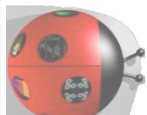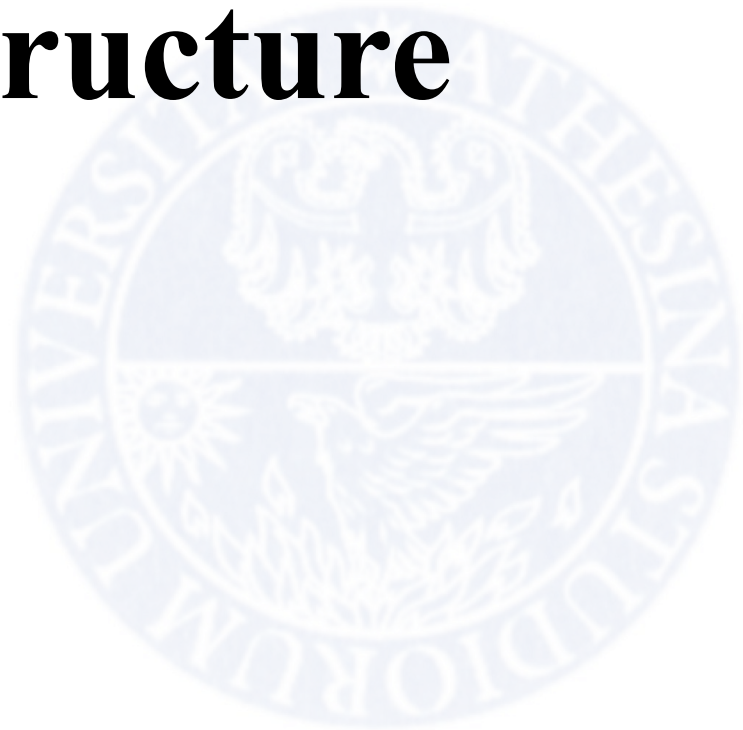# Quantitative phase analysis and microstructure

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Outline

- **Introduction**

- **Traditional methods for QPA**
  - **Internal standard**
  - **Polymorph method**
  - **RIR**

- **Rietveld method for QPA**

- **Problems and errors**

- **Examples**

- **Crystallinity determination and examples**

Quantitative phase analysis (QPA)

◆ **Reflection intensity (reflection k of phase j):**

Incident beam intensity   Phase volume fraction

$$I_j^k = I \frac{f_j}{V_j^2} L_k \left| F_{k,j} \right|^2 P_{k,j} A_j$$

Absorption factor

Cell volume

Lorentz-polarition   Structure factor   Texture factor

◆ **The intensity of a diffraction peak is directly proportional to the volume fraction**

◆ **QPA methods:**
  - Traditional (polymorph, internal standard, RIR….)
  - Rietveld

Quantitative phase analysis

- ◆ **Reflection intensity:**

$$I_j^k = I \frac{f_j}{V_j^2} L_k \left| F_{k,j} \right|^2 P_{k,j} A_j$$

- ◆ **In the case of random texture: $P_{k,j}=1$**

- ◆ **For reflection geometry and flat sample: $A_j = 1/2\mu^*$, μ^*=linear absorption coefficient of the mixture**

- ◆ **First problem: μ^* is unknown, but considering two phases (1 and 2) and measuring a peak k for phase 1 and peak s for phase 2:**

$$\frac{f_1}{f_2} = \frac{I_1^k}{I_2^s} \frac{V_1^2 L_s \left| F_{s,2} \right|^2}{V_2^2 L_k \left| F_{k,1} \right|^2}$$
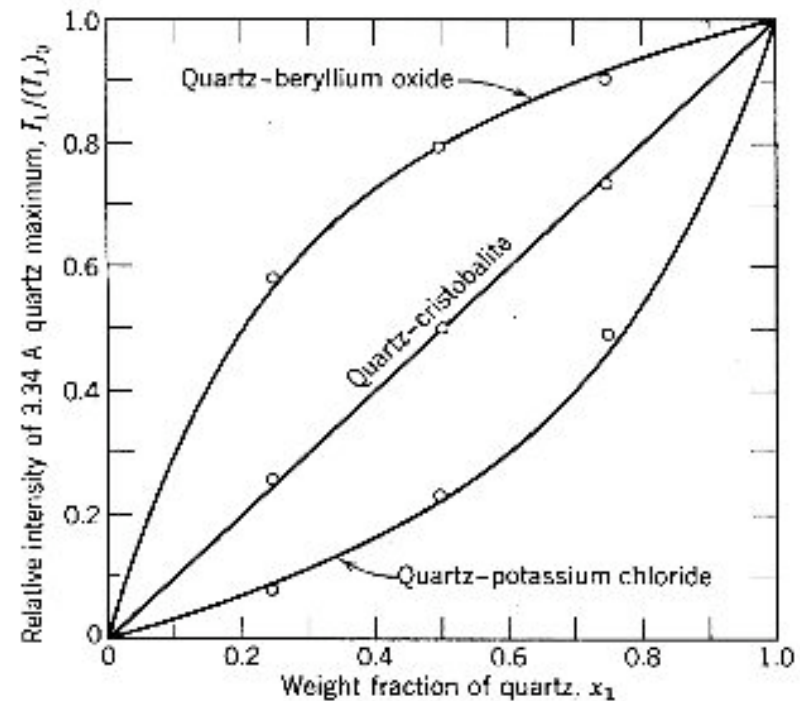
Traditional methods (external standard)

◆ **Require the measurement of a pure sample of one of the two phases at the same conditions (beam intensity, time and packing of the sample) as the mixture. Indicating with ext the peak intensity measured for the external standard or pure phase:**

$$\frac{I_1^k}{I_{1,ext}^k} = \frac{w_1 \mu_1^*}{w_1(\mu_1^* - \mu_2^*) + \mu_2^*}$$

◆ **By graphical representation:**

◆ **The graph can be measured also**
◆ **   (calibration curve)**

Traditional methods (others)

◆ **Internal standard:mixing phases 1 and 2 in know proportion we can measure K. Then when we add a know amount of phase 2 (the internal standard) to a sample containing phase 1, then using K we determine the amount of phase 1.**

$$\frac{I_1^k}{I_2^s} = K \frac{w_1}{w_2}$$

◆ **Polymorph method: used first for polymorph mixture. The same formula is used and K is measured or computed theoretically. But no internal standard is used. For polymorphs the absorption is the same so no matrix effect is present.**

◆ **RIR or Reference Intensity Ratio: same principle as the internal standard that is always the corundum. Values of the RIR or intensity ratio of the more intense peak of each phase respect to the (113) peak of corundum are reported in the PDF of ICDD.**

$$w_1 = \frac{I_1^k}{I_{corundum}^{113}} \frac{w_{corundum}}{RIR_{1,corundum}}$$

Limits of traditional methods and QPA

♦ **Principal errors of traditional methods derive from:**

- Methodology to determine the peak intensity (often the height instead of the peak integral is used)

- Use of only one peak (or few), so the results are affected more by preferred orientation etc.

