ADVANCES IN DATA ANALYSIS OF *IN SITU* X-RAY POWDER DIFFRACTION DATA: A CASE STUDY OF RUBIDIUM OXALATE $(Rb_2C_2O_4)$

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Methods have been developed to facilitate the data analysis of multiple two-dimensional powder diffraction images. These include, among others, automatic detection and calibration of Debye-Scherrer ellipses using pattern recognition techniques, and signal filtering employing established statistical procedures like fractile statistics. All algorithms are implemented in the freely available program package Powder3D which has been developed for the evaluation and graphical presentation of large powder diffraction data sets. As a case study to demonstrate the benefits of this software, the high temperature phases of rubidium oxalate $Rb_2[C_2O_4]$, and its decomposition product rubidium carbonate $Rb_2[CO_3]$, were investigated using fast, angle dispersive X-ray powder diffraction with an image plate detector.

1. Introduction

With the general availability of high intensity parallel synchrotron radiation, the use of twodimensional detectors like CCD-detectors or online image plate readers for fast high resolution data acquisition enjoys a growing popularity. Typical exposure and readout times are now on the order of seconds. Soon, milliseconds will become standard, producing huge amounts of data which need to be processed efficiently. As a consequence, the field of X-ray powder diffraction has experienced a renaissance. One of the major advantages of powder diffraction compared to other analyzing techniques is to (indirectly) measure changes of the entire crystal structure as a function of an external variable. It is possible nowadays to record the entire Debye-Scherrer rings up to high angular range with high angular resolution within a few seconds or even less. The field of applications is vast with current experiments including texture analysis [1] and in situ powder diffraction measurements in dependence on pressure [2], temperature [3], chemical composition [4], electric and magnetic fields [5] or external strains [6].

The experimentalist is faced with two major challenges. Firstly, large area detectors produce large numbers of two-dimensional images which need to be reproducibly reduced to one dimensional powder patterns. Secondly, the sets of hundreds or even thousands of powder

Vol. 23 2006

patterns need to be evaluated and graphically presented.

It is interesting to note that for both tasks only very few generally available programs exist. These are keyed toward single powder patterns involving extensive manual interaction. This approach is unsuitable for mass data analysis: not only is the manual workload exorbitant but the induced subjectivity hinders reproducible results.

The key to solve the first problem lies in the reliable extraction of a powder diffraction pattern unaffected by grain size effects, detector aberrations, and scattering from other sources like reaction cells, diamond anvils, gaskets etc. Almost all signals from a two-dimensional image can be reduced to simple geometric figures like points, lines and ellipses, calling for the application of modern pattern recognition techniques [7, 8]. As to the representation and evaluation of the integrated powder patterns, a high level graphically powerful programming language offers the basis for an efficient solution. We decided on the Interactive Data Language IDL (current version 6.2) [9] to develop a general program for automatic data reduction and evaluation of two-dimensional powder diffraction data called Powder3D [10, 11].

The new software solution presented here aims to provide a tool for just this purpose. The software design and functionality has been optimized to allow a substantial amount of automation, if desired by the user. The maximum num-

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ber of imported powder patterns which can be processed simultaneously is only dependent on the speed and memory of the computer used.

Some of the aspects necessary to solve the problems encountered during the investigation of the high temperature phases of rubidium oxalate $Bb_2[C_2O_4]$, and its decomposition product rubidium carbonate $Bb_2[CO_3]$ are described in this paper. A more detailed description of the crystal structures of the different phases of these compounds has recently been published [12, 13].

2. Powder Diffraction

2.1. Measurement

In-situ X-ray powder diffraction data of rubidium oxalate at high temperature were collected at a wavelength of 0.9184 Å in transmission geometry with a hot small environment cell for real time studies [14-16] on a motorized goniometer head at beamline X7B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The size of the beam was adjusted to a height of approximately 0.5 mm and a width of 2 mm. The detector, a MAR 345 image plate reader was set up perpendicular to the beam path at a distance of approx. 170 mm from the sample. LaB₆ was used as an external standard to determine the beam center, sample-to-detector distance, exact wavelength, and tilting angle of the image plate. The sample was contained in a sealed quartz capillary with a diameter of 0.5 mm, loaded in a sapphire tube of 0.8 mm diameter attached to a flow-reaction cell (Fig. 1). The temperature was monitored and controlled by a 0.01 in. thermocouple (Omega) which was inserted straight into the sapphire tube adjacent to and contacting the sample capillary. The sample was aligned so that the sample closest to the thermocouple was in the X-ray beam path. The sample was heated in the temperature range from room temperature up to T=900 K with a small resistance heater wrapped around the sapphire tube. During exposure, the sample was rocked for several degrees in order to improve the randomization of the crystallites. An exposure time of 30 seconds was chosen depending on the saturation intensity of the image plate. A total of 200 images was recorded, covering the temperature range from T=298 to T=873 (2.4 K/min; scans 1-133) and down to T=298 K (4.8 K/min; scans 134-200). Considering the exposure and development time this leads to a heating rate of 4.2 Kframe⁻¹ and a cooling rate of 7.62 Kframe⁻¹.

