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Thermochemical properties of microporous materials for two borogermanates, β-$K_2[B_2Ge_3O_{10}]$ and $NH_4[BGe_3O_8]$

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ABSTRACT

Two pure dehydrated borogermanates with microporous structure, β-$K_2[B_2Ge_3O_{10}]$ and $NH_4[BGe_3O_8]$, have been synthesized and characterized by XRD, FT-IR, TG techniques. The molar enthalpies of solution of 2.51 mg of GeO_2 (s)/0.99 mg of H_3BO_3 (s)/1.98 mg of H_3BO_3 (s) in 2.00 cm^3 of 1 $mol \cdot dm^{-3}$ NaOH (aq) were measured, respectively. The molar enthalpies of solution of 2.44 mg of $K_2B_4O_7 \cdot 4H_2O$ (s) and 2.18 mg of $NH_4B_5O_8 \cdot 4H_2O$ (s) in the mixture solvent of 2.00 cm^3 of 1 $mol \cdot dm^{-3}$ NaOH (aq) which contains 2.51 mg of GeO_2 (s) were measured, respectively. The molar enthalpies of solution of 3.82 mg of β-$K_2[B_2Ge_3O_{10}]$ (s) in the mixture solvent of 2.00 cm^3 of 1 $mol \cdot dm^{-3}$ NaOH (aq) which contains 0.99 mg of H_3BO_3 (s), and 3.00 mg of $NH_4[BGe_3O_8]$ (s) in the mixture solvent of 2.00 cm^3 of 1 $mol \cdot dm^{-3}$ NaOH (aq) which contains 1.98 mg of H_3BO_3) (s) were also measured, respectively. With the use of standard molar enthalpies of formation for $NH_4B_5O_8 \cdot 4H_2O$ (s), $K_2B_4O_7 \cdot 4H_2O$ (s), GeO_2 (s), H_3BO_3 (s) and H_2O (l), the standard molar enthalpies of formation of – (3937.1 ± 4.7) $kJ \cdot mol^{-1}$ for β-$K_2[B_2Ge_3O_{10}]$ and – (2713.7 ± 6.0) $kJ \cdot mol^{-1}$ for $NH_4[BGe_3O_8]$ at $T = 298.15$ K were obtained on the basis of the appropriate thermochemical cycles, respectively.

1. Introduction

Because of their current widespread applications in catalysis, separation, ion exchange, and adsorption, microporous materials have attracted extensive research efforts worldwide [1]. Borogermanates have many very interesting topological types derived from the flexible coordination geometries for both B and Ge atoms. Until now, many borogermanates have been synthesized, and some of them feature interesting three-dimensional (3D) open frameworks which is a way to create novel microporous materials, such as two borogermanates with microporous structure, β-$K_2[B_2Ge_3O_{10}]$ [2] and $NH_4[BGe_3O_8]$ [3].

Thermodynamic properties play very important roles in scientific research and industrial applications. Thermochemical data can provide information on stabilities and reactivities of molecules that are used, and also are a key factor in the safe and successful scale-up of chemical processes in the chemical industry. Navrotsky group has done much work on the thermochemistry of microporous compounds such as zeolites, pure silica, gallosilicate, and aluminophosphates by using high-temperature calorimetry [4,5]. Recently, our group has reported the determination of standard molar enthalpies of formation of several boron-containing microporous compounds [6–9] including borogermanates [10] by using a heat conduction microcalorimeter.

As part of the continuing study of this work, this paper reports the determination of standard molar enthalpies of formation of two dehydrated borogermanates microporous materials, β-$K_2[B_2Ge_3O_{10}]$ and $NH_4[BGe_3O_8]$, by solution calorimetry.

2. Experimental

2.1. Synthesis and characterization of samples

The β-$K_2[B_2Ge_3O_{10}]$ and $NH_4[BGe_3O_8]$ samples were synthesized referring to literature [2,3], and all reagents and solvents employed in the synthesis were commercially available and used without further purification. Table 1 summarizes relevant information on sample material purities.

