BRASS 2.0

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Training manual for an examplary Rietveld refinement

(fragmentary version)

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1 New concepts of BRASS 2 versus BRASS 1

BRASS 2 devises a number of changes with respect to BRASS 1. Two main changes shall be discussed here shortly, the user interface and the structure of Rietveld jobs.

The user interface has been rewritten completely to provide a much more intuitive access to BRASS. The new *BRASS 2 job explorer*, a Windows Explorer-like folder tree, provides four main branches *raw data viewer*, *rietveld job*, *struplo job* and *fourier job*. The branches *rietveld job* and *struplo job* now provide directly accessible sub-branches for all previously successive layers of BRASS 1-Rietveld or -StruPlo jobs. All major branches in a *rietveld job*, such as *phases*, *raw data* or *BRASS job explorer*, provide a group of context-related buttons, all other branches give direct access to the related editing or information pages. In addition, the user interface now interprets the space group symbol, automatically applies symmetry constraints to the lattice constants and allows for activation of symmetry constraints for each atom individually, by a single mouse click each.

In BRASS 2 every Rietveld job is a single separate file with extension "BRJ". All related data are stored here. On starting a refinement BRASS 2 creates a subfolder to the job's folder with the same name as that of the job, extended by "temp". The files in this subfolder are direct ASCII input to and output from the Rietveld kernel. To continue organizing your Rietveld jobs in a superordinated project, simply store your BRJ-files in the same folder of your computer. Note: In this beta-version of BRASS 2 only a single Rietveld job can be opened and edited at a time. BRASS 2 will ask you for storing your job before opening the next one if anything has been changed.

The Rietveld kernel also has been modified extensively to provide a rigorous separation of instrument and sample contributions to the peak profiles. For this purpose the Pseudo-Voigt function has been redefined according to (Birkenstock *et al.*, 2006). The "classical" profile parameters U, V and W after (Cagliotti *et al.*, 1958), more precisely the respective Gaussian (U_G, V_G, W_G) and Lorentzian parameters (U_L, W_L) in BRASS 2 are now reserved for instrumental contributions and may not be refined but once for a given data set. Consequently these parameters are now located on branch *measurement* in the *raw data* section. In section *raw data* you will also find all other parameters that are closely related to the specific raw data, i.e. profile limits, asymmetry, background parameters, errors in peak positions (ZERO and sample displacement) etc.

The *phases* pages consequently have been revised, too. A phase's *profile* page now provides sample related parameters only, i.e. preferred orientation, crystallite size and microstrain parameters. Two microstrain models are now available, the previously known *Stephens' model* after (Stephens, 1999) and the new *isotropic / simple anisotropic model*. The latter, described in the above reference, is the new default setting and should suffice for most purposes and data qualities.

Note, however, that the microstrain parameters including the new ones iS_L, iS_G, aS_L and aS_G and the instrument parameters UVW (especially U) are highly correlated. The same is true for the crystallite size parameters if the crystallite size is not very pronounced. It is thus not just advisable but indispensable that the two sets be established independently using a standard sample for UVW and your given sample for the sample parameters. Otherwise at least the refined sample parameters are meaningless but beforehand you will probably run into serious problems with stability in the refinement.

Compatibility with BRASS 1 could not be assessed completely since superordinated projects are no longer supported. But any single BRASS 1 Rietveld job may be loaded to BRASS 2: Simply use the open button from either *BRASS job explorer* or *Rietveld job*, set the filter to either "Rietveld job" or "input file", respectively. Then go to the folder of your BRASS 1 project, follow the relative folder path input parameters → rietveld and pick the Rietveld job file with extension INP you are heading for. BRASS 2 then imports all information from that file to the BRASS 2 dialogs. Note that you can also pick single phases from INP files using the *add phase* button on branch *phases*.

This training manual is intended to provide insight into all steps to perform Rietveld refinements with BRASS 2 on samples of a profile standard and on "everyday samples", containing structurally known phases with only crystallite size and simple microstrain effects. It should be noted, though, that BRASS provides numerous capabilities for further tasks, such as high quality structure drawing, crystal chemical calculations, refinement and quantification of phases without structural model ((Birkenstock *et al.*, 2005)) and Le-Bail profile fitting to yield structure factors for structure solution. Finally, currently the familiar BRASS 1 tools for structure completion, fourier and grid search, are being made available in BRASS 2, too.
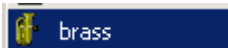
2   First contacts with BRASS 2.0

The example files **LaB6_041008_ref061215.brj** and **Mixture2_041111_ref061215.brj** contain fully refined BRASS2 Rietveld jobs. LaB6~.brj is a Rietveld refinement against data of LaB_6, a material that is widely used in diffraction laboratories as a profile standard. The

refinement has been done to establish the instrumental parameters U_L, U_G, V_G, W_L and W_G. These were used and kept fixed in the refinement of mixture2 to be able to establish the sample contributions to the profile. mixture2 is also intended for demonstration of quantifications with BRASS, especially taking into account the Brindley correction for microabsorption.

Based on the above Rietveld jobs in this chapter some simple exercises are described to get used to BRASS 2.

2.1   Introducing some basic actions with BRASS.

2.1.1 Executing BRASS 2.0

Execute BRASS using the respective desktop symbol or the entry at ![Start] → programs. Alternatively use the Windows® Explorer to execute file brass2_0.exe from the program folder of BRASS 2.0. Depending on the exact version of BRASS 2.0 the program will appear as follows:
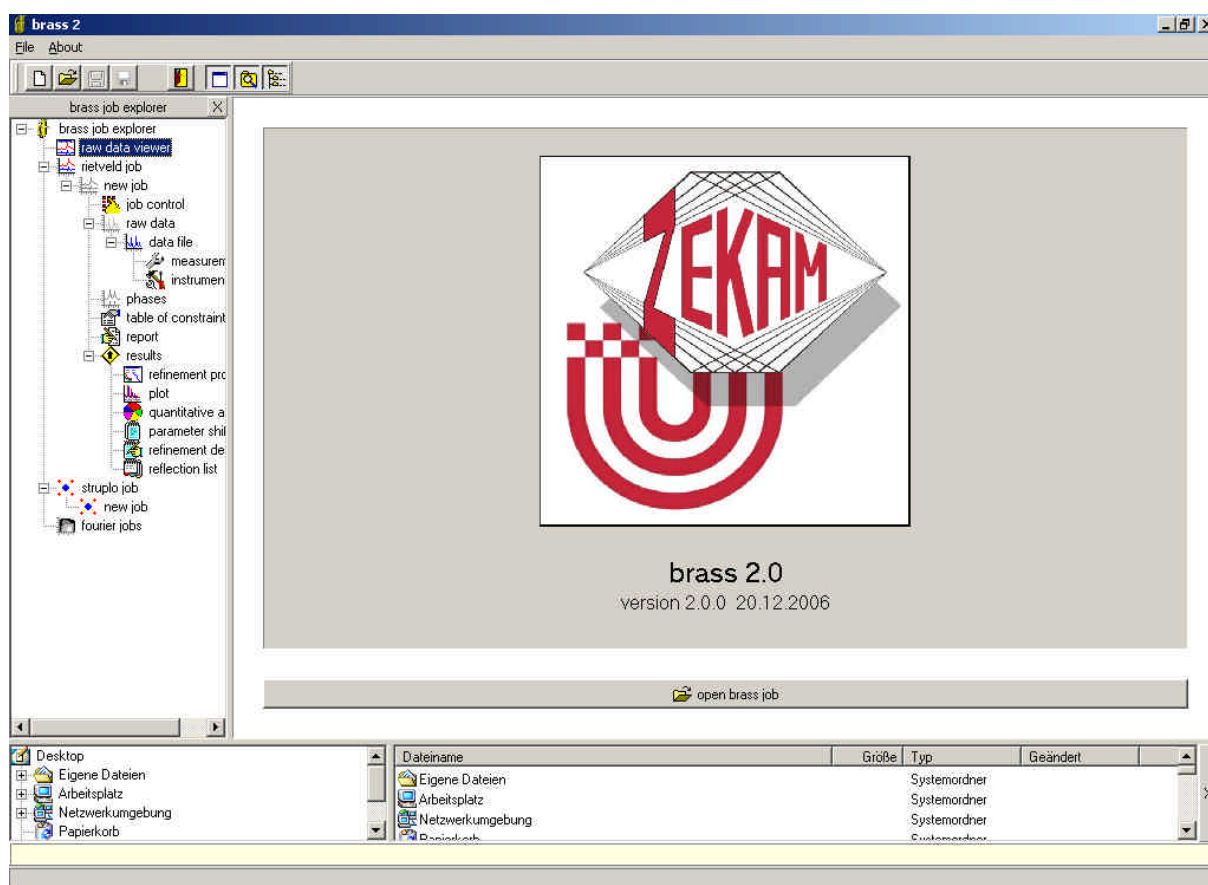
2.1.2   Elements of the BRASS 2 main window

2.1.2.1   The main tool bar ⬚ on top left.

- ⬚ : Creates a new Rietveld job.

- ⬚ : Invokes a standard open dialog. Filters for all types of jobs supported by BRASS 2 are available. The pre-selection of the current filter is determined by the job type currently active in the job explorer window.

- ⬚ : Saves the currently active job. Enabled only if the currently active job has been changed. Invokes the *save as*-dialog if a new job is active.

- ⬚ : Save as button. Invokes the *save as*-dialog for the active job.

- ⬚ : Close BRASS.

- ⬚ : Push *down* to display one job window only at a time. Push *up* to display all job windows containing data at a time.

- ⬚ : Push *down* to show the BRASS file explorer at the bottom, push *up* to hide it.

- ⬚ : Push *down* to show the BRASS job explorer on the left side, push *up* to hide it.

2.1.2.2   The BRASS job explorer

- All job types available in BRASS 2 are displayed as main branch.

- A click on any branch displays the related dialog window in the working area to the right of the job explorer.

- Many types of files are accepted by the job explorer by drag&drop from the Windows® and the BRASS file explorer.

- Some branches accept the appropriate files by drag&drop from the Windows® and the BRASS file explorer:

  raw data viewer → raw data files.

  rietveld job → BRJ, INP, CIF files. Invokes dialog.

  data file → raw data files. Replaces current raw data!

  phases → CIF, INP, BRJ. INP and BRJ: Invokes dialog to select phases to be imported.

