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Thermochemistry of two lead borates; $Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$

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ABSTRACT

Two pure hydrated lead borates, $Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$, have been characterized by XRD, FT-IR, DTA-TG techniques and chemical analysis. The molar enthalpies of solution of $Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$ in $1\,mol\,dm^{-3}$ $HNO_3(aq)$ were measured to be $(-35.00 \pm 0.18)\,kJ\,mol^{-1}$ and $(35.37 \pm 0.14)\,kJ\,mol^{-1}$, respectively. The molar enthalpy of solution of $H_3BO_3(s)$ in $1\,mol\,dm^{-3}$ $HNO_3(aq)$ was measured to be $(21.19 \pm 0.18)\,kJ\,mol^{-1}$. The molar enthalpy of solution of PbO(s) in $(HNO_3 + H_3BO_3)(aq)$ was measured to be $-(61.84 \pm 0.10)\,kJ\,mol^{-1}$. From these data and with incorporation of the enthalpies of formation of PbO(s), $H_3BO_3(s)$ and $H_2O(l)$, the standard molar enthalpies of formation of $-(1820.5 \pm 1.8)\,kJ\,mol^{-1}$ for $Pb(BO_2)_2{\cdot}H_2O$ and $-(4038.1 \pm 3.4)\,kJ\,mol^{-1}$ for $PbB_4O_7{\cdot}4H_2O$ were obtained on the basis of the appropriate thermochemical cycles.

1. Introduction

Borate materials have attracted considerable attention in the past decades because they show a great variety of physical properties ranging from nonlinear optical (NLO), ferroelectric to semiconducting behaviors [1]. Lead borates are of special interest in the search for materials, since some of these compounds have pronounced nonlinear-optical properties [2], such as PbB_4O_7 [3], $Pb_2[B_5O_9](OH){\cdot}H_2O$ [4], $Pb_5B_3O_8(OH)_3{\cdot}H_2O$ [5], $Pb_3B_9O_{16}(OH){\cdot}B(OH)_3$ [6] and $Pb_6B_{11}O_{18}(OH)_9$ [7].

Thermodynamic properties play very important roles in scientific research and industrial applications. As for the thermochemistry of main group borates, the standard molar enthalpies of formation of many alkaline and alkaline-earth metal borates have been measured [8–18]. However, studies of the thermochemistry of the lead borates are not reported in the literature. This paper reports the determination of standard molar enthalpies of formation of two lead borates, $Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$, using a heat conduction microcalorimeter.

2. Experimental

2.1. Synthesis and characterization of samples

$Pb(BO_2)_2{\cdot}H_2O$ is a chemical reagent with analytic grade (mass fraction >0.9900) purchased from commercial source and used as received, which was made in Sinopharm Chemical Reagent Co. Ltd, China.

$PbB_4O_7{\cdot}4H_2O$ was synthesized referring to the literature [19], and all reagents used in the synthesis were of analytic grade. 11.4 g of $Pb(CH_3COO)_2{\cdot}3H_2O$ and 3.7 g of H_3BO_3 were placed in a beaker, and $20\,cm^3$ of deionized water was added, then this mixture was stirred thoroughly until homogeneous. After 2 weeks, this mixture was diluted into $100\,cm^3$ with deionized water. The resulting white crystal was filtered, then washed with 1% boric acid aqueous solution and 60% (v/v) ethanol–water solvent, and finally, dried at room temperature to constant mass. The sample was characterized by FT-IR spectroscopy (recorded over the $400–4000\,cm^{-1}$ region on a Nicolet NEXUS 670 FT-IR spectrometer with KBr pellets at room temperature), X-ray powder diffraction (Rigaku D/MAX-IIIC with Cu target at $8^\circ\,min^{-1}$) and TG-DTA (performed on a TA-SDT Q600 simultaneous thermal analyzer under N_2 atmosphere with a heating rate of $10\,^\circ C\,min^{-1}$). The chemical compositions of the sample were determined by EDTA titration for Pb^{2+}, by NaOH standard solution in the presence of mannitol for B_2O_3, and by the mass loss in the TG curve for H_2O.

2.2. Calorimetric experiment

$Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$ can be regarded as the products of reactions (5) in the designed thermochemical cycles (Fig. 1 and Tables 4 and 5).

