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On the existence of lower hydrates of M(OH)X(M is Sr, Ba; X is Cl, Br, I)

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Abstract

Preparation of the lower hydrates of M(OH)X(M is Ba, Sr; X is Cl, Br, I) was attempted both by dehydration experiments of $Ba(OH)X \cdot 2H_2O$ (X is Cl, Br), $Ba(OH)I \cdot 4H_2O$, and $Sr(OH)X \cdot 4H_2O$ (X is Cl, Br), and by rehydration of the anhydrous salts using infrared, Raman, and high-temperature Raman spectroscopic methods. Thus, the hitherto unknown compound $Ba(OH)I \cdot 2H_2O$ has been established and $Ba(OH)Cl \cdot 0.5H_2O$, but not $Ba(OH)Br \cdot 0.5H_2O$, has been confirmed. $Ba(OH)I \cdot 0.5H_2O$ and lower hydrates of Sr(OH)X were not obtained. $Ba(OH)I \cdot 2H_2O$ is isostructural with $Ba(OH)X \cdot 2H_2O$ (X is Cl, Br). The crystal structure of $Ba(OH)Cl \cdot 0.5H_2O$ is not known so far. The dehydration and fusing temperatures of $M(OH)X \cdot 4H_2O$ and M(OH)X, respectively, are presented.

Keywords: Dehydration; Halide; Hydration; IRS; Raman

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1. Introduction

The higher hydrates of the barium and strontium hydroxy halides $Ba(OH)X \cdot 2H_2O$ (X is Cl, Br), $Sr(OH)X \cdot 4H_2O$ (X is Cl, Br), and $Ba(OH)I \cdot 4H_2O$ are well established [1–6]. The crystal structures of these compounds are noteworthy in so far as that the former belong to the very few structures in which OH^- ions are not coordinated to metal ions [3,4,7]. The latter possess water molecules which are the most distorted ones known so far. This is due to the extremely differently strong hydrogen bonds formed [6,8]. Literature data on the lower hydrates of these basic salts are scarce [1,5]. The only compounds mentioned are $Ba(OH)X \cdot 0.5H_2O$ with X being Cl and Br, apart from the well-established anhydrous salts [1,5,9,10].

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In this paper, we demonstrate the existence of lower hydrates of M(OH)X (M is Ba, Sr; X is Cl, Br, I) by means of IR, Raman, and high-temperature Raman spectroscopic methods, and by thermoanalytical (DTA, TG, DTG) measurements.

2. Experimental

The starting materials were $Ba(OH)X \cdot 2H_2O$ (X is Cl, Br) and $Ba(OH)I \cdot 4H_2O$. They (as well as deuterated specimens) were prepared by crystallization of aqueous solutions of the respective halides and hydroxides in molar ratios of 10: 1; for details, see Refs. [3,9,10].

Preparation of the lower hydrates of the title compounds was attempted by dehydration of the higher hydrated hydroxide halides and by rehydration of anhydrous M(OH)X, respectively.

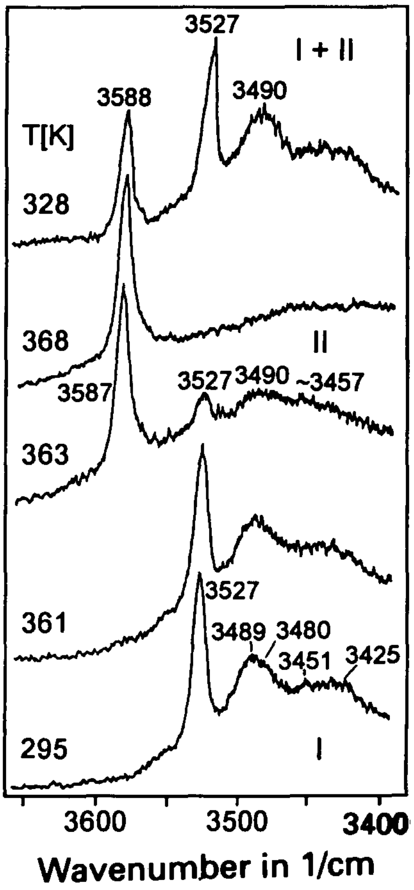

Fig. 1. High-temperature Raman spectroscopic dehydration studies of $Ba(OH)I \cdot 4H_2O$ (closed tube): I, $Ba(OH)I \cdot 4H_2O$; II, Ba(OH)I.

