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Standard molar enthalpies of formation for the two mixed alkali/alkaline earth metal borates of $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$

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ABSTRACT

Two pure mixed alkali/alkaline earth metal borates with three-dimensional framework, $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$, have been synthesized by high-temperature solid state reaction, and characterized by XRD, FT-IR, DTA–TG techniques and chemical analysis. The molar enthalpies of solution of $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$ in 1 mol L^{-1} HCl(aq), and of $LiCl{\cdot}H_2O$(s)/NaCl(s) in [1 mol L^{-1} HCl + H_3BO_3 + $Ba(OH)_2{\cdot}8H_2O$](aq) have been determined by microcalorimeter at 298.15 K, respectively. From these data and with the incorporation of the previously determined enthalpy of solution of H_3BO_3(s) in 1 mol L^{-1} HCl (aq), together with the use of the standard molar enthalpies of formation for $Ba(OH)_2{\cdot}8H_2O$(s), $LiCl{\cdot}H_2O$(s)/NaCl(s), H_3BO_3(s), HCl(aq) and H_2O(l), the standard molar enthalpies of formation of $-(6796.8 \pm 7.3)$ kJ mol^{-1} for $LiBaB_9O_{15}$ and $-(6829.9 \pm 7.3)$ kJ mol^{-1} for $NaBaB_9O_{15}$ were obtained on the basis of the appropriate thermochemical cycles.

1. Introduction

Boron has two kinds of unique coordination, BO_3 and BO_4, which leads to the formation of a large variety of borates. Therefore, borates can be a resource for functional materials. The studies of alkali/alkaline earth metal borates have attracted considerable interest because some of these borates can be as nonlinear optical (NLO) materials, such as $CsLiB_6O_{10}$, BaB_2O_4 (BBO) and $Ba_2Be_2B_2O_7$ (TBO) [1,2]. Some borates have three-dimensional framework, such as $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$ [3], in which both borates crystallize in the trigonal system with space group *R*3*c* and exhibit the same anionic group which is a three-dimensional framework built up from B_3O_7 rings, with channels along the *c* axis in which the alkaline earth Ba^{2+} and the alkaline Li^+/Na^+ ions are located [3]. In addition, nanoborate $LiBaB_9O_{15}$ was also obtained by Pushcharovsky et al. with hydrothermal synthesis systems [4]. Han et al. reported flux growth, spectroscopic studies, and thermal properties (including the thermal expansion, specific heat, thermal diffusion coefficient, and thermal conductivity) of single crystal of $LiBaB_9O_{15}$ [5,6]. However, there are no reports on the standard molar enthalpies of formation for $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$.

Thermodynamic properties play very important roles in scientific research and industrial applications. Until now, the standard molar enthalpies of formation of many alkaline/alkaline-earth metal borates have been reported [7–20]. As part of the continuing study of the thermochemistry of main group borates, this paper reports the determination of the standard molar enthalpies of formation of two mixed alkali/alkaline earth metal borates of $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$ with three-dimensional framework by using a heat conduction microcalorimeter.

2. Experimental

2.1. Chemicals

All reagents were used as obtained from commercial sources without further purification. Table 1 summarizes relevant information on sample material purities. The water contents in $Ba(OH)_2$ and LiCl hydrates are consistent with those of the molecular formula of $LiOH{\cdot}H_2O$ and $Ba(OH)_2{\cdot}8H_2O$, respectively.

2.2. Synthesis and characterization of samples

Single crystals of $LiBaB_9O_{15}$ were synthesized from a mixture of 0.168 g $LiOH{\cdot}H_2O$, 0.197 g $BaCO_3$, 0.188 g Ga_2O_3 and 0.931 g H_3BO_3. This mixture was ground in an agate mortar and transferred to platinum crucible, which was heated in a furnace at 900 °C for 2 days, then cooled to 450 °C at a rate of 2.7 °C h^{-1}, followed by cooling to room temperature at a rate of 20 °C h^{-1}. The resulting colorless crystals were collected, and washed with deionized water and ethanol for three times, respectively. The single crystals of $NaBaB_9O_{15}$ were synthesized referring to literature [3].

