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Short communication

Synthesis and thermochemistry of $SrB_2O_4\cdot4H_2O$ and SrB_2O_4

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Abstract

Two pure strontium borates $SrB_2O_4\cdot4H_2O$ and SrB_2O_4 have been synthesized and characterized by means of chemical analysis and XRD, FT-IR, DTA-TG techniques. The molar enthalpies of solution of $SrB_2O_4\cdot4H_2O$ and SrB_2O_4 in $1\,\mathrm{mol\,dm^{-3}}$ HCl(aq) were measured to be $-(9.92\pm0.20)\,\mathrm{kJ\,mol^{-1}}$ and $-(81.27\pm0.30)\,\mathrm{kJ\,mol^{-1}}$, respectively. The molar enthalpy of solution of $Sr(OH)_2\cdot8H_2O$ in $(HCl+H_3BO_3)(aq)$ were determined to be $-(51.69\pm0.15)\,\mathrm{kJ\,mol^{-1}}$. With the use of the enthalpy of solution of H_3BO_3 in $1\,\mathrm{mol\,dm^{-3}}$ HCl(aq), and the standard molar enthalpies of formation for $Sr(OH)_2\cdot8H_2O(s)$, $H_3BO_3(s)$, and $H_2O(l)$, the standard molar enthalpies of formation of $-(3253.1\pm1.7)\,\mathrm{kJ\,mol^{-1}}$ for $SrB_2O_4\cdot4H_2O$, and of $-(2038.4\pm1.7)\,\mathrm{kJ\,mol^{-1}}$ for SrB_2O_4 were obtained.

Keywords: Strontium borates; Standard molar enthalpy of formation; Solution calorimetry

1. Introduction

There are several types of strontium borates, both natural and synthetic. Some of them have useful properties, such as SrB_2O_4 has excellent dielectric properties [1]. SrB_4O_7 (SBO) is a useful material with some excellent mechanical and luminescence properties [2]. $Sr_2Be_2B_2O_7$ (SBBO) is an excellent nonlinear optical (NLO) material [3].

Thermodynamic properties of materials play very important roles in scientific research and industrial applications. As for the thermochemistry of alkaline-earth metal borates, the standard molar enthalpies of formation of many magnesium and calcium borates have been measured [4–7]. However, studies of the thermochemistry of the strontium borates are limited in the literature. This paper reports in detail the determination of standard molar enthalpies of formation of two strontium borates, $SrB_2O_4\cdot4H_2O$ and SrB_2O_4, by using a heat conduction microcalorimeter.

2. Experimental

2.1. Preparation of $SrB_2O_4\cdot4H_2O$ and SrB_2O_4 samples

All reagents used in the synthesis of the compounds were of analytical grade. $SrB_2O_4\cdot4H_2O$ was prepared by the following procedure. A few drops of strontium chloride solution were added to a solution of 1.1 g of NaOH in 40 ml of water and the formed strontium carbonate filtered off under reduced pressure. A solution of 70 ml water containing 3.8 g of $Na_2B_4O_7\cdot10H_2O$ was added. A solution of 2.66 g of $SrCl_2\cdot6H_2O$ in 10 ml of water was added and the solution was protected from the atmosphere by covering the beaker. The mixture was stirred for 1 h at room temperature. After 2 days, the resulting white suspended precipitate was filtered, washed with absolute alcohol and absolute ether, and finally, dried at 303 K to constant mass. SrB_2O_4 was prepared by dehydration of $SrB_2O_4\cdot4H_2O$ in air for 3 h at 973 K. These two synthetic samples were characterized by X-ray powder diffraction (Rigaku D/MAX-C X-ray diffractometer with Cu target at $8^\circ\,\mathrm{min^{-1}}$), FT-IR spectroscopy (Nicolet NEXUS 670 FT-IR spectrometer by using KBr pellets at room temperature), and TG-DTA (TA-SDT Q600 simultaneous thermal analyzer at a heating rate of $10\,\mathrm{K\,min^{-1}}$ in flowing N_2). The chemical compositions of the samples were determined by EDTA titration for Sr^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the mass lost in the TG curve for H_2O.