The $1\,mol\,dm^{-3}$ $HNO_3(aq)$ solvent can dissolve all components of reaction (5), which was prepared from analytical grade nitric acid and deionized water, and its concentration, $1.0044\,mol\,dm^{-3}$, was determined by titration with standard sodium carbonate. With the use of its density of $1.032\,g\,cm^{-3}$ (taken from chemical handbook), its concentration can also be expressed as the form of $HNO_3{\cdot}53.59H_2O$.

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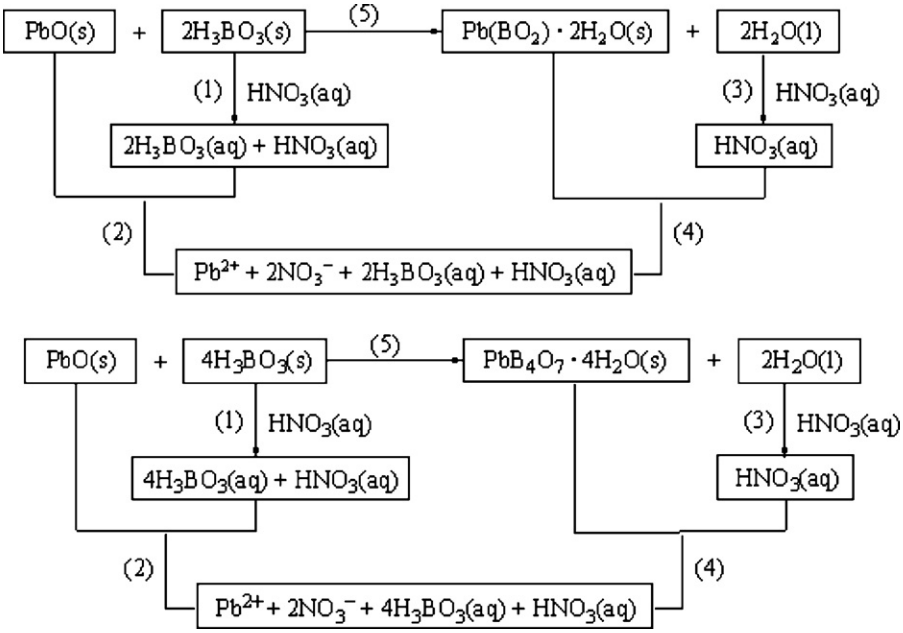

Fig. 1. Schematic drawings of the thermodynamic circles.

The molar enthalpies of solution of $H_3BO_3(s)$, $Pb(BO_2)_2{\cdot}H_2O(s)$ and $PbB_4O_7{\cdot}4H_2O(s)$ in 1 mol dm^{-3} $HNO_3(aq)$ were measured, respectively. The calculated amount of PbO(s) was dissolved in (nitric acid + boric acid) aqueous solution which consisted of 1 mol dm^{-3} $HNO_3(aq)$ and the calculated amount of $H_3BO_3(s)$. In all these determinations, strict control of the stoichiometry in each step of the calorimetric cycle must be observed, with the objective that the dissolution of the reactants give the same composition as those of the products in reaction (5). Applying Hess's law, the enthalpy of reaction (5) can be calculated according to the following expression:

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

The standard molar enthalpies of formation of $Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$ can be obtained from the value of $\Delta_r H_m^\circ$ (5) in combination with the molar enthalpies of formation of $H_3BO_3(s)$, PbO(s), and $H_2O(l)$.

All the enthalpies of solution were measured with an RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China), which has been described in detail previously [14,20]. 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 ≥0.9999) in deionized water was determined to be (17.54 ± 0.10) kJ mol^{-1}, which was in agreement with that of (17.524 ± 0.028) kJ mol^{-1} reported in the literature [21]. This shows that the device used for measuring the enthalpy of solution in this work is reliable.

3. Results and discussion

3.1. Identification of the purity of $Pb(BO_2)_2{\cdot}H_2O$ reagent

The chemical analytical data of $Pb(BO_2)_2{\cdot}H_2O$ are (calcd/found, %), PbO (71.80/71.55), B_2O_3 (22.40/22.10), H_2O (5.80/5.90), which are consistent with the theoretical values.

