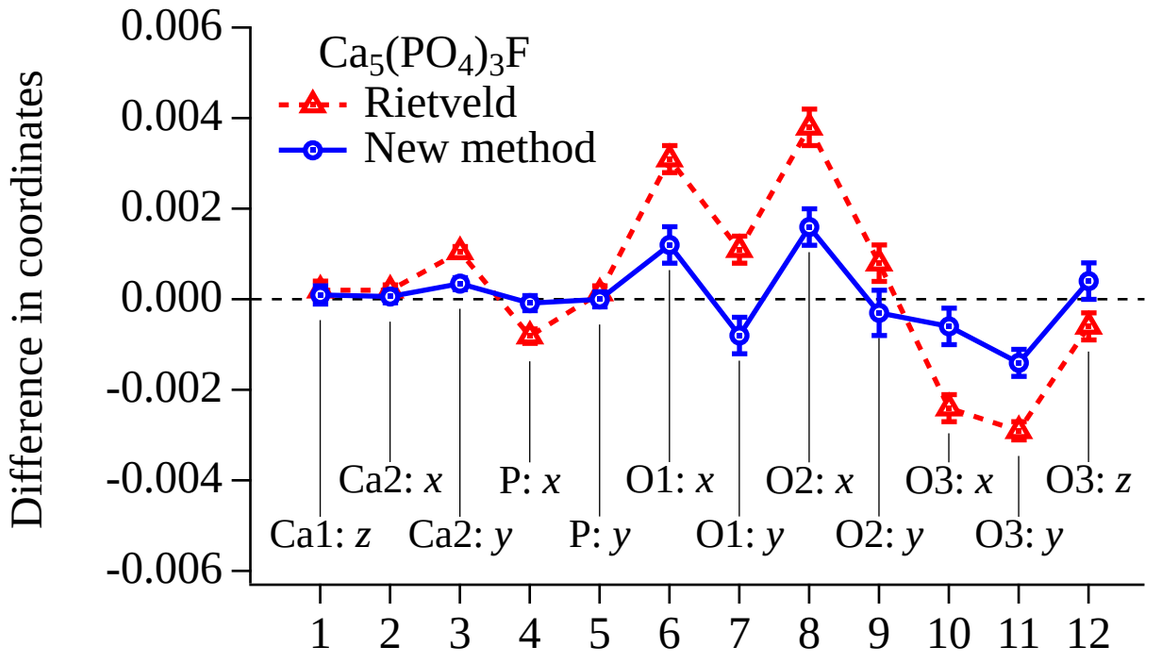

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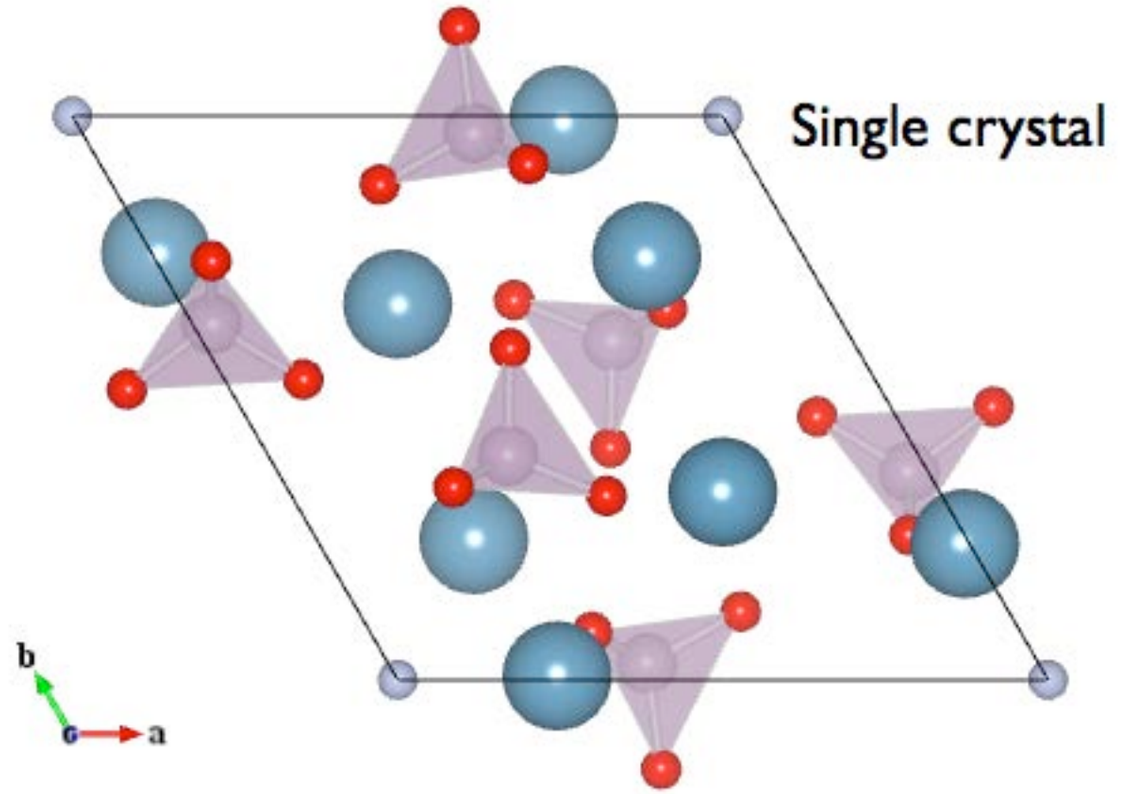


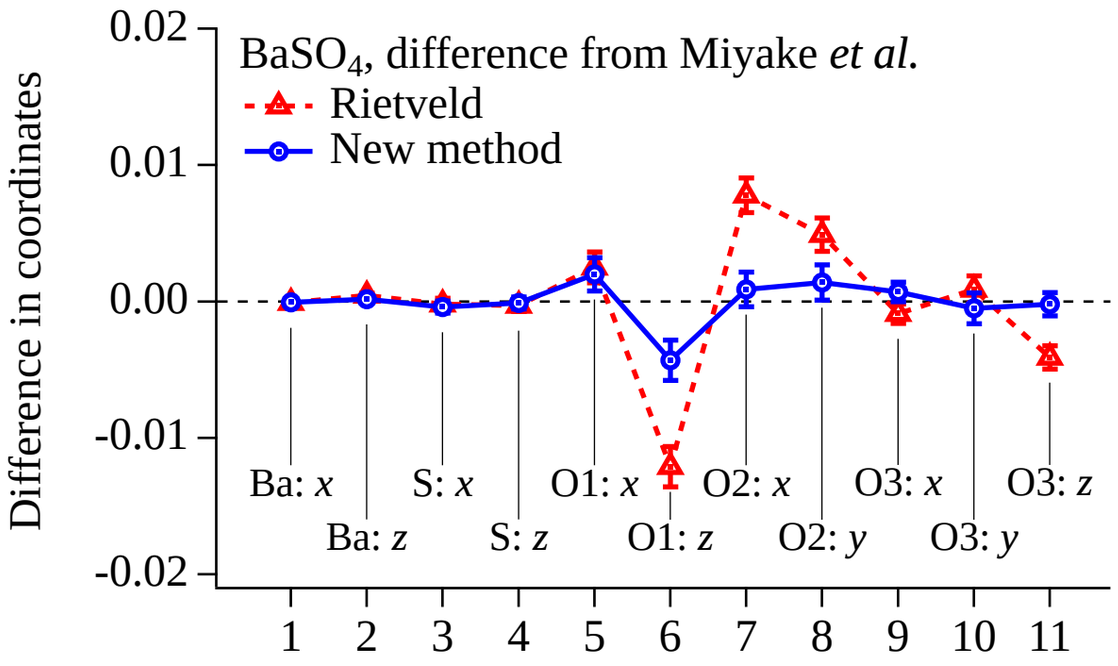
$P6_3/m$

The results of the new (MLE) method are closer to **single-crystal data** rather than **the results of the Rietveld method** from the same data set !

