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Thermochimica Acta 435 (2005) 168–171
thermochimica acta
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Hydrothermal synthesis, characterization and thermochemistry of $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$

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Received 24 December 2004; received in revised form 9 May 2005; accepted 17 May 2005
Available online 24 June 2005

Abstract

A pure calcium borate $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$ 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 $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$ in $HC1\cdot 54.582H_2O$ was determined. From a combination of this result with measured enthalpies of solution of H_3BO_3 in $HC1\cdot 54.561H_2O$ 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 $-(3172.5 \pm 2.5)\,kJ\,mol^{-1}$ of $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$ was obtained.

Keywords: $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$; Synthesis; Standard molar enthalpy of formation

1. Introduction

There are several types of hydrated calcium borates, both natural and synthetic. Some of them are useful chemical industrial materials, which are used in the glass, pottery and porcelain enamel industries, especially in the manufacture of glasses without alkali content. Gurevich and Sokolov [1] determined the standard molar enthalpies of formation of the natural calcium borate minerals of $Ca_2B_6O_{11}\cdot 5H_2O$ and $Ca_2B_6O_{11}\cdot l3H_2O$. Jun et al. [2] also reported the standard molar enthalpy of formation of five other hydrated calcium borates. This paper reports the synthesis and standard molar enthalpy of formation of a new calcium borate, $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$.

2. Experimental

2.1. Synthesis of $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$

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 into a small autoclave (40 ml). The mixture was stirred and placed in an oven at 393 K. The autoclave was cooled naturally and opened after 5 days. The solid phase was filtered, washed with hot distilled water, alcohol and ether and 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, in KBr pellets at room temperature) and TG (METZSCH-Geratebau GmbH STA449C thermal analyzer at a heating rate of $10\,^{\circ}C\,min^{-1}$ in flowing N_2). The chemical composition of the sample was determined by titration with standard EDTA solution for calcium content, by titration with standard NaOH solution in the presence of mannitol for B_2O_3 content, and by difference for H_2O content.

2.2. Method of calorimetric experiment

An RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) 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 and reference cells of the calorimeter to prevent corrosion of the

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doi:10.1016/j.tca.2005.05.018

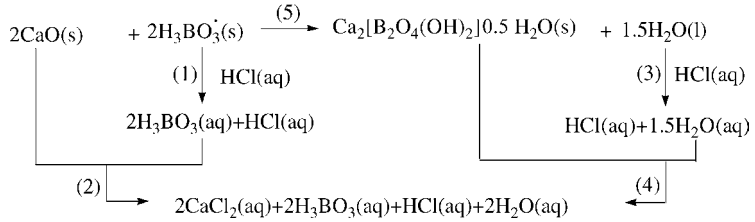

Fig. 1. Schematic drawing of the thermochemical cycle.

stainless steel by HCl(aq). The lining in the double-layer glass tube containing 2.00 ml HCl(aq) was broken by a rod after at least 2 h, when thermal equilibration was reached, and the HCl(aq) was mixed with solid sample (6 mg) in the outer glass tube. The thermal effect was then 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.

To check the performance of the calorimeter, the calorimetric measurements on the enthalpy of solution of KCl (G.R.) in deionized water were made. The average experimental value $(17.31 \pm 0.20)\,\mathrm{kJ\,mol^{-1}}$ of $\Delta_{sol}H_m$ of KCl(s) is in excellent agreement with that of $17.241 \pm 0.0l8\,\mathrm{kJ\,mol^{-1}}$ reported in ref. [5].

$Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$ can be regarded as the product of the reaction (5), and the thermochemical cycle could be established as indicated in Fig. 1. The approximately $1\,\mathrm{mol\,dm^{-3}}$ HCl(aq) solvent dissolves all components of the reaction (5).

3. Results and discussion

3.1. Characterization of the synthetic sample

The analysis of the sample is shown in Table 1 together with the theoretical values.

