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PHASE RELATION AND DEHYDRATION BEHAVIOR OF BARIUM NITRITE HYDRATES

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ABSTRACT

The phase relation and the dehydration behavior of barium nitrite hydrates have been examined by DTA under various external pressures, and by TG–DTA in air The equilibrium water vapor pressures of the mono-, hemi-, and 1/3-hydrates have been measured The temperatures of III–II and II–I phase transitions and melting point of the anhydrate are 469, 497 and 542 K, respectively The dehydration in the atmosphere proceeds as follows

$$\text{monohydrate} \xrightarrow{(372\ \text{K})} \text{hemihydrate} \xrightarrow{(425\ \text{K})} 1/3\text{-hydrate} \xrightarrow{(457\ \text{K})} \text{anhydrate}$$

INTRODUCTION

Since the first report on strong pyroelectricity of barium nitrite monohydrate ($Ba(NO_2)_2\ H_2O$) by Gladkii and Zheludev [11], some efforts [2–10] have been devoted to the investigation of the properties of a series of barium nitrite hydrates Three salts, i e monohydrate, hemihydrate ($Ba(NO_2)_2\ \frac{1}{2}H_2O$) and anhydrate ($Ba(NO_2)_2$), have been known so far above room temperature

For the monohydrate, a sluggish first-order phase transition has been reported to occur at about 350 K [11,12] before dehydration to the hemihydrate at about 430 K [11] upon heating The phase transition has been correlated with the disorder of H_2O molecules in the crystal [11] No phase transition has been reported for the monohydrate below room temperature down to 20 K [2,13] The relation between the pyroelectricity and the displacements of atoms was discussed by Liminga et al [14] on the basis of the crystal structure at low temperatures [13,15]

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In the crystalline hemihydrate, a phase transition was recently discovered at 211 K by the present authors [16] A dielectric dispersion probably due to the reorientation of H_2O and/or NO_2^- was also reported [16] No phase transition has been observed above room temperature up to 457 K, at which the hemihydrate changes to the anhydrate

The anhydrate undergoes two phase transitions at 462 and 495 K before melting at 516 K [17] The crystal structures of the lowest temperature phase III and of the highest temperature phase I have been studied by X-ray diffraction [17] Another phase, IV, has been reported to appear through dehydration in dry air at room temperature [12]

The dehydration process of barium nitrite monohydrate has been studied [11] by thermogravimetry (TG) and differential thermal analysis (DTA), and two steps have been reported as $Ba(NO_2)_2\ H_2O \rightarrow Ba(NO_2)_2\ \frac{1}{2}H_2O \rightarrow Ba(NO_2)_2$ However, the details of the dehydration behavior and the phase relation of barium nitrite hydrates have not been clarified yet The main aim of the present study is to establish the phase relation of barium nitrite hydrates, and to interpret the dehydration behavior The DTA under various external pressures and TG–DTA in air are performed, and the results are analyzed on the basis of the principles of thermal analysis [18–20] The equilibrium water vapor pressures are also measured by mercury manometry

EXPERIMENTAL

The sample of barium nitrite monohydrate was purchased from Kanto Chemical Co , Inc , and purified by repeating recrystallization from aqueous solution several times The purified specimen was identified as the expected monohydrate by the powder X-ray diffraction using Ni-filtered Cu K_α radiation The gravimetric analysis gave 55 51 mass % for barium which compared favorably with the calculated value of 55 52 mass% The sample was ground in an alumina mortar before use for the experiments

DTA in the atmosphere was carried out from room temperature to 700 K using a laboratory-made high-temperature DTA apparatus [21] The temperature difference between the sample and the reference material (α-Al_2O_3) was measured with metal-sheathed thermocouples of type K (0 09 mm in wire diameter, 0 5 mm in sheath diameter (Toyonetsukagaku Co , Ltd)) The amount of the sample was about 300 mg, which was put into the sample vessel made of Pyrex glass The heating rate was about 0 07 K s^{-1}

The DTA experiments under reduced external pressures were performed between 480 and 100 K using a laboratory-made low-temperature apparatus [22] The powdered specimen of about 300 mg was put into the sample vessel, which was unsealed The heating rate was about 0 05 K s^{-1} for each experiment