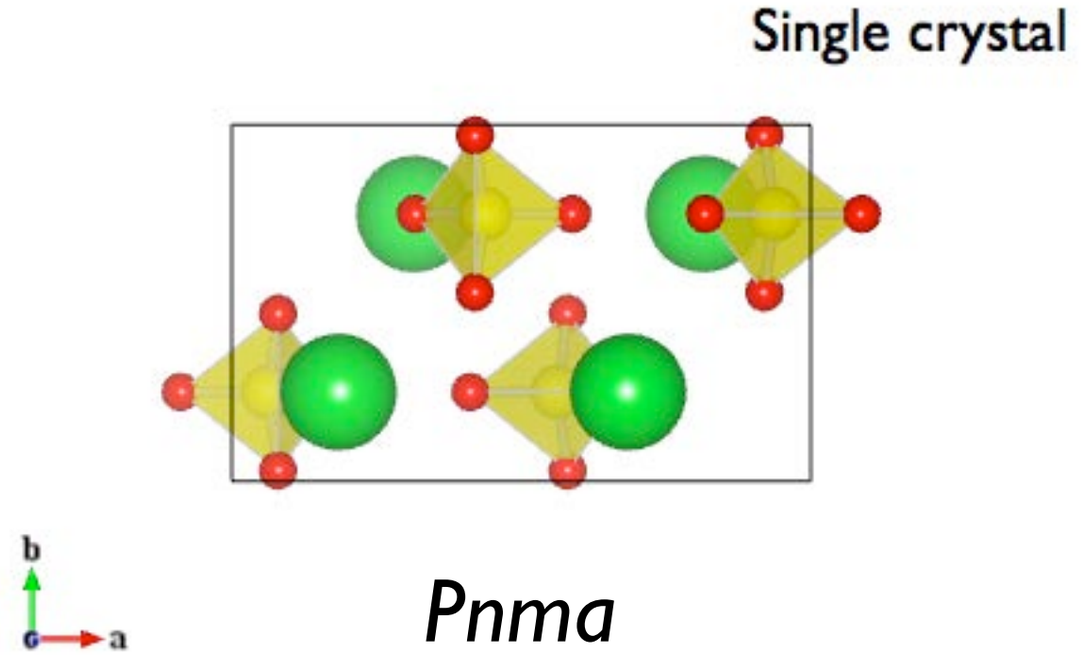
Results (2/4) $BaSO_4$ (open powder data attached to *RIETAN-FP*)

Comparison with single-crystal data

Spherical 0.15 mmΦ (Miyake *et al.* 1978),



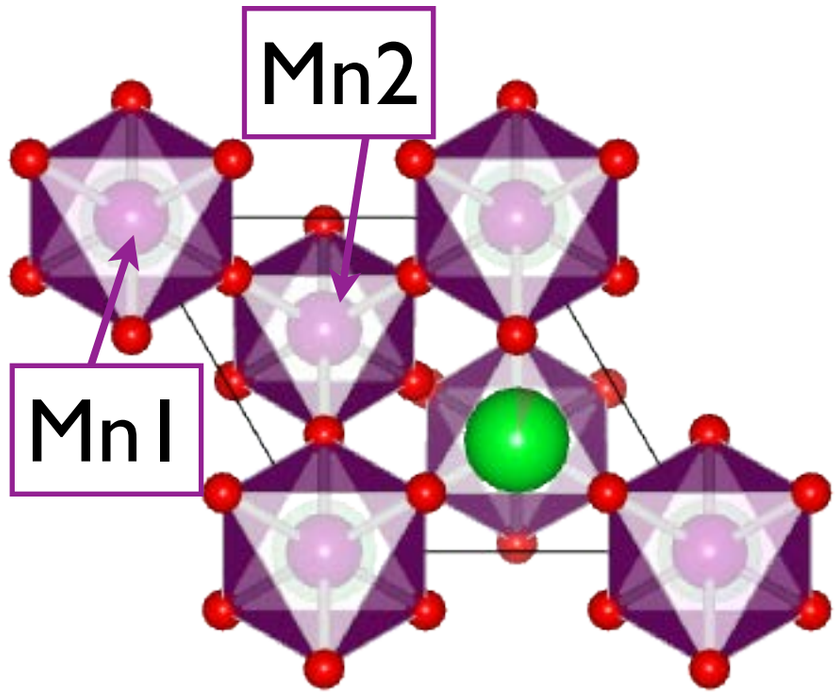
Difference in atomic coordinates
(from results by Miyake *et al.*)



The results of the new (MLE) method coincide with the **single-crystal data** except one structure parameter (O1: z), while the deviations in **the results of the Rietveld method** exceed the error range.

Results (3/4) $La_xSr_{1-x}MnO_3$

$La_{0.03}Sr_{0.97}MnO_3$, *P*6$_3$/*mmc*



SPring-8 BL19B2

$La_{0.03}Sr_{0.97}MnO_3$

Rietveld

BVS(Mn1) = +2.97

BVS(Mn2) = +4.39

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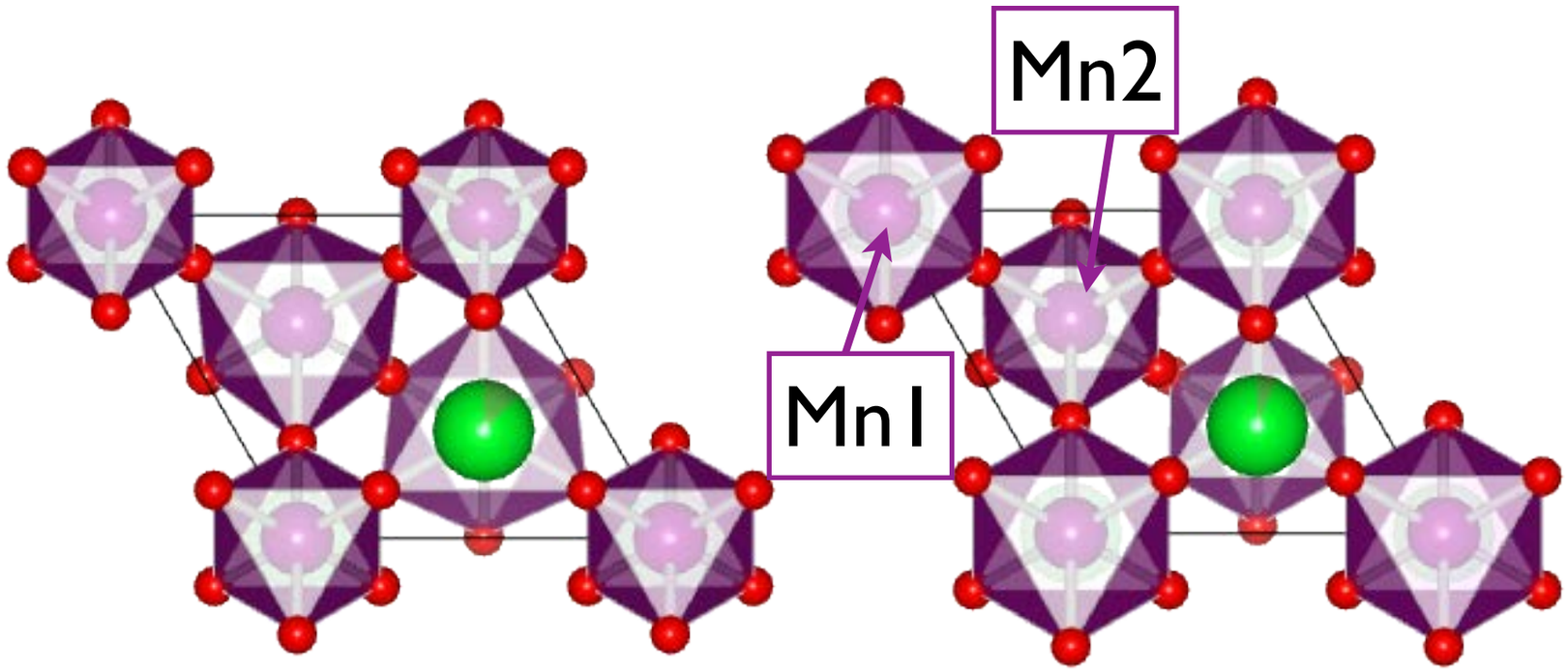

