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Calorimetric study of alkali metal tetrafluoroborates[1]

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Abstract

Adiabatic calorimetric investigation of the low-temperature heat capacity of sodium tetrafluoroborate as well as a DSC study of the thermal behavior of potassium tetrafluoroborate and of lithium tetrafluoroborate and its hydrates were carried out.

Temperatures and enthalpies of phase transitions at temperature above ambient were determined for potassium tetrafluoroborate, lithium tetrafluoroborate, and lithium tetrafluoroborate mono- and trihydrate. It was demonstrated that lithium tetrafluoroborate has only one phase transition in the solid at 300 K.

Keywords: Adiabatic calorimetry; DSC; Lithium tetrafluoroborate; Low-temperature heat capacity; Phase transitions; Potassium tetrafluoroborate; Sodium tetrafluoroborate

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1. Introduction

Thermodynamic properties of alkali metal tetrafluoroborates are of great interest as these substances are promising components of coolant mixtures. It is known that mixtures of tetrafluoroborates were proposed for cooling of molten salts breeder reactor. In recent years information about application of lithium tetrafluoroborate as a component of solid electrolytes was published.

The present study is a part of an investigation of the thermodynamic properties of alkali metal tetrafluoroborates over a wide temperature range. We now present the results of measurements of the low temperature heat capacity of sodium tetrafluoroborate by adiabatic calorimetry and from the study of the thermal behavior of potassium and lithium tetrafluoroborates by differential scanning calorimetry (DSC).

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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In our recent study of the low temperature heat capacity of lithium tetrafluoroborate by adiabatic calorimetry [1] we observed an extended heat capacity anomaly in the range from 120 to 305 K with a sharp peak at 300.7 ± 0.5 K. The entropy value of this transition, 12.0 J K^{-1} mol^{-1} ($\approx R\ln4$) enables it to be attributed to an orientational disorder type transition. One can find confirmation of this assumption in Ref. [2], in which the NMR study of a powder sample of $LiBF_4$ showed that the BF_4 ion reorientates isotropically between 300 and 370 K. Unfortunately it is unknown whether this phase transition is accompanied by change of crystal structure because no information is available about the crystal structure of lithium tetrafluoroborate below and above the transition temperature Ref. [3] alone contains the brief note that at ambient temperatures it has a hexagonal-type structure, probably that of SiO_2. Investigations of the heat capacities of potassium [4, 5] and cesium [6] tetrafluoroborates showed that these substances have no phase transitions at low temperatures.

Information about the thermal behavior of $LiBF_4$ above 300 K is contradictory. Thermodynamic properties of alkali metal tetrafluoroborates at elevated temperatures were studied earlier by DTA [7, 8] and drop-calorimetry [3, 9] methods. For all alkali metal tetrafluoroborates, except $LiBF_4$ temperatures and enthalpies of structural transitions from orthorhombic to cubic phase were determined. For $LiBF_4$ Morano and Shuster [7] attributed the endothermic peak, observed at 381–388 K, to the same type of transition. But later in the investigation of thermal behavior of lithium tetrafluoroborate in the range 298–700 K by DTA and drop-calorimetry methods Dworkin [3] found only one endothermic effect of $LiBF_4$ melting at 583 K and proposed that in Ref. [7] the authors were dealing with the hydrated sample as all experimental operations were performed in air. Except for Ref. [1] no information about the phase transition in $LiBF_4$ near 301 K has appeared in the literature.

We undertook the study of $LiBF_4$ and its crystalline hydrates by differential scanning calorimetry to clarify the thermal behavior of $LiBF_4$ at high temperatures, as it is known that lithium tetrafluoroborate actively reacts with atmospheric moisture and forms hydrates. Plakhotnik et al. [10] in the study of the $LiBF_4$–H_2O system confirmed the existence of two hydrated forms of lithium tetrafluoroborate ($LiBF_4 \cdot H_2O$ and $LiBF_4 \cdot 3H_2O$) and determined the temperature of $LiBF_4 \cdot 3H_2O$ incongruent melting (304.1 ± 0.1 K). DTA and TG study of lithium tetrafluoroborate monohydrate [11] revealed two endotherms in the range 388–403 K, one of which, at 390 K, was related to monohydrate melting, the other, at 403 K, to water removal.

