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THERMAL BEHAVIOUR OF AMMONIUM OXOFLUOROTITANATES(IV)

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Abstract

The thermal behaviour of ammonium oxofluorotitanates $(NH_4)_3TiOF_5$, $(NH_4)_2TiOF_4$ and NH_4TiOF_3 was investigated by thermoanalytical, X-ray and IR spectroscopic methods. The first decomposition stages under quasi-isobaric conditions are characterized by the formation of $(NH_4)_2TiF_6$ and ammonium oxofluorotitanate with the less content of ammonium and fluorine than in the initial compound. The decomposition process is accompanied by the Ti(IV) reducing due to ammonia evolved. The new ammonium oxofluorotitanate of high volatility was isolated and characterized. Ammonium-containing non-stoichiometric titanium oxyfluorides are the final products of thermal decomposition of ammonium oxofluorotitanates.

Keywords: ammonium oxofluorotitanates, quasi-isobaric thermal analysis, thermal decomposition

Introduction

Very little is known about the thermal decomposition of ammonium oxofluorotitanates. Patarin *et al.* [1] reported the two-stage decomposition of $(NH_4)TiOF_4$ in dry argon:

$$(NH_4)_2TiOF_4 \xrightarrow{125-380\,^{\circ}C} TiOF_2 \xrightarrow{380-390\,^{\circ}C} TiO_2 \text{ (anatase).}$$

We synthesized a series of ammonium oxofluorotitanates $(NH_4)_3TiOF_5$, $(NH_4)_2TiOF_4$ and NH_4TiOF_3 during the hydrolysis of $(NH_4)_2TiF_6$ at pH=7–9 and isolated them in a pure form. Ammonium oxopentafluorotitanate was obtained for the first time [2]. In the present paper we describe a path for the thermal degradation of the complexes synthesized and characterize the intermediates.

Experimental

The thermal analysis was carried out with the Derivatograph Q-1500 D MOM Budapest. The following parameters were used:

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Sample mass: 200–400 mg, dynamic heating rate: 5 K min^{-1}, quasi-static heating rate: 2 K min^{-1}; reference: Al_2O_3; air and helium atmospheres, sensitivities for TG=200 mg and DTA=500 μV.

The samples were prepared and characterized as described in [2]. All intermediates and final products of the decomposition reactions were characterized by X-ray analysis (Diffractometer DRON-2, CuK_α radiation), IR (Nicolet Protégé 460 spectrometer, KBr pellets) and ESR spectroscopy (ERS-231 technique) at 300–500 K, and by chemical analysis. Ammonium was determined by Kjeldahl method, fluorine by distillation of H_2SiF_6 and followed by titration with $Th(NO_3)_4$. Titanium was analyzed by atomic absorption after the sample dissolution in HCl or gravimetrically after removing fluoride ions by boiling with H_3BO_3 and NH_4OH. Titanium reduced in the presence of fluoride-ions was titrated as indicated in [3].

Results and discussion

The thermal decomposition of $(NH_4)_3TiOF_5$ under quasi-isobaric conditions (in conic Pt-labyrinth crucible) is shown in Fig. 1a. Its degradation in Q-regime (quasi-isothermal and quasi-isobaric conditions) is presented in Fig. 1b. In the first step (200°C), no HF evolution was detected in accordance with the mass loss of 11.9% and fluorine content in the residue of 51.2 (50.83% calculated value). Since, according to X-ray powder data, the product was a mixture of $(NH_4)_2TiF_6$ and $(NH_4)_2TiOF_4$, the process is described as follows:

$$2(NH_4)_3TiOF_5 \rightarrow (NH_4)_2TiF_6 + (NH_4)_2TiOF_4 + 2NH_3 + H_2O \ (\Delta m=12.21\%)$$

