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New synthetic method and thermochemistry of szaibelyite

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Abstract

A new synthetic method of szaibelyite ($2MgO{\cdot}B_2O_3{\cdot}H_2O$) has been reported. The enthalpy of solution of $2MgO{\cdot}B_2O_3{\cdot}H_2O$ in 2.9842 mol dm^{-3} HCl (aq) was determined. From a combination of this result with measured enthalpies of solution of H_3BO_3 in 2.9842 mol dm^{-3} HCl (aq) and of MgO in (HCl + H_3BO_3) solution, together with the standard molar enthalpies of formation of MgO (s), H_3BO_3 (s), and H_2O (l), the standard molar enthalpy of formation of $-(2884.36 \pm 1.82)$ kJ mol^{-1} of $2MgO{\cdot}B_2O_3{\cdot}H_2O$ was obtained.

Keywords: Szaibelyite; Synthesis; Standard molar enthalpy of formation; Solution calorimetry

1. Introduction

There are many kinds of magnesium borates, both natural and synthetic. Some of them have useful properties, such as $2MgO{\cdot}B_2O_3$ ($Mg_2B_2O_5$) and $2MgO{\cdot}B_2O_3{\cdot}H_2O$ might be prepared as whisker materials [1]. $2MgO{\cdot}B_2O_3{\cdot}H_2O$ named szaibelyite (ascharite) is a magnesium borate mineral with a structure formula of $Mg_2[OH][B_2O_4(OH)]$ [2]. Recently, we also found a new synthetic method for it when we investigated the phase transformation of $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$ in boric acid solution. The advantages of this method consist in the natural material of $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$ which was obtained from the natural concentrated salt lake brine [3], relatively lower hydrothermal reaction temperature.

Thermodynamic properties play very important roles in scientific research and industrial applications. Li et al. [4] reported the standard molar enthalpy of formation of eight hydrated magnesium borates. This paper reports this new synthesis method and the standard molar enthalpy of formation of $2MgO{\cdot}B_2O_3{\cdot}H_2O$.

2. Experimental

$2MgO{\cdot}B_2O_3{\cdot}H_2O$ could be synthesized by the dissolution and phase transformation of double salt $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$ in boric acid solution at hydrothermal condition as follows: 1.86 g (3.28×10^{-3} mol) $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$ (synthesized by modification of the literature method [5]), 1.85 g (2.99×10^{-2} mol) H_3BO_3, and 20 ml H_2O were put in the lining of small autoclave (40 ml). The mixture was stirred for 0.5 h, and placed in an oven at 180 °C. The autoclave was cooled naturally and opened after reaction 3 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 80 °C to constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC), FT-IR spectroscopy (Bruker Equinox 55 spectrometer with KBr pellets at room temperature), TG (Perkin-Elmer TGA7, at a heating rate of 10 K min^{-1} in flowing N_2). The chemical compositions of the sample were determined by EDTA titration for Mg^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by difference for H_2O.

$2MgO{\cdot}B_2O_3{\cdot}H_2O$ can be regarded as the product of the following reaction:

$$2MgO\,(s) + 2H_3BO_3\,(s) = Mg_2B_2O_5 \cdot H_2O\,(s) + 2H_2O \qquad (1)$$

$2MgO{\cdot}B_2O_3{\cdot}H_2O$ is one of the most difficult to dissolve of the magnesium borates, so the enthalpies of solution of $2MgO{\cdot}B_2O_3{\cdot}H_2O$, of H_3BO_3 in approximately 3 mol dm^{-3} HCl (aq), and of the calculated amount of MgO in aqueous (hydrochloric acid + boric acid) which consisted of approximately 3 mol dm^{-3} HCl (aq) and the calculated amount of H_3BO_3 were determined. The standard molar enthalpy of formation of $2MgO{\cdot}B_2O_3{\cdot}H_2O$ could be obtained by

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solution calorimetry as above in combination with the standard molar enthalpies of formation of MgO (s), H_3BO_3 (s), and H_2O (l).The HCl solvent was prepared from analytical grade hydrochloric acid and deionized water, and its concentration, 2.9842 mol l^{-1}, was determined by titration with standard sodium carbonate, and its density, 1.053 g cm^{-3}, was taken from Soviet Chemical Handbook [6].

A RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used and has been described in detail previously [7]. The temperature of the calorimetric experiment was 298.15 K. Additional double-layer glass tubes were put in the 15 ml 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, then the thermal effect was recorded automatically on a computer. Total time required for the complete reaction was about 0.5 h for H_3BO_3 (s) and MgO (s), 1 h for $2MgO{\cdot}B_2O_3{\cdot}H_2O$. There were no solid residues observed after the reactions in each calorimetric experiment.

3. Results and discussion

Chemical analysis results of synthetic sample: MgO, 47.21%; B_2O_3, 41.43%; H_2O, 11.36%; mole ratio of MgO: B_2O_3:H_2O = 1.97:1.00:1.06. TG curve indicates that the total loss is 10.78% in the range of 691 ∼ 933 ∼ 1043 K, which corresponds to the loss of one water molecule and can be compared with calculated value of 10.70%. The d (nm) values of XRD spectrum are 0.6232, 0.5181, 0.3020, 0.2980, 0.2659, 0.2599, 0.2569, 0.2536, 0.2429, 0.2318, 0.2304, 0.2202, 0.2079, 0.1554, 0.1548. FT-IR spectrum of synthetic sample exhibited the following absorptions and they were assigned referring to literature [8]. The band at 3561 and 3427 cm^{-1} is the stretching of O–H. The bands at 1461, 1400 and 1015, 981, 926 cm^{-1} might be the asymmetric and symmetric stretching of B(3)–O, respectively. The band at 1227 cm^{-1} is the in-plane bending of B–O–H. The strong band at 709, 627 cm^{-1} is the out-of-plane bending of B(3)–O. The weak band at 560 cm^{-1} is the in-plane bending of B(3)–O. No impurity lines were observed. The synthetic sample is suitable for the following calorimetric experiments.

To check the performance of RD496-III heat conduction microcalorimeter, calorimetric measurements on the enthalpies of solution of KCl (spectral purity) in deionized water and of THAM (trishydroxymethylaminomethane) in 0.1 mol dm^{-3} HCl (aq) were made, respectively. The average experimental values 17.23 ± 0.04 kJ mol^{-1} of $\Delta_{\rm sol} H_{\rm m}^{\propto}$ of KCl (s) and $-(29.75 \pm 0.04)$ kJ mol^{-1} of THAM are in excellent agreement with those of 17.234 kJ mol^{-1} reported in the literature [9] and $-(29.73 \pm 0.04)$ kJ mol^{-1} reported in the literature [4], respectively. This shows that the device for measuring the enthalpy of solution used in this work is reliable.

Table 1
The molar enthalpies of solution of H_3BO_3 (s) in 2.9842 mol dm^{-3} HCl at 298.15 K[a]

No.	Mass/mg	$\Delta_{\rm sol}H_{\rm m}$ (kJ mol^{-1})
1	5.94	22.60
2	6.26	22.81
3	6.14	22.73
4	6.15	22.32
5	6.17	22.53
Mean		22.60 ± 0.17[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
The molar enthalpies of solution of MgO (s) in ($HCl + H_3BO_3$) solution at 298.15 K[a]

No.	Mass/mg	$\Delta_{\rm sol}H_{\rm m}$ (kJ mol^{-1})
1	1.40	−148.19
2	1.49	−148.44
3	1.47	−148.71
4	1.46	−148.52
5	1.44	−148.64
Mean		−148.50 ± 0.18[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.