2. Experimental

2.1. Samples

The first group of samples of lithium tetrafluoroborate (samples $LiBF_4$-1 and $LiBF_4$-2; synthesized and analyzed by V.N. Plakhotnik, Dnepropetrovsk Transport Institute) was synthesized by the reaction of tetrafluoroboric acid ($\phi = 4.02$) with lithium carbonate (pure grade). The salt obtained was carefully dehydrated and worked up in anhydrous fluorine hydride. Analytical study of the substance showed that it contained 99.9 wt% $LiBF_4$ and less than 0.01 wt% H_2O. The second type of $LiBF_4$ sample (sample $LiBF_4$-3; synthesized by S.I. Bakum, Kurnakov Institute of General and Inorganic Chemistry) was synthesized by fluorination of lithium tetrahydridoborate. This sample contained 99.8 wt% $LiBF_4$.

Hydrates of lithium tetrafluoroborate were produced by precipitation from aqueous solutions of $LiBF_4$ under the suitable conditions. Hydrates ($LiBF_4 \cdot H_2O$ and $LiBF_4 \cdot 3H_2O$) contained $\approx$ 2 wt% of hydrolysis products and 0.5% wt LiF. All samples were stored in sealed glass vessels.

Sodium tetrafluoroborate was synthesized by the reaction of sodium carbonate and tetrafluoroboric acid (both substances were pure grade). Chemical analysis showed that after additional purification the sample contained 99.9 wt% $NaBF_4$ and 0.1 wt% of hydrolysis products; sodium fluoride was not detected in the specimen obtained. The sample was carefully dried and stored in a dry inert gas atmosphere.

Potassium fluoroborate was produced by reaction of tetrafluoroboric acid with potassium carbonate (pure grade). After synthesis the sample was purified and carefully dried. The sample studied contained 99.9 wt% KBF_4.

2.2. *Calorimetric instrumentation and methods*

The low temperature heat capacity of sodium tetrafluoroborate was studied by adiabatic calorimetry with the equipment described in Ref. [12]. A platinum resistance thermometer (R = 50 Ohm at 273 K) was used as the temperature probe. Samples were loaded in a 2 cm^3 stainless steel container. Before sealing the container was filled with helium ($p = 10^4$ Pa) as a heat exchange gas. A two-shield arrangement was applied to provide the adiabatic conditions for heat capacity study. Measurements on high purity benzoic acid as reference substance were carried out for quality control of the data obtained. The difference between measured and reference data was less than 1% in the range 14–50 K and less than 0.2% in the range 50–350 K. The mass of the sample of sodium fluoroborate was 2.4907 g, molecular mass M = 109.7926.

The thermal behavior of alkali metal tetrafluoroborates at temperatures above ambient was studied by differential scanning calorimetry using a Setaram DSC 111 instrument. High purity metal standards (Ga, In, Sn, Pb, Zn, and Al) supplied by the Russian Research Institute of Standard Substances Metrology were used to calibrate the DSC instrument in respect of temperature. The temperature reproducibility was ± 0.1 K at an uncertainty in the temperature scale of ± 0.5 K. The enthalpy calibration of the DSC 111 instrument was carried out by measurement of the Joule effect. Checking by measurement of the melting enthalpy of metals showed that at temperatures below 500 K the error of enthalpy determination was $\pm 1\%$, and at temperatures above 500 K it increased to $\pm 3\%$.

For DSC measurements samples of prepared substances, 0.05–0.1 g, were loaded in stainless steel crucibles with crimped aluminum or nickel seals under a dry nitrogen atmosphere. Phase transition enthalpies (ΔH) were determined by graphic integration of peaks in the DSC curves using the Setaram software. The error of integration was 0.1–3%depending on the configuration and area of the peak. Temperatures of thermal effects were determined as extrapolated peak onset temperature T_e and as maximum peak temperature T_p.

If necessary blank experiments with the empty crucibles were carried out to correct the base line and calculate the specific heat of specimens.