- Peak overlapping that make difficult to extract the intensity of a peak

- In the RIR, the use of tabulated values that may not be representative of the real phase in the sample to be analyzed. The multireflection RIR, where intensity is determine over all peaks in a certain range, has been introduced to mitigate some of these problems.

QPA by Rietveld method

◆ **Recalling the usual intensity formula for Rietveld:**

$$I_i^{calc}(\chi,\phi) = \sum_{n=1}^{Nphases} \frac{S_n}{V_n^2} \sum_k L_k \left| F_{k;n} \right|^2 S\left(2\theta_i - 2\theta_{k;n}\right) P_{k;n}(\chi,\phi) A + bkg_i$$

Where S_n are the scale factors for the phases and remembering the intensity formula for peaks:

$$I_j^k = I \frac{f_j}{V_j^2} L_k \left| F_{k,j} \right|^2 P_{k,j} A_j$$

It is easy to see that the scale factors incorporate the terms: incident beam intensity (equal for all phases) and the phase fraction, so we can write:

Phase density

$$f_j = \frac{S_j}{\sum_{i=1}^{Nphases} S_i} \qquad \text{or} \qquad w_j = \frac{S_j \rho_j}{\sum_{i=1}^{Nphases} S_i \rho_i}$$

Volume fractions

Weight fractions

Errors in QPA

◆ **Preferred orientation (texture): this is one of the main causes for errors in QPA, for powder samples, a correct sample preparation is fundamental**

◆ **Graininess: too few large grains contributing to the scattering; the intensity is not representative and the only solution is to improve the number of scattering grains (either by milling the sample, or spinning or enlarge the beam size)**

◆ **Microabsorption: large absorbing particles scatter more than light absorbing small grains inducing an erroneous quantitative phase analysis**

Examples and problems

- **Nickel-alumina by Cu radiation XRD:**
  - An example of microabsorption problems and how it work the Brindley correction (require knowledge of the grain size)

- **Fe-Cu co-laminate analyzed by neutron diffraction (TOF):**
  - The sample shows moderate texture
  - We will see how the analysis is affected by preferred orientations
  - We will see also how the different correction methods work for QPA

Cermet: Ni-Al$_2$O$_3$

- **Alumina is quite inexpensive as high temperature structural material**

- **Lack of toughness**

- **Ductile metal inclusions**

- **Ni, Ag, FeAl, NiAl….**

- **Nickel is very ductile (relatively low temperature applications)**

Cermet production (Ni-Al$_2$O$_3$)
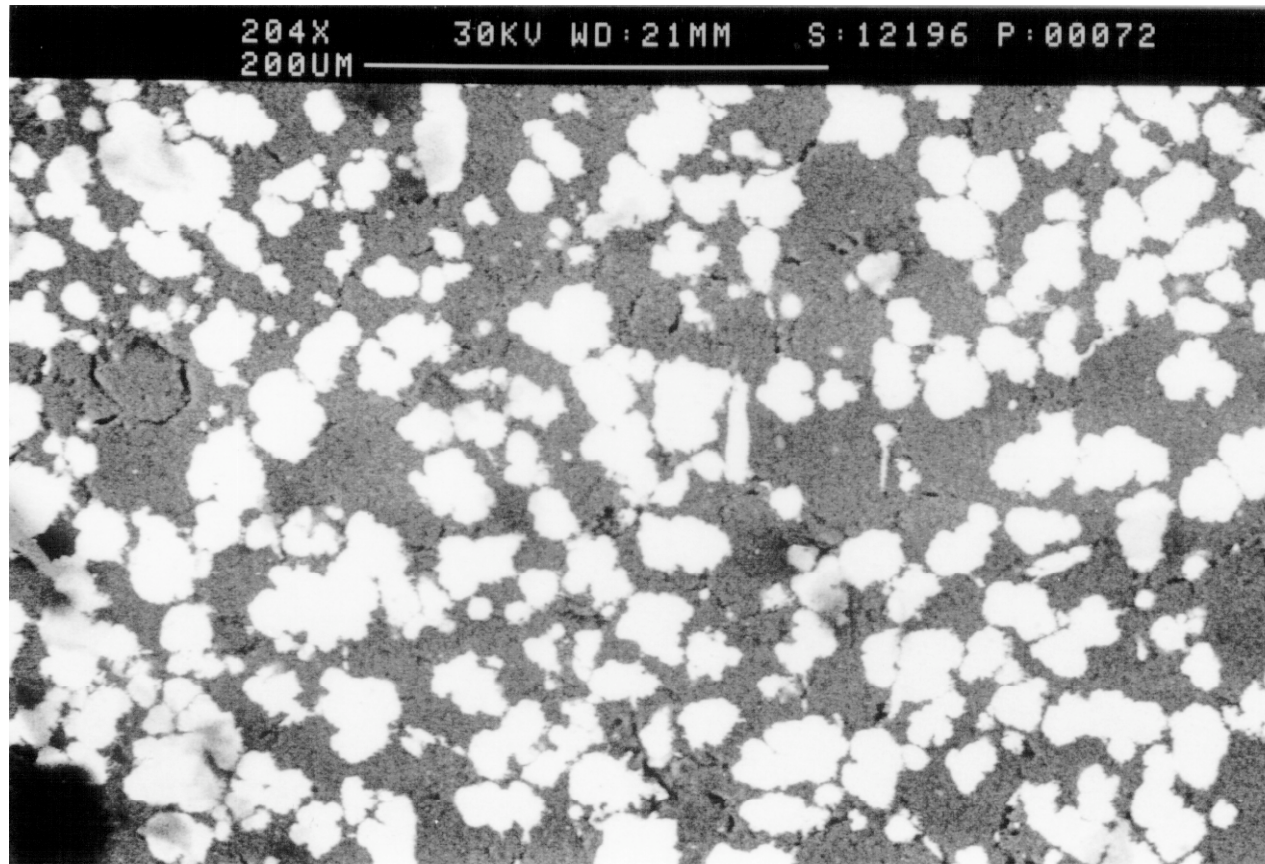
◆ **Powder metallurgy**

