Research Article

Heat Capacity and Thermodynamic Properties of Cesium Pentaborate Tetrahydrate

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This paper reports the molar heat capacities of $\beta$-CsB$_5$O$_8$$\cdot$4H$_2$O, which were measured by an accurate adiabatic calorimeter from 298 to 373 K with a heating rate of 0.1 K/min under nitrogen atmosphere. Neither phase transition nor thermal anomalies were observed. The molar heat capacity against temperature was fitted to a polynomial equation of

$$C_{p,m}(J\cdot mol^{-1}\cdot K^{-1}) = 618.07702 + 39.52669\left[ T - \frac{1}{2}(T_{\text{max}} + T_{\text{min}}) \right] + 3.46888\left[ \frac{T - \frac{1}{2}(T_{\text{max}} + T_{\text{min}})}{T_{\text{max}} - T_{\text{min}}} \right]^2 + 7.9441\left[ \frac{T - \frac{1}{2}(T_{\text{max}} + T_{\text{min}})}{T_{\text{max}} - T_{\text{min}}} \right]^3.$$ 

The relevant thermodynamic functions of enthalpy ($H_T - H_{298.15}$), entropy ($S_T - S_{298.15}$), and Gibbs free energy ($G_T - G_{298.15}$) of cesium pentaborate tetrahydrate from 298 to 375 K of 5 K intervals are also obtained on the basis of relational expression equations between thermodynamic functions and the molar heat capacity.

1. Introduction

Boron and borates are considered as a kind of modern strategic resource worldwide for high melting point, high hardness, high strength, light weight, and abrasion resistance, and they are extensively applied in whisker materials, superconducting materials, fuel-rich propellants, and other high-technology domains [1–4]. Nowadays, the continuously increasing demand for cesium borates owing to the significant physical interest [5], along with their limited production, has led to a situation where the supply fails to meet the market demand. A number of salt lakes with an abundance of boron resources are widely distributed in the western regions of China, and studies on thermodynamic properties are of great importance not only in guiding the comprehensive utilization of the resources but also in evaluating and explaining the corresponding physicochemical properties, as well as exploring novel methods for more effective and efficient extraction for salt lake resources. Hence, in order to provide useful information for extracting cesium borates and synthesizing materials, it is highly desirable to study the thermodynamic properties.

The thermodynamic properties for borates or its aqueous solutions have attracted great attention in these past few years, including the enthalpy of dilution [6], the molar heat capacity [7–10], the apparent molar volumes [11, 12], and the standard molar enthalpies of formation [13–15]. Heat capacity is one of the more valuable thermophysical quantities and reflects the ability of a substance to absorb or release heat without phase transition. Cui et al. [7] reported the heat capacity of lithium pentaborate pentahydrate using an adiabatic calorimeter at the temperature from 297 to 375 K, and relevant thermodynamic functions were obtained at the temperature of 5 K intervals. And the heat capacities and thermodynamic functions of the aqueous Li$_2$B$_4$O$_7$ solution were measured at a concentration of 0.0187 and 0.3492 mol·kg$^{-1}$ from 80 to 355 K [8, 9]. In addition, the heat capacity of cesium tetraborate pentahydrate has been measured with the high-precision TG-DSC LABSYS Evo in the range of 303 to 349 K [10]. However, up to now, there are no data reported on the heat capacity of cesium pentaborate...
tetrahydrate. In this paper, the heat capacity and the related thermodynamic functions of enthalpy, entropy, and Gibbs free energy for \( \beta\)-CsB_5O_8·4H_2O have been determined for the first time.

### 2. Experimental

#### 2.1. Materials.

The purity degree and purification of the chemicals used in this work are tabulated in Table 1. The doubly deionized water (DDW) produced by ULUP-II-10T (Chongqing Jiuyang Co. Ltd., China) with a conductivity less than 1 \( \times \) 10^{-6} S·m^{-1} and pH = 6.60 at 25°C, was used during the whole experiment. On the basis of the method described in the literature [16], \( \beta\)-CsB_5O_8·4H_2O was successfully synthesized in our laboratory. A certain amount of Cs_2CO_3 was added to a solution of H_3BO_3, in which the mol ratio of Cs_2CO_3: H_3BO_3 is 1:10, followed by stirring at room temperature for homogeneity, and heated to the boiling point for releasing CO_2. Then, the solution was stirred at 60°C for 24 h to precipitate out of the solid phase. Finally, the precipitates were filtered, recrystallized, washed with DDW as well as absolute ethyl alcohol separately, and dried at 30°C to obtain the samples. In addition, the samples were dried at 50°C and atmospheric pressure until the weight was constant, and then cooled down to room temperature to store in the desiccators for use.

