

HYDRATES OF BARIUM HYDROXIDE. PREPARATION, THERMAL DECOMPOSITION AND X-RAY DATA

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ABSTRACT

From rehydration experiments the hydrates $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$, $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$, $\beta\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$, and $\gamma\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$ have been found in the system $\text{Ba(OH)}_2\text{—H}_2\text{O}$. Thermoanalytical measurements (DTA, TG, DTG, high temperature X-ray diffraction, high temperature Raman scattering) on these hydrates are reported. Thermal decomposition of $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$ and $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$ always results in the formation of $\beta\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$, the stable form of the monohydrates at ambient temperature. Dehydration of $\beta\text{-}$ and $\gamma\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$, both of which form anhydrous $\beta\text{-Ba(OH)}_2$ as the first product of decomposition, starts at 105 and 115°C, respectively. Single crystals of $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$ and $\gamma\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$ were prepared from $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$ meltings and from ethanolic solutions of Ba(OH)_2 , respectively. The crystal data are: $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$ (orthorhombic, $Pnma$): $a = 764.0(2)$, $b = 1140.3(5)$, $c = 596.5(1)$ pm, $Z = 4$; $\gamma\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$ (monoclinic, $P2_1/m$ or $P2_1$): $a = 704.9(2)$, $b = 418.4(1)$, $c = 633.3(1)$ pm, $\beta = 111.45(2)^\circ$, $Z = 2$.

INTRODUCTION

Whereas magnesium and calcium hydroxide only exist as the anhydrous compounds Mg(OH)_2 and Ca(OH)_2 , the hydroxides of the heavier alkaline earth elements, strontium and barium, form several hydrates. With regard to strontium hydroxide, the two hydrates $\text{Sr(OH)}_2 \cdot 8 \text{H}_2\text{O}$ and $\text{Sr(OH)}_2 \cdot 1 \text{H}_2\text{O}$ have been found besides the anhydrous Sr(OH)_2 . All these compounds have been well established. For barium hydroxide nearly all imaginable hydrates with 1–8 water molecules of crystallization and two polymorphic forms of anhydrous Ba(OH)_2 , $\alpha\text{-}$ and $\beta\text{-Ba(OH)}_2$, have been discussed in literature (refs. 1–9, and the older literature cited in refs. 1, 5 and 9). But X-ray or spectroscopic data have only been given for $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$ [2,10,11], $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$ [5], $\beta\text{-}$ and $\gamma\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$ [2,5–7,12], and for anhydrous $\alpha\text{-}$ and $\beta\text{-Ba(OH)}_2$ [5,6,13].

The obtained results on the hydrates of barium hydroxide are mainly based on the thermal decomposition of the octahydrate and contradictory conclusions have been drawn for the formation of several hydrates in the system $\text{Ba(OH)}_2\text{—H}_2\text{O}$. This is possibly caused by the fact that thermal decomposition of the higher hydrates often occurs in very different ways, depending on operation conditions [7–9]. Therefore, and in order to con-

firm formerly observed polymorphic forms of $\text{Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$ [5,6] and to establish Raman spectroscopic investigations on the hydrates of barium and strontium hydroxide [14], we reinvestigated the system $\text{Ba(OH)}_2\text{—H}_2\text{O}$ both by thermal decomposition (DTA, TG, DTG, high temperature X-ray diffraction, high temperature Raman scattering) and by rehydration experiments. Furthermore, we tried to obtain single crystals of the found hydrates for full X-ray characterization.

EXPERIMENTAL

Starting materials

$\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$ was prepared in the usual way by recrystallization from aqueous barium hydroxide solutions at room temperature. $\beta\text{-Ba(OH)}_2$ was prepared by dehydration of $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$ in a vacuum ($\sim 1 \text{ Pa}$) at 140°C . All preparations were carried out under exclusion of CO_2 . The composition of the obtained samples was confirmed by titrimetric and thermogravimetric measurements.

Apparatus and technique

DTA, TG, and DTG measurements were made in an argon stream (50 ml min^{-1}) using a thermoanalyzer Linseis L62 and a thermobalance Linseis L81, respectively. The sample weight was 30–50 mg. The heating rates were 1, 2 and $5^\circ \text{C min}^{-1}$. Al_2O_3 was used as a reference.

High temperature X-ray diffraction patterns were obtained using an Enraf–Nonius Guinier Simon camera with $\text{CuK}\alpha_1$ radiation. The heating rate was 10°C h^{-1} . Quartz capillaries (0.3 mm diameter) were taken for sample holders.

