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A study of the phase transitions in $Ba(OH)_2$, and a comment on the fusion of $Sr(OH)_2$

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Abstract

The polymorphism of $Ba(OH)_2$ described in the literature, has been investigated by crystallographic, infrared spectroscopic, and calorimetric techniques. From the X-ray powder diffraction pattern it has been found that the β phase has a monoclinic structure (space groups $P2_1$ or $P2_1/m$) with $a = 6.7835(6)$, $b = 7.9268(6)$, $c = 9.4246(10)$ Å and $\beta = 95.823(9)^\circ$. A phase transformation to α-$Ba(OH)_2$ occurs at 526 ± 1 K, which upon cooling in a dry atmosphere remains unchanged. However, a reversible phase transition $\alpha \rightarrow \beta$ is observed in the presence of traces of water vapour, acting as a catalyst. The thermodynamic properties of α-$Ba(OH)_2$, including fusion, have been measured. In addition, the fusion properties of $Sr(OH)_2$ are discussed.

Keywords: Barium hydroxide; Calorimetry; Crystal structure; Enthalpy of formation; Phase transformation

1. Introduction

Two modifications of $Ba(OH)_2$ have been described in the literature [1–4], a low-temperature β phase and a high-temperature α phase, but the nature of the $\beta \rightarrow \alpha$ transition has not been established. Bück and Barnighausen [3] reported that α-$Ba(OH)_2$ has an orthorhombic structure, whereas that of β-$Ba(OH)_2$ has not been reported. These authors, and also Michaud [1,2], observed that the α- phase can be maintained at room temperature upon cooling in a dry atmosphere and that traces of water vapour enhance the back reaction, suggesting that the β-to-α transition may not be reversible.

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As part of a systematic investigation of the thermodynamic properties of the solid hydroxides $Sr(OH)_2$ and $Ba(OH)_2$ [5,6], we have studied the phase transition in $Ba(OH)_2$ in detail by calorimetric, X-ray diffraction, infrared-spectroscopic, and thermal analysis techniques. In addition, the fusion properties of $Sr(OH)_2$ and $Ba(OH)_2$ are reported.

2. Experimental

A sample of β-$Ba(OH)_2$ was prepared either from barium metal (Cerac; 99.7%) or BaO (obtained by decomposition of Sr-free $BaCO_3$) by the reaction with water vapour at a partial pressure of about 1.3 kPa at 460 K. α-$Ba(OH)_2$ was prepared by heating the β form in a dry argon atmosphere at 600 K in a silver boat for about 8 h. $Sr(OH)_2$ was prepared similarly from SrO at 570 K. The syntheses were performed in silver boats in a purified argon atmosphere saturated with water vapour by passing it through a 0.05 M KOH solution kept in a thermostatted bath at 283 K. The samples were stored and handled in an argon-filled glove-box to avoid contact with water or CO_2. The chemical analyses showed them to be of high purity [5].

The X-ray powder diffraction spectra were recorded with a Guinier–de Wolff camera (Enraf Nonius) using $CuK_{\alpha 1}$ radiation ($\lambda = 1.54060$ Å). α-SiO_2 ($a = 4.9133$ and $c = 5.4053$ Å) was used as an internal standard, and a non-linear correction procedure was applied. The sample was enclosed in a sealed polyethylene bag to avoid reaction with the atmosphere during the measurement. The high-temperature X-ray powder diffraction spectra were recorded in helium or helium–water vapour mixtures ($p(H_2O) = 1.3$ kPa) with a Guinier–Lenné camera (Enraf Nonius) using CuK radiation.

Infrared spectra of α- and β-$Ba(OH)_2$ were recorded with a BOMEM DA3.02 Fourier-transform spectrometer. The samples were contained in KBr discs which were pressed in an argon-filled glove-box. In order to avoid the influence of moisture during the transport of the samples from the glove box to the apparatus, both faces of the pellets were prepared from pure KBr by pressing layer-wise. The spectra were recorded at a vacuum better than 13 Pa in the range 450–5000 cm^{-1} with a resolution of 4 cm^{-1}; 64 scans were co-added, and the combination globar light source–KBr beamsplitter–DTGS detector, was used.

