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Controlling the Selective Formation of Calcium Sulfate Polymorphs at Room Temperature**

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Abstract: *Calcium sulfate is a naturally abundant and technologically important mineral with a broad scope of applications. However, controlling $CaSO_4$ polymorphism and, with it, its final material properties still represents a major challenge, and to date there is no universal method for the selective production of the different hydrated and anhydrous forms under mild conditions. Herein we report the first successful synthesis of pure anhydrite from solution at room temperature. We precipitated calcium sulfate in alcoholic media at low water contents. Moreover, by adjusting the amount of water in the syntheses, we can switch between the distinct polymorphs and fine-tune the outcome of the reaction, yielding either any desired $CaSO_4$ phase in pure state or binary mixtures with predefined compositions. This concept provides full control over phase selection in $CaSO_4$ mineralization and may allow for the targeted fabrication of corresponding materials for use in various areas.*

It is well-established that many solid materials, both natural and synthetic, can exist in distinct structural forms.[1] These so-called polymorphs share the same chemical composition, but differ in terms of their (crystal) modification at the atomic level and their macroscopic habit. Nowadays, control over polymorphism is a central goal in materials science, because the properties of solids depend intimately on the underlying structure. This control is achieved in a masterly manner by nature, where polymorphs are precisely selected according to their suitability for a given demand, and can be differentiated even at small scales and under very similar chemical conditions.[2] In the laboratory, such sophisticated control is as yet difficult and often impossible to accomplish, although in some cases deliberate switching between distinct crystal modifications in a single system has been realized.[3] Usually, however, more- or less-elaborate measures have to be taken to obtain certain polymorphs in a pure state (e.g. by carefully adjusting process conditions[4] or by introducing specific additives[5,6]) and thus, phase selection is still a major challenge for many applications.[7]

Calcium sulfate is one prominent example for a mineral system exhibiting fairly rich polymorphism.[8–10] At ambient temperature and pressure, its dihydrate phase (gypsum, $CaSO_4{\cdot}2\,H_2O$) represents the thermodynamically stable modification. Gypsum is the most abundant sulfate mineral on the Earth's surface[11] and serves as an important raw material for construction purposes.[12] Bassanite, the hemihydrate ($CaSO_4{\cdot}0.5\,H_2O$), is generally metastable in nature and therefore much less abundant,[13] but nonetheless, it likewise finds extensive application as a building material (plaster of Paris).[14] The third crystalline polymorph, anhydrite (anhydrous $CaSO_4$), replaces gypsum as the stable phase at temperatures higher than around 50 °C[8,15] and is common in evaporitic deposits,[16] but also in low-temperature hydrothermal settings;[17] it is frequently used as a binder in cements and adhesives.[18] Interestingly, despite its abundance and actual stability in the phase diagram at elevated temperatures, anhydrite does not form spontaneously during precipitation of calcium sulfate below about 120 °C, mainly because of kinetic inhibition.[8,19]

Herein we present a simple, solution-based method that allows for the preparation of phase-pure anhydrite at room temperature. In a recent study,[20] we have shown that well-defined nanoparticles of bassanite can be synthesized by quenching aqueous solutions of $CaSO_4$ into an excess of an organic solvent, such as ethanol. It was found that the polymorphic composition of the product is essentially determined by the amount of water in the mixtures: pure bassanite was obtained below a certain critical water content (ca. 33 wt %), whereas increasing fractions of gypsum (and ultimately only gypsum) formed as more and more water was added. This behavior was ascribed to the limited availability of H_2O in the medium, leading to the preference for the less-hydrated, though actually metastable, phase under these conditions. In the present work, we have extended this methodology to produce anhydrite by a further decrease in the water content. Thus, we have gained full control over $CaSO_4$ polymorphism at ambient temperature, and can switch

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between all three crystalline phases simply by adjusting the concentration of water in organic-solvent-based syntheses.