X-Ray single crystal data were obtained using a Huber precession camera with $\text{MoK}\alpha$ radiation. Unit cell dimensions have been refined by the least squares method using powder data obtained with a Huber Guinier camera with $\text{CrK}\alpha_1$ radiation against quartz as an internal standard.

High temperature Raman spectra were recorded with a Coderg T 800 Raman spectrometer excited by 488.0 nm radiation from an Ar^+ ion laser and analyzed with the usual right-angle geometry. The samples were heated in closed glass tubes by means of a Coderg model CRN2 variable temperature cell.

RESULTS AND DISCUSSION

Besides the thermal decomposition of higher hydrates, rehydration of the anhydrous salts with stoichiometric amounts of water in closed tubes and subsequent Raman spectroscopic characterization of the samples (details have been given elsewhere [15]) is a proper method for analyzing what kinds of crystal hydrates exist. From such rehydration experiments, the

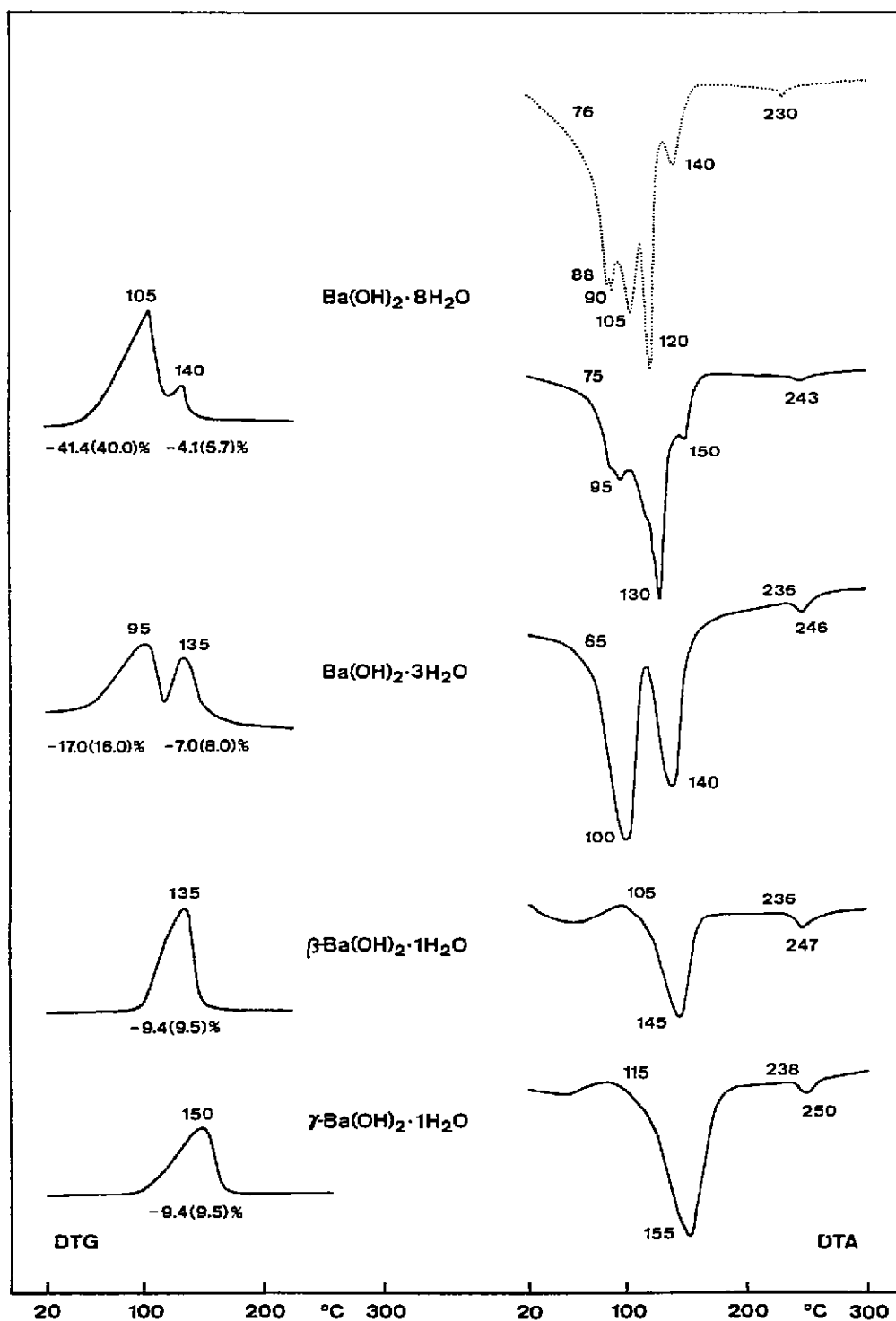


Fig. 1. DTG curves and DTA diagrams of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$, $\text{Ba(OH)}_2 \cdot 3\text{H}_2\text{O}$, $\beta\text{-Ba(OH)}_2 \cdot 1\text{H}_2\text{O}$, and $\gamma\text{-Ba(OH)}_2 \cdot 1\text{H}_2\text{O}$: full line, heating rate 5°C min^{-1} ; dotted line, 2°C min^{-1} , given temperatures, intersections and peak maxima; peaks (maxima): $90\text{--}130^\circ\text{C}$, dehydration of $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Ba(OH)}_2 \cdot 3\text{H}_2\text{O}$, respectively; $135\text{--}150^\circ\text{C}$, dehydration of $\beta\text{-Ba(OH)}_2 \cdot 1\text{H}_2\text{O}$; $150\text{--}155^\circ\text{C}$, dehydration of $\gamma\text{-Ba(OH)}_2 \cdot 1\text{H}_2\text{O}$; $230\text{--}250^\circ\text{C}$, phase transition $\beta\text{-Ba(OH)}_2$ to $\alpha\text{-Ba(OH)}_2$.

hydrates $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$, $\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$, and two forms of the monohydrate, viz. β - and γ - $\text{Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, were found in the system $\text{Ba}(\text{OH})_2$ — H_2O . In contrast to this method, dehydration experiments on $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ and $\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$ always result in the formation of β - $\text{Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ as the only dehydration product besides anhydrous barium hydroxides. The DTG curves and the DTA diagrams of the four barium hydroxide hydrates are shown in Fig. 1. A detailed discussion of the obtained IR and Raman spectroscopic data will be given elsewhere [14].

