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Vapour pressure and standard enthalpy of sublimation of alkali-metal fluoroborates

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Abstract

The temperature dependence of the vapour pressures of solid alkali-metal fluoroborates MBF_4 (M = Na, Rb or Cs) were experimentally determined using an improvised transpiration technique. The vapour pressure of $NaBF_4$ could be represented by the following least-squares expressions:

$$\log(p/\mathrm{Pa})\,[\mathrm{NaBF_4,\ orthorhombic}] = 7.06(\pm 0.03) - 3734(\pm 360)\,(\mathrm{K})/T$$

$$\log(p/\mathrm{Pa})\,[\mathrm{NaBF_4,\ monoclinic}] = 6.03(\pm 0.04) - 3192(\pm 80)\,(\mathrm{K})/T$$

The enthalpy pertaining to the transition from the orthorhombic to the monoclinic phase at 527 K, was found to be 10.4 kJ mol^{-1}.

The measured vapour pressures of $RbBF_4$ and $CsBF_4$ could be represented by the following least-squares expressions:

$$\log(p/\mathrm{Pa})\,[\mathrm{RbBF_4}] = 6.21(\pm 0.04) - 4020(\pm 87)\,(\mathrm{K})/T$$

$$\log(p/\mathrm{Pa})[\mathrm{CsBF_4}] = 7.77(\pm 0.04) - 5209(\pm 108)\,(\mathrm{K})/T$$

By using the third law analyses of the data, $\Delta H^\circ_{\mathrm{sub}}$ of MBF_4 (M = Na, Rb or Cs) at 298 K were determined to be 89.4 ± 1.5, 123.4 ± 1.9 and 135.7 ± 0.8 kJ mol^{-1}, respectively.

Keywords: Alkali fluoro borate; Vapour pressure; TG based transpiration technique; Enthalpy of sublimation

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1. Introduction

High-density boron carbide (^{10}B-enriched) pellets will be used as neutron absorbers in the control and safety rods (CSR) and diverse safety rods (DSR) of the first Indian commercial fast breeder reactor [1]. These carbide pellets will be produced by the direct reaction between elemental boron and graphite at high temperature followed by consolidation by hot pressing [2]. Enriched elemental boron will be produced by the electrolysis of KBF_4 dissolved in a molten mixture of KCl and KF [3]. Data on the vapour pressure of KBF_4 would be useful for predicting and minimizing the loss of the precious enriched boron during high temperature electrolysis. Hence, the vapour pressure of this compound was measured in our laboratory [4]. In addition to these applications, experimental data on the vapour pressure and enthalpies of phase transitions are required for the basic understanding of the thermochemistry of this class of compounds. Hence, in the present study, the vapour pressures of MBF_4 (where M = Na, Rb or Cs) were measured in order to study the systematics in the vapour pressure as well as the standard enthalpy of sublimation of these compounds.

2. Experimental

2.1. Starting materials

Analytical reagent grade $NaBF_4$ of purity better than 99.9% (supplied by M/s Acros organics, USA) was used for the transpiration experiments. $RbBF_4$ and $CsBF_4$ were prepared by carrying out the following chemical reactions.

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2.2. Synthesis of alkali metal flouroborates

$RbBF_4$ and $CsBF_4$ were prepared through the following chemical reactions:

$$4HF(aq) + H_3BO_3(s) \rightarrow HBF_4(aq) + 3H_2O(l) \qquad (1)$$

$$HBF_4(aq) + \frac{1}{2}M_2CO_3(aq)\,(M = Rb\,(or)\,Cs)$$
$$\rightarrow MBF_4(s) + \frac{1}{2}H_2O(l) + \frac{1}{2}CO_2(g) \qquad (2)$$

Both the above reactions are highly exothermic. Hence, it was necessary to carry out these reactions at 278 K. In the first reaction, HBF_4 was prepared by dissolving stoichiometric quantity of boric acid in 27N hydrofluoric acid, by adding small lots of H_3BO_3 to HF with continuous stirring. After the completion of dissolution, a saturated solution of M_2CO_3 (where M = Rb or Cs) was added to the HBF_4 solution at 278 K. A gelatinous white precipitate of MBF_4 (M = Rb or Cs) was obtained. This precipitate was filtered under suction using a G4 glass frit, washed with water (278 K) and with methanol, and dried under an IR lamp for 1 h. The XRD patterns of the compounds prepared in this study match with the patterns reported in JCPDS [JCPDS file no.: 11-0671 for $NaBF_4$, 73-1521 for $RbBF_4$ and 73-0206 for $CsBF_4$].

