Research Article

Heat Capacity and Thermodynamic Property of Lithium Pentaborate Pentahydrate

Wanjin Cui,¹ Long Li,¹ Yafei Guo ,^{1,2} Sisi Zhang,¹ and Tianlong Deng ¹

¹Tianjin Key Laboratory of Marine Resources and Chemistry, College of Chemical Engineering and Material Science, Tianjin University of Science and Technology, Tianjin 300457, China

²College of Chemistry and Materials Science, Northwest University, Xi'an 710127, China

Correspondence should be addressed to Yafei Guo; guoyafei@tust.edu.cn and Tianlong Deng; tldeng@tust.edu.cn

Received 2 October 2017; Accepted 18 December 2017; Published 17 January 2018

Academic Editor: Elena Gomez

Copyright © 2018 Wanjin Cui et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The heat capacity of lithium pentaborate pentahydrate has been measured using an adiabatic calorimeter at the temperature from 297 to 375 K. No phase transition and thermal anomalies were observed. The molar heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ can be expressed as $C_{p,m} (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 396.79376 + 35.87528 [T - (T_{\max} + T_{\min})/2] / [(T_{\max} - T_{\min})/2] + 0.16494 \{ [T - (T_{\max} + T_{\min})/2] / [(T_{\max} - T_{\min})/2] \}^2 + 8.3083 \{ [T - (T_{\max} + T_{\min})/2] / [(T_{\max} - T_{\min})/2] \}^3$, where T is the temperature in Kelvin, $T_{\max} = 375 \text{ K}$, and $T_{\min} = 297 \text{ K}$. The thermodynamic functions of $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$ of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ are obtained via the molar heat capacity at the temperature of 5 K intervals.

1. Introduction

Studies of alkali borates have attracted much interest in recent years because some of these compounds especially the alkali pentaborates show significant physical interest, such as nonlinear optical behavior [1]. The $[\text{B}_5\text{O}_{10}]^{2-}$ boron oxycyclic structure of the alkali metal pentaborate crystal contains the BO_3 group, which has a strong macro frequency effect and can be used in the field of nonlinear optical materials [2]. In addition, the lithium pentaborate ($\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$) also can be used in special glass, lubricating oil additives, and production of boron oxide [3, 4].

Heat capacity is one of the important parameters of thermodynamic properties to optimize the producing process. And reliable calculation of such thermodynamic functions of entropy, enthalpy, and Gibbs free energy requires data on heat capacity [5]. Furthermore, heat capacity is inherent characteristic of crystals, closely related to the specific features of their composition and structure. To better understand the industrial application of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ and perform the corresponding theoretical studies, the thermodynamic properties of this compound are essential. Li et al. [6] reported the standard molar enthalpy of formation of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$. Ge et al. [7] determined the physicochemical properties of LiB_5O_8

solutions, including the density, viscosity, conductivity, and pH. However, there is no data reported on the heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ in the literature. In this paper, the heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ has been determined using an adiabatic calorimeter in the temperature range from 297 to 375 K, and the values of the thermodynamic functions, heat capacity, entropy, enthalpy, and Gibbs free energy, were calculated at temperature 5 K intervals.

2. Experimental

2.1. Synthesis. The chemical of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ was synthesized in our laboratory according to the phase diagram of system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ [8]. Certain amounts of H_3BO_3 and $\text{LiOH} \cdot \text{H}_2\text{O}$ were dissolved in the quantificational deionized water under stirring for 24 h at 333.15 K. Then, the product was filtered by suction filtration and washed three times with deionized water and absolute ethyl alcohol, respectively. Finally, the samples were dried until the weight was constant and stored in the desiccators for use.

2.2. Characterization and Analytical Methods. The synthesized chemical of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ was identified by X-ray powder diffraction (PERSEE XD-3 polycrystalline X-ray

FIGURE 1: The X-ray diffraction pattern of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$.