   ↪ **Forming and sintering**

   ↪ **Cold Isostatic Pressing and sintering**

   ↪ **Hot Pressing**

◆ **Active binder**

   • **Binder + powder Al$_2$O$_3$ - Ni**

   • **Polimerization and forming**

   • **Thermal treatment (decomposition) + sintering**

SEM: Al2O3 - 40 % Ni

204X   30KV WD:21MM   S:12196 P:00072
200UM

Quantitative phase analysis
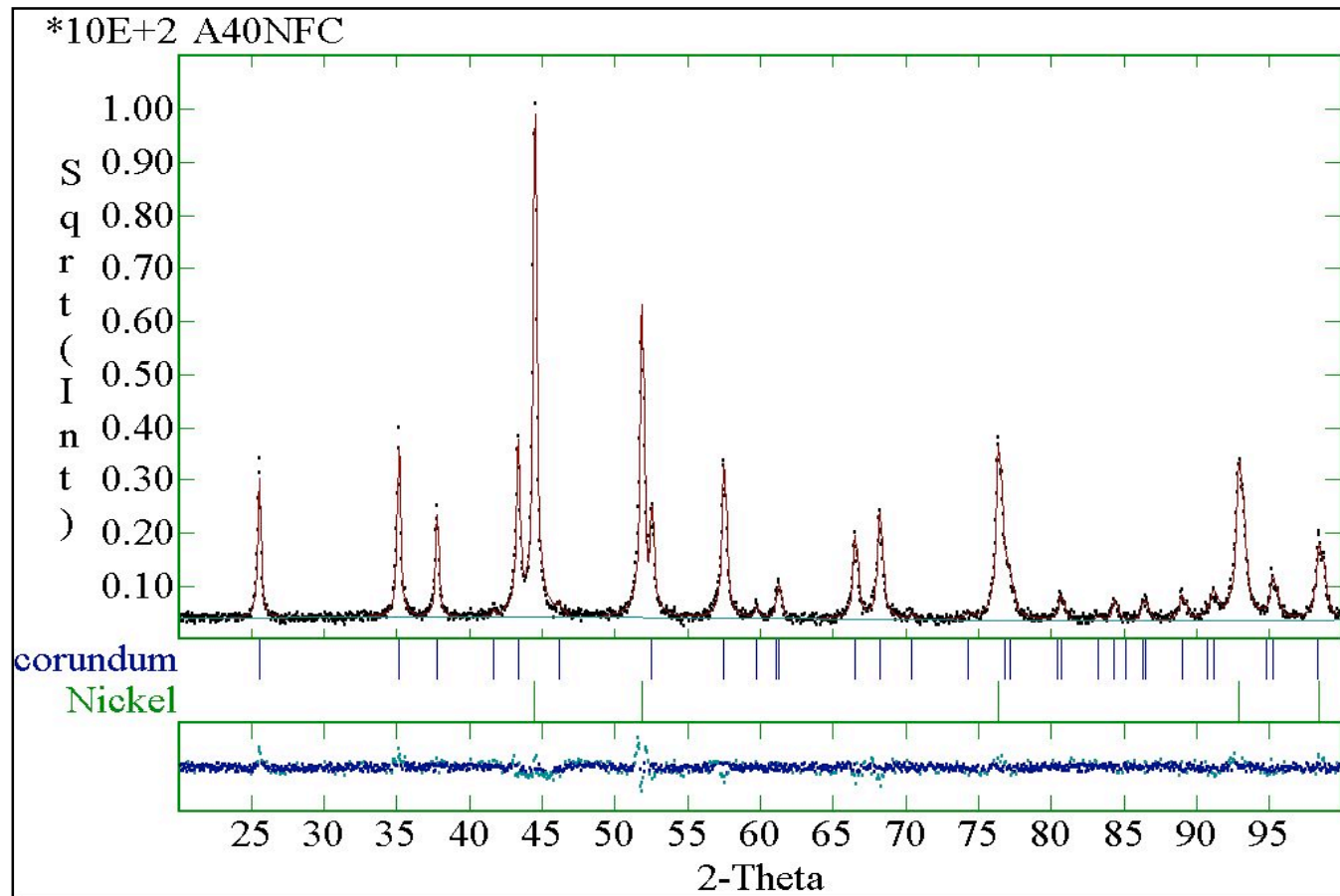
Quantitative phase analysis: problems

