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1 + 1 = 3: Coupling μ-XRD^2 and DTA New insights in temperature-dependent phase transitions

The gypsum–bassanite–anhydrite system as an example

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Abstract The article shows how additional information can be obtained from coupling a self constructed DTA-system with a commercially available BRUKER D8 DISCOVER GADDS XRD^2-microdiffractometer. The dehydration process of gypsum to anhydrite in the temperature range from room temperature up to 723 K is used as an example. Due to the short measurement times of 10 s for each diffraction pattern the three phase transformations from gypsum to anhydrite (anhydrite II) via the hemihydrate bassanite, a water-free bassanite structure (γ-anhydrite, anhydrite III) were resolved in detail by recording the thermal signal and the diffraction pattern simultaneously. To the best of our knowledge, this is the first observation of a completely reversible dehydration/rehydration process of the bassanite/γ-anhydrite-structure around 373 K which is studied by coupled XRD and differential thermal analysis (DTA) measurements.

Keywords DTA · Thermal analysis · Capillary optics · Microdiffraction · Gypsum · Anhydrite · Bassanite

Introduction

Combining time and temperature resolved X-ray powder diffraction with differential thermal analysis (DTA) or differential scanning calorimetry (DSC) is a promising technique for a more detailed understanding of all kinds of temperature-dependent processes, such as phase transformations, dehydration processes with or without structural changes, or isothermal reactions in geopolymers or cements, and many more.

Coupling a DTA reaching temperatures up to 1873 K with a commercially available X-ray diffractometer was first described by Wefers in 1965 [1] and later, in 1985 and 1989, the combination of a X-ray diffractometer with a thermal analyzer for temperatures up to 723 K was realized by Fawcett et al. [2, 3]. These early setups had one shortcoming in common: they lacked sufficiently small spot sizes with high intensities. Small X-ray spotsizes, however, are essential for thermal analysis in combination with XRD to be able to investigate the small sample inside the DTA or DSC sample holder. Until recently, the reduction of the spot size of a common X-ray tube down to a diameter of a few millimeters could only be realized using pinhole collimators. This dramatically decreased the intensities of the X-ray beam and, hence, increased the measurement times accordingly. This is why it was not possible to continuously monitor DTA experiments with typical heating rates of around 10 K/min via XRD because of the poor time resolution.

Wefers [1], therefore, used two different samples in his setup: a large one for XRD analysis and a small one for the DTA measurements. Both samples were mounted on the same sample holder. With this setup a continuous heating rate up to 10 K/min could be realized, but the theta range covered only 8°. But this way, not the exact same sample

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was subject to XRD and DTA measurements. In a later setup, Fawcett et al. [2, 3] performed truly coupled DSC/XRD measurements, but due to the low intensity of the X-ray beam, a typical measurement time for one XRD pattern was at least 2 min. As a result, the typical heating rates for DTA measurements of around 10 K/min could not be resolved as each individual XRD pattern covered a temperature range of approximately 20 K. Fawcett et al. [2, 3] tried to solve this problem by either reducing the heating rates to around 1 K/min to monitor structural changes continuously or they performed step-by-step measurements, where the temperature was increased first step-by-step, and the diffraction data were then collected for each isothermal position separately. Both ways are not ideal for real temperature and time resolved DTA experiments.

Another description of coupling a commercial X-ray diffractometer with a differential scanning calorimeter (DSC) was given by Kishi et al. [4]. Like Fawcett et al. [2, 3], they used one sample for both, the XRD and DSC measurements but the total measurement time for one pattern covering 35°2θ was still high (>1 min.) and the maximum temperature of their setup was limited to 623 K. An advantage of this system was a controlled atmosphere unit to perform measurements under different humidity conditions which is known to be an important feature for the study of dehydration processes.

To realize short measurement times and yet high spatial resolution, DTA or DSC devices were typically integrated into diffractometers, which used a high flux synchrotron X-ray source combined with rapid X-ray detection systems in the last decades [5–7]. This way, measurements over a wide 2θ range and measurement times of a few seconds were possible while having both, small beam diameters (millimeter range) and high signal intensities.