The next step (270°C, Fig. 1) is connected with the thermal behaviour of $(NH_4)_2TiOF_4$ (Fig. 2), because the decomposition of $(NH_4)_2TiF_6$ under quasi-isobaric conditions begins at 380°C [4]. The first three steps of thermal decomposition of $(NH_4)_2TiOF_4$ are caused by reconstruction of chain-structure of this compound and formation of $(NH_4)_2TiF_6$ with isolated (TiF_6)-octahedra and layered NH_4TiOF_3. The process is accompanied with NH_3 and H_2O evolution that is in good agreement with the observed value of mass loss 10.0% (Fig. 2):

$$3(NH_4)_2TiOF_4 \rightarrow (NH_4)_2TiF_6 + 2NH_4TiOF_3 + 2NH_3 + H_2O \ (\Delta m=9.85\%)$$

In Fig. 1 this reaction is characterized by 4.1% mass loss that is in agreement with theoretical one of 4.08%. The analytical data are close to the composition $(NH_4)_2TiF_6$+ $2NH_4TiOF_3$.

NH_4TiOF_3 (Fig. 3) exhibits similar thermal behaviour in the first steps also giving $(NH_4)_2TiF_6$ and oxofluorocomplex with the less contents of ammonium and fluorine. This compound has a structure relative to NH_4TiOF_3 and contains the detectable amount of the reduced titanium. There is no loss of fluorine in this case either:

$$4NH_4TiOF_3 \rightarrow (NH_4)_2TiF_6 + 3(NH_4)_{0.3}TiOF_2 + 0.15N_2 + 0.8NH_3 + H_2O \ (\Delta m=6.44\%)$$

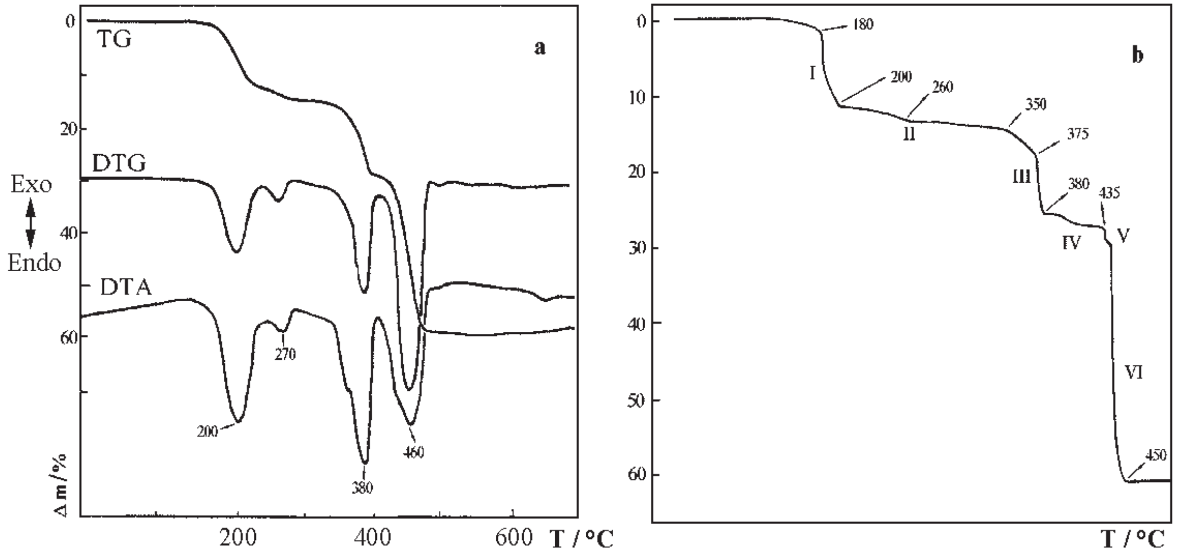

Fig. 1 Thermal decomposition of $(NH_4)_3TiOF_5$: a – quasi-isobaric conditions, b – quasi-isothermal and quasi-isobaric conditions
I. $2(NH_4)_3TiOF_5 \rightarrow (NH_4)_2TiF_6+(NH_4)_2TiOF_4+2NH_3+H_2O$; II.$3(NH_4)_2TiOF_4 \rightarrow (NH_4)_2TiF_6+2NH_4TiOF_3+2NH_3+H_2O$
III. $(NH_4)_2TiF_6 \xrightarrow{0.4H_2O} (NH_4)_{0.9}TiO_{0.4}F_{4.1}+1.1NH_3+1.9HF$; IV. $4NH_4TiOF_3 \rightarrow (NH_4)_2TiF_6+3(NH_4)_{0.3}TiOF_2+0.15N_2+0.8NH_3+H_2O$
V. $(NH_4)_2TiF_6 \xrightarrow{0.4H_2O} (NH_4)_{0.9}TiO_{0.4}F_{4.1}+1.1NH_3+1.9HF$; VI. sublimation of $(NH_4)_{0.9}TiO_{0.4}F_{4.1}$

