

Electronic Supplementary Information (ESI)

A simple and scalable strategy for the synthesis of well-defined bassanite nanorods

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Section S1. Experimental Details

S1.1. Chemicals

Sodium sulfate (anhydrous, ACS reagent) and calcium chloride dihydrate ($\geq 99\%$) were purchased from Merck and Sigma-Aldrich, respectively, and used as received. All solvents (i.e. ethanol, methanol, acetone, isopropanol, tetrahydrofuran (THF)) were of technical grade and contained ca. 4 vol% water.

S1.2. General procedure for the synthesis of bassanite/gypsum particles

Supersaturated calcium sulfate solutions (containing 25, 50, 75, 100, or 150 mM CaSO_4) were prepared by mixing equal volumes of $\text{CaCl}_{2(\text{aq})}$ and $\text{Na}_2\text{SO}_{4(\text{aq})}$ (both 50, 100, 150, 200 or 300 mM, respectively). After shaking for 5 s, a certain volume (typically 50 mL) of the aqueous solution was poured into an excess of organic solvent (100-500 mL). The resulting dispersion was shaken for another few seconds before the formed particles were isolated by centrifugation (9000 rpm for 1 min) and subsequent drying in vacuum at room temperature. Note that 16 wt% is the minimum final water content achievable in these syntheses, because the used ethanol was of technical grade and thus already contained about 4 wt% water. Higher final water contents were realised by using $\text{H}_2\text{O}/\text{EtOH}$ mixtures instead of pure ethanol for quenching.

In order to mimic the industrially applied process for the synthesis of bassanite, some of the as-obtained gypsum particles were re-transformed into bassanite by heating the dry samples for 3.5 days in air at 155° .

S1.3. Analytical methods

Infrared (IR) spectra were acquired on a Perkin-Elmer Spectrum 100 instrument, equipped with an attenuated total reflectance (ATR) unit for direct analysis of the obtained solids. Data were

collected at a resolution of 1 cm^{-1} and were averaged over 4-8 scans. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer, using Cu-K_α radiation and covering a 2θ range of $5\text{-}60^\circ$ at a step resolution of 0.02° (integration time per step: 6 s). For scanning electron microscopy (SEM), the dry powders were fixed onto standard aluminum stubs by means of double-sided adhesive carbon tape and were subsequently sputtered with gold. SEM analyses were performed on a Zeiss CrossBeam 1540XB microscope at a typical acceleration voltage of 3 kV. Samples for transmission electron microscopy (TEM) were prepared by dispersing suitable amounts of the isolated particles in absolute ethanol and placing a small drop of the resulting suspension onto conventional TEM grids (carbon-filmed copper grids, 300 mesh, supplied by Plano GmbH) or, when observing the transformation of bassanite to gypsum, by blotting aliquots of the aqueous reaction mixture directly on the grids. After evaporation of the solvent in air, the deposited particles were investigated with the aid of a Zeiss Libra 120 microscope operated at 120 kV.

Section S2. Additional Figures and Tables

$c(\text{CaSO}_4)_{(\text{aq})} / \text{mM}$	$\text{IAP} / 10^{-4} \text{M}^2$	$\text{SI}_{\text{Gypsum}}$	$\text{SI}_{\text{Bassanite}}$
25	0.40	0.22	-0.66
50	0.92	0.59	-0.30
75	1.51	0.80	-0.08
100	2.16	0.95	0.07
150	3.62	1.18	0.29

Table S1. Analytical molar concentrations of calcium sulfate in the aqueous precursor solutions ($c(\text{CaSO}_4)_{(\text{aq})}$), ionic activity products (IAP) calculated with the geochemical software PHREEQC (v. 3.0.6),^[S1] and saturation indexes ($\text{SI} = \log(\text{IAP}/K_{\text{sp}})$) derived for gypsum ($\text{SI}_{\text{Gypsum}}$) and bassanite ($\text{SI}_{\text{Bassanite}}$) at the different concentrations using thermodynamic solubility products (K_{sp}) reported by Amathieu et al.^[S2] Note that all solutions are supersaturated with respect to gypsum, whereas the solubility limit of bassanite is exceeded only in the case of 100 and 150 mM $\text{CaSO}_4_{(\text{aq})}$.