FIGURE 2: The TG curve of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$.

diffractometer with $\text{Cu-K}\alpha$ radiation at 4° min^{-1}) and thermogravimetric (TG) (performed on a SETARAM LABSYS thermal analyzer under argon atmosphere with a heating rate of 10 K min^{-1}). The X-ray powder pattern of the synthesized $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ in Figure 1 shows that the diffraction peaks on patterns correspond well in position, indicating the phase purity of the synthesized samples. The weight loss of 32.26% from the TG curve in Figure 2 corresponds to the loss of five water molecules and can be compared with the calculated value of 32.26%.

The B_2O_3 concentration was analyzed using gravimetric method with sodium hydroxide standard solution in the presence of mixture indicators of methyl red plus phenolphthalein and the excessive mannitol conditions, and the standard uncertainty $u(\text{BO}_2^-)$ was 0.0005 in mass fraction [9]. The lithium ion content was measured by inductively coupled plasma optical emission spectrometer (Prodigy, Leman Corporation, America) with precision of $\pm 0.5\%$. The crystallized water content was calculated through subtraction. The chemical analytical result of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ is listed in Table 1.

2.3. Adiabatic Calorimetry and Experiment Method. Heat capacity measurements were carried out in a high-precision SETARAM BT 2.15 adiabatic calorimeter. The BT 2.15 calorimeter comprises a calorimetric chamber, electrical or pneumatic peripherals, and the liquid nitrogen supply. The calorimetric chamber can receive the heat capacity cell, which

TABLE 1: Chemical analytical result of lithium pentaborate pentahydrate in mass fraction.

	Li_2O	B_2O_3	H_2O	$n (\text{Li}_2\text{O} : \text{B}_2\text{O}_3 : \text{H}_2\text{O})$
Experimental	0.0538	0.6262	0.3200	1.00 : 4.99 : 9.87
Theoretical	0.0536	0.6239	0.3226	1.00 : 5.00 : 10.00

FIGURE 3: Experimental molar heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ in the range of 297 to 375 K.

is provided with a syringe for sample introduction. The sample mass used for the heat capacity measurement was 8877.74 mg. The performance of this calorimetric apparatus has been verified by measuring the heat capacity of KCl where the average result is $0.6877 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ in seven times and the deviation of the results is 0.0007, compared with the reference data of $0.6879 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ [10]. The heat capacity $C_{p,m}$ of the sample was measured ranging from 297 to 375 K by an adiabatic continuous heating technique with a heating rate of 0.1 K/min .

3. Results and Discussion

3.1. Heat Capacity. According to the experimental method, the heat capacity C_p of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ was measured using the adiabatic calorimeter from 297 to 375 K with standard uncertainty $0.05 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and the result of the molar heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ is shown in Table 2 and Figure 3.

In Figure 3, it is shown that the heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ sample increases smoothly with the increasing of temperature in the range between 297 and 375 K without any phase transition and thermal anomaly.

On the basis of the Debye Law [11], the molar heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ determined in this work has been fitted and shown in (1). On the basis of (1), the molar heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ at 298.15 K can be obtained as $354.54 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

$$C_{p,m} (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 396.79376 + 35.87528 \frac{[T - (T_{\max} + T_{\min})/2]}{[(T_{\max} - T_{\min})/2]}$$

TABLE 2: Molar heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ (molecular mass $M = 278.99 \text{ g mol}^{-1}$).