DTA (difference thermal analysis), TG (thermogravimetry) and DSC (differential scanning calorimetry) measurements were carried out on Linseis L 62, Mettler TA 4000, and Perkin-Elmer DSC 7 systems, using silica tubes and gold crucibles as sample holders, respectively. Heating rates were 5–10°C min^{-1}. Al_2O_3 was used as reference.

IR spectra of dehydrated and rehydrated samples, respectively, were recorded on a Perkin-Elmer model 580 spectrophotometer (resolution < 1 cm^{-1}) using KBr and CsI discs as well as Nujol and Fluorolub mulls. Raman spectra, with the samples in

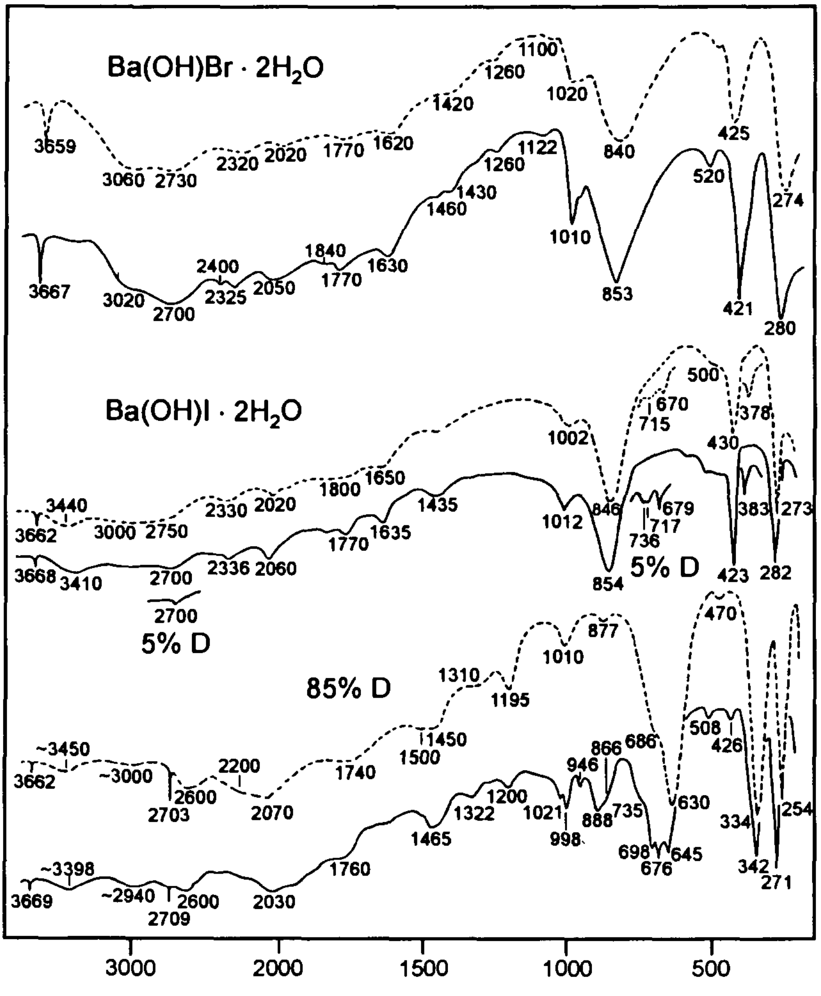

Fig. 2. Infrared spectra (CsI discs) of Ba{O(H, D)}X·2(H, D)$_2$O (X is Br, I) at ambient (- - -) and liquid nitrogen temperature (——). Assignment of the observed bands (cm^{-1}) [3]: 3662 and 2703, stretches of OH$^-$ and OD$^-$; 2700–3000, stretches of H_2O; 846 and 630, librations of H_2O and D_2O; 430 and 334, librations of OH$^-$ and OD$^-$; < 300 cm^{-1}, translational modes (data for X is I).

glass capillaries, were measured on a Dilor OMARS 89 multichannel Raman spectrograph (resolution $< 4\,\mathrm{cm}^{-1}$) with the usual right-angle geometry. For excitation, the 514.5 nm line of an Ar^+ ion laser was employed. Further details, especially with respect to high-temperature Raman measurements, are given elsewhere [9, 11].