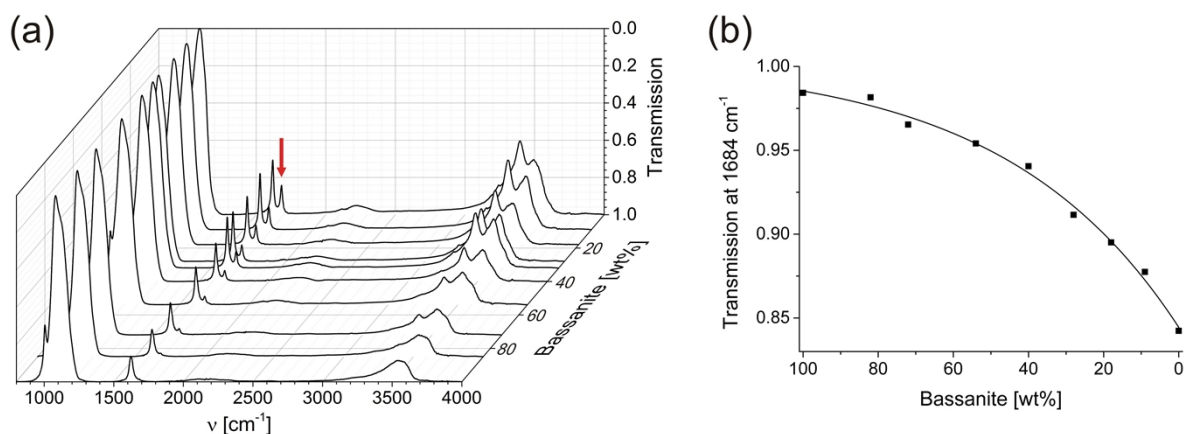


Figure S1. (a) IR spectra of samples containing bassanite and gypsum in varying defined mass ratios (obtained by mixing the two polymorphs in dry state and homogenizing the conglomerate by careful grinding in a mortar). The red arrow marks the peak at 1684 cm^{-1} , which only occurs for gypsum. (b) Plot of the intensity of the band at 1684 cm^{-1} (in units of transmission) as a function of the bassanite content ($w_{\text{Bassanite}}$) in the mixtures. Squares represent experimental data, while the full line is an exponential fit giving the following “calibration” equation: $w_{\text{Bassanite}} = 46.3 \cdot \ln[(1 - T_{1684})/0.16]$.