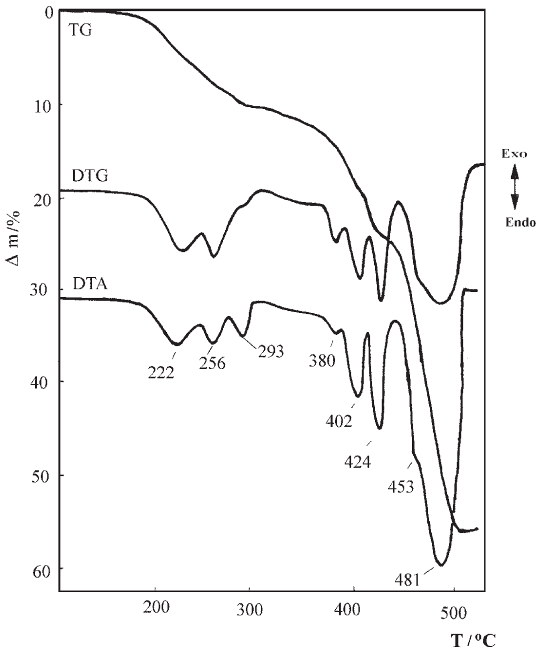

Fig. 2 Thermal curves of $(NH_4)_2TiOF_4$

The next step (437°C) is connected with the evolution of approximately $1.1NH_4F$ (Δm=7.2% on TG curve, that matches to the calculated value of 7.3%). The process described is proved by analytical data of the residue (by ammonium and fluorine contents). This reaction takes place at 350–380°C in the case of $(NH_4)_3TiOF_5$ and $(NH_4)_2TiOF_4$ and relates to $(NH_4)_2TiF_6$ decomposition. It is accepted that thermal behaviour of $(NH_4)_2TiF_6$ is described by the following reaction scheme:

$$(NH_4)_2TiF_6 \rightarrow NH_4TiF_5 \rightarrow TiF_4 \quad [4\text{–}7]$$

However, the intermediate reported as NH_4TiF_5 contained oxygen (see its IR spectrum, Fig. 4a; the vibration at 859 cm^{-1} can be attributed to Ti=O stretching bond). It was very hygroscopic and not stable in air forming $(NH_4)_{0.8}TiOF_{2.8}$ which is isostructural with NH_4TiOF_3. We managed to isolate this compound in a pure single crystal form from the gas phase at 300°C in argon during the decomposition of $(NH_4)_2TiF_6$. Its X-ray data are given in Table 1 and very similar to those presented in [4]. Moreover, it is isostructural with NH_4VOF_3 [8]. Chemical analyses of this intermediate gave the ratio $F:NH_4$ not to be exceeded 4.6, so its composition was close to $(NH_4)_{0.9}TiO_{0.4}F_{4.1}$. Returning to Fig. 1a the cumulative process in the third step of thermal degradation of $(NH_4)_3TiOF_5$ can be expressed as follows:

$$(NH_4)_3TiOF_5 \rightarrow (NH_4)_{0.9}TiO_{0.4}F_{4.1} + 2.1NH_3 + 0.9HF + 0.6H_2O \; (\Delta m = 30.30\%).$$

Table 1 Powder pattern of $(NH_4)_{0.9}Ti_{0.4}F_{4.1}$

d/Å	*I*/*I*o	*d*/Å	*I*/*I*o
6.86	14	2.530	5
5.79	100	2.430	5
4.87	43	2.260	5
4.32	7	2.100	5
3.72	7	2.070	9
3.48	53	1.993	5
3.44	51	1.895	5
3.19	16	1.834	4
3.11	7	1.810	7
2.90	5	1.719	4
2.73	4	1.628	4
2.62	4	1.605	4
2.61	4		

The mass loss observed is 30.0 under quasi-isobaric conditions and 26.0% under quasi-isothermal conditions (Fig. 1b) that can be explained by partial refluorination of the intermediate with HF released. Really, this stage (III) is connected with the thermal decomposition of $(NH_4)_2TiF_6$ formed from $(NH_4)_3TiOF_5$ and $(NH_4)_2TiOF_4$.