- Push ⊠ to hide the job explorer. To show again push ⬚ in the main tool bar.
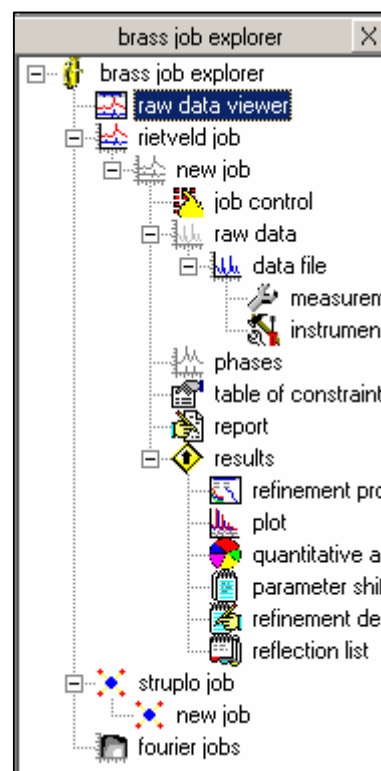
2.1.2.3 The BRASS working area

- Each click on a branch in BRASS job explorer displays the related dialog in the respective job window located in the BRASS working area.

- If the button ▣ is pushed *down* only the job window of the active job is displayed.

- If the button ▣ is pushed *up* all job windows currently containing data share the working area. Place the mouse between the job windows and use click&draw to resize the job windows.
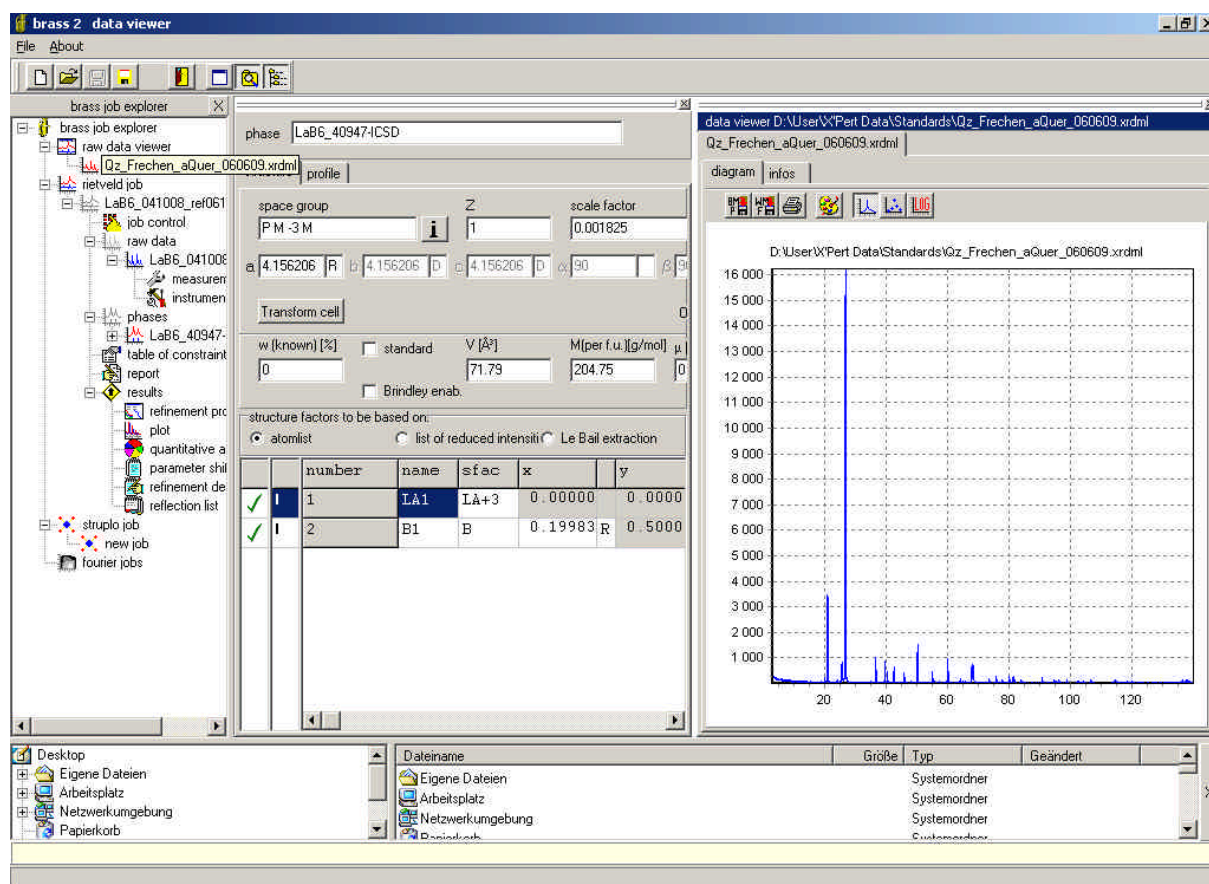
2.1.2.4 The BRASS file explorer

- Located at the bottom of the BRASS main window (see figure above).

- Resizable by a splitter on top of the file explorer.

- Behaviour identical to that of the Windows® Explorer.

2.1.2.5   The BRASS main menu and why it is so sparse.

- Only a few standard commands are placed here. The majority of commands is located in a context related environment, i.e. as branches, on the job pages related to the job branches and/ or in context menus. Many commands are doubly or triply available at either one of these locations. If you expect a useful command at some lactaion use the right mouse button for "missing" context sensitive menus.

2.1.3   The raw data viewer

Currently the following file types with diffraction data are supported:

- ***.xrdml, *.sd, *.rd**: raw data from PANalytical (former Philips) diffractometers
- ***.udf**: ASCII export format from PANalytical (former Philips) diffractometers
- ***.dat**: ASCII file used with many Rietveld programs based on the Young&Wiles code, format: 1 header (3F16.N, 32A) or (3F8.N, 66A), N/10 lines with intensities (10I8) or intensities + repetition counter (10I1I7) or sometimes (10I2I6), with N = No. of steps+1.
- ***.raw**: Siemens raw data files, versions 1 and 2.
- ***.nja**: ASCII export format from Seifert diffractometers. Note: only one scan per file is supported.
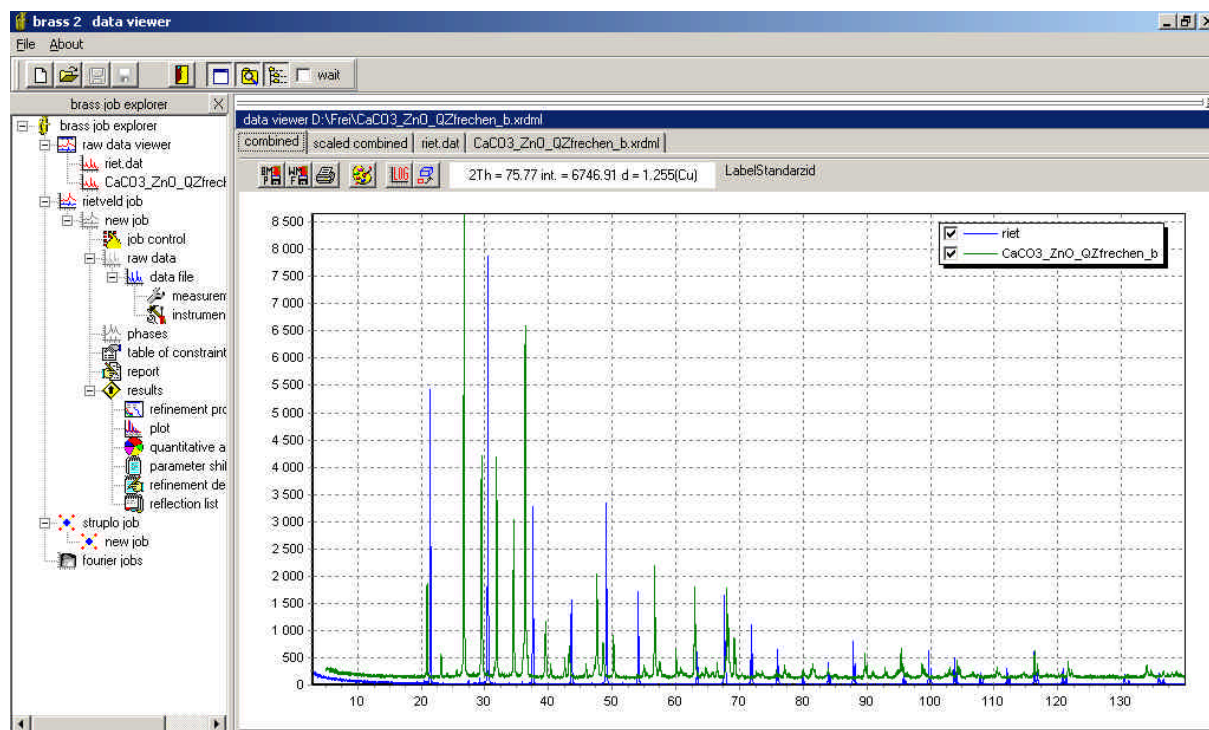
To display single or multiple diffraction data from supported file types:

- Drag&drop files from the Windows® or BRASS file explorer on the branch raw data viewer

- Use one of the ways to open files and select the file filter data viewer.

Display modes in the *raw data viewer*

- Each file with diffraction data is displayed on a separate page.

- On each single file's page you find both the diffraction diagram and the *infos* sub-page

- In addition all files are plotted together in both the *combined* and the *scaled combined* plot. On page *scaled combined* all diagrams are scaled to 10000 counts for the maximum step intensity. On both combined pages you can select individually which data are to be displayed.

Actions with the *raw data viewer*

- On top of the diagram the position of the mouse cursor is displayed. Reported d-values are currently based on the wavelength of Cu-$K_{\alpha 1}$ radiation.

- Use click&draw to zoom a selected part of the plot.

- To move the plot when data are zoomed click&draw with the right mouse button.

- To unzoom double click on the diagram.

- To change some display attributes of the single data plots use the respective buttons on top of the plot.

2.1.4 Exploring a Rietveld or a StruPlo job

BRASS 2.0 jobs are stored in BRASS' proprietary files with extension *.BRJ for Rietveld jobs and *.BST for BRASS StruPlo jobs.

1) To open a BRASS Rietveld or StruPlo job file you may either

   - Push the button from the main tool bar

   - Use the command *open job* from menu *file* and setting the filter of the open dialog to *brass job file* or *Rietveld job* or *struplo job*, respectively.

   - Press the shortcut *crtl + o* with the same filter settings.

   - For Rietveld jobs you may also go to branch *Rietveld job* on the *BRASS job explorer* tree and use the button from the related dialog in the working space.

2) If you wish to open a file you have edited lately you may open it more conveniently

   - Right mouse click on the button and select the file from the drop down list.

   - Use command *reopen job* from menu *file*.

3) Direct access to all dialogs

- To access any of the dialogs related to the current Rietveld or StruPlo job simply click on the related branch in the BRASS job explorer.

- For details on the respective dialogs of a Rietveld job see the exercises in sections 2.2 (fragment) and 2.3 (to come).

