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Determination of Standard Molar Enthalpies of Formation for the Two Barium Borates $BaB_2O_4 \cdot xH_2O$ ($x = 4, 0$) by Microcalorimetry

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Two pure barium borates, $BaB_2O_4 \cdot 4H_2O$ and β-BaB_2O_4, have been prepared and identified by X-ray diffraction, infrared spectral and thermogravimetric analysis, and chemical analysis. The molar enthalpies of solution of $BaB_2O_4 \cdot 4H_2O$ and β-BaB_2O_4 in 1 $mol \cdot dm^{-3}$ HCl(aq) were measured to be $-(7.63 \pm 0.10)$ $kJ \cdot mol^{-1}$ and $-(93.06 \pm 0.24)$ $kJ \cdot mol^{-1}$, respectively. The molar enthalpy of solution of $Ba(OH)_2 \cdot 8H_2O$ in ($HCl + H_3BO_3$)(aq) was determined to be $-(55.42 \pm 0.36)$ $kJ \cdot mol^{-1}$. With the incorporation of the enthalpy of solution of H_3BO_3 in 1 $mol \cdot dm^{-3}$ HCl(aq) and the standard molar enthalpies of formation of $Ba(OH)_2 \cdot 8H_2O(s)$, $H_3BO_3(s)$, and $H_2O(l)$, the standard molar enthalpies of formation of $BaB_2O_4 \cdot 4H_2O$ and β-BaB_2O_4 were found to be $-(3249.1 \pm 1.7)$ $kJ \cdot mol^{-1}$ and $-(2020.3 \pm 1.7)$ $kJ \cdot mol^{-1}$, respectively.

Introduction

Borates are a resource for functional materials, particularly for nonlinear optical (NLO) materials. Some barium borates have appropriate properties for these materials, such as β-BaB_2O_4 (BBO), which is an important NLO material because it has a variety of favorable properties,[1] and $Ba_2Be_2B_2O_7$ (TBO).[2]

Thermodynamic properties play very important roles in scientific research and industrial applications. As to the thermochemistry of alkaline−earth metal borates, the standard molar enthalpies of formation of many magnesium and calcium borates have been measured.[3−7] However, studies of the thermochemistry of the barium borates are not reported in the literature. This paper reports the determination of the standard molar enthalpies of formation of two barium borates, β-BaB_2O_4 and its precursor $BaB_2O_4 \cdot 4H_2O$, using a heat conduction microcalorimeter.

Experimental Section

Preparation of $BaB_2O_4 \cdot 4H_2O$* and *β-BaB_2O_4 Samples. All reagents used in the synthesis were of analytic grade. A few drops of barium chloride solution was added to a solution of 1.85 g of NaOH in 10 cm^3 of water, and the formed carbonate was filtered off under reduced pressure. A solution of 65 cm^3 water containing 7.61 g of $Na_2B_4O_7 \cdot 10H_2O$ was added. A solution of 5.01 g of $BaCl_2 \cdot 2H_2O$ in 15 cm^3 of water was added, and the solution was left in a closed beaker. The mixture was stirred for 1 h at room temperature. After 2 days, the resulting white suspended precipitate was filtered, then washed with absolute alcohol and absolute ether, and finally, dried at 303 K to constant mass. β-BaB_2O_4 was prepared by a literature[1] method by dehydration of $BaB_2O_4 \cdot 4H_2O$ in air for 3 h at 973 K. These two synthetic samples were identified by X-ray powder diffraction (Rigaku D/MAX- IIIC with Cu target at 8° min^{-1}), FT-IR spectroscopy (Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature), and TG-DTA (TA-SDT Q600 simultaneous thermal analyzer at a heating rate of 10 $K \cdot min^{-1}$ in flowing N_2). The chemical compositions of the samples were determined by EDTA titration for Ba^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by difference for H_2O.

Thermochemical Cycles. $BaB_2O_4 \cdot 4H_2O$ and β-BaB_2O_4 can be regarded as the products of the following reactions I and II, respectively:

$$Ba(OH)_2 \cdot 8H_2O(s) + 2H_3BO_3(s) \rightarrow BaB_2O_4 \cdot 4H_2O(s) + 8\ H_2O \qquad (I)$$

$$Ba(OH)_2 \cdot 8H_2O(s) + 2H_3BO_3(s) \rightarrow BaB_2O_4(s) + 12H_2O \qquad (II)$$

The 1 $mol \cdot dm^{-3}$ HCl(aq) solvent can rapidly dissolve all components of reactions I and II, which was prepared from analytical grade hydrochloric acid and deionized water. Its concentration, 0.9996 $mol \cdot dm^{-3}$, was determined by titration with standard sodium carbonate.

