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THERMAL DECOMPOSITION OF AMMONIUM FLUOROFERRATES $(NH_4)_xFeF_{2x}$ $(2 \le x \le 3)$

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Abstract

Different ammonium fluoroferrates $(NH_4)_xFeF_{2x}$ $(2 \le x \le 3)$ have been investigated. The thermal decomposition of the compounds obtained can be interpreted by their identical crystal structures (cryolite type). The decomposition products of all ammonium fluoroferrates formed in initial stage are isostructural of NH_4FeF_4. The decomposition is accompanied by the partial reduction of Fe(III) to Fe(II) by ammonium isolated. The end product of the thermal decomposition is FeF_2 and FeF_3 mixture.

Keywords: ammonium fluoroferrates, thermal decomposition

Introduction

The thermal decomposition of ammonium hexafluoroferrate $(NH_4)_3FeF_6$ is known [1]. The process was carried out in dry nitrogen, it can be expressed by the scheme:

$$(NH_4)_3FeF_6 \xrightarrow{280^\circ C} NH_4FeF_4 \xrightarrow{410^\circ C} FeF_3.$$

However, by Menz and Bentrup [2], ammonium hexafluorochromate to be isostructural with $(NH_4)_3FeF_6$ decomposes in quasi-isobaric conditions via NH_4CrF_4 to CrF_3 and additional Cr_2F_5 is formed caused by the partial reduction of CrF_3 by NH_3. We suppose that the thermal decomposition of $(NH_4)_3FeF_6$ is accompanied by the same effect because there is a mobile equilibrium of Fe(III) $\rightleftarrows$ Fe(II).

In present work different ammonium fluoroferrates were obtained and detailed studied of thermal decomposition in quasi-isobaric conditions was carried out.

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Experimental

The chemical analysis data and synthetic methods of ammonium fluoroferrates are listed in Table 1. The products formed were analysed for ammonia, fluorine and metal contents. Ammonia was determined by the Kjeldahl method, fluorine by distillation of H_2SiF_6 and ferrum by atomic absorption method.

TG, DTG and DTA curves were recorded with a Q 1000 derivatograph. 200–300 mg of powder samples were heated in a Pt-crucible in the range 25–500°C at a constant rate of 5 and 10 deg·min^{-1}.

The IR spectra of the complexes formed were obtained using a Specord M 80 spectrophotometer over the range 4000–400 cm^{-1}.

The diffractograms of ammonium fluoroferrates were recorded with a DRON-3 diffractometer by CuK_α (with monochromator) or FeK_α radiation.

Results and discussion

Interaction of Fe_2O_3 with NH_4HF_2

Ammonium hexafluoroferrate $(NH_4)_3FeF_6$ was first prepared by the reaction of the metal bromide with ammonium fluoride in methanol [1]. We obtained $(NH_4)_3FeF_6$ by a more easy method by caking of Fe_2O_3 with NH_4HF_2 at 200°C (Fig. 1):

$$Fe_2O_3 + 6NH_4HF_2 \rightarrow 2(NH_4)_3FeF_6 + 3H_2O \qquad (1)$$

The reaction takes place in molted NH_4HF_2 (exothermic peak at 130°C); mass loss is 10.6%, that corresponds to a mass loss 10.8% calculated for reaction 1. The chemical analysis data are given in Table 1. $(NH_4)_3FeF_6$ is crystallized in cubic form (cryolite type), a= 9.10 Å.

The next peak at 235°C is thermal decomposition of $(NH_4)_3FeF_6$. The mass loss may be due to the elimination of 0.5 mol of NH_4F and formation of the intermediate compound $(NH_4)_{2.5}FeF_{5.5}$, which was not found by Shinn and coauthors [1]. The calculated ammonium fluoride loss is 14.4% (obs. 15.0%). The compound formed is isostructural with initial $(NH_4)_3FeF_6$. At 330°C a larger endothermic effect was observed, a mass loss is equivalent of 1.5 mol NH_4F and NH_4FeF_4 formation (Δm_{obs}= 39.9; Δm_{calc}= 40.2%). The further heating was accompanied by endothermic effects at 400, 445, 490°C, what may be due to the elimination of NH_4F (NH_3, HF) and partial reduction of Fe(III) to Fe(II) by ammonia isolated, as in the case of $(NH_4)_3CrF_6$. According to X-ray data the end-product is FeF_3 and FeF_2 mixture. The stoichiometry of this interaction can be expressed by the following scheme:

Table 1 Ammonium fluoroferrates

N° Sp.	Compound	Synthetic method	Content/mass.%					
			Found			Calculated		
			NH_4	Fe	F	NH_4	Fe	F
1	$(NH_4)_3FeF_6$	$Fe_2O_3+6NH_4HF_2$ cake, 200°C	23.8	25.0	50.3	24.11	25.00	50.89
2	$(NH_4)_{2.5}FeF_{5.5}$	Decomposition of $(NH4)_3FeF_6$ at 270°C	21.9	27.0	50.2	21.90	27.25	50.85
3	$(NH_4)_{2.8}FeF_{5.6}$	Evaporation of $(NH4)_3FeF_6$ aqueous solution	22.9	25.4	48.4	23.68	26.32	50.00
4	$(NH_4)_{2.5}FeF_5$	Monocrystals from aqueous solution of cake of pyrrhotine with NH_4HF_2	22.8	28.7	48.9	22.96	28.57	48.47
5	$(NH_4)_{2.4}FeF_{4.8}$	Solid after leaching of cake pyrrhotine with NH_4HF_2	21.5	28.0	45.5	22.69	29.41	47.90

$$Fe_2O_3 + 6NH_4HF_2 \rightarrow FeF_3 + FeF_2 + 0.165N_2 + 5.67NH_3 + 7HF + H_2O$$

$$(\Delta m = 58.8\%) \qquad (2)$$

The mass loss on the final step depends on degree of Fe(III) reduction.