A commercially available apparatus (TG-20, Seiko I&E Ltd) was used for TG–DTA in air The sample of about 10 mg was loaded on an open aluminum dish, and the experiment was done at a heating rate of about 0 17 K s^{-1}

The equilibrium water vapor pressures of the hydrates were measured by mercury manometry A powdered sample of about 2 g was used The sample and the manometer were put in an oil bath, which was thermostatted to within ±0 2 K The precision of the pressure measurements was ±0 2 kPa

RESULTS AND DISCUSSION

Prior to the detailed studies of the dehydration behavior, high-temperature DTA was carried out on the anhydrate sample The result is shown in Fig 1 The two solid phase transitions III–II and II–I occur at 469 and 497 K, and melting at 542 K The melting anomaly is rather small, which indicates that the solid phase I is a kind of ionic plastic crystal [23,24] It must be noted that the sample holder was broken on cooling from the melt, which was probably caused by the expansion upon solidification

The results of low-temperature DTA on the monohydrate under various external pressures are shown in Fig 2 The onset temperatures of the anomalies [18–20] are given in Fig 3 The anomaly at 469 K which is hardly affected by the external pressures is due to the III–II phase transition and should obey the Clapeyron–Clausius relation The other anomalies show apparent pressure dependence and should be related to the dehydration

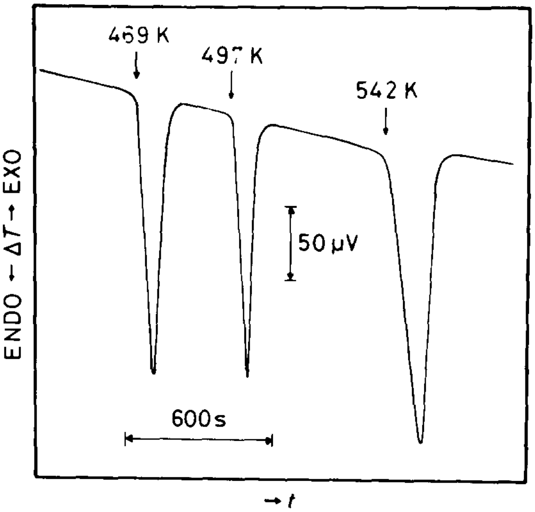

Fig 1 DTA trace of barium nitrite anhydrate in the atmosphere at a heating rate of about 0 07 K s^{-1}

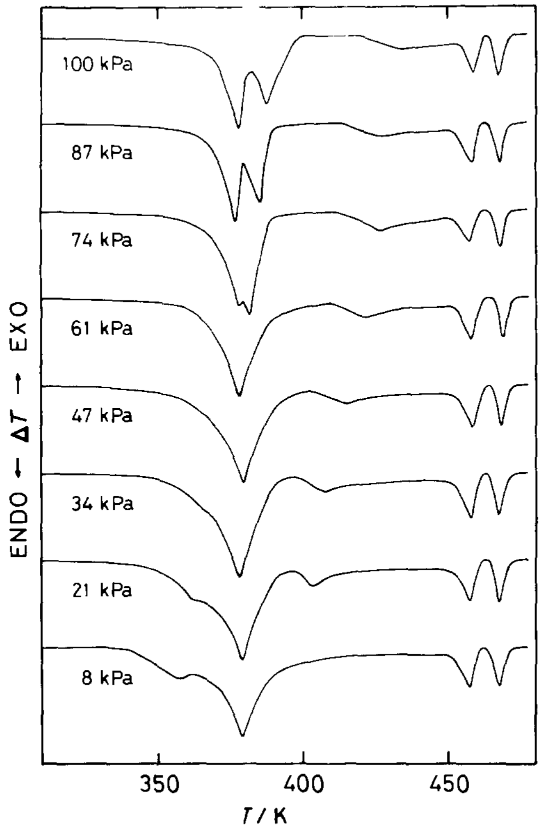

Fig 2 DTA traces of barium nitrite monohydrate under various pressures at a heating rate of about 0 05 K s^{-1}

processes With regard to the dehydration temperatures, these are two types of pressure dependence, large (at 387 and 425 K under atmospheric pressure) and small (at 372 and 457 K) The anomalies of large pressure dependence are attributed to dehydration associated with a gradual increase in equilibrium water vapor pressure The anomalies of small pressure dependence should be correlated with a change in phase relation

