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Hydrothermal Synthesis and Standard Molar Enthalpy of Formation of Zinc Borate of $4ZnO \cdot B_2O_3 \cdot H_2O$[†]

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The zinc borate $4ZnO \cdot B_2O_3 \cdot H_2O$ has been synthesized and characterized by means of chemical analysis, X-ray diffraction (XRD), FT-IR, and DTA-TG. The measured molar enthalpy of solution of $4ZnO \cdot B_2O_3 \cdot H_2O(s)$ in $HCl \cdot 54.572H_2O$ is $-(265.64 \pm 0.11)$ $kJ \cdot mol^{-1}$. With previously determined enthalpies of solution of $H_3BO_3(s)$ in 1 $mol \cdot dm^{-3}$ HCl(aq) and of ZnO(s) in ($HCl + H_3BO_3$) aqueous solution, together with the use of the standard molar enthalpies of formation for ZnO(s), $H_3BO_3(s)$, and $H_2O(l)$, the standard molar enthalpy of formation for $4ZnO \cdot B_2O_3 \cdot H_2O(s)$ was calculated as $-(3030.46 \pm 1.72)$ $kJ \cdot mol^{-1}$.

Introduction

Zinc borates, such as $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$ and $4ZnO \cdot B_2O_3 \cdot H_2O$, are frequently used as fire retardants and smoke suppressants for polymers, rubbers, and coatings.[1,2] Because of its relatively high dehydration temperature, $4ZnO \cdot B_2O_3 \cdot H_2O$ (FB415)[2] offers significant advantages for compounding with polymers requiring processing at high temperatures. Its structure was determined as $Zn_2(OH)BO_3$ by single-crystal X-ray diffraction in 2003.[3] As part of the continuing study of the thermochemistry of hydrated zinc borates,[4] this paper reports its standard molar enthalpy of formation.

Experimental Section

Synthesis and Characterization of the $4ZnO \cdot B_2O_3 \cdot H_2O$ Sample. All reagents used in the synthesis of the $4ZnO \cdot B_2O_3 \cdot H_2O$ were of analytical grade. A mixture of 1.4293 g of $Na_2B_4O_7 \cdot 10H_2O$ in 15 mL of distilled water (stirred for 1 h at 40 °C) and 1.0782 g of $ZnSO_4 \cdot 7H_2O$ in 15 mL of distilled water (stirred for 1 h at room temperature) was sealed in a Teflon-lined stainless steel vessel and heated at 160 °C for 4 days. The solids were separated and washed thoroughly with distilled water, then with alcohol and ether, and finally dried at 120 °C to a constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu target at $8° \cdot min^{-1}$), FT-IR spectroscopy (recorded over the (400 to 4000) cm^{-1} region on a Bruker Equinox 55 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 sample were determined by EDTA titration for Zn^{2+} and by NaOH standard solution in the presence of mannitol for B_2O_3.

Calorimetric Experiment. All the enthalpies of solution were measured with an RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which has been 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 (17.563 ± 0.099) $kJ \cdot mol^{-1}$, which was in agreement with that of (17.524 ± 0.028) $kJ \cdot mol^{-1}$ reported in the literature.[7]

Table 1. Thermochemical Cycle and Results for the Derivation of $\Delta_f H_m^o$ ($4ZnO \cdot B_2O_3 \cdot H_2O$, 298.15 K)[a]

no.	reaction	$\Delta_r H^o$ ($kJ \cdot mol^{-1}$)	ref
(1)	$2H_3BO_3(s) + 186.725 (HCl \cdot 54.561H_2O) = 2H_3BO_3(aq) + 186.725 (HCl \cdot 54.561H_2O)$	43.68 ± 0.10	6
(2)	$4ZnO(s) + 2H_3BO_3(aq) + 186.725 (HCl \cdot 54.561H_2O) = 4ZnCl_2(aq) + 2H_3BO_3(aq) + 178.725 (HCl \cdot 57.026H_2O)$	-320.04 ± 0.60	4
(3)	$186.725 (HCl \cdot 54.561H_2O) + 2H_2O(l) = 186.725 (HCl \cdot 54.572H_2O)$	-0.04 ± 0.01	9
(4)	$4ZnO \cdot B_2O_3 \cdot H_2O(s) + 186.725 (HCl \cdot 54.572H_2O) = 4ZnCl_2(aq) + 2H_3BO_3(aq) + 178.725 (HCl \cdot 57.026H_2O)$	-265.64 ± 0.11	this work
(5)	$4ZnO(s) + 2H_3BO_3(s) = 4ZnO \cdot B_2O_3 \cdot H_2O(s) + 2H_2O(l)$	-10.68 ± 0.62[b]	

[a] $\Delta_f H_m^o$ ($4ZnO \cdot B_2O_3 \cdot H_2O$, s) $= \Delta_r H_m^o (5) + 4\Delta_f H_m^o$ (ZnO, s) $+ 2\Delta_f H_m^o$ (H_3BO_3, s) $- 2\Delta_f H_m^o$(H_2O, l). [b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

The reaction in the calorimeter in this study was the reverse of $4ZnO(s) + 2H_3BO_3(s) = 4ZnO \cdot B_2O_3 \cdot H_2O(s) + 2H_2O(l)$, reaction (5) in Table 1. The 1.0004 $mol \cdot dm^{-3}$ HCl(aq) solvent, prepared from analytical grade hydrochloric acid and deionized water and standardized by titration with standard sodium carbonate, rapidly dissolves all components of the reaction. With density, 1.019 $g \cdot cm^{-3}$, its concentration is $HCl \cdot 54.561H_2O$.

