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Synthesis and thermochemistry of $2CaO \cdot B_2O_3 \cdot H_2O$

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Abstract

A pure calcium borate $2CaO \cdot B_2O_3 \cdot H_2O$ has been synthesized under hydrothermal condition and characterized by XRD, FT-IR and TG as well as by chemical analysis. The molar enthalpy of solution of $2CaO \cdot B_2O_3 \cdot H_2O$ in $HCl \cdot 54.579H_2O$ was determined. From a combination of this result with measured enthalpies of solution of H_3BO_3 in $HCl \cdot 54.561H_2O$ and of CaO in $HCl + H_3BO_3$ solution, together with the standard molar enthalpies of formation of CaO(s), H_3BO_3(s), and H_2O(l), the standard molar enthalpy of formation of $-(3041.8 \pm 2.5)\,\text{kJ}\,\text{mol}^{-1}$ of $2CaO \cdot B_2O_3 \cdot H_2O$ was obtained.

Keywords: $2CaO \cdot B_2O_3 \cdot H_2O$; Synthesis; Standard molar enthalpy of formation

1. Introduction

There are many kinds of hydrated calcium borates, both natural and synthetic. Some of them are useful chemical industrial materials, which are used in glass, pottery and porcelain enamel industry, especially in unalkali glass industry. Thermodynamic properties play very important roles in scientific research and industrial applications. Gurevich et al. [1] determined the standard molar enthalpies of formation of the natural calcium borate minerals of $Ca_2B_6O_{11} \cdot 5H_2O$ and $Ca_2B_6O_{11} \cdot 13H_2O$. Li et al. [2] also reported the standard molar enthalpy of formation of five other hydrated calcium borates. This paper reports the synthesis method and the standard molar enthalpy of formation of $2CaO \cdot B_2O_3 \cdot H_2O$, which is a calcium borate mineral named Parasibirskite.

2. Experimental

2.1. Synthesis of $2CaO \cdot B_2O_3 \cdot H_2O$

2.806 g of CaO (obtained by the decomposition of $CaCO_3$ (A.R.) at 1223 K for 3 h), 3.093 g of H_3BO_3 (A.R.), and 30 cm^3 of H_2O were put in the lining of small autoclave (40 cm^3). The mixture was stirred and placed in a oven at 453 K. The autoclave was cooled naturally and opened after reaction 5 days. The solid phase was separated, washed thoroughly with hot distilled water, and then with alcohol and ether. Finally, the solid phase was dried at 353 K to constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC), FT-IR spectroscopy (Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature), and TG (Perkin-Elmer TGA7, heating rate of $0.167\,\text{K}\,\text{s}^{-1}$ in flowing N_2). The chemical compositions of the sample were determined by EDTA titration for Ca^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by difference for H_2O.

2.2. Method of calorimetric experiment

$2CaO \cdot B_2O_3 \cdot H_2O$ can be regarded as the product of the following reaction (5), and the thermochemical cycle was designed as Fig. 1.

The approximately $1\,\text{mol}\,\text{dm}^{-3}$ HCl(aq) solvent can dissolve instantaneously all components of the reaction (5), which was prepared from analytical grade hydrochloric acid and deionized water, and its concentration was determined by titration with standard sodium carbonate.

The standard molar enthalpy of formation of $2CaO \cdot B_2O_3 \cdot H_2O$ could be obtained by the value of $\Delta_r H_m^\circ$ (5) in combination with the standard molar enthalpies of formation of

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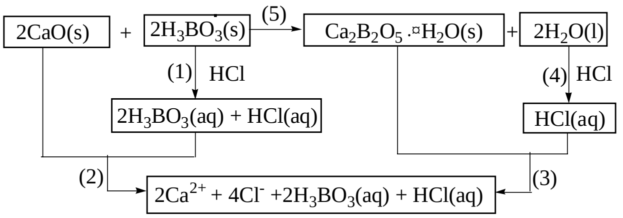

Fig. 1. Schematic drawing of the thermochemical cycle.

