Quantitative Phase Analysis using FullProf

Juan Rodríguez-Carvajal
Laboratoire Léon Brillouin (CEA-CNRS), CEA/Saclay FRANCE

Quantitative Phase analysis with the Rietveld Method

The scale factor used in the Rietveld method is proportional to the quantity of corresponding crystalline phase

$$y_i = \sum_\phi S_\phi \left(\sum_\mathbf{h} \mathbf{I_h} \Omega(T_\mathbf{h} - T_i) \right)_\phi + b_i$$

$$S_\phi = \frac{C}{\bar{\mu}} \frac{W_\phi}{(ZMV)_\phi}$$

D.L.Bish & S.A.Howard, J.Appl.Cryst. **21**, 86 (1988)

Scale Factors

Experimental constant

Weight fraction of phase ϕ

$$S_\phi = \frac{C}{\bar{\mu}} \frac{W_\phi}{(ZMV)_\phi}$$

Average absorption coefficient

Unit cell volume of phase ϕ

Molecular weight of phase ϕ

Number of formula units of phase ϕ

D.L.Bish & S.A.Howard, J.Appl.Cryst. **21**, 86 (1988)

Quantitative Phase analysis with the Rietveld Method

If all phases are well crystallized one can constraint the sum of the weight fractions to 1, so that:

$$W_\phi = \frac{S_\phi (ZMV)_\phi}{\sum_{i=1,\ldots n} S_i (ZMV)_i}$$

$$W_\phi = \frac{S_\phi (ZMV)_\phi / \tau_\phi}{\left[\sum_{i=1,\ldots n} S_i (ZMV)_i / \tau_i \right]}$$

Micro-absorption
Brindley coefficients

D.L.Bish & S.A.Howard, J.Appl.Cryst. **21**, 86 (1988)

Quantitative phase analysis in FullProf

Micro-absorption phenomena can be accounted through Brindley considerations:

Classification of powders according to the value of μr product (μ: linear absorption coefficient; r: linear size of particles)

. Fine powders: $\mu r < 0.01$
. Medium powders: $0.01 < \mu r < 0.1$
. Coarse powders: $0.1 < \mu r < 1.0$
. Very coarse powders: $\mu r > 1.0$

Brindley coefficients

The Brindley coefficients can be calculated iteratively by starting with the weight fractions obtained when all $\tau = 1$ and using the empirical formula:

$$\tau_\phi = 1 - 1.450(\mu_\phi - \bar{\mu})r + 1.426\left[(\mu_\phi - \bar{\mu})r\right]^2$$

Expression valid for low absorption contrast $-0.1 \leq (\mu_\phi - \bar{\mu})r \leq 0.1$

Mean Powders (Brindley): $0.01 \leq 2r\mu_\phi \leq 0.1$

r is the mean crystallite radius and μ_ϕ the linear absorption coefficient

G.W. Brindley, Philosophical Magazine. **36**, 347 (1945)

Quantitative phase analysis in FullProf

$$W_\phi = \frac{S_\phi (ZMV)_\phi . f_\phi^2 / \tau_\phi}{\displaystyle\sum_{i=1}^{N_\phi} S_i . (ZMV)_i . f_i^2 / \tau_i} = \frac{S_\phi ATZ_\phi . V_\phi}{\displaystyle\sum_{i=1}^{N_\phi} S_i ATZ_i . V_i}$$

with

S_ϕ Scale factor in FullProf (refinable variable)

$ATZ_i = Z_i M_i f_i^2 / \tau_i$ FullProf parameter

τ_i Brindley factor (particle absorption contrast factor). τ is tabulated as a function of ($\mu_i - \mu$).r FullProf parameter

Quantitative phase analysis in FullProf

f_i Used to transform the site multiplicities in PCR FullProf input file, to their real values. For a stoichiometric phase, $f = 1$ if these multiplicities are calculated by dividing the Wyckoff multiplicity m of the site by the general multiplicity M of the space group. Otherwise, $f=occ.M/m$, where $occ.$ is the occupation number in the PCR file

☺   In order to GET PROPER VALUES OF WEIGHT FRACTIONS LET THE PROGRAM RE-CALCULATE **ATZ** by putting them to ZERO.

The correct **ATZ** value is rewritten in the PCR file.

