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Thermochimica Acta 454 (2007) 23–25
thermochimica acta
www.elsevier.com/locate/tca

Synthesis, characterization and thermochemistry of $K_2B_5O_8(OH)\cdot 2H_2O$

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Received 15 October 2006; received in revised form 23 November 2006; accepted 6 December 2006
Available online 12 December 2006

Abstract

A pure hydrated potassium borate $K_2B_5O_8(OH)\cdot 2H_2O$ has been synthesized under mild hydrothermal conditions and characterized by single-crystal X-ray diffraction, XRD, FT-IR, Raman spectra and DTA-TG. The crystal structure consists of two K–O polyhedra and $[B_5O_8(OH)]^{2-}$ polyborate anion. The enthalpy of formation was determined to be $-4772.6 \pm 4.0\,\mathrm{kJ\,mol^{-1}}$ by solution calorimetry.

Keywords: Hydrothermal synthesis; Borate; Characterization; Thermochemistry

1. Introduction

Boron atoms coordinate with oxygen not only in tetrahedral BO_4 but also in triangular BO_3. These BO_3 and BO_4 groups may further link together via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets and networks, which result in the complexity of the structures of borates. Much interest has been focused on alkali borate compounds because some of these compounds show interesting physical properties, such as nonlinear optical behavior for $CsLiB_6O_{10}$ [1], CsB_3O_5 [2] and $KB_5O_8\cdot 4H_2O$ [3]. Several phases had been obtained in the K_2O–B_2O_3–H_2O system [3–8]. The polyborate $K_2B_5O_8(OH)\cdot 2H_2O$ was prepared for the first time by Auger, and single crystals of $K_2B_5O_8(OH)\cdot 2H_2O$ were grown by Carpeni et al. through evaporating a very viscous supersaturated solution of $5H_3BO_3$ and 2KOH at ∼90 °C. The crystal structure of this compound was determined by Marezio [5] using the samples synthesized by Carpeni et al. This paper describes the hydrothermal synthesis, characterization and determination of the enthalpy of formation of $K_2B_5O_8(OH)\cdot 2H_2O$.

2. Experimental

2.1. Hydrothermal synthesis and characterization

All reagents used in the synthesis of the compounds were of analytical grade. A mixture of 2.105 g of K_2CO_3, 2.803 g of H_3BO_3 and 0.5 ml of H_2O was sealed in a Teflon-lined bomb and heated at 170 °C for 7 days and then cooled to room temperature. The resulting colorless and transparent crystals of $K_2B_5O_8(OH)\cdot 2H_2O$ were recovered by filtration, washed with deionized water and dried in a vacuum dryer to a constant mass at room temperature. The samples were characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu target at $8^\circ\,\mathrm{min^{-1}}$), FT-IR spectroscopy (recorded over the 400–4000 $\mathrm{cm^{-1}}$ region on a Bruker Equinox 55 spectrometer with KBr pellets at room temperature), Raman spectroscopy (recorded over the 300–4000 $\mathrm{cm^{-1}}$ region on a Nicolet Almega Dispersive Raman spectrometer) and thermogravimetric analysis (TGA) and differential thermal analysis (DTA) (performed on an SDT Q600 thermal analyzer under N_2 atmosphere with a heating rate of $10\,^\circ\mathrm{C\,min^{-1}}$). B_2O_3 content was determined by NaOH titration in the presence of mannitol. H_2O content was determined by the mass lost in the TG curve.

A colorless, transparent crystal 0.48 mm × 0.42 mm × 0.22 mm was selected for the crystal structure measurements. X-ray diffraction intensities were recorded by a Bruker Smart-1000

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doi:10.1016/j.tca.2006.12.008

Table 1
Thermochemical cycle and results for the calculation of $\Delta_f H_m^\circ$ ($K_2B_5O_8(OH)\cdot 2H_2O$, 25.00 °C)

No.	Reaction	$\Delta_f H_m^\circ$ ($kJ\,mol^{-1}$)
1.	$K_2B_5O_8(OH)\cdot 2H_2O\ (s) + 147.37(HCl\cdot 54.506H_2O) = 2K^+(aq) + 2Cl^-(aq) + 5H_3BO_3(aq) + 145.37\ (HCl\cdot 55.228H_2O)$	41.59 ± 0.19
2.	$5H_3BO_3(aq) + 145.37(HCl\cdot 55.228H_2O) = 5H_3BO_3(s) + 145.37(HCl\cdot 55.228H_2O)$	−109.15 ± 0.40
3.	$2K^+(aq) + 2Cl^-(aq) + 5H_3BO_3(aq) + 145.37(HCl\cdot 55.228H_2O) = 2KCl(s) + 5H_3BO_3(aq) + 145.37(HCl\cdot 55.228H_2O)$	−35.26 ± 0.22
4.	$147.37(HCl\cdot 55.228H_2O) = 147.37(HCl\cdot 54.506H_2O) + 106.456H_2O(l)$	2.10 ± 0.08
5.	$H_2(g) + Cl_2(g) + 110.456H_2O(l) = 2(HCl\cdot 55.228H_2O)$	−330.86 ± 0.20
6.	$2KCl(s) = 2K(s) + Cl_2(g)$	873.50 ± 0.20
7.	$5H_3BO_3(s) = 5B(s) + \frac{15}{2}H_2(g) + \frac{15}{2}O_2(g)$	5474.0 ± 4.0
8.	$4H_2(g) + 2O_2(g) = 4H_2O(l)$	−1143.32 ± 0.16
9.	$K_2B_5O_8(OH)\cdot 2H_2O(s) = 2K(s) + 5B(s) + \frac{5}{2}H_2(g) + \frac{11}{2}O_2(g)$	4772.6 ± 4.0[a]

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

CCD automatic diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.071073 nm). Crystal data and conditions of the intensity measurements are given in Table 1 in Supplementary data file.

