Synthesis, Characterization and Thermochemistry of $2MgO\cdot B_2O_3\cdot 1.5H_2O$

LIU, Zhi-Hong[*,a] **(刘志宏)** **ZHAO, Li**[b] **(赵莉)** **HU, Man-Cheng**[a] **(胡满成)**

[a] *School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an, Shaanxi 710062, China*

[b] *Department of Biochemistry, Shaanxi Institute of Education, Xi'an, Shaanxi 710061, China*

A new magnesium borate $2MgO\cdot B_2O_3\cdot 1.5H_2O$ has been synthesized by the method of phase transformation of double salt under hydrothermal condition and characterized by XRD, IR, Raman spectra and TG. The enthalpy of solution of $2MgO\cdot B_2O_3\cdot 1.5H_2O$ in 2.9842 mol·L^{-1} HCl was determined. From a combination of this result with measured enthalpies of solution of H_3BO_3 in 2.9842 mol·L^{-1} 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 −(3019.76 ± 1.79) kJ·mol^{-1} of $2MgO\cdot B_2O_3\cdot 1.5H_2O$ was obtained.

Keywords $2MgO\cdot B_2O_3\cdot 1.5H_2O$, synthesis, characterization, standard molar enthalpy of formation

Introduction

$2MgO\cdot B_2O_3$ ($Mg_2B_2O_5$) 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 is a magnesium borate mineral with a structural formula of $Mg_2[B_2O_4(OH)_2]$.[2] It is difficult to synthesize this compound in the laboratory. Recently, we obtained a similar compound $2MgO\cdot B_2O_3\cdot 1.5H_2O$ when we tried to prepare whisker of $2MgO\cdot B_2O_3\cdot H_2O$ by the phase transformation of $2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O$ in H_3BO_3 solution under hydrothermal condition. It is hopeful to prepare whisker of $2MgO\cdot B_2O_3$ through the dehydration of $2MgO\cdot B_2O_3\cdot 1.5H_2O$. In this paper the synthetic method and the standard molar enthalpy of formation of $2MgO\cdot B_2O_3\cdot 1.5H_2O$ are reported.

Experimental

Reagents and instruments

H_3BO_3, $MgCl_2\cdot 6H_2O$, $Mg(OH)_2\cdot 4MgCO_3\cdot 6H_2O$ and HCl were of analytical grade, and KCl was spectral purity. X-ray powder diffraction meter (Rigaku D/MAX-ⅢC), FT-IR spectrometer (Bruker Equinox 55, with KBr pellet), Dispersive Ramanmeter (Nicolet Almega), thermograph analyzer (Perkin-Elmer TGA7, at a heating rate of 10 ℃/min in flowing N_2), Abbe refractometer (2WA-J, Shanghai, China) and heat conduction microcalorimeter (RD496-Ⅲ, Southwest Institute of Electron Engineering, China) were used.

Synthesis of $2MgO\cdot B_2O_3\cdot 1.5H_2O$

1.86 g of $2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O$ (synthesized by the modified method in literature[3]), 1.85 g of H_3BO_3, and 20 mL of H_2O were put in the lining of a small autoclave, then placed in an oven at 140 ℃. After 3 d, the solid phase was separated and washed thoroughly, first with hot distilled water, then with alcohol and ether. Finally, the obtained solid was dried at 80 ℃ to constant mass, and characterized by X-ray powder diffraction, FT-IR spectroscopy, Raman spectroscopy and TG. The chemical composition of the synthetic sample was determined by EDTA titration for Mg^{2+}, by standard NaOH solution in the presence of mannitol for B_2O_3, and by difference for H_2O.

Method of calorimetric experiment

$2MgO\cdot B_2O_3\cdot 1.5H_2O$ can be regarded as the product of the following reaction (5), and the thermochemical cycle was designed as Fig. 1.

$2MgO\cdot B_2O_3\cdot 1.5H_2O$ is difficult to dissolve in HCl (aq.), so the enthalpies of solution of $2MgO\cdot B_2O_3\cdot 1.5H_2O$, of H_3BO_3 in 2.9842 mol·L^{-1} HCl(aq.), and of the calculated amount of MgO in aqueous (hydrochloric acid + boric acid) which was consisted of 2.9842 mol·L^{-1} HCl(aq.) and the calculated amount of H_3BO_3 were determined. The two solutions after reactions (2) and (3) had the same value of refraction index n^{25} of 1.3555, indicating that their thermodynamic states were the same

* E-mail: liuzh@snnu.edu.cn

Received February 27, 2003; revised July 17, 2003; accepted September 28, 2003.