The designed thermochemical cycles are given in Tables 3 and 4. The molar enthalpies of solution of $H_3BO_3(s)$, $BaB_2O_4 \cdot 4H_2O(s)$, and β-$BaB_2O_4(s)$ in 1 $mol \cdot dm^{-3}$ HCl(aq) were measured, namely, $\Delta_r H_m^\circ(1)$ and $\Delta_r H_m^\circ$ (4), respectively. The calculated amount of $Ba(OH)_2 \cdot 8H_2O(s)$ was dissolved in (hydrochloric acid + boric acid) aqueous solution which consisted of 1 mol dm^{-3} HCl(aq) and the calculated amount of $H_3BO_3(s)$ ($\Delta_r H_m^\circ$ (2)). In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycle must be maintained, with the objective that the dissolution of the reactants gives the same composition as those of the products. Applying Hess's law, the enthalpy of reaction 5 ($\Delta_r H_m^\circ$ (5)) can be calculated according to the following expression:

$$\Delta_r H_m^\circ (5) = \Delta_r H_m^\circ (1) + \Delta_r H_m^\circ (2) - \Delta_r H_m^\circ (3) - \Delta_r H_m^\circ (4)$$

where $\Delta_r H_m^\circ$ (3) is the enthalpy of dilution of HCl(aq).

The standard molar enthalpies of formation of $BaB_2O_4 \cdot 4H_2O$ and β-BaB_2O_4 can be obtained from the values of $\Delta_r H_m^\circ$ (5) in combination with the molar enthalpies of formation of $H_3BO_3(s)$, $Ba(OH)_2 \cdot 8H_2O(s)$, and $H_2O(l)$.

Calorimetric Experiments. All the enthalpies of solution were measured using a RD496- III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is

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Table 1. Molar Enthalpies of Solution of $Ba(OH)_2\cdot 8H_2O$ in the Mixed Solvent Consisting of 1 mol dm^{-3} HCl(aq) and Calculated Amount of H_3BO_3 at 298.15 K[a]

no.	m/mg	$\Delta_{sol}H$/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
1	13.26	−2340.270	−55.68
2	13.37	−2367.120	−55.85
3	13.39	−2348.214	−55.32
4	13.57	−2356.591	−54.79
5	13.52	−2376.197	−55.45
mean			−55.42 ± 0.36[b]

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used. [b] Uncertainty is twice the standard deviation of the mean, namely, $\delta = 2\sqrt{\Sigma(x_i-\bar{x}^2)/n(n-1)}$, in which n is the number of experimentals ($n = 5$); x_i is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value.

Table 2. Molar Enthalpies of Solution of $BaB_2O_4\cdot 4H_2O$ and β-BaB_2O_4 in 1 mol dm^{-3} HCl(aq) at 298.15 K[a]

no.	m/mg	Δ_rH/mJ	$\Delta_{sol}H_m$/kJ·mol^{-1}
		$BaB_2O_4\cdot 4H_2O$	
1	12.69	−331.372	−7.70
2	12.64	−332.724	−7.77
3	12.76	−330.992	−7.65
4	12.69	−323.671	−7.52
5	12.42	−316.286	−7.51
mean			−7.63 ± 0.10[b]
		β-BaB_2O_4	
1	9.49	−3955.312	−92.92
2	9.40	−3937.310	−93.38
3	9.54	−3969.588	−92.77
4	9.40	−3933.975	−93.31
5	9.57	−3989.011	−92.93
mean			−93.06 ± 0.24[b]

[a] In each experiment, 2.00 cm^3 of HCl(aq) was used. [b] Uncertainty $\delta = 2\sqrt{\Sigma(x_i-\bar{x}^2/n(n-1)}$, in which n is the number of experimentals ($n = 5$); x_i is the experimental value of each repeated measurement; and $\bar{x}$ is the mean value.

