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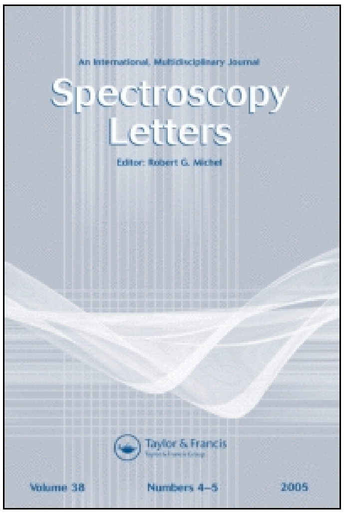

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VOLATILE AMMONIUM FLUOROTITANATE

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VOLATILE AMMONIUM FLUOROTITANATE

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ABSTRACT

Single crystals of $NH_4TiO_xF_{5-2x}$ $(x = 0.4)$ have been synthesized by gaseous product condensation at 300–400°C during the thermal decomposition of crystalline $(NH_4)_2Ti(OH)_xF_{6-x}(x = 0.6)$. The compound consists of kinked parallel infinite chains of cis-corner-connected TiF_6 octahedra along the [1 0 1]-direction separated from each other by NH_4^+-ions. The crystal parameters of this compound are as follows: monoclinic $P2_1/n$, $a = 14.683$ (1), $b = 6.392$ (1), $c = 20.821$ (2) Å, $\beta = 110.538$ (2)°, $V = 1829.9$ (3) Å^3, $Z = 16$. The presence of oxygen was proved by chemical analyses, IR and NMR spectroscopy. Oxygen atoms must be randomly distributed in the crystal lattice. Fluorine and ammonium diffusion above 480 K can be the evidence of high ionic conductivity of this complex.

Key Words: Ammonium fluorotitanate; Nonstoichiometry; Crystal structure; IR, NMR spectra; Ionic diffusion

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COMMENT

It is assumed that the decomposition of $(NH_4)_2TiF_6$ under non-reciprocal quasi-isobaric conditions leads to NH_4TiF_5 as new intermediate[1] which is hygroscopic and unstable in air. We isolated similar compound in a more stable form from the gas phase during the thermal decomposition of $(NH_{4)_2}Ti(OH)_xF_{6-x}$ $(x = 0.6)$[2,3]. Its X-ray powder data are very close to those of NH_4TiF_5[1]. They are presented in Table 1.

However, our compound contained some oxygen because of its presence in the initial complex $(NH_4)_2Ti(OH)_xF_{6-x}$. It is impossible to obtain fully stoichiometric $(NH_4)_2TiF_6$ from aqueous fluoride solution (even from concentrated HF). As a consequence, the first-step decomposition product of diammonium fluorotitanate also contains oxygen:

$$(NH_4)_2Ti(OH)_xF_{6-x} \rightarrow NH_4TiO_{0.5x}F_{5-x} + NH_3 + HF + 0.5xH_2O$$

Further heating is accompanied by sublimation of $NH_4TiO_{0.5x}F_{5-x}$ because the chemical analyses and X-ray powder data of the solid (residue after the first-stage decomposition of $(NH_4)_2Ti(OH)_xF_{6-x}$) are identical with those of

