

Fluoride Processing of Titanium-Containing Minerals

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ABSTRACT

Fluoride processing of natural ilmenite with the use of ammonium hydrogen difluoride (NH_4HF_2) as an effective fluorinating agent is suggested. Chemistry, composition, structure, thermal and hydrolytic properties of fluorination products were investigated. Ammonium fluoro- and oxofluorotitanates are suitable for preparing of titanium dioxide as pigmentary product or as doped by nitrogen and fluorine.

Keywords: Ilmenite; Fluorination Reactions; Ammonium Hydrogen Difluoride; Ammonium Fluoro- and Oxofluorometallates; Thermal Behavior; Hydrolysis; N-F-TiO₂.

1. Introduction

Titanium dioxide (TiO₂) has long been at the center of photocatalyst research due to its catalytic efficiency coupled with wide availability, biocompatibility, chemical stability, low cost, and safety toward both humans and the environment. It is much more effective as photocatalyst in the form of nanoparticles modified by doping with cations and anions [1,2]. The nitrogen and fluorine-doped titanium dioxide (N-F-TiO₂) nanomaterials exhibit high photocatalytic activity for water-splitting and photodegradation of organic pollutants [3–8]. It was shown that co-doping with nitrogen and fluorine is advantageous for the reduction of defect formation and lowers the energy cost for the incorporation of nitrogen owing to the charge compensation effect between the donor (F) and acceptor (N) [9].

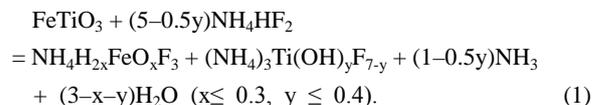
Multifunctional properties and vast applications of nano-TiO₂ require its production in a mass scale. The large-quantity production of rutile nanorods from ilmenite sands was recently suggested [10,11]. Ilmenite (FeTiO₃) is abundant feedstock for industrial production of TiO₂. At present, ilmenite is commonly used in industry for making white pigment *via* a sulfate or chlorine route having serious disadvantages, such as the treatments of byproducts in the former and the lack of raw rutile minerals in the latter. Fluoride processing of titanium-bearing minerals can serve as an alternative. Ammonium hydrogen difluoride (NH_4HF_2 , solid, melting point is 126°C, boiling point is 240°C) was recognized as versatile fluorinating agent for recovering of titanium-containing raw materials [12,13]. It should be noted that foundation of ilmenite processing with ammonium hydrogen difluoride was created by Svendsen as early as the thirties [14,15]. The suggested methods comprised fluorination with molten NH_4HF_2 followed by sublimation of fluoride titanium compound but the detailed chemistry was not completely understood. Since the fluorination products are ammonium fluoro- or oxofluorotitanates, it is reasonable to consider them as precursors for the N-F-TiO₂ obtaining.

Indeed, the N-F-TiO₂ nanoparticles of anatase crystalline structure were recently prepared by a facile method of $(\text{NH}_4)_2\text{TiF}_6$ pyrolysis [16]. The synthesis of N-F-codoped TiO₂

powders with a homogenous anatase structure via a thermal decomposition of different ammonium oxofluorotitanate precursors at 550°C was reported [17]. Uniform ammonium oxofluorotitanate (NH_4TiOF_3) mesocrystals and their conversion to mesocrystals of TiO₂ were described [18–20]. Titanium oxyfluoride TiOF₂ was synthesized for obtaining of thermally stable TiO₂ of high photocatalytic activity [21] and for its use as anode material for lithium-ion battery [22]. The synthesis of the above precursors from natural ilmenite and investigation of their physicochemical properties is the aim of present paper.