♦ **High contrast in absorption between Ni and alumina**

|	No Correction		Brindley Cubic Corr.		Brindley Spheric Corr.	
	%Al$_2$O$_3$ $_{VOL}$	%Ni $_{VOL}$	%Al$_2$O$_3$ $_{VOL}$	%Ni $_{VOL}$	%Al$_2$O$_3$ $_{VOL}$	%Ni $_{VOL}$
Al$_2$O$_3$ + 40%$_{VOL}$ Ni Powders	72.1 (2)	27.9 (2)	61.3 (2)	38.7 (2)	63.8 (2)	36.2 (2)
Pure Al$_2$O$_3$ F1	100 (0)	0 (0)	100 (0)	0 (0)	100 (0)	0 (0)
Al$_2$O$_3$ + 10%$_{VOL}$ Ni F1	94.7 (1)	5.34 (1)	89.9 (1)	10.1 (1)	91.2 (1)	8.8 (1)
Al$_2$O$_3$ + 20%$_{VOL}$ Ni F1	88.1 (1)	11.9 (1)	79.9 (1)	20.1 (1)	82.0 (1)	18.0 (1)
Al$_2$O$_3$ + 30%$_{VOL}$ Ni F1	80.7 (2)	19.3 (2)	70.4 (2)	29.6 (2)	72.9 (2)	27.1 (2)
Al$_2$O$_3$ + 40%$_{VOL}$ Ni F1	70.1 (3)	29.9 (2)	59.2 (3)	40.8 (2)	61.7 (3)	58.1 (2)
Pure Al$_2$O$_3$ F1C23	100 (0)	0 (0)	100 (0)	0 (0)	100 (0)	0 (0)
Al$_2$O$_3$ + 10%$_{VOL}$ Ni F1C23	91.4 (1)	8.6 (1)	84.6 (1)	15.4 (1)	86.4 (1)	13.6 (1)
Al$_2$O$_3$ + 20%$_{VOL}$ Ni F1C23	88.2 (1)	11.8 (1)	79.8 (1)	20.2 (1)	82.0 (1)	18.0 (1)
Al$_2$O$_3$ + 30%$_{VOL}$ Ni F1C23	79.8 (2)	20.2 (2)	69.4 (2)	30.6 (2)	71.9 (2)	28.1 (2)
Al$_2$O$_3$ + 40%$_{VOL}$ Ni F1C23	70.6 (3)	29.4 (3)	60.4 (3)	39.6 (3)	62.9 (3)	37.1 (3)
Al$_2$O$_3$ + 20%$_{VOL}$ Ni HP (b)	88.4 (1)	11.6 (1)	80.4 (1)	19.6 (1)	82.4 (1)	17.6 (1)
Al$_2$O$_3$ + 20%$_{VOL}$ Ni HP (w)	88.4 (1)	11.6 (1)	80.3 (1)	19.7 (1)	82.4 (1)	17.6 (1)
Al$_2$O$_3$ + 20%$_{VOL}$ Ni HP (Mo)	89.7 (1)	10.3 (1)	78.8 (1)	21.2 (1)	81.4 (1)	18.6 (1)
Al$_2$O$_3$ + 40%$_{VOL}$ Ni HP (b)	73.8 (2)	26.2 (2)	63.1 (2)	36.9 (2)	65.6 (2)	34.4 (2)
Al$_2$O$_3$ + 40%$_{VOL}$ Ni HP (w)	70.2 (2)	29.8 (2)	59.2 (2)	40.6 (2)	61.9 (2)	38.1 (2)
Al$_2$O$_3$ + 40%$_{VOL}$ Ni HP (Mo)	76.1 (3)	23.9 (2)	61.5 (3)	38.5 (2)	64.7 (3)	35.3 (2)

Use neutron

Analysis of rolled Cu67-Fe33 samples

- **Production: Powder metallurgy (Technical University of Hamburg-Harburg, B. Commentz)**

- **67% of Cu - 33% of Fe**

- **Cold Isostatic Pressing (115 Mpa)**

- **Hot Pressing (750°C, 50 Mpa, 30 min)**

- **Resulting compacts: 1% porosity**

- **Rolling at 5 m/min**
  - **I: not deformed**
  - **II: 6 pass for -0.1/pass, plastic deformation: -0.607**
  - **III: 6 pass for -0.2/pass, plastic deformation: -1.142**
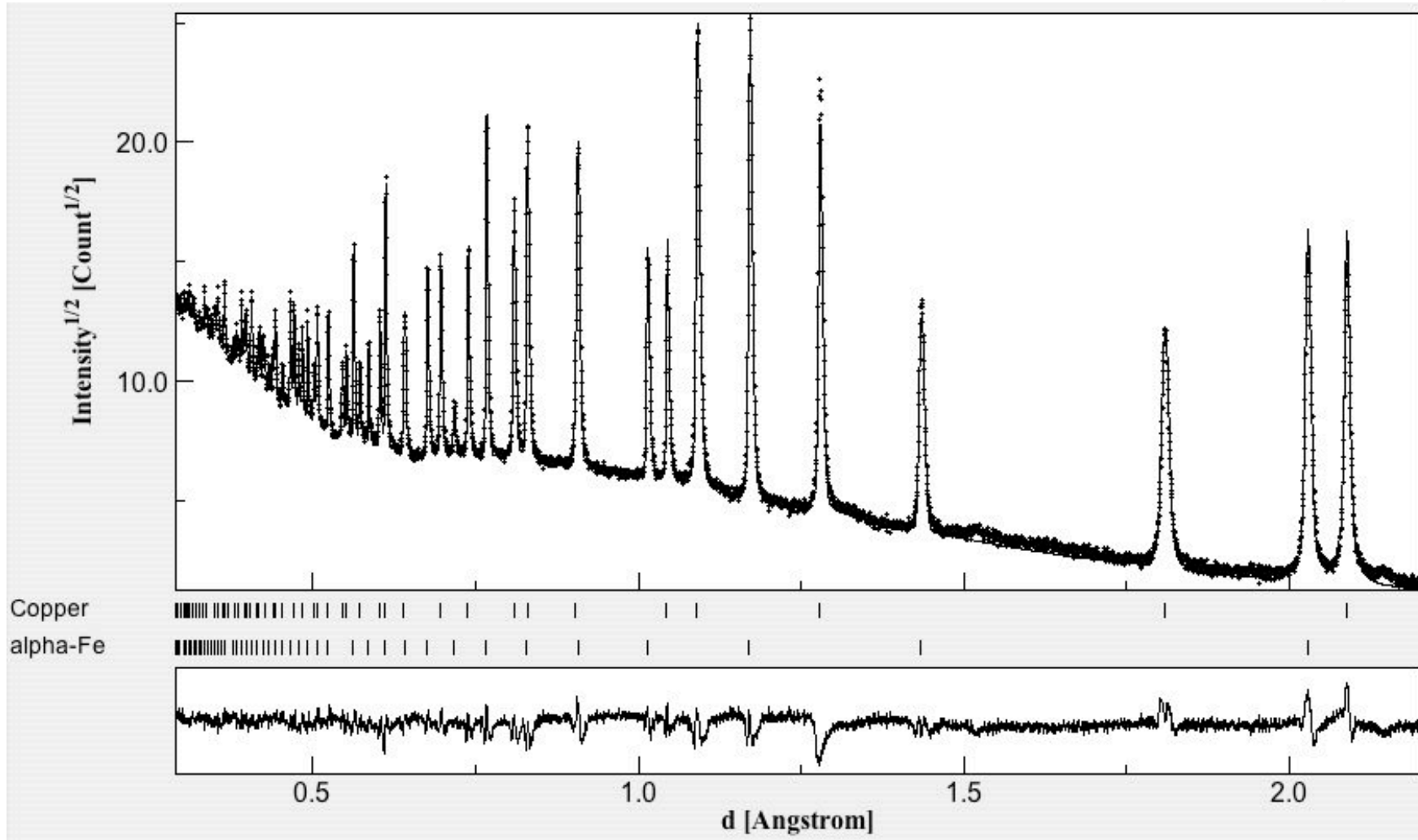
- **Measurements by Neutron TOF at IPNS**