#### 2.2. Characterization.

The synthesized CsB_5O_8·4H_2O was identified by the X-ray diffractometer (MSAL XD-3, Beijing Purkinje Instrument Co. Ltd., China) with Cu-Kα radiation at 4 min^{-1} in the scan range of 2θ from 5 to 70°, and the results are shown in Figure 1 and it can clearly be seen that the peak position and intensity of the synthesized CsB_5O_8·4H_2O were in great agreement with the standard card (22–0175), indicating that the compound for CsB_5O_8·4H_2O is the beta phase (\( \beta\)-CsB_5O_8·4H_2O) [16]. TG and DSC were conducted by SETARAM LABSYS thermal analyzer under an N_2 atmosphere with a heating rate of 10 K·min^{-1} from 298.15 to 823.15 K, as shown in Figure 2. Furthermore, the output of water molecules proceeds in two stages [17]. The first stage is observed from 393 K to 473 K with a loss of three water molecules and the compound transforms into the amorphous, and the second stage is observed with the loss of only one water molecule. The total weight loss of the sample was 0.1863 in mass fraction, which is essentially consistent with the theoretical value of 0.1862, the deviation being only 0.05%.

The concentration of B_2O_3 was determined by the mannitol gravimetric method with a known content of NaOH aqueous solution in the presence of double indicator of methyl red and phenolphthalein with the standard uncertainty of 0.0005 in mass fraction [18], and the reaction equation can be written as follows. The content for cesium ion was measured by inductively coupled plasma optical emission spectrometer (Prodigy, Leman Corporation, America) with a precision of ±0.005 in mass fraction. The H_2O content was calculated through differential subtraction and the calculated value of 18.63% corresponds to the four water molecules. The chemical analysis results presented in Table 2, together with the X-ray diffractometer map and TG analysis, testify that the purity of the synthesized \( \beta\)-CsB_5O_8·4H_2O reaches 0.995 in mass fraction:

\[
\begin{align*}
H_2BO_3 + C_6H_{14}O_6 & \rightarrow C_6H_8(OH)_2 \cdot (BO_3H)_2 \cdot (BO_3Na)_2 + 4H_2O \\
C_6H_8(OH)_2 \cdot (BO_3H)_2 + NaOH & \rightarrow C_6H_8(OH)_2 \cdot (BO_3Na)_2 + 4H_2O
\end{align*}
\]

#### 2.3. Apparatus and Procedure.

A high-precision adiabatic microcalorimeter (BT2.15, SETARAM, France), which mainly comprised a calorimetric chamber, electrical or pneumatic peripherals, and the liquid nitrogen supply, was used for measuring the heat capacity of \( \beta\)-CsB_5O_8·4H_2O over the temperature range of 298 to 373 K with a heating rate of 0.1 K/min under nitrogen atmosphere and the sample mass in the sample cell used for the heat capacity measurement was 16044.01 mg weighted with an accuracy of 0.00001 g. To verify the accuracy of the calorimeter, the heat capacity of a reference standard material (KCl) was carried out at 298.15 K where the average result is 0.6876 J·g^{-1}·K^{-1} for seven times, which agrees well with 0.6879 J·g^{-1}·K^{-1}, reported in the literature [19], and the deviation is 0.0004.

