Raman Analysis of $CaSO_4$-based Materials

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Introduction

$CaSO_4$-based materials, commonly referred to as plaster are widely used in many different fields such as building, construction and arts to name a few. The setting process implies the hydration of the hemihydrate bassanite (2CaSO4.H2O), thus forming the dihydrate gypsum (CaSO4.2H2O) via a dissolution/precipitation process. Since those two compounds exhibit distinctly different Raman spectra, Raman imaging was chosen as primary analytical approach for the characterization of two different samples, exhibiting different macroscopic properties and for the estimation of the bassanite/gypsum ratio therein as well. The results of the imaging analysis were compared with those from the averaged spectra. Additionally, the ratio bassanite/gypsum was calculated from the X-ray powder diffraction data.

Methods

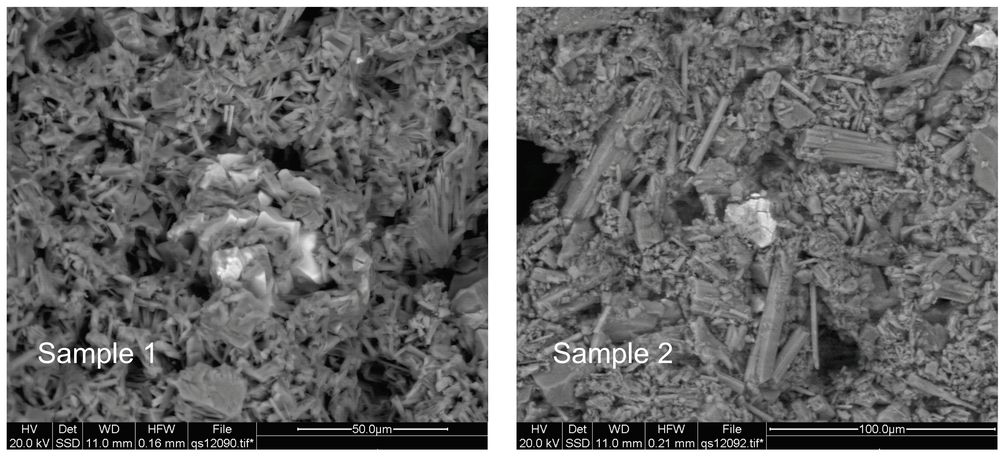
Raman images were collected using a HORIBA LabRAM HR 800 confocal Raman microscope: 800 mm focal length; He-Ne laser (6333 nm, 15 mW); CCD: 1024x256 pixel (spectral range: 200-1050 nm); DuoScan™ Imaging system (for fast and uniform scanning over small and large sample areas with variable pixel size); LabSPEC software (with SWIFT™ module).

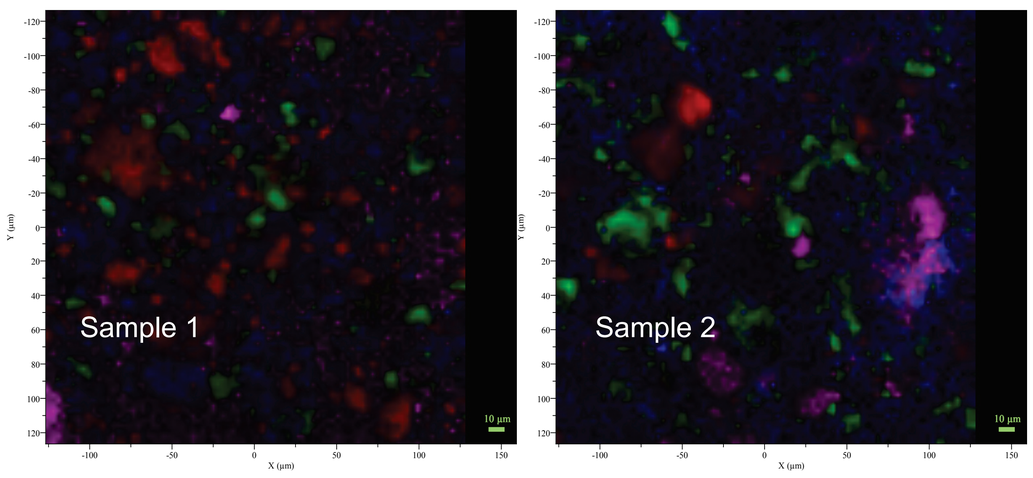
Image evaluation: MCR analysis with MIA Solo.