Octahydrate

$\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$, which crystallizes from aqueous solutions at ambient temperature, is well known. The crystal structure was established by Manohar and Ramaseshan [10]. The octahydrate melts in its own water of crystallization at 78°C , as confirmed by visual examination.

Thermogravimetric experiments indicate that $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ dehydrates in two steps (see Fig. 1). During the first step (60 – 125°C) 7 moles of water are lost (weight loss: 41.4%, theory: 40.0%), forming β - $\text{Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$. In the second step (125 – 150°C) another mole of water is lost (weight loss: 4.1%, theory: 5.7%) under formation of β - $\text{Ba}(\text{OH})_2$. Both reactions were confirmed by high temperature X-ray diffraction. The DTA diagrams (see Fig. 1) show up to four peaks in the first dehydration stage (60 – 135°C). These peaks might be assigned to the melting point of the octahydrate, to evaporation of H_2O from the melt and to formation and decomposition of the trihydrate. But the latter could not be supported by high temperature X-ray diffraction.

Trihydrate

$\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$, first described by Bauer [16], was controversially discussed in literature for a long time [1,9]. But the existence of $\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$ was confirmed by solubility [5] and gas-phase equilibrium [3] measurements. Pure samples of $\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$ can be prepared by simple annealing of stoichiometric amounts of anhydrous $\text{Ba}(\text{OH})_2$ and H_2O in closed glass tubes at 80°C . Single crystals were obtained from $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ meltings as described by Bauer [16]. $\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$ crystallizes in the orthorhombic space group $Pnma$ (from both systematic absences and the mutual exclusions of IR and Raman frequencies [14]) with four formula units in a cell of dimensions: $a = 764.0(2)$, $b = 1140.3(5)$, $c = 596.5(1)$ pm. Dehydration of the trihydrate, which starts at 65°C [intersection of the first endothermic peak in the DTA curves (see Fig. 1)], occurs in two stages. During the first stage (65 – 120°C) 2 moles of water are lost (weight loss: 17.0%, theory: 16.0%), forming β - $\text{Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, as shown by high temperature X-ray diffraction patterns (see Fig. 2) and high temperature Raman studies (see Fig. 3).