2. Fluorination of Ilmenite with NH_4HF_2

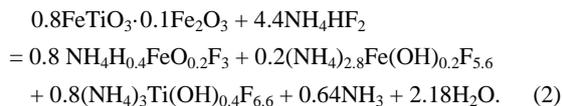
Interaction of ilmenite with NH_4HF_2 proceeds exothermally at room temperature under grinding the initial components [23]. Similar reactions when two solids interact under mechanical grinding with the formation of a new compound were being studied by Indian authors since 1982 [24]. One should concentrate attention on nonstoichiometric composition of fluorinating products due to some OH⁻ groups substituting for fluorine since water molecules are formed during fluorination:



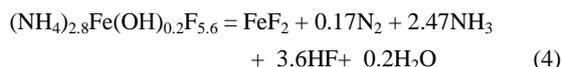
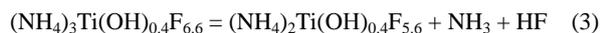
The main titanium fluoride product is a double salt isostructural with $(\text{NH}_4)_3\text{TiF}_7 = (\text{NH}_4)_2\text{TiF}_6 \cdot \text{NH}_4\text{F}$ which was isolated in a single crystal form from fluoride aqueous solution. Its crystal structure was determined. The parameters of tetragonal unit cell were changed under X-rays, the stable phase is characterized by the following parameters: sp. gr. P4nc; a = 11.97, b = 11.68 Å; z = 8. One of the three independent Ti octahedra is disordered so a phase transition (PT) at about 280 K takes place. Fe(II) forms a cubic fluoroperovskite type structure and easily oxidized in air and in aqueous solution, and Fe(III) fluoride compound crystallizes in cubic fluoroelpasolite structure. Its octahedral single crystals of the $(\text{NH}_4)_x\text{Fe}(\text{OH})_{3-x}\text{F}_{2x}$ (x = 2.70–2.85) composition were grown. Usually, natural ilmenite

contains some Fe(III). We dealt with the real composition of $0.8\text{FeTiO}_3 \cdot 0.1\text{Fe}_2\text{O}_3$ and investigated carefully its fluorinated process. The corresponding thermal curves are shown in **Figure 1**. An exoeffect at 125°C is evident.

The corresponding equation can be expressed as follows:



The endoeffect at 280°C corresponds to thermal decomposition of titanium double salt. Further effects are connected with thermal behavior of $(\text{NH}_4)_2\text{Ti}(\text{OH})_{0.4}\text{F}_{5.6}$ and ammonium fluoroferrates:



One should mention the evolution of volatile titanium fluoride compound $\text{NH}_4\text{TiO}_{0.4}\text{F}_{4.2}$ which sublimes incongruently with the formation, probably, of the titanium adduct with NH_3 . We succeeded in obtaining of single crystal of this volatile compound and determined its chain structure (**Figure 2**). Infinite chains of *cis*-connected $[\text{TiF}_6]$ -octahedra are joint via NH_4 groups by $\text{N}\cdots\text{H}\cdots\text{F}$ hydrogen bonds with the average $\text{N}\cdots\text{F}$ distance of $2.85\text{--}2.98\text{ \AA}$ [25]. It is necessary to take into account that some Ti^{4+} is reduced to Ti^{3+} by NH_3 evolved, so we used simple aqueous leaching of the cake to separate titanium from iron. One can expect the formation of ammonium oxofluorotitanate $(\text{NH}_4)_3\text{TiOF}_5$ at this stage at $\text{pH} = 7\text{--}8$ [26]. This compound is isostructural with iron fluoroelpasolite, their crystal structures were determined [27].

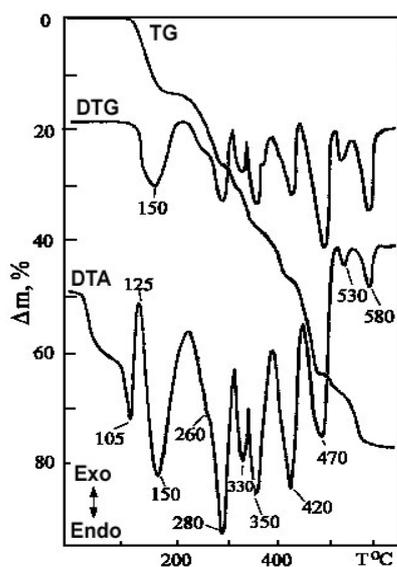


Figure 1. Thermal curves of the mixture of ilmenite with NH_4HF_2 .