To prepare pure anhydrite, several modifications had to be made to the method we developed for the formation of bassanite.[20] First, the reagents (i.e. Ca^{2+} and SO_4^{2-}) were not pre-mixed in water and then quenched into ethanol, but were rather combined directly in the organic medium. However, when dissolving $CaCl_2$ in ethanol and adding a concentrated aqueous solution of Na_2SO_4 (see Section S1 in the Supporting Information for experimental details), we observed immediate precipitation of crystalline sodium sulfate owing to its very low solubility in alcohol (giving peculiar spherical superstructures, as shown by Figure S1). Therefore, as a second measure, Na_2SO_4 was replaced as the sulfate source by sulfuric acid; this led to the crystallization of bassanite particles with interesting fiber-like morphologies (see Figure S2), but still no anhydrite could be detected. The third and decisive modification was to switch from ethanol to dry methanol as the solvent. In this way, the effective water content in the medium could be decreased to below 0.1 wt %, ultimately enabling the spontaneous formation of anhydrite.

Thus, in a typical experiment, $CaCl_2$ (10 mmol) was dissolved in absolute methanol (50 mL) and an equimolar portion of H_2SO_4 was added by dosing aliquots of concentrated sulfuric acid (assumed to contain 5 vol % H_2O); the amount of water in the final mixture was about 1.6 mmol (ca. 0.07 wt %) and hence, there was a more than sixfold molar excess of $CaSO_4$ over H_2O in the reaction volume. Upon addition of H_2SO_4, the initially transparent solution turned cloudy immediately, indicating rapid formation of calcium sulfate particles that remained dispersed in the resulting viscous slurry. The product was isolated by centrifugation, washed and dried, and subsequently analyzed by means of transmission electron microscopy (TEM, Figure 1), infrared (IR) spectroscopy (Figure 2), and X-ray diffraction (XRD, Figure 3).

TEM images show that the precipitates consist of approximately 10–20 nm primary particles, either spherical or elongated, which have aggregated and partially fused into larger, less-defined structures (Figure 1 a). Electron-diffraction (ED) patterns of such agglomerates demonstrate that they are composed of crystalline anhydrite (Figure 1 b). In some cases, reflections corresponding to calcium oxide were detected (see Figure S3), likely due to rapid transformation of anhydrite into CaO under the influence of the electron beam. IR spectra confirm the selective formation of anhydrite, as is evident from the position (and splitting) of the ν_4 antisymmetric bending modes of the sulfate ion (Figure 2): anhydrite shows three distinct bands at 594, 617, and 673 cm^{-1} in this region whereas, owing to higher symmetry, there are only two peaks at different wavenumbers in the case of bassanite (601 and 659 cm^{-1}, cf. Figure 2 b) as well as gypsum (594 and 667 cm^{-1}, see Figure S4).[6,21] This notion is further supported by the absence of defined water vibrations at about 1600 and 3500 cm^{-1}, which would be expected for both bassanite and gypsum (cf. Figure S4).

Finally, the presence of phase-pure anhydrite is verified by XRD patterns (Figure 3 a), where all occurring reflections can be indexed to crystalline anhydrite and no signs of bassanite or gypsum could be discerned. To our knowledge, this is the first time that pure anhydrite has been successfully prepared by spontaneous precipitation in a solution-based method at room temperature. In fact, early work on the crystallization of calcium sulfate in completely water-free alcoholic solutions reported the formation of a solvate adduct ($CaSO_4 \cdot 0.5\,MeOH$) with a structure analogous to that of bassanite,[22] which however was not observed in any of the present experiments. Other studies have indicated that the formation of anhydrite "under moderate conditions" may be facilitated by adding certain crystallization inhibitors (namely polycarboxylates and phosphate esters);[23] however, this process still required a minimum temperature of 60 °C.