3. Results and discussion

3.1. Low temperature heat capacity of sodium tetrafluoroborate

The heat capacity of $NaBF_4$ was determined in the range 15–320 K using 125 experimental points. No anomalies were observed in the $C_p(T)$ curve. Experimental data were smoothed by the spline approximation using Ivtantermo DataBase software [13]. Calculation of the thermodynamic properties of sodium tetrafluoroborate (Table 1) was carried out using smoothed heat capacity data. Extrapolation of $C_p(T)$-dependence to absolute zero was performed by use of the Debye equation ($C_p = AT^3$).

Comparison of the temperature-dependence of the heat capacity of sodium tetrafluoroborate with those for the potassium and cesium salts, obtained in our previous work [5, 6], shows that at very low temperatures the sodium salt heat capacity curve passes below those of KBF_4 and $CsBF_4$ (Fig. 1). This may be explained by the influence of the mass of the ions on the frequency of lattice translational vibrations. Near ambient temperatures the $C_p(T)$ curve for $NaBF_4$ intersects the curves for potassium and cesium tetrafluoroborates, which may be related to the different structures of these substances. One has to pay attention to the anomalous behavior of the lithium tetrafluoroborate heat capacity at very low temperatures where its $C_p(T)$ curve intersects not only that of sodium tetrafluoroborate, but also that of potassium tetrafluoroborate. Data on the temperature-dependences of the Debye temperature for different tetrafluoroborates are shown in Fig. 2. The general appearance of the $\theta_D(T)$ dependence for $LiBF_4$ is very similar to that for substances with layer or chain structures. Unfortunately no reliable information about the structure of $LiBF_4$ even above the phase transition ($T = 300.7$ K) was found in the literature.

3.2. High temperature calorimetric study

3.2.1. Lithium tetrafluoroborate $LiBF_4$ ($M = 93.7446$)

Heating of samples was carried out as follows:

(1) The first run for $LiBF_4$-1: heating in the range 283–333 K (heating rate $v = 1$ K min^{-1})–isothermal stage ($t = 10$ min)–heating in the range 333–443 K ($v = 2$ K min^{-1}).

(2) The second run for $LiBF_4$-1: heating (288–323 K; $v = 2$ K min^{-1})–isothermal stage ($t = 5$ min)–heating (323–443 K; $v = 1$ K min^{-1}).

(3) The third run for $LiBF_4$-1: heating (288–423 K, $v = 1$ K min^{-1}).

(4) The fourth run for $LiBF_4$-1 and the first run for $LiBF_4$-2: heating (293–423 K, $v = 1$ K min^{-1}).

Table 1
Thermodynamic properties of sodium tetrafluoroborate (heat capacity, entropy, and reduced Gibbs energy in J K^{-1} mol^{-1}, enthalpy change in J mol^{-1})

T/K	$C_p^0(T)$	$S^0(T)$	$H^0(T)-H^0(0)$	$\Phi^0(T)$[a]
15	2.009	0.6697	7.534	0.1674
20	5.266	1.665	25.25	0.4025
25	9.564	3.286	61.97	0.8072
30	14.54	5.461	122.0	1.394
35	19.78	8.095	207.8	2.158
40	24.92	11.07	319.7	3.078
45	29.67	14.29	456.4	4.148
50	33.89	17.64	615.5	5.330
60	41.14	24.48	992.0	7.947
70	47.50	31.31	1463	10.80
80	53.15	38.03	1940	13.78
90	58.14	44.59	2497	16.85
100	62.60	50.95	3101	19.94
110	66.62	57.10	3747	23.04
120	70.32	63.06	4432	26.13
130	73.77	68.83	5153	29.19
140	77.05	74.42	5907	32.23
150	80.19	79.84	6693	35.22
160	83.22	85.11	7510	38.17
170	86.15	90.25	8357	41.09
180	88.99	95.25	9233	43.96
190	91.72	100.1	10140	46.73
200	94.35	104.9	11070	49.55
210	96.87	109.6	12020	52.36
220	99.29	114.1	13000	55.01
230	101.6	118.6	14010	57.69
240	103.9	123.0	15040	60.33
250	106.1	127.3	16090	62.94
260	108.3	131.5	17160	65.50
270	110.4	135.6	18250	68.01
273.15	111.1	136.3	18600	68.21
280	112.6	139.6	19370	70.42
290	114.8	143.6	20500	72.91
298.15	116.6	146.9	21450	74.96
300	117.0	147.6	21660	75.40
310	119.1	151.4	22840	77.72
320	121.0	155.2	24040	80.08

[a] Reduced Gibbs energy $\Phi^0(T) = -[G^0(T) - H^0(0)]/T$

(5) The first and the second runs for $LiBF_4$-3: heating in the ranges 293–413 K and 293–423 K, respectively, with $v = 1$ K min^{-1}.

