Journal of Thermal Analysis and Calorimetry, Vol. 75 (2004) 73–78

STUDIES ON SYNTHESIS, CHARACTERIZATION AND THERMOCHEMISTRY OF $Mg_2[B_2O_4(OH)_2]\cdot H_2O$

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(Received March 5, 2003; in revised form September 11, 2003)

Abstract

A new magnesium borate $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ has been synthesized by the method of phase transformation of double salt at hydrothermal condition and characterized by XRD, IR, TG and DSC. The enthalpy of solution of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ in 0.9764 mol L^{-1} HCl was determined. With the incorporation of the enthalpies of solution of H_3BO_3 in HCl (*aq*), of MgO in (HCl+H_3BO_3) (*aq*), and the standard molar enthalpies of formation of MgO(*s*), H_3BO_3(*s*), and H_2O(*l*), the standard molar enthalpy of formation of –(3185.78±1.91) kJ mol^{-1} of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ was obtained.

Keywords: $Mg_2[B_2O_4(OH)_2]\cdot H_2O$, solution calorimetry, standard molar enthalpy of formation, synthesis

Introduction

There are many kinds of magnesium borates, both natural and synthetic. Some of them have useful properties, such as $Mg_2B_2O_5$ and $Mg_2B_2O_5\cdot H_2O$ might be prepared as whisker materials [1]. $Mg_2B_2O_5\cdot H_2O$ named szaibelyite is a magnesium borate mineral with a structure formula of $Mg_2[B_2O_4(OH)_2]$ [2]. It is difficult to obtain this pure compound in laboratory. Recently, we obtained a similar compound $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ when we tried to prepare whisker of $Mg_2B_2O_5\cdot H_2O$ by the phase transformation of $2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O$ in water at hydrothermal condition. It is hopeful to prepare whisker of $Mg_2B_2O_5$ through the dehydration of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$.

Thermodynamic properties play very important roles in scientific research and industrial applications. Li Jun *et al*. Reported [3] the standard molar enthalpy of formation of eight hydrated magnesium borates. This paper reports the synthesis, characterization and the standard molar enthalpy of formation $Mg_2[B_2O_4(OH)_2]\cdot H_2O$.

Experimental

1.86 g $2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O$ (synthesized by modification of the literature method [4]) and 40 mL H_2O were put in the lining of small autoclave, and placed in

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1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

an oven at 120°C. After 3 d, the power of oven was off. When cooling down to room temperature, the autoclave was opened. The solid was separated, washed thoroughly with hot distilled water, and then with alcohol and ether. Finally, the solid was dried at 80°C to constant mass. The synthetic sample was characterized by X-ray powder diffraction (recorded on a Rigaku D/MAX-IIIC), FT-IR spectroscopy (recorded on a Bruker Equinox 55 spectrometer with KBr pellets at room temperature), simultaneous TG-DSC (determined on a Netzsch-Geratebau GmbH STA449C thermal analyzer at a heating rate of 10°C min^{-1} in flowing N_2). The chemical composition of the sample was 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.

$Mg_2[B_2O_4(OH)_2]\cdot H_2O$ can be regarded as the product of the following reaction:

$$2MgO(s)+2H_3BO_3(s)=Mg_2[B_2O_4(OH)_2]\cdot H_2O(s)+H_2O(l)$$

The enthalpies of solution of H_3BO_3, of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ in approximately 1 mol L^{-1} HCl(*aq*), and of the calculated amount of MgO in aqueous (hydrochloric acid+boric acid) which consisted of approximately 1 mol L^{-1} HCl (*aq*) and the calculated amount of H_3BO_3 were determined. The standard molar enthalpy of formation of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ could be obtained by 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, 0.9764 mol L^{-1}, was determined by titration with standard sodium carbonate, and its density, 1.0168 g cm^{-3}, was taken from chemical handbook.

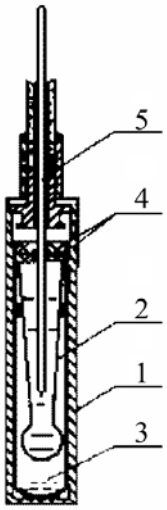

Fig. 1 Schematic drawing of the device used for the study of enthalpy of solution
1 – calorimetric cell; 2 – tube containing approximately 1 mol L^{-1} HCl(*aq*);
3 – tube containing solid sample; 4 – silicone rubber cover; 5 – glass rod

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 [5, 6]. 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*). This device used for calorimetry is shown in Fig. 1. The lining in the double-layer glass tube containing HCl(*aq*) was broken by a rod after thermal equilibration for at least 3 h, and the HCl(*aq*) was mixed with solid sample in the outer glass tube, then the thermal effect was recorded automatically by 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.