The FT-IR spectrum of $Pb(BO_2)_2{\cdot}H_2O$ reagent (Fig. 2a) exhibited the following absorption bands and they were assigned referring to the literature [22]. The bands at 3446 cm^{-1} is the stretching vibration of the O–H group. The band at 1632 cm^{-1} is assigned to the H–O–H bending mode, which shows this compound contains crystal water. The bands at (1392, 1342) cm^{-1} and 1004 cm^{-1} are the asymmetric and symmetric stretching of B(3)–O, respectively. The band at 692 cm^{-1} is assigned to out-of-plane bending of B(3)–O. These assignments are consistent with the structure of $Pb(BO_2)_2{\cdot}H_2O$, in which the polyborate anion only contains BO_3 group.

The TG curve of the $Pb(BO_2)_2{\cdot}H_2O$ sample (Fig. 3) indicates that the total mass loss is 5.90% from 303 K to 993 K, which corresponds to the loss of one water molecule and agrees with the calculated value of 5.80%.

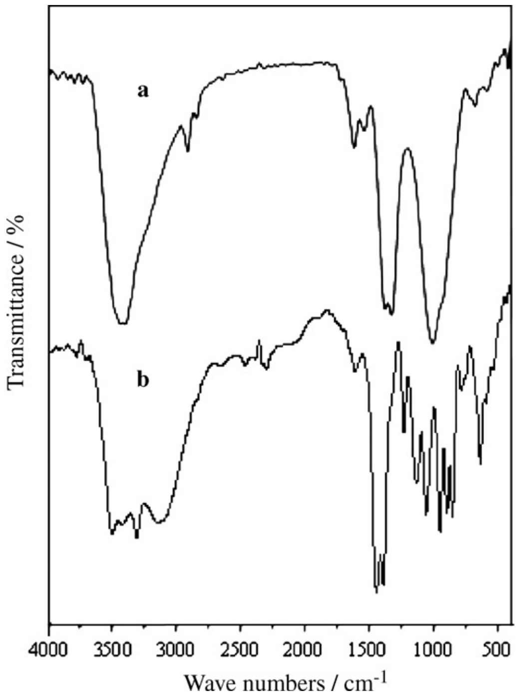

Fig. 2. FT-IR spectra of samples: (a) $Pb(BO_2)_2{\cdot}H_2O$ and (b) $PbB_4O_7{\cdot}4H_2O$.

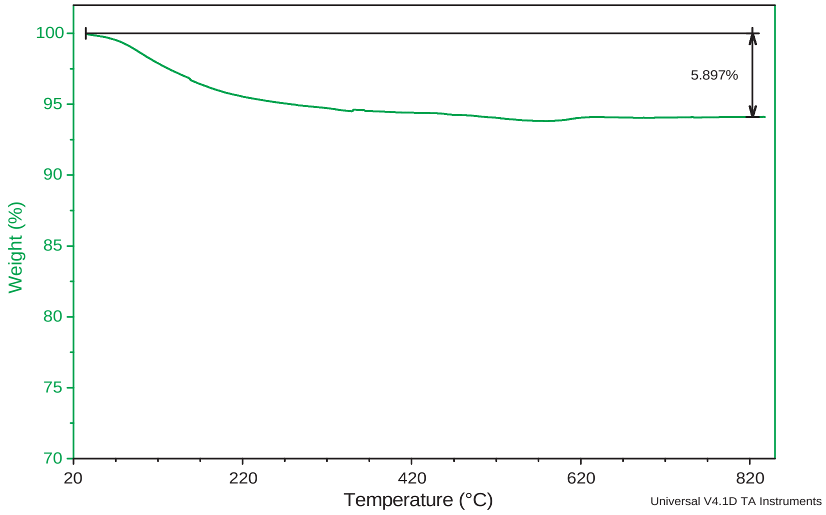

Fig. 3. TGA curve of $Pb(BO_2)_2{\cdot}H_2O$ sample.

3.2. *Characterization of synthetic $PbB_4O_7{\cdot}4H_2O$ sample*

The chemical analytical data of $PbB_4O_7{\cdot}4H_2O$ are (calcd/found, %), PbO (51.37/51.69), B_2O_3 (32.05/31.60), H_2O (16.57/17.06), which are consistent with the theoretical values.

Fig. 4 shows the powder XRD pattern of the synthetic sample of $PbB_4O_7{\cdot}4H_2O$. The main characteristic *d* values of the XRD pattern are 10.1085, 8.0966, 5.0179, 4.8177, 4.6719, 4.2358, 4.0735, 3.8275, 3.4849, 3.3458, 3.2711, 3.0848, 3.0035, 2.7105, 2.2337, 2.2119, 2.1426, 2.0439, 1.9754, 1.9482, and 1.8864 Å. No peaks from H_3BO_3 or $Pb(CH_3COO)_2{\cdot}3H_2O$ were observed.

