



Thermodynamic properties for two mixed alkali-transition metal borates of $\text{Li}_6\text{Zn}_3\text{B}_4\text{O}_{12}$ and $\text{Na}_3\text{ZnB}_5\text{O}_{10}$



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ABSTRACT

Two pure mixed alkali-transition metal borates, $\text{Li}_6\text{Zn}_3\text{B}_4\text{O}_{12}(\text{s})$ and $\text{Na}_3\text{ZnB}_5\text{O}_{10}(\text{s})$ have been synthesized and characterized by XRD, FT-IR, and chemical analysis. For $\text{Li}_6\text{Zn}_3\text{B}_4\text{O}_{12}$, the molar enthalpy of solution of $\text{Li}_6\text{Zn}_3\text{B}_4\text{O}_{12}$ in the mixture solvent of $\{2.00 \text{ mL of } 1 \text{ mol}\cdot\text{L}^{-1} \text{ HCl} + \text{H}_3\text{BO}_3(\text{aq})\}$ was measured. The molar enthalpies of solution of $\text{ZnO}(\text{s})$ in $1 \text{ mol}\cdot\text{L}^{-1} \text{ HCl}(\text{aq})$, and $\text{LiBO}_2(\text{s})$ in the mixture solvent of $\{2.00 \text{ mL of } 1 \text{ mol}\cdot\text{L}^{-1} \text{ HCl}(\text{aq}) + \text{ZnO}(\text{aq})\}$ were also measured. For $\text{Na}_3\text{ZnB}_5\text{O}_{10}$, the molar enthalpy of solution of $\text{Na}_3\text{ZnB}_5\text{O}_{10}$ in $2.00 \text{ mL of } 1 \text{ mol}\cdot\text{L}^{-1} \text{ HCl}(\text{aq})$ was measured. The molar enthalpy of solution of $\text{NaBO}_2\cdot 4\text{H}_2\text{O}(\text{s})$ in the mixture solvent of $\{2.00 \text{ mL of } 1 \text{ mol}\cdot\text{L}^{-1} \text{ HCl}(\text{aq}) + \text{H}_3\text{BO}_3 + \text{ZnO}(\text{aq})\}$ was also measured. With the incorporation of the previously determined enthalpy of solution of $\text{H}_3\text{BO}_3(\text{s})$ in $1 \text{ mol}\cdot\text{L}^{-1} \text{ HCl}(\text{aq})$, and $\text{ZnO}(\text{s})$ in $\{1 \text{ mol}\cdot\text{L}^{-1} \text{ HCl}(\text{aq}) + \text{H}_3\text{BO}_3\}$, together with the use of the standard molar enthalpies of formation for $\text{LiBO}_2(\text{s})/\text{NaBO}_2\cdot 4\text{H}_2\text{O}(\text{s})$, $\text{ZnO}(\text{s})$, $\text{H}_3\text{BO}_3(\text{s})$ and $\text{H}_2\text{O}(\text{l})$, the standard molar enthalpies of formation of $-(5867.5 \pm 4.8) \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{Li}_6\text{Zn}_3\text{B}_4\text{O}_{12}$ and $-(4655.3 \pm 6.6) \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{Na}_3\text{ZnB}_5\text{O}_{10}$ at $T = 298.15 \text{ K}$ were obtained on the basis of two appropriate thermochemical cycles.

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1. Introduction

Borate materials have attracted much attention in the past decades because of their structural chemistry and potential applications in luminescence, nonlinear optics and industrial importance [1–3]. For example, zinc borates with different chemical formula such as $2\text{ZnO}\cdot 3\text{B}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ are the fire retardant materials used in plastics [4].

Thermodynamic property plays an important role in scientific research and industrial application. We have reported the measurement of standard molar enthalpies of formation of a few transition metal zinc borates by using a heat conduction microcalorimeter [5–8]. However, studies of the thermochemistry of the mixed alkali-transition metal borates are few [9,10]. As a continuation of this work, this paper reports the measurement of standard molar enthalpies of formation of $\text{Li}_6\text{Zn}_3\text{B}_4\text{O}_{12}$ and $\text{Na}_3\text{ZnB}_5\text{O}_{10}$ by solution calorimetry.