Results and discussion

Chemical analysis results of synthetic sample: MgO, 43.31%; B_2O_3, 37.29%; H_2O, 19.40%; mole ratio of $MgO:B_2O_3:H_2O$=2.01:1.00:2.01. TG curve (Fig. 2) indicates that the total mass loss is 19.00% from 60 to 600°C, which corresponds to the loss of 2 water molecules and can be compared with calculated value of 19.33%. On the DSC curve (Fig. 2), there are two peaks: one endothermic peak appeared at 548.2°C corresponds to the loss of 2 water molecules and formed amorphous $Mg_2B_2O_5$; the other greater exothermic peak appeared at 653.7°C corresponds to a recrystallization of $Mg_2B_2O_5$. The *d* (nm) values of XRD spectrum (Fig. 3): 0.6357, 0.6155, 0.2984, 0.2693, 0.2656, 0.2629, 0.2585, 0.2546, 0.2523, 0.2437, 0.1551. The FT-IR spectrum (Fig. 4) of synthetic sample exhibited the following absorptions and they were assigned referring to literature [7]: The band at 3561 and 3438 cm^{-1} is the stretching of O–H. The band at 1645 cm^{-1} is assigned to the H–O–H bending mode, which shows the compound containing the crystal water. The bands at 1461, 1387 cm^{-1} and 980, 922 cm^{-1} might be the asymmetric and symmetric stretching of B(3)–O, respectively. The band at 1226 cm^{-1} is the in-plane bending of