PDF#04-010-5038
(Star Quality / ND)
$La_{0.1}Sr_{0.9}MnO_3$
Rietveld
BVS(Mn1) = +4.65
BVS(Mn2) = +3.04

SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
Rietveld
BVS(Mn1) = +2.97
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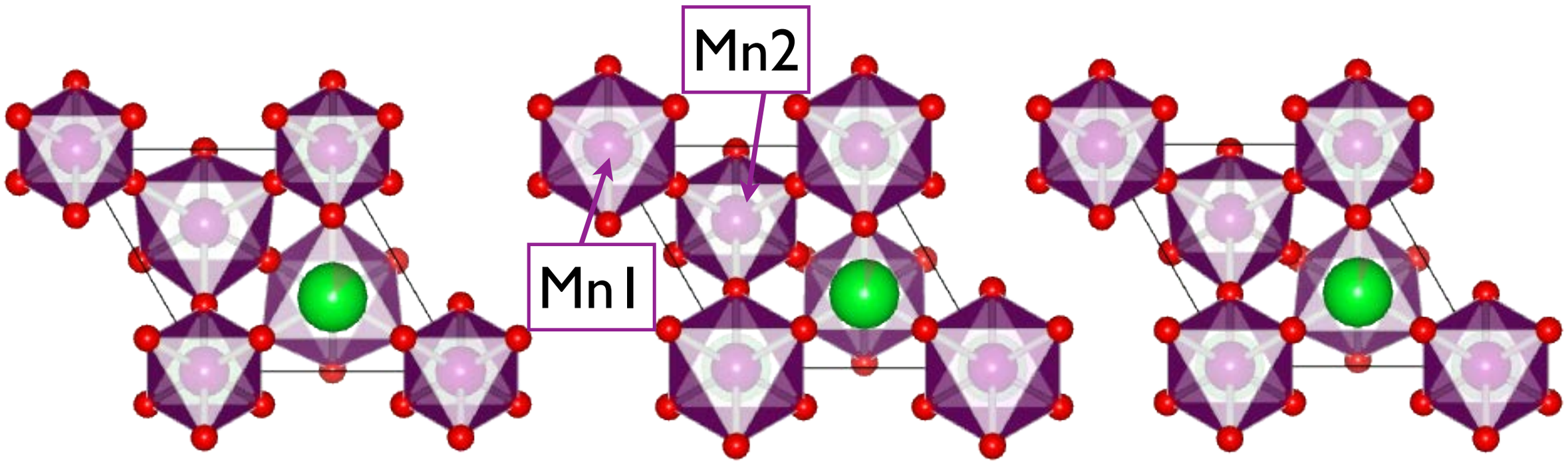

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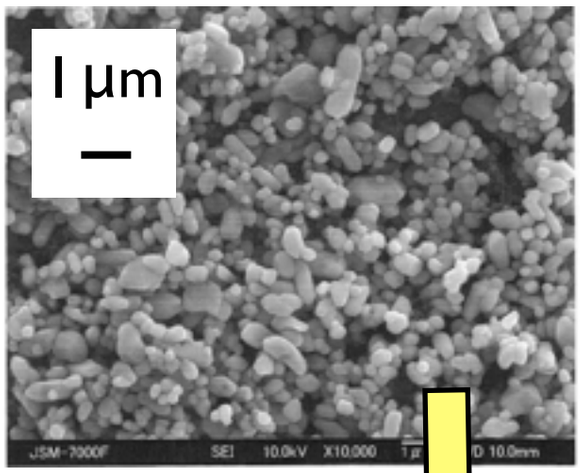
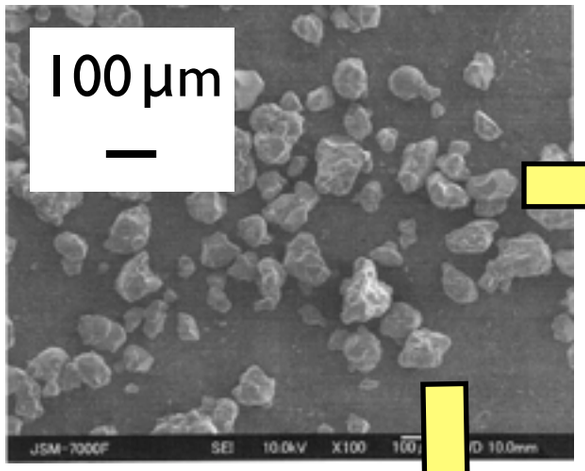
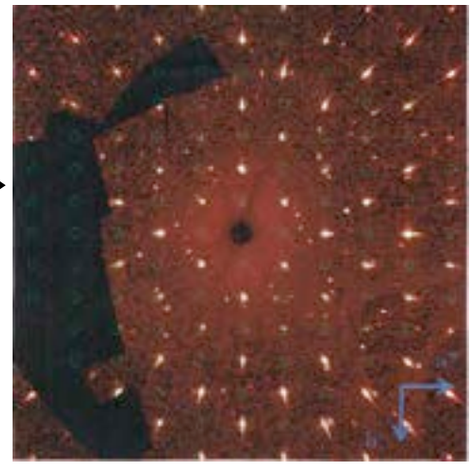
SPring-8 BL19B2
$La_{0.03}Sr_{0.97}MnO_3$
MLE
BVS(Mn1) = +3.82
BVS(Mn2) = +3.90

