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HYDROTHERMAL SYNTHESIS AND THERMODYNAMIC PROPERTIES OF $2CaO{\cdot}3B_2O_3{\cdot}H_2O$

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$2CaO{\cdot}3B_2O_3{\cdot}H_2O$ which has non-linear optical (NLO) property was synthesized under hydrothermal condition and identified by XRD, FTIR and TG as well as by chemical analysis. The molar enthalpy of solution of $2CaO{\cdot}3B_2O_3{\cdot}H_2O$ in $HCl{\cdot}54.572H_2O$ was determined. From a combination of this result with measured enthalpies of solution of H_3BO_3 in $HCl{\cdot}54.501H_2O$ 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 $-(5733.7\pm5.2)$ kJ mol^{-1} of $2CaO{\cdot}3B_2O_3{\cdot}H_2O$ was obtained. Thermodynamic properties of this compound were also calculated by a group contribution method.

Keywords: *$2CaO{\cdot}3B_2O_3{\cdot}H_2O$, hydrothermal synthesis, solution calorimetry, thermodynamic properties*

Introduction

Among all the present NLO materials, the series of borate salts has attracted special interest because of their outstanding advantages for generating ultraviolet as well as blue and green light, especially, β-BaB_2O_4(BBO) and LiB_3O_5(LBO) crystals. A great variety of similar NLO materials, including CsB_3O_5(CBO), $CsLiB_6O_{10}$(CLBO) and $2CaO{\cdot}3B_2O_3{\cdot}H_2O$, have been found in recent years [1, 2]. But there is no report on its thermodynamic properties. Thermodynamic properties play very important roles in scientific research and industrial applications. This paper reports the hydrothermal synthesis and thermodynamic properties of $2CaO{\cdot}3B_2O_3{\cdot}H_2O$.

Experimental

Hydrothermal synthesis of $2CaO{\cdot}3B_2O_3{\cdot}H_2O$

1962.8 mg of CaO (obtained by the decomposition of $CaCO_3$ (analytical grade) at 1223 K for 3 h), 19493.6 mg of H_3BO_3 (analytical grade), and 160 mL of H_2O were put in the lining of autoclave (250 mL). The mixture was stirred and placed in an oven at 573 K. 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 353 K to constant mass. The synthetic sample was characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC), FTIR spectroscopy (Nicolet NEXUS 670 FTIR spectrometer with KBr pellets at room temperature), and TG (Perkin-Elmer TGA7, heating rate of 10 K min^{-1} in flowing N_2). The chemical compositions of the sample were determined by EDTA titration for Ca^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by difference for H_2O.

Method of calorimetric experiment

$2CaO{\cdot}3B_2O_3{\cdot}H_2O$ can be regarded as the product of the following reaction (5), and the thermochemical cycle was designed as Fig. 1:

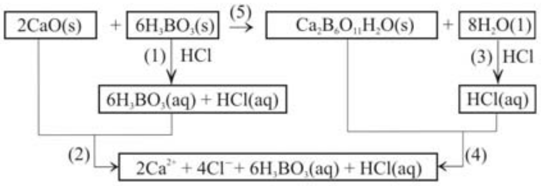

Fig. 1 Schematic drawing of the thermochemical cycle

The approximately 1 mol L^{-1} HCl(aq) solvent can dissolve instantaneously all components of the reaction (5), which was prepared from analytical grade hydrochloric acid and deionized water, and its concentration was determined by titration with standard sodium carbonate.