2.2. Data Reduction and Filtering

Information required for powder diffraction analysis is contained in Debye-Scherrer cones. These are projected as ellipses onto two-dimensional detectors [17]. A precise calibration of the experiment necessitates the exact definition of these cones. Currently, solving this task is a rather cumbersome ordeal. We have thus developed a robust method for the automatic detection and characterization of ellipses using a modified Hough transformation [18]. The method involves no mathematical complexity and exhibits excellent overall efficiency.

2.3. Ellipse Detection

An ellipse can be described by five parameters, the major-axis *a*, minor-axis *b*, centre coordinates x_0 and y_0 and angle of orientation α . Computing all five parameters simultaneously using Hough transformation is computationally very expensive [19], as a huge quantized five-di-



Fig. 1. Left: reaction cell with internal heater in front of a MAR345 image plate system (X7B, NSLS). Right: reaction cell with external hot air blower (ID31, ESRF).

mensional parameter space has to created. In practice the transformation scales to the number of dimensions in parameter space. In order to reduce the size of the required parameter space, the complete process of ellipse detection is decomposed into different steps. Hough transformation is used for the calculation of the parameter *b* alone. Hence we require only a one-dimensional parameter space.

2.4. Reduction of Resolution

The spatial resolution of digitized powder diffraction images is typically in the order of a few thousand pixels squared. Manipulation of such an amount of data is impractical. The computational complexity of an image of size $N \times N$ is $(N \times N)_4$. To improve the execution speed the image resolution is reduced by a factor of five.

2.5. Approximate Centre Determination

Many methods have been used for the determination of the centre of an ellipse [20, 21]. Most of the methods suffer either a lack of accuracy or inefficient memory usage. We propose a generic two-step approach to determine the centre coordinates of an ellipse. In the first step we find the approximate centre by using the intensity patterns of vertical and horizontal grids (Fig. 2) drawn on the image.

All pixel intensities along a grid are copied to an array (Fig. 3). The mirror plane of this distribution is detected by finding the absolute difference of the mirrored intensities. This absolute difference is calculated for each possible mirror plane position and copied to another array (Fig. 4). The lowest point in this difference plot is the position of maximum peak overlap and represents the approximate mirror plane. Each grid line results in one such point.

Two lines, one for the points from the vertical grids and the other from the horizontal grid, are fitted, using the robust least absolute deviation



Fig. 2. Centre detection grid.

[22] method. The approximate centre of the ellipse is the point of intersection. This algorithm for centre determination is both robust against the outliers in the image and against the position of the ellipses with respect to the image centre. This method requires the centre of the ellipses to be on the image.

2.6. Masking of High Intensity Spikes

High intensity pixels have to be masked to enhance the accuracy of the ellipse parameter determination. Masking is done by capping the intensities to six times the median of the entire image.

2.7. Background Reduction and Thresholding

Thresholding is an important step in preparing an image for a Hough transformation and the importance of a preceding background reduction shall be shown. Diffraction images often suffer from a diffuse background resulting from the scattering of X-rays by air molecules. Hence the background intensity is high near the incident beam and decreases towards higher 2Θ angles. Subtracting the background for such images with non-uniform intensity distribution is







Fig. 4. Difference histogram of profile.



Fig. 5. Binary images without (left) and with (right) initial background subtraction.

crucial.

The entire image is divided into broad circular segments whose average intensities decrease toward higher radii. Background reduction is accomplished by subtracting twice the median of the pixel intensities within a segment from those same pixel intensities.

Following the background subtraction, the image is converted into a binary image. This conversion is beneficial to an efficient Hough transformation, as the number of transformed pixels is reduced and the space required for their storage is substantially smaller [23]. We set the pixels of high intensity to 1 and the remaining to 0 by applying a threshold of 10% of the maximum intensity. The result and the importance of an initial background reduction is visible in Fig. 5. In the further process of ellipse detection, only pixels with the value of 1 are subject to analysis.

