



Tricritical point in ferroelastic ammonium titanyl fluoride: NMR study

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ARTICLE INFO

Article history:

Received 28 March 2010

Received in revised form

12 July 2010

Accepted 17 July 2010

Available online 24 July 2010

Keywords:

Ferroelastic phase transitions

Jahn–Teller effect

Titanyl fluoride complex

¹⁹F NMR

Anisotropic rotation

Tricritical point

ABSTRACT

Ionic mobility and phase transitions in ammonium titanyl pentafluoride $(\text{NH}_4)_3\text{TiOF}_5$ were studied using the ¹⁹F and ¹H NMR data. The high-temperature phase (I) is characterized by spherically symmetric (isotropic) reorientation of $[\text{TiOF}_5]^{3-}$ anions and by uniaxial reorientation of these anions in the ferroelastic phase II. A previously unknown second-order phase transition to the low-temperature modification $(\text{NH}_4)_3\text{TiOF}_5(\text{III})$ was found at 205 K. The transition is accompanied by hindering of uniaxial rotations of $[\text{TiOF}_5]^{3-}$ anions and by noticeable change of ¹⁹F magnetic shielding tensor associated with the influence of pseudo-Jahn–Teller effect. A pressure-induced tricritical point with coordinates $p_{\text{TCR}} \approx 2$ kbar and $T_{\text{TCR}} \approx 170$ K is estimated on the base of ¹⁹F NMR chemical shift data, and previously studied p – T diagram of $(\text{NH}_4)_3\text{TiOF}_5$.

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1. Introduction

Complex titanyl fluorides belong to a new family of coordinate compounds of titanile. Among them, potassium titanyl pentafluoride, K_3TiOF_5 , is both ferroelectric and ferroelastic below 490 K [1]. Ferroelastic phase transitions in ammonium titanyl pentafluoride complex $(\text{NH}_4)_3\text{TiOF}_5$ was found at $T_1 = 264.7 \pm 0.1$ K with the entropy change $\Delta S = \sim R \ln 8$ [2]. In the p – T diagram of this complex four phases and two triple points were found below 300 K and 5 kbar [2]. From a linear extrapolation of low-temperature high-pressure data to $p = 1$ bar a low-temperature phase transition at nearly ~ 120 K was predicted. However, the scanning calorimetric study [2] did not discover any thermal anomalies of $(\text{NH}_4)_3\text{TiOF}_5$ between T_1 and ~ 80 K, and the structural mechanism of the phase transitions has not been studied.

The crystal structure of high-temperature (paraelectric) phase of $(\text{NH}_4)_3\text{TiOF}_5$ belongs to the family of elpasolite, space group $Fm\bar{3}m$; $a = 9.113$ Å, $Z = 4$ [2]. The asymmetric titanyl pentafluoride ions (Fig. 1) occupy the 4(a) position of the O_h point symmetry, while the ammonium ions occupy 4(b) and 8(c) positions. It was supposed that F and O atoms in the paraelectric phase of $(\text{NH}_4)_3\text{TiOF}_5$ were distributed uniformly over the positions of perfect octahedrons. Here we show that isotropic reorientation of $[\text{TiOF}_5]^{3-}$ anions takes place in this case. The previously unknown first-order phase transition is revealed at 205 K. We also studied the variations of internal mobility

under the phase transitions, order–disorder phenomena and related electronic structure changes in $(\text{NH}_4)_3\text{TiOF}_5$ using the ¹⁹F and ¹H NMR solid-state spectroscopy and the density functional theory (DFT) calculations. The low-temperature phase transition is shown to be caused by hindering of uniaxial rotation of $[\text{TiOF}_5]^{3-}$ anions and symmetry lowering due to pseudo-degeneration of the electronic basic state resulting in the second-order Jahn–Teller effect.