Measurement and texture

- ◆ **Pole figure coverage showing the measuring points for the different banks**
- ◆ **Texture is only moderate**
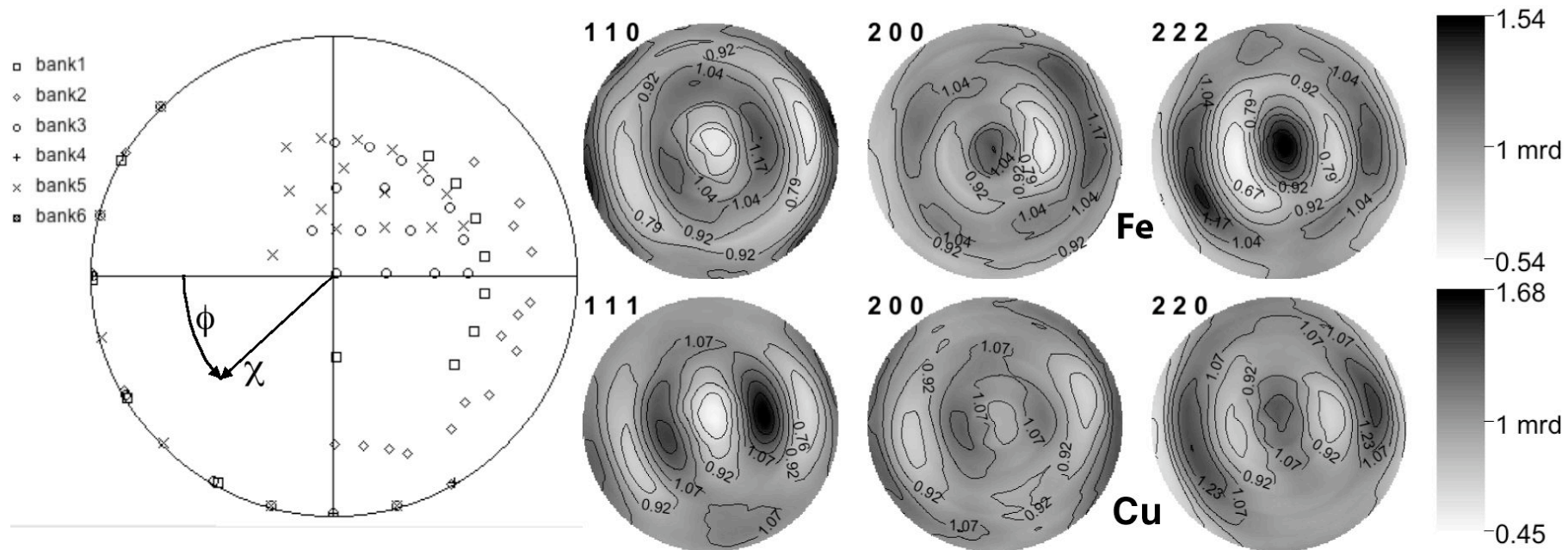
Spectra sum for bank 2 with fitting by RTA

QPA analysis on one spectrum

- ◆ **Only the spectrum at the center of pole figure was used**
- ◆ **For the ODF given by EWIMV we assumed the ODF was measured externally and used only to correct the spectrum**
- ◆ **We tested different texture corrections to see the effect on the QPA results**
- ◆ **The harmonic and March-Dollase corrections give erroneous quantities**
- ◆ **If the ODF is unknown, better to assume random ODF for QPA analysis**

Methods	Full range		Range 0.79-2.2 Å	
	% Cu	R_w (%)	% Cu	R_w (%)
ODF given (EWIMV)	68.8(14)	14.5	66.5(19)	15.6
Random ODF	65.5(25)	31.5	63.3(37)	35
March-Dollase Fe(100) Cu(110)	58.3(20)	25	57.3(38)	29
Harmonic (fiber), L_{max} = 4	67.4(23)	27.5	62.7(41)	30.5
Harmonic (fiber), L_{max} = 6	70.0(13)	13	66.0(25)	14.5
Harmonic (fiber), L_{max} = 8	71.4(14)	12.7	70.2(40)	14.4

Crystalline determination

- The standard procedure is to determine the amorphous fraction by the internal standard method. The amorphous is obtained as the complement to 1 of the total amount of crystalline phases

- As an alternative and when no internal standard can be used, we can simulate the amorphous with the Le-Bail nanocrystalline approximation and use the standard Rietveld method

