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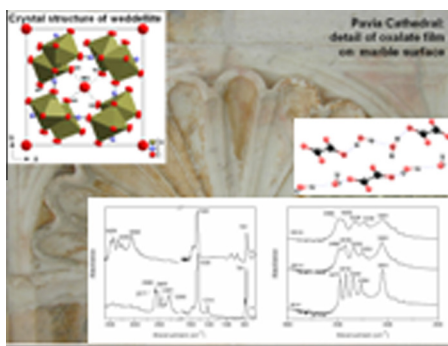
Phase transformation of calcium oxalate dihydrate–monohydrate: Effects of relative humidity and new spectroscopic data

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HIGHLIGHTS

- We study the vibrational properties of monohydrate and dihydrate phases of calcium oxalate.
- We investigate the phase transformation of calcium oxalate dihydrate.
- We report a re-investigation of the vibrational spectra (Raman and IR) of whewellite.
- X-ray diffraction show the influence of relative humidity on the stability of weddellite.
- The new data achieved will provide essential information in medical and Cultural Heritage fields.

GRAPHICAL ABSTRACT



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ABSTRACT

New data on vibrational properties of calcium oxalates and their controversial transformation mechanism are presented. We have focused on whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and weddellite [$\text{CaC}_2\text{O}_4 \cdot (2 + x) \text{H}_2\text{O}$], the most common phases of calcium oxalate; these compounds occur in many organisms, in kidney stones and in particular kinds of films found on the surface of many works of art. Low temperature experiments carried out by Fourier transform infrared spectroscopy have highlighted both the high structural order in the crystalline state of whewellite and the disordered distribution of the zeolitic water molecules in weddellite. The synthesised nanocrystals of weddellite have been kept under different hygrometric conditions in order to study, by X-ray powder diffraction, the role of “external” water molecules on their stability. Moreover, in order to identify the different kinds of water molecules, a re-investigation, supported by quantum chemical calculations, of the observed vibrational spectra (IR and Raman) of whewellite has been conducted.

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Introduction

Calcium oxalates occur in nature in three different crystalline forms: (1) calcium oxalate monohydrate, or whewellite (CaC_2O_4

$\cdot \text{H}_2\text{O}$), which represents the most common form, stable at environmental conditions; (2) calcium oxalate dihydrate, or weddellite ($\text{CaC}_2\text{O}_4 \cdot (2 + x) \text{H}_2\text{O}$) which is unstable at environmental conditions and is less frequently observed than whewellite; (3) calcium oxalate trihydrate, or caoxite ($\text{CaC}_2\text{O}_4 \cdot 3 \text{H}_2\text{O}$), is rarely observed. Calcium oxalates are well known in the field of medicine as they are the primary constituents of more than 70% of all human kidney

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stones in Western countries [1]. Moreover, these minerals occur in many organisms [2–6] and are also observed in particular kinds of films found on the surface of many works of art [7–10].

The frequent occurrence of whewellite and weddellite led researchers to investigate their crystallographic structures [11–15]; whewellite crystallizes in a monocline lattice [P21/c (C2h) space group] while the crystal of weddellite has a tetragonal structure [I4/m (C4h) space group]. In weddellite each polyhedron of calcium is linked to two adjacent polyhedra, thus generating chains running along the *c*-axis. The link between these chains is achieved by means of oxalate–water–oxalate ribbons, lying in planes parallel to the (100) plane. In weddellite the repetition around the four-fold axis of the calcium chains and the oxalate–water ribbons generates channels in which zeolitic water occurs with partial site occupancy. Taken together these findings suggest that in whewellite all water molecules are strongly linked in the crystalline structure, while in weddellite there is a fraction of water that is quite mobile in the channels inside the crystal.

