



SEIFERT SOFTWARE

THE NEW SEIFERT RIETVELD PROGRAM BGMN AND ITS APPLICATION TO QUANTITATIVE PHASE ANALYSIS

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Abstract

The new Rietveld program BGMN is introduced with its unique features especially useful for fully automatic quantitative phase analysis. Some examples including layer silicates are presented.

1 Introduction

The Rietveld Method has become a powerful tool for quantitative phase analysis since 1987. Nevertheless some inconveniences have limited its use in routine analysis. Perhaps the most important limitation is the setup and test of the refinement strategy which requires a comprehensive knowledge of the working principles of the Rietveld Program used.

Some problems have to be mentioned, which are reasons for the difficulties in the routine use of conventional Rietveld code:

- analytic profile model which parameters (mostly used u , v , w ...) have to be refined simultaneously with structural parameters
- due to this joint refinement there is always a correlation between the two profile and structure parameters
- as a result parameters often reach physically meaningless values

Although this list is not complete, it illustrates the possible frustration of the novice Rietveld user. Everybody who has ever used a Rietveld program knows the annoying message 'Fatal error - program stopped'. The only solution to get reliable results is a carefully planned refinement strategy, in which - step by step - the number of free parameters increases. Of course this requires long computer sessions if the problem is not simple.

Recently some Rietveld programs targeting only the quantitative phase analysis were developed. They have in theory less problems because they don't refine structural parameters. But they are basing on older Rietveld code and inherit in principle the above mentioned problems.

The goal of the development of the new BGMN Rietveld program from the ground up was the complete elimination of numerical instability and bad convergence. As a result the user only has to take into account the crystallographic or mineralogical problem. In the next section it will be explained, how that goal was reached.

2 Features of the Program

2.1 Numerical Background: Advanced Peak Model and New Optimization Algorithm

First, the strong correlation between profile and other parameters had to be eliminated. The only solution was a development of a complete new profile model (Fig. 1).

This new profile model

- strictly distinguishes between wavelength distribution of the X-ray tube, the instrumental function and the sample function
- contains a sophisticated model of the instrumental function (it consists of an individual sum of a variable number of Lorentz-squared functions at each angular position)
- models the sample function taking into account peak broadening due to crystallite size and microstrain

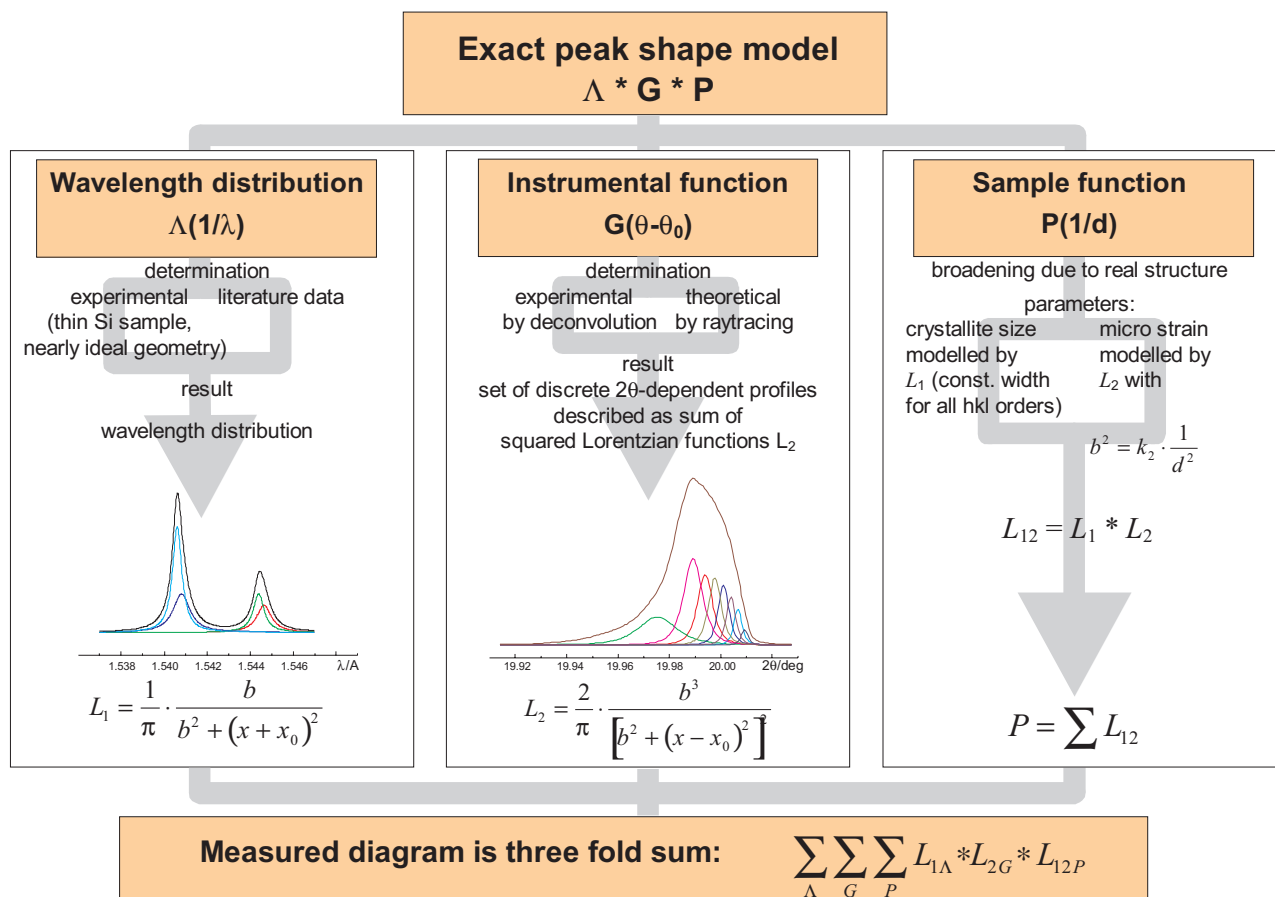
The wavelength distributions of X-ray tubes are already determined. Before starting the refinement the user has only to check if he has already computed the instrumental function. If not, he has to compute this function only once for a given geometrical setup.