The XRD pattern of the synthetic sample is shown in Fig. 2. The characteristic *d* values are 0.2967, 0.6681, 0.2828, 0.2229, 0.2068, 0.4217, 0.1838, 0.1787, 0.1821, 0.9929, 0.1774, 0.1774 and 0.1746 nm. The absorption bands in the IR spectrum of the synthetic sample (Fig. 3) are assigned according to ref. [6]. The band at 3355 $\mathrm{cm^{-1}}$ is the stretching vibration of the O–H group. The weak band at 1600 $\mathrm{cm^{-1}}$

Table 1
The chemical composition of the sample as mass fraction (%)

	CaO	B_2O_3	H_2O	CaO:B_2O_3:H_2O (mole ratio)
Theoretical	53.71	33.31	12.93	2.00:1.00:1.50
Analytical	53.64	33.13	13.23	2.01:1.00:1.54

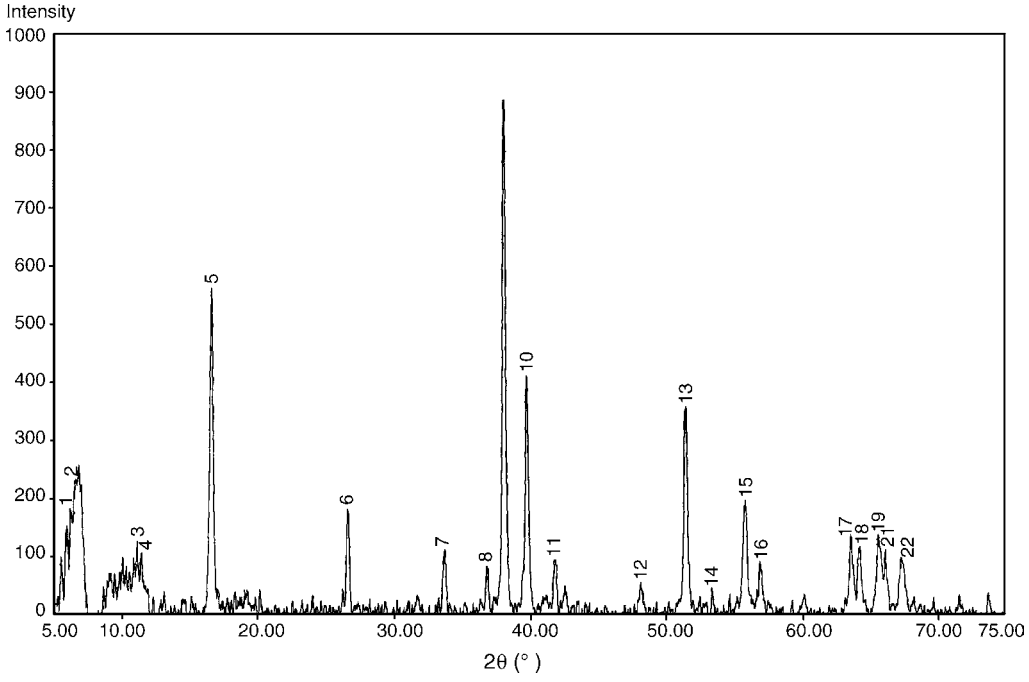

Fig. 2. X-ray powder diffraction pattern of $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$.