Table 1 gives the thermochemical cycle used in this study. Strict control of the stoichiometry in each step of the calorimetric cycle must be observed, with the objective that the dissolution of the reactants gives the same composition as those of the products in the reaction. Applying Hess's law, the enthalpy of reaction 5 ($\Delta_r H_m^o$ (5)) can be calculated by

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

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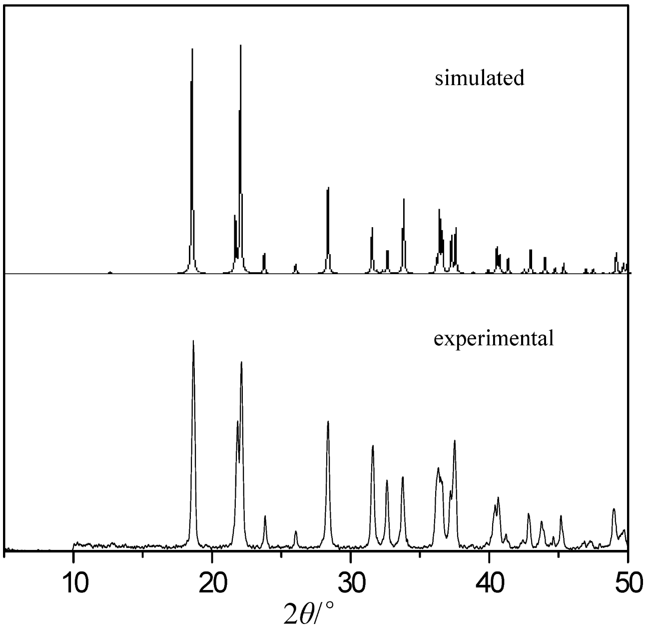

Figure 1. X-ray powder diffraction pattern of the synthetic sample.

The standard molar enthalpy of formation of $4ZnO\cdot B_2O_3\cdot H_2O$ can be obtained from the value of $\Delta_r H_m^o$ (5) in combination with the molar enthalpies of formation of H_3BO_3(s), ZnO(s), and H_2O(l).

Results

Chemical analysis of synthetic sample gave (calcd/found, %) ZnO (78.79/79.36) and B_2O_3 (16.85/16.22).

Figure 1 shows the powder XRD pattern of the as-synthesized compound and the simulated pattern on the basis of the single-crystal structure of $4ZnO\cdot B_2O_3\cdot H_2O$.[3] The diffraction peaks on patterns corresponded well in position, indicating the phase purity of the as-synthesized sample.

The FT-IR spectrum exhibited the following absorption bands, and they were assigned referring to the literature.[8] The bands at (3361 and 3404) cm^{-1} are the stretching vibration of the O−H group. The band at 1305 cm^{-1} is the asymmetric stretching mode of B(3)−O. The band at 1246 cm^{-1} is the in-plane bending of B−O−H. The bands at (714 and 625) cm^{-1} are assigned to out-of-plane bending of B(3)−O. The band at 532 cm^{-1} is assigned to the bending mode of B(3)−O. The bands at (1024 and 478) cm^{-1} are assigned to the bending mode of Zn−O. These assignments are consistent with the result of its structure not containing the BO_4 group.

The simultaneous TG-DTA curves of the sample of $4ZnO\cdot B_2O_3\cdot H_2O$ indicate that the total mass loss is 4.90 % from (447 to 614) °C, which corresponds to the loss of 1 water molecule and is near the calculated value of 4.36 %. The mass loss at (50 to 447) °C, 1.2 %, might be from moisture on the surface of the sample.

The molar enthalpy of solution of $4ZnO\cdot B_2O_3\cdot H_2O$(s) in 2.00 cm^3 of $HCl\cdot 54.572H_2O$ at 298.15 K was measured to be $-(265.64 \pm 0.11)\ kJ\cdot mol^{-1}$, where the uncertainty is estimated as twice the standard deviation of the mean with experimental number $n = 5$.

Table 1 gives the thermochemical cycle used for the derivation of the standard molar enthalpy of formation of $4ZnO\cdot B_2O_3\cdot H_2O$. Using the standard molar enthalpies of formation of ZnO(s), H_3BO_3(s), and H_2O(l), namely, $-(350.46 \pm 0.27)\ kJ\cdot mol^{-1}$, $-(1094.8 \pm 0.8)\ kJ\cdot mol^{-1}$, and $-(285.830 \pm 0.040)\ kJ\cdot mol^{-1}$, respectively,[10] the standard molar enthalpy of formation of $4ZnO\cdot B_2O_3\cdot H_2O$ at 298.15 K was calculated to be $-(3030.46 \pm 1.72)\ kJ\cdot mol^{-1}$.

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