Thermogravimetric analyses were done in a Seiko TG–DTA module, type 320 U in a dried argon atmosphere with a heating rate of 10 K min^{-1}. The DSC runs were recorded in both a commercial Mettler TA-13 apparatus, and a Seiko DSC apparatus, type 220 CU with a heating rate of 5 K min^{-1}, using Zn and Sn as the reference materials. The samples of $Ba(OH)_2$ were measured in open as well as in sealed silver ampoules. Transition temperatures were recorded as onset temperatures; the indicated uncertainties are the standard deviations from a series of different DSC runs.

Enthalpy increments of α-$Ba(OH)_2$ were measured in a drop calorimeter developed by Cordfunke et al., as described previously [7]. The masses of the sample and capsule were almost identical to our previous measurements for β-$Ba(OH)_2$ [6].

3. Results and discussion

3.1. The crystal structure of β-Ba(OH)$_2$

The experimental d-values for β-Ba(OH)$_2$ recorded at room temperature and listed in Table 1, have been indexed using the computer programme ITO [8]. The least squares refinement based on a monoclinic cell gave the following results: $a = 6.7835(6)$ Å, $b = 7.9268(6)$ Å, $c = 9.4246(10)$ Å, $\beta = 95.823(9)°$, $V = 504.16$ Å^3. The systematic extinctions agree with the space groups P2$_1$ or P2$_1$/m. The X-ray density has been calculated on the basis of eight units in the cell as: $d_x = 4.515$ g cm^{-3}. The present d-values are in good agreement with those reported by Michaud [2]. It should be noted that the crystal structure of β-Ba(OH)$_2$ is related to that of γ-Ba(OH)$_2 \cdot$H$_2$O, as reported by Lutz et al. [9].

3.2. The β-to-α transition

Upon transferring the Ba(OH)$_2$ sample to the high-temperature X-ray diffraction camera, the monohydrate Ba(OH)$_2 \cdot$H$_2$O is formed, which decomposes at about 360 K to β-Ba(OH)$_2$. This phase is stable to about 526 K where it transforms into α-Ba(OH)$_2$.

The β-to-α transition in Ba(OH)$_2$ was located in DSC runs as a sharp peak at (526 ± 1)K (Fig. 1). The enthalpy change associated with this transition is $\Delta_{\mathrm{trs}}H° = (3.0 \pm 0.3)$ kJ mol^{-1}, as obtained by integration of the peak area. Upon

Table 1
X-ray powder diffraction data of β-Ba(OH)$_2$

hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}
−101	5.7665	5.7614	10	212	2.4831	2.4839	70
110	5.1391	5.1386	5	023	2.4549	2.4541	60
−111	4.6687	4.6604	20	221	2.4301	2.4305	5
111	4.3689	4.3662	10	−123	2.3668	2.3677	5
012	4.0356	4.0351	30	004	2.3445	2.3440	20
020	3.9652	3.9634	15	−222	2.3296	2.3302	10
−112	3.6056	3.6047	60	032	2.3012	2.3018	40
120	3.4180	3.4176	100	−132	2.2121	2.2125	5
200	3.3759	3.3743	80	−114	2.1971	2.1977	10
112	3.3398	3.3372	80	310	2.1641	2.1641	20
−121	3.2652	3.2654	50	213	2.1060	2.1065	20
121	3.1584	3.1591	30	−223	2.0643	2.0645	40
022	3.0286	3.0267	30	−312	2.0419	2.0421	20
−103	2.9526	2.9525	60	033	2.0179	2.0178	30
013	2.9080	2.9075	50	231	2.0045	2.0046	40
−122	2.8333	2.8318	20	040	1.9818	1.9817	20
103	2.7328	2.7322	30	320	1.9567	1.9564	40
−212	2.7090	2.7075	60	−232	1.9476	1.9472	20
220	2.5693	2.5693	40	041	1.9385	1.9389	30
031	2.5438	2.5432	70	−303	1.9203	1.9205	30