The obtained products were washed with distilled water and ethanol repeatedly, then dried at $T = 313$ K. The samples were characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu target at $8° \cdot min^{-1}$), FT-IR spectroscopy (recorded over the 400–4000 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellet at room temperature), and TG-DTA (performed on a TA-SDT Q600 simultaneous

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TABLE 1
Provenance and mass fraction purity of the chemical reagents used in this study.

Chemical name	Source	State	Mass fraction purity[a]
$K_2B_4O_7 \cdot 4H_2O$	Sinopharm Chemical Reagent Co., Ltd	Solid	$\geqslant$0.995
$NH_4B_5O_8 \cdot 4H_2O$	Sinopharm Chemical Reagent Co., Ltd	Solid	$\geqslant$0.990
GeO_2	Sinopharm Chemical Reagent Co., Ltd	Solid	0.9999
H_3BO_3	Xian Chemical Reagent Factory	Solid	$\geqslant$0.990
Ethylene glycol	Sinopharm Chemical Reagent Co., Ltd	Liquid	$\geqslant$0.990
1,4-Diaminobutane	Aladdin	Solid	$\geqslant$0.980
Ethylenediamine	Sinopharm Chemical Reagent Co., Ltd	Liquid	$\geqslant$0.990
$KHC_8H_4O_4$	Sinopharm Chemical Reagent Co., Ltd	Solid	$\geqslant$0.9995
KCl	Aladdin	Solid	$\geqslant$0.9999
β-$K_2[B_2Ge_3O_{10}]$	Synthesized	Solid	0.9932[b]
$NH_4[BGe_3O_8]$	Synthesized	Solid	0.9896[c]

[a] Stated purity from the commercial supplier.
[b] Evaluated by averaging based on the measured contents of B_2O_3 and K.
[c] Evaluated by averaging based on the measured contents of B_2O_3 and N.

thermal analyzer under N_2 atmosphere with a heating rate of $10\ K \cdot min^{-1}$). The chemical compositions of the samples were determined by NaOH standard solution in the presence of mannitol for B_2O_3, and by elemental analyzer (GmbH Vario EL III) for N and H content in $NH_4[BGe_3O_8]$ sample. The content of potassium was determined by ICP-MS (performed on a Bruker M90).

2.2. Calorimetric experiments

The thermochemical cycles designed for the derivation of the molar enthalpies formation of β-$K_2[B_2Ge_3O_{10}]$ and $NH_4[BGe_3O_8]$ were shown in figure 1.

The $1\ mol \cdot dm^{-3}$ NaOH (aq) solvent dissolves all components of the reaction (6), and its concentration of $1.0210\ mol \cdot dm^{-3}$ was determined by titration with standard potassium hydrogen phthalate. With the use of its density of $1.042\ g \cdot cm^{-3}$ (taken from chemical handbook [11]), its concentration can also be expressed as the form of $NaOH \cdot 54.476H_2O$.

The molar enthalpies of solution of 2.51 mg of GeO_2 (s), 0.99 mg of H_3BO_3 (s) and 1.98 mg of H_3BO_3 (s) in $2.00\ cm^3$ of $1\ mol \cdot dm^{-3}$ NaOH (aq) were measured, respectively. The molar enthalpies of solution of 2.44 mg of $K_2B_4O_7 \cdot 4H_2O$ (s) and 2.18 mg of $NH_4B_5O_8 \cdot 4H_2O$ (s) in the mixture solvent of $2.00\ cm^3$ of $1\ mol \cdot dm^{-3}$ NaOH (aq) in which 2.51 mg of GeO_2 (s) being added were measured, respectively. The molar enthalpies of solution of 3.82 mg of β-$K_2[B_2Ge_3O_{10}]$ (s) in the mixture solvent of $2.00\ cm^3$ of $1\ mol \cdot dm^{-3}$ NaOH (aq) which contains 0.99 mg of H_3BO_3 (s), and of 3.00 mg of $NH_4[BGe_3O_8]$ (s) in the mixture solvent of $2.00\ cm^3$ of $1\ mol \cdot dm^{-3}$ NaOH (aq) which contains 1.98 mg of H_3BO_3 (s) were also measured, respectively. In all these determinations, strict control of the stoichiometries in each step of the calorimetric cycles must be observed, with the objective that the dissolution of the reactants give the same composition as those of the products.