The obtained samples were characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu Kα1

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Table 1
Chemical sample used in this study.

Chemical name	Source	State	Initial mole fraction
$LiCl{\cdot}H_2O$	Aladdin	Solid	≥0.999
$BaCO_3$	Sinopharm Chemical Reagent Co., Ltd.	Solid	≥0.990
H_3BO_3	Aladdin	Solid	≥0.998
Ga_2O_3	Aladdin	Solid	≥0.999
Na_2CO_3	Sinopharm Chemical Reagent Co., Ltd.	Solid	≥0.998
$Ba(OH)_2{\cdot}8H_2O$	Jinjing Barium Salt Chemical Co., Ltd.	Solid	≥0.9948

target ($\lambda = 1.5406$ Å) scanning the 2θ range with a speed of $8^\circ\,min^{-1}$), FT-IR spectroscopy (recorded over the 400–4000 cm^{-1} region on a Nicolet NEXUS 670 spectrometer with KBr pellets at room temperature), single crystal X-ray diffraction (recorded by a CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.34.36 CCD automatic diffractometer with graphite monochromatized Mo Kα1 radiation ($\lambda = 0.7093$ Å)), and thermogravimetric analysis (TGA) (performed on a SDT Q600 simultaneous thermal analyzer under N_2 atmosphere with a heating rate of $10\,^\circ C\,min^{-1}$). The chemical compositions of the samples were determined by EDTA titration for Ba^{2+}, by NaOH titration in the presence of mannitol for B_2O_3 [21], and by ICP-AES elemental analysis (IRIS Advantage, charge-injection detector (CID), Thermo Scientific) for Li^+ and Na^+. The relative standard uncertainty $u(r)$ in the titration experiments was estimated to be 0.2%.

2.3. Calorimetric experiment

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 [20,22]. To check the performance of the calorimeter, the enthalpy of solution of KCl (mass fraction ≥ 0.9999) in deionized water was determined to be $(17.54 \pm 0.10)\,kJ\,mol^{-1}$, which was in agreement with that of $(17.524 \pm 0.028)\,kJ\,mol^{-1}$ reported in the literature [23]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

The thermochemical reactions designed for the derivation of the $\Delta_f H_m{}^0$ of $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$ are expressed as follows:

$$LiBaB_9O_{15}(s) + (HCl{\cdot}54.561H_2O) = LiCl{\cdot}H_2O(s) + Ba(OH)_2{\cdot}8H_2O(s) + 9H_3BO_3(s) + 31.561H_2O(l)$$

$$NaBaB_9O_{15}(s) + (HCl{\cdot}54.561H_2O) = NaCl(s) + Ba(OH)_2{\cdot}8H_2O(s) + 9H_3BO_3(s) + 32.561H_2O(l)$$

The 1 mol dm^{-3} HCl(aq) solvent can dissolve all components of designed reactions, and its concentration, 1.0004 mol dm^{-3}, was determined by titration with standard sodium carbonate. With the use of its density of 1019 kg m^{-3} (taken from chemical handbook), its concentration can also be expressed as the form of $HCl{\cdot}54.561H_2O$. 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.

The standard molar enthalpies of formation of $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$ could be obtained by solution calorimetries in combination with the standard molar enthalpies of formation of $Ba(OH)_2{\cdot}8H_2O(s)$, $LiCl{\cdot}H_2O(s)$/NaCl(s), $H_3BO_3(s)$, HCl(aq) and $H_2O(l)$.