2.3. Transpiration set-up

A horizontal thermal analyzer (Model-Seiko 320) was adapted as a transpiration set-up for vapour pressure measurements. The configuration of the dual arm balance with a narrow furnace chamber minimizes errors arising from convection, buoyancy, thermo molecular and electrostatic charge effects. A Pt-13% Rh/Pt thermocouple (Type-R) was used for the measurement of temperatures with an accuracy of ±0.5 K. The thermocouple was calibrated at the freezing point of pure metals such as tin, lead, antimony, aluminium, silver and gold. These calibration experiments revealed that the measured values of the temperature conform to the scale prescribed by ITS-90 [5] within ±0.5 K. Helium gas (99.995% pure) was used as the carrier gas. Since the flow rate of the carrier gas is the critical parameter in the transpiration experiments, precise flow calibration of the carrier gas was done using a capillary glass flow meter, which in turn was calibrated by a soap bubble method using a horizontal burette. Though the precision in the flow rate by the glass capillary flow meter was ±0.5%, the overall precision in the integral volume was of the order of ±1% of the total volume of the carrier gas. In order to facilitate the saturation of the carrier gas with the vapourising species, the powdered sample was spread over the surface of a shallow platinum crucible. Further, the narrow chamber tube was found to be conducive for the saturation of the vapour with carrier gas. Prior to the vapour pressure measurements, blank runs were taken with flow rates of 3–30 dm^3/h of helium gas at a temperature range from 400 to 800 K keeping both the sample and the reference pans empty. The apparent mass gain was found to be of the order of 2–4 μg/100 K change in temperature encompassing the full range of flow rate. However at any given temperature in this range, the drift in mass over a period of 1 h was of the same magnitude. The apparent mass loss was subtracted from all the recorded isothermal mass losses. The details of the experimental set-up and the method of measurement of the vapour pressure are described elsewhere [4,6,7].

2.4. Differential scanning calorimetry (DSC)

A heat flux type differential scanning calorimeter (model DSC 821 e/700, M/s. Mettler Toledo, GmbH, Switzerland) was used for the measurement of transition enthalpy of alkali-metal fluoroborates. The measurements were carried out at a heating rate of 0.17 $K\,s^{-1}$ and with a flow of 100 $ml\,min^{-1}$ of 99.995% pure argon. The DSC equipment was calibrated for the temperature measurement using the melting points of In, Pb, Zn, Sb, Al and Au. The enthalpies of these transitions were in agreement within ±1 kJ with those cited in the literature [8].

3. Results and discussion

3.1. TG and DSC measurements

Non-isothermal TG experiments were carried out with $NaBF_4$, $RbBF_4$ and $CsBF_4$ at a linear heating rate of 0.07 $K\,s^{-1}$ using the TG/DTA thermal analyser in order to identify the mass-loss steps and to fix the maximum temperature for vapour pressure measurements. Typical thermograms of these compounds are shown in Fig. 1. The range of temperature was so chosen that they are significantly below the melting/decomposition temperature of alkali-metal fluoroborates. The thermograms shown in Fig. 1 reveal the phase transition temperatures of $NaBF_4$ (orthorhombic to monoclinic), $RbBF_4$ and $CsBF_4$ (orthorhombic to cubic) to be 519, 527 and 442 K, respectively. These values are in excellent agreement with the corresponding values of 519, 529 and 443 K, respectively, obtained by the Differential Scanning Calorimetry (DSC) in this study (Fig. 2). From the DSC curves the enthalpies of phase transitions were calculated to be 7.2, 10.97