- In the nanocrystalline approximation we assume a crystal structure for the amorphous (that simulate the local order) and broaden the peaks assuming very small crystallite sizes (in the order of the length at which the order is loosed)
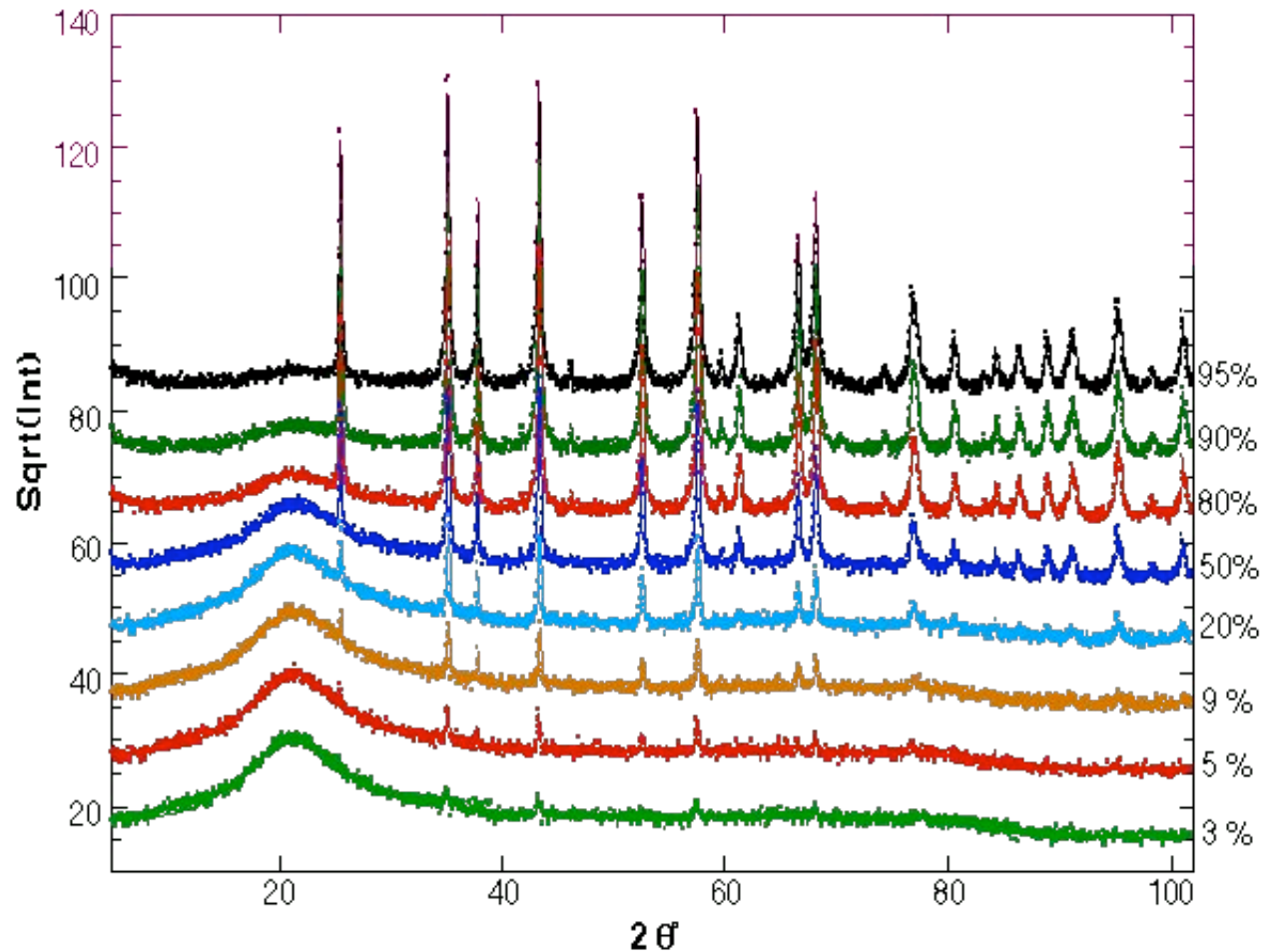
Pseudo-amorphous approximation

