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*Short Communication*

# SYNTHESIS, THERMAL INVESTIGATIONS AND KINETIC DATA OF $Zn(BF_4)_2 \cdot 6H_2O$

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The thermal dehydration and decomposition of $Zn(BF_4)_2 \cdot 6H_2O$ have been studied by TG, DTA and DSC analyses. It is found that the dehydration occurs in two steps. Following the experimental results a thermal decomposition scheme of the compound under investigation is proposed. The enthalpies of dehydration have been determined as well as the formal kinetic parameters are presented.

***Keywords:*** *DSC, DTA, kinetic parameters, phase transitions, zinc(II) tetrafluoroborate hexahydrate*

## Introduction

There are scarce data about the synthesis and properties of tetrafluoroborates in the literature. Phase transition, thermal decomposition and kinetic parameters of $Cd(BF_4)_2 \cdot 6H_2O$ have been studied in [1]. Crystalline compounds of the type $[M(H_2O)_6](BF_4)_2$, where *M*=Mn, Fe, Co, Ni, Zn have been prepared and TG, DTA curves presented in [2]. Synthesis and dehydration process of $[Cd(H_2O)_6](BF_4)_2$ is described in [3]. Only TG, DTA curves of hydrates and ammoniacates of zinc-, cadmium- and copper tetrafluoroborates are presented in [4]. There are several recent publications dealing with the properties of 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) [5] and 1-butylpiridinium tetrafluoroborate ($BPBF_4$) [6]. Furthermore, new complexes $[Co(MH)_2(Thio)_2]BF_4 \cdot H_2O$ and $[Co(DH)_2(NH_3)_2]BF_4$ have been synthesized and their crystal structure has been determined [7].

The aim of the present study is to prepare a compound with defined composition and to investigate the thermal decomposition of $Zn(BF_4)_2 \cdot 6H_2O$, the kinetic parameters of the dehydration process as well as the enthalpy changes accompanying the most important phase transitions determined by DSC.

## Experimental

Zinc(II) tetrafluoroborate hexahydrate was synthesized by treating zinc(II) oxide (Merck p.a.) with tetrafluoroboric acid (35%, Merck p.a.) and stirring at ambient temperature. The resulting solution was filtered and concentrated by vacuum at 328 K for 6 h. The colorless crystals were obtained after cooling and dried in a desiccator over $CaCl_2$.

The compound was characterized by quantitative analysis: $Zn^{2+}$ complexometrically and $BF_4^-$ according to [8].

Thermogravimetric (TG) and differential thermal analysis (DTA) measurements were performed using a Paulik–Paulik–Erdey MOM OD-101 apparatus at a heating rate of 3 K $min^{-1}$ and a sample mass of 184 mg up to 673 K. Differential scanning calorimetric (DSC) measurements were performed on a Perkin-Elmer DSC-4 apparatus in the temperature range 303–483 K at a heating rate of 3 K $min^{-1}$ and sample mass of 6.4 mg. The X-ray analysis of the solid products of the decomposition was performed on a Zeiss TUR-M 62 apparatus with $CuK_\alpha$ radiation.

## Results and discussion

The TG and DTA curves of $Zn(BF_4)_2 \cdot 6H_2O$ are shown in Fig. 1. A small endothermic peak of the DTA curve in the temperature range 333–353 K, which is not related to any mass loss in TG curve was observed. It corresponds to a phase transition in the solid-state. The next endothermic process of complex character in the range 353–443 K was observed. It is related to the dehydration of $Zn(BF_4)_2 \cdot 6H_2O$ to $Zn(BF_4)_2 \cdot 4H_2O$ at $T_{max}$=413 K.

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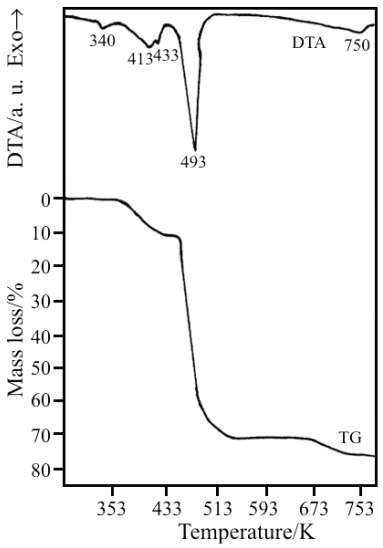


**Fig. 1** TG and DTA curves of $Zn(BF_4)_2 \cdot 6H_2O$

$$Zn(BF_4)_2 \cdot 6H_2O \rightarrow Zn(BF_4)_2 \cdot 4H_2O + 2H_2O$$

The decrease in sample mass for two water molecules is 11.1%, which is an, agreement with the value calculated – 10.4%. The small endothermic effect in the DTA curve at $T_{max}$=433 K which is not connected with any mass loss by TG, corresponding to the sample melting:

$$Zn(BF_4)_2 \cdot 4H_2O_{(s)} \rightarrow Zn(BF_4)_2 \cdot 4H_2O_{(l)}$$

The endothermic peak observed in DTA curve at $T_{max}$=493 K is connected with dehydration of $Zn(BF_4)_2 \cdot 4H_2O$ at a liquid phase and simultaneous decomposition of $Zn(BF_4)_2$ to $BF_3$ and $ZnF_2$.

$$Zn(BF_4)_2 \cdot 4H_2O_{(l)} \rightarrow ZnF_2 + 2BF_3 + 4H_2O$$

The X-ray diffraction patterns for the intermediate phase confirm the formation of $ZnF_2$ (Fig. 2a) [9].