CaO(s), H_3BO_3(s) and H_2O(l). Value of $\Delta_r H_m^\circ$ (5) could be obtained by means of the following reactions:

$$2H_3BO_3(s) + HCl \cdot 54.561H_2O(aq) = \text{Soln}\,X_1 \qquad (1)$$

$$2CaO(s) + \text{Soln}\,X_1 = \text{Soln}\,X_2 \qquad (2)$$

$$2CaO \cdot B_2O_3 \cdot H_2O(s) + \text{Soln}\,X_4 = \text{Soln}\,X_3 \qquad (3)$$

$$2H_2O(l) + HCl \cdot 54.561H_2O(aq) = \text{Soln}\,X_4 \qquad (4)$$

$$\text{Soln}\,X_2 = \text{Soln}\,X_3$$

In all these determinations, a strict control of the stoichiometries in each step of the calorimetric cycle must be obeyed, with the objective that the dissolution of the reactants give the same composition as those of the products. Applying Hess's law, $\Delta_r H_m^\circ$ (5) could be calculated according to the following expression:

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

An RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is a totally automatic instrument utilizing computer control, was used and has been described in detail previously [3,4]. 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. 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 RD496-III heat conduction microcalorimeter, calorimetric measurements on the enthalpy of solution of KCl (G.R.) in deionized water were made. The average experimental value $17.23 \pm 0.04\ kJ\,mol^{-1}$ of $\Delta_{sol}H_m$ of KCl(s) is in excellent agreement with that of $17.241 \pm 0.018\ kJ\,mol^{-1}$ reported in the literature [5]. This shows that the device for measuring the enthalpy of solution used in this work is reliable.

3. Results and discussion

3.1. Characterization of the synthetic sample

Chemical analysis results of synthetic sample: CaO, 55.90%; B_2O_3, 34.89%; H_2O, 9.21%; mole ratio of $CaO:B_2O_3:H_2O = 1.99:1.00:1.02$.

XRD pattern of synthetic sample is showed in Fig. 2. The characteristic d values are 0.6689, 0.4214, 0.3349, 0.2967,

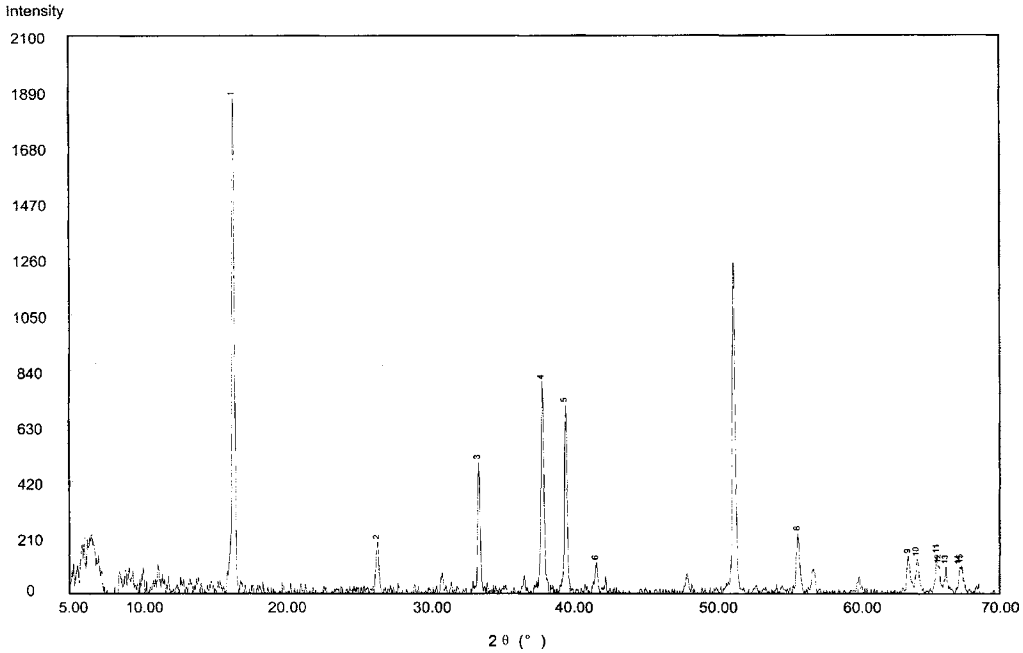

Fig. 2. X-ray powder diffraction pattern of $2CaO \cdot B_2O_3 \cdot H_2O$.