### 3. Results and Discussion

#### 3.1. Heat Capacity.

The values for the molar heat capacity of \( \beta\)-CsB_5O_8·4H_2O measured by the adiabatic calorimeter from 298 to 373 K with the standard uncertainty of 0.05 J·mol^{-1}·K^{-1} are listed in Table 3 and plotted in Figure 3. As shown in Figure 3, the heat capacities of \( \beta\)-CsB_5O_8·4H_2O increase slowly in the rise of temperature from 298 to 373 K, which shows that the structure of \( \beta\)-CsB_5O_8·4H_2O is stable in this temperature range, that is, no phase transition is observed and no other thermal anomalies take place within the temperature range of the experiment. Compared with the Cs_2B_4O_7·5H_2O as well as LiB_2O_5·5H_2O [7, 10], the molar heat capacity of \( \beta\)-CsB_5O_8·4H_2O is much larger than that of Cs_2B_4O_7·5H_2O from 303 to 335 K, and that of LiB_2O_5·5H_2O is smaller than that of Cs_2B_4O_7·5H_2O and \( \beta\)-CsB_5O_8·4H_2O at the same temperature. For \( \beta\)-CsB_5O_8·4H_2O and CsB_5O_8·5H_2O, the types of elements are the same including the cesium, boron, hydrogen, and oxygen, and the distinction in the heat capacity may be caused by the diverse internal structures of the molecules. However, for \( \beta\)-CsB_5O_8·4H_2O and LiB_2O_5·5H_2O, cesium and lithium belong to the same group and the radius of cesium ion is larger than that of lithium ion, resulting in more electrons around the cesium.
ion, which leads to the difference of the energy when the temperature varies and further causes the imparity of heat capacity. Therefore, the molar heat capacities of \( \text{Cs}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O} \) and \( \beta \)-\( \text{CsB}_5\text{O}_8 \cdot 4\text{H}_2\text{O} \) are larger than that of \( \text{LiB}_5\text{O}_8 \cdot 5\text{H}_2\text{O} \).

In order to obtain the heat capacity quickly at a certain temperature, the molar heat capacity of \( \beta \)-\( \text{CsB}_5\text{O}_8 \cdot 4\text{H}_2\text{O} \) determined in this work has been fitted by means of a least-squares method and the polynomial equation with the correlation coefficient \( r = 0.99722 \) can be expressed as follows:

\[
C_{p,m}(J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) = 618.07702 + 39.52669 \frac{T - (T_{\text{max}} + T_{\text{min}})/2}{(T_{\text{max}} - T_{\text{min}})/2} \]

\[
- 3.46888 \left[ \frac{T - (T_{\text{max}} + T_{\text{min}})/2}{(T_{\text{max}} - T_{\text{min}})/2} \right]^2
\]

\[
+ 7.9441 \left[ \frac{T - (T_{\text{max}} + T_{\text{min}})/2}{(T_{\text{max}} - T_{\text{min}})/2} \right]^3
\]

where \( C_{p,m} \) is the molar heat capacity of \( \beta \)-\( \text{CsB}_5\text{O}_8 \cdot 4\text{H}_2\text{O} \) (\( J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \)), \( T \) is the thermodynamic temperature (K), and \( T_{\text{max}} \) and \( T_{\text{min}} \) are the maximum and minimum in the experimental temperature range, which are 373.01 and 298.02 K, respectively. According to the above equation, the molar heat capacity of \( \beta \)-\( \text{CsB}_5\text{O}_8 \cdot 4\text{H}_2\text{O} \) at 298.15 K can be calculated as 567.37 \( J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \), and the standard deviations between experimental values, \( C_{p,\text{exp}} \), and fitted values \( C_{p,\text{fit}} \) through the polynomial equation are within 0.005, as shown in Figure 4.

3.2. Thermodynamic Functions. Thermodynamic functions \( (H_T - H_{298.15}) \), \( (S_T - S_{298.15}) \), and \( (G_T - G_{298.15}) \) of

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Table 1: Reagents used in the study.

| Chemicals | CAS reg. no. | Initial mass fraction purity | Purification method | Final mass fraction purity | Analysis method |
|-----------|--------------|-----------------------------|---------------------|---------------------------|----------------|
| \( \text{H}_3\text{BO}_3 \)\textsuperscript{a} | 10043-35-3 | 0.9999 | Without purification | 0.9999 | Gravimetric method for boron |
| \( \text{CsCO}_3 \)\textsuperscript{b} | 534-17-8 | 0.9990 | Without purification | 0.9990 | Gravimetric method for carbonate |
| \( \beta \)-\( \text{CsB}_5\text{O}_8 \cdot 4\text{H}_2\text{O} \)\textsuperscript{c} | — | 0.9900 | Recrystallization | 0.9950 | Gravimetric method for boron |