Nowadays, the application of focusing X-ray microlenses in laboratory X-ray diffractometers offers an easy way to reduce the spot size of the X-ray beam while maintaining a high intensity [8–12], making simultaneous DTA/DSC + diffractometry measurements possible. The combination of X-ray microlenses with a two-dimensional detector system provides the possibility to perform μ-XRD^2-analyses on samples smaller than 1 mm with measurement times of only a few seconds and yet covering a large 2θ/Chi range (around 30° per frame).

The potential of such a setup combining a polycapillary microlens (IFG-Adlershof) with a spotsize of 200 μm (FWHM) with a two-dimensional HI-STAR detector in a commercially BRUKER D8 DISCOVER GADDS XRD^2-microdiffractometer was demonstrated in a recent publication [12]. The dehydration behavior of gypsum ($CaSO_4 \cdot 2H_2O$) in the temperature range from 313 up to 543 K was investigated with a heating rate of approximately 140 K/min by using a simple heating stage incorporated into the microdiffractometer. In this experiment, the sample was 4 mm in diameter, and it was possible to reduce the measurement time for each diffraction pattern to 3 s covering a theta range of 30°2θ. 17 XRD patterns were recorded during the 96 s of rapid sample heating. The phase transition from gypsum to a water-free bassanite structure (γ-anhydrite or anhydrite III) during the heating process took 36 s and was documented by seven diffraction patterns, hence evidencing the possibility to resolve even such fast kinetic processes. No evidence of the anhydrite structure at the maximum temperature of 543 K at the end of the experiment was observed. These first results demonstrated two things: first, the feasibility of modular heating cells for regular laboratory diffractometers and second, the surplus in information when combining real-time monitor heating and dehydration processes with X-ray diffraction.

The calcium sulfate system with hydrate ($CaSO_4 \cdot 2H_2O$), hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and anhydrate phase ($CaSO_4$) is of particular interest because of its widespread use in industry: gypsum is used for a large number of applications such as building material, plaster and casting molds. In all these fields, a detailed understanding of the dehydration behavior of the different $CaSO_4 \cdot xH_2O$ phases is essential. However, the literature on the stability ranges of the different structures as well as the crystallographic structures present at a specific temperature, differs significantly (reviews given in [13, 14]). Morris [15], for example, introduced a rather arbitrary definition by distinguishing between an α- and β-phase of bassanite based on crystallinity what is not based on crystallographic aspects leading to a confusing use of phase nomenclature.

All studies performed so far on this system suffer significantly from the fact that thermoanalysis and the corresponding phase analysis by XRD or different spectroscopic techniques were performed in different—that is uncoupled—systems [13, 16–27]. The integration of a DTA system in a microdiffractometer now closes the gap between diffraction- or spectroscopy-based data on the one hand and thermal analysis on the other hand. When we look at the numerous contradictions in the literature, it is evident that an approach using combined methods must be considered mandatory for a more comprehensive understanding of the dehydration behavior of even rather simple systems such as calcium sulfate.

Experimental

In our study, a BRUKER D8 DISCOVER GADDS XRD^2-microdiffractometer was used, equipped with a standard sealed tube with Co-anode, a primary graphite monochromator, a standard collimator base equipped with a special designed polycapillary optic (IFG Adlershof) with a spot size of 200 µm (FWHM) for the used Co-Kα radiation and a two-dimensional HI-STAR-detector [12]. The focal distance between the exit of this microlens and the sample surface was 70 mm.

The DTA module was engineered by the workshop at the IFG Tübingen inspired by a setup which was described by Lippmann in 1952 [28] and 1959 [29]. As block material pure nickel was used and holes for sample and reference, respectively, were introduced. Only heating experiments could be monitored via DTA as no active cooling system has yet been adapted to the setup (whereas both, cooling and heating was monitored by means of XRD). Sample and reference temperatures were recorded using type-K thermocouples and a schematic sketch of the setup is shown in Fig. 1.