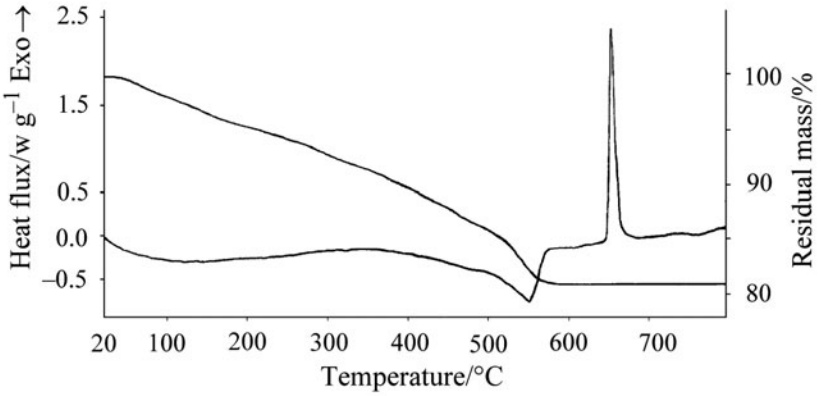

Fig. 2 Simultaneous TG-DSC curves of synthetic sample

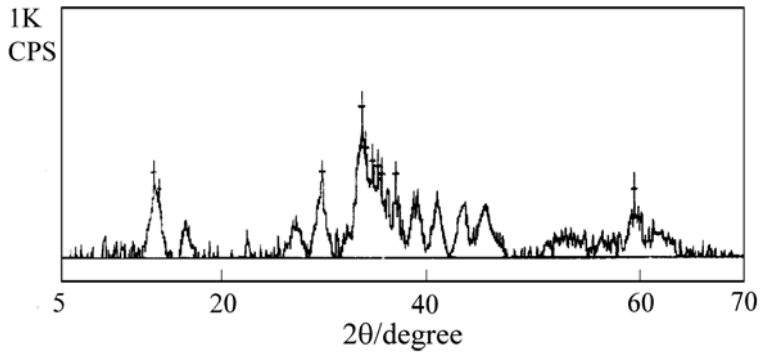

Fig. 3 XRD spectrum of synthetic sample

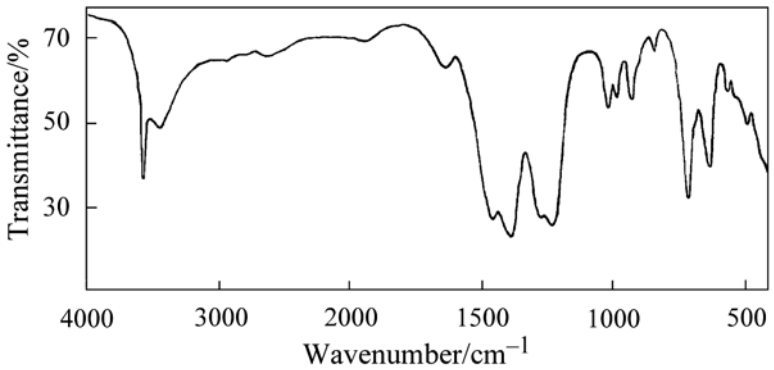

Fig. 4 FT-IR spectrum of synthetic sample

B–O–H. The bands at 1011 cm^{-1} and 836 cm^{-1} are assigned as the asymmetric and symmetric stretching of B(4)–O, respectively. The strong band at 711 cm^{-1} is the out-of-plane bending of B(3)–O. The very strong peak 628 cm^{-1} might be the characteristic symmetric pulse vibration of $[B_2O_4(OH)_2]^{4-}$. The weak band at 560 cm^{-1} is the in-plane bending of B(3)–O. The weak band at 484 cm^{-1} is the bending modes of B(4)–O. It can be seen that the shape of XRD spectrum and the vibration frequencies of FT-IR of synthetic sample are similar to those of $Mg_2[B_2O_4(OH)_2]$. Therefore, the structural formula of this compound can be written as $Mg_2[B_2O_4(OH)_2]\cdot H_2O$. The synthetic sample is suitable for the following calorimetric experiments.

To check the performance of RD496-III heat conduction microcalorimeter, calorimetric measurements on the enthalpy of solution of KCl (spectral purity) in deionized water were made, and the results are listed in Table 1. The experimental value (17.23±0.04) kJ mol^{-1} of $\Delta_{sol}H_m$ is in excellent agreement with that of 17.234 kJ mol^{-1} reported in the literature [8].This shows that the device for measuring the enthalpy of solution used in this work is reliable.

Table 1 The enthalpy of solution in water of KCl(*s*) at 298.15 K[a]

No.	*m*/mg	$\Delta_{sol}H_m$/kJ mol^{-1}
1	8.01	17.23
2	8.19	17.15
3	12.02	17.29
4	13.16	17.25
5	15.00	17.27
6	15.02	17.24
7	15.04	17.21
Mean		17.23±0.04[b]

[a]In each experiment, 8.00 mL of H_2O was used.
[b]Uncertainty is twice the standard deviation of the mean.

Table 2 The molar enthalpies of solution of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ in 0.9764 mol L^{-1} HCl at 298.15 K[a]

No.	*m*/mg	$\Delta_{sol}H_m$/kJ mol^{-1}
1	4.07	–169.58
2	3.98	–170.52
3	3.95	–169.34
4	4.06	–169.83
5	3.96	–170.28
Mean		–169.91±0.44[b]

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

Table 3 Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($Mg_2[B_2O_4(OH)_2]\cdot H_2O$, 298.15 K)

No.	Reaction	$\Delta_r H_m$/kJ mol^{-1}
1	$2H_3BO_3(s)+90.912(HCl\cdot 55.826H_2O)=$ $2H_3BO_3(aq)+90.912(HCl\cdot 55.826H_2O)$	43.66±0.16
2	$2MgO(s)+2H_3BO_3(aq)+90.912(HCl\cdot 55.826H_2O)=$ $2MgCl_2(aq)+2H_3BO_3(aq)+86.912(HCl\cdot 58.418H_2O)$	–292.4±0.72
3	$2MgCl_2(aq)+2H_3BO_3(aq)+86.912(HCl\cdot 58.418H_2O)=$ $Mg_2[B_2O_4(OH)_2]\cdot H_2O(s)+90.912(HCl\cdot 55.837H_2O)$	169.91±0.44
4	$90.912(HCl\cdot 55.837H_2O)=90.912(HCl\cdot 55.826H_2O)+H_2O(l)$	0.02±0.01
5	$2MgO(s)+2H_3BO_3(s)=Mg_2[B_2O_4(OH)_2]\cdot H_2O(s)+H_2O(l)$	–78.81±0.86

The results of the calorimetric measurements are given in Table 2, in which m is the mass of sample, $\Delta_{sol}H_m$ is the molar enthalpy of solution of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$, and the uncertainty is twice the standard deviation of the mean. The molar mass of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ is 186.2 g mol^{-1}. Table 3 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$. The molar enthalpy of solution of $H_3BO_3(s)$ of (21.83±0.08) kJ mol^{-1} in approximately 1 mol L^{-1} HCl(aq), and of MgO(s) of –(146.20±0.36) kJ mol^{-1} in the mixture of HCl and H_3BO_3 were taken from previous work [3]. The standard molar enthalpies of formation of $H_2O(l)$, MgO(s), and $H_3BO_3(s)$ were taken from the Codata Key Values [9], namely –(285.830±0.040) kJ mol^{-1}, –(601.60±0.30) kJ mol^{-1}, and –(1094.8±0.8) kJ mol^{-1}, respectively. The enthalpy of dilution HCl(aq) was calculated from the NBS tables [10]. From these data, the standard molar enthalpy of formation of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ was calculated to be –(3185.78±1.91) kJ mol^{-1}.

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