- Details on the dialogs of a BRASS StruPlo job are under construction …

2.2   Exercise (fragment): Explore the fully refined Rietveld job on a profile standard sample (LaB$_6$)

2.2.1 Loading Rietveld jobs and understanding refinement flags "R" and "D"

Execute BRASS 2 and open the Rietveld job file *LaB6_041008_ref061215.brj*. The dialog linked to phase *LaB6_40947-ICSD* is automatically displayed.
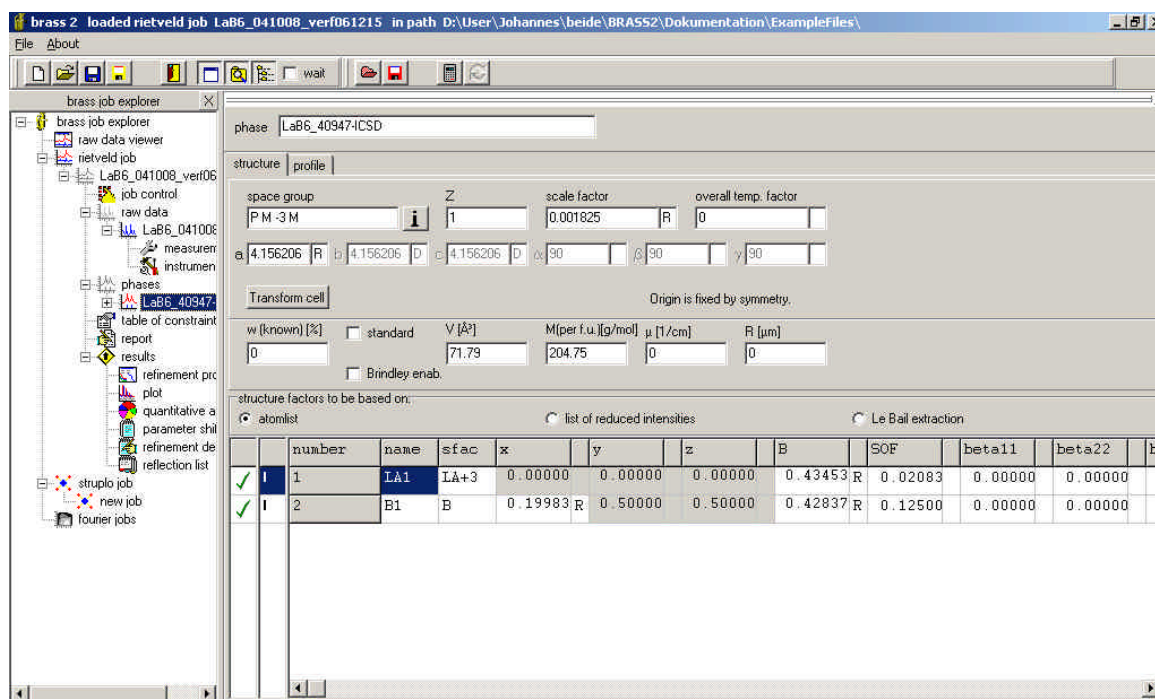
Next to some of the parameters' values there is a small box which is either empty or is filled with an "R" or "D". A parameter with an empty box is principally refinable but is currently not refined. It is said to be "not flagged" or "unflagged". Other parameters, such as the scale factor or lattice constant a, with an "R" were refined as independent parameters and are said to be "flagged" for independent refinement. The parameters with a "D", such as lattice constants b and c, are "flagged" for refinement with a linear dependance on one of the parameters flagged "R". I.e. these parameters may not change independently but follow the changes of the related parameter flagged "R" in a fixed ratio.

Click on one of the "R" flags to toggle it on or off. Note that if you click on the flag of lattice constant *a* the "D"-flagged lattice parameters are automatically unflagged or flagged since the dependencies are derived from symmetric restrictions.

To set a dependent flag for parameters which are not constrained by symmetry first set an "R" flag on one of the parameters and immediately set "D" flags for all dependent parameters. Note that the setting of each "D" is followed by a dialog asking for the linear factor relating its shift to the shift of the first parameter flagged "R".

Try setting the displacement parameters B of the atoms La and B dependent by a factor of 1, i.e. first unflag both B parameters, then flag either B(La) or B(B) first by a left mouse click and then flag the second one "D" by a right mouse click. In the subsequent dialog *constrain factor* set the factor to 1.

Note: Information on which parameters are related by dependencies is displayed and may be edited using the branch *table of constraints*. The constrain factors may be edited and dependencies may be deleted by the respective context menu of the currently selected row.

2.2.2 The *raw data* branch

1. At branch *raw data* you only find a button which allows for replacement of the current diffraction raw data. This is the fastest way to perform a series analysis of samples which comprise the same overall set of phases but vary e.g. in phase fractions: You would refine your model for the first sample, then save it with a new name and load the data of the next sample. Then you usually can refine the robust parameters in one first step and all the others at a time in a second step. I.e. after doing some profound and rather lengthy work on a representative sample you can work very fast on similar samples.

2. At branch *LaB6_041008.xrdml* you find the dialogs related to the diffraction data, i.e. the plot and – using the side bar and the options on top of the graph – the dialogs to define the background model (side bar page *background*), the model for handling position errors (side bar page *2 theta shifts*), some other side bar pages to adapt display options of the graph and, to the upper left, some buttons for exporting the plot.
   In section 3.1.1 you will learn how to set up the parameters for background and 2 Theta shifts. Here you may simply check the "mouse action mode" *zoom* on top of the graph and use click&draw to zoom the plot and double click to unzoom it.

3. At sub-branch *measurement* note that all instrumental parameters for 2?-dependent peak width parameters of the instrumentally produced peak widths FWHM (full width at half maximum) have been refined. In addition the parameter *AS* for the description of asym-

metric peaks up to a *2-theta limit* of 50° using Rietveld's original approach has been re-fined.
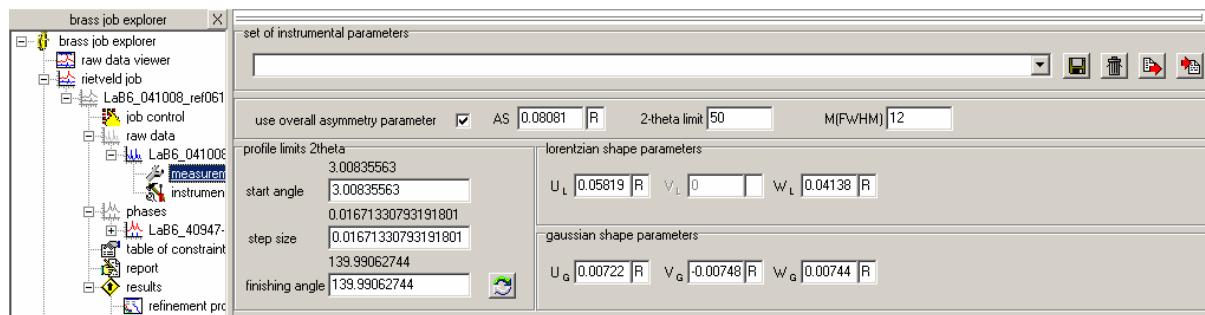
The parameter *M(FWHM)* determines to which angle below and above the peak center the peak is to be calculated. The lower and upper limiting angles each are M(FWHM) · FWHM ° apart from the center. Set M(FWHM) to a value that guarantees that the peak's intensity has dropped to zero below and above the limiting angles. This limiting saves a lot of time compared to the calculation of each peak over the full range of the diagram for just adding a lot of zeroes.

Hint: In early stages of a refinement or in case of very large unit cells you can speed up the calculations by reducing *M(FWHM)* down to about 4.

Sets of instrumental parameters are templates with values for all parameters on the pages *measurement* and *instrumental* except for the *profile limits in 2theta*. At the end of section 3.1.2 you will save a new template and at the beginning of section 3.2 you will make use of it.

Note that you must save edited sets using the 🖫 button. Single sets may also be deleted from the list using 🗑. You may also save a single set to a *.ris file by 🖹 or load sets from *.ris files by 🗎.

4. At branch *instrument* specifications on the instrument are listed. All entries must be given by the user and may be stored – together with the entries on page *measurement* – as a template *set of instrumental parameters* which may be called from the drop down list for all datasets that were measured with the same configuration.

Note that you must save edited sets using the 🖫 button. Single sets may also be deleted from the list using 🗑. You may also save a single set to a *.ris file by 🖹 or load sets from *.ris files by 🗎.
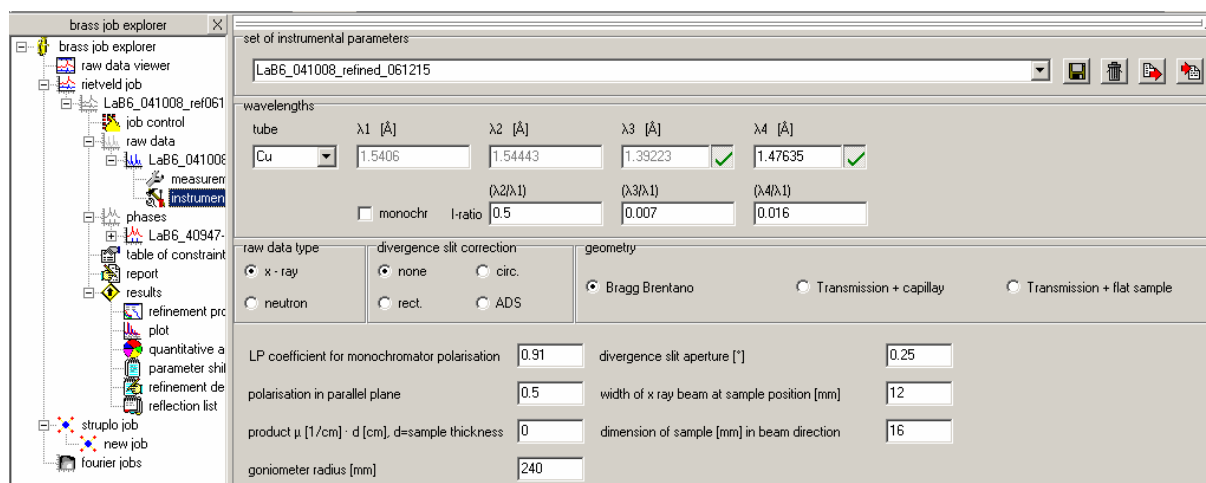
- *tube*: A set of stored wavelengths. If you have to edit the wavelengths, confer to the warning below and select the entry "other".

  Warning: Note that BRASS currently does not support manual editing of parameters for the calculation of scattering factors. I.e. in case of x-ray data, scattering factors are only calculated correctly for the pre-defined sets of wavelengths.