The measurement parameters for all experiments were as follows: standard Co-sealed tube operating at 40 kV/30 mA, fixed incident angle 14°, detector distance from the sample 18.8 cm, fixed detector angle 18° covering a θ range from 11°– 40°2θ, 10 s measuring time for each pattern, sample heating/cooling rate 10 K/min.

High purity natural gypsum minerals were used for the experiments, characterized by XRD and showing no impurities in the sample material. The minerals were carefully ground in an agate mortar, and $\approx$20 mg of the powder was used for each experiment. As reference material a fine ground corundum powder (Alcoa Inc.) was used.

Results

In the first experiment, the effects of continuous heating of the sample up to 723 K was studied by means of coupled DTA/μ-XRD. The results are presented in Fig. 2. In Fig. 2, ranges where significant phase transformations take place (A: 373–423 and B: 623–673 K), are marked (black) in both, the waterfall diagram of the XRD diffractograms and the DTA curve.

In detail, around 393 K, the dehydration process starts. Latter is visible by the onset of the endothermal peak in the DTA curve (A). In the XRD pattern, this onset correlates with a constant decrease in the gypsum signal intensity and an increase in the bassanite reflections. The phase transition from gypsum to bassanite can be observed up to 423 K via XRD. The end of the phase transformation correlates with the onset of the dehydration of the hemihydrate ($-0.5H_2O$) as seen from the second endothermal peak in the DTA curve. It is important to note that the corresponding XRD patterns show no evidence for a second reconstructive phase transformation when bassanite (hemihydrate) transients into a water-free bassanite structure (γ-anhydrite/anhydrite III).

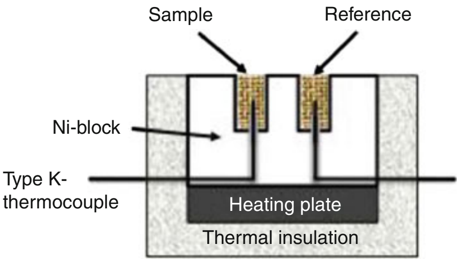

Fig. 1 Schematic setup of the modular DTA system for use with a μ-XRD^2-diffractometer

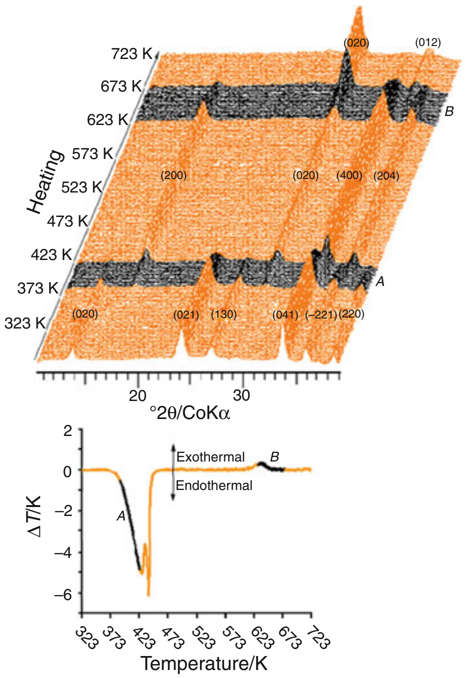

Fig. 2 Coupled XRD and DTA measurement of the dehydration process of gypsum in the temperature range from 303 to 723 K

Upon further heating up to 623 K, no structural changes/reactions can be observed via XRD or DTA. At around 623 K, a small exothermal peak is visible in the DTA curve (B) which correlates with the decrease of the bassanite-related intensities and an increase of the anhydrite signal in the XRD measurements (range B in Fig. 2). The transition from water-free bassanite to anhydrite can be observed up to 673 K. At higher temperatures, no further structural changes occur. As a result, it is clearly visible that first, gypsum transients into bassanite as the hemihydrate and upon further dehydration, not anhydrite but a nominally water-free, bassanite-type structure is obtained.