2.8. Range of the Major and Minor Axes

To restrict the search area for the major and minor axes of the ellipse we find the approximate range of *a*. The range of *a* and *b* is determined for each ellipse by calculating the radial distances. This is done only for a thin wedge of the image. For better averaging, 16 wedges are drawn with an opening angle of 2.5° . An opening angle of 2.5° seemed a good compromise between a local probe and a statistically acceptable sample.

After computing 16 radii of all the ellipses, the entire array of distances is converted into a histogram, containing the density of distances falling within certain intervals (Fig. 6). An algorithm that scans through the histogram identifies the ranges of the filled bins. These ranges, which correspond to the minimum and maximum distances to the centre, are initial estimates of the minor and major axes.

2.9. Determination of Major Axis and Orientation

A routine based on Chellali *et al.*, 2003 [24] is used for the final steps. We assume a pair of



Fig. 6. Radial distances of ellipses.

pixels to be the vertices of the major axis of the ellipse. Their distance to one another is calculated, and should it lie within the range estimated previously, the midpoint is calculated. Should this again agree within a certain tolerance to the initial centre, then it is stored. The corresponding orientation of the ellipse is then calculated. Finally the maximum distance is taken to be the most probable value of the major axis of the ellipse.

2.10. Determination of Minor Axis Using Hough Transformation

Hough transformation is a standard tool in image analysis and is widely applied to detect geometrical shapes. This Hough space spans all possible parameters that could describe the required shape. It is clear that the size of this space depends strongly on the number of parameters, which translate to Hough space dimensions, as well as the range of these parameters, which correspond to the lengths of the dimensions. The transformation is implemented by guantizing the Hough space into finite intervals. After processing all the pixels of the reduced image, the local peaks in the parameter space correspond (Fig. 7) to the parameters of the most successful shapes. We have reduced the size of the transformation from five dimensions down to one by previously locating estimates for the centre, major axis and rotation angle. All pixels are checked for validity with regard to these estimates and the parameter space is incremented for all the pixels satisfying the constraints. After processing all the points in the image, the local maxima of the parameter space is the minor axis length (Fig. 7). As we use the Hough transformation to determine the minor axis only, a mere one-dimensional parameter space is required. This is both beneficial to



Fig. 7. The accumulator array.

computing and memory costs.

In the process of ellipse detection we determine the parameters of the innermost ellipse first and then proceed outwards. The reason is that the X-ray diffraction intensities have high gradients with the maximum near the centre of diffraction pattern. Outer ellipses thus have a lower signal density than inner ellipses. This results in better statistics for inner ellipses. After detecting an ellipse, its pixels are removed from the image, the rest of the ellipses are detected iteratively. As a result the computational time for *b* decreases with every detected ellipse.

Signal Filtering 2.11.

Many powder diffraction experiments impede the realization of ideal circumstances, namely the contribution of a very large number of evenly sized and randomly oriented crystals to the diffraction pattern. This would in turn lead to an ideal normal intensity distribution. Despite the great experimental effort expended to ensure good quality data, in situ powder diffraction often suffers from 'spotty' diffraction cones, the result of relatively few crystallites passing through a diffraction position, an effect that is enhanced by highly parallel synchrotron beams. The reasons for this are manifold. High pressure powder diffraction traditionally suffers from weaker signal quality than other in situ experiments. Sample rotation is confined to small angular rocking due to the diamond anvil cell's (DAC) opening angle, the wish to limit the effect of gasket shadowing and the avoidance of diamond reflections. The same effect occurs for high/low temperature diffraction after re-crystallization in the course of first order phase transitions. To remedy this effect the intensity of the entire diffraction cone is integrated to a peak. This method generally results in powder pat-





Fig. 8. Rendered 2D image plate data from a high pressure experiment using a false colour texture map. Intensity is represented by the elevation along the z-axis. In addition the false colours have been scaled to the intensity. The scale has been adjusted to highlight the weak intensities.

terns with reliable intensities.

One effect that is however not alleviated by a mere integration is that of highly dispersed intensities within the diffraction cone. These result from large grain size differences within the sample. Strong peaks resulting from larger grains lie within a ring of moderate intensities generated by small crystallites (Fig. 8). In most cases the number of large grains tends to be a couple of orders of magnitude lower than the number of small grains. On account of the small number of large crystallites they inevitably fail to ensure a 'statistical' distribution. Due to their high intensity, they have a great effect on the integrated pattern, falsifying the intensities considerably.