In the DSC curves of lithium tetrafluoroborate we found two endothermic peaks, noted below by the Roman figures I and II (see Fig. 3). Experimental results are

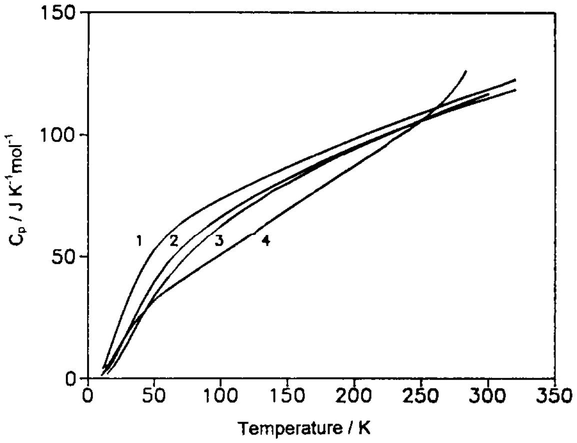

Fig. 1. Heat capacity-dependences for alkali metal tetrafluoroborates at low temperatures: 1, $CsBF_4$; 2, KBF_4; 3, $NaBF_4$; 4, $LiBF_4$.

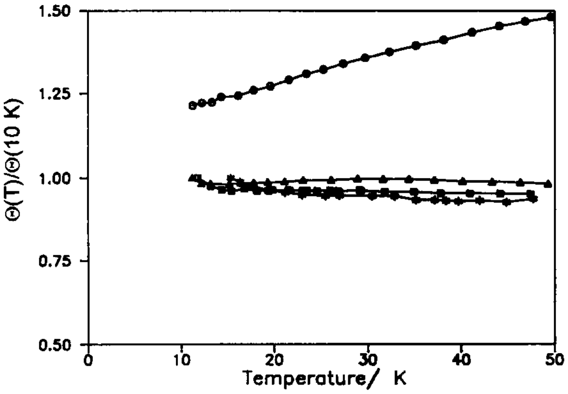

Fig. 2. Temperature-dependences of the Debye temperature for alkali metal tetrafluoroborates: ●, $LiBF_4$; ▲, $CsBF_4$; ■, KBF_4; *, $NaBF_4$.

presented in Table 2 (in all tables values of ΔH effects are related to whole mass of the sample).

Endotherm I at $T_p(I) = 300.9 \pm 0.3$ K (from six runs with a heating rate 1 K min^{-1}) corresponds to heat capacity anomaly reported in Ref. [1]. As in accordance with low temperature calorimetry data this phase transition starts at 120 K, integration of peak I in the range 289–309 K leads to underestimation of transition enthalpy value by a factor of 3.5. A feature of this reversible transition is that thermal equilibrium in the sample under study is reached sufficiently fast at any temperature in the anomaly region and an appropriate fraction of transition enthalpy, $\Delta' H$, can be determined for any temperature range with sufficiently high reliability. For the $LiBF_4$-1 and $LiBF_4$-2

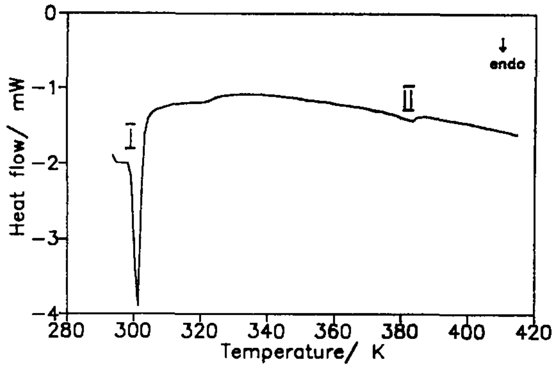

Fig. 3. DSC curve of $LiBF_4$-1 (run 4).