\textsuperscript{a}From the Shanghai Macklin Biochemical Co. Ltd. \textsuperscript{b}From the Aladdin Industrial Co. Ltd. \textsuperscript{c}Synthesized in our laboratory.
Table 2: Chemical analytical results of $\beta$-CsB$_5$O$_8$·4H$_2$O in mass fraction$^a$.

| CsB$_5$O$_8$·4H$_2$O | Cs$_2$O | B$_2$O$_3$ | H$_2$O | $n$ (Cs$_2$O : B$_2$O$_3$ : H$_2$O) |
|---------------------|--------|----------|--------|-----------------------------|
| Experimental        | 0.3663 | 0.4474   | 0.1863 | 1.00 : 4.94 : 7.96          |
| Theoretical         | 0.3641 | 0.4497   | 0.1862 | 1.00 : 5.00 : 8.00          |
| Relative error (%)  | 0.60   | 0.50     | 0.05   |                             |

$^a$Standard uncertainties $u$ are $u$(Cs$_2$O) = 0.0053, $u$(B$_2$O$_3$) = 0.0005, and $u$(H$_2$O) = 0.0055 in mass fraction.

Table 3: Molar heat capacity of $\beta$-CsB$_5$O$_8$·4H$_2$O (molecular mass $M$ = 386.95 g·mol$^{-1}$).

| $T$ (K)$^b$ | $C_{p,m}$ (J·mol$^{-1}$·K$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·mol$^{-1}$·K$^{-1}$) | $T$ (K) | $C_{p,m}$ (J·mol$^{-1}$·K$^{-1}$) |
|-------------|----------------------------------|--------|----------------------------------|--------|----------------------------------|
| 298.02      | 565.49                           | 324.04 | 606.12                           | 350.01 | 632.08                           |
| 299.01      | 567.42                           | 325.05 | 607.88                           | 351.01 | 634.06                           |
| 300.01      | 569.35                           | 326.00 | 608.30                           | 352.04 | 635.99                           |
| 301.06      | 571.66                           | 327.01 | 609.28                           | 353.00 | 636.81                           |
| 302.01      | 573.85                           | 328.02 | 609.80                           | 354.06 | 638.94                           |
| 303.05      | 575.71                           | 329.08 | 610.97                           | 355.02 | 640.93                           |
| 304.00      | 577.75                           | 330.06 | 612.01                           | 356.04 | 642.12                           |
| 305.01      | 579.77                           | 331.04 | 612.25                           | 357.04 | 643.19                           |
| 306.01      | 581.49                           | 332.00 | 614.00                           | 358.04 | 644.83                           |
| 307.07      | 583.69                           | 333.00 | 614.71                           | 359.01 | 646.08                           |
| 308.01      | 585.50                           | 334.01 | 615.94                           | 360.03 | 647.90                           |
| 309.01      | 586.48                           | 335.00 | 616.34                           | 361.08 | 648.30                           |
| 310.06      | 588.54                           | 336.04 | 617.34                           | 362.07 | 649.39                           |
| 311.06      | 590.00                           | 337.08 | 618.49                           | 363.04 | 650.39                           |
| 312.02      | 591.22                           | 338.05 | 619.12                           | 364.03 | 651.17                           |
| 313.10      | 592.50                           | 338.97 | 620.37                           | 365.00 | 651.98                           |
| 314.01      | 593.08                           | 340.02 | 621.15                           | 366.05 | 652.52                           |
| 315.07      | 593.96                           | 341.06 | 622.30                           | 367.07 | 653.01                           |
| 316.07      | 595.69                           | 342.08 | 623.74                           | 368.14 | 654.35                           |
| 317.01      | 597.06                           | 343.05 | 624.55                           | 369.21 | 655.23                           |
| 318.01      | 598.19                           | 344.02 | 625.64                           | 370.12 | 656.94                           |
| 319.07      | 599.67                           | 345.10 | 626.27                           | 371.01 | 657.83                           |
| 320.03      | 601.75                           | 346.01 | 627.05                           | 372.02 | 658.27                           |
| 321.04      | 602.34                           | 347.06 | 628.44                           | 373.02 | 659.07                           |
| 322.01      | 603.82                           | 348.03 | 629.64                           |        |                                  |
| 323.02      | 604.84                           | 349.01 | 631.44                           |        |                                  |

$^b$Uncertainty of temperature $u(T) = 0.01$ K, and the molar heat capacity uncertainty $u(C_{p,m}) = 0.05$ J·mol$^{-1}$·K$^{-1}$.
Figure 3: Experimental molar heat capacity of $\beta$-CsB$_5$O$_8$·4H$_2$O in the range of 298 to 373 K.