The accepted manner of filtering such data is to mask the high intensity peaks manually using software such as Fit2D [25]. This well known software represents the state of the art in the integration of two-dimensional powder diffraction data. Manual masking is however time consuming, lacks reproducibility and relies too heavily on visual inspection to produce reliable results. Therefore we devised a two-dimensional signal filtering algorithm which should be generally applicable.

2.12. Fractile Masking

The general goal of signal filtering is the separation of the required signal from artefacts or noise. We implement robust type of band pass filter based on fractile statistics. An arbitrary fraction of the highest intensities collected for a 2Θ range is masked. In our case, by selecting



Fig. 9. An excerpt of the azimuthal intensity distribution of the typical Bragg reflection. Red diamonds represent data masked using the fractile threshold of 5%.



Fig. 10. Same as Fig. 9. In addition the mask is dilated by two pixels.

5% of the highest peaks, most of the pixels contributing to the high intensity data are masked (Fig. 9). Mask dilation applied afterward suffices to mask the tails of the peaks (Fig. 10), leading to a significant improvement in intensity distribution of the signal (Fig. 11). The diffraction intensities originating from the finely crystalline matrix are in effect the base line displayed as black diamonds in Figs. 9 and 10.

For the application of such intensity sensitive filtering procedures it is of ultimate importance to have previously applied all possible two dimensional corrections affecting the intensity. Of greatest are those corrections which are a function of the azimuth. These include polarization and Lorentz corrections, for which the experimental geometry has to be determined. As the filter is applied sequentially to a small 2Θ range, the effect of corrections which are only a function of 2Θ have little impact.

In particular, all reflections due to the singlecrystal sapphire capillary were excluded. It was observed that in the present study, the diffracted intensity of all phases was quite uniformly distributed over the Debye-Scherrer rings, ruling out severe grain size effects and



Fig. 11. An example of a masked image plate data in the Powder3D software. Note the intensity difference in the integrated patterns.

preferred orientation.

2.13. Data Import

In the case of $Rb_2[C_2O_4]$, 200 integrated data sets were produced with the procedure described above and were simultaneously loaded in Powder3D. It should be noted that Powder3D supports a variety of different formats for powder diffraction data including non-equidistant data sets. To allow the combination of powder patterns coming from different sources, wavelengths can be converted and arbitrary step width can be selected by linear, quadratic or spline interpolation of the intensities.

2.14. Data Normalization and Background Correction

Data collected using image plates generally lacks a beam decay or refill correction. This can be partially alleviated by a normalization (Fig. 12). The normalized powder patterns were automatically background corrected using a robust algorithm based on an adaptive lowpass filter as proposed by Bruckner [26]. Due to the fact that the shape of the background often changes, several background points were subject to manual post-processing using a comfortable editing tool.

2.15. Graphics

The importance of a significant 2D and 3D graphical representation of multiple powder patterns is often underestimated. Powder3D makes extensive use of the graphical possibilities of the IDL_{TM} graphics language as is



Fig. 12. Normalization function.



Fig. 13. Background reduction.

demonstrated with the following pictures (Figs. 14–16).

In addition, the powerful and independent data visualization and manipulation software iTools[™], developed by RSI Inc. allows all kinds of modification to the graphics by the user (Fig. 17).

2.16. Peak Hunting and Indexing

Peaks for the different phase were searched by a multiple pass, variable FWHM [27] second derivative method. Only in few cases, manual interaction was necessary to alter the peak list (Fig. 17).

The peak positions and intensities were forwarded to the Crysfire indexing suite [28]. The results of Crysfire were directly be imported by Powder3D.

2.17. Le-Bail Refinement

The next step consisted in setting the temperature increments and phase ranges which are necessary for the Le Bail/Rietveld refinement (Fig. 18).

Starting values for the peak profile analysis were obtained by using the single peak fitting tool of Powder3D, applying a pseudo-Voigt



Fig. 14. 2D-film plot (simulated heating-'Gunier-film) using bicubic interpolation between the patterns.



Fig. 15. Rendered 3D surface plot after positioning of different light sources.

Fig. 16. User defined modification of the plot in Fig. 15 using the $iTools^{TM}$ software.

function corrected for axial divergence [29]. This feature has also been used to fit at least 6 peaks of the LaB_6 reference pattern in order to

Fig. 17. Peak searching.

(automatically) create an instrument resolution file which allowed meaningful starting values for the profile parameters of the consecutive LeBail-refinements [30] using the Fullprof program [31]. The cell dimensions of the first patterns of the different phases were imported from the Crysfire summary file (Fig. 19). The previously determined background points were automatically forwarded to the Fullprof program for interpolation respectively refinement.