Table 2
DSC data for $LiBF_4$

Samples	Endotherm I (polymorphous transition)		Endotherm II (melting of impurity)			
	$v/(K\ min^{-1})$	T_p/K	$v/(K\ min^{-1})$	T_e/K	T_p/K	$\Delta H(II)/(J\ g^{-1})$
$LiBF_4$-1 (0.0516 g)						
Run 1	1	301.2	2	379.0	385.0	(0.89)
Run 2	2	301.8	1	379.6	383.2	0.89
Run 3	1	301.0	1	378.3	383.1	0.87
Run 4	1	301.1	1	378.5	383.0	0.69
$LiBF_4$-2 (0.0636 g)						
Run 1	1	301.3	1	380.3	384.6	2.15
$LiBF_4$-3 (0.0404 g)						
Run 1	1	300.9	1	373.1	377.4	0.124
Run 2	1	300.2	1	373.2	378.3	0.123

samples calculation of $\Delta' H(I)$ by integration of peak areas for the same temperature ranges leads to values in close agreement (difference < 5%). For the $LiBF_4$-3 sample the $\Delta' H(I)$ enthalpy increases by 15% on second heating and comes very close to $\Delta' H(I)$ values for $LiBF_4$-1 and $LiBF_4$-2.

In heating curves of $LiBF_4$ the diffuse endothermic peak II was observed in the range 365–390 K. This endotherm was caused by the presence of admixed lithium monohydrate $LiBF_4 \cdot H_2O$ (see section 3.2.3). From Table 2 one can see that for sample $LiBF_4$-2 the enthalpy $\Delta H(II)$ increased by a factor of 2.5 in comparison with $LiBF_4$-1. So, as a result of the second unsealing of glass vessel the sample of lithium tetrafluoroborate humidified.

On first heating of sample $LiBF_4$-3 a small endothermic peak was revealed in the range 332–348 K; this anomaly was not detected later on heating for a second time. We suggest that this endotherm was caused by the presence of an unreacted impurity, which is transformed to $LiBF_4$ when the sample is first heated. This suggestion was confirmed by the increased $\Delta' H(\mathrm{I})$ value on the disappearance of this endotherm from sample $LiBF_4$-3.

3.2.2. *Lithium tetrafluoroborate monohydrate* $LiBF_4 \cdot H_2O$ *(0.0928 g; M = 111.7598)*

Thermal study was carried out using the following program:

(1) The first cycle: heating in the range 293–353 K ($v = 5$ K min^{-1}) – isothermal stage for 10 min – heating in the range 353–433 K ($v = 1$ K min^{-1}) – cooling from 433 K ($v = 4$ K min^{-1}).

(2) The second cycle: heating in the range 283–403 K ($v = 1$ K min^{-1}) – cooling from 403 K ($v = 4$ K min^{-1}).

(3) The third and the fourth cycles: heating in the range 287–343 K ($v = 2$ K min^{-1}) – isothermal stage for 5 min — heating in the range 343–403 K ($v = 1$ K min^{-1}) – cooling from 403 K ($v = 2$ K min^{-1}).

(4) The fifth run: heating in the range 283–323 K ($v = 1$ K min^{-1}).

Two endothermic peaks were found in the heating curves of $LiBF_4 \cdot H_2O$. The enthalpies of both effects changed after the first heating (see Table 3).

The temperature of endothermic peak I ($T_e(\mathrm{I}) = 299.8$ K, $T_p(\mathrm{I}) = 303.5$ K) is very near to the melting temperature of $LiBF_4 \cdot 3H_2O$ (see section 3.2.3). On first heating the $\Delta H(\mathrm{I})$ enthalpy was 12.6 J g^{-1}. On second heating the $\Delta H(\mathrm{I})$ value decreased to 1.28 ± 0.05 J g^{-1} and on subsequent heating this effect did not occur.