- *monochr*: Check if the data were measured with a single wavelength such as $K_{\alpha1}$.

- *I-ratio*: The relative intensity ratios for the second, third and fourth wavelength with respect to the intensity of the first wavelength. For $K_{\alpha2}$ it is usually 0.5 or more exactly 0.497.

- *raw data type*: select the type of radiation used for raw data collection.

- *divergence slit correction*: Using Bragg-Brentano diffractometers with a fixed divergence slit the sample is often over-irradiated at small diffraction angles. Peaks in this region are systematically underestimated and should be corrected for either rectangular sample surface areas (Fischer, 1996) or circular ones (Krüger & Fischer, 2004).

  Note that for fixed slit corrections you must also enter the correct values for the goniometer radius, the divergence slit aperture, the width of the x-ray beam and the dimension of the sample in the edit fields below.

  If an automatic or variable divergence slit was used select *ADS*.

- *geometry*: Select the correct type of diffractometers geometry. For the different geometries enter at least the following values in the edit fields below:

  Bragg-Brentano: All but *product µ·d*.

  Transmission + capillary: All four values on the left.

  Transmission + flat sample: All four values on the left.

- *LP coefficient*: factor due to pre- (or post-) polarization of the primary (or secondary) beam invoked by a primary (or secondary) monochromator. For Cu tubes the default

value is 0.91.

Note that errors in the LP coefficient will be taken up by the displacement parameters due to their similar long term variation with the diffraction angle.

- *polarization in parallel plane*: factor for pre-polarized primary beams such as in synchrotron facilities. For laboratory radiation there is no pre-polarization resulting in a factor of 0.5.

- *product µ·d*: Needed for the calculation of absorption correction in case of transmission geometries only. It is mandatory to leave it 0 for Bragg-Brentano geometry!

- *goniometer radius*: Needed for the calculation of various corrections.

- *divergence slit aperture*: primary beam divergence. Needed for fixed divergence slit corrections only (see above).

- *width of X-ray beam at sample position*: Needed for fixed divergence slit corrections only (see above).

- *dimension of sample in beam direction*: Needed for fixed divergence slit corrections only (see above).

2.2.3 The *phases* branch

1. On the main branch *phases* some basic commands on phases are available
   new phase: Creates a new sub-branch with a corresponding form to enter structural and profile parameters from the scratch.
   add phase: Calls an open dialog to import phases from CIF, INP and BRJ files. If an INP or BRJ file is selected you can pick one or several phases from a subsequent dialog. For each imported phase a new sub-branch to *phases* is created.
   show selected phase: Switches to the branch of the phase selected in the box.
   del. selected phase: Deletes the phase selected in the box.
   The branch *phases* is also visible when a new Rietveld job is started from the scratch.

2. *phases – structure*
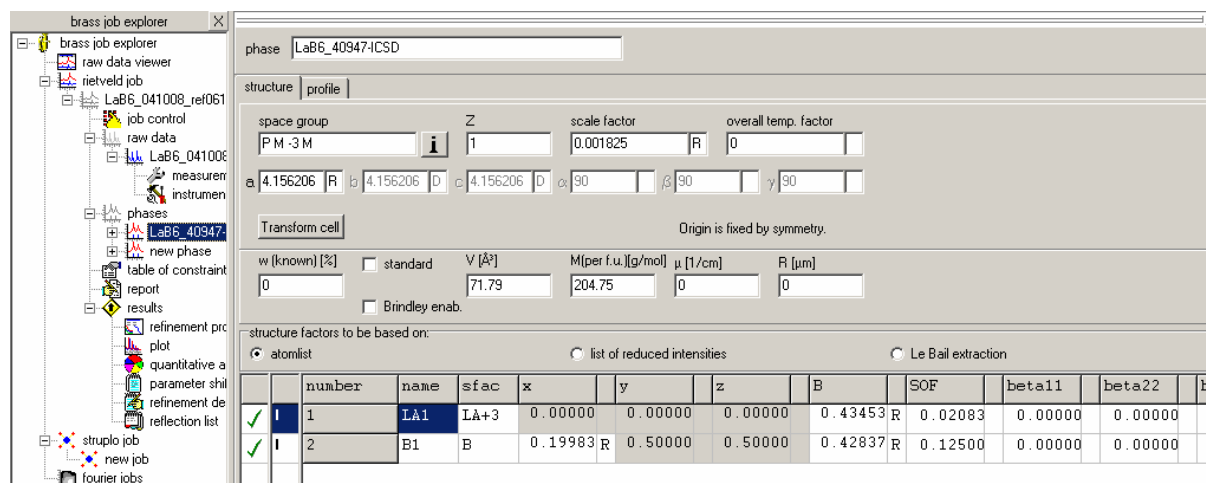
Minimum information to be given: *space group*, *lattice constants* and an *atom list* (or a *list of reduced intensities* or check *LeBail* extraction).

Push [i] to see a list of all symmetry operators of the given space group and an expansion of the atom list all atomic positions calculated from the symmetry operators.

Information in the row *w (known)* to *R [µm]* is optionally needed if the Brindley correction is applied to quantification results. *V* and *M* are recalculated by the program each time a Rietveld refinement is invoked.

3. *phases – profile*

As LaB_6 is expected to be a profile standard no sample parameters were refined. It was arbitrarily assumed that the known crystallite size D of about 10 µm is a purely lorentzian contribution. The resulting peak width parameter iP_L is calculated from $D = \frac{180}{p} \cdot \frac{1}{iP_L}$ to 0.00088 which is so small that it barely contributes to the peak widths. Thus the selection of either iP_G or iP_L for the description of this small crystallite size effect is in fact arbitrary.

All other parameters were set to zero-effect values, i.e. to 0 for peak width contributions and to 1 for the preferred orientation. The asymmetry parameter is disabled here because it is assumed as an instrumental effect and is thus used on page *measurement*.
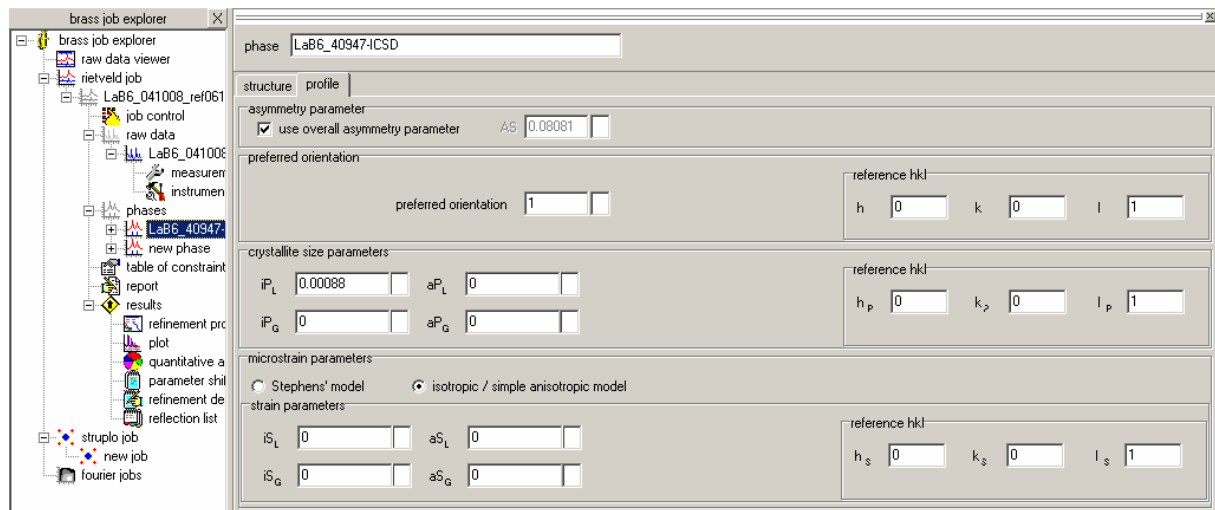
To come:

4. table of constraints

5. results – refinement progress

6. results – plot

7. results – quantitative analysis

8. results – parameter shifts

9. results – refinement details

10. results – reflection list

11. report

12. ASCII files in folder temp

2.3   Exercise (to come): Explore the fully refined Rietveld job on mixture2, containing the phases quartz, calcite and zincite

3   Training exercise on *lab6*.brj* and *mixture2*.brj*

The same examples are used here as in chapter 2. Thus, by following these instructions, you will be able to control the success of your exercises by comparing it to the provided example files. You will learn how to create a Rietveld job, how to establish instrumental parameters using a standards' data and how to fully analyze a sample containing several phases (here: three).