Sequential LeBail fits of 7 distinguishable phases (4 for $Rb_2[C_2O_4]$ and 3 for $Rb_2[CO_3]$) (Table 1) were obtained for the 200 powder patterns (e.g. Fig. 20).

A summary graphics shows the dependency of the lattice parameters and the cell volume of the high temperature phases of $Rb_2[C_2O_4]$ and $Rb_2[CO_3]$ from temperature (Fig. 21).

| 👩 Set increments and phase ranges | | | | | | | _ 🗆 🗵 | Set increments and phase ranges | | |
|--|------------------|---------|--------|--------|--------|----------|----------------------------------|---|--|--|
| Increments | Phase ranges | | | | | | | Increments Phase ranges | | |
| | Dataset No. | K | Phase1 | Phase2 | Phase3 | Phase4 | Phase5 | Dataset No. K Set increment values | | |
| 32 | 32 | 278.000 | xyz | | | | <u> </u> | 1 1.00000 154.000 K Junear A | | |
| 33 | 33 | 282.000 | xyz | | | | | 2 2.00000 158.000 Increment 4 | | |
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| 35 | 35 | 290.000 | xyz | zyx | | | | 4 4.00000 166.000 Prist Value: Det | | |
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| 10 10.0000 190.000 V To set no. /9 | | | | | | | | | | |
| | To set no | .: 79 | | | | | | | | |
| | | | | | | | | | | |
| | | | | | | Insert I | Insert Done | Cancel | | |

Fig. 18. Inserting increments and setting phase ranges.

| 📶 LeBail refinement | 🗐 LeBail refinement | |
|--|--|--------|
| Phase information: | Phase information: | |
| Phase Selected phase ranges from set number 0 to 0. Ranges Phase Current set for refinement: | Phase3 Selected phase ranges from set number 0 to 33. Phase3 Current set for refinement: | |
| Paltern: Zero offset: 0.015760 Trefine Import Fullprof Reset Remove HKL | Pattern: Zero offset: 0.005340 🗖 refine Import Fullprof Reset Remove HKL | |
| Cell Profile | Cell Profile | |
| Spacegroup: P b a m 🛛 🗖 refine cell | FWHM: C constant Image: Translation of the state of | |
| a: 11.2244 alpha: 90.0000 | X: 0.021825 Y: 0.021965 ▼ refine | |
| b: 6.25995 beta: 90.0000 | Asymmetry: S/L: 0.001730 Trefine D/L: 0.014000 Trefine | Import |
| c: 3.60249 gamma: 90.0000 Import | | |
| Refinement information: Cancel Refine Auto | Refinement information: Cancel Refine | Auto |

Fig. 19. Le Bail refinement, profile parameters and cell data.

| Phase | SG | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å | β/° | Range |
|--|----------------------|-------------|-------------|-------------|-------|--------|
| δ -Rb ₂ [C ₂ O ₄] | Pbam | 11.29 | 6.29 | 3.62 | | →522 K |
| γ -Rb ₂ [C ₂ O ₄] | $P2_1/c$ | 6.33 | 10.45 | 8.22 | 98.02 | →653 K |
| β -Rb ₂ [C ₂ O ₄] | Pnma | 8.16 | 6.58 | 10.9 | | →661 K |
| α -Rb ₂ [C ₂ O ₄] | P6 ₃ /mmc | 6.47 | | 8.26 | | →723 K |
| α -Rb ₂ [CO ₃] | P6 ₃ /mmc | 5.89 | | 7.80 | | |
| β -Rb ₂ [CO ₃] | Pnma | 7.68 | 5.89 | 10.14 | | →830 K |
| γ -Rb ₂ [CO ₃] | P2 ₁ /c | 5.87 | 10.13 | 7.31 | 97.3 | →600 K |

Table 1. Phases identified in the sample data set.

Fig. 20. Plot of the Le Bail refinement of the first data set of the δ -phase of Rb₂C₂O₄.

Fig. 21. Powder diffraction patterns, lattice parameters, and cell volumes of $Rb_2[C_2O_4]$ and $Rb_2[CO_3]$ as a function of temperature in the range from 298 to 838 K (2.4 K min⁻¹ and back down to 298 K (4.8 K min⁻¹)).