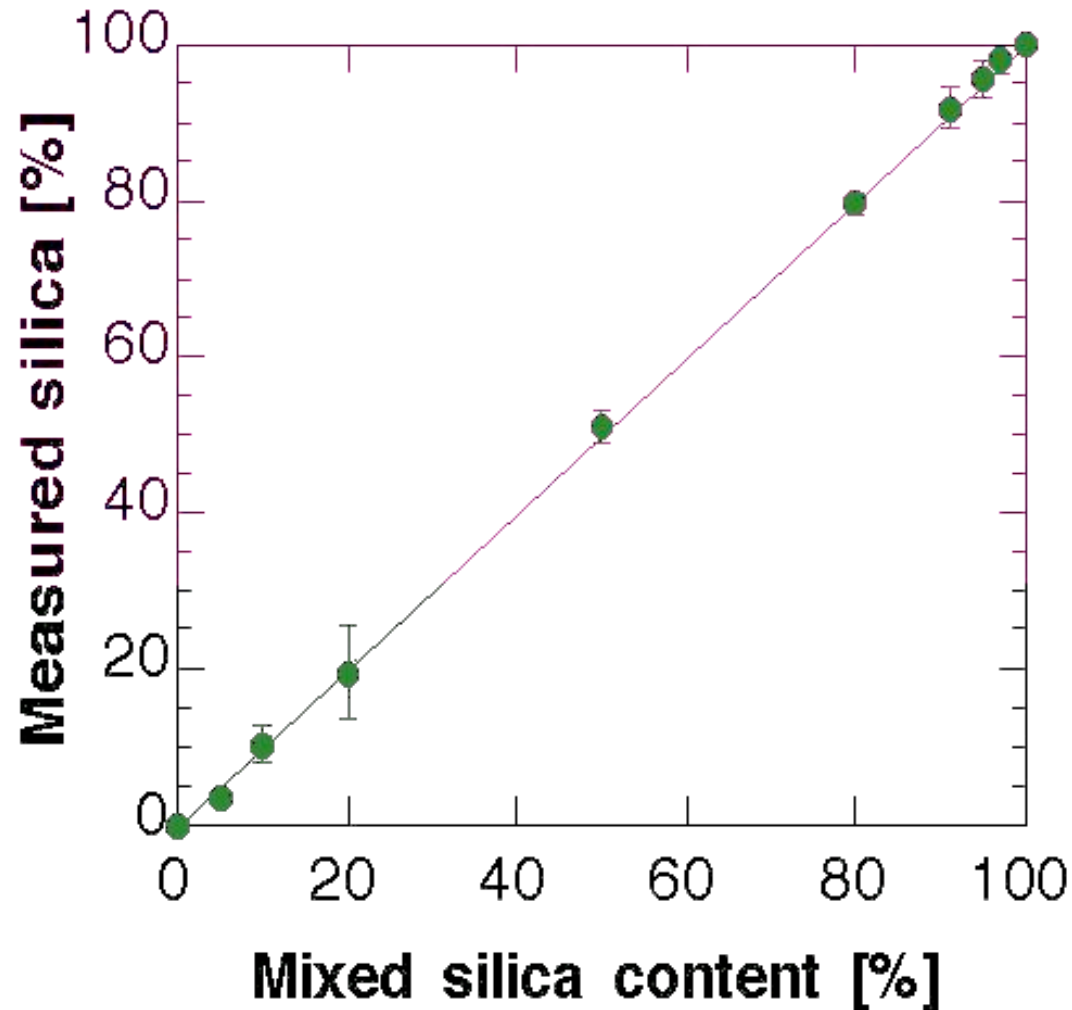◆ Le Bail, A., *J. Non-Cryst. Solids*, 183, pp. 39-42, 1995
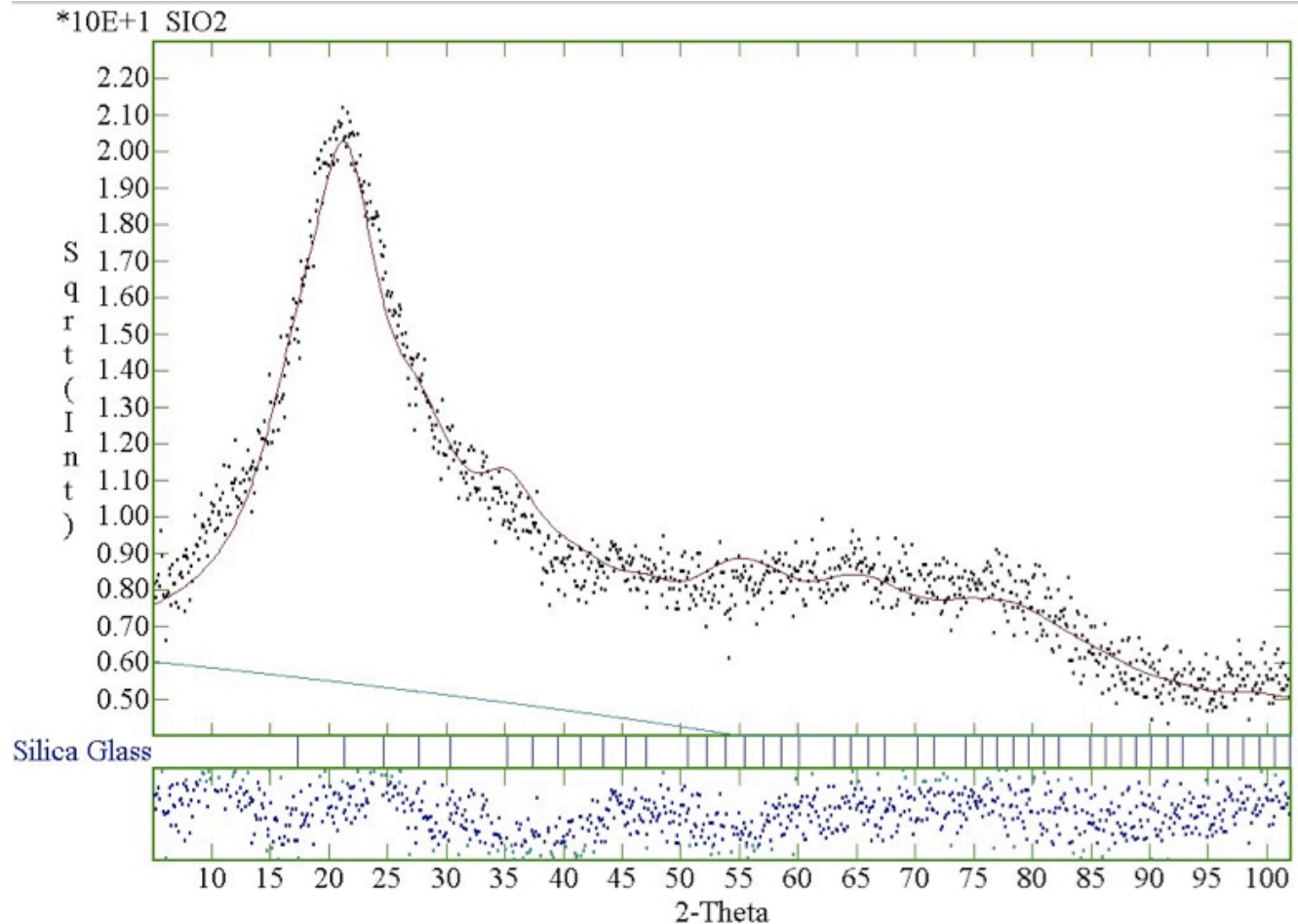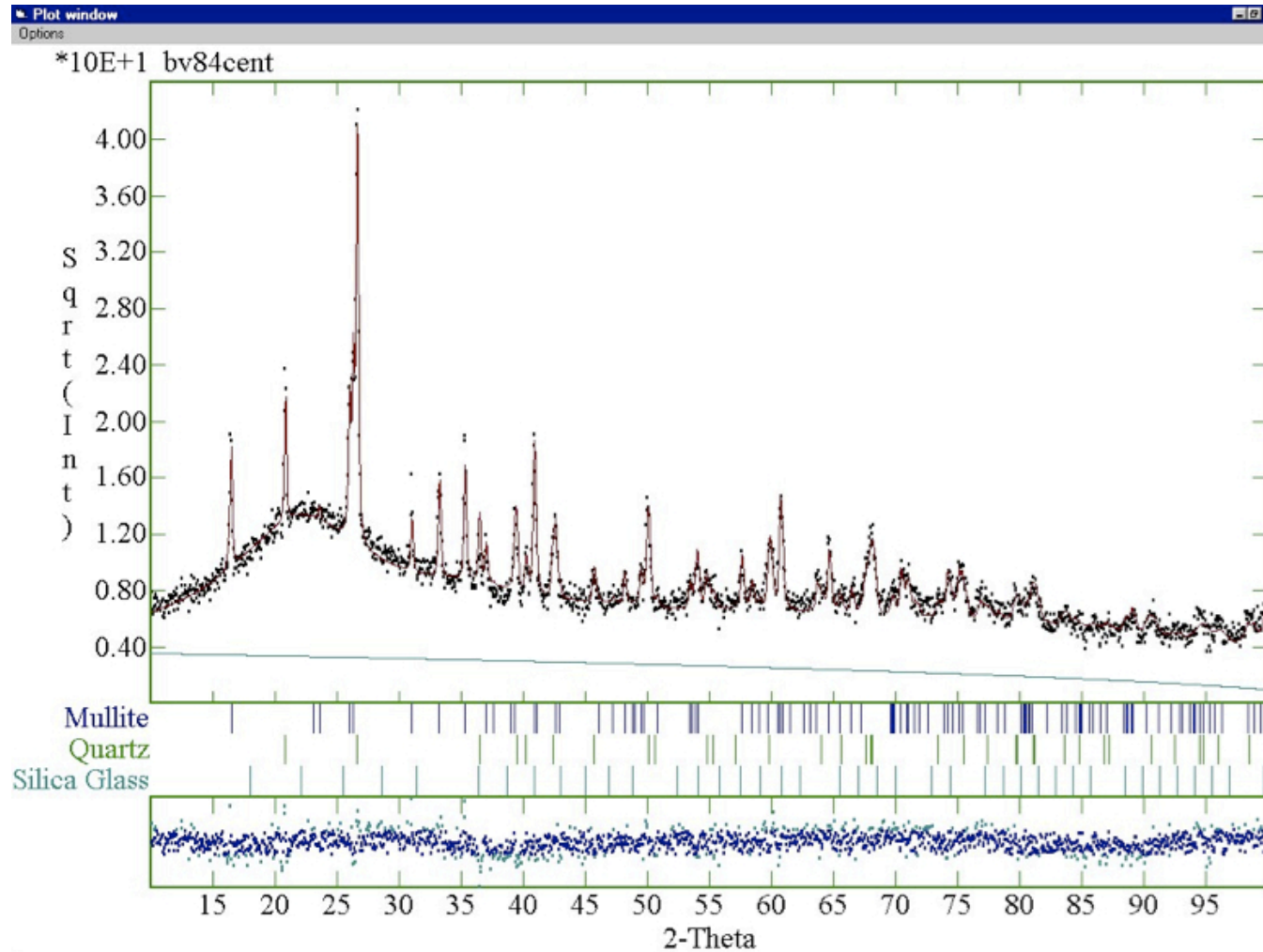
Corundum+amorphous silica mixed