3.1   Rietveld analysis of the LaB₆ standard to establish the instrument parameters

3.1.1   Preparation and run of the first refinement step

1. Start BRASS 2 and find the following situation:
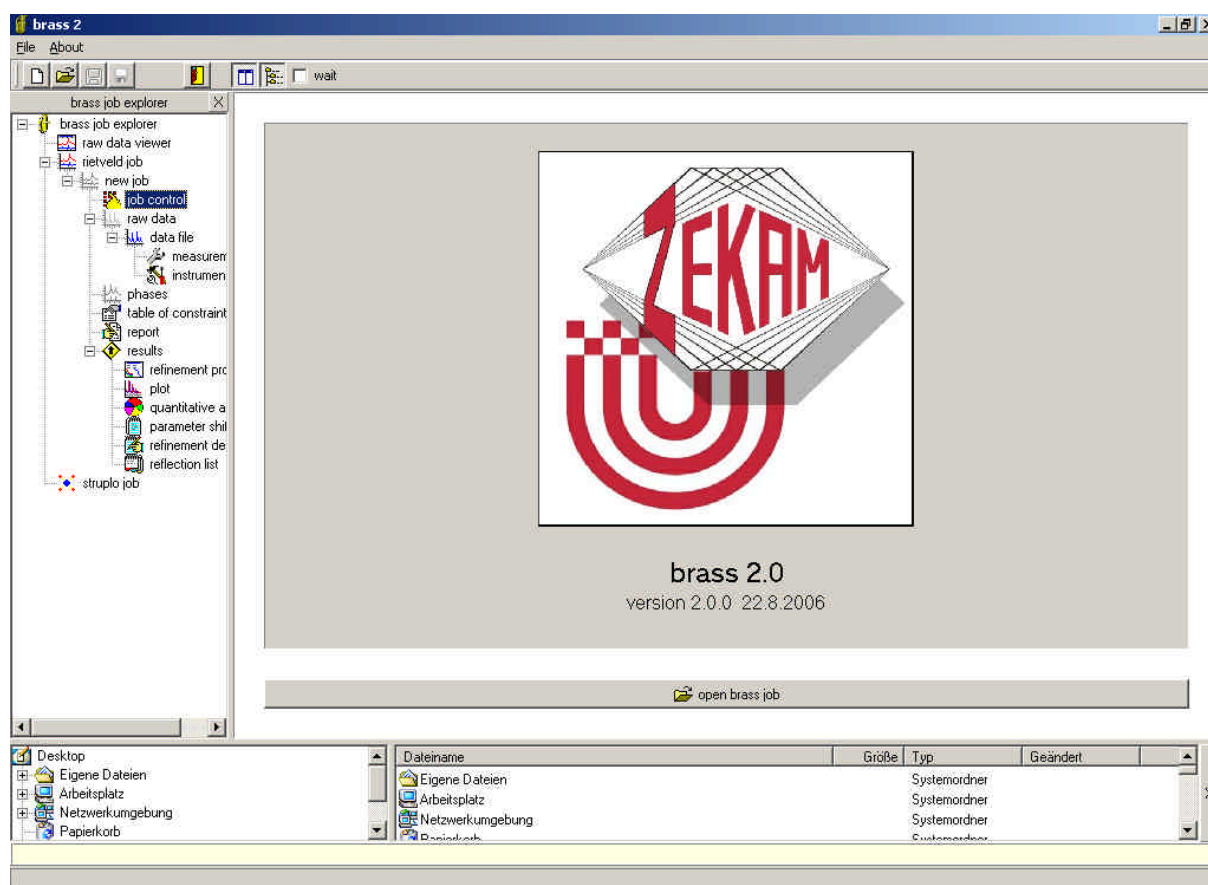
2. The branch *rietveld job → new job* provides all necessary containers for the new Rietveld job. Select branch *raw data* and load the data *LaB6_041008.xrdml* provided in your folder with stored example data. To see the raw data select the branch next to *raw data* now labeled *LaB6_041008.xrdml*.
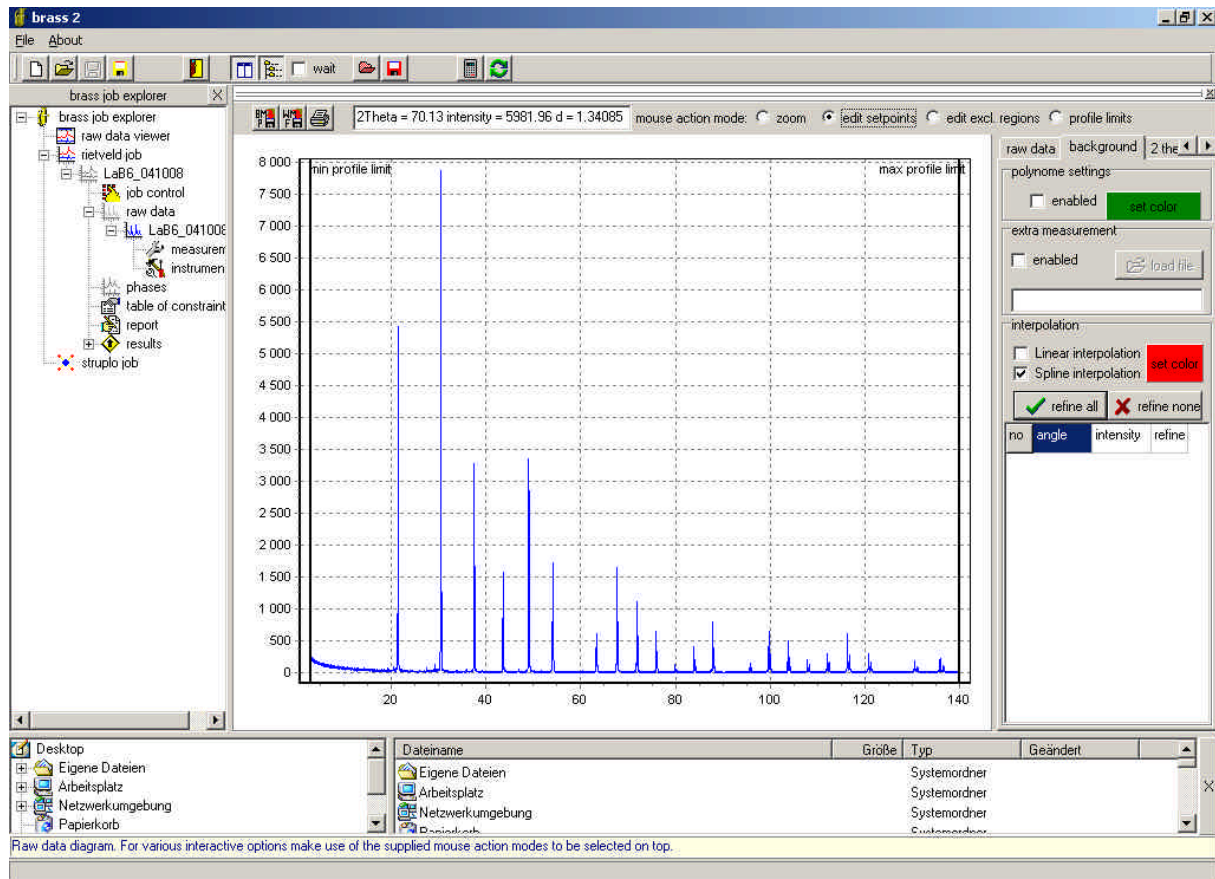
3. In mouse action mode *zoom* (on top of the graph) zoom the background region of the plot.

   Hint: Select a small interval in intensity and a rather large one in 2? by left mouse click&draw.

   Select *edit setpoints* on top and *spline interpolation* (sub-page *background*). Now set some background points by left mouse click on the graph. Preferably do not select points right below a peak. Remove bad setpoints by right click or move it by left drag&draw action. Set refinement flags for all background points by pushing

   refine all on the side bar page.

   Finally select page *2 theta shifts* on the side bar and set a refinement flag **R** on *constant zero* by a left click next to the parameters' value.

   Notes: For a smooth background, like the one here, set roughly between 8 and 15 setpoints with a higher density of setpoints in areas where a stronger curvature is observed. No great care has to be taken to match the observed intensity, since the setpoints' intensity values will be refined. The 2? values usually are not chosen directly below peaks.
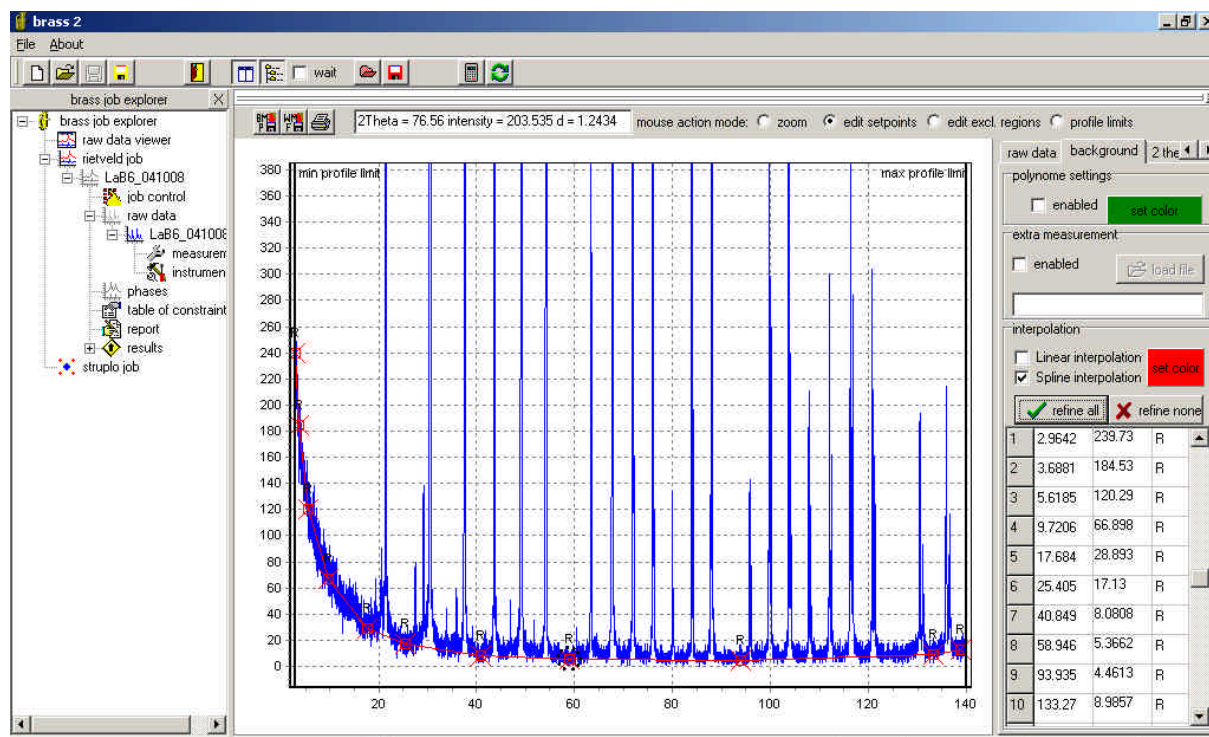
4. In the above figure note the small peaks left to the large ones e.g. near 20° and 30° 2?. These are spurious peaks coming from two extra wavelengths, Cu-K$_\beta$ and W-L$_\alpha$, present in the primary beam – both resulting from incomplete monochromatization and W-L$_\alpha$ from pollution of the anode by vaporizing W filament. In addition to Cu-K$_{\alpha1}$ and Cu-K$_{\alpha2}$ these two wavelengths must be taken into account for the Rietveld calculation. To do this, switch to branch *instrumental* and activate λ_3 and λ_4 with the default intensity ratios as shown below. Also set the values in the edit fields at the bottom to the correct values shown in the figure.

Note: The material used here is known to have no noticeable microstrain but an average crystallite size of about 10 µm yielding a small size effect of peak widths. It is more or less negligible but may be accounted for by setting the lorentzian crystallite size parameter iP_L[1] to the value 0.00088 on sub-page "profile" of the phase.