The standard molar enthalpy of formation of $2CaO{\cdot}3B_2O_3{\cdot}H_2O$ could be obtained by the value of $\Delta_r H_m^0$ (5) in combination with the standard molar enthalpies of formation of CaO(s), H_3BO_3(s) and

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H_2O (l). The value of $\Delta_r H_m^0$ (5) could be obtained by means of the following reactions:

$$6H_3BO_3(s)+HCl\cdot 54.501H_2O(aq)=\text{Soln }X_1 \quad (1)$$

$$2CaO(s)+\text{Soln }X_1=\text{Soln }X_2 \quad (2)$$

$$8H_2O(l)+HCl\cdot 54.501H_2O\ (aq)=\text{Soln }X_3 \quad (3)$$

$$2CaO\cdot 3B_2O_3\cdot H_2O(s)+\text{Soln }X_3=\text{Soln }X_4 \quad (4)$$

$$\text{Soln }X_2=\text{Soln }X_4$$

In all these determinations, a strict control of the stoichiometries in each step of the calorimetric cycle must be obeyed, with the objective that the dissolution of the reactants give the same composition as those of the products. Applying Hess's law, $\Delta_r H_m^0$ (5) could be calculated according to the following expression:

$$\Delta_r H_m^0\ (5)=\Delta_r H_m^0\ (1)+\Delta_r H_m^0\ (2)-$$
$$-\Delta_r H_m^0\ (3)-\Delta_r H_m^0\ (4)$$

A 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 [3, 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, and the HCl (aq) was mixed with solid sample in the outer glass tube. The thermal effect was then recorded automatically on 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 RD496-III heat conduction microcalorimeter, calorimetric measurements on the enthalpy of solution of KCl (mass fraction≥0.9999) in deionized water and of THAM (trishydroxymethylaminomethane mass fraction≥ 0.9999) in 0.1 mol L^{-1} HCl(aq) were made, respectively. The average experimental values (17.31±0.20) kJ mol^{-1} of $\Delta_{sol}H_m$ of KCl(s) and –(29.75±0.04) kJ mol^{-1} of THAM are in excellent agreement with those of 17.241 kJ mol^{-1} reported in the literature [5] and –(29.73±0.04) kJ mol^{-1} reported in the literature [6], respectively. This shows that the device for measuring the enthalpy of solution used in this work is reliable.

Results and discussion

Characterization of the synthetic sample

The chemical analysis of synthetic sample is showed in Table 1. The analytical results are consistent with the theoretical values.

Table 1 The chemical composition of the sample/%

	CaO	B_2O_3	H_2O	mol ratio
				$CaO:B_2O_3:H_2O$
Theoretical	33.08	61.61	5.31	2.00:3.00:1.00
Analytical	33.05	61.53	5.42	2.00:2.99:1.02
	33.09	61.71	5.20	2.00:3.00:0.97

XRD pattern of synthetic sample is showed in Fig. 2. The characteristic *d* values are 0.6773, 0.3786, 0.3717, 0.3686, 0.3584, 0.3484, 0.3735, 0.3255, 0.3093, 0.2869, 0.2675, 0.253, 0.2495, 0.2253, 0.2197, 0.2122, 0.2052, 0.2031, 0.2001, 0.1924 and 0.1890 nm, which corresponds with those of JCPDS card (File No.14-437), and shows absence of other crystalline forms in the synthetic sample.

The FTIR spectrum of synthetic sample (Fig. 3) exhibited the following absorptions and they were assigned referring to literature [7]. The band at 3460 cm^{-1} is the stretching of O–H. The bands at 1438, 957 cm^{-1} might be the asymmetric and symmetric stretching of $B_{(3)}$–O, respectively. The band at 1287 and 1172 cm^{-1} are the in-plane bending of B–O–H. The bands at 1021, 1066 and 841, 767 cm^{-1} are the asymmetric and symmetric stretching of $B_{(4)}$–O, respectively. The band at 634 cm^{-1} is assigned as the characteristic peak of triborate anion. The band at 691 cm^{-1} is assigned as the out-of-plane bending. The bands at 562, 524 cm^{-1} and 476 cm^{-1} are the in-plane bending of $B_{(3)}$–O and $B_{(4)}$–O, respectively.