3. Results and discussion

3.1. $Ba(OH)I \cdot 2H_2O$

The existence of the hitherto unknown $Ba(OH)I \cdot 2\,H_2O$ compound was first detected by dehydration of $Ba(OH)I \cdot 4\,H_2O$ in a CsI matrix in the course of IR spectroscopic measurements [9]. The tetrahydrate dehydrates very easily to the anhydrous salt. With

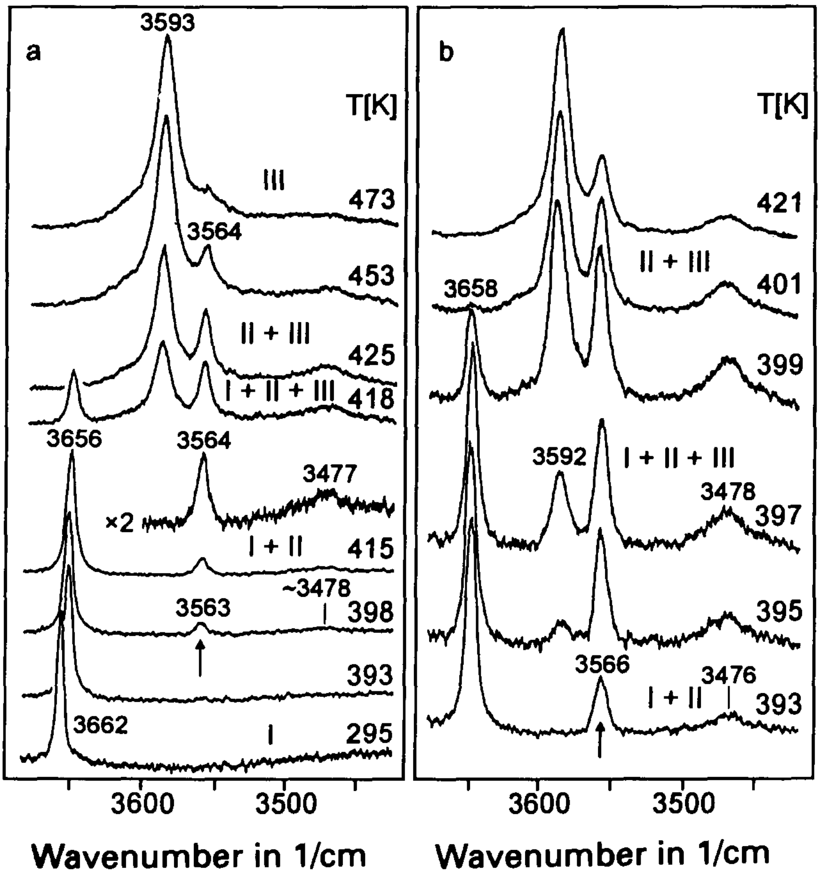

Fig. 3. High-temperature Raman spectroscopic dehydration studies of $Ba(OH)Cl \cdot 2H_2O$: a, closed tube; b, open tube; I, $Ba(OH)Cl \cdot 2H_2O$; II, $Ba(OH)Cl \cdot 0.5\,H_2O$; III, $Ba(OH)Cl$; ↑, OH stretching mode (OH^- ions) of $Ba(OH)Cl \cdot 0.5H_2O$.

thermal analyses (DTA, etc.), dehydration starts at 348 K (onset, T_{max}, 368 K; open crucible). The dihydrate is obtained if the disc is produced with a pressure of 10^9 Pa (10 t cm^{-2}) using a cooled mortar. High-temperature Raman studies, however, do not reveal the existence of this compound, either on dehydration of the tetrahydrate or on rehydration of Ba(OH)I (see Fig. 1).