The anomaly at 387 K under the atmospheric pressure shifts to lower temperatures with decreasing external pressure and seems to cross the anomaly at 372 K which shows small pressure dependence However, the pressure dependence of the anomaly changes discontinuously at the crossing point (50 kPa, 372 K), which suggests a change in phase relation at that point The peak area of the anomaly increases as the external pressure decreases, while that of the anomaly at 372 K decreases, and thus the sum of the two peak areas is constant The dehydration at 387 K seems to be of "super-heated" monohydrate On the other hand, the peak area of the anomaly at 425 K under the atmospheric pressure shows small pressure

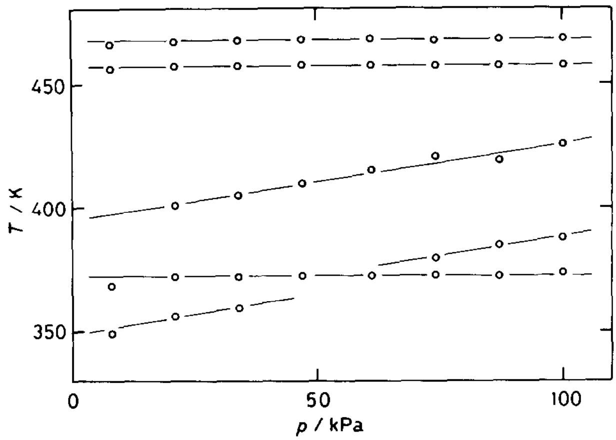

Fig 3 Onset temperatures of the anomalies in DTA of barium nitrite monohydrate under various external pressures at a heating rate of about 0 05 K s^{-1} Solid lines are drawn as guides

dependence in spite of its large pressure dependence in the dehydration temperature This behavior is rationalized if we assume the existence of a lower hydrate such as 1/3-hydrate

The following dehydration sequence on heating under the atmospheric pressure is suggested from the above analysis on the results of low-temperature DTA under various external pressures The monohydrate loses the water at 372 K to the hemihydrate due to the change in the phase relation However, the dehydration needs a time interval, and the dehydration owing to a gradual increase in equilibrium water vapor pressure of the remaining monohydrate becomes apparent at about 387 K The equilibrium water vapor pressure of the hemihydrate gradually increases and dehydration occurs again at about 425 K to a lower hydrate such as $\frac{1}{3}$-hydrate Then, the change in the phase relation at 457 K results in the anhydrate

In order to examine the formation of lower hydrate during the dehydration of the monohydrate, the TG-DTA experiment was undertaken The result is represented in Fig 4 The DTA trace below 400 K is somewhat different from that of low-temperature DTA (Fig 2). The anomaly observed at 387 K in low-temperature DTA is absent, and instead two anomalies appear at 340 and 356 K The anomaly at 340 K is due to the phase transition of the monohydrate and that at 356 K is possibly related to dehydration of the monohydrate The TG curve apparently shows three steps of mass loss The first mass loss between 350 and 380 K corresponds to dehydration from the monohydrate to the hemihydrate, which is in good agreement with the results reported by Gallagher et al [11] The second one gives a plateau corresponding to the mass of the 1/3-hydrate This step of dehydration is observed as a broad anomaly around 420 K in DTA The final mass loss at 457 K is sharp in comparison with the preceding two steps

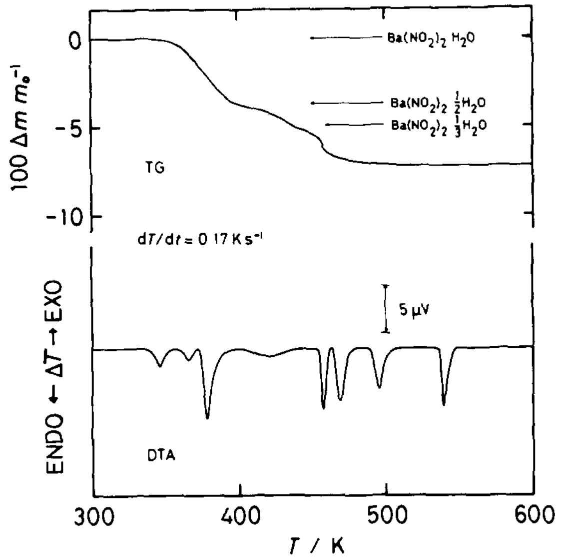

Fig. 4. TG–DTA curves of barium nitrite monohydrate in air at a heating rate of about 0.17 K s^{-1}.

