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Standard Molar Enthalpies of Formation for the Two Polymorphs of $Na_2B_5O_8(OH)\cdot 2H_2O$

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Two pure hydrated sodium borates, α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and β-$Na_2B_5O_8(OH)\cdot 2H_2O$, have been synthesized under mild hydrothermal conditions and characterized by X-ray diffraction, infrared spectral, and thermogravimetric analysis and chemical analysis. The molar enthalpies of solution of α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and β-$Na_2B_5O_8(OH)\cdot 2H_2O$ in 1 $mol\cdot dm^{-3}$ HCl(aq) were measured by solution calorimetry to be (20.36 ± 0.33) $kJ\cdot mol^{-1}$ and (14.27 ± 0.20) $kJ\cdot mol^{-1}$, respectively. With the incorporation of other thermodynamic data, the standard molar enthalpies of formation were found to be −(4725.1 ± 4.0) $kJ\cdot mol^{-1}$ for α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and −(4719.0 ± 4.0) $kJ\cdot mol^{-1}$ for β-$Na_2B_5O_8(OH)\cdot 2H_2O$. The result shows that α-$Na_2B_5O_8(OH)\cdot 2H_2O$ is more stable than β-$Na_2B_5O_8(OH)\cdot 2H_2O$, which is consistent with their thermal behavior.

Introduction

During recent years, much interest has been focused on the studies of alkali borates because some of these compounds show interesting physical properties, such as nonlinear optical behavior for CsB_3O_5[1] and $KB_5O_8\cdot 4H_2O$.[2] Several phases, such as $Na_2B_5O_8(OH)\cdot 2H_2O$ (nasinite), had been obtained in the $Na_2O-B_2O_3-H_2O$ system under hydrothermal conditions.[3] Recently, we obtained a new form of nasinite, and its synthesis and crystal structure have been reported.[4] In this paper, we report the determination of the standard molar enthalpies of formation of the two polymorphs using a heat conduction microcalorimeter. In the following, nasinite will be named α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and our sample will be named β-$Na_2B_5O_8(OH)\cdot 2H_2O$.

Experimental Section

Synthesis and Characterization of Samples. A β-$Na_2B_5O_8(OH)\cdot 2H_2O$ single-crystal sample was taken from our previous work.[4] All reagents used in the synthesis of α-$Na_2B_5O_8(OH)\cdot 2H_2O$ were of analytical grade. A mixture of 0.218 g of Na_2CO_3, 0.618 g of H_3BO_3, and 0.5 mL of H_2O was sealed in a Teflon-lined bomb and heated at 150 °C for 3 days and then cooled to room temperature. The resulting colorless and transparent crystals were recovered by filtration, washed with distilled water, and dried in a vacuum dryer to a constant mass at room temperature. The samples were characterized by FT-IR spectroscopy (recorded over the (400 to 4000) cm^{-1} region on a Bruker Equinox 55 spectrometer with KBr pellets at room temperature), X-ray powder diffraction (Rigaku D/MAX-IIIC with a Cu target at 8 $°C\cdot min^{-1}$), thermogravimetric analysis (TGA), and differential thermal analysis (DTA) (performed on an SDT Q600 simultaneous thermal analyzer under an N_2 atmosphere with a heating rate of 10 $°C\cdot min^{-1}$). The B_2O_3 content was determined by NaOH titration in the presence of mannitol. The H_2O content was determined by the weight loss in the TG curve.

Calorimetric Experiment. The thermochemical reaction designed for the derivation of the $\Delta_f H_m^o$ of $Na_2B_5O_8(OH)\cdot 2H_2O$ is given below

$$Na_2B_5O_8(OH)\cdot 2H_2O(s) + 2(HCl\cdot 54.506H_2O) \rightarrow 2NaCl(s) + 5H_3BO_3(s) + 105.012H_2O$$

The 1 $mol\cdot dm^{-3}$ HCl(aq) solvent can dissolve all components of reaction, and its concentration of 0.9996 $mol\cdot dm^{-3}$ was determined by titration with standard sodium carbonate. The standard molar enthalpy of formation of $Na_2B_5O_8(OH)\cdot 2H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of NaCl(s), H_3BO_3(s), HCl(aq), and H_2O(l).