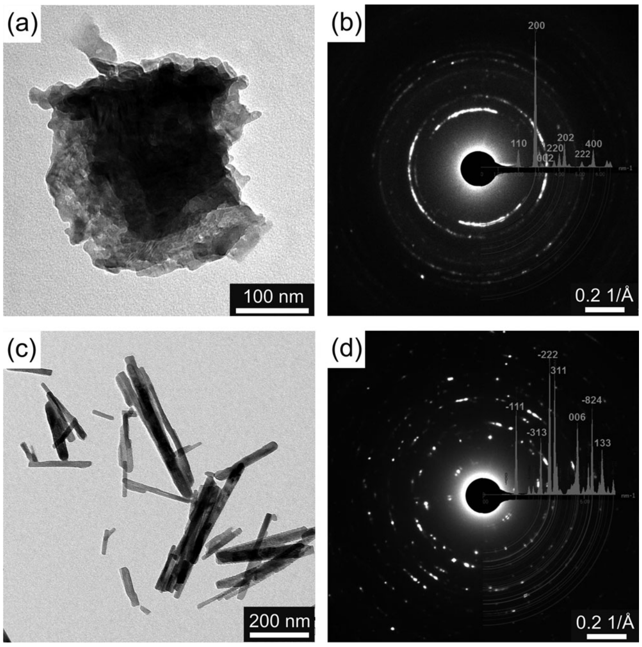

Figure 1. Left: TEM micrographs and Right: electron diffraction patterns of particles formed after addition of concentrated H_2SO_4 to $CaCl_2$ solutions in a,b) dry methanol (containing about 0.07 wt % H_2O, $CaSO_4$:H_2O molar ratio of 1:0.16) and c,d) methanol with a total water content of 4.14 wt % ($CaSO_4$:H_2O = 1:10). Precipitation in pure methanol yields aggregates of spherical nanoparticles (a), which consist of pure anhydrite (b). In the presence of more water, rod-shaped particles are obtained (c), which were confirmed to be bassanite (d).

To further characterize the experimental parameters leading to the formation of anhydrite and to trace the transition from bassanite to anhydrite in alcohol-based syntheses, the amount of water present in the final reaction medium was systematically increased while keeping constant the concentration of calcium sulfate. This was achieved by adding defined volumes of water to the methanolic $CaCl_2$ solution and combining this mixture with H_2SO_4 under otherwise identical conditions. The composition of the precipitates obtained was analyzed by IR spectroscopy (Figure 2 b) and XRD (Figure 3 and Figure S5).

To quantify the fractions of bassanite and anhydrite in the products, the intensities of the IR bands at 673 cm^{-1} (which only occurs for anhydrite) and 659 cm^{-1} (characteristic of bassanite) were determined for each sample. The ratio of these intensities turned out to scale linearly with the mass