The decrease in sample mass by TG during the whole process of thermal dehydration and decomposition is 70.0%, which was compared with that calculated – 70.2%.

The last small endothermic peak of the DTA curve at $T_{max}$=750 K is connected with partial oxidation of $ZnF_2$ to ZnO. The phase isolated at 750 K is proved by X-ray diffraction data in Fig. 2b. In this figure reflections for both $ZnF_2$ and ZnO [10] can be seen.

DSC curve for $Zn(BF_4)_2 \cdot 6H_2O$ as registered on heating rate of 3 K $min^{-1}$ in the temperature range of 300–500 K is shown in Fig. 3. A large endothermic process is observed in the range 353–408 K with

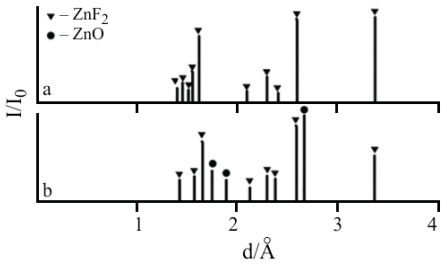


**Fig. 2** Schematic diagram of the X-ray diffraction lines for: a – intermediate phase at 593 K, b – phase at 750 K

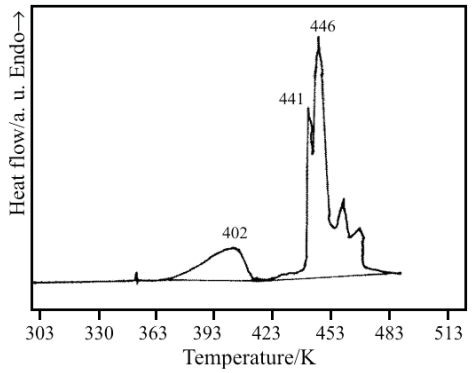


**Fig. 3** DSC curves of $Zn(BF_4)_2 \cdot 6H_2O$

$T_{max}$=402 K. It is connected with the 'solid–solid' transformation, releasing and evaporation two water molecules, thus forming $Zn(BF_4)_2 \cdot 4H_2O$. The value of $\Delta H$ for this temperature range is 141.9 kJ $mol^{-1}$. An endothermic process of complex character is observed in the range 408–483 K. The peak at 441 K is connected with the process of melting $Zn(BF_4)_2 \cdot 4H_2O$ which is in agreement with the data from DTA curve. Subsequent heating of the melted sample leads to the dehydration and evaporation of four water molecules, thus producing an anhydrous salt, which decomposes immediately. The total enthalpy for this complex process is $\Delta H_{Ph.tr.}$=487.6 kJ $mol^{-1}$. The basic part of this value is due to $\Delta H_{vap}$ of water of crystallization 38.63·4=154.52 kJ $mol^{-1}$ [11].

Based on TG data, the kinetics of the dehydration and decomposition in the temperature range 333–433 and 443–533 K was characterized in the isothermal mode. A computer program was used, including 25 kinetic equations described in the literature, for which – upon comparison with experimental data from the TG curve – the value of $E^*$ and the correlation coefficient are obtained [12]. The kinetic data show that the both processes take place in the diffusion area (Table 1).

**Table 1** Kinetic parameters of the thermal decomposition of $Zn(BF_4)_2 \cdot 6H_2O$

| Temperature range/K | Kinetic equation | $E^*$/kJ $mol^{-1}$ | $R$ |
|---|---|---|---|
| 333–433 | $F=[(1-\alpha)^{-1/3}-1]^{-1}$ | 73.9 | 0.9504 |
| 443–533 | $F=[(1-\alpha)^{-1/3}-1]^{-1}(1-\alpha)^{4/3}$ | 290.2 | 0.9876 |

## Conclusions

The scheme of thermal dehydration and decomposition of $Zn(BF_4){\cdot}6H_2O$ is proposed.

- The endothermic peak of the DTA curve in the temperature range 333–353 K corresponds to a phase transition in the solid-state.
- The dehydration process starts at $T_{max}$=413 K and $Zn(BF_4){\cdot}4H_2O$ is obtained.
- $Zn(BF_4){\cdot}4H_2O$ melts at $T_{max}$=433 K.
- Dehydration at $T_{max}$=493 K of $Zn(BF_4){\cdot}4H_2O$ in a liquid phase and simultaneous decomposition to $BF_3$ and $ZnF_2$ are observed.
- Partial oxidation of $ZnF_2$ to ZnO.

The kinetic data of dehydration and decomposition in the temperature range 333–433 and 443–533 K are defined.

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