The RD496−III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously.[5,6] To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ≥ 0.9999) in deionized water was determined to be (17.31 ± 0.20) $kJ\cdot mol^{-1}$, in agreement with that of 17.234 $kJ\cdot mol^{-1}$ reported in the literature.[7] This shows that the device used for measuring the enthalpy of solution in this work is reliable.

The calorimetric experiment was performed five times at 298.15 K. Double-layer glass tubes were put in the 15 cm^3 stainless steel sample and reference cells of the calorimeter to prevent corrosion by HCl(aq). The inner glass tube containing 2.00 cm^3 of HCl(aq) was broken by a rod after thermal equilibration for at least 2 h, and the HCl(aq) mixed with the solid sample in the outer glass tube. The total time required for the complete reaction was about 0.5 h. No solid residues were observed after the reactions.

Results and Discussion

Characterization of the Synthetic Samples. The chemical analytical data of synthetic samples are (found/calcd, %) B_2O_3 (62.26/61.92) and H_2O (16.06/16.01) for α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and B_2O_3 (62.11/61.92) and H_2O (15.58/16.01) for β-$Na_2B_5O_8(OH)\cdot 2H_2O$. The chemical analytical results are consistent with

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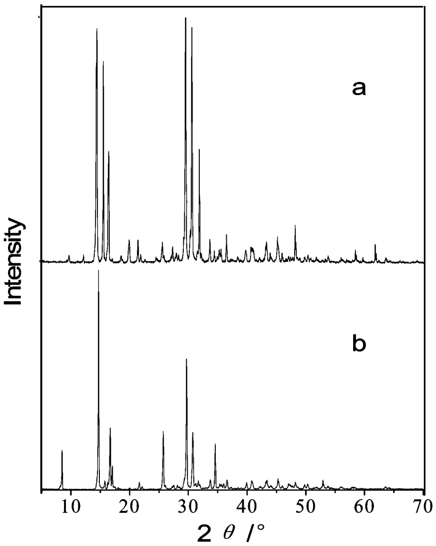

Figure 1. Powder XRD patterns of synthesized samples (a) α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and (b) β-$Na_2B_5O_8(OH)\cdot 2H_2O$.

the theoretical values. The uncertainties in the measurement of the mass fraction of each species were estimated to be ± 0.2 %.

Figure 1 shows the powder XRD patterns of synthesized samples of α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and β-$Na_2B_5O_8(OH)\cdot 2H_2O$. The main characteristic *d* values of the XRD pattern for α-$Na_2B_5O_8(OH)\cdot 2H_2O$ are (6.095, 5.646, 5.361, 4.125, 3.017, 2.910, 2.803, 2.525, and 2.262) Å, which correspond with those of the JCPDS card (File No. 29-1180) and show the absence of any other crystalline forms in this synthetic sample. The main *d* values for β-$Na_2B_5O_8(OH)\cdot 2H_2O$ are (10.876, 10.422, 6.022, 5.619, 5.436, 5.316, 5.195, 3.007, 2.904, 2.594, 2.821, 2.656, 2.5364, 2.455, and 2.257) Å. It can be seen that the latter shape and data of XRD patterns are different from those of the former, which confirms that β-$Na_2B_5O_8(OH)\cdot 2H_2O$ is a new compound.[4]