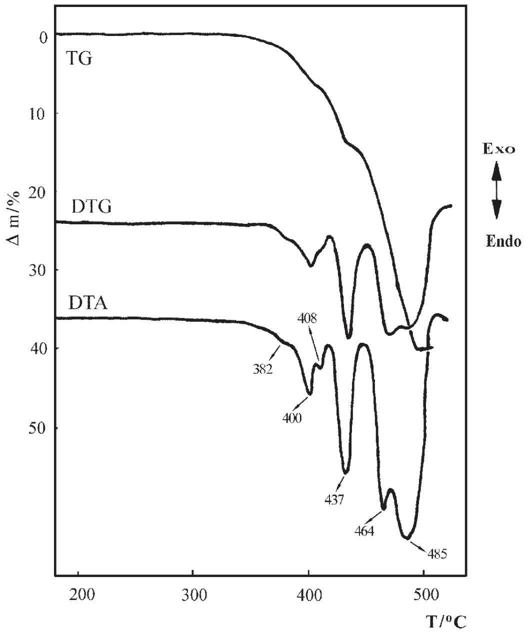

Fig. 3 Thermal curves of NH_4TiOF_3

The same reaction is observed in the fifth step and relates to the thermal degradation of $(NH_4)_2Ti\ F_6$ arisen from NH_4TiOF_3. $(NH_4)_{0.9}TiO_{0.4}F_{4.1}$ has high volatility, so the final degradation of all ammonium oxofluorotitanates investigated is accompanied by the evolution of titanium into gas phase that is corroborated by mass loss (Table 2) at 500°C.