2.2. *Calorimetric experiment*

The thermochemical reaction designed for the derivation of the $\Delta_f H_m^\circ$ of $K_2B_5O_8(OH)\cdot 2H_2O$ is

$$\begin{aligned} &K_2B_5O_8(OH)\cdot 2H_2O(s) + 147.37\,(HCl\cdot 54.506H_2O) \\ &\quad = 2KCl(s) + 5H_3BO_3(s) + 145.37\,(HCl\cdot 54.506H_2O) \\ &\qquad + 105.012H_2O \end{aligned}$$

The 0.9996 $mol\,dm^{-3}$ HCl(aq) solvent dissolves all components of reaction, and its concentration was determined by titration with standard sodium carbonate. The enthalpy of formation of $K_2B_5O_8(OH)\cdot 2H_2O$ was obtained by solution calorimetry in combination with the standard molar enthalpies of formation of KCl(s), $H_3BO_3(s)$, HCl(aq) and $H_2O(l)$.

The RD496-III heat conduction calorimeter (Southwest Institute of Electron Engineering, China) used was described in detail previously [9,10]. To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ≥0.9999) in deionized water was determined to be 17.31 ± 0.20 $kJ\,mol^{-1}$, in agreement with that of 17.234 $kJ\,mol^{-1}$ reported in the literature [11].

Calorimetric experiment was performed five times at 25.00 °C. Double-layer glass tubes were put in the 16 cm^3 stainless steel sample and reference cells of the calorimeter to prevent corrosion by HCl(aq). The inner glass tube containing 2.00 cm^3 HCl(aq) was broken by a rod after thermal equilibration for at least 2 h and the HCl(aq) mixed with the solid sample in the outer glass tube. The total time required for the complete reaction was about 0.5 h. No solid residues were observed after the reactions.

3. Results and discussion

3.1. *Description of the structure*

See Supplementary data files.

3.2. *Characterization of the synthetic sample*

The chemical analytical data of synthetic sample are (found/calcd., %), B_2O_3 (55.64/55.56), H_2O (14.44/14.36).

The powder XRD pattern of synthesized compound and the simulated pattern on the basis of single-crystal structure of $K_2B_5O_8(OH)\cdot 2H_2O$ are given in Supplementary data files. No impurity lines were observed.

The FT-IR and Raman spectra of this compound were assigned referring to literature [12,13], which are given in Supplementary data files.

The thermal behavior of this compound is shown in Fig. 4 in Supplementary data file. TG curve shows two weight losses between 25 and 600 °C. The first weight loss (11.92%) at 25–330 °C corresponds to the loss of two water molecules and is in good agreement with calculated value of 11.49%. In the second step, the weight loss (2.52%) at 330–600 °C corresponds to the loss of one hydroxyl group and correlates with calculated value of 2.87%. This dehydration process can be expressed as follows:

$$K_2[B_5O_8(OH)]\cdot 2H_2O \xrightarrow{-2H_2O} K_2[B_5O_8(OH)] \xrightarrow{-0.5H_2O} \tfrac{1}{2}K_4B_{10}O_{17}$$

In the DTA curve, there are six peaks. The endothermic peaks at 99, 239 and 437 °C are related to the two-step dehydration and formation of the amorphous phase $K_4B_{10}O_{17}$. This amorphous phase recrystallizes as proven by the exothermic peaks at 508 and 661 °C. The endothermic peak at 756 °C is related to the melting of the solid phase.

3.3. *Results of calorimetric experiment*

The molar enthalpies of solution of $K_2B_5O_8(OH)\cdot 2H_2O$ in 1 $mol\,dm^{-3}$ HCl(aq) at 25.00 °C is (41.59 ± 0.19, $n = 5$, $kJ\,mol^{-1}$) (see Supplementary file). The uncertainty is estimated as the twice the standard deviation of the mean. Table 1 gives the thermochemical cycle for determination of the enthalpy of formation of $K_2B_5O_8(OH)\cdot 2H_2O$. The 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 [14]. The enthalpy of solution of KCl(s) of 17.63 ± 0.11 $kJ\,mol^{-1}$ in (1 $mol\,dm^{-3}$ HCl + H_3BO_3) (aq) was taken from [15]. The enthalpy of formation of HCl(aq) and the enthalpy of dilution of HCl(aq) was calculated from NBS tables [16]. The standard molar enthalpy of formation of KCl(s) was taken from NBS tables [16], namely $-436.75 \pm 0.10\,\mathrm{kJ\,mol^{-1}}$ and the enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values [17], namely -1094.8 ± 0.8 and $-285.830 \pm 0.040\,\mathrm{kJ\,mol^{-1}}$.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2006.12.008.

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