In order to investigate the reversibility of the dehydration/rehydration of bassanite/water-free bassanite, a series of heating and cooling experiments were performed (Fig. 3). In a first step, gypsum was heated up to 523 K to form the dehydrated bassanite (i.e., well below the exothermal phase transition into anhydrite), followed by

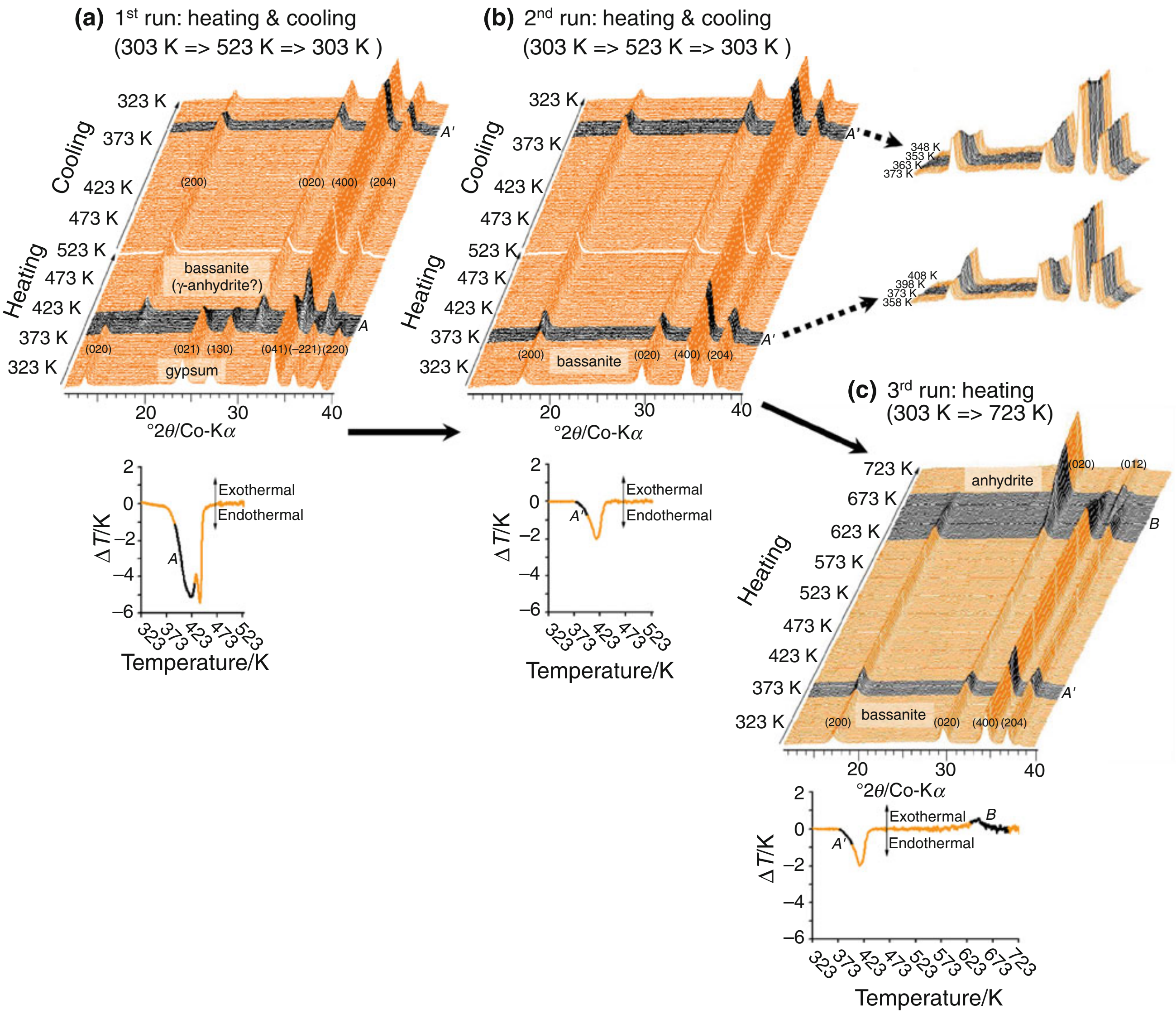

Fig. 3 Coupled XRD and DTA measurements of the dehydration/rehydration process of gypsum in the temperature range from 303 to 523 K (**a** first run, **b** second run) and the final dehydration up to 723 K (**c** third run). All measurements were performed with the same sample remaining in the DTA-module