Table 1. X-ray Diffraction Data for $NH_4TiO_xF_{5-2x}$ $(x = 0.15)$

	d, Å				*d*, Å		
I/I_0	Obs.	Calc.	*h k l*	I/I_0	Obs.	Calc.	*h k l*
14	6.84	6.85	−2 0 2	4	2.269	2.268	−6 1 2
100	5.79	5.79	1 1 0	3	2.222	2.221	−6 1 5
35	4.85	4.85	−3 0 1	4	2.103	2.103	−1 3 1
4	4.54	4.55	0 1 3	12	2.071	2.071	−3 0 10
6	4.31	4.31	−2 1 3	4	2.021	2.021	−7 0 6
8	3.71	3.72	−3 1 3	4	1.999	2.000	−2 3 3
73	3.47	3.47	−3 1 4	7	1.987	1.988	−7 1 4
69	3.43	3.43	−4 0 4	6	1.895	1.894	1 3 4
2	3.24	3.24	0 0 6	3	1.868	1.868	0 3 5
20	3.18	3.18	−4 1 2	4	1.834	1.834	−8 0 4
3	3.11	3.11	−1 2 1	11	1.810	1.810	−1 3 6
3	3.03	3.03	−1 1 6	5	1.737	1.737	−7 2 2
4	2.89	2.89	3 1 3	4	1.717	1.717	−4 0 12
4	2.60	2.60	5 0 1	4	1.626	1.626	7 2 1
3	2.53	2.53	−1 2 5	4	1.577	1.577	−7 1 11
4	2.430	2.432	5 0 2	3	1.447	1.447	6 2 6

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the condensed phase. Moreover, if an ammonium fluorocompound decomposes, the NH_3 evolution can be always detected by green coloring of wet indicator paper in the gas phase because of its diffusion rate faster than that of HF. In our case, this effect was absent. We also controlled the first step of thermal decomposition of the initial diammonium fluorotitanate (reagent grade, 20–30 g were used) at 250–300℃ by stopping the green coloring of indicator paper and appearing the red coloring due to partial hydrolysis with HF formation. The solid residue was then heated up to 500℃ in a covered graphite vessel. Transparent needles were grown on the cover at 300–400℃. The recurring sublimation leads to obtaining of transparent thin plates. The analytical data for all specimens obtained are given in Table 2. Sp.3 contains more fluorine than Sp.2 due to the following processes:

Table 2. Analytical Data for $NH_4TiO_xF_{5-2x}$

		Content, mass. %					
		Found			Calculated		
Sample	Synthetic Method	NH_4	Ti	F	NH_4	Ti	F
1. $NH_4TiO_{0.4}F_{4.2}$	Powder after the first step decomposition of $(NH_4)_2Ti(OH)_{0.4}F_{5.6}$ or crystal needles from the gas phase condensed at 300–350 °C, nitrogen atmosphere	11.41	30.80	52.71	11.83	31.39	52.47
2. $NH_4TiO_{0.2}F_{4.6}$	Transparent needles during desublimation at 300–400 °C of $NH_4TiO_{0.4}F_{4.2}$, covered vessel, air atmosphere, humidity 45–50%	11.27	31.04	55.47	11.50	30.61	55.85
3. $NH_4TiO_{0.15}F_{4.7}$	Transparent plates during desublimation of $NH_4TiO_{0.2}F_{4.6}$, covered vessel, air atmosphere, humidity 40–45%	11.36	30.37	56.64	11.42	30.39	56.66

*At 80–100% humidity the crystals of $NH_4TiO_xF_{5\text{-}2x}$ are hydrolyzed rapidly and grow turbid.

$$NH_4TiO_{0.2}F_{4.6} + 0.8H_2O \rightarrow TiOF_2 + NH_3 + 2.6HF \text{ (partial hydrolysis);}$$

The evolved HF refluorinates then the initial ammonium fluorotitanate:

$$NH_4TiO_{0.2}F_{4.6} + 0.1HF \rightarrow NH_4TiO_{0.15}F_{4.70} + 0.05H_2O.$$

A suitable transparent plate of the latter sample was chosen for X-ray diffraction experiment. The crystal parameters of this compound are as follows: monoclinic $P2_1/n$, $a = 14.683$ (1) Å, $b = 6.392$ (1) Å, $c = 20.821$ (2) Å, $\beta = 110.538$ (2)°, $V = 1829.9$ (3) Å^3, $Z = 16$, $Dx = 2.326$ g/cm^3.