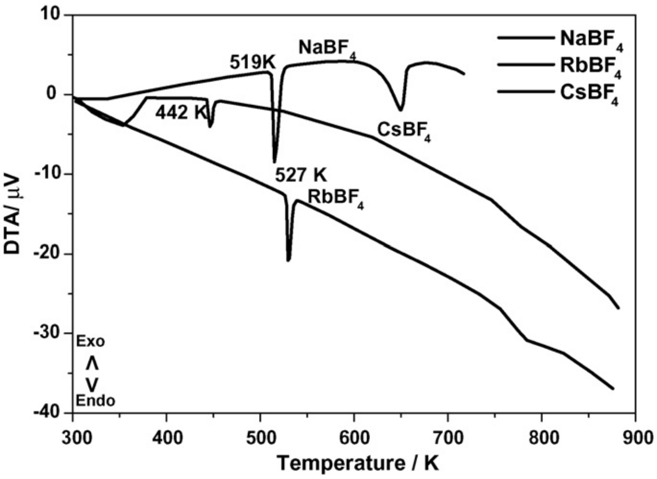

Fig. 1. DTA traces of MBF_4 (M = Na, Rb or Cs).

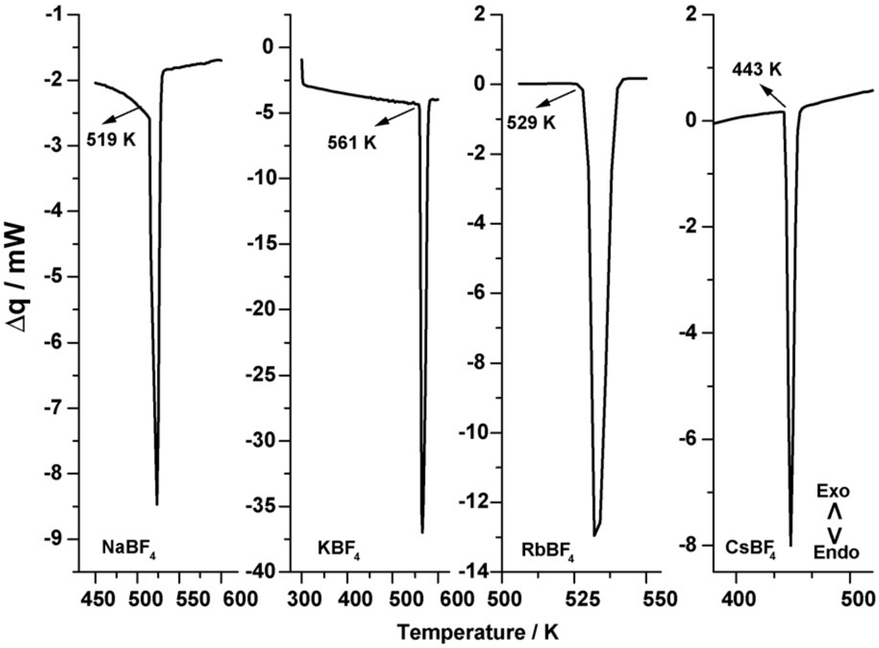

Fig. 2. DSC traces of MBF_4 (M = Na, Rb or Cs).

and 8.26 kJ mol^{-1}, respectively for $NaBF_4$, $RbBF_4$ and $CsBF_4$. These values are in excellent agreement with the values of 6.7, 11.96 and 8.11 kJ mol^{-1} recommended by Dworkin and Bredig [9]. The experimentally determined quantities along with those reported in earlier investigations are compared in Table 1.

3.2. Transpiration experiments

The apparent vapour pressures, p^{app}, over solid $NaBF_4$, $RbBF_4$ and $CsBF_4$ were calculated from the mass-loss of the sample using the relation:

$$p^{\mathrm{app}} = \frac{WRT_{\mathrm{c}}}{MV_{\mathrm{c}}} \qquad (3)$$

Table 1
Comparison of $\Delta H^{\circ}_{\mathrm{trans}}$ and T_{trans} of MBF_4 (M = Na, K, Rb or Cs)