2. Experimental

Ammonium oxofluotitanate $(\text{NH}_4)_3\text{TiOF}_5$ was synthesized in the form of well-shaped octahedral single crystals as a result of the ammoniac hydrolysis of the $(\text{NH}_4)_2\text{TiF}_6$ hot aqueous solution in the excess of NH_4F according to the original method described in [3]. The obtained crystals had dimensions of ~ 5 μm at fast crystallisation and up to ~ 40 μm at slow evaporation. According to IR spectroscopy data, the samples did not contain hydroxide ions within the detection limits (10^{-4} at%).

The ¹⁹F and ¹H NMR spectra were recorded using the spectrometers Bruker AV-300 (at the Larmor frequency $\nu_L = 282.404$ and 300.0 MHz), and Bruker SWL 3-100 ($\nu_L = 84.66$ MHz). The temperature varied in a stepwise manner between 150 and 360 K, the accuracy of temperature stabilization at each step was ± 3 K. A series of representative ¹⁹F and ¹H NMR spectra is shown in Fig. 2.

The calculation of the spectra second moments M_2 (mean-square width of the NMR spectrum in G^2 , see Fig. 3 and Table 1) has been carried out with the accuracy of $\sim 5\%$. The ¹⁹F NMR

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chemical shifts were measured using C_6F_6 as a reference with $\sim 3\%$ accuracy. The ^{19}F NMR chemical shift of C_6F_6 relatively to an idealized fluorine ion $[F]^-$ is $\delta_{[F]^-}(C_6F_6) = 125$ ppm [4].

3. Results and data analysis

3.1. Intracrystalline ionic mobility in $(NH_4)_3TiOF_5$

Fig. 3 shows the temperature dependence of the second moment (M_2) for the ^{19}F NMR spectra of $(NH_4)_3TiOF_5$. Stepwise changes of M_2 are observed at temperatures of ~ 265 (PT_1) and

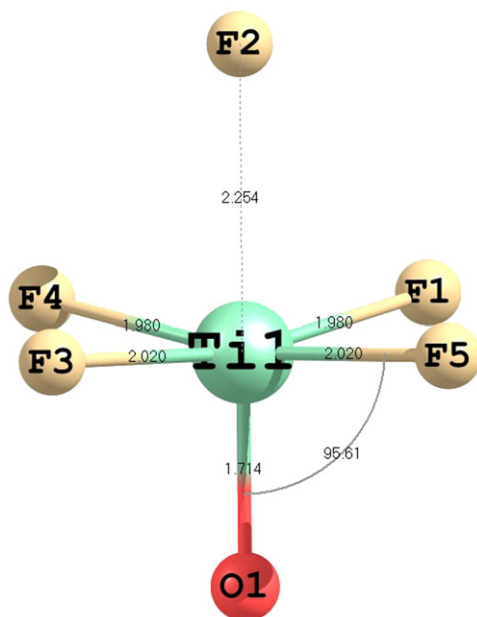


Fig. 1. Distorted structure of complex anion $[TiOF_5]^{3-}$ in phase $(NH_4)_3TiOF_5(III)$.

~ 205 K (PT_2). The first value is in close agreement with the temperature $T_1 = 264.7 \pm 0.1$ K of the first-order phase transition reported earlier [2]. The second stepwise change of M_2 observed at $T_2 \approx 205$ K can be related to the low-temperature phase transition PT_2 predicted previously in [2].

The uneven variations of $M_2(F)$ at PT_1 and PT_2 (Fig. 3) result in abrupt changes of structural ordering and intracrystalline ionic mobility accompanying the solid–solid phase transitions. According to the fundamentals of the NMR theory [5], the above intracrystalline ionic mobilities are represented by orientation diffusion of constituent molecular anions $[TiOF_5]^{3-}$ and cations $[NH_4]^+$ and fast proton exchange in the high-temperature phase I. In Table 1 the experimental M_2 data are juxtaposed with the expected ones calculated for different modes of intracrystalline mobility in different phases of $(NH_4)_3TiOF_5$.