Figure 4: The deviations of the experimental and fitting values.

Table 4: Molar heat capacity and thermodynamic functions of $\beta$- CsB$_5$O$_8$·4H$_2$O.

| $T$ (K) | $C_{p,m}$ (J·mol$^{-1}$·K$^{-1}$) | $H_T - H_{298.15}$ (kJ·mol$^{-1}$) | $S_T - S_{298.15}$ (J·mol$^{-1}$·K$^{-1}$) | $G_T - G_{298.15}$ (kJ·mol$^{-1}$) |
|---------|-------------------------------|----------------------------------|---------------------------------|---------------------------------|
| 298.15  | 567.37                        | 0.00                             | 0.00                            | 0.00                            |
| 300     | 570.77                        | –10.46                           | 63.64                           | –29.55                          |
| 305     | 579.32                        | –37.84                           | 233.99                          | –109.21                         |
| 310     | 587.06                        | –63.93                           | 402.10                          | –188.58                         |
| 315     | 594.10                        | –88.77                           | 567.93                          | –267.67                         |
| 320     | 600.56                        | –112.40                          | 731.47                          | –346.47                         |
| 325     | 606.54                        | –134.84                          | 892.72                          | –424.98                         |
| 330     | 612.16                        | –156.15                          | 1051.66                         | –503.20                         |
| 335     | 617.53                        | –176.35                          | 1208.30                         | –581.13                         |
| 340     | 622.76                        | –195.48                          | 1362.63                         | –658.78                         |
| 345     | 627.98                        | –213.57                          | 1514.66                         | –736.13                         |
| 350     | 633.28                        | –230.66                          | 1664.39                         | –813.20                         |
| 355     | 638.79                        | –246.78                          | 1811.82                         | –889.97                         |
| 360     | 644.62                        | –261.96                          | 1956.95                         | –966.46                         |
| 365     | 650.87                        | –276.23                          | 2099.80                         | –1042.66                        |
| 370     | 657.67                        | –289.63                          | 2240.36                         | –1118.56                        |
| 375     | 665.12                        | –302.18                          | 2378.66                         | –1194.18                        |
The polynomial fitted values for the molar heat capacity and thermodynamic functions of $\beta$-CsB$_5$O$_8$·4H$_2$O are obtained in the temperature range from 298 to 375 K at intervals of 5 K and listed in Table 4. It can clearly be seen that from Table 4 the values of the molar heat capacity and entropy ($S_T - S_{298.15}$) are increased with the increase of temperature from 298.15 K to 375 K, but the enthalpy ($H_T - H_{298.15}$) and Gibbs free energy ($G_T - G_{298.15}$) are decreased.

4. Conclusions

The molar heat capacities of $\beta$-CsB$_5$O$_8$·4H$_2$O were measured by an adiabatic calorimeter in the temperature range from 298 to 373 K with a heating rate of 0.1 K/min without the phase transition and other thermal anomalies and were fitted to a polynomial equation of $C_{p,m} (\text{J mol}^{-1} \text{K}^{-1}) = 618.07702 + 39.52669[T - (T_{\text{max}} + T_{\text{min}})/2]/(T_{\text{max}} - T_{\text{min}})/2] - 3.46888[(T - (T_{\text{max}} + T_{\text{min}})/2)/T_{\text{max}} - T_{\text{min}}/2]^2 + 7.9441[(T - (T_{\text{max}} + T_{\text{min}})/2)/(T_{\text{max}} - T_{\text{min}}/2)^3]$. The relevant thermodynamic functions of enthalpy, entropy, and Gibbs free energy of cesium pentaborate tetrahydrate are also obtained at intervals of 5 K from 298 to 375 K.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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