Characterization of vaterite synthesized at various temperatures and stirring velocities without use of additives

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A B S T R A C T

Conditions for the synthesis of vaterite without additives have been investigated ($T = 30 – 90$ °C, stirring velocity = 200–600 rpm). The obtained different $CaCO_3$ polymorphs were characterized with Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRPD) and scanning electron microscopy (SEM). Quantitative phase analysis (QPA) was performed by the Rietveld method. To describe vaterite diffraction patterns, two structural models were employed. Their relative abundance was found to change with the temperature of synthesis. The optimal synthesis conditions for preparing pure vaterite (≥99 wt.%) were found at 60 °C and 600 rpm. This is the first time pure vaterite is obtained at such high temperature without additives. The conditions under which the different polymorphs formed, and their microstructural features, are discussed. In addition, nanoindentation measurements on synthesized vaterite and calcite are firstly reported. The vaterite elastic modulus is higher than that of calcite ($E = 16–48$ GPa and $E = 9–35$ GPa, respectively), whereas the range in hardness was found to be the same for both polymorphs ($H = 0.4–2.8$).

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1. Introduction

Calcium carbonate ($CaCO_3$) has got a remarkable importance in nature as well as in different fields of human activities [1–5]. It is largely employed by living organisms in biomineralization processes and finds widespread use as filler, extender and pigment in the production of paper, rubber, plastic, pharmaceuticals, food, paint, textiles and many other different materials [1–6]. $CaCO_3$, as the main constituent of limestone rocks, has got significant application in the building industry. In the recent years, lime, which is produced from them, has become an important material in the cultural heritage conservation for designing repair mortars compatible with the existing historic materials [7,8].

In its different mineral modifications, calcium carbonate is highly abundant in the earth crust, occurring as calcite, aragonite and vaterite (anhydrous crystalline polymorphs) or, ikaite (calcium carbonate hexahydrate) and calcium carbonate monohydrate, (hydrated crystal form) [9]. Amorphous $CaCO_3$ (ACC) was also described [10]. However, ACC is thermodynamically unstable under ambient conditions and transforms at the initial stages of the carbonation process into vaterite and/or calcite [10–13]. Of the three anhydrous crystalline forms of calcium carbonate, calcite is the most thermodynamically stable under ambient conditions. During synthesis, crystallization of the three anhydrous crystalline polymorphs of $CaCO_3$ was found to be strongly dependent upon the reaction conditions, as pH of the solution, temperature,

pressure, degree of supersaturation, ion concentration, ionic strength, type and concentration of additives, the presence of impurities etc. [14–17]. It was found that high CO_2 pressure and pH in the range 8.5–10.5 favor vaterite formation [17–20]. On the other hand, pH values close to 7 and higher than 11, as well as low CO_2 pressure, favor calcite precipitation [16,21]. It has been also reported that excess of Ca^{2+} ions may favor the rapid transformation of vaterite into calcite [22]. Aragonite typically precipitates at higher temperatures and at pH < 11 in the presence of magnesium and Mg^{2+} ions [16]. Several other publications were focused on the synthesis of vaterite at various temperatures [23–27], however, the experimental procedures were varied by using different reactants (Na_2CO_3, NH_4HCO_3), their concentrations and volumes, rate of additions, stirring procedures, aging times.

As part of a project aimed at the study of carbonation processes and the occurrence of the different $CaCO_3$ polymorphs in lime mortars, this work is focused on the synthesis of vaterite without use of additives. The influence of reaction conditions, temperature and stirring velocities, on vaterite formation, has been investigated. Results of spectroscopic and microscopic analysis as well as mechanical testing with nanoindentation technique are reported.

2. Materials and methods

2.1. Synthesis of vaterite and calcite

The synthesis of vaterite was conducted modifying an existing procedure described elsewhere [28,29]. The reagents, their concentration and rate of addition were the same as reported in [29].