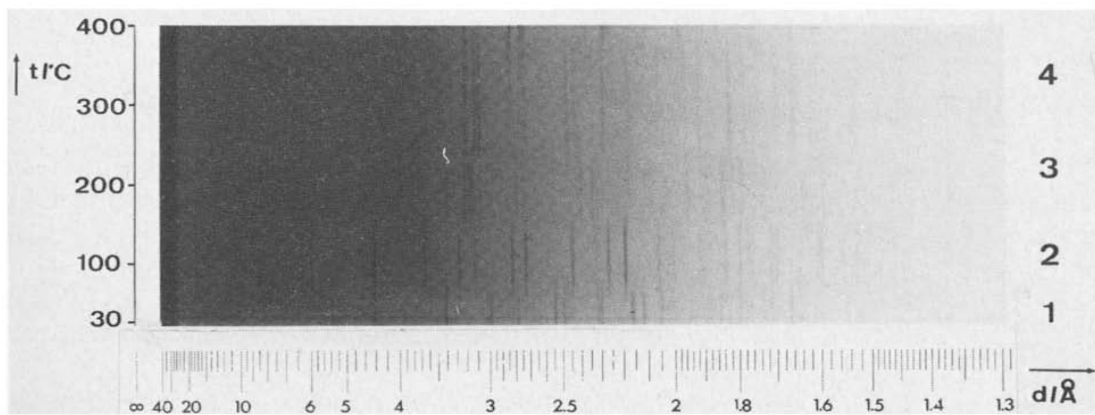


Fig. 2. High temperature X-ray diffraction patterns of $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$: 1, $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$; 2, $\beta\text{-Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$; 3, $\beta\text{-Ba(OH)}_2$; 4, $\alpha\text{-Ba(OH)}_2$.