The structure of the complex[4] consists of infinite chains of cis corner-sharing TiF_6 octahedra that extend along the [010] direction as shown in Fig. 1a (the hydrogen atoms are not observable). The cis linkages in $(TiF_5^-)_n$

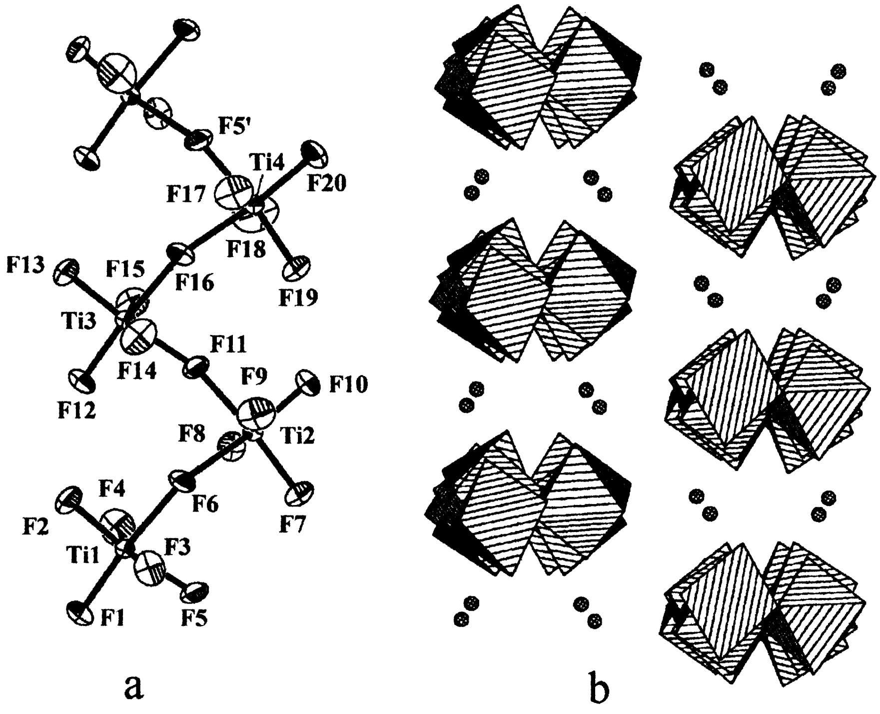

Figure 1. Crystal structure of $NH_4TiO_xF_{5\text{-}2x}$: **a** – part of the chain built from cis corner-connected TiF_6 octahedra; **b** – zigzag chains of corner-connected TiF_6 octahedra with ammonium ions in between.

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are quite unusual and were observed in the case of $H_3O^+TiF_5^-$[5] while in the related $(NH_4)_2TiF_5$ containing rare reduced paramagnetic titanium Ti^{3+}, trans corner-sharing octahedra are present[6]. The ammonium ions link the chains via hydrogen bonds as on a chess-board (Figure 1b). The average distances $N\ldots F$ are 2.85–2.98 Å. The crystal structure of our complex is different from that of an other volatile titanium (IV) fluorocompound TiF_4, which consists of $[Ti_3F_{15}]$ – rings connected by trans-F^- to isolated parallel columns[7].

As in this case, it seemed impossible to distinguish between O^{2-} and F^- by X-ray diffraction, but the chemical analyses data give evidence of nonstoichiometry of the compound (Table 2). Fluorine content was determined by two methods: by distillation of H_2SiF_6 and by pyrohydrolysis at 400°C followed by titration with $Th(NO_3)_4$ (accuracy ±0.5%). Ammonium was analyzed by the Kjeldahl method (accuracy ±0.2%) and titanium was determined by atomic absorption and pyrohydrolysis (accuracy ±0.5%). IR and NMR spectroscopies confirmed the composition of the crystals.