The XRD-measurements were performed on a Siemens D501 which works in Bragg–Brentano geometry. The obtained data were analysed with the DIFFRAC.EVA software V2.0 from Bruker.

Results and Discussion

Two different plaster samples were analysed with Raman imaging and XRD, the results are summarised below.

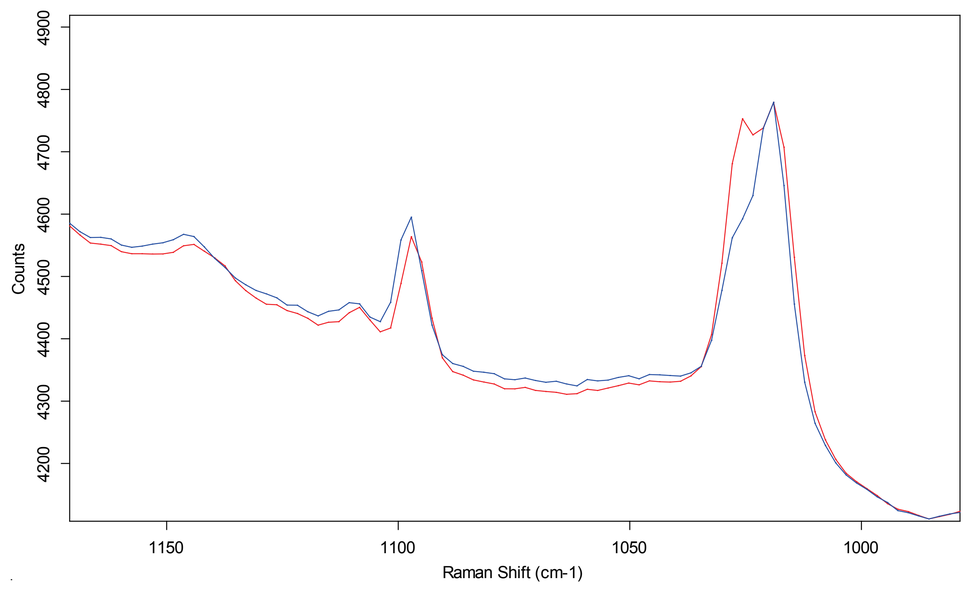




RGB-Images after PCA of the two samples. Red – $CaCO_3$ (filler), blue/violett – gypsum, green – bassanite.

Total imaged area: **250 µm * 250 µm**; step size: 2.5 µm (DUOSCAN™) ;
Total number of spectra collected: **10 000**

The areas calculated from the Raman image have been corrected for the density of the two compounds of interest.
Calculated values rely on the confocality of the Raman measurements (about 2 µm).
Results have been compared to those, obtained from the averaged Raman spectra and also to the XRD data.



Averaged Raman spectra with indexed Raman modes for bassanite and gypsum

	Raman (MCR)	Raman (averaged)	XRD
Sample 1	0.63	0.66	0.33
Sample 2	0.96	1.24	1.00

Table: Bassanite/gypsum ratio, calculated from the Raman and XRD data

⇒ Semi quantitative data (bassanite/gypsum) ratio could be extracted from the Raman data
⇒ Information about the filler distribution was obtained simultaneously, showing distinct differences between the samples (agglomerates in sample 1)
⇒ a good agreement between the Raman and XRD data could be found.
⇒ the non-destructive Raman measurement allows the subsequent analysis of the same unaltered sample with other analytical techniques

References

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Das Land Steiermark

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