Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 403 (2003) 181–184
thermochimica acta
www.elsevier.com/locate/tca

Synthesis and thermochemistry of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$

Liu Zhihong*, Hu Mancheng

School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an, Shaanxi 710062, PR China

Received 17 August 2002; accepted 28 November 2002

Abstract

A new magnesium borate $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ has been synthesized by the method of phase transformation of double salt and characterized by XRD, IR and Raman spectroscopy as well as by TG. The structural formula of this compound was $Mg[B_6O_9(OH)_2]{\cdot}2.5H_2O$. The enthalpy of solution of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ in approximately 1 mol dm^{-3} HCl was determined. With the incorporation of the standard molar enthalpies of formation of MgO(s), H_3BO_3(s), and H_2O(l), the standard molar enthalpy of formation of $-(5595.02 \pm 4.85)$ kJ mol^{-1} of $MgO{\cdot}3B_2O_33.5H_2O$ was obtained. Thermodynamic properties of this compound was also calculated by group contribution method.

Keywords: $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$; Synthesis; Standard molar enthalpy of formation; Solution calorimetry

1. Introduction

There are many kinds of magnesium borates, both natural and synthetic. Up to now, four hydrated magnesium borates belong to $MgO{\cdot}3B_2O_3{\cdot}nH_2O$ ($n = 7.5$, 7, 6, 5) are found. The polyborate anion of all these borates is $[B_6O_7(OH)_6]^{2-}$. Recently, we discovered a new magnesium hexaborate when investigating the phase transformation of $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$ in boric acid aqueous solution. Its structure has been studied using XRD, FT-IR and Raman spectra as well as TG.

Thermodynamic properties play very important roles in scientific research and industrial applications. Li et al. reported [1,2] the standard molar enthalpy of formation of nine hydrated magnesium borates. As part of the continuing study of the thermochemistry of hydrated borates, this paper reports the synthesis and the standard molar enthalpy of formation of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$.

2. Experimental

2.1. Synthesis of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$

$MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ was synthesized by the method of phase transformation of double salt. The $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$ (3.72 g, synthesized by modification of the literature method [3]), H_3BO_3 (5.96 g), and H_2O (40 ml) were transferred to a flask with a reflux condenser, the mixture was heated to the boiling point and became a clear solution. After 3 days, Mg-borate crystallized from the clear solution. The solid was separated, washed thoroughly with hot distilled water, and then with alcohol and ether. Finally, the solid was dried at $T = 353$ K 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

* Corresponding author. Tel.: +86-29-5307765; fax: +86-29-5307774.
E-mail address: liuzh@snnu.edu.cn (L. Zhihong).

0040-6031/03/$ – see front matter
doi:10.1016/S0040-6031(03)00058-3

spectrometer with KBr pellets at room temperature), Raman spectroscopy (recorded on a Nicolet Almega Dispersive Ramanmeter), and TG (determined on a Perkin-Elmer TGA7 thermograph analyser 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.

2.2. Method of calorimetric experiment

$MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ can be regarded as the product of the following reaction:

$$MgO(s) + 6H_3BO_3(s) = MgB_6O_{10} \cdot 3.5H_2O(s) + 5.5H_2O \quad (1)$$

The standard molar enthalpy of formation of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of MgO(s), H_3BO_3(s), and H_2O(l). The H_3BO_3 and $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ were dissolved in approximately 1 mol dm^{-3} HCl(aq), respectively, and then the calculated amount of MgO was dissolved in aqueous (hydrochloric acid + boric acid) which consisted of approximately 1 mol dm^{-3} HCl(aq) and the calculated amount of H_3BO_3. The HCl solvent was prepared from analytical grade hydrochloric acid and deionized water, and its concentration was determined by titration with standard sodium carbonate.

A RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used and has been 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. 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. The HCl(aq) was mixed with solid sample in the outer glass tube, then the thermal effect was recorded automatically on an 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 (spectral purity) in deionized water were made. 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 [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 synthetic sample

Chemical analysis results of synthetic sample: MgO, 13.06%; B_2O_3, 66.44%; H_2O, 20.50%; mole ratio of $MgO{:}B_2O_3{:}H_2O$, 1.00:2.95:3.51. XRD data of synthetic sample, *d* (Å): 7.167, 6.223, 5.720, 4.048, 3.596, 3.417, 3.104, 2.688, 2.497, 2.152, 2.082, 2.070. The IR and Raman spectra of synthetic sample exhibited the following absorptions and they were assigned referring to literature [6]. The band at 3433 cm^{-1} is the stretching of O–H. The band at 1635 cm^{-1} is assigned to the H–O–H bending mode, which shows the compound containing the crystal water. The bands at 1443, 1335 cm^{-1} and 946, 904 cm^{-1} might be the asymmetric and symmetric stretching of B(3)–O, respectively. The band at 1200 cm^{-1} is the in-plane bending of B–O–H. The bands at 1111, 1043 cm^{-1} and 802, 875 cm^{-1} (Raman) are assigned as the asymmetric and symmetric stretching of B(4)–O, respectively. The bands at 742 cm^{-1} (very weak) in FT-IR spectra and 744 cm^{-1} in Raman spectra are the out-of-plane bending of B(3)–O. The very strong Raman spectra peak 636 cm^{-1} is assigned as the characteristic of hexaborate anion. The bands at 475 cm^{-1} in FT-IR and 399 cm^{-1} in Raman are the bending modes of B(4)–O. It can be seen that the shape of XRD spectra and the vibration frequencies of FT-IR and Raman are more similar to those of $CaO{\cdot}3B_2O_3{\cdot}4H_2O$ which structure is $Ca[B_6O_9(OH)_2]{\cdot}3H_2O$ than $MgO{\cdot}3B_2O_3{\cdot}nH_2O$ (n = 7.5, 7, 6, 5). TG curve indicates that the total loss is 20.02%, and there exist two weight loss stages from 60 to 733 °C. The first weight loss from 60 to 310 °C, 14.13%, corresponds to the loss of 2.5 water molecules and can be compared with calculated value of 14.42%. The second weight loss from 310 to 733 °C, 5.88%, corresponds to the loss of one water

Table 1
The molar enthalpies of solution of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ in approximately 1 mol dm^{-1} HCl at 298.15 K[a]

No.	m (mg)	$\Delta_{sol}H$ (mJ)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	4.06	−239.36	−18.40
2	4.08	−240.77	−18.42
3	4.04	−239.06	−18.47
4	4.01	−236.67	−18.42
5	3.31	−195.46	−18.43
Mean			−18.43 ± 0.02[b]

[a] In each experiment 2.00 cm^3 of HCI(aq) was used.
[b] Uncertainty is estimated as twice the standard deviation of the mean.

molecule and can be compared with calculated value of 5.77%.

Therefore, the structural formula of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ can be written as $Mg[B_6O_9(OH)_2]{\cdot}2.5\ H_2O$. No impurity lines were observed, and the synthetic sample 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, $\Delta_{sol}H$ is the enthalpy of solution of solute, $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute, and the uncertainty is estimated as twice the standard deviation of the mean. Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$. The molar enthalpy of solution of H_3BO_3(s) of (21.83 ± 0.08) kJ mol^{-1} in approximately 1 mol dm^{-3} 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 literature [1]. The standard molar enthalpies of formation of H_2O(l), MgO(s), and H_3BO_3(s) were taken from the CODATA Key Values [7], 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 [8]. From these data, the standard molar enthalpy of formation of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ was calculated to be −(5595.02 ± 4.85) kJ mol^{-1}. The enthalpy of formation of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ can also be estimated by a group contribution method [9] as the sum of the contributions of Mg^{2+}(aq), $[B_6O_9(OH)_2]^{2-}$(aq) and of structural water. The standard molar enthalpy of formation is, using this scheme, −5597.73 kJ mol^{-1}. The calculated value is close to the experimental result. The relative error is −0.05%. This result shows that the proposed structural formula of this compound, $Mg[B_6O_9(OH)_2]{\cdot}2.5H_2O$, is correct. So we also used a group contribution method to calculate $\Delta_f G^\circ_m$ of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ to be −5149.07 kJ mol^{-1}. Combining the $\Delta_f H^\circ_m$ of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$, the standard molar entropy of formation of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ has been calculated at −1504.81 J mol^{-1} K^{-1} according to following equation:

$$\Delta_f S^\circ_m = \frac{\Delta_f H^\circ_m - \Delta_f G^\circ_m}{T}$$

Finally, the standard molar entropy of $MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$ was calculated to be 404.30 J mol^{-1} K^{-1} according to following reaction:

$$Mg(s) + 6B(s) + 3.5H_2(g) + \tfrac{13.5}{2}O_2(g) = MgB_6O_{10}\cdot 3.5H_2O(s)$$

The standard molar entropies of the elements were taken from CODATA Key Values to be 32.67, 5.90, 130.571, and 205.043 J mol^{-1} K^{-1} for Mg(s), B(s), H_2(g), and O_2(g), respectively.

Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H^\circ_m$ ($MgO{\cdot}3B_2O_3{\cdot}3.5H_2O$, 298.15 K)

S.No.	Reaction	$\Delta_r H_m$ (kJ mol^{-1})
1	$6H_3BO_3(s) + 156.117\ (HCl{\cdot}54.561H_2O) = 6H_3BO_3(aq) + 156.117\ (HCl{\cdot}54.561H_2O)$	130.98 ± 0.48
2	$MgO(s) + 6H_3BO_3(aq) + 156.117\ (HCl{\cdot}54.561H_2O) = MgCl_2(aq) + 6H_3BO_3(aq) + l54.117(HCl{\cdot}55.276H_2O)$	−146.20 ± 0.36
3	$MgCl_2(aq) + 6H_3BO_3(aq) + 154.117\ (HCl{\cdot}55.276H_2O) = MgB_6O_{10}{\cdot}3.5H_2O(5) + 156.117\ (HCl{\cdot}54.596H_2O)$	18.43 ± 0.02
4	$156.117\ (HCl{\cdot}54.596H_2O) = 156.117\ (HCl{\cdot}54.561H_2O) + 5.5H_2O$	0.11 ± 0.01
5	$MgO(s) + 6H_3BO_3(s) = MgB_6O_{10}{\cdot}3.5H_2O(s) + 5.5H_2O(l)$	3.32 ± 0.60

References

[1] J. Li, S.Y. Gao, S.P. Xia, B. Li, R.Z. Hu, J. Chem. Thermodyn. 29 (1997) 491.
[2] Y.Z. Jia, J. Li, S.Y. Gao, S.P. Xia, J. Chem. Thermodyn. 31 (1999) 1605.
[3] S.Y. Gao, X.A. Chen, S.P. Xia, Acta Chim. Sin. 11 (1990) 1049.
[4] M. Ji, M.Y. Liu, S.L. Gao, Q.Z. Shi, Instrum. Sci. Technol. 29 (1) (2001) 53.
[5] R.C. Weast, CRC Handbook of Chemistry and Physics, 70th ed., CRC Press, Boca Raton, FL, 1989.
[6] J. Li, S.P. Xia, S.Y. Gao, Spectrochim. Acta 51A (1995) 519.
[7] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics Hemisphere, New York, 1989.
[8] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Chumey, R.L Nuttall (Eds.), The NBS Tables of Chemical Thermodynamic Properties, J. Phys. Chem. Data 11 (Suppl. 2) (1982).
[9] J. Li, B. Li, S.Y. Gao, Phys. Chem. Miner. 27 (2000) 342.