M	$\Delta H^{\circ}_{\mathrm{trans}}$(kJ mol^{-1})	T_{trans}(K)	Reference
Na	6.7	516	[9]
	7.2	519	This work—DSC
	10.4	527	This work—TG transpiration
	–	519	This work—DTA
K	14.1	556	[9,11]
	16.8	556	[10]
	14.1	561	[4]—TG Transpiration
	14.5	561	[4]—DSC
	–	560	[4]—DTA
Rb	11.96	518	[9]
	10.97	529	This work—DSC
	–	527	This work—DTA
Cs	8.11	443	[9]
	8.26	443	This work—DSC
	–	442	This work—DTA

where 'W' is the mass-loss of the sample, V_{c} is the total volume of the carrier gas (saturated with the vapour species), T_{c} is the ambient temperature of the carrier gas and M is the molecular weight of the vapour species. In the case of KBF_4, the vapour phase in equilibrium with the solid compound contains monomeric species [10,11]. This supposition is substantiated from the observation made in our earlier work [4]. In the present study, we derived the enthalpy of transition and transition temperature of $NaBF_4$ from the vapour pressure measurements assuming that the gaseous species were only monomeric. It is observed that there is a good agreement between the enthalpy values derived from vapour pressure measurements (free vapourization) and closed capsule DSC measurements. Similarly, we derived the enthalpy of transition and transition temperature of $RbBF_4$ and $CsBF_4$ from DSC measurements. It is observed that there is a good agreement between the enthalpy values derived from DSC measurements made in this study and the enthalpy values derived from calorimetric measurements reported in the literature [9]. Thus, the absence of gas phase decomposition of the vapour species, as well as preferential removal of any particular species (other than the monomeric species) from the gas phase during the vapour pressure experiments is confirmed. This testifies the validity of the assumption that the vapourization is congruent in MBF_4 and that the vapour comprises only monomers. The vapour pressures of alkali-metal fluoroborates were measured after establishing the equilibrium conditions. In order to establish that the measured values of p^{app} are the equilibrium vapour pressure values at a given temperature, it is necessary to demonstrate the existence of a chair-shaped curve in the plot of p^{app} versus flow rate of the carrier gas. This chair-shaped curve is characteristic of isothermal equilibrium vapourization in a transpiration technique. Such plots for MBF_4 (M = Na, Rb or Cs) are shown in Fig. 3. The plateau in these plots shows that the vapourization rate was adequate to saturate the carrier gas for any

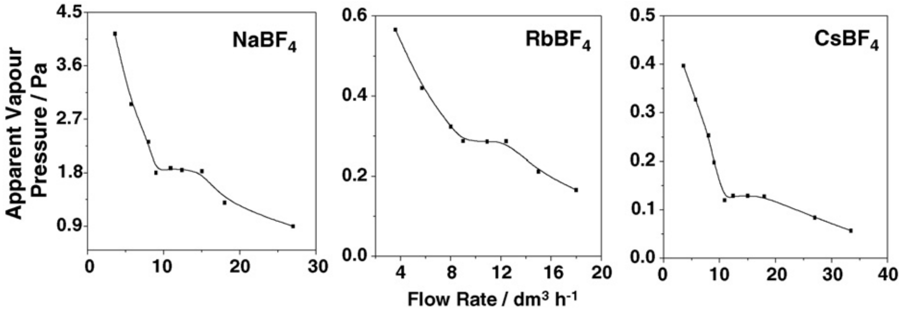

Fig. 3. Plots of p^{app} vs. flow rate of the carrier gas for $NaBF_4$, $RbBF_4$ and $CsBF_4$.

Table 2
Vapour pressure of $NaBF_4$

Experiment number	Temperature (K)		Mass loss[a] (μg)	V_c (dm^3)	Pressure (mPa)
	Ambient	Experimental			
1	297	483	107	10.909	221.5
2	297	493	133	9.955	300.8
3	295	498	140	9.0	347.9
4	297	503	192	10.909	396.3
5	299	514	320	10.909	664.9
6	301	519	306	10.909	640.1
7	299	523	420	10.909	872.7
8	299	533	570	10.909	1184.3
9	299	544	800	10.909	1662.2
10	299	545	710	9.0	1475.2
11	299	554	778	9.0	1959.4
12	299	554	716	9.0	1803.3
13	299	554	1000	12.414	1825.9
14	299	554	957	11.662	1847.7
15	299	554	904	10.909	1878.3
16	299	566	1017	9.0	2561.3
17	295	575	1287	10.909	2638.4
18	299	576	1202	9.0	3027.2
19	295	580	1950	12.414	3512.9
20	299	586	1524	9.0	3838.2
21	295	602	3090	12.414	3512.9
22	295	612	3270	12.414	5890.8
23	295	622	4875	12.414	8782.2
24	295	663	4390	6.200	15817