2.18. Crystal Structure Determination and Refinement

All previously unknown crystal structures of $Rb_2[C_2O_4]$ and $Rb_2[CO_3]$ were solved using the DASH structure solution package [32]. The measured powder patterns were subjected to Pawley refinements [33] in order to extract correlated integrated intensities from the pattern. Good fits to the data were obtained. An internal coordinate description of the oxalate and carbonate moieties was constructed using bond lengths, angles, and torsion angles (in case of

Fig. 22. Scattered X-ray intensity for $Rb_2[CO]_3$ at T=385 K as a function of diffraction angle 2 θ . Shown are the observed patterns (diamonds), the best Rietveld-fit profiles (line), and the difference curves between observed and calculated profiles in an additional window below. The high angle parts are enlarged by a factor of 5, starting at 25° 2 θ .

the oxalate anion) from corresponding alkali oxalate and alkali carbonate phases [12]. The torsion angle between the two carboxylate groups of the oxalate anion could not be assigned a precise value in advance, and was thus treated as an internal degree of freedom in the simulated annealing procedure. The positions of the two crystallographically independent alkali cations as well as the position, orientation, and conformation of the oxalate and carbonate anions in the unit cell were postulated and the trial structure was subjected to a global optimization in direct space using DASH. The structure giving the best fit to the data was validated by Rietveld refinement [34] of the fractional coordinates obtained at the end of the simulated annealing run.

Rigid body Rietveld refinements using the program GSAS [35] were performed on all powder patterns of Rb₂[C₂O₄] (α , β , γ , and δ), and $Rb_{2}[CO_{2}]$ (α , β , and γ) (e.g. Fig. 22). The unit cell parameters, the background, and the peak profile were taken from the corresponding LeBail fits. The strong (presumably) dynamic disorder of the high temperature phases of the alkali oxalates and carbonates was modeled in dependence on the quality of the powder diffraction patterns by rigid body TLS refinement and/or by split positions according to space group symmetry (up to 24-fold for P63/mmc). Due to the disorder, the packing is discussed on the basis of the center of gravity locations of the oxalate and carbonate anions, respectively.

3. Results and Discussion

The phase transitions and the decomposition

of anhydrous rubidium oxalate have been monitored in-situ using synchrotron radiation in the temperature range from room temperature up to T=900 K at ambient pressure. The nomenclature of the phases was chosen in such a way that the aristotype in space group $P6_3/mmc$ which is found for all investigated alkali oxalates and carbonates is denoted the α -phase. All phases occurring upon cooling are given consecutive Greek letters in the order they appear (Table 1). During the in-situ synchrotron powder diffraction experiments, rubidium oxalate was first heated until complete decomposition into the corresponding high temperature carbonate phases occurred. Three phase transitions $(\delta \rightarrow \gamma \rightarrow \beta \rightarrow \alpha)$ were observed. Subsequently, the decomposition product rubidium carbonate was also monitored by X-ray diffraction upon cooling. At cooling to room temperature, two phase transitions $(\alpha \rightarrow \beta \rightarrow \gamma)$ for rubidium carbonate were observed. The dependence of the lattice parameters on temperature and the range of existence of the different alkali oxalate and carbonate phases is given in Fig. 21. The crystal structures of α -, β -, γ -, and δ - $Rb_2[C_2O_4]$, and α -, β -, and γ - $Rb_2[CO_3]$ were solved and/or refined from the powder diffraction data [12, 13].

The crystal structures of the γ - and δ -modifications of the higher homologues of the alkali oxalates have been described (*ibid.*). In the δ - and γ -phases, the oxalate anions can be considered static with the oxalate anions in two different conformations: Planar in the δ -phase and staggered in the γ -phase (94°). The layered crystal structure of the δ -modification of rubidium oxalate anions and alkali cations. In the β - and α -phases, the oxalate anions are staggered and disordered. Therefore, only the conformation of the oxalate anions in the different modifications and the principal packing motifs are further investigated.

The basic packing of the γ -phase is preserved also for the β - and α -phases. For the β -phase, a two-fold disorder model with the oxalate anion rotating around an axis perpendicular to the principal axis proved sufficient to describe the powder diffraction data reasonably well. The disorder increases significantly for the α -phase. In addition to the rotation as described for the β -phase, there exist additional rotations of the carboxyl groups, leading to a quasispherical entity. In this case, the powder diffraction data suggest a 24-fold disorder model. In addition, the mobility of the cations increases drastically in a non-uniform way with increasing temperature, which could be satisfactorily modeled by refining an anisotropic temperature factor.