IR spectra of Ba{O(H, D)} I·2 H_2O are shown in Fig. 2. The spectra are very similar to those of Ba(OH)Br·2 H_2O [3] indicating that the hydrogen bonds formed are very similar in these compounds. Obviously, the hydrogen bond system present in Ba(OH)Cl·2 H_2O-type structures cannot be further expanded on substitution of Br by I without destabilization of the structure. This also explains the low stability of the iodide under discussion.

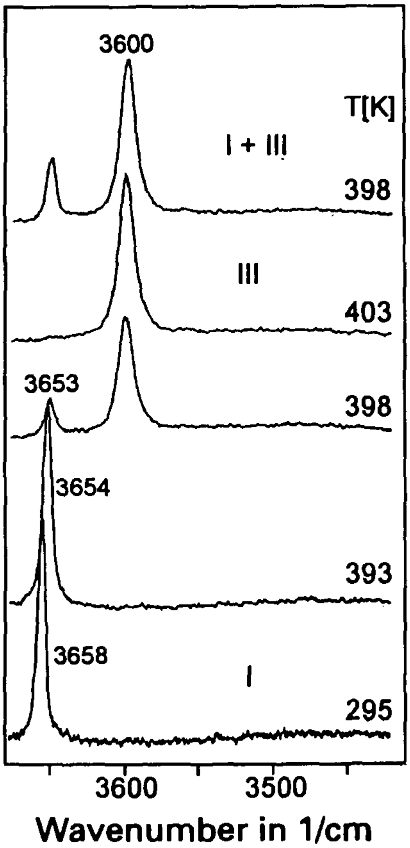

Fig. 4. High-temperature Raman spectroscopic dehydration studies of Ba(OH)Br·$2H_2O$ (closed tube): I, Ba(OH)Br·$2H_2O$; III, Ba(OH)Br.

Table 1
Fusing temperatures (K) and fusing energies (kJ mol^{-1}) of M(OH)X (DSC measurements, Au crucibles)

	Ba(OH)Cl	Ba(OH)Br	Ba(OH)I	Sr(OH)Cl	Sr(OH)Br	Sr(OH)I
T_{onset}	805	850	937	782	848	934
T_{max}	814	863	949	793	863	943
H_M	21.4	22	36.5	22.4	17.2	29.0

3.2. Ba(OH)X·0.5 H_2O (X is Cl, Br)

Unlike Ba(OH)Br·0.5 H_2O, Ba(OH)Cl·0.5 H_2O can be prepared by both dehydration of the dihydrate at ambient temperature over P_2O_5 and by rehydration of the anhydrous compound with stoichiometric amounts of H_2O[3, 5]. On dehydration of Ba(OH)Cl·2H_2O at higher temperatures (DTA and DSC studies [2,3,9,12]), the two water molecules are usually emitted in one step. These findings were confirmed by high-temperature Raman experiments (see Figs. 3 and 4), which indicate that Ba(OH)Cl·0.5 H_2O, but not Ba(OH)Br·0.5 H_2O, is a real compound. Formation of Ba(OH)Cl·0.5 H_2O starts at 390 K, and that of Ba(OH)Cl starts at 410 K (closed tube). The hemihydrate can be detected and distinguished from other barium hydroxide chlorides by the Raman band at 3564 cm^{-1} which is due to the stretching mode of the OH^- ions.

3.3. Lower hydrates of Sr(OH)X

Compounds like Sr(OH)X·0.5 H_2O and Sr(OH)X·2 H_2O (X is Cl, Br) have not been established. Sr(OH)X·4 H_2O (X is Cl, Br) dehydrate to the anhydrous compounds in one step. Dehydration starts at 321 and 335 K, respectively (onset, T_{max}, 351 and 361 K, open tube, DTA) [9]. In the case of the iodide, the tetrahydrate reported in Refs. [1, 5] could not be prepared. Therefore, its existence is debatable.

3.4. M(OH)X (M is Ba, Sr; X is Cl, Br, I)

Anhydrous Ba(OH)X (X is Cl, Br, I) and Sr(OH)I (all laurionite type [9, 10, 13, 14]), Sr(OH)Br (space group $P2_13$ [13]), and Sr(OH)Cl, Cd(OH)Cl-type [13], melt undecomposed at 780–940 K (see Table 1). On further heating, decomposition to MO and M_4OX_6 [15] occurs.

Acknowledgments

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