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Note

DETERMINATION OF HEAT CAPACITY AND ENTHALPIES OF PHASE TRANSITIONS OF AMMONIUM, SODIUM AND POTASSIUM TETRAFLUOROBORATES

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Tetrafluoroborates, ABF_4 (where A is ammonium or alkali metal), have been widely investigated recently due to their use in a number of processes.

A specific feature of ABF_4 is the presence of polymorphous transitions above room temperature, but the literature provides differing data on the temperatures and enthalpies of tetrafluoroborate transitions [1–3]. Data on direct measurements of the heat capacities of these compounds above room temperature are completely missing.

The aim of this paper is to study the heat capacity and enthalpy of phase transitions of NH_4BF_4, $NaBF_4$ and KBF_4 compounds.

METHODS

NH_4BF_4 was prepared by the interaction of ammonium hydrogen fluoride, NH_4HF_2 (AR grade), with H_3BO_3 (suprapur) keeping them at a temperature of about 523 K for 3–4 h.

$NaBF_4$ was prepared by recrystallization of a reagent (AR grade) from aqueous solution containing hydrofluoric acid (suprapur).

KBF_4 (AR grade) was previously remelted at 823 K in a graphite crucible in a purified argon atmosphere.

X-ray diagrams of the samples obtained were in good agreement with those known from the literature.

Heat capacity measurements were conducted by means of the dynamic triple heat bridge (THB) method [4] with an error not exceeding 3%. The samples were pressed into polycrystal cylinders of 1.2–2.0 g mass. Copper (99.95% purity) was used as a reference. Its heat capacity values were taken from ref. 5. The heating rate was 2 K min^{-1}.

Investigation of the above tetrafluoroborates was also carried out on a quantitative DTA apparatus of original construction [6]. The apparatus was previously calibrated during heating with temperatures and phase transition

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enthalpies of a number of metals and salts. The error in determination of enthalpy amounted to 5–7%. Powdery sample masses amounted to about 1.5–2.0 g. Calcined aluminium oxide was used as a reference. The heating rate was 5 K min^{-1}.

RESULTS AND DISCUSSION

Heat capacity measurement data are given in Fig. 1.

As can be seen from Fig. 1, heat capacity anomalies with maxima at 480 ± 2 K for NH_4BF_4, 520 ± 2 K for $NaBF_4$ and 562 ± 2 K for KBF_4 are due to changes in the structure of the tetrafluoroborates.

We calculated their transition enthalpy by integration of the $C_p(T)$ dependence in the transition region, ΔH (kJ mol^{-1}): $\Delta H(NH_4BF_4) = 10.0 \pm 0.4$, $\Delta H(NaBF_4) = 8.4 \pm 0.4$, $\Delta H(KBF_4) = 14.2 \pm 0.4$.

Temperatures and enthalpies of NH_4BF_4, $NaBF_4$ and KBF_4 phase transitions, which were determined on the basis of heating curves by the quantitative DTA method, within experimental error, agree with the values calculated using heat capacity measurements. The enthalpy values are: $\Delta H(NH_4BF_4) = 9.2 \pm 0.7$, $\Delta H(NaBF_4) = 8.1 \pm 0.6$, $\Delta H(KBF_4) = 14.2 \pm 0.8$ kJ mol^{-1}.

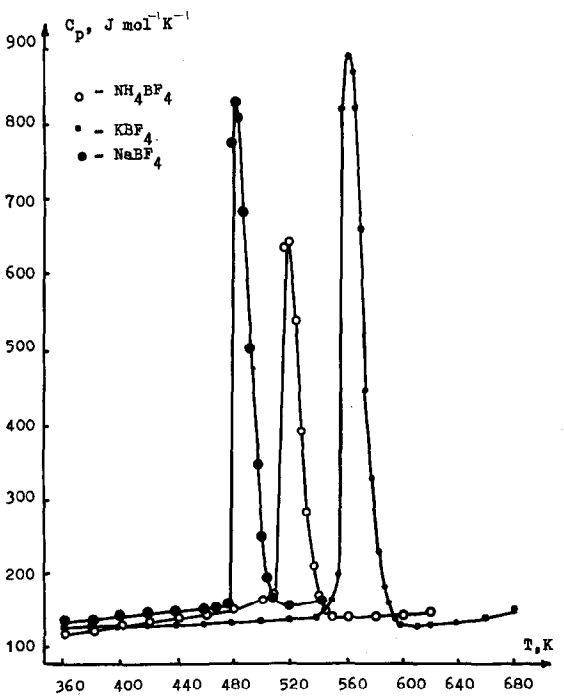

Fig. 1. Heat capacity of NH_4BF_4, $NaBF_4$ and KBF_4 compounds.

Previously publsihed work [3] describes the transition process from the low-temperature into a high-temperature modification of $NaBF_4$ and shows an explicit difference in temperature and the phase transition enthalpy value, which were measured during the process of heating and cooling of a sample. For all compounds studied, the DTA method also revealed that the values of phase transition enthalpy calculated from the heating curves were approximately 1.5–2.0 kJ mol^{-1} less than those found from the cooling curves.

In order to gain more accurate data on the thermal behaviour of $NaBF_4$ and to study the peculiarities of the KBF_4 phase transition process, we carried out measurements of the total conductivity of these compounds. Measurements were carried out by AC technique (1000 Hz) on pressed polycrystal samples of 90% X-ray density using graphite contacts. It is shown that the phase transition process is accompanied by a considerable increase in electrical conductivity of the compounds (10^{-6} to 10^{-3} ohm^{-1} cm^{-1}). In the case of $NaBF_4$ we observed a difference in the phase transition temperature for heating and cooling the sample: T(heat) = 531 ± 2 K; T(cool) = 495 ± 2 K. We also found a similar behaviour for KBF_4: T(heat) = 562 ± 2 K; T(cool) = 543 ± 2 K.

Thus, the tetrafluoroborate phase transition process is of complex character and the known differences in temperature and phase transition enthalpy may be due to different experimental conditions.

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