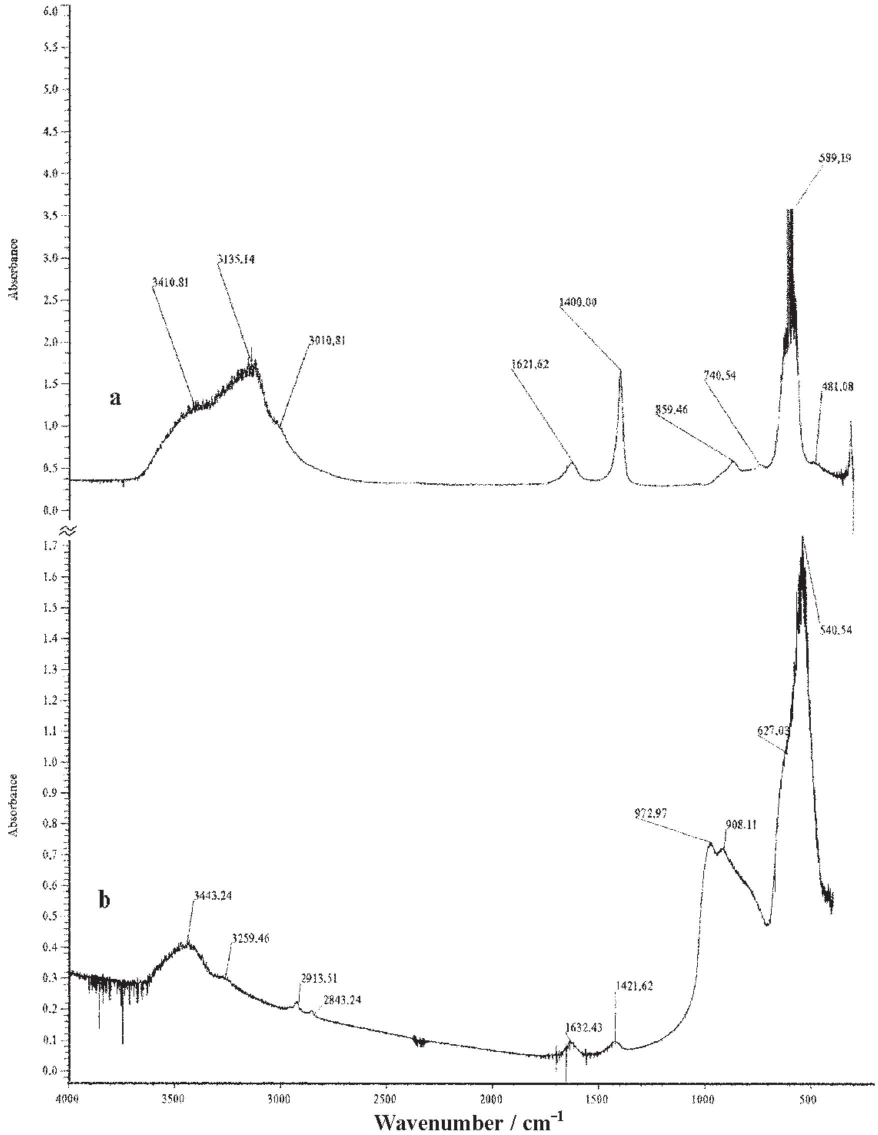

Fig. 4 IR spectra of a – $(NH_4)_{0.9}TiO_{0.4}F_{4.1}$ and b – ammonium-containing non-stoichiometric titanium oxyfluoride

The reduction of Ti(IV) by ammonia evolved is evident because of the coloring of the decomposition residues (from cream and gray to brown and black) and deposits on the outer side of the labyrinth crucible (gray violet mixture with rutile and anatase forms containing about 5% fluorine was deposited because of hydrolysis of the volatile titanium product). ESR spectrum (Fig. 5) indicates the presence of Ti(III) (g=1.92 which disappears at heating and appears again at room temperature) in the products of thermal decomposition of ammonium oxofluorotitanates. Their IR spectra (Fig. 4b) reveal the existence of ammonium (the band at 3259 is stretching mode and the band at 1421 cm^{-1} is deformation vibration of ammonium). So their general formula can be ascribed to $(NH_4)_xTiO_{2-y}F_y$, $0<x<0.2$; $0<y<0.3$.

Table 2 The mass loss data of thermal decomposition of ammonium oxofluorotitanates at 500°C

Compound	Experimental conditions	Δm_1	Δm_2
$(NH_4)_3TiOF_5$	quasi-isobaric conditions (labyrinth crucible), air	63.0	96.2
$(NH_4)_3TiOF_5$	labyrinth crucible, helium	65.7	99.5
$(NH_4)_3TiOF_5$	open crucible, helium	73.9	89.2
$(NH_4)_2TiOF_4$	quasi-isobaric conditions	56.6	68.6
NH_4TiOF_3	quasi-isobaric conditions	42.5	56.0

Δm_1 – registered on TG curve
Δm_2 – measured from the mass of residue in crucible

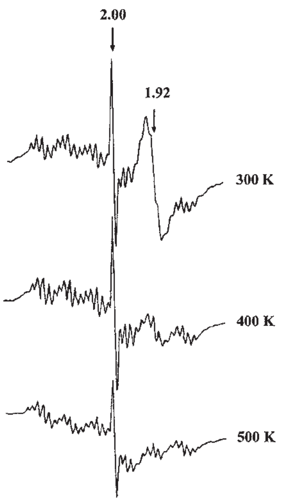

Fig. 5 ESR spectrum of ammonium-containing non-stoichiometric titanium oxyfluoride

Conclusions

Using quasi-isobaric techniques, thermal decomposition of ammonium oxofluorotitanates was investigated. Having reconstructed their initial structure all the complexes examined do not lose fluorine in the first stages of the degradation process. The existence of NH_4TiF_5 is questionable. More precise definition of stoichiometry of volatile ammonium oxofluorotitanate by a direct structural determination is needed. It is necessary to take into account that titanium oxyfluorides, which are the products of the initial oxofluorocomplexes decomposition and isostructural with $TiOF_2$, TiOF or TiO_2, contain ammonium and reduced titanium and can be attributed to non-stoichiometric ammonium-containing titanium oxyfluorides.

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