5. Now switch to branch *phases* and push the button [add phase] or choose the command *add phase* from the context menu of the branch *phases*. In the dialog open the file " LaB6_40947.cif" with structural information on the phase LaB_6. Since not all symbols for scattering factors used in CIF files are known to BRASS, the following dialogs ask you to select valid scattering factor symbols for the atoms. For atom La1 select La+3 as shown here, for B1 select B.
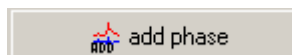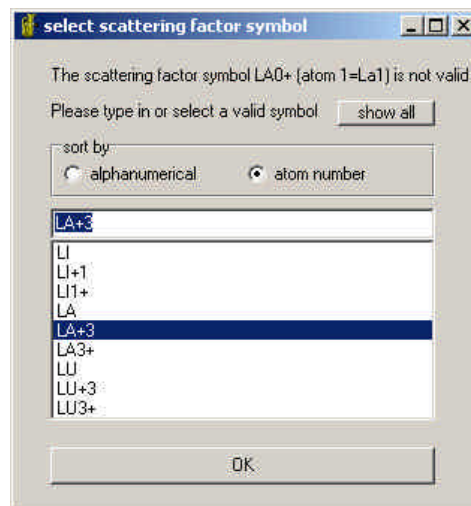
Now the phase "data_40947-ICSD" is added to to the *phases*-branch. To speed up convergence in the subsequent refinement increase the scale factor to 1E-3 instead of the default 1E-5 and then flag [R] the scale factor for refinement by left mouse click: [scale factor 1E-3 R] .
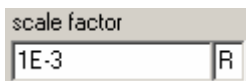
Hint: For better phase recognition in other dialogs it is recommended to rename the phase to "LaB6_40947-ICSD" using either the respective branch entry or the *phase* field on the phases' page.

6. Before running the refinement, save the job using either the blue disk button [🖫] on the main tool bar or the command *Save job* from the menu item *file* or by selecting the job header branch right below the branch *rietveld job* and pushing the button

[🖫 save job] .

Note: At any time you may save a backup of your current project using the red disk button [🖫]. The file is stored in the same folder as your current project with same name extended by a serial number between 000 and 999 and with extension BRB, e.g. the first backup of test.brj is test001.brb. From the backup the stored state of the project may be restored to the current project at any time using [📂].

Hint: Switch to branch *report*. All major Rietveld job actions are reported here for your convenience: saving the job by [🖫], running a refinement by [▦], accepting the new parameters by [🔄] after a refinement is done, saving a backup *.BRB file by [🖫] and overwriting the current job by the values of a

---

[1] Using the adapted Scherrer formula: $iP_L = 180 \cdot D / (p \cdot \lambda)$, crystallite size D and wavelength λ given in Å.

backup file using . When running a Rietveld refinement, all parameters being refined will be listed here as well as the major R values and the convergence status. In addition you may add text to the report at any time. This way it is possible to store your personal comments on any step to be able to reconstruct what you have done afterwards. In combination with the backups this will help you to go back to a specific stage of the refinement when you have run into trouble or if you want to follow a different route in the refinement.

7. Visit the branch *job control*. Some major controls of the refinement may be set here. Ask for a maximum of 36 least squares cycles. The other setting usually will do.
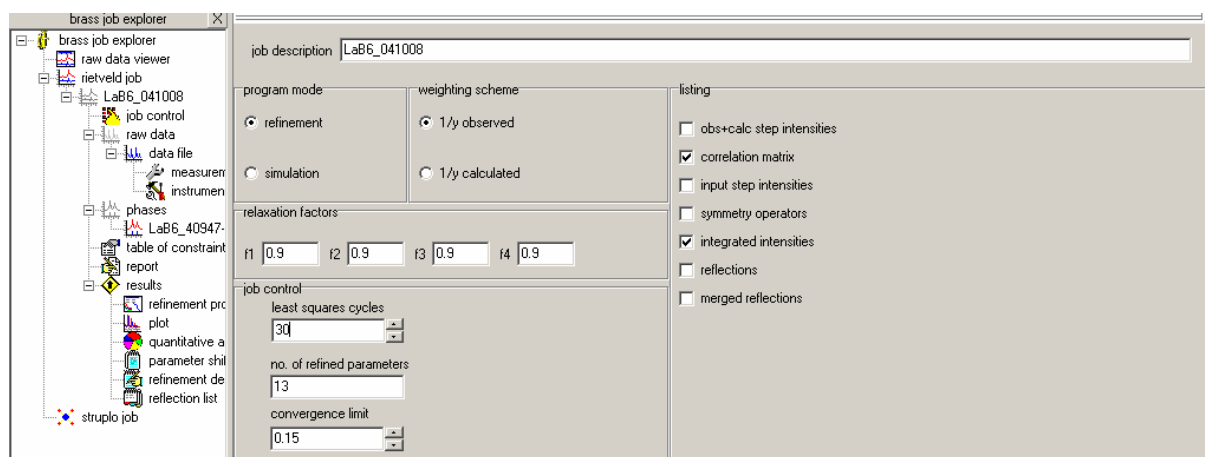
8. Run the first refinement using the *calculate* button . The program switches to the branch *refinement progress* displaying a plot similar to this one:
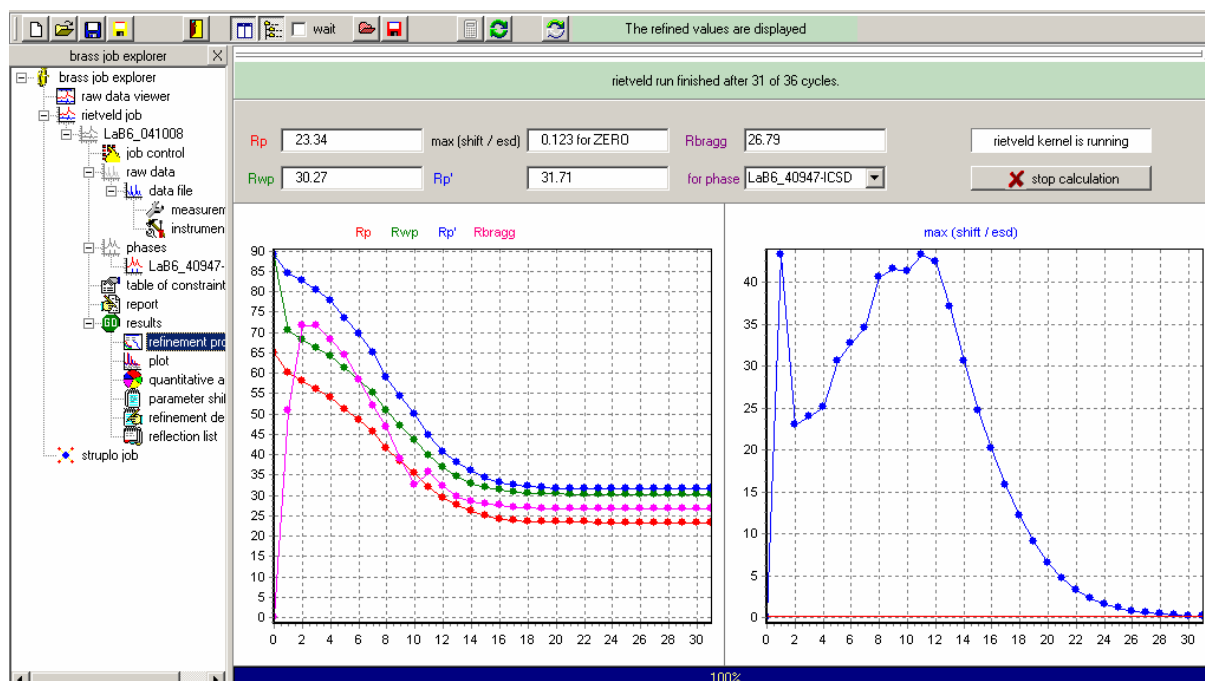
Note the large green bar[2] on top of the plot is declaring that the refinement has converged, i.e. in the last cycle the largest ratio shift(parameter)/s (parameter) of any parameter was smaller than the value of the *convergence limit* on branch *job control*. In addition a new button is now displayed in the main tool bar for toggling between start and refined parameter sets. E.g. display the raw data and toggle with between refined and start values. Note the change in the setpoints' positions on the *raw data* display and in the numerical values of the setpoints while toggling. Also toggle between start and refined values while displaying the sub-page *2 theta shifts* on *data file* or the *structure* page of LaB_6. You should also look at the Rietveld *plot* branch[3] to judge if the peak positions are more or less hit. These, as well as the calculated profiles, will improve on further steps.

Hint: Before accepting the new parameters for further refinement steps you may wish to back up the current state of the refinement using the red .

9. Accept the new values using the button . The toggle button disappears. Optionally save the current state of the Rietveld job using the blue to the left.

3.1.2 Running the further refinement steps of the LaB_6 refinement

Now every further refinement step should follow a similar procedure as described above with respect to user actions, i.e.: At first prepare the next step by applying modifications to the model as indicated below. Then optionally write down a comment to the last line of the report with the step's numbering and a description of what will be done next. Secondly run the refinement and head for convergence. At third carefully check if the refinement has yielded improvements or at least no changes for the worse with respect to R values and parameters. Fourthly, if all is fine, accept the parameters and, if necessary, make sure by repeated refinements that convergence is achieved. At fifth (optionally, but strongly recommended) save a backup version of the current state. Then turn to the next step.

For the LaB_6 standard sample now complete the refinement in these steps:

---

[2]   Either a green, a yellow or a red bar may appear. Green means that convergence has been achieved. Examine and accept the new parameters and continue with further steps. Yellow means "no crash but no convergence either". If R values have evolved to lower values and parameters are O.K. then accept the new parameters and run further cycles. In case that a red bar appears, the refinement has crashed. Shut down BRASS reload your Rietveld job and modify the flags and or parameters to prevent the program from crashing.

[3]   Sometimes the Rietveld plot looks all grey or the difference plot is not scaled correctly. In this case double click on the graph to reset it to defaults.

Step 2) Additional refinement of lattice constant a (*phase* branch), constant instrumental peak width parameters W$_{Lorentz}$ and W$_{Gauss}$ (*measurement* branch) and possibly some more setpoints (sub-branch to *raw data*).

Comments: Always (try to) <u>add</u> all further refinement flags, i.e. (try to) extend the set of refined parameters until finally all parameters may be refined altogether in the end. If this may not be achieved this is usually not a good sign or at least must be discussed explicitely.

Set all flags for this step. Flags for further setpoints: On page *plot* zoom the background area of the plot. If long-ranged regions (ranging over much more than a peak width) are observed where differences (grey plot at the bottom) systematically are all positive or negative, a need for further setpoints in between may be indicated. Note the respective 2? regions, switch to the *data file* plot and set further setpoints. Do not forget to flag these for refinement.

Result: Note the strong improvements in the R values in the *refinement progress* branch and – by toggling between start and refined values – in the difference curve of the Rietveld *plot*. This is due to the fact that the default instrumental peak width parameters UVW gave much too narrow peaks. Looking at peaks at various angels you can still observe that some are calculated a bit too narrow or too wide. Thus, angle dependent parameters have to be refined, too.

Step 3) Additional refinement of the 2? dependent instrumental width parameters V$_G$, U$_G$, and U$_L$, and the asymmetry parameter AS (all on *measurement*)

Results: The improvement is small but since the profile R values all have improved a bit the step is acceptable.