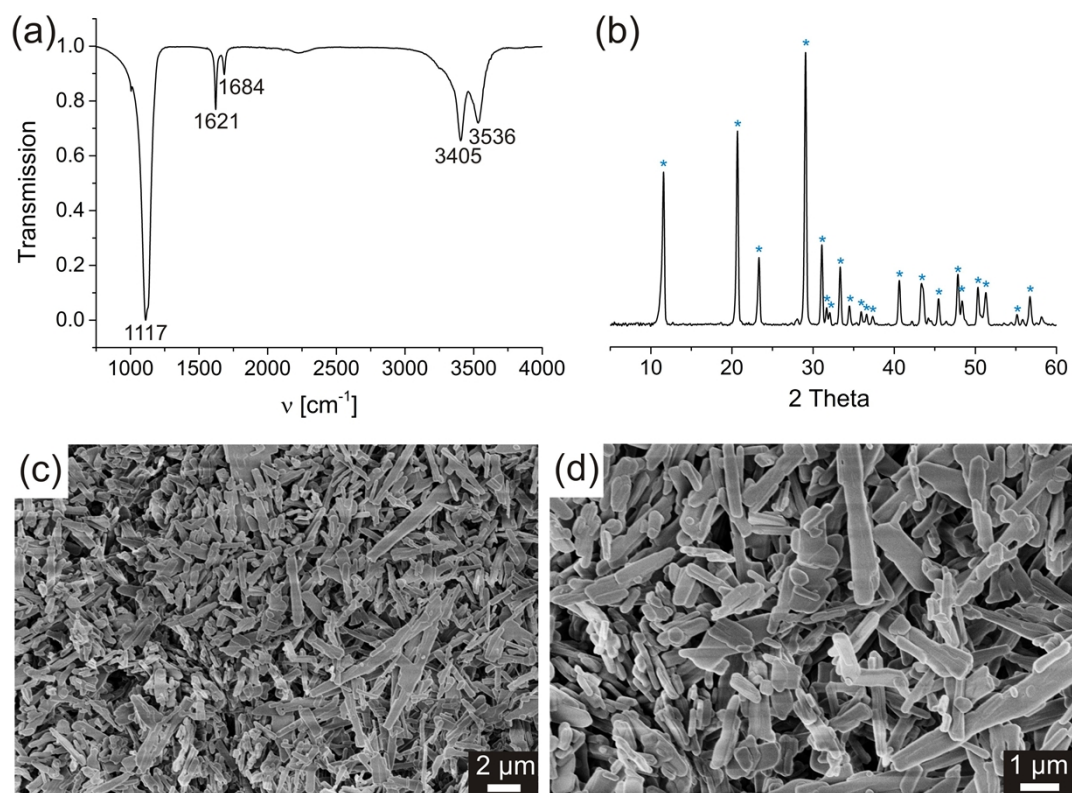


Figure S2. Characterization of calcium sulfate particles precipitated from reaction mixtures containing 54 wt% water (addition of 50 mL 150 mM CaSO_{4(aq)} to 500 mL ethanol/water mixture). (a) IR and (b) XRD pattern of the isolated precipitates, showing signals that can all be assigned to crystalline gypsum (XRD reflections marked by red asterisks). (c-d) SEM images of the samples, revealing micron-sized gypsum needles.