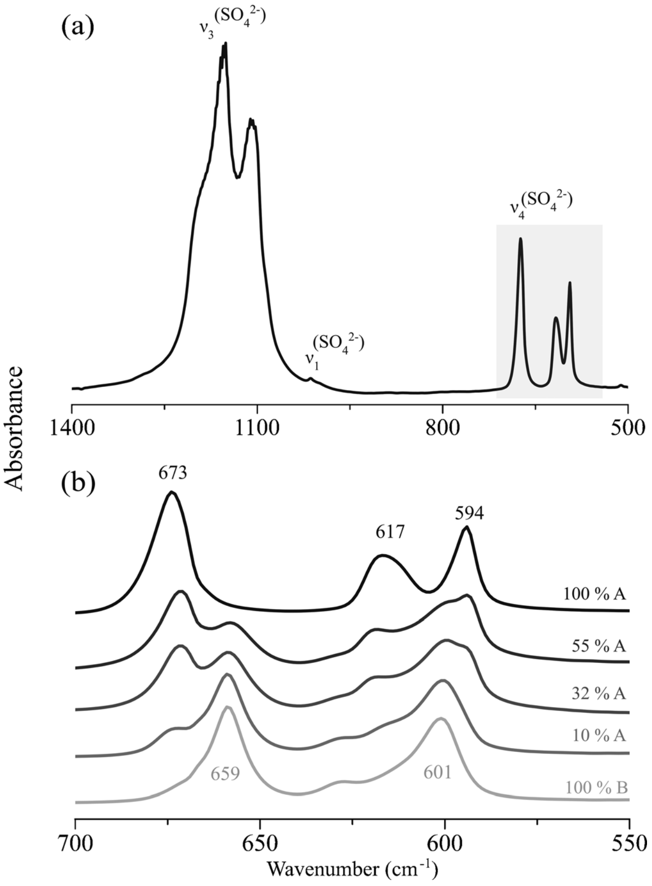

Figure 2. Infrared spectra of a) pure anhydrite, formed by precipitation from methanolic solutions at a water content of 0.07 wt % ($CaSO_4$:H_2O ratio of 1:0.16), and b) anhydrite, bassanite, and anhydrite/bassanite mixtures obtained in the presence of increasing amounts of water, namely (from top to bottom, corresponding $CaSO_4$:H_2O ratios in brackets) 0.07 (1:0.16, pure anhydrite, A), 0.54 (1:1.25), 0.60 (1:1.4), 1.49 (1:3.5), and 3.14 wt % (1:7.5, pure bassanite, B). Relative percentages of the two polymorphs, as determined by calibration with a series of defined anhydrite/bassanite mixtures (cf. Figure S6) are indicated.

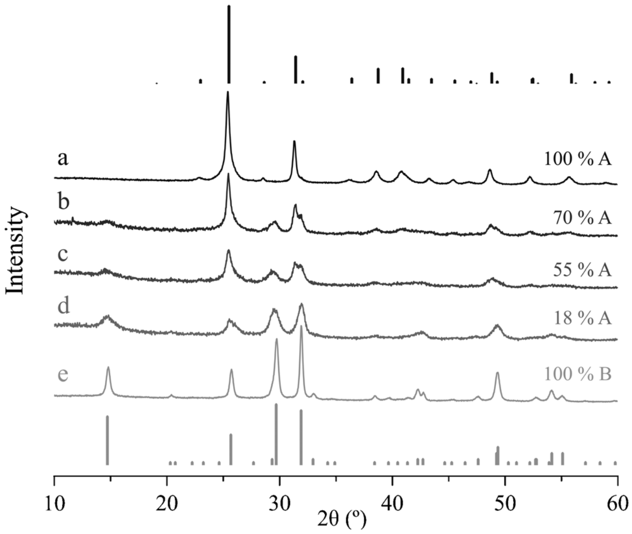

Figure 3. X-ray diffraction patterns of calcium sulfate powders obtained by precipitation from methanolic solutions at final water contents (corresponding $CaSO_4$:H_2O ratios in brackets) of a) 0.07 (1:0.16), b) 0.43 (1:1), c) 0.54 (1:1.25), d) 0.86 (1:2), and e) 4.14 wt % (1:10). Reflections in (a) and (e) can be assigned to pure anhydrite (A) and bassanite (B), respectively, whereas (b)–(d) are mixtures of the two polymorphs with compositions as indicated (values derived from IR data). The vertical lines at the top and bottom of the graph represent peak positions theoretically expected for anhydrite and bassanite, respectively.

fraction of anhydrite in the solids, as demonstrated by calibration using a series of anhydrite-bassanite mixtures with known polymorph contents (see Figure S6). In this way, the amount of bassanite formed with increasing concentration of water could be derived from the IR data, leading to the results shown in Figure 4. Up to a final water content of 0.22 wt % (i.e. a $CaSO_4$:H_2O ratio of 1:0.5), phase-pure anhydrite was produced, as confirmed by XRD. Beyond this threshold, increasing amounts of bassanite were detected in the precipitates (e.g. ca. 50 wt % bassanite at 0.54 wt % H_2O, cf. also Figure 2 b and Figure 3). Starting from a water content of 0.86 wt % ($CaSO_4$:$H_2O = 1$:2), the measured fractions of anhydrite were generally less than 20 wt % and hence close to the experimental error estimated for the used procedure (ca. ± 10 wt %). In the presence of 2.11 wt % water or more (1:5 $\leq$ $CaSO_4$:H_2O $\leq$ 1:10), bassanite was the only phase found in the products. Thus, an overall sigmoidal progression was obtained for the evolution of the bassanite mass fraction as a function of the water content in the medium (Figure 4).