During the refinement only the parameters of crystallite size and microstrain are varied. The profile portion which describes the instrument remains constant.

Next, a new numerical algorithm was introduced. This algorithm has in common optimal convergence behavior for the refinement of X-ray data. But it has a very valuable extension:

In conventional Rietveld programs parameters only can be fixed or freed. In the new algorithm physical meaningful Parameter Ranges with lower and upper limits can be defined without lengthening the computation time. This is extremely useful to avoid physically meaningless parameter values, for example negative peak widths.

In sum the above mentioned developments lead to a very useful feature of the program:



2.2 The full parameter set of the starting model is calculated in only one step.

Any user interaction during the refinement isn't necessary nor possible. The success of the refinement depends only on the chosen start model. A careful examination of the result list shows if the parameters have reasonable error values and if they didn't reach their limits. If not, one has only to modify the start model and run the refinement again.

So, a fully automatic refinement of samples with varying compositions and phase contents using the same starting model becomes a routine task (see example below).

2.3 Correction of Preferred Orientation

One of the most important rules in X-ray powder diffractometry is: 'the sample has to be prepared carefully to avoid preferred orientation'. But often it's not possible to prepare such an ideal sample. Many minerals have preferred cleavage planes or were grown in a manner which force preferred orientation. As an example the figure shows needle-shaped crystallites of synthetic diaspor for use in ceramics.

Analyzing a sample prepared from such crystallites requires a suitable model for correction of preferred orientation. The well known March model doesn't work because of the multiple preferred orientation combined with strong correction factors.

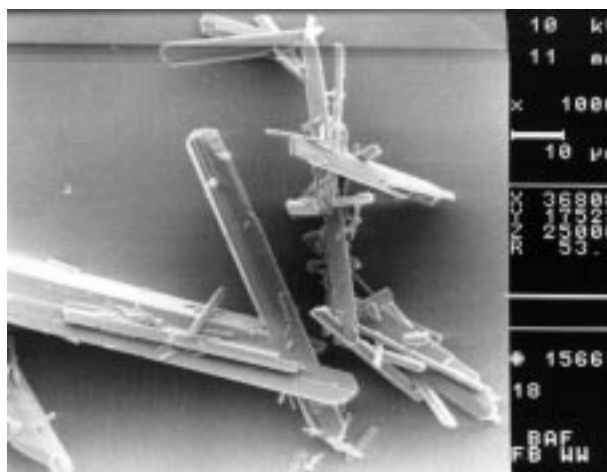


Fig. 2: Needle-shaped diaspor crystallites grown in b direction

Therefore a model using spherical harmonics was implemented. This model can correct not only strong preferred orientation in one direction but also multiple ones. The program uses spherical harmonics up to the 8th order. This leads in maximum to 45 free parameters in the triclinic crystal system. Because of restrictions due to crystal symmetry the number of free parameters reduces according to table 1. As a rule one must choose a higher order model if the crystal symmetry is higher. Up to 10 or more parameters are required to describe strong preferred orientation in non-cubic crystal systems.