Step 4) Additional refinement of the structure parameters x(B), B(La), B(B) (all on the branch of the respective phase)

Comments: Clearly there is no doubt that such a simple structure model as that of LaB$_6$ cannot be "improved" based on powder data. In fact we do not expect large changes on positional parameters. Vice versa it is a good sign when only minor changes occur, since that means that the reported model fits our data and there is no big error in our inputs. On the other hand minor changes will always occur, since structure parameters are e.g. a function of the ambient conditions and this justifies refining these parameters in addition to the above purpose. Keep in mind that during a refinement of instrument parameters it is also a major target to yield the best fit, beyond plausibility considerations. You might even prefer a Le-Bail profile fit without using a structure model.

Usually isotropic temperature factors B for powder data differ significantly from those based on single crystal data. Thus, for major phases these should always be refined, but always <u>in the end</u> of the whole refinement!

Results: No big change in structural parameters. Even the B values are in close agreement with the literature values.

Step 5) Check and adapt intensity ratios for wavelengths Cu-K$_ß$ and W-L

Comment: The intensity ratio I(Cu-K$_ß$)/ I(Cu-K$_{\alpha1}$) for Cu-K$_ß$ is different for each instrument since the degree of suppression depends on the very monochromator in use. The situation is even worse for W-L$_\alpha$: The intensity ratio I(W-L$_\alpha$)/ I(Cu-K$_{\alpha1}$) is a function of time since the W filament of the x-

ray tube degrades slowly with time. I.e. the first ratio must be established once for each apparatus, the latter one even for a specific period of time. On branch *instrumental* you find the four wavelengths involved: Cu-K$_{\alpha 1}$ = ?$_1$, Cu-K$_{\alpha 2}$ = ?$_2$, Cu-K$_ß$ = ?$_3$, W-L$_\alpha$ = ?$_4$. The ratio I(Cu-K$_{\alpha 2}$)/ I(Cu-K$_{\alpha 1}$) is constantly 0.5 (or more precisely 0.497) while the other two shall be established here: In the Rietveld *plot* display the wavelengths λ_3 and λ_4 by checking the respective options of the phase in the side bar. Now zoom a small window with some λ_3- and λ_4-peaks. Check for a number of such peaks if the heights are hit more or less. If this is not the case, for both, λ_3 and λ_4 separately, calculate a factor in peak height for which the heights are hit better and on branch *instrument* apply these factors to the ratios I(Cu-K$_ß$)/ I(Cu-K$_{\alpha 1}$) and I(W-L$_\alpha$)/ I(Cu-K$_{\alpha 1}$), respectively.

Then run a final refinement, accept parameters and save the Rietveld job. Though R values are not much affected you will find, looking at the Rietveld *plot*, that the spurious peaks are described much better. If that is not true, repeat the procedure.

After step 5 is completed there is no way to improve the fit for the instrument standard. If you have a closer look at the Rietveld *plot* you will find that there are still some differences between observed and calculated data, especially this is true for peaks at low 2? angles, having "lying-S shaped" difference curves. This is due to the insufficient model for asymmetry while differences at various angles may be due to shortcomings of the Pseudo-Voigt function itself. Other differences may simply be due to data statistics, i.e. fluctuations of count rates in the raw data. Anyhow the best possible fit is achieved and we thus consider it as the final result of the refinement.

10. Finally store a set of instrumental parameters for further use with other samples: On branch *instrument* or on branch *measurement* enter a new name for a set of instrumental parameters (e.g. LaB6_041008_refined_*NewDate*) and then push the save button next to the edit field. The sets of parameters are saved to the file *instrumental.ris* in the main program folder.

The new set of instrumental parameters is now ready for use with other samples that have been measured on the same instrument at a similar date[4] and under the same instrumental conditions, except for data range, counting time and step width. To use it with other data start a new Rietveld job, load the respective data and then load the set of instrumental parameters by simply selecting it from the drop-down list.

Concluding remarks: The refinement of a profile standard should succeed routinely since there are not many independent parameters and the peaks are well defined. For other sam-

---

[4]   "Similar date" is not determined very well. The only reason for this requirement is the change in intensity of the W-L$_\alpha$ peaks, if any. The other instrumental parameters usually will not change significantly for a given configuration of the instrument. So check the changes in the standard's W-L$_\alpha$ intensities from time to time.

ples this may be much different. The establishment and fixation of the instrument parameters will ease and stabilize the refinement since for each phase five parameters (U_L, W_L, U_G, V_G und W_G) are fixed in advance. In some cases it will even be precondition for any success of the refinement. Additionally the sample effects may be analyzed alongside.

3.2   *Rietveld analysis of mixture2 (Calcite, Zincite und Quartz)*

The sample was prepared from equal amounts of pure powders of the above three phases. The powders were found to be finely grained in advance and homogenization was done by routine mixing and grinding in an agate mortar. Note that you must have completed the exercise in chapter 3.1 to have the LaB6-based "set of instrumental parameters" ready for use.

3.2.1 Preparation of the refinement

1. Start a new Rietveld job on branch *rietveld job*. The situation is identical to that after starting BRASS.

2. Raw data preparation: Switch to branch *raw data* and load the data "mixture2_041111.xrdml". Set about 8 to 15 background points in mouse action mode *edit setpoints* and set refinement flags for all setpoints (button *refine all*). On sub-page *2 theta shifts* flag *constant zero* ⟦R⟧ for refinement.

3. On branch *measurement* or *instrumental* load the set of instrumental parameters that you have prepared in chapter 3.1.

4. Phase model preparation: Switch to branch *phases* and subsequently add the three phases from the CIF files "Quartz_I90145.cif", "Calcite_I80869.cif" and "Zincite_I65120.cif".

   Note: For each phase BRASS immediately applies some tests based on the supplied space group symbol. Since for coordinates BRASS works with an accuracy of 5 decimals while in CIF files only 4 are stored, BRASS detects that some atoms are very close to special positions and asks if you wish to move atoms to special positions, which you should confirm here. For the missing scattering factor symbol (C4+) of Calcite C should be selected. Furthermore in the CIF files of Calcite and Zincite there are no isotropic temperature parameters B supplied. BRASS automatically sets these to the value B = 0.6 each. For major phases (as given here) you will always refine these at some later step anyhow, for minor phases this will usually not introduce significant errors.

   Set refinement flags ⟦R⟧ for the scale factor of each phase.

5. Run preparation (optional): Using branch *job control* preferably increase the maximal number of cycles (e.g. 36) and adapt the job description.

3.2.2 Running the refinement in strategic steps

For each refinement step remember the following procedure:

1) Modify the model, i.e. set the refinement flags according to the steps history below. Pay attention to the details given in notes and hints. Optionally save your input using the red ![save].

2) Run the refinement using the *calculate* button ![calc].

3) Carefully judge the results by extensive use of the *refinement progress* (do not accept a refinement that has worsened profile R values or obscured parameters), the toggling button ![toggle], the inspection of the raw data and related sub-pages on its side bar, the phases' pages, the Rietveld *plot* and possibly the details given by branches *parameter shifts* and *refinement details*. If something is suspicious or unsatisfactory, switch to the start parameters, modify the model or flags and try again.

4) Option: Save a backup of the job using the blue ![backup] for unforeseeable restoration needs.

5) If everything is fine accept the new parameters using ![accept], save your project using the red ![save] and go to the next step.

Now go through the following steps to refine the model up to the best fit:

> **Step 1) Refine ZERO (data file's branch, side bar *2 theta shifts*), scale factors S for all phases (Phases' branches), all setpoints (data file's branch, side bar *background*).**
>
> Remarks: Take a look at the Rietveld *plot*. The button *show all profiles* invokes the display of the individual profiles of the three phases on top of the calculated background. The peak positions of all three phases are well hit. The peak widths and profiles are not hit well yet. The calculated profiles are now based on instrumental widths and profiles, i.e. the differences between observation and calculation must result from sample effects such as small crystallite sizes and/ or microstrain. The largest differences in widths are observed for Calcite.
>
> Note: Step 1 will do in most cases. You may wish to write the quantification results to the report for comparison with later steps.
>
> Hints: Sometimes, especially with small cells and strong scatterers, the default scale of 1E-5 is way too small. The refinement may not lock in. In that case increase the starting value of the scale. If the scale is more or less O.K. and the lattice constants are not too far off, it may be possible to combine step 1 and 2 from the very beginning.

> **Step 2) Add refinement of lattice constants for all three phases.**
>
> Remarks: All independent parameters must be flagged, e.g. a and c for quartz. The symmetry constraints on the lattice constants are automatically set by BRASS as interpreted from the space group symbol.
>
> The refinement converges rather slowly. Consider that in this step narrow calculated peak shall be fit to broad observed ones while their positions shall be optimized. The solution to this problem is not very sharp. Consequently the refinement takes some time for the best solution. The convergence to the best solution will be much faster as soon as the first parameter for the peak width is flagged.

Hint: The refinement may not converge within your maximum number of cycles but the tendency of R values and convergence parameter *max(shift/esd)* should be stable. Then you should accept the new parameters and refine again until convergence is reached. Possibly you have to repeat this several times.

Step 3) Add refinement of the overall asymmetry parameter AS (*measurement*), the isotropic crystallite size parameter iP_L for all phases (sub-page *profile* of each phase) and the preferred orientation parameter PO for all phases (same page as iP_L).

Note: For quartz no pronounced preferred orientation is expected but still it should be tested, here with respect to the reference direction (0 0 1). For zincite the same direction is appropriate. For Calcite use (1 0 1) which is the well known cleavage plane.

Remarks: The asymmetry of the peaks is most pronounced at small angles. In BRASS it is corrected by Rietveld's original approach which in fact does not really perform perfectly but it does at least part of the job. At the present time no other algorithm is available in BRASS. iP_L is the first parameter we use to describe sample effects contributing to the peak widths – P parameters describing a crystallite effect. A Lorentzian shape of the contribution to the profiles is assumed at this stage.

In the Rietveld *plot* after the refinement zoom at fine detail into the reflection of a given phase at much different angles. For one phase (_____?) the peak width are matched much worse than for the other two. This indicates that the description of the peak broadening as a lorentzian crystallite size effect is not appropriate. In the next step we will allow for freedom of choice between crystallite size and microstrain effect. Also note the preliminary results on the quantification for later comparison.

Step 4) For all three phases add refinement of all isotropic sample parameters for peak widths: gaussian size parameter iP_G and lorentzian and gaussian microstrain parameters iS_L, iS_G (all on phases' sub-pages *profile*).

Remarks: Remember that iP_L is already flagged "R". Together with the other three parameters iP_G, iS_L and iS_G for each phase there is a maximum degree of freedom to decide what causes the phases' peak broadening. The Rietveld kernel will not allow for negative values of these parameters since the instrumental peak widths are the narrowest ones possible. Some parameters will be unflagged and set to zero by the kernel and you should receive a related message after the run is terminated. You may accept this for good or try refining these parameters again at a later stage.