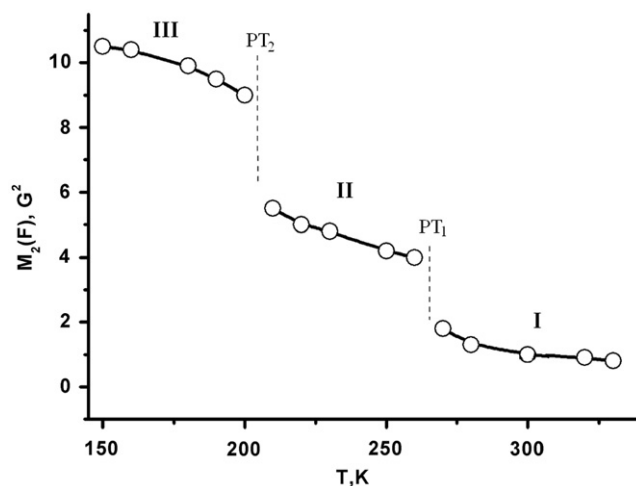


Fig. 3. Temperature dependence of the second moments of ^{19}F NMR spectra of $(NH_4)_3TiOF_5$ measured in the magnetic field of $B_0 = 21.140$ kG at the Larmor frequency $\nu_L = 84.66$ MHz.

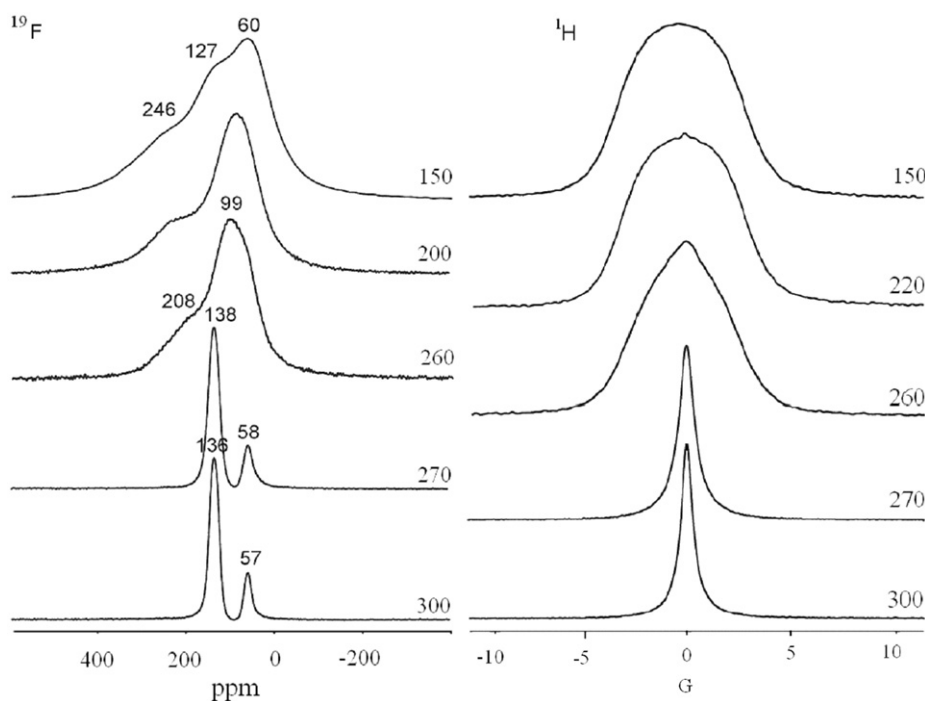


Fig. 2. Temperature variations of ^{19}F and 1H NMR spectra of $(NH_4)_3TiOF_5$ recorded in the magnetic field of $B_0 = 70.5$ kG at the Larmor frequencies $\nu_L = 282.404$ and 300.0 MHz.

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