Project supported by the Natural Science Foundation of Shaanxi Province of China (No. 2002B13).

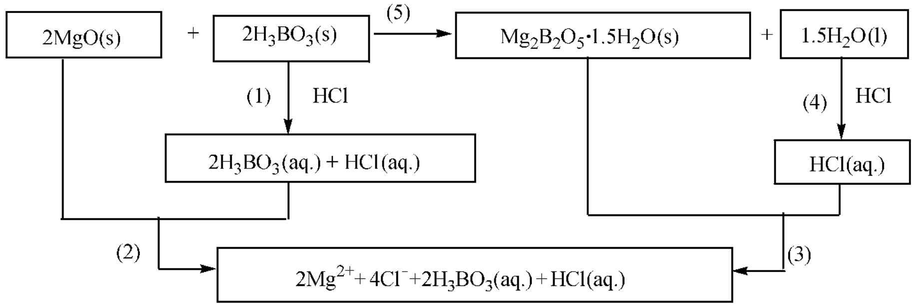

Fig. 1 Schematic drawing of the thermochemical cycle.

and the designed thermochemical cycle was correct. The standard molar enthalpy of formation of $2MgO \cdot B_2O_3 \cdot 1.5H_2O$ could be obtained by solution calorimetry as stated 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 $mol \cdot L^{-1}$, was determined by titration with standard sodium carbonate, whose density, 1.053 $g \cdot cm^{-3}$, was taken from Soviet Chemical Handbook.

The RD496-Ⅲ heat conduction microcalorimeter was used and described in detail previously.[4] 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. The device of double-layer glass tubes used for calorimetry was referred to the method of literature.[5] 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 equilibrium for at least 2 h, and the HCl(aq.) was mixed with solid sample in the outer glass tube, then the heat 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 $2MgO \cdot B_2O_3 \cdot 1.5H_2O$. There were no solid residues observed after the reactions in each calorimetric experiment ended.

To check the performance of RD496-Ⅲ heat conduction microcalorimeter, calorimetric measurements on the enthalpy of solution of KCl in deionized water were made. The experimental mean value (17.23 ± 0.04) $kJ \cdot mol^{-1}$ of $\Delta_{sol}H_m^{\ominus}$[6] is in excellent agreement with that of 17.234 $kJ \cdot mol^{-1}$ reported in the literature.[7] This shows that the device for measuring the enthalpy of solution used in this work is reliable.

Results and discussion

Characterization of synthetic sample

Anal. calcd for $2MgO \cdot B_2O_3 \cdot 1.5H_2O$: MgO 45.48, B_2O_3 39.28, H_2O 15.24; found MgO 45.54, B_2O_3 39.30, H_2O 15.16; molar ratio of $MgO : B_2O_3 : H_2O$ is 2.00∶1.00∶1.49. TG curve (Fig. 2) indicates that the total mass loss is 14.87% in the range of 191—608—785 ℃, which corresponds to the loss of 1.5 water molecule and can be compared with calculated value of 15.24%. XRD spectrum of synthetic sample has the following characteristic d (nm) values: 0.6412, 0.6285, 0.6095, 0.5242, 0.3024, 0.2988, 0.2709, 0.2684, 0.2668, 0.2653, 0.2617, 0.2590, 0.2534, 0.2510, 0.2435, 0.2320, 0.2311, 0.2220, 0.2094, 0.2001, 0.1990, 0.1980, 0.1550, 0.1542. FT-IR spectrum (Fig. 3) of synthetic sample exhibits the following absorptions and they are assigned referring to literature.[8] The bands at 3562 and 3436 cm^{-1} are the stretching of O—H. The band at 1636 cm^{-1} is assigned to the H—O—H bending mode, which shows that the compound contains the crystal water. The bands at 1461, 1387 cm^{-1} and 1013, 981, 923 cm^{-1} might be the asymmetric and symmetric stretching of B(3)—O, respectively. The band at 1224 cm^{-1} is the in-plane bending of B—O—H. The strong bands at 627, 710 cm^{-1} are the out-of-plane bending of B(3)—O. The weak band at 836 cm^{-1} might be the characteristic peak of $[B_2O_4(OH)_2]^{4-}$, which also appears in that of $Mg_2[B_2O_4(OH)_2]$.[9] The weak band at 562 cm^{-1} is the in-plane bending of B(3)—O. In Raman spectrum, the weak band at 617 cm^{-1} is the out-of-plane bending of B(3)—O. The strong band at 833 cm^{-1} might be the characteristic peak of $[B_2O_4(OH)_2]^{4-}$, which also appears in that of $Mg_2[B_2O_4(OH)_2]$.[9] The band at 1606