Endothermic effect II ($T_{e,m} = 381.3 \pm 0.7$ K (from 3 runs) and $T_{p,m} = 386 \pm 0.2$ (from the two last runs)) is related to the melting of $LiBF_4 \cdot H_2O$ (Fig. 4). The melting enthalpy was equal to $\Delta_m H(LiBF_4 \cdot H_2O) = 23.28$ kJ mol^{-1}. After the first heating the amount of admixed $LiBF_4 \cdot 3H_2O$ decreased by a factor of 10 (from the $\Delta H(\mathrm{I})$ values) and the melting enthalpy of the monohydrate increased by 3% (possibly because of the transformation of trihydrate to the monohydrate during the first melting and crystallization processes). The parameters of endothermic peak II were, therefore, taken from runs other than the first.

Crystallization of the melt begins at $T_{e,cr} = 379 \pm 0.3$ K (exotherm) and supercooling of the melt was not observed (difference between $T_{e,m}$ and $T_{e,cr}$ is only 2 K). The crystallization enthalpy for the remelted sample is 3% higher than the melting enthalpy.

3.2.3. *Lithium fluoroborate trihydrate* $LiBF_4 \cdot 3H_2O$ *(0.1242 g; M = 147.7902).*

Heating of the sample was carried out four times at a rate of 1 K min^{-1}: the first in the range 288–348 K, the others in the range 283–323 K. The results of these studies are presented in Table 4 and Fig. 5.

The endothermic peak of trihydrate melting with $T_{e,m} = 303.5 \pm 0.3$ K and $T_{p,m} = 306.7 \pm 0.1$ K (from four runs) is observed in the DSC curves in this temperature range. At 307.5 K one can see the weak inflection of the descending peak slope. From

Table 3
DSC data for $LiBF_4 \cdot H_2O$

Run no.	Endotherm I (impurity)				Endotherm II (melting)				Exotherm (crystallization			
	$v/(K\ min^{-1})$	T_e/K	T_p/K	$\Delta H(I)/(J\ g^{-1})$	$v/(K\ min^{-1})$	T_e/K	T_p/K	$\Delta_m H/(J\ g^{-1})$	$v/(K\ min^{-1})$	T_e/K	T_p/K	$\Delta_{cr} H/(J\ g^{-1})$
1	5	299.7	305.7	12.6	1	382.0	387.5	202.0	4	379.7	372.7	223.7
2	1	299.8	303.5	1.28	1	381.3	386.5	208.3				
4	2	–	–	–	1	380.6	386.1	208.3	2	379.2	374.7	211.7

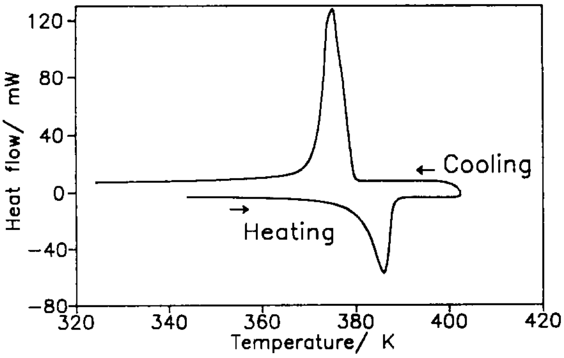

Fig. 4. Heating and cooling cycle of $LiBF_4 \cdot H_2O$ (run 4).

Table 4
Temperature and enthalpy of melting of $LiBF_4 \cdot 3H_2O$

Run	T_e/K	T_p/K	$\Delta_m H/(J\ g^{-1})$	Purity/mol%
1	303.8	306.8	144.2	97.7
2	303.6	306.7	126.3	96.5
3	303.4	306.7	151.4	97.3
4	303.0	306.7	187.0	93.6

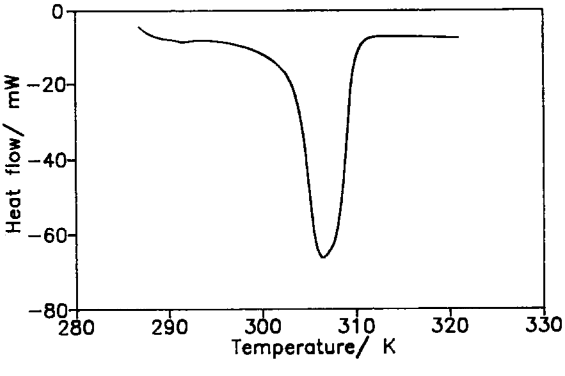

Fig. 5. DSC curve of $LiBF_4 \cdot 3H_2O$ (run 1).