Results (4/4) $BaSO_4$, heat-treated coarse-grain powder

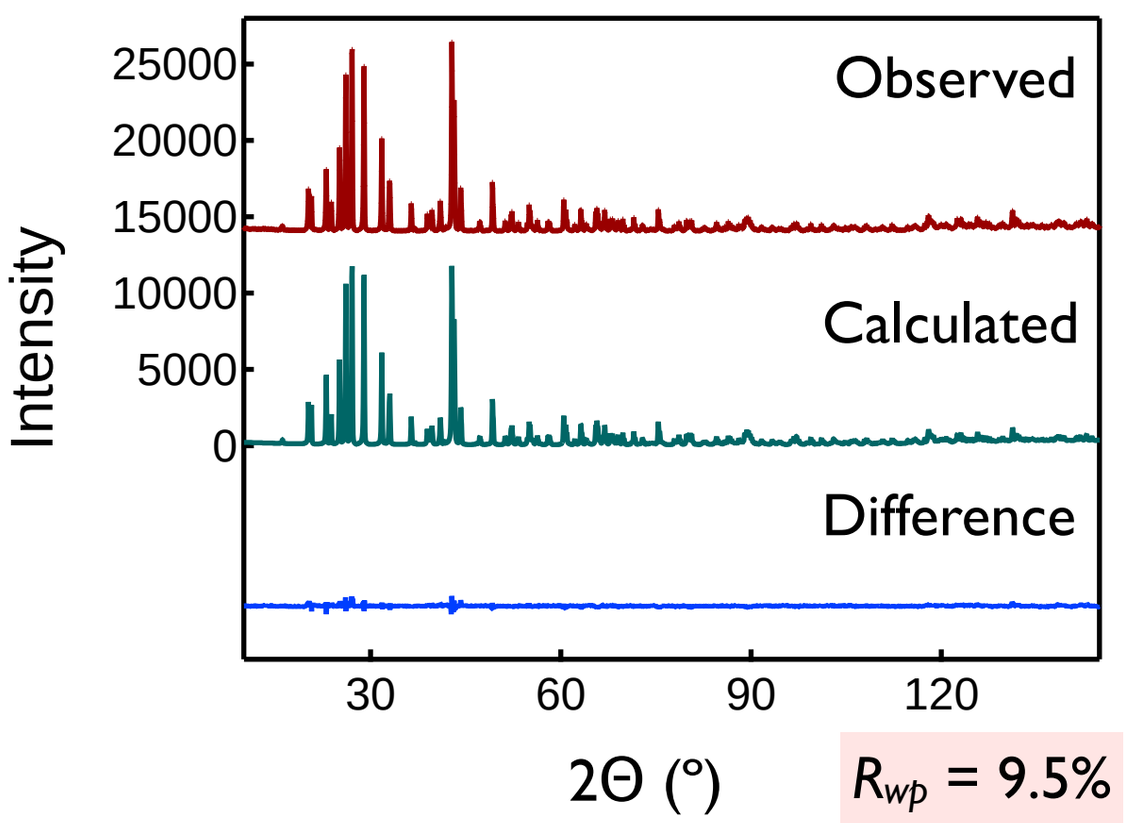


1000°C



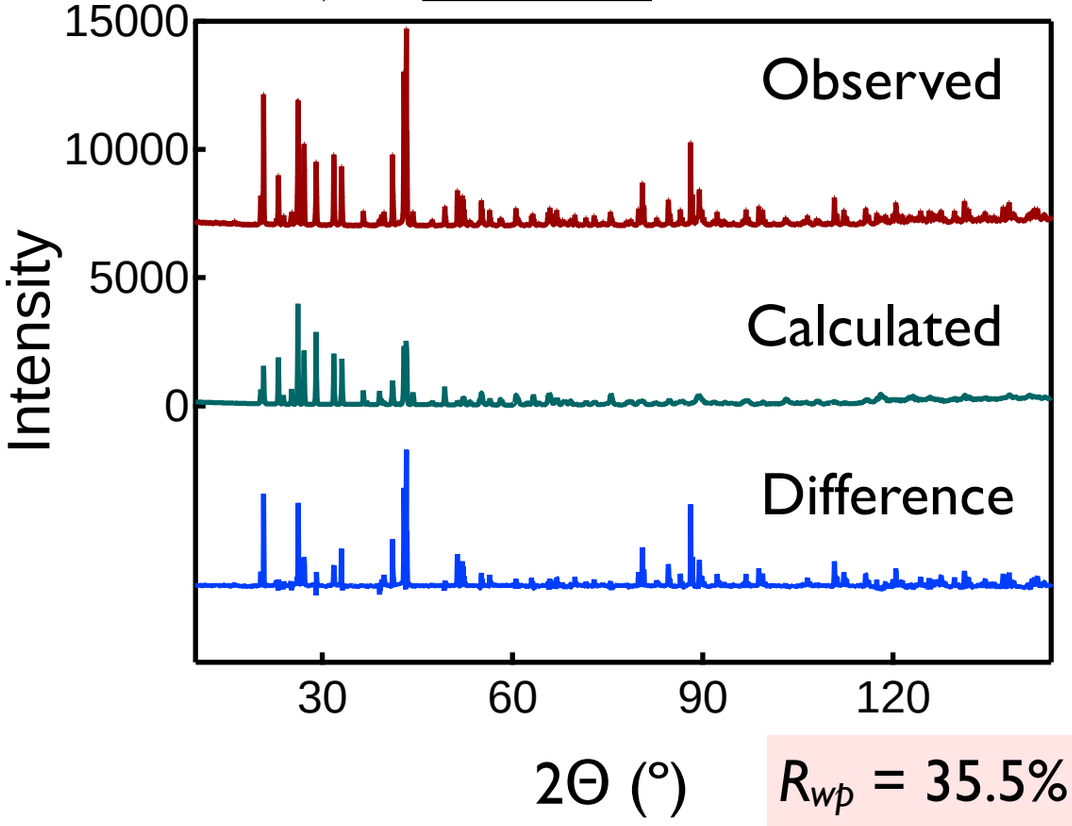


Rietveld



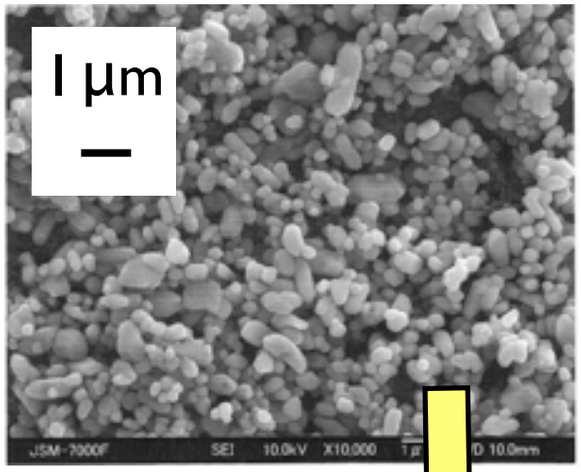
R_{wp} = 9.5%

Rietveld

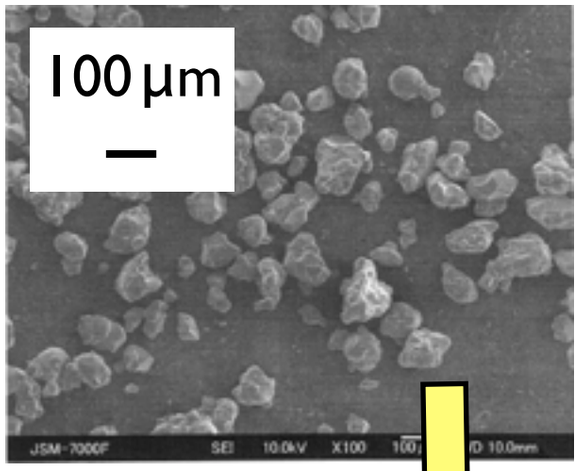


R_{wp} = 35.5%

Results (4/4) $BaSO_4$, heat-treated coarse-grain powder

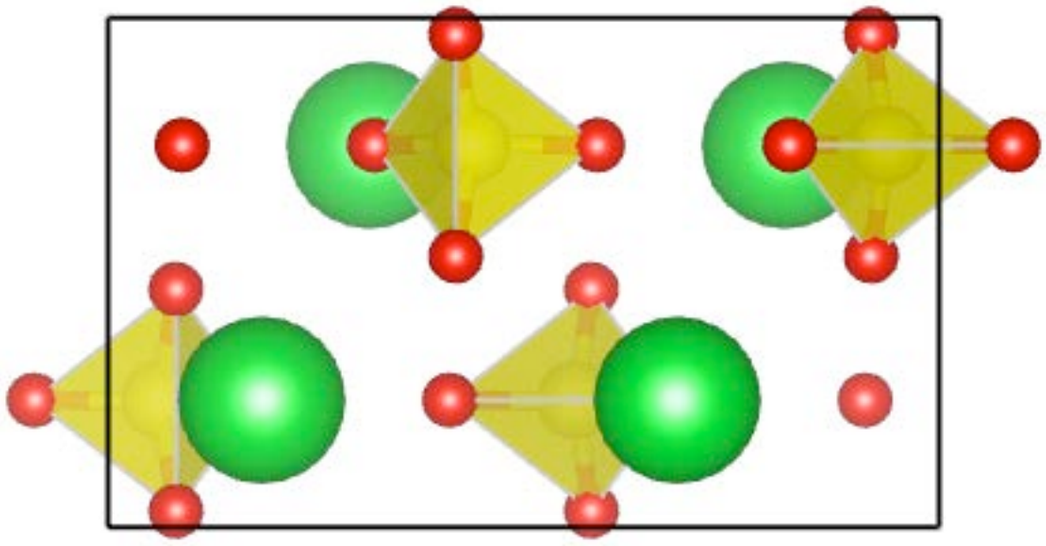


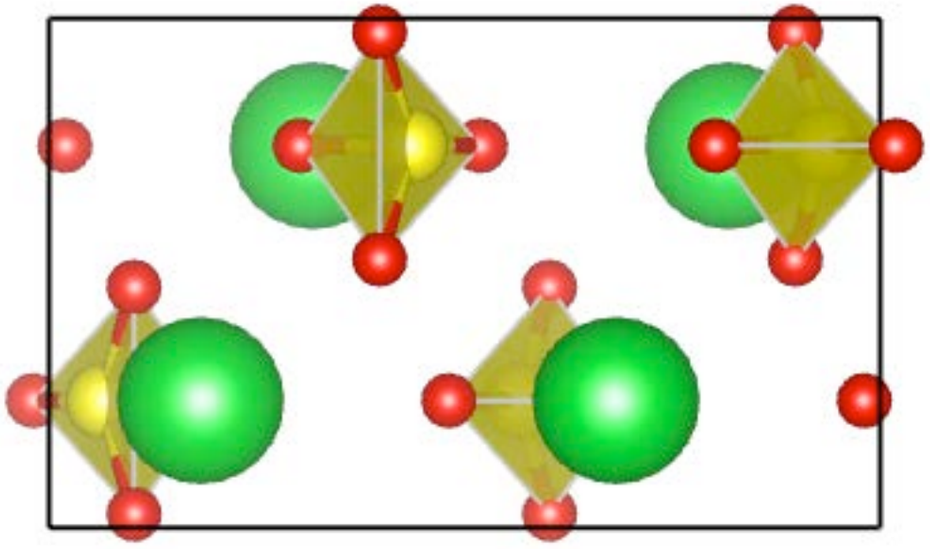
1000°C