Validation of the method testing on know amount of silica-alumina

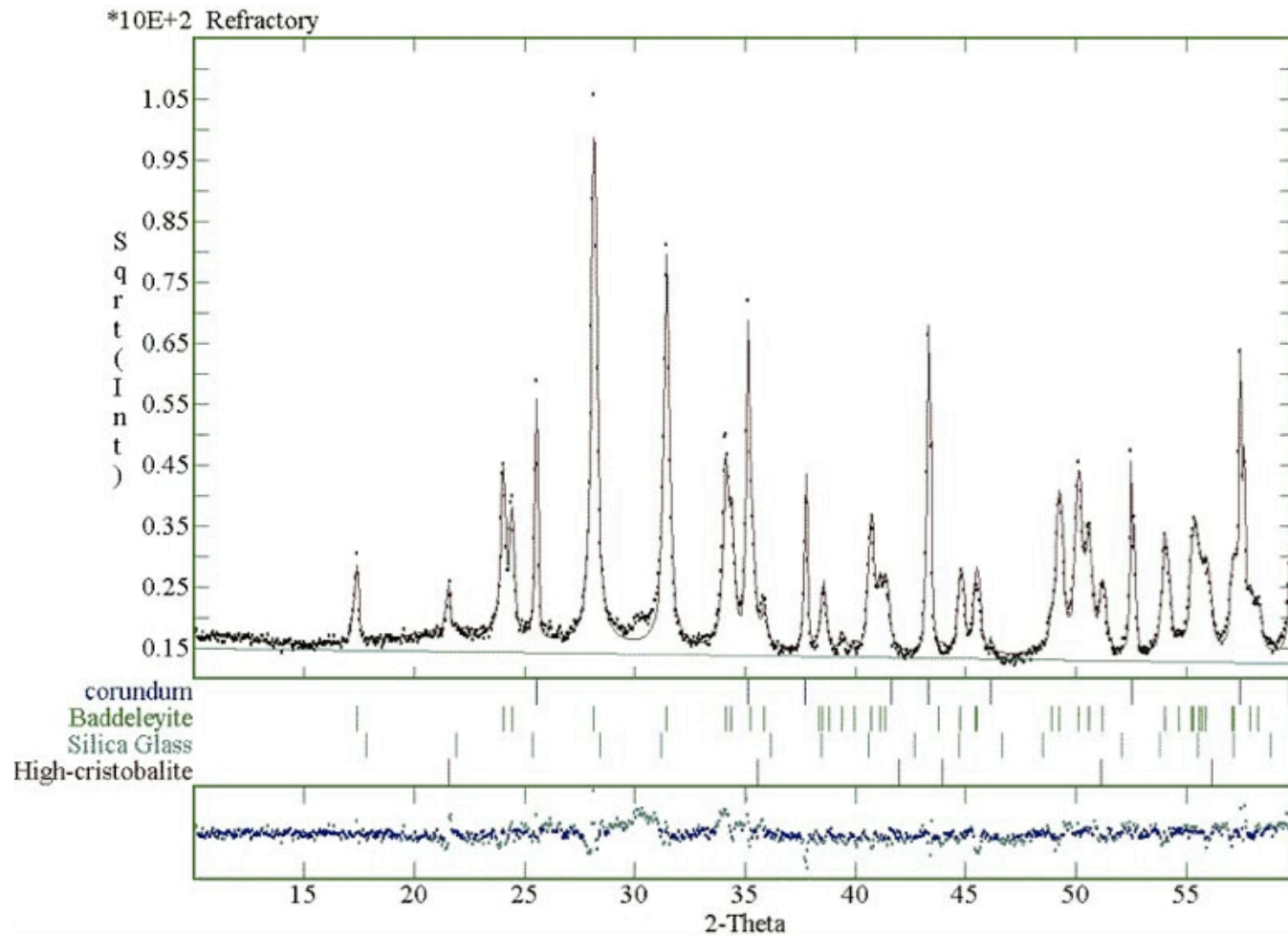# Result of the Rietveld analysis using the pseudo-amorphous approx.

Sanitary ware (>60% silica glass)

Ceramics for high temperature

Results

	Sanitary-ware		Refractory material
	Monochromator	Filtered radiation	Filtered radiation
Mullite	24.2(5)	20.5(7)	-
Quartz Low	13.3(2)	15.1(10)	-
Silica Glass	62.5(26)	64.4(6)	11(1)
Corundum	-	-	49(4)
Baddeleyite	-	-	39(1)
High Cristobalite	-	-	1(0.2)

Crystalline fraction for polypropylene

◆ **Same crystal structure for amorphous and crystalline**

◆ **Results: 43(1) % crystalline - 57(1) % amorphous**