The FT-IR spectrum of $PbB_4O_7{\cdot}4H_2O$ sample (Fig. 2b) exhibited the following absorption bands and they were assigned referring to the literature [22]. The bands at (3512, 3319 and 3150) cm^{-1} are the stretching vibration of the O–H group. The band at 1630 cm^{-1} is assigned to the H–O–H bending mode, which shows this compound contains crystal water. The bands at 1252 cm^{-1} and 1153 cm^{-1} are the in plane bending of B–O–H. The bands at (1460, 1406) cm^{-1} and 966 cm^{-1} are the asymmetric and symmetric stretching of B(3)–O, respectively. The bands at 1078 cm^{-1} and (875, 802) cm^{-1} might be the asymmetric and symmetric stretching modes of B(4)–O, respectively. The band at 657 cm^{-1} is assigned to out-of-plane bending of B(3)–O. These assignments are consistent with its structure of $Pb[B_4O_5(OH)_4]{\cdot}2H_2O$, in which the polyborate anion contains BO_3 and BO_4 groups.

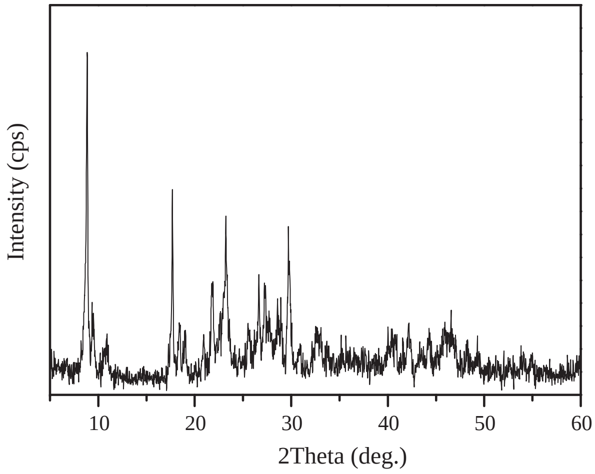

Fig. 4. The powder XRD pattern of $PbB_4O_7{\cdot}4H_2O$ sample.

The thermal behavior of $PbB_4O_7{\cdot}4H_2O$ is shown in Fig. 5. The TG curve shows that $PbB_4O_7{\cdot}4H_2O$ has a two-step weight loss from 313 K to 823 K, and the total mass loss is 17.06%, which corresponds to the loss of four water molecules and agrees with the calculated value of 16.57%. The first mass loss (4.20%) at 313–373 K corresponds to the loss of one crystal water molecule and is in good agreement with the calculated value of 4.14%. In the second step, the mass loss (12.86%) at 373–823 K corresponds to the loss of the others three water molecules and can be compared with the calculated value of 12.43%. In the DTA curve, the endothermic peak appearing at 349, 461 and 489 K are related to the two-step dehydration and formation of the PbB_4O_7 phase.

All of above results indicate that the synthetic sample is pure and suitable for the calorimetric experiments.

3.3. *Results of calorimetric experiment*

The molar enthalpy of solution of $H_3BO_3(s)$ of (21.19 ± 0.18) kJ mol^{-1} in 2.00 cm^3 of 1 mol dm^{-3} $HNO_3(aq)$ at 298.15 K is listed in Table 1. The molar enthalpy of solution of PbO(s) of (-61.84 ± 0.10) kJ mol^{-1} in 2.00 cm^3 of (1 mol dm^{-3} $HNO_3 + H_3BO_3$)(aq) at 298.15 K is listed in Table 2. The molar enthalpies of solution of $Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$ in 2.00 cm^3 of 1 mol dm^{-3} $HNO_3(aq)$ at 298.15 K are listed in Table 3, in which *m* is the mass of samples, $\Delta_{sol}H_m$ is the molar enthalpy of solution of solute, and the uncertainty is estimated as twice the standard deviation of the mean with $n = 5$.

Tables 4 and 5 give the thermochemical cycles used for the derivation of the standard molar enthalpy of formation of $Pb(BO_2)_2{\cdot}H_2O$ and $PbB_4O_7{\cdot}4H_2O$, respectively. The enthalpy of dilution of $HNO_3(aq)$ was calculated according to the standard molar

Table 1
Molar enthalpies of solution of $H_3BO_3(s)$ in 1 mol dm^{-3} $HNO_3(aq)$ at 298.15 K[a].