subsequent cooling to 303 K (Fig. 3a). In a second step, the obtained bassanite sample was heated up again to 523 K and subsequently cooled to 303 K (Fig. 3b), finally the heating of the bassanite to 723 K (Fig. 3c) completed this series.

For the first hydration/rehydration experiment, the same DTA and XRD signals (Fig. 3a) as for the simple dehydration experiment (Fig. 2) could be observed. In general, the onset temperatures were well reproducible when repeating the experiment. Only one phase transformation is detectable from the XRD patterns in the temperature range from 393 up to 423 K (A). The second dehydration step (removal of $0.5H_2O$) only gives rise to a thermal signal as completely water-free bassanite is obtained. After heating, the sample was cooled down to 303 K, which was only monitored by means of XRD, because it was not possible to maintain a constant cooling rate of 10 K/min to room temperature at temperatures below 423 K due to the missing active cooling unit of the DTA block.

During cooling small intensity changes of the bassanite (200), (020), (400) reflections occur (A′) at around 363 K. This indicates slight structural changes due to the incorporation of water molecules from air humidity into the channels of the bassanite structure. It is important to note that only the hemihydrates reforms and not gypsum! A second heating and cooling run was performed with the

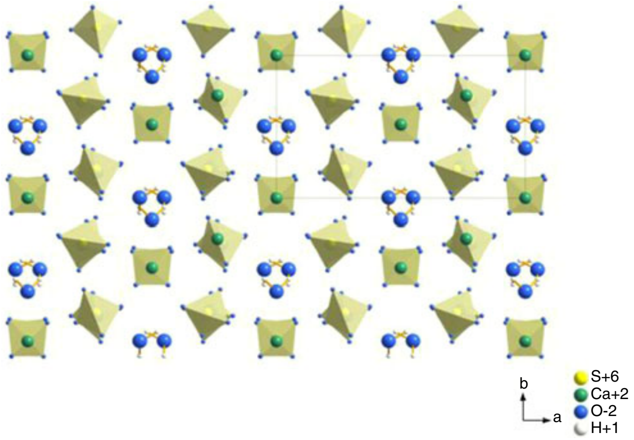

Fig. 4 Bassanite crystal structure showing the pronounced channel structure for water

same sample which remained in the DTA module (Fig. 3b). During heating, the exactly opposed intensity changes of the same bassanite reflections start around 373 K (A′). This correlates with a single broad endothermal peak in the DTA curve (Fig. 3b). During cooling of the sample, the XRD pattern show the same intensity changes like in Fig. 3a. Detailed XRD sections of these two temperature ranges are shown in Fig. 3b.

After the two heating-and-cooling runs, the sample was finally heated up to 723 K to transform the water-free bassanite into anhydrite (Fig. 3c) For this, the very same sample as shown in Fig. 3a and b was used to address reversibility undiluted from sample preparation or other detrimental effects. Just like in the runs before, slight intensity changes were observed in the bassanite diffraction pattern at around 373 K (A′) corresponding to a single broad endothermal peak in the DTA signal. As expected, no further thermal or structural changes occurred up to approximately 623 K, where the phase transformation from water-free bassanite to anhydrite occurred (B).

Discussion

The presented results regarding the dehydration behavior of gypsum especially around 373 K are in good agreement with the recent results of Carbone and Ballirano et al. [23, 26]. They observed similar effects in the XRD patterns during heating in the temperature interval from 343 to 383 K, and concluded that this is due to a rapid dehydration and rehydration of the bassanite => γ-anhydrite => bassanite structures. However, it is clear from our measurements that these intensity changes are related to an endothermic DTA peak during heating which is caused by the removal of the water molecules from the channels in the bassanite structure. As depicted in Fig. 4, the zeolite-like channels in bassanite easily serve as pathways for reversible dehydration–rehydration without causing significant reorganization of the calcium sulfate crystal structure itself.