Crystal system	Laue Group	2 nd order	4 th order	6 th order	8 th order
triclinic	-1	6	15	28	45
monoclinic	2/m	4	9	16	25
orthorhombic	2/m 2/m 2/m	3	6	10	15
tetragonal	4/m	2	5	8	13
tetragonal	4/mmm	2	4	6	9
rhombohedral	-3	2	5	10	15
rhombohedral	-3m	2	4	7	10
hexagonal	6/m	2	3	6	9
hexagonal	6/mmm	2	3	5	7
cubic	m3	1	2	4	5
cubic	m3m	1	2	3	4

Table 1: Effective number of free parameters in the spherical harmonics model for correction of preferred orientation

In the next refinement the orientation distribution function for diaspore calculated with an 8th order correction function (15 parameters) was applied. This example shows correction factors of about 2.5 to 3 in the directions 101, 002, 102, 103 and 203. A satisfactory agreement between measured and calculated data is the result (Fig. 3).

In addition to the implementation of this extended correction model the program includes an algorithm which automatically reduces the order of the model if the intensities of the peaks are too low. So you can always start with the maximum model even if the sample contains only low content of the phase.

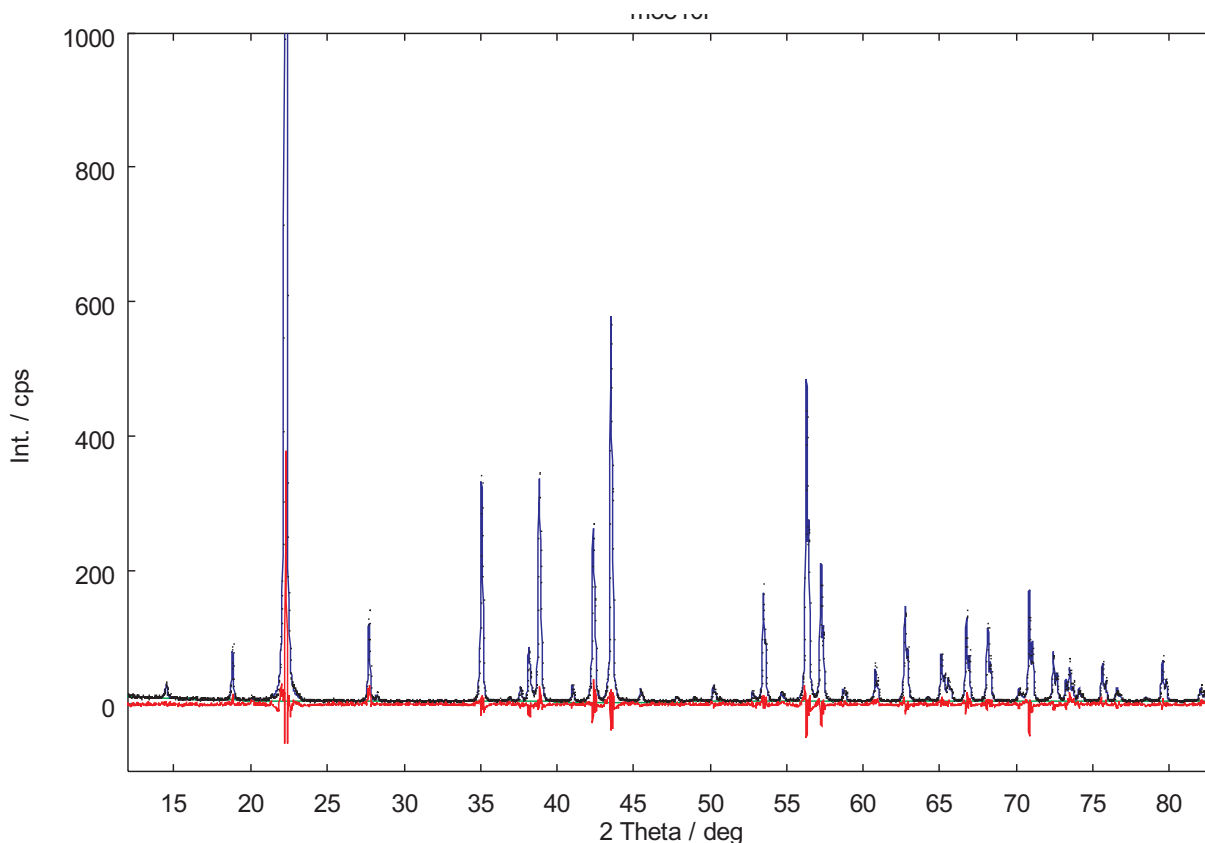


Fig. 3: Refinement result for a sample containing 99 % Diaspore and 1 % Boehmite; $R_{wp} = 14.2\%$ (without pref. Orient. 36 %)



2.4 Anisotropic Peak Broadening

Some minerals form crystallite shapes with strong differing axis lengths. An example for that behavior combined with strong preferred orientation is muscovite, here presented in a mixture with quartz (Fig. 4).