a totally automatic instrument utilizing computer control and has been described in detail previously.[8] The temperature of the calorimetric experiment was 298.15 K. Additional double-layer glass tubes were put in the 15 cm^3 stainless steel sample cell and reference cell of the calorimeter. This was done to prevent corrosion of the stainless steel sample and reference cell by HCl(aq). The lining in the double-layer glass tube containing HCl(aq) was broken by a rod after thermal equilibration for at least 2 h, and the HCl(aq) was mixed with solid sample in the outer glass tube. The thermal effect was then recorded automatically on a computer. The total time required for the complete reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

To check the performance of the RD496-III heat conduction microcalorimeter, the calorimetric constant at 298.15 K was determined by the Joule effect before the experiments. The Joule cell was supplied with 100 mW electric power for 100 s. The calorimetric constant obtained in this way was (63.99 ± 0.03) μV·mW^{-1}. The reliability of the calorimeter was verified by measuring the enthalpy of solution of KCl (mass fraction $\geqslant$ 0.9999) in deionized water. The average experimental value of $\Delta_{sol}H_m$(KCl) was determined to be (17.31 ± 0.20) kJ mol^{-1}, which is in excellent agreement with that of 17.234 kJ mol^{-1} reported in the literature.[9] This shows that the device used for measuring the enthalpy of solution in this work is reliable.

Results and Discussion

Identification of Synthetic Samples. Anal. Calcd for $BaB_2O_4\cdot 4H_2O$: BaO, 51.97 %; B_2O_3, 23.60 %; H_2O, 24.43 %. Found: BaO, 51.92 %; B_2O_3, 23.92 %; H_2O, 24.16 %. The chemical analytical results are consistent with the theoretical values. The uncertainties in the measurement of the mass fraction of each species were estimated to be ± 0.2 %.

The XRD pattern of a synthetic sample of $BaB_2O_4\cdot 4H_2O$ is shown in Figure 1. The characteristic d values are 0.5779, 0.5507, 0.4924, 0.4191, 0.4005, 0.3821, 0.3657,0.3409, 0.3169, 0.2741, 0.2635, 0.2583, 0.2563, 0.2447, 0.2284, 0.2140, 0.2112, 0.2071, 0.2026, 0.1961, and 0.1852 nm, which correspond with those of the relevant JCPDS card (File No. 48-941) and show an absence of other crystalline forms in the synthetic sample. The XRD pattern of a synthetic sample of β-BaB_2O_4 is also shown in Figure 1. The characteristic d values are 0.6330, 0.3636, 0.3534, 0.3149, 0.3066, 0.2531, 0.2376, 0.2073, and 0.1834 nm. All the diffraction peaks can be exactly indexed with those of β-BaB_2O_4 (JCPDS File No. 38-772), and no other crystalline forms in this synthetic sample were observed.

The FT-IR spectra of these two samples exhibit the following absorption bands, and they have been assigned by referring to literature.[10] In $BaB_2O_4\cdot 4H_2O$, the bands at (3416 and 3238) cm^{-1} are the stretching vibration of the O−H group. The band at 1641 cm^{-1} is assigned to the H−O−H bending mode, which shows this compound contains crystal water. The band at 1199 cm^{-1} might be the in plane bending of B(3)−O. The bands at (1282 and 934) cm^{-1} are the asymmetric and symmetric stretching modes of B(3)−O, respectively. The bands at (732 and 674) cm^{-1} are assigned to out-of-plane bending of B(3)-O. The band at 518 cm^{-1} is assigned to the bending mode of B(3)-O. In β-BaB_2O_4, the bands at (1416 and 955) cm^{-1} are the asymmetric and symmetric stretching vibration modes of B(3)−O, respectively. The band at 1247 cm^{-1} is assigned to the in plane bending of B(3)−O. The bands at 702 cm^{-1} is the out-of-plane bending mode of B(3)-O. These assignments are consistent with the structure containing the $[B_3O_6]^{3-}$ rings. The β-BaB_2O_4 crystal is built up by the Ba^{2+} cations and the $[B_3O_6]^{3-}$ anion rings by turns. The anionic group contains three coplanar BO_3^{3-} groups joined by three common oxygen atoms.[11]

The simultaneous TG-DTA curves of a synthetic sample of $BaB_2O_4\cdot 4H_2O$ are shown in Figure 2. The TG curve indicates that the total mass loss is 25.01 % from (373 to 773) K, which corresponds to the loss of four water molecules and can be