[a] Initial weight of the sample: 70 mg.

flow rate within this range. It is well known that at higher flow rates the carrier gas is under-saturated with slow vapourization of the sample while at lower flow rates than that in plateau region p^{app} is greater than $p_{\mathrm{equilibrium}}$ owing to diffusion of the heavier species down the temperature gradient at a different mean velocity than the carrier gas atoms [12]. The mass losses, T, V_c and p^{app} calculated using the expression (3) for MBF_4 are listed in Tables 2–4. The measured data could be represented by the following least-squares expressions:

$$\log(p/\mathrm{Pa})\,[\mathrm{NaBF_4},\ \text{orthorhombic}] = 7.06(\pm 0.03) - 3734(\pm 360)\,(\mathrm{K})/T \tag{4}$$

$$\log(p/\mathrm{Pa})\,[\mathrm{NaBF_4},\ \text{monoclinic}] = 6.03(\pm 0.04) - 3192(\pm 80)\,(\mathrm{K})/T \tag{5}$$

Table 3
Vapour pressure of $RbBF_4$

Experiment number	T (K)	Mass loss[a] (μg) (cumulative)	V_c (dm^3)	Pressure (mPa)
1	550	34	12.414	39.3
2	555	46	12.414	53.2
3	566	56	12.414	64.7
4	576	74	10.909	97.3
5	581	86	12.414	99.4
6	592	106	10.909	139.4
7	602	142	12.414	164.1
8	613	188	12.414	217.3
9	622	180	9	287.0
10	622	217	10.909	285.4
11	622	248	12.414	286.7
12	629	260	12.414	300.5
13	641	320	10.909	420.9
14	655	442	12.414	510.9
15	676	600	10.909	789.2
16	697	936	12.414	1081.9

Ambient temperature is 297 K.
[a] Initial weight of the sample: 45 mg.

Table 4
Vapour pressure of $CsBF_4$

Experiment number	T (K)	Mass loss[a] (μg) (cumulative)	V_c (dm^3)	Pressure (mPa)
1	586	40	12.414	36.3
2	592	46	12.414	41.7
3	602	73	12.414	66.2
4	608	93	12.414	84.3
5	611	92	12.414	83.4
6	623	156	12.414	141.4
7	627	116	10.909	119.7
8	627	142	12.414	128.7
9	627	172	15	129.0
10	627	204	18	127.5
11	634	201	12.414	182.2
12	648	348	15	261.1
13	654	383	12.414	347.2
14	666	394	12.414	357.2
15	682	617	12.414	559.3
16	692	1030	15	772.7
17	703	868	10.909	895.4
18	705	920	10.909	949.0

Ambient temperature is 297 K.
[a] Initial weight of the sample: 45 mg.

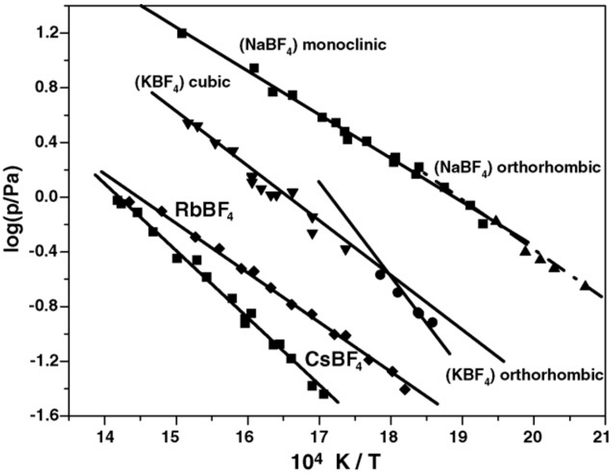

Fig. 4. Temperature dependence of equilibrium vapour pressure of MBF_4 (M = Na, K, Rb or Cs).