One of the most controversial issues in the chemistry of oxalates is the process which accounts for the transformation of weddellite into whewellite [16] and the understanding of the conditions that favour or hamper this process. Many variables, e.g. temperature and humidity, have been taken into account by various authors. Several studies concerning the thermal transformation of the two calcium oxalates have been carried out: Frost and Weier [17], using Raman spectroscopy, a mechanism of thermal decomposition of whewellite have suggested. It exhibits three distinct mass loss steps: in the first step water is developed around 434 K; in the second step carbon monoxide around 752 K and in the third step carbon dioxide around 957 K. White and Ai [18], using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) combined with quadrupole mass spectrometry, highlighted the existence of three temperature-dependent phase transitions within whewellite before transformation: all these phases can be distinguished from their DRIFTS spectra even though the phase transitions involve only slight displacement of the oxalate units. Christy et al. [19], using diffuse reflectance FT-IR spectroscopy, carried out a study of dehydration of whewellite in order to determine the kinetic parameters and to assign the O–H stretching modes. Also the thermal decomposition of weddellite is well known [20,21]: as in the case of whewellite, the decomposition of weddellite shows three major mass-loss events. The first near 393 K corresponds to the dehydration reaction, the second mass loss near 698 K results from the transformation of the dehydrated oxalate to carbonate. In the final reaction, near 873–923 K, the calcium carbonate transforms into the calcium oxide. Morphological and chemical changes occurring during the thermal decomposition of weddellite were studied by Klopogge et al. [22]: the gases formation temperatures are significantly higher for whewellite than for weddellite. In particular, the most significant difference corresponds to the first mass-loss event: the mineralogical phase with two water molecules (weddellite) shows the dehydration reaction at a significantly lower temperature than the mineralogical phase with only one water molecule (whewellite). This finding confirms that in weddellite the water molecules are more weakly bound in the crystal in comparison with whewellite.

Few data have been found regarding the studies of calcium oxalates at low temperatures. Frost and Weier [17,23], using Raman spectroscopy at 77 K, observed the evolution of the bands of whewellite and weddellite. Trpkovska et al. [24] showed FT-IR spectra at low temperature (80 K) of these phases and provided relevant information on the O–H stretching of water in whewellite. Indeed FT-IR shows a high sensitivity in the OH spectral regions and, at low temperature bands of whewellite clearly sharpen. This work was undertaken to provide additional information on the role of

water molecules in the transformation of weddellite and to present the infrared spectra of calcium oxalates obtained at low temperatures (95 and 173 K).

As already shown in a previous paper [25], contrasting opinions exist on the role of humidity in the behaviour of calcium oxalates. However, whilst all the experimental studies agree on the instability of weddellite at ambient conditions, this fact is in apparent discrepancy with the findings achieved studying Cultural Heritage materials [26], where weddellite is often detected in oxalate films occurring on the surface of several ancient monuments. This suggests that weddellite is stable for centuries at ambient conditions. The influence of relative humidities (RH) on the stability of weddellite has been explored to offer some insight into the mechanisms of formation and transformation phases of calcium oxalate.

Materials

Synthetic weddellite, in the form of nanocrystalline powder [25], was prepared by slowly mixing stoichiometric amounts of sodium oxalate (Sigma Aldrich) and calcium chloride (Sigma Aldrich) at 273 K in water. To remove the excess sodium chloride the nanocrystals of weddellite were filtered, washed with deionized water and carefully dried. In order to evaluate their stability over the time they were kept for two months at three different hygrometric conditions: (1) 35%, (2) 76% and (3) 95% of RH. Constant values of RH were obtained using desiccators with saturated aqueous solutions of different salts, namely CaCl_2 (RH 35%), NaCl (RH 76%) and Na_2HPO_4 (RH 95%).

Temperature dependent experiments were carried out by FT-IR on thin layers of whewellite and weddellite deposited on an aluminium mirror.

Analytical techniques

- (1) Micro-Infrared spectra were collected with a Nicolet Nexus FT-IR spectrometer coupled to a Continuum Thermo-Electron microscope equipped with a liquid nitrogen cooled MCTA detector (4000–600 cm^{-1} spectral range). Temperature controlled spectra have been obtained placing the samples into a FTIR-600 Linkam cell placed under the Cassegrain 15× reflector microscope objective. Spectra were recorded in double transmission, collecting 256 scan on a $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$ area of the sample at 2 or 4 cm^{-1} of resolution.
- (2) A Panalytical X'Pert PRO X-ray powder diffractometer (XRPD) was used to study the transformation of synthesized weddellite at different hygrometric conditions. The instrument is equipped with a X'Celerator detector PW3015/20 and diffraction patterns have been collected from 5° to 60° 2 θ , scan speed 0.21°/s, with a Cu K α -radiation source, working conditions 40 kV and 40 mA. Powdered samples have been spread on an amorphous silicon holder and then analysed.
- (3) Micro-Raman spectra were obtained with a Senterra dispersive μ -Raman spectrometer (Bruker) coupled to an Olympus BX51 microscope with 20×, 50× and 100× objectives (in light and dark field) and equipped with a 1024 × 256 pixels Peltier cooled CCD detector. Measurements were carried out with the 532 nm exciting laser line using a 1200 grooves/mm gratings (3–5 cm^{-1} of spectral resolution). The spectra were recorded with an exposure time of 60 s, 3 accumulations and a maximum of 5 mW laser power at the sample. Spectra were MIN-MAX normalized and baseline corrected.

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