Table 3. Thermochemical Cycle and Results for the Derivation of $\Delta_fH_m°(BaB_2O_4\cdot 4H_2O$, 298.15 K)

no.	reaction	$\Delta_rH°$/kJ mol^{-1}
1	$2H_3BO_3(s) + 46.660(HCl\cdot 54.506H_2O) = 2H_3BO_3(aq) + 46.660(HCl\cdot 54.506H_2O)$	43.68 ± 0.10
2	$Ba(OH)_2\cdot 8H_2O(s) + 2H_3BO_3(aq) + 46.660(HCl\cdot 54.506H_2O) = BaCl_2(aq) + 2H_3BO_3(aq) + 44.660(HCl\cdot 55.171H_2O)$	−55.42 ± 0.36
3	$46.660(HCl\cdot 54.506H_2O) + 8H_2O(l) = 46.660(HCl\cdot 54.677H_2O)$	−0.16 ± 0.04
4	$BaB_2O4\cdot 4H_2O(s) + 46.660(HCl\cdot 54.677H_2O) = BaCl_2(aq) + 2H_3BO_3(aq) + 44.660(HCl\cdot 57.171H_2O)$	−7.63 ± 0.10
5	$Ba(OH)_2\cdot 2H_2O(s) + 2H_3BO_3(s) = BaB_2O_4\cdot 4H_2O(s) + 8H_2O(l)$	−3.95 ± 0.39[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.

Table 4. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^\circ(\beta\text{-BaB}_2O_4, 298.15\ K)$

no.	reaction	$\Delta_r H^\circ$/kJ·mol^{-1}
1	$2H_3BO_3(s) + 47.016(HCl·54.506H_2O) = 2H_3BO_3(aq) + 47.016(HCl·54.506H_2O)$	43.68 ± 0.10
2	$Ba(OH)_2·8H_2O(s) + 2H_3BO_3(aq) + 47.016(HCl·54.506H_2O) = BaCl_2(aq) + 2H_3BO_3(aq) + 45.016(HCl·57.150H_2O)$	-55.42 ± 0.36
3	$47.016(HCl·54.506H_2O) + 12H_2O(l) = 47.016(HCl·54.761H_2O)$	-0.24 ± 0.06
4	$BaB_2O_4(s) + 47.016(HCl·54.761H_2O) = BaCl_2(aq) + 2H_3BO_3(aq) + 45.016(HCl·57.150H_2O)$	-93.06 ± 0.24
5	$Ba (OH)_2·8H_2O(s) + 2H_3BO_3(s) = BaB_2O_4(s) + 12H_2O(l)$	81.56 ± 0.45[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.

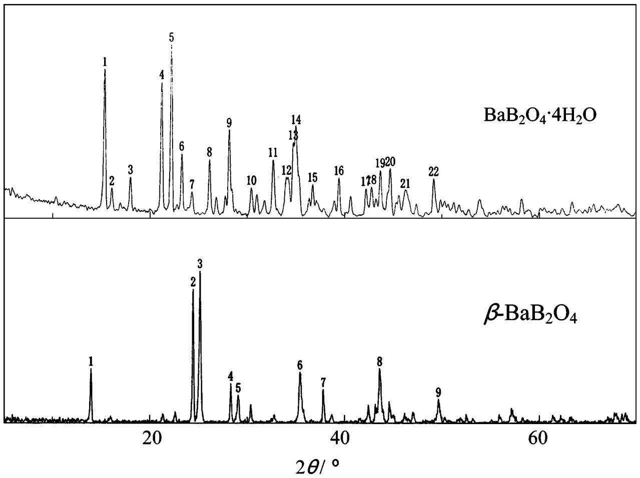

Figure 1. X-ray powder diffraction patterns of synthetic samples.