The FT-IR spectrum of an α-$Na_2B_5O_8(OH)\cdot 2H_2O$ sample exhibited the following absorption bands, and they were assigned referring to the literature.[8] The band at 3454 cm^{-1} is the stretching of O−H. The band at 1643 cm^{-1} is assigned to the H−O−H bending mode, which shows the compound contains crystalline water. The band at 1252 cm^{-1} might be the in-plane bending of B−O−H. The bands at 1362 cm^{-1} and 933 cm^{-1} are the asymmetric and symmetric stretching of B(3)−O. The band at 1034 cm^{-1} is the asymmetric stretching of B(4)−O. The band at 737 cm^{-1} is the out-of-plane bending mode of B(3)−O. The band at 589 cm^{-1} is assigned as the characteristic peak of the pentaborate anion, $[B_5O_8(OH)]^{2-}$. The band at 457 cm^{-1} might be the bending mode of B(4)−O. These absorption bands are different from those of β-$Na_2B_5O_8(OH)\cdot 2H_2O$.[4]

The thermal behavior of an α-$Na_2B_5O_8(OH)\cdot 2H_2O$ sample is shown in Figure 2. The TG curve shows that α-$Na_2B_5O_8(OH)\cdot 2H_2O$ has a three-step weight loss between (40 and 650) °C, and the total weight loss is 16.06 %, which corresponds to the loss of 2.5 water molecules and can be compared with a calculated value of 16.01 %. The first weight loss (6.35 %) at (40 to 167) °C corresponds to the loss of one crystalline water molecule and is in good agreement with a calculated value of 6.40 %. In the second step, the weight loss (6.15 %) at (167 to 375) °C corresponds to the loss of another crystalline water molecule and can be compared with a calculated value of 6.40 %. In the third step, the weight loss is 3.56 % from (375 to 650) °C, which corresponds to the loss of 1/2 structural water from one hydroxyl group and can be compared with a calculated value of 3.21 %. In the DTA curve, there are four endothermic peaks. The peaks at (151, 273, and 523) °C are related to the three-step dehydration and formation of the $Na_4B_{10}O_{17}$ phase. The peak at 691 °C is related to melting of the solid phase. This dehydration process can be expressed as follows

$$\alpha\text{-}Na_2[B_5O_8(OH)]\cdot 2H_2O \xrightarrow{-H_2O} Na_2[B_5O_8(OH)]\cdot H_2O \xrightarrow{-H_2O} Na_2[B_5O_8(OH)] \xrightarrow{-0.5H_2O} 1/2Na_4B_{10}O_{17}$$

The thermal behavior of a β-$Na_2B_5O_8(OH)\cdot 2H_2O$ sample has been given in a previous paper.[4] The TG curve shows that