Table 4 it is obvious that $T_{p,m}$ does not vary in different runs, and $T_{e,m}$ gradually decreases. Calculation of sample purity by the Van't-Hoff equation (Setaram software) revealed that purity decreases from 97.7 mol% in the first run to 93.6 mol% in the last (it should be noted that the calorimetric method for purity determination gives the correct results only for purity higher than 99% and that the listed data are rough values.

The melting enthalpy of the trihydrate increases by approximately 30% from the first to the last run (the second run was not taken into account as in this experiment we encountered incomplete crystallization). This increase may be explained as follows – in our DSC study the small change in the starting composition of sample to monohydrate occurred during incongruent melting of the trihydrate (see Ref. [10]). Therefore temperature and enthalpy of trihydrate melting $T_m(LiBF_4 \cdot 3H_2O) = 303.8$ K and $\Delta_m H(LiBF_4 \cdot 3H_2O) = 21.3$ kJ mol^{-1} were determined from the first run.

Table 5 lists the temperatures of endothermic peaks in the DSC curves of lithium tetrafluoroborate and its hydrates and the corresponding literature data; it is apparent that water was the major impurity in all the samples studied — as monohydrate in $LiBF_4$ and as trihydrate in $LiBF_4 \cdot H_2O$. We evaluated the amount of impurities in the studied samples from values of melting enthalpies of the hydrates. For instance, sample $LiBF_4$-1 contained 0.3–0.4 wt% of $LiBF_4 \cdot H_2O$ (or 0.06 wt% of H_2O). In sample $LiBF_4$-2 the amount of monohydrate increased to 1.1 wt%. The starting $LiBF_4 \cdot H_2O$ contained 9 wt% of $LiBF_4 \cdot 3H_2O$ (or 3 wt% of H_2O), but as a result of the first melting of the sample the amount of impurity decreased to 0.9 wt % of trihydrate (or 0.3 wt% of H_2O), i.e. by a factor of ten.

So we deduce that this type of hygroscopic substances DSC is the method applicable to identification and evaluation of purity of samples synthesized in different ways.

We suggest that our DSC results provide evidence that the endothermic peak found in Ref. [7] at 381–388 K is related to melting of lithium tetrafluoroborate monohydrate and not to the structural phase transition of $LiBF_4$.

Our DSC data confirmed the occurrence of a phase transition in $LiBF_4$ at 300.7 ± 0.5 K [1]. In [3] and [8] this transition was not detected as the authors did not cool the substance below 299 K (see, for example, Ref. [14]) and dealt with the high-temperature phase of $LiBF_4$.

3.2.4. *Potassium tetrafluoroborate* KBF_4 *(0.0969 g; M = 125.9019)*

The first "heating-cooling" cycle was carried out with the following program: heating in the range 293–513 K ($v = 5$ K min^{-1})–isothermal stage for 10 min–heating from 513 to 603 K ($v = 2$ K min^{-1})–cooling from 603 ($v = 5$ K min^{-1}). The next three runs were

Table 5
Temperatures of endothermic effects in the DSC curves for lithium tetrafluoroborate and its hydrates.

Substance	$T_{tr}(LiBF_4)$ T_p/K	$T_m(LiBF_4 \cdot 3H_2O)$		$T_m(LiBF_4 \cdot H_2O)$	
		T_e/K	T_p/K	T_e/K	T_p/K
$LiBF_4$-1	300.9 ± 0.3 300.7 ± 0.5 [1]			378.9 ± 0.5	383.6 ± 0.7
$LiBF_4 \cdot H_2O$		≈ 300	304.6 ± 1.0	381.3 ± 0.7 381–388 [7]	386.3 ± 0.2 390 [11]
$LiBF_4 \cdot 3H_2O$		303.5 ± 0.3	306.7 ± 0.1 304.0 ± 0.1 [10]		