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$CaCl_2 \cdot 2H_2O$ (p.a.) and K_2CO_3 (p.a.) were purchased from Lach-Ner (Czech Republic) and used as received. Aqueous solutions ($c = 2$ mol l^{-1}, $V = 50$ ml) of these reactants were prepared using deionization water (Barhstead Smart2pure, Thermo Scientific). Deionization water employed had the following characteristics: $\chi = 0.055$ μS cm^{-1}; $R = 18.2$ MΩcm; pH = 8.2.

The synthesis of vaterite was conducted in a 250 ml beaker placed in a water bath Wisebath® WB (Witeg). Solutions were continuously mixed using an overhead stirrer Wisd HT120DX (Witeg) with 3-bladed stainless steel impeller (Ø = 8 mm, l_{rod} = 500 mm, Ø$_{blade}$ = 50 mm). The aqueous solution of $CaCl_2 \cdot 2H_2O$ was added to aqueous solution of K_2CO_3 at 25 ml min^{-1} rate with the help of a peristaltic pump (type 3200, Welch).

Reactions between aqueous solutions of $CaCl_2 \cdot 2H_2O$ and K_2CO_3 were followed at different temperatures (30 °C, 60 °C, 80 °C, 90 °C) at 600 rotations per minute (rpm) stirring velocity and with different stirring velocities (200 rpm, 400 rpm and 600 rpm) at 60 °C. After the addition of the whole aqueous solution of $CaCl_2 \cdot 2H_2O$, the mixture was immediately filtered on filter paper (pore size 5–8 μm, Grade 292 Munktell) in a Buchner funnel and then the precipitate was washed with deionization water several times to ensure the complete removal of mother liquor. Small volume of acetone was used for speed-up drying. The precipitate was then stored in a vacuum desiccator containing silica gel. Finally, the dried white powder was carefully grinded in an agate mortar.

Pure calcite was prepared from non-pure vaterite synthesized at 30 °C and 600 rpm (mixture of vaterite and calcite in the ratio 86 wt.%:14 wt.%). About 10 g of this mixture was dispersed in 200 ml of deionized water in a round-bottom flask fitted with condenser. The suspension was refluxed at 100 °C for 60 min. Subsequently, the suspension was filtered, dried and stored as described above.

2.2. Fourier transform infrared spectrometry analysis

Approximately 0.5 g of powder was gently ground by hand in an agate mortar and then 1 mg of each sample was added to 150 mg of dried KBr (IR-grade, Sigma-Aldrich). These mixtures were then carefully homogenized by hand and pressed into pellets (13 mm diameter). Pellets were measured in transmission mode by Fourier transform infrared spectrometer (FTIR) Nicolet iN10 equipped with the secondary module iZ10 (both Thermo Scientific). IR spectra were collected in spectral range of 4000–400 cm^{-1} at 2 cm^{-1} spectral resolution with 32 scans. Data were analyzed with the OMNIC software v. 8.3.103.

2.3. X-ray diffraction analysis

The phase composition of the samples was studied by X-ray powder diffraction (XRPD) employing a Bragg–Brentano D8 advance diffractometer (Bruker) equipped with a LynxEye 1-D silicon strip detector, using CuKα radiation and Ni filter. Patterns were recorded at 40 kV and 40 mA at ambient temperature in the angular range of 15–90° 2θ with a virtual step scan of 0.01° and counting time 0.4 s per step. The samples were allowed to spin at 15 rpm to increase the particle statistics. Quantitative phase analysis (QPA) was performed by the Rietveld method [30] using Topas 4.2 from Bruker AXS.

2.4. Scanning electron microscopy analysis

Products of the vaterite and calcite formation were examined with a high-resolution scanning electron microscope (SEM) Quanta 450 FEG (FEI) using a secondary electron detector. Analyses were performed at accelerating voltage between 5 and 20 kV. Powder samples were dispersed on carbon tape and gold coated with a 5 nm thick layer.