TG curve indicates that the total mass loss is 5.62% from 500 to 760°C, which corresponds to the

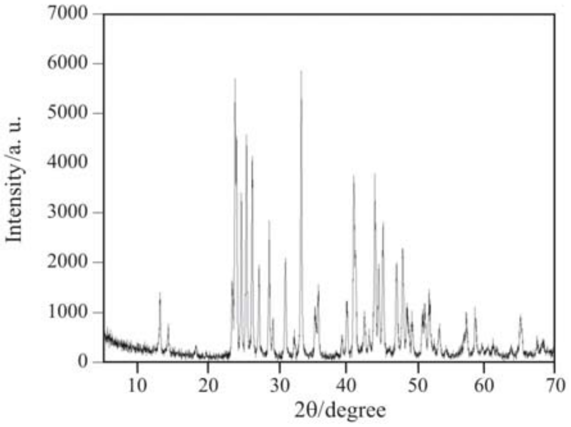

Fig. 2 X-ray powder diffraction pattern of $2CaO\cdot 3B_2O_3\cdot H_2O$

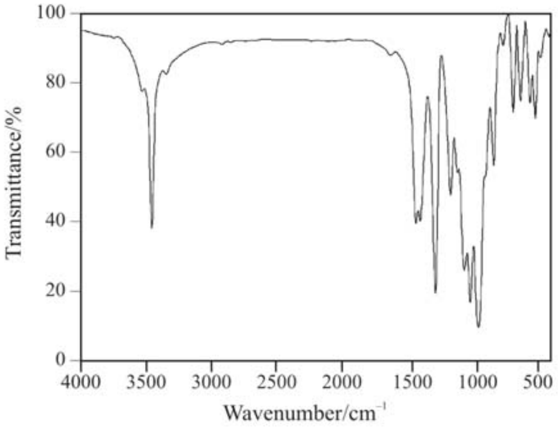

Fig. 3 FTIR spectrum of $2CaO\cdot 3B_2O_3\cdot H_2O$

loss of 1 water molecule and can be compared with calculated value of 5.31% . High temperature to start losing water shows that the H_2O in $2CaO\cdot 3B_2O_3\cdot H_2O$ molecules is the structural water.

FTIR spectrum and TG results of synthetic sample are consistent with the structural formula of $Ca[B_3O_5(OH)]$. XRD, chemical analysis and TG results of synthetic sample indicate that the synthetic sample is pure $2CaO\cdot 3B_2O_3\cdot H_2O$ and is suitable for the calorimetric experiments, and there was no need for impurity correction.

Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 2 , in which *m* is the mass of sample, $\Delta_{sol}H_m^0$ is the molar enthalpy of solution of solute, and the uncertainty is twice the standard deviation of the mean. Table 3 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of $2CaO\cdot 3B_2O_3\cdot H_2O$. The molar enthalpy of solution of $H_3BO_3(s)$ of (21.83±0.08) kJ mol^{-1} in $HCl\cdot 54.501H_2O$, and of CaO(s) of –(188.63± 0.36) kJ mol^{-1} in the mixture of HCl and calculated amount of H_3BO_3 were taken from the literature [8]. The standard molar enthalpies of formation of $H_2O(l)$, CaO(s), and $H_3BO_3(s)$ were taken from the CODATA Key Values [9], namely –(285.83±0.04), –(634.92± 0.90), and –(1094.8±0.8) kJ mol^{-1}, respectively. The enthalpy of dilution of HCl(aq) was calculated from the NBS tables [10]. From these data, the standard molar enthalpy of formation of $2CaO\cdot 3B_2O_3\cdot H_2O$ was calculated to be –(5733.7±5.2) kJ mol^{-1}.