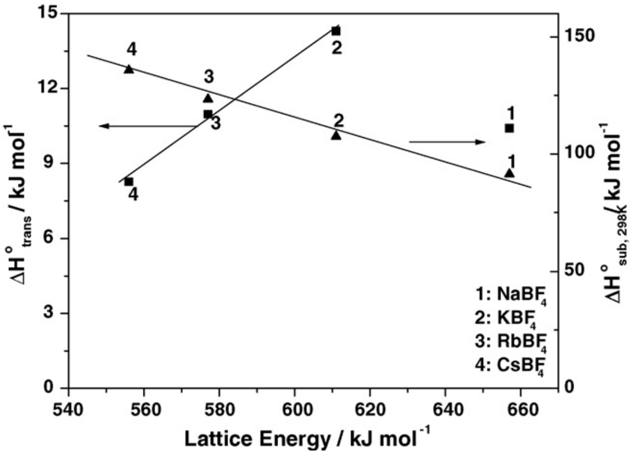

Fig. 5. Systematic trend in Enthalpy of transition (axis Y1) and enthalpy of sublimation at 298 K (axis Y2) with lattice energy of the alkali metal.

$$\log(p/\text{Pa})\,[\text{RbBF}_4] = 6.21(\pm 0.04) - 4020(\pm 87)\,(\text{K})/T \qquad (6)$$

$$\log(p/\text{Pa})\,[\text{CsBF}_4] = 7.77(\pm 0.04) - 5209(\pm 108)\,(\text{K})/T \qquad (7)$$

The vapour pressures of $NaBF_4$ were represented by the expressions (4) and (5) in the temperature ranges, 483–513 and 518–663 K, respectively. From these expressions a value of 527 K was obtained for the orthorhombic to monoclinic transformation temperature of $NaBF_4$, which is in good agreement with the value of 516 K cited in Ref. [9]. From the slopes of the above equations, values of 71.5 ± 1.5 and 61.1 ± 6.9 kJ mol^{-1} could be derived for the enthalpy of sublimation, $\Delta H^\circ_{\text{sub}}$ of orthorhombic and monoclinic phases of $NaBF_4$, respectively at the mean temperature of the measurements, i.e., 498 and 591 K, respectively. The difference between these results yielded a value of 10.4 kJ mol^{-1} for the enthalpy of phase transition of $NaBF_4$ which is in good agreement with the data reported in Ref. [9] as well as those obtained using DSC, in the present work. From the slopes of the Eqs. (6) and (7), the mean enthalpies of sublimation ($\Delta H^\circ_{\text{sub}}$) of $RbBF_4$ and $CsBF_4$ in the respective temperature ranges of 550–697 K and 586–705 K, were derived to be 77.0(±1.7) and 99.7(±2.1) kJ mol^{-1}.

The plots of $\log p$ against $1/T$ for the compounds MBF_4 (M = Na, Rb or Cs) are given in Fig. 4 along with our results for KBF_4 [4] for the purpose of comparison. It is clear from Fig. 4 that the vapour pressure of the alkali-metal decreases systematically from Na to Cs. A similar systematic trend is observed when enthalpies of transitions are plotted as a function of lattice energy of the alkali-metal fluroborates, as can be seen from Fig. 5 except for $NaBF_4$. In the case of $NaBF_4$, the phase transformation is from orthorhombic to monoclinic whereas in other alkali fluoroboates, the transformation is from orothorhombic to cubic and therefore the deviation exists. The present vapour pressure results of MBF_4 (M = Na, Rb or Cs) are compared in Table 5 along with the data on KBF_4 reported earlier from this laboratory.

3.3. ΔH°_{sub} of MBF_4 (M = Na, Rb or Cs)

In order to assess the temperature dependent errors in the present measurements, a third-law analysis of the vapour pressure data was carried out. The change in the Gibbs energy functions for the vapourization reaction was calculated using the Gibbs energy functions of each participating member of the reaction in the temperature range of the present measurements. Among the fluroborates studied the values of the free energy functions were available only for KBF_4 [10] and not for the other alkali-metal fluoroborates. For MBF_4 (M = Na, Rb or Cs) solids, the Gibbs energy functions were calculated using data given in Ref. [9]. Since data on the Gibbs energy functions for gaseous MBF_4 (M = Na, Rb or Cs) are not available in the literature, they were estimated by using respective thermal functions of MF(s) (M = Na, Rb or Cs) and BF_3 (g) [10,11] and considering