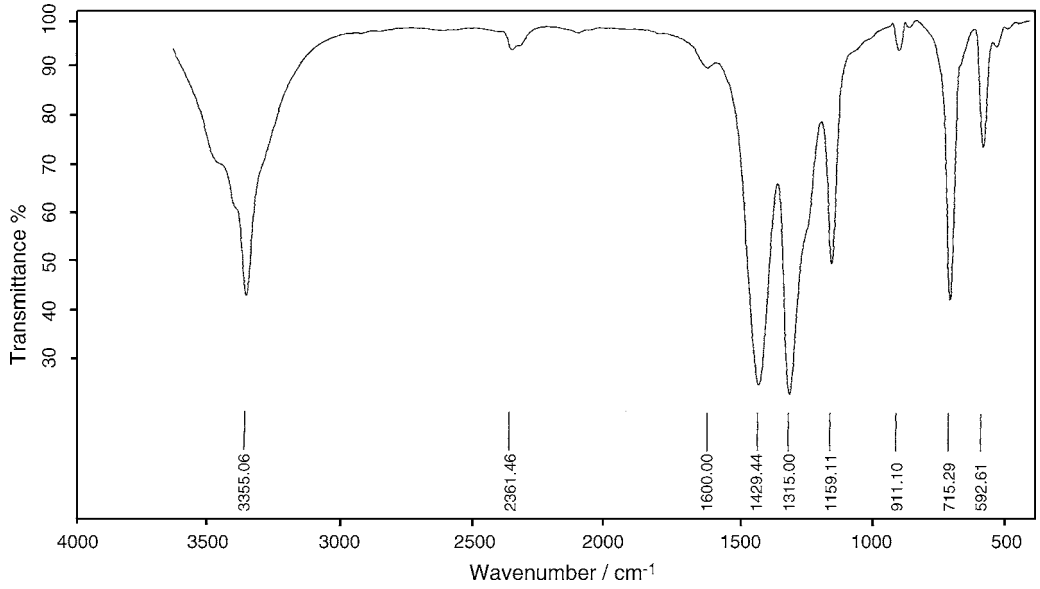

Fig. 3. FT-IR curve of $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$.

is assigned to the H–O–H bending mode. This confirms the presence of crystallization water in the compound. The bands at 1429, 1315 and 911 cm^{-1} are, respectively, assigned to the asymmetric and symmetric stretching vibrations of B(3)–O group. The band at 1159 cm^{-1} is the in-plane bending of B–O–H. The very strong band at 715 cm^{-1} is assigned to out-of-plane bending of the group B(3)–O, which was also observed in the compound of $Mg_2[B_2O_4(OH)_2]\cdot H_2O$ [7]. The band at 592 cm^{-1} is assigned to the in-plane bending of B(3)–O.

TG–DSC curves (Fig. 4) indicate that the total weight loss is 13.09% from 50 to 750 °C, which corresponds to the loss of 1.5 water molecules and is near to the calculated value of 12.94%.