Applying Hess's law, $\Delta_r H_m^0$ (6) can be calculated according to the following expressions:

$$\Delta_r H_m^0(6) = \Delta_r H_m^0(1) + \Delta_r H_m^0(2) - \Delta_r H_m^0(3) - \Delta_r H_m^0(4) - \Delta_r H_m^0(5), \qquad (a)$$

$$\Delta_r H_m^0(6) = \Delta_r H_m^0(1) + \Delta_r H_m^0(2) + \Delta_r H_m^0(3) - \Delta_r H_m^0(4) - \Delta_r H_m^0(5). \qquad (b)$$

The standard molar enthalpies of formation of β-$K_2[B_2Ge_3O_{10}]$ (s) and $NH_4[BGe_3O_8]$ (s) can be obtained by the values of $\Delta_r H_m^0$ (6) in combination with the standard molar enthalpies of formation of GeO_2 (s), $K_2B_4O_7 \cdot 4H_2O$ (s)/$NH_4B_5O_8 \cdot 4H_2O$, H_3BO_3 (s) and H_2O (l).

All the enthalpies of solution were measured with a RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China), which has been described in detail previously [12,13]. Calorimetric experiments were performed five times at $T = 298.15$ K. The total time required for the complete dissolution 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 enthalpy of solution of KCl (mass fraction $\geqslant$0.9999) in deionized water was determined to be $(17.54 \pm 0.10)\ kJ \cdot mol^{-1}$, which was in agreement with that of $(17.524 \pm 0.028)\ kJ \cdot mol^{-1}$ reported in the literature [14]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

3. Results and discussion

3.1. Characterization of synthetic samples

Figures 2 and 3 show the powder XRD patterns of as-synthesized samples and the simulated patterns (obtained by a software of Diamond Crystal and Molecular Structure Visualization) on the basis of single-crystal structures of β-$K_2[B_2Ge_3O_{10}]$ and $NH_4[BGe_3O_8]$, respectively. The diffraction peaks on patterns corresponded well in position, indicating the phase purity of the as-synthesized samples.

The FT-IR spectra of the two synthetic samples are shown in figure 4, which are similar to values in the literature [2,3] respectively. For sample β-$K_2[B_2Ge_3O_{10}]$: The bands for the BO_4 group appear at (995 and 940) cm^{-1} [15]. The absorption peak of $795\ cm^{-1}$ can be assigned to the asymmetrical stretch of Ge—O bonds in the GeO_4 group [2]. The absorption bands at (545 and 471) cm^{-1} can be assigned to the symmetrical stretch of Ge—O bonds. For sample $NH_4[BGe_3O_8]$: The bands at (3191–2861) cm^{-1} and $1441\ cm^{-1}$ can be attributed to the stretching and bending vibrations of the N—H groups, respectively. A strong band at about $1022\ cm^{-1}$ agrees with the existence of tetrahedral BO_4 in the crystal structure [3,15]. The peaks at (884 and 829) cm^{-1} can be assigned to the asymmetrical stretch of Ge—O in the GeO_4 group. The absorption bands at (596 and 531) cm^{-1} are caused by the symmetrical stretch of Ge—O. The peaks at (485 and 433) cm^{-1} are due to bending vibrations of Ge—O [3].

The TG curves of two synthetic samples are shown in figure 5. The TG analysis shows that β-$K_2[B_2Ge_3O_{10}]$ sample has no weight loss from room temperature to 1073 K, which are consistent with this compound having no water or OH group, indicating its good thermal stability. The TG analysis of synthetic sample $NH_4[BGe_3O_8]$ indicates that it is stable up to $T = 723$ K and then it begins to decompose.

The elemental analytical data of $NH_4[BGe_3O_8]$ sample: N, 3.68%; H,1.12%, which are consistent with the theoretical values, N, 3.73%;