Quantitative phase analysis in FullProf

1. Crystal structure has to be refined:

   `JBT=0` (`IRF=0`)

   ➔ Refine the structural parameters as usually

2. **Crystal structure is well known:**

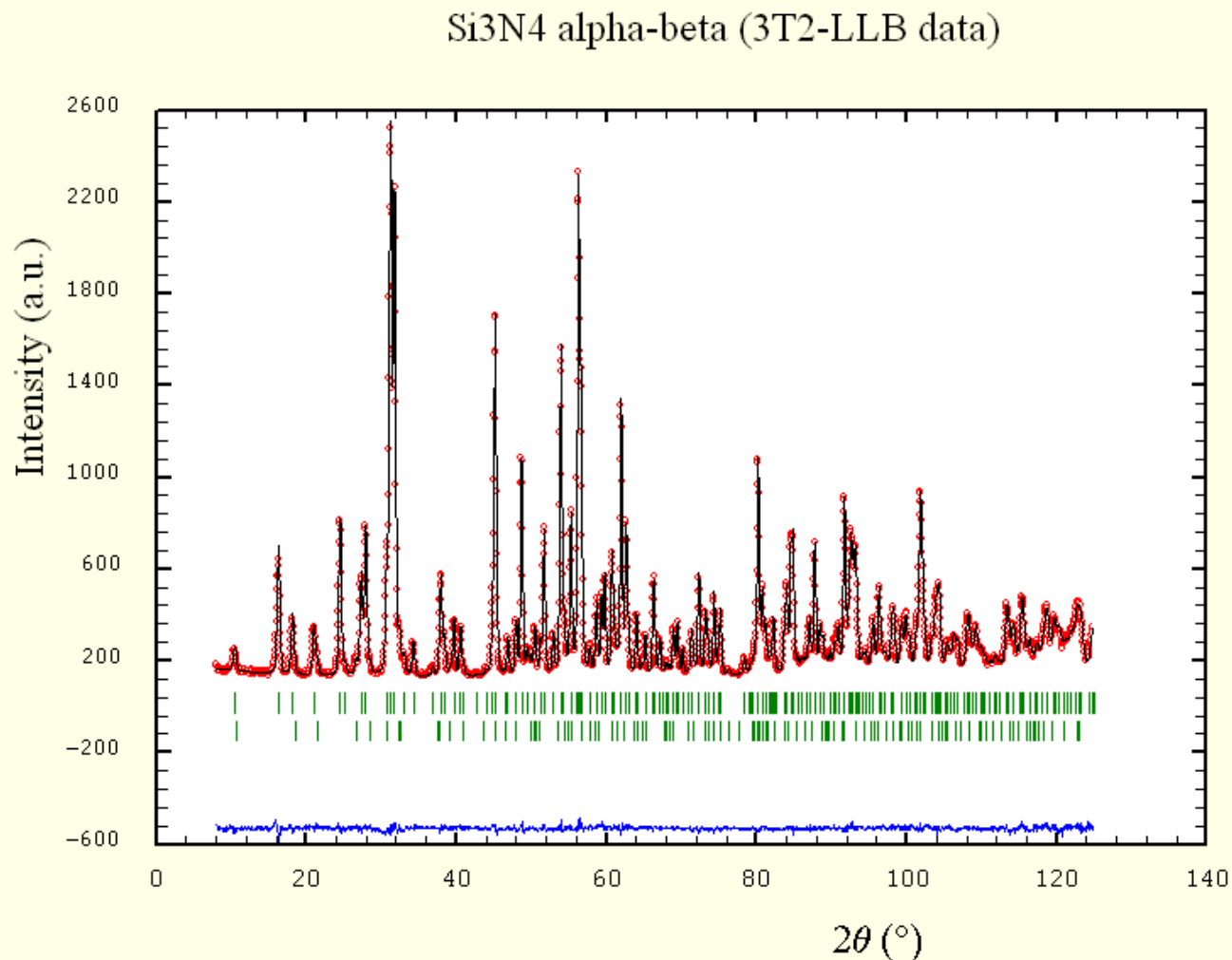   2.1 Create hkl file containing hkl list with corresponding F^2 (`JLKH=5`)