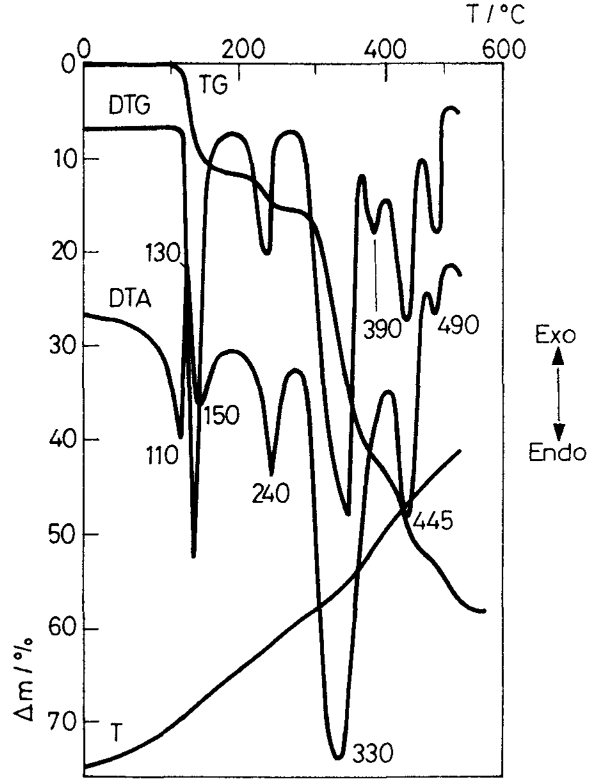

Fig. 1 DTA/TG curves of mixture of α-Fe_2O_3+$6NH_4HF_2$ in labirinth crucible

Thermal decomposition of $(NH_4)_xFeF_{2x}$ $(2 \leq x \leq 3)$

$(NH_4)_3FeF_6$ is water-soluble (~50 g/l). By evaporation of the solution the crystals formed have no $(NH_4)_3FeF_6$ composition: modulus of solid (NH$_4$:Fe ratio) is less than 3. Cox and Sharpe [3] observed that the cubic $(NH_4)_{2.6}FeF_{5.6}\cdot 0.4H_2O$ was the only compound precipitated from the solution of ammonium hexafluoroferrate. An analogous fact takes place also in the case of cryolite Na_3AlF_6. The modulus of solids obtained from aqueous solutions of cryolite was not high than 2.8–2.9 [4]. Brosset [5] explained this fact by the partial substitution of fluorine by water molecules with displacing from the lattice an equivalent number of alkaline metal. However, we can not apply such argument in our case. From aqueous solutions of $(NH_4)_3FeF_6$ the cubic $(NH_4)_{2.8}FeF_{5.6}$ (Sp.3, Table 1) falls out. There are not crystallization water bands in its IR-spectrum (Fig. 2). In the present case the formal oxidation state of ferrum is lower than 3 and it is equivalent to the modulus of solid (2.8). This appears to be due to a partial reduction of Fe(III) to Fe(II) in ammonium fluoroferrate solutions. The complex compositions depend on Fe(III): Fe(II) ratio.

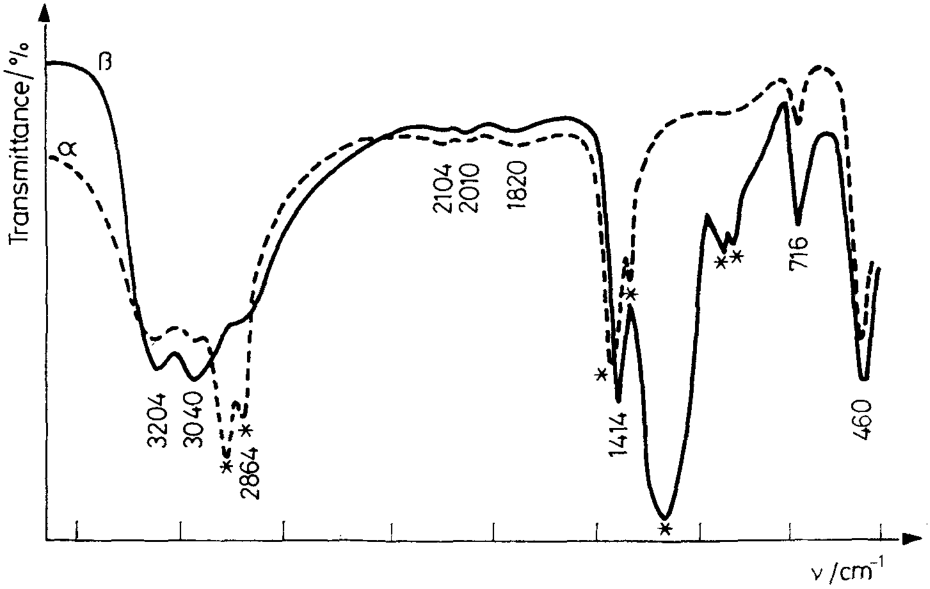

Fig. 2 Infrared spectra of ammonium fluoroferrates $(NH_4)_xFeF_{2x}$: a - in Nujol mull, b - in Flurine oil

The ammonium fluoroferrates with the lower modulus value were obtained by water leaching of the cake of pyrrhotine ($Fe_{1-x}S$) with ammonium bifluoride (solid:liquor= 1:4). The solid after leaching was a composition $(NH_4)_{2.4}FeF_{4.8}$ (Sp.5). The octahedral crystals $(NH_4)_{2.5}FeF_5$ (Sp.4) of a good quality were precipitated by slow evaporation of the aqueous solution. The thermal decomposition of the former solid under quasi-isobaric conditions leads only to FeF_2. In the second case the mixture of FeF_2 and FeF_3 was formed. The schemes of these reactions can be expressed as follows:

$$(NH_4)_{2.4}FeF_{4.8} = FeF_2 + 0.065N_2 + 2.27NH_3 + 2.8HF \qquad (3)$$

$$(NH_4)_{2.5}FeF_5 = 0.75FeF_2 + 0.25FeF_3 + 0.04N_2 + 2.42NH_3 + 2.75HF \qquad (4)$$

The thermal decomposition of $(NH_4)_{2.8}FeF_{5.6}$ results in also FeF_2 and FeF_3 mixture:

$$(NH_4)_{2.8}FeF_{5.6} = 0.3FeF_2 + 0.7FeF_3 + 0.016N_2 + 2.77NH_3 + 2.9HF \quad (5)$$

The mass loss data by thermal decomposition of $(NH_4)_xFeF_{2x}$ (T= 500°C) are shown in Table 2.