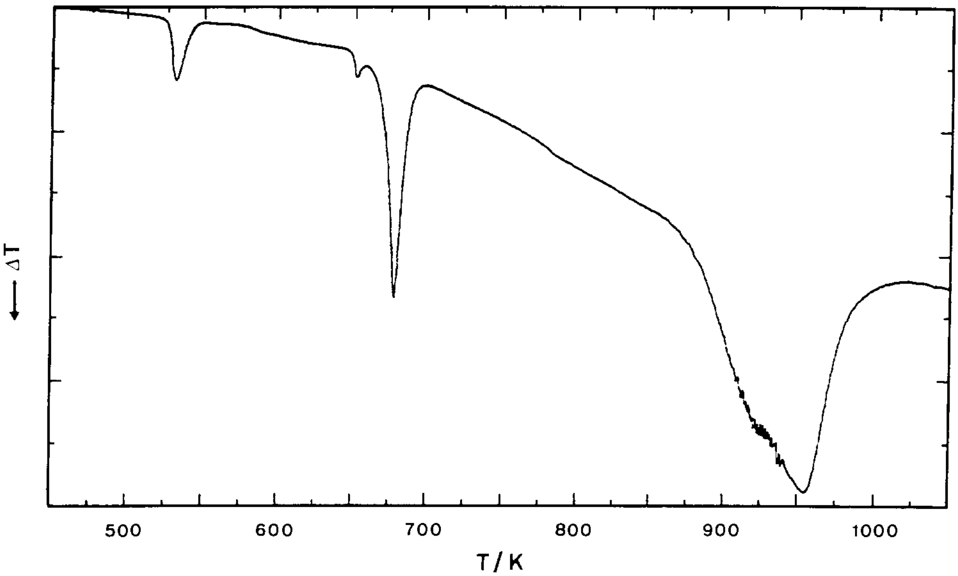

Fig. 1. The DSC diagram of $Ba(OH)_2$.

cooling the transition is not observed, and the alpha modification is maintained to room temperature. These observations are in agreement with the results of Michaud [1, 2] who observed the transition to α-$Ba(OH)_2$ at 523.15 and 518.15 K in two different samples, and reported that it was of a non-reversible nature in the absence of water. Maneva-Pertrova and Nikolova [10] observed the β-to-α transition at 533 and 534.2 K in DTA runs using $Ba(OH)_2 \cdot 8H_2O$ and $Ba(OH)_2 \cdot 8D_2O$ as starting materials, respectively. Using the dihydrates as starting materials their results were, however, 50 K lower.

The dependence of the reversibility on the presence of water was also observed in the present study:

(1) in the absence of water, for example, in an argon-filled dry box, or a closed ampoule, α-$Ba(OH)_2$ can be maintained at room temperature;

(2) by performing DSC or high-temperature diffraction measurements in ($Ar + H_2O$) gas mixtures, the reverse $\alpha \rightarrow \beta$ reaction takes place rapidly upon cooling;

(3) a combined TG–DTA analysis using the sensitive Seiko apparatus, showed that the phase transition of β-$Ba(OH)_2$ to α-$Ba(OH)_2$ takes place without any weight loss.

Infrared spectra of β-$Ba(OH)_2$ and α-$Ba(OH)_2$ obtained in our study, shown in Fig. 2, are clearly different in that the strong –OH stretching vibrations of β-$Ba(OH)_2$ at 3260 and 3490 cm^{-1} are almost absent in α-$Ba(OH)_2$ at 298 K. Instead, broad absorption bands are observed, indicating the formation of strong hydrogen bridges in α-$Ba(OH)_2$, in agreement with the infrared and Raman spectroscopic