All investigated rubidium carbonate phases (Fig. 23) are isotypic to their corresponding alkali oxalate phases given by the same phase identifier, despite the different shapes of the anions. The differences between the γ -, β -, and α phases for rubidium carbonate are mainly given by the different orientations of the rigid carbonate anion. Whereas in the γ -modification, the carbonate anions are inclined around two axes with respect to each other, they are inclined around one axis in the β -phase because of an additional mirror plane running through the $[CO_3]^{2-}$ anions. Therefore, no disorder model is necessary to match the powder diffraction pattern of the β -modification. The principal orientation of the carbonate anion in the β -modification still exists in the α -modification except for the 24-fold disorder which causes the oxygen positions to be smeared out. It is noteworthy that the "sphericity" created by disorder is much less pronounced for the carbonate than it is for the oxalate phases (Fig. 23).

In order to get an easy access to the crystal structures and the topologies of the different high temperature phases of the alkali oxalates and alkali carbonates, one may replace the oxalate respectively carbonate anions by a sphere at their center of gravity, i.e. either the center between the carbon-carbon bond of the oxalate anion or the location of the carbon atoms in the case of the carbonate anion (Fig. 23).

All crystal structures of rubidium oxalate and -carbonate, at different temperatures, belong to the AlB₂ family. Depending on the size of the cations and the anions, two idealized structure types occur within this family: The AlB₂-type (*P*6/*mmm*; anion at 0, 0, 0 and cation at $1/_3$, $2/_3$, $1/_2$) and the Ni₂In type (*P*6₃/*mmc*; anion at $1/_3$, $2/_3$, $1/_4$ and cations at 0, 0, 0 and $1/_3$, $2/_3$, $1/_4$). The hexagonal layers of the anions as well as the positions of the alkali cations deviate from the idealized ones for all crystal structures in space groups other than those of the aristotypes. Furthermore, the degree of distortion with respect to the idealized structure types varies greatly with temperature, and with the conformation resp. disorder of the anion.

4. Conclusions

The complicated and time consuming evaluation process from *in situ* 2D-powder diffraction pattern to crystal structures in dependence of an external variable has been simplified and

Fig. 23. Comparison of the crystal structures (upper two rows) and crystal packing (lower row) of the crystal structures of the 4 phases of $Rb_2[C_2O_4]$ and the three phases $Rb_2[CO_3]$ n projections perpendicular to the (pseudo)-hexagonal layers of the anions. The packing diagrams show the centres of gravity locations of the oxalate and carbonate anions (white balls) and the positions of the alkali cations (grey balls) are drawn. The fractional height of the cations is given. Solid lines connect anions at height 0, while hollow lines connect anions at height $\frac{1}{2}$.

partly automated. Furthermore, the general applicability of two-dimensional signal filtering to powder diffraction data has been demonstrated. A comprehensive software package called Powder3D has been written. The compiled object oriented code can be run using the IDL Virtual MachineTM that is freely available for various platforms. As a case study to demonstrate the advances in the data analysis, the high temperature phases of rubidium oxalate $Rb_2[C_2O_4]$, and its decomposition product rubidium carbonate $Rb_2[CO_3]$, were investigated, successfully identifying a variety of phases and decomposition products.

The sequence of high temperature phase transitions of rubidium alkali oxalate and carbonate can best be understood from geometrical and energetic considerations. The disorder of the oxalate and carbonate groups, respectively, at high temperatures provides significant entropic stabilization of the high temperature phases relative to the low temperature ordered

structures. The different phases tend towards hexagonal closed packed crystal structures and are mainly distinguished by changes in the anionic packing. The driving force for the structural phase transitions is clearly related to the steric requirements of the anions, which change due to the increasing dynamics at higher temperature. Interestingly, the "sphericity" of the anions either static or dynamic proved to be more important than the actual radius of the "spheres". Despite of the different shapes of the oxalate and the carbonate anions, both families of rubidium metal salts exhibit the same basic structural features. As a general tendency, the Ni₂In arrangement gains preference over the AIB₂ packing type with increasing temperature. From the structural observations, convincing evidence can be derived for the process of thermal degradation of the alkali oxalates to the alkali carbonates to be topochemical in nature.

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References

When publishing please give reference to Powder3D in the following manner: Hinrichsen, B., Dinnebier, R. E. and Jansen, M. (2006) Powder3D: An easy to use program for data reduction and graphical presentation of large numbers of powder diffraction patterns. *Proc. Eur. Powder Diffraction Conf. 9, Z. Krist. Suppl 23*, 231–236, in press.