3. Dynamic Orientational Disorder in Crystals of Iron and Titanium Fluoroelpasolites

Classical cubic structure of A_2BMX_6 ($\text{A} > \text{B}$) elpasolite ($\text{Fm}\bar{3}\text{m}$, $Z = 4$) comprises a central atom M to be in the 4a position, ligands in 24e, larger cations in 8c, and smaller cations in 4b. NH_4 in the latter position is accepted to be disordered on two orientations. We advanced in the refining of this structure and published recently the paper on this subject [28]. In fact, the ligand atoms are distributed on mixed $24e + 96j$ positions, and ammonium group in the 4b position is distributed on the 32f position taking 8 equivalent orientations. Ammonium groups in the 8c position are tetrahedrally shifted into the 32f position. In the Ti oxofluoroelpasolite, a central atom is disordered on 6 orientations. The Ti atom is shifted towards the O atom with the formation of short triple $\text{Ti}\text{--}\text{O}$ bond that allows to determine the real geometry of TiOF_5 octahedron. **Figure 3** presents disordered structure of the discussed elpasolites.

The observed disorder has a dynamic nature that the NMR data support (**Figure 4**). Two phase transitions at lower temperature are evident. The M_2 jump at 265 K coincides with the temperature of phase transition (PT) detected by the differential scanning microcalorimetry method (DSM). The rather large value of entropy change ΔS at this PT ($18.1\text{ J mol}^{-1}\text{ K}^{-1}$ or $\text{Rln}9$) characterizes this first order PT as of order-disorder type [29]. High anionic and cationic mobility is reflected in thermal behavior of this complex. The easy transfer of hydrogen from ammonium group to the O atom emerges in the IR spectrum as the appearance of strong hydrogen bond of the $\text{O}\text{--}\text{H}\cdots\text{F}$ type at $700\text{--}800\text{ cm}^{-1}$. As a result, only NH_3 and H_2O , but no HF evolve during the thermal decomposition of the compound.

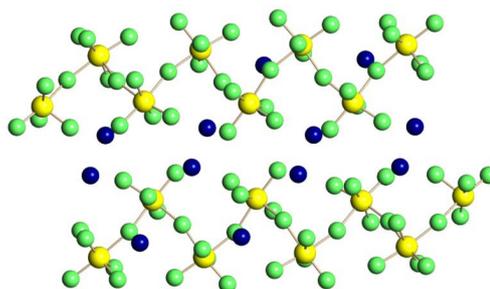


Figure 2. Crystal structure of $\text{NH}_4\text{TiO}_x\text{F}_{5-2x}$ ($x = 0.15$): sp. gr. $\text{P}2_1/n$, $a = 14.683$, $b = 6.392$, $c = 20.821\text{ \AA}$; $\alpha, \gamma = 90^\circ$, $\beta = 110.538^\circ$, $Z = 16$.

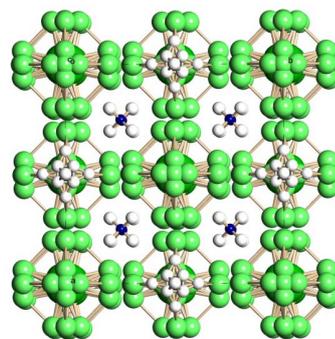
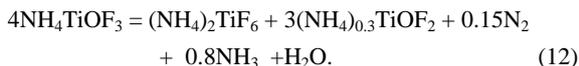
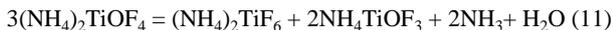
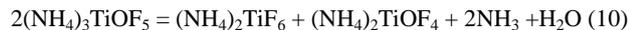


Figure 3. Disordered crystal structure of $(\text{NH}_4)_3\text{FeF}_6$ or $(\text{NH}_4)_3\text{TiOF}_5$.

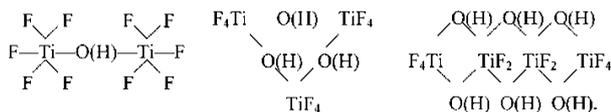
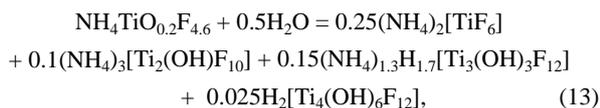
4. Thermal and Hydrolytic Properties of Ammonium Fluorometallates

Thermal behavior of ammonium oxofluorotitanates were examined [30]. Thermal curves of the $(NH_4)_3TiOF_5$ decomposition are presented in **Figure 5**. The corresponding reactions can be expressed as follows:



The process is accompanied by sublimation of volatile titanium compound and by the formation of hexagonal ammonium-containing $TiOF_2$.