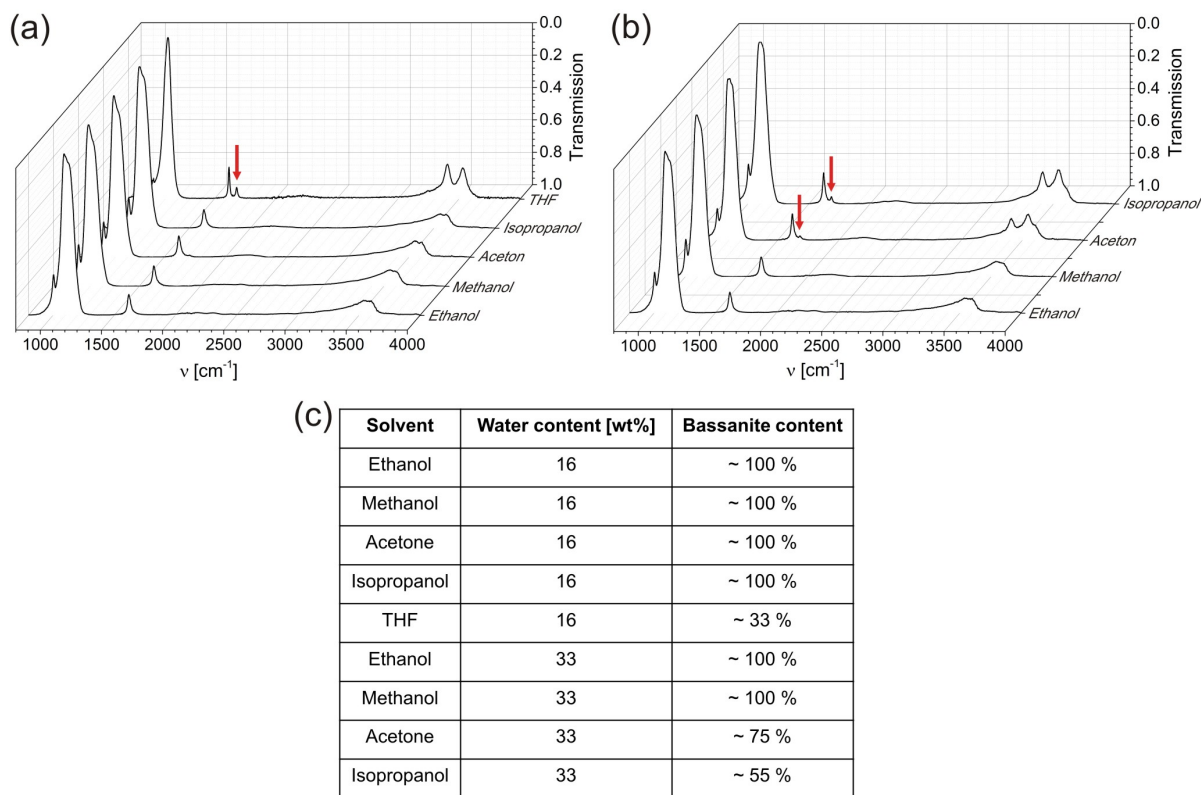


Figure S3. Results of IR measurements on products formed by adding 50 mL of 50 mM $\text{CaSO}_{4(\text{aq})}$ solution to 500 mL of different organic solvents, with final water contents of (a) 16 wt% and (b) 33 wt%. The intensity of the peak at 1684 cm^{-1} (highlighted by red arrows) indicates the presence of varying amounts of bassanite and gypsum in the samples. c) Bassanite contents estimated for the different solvents and conditions on the basis of the IR data.

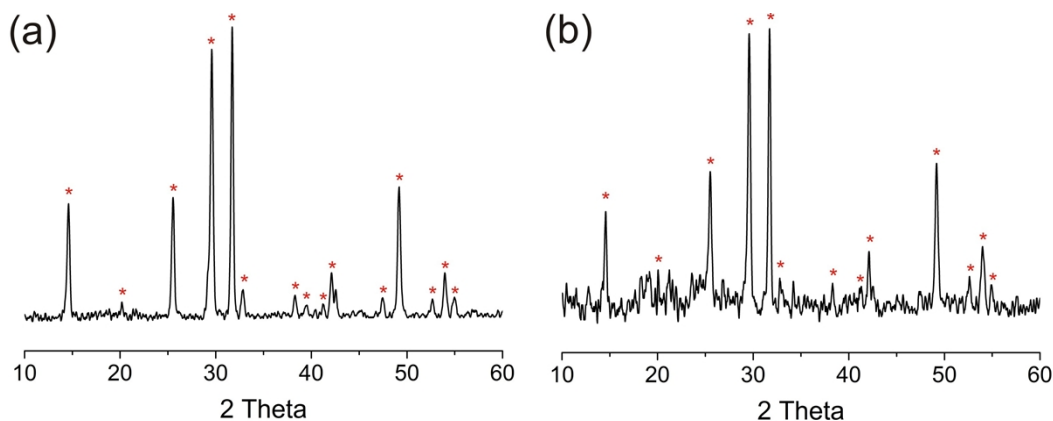


Figure S4. Bassanite stability in dry state: XRD patterns of solid bassanite after ageing the isolated particles for (a) 1 week and (b) 3 weeks in closed vials at room temperature. All observed reflections can be indexed to crystalline bassanite (red asterisks).