Figure 2 shows the IR spectrum of the $NH_4TiO_{0.15}F_{4.7}$ recoded in KBr pellet (one transparent single crystal was ground with KBr). The band at 855 cm^{-1} indicates the presence of ? (Ti=O), where the oxygen atom is terminal. The band at 740 cm^{-1} (which is more obvious in the case of $NH_4TiO_{0.4}F_{4.2}$[2])

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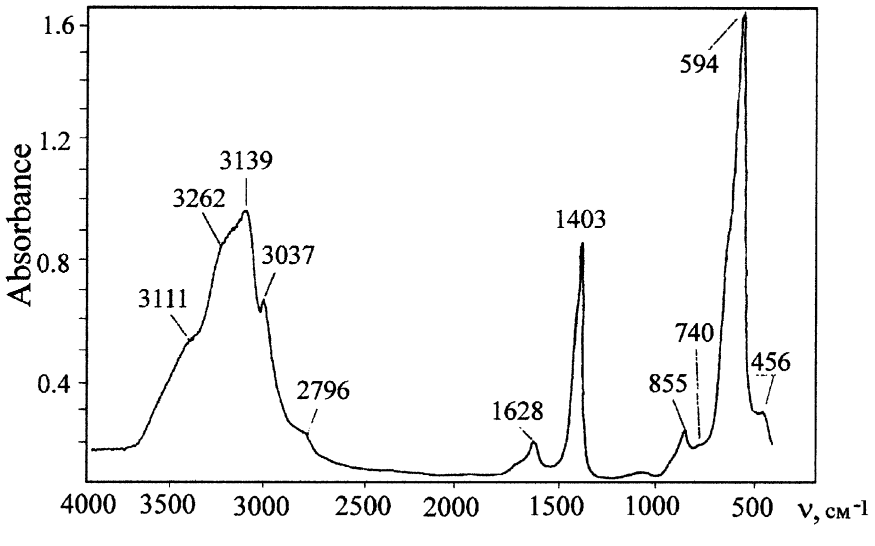

Figure 2. IR spectrum of $NH_4TiO_xF_{5\text{-}2x}$ ($x = 0.15$) at room temperature.

must be assigned to a combination or lattice mode of Ti-O and Ti-F bands[8], when O^{2-} and F^- anions are randomly distributed in the crystal lattice.

The ratio of integral intensities of NMR ^{19}F and NMR ^1H signals measured with the accuracy of 5% gives 1.15 for Sp.2 and 1.18 for Sp.3 instead of 1.25 for stoichiometric NH_4TiF_5. The ionic dynamics in the compound obtained was also examined at 270–530 K. The relatively large magnitude of the second moment S_2 of NMR ^{19}F spectra ($\sim 19\,G^2$) at 270–390 K and their lineshape indicate the rigidity of fluorine sites and the absence of any fluorine mobility with the frequencies more than 10^4–10^5 Hz. Fluorine lineshape transformation begins above 400 K, and S_2 decreases sharply up to $1.8\,G^2$ at 475 K that is the evidence of motional reorientations of fluorine octahedra around the bridging fluorines. Activation energy E_a for this process is ~ 62 kJ/mol. As temperature rises, the frequency of reorientational motion increases that leads to destruction of bridging bonds and isotropic reorientations of the fluoride fragments formed ($S_2 \sim 0.65\,G^2$). Above 520 K S_2 decreases to 0.25 G^2 that means the appearance of translational diffusion in the crystal lattice ($E_a = 80.3$ kJ/mol).

The value of S_2 for NMR ^1H spectra of $NH_4TiO_xF_{5\text{-}2x}$ (narrow symmetrical line) is practically constant in the temperature range 230–390 K (3.5 ± 0.2 G^2). According to the different models of NH_4^+-motion[9], this shows isotropical reorientations of NH_4^+-ions in the crystal lattice. Above 480 K a narrow component is registered at the expence of the broad line that is connected with NH_4^+-diffusion which increases with temperature rising. E_a of this process is 74.2 kJ/mol.

Thus, volatile ammonium fluorotitanate should be considered as non-stoichiometric compound of general formula $NH_4TiO_xF_{5\text{-}2x}$ ($x = 0.4$). Probably, pure NH_4TiF_5 can be obtained in dry HF atmosphere. This complex is more likely the final product of $(NH_4)_2TiF_6$ decomposition rather than TiF_4. Above 480 K fluorine and ammonium diffusion is observed that can be the evidence of high ionic conductivity in the compound examined.

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