- H. R. Wenk and S. Grigull: J. Appl. Cryst., 36 (2003), 1040–1049.
- [2] M. Hanfland, U. Schwarz, K. Syassen and K. Takemura: *Physical Review Letters*, 82 (1999), 1197–1200.
- [3] P. Norby: J. Appl. Cryst., **30** (1997), 21–30.
- [4] C. Meneghini, G. Artioli, A. Balerna, A. F. Gualtieri, P. Norby and S. Mobiliob: J. Synchrotron Rad., 8 (2001), 1162–1166.
- [5] M. Knapp, C. Baehtz, H. Ehrenberg and H. Fuess: J. Synchrotron Rad., 11 (2004), 328–334.
- [6] H. F. Poulsen, J. A. Wert, J. Neuefeind, V. Honkimaki and M. Daymond: *Nature Materials*, 4 (2005), 33–36.
- [7] S. Theodoridis and K. Koutroumbas: *Pattern Recogni*tion, (1999), Academic Press.
- [8] D. Paulus and J. Hornegger: Pattern Recognition and Image Processing in C++, (1995), Vieweg, Braunschweig.
- [9] RSI 2005 Interactive Data Language—IDL (USA: Boulder, CO).
- [10] B. Hinrichsen, R. E. Dinnebier and M. Jansen: Proc. Eur. Powder Diffraction Conf. 9, Z. Krist. Suppl., 23 (2006), 231–236, in press.
- [11] B. Hinrichsen, R. E. Dinnebier, P. Rajiv, M. Hanfland, A. Grzechnik and M. Jansen: *Journal of Physics: Condensed Matter*, (2006), in press.
- [12] R. E. Dinnebier, S. Vensky, M. Panthöfer and M. Jansen: *Inorg. Chem.*, **42** (2003), 1499–1507.
- [13] R. E. Dinnebier, S. Vensky, M. Jansen and J. Hanson:

Chem. Eur. J., 11 (2005), 1119-1129.

- [14] P. Norby, C. Cahill, C. Koleda and J. B. Parise: J. Appl. Cryst., 31 (1998), 481–483.
- [15] J. B. Parise, C. L. Cahill and Y. J Lee: *Canadian Miner-alogist*, **38** (2000), 777–800.
- [16] P. J. Chupas, M. F. Ciraolo, J. C. Hanson and C. P. Grey: J. Am. Chem. Soc., **123** (2001), 1694–1702.
- [17] B. He: Powder Diffraction, **18** (2003), 71–85.
- [18] P. V. C. Hough: Method and means for recognizing complex patterns (1962), US Patent 3069654.
- [19] N. Bennett, R. Burridge and N. Saito: IEEE Transactions on Pattern analysis and Machine Intelligence, 21 (1999), 652–657.
- [20] Y. Lei and K. C. Wong: Pattern Recognition Letters, 20 (1999), 41–47.
- [21] C. Dammer, P. Leleux, D. Villers and M. Dosiere: Nuclear Instruments and Methods in Physics Research, B132 (1997), 214–220.
- [22] W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery: *Numerical Recipes in C*, (2002), Cambridge University Press.
- [23] P. F. Fung, W. S. Lee and I. King: Proceedings of the 13th International Conference on Pattern Recognition, (1996) Vol. 2, 511–515.
- [24] R. Chellali and V. Fremont: Ellipse detection using hough transform, 13th International Conference on Artificial reality and Telexistence, Japan, Dec. 3–5, 2003.
- [25] A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hausermann: *High Pressure Research*, **14** (1996), 235–248.
- [26] S. Bruckner: J. Appl. Cryst., 33 (2000), 977-979.
- [27] R. E. Dinnebier: Powder Diffraction, 18 (2003), 199–204.
- [28] R. Shirley: The Crysfire 2002 System for Automatic Powder Indexing: User's Manual, (2002).
- [29] L. W. Finger: J. Appl. Cryst., **31** (1998), 111.
- [30] A. Le Bail, H. Duroy and J. L. Fourquet: *Mat. Res. Bull.*, 23 (1988), 447–452.
- [31] J. R. Carvajal: Commission on Powder Diffraction Newsletter, 26 (2001), 12–19.
- [32] W. I. F. David, K. Shankland and N. Shankland: Chem. Commun., (1998), 931–932.
- [33] G. S. Pawley: J. Appl. Cryst., 14 (1981), 357–361.
- [34] H. M. Rietveld: J. Appl. Cryst., 2 (1969), 65-71.
- [35] A. C. Larson and R. B. Von Dreele: Los Alamos National Laboratory Report LAUR (1994), 86–748.

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