Now look at the values of the parameters. To learn about the size of the respective effect take a closer look at the branch *refinement details*: On top a report on start parameters is given. Below, for each cycle, a full list of the parameters is given - no matter if refined or not. Scroll down to the last cycle (or use the find dialog with keyword ") find the entries for either phase and for that phase scroll up or down to listings on crystallite size and microstrain. Here the respective values are listed as well as the percental lorentzian character. Note that the three phases all display different mixtures of sample effects. Especially for calcite a large strain effect is found while for quartz some mixture of strain and size effect is present and for zincite there is only a size effect.

A closer look at the Rietveld *plot* confirms that for calcite the largest improvement is observed compared to the previous step in which we only allowed for a crystallite size effect.

Step 5) Add refinement of all free coordinates x, y and z for all atoms of all phases and check the background description.

Remarks: As for the LaB_6 refinement it cannot be expected that we may "improve the structure models" of these well known phases. The refinement serves as test for the validity of the model for our data and to give the best fit allowed for the respective model. Note that for complicated structures a step by step addition of further coordinates may be necessary for a stable refinement. Note that the Si coordinates in Quartz should be (x 0 1/3). If no special position is recognized set the value of z to exactly 1/3 (0.33333 instead of 0.3333). For Zincite there is no fixation of the origin with respect to z, i.e. you MUST leave the z coordinate of one atom unchanged. Here: only refine z(O1).

The background description should be checked before running the refinement and in regions - ranging over much more than a few peak width - where the difference curve systematically is positive or negative one or two setpoints should be added and refined.

Hint: No big changes in coordinates have occurred. You can check this by using the sub-branch *distances and angles* next to each phase and compare some values for the starting and the refined model, respectively.

Step 6) Add refinement of all isotropic temperature parameters B of all three phases (sub-page *phase* on the respective phases' branch).

Remarks: Temperature parameters often consume errors prevailing in other parts of the structure model. Some people call them waist basket for structural errors. For this reason all other relevant structure parameters have been and always should be refined in advance. The refinement of the B parameters should generally be done for major phases only, since for minor phases not enough peaks are observable at high angles. The refinement should yield "meaningful values" for all atoms except for the lightest ones. Meaningful are e.g. small values between 0.x and 1 for tightly bonded atoms, usually high charged cations auch as Si^{4+}. For bonded oxygen you often find values between 0.5 and 2.5. For loosely bonded atoms (water, low charged cations in channels or cavities, ...) even higher values are calculated. Values above 10 or 15 are absolutely exceptional and usually will not be significant in the second digit.

After completion of this step all temperature parameters should be reasonable. For Zincite the smallest values are calculated. The overall changes are significant but remember that at least for Zincite and Calcite we had started with default values of 0.6 which surely is not appropriate for all atoms. If a phase fraction were small you should not refine its atomic parameters but the absolute error on quantification would be small compared to the relative one. This is different for phases with large fractions as is true here. Look at the phases' scale factors before and after this step, demonstrating the large impact of the B parameters on them and consequently on the quantification results at *quantitative analysis.*

Final remarks: After step 6 the quality of the refinement is similar to that of the LaB_6 refinement. And specifically it should be very similar to that of the example Rietveld jobs that were run with the same data and merely the same models, possibly except for the choice of the background setpoints.

You could try to refine some more parameters, e.g. the parameters aP_G, aP_L, aS_G and aS_L for anisotropic gaussian and lorentzian size and strain effects, respectively. This would

not make much sense, though: The quality of the fit is as good as for the standard material, i.e. differences of that magnitude must be expected for any other sample. If you would like to refine more parameters there must be some evidence for it. Anisotropic sample effects would yield significantly varying peak widths for closely neighbored peaks of the same phase. If that is not noticeable after the current stage of refinement there is no basis for such a refinement. Probably the refinement would either converge very slowly or even diverge and produce meaningless numbers. Still, do not hesitate to try it just to see what happens...

There is just one problem with that refinement: The quantification results on branch *quantitative analysis* are far off the weighed in phase fractions. All three phases were weighed in with the same amount by weight, i.e. the result should be $33^{1}/_{3}$ % for each phase. Instead the calculation yields ~39.5 % for quartz, ~32.9 % for calcite and 27.6 % for zincite. These large absolute errors from weighed-in fractions are rather exceptional. In the next section we will see that it can well be explained by microabsorption and be corrected for by Brindley's method.

3.3 *Brindley's microabsorption correction applied to mixture2*

Microabsorption effects may largely obscure quantification results from powder diffraction data. The problem will always be present when the so called absorption contrast, the product $\mu \cdot R$ of absorption factor μ and mean particle radius R, differs significantly between the present phases. (Brindley, 1945) discussed that problem extensively and developed a numerical correction method. (Taylor & Matulis, 1991) first introduced the correction method to a Rietveld program and demonstrated its necessity and success.

In BRASS 2 Brindley's correction method has been implemented as a post-refinement procedure. I.e. after completion of the refinement switch to the branch *quantitative analysis* and enter the absorption factors and mean particle radii of the phases. On checking *enabled* in the *Brindley correction* side bar the quantification results will be recalculated according to Brindley's formulas. Actually, expecting that all radii are equal, you can try to find the average particle radius for which the quantification is correct. In the case of mixture2 follow this procedure, using the *Brindley correction side bar* at branch *quantitative analysis*:

1) Enter the absorption factors μ [1/cm] for the three phases: $\mu_{quartz} = 91.25$, $\mu_{calcite} = 192.27$ and $\mu_{zincite} = 287.85$.

2) Check the boxes ☑ keep radii identical and ☑ enabled .

3) Step by step increase the mean Brindley radius R by pushing the up-down button ⬍ next to the $R_{Brindley}$ field of one of the phases. The step size may be adapted by pressing one of the buttons `0.01` `0.1` `1` . The $R_{Brindley}$ of the other phases will be adapted accordingly.

4) This way, by trial and error, find the average $R_{Brindley}$ for which the true weighed-in fractions are calculated. For mixture2 this will be true for R ≈ 12 µm. (compare to fig. on next page)

The result is alarming in several respects: The sample was prepared from pure phases in a routine procedure. Since all powders are white and finely grained it was not easy to assess by microscopy if the sample was well homogenized or not. Obviously it was not and this puts a spotlight on the importance of thorough sample preparation. Secondly, in agreement with (Taylor & Matulis, 1991), it is highlighted that even for everyday phases and samples the microabsorption may be significant and must not be neglected for quantification.
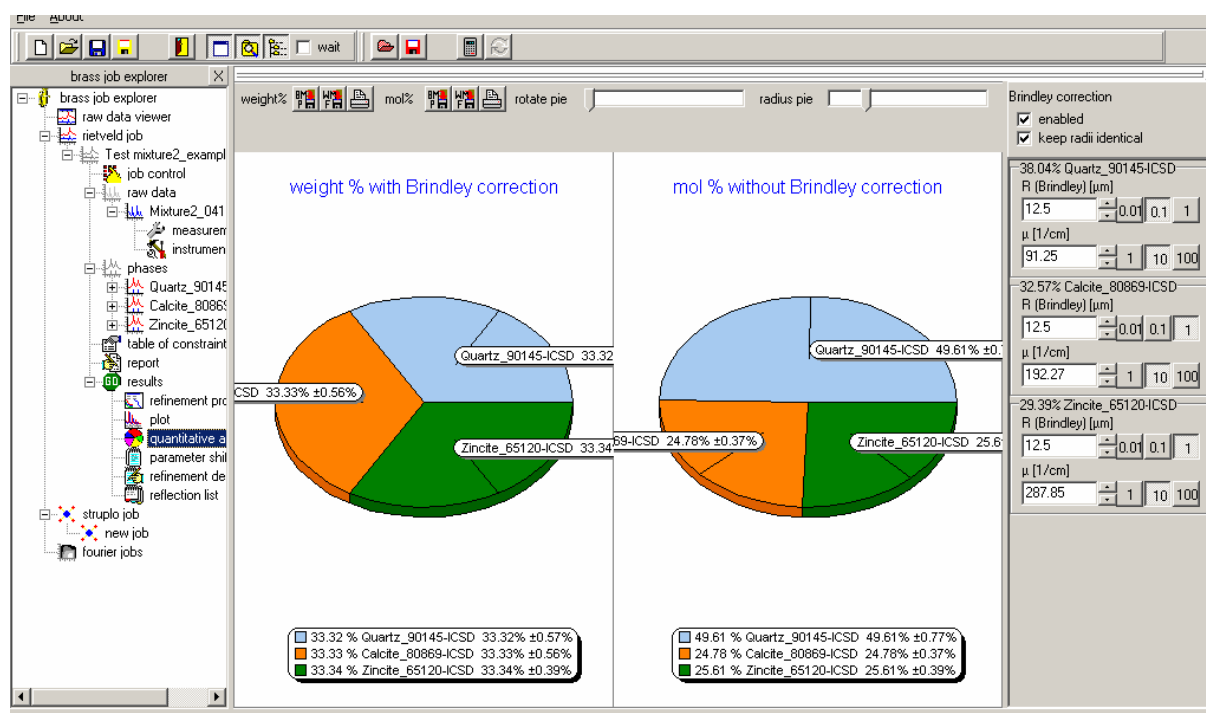
After this finding the same sample was prepared for a second time, this time it was homogenized in acetone. The Rietveld analysis of the second preparation yielded much more closely the weighed-in fraction: Quartz 34.7 %, calcite 32.6 % and zincite 32.7 %. The Brindley correction yielded 33.7 % quartz, 32.6 % calcite and 33.7 % zincite using a common average $R_{Brindley}$ ≈ 2 µm for all phases. This finding nicely confirms the hypothesis that the first sample simply was not homogenized well enough.

With these results the example refinement is finished. We hope you enjoy using BRASS.

4 Some final remarks on the free software BRASS

Good look with further using BRASS 2. If you find BRASS useful don't hesitate to tell people and direct them to BRASS' homepage http://www.brass.uni-bremen.de/ for free download.

For the free version of BRASS please do not expect too much support since it is primarily developed for our own purposes. But if you encounter problems that – to your conviction – lie within BRASS bugs and not within too little experience with the Rietveld method, we would appreciate if you tell us. Non-experienced users might be interested to participate in a BRASS workshop: Please look at http://www.brass.uni-bremen.de/. If you think you have encountered limitations of BRASS which might be crossed by some further development please don't hesitate to contact us.

Clearly we welcome collaboration if you have some interesting idea. Note, that we also develop special automated editions of BRASS for special purposes, i.e. to control the outcome of production steps. To contact us look at www.brass.uni-bremen.de or www.zekam.uni-bremen.de.

5 References

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