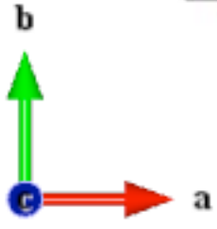


Rietveld

Rietveld



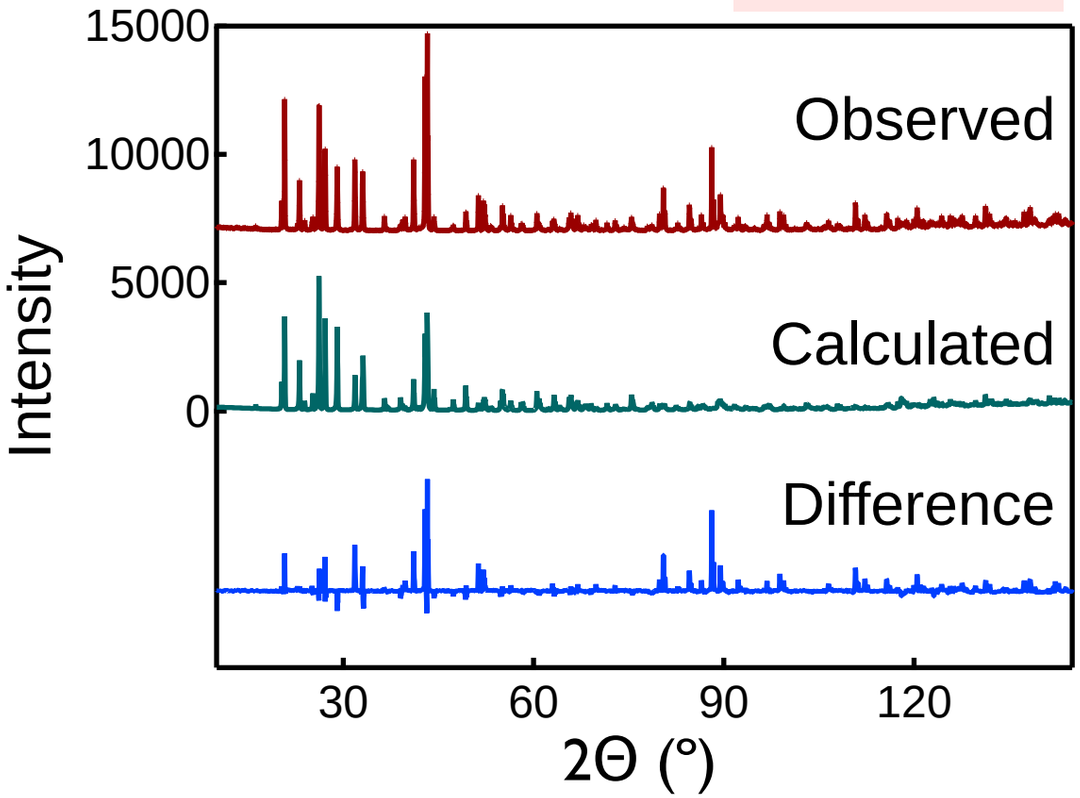




Results (4/4) $BaSO_4$, heat-treated coarse-grain powder

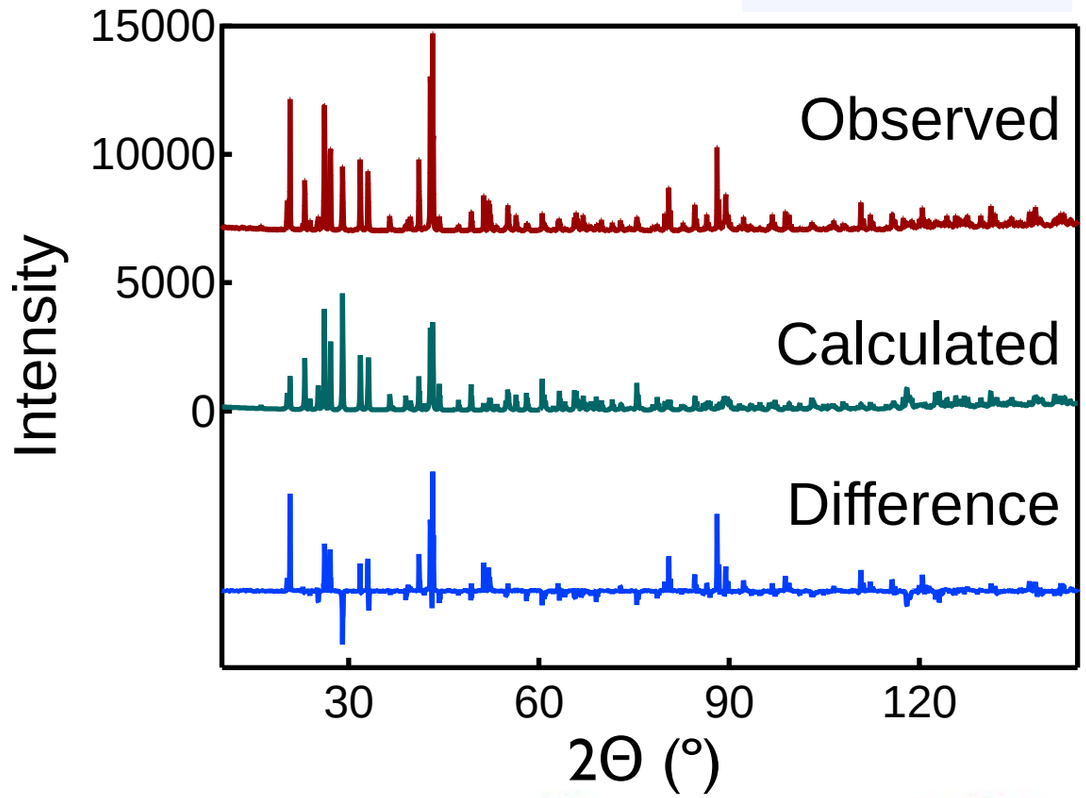
Rietveld

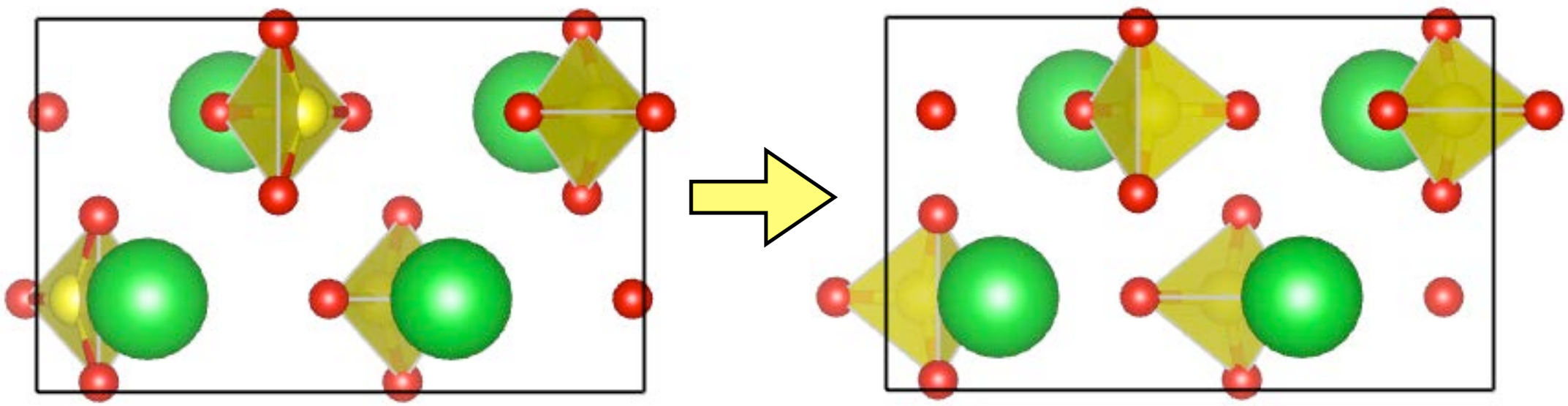
R_{wp} = 35.5 %
R_p = 27.5 %



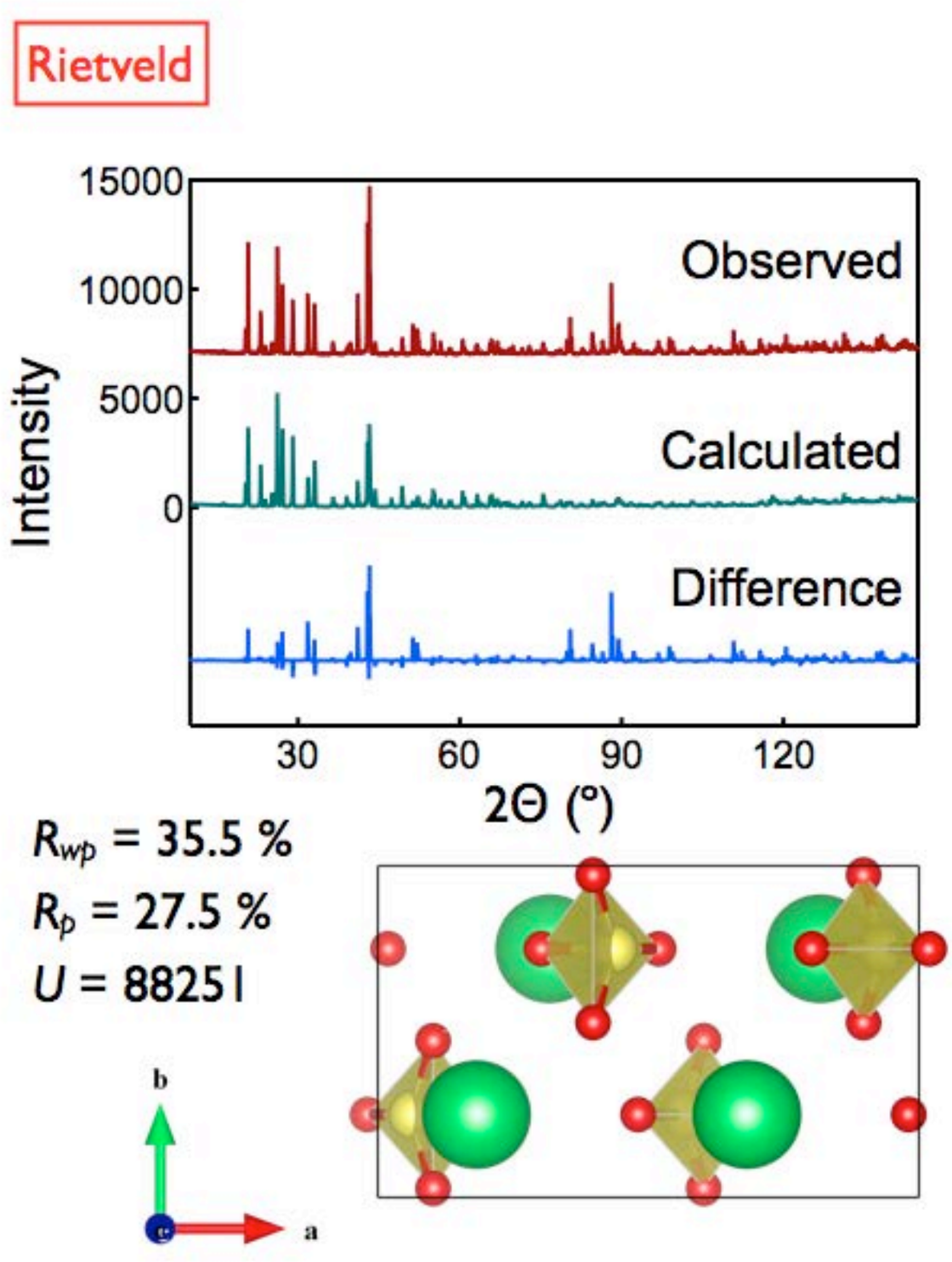
ML Optimization

R_{wp} = 21.5 %
R_p = 30.6 %





Results (4/4) $BaSO_4$, heat-treated coarse-grain powder



	Rietveld	MLE	single crystal
Bond length (Å)			
S–O1	2.04	1.39	1.47
S–O2	1.47	1.41	1.47
S–O3	1.84	1.60	1.49
Bond angles (°)			
O1-S-O2	74.6	112.2	111.9
O1-S-O3	137.8	114.2	109.6
O2-S-O3	107.7	109.3	108.9
O3-S-O3’	82.9	96.5	107.9

Conclusion

A new analytical method for powder diffraction intensity data based on MLE, superordinate concept of the LSQ method, has been developed. The method includes estimation of statistical errors on structure refinement.