For muscovite a peak broadening of 0 was calculated which means an unlimited large crystallite size. The difference diagram shows volcanic shaped segments at the muscovite hkl peak positions except 001, which can be nearly completely removed by introduction of anisotropic peak broadening (Fig. 5)

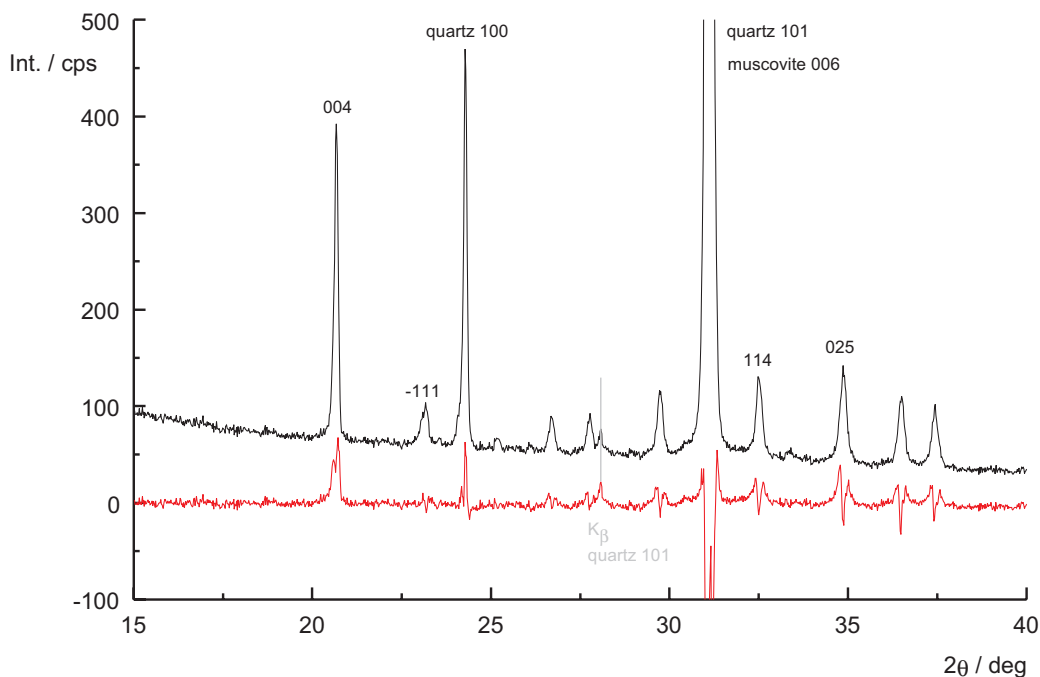


Fig. 4: Refinement result for a sample containing 50 % muscovite and 50 % quartz; isotropic peak broadening due to crystallite size; $R_{wp} = 12.7\%$