T/K	$C_{p,m}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	T/K	$C_{p,m}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	T/K	$C_{p,m}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
297.44	350.85	324.19	385.60	350.08	410.17
298.38	353.23	325.32	386.75	351.22	411.46
299.13	355.08	326.23	387.85	352.36	412.27
300.21	357.20	327.24	388.59	353.39	414.08
302.18	361.25	328.58	389.95	354.39	415.41
303.19	363.14	329.53	390.38	355.37	416.69
304.28	364.46	330.19	391.17	356.16	417.34
305.11	365.22	331.15	392.06	357.13	418.45
306.21	366.60	332.13	392.83	358.21	419.13
307.28	367.77	333.16	393.24	359.31	420.45
308.16	369.14	334.14	394.20	360.23	421.34
309.21	370.16	335.16	395.38	361.34	422.37
310.16	371.33	336.21	396.66	362.26	423.94
311.18	372.58	337.16	397.30	363.12	425.24
312.29	373.40	338.21	398.18	364.13	426.12
313.20	374.52	339.19	399.46	365.21	427.13
314.18	375.55	340.17	400.85	366.28	428.43
315.31	376.60	341.29	401.88	367.53	429.91
316.24	377.63	342.16	402.22	368.19	431.01
317.18	378.66	343.15	403.16	369.33	432.70
318.40	379.72	344.15	404.66	370.49	433.92
319.35	380.80	345.41	405.60	371.18	435.44
320.18	381.48	346.10	406.09	372.12	436.70
321.26	382.09	347.10	407.30	373.09	437.91
322.15	383.11	348.30	408.37	374.18	439.08
323.16	384.23	349.39	409.37		

Note. Standard uncertainty of temperature $u(T) = 0.01 \text{ K}$, and the molar heat capacity $u(C_{p,m}) = 0.05 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

$$\begin{aligned}
& + 0.16494 \left\{ \frac{[T - (T_{\max} + T_{\min})/2]}{[(T_{\max} - T_{\min})/2]} \right\}^2 \\
& + 8.3083 \left\{ \frac{[T - (T_{\max} + T_{\min})/2]}{[(T_{\max} - T_{\min})/2]} \right\}^3,
\end{aligned} \quad (1)$$

where T is the absolute temperature in Kelvin, $T_{\max}$ is the upper temperature (375 K), and $T_{\min}$ is the lower temperature (297 K). The deviations between the experimental and the fitted values are within 0.005 and shown in Figure 4.

3.2. Enthalpy, Entropy, and Gibbs Free Energy. The thermodynamic functions of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ relative to the standard status, that is, 298.15 K and 0.1 MPa, can be derived based on the following thermodynamic equations:

$$\begin{aligned}
H_T - H_{298.15} &= \int_{298.15}^T C_{p,m} dT, \\
S_T - S_{298.15} &= \int_{298.15}^T \left[\frac{C_{p,m}}{T} \right] dT,
\end{aligned}$$

TABLE 3: Calculated molar heat capacities and thermodynamic functions of $\text{LiB}_5\text{O}_8 \cdot \text{H}_2\text{O}$.

T/K	$C_{p,m}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$H_T - H_{298.15}$ $\text{kJ}\cdot\text{mol}^{-1}$	$S_T - S_{298.15}$ $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$G_T - G_{298.15}$ $\text{kJ}\cdot\text{mol}^{-1}$
298.15	354.54	0	0	0
300	357.28	0.6590	2.2035	-0.0020
305	364.21	2.465	8.17	-0.0280
310	370.49	4.303	14.15	-0.0838
315	376.23	6.172	20.13	-0.1695
320	381.53	8.068	26.10	-0.2851
325	386.50	9.990	32.06	-0.4305
330	391.25	11.936	38.01	-0.6057
335	395.87	13.906	43.93	-0.8105
340	400.48	15.898	49.83	-1.0449
345	405.18	17.915	55.72	-1.3088
350	410.08	19.955	61.59	-1.6021
355	415.27	22.020	67.45	-1.9247
360	420.87	24.112	73.30	-2.2766
365	426.98	26.234	79.15	-2.6577
370	433.70	28.387	85.01	-3.0681
375	441.14	30.576	90.89	-3.5079

FIGURE 4: Plot of deviations of experimental data from fitted.

$$G_T - G_{298.15} = \int_{298.15}^T C_{p,m} dT - T \int_{298.15}^T \left[\frac{C_{p,m}}{T} \right] dT. \quad (2)$$

The results of the molar heat capacity and thermodynamic functions of $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$ are obtained and listed in Table 3 with a temperature of 5 K interval. From the entropy function data in Table 3, it is shown that the molar heat capacity and the changes of enthalpy $(H_T - H_{298.15})$ and entropy $(S_T - S_{298.15})$ are increased with the increasing of temperature from 298.15 K to 375 K and the changes of free energy $(G_T - G_{298.15})$ are just the opposite.