The structure parameters of $Ca_3(PO_4)_3F$ & $BaSO_4$ optimized by the new method have become closer to the single-crystal data, as compared with the results of the Rietveld refinement. The structure of a La-Sr-Mn-O system optimized by the new method is clearly different from those refined by the Rietveld analyses.

Reasonable structure parameters was obtained from powder diffraction data of coarse $BaSO_4$ powder by applying the ML optimization.

published in *J. Appl. Cryst.* **44**(5) 921-927 (2011).

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Appendix: Background/Theory

Statistical analysis of experimental data

Baysian inference

↓ application of mode

Maximum A Posteriori estimation

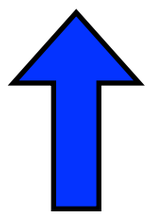
↓ uniform prior distribution

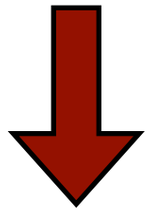
Maximum Likelihood Estimation

↓ experimental error known

Least Squares Method

general





special

Appendix 2: $Ca_5(PO_4)_3F$, $PbSO_4$, $BaSO_4$

Likelihood estimator = probability that observed dataset should appears

	$Ca_5(PO_4)_3F$	$PbSO_4$	$BaSO_4$
$P_{Rietveld}$	10^{-14698}	10^{-17386}	10^{-9567}
$P_{Ida\text{-}Izumi}$	10^{-13654}	10^{-15305}	10^{-8682}
$P_{Ida\text{-}Izumi}$ / $P_{Rietveld}$	10^{1044}	10^{2081}	10^{885}

The statistical model of the newmethod is $10^{885} \sim 10^{2081}$ times more likely than that used in Rietveld analysis

Appendix: errors in the goniometer angles

A theoretical model for statistical errors

$$\sigma_j^2 = \left(\sigma_{\mathrm{c}}\right)_j^2 + \left(\sigma_{\mathrm{p}}\right)_j^2 + \left(\sigma_{\mathrm{r}}\right)_j^2 + \left(\sigma_{2\Theta}\right)_j^2$$

(1) σ_{c} : Error caused by counting (Poisson) statistics for count-loss negligible case

(2) σ_{p} : Error caused by particle (sampling) statistics (Alexander et al. 1948)

(3) σ_{r} : Error proportional to intensity (Toraya 1998, 2000)

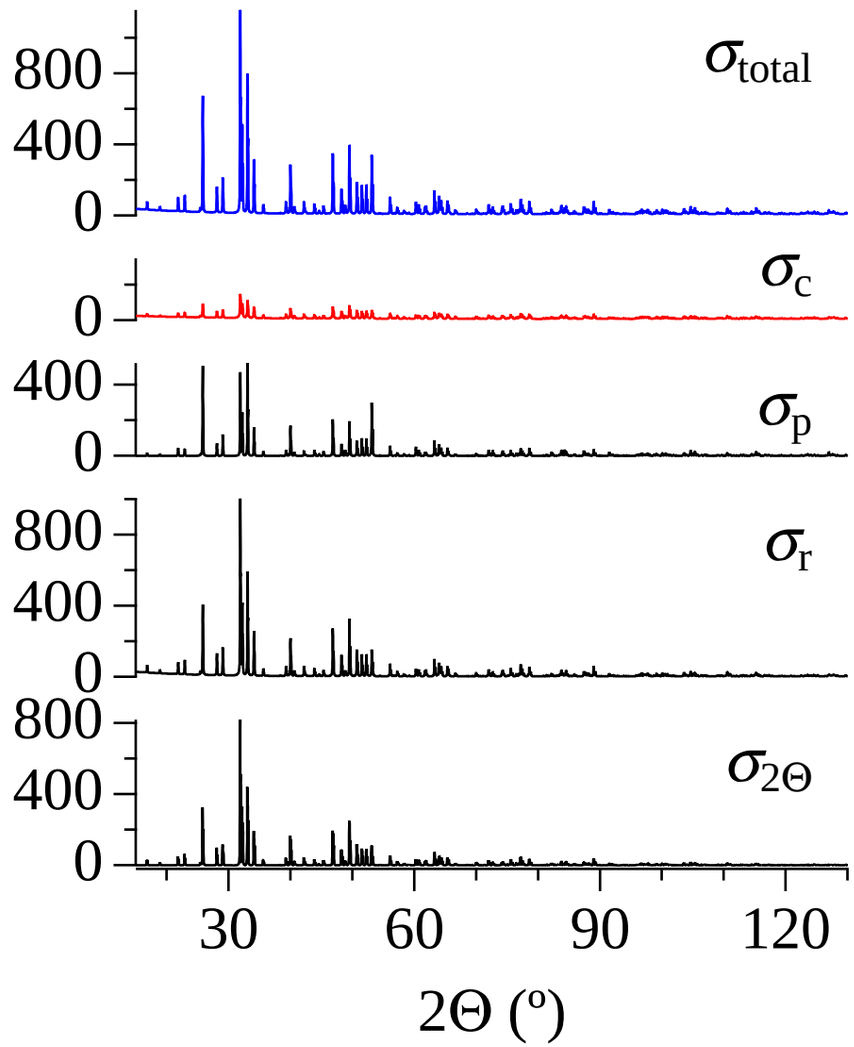
(4) $\sigma_{2\Theta}$: Error caused by statistical error in goniometer angle

$$\sigma_{2\Theta} = C_{2\Theta}\left(\Delta 2\Theta\right)$$

$$C_{2\Theta} = \left(\frac{\partial y_{\mathrm{calc}}}{\partial 2\Theta}\right)^{-1}$$

Errors in 2Θ ? (1) $Ca_5(PO_4)_3F$ (open powder data)