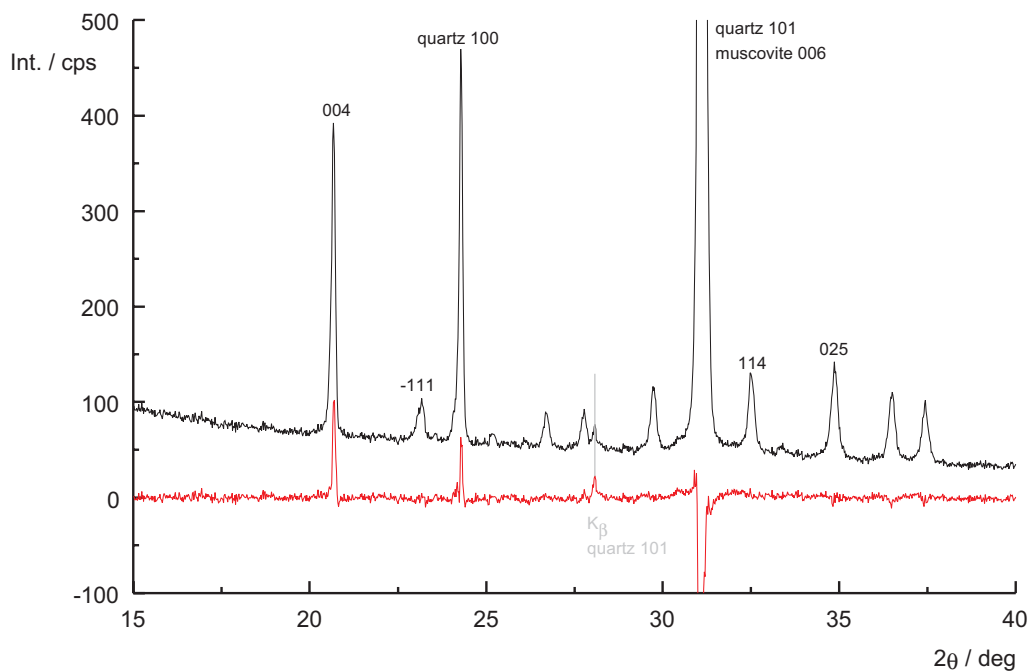


Fig. 5: Refinement result for a sample containing 50 % muscovite and 50 % quartz; anisotropic peak broadening due to crystallite size; $R_{wp} = 10.5\%$



The quantitative results also improved dramatically:

- isotropic peak broadening: 44.9 % muscovite;
 $R_{wp} = 12.7 \%$
- anisotropic peak broadening: 50.5 % muscovite;
 $R_{wp} = 10.5 \%$

Now also the calculated crystallite sizes have reasonable values. The site occupation factor for K^+ in muscovite was refined to approximately 0.85 in both cases.

Note that the correction factor of the 004 peak of muscovite due to preferred orientation is about 5, the measured peak is five-fold too high. A 2th order spherical harmonics model was used to correct this behavior.

2.5 Complex Disordering Models

There are a number of minerals which crystalline order is noticeable disturbed. Important examples of this behavior are layer silicates.

They show stacking faults by shifting the layers against each other. These shifts may be well defined and have discrete values or can be poorly defined and yield to two-dimensional diffraction effects. Natural samples may contain domains of different degree of disorder.

In comparison to an ideal structure, the resulting diffraction pattern shows depending on hkl:

- variable peak broadening
- shifted peak positions and
- asymmetric, tailed reflections.

Conventional Rietveld programs are of limited use in this case. At maximum they model anisotropic peak broadening with a simple ellipsoidal model or spherical harmonics. It's not possible to compute individual peak shape parameters for selected Bragg reflections. The description of peak asymmetry is only used to correct instrumental effects. It's a smooth function which is not applicable to individual reflections. Real structure induced shifted peak positions cannot be calculated.

To handle this complex requirements a new approach to introduce real structure models into Rietveld refinement was implemented. A hard coded model was not practicable because the nature of real structure varies between different mineral groups (or structure types). Therefore an interpreter for a structure description language was developed. It can be used to introduce additional parameters for describing disordering effects. Unlimited coupling of parameters is possible. To approximate the presence of domains having different degrees of disorder sub-phases are definable. They share global parameters, for instance lattice constants, and have individual parameters, for instance broadening models for definite Bragg peaks. Individual shifting of peak positions can be introduced to approximate the two-dimensional diffraction effects.

Chlorite minerals are an example for an already implemented real structure model. They show a well defined dis-

ordering (semi-random stacking). The layers are shifted from one to another by exactly $b/3$ along the three pseudo-hexagonal Y axes. The resulting X-ray diagram shows

- sharp and intensive 00l reflections
- relatively sharp, less intensive reflections with $k=3n$
- broadened or vanished/erased reflections with $k \neq 3n$

The first refinement using the structure model of Steinfink (Steinfink 1958) without disordering model showed correct fitting of the $k=3n$ peaks and the problem of the disappeared lines with $k \neq 3n$. The tailed band 02, 11 wasn't fitted at all by the peaks in this region (Fig.6).

Finally, a far more complex model had to be formulated. A rod-like intensity distribution in reciprocal space was assumed for the peaks with $k \neq 3n$. These rods are projected by the cosine of the direction on the diffractogram. The lengths of the rods are a new parameter introduced in the structure description. As an approximation, the resulting band was described by individually broadened hkl reflections. The angular shift of 0k0 peaks with $k=3n$ was refined by a new parameter depending on the dimension of the rods. The width of 0k0 was also parametrized. The relatively sharp peaks with $k=3n$ were described by an anisotropic broadening model due to anisotropic crystallite size and an isotropic broadening model due to microstrain. We used two sub-phases to match differing degrees of disorder in the sample. The sub-phases were refined with identical lattice parameters and identical preferred orientation correction. Their mixing ratio was also calculated. The dimension of reciprocal lattice rods and the normal peak broadening of the sub-phases were refined in a constrained ratio.

