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Thermodynamic properties of two zinc borates: $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$

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ABSTRACT

Two pure zinc borates with microporous structure $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ have been synthesized and characterized by XRD, FT-IR, TG techniques and chemical analysis. The molar enthalpies of solution of $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$(s) and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$(s) in 1 mol · dm^{-3} HCl(aq) were measured by microcalorimeter at T = 298.15 K, respectively. The molar enthalpies of solution of ZnO(s) in the mixture solvent of 2.00 cm^3 of 1 mol · dm^{-3} HCl(aq) in which 5.30 mg of H_3BO_3 were added were also measured. With the incorporation of the previously determined enthalpy of solution of H_3BO_3(s) in 1 mol · dm^{-3} HCl(aq), 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 enthalpies of formation of $-(6115.3 \pm 5.0)$ kJ · mol^{-1} for $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $-(9606.6 \pm 8.5)$ kJ · mol^{-1} for $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ at T = 298.15 K were obtained on the basis of the appropriate thermochemical cycles.

1. Introduction

Borate materials have attracted a great deal of attention in the past decades owing to their structural chemistry and potential applications in mineralogy, luminescence, nonlinear optical properties and industrial importance [1–4]. So far, there are many kinds of zinc borates found in nature as well as synthesized in the laboratory [5]. Some of these borates have useful properties. For example, $2ZnO{\cdot}3B_2O_3{\cdot}3.3–3.7H_2O$ can be used as a flame retardant [6]. Some of these borates possess three-dimensional open framework structures and might be used as microporous materials, such as $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ [7].

Thermodynamic properties play very important roles in scientific research and industrial applications. Thermochemical data can provide information on stability and reactivity of molecules that are used, and also are a key factor in the safe and successful scale-up of chemical processes in the chemical industry. Our group has reported the thermodynamic properties of several boron-containing microporous materials [8–10] and a few zinc borates for $2ZnO{\cdot}3B_2O_3{\cdot}3H_2O$, $2ZnO{\cdot}3B_2O_3{\cdot}7H_2O$ and $3ZnO{\cdot}5B_2O_3{\cdot}14H_2O$ [11,12]. However, investigation of the thermodynamic properties of the zinc borates with microporous structure was not reported in the literature. This paper reports the determination of standard molar enthalpies of formation of two zinc borates, $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ with microporous structure and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$, by using a heat conduction microcalorimeter.

2. Experimental

2.1. Synthesis and characterization of samples

Samples of $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ were synthesized referring to literature [7] under mild hydrothermal conditions. All reagents used in the synthesis were commercially available with analytic grade and used without further purification. Table 1 summarizes relevant information on sample material purities.

In a typical synthesis, 0.40 g of ZnO, 1.008 g of H_3BO_3 and 4.60 cm^3 of distilled water were added in 25 cm^3 of Teflon-lined stainless steel vessels, and heated at T = 453 K for about 2 days, then cooled to room temperature. The resulting white solid powder was washed with hot distilled water, and dried in air at ambient temperature. It need to indicate that the $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ sample was obtained when the leakage taken place for the used Teflon-lined stainless steel vessel.

The samples obtained were characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu target at 8° min^{-1}), FT-IR spectroscopy (recorded over the 400 to 4000 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellet at room temperature), and TG (TA-SDT Q600 simultaneous thermal analyser under N_2 atmosphere with a heating rate of 10 K · min^{-1}).

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The chemical compositions of the samples were determined by EDTA titration for Zn^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the mass loss in the TG curve for H_2O.

2.2. Calorimetric experiment

The thermochemical cycles designed for the derivation of the molar enthalpies formation of $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ were shown in figures 1 and 2, respectively. The 1 mol · dm^{-3} HCl(aq) solvent can dissolve all components of virtual reaction (5), and its concentration, (1.0004 ± 0.0001) mol · dm^{-3}, was determined by titration with standard sodium carbonate. With the use of its density of 1.019 g · cm^{-3} (taken from chemical handbook [13]), its concentration can also be expressed as the form of HCl 54.561H_2O.

The molar enthalpies of solution of $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ in 1 mol · dm^{-3} HCl(aq) were measured, respectively. The molar enthalpies of solution of H_3BO_3(s) in HCl 54.561H_2O, of ZnO(s) in the mixture of HCl 54.561H_2O and calculated amount of H_3BO_3(s) were also measured, respectively. In all these determinations, strict control of the stoichiometry in each step of the calorimetric cycle must be observed with the objective that the dissolution of the reactants give the same composition as those of the products. Hence the masses of ZnO, $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ samples were calculated respectively when the mass of sample H_3BO_3 was used as 5.30 mg as per the literature [14] according to the stoichiometry of reaction (5) in figures 1 and 2.