2. Experimental

2.1. Synthesis and characterization of samples

All used reagents in the synthesis were commercially available with analytic grade and used without further purification. Table 1 gives the purities of materials used.

Both samples were synthesized through a conventional high temperature solid-state reaction method. The polycrystalline powder for $\text{Li}_6\text{Zn}_3\text{B}_4\text{O}_{12}$ was obtained by using Li_2CO_3 , ZnO and H_3BO_3 referring to literature [11]. The polycrystalline powder for $\text{Na}_3\text{ZnB}_5\text{O}_{10}$ was obtained by using Na_2CO_3 , ZnO and H_3BO_3 referring to literature [12]. The resulting white solid powder was washed with hot distilled water (60°C) and ethanol for three times respectively, and then dried in air at ambient temperature.

X-ray powder diffraction (Bruker D8 Advance X-ray diffractometer with Cu target at $8^\circ\cdot\text{min}^{-1}$) and FT-IR spectroscopy (recorded over the 400 cm^{-1} to 4000 cm^{-1} region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellet at room temperature) were used to characterize the obtained samples. The chemical compositions of the samples were measured by EDTA titration for Zn^{2+} , and by NaOH standard solution in the presence of mannitol for B_2O_3 .

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¹ Both authors contributed equally to this work and should be considered co-first authors.

Table 1

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

Chemical name	Source	State	Mass fraction purity ^a
LiBO ₂	Shanghai Macklin Biochemical Co., Ltd.	Solid	≥0.999
NaBO ₂ ·4H ₂ O	Sinopharm Chemical Reagent Co., Ltd.	Solid	≥0.990
Na ₂ CO ₃	Guangdong Guanghua Sci-Tech Co., Ltd.	Solid	≥0.990
Li ₂ CO ₃	Shanghai Macklin Biochemical Co., Ltd.	Solid	≥0.990
H ₃ BO ₃	Xian Chemical Reagent Factory	Solid	≥0.990
ZnO	Shanghai Macklin Biochemical Co., Ltd.	Solid	≥0.995
KCl	Aladdin	Solid	≥0.9999
HCl	Sinopharm Chemical Reagent Co., Ltd.	aqueous	0.38 ^b
Li ₆ Zn ₃ B ₄ O ₁₂	Synthesized	Solid	0.990 ^c
Na ₃ ZnB ₅ O ₁₀	Synthesized	Solid	0.994 ^c

^a Stated purity from the commercial supplier.^b Concentration of HCl aqueous solution.^c Evaluated based on the measured content of B₂O₃.

2.2. Method of obtaining standard molar enthalpy of formation

The thermochemical cycles designed for the derivation of the molar enthalpies formation of Li₆Zn₃B₄O₁₂ and Na₃ZnB₅O₁₀ were shown in Figs. 1 and 2, respectively. The 1 mol·L⁻¹ HCl (aq) solvent can dissolve all components of virtual reaction (6), and its concentration, 1.0004 ± 0.0001 mol·L⁻¹, was determined by titration with standard sodium carbonate. With the use of its density of 1.019 g·cm⁻³ (taken from chemical handbook [13]), its concentration can be expressed in the form of HCl·54.561H₂O.

In order to give the same composition for the dissolution of the reactants and the dissolution of the products, the stoichiometries in each step of the calorimetric cycles must be observed in all determinations.

To the Li₆Zn₃B₄O₁₂ cycle, the molar enthalpy of solution of 6.75 mg Li₆Zn₃B₄O₁₂ in the mixture solvent of {2.00 mL of 1 mol·L⁻¹ HCl + 1.77 mg of H₃BO₃(aq)} was measured. The molar enthalpy of solution of 3.48 mg ZnO(s) in 2.00 mL of 1 mol·L⁻¹ HCl(aq) was also measured. The molar enthalpy of solution of 4.26 mg LiBO₂(s) in the mixture solvent of {2.00 mL of 1 mol·L⁻¹ HCl(aq) + 3.48 mg of ZnO}(aq) was also measured.