The result is a much better difference plot and a dramatic decrease of reliability factor (Fig. 7). The separately broadened $k \neq 3n$ reflections merge into a sufficient described band-like region. The other reflections are better fitted because of the distinct shape parameters for different classes of peaks.

3 Application in Phase Analysis

Minor phases in aluminum oxide-hydroxide system

A number of samples containing Diaspore, Bayerite, Boehmite, Corundum and Gibbsite with strong varying compositions had to be analyzed. These sample system is a good example for the program use in principle:

- First, the device function has to be chosen
- Next, all phases have to be included in the starting model
- Next, the calculation has to be done in fully automatic mode
- Finally, the results have to be verified

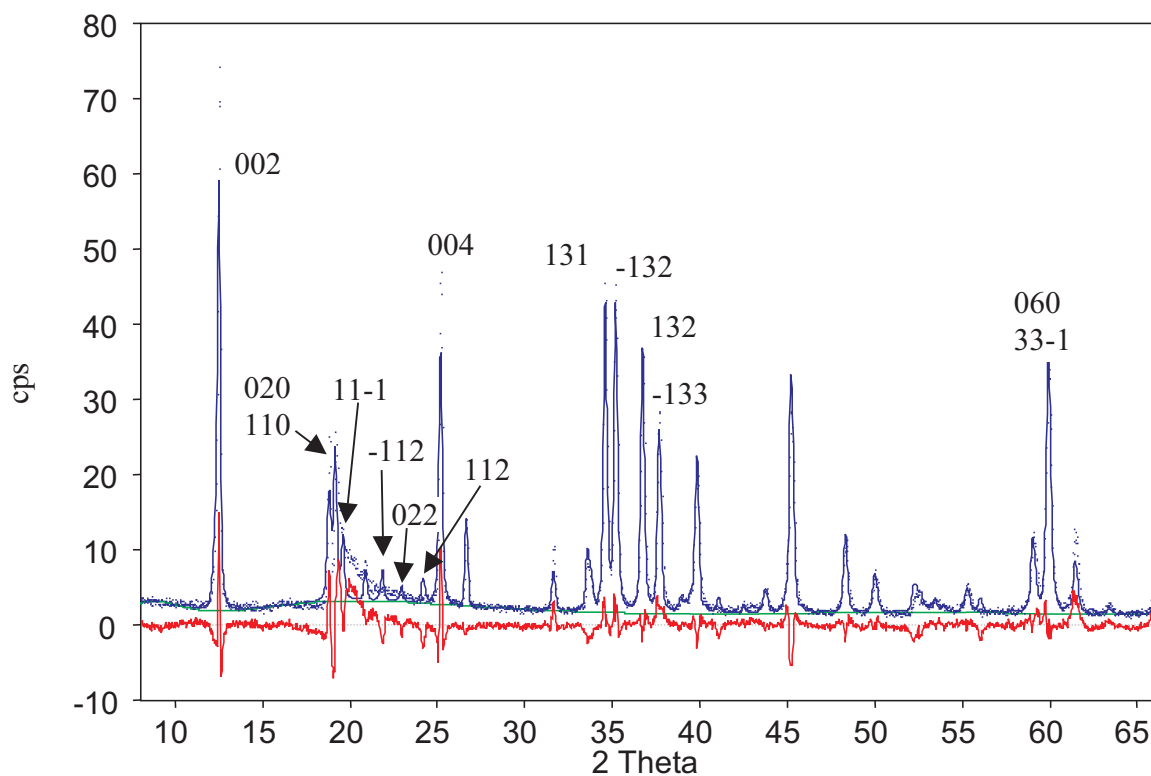


Fig. 6: Refinement result for ripidolite using ideal structure; $R_{wp} = 21.4\%$. The introduction of the traditional anisotropic peak broadening resulted in a somewhat better reliability factor ($R_{wp} = 19.5\%$) but the difference plot showed in principle the same problems.