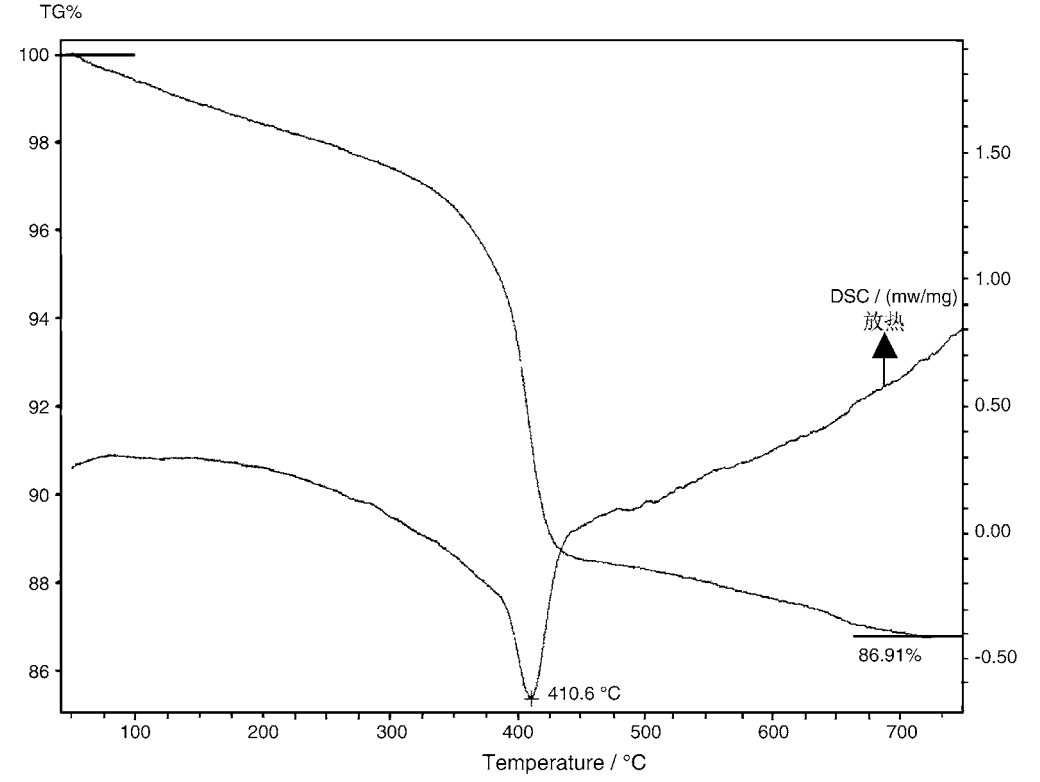

Fig. 4. Simultaneous TG–DSC curves of $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$.

Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$, 298.15 K)

Reaction		$\Delta_r H_m$ (kJ mol^{-1})
$2H_3BO_3(s) + 70.921(HCl \cdot 54.561H_2O) = 2H_3BO_3(aq) + 70.921(HCl \cdot 54.561H_2O)$	(1)	43.67 ± 0.16
$CaO(s) + 2H_3BO_3(aq) + 70.921(HCl \cdot 54.561H_2O) = 2CaCl_2(aq) + 2H_3BO_3(aq) + 66.921(HCl \cdot 57.852H_2O)$	(2)	−377.26 ± 0.72
$70.921(HCl \cdot 54.561H_2O) + 1.5H_2O(l) = 70.921(HCl \cdot 54.582H_2O)$	(3)	−0.03 ± 0.02
$Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O(s) + 70.921(HCl \cdot 54.582H_2O) = 2CaCl_2(aq) + 2H_3BO_3(aq) + 66.921(HCl \cdot 57.852H_2O)$	(4)	−191.75 ± 0.34
$2CaO(s) + 2H_3BO_3(s) = Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O(s) + 1.5H_2O(l)$	(5)	−141.81 ± 0.81

Thus, the general formula for $2CaO\cdot B_2O_3\cdot 1.5H_2O$ can be written as $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$. All of above results indicate that the synthetic sample is pure and suitable for the calorimetric experiments.

3.2. Results of calorimetric experiment

The results of five calorimetric measurements gave -191.75 ± 0.34 kJ mol^{-1} for $\Delta_{sol} H_m^\circ$, the molar enthalpy of solution of the compound. Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$. The molar enthalpy of solution of H_3BO_3(s) of 21.83 ± 0.08 kJ mol^{-1} in HC1 $54.561H_2O$ 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 ref. [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 $-(285.83 \pm 0.04)$, $-(634.9 \pm 0.90)$ 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 $Ca_2[B_2O_4(OH)_2]\cdot 0.5H_2O$ was calculated to be $-(3172.5 \pm 2.5)$ kJ mol^{-1}.

Acknowledgement

This research was supported by the Innovative Foundation of Shaanxi Normal University, PR China.

References

[1] V.M. Gurevich, V.A. Sokolov, Geokhimiya 3 (1976) 455.
[2] L. Jun, G. Shiyang, X. Shuping, L. Bing, H. Rongzu, J. Chem. Thermodyn. 29 (1997) 1071.
[3] M. Ji, M.Y. Liu, S.L. Gao, Q.Z. Shi, Instrum. Sci. Technol. 29 (1) (2001) 53.
[4] L. Zhihong, H. Mancheng, Thermochim. Acta 414 (2004) 215.
[5] M.V. Kilday, J. Res. Natl. Bur. Stand (US) 85 (1994) 467.
[6] L. Jun, X. Shuping, G. Shiyang, Spectrochim. Acta 51A (1995) 519.
[7] L. Zhihong, H. Mancheng, G. Shiyang, J. Therm. Anal. Calorim. 75 (2004) 73.
[8] J.D. Cox, D.D. Wagman, V.A. Medvedev, CODATA Key Values for Thermodynamics, Hemisphere, New York, 1989, pp. 25–26.
[9] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, in: 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) 47.