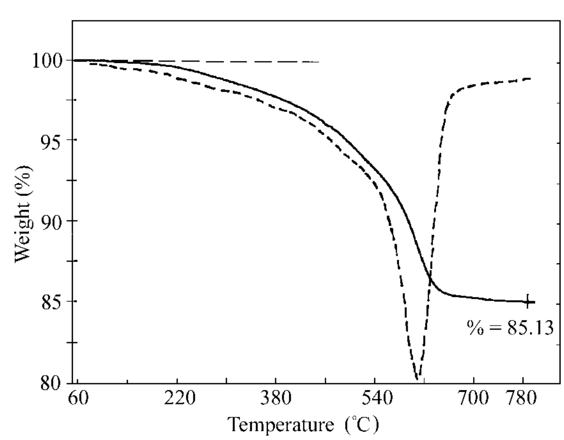

Fig. 2 TG curve of synthetic sample.

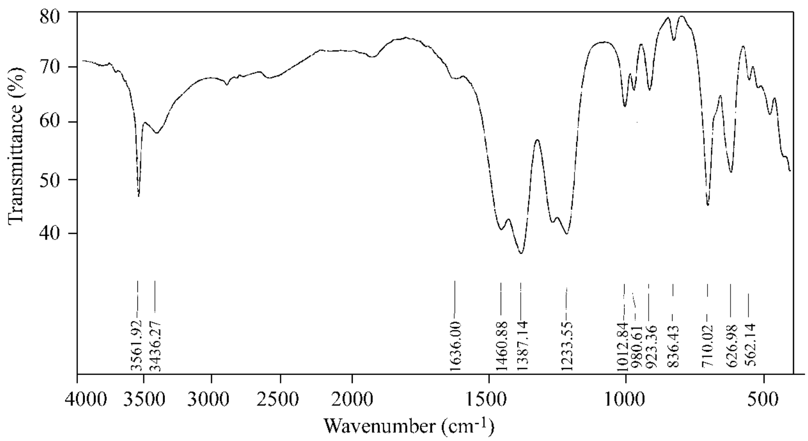

Fig. 3 FT-IR spectrum of synthetic sample.

cm^{-1} is the H—O—H bending mode. The bands at 2519 and 3560 cm^{-1} are the stretching of O—H. The results of chemical analysis and TG indicates that the synthetic sample is pure $2MgO \cdot B_2O_3 \cdot 1.5H_2O$ and is suitable for the following calorimetric experiments.

Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 1 to Table 3, in which m is the mass of sample, $\Delta_{sol}H_m^{\ominus}$ is the molar enthalpy of solution of solute, and the uncertainty is estimated as twice the standard deviation of the mean.

Table 1 Molar enthalpies of solution of H_3BO_3(s) in 2.9842 mol·L^{-1} HCl at 298.15 K[a]

No.	m (mg)	n_{HCl}(mol)	n_{H_2O}(mol)	$\Delta_{sol}H_m^{\ominus}$(kJ·$mol^{-1}$)
1	5.94	5.9684×10^{-3}	0.1049	22.60
2	6.26	5.9684×10^{-3}	0.1049	22.81
3	6.14	5.9684×10^{-3}	0.1049	22.73
4	6.15	5.9684×10^{-3}	0.1049	22.32
5	6.17	5.9684×10^{-3}	0.1049	22.53
Mean				22.60 ± 0.17[b]

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

Table 2 Molar enthalpies of solution of MgO(s) in (HCl + H_3BO_3) solution at 298.15 K[a]

No.	m (mg)	n_{HCl}(mol)	n_{H_2O}(mol)	$\Delta_{sol}H_m^{\ominus}$(kJ·$mol^{-1}$)
1	1.40	5.9684×10^{-3}	0.1049	−148.19
2	1.49	5.9684×10^{-3}	0.1049	−148.44
3	1.47	5.9684×10^{-3}	0.1049	−148.71
4	1.46	5.9684×10^{-3}	0.1049	−148.52
5	1.44	5.9684×10^{-3}	0.1049	−148.64
Mean				-148.50 ± 0.18[b]

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

Table 3 Molar enthalpies of solution of $2MgO \cdot B_2O_3 \cdot 1.5H_2O$ in 2.9842 mol· L^{-1} HCl at 298.15K[a]