Table 5
Comparison of vapour pressure and enthalpy of sublimation at 298 K for MBF_4 (M = Na, K, Rb or Cs)

M	$\log p$ (Pa) = $A - B/T$ (K)		T range (K)	p (Pa) at 600 K	$\Delta H^\circ_{\text{sub,298 K}}$ (kJ mol^{-1})	Reference
	A	B				
Na	7.06	−3734	483–513	6.9	89.4	This work
	6.03	−3192	518–663	5.3	89.4	This work
K	8.16	−4892	538–560	1.0	104.5	[4]
	6.85	−4158	576–660	0.8	104.5	[4]
Rb	6.21	−4020	550–697	0.3	123.4	This work
Cs	7.77	−5209	586–705	0.1	135.7	This work

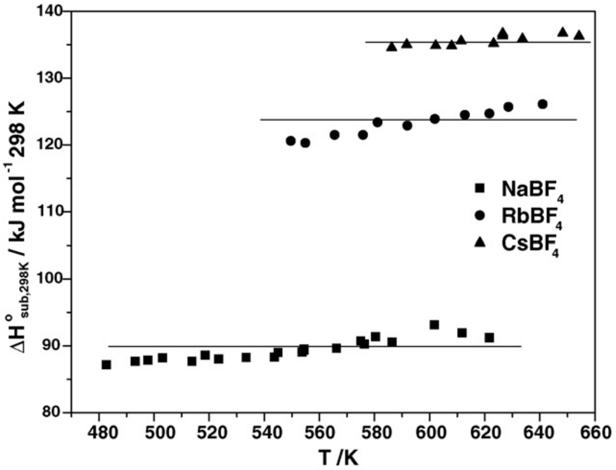

Fig. 6. Third-law plots for the enthalpy of sublimation of MBF_4 (M = Na, Rb or Cs).

the following chemical equilibrium:

$$MF(s) + BF_3(g) \rightarrow MBF_4(g)$$

The enthalpy of sublimation at 298 K was then derived using Eq. (8).

$$\Delta H^\circ_{sub}(MBF_4) = \Delta G^\circ_{vap} - T\Delta\left(\frac{G^\circ_T - H^\circ_{298}}{T}\right). \qquad (8)$$

For the vapourization process, the values of ΔH°_{sub} of $MBF_4(s)$ were calculated for the experimental data given in Tables 2–4. Plots of ΔH°_{sub} of $MBF_4(s)$ against experimental temperatures are shown in Fig. 6. The mean values of ΔH°_{sub} at 298 K were found to be 89.4 ± 1.5, 123.4 ± 1.9 and 135.7 ± 0.8 kJ mol^{-1} for $NaBF_4$, $RbBF_4$ and $CsBF_4$, respectively. The plots indicate that the systematic errors in the present measurements are insignificant. The values of ΔH°_{sub} at 298 K are compared in Table 5 and also plotted in Fig. 5. It is seen from Fig. 5 that there is a systematic increase in the enthalpy of sublimation at 298 K for the alkali-metal fluoroborates as the lattice energy of the alkali-metal fluroborates decreases.

4. Conclusion

The vapour pressures of solid $NaBF_4$ $RbBF_4$ and $CsBF_4$ were measured by transpiration technique for the first time. The enthalpy of sublimation of orthorhombic and monoclinic phases of $NaBF_4$ were derived to be 71.5 ± 1.5 kJ mol^{-1} (valid over 483–513 K) and 61.1 ± 6.9 kJ mol^{-1} (valid over 518–663 K), respectively. Likewise, enthalpy of sublimation of $RbBF_4$ and $CsBF_4$ were derived to be 77.0(±1.7) and 99.7(±2.1) kJ mol^{-1} valid over the temperature ranges 550–697 and 586–705 K, respectively. Third-law analysis of the experimental data yielded enthalpy of sublimation values of 89.4 ± 1.5, 123.4 ± 1.9 and 135.7 ± 0.8 kJ mol^{-1}, respectively for Na, Rb and Cs fluoroborates at 298 K.

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