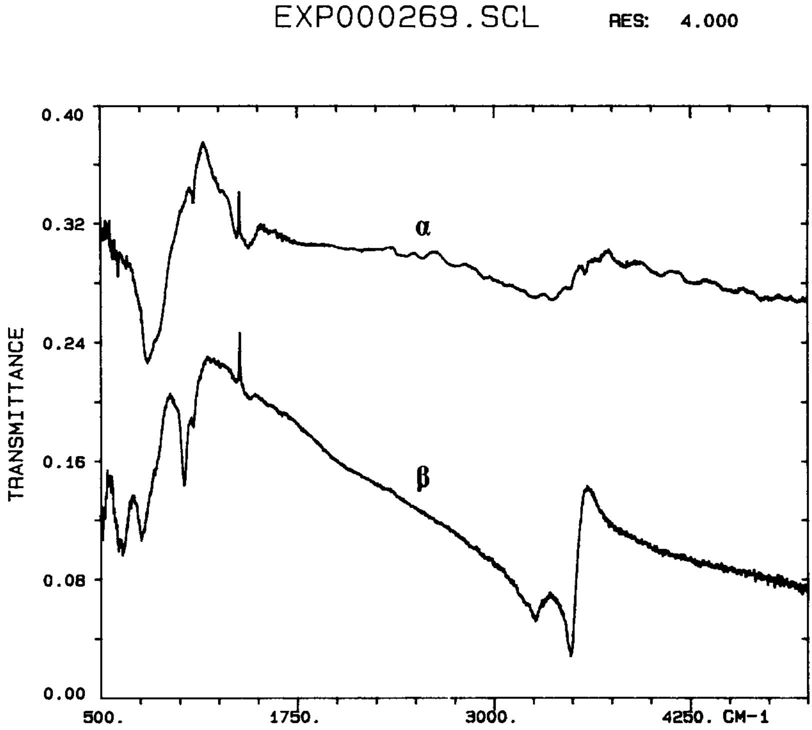

Fig. 2. The infrared spectra of α-$Ba(OH)_2$ (top) and β-$Ba(OH)_2$ (bottom).

measurements by Lutz et al. [4]. It can be concluded that β-$Ba(OH)_2$ should be considered as an anhydrous phase, the phase transition $\alpha \rightarrow \beta$ being catalyzed by traces of water.

3.3. Thermodynamic properties

The enthalpy of formation of α-$Ba(OH)_2$ has been determined from enthalpy of solution measurements in a way similar to that described previously [5]. From the enthalpy of solution of α-$Ba(OH)_2$ in 1.01 M HCl, $-(169.98 \pm 0.36)$ kJ mol^{-1} (mean of three measurements), we obtain for the enthalpy of formation the value $\Delta_f H^\circ$ (298.15 K) $= -(937.0 \pm 1.8)$ kJ mol^{-1}. For the β form we previously found the value $-(940.6 \pm 1.8)$ kJ mol^{-1}—a small summation error was made in the original publication—from which the enthalpy of transition of β- to α-$Ba(OH)_2$ can be calculated, $\Delta_{tr} H^\circ = +3.6$ kJ mol^{-1}. This value is in good agreement with the value found in the DSC measurements at the transition temperature.

Enthalpy increments of α-$Ba(OH)_2$ measured by drop calorimetry, are listed in Table 2. The results, to which 3600 J mol^{-1} have to be added because of the irreversible nature of the phase transition, have been fitted with the constraints C_p° (298.15 K) = 91.2 J mol^{-1} K^{-1} and $\{H^\circ(T) - H^\circ \text{ (298.15 K)}\} = 3600$ J mol^{-1}, to give:

$$\{H^\circ(T) - H^\circ(298.15\,\mathrm{K})\}/\mathrm{J\,mol^{-1}} = 104.290(T/\mathrm{K}) + 7.80781\cdot10^{-3}(T/\mathrm{K})^2 + 15.7744\cdot10^{5}(T/\mathrm{K})^{-1} - 33478.8$$