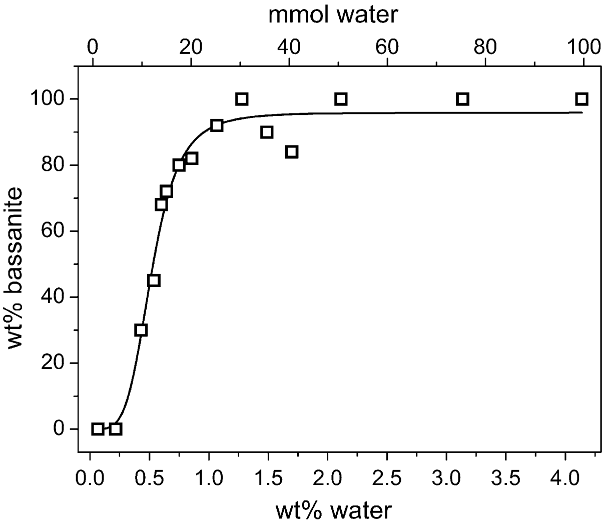

Figure 4. Plot of the bassanite content (weight fraction relative to anhydrite) of precipitates formed in the presence of different total amounts of water, given as mmol H_2O per 50 mL of methanol (top axis) and wt % H_2O (bottom axis). The solid line represents a dose-response fit showing the sigmoidal behavior of the data.

The bassanite particles formed at higher water concentrations were well-defined nanorods with sizes and morphologies quite similar to those reported in our previous study[20] and other work,[9] as shown by TEM (Figure 1 c,d) and SEM (see Figure S7). Some of these nanoparticles display pronounced porosity (see Figure S8); the observed voids (or cracks), typically about 10 nm in size, are likely to originate from rapid and uncontrolled expulsion of water during abrupt precipitation of bassanite in the organic medium.[20]

Finally, we have investigated the stability of the anhydrite particles formed, both in dry state and in aqueous dispersion. IR analyses of anhydrite powders that were exposed to air for 8 weeks did not show any signs for noticeable conversion into bassanite or gypsum (see Figure S9), suggesting that the material can be stored and processed in air without significant structural changes. In contrast, fast transformation was observed when the particles were dispersed in water ($10\,\mathrm{mg\,mL^{-1}}$ $CaSO_4$) and stirred: even after 5 min, the isolated solids consisted mainly of gypsum (see Figure S10). Thus, the anhydrite obtained by our method displays characteristics typical of type-II (stable in air, dehydration product of gypsum/bassanite at relatively mild temperatures (>100 °C) and type-III anhydrite (high reactivity with water, resulting from dehydration at >300 °C).[12,24] However, XRD analyses clearly show that our product is phase-pure anhydrite II (see Figure S11). This type of anhydrite corresponds to the dominant calcium sulfate phase formed during direct precipitation from solution in geological environments at elevated temperatures.[19]

In conclusion, we have developed a procedure by which phase-pure nanoparticles of anhydrite can be obtained by spontaneous precipitation from organic media. The key to produce the anhydrous form of calcium sulfate was to decrease the effective water content in the reaction mixture to levels significantly below 1 wt %. Unlike common approaches to prepare anhydrite (e.g. by thermal dehydration of gypsum), this solution-based method does not require heating and can be conducted at ambient temperature, thus avoiding major energetic costs associated with currently applied procedures. Moreover, combined with the results of our previous study,[20] the data collected in the present work show that precipitation of calcium sulfate in organic solvents as described herein is a simple, but powerful strategy to control the polymorphism of this important mineral. In fact, by tuning the water content in such syntheses, all three crystalline polymorphs can be selectively obtained in pure state (anhydrite at ≤ 0.2 wt % H_2O, bassanite for $2 \leq$ wt % $H_2O \leq 33$, and gypsum at ≥ 50 wt % H_2O), as well as in binary mixtures with pre-defined compositions (0.3–2 and 33–50 wt % H_2O, respectively). These findings may be used to synthesize calcium sulfate powders with specific properties for various applications. Beyond that, it is conceivable that similar control over polymorphism could also be gained for other mineral systems comprising phases that differ with respect to their water content.

Keywords: anhydrite · bassanite · calcium sulfate · nanoparticles · polymorphism

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