Hydrolysis process of volatile ammonium fluorotitanate, $NH_4TiO_xF_{5-2x}$, is practically important. Its aqueous solution has an acid reaction meaning the strong hydrolysis [31]. According to ^{19}F , ^{17}O , and ^{49}Ti NMR data, dimers with bridging OH or even trimers (cyclic or linear) are formed:



Oligomerization (polymerization) is the main feature of pyrohydrolysis of ammonium fluorotitanates and fluoroferrates. Kinetic curves show that it takes about 40 min to convert ammonium fluorometallates to oxides [32,33]:

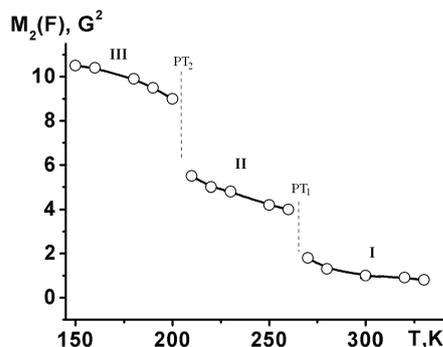


Figure 4. Temperature dependence of the second moment (M_2) of the ^{19}F NMR spectrum of $(NH_4)_3TiOF_5$.

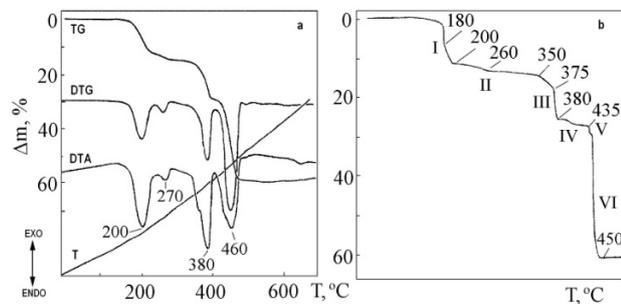
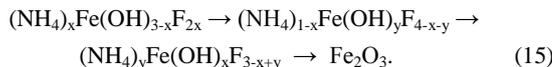
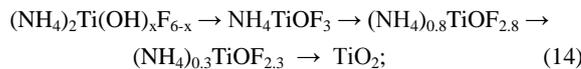


Figure 5. Thermal curves of $(NH_4)_3TiOF_5$.



Using the data obtained we suggested pyro-hydro-metallurgical method of ilmenite processing [34] which comprises the fluorination of ilmenite with NH_4HF_2 at 20–200 °C followed by a simple aqueous leaching of the cake. Combination of hydrolysis and pyrohydrolysis processes gives pigmentary Ti and Fe oxides. We tried to burn volatile ammonium fluorotitanate in an oxygen atmosphere at 1000°C and obtained N–F-doped TiO_2 with rutile structure. Crystals with splendid color like sapphire were grown. They are good UV- and visible light absorbers. We suspect that selecting conditions of hydrolysis (pyrohydrolysis) or/and pyrolysis of ammonium fluorotitanates, it will be possible to design nanosized N–F-doped TiO_2 .

Thus, to obtain useful product from natural raw materials using NH_4HF_2 we should to take into account that thermodynamically possible fluorination reactions proceed spontaneously (exothermally) with the formation of high symmetry phases of ammonium fluoro- and oxofluorometallates. The essence of high symmetry is dynamic orientation disorder of both ammonium groups and anionic polyhedra.

Under dynamic disorder, it is possible to identify O and F atoms on local scale by common X-ray diffraction and to find the real geometry of oxofluoride polyhedron. Orientational dynamic disorder is responsible for PTs at lower temperatures which proceed with rather large ΔS and are characterized as PT of order-disorder type.

Oligomerization is the main feature of thermal and hydrolytic decomposition of ammonium fluoro- and oxofluorometallates which can be used for designing perspective functional materials doped by F and N atoms.

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