   2.2 Refine the pattern without entering atomic positions `JBT=-3, IRF=2` (Le Bail fit mode with constant relative intensities for the current phase, but refinable scale factor)
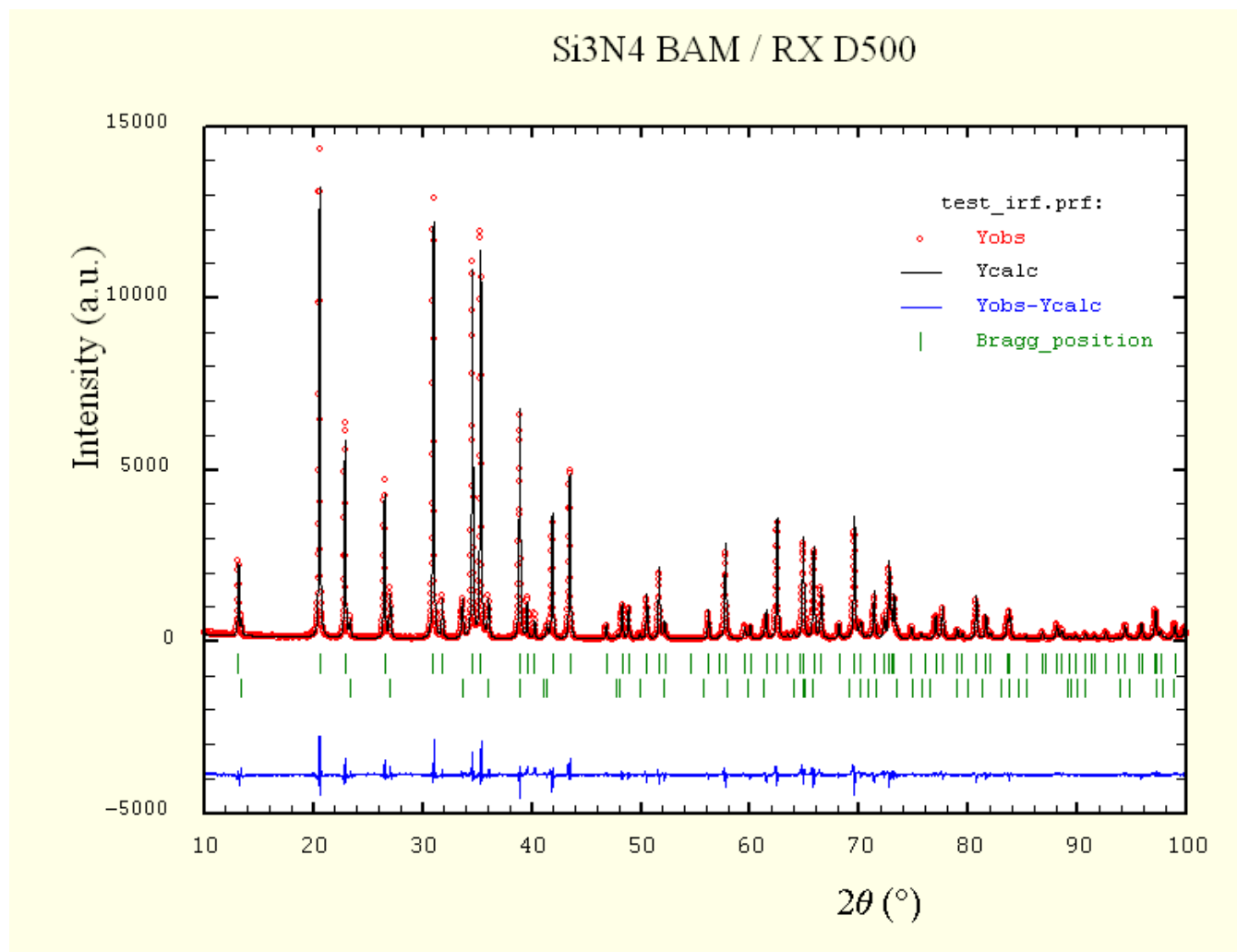
Rietveld Q.P.A.

☺ ✓ **easy to operate (automatic analysis in FullProf)**

✓ **no internal standard**

✓ **non destructive method**

✓ **up to 16 phases in FullProf**

✓ **polymorphism, microstructure**

✓ **neutron case: large amounts of powder analysis (real samples)**

✓ **industrial applications (cements, clays …)**

☹

✓ **structure model dependent: $\{F_{hkl}\}$ have to be known**

✓ **beware of preferred orientation**

Rietveld Q.P.A.: α-Si$_3$N$_4$ and β_Si$_3$N$_4$ mixture

Si3N4 alpha-beta (3T2-LLB data)