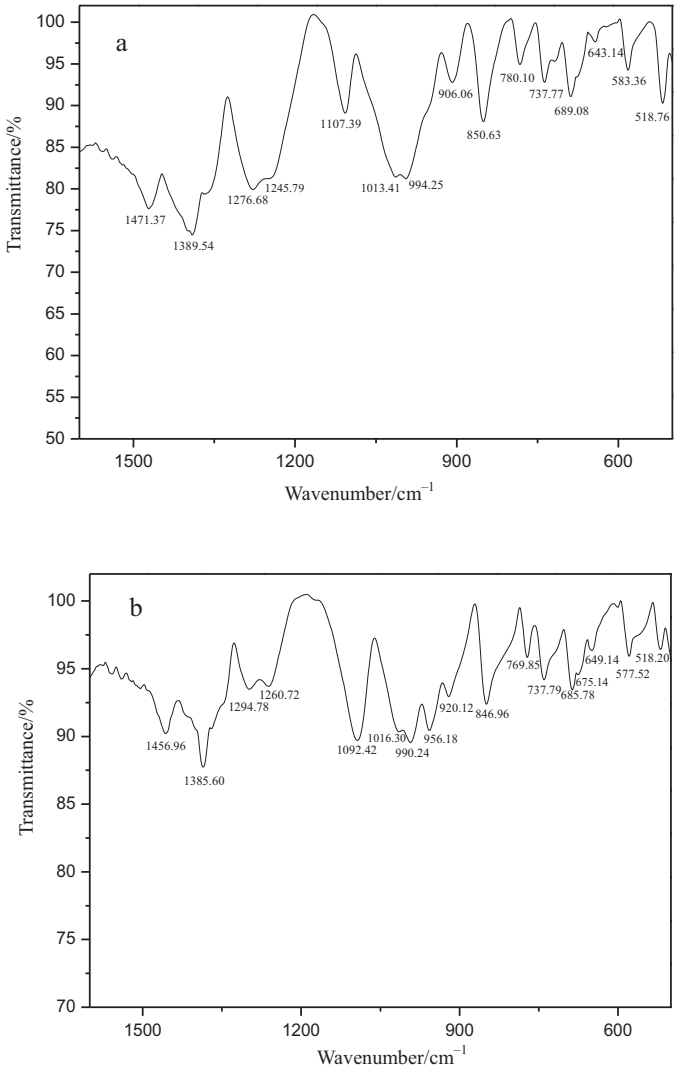

Fig. 1. FT-IR spectra of samples: (a) $LiBaB_9O_{15}$ and (b) $NaBaB_9O_{15}$.

3. Results and discussion

3.1. Characterization of the synthetic samples

Single X-ray diffraction indicated that the samples of $LiBaB_9O_{15}$ and $NaBaB_9O_{15}$ crystallized in the trigonal system with space group *R3CH*, and the unit cell dimensions are $a = b = 10.967(7)$ Å, $c = 17.060(14)$ Å, $\gamma = 120^\circ$ for $LiBaB_9O_{15}$ sample; $a = b = 11.102(6)$ Å, $c = 17.400(9)$ Å, $\gamma = 120^\circ$ for $NaBaB_9O_{15}$ sample, which are consistent with the reported unit cell values in the literature [3], respectively.

As shown in Fig. 1, the IR spectrum of $NaBaB_9O_{15}$ sample is very similar to that of $LiBaB_9O_{15}$ sample, which indicates their similar structures. Referring to the literature [5,24], we only assigned the absorption bands of FT-IR spectrum for sample $LiBaB_9O_{15}$ as follows: the bands at (1471, 1390 and 1277) cm^{-1} and 906 cm^{-1} might be asymmetric and symmetric stretching mode of B(3)—O in the triangular BO_3 unit. The bands at (1107, 1013, and 994) cm^{-1} and (851 and 780) cm^{-1} were the asymmetrical and symmetric stretching mode of B(4)—O in the tetrahedral BO_4 unit, respectively. The bands at (738, 689, and 643) cm^{-1} are the out of plane bending of B(3)—O. The peaks at (583 and 519) cm^{-1} might be bending modes of B(3)—O and B(4)—O.