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Thermochemical properties of two mixed alkali-alkaline earth metal borates as non-linear optical materials: $NaSrBO_3$ and $KSr_4B_3O_9$

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Two mixed alkali-alkaline earth metal borates of $NaSrBO_3$ and $KSr_4B_3O_9$ have been synthesized by high-temperature solid state reaction, which were further characterized by XRD, FT-IR, DTA-TG techniques and chemical analysis. The molar enthalpies of solution of $NaSrBO_3$(s) and $KSr_4B_3O_9$(s) in 2.00 cm^3 of 1 $mol \cdot dm^{-3}$ HCl(aq), at T = 298.15 K were measured to be $-(206.84 \pm 0.43)$ $kJ \cdot mol^{-1}$ and $-(494.59 \pm 0.53)$ $kJ \cdot mol^{-1}$, respectively. The molar enthalpy of solution of NaCl(s) in 2.00 cm^3 of {1 $mol \cdot dm^{-3}$ HCl + H_3BO_3 + $Sr(OH)_2 \cdot 8H_2O$}(aq) mixed solvent at T = 298.15 K was measured to be (5.17 ± 0.02) $kJ \cdot mol^{-1}$. From these data and with the incorporation of the previously determined enthalpies of solution of H_3BO_3(s) in HCl(aq) of $Sr(OH)_2 \cdot 8H_2O$(s) in (HCl + H_3BO_3)(aq), and of KCl(s) in {HCl + H_3BO_3 + $Sr(OH)_2 \cdot 8H_2O$}(aq), together with the use of the molar enthalpies of formation for NaCl(s)/KCl(s), $Sr(OH)_2 \cdot 8H_2O$(s), H_3BO_3(s), HCl(aq) and H_2O(l), the standard molar enthalpies of formation of $NaSrBO_3$(s) and $KSr_4B_3O_9$ were calculated to be $-(1653.1 \pm 1.4)$ $kJ \cdot mol^{-1}$ and $-(5071.1 \pm 3.4)$ $kJ \cdot mol^{-1}$ on the basis of the designed thermochemical cycles, respectively.

1. Introduction

The studies of alkali/alkaline earth metal borates have attracted considerable interest because some of these borates can be as non-linear optical (NLO) materials, such as $CsLiB_6O_{10}$, BaB_2O_4 (BBO) and $Ba_2Be_2B_2O_7$ (TBO) [1,2]. The title two borates $NaSrBO_3$ [3] and $KSr_4B_3O_9$ [4] are also likely to be good candidates for future deep-UV NLO and birefringent materials [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. Until now, the standard molar enthalpies of formation of several mixed alkali-alkaline earth metal borates have been reported [5–9]. This paper reports the determination of the standard molar enthalpies of formation of $NaSrBO_3$ and $KSr_4B_3O_9$ by using a heat conduction microcalorimeter.

2. Experimental

2.1. Synthesis and characterization of samples

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.

Polycrystalline $NaSrBO_3$ sample was synthesized by high-temperature solid state reaction referring to literature [3]. A mixture of 0.42 g Na_2CO_3, 1.18 g $SrCO_3$ and 0.49 g H_3BO_3 was ground in an agate mortar and transferred to platinum crucible, which was heated in a furnace at T = 923 K for 4 h, then elevated to 1123 K for 72 h. The sample was cooled and then ground.

The polycrystalline $KSr_4B_3O_9$ sample was synthesized by high-temperature solid state reaction according to the literature [4]. A mixture of 0.55 g K_2CO_3, 1.25 g $SrCO_3$ and 0.49 g H_3BO_3 was ground in an agate mortar and transferred to platinum crucible, which was heated in a furnace at T = 673 K for 5 h, then elevated to 1173 K for 48 h. The sample was cooled to 673 K at a rate of 0.2 $K \cdot min^{-1}$, followed by cooling to room temperature, and then ground.

The resulting colourless powders were collected, and washed with deionized water and ethanol for three times, respectively.

The samples obtained were characterized by X-ray powder diffraction (Rigaku D/MAX-IIIC X-ray diffractometer with Cu target at 8 min^{-1}), FT-IR spectroscopy (recorded on a Nicolet NEXUS 670 spectrometer with KBr pellets at room temperature), and TG-DTA (performed on a SDT Q600 simultaneous thermal analyser under a N_2 atmosphere with a heating rate of 10 $K \cdot min^{-1}$). The chemical composition of the sample was determined by EDTA titration for Sr^{2+}, and by NaOH standard solution titration in the presence of mannitol for boron.

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TABLE 1
Chemical reagents used in this study.