of mass loss. Hence, the lower hydrate predicted in low-temperature DTA should be the 1/3-hydrate. It seems very likely that the 1/3-hydrate is stable above 356 K and the hemihydrate above 372 K. This situation possibly leads

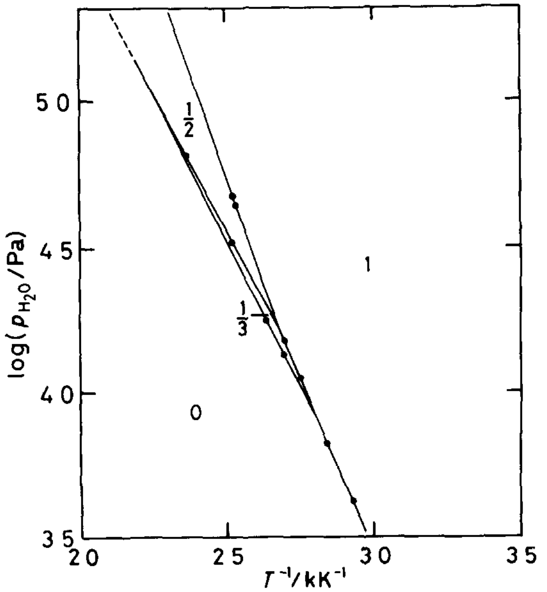

Fig. 5. T–P phase diagram of barium nitrite hydrates.

TABLE 1

Enthalpies of dehydration of $Ba(NO_2)_2\ nH_2O$

n	ΔH (kJ mol^{-1})
$1 \rightarrow 1/2$	56
$1/2 \rightarrow 1/3$	34
$1/3 \rightarrow 0$	37

instability of the 1/3-hydrate at 457 K It is worth noting that dehydration below 350 K gives the anhydrate (see Fig 5)

The reason that the dehydration behavior in TG–DTA is different from that in low-temperature DTA is probably the difference in the positions at which the samples are located In the case of low-temperature DTA, the sample is loaded into a deep well of a sample holder [22], and thus is in contact with rather humid air On the other hand, in the TG–DTA the sample is put on an open dish The phase transition of the monohydrate at 350 K has been reported to be very sensitive to humidity [11,12]

A knowledge of the equilibrium phase relation of the system is necessary to reach a full interpretation of dehydration The measured equilibrium water vapor pressures are shown in Fig 5 The 1/3-hydrate is stable above 356 K and the hemihydrate above 372 K The linearly extrapolated vapor pressure curves of the hemihydrate and of the 1/3-hydrate cross each other at about 460 K, which is reasonably close to the dehydration temperature 457 K of the 1/3-hydrate The enthalpies of dehydration estimated from the slopes of the plots are tabulated in Table 1 The values of enthalpies of dehydration satisfy thermodynamic requirements such as

$$\Delta H_{1-0} = \Delta H_{1-\frac{1}{3}} + \Delta H_{\frac{1}{3}-0}$$

CONCLUSIONS

The phase relation and the dehydration behavior of barium nitrite hydrates were studied on the basis of DTA under various external pressures, TG–DTA in air, and measurements of equilibrium water vapor pressure The temperatures of the III–II, II–I phase transitions and melting were determined as 469, 497 and 542 K, respectively The T–P phase diagram was obtained, and the enthalpy changes among the mono-, hemi-, and 1/3-hydrates were estimated.

The dehydration process of the monohydrate in the atmosphere is represented as monohydrate $\xrightarrow{(372\ K)}$ hemihydrate $\xrightarrow{(425\ K)}$ 1/3-hydrate $\xrightarrow{(457\ K)}$ anhydrate While dehydration at about 425 K is due to a gradual increase in equilibrium water vapor pressure of the hemihydrate, dehydrations at 372 and 457 K reflected the change in the phase relation

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