2.2. Calorimetric experiment

$SrB_2O_4\cdot4H_2O$ and SrB_2O_4 can be regarded as the products of the following reactions (1) and (2), respectively:

$$Sr(OH)_2\cdot8H_2O(s) + 2H_3BO_3(s) \rightarrow SrB_2O_4\cdot4H_2O(s) + 8H_2O \quad (1)$$

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$$Sr(OH)_2{\cdot}8H_2O(s) + 2H_3BO_3(s) \rightarrow SrB_2O_4(s) + 12H_2O \qquad (2)$$

The 1 mol dm^{-3} HCl(aq) solvent can rapidly dissolve all components of reactions (1) and (2). It was prepared from analytical grade hydrochloric acid and deionized water, and its concentration, 0.9996 mol dm^{-3}, was determined by titration with standard sodium carbonate.

The thermochemical cycles used are given in Tables 2 and 3. The molar enthalpies of solution of $H_3BO_3(s)$, $SrB_2O_4{\cdot}4H_2O(s)$ and $SrB_2O_4(s)$ in 1 mol dm^{-3} HCl(aq) were measured, namely $\Delta_r H_m^\circ$ (1), $\Delta_r H_m^\circ$ (4), respectively. The calculated amount of $Sr(OH)_2{\cdot}8H_2O(s)$ was dissolved in (hydrochloric acid + boric acid) aqueous solution which consisted of 1 mol dm^{-3} HCl(aq) and the calculated amount of $H_3BO_3(s)$ ($\Delta_r H_m^\circ$ (2)). In all these determinations, strict control of the stoichiometry in each step of the calorimetric cycle must be observed, with the objective that the dissolution of the reactants give the same composition as those of the products in reactions (1) and (2). Applying Hess's law, the enthalpy of reaction (5) ($\Delta_r H_m^\circ$ (5)) can be calculated according to the following expression:

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

where $\Delta_r H_m^\circ$ (3) is the enthalpy of dilution of HCl(aq).

The standard molar enthalpies of formation of $SrB_2O_4{\cdot}4H_2O$ and SrB_2O_4 can be obtained from the values of $\Delta_r H_m^\circ$ (5) in combination with the molar enthalpies of formation of $H_3BO_3(s)$, $Sr(OH)_2{\cdot}8H_2O(s)$, and $H_2O(l)$.

All the enthalpies of solution were measured with an RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which is a totally automatic instrument by using a computerized control that has been described in detail previously [6,8]. 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 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. 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.

3. Results and discussion

3.1. Characterization of synthetic samples

The chemical analytical data of synthetic sample are (found/calcd., %), SrO (42.27/42.24), B_2O_3 (27.69/28.38), H_2O (29.17/29.38).

The data of XRD pattern of the synthetic samples are listed in Table 1, which agree with those of JCPDS cards (File Nos. 41-538 and 15-779) and show absence of other crystalline forms in the synthetic samples, respectively.

Table 1
XRD data of synthetic samples

$SrB_2O_4{\cdot}4H_2O$		SrB_2O_4	
d (nm)	I/I_0	*d* (nm)	I/I_0
0.5764	100	0.6013	46
0.4881	16	0.3466	100
0.4160	71	0.3295	29
0.3994	73	0.3177	40
0.3625	56	0.3002	31
0.3361	32	0.2888	28
0.3112	90	0.2684	64
0.2703	19	0.2218	20
0.2614	22	0.2166	27
0.2556	13	0.2038	15
0.2532	76	0.2000	42
0.2517	65	0.1933	34
0.2405	51	0.1758	16
0.2243	31	0.1588	8
0.2093	15	0.1550	16
0.2054	11		
0.1975	19		
0.1925	21		
0.1809	22		

The FT-IR spectra of these two samples are given in supplementary data files.

The simultaneous TG-DTA curves of the synthetic sample of $SrB_2O_4{\cdot}4H_2O$ are shown in Fig. 1. TG curve indicates that the total mass lost is 29.17% from 373 to 1073 K, which corresponds to the loss of four water molecules and agrees with the calculated value of 29.38%. In the DTA curve, there are three peaks. The first endothermic peak appearing at 434 K is related to the elimination of crystal water. The amorphous phase formed recrystallizes as shown by the exothermic peaks at 898 and 989 K. The simultaneous TG-DTA curves of the synthetic sample of SrB_2O_4 (Fig. 2) indicate that there is no weight loss from 323 to 1073 K.

All of above results indicate that the two synthetic samples are pure and suitable for the calorimetric experiments.