Chemical name	Provenance	State	Initial mole fraction	CAS numbers
Na_2CO_3	Aladdin Reagent Co., Ltd	Solid	0.998	497-19-8
K_2CO_3	Aladdin Reagent Co., Ltd	Solid	0.995	584-08-7
$SrCO_3$	Aladdin Reagent Co., Ltd	Solid	0.99	1633-05-2
H_3BO_3	Aladdin Reagent Co., Ltd	Solid	0.998	10043-35-3
NaCl	Aladdin Reagent Co., Ltd	Solid	0.998	7647-14-5
KCl	Aladdin Reagent Co., Ltd	Solid	0.9998	7447-40-7

2.2. Calorimetric experiment

The thermochemical cycles designed for the derivation of the $\Delta_f H_m^o$ of $NaSrBO_3$ and $KSr_4B_3O_9$ are shown in figure 1. The $1\ mol \cdot dm^{-3}$ HCl(aq) solvent can dissolve all components of designed reaction (6), and its concentration, $1.0004\ mol \cdot dm^{-3}$, was determined by titration with standard sodium carbonate. With the use of its density of $1.019\ g \cdot cm^{-3}$ (taken from chemical handbook [10]), its concentration can also be expressed as the form of HCl $54.561H_2O$. 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 [11]. In all these determinations, strict control of the stoichiometry in each step of the calorimetric cycle has been observed, with the objective that the dissolution of the reactants give the same composition as those of the products. The total time required for the complete dissolution reaction of $NaSrBO_3$, $KSr_4B_3O_9$ and NaCl(s) solutes in corresponding solvents was about 0.5 h for each compound. 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 ⩾ 0.9998) in deionised water was determined to be $(17.54 \pm 0.10)\ kJ \cdot mol^{-1}$, which is in agreement with that of $(17.524 \pm 0.028)\ kJ \cdot mol^{-1}$ reported in the literature [12]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

The standard molar enthalpies of formation of $NaSrBO_3$ and $KSr_4B_3O_9$ were obtained by solution calorimetry in combination

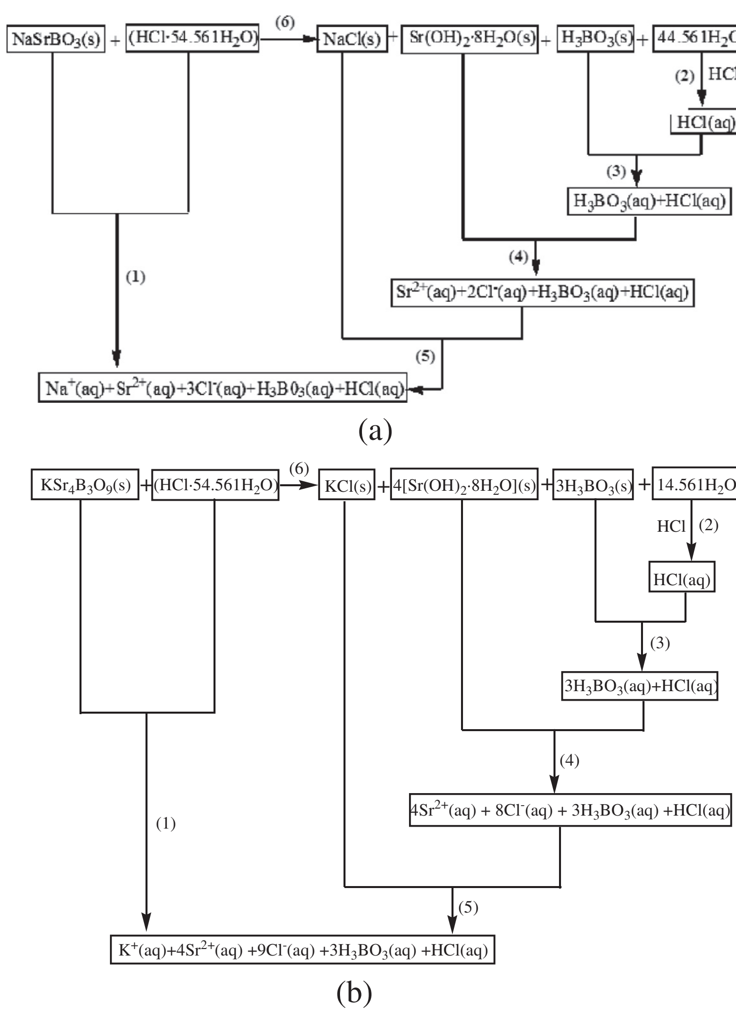

FIGURE 1. The designed thermochemical cycles: (a) $NaSrBO_3$, (b) $KSr_4B_3O_9$.