To the Na₃ZnB₅O₁₀ cycle, the molar enthalpy of solution of 3.73 mg Na₃ZnB₅O₁₀ in 2.00 mL of 1 mol·L⁻¹ HCl(aq) was measured. The

molar enthalpy of solution of 4.43 mg NaBO₂·4H₂O(s) in the mixture solvent of {2.00 mL of 1 mol·L⁻¹ HCl(aq) + 1.33 mg of H₃BO₃ + 0.87 mg of ZnO(aq)} was also measured.

Applying Hess's law, Δ_rH_m^θ (6) can be calculated according to the following expression:

$$\Delta_r H_m^\theta (6) = \Delta_r H_m^\theta (1) + \Delta_r H_m^\theta (2) + \Delta_r H_m^\theta (3) - \Delta_r H_m^\theta (4) - \Delta_r H_m^\theta (5)$$

The standard molar enthalpy of formation of Li₆Zn₃B₄O₁₂ can be obtained by the values of Δ_rH_m^θ (6) in combination with the standard molar enthalpies of formation of LiBO₂(s), ZnO(s), H₃BO₃(s) and H₂O(l). The standard molar enthalpy of formation of Na₃ZnB₅O₁₀ can be obtained by the values of Δ_rH_m^θ (6) in combination with the standard molar enthalpies of formation of NaBO₂·4H₂O(s), ZnO(s), H₃BO₃(s) and H₂O(l).

2.3. Calorimeter

All the enthalpies of solution were measured by using a RD496-2000 heat conduction microcalorimeter (Mianyang CP Thermal Analysis Instrument Co., LTD, China), which has been described in detail previously [14,15]. Calorimetric experiments were performed five times at T = 298.15 K. The total time required for the complete dissolution reaction was about 30 min. After finishing each calorimetric experiment, no solid residue was observed in the reactions system.

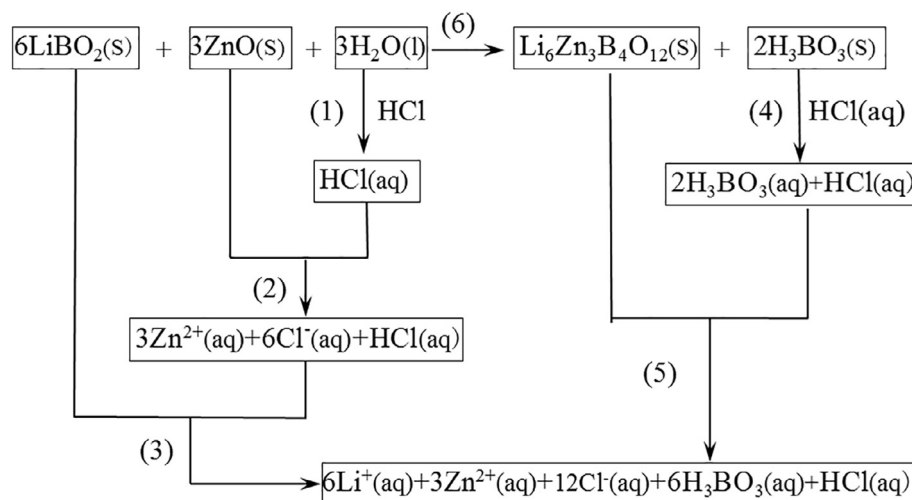
In order to check the performance of the calorimeter, the enthalpy of solution of KCl in deionized water was determined to be (17.54 ± 0.10) kJ·mol⁻¹, which was in accord with that reported in the literature [16]. It shows that the calorimeter used for measuring the enthalpy of solution in this work is reliable.

3. Results and discussion

3.1. Characterization of the synthetic samples

Figs. 3 and 4 give the powder XRD patterns of as-synthesized samples and the simulated patterns (obtained by software of Diamond Crystal and Molecular Structure Visualization) on the basis of single-crystal structures of Li₆Zn₃B₄O₁₂ and Na₃ZnB₅O₁₀, respectively. The diffraction peaks on patterns accord well within position, which indicates that synthesized samples are pure.

The FT-IR spectra of synthetic samples are shown in Fig. 5, which exhibit the following absorption bands, and they were

**Fig. 1.** The designed thermochemical cycle of sample Li₆Zn₃B₄O₁₂.

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