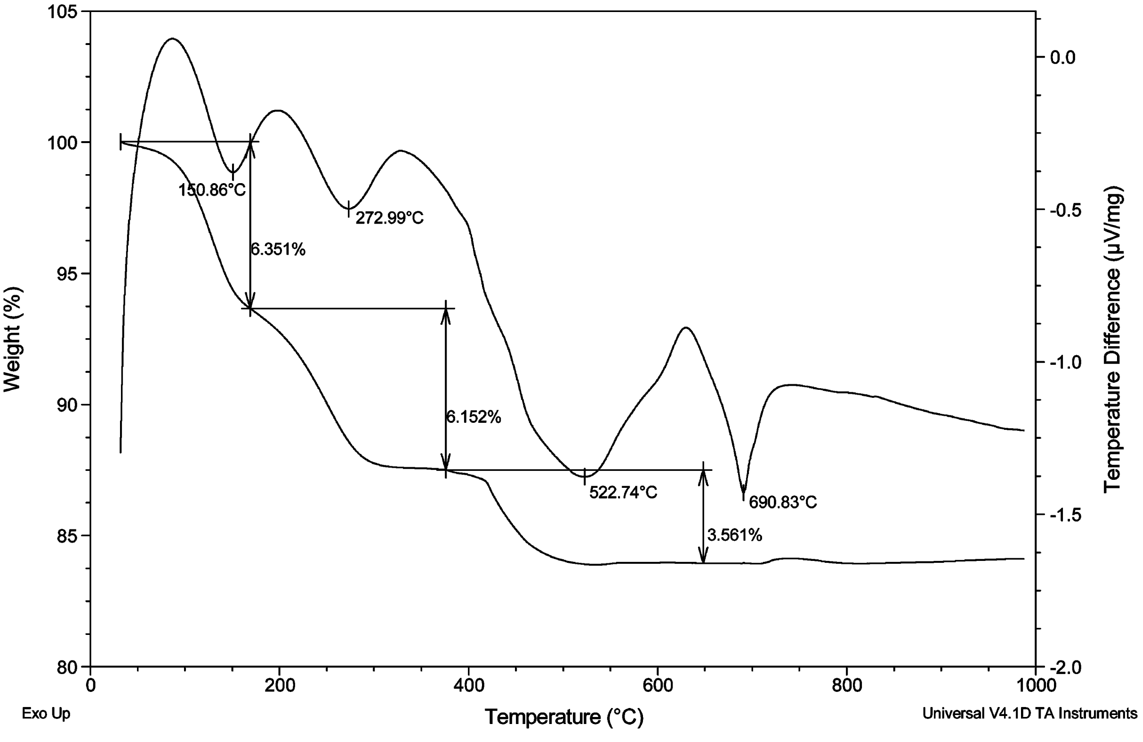

Figure 2. Simultaneous TG−DTA curves of an α-$Na_2B_5O_8(OH)\cdot 2H_2O$ sample.

Table 1. Molar Enthalpies of Solution of α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and β-$Na_2B_5O_8(OH)\cdot 2H_2O$ in 1 mol·dm^{-3} HCl(aq) at 298.15 K[a]

no.	m mg	$\Delta_r H$ mJ	$\Delta_{sol}H_m$ kJ·mol^{-1}
	α-$Na_2B_5O_8(OH)\cdot 2H_2O$		
1	7.48	538.419	20.223
2	7.88	554.340	19.773
3	7.77	571.575	20.694
4	7.77	574.464	20.621
5	8.05	586.119	20.475
mean			20.36 ± 0.33[b]
	β-$Na_2B_5O_8(OH)\cdot 2H_2O$		
1	7.63	382.795	14.100
2	7.51	381.159	14.265
3	7.44	371.606	14.039
4	8.38	434.926	14.587
5	8.05	411.348	14.362
mean			14.27 ± 0.20[b]

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used. [b] Uncertainty is estimated as twice the standard deviation of the mean.

Table 2. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^o$ ($Na_2B_5O_8(OH)\cdot 2H_2O$, 298.15 K)

no.	reaction	$\Delta_r H_m^o$/ (kJ·mol^{-1})
1	α-$Na_2B_5O_8(OH)\cdot 2H_2O(s) + 72.13(HCl\cdot 54.506H_2O) = 2Na^+(aq) + 2Cl^-(aq) + 5H_3BO_3(aq) + 70.13(HCl\cdot 56.003H_2O)$	20.36 ± 0.33
	β-$Na_2B_5O_8(OH)\cdot 2H_2O$ (s):	14.27± 0.20
2	$70.13(HCl\cdot 56.003H_2O) = 70.13(HCl\cdot 54.506H_2O) + 105.012H_2O(l)$	2.10 ± 0.08
3	$5H_3BO_3(aq) + 70.13(HCl\cdot 56.003H_2O) = 5H_3BO_3(s) + 70.13(HCl\cdot 56.003H_2O)$	−109.15 ± 0.40
4	$2Na^+(aq) + 2Cl^-(aq) + 5H_3BO_3(aq) + 70.13(HCl\cdot 56.003H_2O) = 2NaCl(s) + 5H_3BO_3(aq) + 70.13(HCl\cdot 56.003H_2O)$	−10.28 ± 0.04
5	$H_2(g) + Cl_2(g) + 109.012H_2O(l) = 2(HCl\cdot 54.506H_2O)$	−330.91 ± 0.20
6	$2NaCl(s) = 2Na(s) + Cl_2(g)$	822.30 ± 0.20
7	$5H_3BO_3(s) = 5B(s) + (15/2)H_2(g) + (15/2)O_2(g)$	5474.0 ± 4.0
8	$4H_2(g) + 2O_2(g) = 4H_2O(l)$	−1143.32 ± 0.16
9	α-$Na_2B_5O_8(OH)\cdot 2H_2O(s) = 2Na(s) + 5B(s) + (5/2)H_2(g) + (11/2)O_2(g)$	4725.1 ± 4.0[a]
	β-$Na_2B_5O_8(OH)\cdot 2H_2O(s)$:	4719.0 ± 4.0[a]