Table 2 Results of thermal decomposition of ammonium fluoroferrates at 500°C

Compound	Mass loss/%	
	Calc.	Found
$(NH_4)_3FeF_6$	51.3	52.0
$(NH_4)_{2.8}FeF_{5.6}$	49.6	50.6
$(NH_4)_{2.5}FeF_5$	49.6	49.2
$(NH_4)_{2.4}FeF_{4.8}$	50.6	50.3

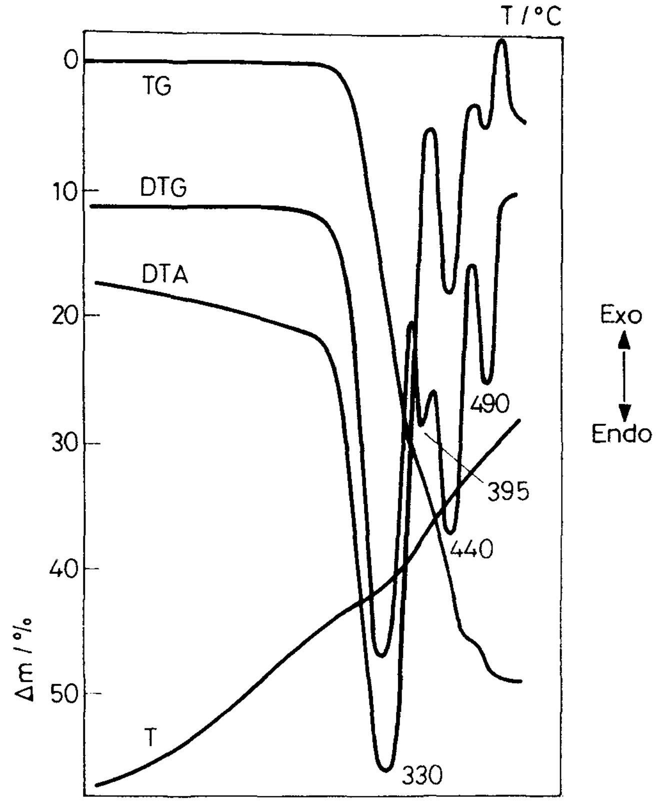

Fig. 3 DTA/TG curves of ammonium fluoroferrates $(NH_4)_xFeF_{2x}$ (x=2.5) in labirinth crucible

The data showed that the thermal decomposition of ammonium fluoroferrates is accompanied by partial reduction of Fe(III) with ammonium isolated. The composition of complexes can be expressed as $(NH_4)_xFeF_{2x}$ where $2 \leq x \leq 3$. The decomposition of the compounds investigated is practically identical which seems to be closely related with their identical structure. All the complexes formed are crystallized in cubic form (cryolite type). During the first step of decomposition at 330°C (Fig. 3) the ammonium fluoroferrates isostructural with NH_4FeF_4 are produced. This structure retains up to the final stage when the FeF_2 and FeF_3 mixture is formed. Such a mixture can be used for obtaining of crystalline form of FeF_3 by fluorination with F_2 at 350–400°C. The FeF_3 crystals were previously prepared with a more difficult method at 1000°C in unaqueous HF.

References

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Zusammenfassung — Es wurden verschiedene Ammoniumfluoroferrate $(NH_4)_xFeF_{2x}$ $(2 \leq x \leq 3)$ untersucht. Die thermische Zersetzung der erhaltenen Verbindungen kann anhand ihrer gleichen Kristallstruktur (Kryolith-Typ) erklärt werden. Alle beim ersten Zersetzungsschritt geformten Ammoniumfluoroferrate sind isostrukturell mit NH_4FeF_4. Die Zersetzung wird von einer teilweisen Reduktion von Fe(III) zu Fe(II) begleitet. Das Endprodukt der thermischen Zersetzung ist ein Gemisch aus FeF_2 und FeF_3.