3.2. Results of calorimetric experiment

The molar enthalpies of solution of $Sr(OH)_2{\cdot}8H_2O$ in $(HCl + H_3BO_3)$(aq), of $SrB_2O_4{\cdot}4H_2O$ and SrB_2O_4 in HCl(aq) at 298.15 K are (−51.69 ± 0.15, $n = 5$, kJ mol^{-1}), (−9.92 ± 0.20, $n = 5$, kJ mol^{-1}), and (−81.27 ± 0.30, $n = 5$, kJ mol^{-1}), respectively. The uncertainty is estimated as twice the standard deviation of the mean.

Tables 2 and 3 give the thermochemical cycles used for the derivation of the standard molar enthalpies of formation of $SrB_2O_4{\cdot}4H_2O$ and SrB_2O_4. The molar enthalpy of solution of $H_3BO_3(s)$ of (21.83 ± 0.08) kJ mol^{-1} in 1 mol dm^{-3} HCl(aq) was taken from reference [4]. The enthalpy of dilution of HCl(aq) was calculated from NBS tables [9]. The enthalpy change for the formation of $SrB_2O_4{\cdot}4H_2O$ and SrB_2O_4 from solid reagents (reactions (1) and (2)), −(2.05 ± 0.30) kJ mol^{-1} and −(73.48 ± 0.38) kJ mol^{-1}, respectively, were calculated by

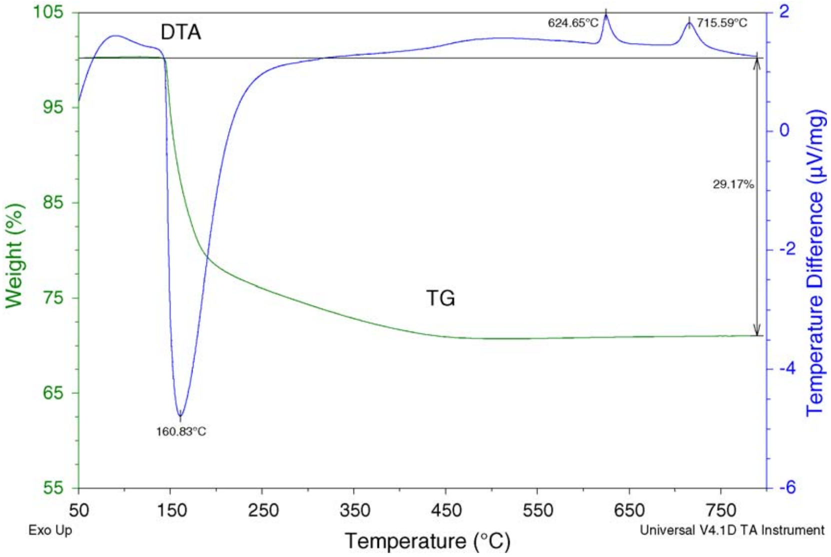

Fig. 1. Simultaneous TG-DTA curves of $SrB_2O_4{\cdot}4H_2O$.

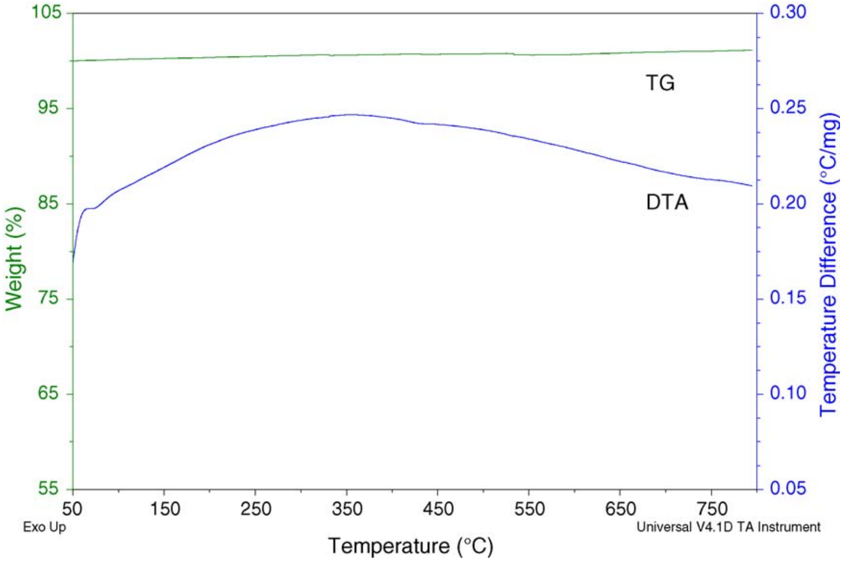

Fig. 2. Simultaneous TG-DTA curves of SrB_2O_4.