No.	m (mg)	$\Delta_r H$ (mJ)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	2.65	922.197	21.52
2	2.47	849.612	21.27
3	2.55	869.204	21.08
4	2.59	881.921	21.05
5	2.50	851.279	21.05
Mean			21.19 ± 0.18[b]

[a] In each experiment, 2.00 cm^3 of $HNO_3(aq)$ was used.

[b] Uncertainty is estimated as twice the standard deviation of the mean.

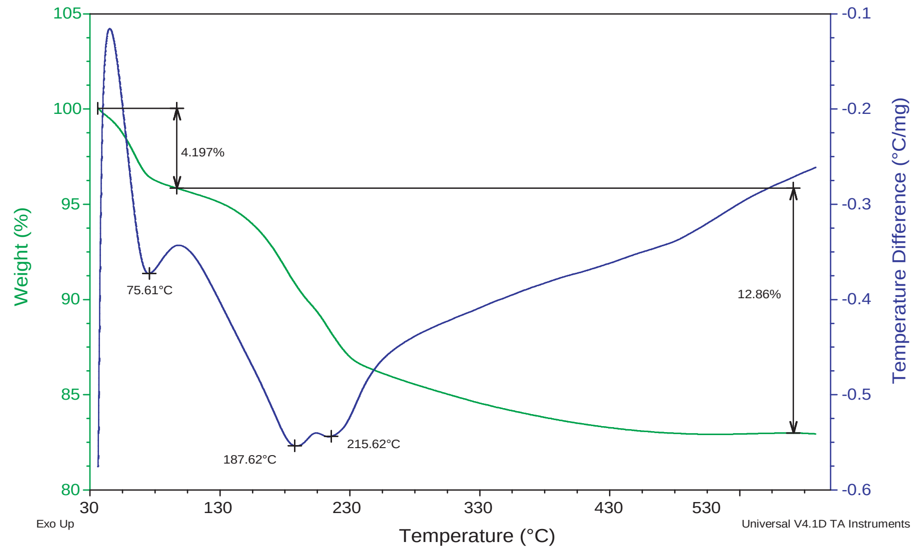

Fig. 5. Simultaneous TG-DTA curves of $PbB_4O_7·4H_2O$ sample.

Table 2
Molar enthalpies of solution of PbO(s) in the mixed solvent that consisted of 1 mol dm^{-3} HNO_3(aq) and calculated amount of H_3BO_3 at 298.15 K[a].

No.	m (mg)	$\Delta_r H$ (mJ)	$\Delta_{sol}H_m$ (kJ mol^{-1})
1	4.50	−1246.679	−61.84
2	4.50	−1246.118	−61.81
3	4.45	−1229.383	−61.67
4	4.47	−1239.905	−61.92
5	4.40	−1221.616	−61.97
Mean			−61.84 ± 0.10[b]

[a] In each experiment, 2.00 cm^3 of HNO_3(aq) was used.
[b] Uncertainty is estimated as twice the standard deviation of the mean.

Table 3
Molar enthalpies of solution of $Pb(BO_2)_2·H_2O$ and $PbB_4O_7·4H_2O$ in 1 mol dm^{-3} HNO_3(aq) at 298.15 K[a].

No.	m (mg)	$\Delta_r H$ (mJ)	$\Delta_{sol}H_m$ (kJ mol^{-1})
$Pb(BO_2)_2·H_2O$			
1	6.31	−710.877	−35.02
2	6.25	−703.841	−35.01
3	6.49	−735.953	−35.25
4	6.28	−700.981	−34.70
5	6.49	−731.110	−35.02
Mean			−35.00 ± 0.18[b]
$PbB_4O_7·4H_2O$			
1	4.31	350.480	35.33
2	4.39	356.700	35.30
3	4.29	349.444	35.39
4	4.32	354.016	35.61
5	4.30	348.361	35.20
Mean			35.37 ± 0.14[b]

[a] In each experiment, 2.00 cm^3 of HNO_3(aq) was used.
[b] Uncertainty is estimated as twice the standard deviation of the mean.