The results of the calorimetric measurements are given in Tables 1–3, in which $\Delta_{\rm sol}H_{\rm m}$ is the molar enthalpy of solution of solute, and the uncertainty is estimated as twice the standard deviation of the mean, namely, $\delta = 2\sqrt{\sum(x_i - \bar{x})^2/n(n-1)}$, in which n is the experimental number ($n = 5$), x_i the experimental value of each series of repeated measurement and $\bar{x}$ the mean value.

Table 4 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $2MgO{\cdot}B_2O_3{\cdot}H_2O$. The two solutions after reactions (2) and (3) had the same value of refraction index n^{25} of 1.3558 (A 2WA-J type of Abbe refractometer, Shanghai, China), indicating that their thermodynamic states were the same and the thermochemical cycle designed in Table 4

Table 3
The molar enthalpies of solution of $2MgO{\cdot}B_2O_3{\cdot}H_2O$ in 2.9842 mol dm^{-3} HCl at 298.15 K[a]

No.	Mass/mg	$\Delta_{\rm sol}H_{\rm m}$ (kJ mol^{-1})
1	1.00	−188.36
2	1.04	−189.08
3	1.08	−188.74
4	1.03	−187.94
5	1.04	−188.56
Mean		−188.54 ± 0.38[b]

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

Table 4
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($2MgO \cdot B_2O_3 \cdot H_2O$, 298.15 K)

Reaction	$\Delta_r H_m$ ($kJ\,mol^{-1}$)
(1) $2H_3BO_3$ (s) + 1003.936($HCl \cdot 17.576H_2O$) = $2H_3BO_3$ (aq) + 1003.936($HCl \cdot 17.576H_2O$)	45.20 ± 0.34
(2) 2MgO (s) + $2H_3BO_3$ (aq) + 1003.936($HCl \cdot 17.576H_2O$) = $2MgCl_2$ (aq) + $2H_3BO_3$ (aq) + 999.936($HCl \cdot 17.648H_2O$)	−297.00 ± 0.36
(3) $2MgCl_2$ (aq) + $2H_3BO_3$ (aq) + 999.936($HCl \cdot 17.648H_2O$) = $Mg_2B_2O_5 \cdot H_2O$ (s) + 1003.936($HCl \cdot 17.578H_2O$)	188.54 ± 0.38
(4) 1003.936($HCl \cdot 17.578H_2O$) = 1003.936($HCl \cdot 17.576H_2O$) + $2H_2O$ (l)	0.04 ± 0.01
(5) 2MgO (s) + $2H_3BO_3$ (s) = $Mg_2B_2O_5 \cdot H_2O$ (s) + $2H_2O$ (l)	−63.22 ± 0.62

was correct. The standard molar enthalpies of formation of H_2O (l), MgO (s), and H_3BO_3 (s) were taken from the CODATA Key Values [10], namely −(285.830 ± 0.040), −(601.60 ± 0.30), and −(1094.8 ± 0.8) $kJ\,mol^{-1}$, respectively. The enthalpy of dilution HCl (aq) was calculated from the NBS tables [11]. From these data, the standard molar enthalpy of formation of $2MgO \cdot B_2O_3 \cdot H_2O$ was calculated to be −(2884.36 ± 1.82) $kJ\,mol^{-1}$.

A similar compound $2MgO \cdot B_2O_3 \cdot 2H_2O$ was obtained by the phase transformation of $2MgO \cdot 2B_2O_3 \cdot MgCl_2 \cdot 14H_2O$ in water at 120 °C. It is easy to dissolve in 1 $mol\,dm^{-3}$ HCl (aq). So the standard molar enthalpy of formation of −(3185.78 ± 1.91) $kJ\,mol^{-1}$ of $2MgO \cdot B_2O_3 \cdot 2H_2O$ was obtained by solution calorimetry of it in 1 $mol\,dm^{-3}$ HCl (aq) [12]. The difference between the two values is −301.42, which near the −290.42 $kJ\,mol^{-1}$ of $\Delta_f H_m^\circ$ of structural water and might result from the difference of one structural water between these two molecules.

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