Research Article

Heat Capacity and Thermodynamic Property of Lithium Pentaborate Pentahydrate

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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 LiB₃O₅·5H₂O can be expressed as

\[ C_{pm}(\text{J mol}^{-1} \cdot \text{K}^{-1}) = 396.79376 + 35.87528[T−(T_{\text{max}} + T_{\text{min}})/2]/[(T_{\text{max}}−T_{\text{min}})/2] + 0.16494[(T−(T_{\text{max}} + T_{\text{min}})/2)/[(T_{\text{max}}−T_{\text{min}})/2]]^2 + 8.3083[(T−(T_{\text{max}} + T_{\text{min}})/2)/[(T_{\text{max}}−T_{\text{min}})/2]]^3, \]

where \(T\) is the temperature in Kelvin, \(T_{\text{max}} = 375\) K, and \(T_{\text{min}} = 297\) K. The thermodynamic functions of \((H−H_{298.15}),(S−S_{298.15}),\) and \((G−G_{298.15})\) of LiB₃O₅·5H₂O 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 \([B_2O_3]^{2–}\) boron oxycyclic structure of the alkali metal pentaborate crystal contains the BO₃ 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 (LiB₃O₅·5H₂O) 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 LiB₃O₅·5H₂O 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 LiB₃O₅·5H₂O. Ge et al. [7] determined the physicochemical properties of LiB₃O₅ solutions, including the density, viscosity, conductivity, and pH. However, there is no data reported on the heat capacity of LiB₃O₅·5H₂O in the literature. In this paper, the heat capacity of LiB₃O₅·5H₂O 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 LiB₃O₅·5H₂O was synthesized in our laboratory according to the phase diagram of system Li₂O-B₂O₃·H₂O [8]. Certain amounts of H₂BO₃ and LiOH·H₂O were dissolved in the quantificationation 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 LiB₃O₅·5H₂O was identified by X-ray powder diffraction (PERSEE XD-3 polycrystalline X-ray...
differential calorimeter with Cu-Kα 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 LiB₂O₅·5H₂O 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 B₂O₃ 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(BO₂⁻) 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 ±0.5%. The crystallized water content was calculated through subtraction. The chemical analytical result of LiB₂O₅·5H₂O 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 is provided with a syringe for sample introduction. The sample mass used for the heat capacity measurement was 887.74 mg. The performance of this calorimetric apparatus has been verified by measuring the heat capacity of KCl where the average result is 0.6877 J g⁻¹·K⁻¹ in seven times and the deviation of the results is 0.0007, compared with the reference data of 0.6879 J g⁻¹·K⁻¹ [10]. The heat capacity Cₚ,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 Cₚ of LiB₂O₅·5H₂O was measured using the adiabatic calorimeter from 297 to 375 K with standard uncertainty 0.05 J mol⁻¹·K⁻¹, and the result of the molar heat capacity of LiB₂O₅·5H₂O is shown in Table 2 and Figure 3.

In Figure 3, it is shown that the heat capacity of LiB₂O₅·5H₂O 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 LiB₂O₅·5H₂O determined in this work has been fitted and shown in (I). On the basis of (I), the molar heat capacity of LiB₂O₅·5H₂O at 298.15 K can be obtained as 354.54 J mol⁻¹·K⁻¹.

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

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

<table>
<thead>
<tr>
<th></th>
<th>B₂O₅</th>
<th>H₂O</th>
<th>Li₂B₁₀O₁₆·10H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O</td>
<td>0.0538</td>
<td>0.3200</td>
<td>1.00:5.00:10.00</td>
</tr>
<tr>
<td>B₂O₅</td>
<td>0.6262</td>
<td>0.3226</td>
<td>1.00:4.99:9.87</td>
</tr>
</tbody>
</table>

**Figure 1:** The X-ray diffraction pattern of LiB₂O₅·5H₂O.

**Figure 2:** The TG curve of LiB₂O₅·5H₂O.

**Figure 3:** Experimental molar heat capacity of LiB₂O₅·5H₂O in the range of 297 to 375 K.
The following thermodynamic equations:

\[ \frac{d}{dT} \left( T \frac{\partial H}{\partial T} \right) = T \frac{\partial S}{\partial T} \]

\[ S_T - S_{298.15} = \int_{298.15}^{T} \frac{C_{p,m}}{T} \, dT \]

\[ G_T - G_{298.15} = \int_{298.15}^{T} C_{p,m} \, dT - T \int_{298.15}^{T} \frac{C_{p,m}}{T} \, dT \]

\[ \frac{d}{dT} \left( T \frac{\partial H}{\partial T} \right) = T \frac{\partial S}{\partial T} \]

\[ H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m} \, dT \]

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

\[ + \frac{0.16494}{2} \left( \frac{T - (T_{\text{max}} + T_{\text{min}})}{2} \right)^2 \]

\[ + \frac{8.3083}{3} \left( \frac{T - (T_{\text{max}} + T_{\text{min}})}{2} \right)^3 \]

where \( T \) is the absolute temperature in Kelvin, \( T_{\text{max}} \) is the upper temperature (375 K), and \( T_{\text{min}} \) 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 LiB\(_2\)O\(_3\)-5H\(_2\)O relative to the standard status, that is, 298.15 K and 0.1 MPa, can be derived based on the following thermodynamic equations:

\[ H_T - H_{298.15} = \int_{298.15}^{T} C_{p,m} \, dT \]

\[ S_T - S_{298.15} = \int_{298.15}^{T} \frac{C_{p,m}}{T} \, dT \]

\[ G_T - G_{298.15} = \int_{298.15}^{T} C_{p,m} \, dT - T \int_{298.15}^{T} \frac{C_{p,m}}{T} \, dT \]

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 LiB$_5$O$_8$·5H$_2$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 LiB$_5$O$_8$·5H$_2$O obeys a polynomial of $C_{p,m} (\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 396.79376 + 35.87528 \frac{(T - (T_{\text{max}} + T_{\text{min}})/2)}{(T_{\text{max}} - T_{\text{min}})/2} + 0.16494 \frac{(T - (T_{\text{max}} + T_{\text{min}})/2)}{(T_{\text{max}} - T_{\text{min}})/2}^2 + 8.3083 \frac{(T - (T_{\text{max}} + T_{\text{min}})/2)}{(T_{\text{max}} - T_{\text{min}})/2}^3$. 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 LiB$_5$O$_8$·5H$_2$O are obtained for the first time.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References