4. Conclusions

The heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ was measured using an adiabatic calorimeter at temperatures from 297 to 375 K, and it did not contain anomalous contributions at the experimental temperature regions. The molar heat capacity of $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ obeys a polynomial of $C_{p,m}$ ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) = $396.79376 + 35.87528[T - (T_{\max} + T_{\min})/2]/[(T_{\max} - T_{\min})/2] + 0.16494\{[T - (T_{\max} + T_{\min})/2]/[(T_{\max} - T_{\min})/2]\}^2 + 8.3083\{[T - (T_{\max} + T_{\min})/2]/[(T_{\max} - T_{\min})/2]\}^3$. The molar heat capacity and thermodynamic functions of $(H_T - H_{298.15})$, $(S_T - S_{298.15})$, and $(G_T - G_{298.15})$ for $\text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O}$ are obtained for the first time.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (U1607123 and 21773170), the Yangtze Scholars and Innovative Research Team in Chinese University (IRT-17R81), the Postdoctoral Science Foundation (2016M592827), and the Laboratory Foundation of Chinese Universities (SY2015018).

References

- [1] Y. Wu, T. Sasaki, S. Nakai, A. Yokotani, H. Tang, and C. Chen, "CsB₃O₅: a new nonlinear optical crystal," *Applied Physics Letters*, vol. 62, no. 21, pp. 2614–2615, 1993.
- [2] S. S. Zhang, L. Li, Y. F. Guo, and T. L. Deng, "Study on the syntheses of alkalis pentaborates," *Journal of Salt Science and Chemical Industry*, vol. 46, no. 6, pp. 31–34, 2017.
- [3] L. J. Jiang and G. S. Wang, "Synthesis of potassium pentaborate," *Journal of Shenyang University of Chemical Technology*, vol. 23, no. 3, pp. 222–225, 2009.
- [4] Rio Tinto American boron Asia Technology Center, "Application of borate in oil and gas field development," in *Proceedings of the Twentieth Seminar of the Development and Application on Chinese Oil and Gas Field Chemicals*, pp. 55–57, Beijing, China, March 2014.
- [5] M. A. Bespyatov, I. S. Chernyaikin, V. N. Naumov, P. A. Stabnikov, and N. V. Gelfond, "Low-temperature heat capacity of $\text{Al}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$," *Thermochimica Acta*, vol. 596, pp. 40–41, 2014.
- [6] J. Li, B. A. Li, and S. Gao, "Thermochemistry of hydrated lithium borates," *The Journal of Chemical Thermodynamics*, vol. 30, no. 6, pp. 681–688, 1998.
- [7] H. W. Ge, C. H. Fang, Y. Fang et al., "Study on physical and chemical properties of LiB_5O_8 solution," *Journal of Salt Lake Research*, vol. 23, no. 001, pp. 44–50, 2015.
- [8] W. T. Reburn and W. A. Gale, "The system lithium oxide-boric oxide-water," *The Journal of Physical Chemistry*, vol. 59, no. 1, pp. 19–24, 1955.
- [9] Qinghai institute of salt lakes of CAS, *Analytical Methods of Brines and Salts*, Chinese Science Press, Beijing, China, 2nd edition, 1988.
- [10] J. G. Speight, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, NY, USA, 16th edition, 2005.
- [11] M. R. Bissengaliyeva, D. B. Gogol, and N. S. Bekturganov, "Low temperature measurements of the heat capacity and thermodynamic functions of pseudo-malachite $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$," *Thermochimica Acta*, vol. 532, pp. 139–144, 2012.