Optimized errors in 2Θ : Δ2Θ = 0.0030°



← Total errors evaluated by the maximum likelihood estimation

← Counting statistical errors

← Particle statistical errors

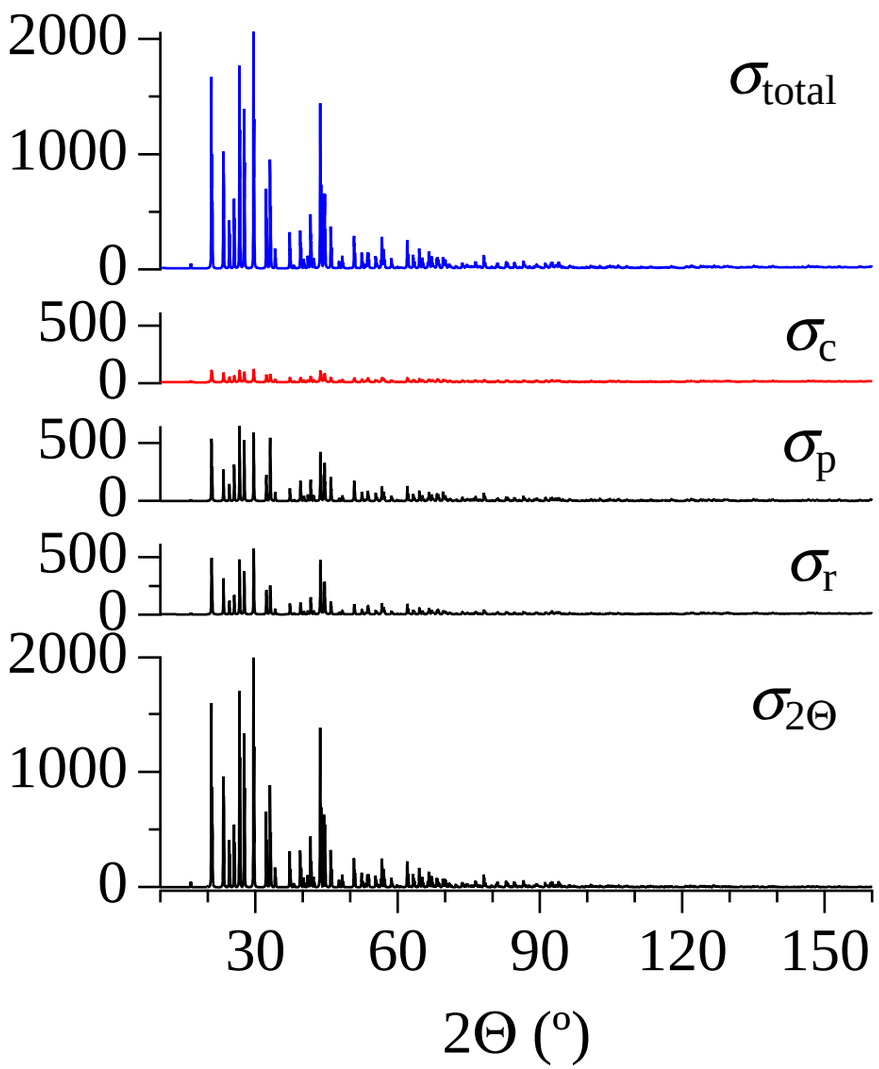
← Errors proportional to intensities

← Errors calculated with Δ2Θ = 0.003°

Total & component errors optimized by maximum likelihood estimation

Errors in 2Θ ? (2) $PbSO_4$ (open powder data attached to *FULLPROF*)

Optimized errors in 2Θ : Δ2Θ = 0.0099°



Total & component errors optimized by maximum likelihood estimation

← Total errors evaluated by the maximum likelihood estimation

← Counting statistical errors

← Particle statistical errors

← Errors proportional to intensities

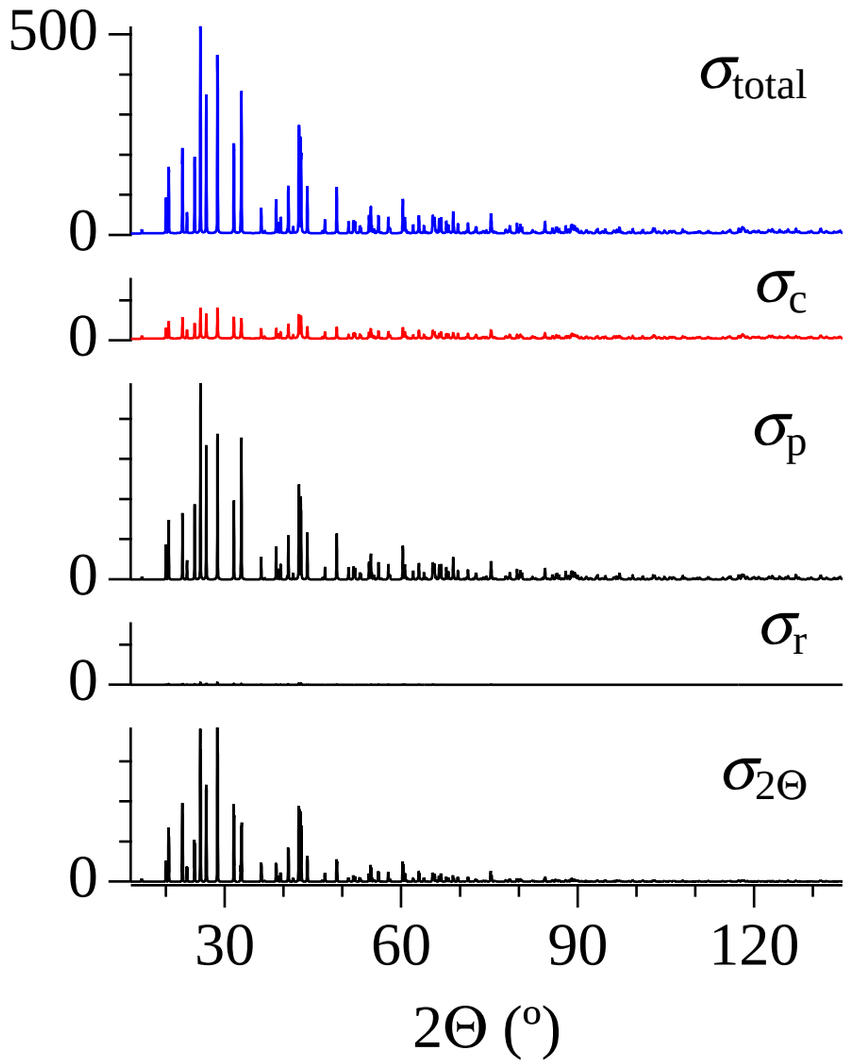
← Errors calculated with Δ2Θ = 0.0099°

a = 9.37102(10) Å
c = 6.88533(6) Å ⇐ MLE

a = 9.37124(10) Å
c = 6.88548(6) Å ⇐ Rietveld

Errors in 2Θ ? (3) (open powder data attached to *RIETAN-FP*)

Optimized errors in 2Θ : Δ2Θ = 0.0036°



Total & component errors optimized
by maximum likelihood estimation

← Total errors evaluated by the maximum likelihood estimation

← Counting statistical errors

← Particle statistical errors

← Errors proportional to intensities

← Errors calculated with Δ2Θ = 0.0036°

Discussions on DXC 2012:

Q1 (Jim Kaduk, chairman): "Your talk makes us think many things before the excursion. There have been some suggestions to change how to weight the data in the Rietveld analysis, and do you think adjustment of weighting scheme can make similar results as your method ?"
A1: "Yes, I think it is possible, but I think the maximum likelihood method is easier."

Q2 (D. Balzar): "As you have mentioned, the errors in the optimized parameters were almost unchanged. Do you have any idea to explain that ?"
A2: "Good question... Actually, the results are different from what I expected, and I am not sure about the reason... But as I showed in equations, I have changed the treatment of the PEAK PROFILE intensity, but NOT changed the treatment of the BACKGROUND intensity in the statistical model. You know most of the powder diffraction intensity data are background intensity, so I think that can be a reason why the estimated errors are not significantly changed... but I am not sure about that now."