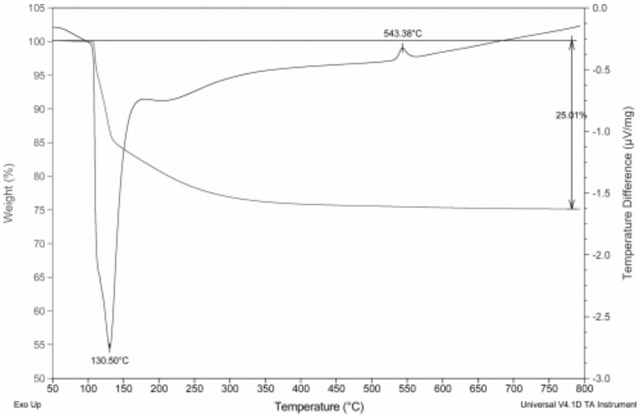

Figure 2. Simultaneous TG-DTA curves of $BaB_2O_4·4H_2O$.

compared with the calculated value of 24.43 %. In the DTA curve, there are two peaks. The first endothermic peak appearing at 403.5 K is related to the dehydration of crystal water. The forming amorphous phase recrystallizes as shown by the exothermic peak at 816.4 K. The simultaneous TG-DTA curves of a synthetic sample of β-BaB_2O_4 (Figure 3) indicate that there is no mass loss from (323 to 1073) K. All of above results indicate that the two synthetic samples are pure and suitable for the calorimetric experiments.

Results of Calorimetric Experiments. The molar enthalpies of solution of $Ba(OH)_2·8H_2O$ in $(HCl + H_3BO_3)$(aq) and of $BaB_2O_4·4H_2O$ and β-BaB_2O_4 in HCl(aq) at 298.15 K are listed in Tables 1 and 2, respectively, in which m is the mass of sample; $\Delta_{sol}H_m$ is the molar enthalpy of solution of the solute; and the uncertainty is estimated as twice the standard deviation of the mean.

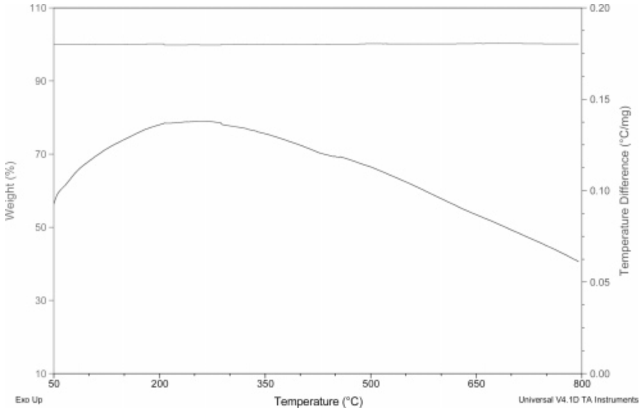

Figure 3. Simultaneous TG-DTA curves of β-BaB_2O_4.

Tables 3 and 4 give the thermochemical cycles for the derivation of the standard molar enthalpies of formation of $BaB_2O_4·4H_2O$ and β-BaB_2O_4. The molar enthalpy of solution of $H_3BO_3(s)$ of (21.84 ± 0.05) kJ·mol^{-1} in 1 mol·dm^{-3} HCl(aq) was taken from our previous work.[7] The enthalpy of dilution of HCl(aq) was calculated from the NBS tables.[12] The enthalpy change in the formation of $BaB_2O_4·4H_2O$ and β-BaB_2O_4 from the reaction of reagents in the solid phase, $-(3.95 \pm 0.39)$ kJ·mol^{-1} and (81.56 ± 0.45) kJ·mol^{-1} were calculated on the basis of the thermochemical cycles. The standard molar enthalpies of formation of $H_3BO_3(s)$ and $H_2O(l)$ were taken from the CODATA Key Values,[13] namely, $-(1094.8 \pm 0.8)$ kJ·mol^{-1} and $-(285.830 \pm 0.040)$ kJ·mol^{-1}, respectively. The standard molar enthalpy of formation of $Ba(OH)_2·8H_2O(s)$ of -3342.2 kJ·mol^{-1} was taken from the NBS tables.[12] From these data, the standard molar enthalpies of formation of $BaB_2O_4·4H_2O$ and β-BaB_2O_4 were calculated to be $-(3249.1 \pm 1.7)$ kJ·mol^{-1} and $-(2020.3 \pm 1.7)$ kJ·mol^{-1}, respectively.

Conclusions

Through an appropriate thermochemical cycle, the standard molar enthalpies of formation of $BaB_2O_4·4H_2O$ and β-BaB_2O_4 have been obtained from measured enthalpies of solution, together with the standard molar enthalpies of formation of $H_3BO_3(s)$, $Ba(OH)_2·8H_2O(s)$, and $H_2O(l)$.

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