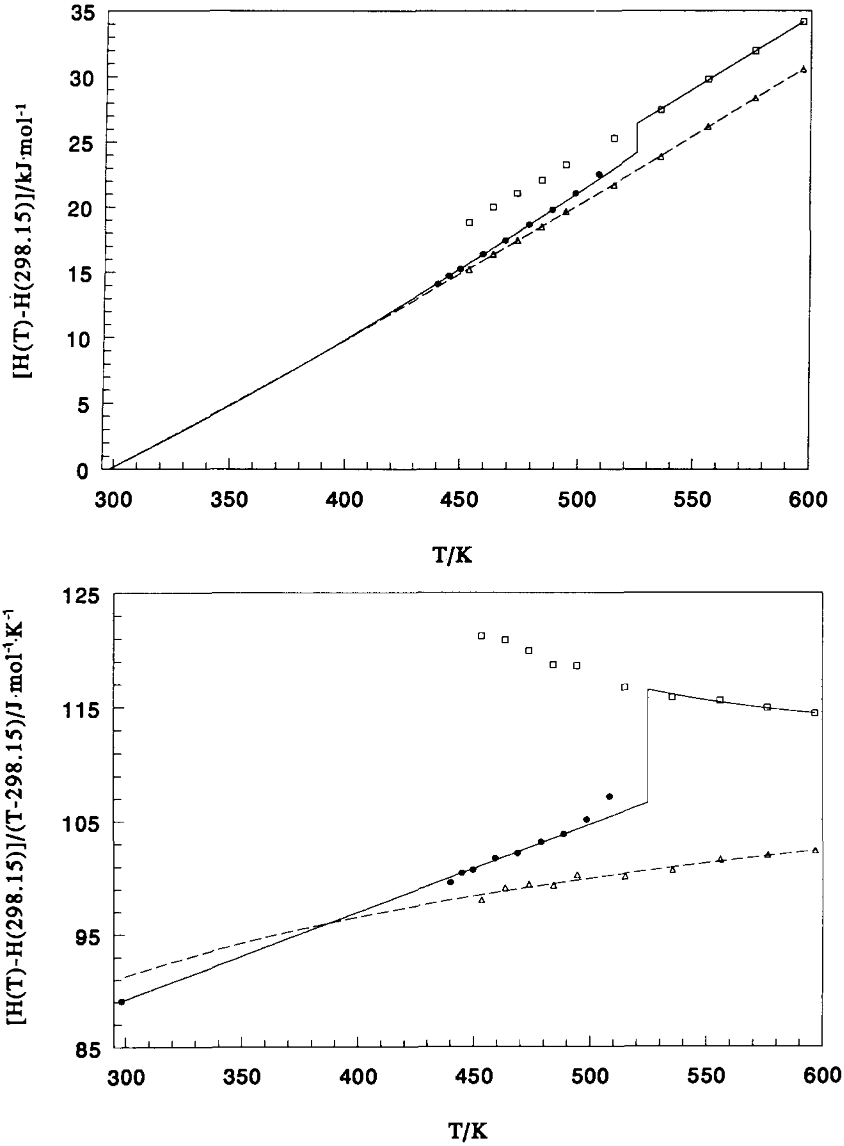

Fig. 3. The enthalpy increment (top) and the reduced enthalpy increment (bottom) of $Ba(OH)_2$ as a function of temperature: ●, β-$Ba(OH)_2$; Δ, α-$Ba(OH)_2$; □, α-$Ba(OH)_2$ relative to β-$Ba(OH)_2$ at 298.15 K.

Table 2
The enthalpy increments of α-$Ba(OH)_2$

T/K	$\{H^\circ(T) - H^\circ(298.15\,K)\}$/(J mol^{-1})		δ %
	Exp.	Calc.	
453.4	15217	15290	−0.48
463.6	16395	16351	0.27
473.8	17460	17416	0.25
484.3	18486	18517	−0.17
494.4	19672	19581	0.46
515.0	21705	21764	−0.27
535.4	23880	23942	−0.26
555.9	26184	26146	0.14
576.3	28368	28354	0.05
596.7	30568	30574	−0.02

The results are presented graphically in Fig. 3 in plots of the reduced enthalpy increment and the enthalpy increment as a function of the temperature.

3.4. *The fusion of* $Ba(OH)_2$ *and* $Sr(OH)_2$

Diagrams of the DSC runs of $Ba(OH)_2$ as well as $Sr(OH)_2$ between 573 and 750 K are shown in Figs. 1 and 4, respectively. For both compounds a large melting peak was found; this was preceded by a small endothermic effect, probably due to eutectic