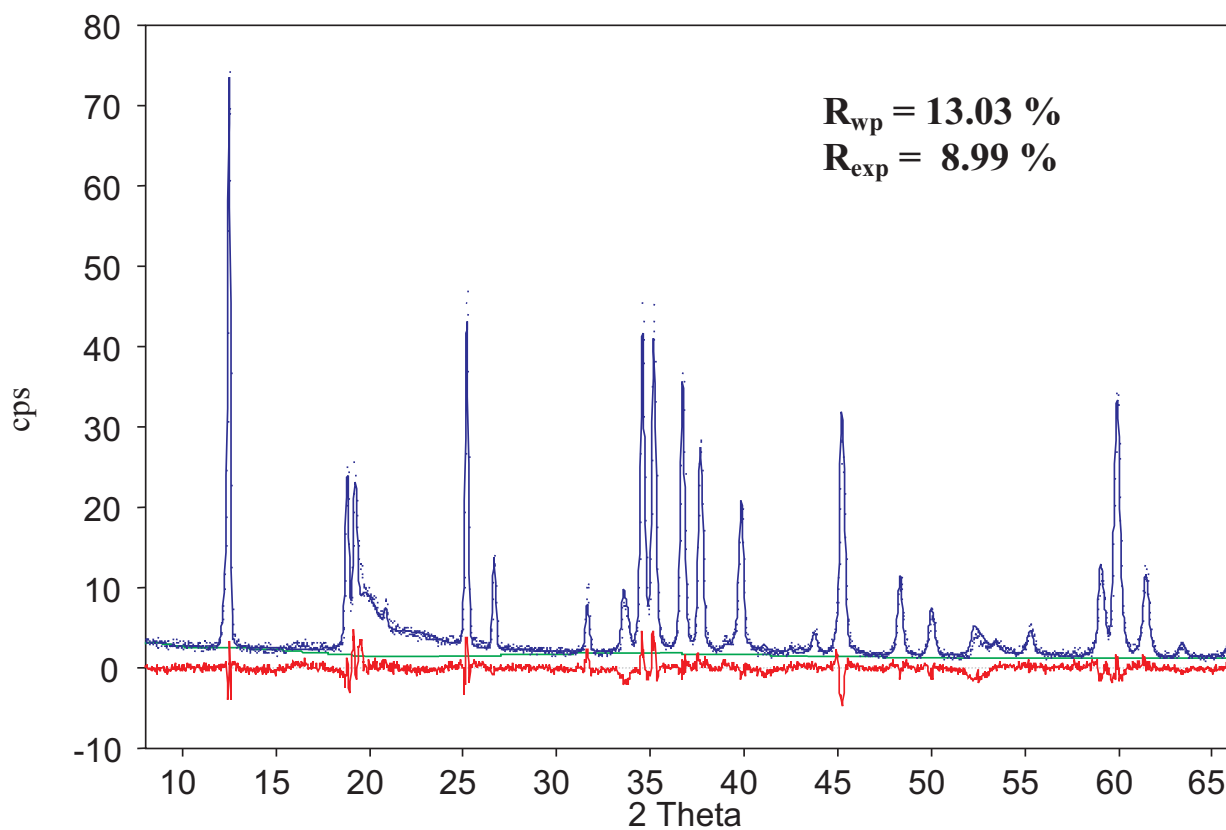


Fig. 7: Refinement result for ripidolite using disordering model; $R_{wp} = 13.0\%$



The measurements were carried out on an URD-6 (Seifert-FPM GmbH, Freiberg/Germany) in reflection mode with an angular range from 10° to $80^\circ 2\theta$. The step width was 0.05° (except samples 10 and 44 with 0.02°) and the measuring time per step was 5 s. An appropriate instrumental function was calculated.

The following starting model was set up:

- Diaspore: correction of preferred orientation with 8th order spherical harmonics; isotropic peak broadening due to crystallite size with an upper limit (maximum 20 parameters)
- Corundum: no preferred orientation; isotropic peak broadening due to crystallite size with an upper limit (4 parameters)
- Bayerite, Boehmite and Gibbsite: correction of preferred orientation with 6th order spherical harmonics; isotropic peak broadening due to crystallite size with an upper limit (each maximum 22 parameters except Boehmit with maximum 15 Parameters)

All lattice constants were free with an variation range of about 2 %. Of course the angle correction parameters for zero shift and sample displacement were free. In sum the number of free parameters varied between 26 and 58 due to the complex modeling of preferred orientation.

All calculations were carried out in one step without user interaction. The actual choice of the model for preferred orientation was done automatically by the program.

The needed calculation time depends on the number of measuring points, the counting statistics and the quality of the model used. On a Pentium 133 the calculation time varied between 10 and 40 minutes.

For all samples except number 30 a good result for the phase content was calculated. Some minor phases with contents below 1 % had parameter values which were shifted to their limits. Such phases can be excluded in a final calculation if one needs a more exact numeric result. But in general this is not necessary because of their small contents.

Samples 19, 20 and 23 showed a noticeable amount of gibbsite. Because of the very strong overlapping with peaks of bayerite some gibbsite parameters moved to their limits.

Only sample 30 stepped out of line. It had a very large reliability value and the large content of Boehmite was refined only with an isotropic model for preferred orientation. A short view on the diagram showed the reason. The Boehmite exhibited a strong peak broadening due to very small crystallites. A second calculation with a 20 times higher upper limit for the peak broadening gave a good fit also for Boehmite in sample 30.