2.5. Nanoindentation analysis

Samples were tested with TI 750 L Ubi (Hysitron) nanoindentor. A three-sided pyramidal diamond Berkovich indenter and the Oliver–Pharr method [31,32] were used to measure the elastic modulus and hardness. For each sample tested, 400 individual indentations were performed on a grid 20 × 20 with spacing between indents of 10 μm. Maximum load was $P_{max} = 0.5$ mN, load increased linearly for 5 s to reach maximum load, held at P_{max} for 2 s and then unloaded linearly for 5 s.

Sample of pure vaterite and calcite were prepared in form of pellets to assure identical shape for comparison of results. Pellets (13 mm diameter) were made from 0.250 mg of samples and pressed for 30 s with force of 40 kN and then pressed for the same time with force 80 kN by means of an hydraulic press. In our specimens, force and depth of penetration were recorded. Initial unloading stiffness is expressed as follows:

$$S = \frac{dP}{dh} = \frac{2E^* \sqrt{A}}{\sqrt{\pi}} \Rightarrow E^* = \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}} \frac{dP}{dh} \tag{1}$$

$$\frac{1}{E^*} = \frac{(1-v^2)}{E} + \frac{(1-v_i^2)}{E_i} \tag{2}$$

where A is the projected contact area at load values peak, E^* is the reduced elastic modulus and E and v are Young's modulus and Poisson's ratio for the sample and E_i and v_i are the same parameters for the indenter tip [32,33]. For Berkovich indenter used in the experiments, the elastic modulus E_i is 1140 GPa and Poisson's ratio v_i was 0.07. Each calcium carbonate polymorph sample was scanned by in-situ Scanning Probe Microscopy (SPM) imaging to select a suitable place for experimental testing with minimum roughness. Average roughness of all samples was below 50 nm. All measurements were performed in load controlled mode.

3. Results and discussion

The synthesis of vaterite was performed at four different temperatures, while the effect of the stirring velocity was tested for samples prepared at 60 °C. Band assignment for FTIR of $CaCO_3$ polymorphs is well established [34–36]. These absorption bands correspond to symmetric C—O stretching mode (v_1), CO_3 out-of-plane bending mode (v_2), doubly degenerated asymmetric C—O stretching mode (v_3) and doubly degenerated in-plane OCO deformation bending mode (v_4).

The spectral region between 1000 cm^{-1} and 600 cm^{-1} was selected for qualitative analysis, because of severe peak overlapping of the different polymorphs in other spectral regions. As evident from Fig. 1, the prepared polymorphs have characteristic absorption bands in the selected region. Vaterite: v_2 at 849 cm^{-1} and 877 cm^{-1}, v_4 at 744 cm^{-1}. Calcite: v_2 at 877 cm^{-1}, v_4 at 712 cm^{-1}. Aragonite: v_2 at 854 cm^{-1}, v_4 at 700 cm^{-1} and 712 cm^{-1}. At 877 cm^{-1}, overlapping of vaterite and calcite absorption bands is present. The same occurs at 712 cm^{-1} for calcite and aragonite. The transformation of the less thermodynamic stable polymorphs into calcite was not observed during preparation of samples for FTIR analysis.

As depicted in Fig. 1, the sample synthesized at 30 °C was a mixture of calcite and vaterite. Only absorption bands of vaterite were detected in the sample prepared at 60 °C and all three anhydrous crystalline $CaCO_3$ polymorphs were obtained at 80 °C and 90 °C.

Quantification of calcium carbonate polymorphs by XRPD is not trivial, because of the lack of a reliable structural model for the description of the diffraction pattern of vaterite. Its crystal structure has puzzled scientists for almost a century. The first structural model was proposed by Meyer in 1959 who described it with a pseudo-hexagonal unit cell [37]. This structural model was later improved with the introduction of a superstructure rotated 30º about the c axis from the main one [38,39]. More recently, other models have been proposed with orthorhombic