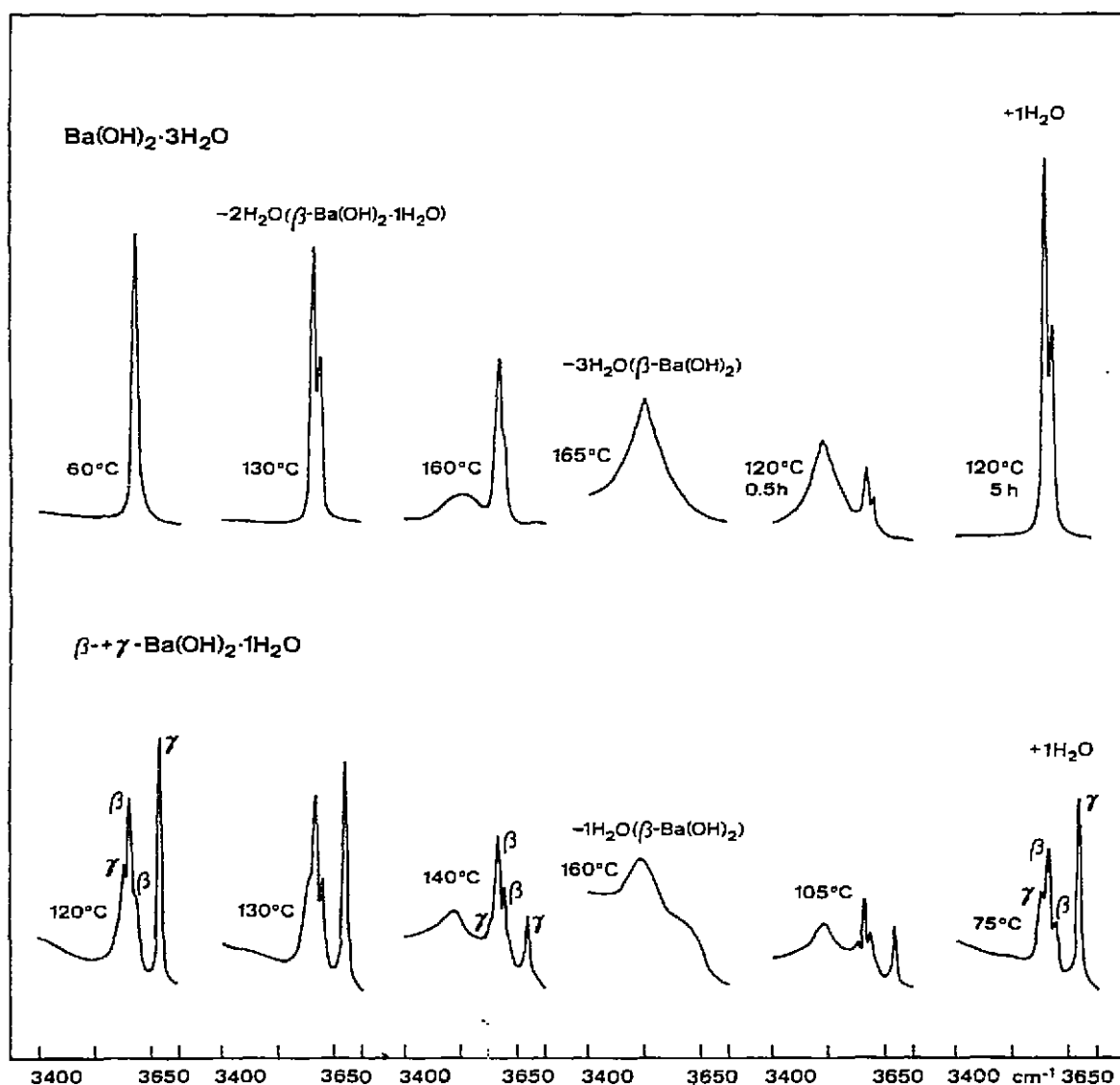


Fig. 3. Dehydration and rehydration studies (closed system) on $\text{Ba(OH)}_2 \cdot 3 \text{H}_2\text{O}$ and on a mixture of γ - and β - $\text{Ba(OH)}_2 \cdot 1 \text{H}_2\text{O}$ with the help of high temperature Raman spectroscopic measurements (stretching mode region of the hydroxide ions, see also refs. 14 and 15).

Monohydrates

Three polymorphic forms of $\text{Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ have been described in literature: the well-known $\beta\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, which is stable at ambient temperature, $\alpha\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, a high temperature modification [5], and $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, which we found by rehydration experiments [6].

$\beta\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, which can be obtained both by dehydration of the two higher hydrates and by rehydration experiments, crystallizes in the orthorhombic space group $P2_1am$ [12].

$\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ is formed as the first product both by rehydration of anhydrous $\text{Ba}(\text{OH})_2$ at room temperature and by isothermal dehydration of $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ at temperatures below 60°C . Hydrolysis of other barium compounds, e.g., $\text{Ba}(\text{OR})_2$ or Ba_3N_2 [17], also gives $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, generally together with other hydrates of $\text{Ba}(\text{OH})_2$. $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ cannot be obtained by non-isothermal dehydration of $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ or $\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$.

Pure samples and single crystals of the γ -monohydrate were obtained by crystallization from an ethanolic solution of $\text{Ba}(\text{OH})_2$ (see also Bergmann et al. [18]). The solutions were prepared by extracting anhydrous $\beta\text{-Ba}(\text{OH})_2$ with dry ethanol in a closed reflux apparatus, whereby the condensed alcohol slowly dropped onto the hydroxide and then back into the vessel, under dissolving small amounts of the hydroxide. The alcohol reacts with $\text{Ba}(\text{OH})_2$, forming the ethoxide, which is easily soluble in ethanol [19], and the hardly soluble $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$. $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ was isolated by decanting the ethoxide solution. $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ crystallizes in the monoclinic space groups $P2_1/m$ or $P2_1$ with two formula units in a cell of dimensions: $a = 704.9(2)$, $b = 418.4(1)$, $c = 633.3(1)$ pm, $\beta = 111.45(2)^\circ$.

The thermal decomposition of the γ -monohydrate starts at 115°C (intersection of the first peak in the DTA), that of $\beta\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ at 105°C (see Fig. 1). Both monohydrates decompose to anhydrous $\beta\text{-Ba}(\text{OH})_2$, as confirmed by high temperature X-ray diffraction. Annealing of $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ at temperatures below 140°C results in the formation of the β -modification (see Fig. 3). Obviously $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ is unstable compared with $\beta\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$, at least at ambient temperature.

A monoclinic form of $\text{Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ is also described by Evans et al. [4]. Whether this monohydrate is identical with γ -monohydrate cannot be proved, because X-ray or spectroscopic data are not published.

$\alpha\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ was found by Michaud [5] with the help of solubility studies and was claimed to be the stable form at temperatures near 200°C under the equilibrium pressure of the solution. We are not able to decide whether this $\alpha\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ is identical with $\gamma\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$. All our experiments, e.g., annealing of $\text{Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ or $\text{Ba}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$ at elevated temperatures, high temperature X-ray diffraction, high temperature Raman studies (see Fig. 3), to find Michaud's $\alpha\text{-Ba}(\text{OH})_2 \cdot 1 \text{H}_2\text{O}$ or to convert the β -monohydrate into the γ -form were negative.

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