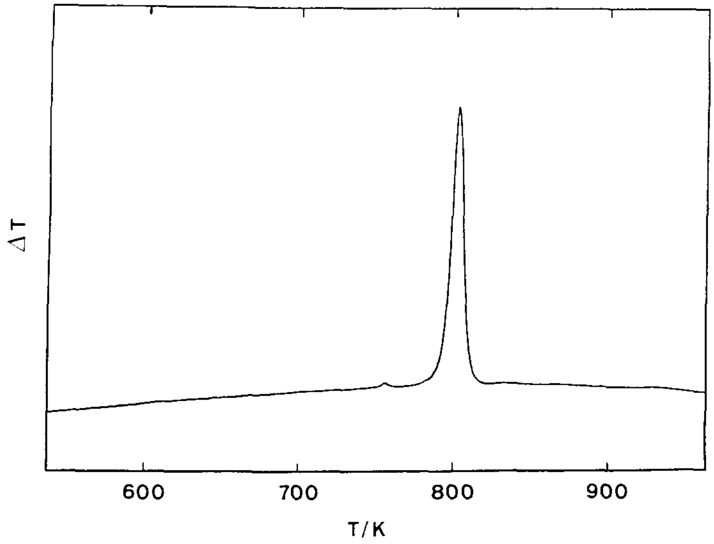

Fig. 4. The DSC diagram of $Sr(OH)_2$.

Table 3
Fusion data for $Sr(OH)_2$ and $Ba(OH)_2$

Authors	T_{fus}/K	$\Delta_{fus}H^\circ$/(J mol^{-1})
$Sr(OH)_2$		
Powers and Blalock [11]	783.2	21882
Brcic and Jernejcic [12]	771	–
Berggren and Brown [13]	723	–
Present study	794.7 ± 1.0	[21500 ± 500] [a]
$Ba(OH)_2$		
Seward [14]	681 ± 1	14226 ± 420
Powers and Blalock [11]	668	17207
Kondakov et al. [15]	682	–
Michaud [1,2]	681	15564 ± 840
Maneva-Petrova and Nikolova [10]	666 [b]	–
Present study	678.2 ± 1.0	18180 ± 300

[a] Estimated value, see text.

[b] Mean of two determinations.

melting of carbonate impurities. The derived data for the melting points and the enthalpies of fusion are compared with previous results in Table 3.

The melting point of $Ba(OH)_2$ was located at (679.3 ± 1.0) K in open silver capsules and at (677.1 ± 0.8) K in a closed silver ampoule. As the "best" value we take the mean: $T_{fus} = (678.2 \pm 1.0)$ K. This value is in good agreement with previous data by Seward [14], Kondakov et al. [15], and Michaud [1,2]. The enthalpy of fusion, as obtained by integration of the peak area of the DSC run in the open crucible, is $\Delta_{fus}H^\circ = (18180 \pm 300)$ J mol^{-1}. This value is significantly higher than previous results by Seward [14], Powers and Blalock [11], and Michaud [1,2], but is in good agreement with the value $\Delta_{fus}H^\circ = 18311$ J mol^{-1} calculated from the mean entropy of fusion in the isostructural alkaline earth halides, $\Delta_{trs}S^\circ = (27.0 \pm 1.3)$ J mol^{-1} K^{-1} (Table 4). Data for the latter group of compounds were taken from Glushko et al. [16].

Table 4
Thermodynamic data for orthorhombic–liquid transformations in alkaline earth halides and hydroxides

Compound	T_{fus}/K	$\Delta_{fus}H^\circ$/(J mol^{-1})	$\Delta_{fus}S^\circ$/(J mol^{-1} K^{-1})
$CaCl_2$	1048	28050	26.77
$CaBr_2$	1015	29100	28.67
SrI_2	811	19700	24.29
$BaBr_2$	1130	32200	28.50
BaI_2	984	26500	26.93
		Average:	27.0 ± 1.3

The measurements for $Sr(OH)_2$ in open silver capsules were hindered by severe dissociation effects and quantitative results could not be obtained. However, in closed silver ampoules the melting point could be located at (794.7 ± 0.9) K. This value is significantly higher than previous data from the literature, which are probably less precise as a result of the presence of (carbonate) impurities. The enthalpy of melting of $Sr(OH)_2$ could not be obtained from the DSC runs in the closed ampoules since no appropriate reference materials could be measured under the same conditions. By combining the mean entropy of fusion, as discussed above, with T_{fus} we obtain for $Sr(OH)_2$: $\Delta_{\mathrm{fus}}H^\circ = (21500 \pm 500)\ \mathrm{J\ mol^{-1}}$. This estimate is in reasonable agreement with the value reported by Powers and Blalock [11] which was derived from rather unreliable drop calorimetric measurements.

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