The presented set of samples showed that a wide range of phase content can be refined without user interaction with only one common starting model. That works because the program reaches many decisions automatically.

Sample	Diaspore		Corundum		Bayerite		Boehmite		Gibbsite		Parameters	R _{wp} /%
	wt.-%	PO	wt.-%	PO	wt.-%	PO	wt.-%	PO	wt.-%	PO		
05	98.4	8 th	0.1	i	0.3*	i	1.0	i	0.2*	i	41	14.4
10	98.5	8 th	0.1*	i	0.1*	i	1.0	i	0.3*	i	41	14.2
19	16.5	6 th	0.5	i	76.3	6 th	0.6*#	i	6.1*#	2 nd	52	16.1
21	0.9*	i	13.9	i	78.6	6 th	0.5	i	6*#	2 nd	43	15.9
23	13.1	6 th	0.6	i	77.2	6 th	0.4*#	i	8.7#	2 nd	52	16.1
29	0.1	i	99.8	i	0.1*	i	0	i	0	i	26	13.0
30	59.2	4 th	0	i	3.5*	i	33.3#	i	4.0*	i	31	27.7
30 2 nd	20.9	4 th	0.2*	i	1.2	i	77.4	6 th	0.3*	i	31	9.4
31	29.8	8 th	1.0	i	0.1	i	69.1	6 th	0	i	58	13.5
44	98.5	8 th	1.0	i	0.3*	i	0.2	i	0	i	41	13.6

Table 2: Refinement results of samples containing phases with strong preferred orientation and varying phase content

*: at least one lattice constant moved to one of its limits

#: the peak width moved to its upper limit

i: no preferred orientation (isotropic model)



Chlorite mineral	Refined Fe	Chlorite wt. %		Quartz wt. %		Muscovite wt. %		Oligoclase wt. %		R _{wp} /%
		norm.	ref.	norm.	ref.	norm.	ref.	norm.	ref.	
penninite	0.7	50	50.9	50	49.1	-	-	-	-	15.5
penninite	0.6	33.3	36.2	33.3	31.1	33.3	32.7	-	-	14.2
penninite	0.7	30	31.4	30	28.7	30	31.2	10	8.7	13.9
ripidolite	2.7	48	46.6	52	53.4	-	-	-	-	21.3
ripidolite	2.1	32	32	34.7	32.9	33.3	34.2	-	-	17.6
thuringite	3.9	47	47.4	50	50.4	-	-	-	-	25.8

Table 3. Refinement results of reference mixtures containign chlorites; transmission measurements.

3.1 Chlorite Minerals

To check the behavior of the above mentioned disordering model for Chlorite in quantitative phase analysis, mixtures of different chlorites with quartz, muscovite and oligoclase were prepared. Muscovite was refined using an anisotropic peak broadening model. All refinements were done in a single run without any interaction of the user, starting from the same structures. The calculation times for such mixtures vary between one to four hours.

The quantitative results are satisfactory (Table 3). The refined total Iron content of Chlorite differs between the measurements and is in general correspondence to the mineralogical classification of the samples used.

The modeling of disorder in chlorites is a first step of implementing disordering models for layer silicates which will be followed by more complicated phases in the future.

4 Summary

The presented program BGMN has a set of unique features which are very useful for quantitative phase analysis.

Because of the underlying numerical algorithms the program can handle samples with a wide varying phase content and strong preferred orientation in a fully automatic way. After application of a suitable starting model based on the qualitative analysis no user interactions during the calculation are required.

Furthermore, the structure-based modeling of broadening and shifting of individual Bragg peaks is an useful tool to approximate the diffraction patterns of disordered layer silicates. The problem of refining such a complicated set of parameters is soluble by means of the program. If the formulation of the dependencies was carried out once, a convenient refinement of multiphase samples including disordered layer silicates is possible.

References

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2. Kleeberg, R and Bergmann, J., 1997. Rietveld Analysis of Disordered Layer Silicates. Lecture held at EPDIC-V, Parma 1996
3. Steinfink, H, 1958. *Acta Cryst.* **11** (1958), 191-195.



Vzorek	Analyzovaná oblast	Přítomné fáze
1a - DK	vnější povrch	α , β , γ , Sn
1b - DK	vnitřní povrch	α , β , γ , Sn
2a - ŠK	vnější povrch	α
2b - ŠK	vnitřní povrch	α , β , γ , Sn
2c - ŠK	fólie s cínovou vrstvou	β , Al