[a] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

β-$Na_2B_5O_8(OH)\cdot 2H_2O$ has a three-step weight loss between (40 and 600) °C, and the total weight loss is 15.58 % (calcd, 16.01 %).

It can be seen that the two borates have different thermal behaviors not only in the dehydration mechanism but also in the DTA curves, which result from the difference in their structure. In their DTA curves, the temperatures of three peaks related to the three-step dehydration for α-$Na_2B_5O_8(OH)\cdot 2H_2O$ are higher than those of β-$Na_2B_5O_8(OH)\cdot 2H_2O$, which shows that α-$Na_2B_5O_8(OH)\cdot 2H_2O$ is more stable than β-$Na_2B_5O_8(OH)\cdot 2H_2O$.

As stated above, no impurity lines were observed, and the synthetic samples are suitable for calorimetric experiments.

Results of Calorimetric Experiments. The molar enthalpies of solution of α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and β-$Na_2B_5O_8(OH)\cdot 2H_2O$ in 1 mol·dm^{-3} HCl(aq) at 298.15 K are listed in Table 1, in which m is the mass of sample; $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute; and the uncertainty is estimated as twice the standard deviation of the mean.

Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and β-$Na_2B_5O_8(OH)\cdot 2H_2O$. The molar enthalpy of solution of H_3BO_3(s) of (21.83 ± 0.08) kJ·mol^{-1} in 1 mol·dm^{-3} HCl(aq) was taken from the literature.[9] The molar enthalpy of solution of NaCl(s) of (5.14 ± 0.02) kJ·mol^{-1} in 1 mol·dm^{-3} (HCl + H_3BO_3)(aq) was also taken from the literature.[10] The standard molar enthalpy of formation of HCl(aq) and the enthalpy of dilution of HCl(aq) were calculated from the NBS tables.[11] The standard molar enthalpy of formation of NaCl(s) was taken from the NBS tables,[11] namely, −(411.15 ± 0.10) kJ·mol^{-1}, and the standard molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values,[12] namely, −(1094.8 ± 0.8) kJ·mol^{-1} and −(285.830 ± 0.040) kJ·mol^{-1}, respectively. From these data, the standard molar enthalpies of formation of α-$Na_2B_5O_8(OH)\cdot 2H_2O$ and β-$Na_2B_5O_8(OH)\cdot 2H_2O$ were calculated to be −(4725.1 ± 4.0) kJ·mol^{-1} and −(4719.0 ± 4.0) kJ·mol^{-1}, respectively.

Conclusions

The very big values of the standard molar enthalpies of formation show that the two sodium borates are quite thermodynamically stable. However, the $\Delta_f H_m^o$ determined for α-$Na_2B_5O_8(OH)\cdot 2H_2O$ is bigger than that of β-$Na_2B_5O_8(OH)\cdot 2H_2O$. This result shows that α-$Na_2B_5O_8(OH)\cdot 2H_2O$ is more stable than β-$Na_2B_5O_8(OH)\cdot 2H_2O$, which is consistent with their thermal behavior.

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