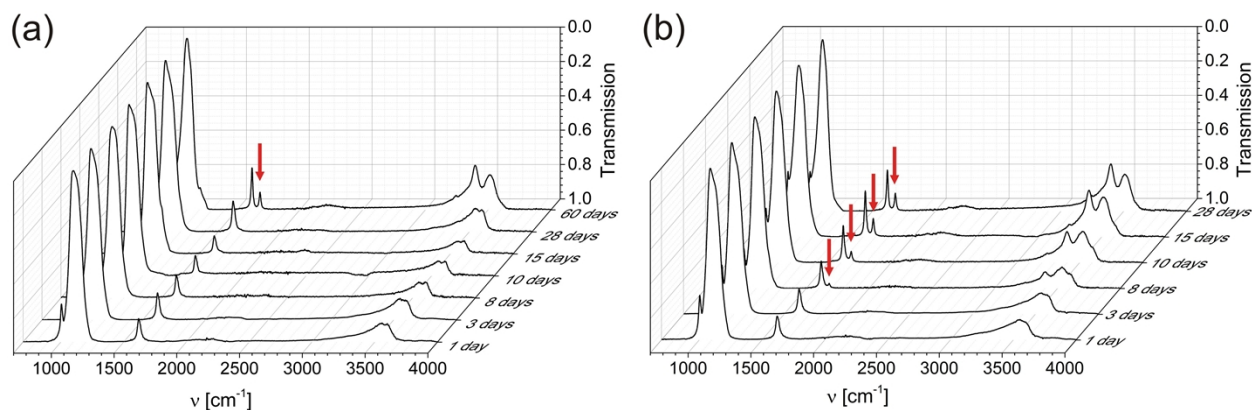


Figure S5. Bassanite stability in dispersion: IR patterns of samples drawn after different ageing times from ethanolic dispersions prepared by adding 50 mL of (a) 50 mM and (b) 150 mM $\text{CaSO}_{4(\text{aq})}$ solution to 500 mL ethanol (final water content: 16 wt%). Note that bassanite was stable for at least 28 days at the lower CaSO_4 concentration (absence of the band at 1684 cm^{-1}), whereas significant amounts of gypsum (ca. 25%) were present after 8 days at the higher concentration. With time, transformation of bassanite proceeded gradually at 150 mM CaSO_4 , and about 85% of gypsum were detected after 28 days.

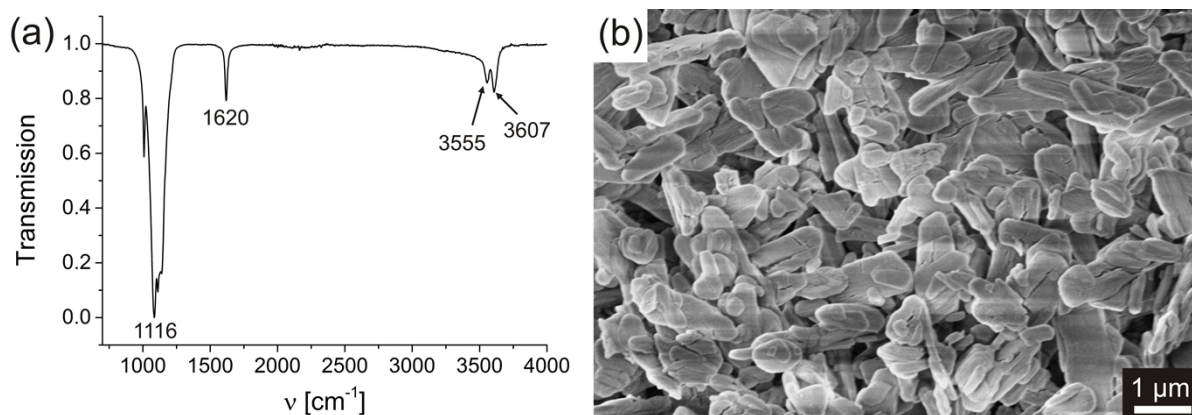


Figure S6. Transformation of gypsum into bassanite via heating. (a) IR spectrum of a sample obtained by heating gypsum particles at 155°C for 3.5 days. The observed absorption bands suggest complete conversion to bassanite. (b) SEM image of the as-formed bassanite particles. Note that the heating procedure yields rather undefined micron-sized grains, in contrast to the fairly uniform nanoparticles generated by ethanol quenching at room temperature.

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- [S1] D. L. Parkhurst, C. A. J. Appelo, *PHREEQC (Version 3) – A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, United States Geological Survey (USGS), **2013**, available at: http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/.
- [S2] L. Amathieu, R. Boistelle, *J. Cryst. Growth*, 1988, **88**, 183-192.
- [S3] Y.-W. Wang, F. C. Meldrum, *J. Mater. Chem.*, 2012, **22**, 22055-22062.