using the thermochemical cycles. The standard molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values [10], namely $-(1094.8 \pm 0.8)\,\mathrm{kJ\,mol^{-1}}$ and $-(285.830 \pm 0.040)\,\mathrm{kJ\,mol^{-1}}$, respectively. The standard molar enthalpy of formation of $Sr(OH)_2{\cdot}8H_2O$(s) of $-(3352.2 \pm 0.04)\,\mathrm{kJ\,mol^{-1}}$ was taken from NBS tables [9]. From these data, the standard molar enthalpies of formation of $SrB_2O_4{\cdot}4H_2O$ and SrB_2O_4 were calculated to be $-(3253.1 \pm 1.7)\,\mathrm{kJ\,mol^{-1}}$ and $-(2038.4 \pm 1.7)\,\mathrm{kJ\,mol^{-1}}$, respectively.

Table 2
Thermochemical cycle and results for the derivation of $\Delta_f H^\circ_m$ ($SrB_2O_4{\cdot}4H_2O$, 298.15 K)[a]

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$2H_3BO_3(s) + 95.410(HCl{\cdot}54.506H_2O) = 2H_3BO_3(aq) + 95.410(HCl{\cdot}54.506H_2O)$	43.66 ± 0.16
2	$Sr(OH)_2{\cdot}8H_2O(s) + 2H_3BO_3(aq) + 95.410(HCl{\cdot}54.506H_2O) = SrCl_2(aq) + 2H_3BO_3(aq) + 93.410(HCl{\cdot}55.780H_2O)$	−51.69 ± 0.15
3	$95.410(HCl{\cdot}54.506H_2O) + 8H_2O(l) = 95.410(HCl{\cdot}54.590H_2O)$	−0.16 ± 0.04
4	$SrB_2O_4{\cdot}4H_2O(s) + 95.410(HCl{\cdot}54.590H_2O) = SrCl_2(aq) + 2H_3BO_3(aq) + 93.410(HCl{\cdot}55.780H_2O)$	−9.92 ± 0.20
5	$Sr(OH)_2{\cdot}8H_2O(s) + 2H_3BO_3(s) = SrB_2O_4{\cdot}4H_2O(s) + 8H_2O(l)$	2.05 ± 0.30[b]

[a] $\Delta_f H^\circ_m$ ($SrB_2O_4{\cdot}4H_2O$, s) = $\Delta_r H^\circ_m$ (5) + $\Delta_f H^\circ_m$($Sr(OH)_2{\cdot}8H_2O$, s) + $2\Delta_f H^\circ_m$ (H_3BO_3, s) − $8\Delta_f H^\circ_m$ (H_2O, l).

[b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

Table 3
Thermochemical cycle and results for the derivation of $\Delta_f H^\circ_m$ (SrB_2O_4, 298.15 K)[a]

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$2H_3BO_3(s) + 96.745(HCl\cdot 54.506H_2O) = 2H_3BO_3(aq) + 96.745(HCl\cdot 54.506H_2O)$	43.66 ± 0.16
2	$Sr(OH)_2\cdot 8H_2O(s) + 2H_3BO_3(aq) + 96.745(HCl\cdot 54.506H_2O) = SrCl_2(aq) + 2H_3BO_3(aq) + 94.745(HCl\cdot 55.762H_2O)$	-51.69 ± 0.15
3	$96.745(HCl\cdot 54.506H_2O) + 12H_2O(l) = 96.745(HCl\cdot 54.630H_2O)$	-0.24 ± 0.06
4	$SrB_2O_4(s) + 96.745(HCl\cdot 54.630H_2O) = SrCl_2(aq) + 2H_3BO_3(aq) + 94.745(HCl\cdot 55.762H_2O)$	-81.27 ± 0.30
5	$Sr(OH)_2\cdot 8H_2O(s) + 2H_3BO_3(s) = SrB_2O_4(s) + 12H_2O(l)$	73.48 ± 0.38[b]

[a] $\Delta_f H^\circ_m (SrB_2O_4, s) = \Delta_r H^\circ_m (5) + \Delta_f H^\circ_m(Sr(OH)_2\cdot 8H_2O, s) + 2\Delta_f H^\circ_m(H_3BO_3, s) - 12\Delta_f H^\circ_m(H_2O, l)$.

[b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.05.018.

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