This process is reversible and fast, as shown by sudden opposite intensity changes in the XRD patterns during cooling of the water-free bassanite structure. Correspondingly, the opposite intensity changes are visible during heating of the rehydrated sample. The coupled DTA/XRD data show that gypsum irreversibly transforms into bassanite which may be present as hemihydrate or, at higher temperatures, completely anhydrous. Only at higher temperatures, an irreversible phase transition of the water-free bassanite into anhydrite is observable. At lower temperatures, no transition of the hemihydrates into the original gypsum structure can be observed.

In the light of these results, the authors feel that the definition of the water-free bassanite as an independent γ-anhydrite or anhydrite III is questionable and even misleading because incooperation and removal of water molecules from the channels of the bassanite structure have only minor influence on the bassanite crystal lattice (as evidenced from the slight intensity changes from XRD scans). From this point of view, it is preferable to distinguish between gypsum (hydrate), bassanite (hemihydrate), a water-free bassanite and, finally, the anhydrite structure.

Summary and outlook

The in situ real-time combination of time and temperature resolved X-ray powder diffraction with differential thermal analysis (DTA) or differential scanning calorimetry (DSC) is a promising technique for a more detailed understanding of many temperature-dependent processes like phase transformations or dehydration processes with or without structural changes. In our study, the combination of a self-constructed DTA system with a commercially available BRUKER D8 DISCOVER GADDS XRD-microdiffractometer equipped with a two-dimensional HI-STAR detector covering a range of 30°2θ and Chi per measurement was used. Adding a polycapillary optic with a spot size of 200 µm, it was possible to perform in situ measurements inside the DTA module with small measuring times of only 10 s per XRD pattern. With the current setup even faster measurements (3 s or less), are possible, too.

In particular, the dehydration process of gypsum ($CaSO_4 \cdot 2H_2O$) to anhydrite ($CaSO_4$) in the temperature range from room temperature up to 723 K was examined. Short measuring times allowed to study and resolve all three phase transformations from gypsum to the hemihydrate bassanite ($CaSO_4 \cdot 0.5H_2O$), a water-free bassanite structure (in literature referred to as γ-anhydrite, anhydrite

III) and finally the formation of the anhydrite (anhydrite II) structure. For the first time, a detailed study of the reversible dehydration/rehydration process was presented, that is, the incorporation of H_2O molecules into the free channels of the bassanite/γ-anhydrite-structure at around 373 K by combining μ-XRD^2 and DTA. From these results, the definition of the so called γ-anhydrite, anhydrite III, or soluble anhydrite in this temperature range is a misleading nomenclature, because the real anhydrite (anhydrite II) structure exists only at temperatures higher than 623 K and should, therefore, not be mistaken with a nominally water-free bassanite structure.

Demonstrating the striking advantages of the coupled X-ray and thermal analysis setup, we see a high potential of this method not only for inorganic solids like the gypsum dehydration outlined in this study, but also for organic materials and especially pharmaceutical compounds where coupled DSC and Raman systems have attracted much attention. In addition, information on texture and domain size changes is also monitored real time by the two-dimensional Hi-Star-detector during the phase transformations. This may provide useful insights, for example, in case of recrystallization processes. Latter may even include phase transitions into a liquid phase and reprecipitation of crystals from it. The increase in the XRD signal will act as a measure of crystallization, while the thermal information provides valuable information on the process itself.

Another advantage of the described modular DTA system is that it can easily be adapted to spectrometers—ideally in combination with XRD. This way, information on the crystal structure, dehydration, and chemical bonding with different methods could be obtained, enabling us to gain a much more comprehensive understanding of temperature-dependent processes and kinetics.

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