Applying Hess's law, $\Delta_r H^\theta_m$ (5) can be calculated according to the following expression:

$$\Delta_r H^\theta_m(5) = \Delta_r H^\theta_m(1) + \Delta_r H^\theta_m(2) - \Delta_r H^\theta_m(3) - \Delta_r H^\theta_m.$$

The standard molar enthalpies of formation of $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$ and $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$ can be obtained by the values of $\Delta_r H^\theta_m$ (5) in combination with the standard molar enthalpies of formation of ZnO(s), H_3BO_3(s) and H_2O(l).

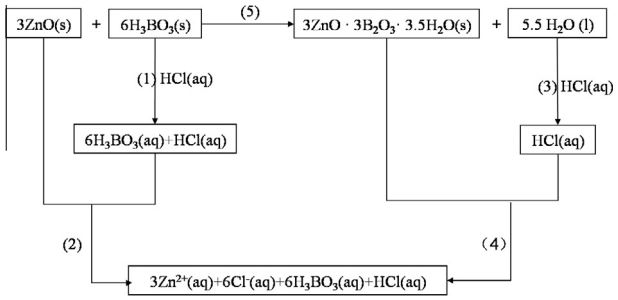

FIGURE 1. The designed thermochemical cycle of $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$.

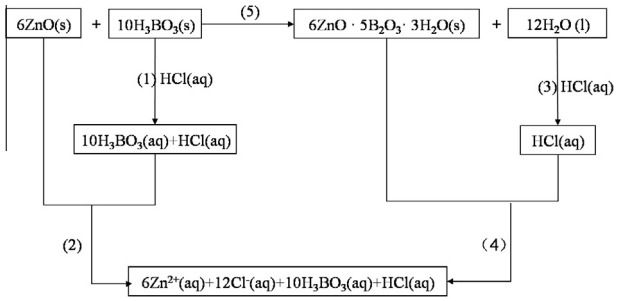

FIGURE 2. The designed thermochemical cycle of $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$.

TABLE 1
Provenance and mass fraction purity of the chemical reagents used in this study.

Chemical name	Source	State	Mass fraction purity[a]
ZnO	Xian Chemical Reagent Factory	Solid	⩾0.995
H_3BO_3	Xian Chemical Reagent Factory	Solid	⩾0.990
Na_2CO_3	Aladdin	Solid	⩾0.9980
KCl	Aladdin	Solid	⩾0.9999
HCl	Sinopharm Chemical Reagent Co., Ltd	Aqueous	0.38

[a] Stated purity from the commercial supplier.

All values of the enthalpy of solution were measured using a RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China), which has been described in detail previously [15]. Calorimetric experiments were performed five times at T = 298.15 K. The total time required for the complete dissolution reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

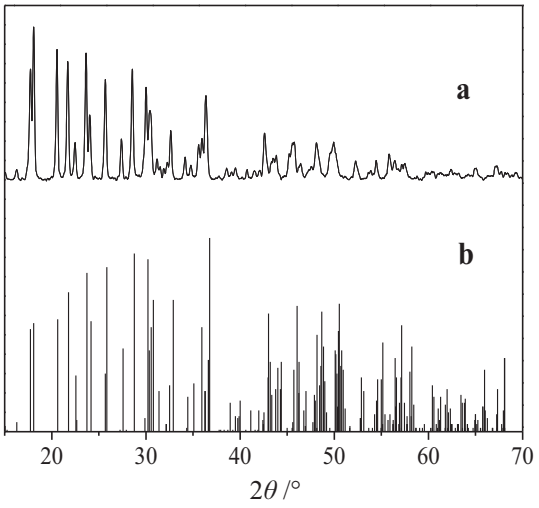

FIGURE 3. X-ray powder diffraction pattern of $3ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$: (a) experimental, (b) simulated.

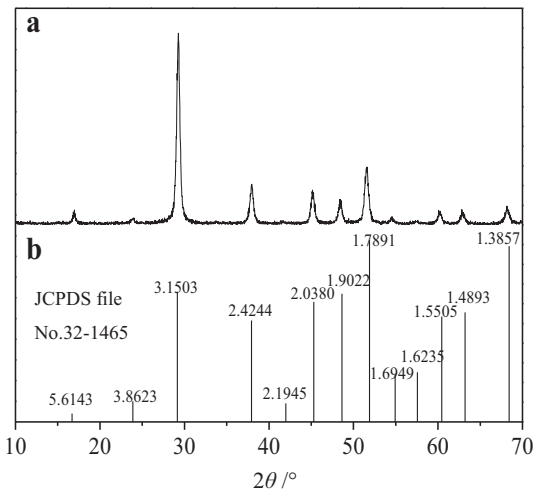

FIGURE 4. X-ray powder diffraction pattern of $6ZnO{\cdot}5B_2O_3{\cdot}3H_2O$: (a) experimental, (b) JCPDS file No. 32-1465.