Neutron data: αSi$_3$N$_4$: 93% wgt
βSi$_3$N$_4$:   7% wgt

Rietveld Q.P.A.: α-Si$_3$N$_4$ and β_Si$_3$N$_4$ mixture

Si3N4 BAM / RX D500

X-rays data: αSi$_3$N$_4$: 91.6% wgt
               βSi$_3$N$_4$:   8.4% wgt

Bauxite / 8 phases /Delphes Comptage long

2θ (°)
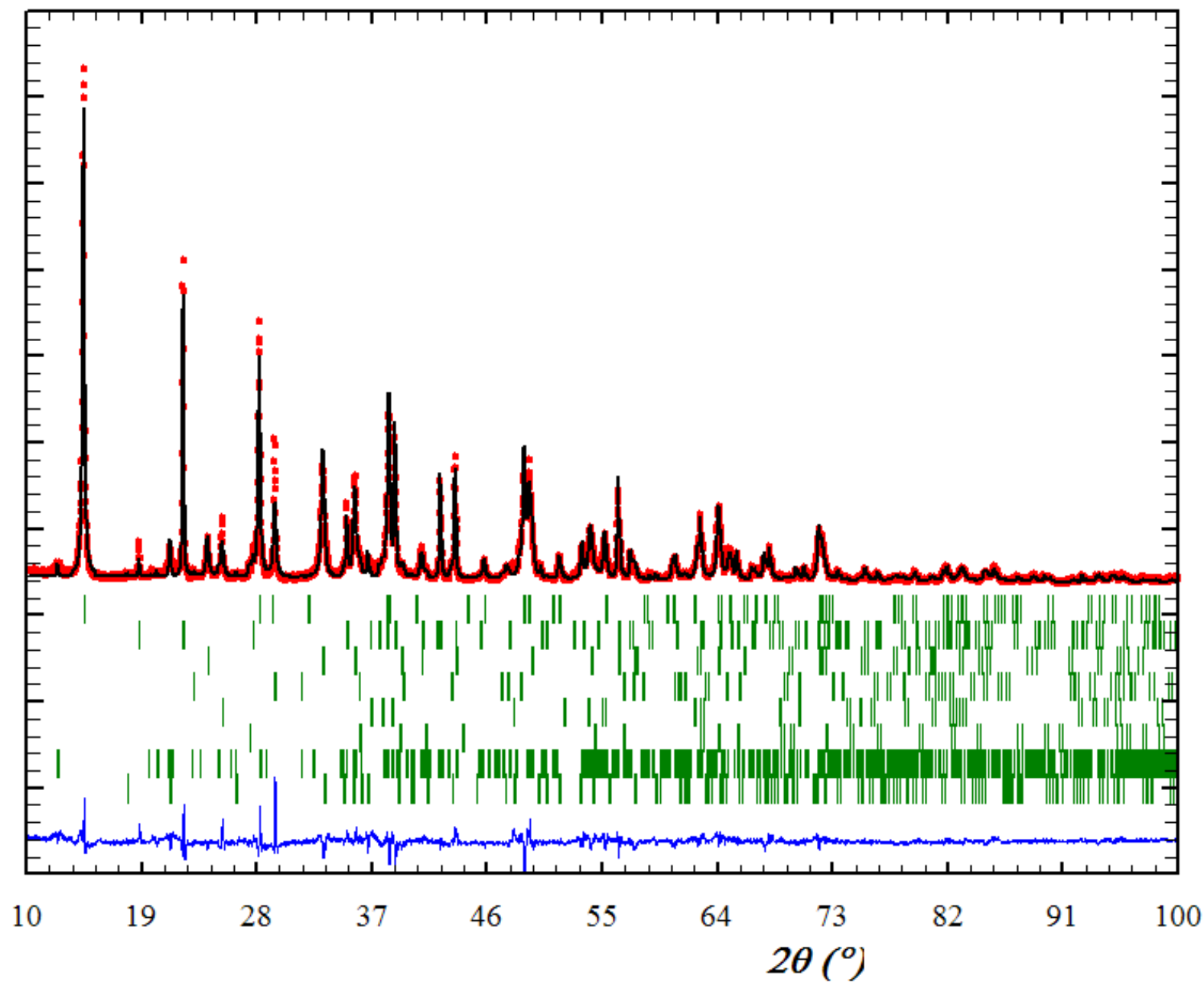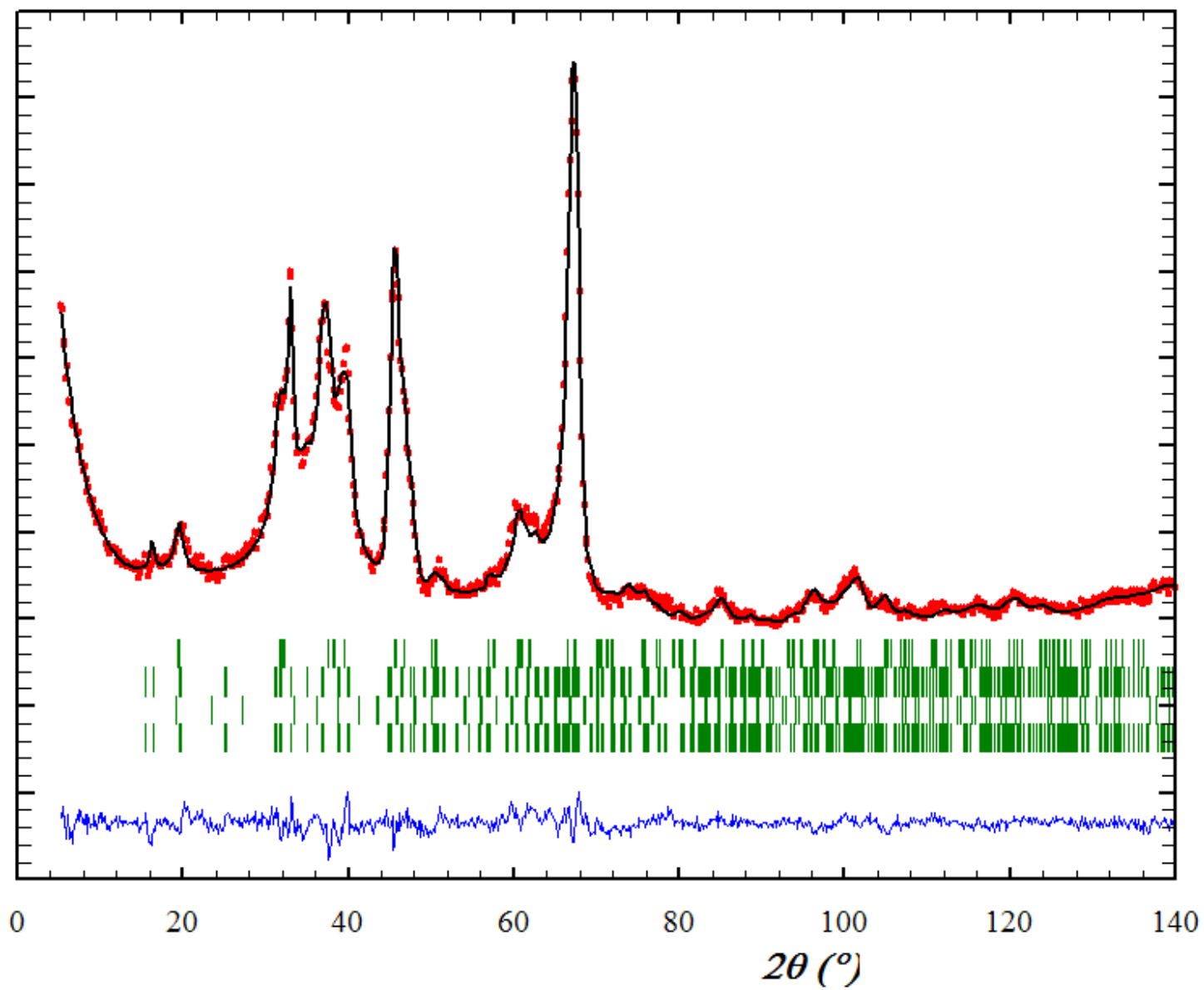
Some references on Q.P.A. by Rietveld method

➢R.J. Hill & C.J. Howard, J. Appl. Cryst. 20, 467-476 (1987)
    Quantitative phase analysis from neutron powder diffraction data using the Rietveld method

➢G.W. Brindley, Phil. Mag. 36, 347-369 (1945)
    The effect of grain or particle size on X-ray reflections from mixed powders and alloys considered in relation to the quantitative determination of crystalline substances by X-ray methods

➢D.L. Bish & S.A. Howard, J. Appl. Cryst. 21, 86-91 (1988)
    Quantitative phase analysis using the Rietveld method

➢J.C. Taylor, Powder Diffraction 6, 2-9 (1991)
    Computer programs for standardless quantitative analysis of minerals using the full powder diffraction profile

➢R.J. Hill, Powder Diffraction 6, 74-77 (1991)
    Expanded use of Rietveld method in studies of phase abundance in multiphase mixtures