No.	m (mg)	n_{HCl}(mol)	n_{H_2O}(mol)	$\Delta_{sol}H_m^{\ominus}$(kJ·$mol^{-1}$)
1	0.98	5.9684×10^{-3}	0.1049	−196.12
2	1.03	5.9684×10^{-3}	0.1049	−196.06
3	1.05	5.9684×10^{-3}	0.1049	−195.93
4	1.04	5.9684×10^{-3}	0.1049	−195.84
5	1.08	5.9684×10^{-3}	0.1049	−196.41
Mean				-196.07 ± 0.20[b]

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

Table 4 Thermochemical cycle and results for the derivation of $\Delta_f H_m^{\ominus}(2MgO \cdot B_2O_3 \cdot 1.5H_2O$, 298.15 K)

No.	Reaction	$\Delta_r H_m^{\ominus}$(kJ·mol^{-1})
1	$2H_3BO_3$(s) + 1057.664 ($HCl \cdot 17.576H_2O$) = $2H_3BO_3$(aq.) + 1057.664 ($HCl \cdot 17.576H_2O$)	45.20 ± 0.34
2	2MgO(s) + $2H_3BO_3$(aq.) + 1057.664 ($HCl \cdot 17.576H_2O$) = $2Mg^{2+}$(aq.) + $4Cl^-$(aq.) + $2H_3BO_3$(aq.) + 1053.664 ($HCl \cdot 17.645H_2O$)	-297.00 ± 0.36
3	$2Mg^{2+}$(aq.) + $4Cl^-$(aq.) + $2H_3BO_3$(aq.) + 1053.664 ($HCl \cdot 17.645H_2O$) = $Mg_2B_2O_5 \cdot 1.5H_2O$(s) + 1057.664 ($HCl \cdot 17.577H_2O$)	196.07 ± 0.20
4	1057.664 ($HCl \cdot 17.577H_2O$) = 1057.664 ($HCl \cdot 17.576H_2O$) + $1.5H_2O$(l)	0.03 ± 0.01
5	2MgO(s) + $2H_3BO_3$(s) = $Mg_2B_2O_5 \cdot 1.5H_2O$(s) + $1.5H_2O$(l)	-55.70 ± 0.53

Table 4 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $2MgO \cdot B_2O_3 \cdot 1.5H_2O$. The standard molar enthalpies of formation of H_2O(l), MgO(s), and H_3BO_3(s) are taken from the CODATA key values,[10] namely $-(285.830 \pm 0.040)$ kJ·mol^{-1}, $-(601.60 \pm 0.30)$ kJ·mol^{-1}, and $-(1094.8 \pm 0.8)$ kJ·mol^{-1}, respectively. The enthalpy of dilution HCl(aq.) is calculated from the NBS tables.[11] From these data, the standard molar enthalpy of formation of $2MgO \cdot B_2O_3 \cdot 1.5H_2O$ is calculated to be $-(3019.76 \pm 1.79)$ kJ·mol^{-1}.

References

1 Sakane, K.; Wada, H.; Kitamura, T. *Gypsum Lime* **1991**, 235.

2 Hawthorne, F. C. *Can. Mineral*. **1986**, *24*, 625.

3 Gao, S.-Y.; Chen, X.-A.; Xia, S.-P. *Acta Chim. Sinica* **1990**, *48*, 1049 (in Chinese).

4 Ji, M.; Liu, M.-Y.; Gao, S.-L.; Shi, Q.-Z. *Instrum. Sci. Technol*. **2001**, *29*, 53.

5 Gao, S.-L.; Ji, M.; Chen, S.-P.; Hu, R.-Z.; Shi, Q.-Z. *Acta Chim. Sinica* **2001**, *59*, 931 (in Chinese).

6 Liu, Z.-H.; Gao, S.-Y.; Hu, M.-C.; Xia, S.-P. *Chin. J. Chem*. **2002**, *20*, 1519.

7 Weast, R. C. *CRC Handbook of Chemistry and Physics*, 70th Edition, CRC Press, Boca Raton, **1989**.

8 Li, J.; Xia, S.-P.; Gao, S.-Y. *Spectrochim. Acta* **1995**, *51A*, 519.

9 Liu, Z.-H. *Ph.D. Dissertation*, Lanzhou University, Lanzhou, **2003** (in Chinese).

10 Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*, Hemisphere, New York, **1989**.

11 Wagman, D. D.; Evans, W. H.; Pariker, V. B. *The NBS of Chemical Thermodynamic Properties*, translated by Liu, T. H.; Zhao, M. K., Chinese Standards Press, Beijing, **1998** (in Chinese).

(E0302272 ZHAO, X. J.)