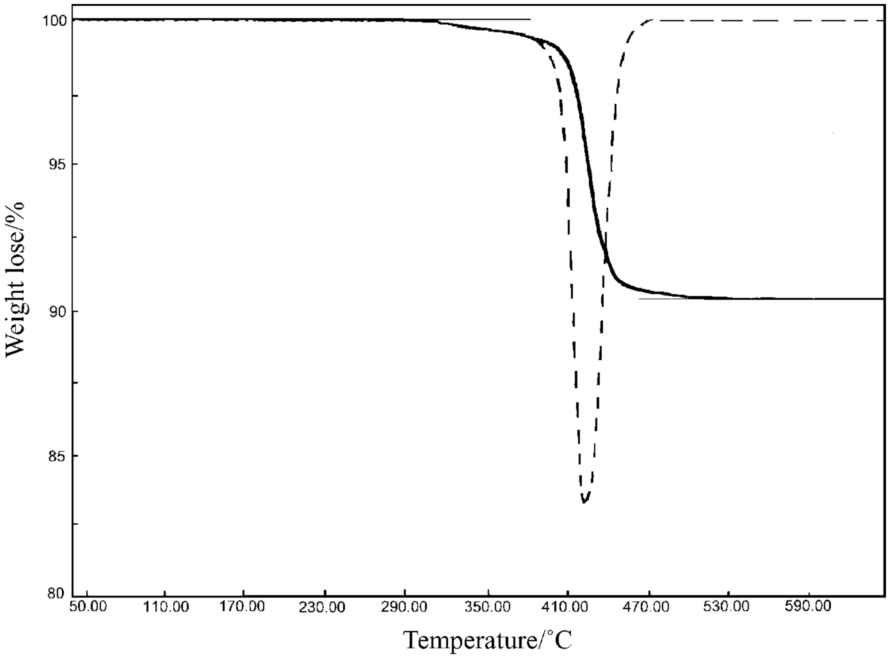

Fig. 3. TG-DTG curve of $2CaO{\cdot}B_2O_3{\cdot}H_2O$.

0.2849, 0.2709, 0.2232, 0.2068, 0.1838, 0.1822, 0.1787, 0.1772, and 0.1750 nm, which corresponds with those of Parasibirskite (see JCPDS File No. 22-0145) and shows absence of other crystalline forms in the synthetic sample.

The IR spectrum of synthetic sample exhibited the following absorptions and they were assigned referring to literature [6]. The band at 3356 cm^{-1} is the stretching of O–H. There is no band at 1600–1700 cm^{-1} which is assigned to the H–O–H bending mode, and this result shows that the compound does not contain the crystal water. The bands at 1430, 1305 and 910 cm^{-1} might be the asymmetric and symmetric stretching of B(3)–O, respectively. The band at 1158 cm^{-1} is the in-plane bending of B–O–H. The very strong band at 716 cm^{-1} is the out-of-plane bending of B(3)–O, which also exist in the compound of $Mg_2[B_2O_4(OH)_2]{\cdot}H_2O$ [7]. The bands at 592 and 560 cm^{-1} are the in-plane bending of B(3)–O.

TG-DTG curve (Fig. 3) indicates that the total weight loss is 9.62% from 623 to 873 K, which corresponds to the loss of 1 water molecule and can be compared with calculated value of 9.02%. High temperature of starting lose water shows that the H_2O in $2CaO{\cdot}B_2O_3{\cdot}H_2O$ molecules is the structural water.

Therefore, the structural formula for $2CaO{\cdot}B_2O_3{\cdot}H_2O$ can be written as $Ca_2[B_2O_4(OH)_2]$. All of above results indicates that the synthetic sample is pure $2CaO{\cdot}B_2O_3{\cdot}H_2O$ and is suitable for the calorimetric experiments.