Table 6
Thermal parameters of structural phase transition in KBF_4

Heating–cooling cycle	Endotherm ($\alpha \rightarrow \beta$ transition)				Exotherm ($\beta \rightarrow \alpha$ transition)			
	v/(K min^{-1})	T_e/K	T_p/K	$\Delta_{tr}H(\alpha \rightarrow \beta)$(kJ mol^{-1})	v/(K min^{-1})	T_e/K	T_p/K	$\Delta_{tr}H(\beta \rightarrow \alpha)$/(kJ mol^{-1})
Run 1	2	555.8	559.0	14.60	5	547.3	541.1	14.92
Run 2	2	555.5	559.6	14.47	5	546.5	541.1	14.84
Run 3	1	555.6	558.2	14.40	5	546.5	541.1	14.83
Run 4	4	556.4	562.2	14.49	5	546.1	540.4	14.69

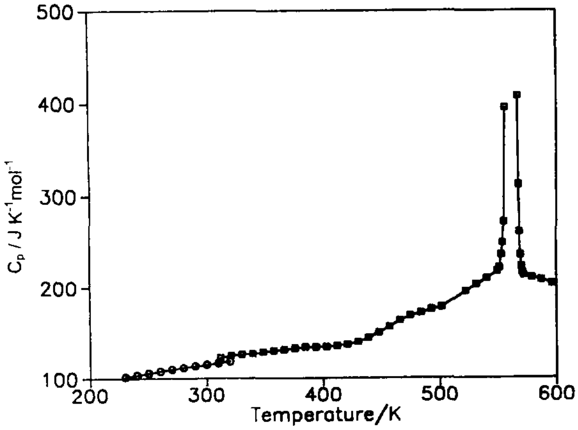

Fig. 6. Heat capacity of potassium tetrafluoroborate: ●, adiabatic calorimetry [4, 5]; ■, DSC data.

performed in the temperature range 323–603 K (heating rates 2, 1, and 4 K min^{-1} and cooling rate 5 K min^{-1}). Experimental data are presented in Table 6.

In the DSC curves in the range 548–573 K the sharp endothermic peak caused by the reversible structural $\alpha \leftrightarrow \beta$ transition from orthorhombic to cubic phase was observed. The parameters of the phase transition were: $T_e = 555.6 \pm 0.1$ K, $T_p = 558.9 \pm 0.5$ K (from the first three runs), $\Delta_{tr}H(\alpha \rightarrow \beta\text{-KBF}_4) = 14.49 \pm 0.07$ kJ mol^{-1} (from four runs); the transition entropy $\Delta_{tr}S(\alpha \rightarrow \beta) = \Delta_{tr}H(\alpha \rightarrow \beta)/T_p = 25.9$ J K^{-1} mol^{-1}. The value of the transition enthalpy obtained from DSC data was 5% more than that from drop-calorimetric measurements [9], but the experimental error in Ref. [9] was ± 2% and in our DSC study at this temperature it is nearly 3%. It is possible that our $\Delta_{tr}H(\alpha \rightarrow \beta\text{-KBF}_4)$ value is an underestimate because in the $C_p(T)$ curve of KBF_4, calculated from the data from run 1, an obvious bend is observed at 430 K (Fig. 6). Apparently the phase transition in KBF_4 takes place over a wide temperature range (as in $LiBF_4$ also) as it is known that in the DSC curves the anomalous enthalpy is not recognized in the early stages of the slowly developing process.

The exothermic peak of the $\beta \rightarrow \alpha$ reverse transition was observed in the cooling curves of potassium tetrafluoroborate recorded at a rate of 5 K min^{-1}. The phase transition interval is 558–508 K with supercooling of nearly 10 K. The parameters of the $\beta \rightarrow \alpha$ transition are: $T_e = 546.6 \pm 0.4$ K, $T_p = 540.9 \pm 0.3$ K, $\Delta_{tr}H(\beta \rightarrow \alpha\text{-KBF}_4) = 14.82 \pm 0.07$ kJ mol^{-1}. The value of the transition enthalpy is close to that obtained from heating. Errors of integration both for endothermic and for exothermic peaks did not exceed 0.1%.

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