Table 2 The molar enthalpies of solution of $2CaO\cdot 3B_2O_3\cdot H_2O$ in $HCl\cdot 54.572H_2O$ at 298.15 K[a]

No.	*m*/mg	Δ_rH/mJ	$\Delta_{sol}H_m$/kJ mol^{-1}
1	5.96	–1141.30	–64.92
2	6.05	–1143.87	–64.10
3	6.04	–1153.92	–64.77
4	5.99	–1133.56	–64.16
5	6.02	–1155.42	–64.07
Mean			–64.40±0.36[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

For comparison, the enthalpy of formation of $2CaO\cdot 3B_2O_3\cdot H_2O$ can also be estimated by a group contribution method [11], which can be expressed in following equation:

$$\Delta_f H_m^0(Ca_2[B_3O_5(OH)]_2,s)=$$
$$2\Delta_f H_m^0(Ca^{2+},aq)+2\Delta_f H_m^0([B_3O_5(OH)]^{2-})$$

in which the $\Delta_f H_m^0$ of –542.83 kJ mol^{-1} of Ca^{2+}(aq) was taken from the literature [11], the $\Delta_f H_m^0$ of –2341.2 kJ mol^{-1} of $[B_3O_5(OH)]^{2-}$ was calculated from the $\Delta_f H_m^0$ of $[B_3O_3(OH)_5]^{2-}$ according to the group contribution method [11] as follows:

$$[B_3O_3(OH)_5]^{2-}=[B_3O_5(OH)]^{2-}+2H_2O$$

The standard molar enthalpy of formation is, using this scheme, –5768.1 kJ mol^{-1}. The calculated value is close to the experimental result. The relative error is 0.6%.

We also used a group contribution method to calculate $\Delta_f G_m^0$ of $Ca_2[B_3O_5(OH)]_2$ to be –5375.5 kJ mol^{-1}, in which the $\Delta_f G_m^0$ of –553.54 kJ mol^{-1} of Ca^{2+}(aq) was taken from the literature [11], the $\Delta_f G_m^0$ of –2134.23 kJ mol^{-1} of $[B_3O_5(OH)]^{2-}$ was calculated from the $\Delta_f G_m^0$ of $[B_3O_3(OH)_5]^{2-}$.

Combining its $\Delta_f H_m^0$, the standard molar entropy of formation of $Ca_2[B_3O_5(OH)]_2$ has been

Table 3 Thermochemical cycle and results for the derivation of $\Delta_f H_m^0$($2CaO\cdot 3B_2O_3\cdot H_2O$, 298.15 K)

No.	Reaction	Δ_rH^0/kJ mol^{-1}
1	$6H_3BO_3(s)+112.965(HCl\cdot 54.501H_2O)=6H_3BO_3(aq)+112.965(HCl\cdot 54.501H_2O)$	130.98±0.48
2	$2CaO(s)+6H_3BO_3(aq)+112.965(HCl\cdot 54.501H_2O)=2CaCl_2(aq)+6H_3BO_3(aq)+108.965(HCl\cdot 56.520H_2O)$	–377.26±0.72
3	$112.965(HCl\cdot 54.501H_2O)+8H_2O(1)=112.965(HCl\cdot 54.572H_2O)$	–0.16±0.04
4	$2CaO\cdot 3B_2O_3\cdot H_2O(s)+112.965(HCl\cdot 54.572H_2O)=2CaCl_2(aq)+6H_3BO_3(aq)+108.965(HCl\cdot 56.520H_2O)$	–64.40±0.36
5	$2CaO(s)+6H_3BO_3(s)=2CaO\cdot 3B_2O_3\cdot H_2O(s)+8H_2O(1)$	–181.72±0.91

calculated at –1317.18 J mol^{-1} K^{-1} according to following equation:

$$\Delta_f S_m^0=(\Delta_f H_m^0-\Delta_f G_m^0)/T.$$

Finally, the standard molar entropy of $Ca_2[B_3O_5(OH)]_2$ was calculated to be 162.23 J mol^{-1} K^{-1} according to following reaction:

$$2Ca(s)+6B(s)+H_2(g)+6O_2(g)=Ca_2[B_3O_5(OH)]_2(s)$$

The standard molar entropies of the elements were taken from CODATA Key Values [9] to be 41.59, 5.90, 130.571 and 205.043 J mol^{-1} K^{-1} for Ca(s), B(s), H_2(g), and O_2(g), respectively.

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