3.2. Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 1, in which m is the mass of sample, $\Delta_{sol}H^\circ_m$ is the molar enthalpy of solution of solute, and the uncertainty is twice the standard deviation of the mean. Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $2CaO{\cdot}B_2O_3{\cdot}H_2O$. The molar enthalpy of solution of $H_3BO_3(s)$ of $21.83 \pm 0.08\,kJ\,mol^{-1}$ in $HCl{\cdot}54.561H_2O$, and of CaO(s) of $-(188.63 \pm 0.36)\,kJ\,mol^{-1}$ in the mixture of HCl and H_3BO_3 were taken from the literature [2]. The standard molar enthalpies of formation of $H_2O(l)$, CaO(s), and $H_3BO_3(s)$ were taken from the CODATA Key Values [8], namely $-(285.830 \pm 0.040)\,kJ\,mol^{-1}$, $-(634.92 \pm 0.90)\,kJ\,mol^{-1}$, and $-(1094.8 \pm 0.8)\,kJ\,mol^{-1}$, respectively. The enthalpy of dilution of HCl(aq) was calculated from the NBS tables [9]. From these data, the standard molar enthalpy of formation of $2CaO{\cdot}B_2O_3{\cdot}H_2O$ was calculated to be $-(3041.8 \pm 2.5)\,kJ\,mol^{-1}$.

For comparison, the enthalpy of formation of $2CaO{\cdot}B_2O_3{\cdot}H_2O$ can also be estimated by a group contribution method [10], which can be expressed in following equation:

Table 1
The molar enthalpies of solution of $2CaO{\cdot}B_2O_3{\cdot}H_2O$ in $HCl{\cdot}54.579H_2O$ at 298.15K[a]

No.	m (mg)	Δ_rH (mJ)	$\Delta_{sol}H_m$ ($kJ\,mol^{-1}$)
1	3.56	−3196.58	−179.39
2	3.45	−3095.41	−179.26
3	3.50	−3152.88	−179.97
4	3.51	−3151.24	−179.37
5	3.54	−3182.97	−179.64
Mean			−179.53±0.25[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 $\Delta_f H_m^\circ$ ($2CaO{\cdot}B_2O_3{\cdot}H_2O$, 298.15 K)

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$2H_3BO_3(s) + 114.20(HCl{\cdot}54.561H_2O) = 2H_3BO_3(aq) + 114.20(HCl{\cdot}54.561H_2O)$	43.66 ± 0.16
2	$2CaO(s) + 2H_3BO_3(aq) + 114.20(HCl{\cdot}54.561H_2O) = 2CaCl_2(aq) + 2H_3BO_3(aq) + 110.20(HCl{\cdot}56.560H_2O)$	−(377.26 ± 0.72)
3	$2CaCl_2(aq) + 2H_3BO_3(aq) + 110.20(HCl{\cdot}56.560H_2O) = 2CaO{\cdot}B_2O_3{\cdot}H_2O(s) + 114.20(HCl{\cdot}54.579H_2O)$	179.53 ± 0.25
4	$114.20(HCl{\cdot}54.579H_2O) = 114.20(HCl{\cdot}54.561H_2O) + 2H_2O(l)$	0.04 ± 0.01
5	$2CaO(s) + 2H_3BO_3(s) = 2CaO{\cdot}B_2O_3{\cdot}H_2O(s) + 2H_2O(l)$	−(154.03 ± 0.78)

$$\Delta_f H_m^\circ(Ca_2[B_2O_4(OH)_2], s) = 2\Delta_f H_m^\circ(Ca^{2+}, aq) + \Delta_f H_m^\circ([B_2O_4(OH)_2]^{4-}, aq)$$

in which the $\Delta_f H_m^\circ$ of −542.83 kJ mol^{-1} of Ca^{2+}(aq) was taken from the literature [10], the $\Delta_f H_m^\circ$ of −1671.24 kJ mol^{-1} of $[B_2O_4(OH)_2]^{4-}$ was calculated from the $\Delta_f H_m^\circ$ of $Mg_2[B_2O_4(OH)_2]{\cdot}H_2O$ [7] according to the group contribution method [10]. The standard molar enthalpy of formation is, using this scheme, −3047.32 kJ mol^{-1}. The calculated value is close to the experimental result. The relative error is 0.18%.

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