enthalpy of formation of HNO_3(aq) from the NBS tables [23], which was near 0. The enthalpies change of (15.54 ± 0.41) kJ mol^{-1} for the formation of $Pb(BO_2)_2·H_2O$ and −(12.45 ± 0.80) kJ mol^{-1} for the formation of $PbB_4O_7·4H_2O$ from the reagents in the solid phase (reactions (5)) were calculated on the basis of the thermochemical cycles. The standard molar enthalpy of formation of PbO (s) of −(218.06 ± 0.63) kJ mol^{-1} was taken from the JANAF Thermochemical Tables [24]. The standard molar enthalpies of formation of H_3BO_3(s) and H_2O(l) were taken from the CODATA Key Values [25], namely −(1094.8 ± 0.8) kJ mol^{-1} and −(285.830 ± 0.040) kJ mol^{-1}, respectively. From these data, the standard molar enthalpies of formation of $Pb(BO_2)_2·H_2O$ and $PbB_4O_7·4H_2O$ were calculated to

Table 4
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($Pb(BO_2)_2·H_2O$, 298.15 K)[a].

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$2H_3BO_3(s) + 98.14\ (HNO_3·53.59H_2O) = 2H_3BO_3(aq) + 98.14\ (HNO_3·53.59H_2O)$	42.38 ± 0.36
2	$PbO(s) + 2H_3BO_3(aq) + 98.14(HNO_3·53.59H_2O) = Pb(NO_3)_2(aq) + 2H_3BO_3(aq) + 96.14(HNO_3·54.72H_2O)$	−61.84 ± 0.10
3	$98.14(HNO_3·53.59H_2O) + 2H_2O(l) = 98.14(HNO_3·53.61H_2O)$	0
4	$Pb(BO_2)_2·H_2O\ (s) + 98.14(HNO_3·53.61H_2O) = Pb(NO_3)_2(aq) + 2H_3BO_3(aq) + 96.14(HNO_3·54.72H_2O)$	−35.00 ± 0.18
5	$PbO(s) + 2H_3BO_3(s) = Pb(BO_2)_2·H_2O(s) + 2H_2O(l)$	15.54 ± 0.41[b]

[a] $\Delta_f H_m^\circ(Pb(BO_2)2·H_2O, s) = \Delta_f H_m^\circ(5) + \Delta_f H_m^\circ(PbO, s) + 2\Delta_f H_m^\circ(H_3BO_3, s) - 2\Delta_f H_m^\circ(H_2O, l)$.
[b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

Table 5
Thermochemical cycle and results for the derivation of $\Delta_f H_m^\circ$ ($PbB_4O_7·4H_2O$, 298.15 K)[a].

No.	Reaction	$\Delta_r H^\circ$ (kJ mol^{-1})
1	$4H_3BO_3(s) + 201.03(HNO_3·53.59H_2O) = 4H_3BO_3(aq) + 201.03(HNO_3·53.59H_2O)$	84.76 ± 0.72
2	$PbO(s) + 4H_3BO_3(aq) + 201.03(HNO_3·53.59H_2O) = Pb(NO_3)_2(aq) + 4H_3BO_3(aq) + 199.03(HNO_3·54.13H_2O)$	−61.84 ± 0.10
3	$201.03(HNO_3·53.59H_2O) + 2H_2O(l) = 201.03(HNO_3·53.60H_2O)$	0
4	$PbB_4O_7·4H_2O(s) + 201.03(HNO_3·53.60H_2O) = Pb(NO_3)_2(aq) + 4H_3BO_3(aq) + 199.03(HNO_3·54.13H_2O)$	35.37 ± 0.14
5	$PbO(s) + 4H_3BO_3(s) = PbB_4O_7·4H_2O(s) + 2H_2O(l)$	−12.45 ± 0.74[b]

[a] $\Delta_f H_m^\circ(PbB_4O_7·4H_2O, s) = \Delta_f H_m^\circ(5) + \Delta_f H_m^\circ(PbO, s) + 4\Delta_f H_m^\circ(H_3BO_3, s) - 2\Delta_f H_m^\circ(H_2O, l)$.
[b] Uncertainty of the combined reaction is estimated as the square root of the sum of the squares of uncertainty of each individual reaction.

be $-(1820.5 \pm 1.8)\,\mathrm{kJ\,mol^{-1}}$ and $-(4038.1 \pm 3.4)\,\mathrm{kJ\,mol^{-1}}$, respectively.

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