

THE FLUORINATION OF SCHEELITE WITH AMMONIUM BIFLUORIDE

*N. M. Laptash, E. I. Melnichenko, S. A. Polyshchuk and
T. A. Kaidalova*

INSTITUTE OF CHEMISTRY, FAR EAST BRANCH OF RUSSIAN ACADEMY OF
SCIENCES, VLADIVOSTOK, RF

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The interaction of scheelite with ammonium bifluoride was studied. It was shown that scheelite reacts with NH_4HF_2 at room temperature, in contrast with tungstic oxide and other tungsten compounds. Two complexes are formed $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and the previously unknown $(\text{NH}_4)_2\text{WO}_3\text{F}_2$. The compounds obtained were fluorinated to $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ (endothermic peaks at 170° and 90°C, respectively).

Cubic monocrystals of $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ were obtained. The cubic form is unstable and underwent a lattice transformation at room temperature to the more stable tetragonal form, which was transformed reversibly into the cubic form at 140°C. The thermal decomposition of $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ was studied.

Keywords: fluorination, $(\text{NH}_2)\text{WO}_3\text{F}_2$

Introduction

The reaction of scheelite with ammonium bifluoride is of practical interest. A poorly soluble compound $(\text{NH}_4\text{WO}_3\text{F})$ is obtained on the interaction of scheelite with ammonium bifluoride solutions [1]. The solid-phase reactions of W(VI) salts with NH_4HF_2 in the range 120°–210°C result in the compound $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ [2]. However, thermal effects were detected at lower temperatures in the solid-state reactions of scheelite with ammonium bifluoride. The aim of the present paper was to study the nature of these effects.

Experimental

Reagent grade CaWO_4 and NH_4HF_2 in a ratio of 1:3.5 were used as starting materials to ensure full fluorination according to the equation $\text{CaWO}_4 + 3.5 \text{NH}_4\text{HF}_2 = \text{CaF}_2 + (\text{NH}_4)_3\text{WO}_2\text{F}_5 + 0.5 \text{NH}_3 + 2\text{H}_2\text{O}$

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 tungsten by photocolourimetry and atomic absorption methods.

TG, DTG and DTA curves were recorded with a Q1000 derivatograph. 200–400 mg of powder samples was heated in a Pt-crucible in the range 25° to 500°C at a constant rate of 10 deg/min. X-ray, IR and NMR spectroscopy were also used to investigate the solid products.

Monocrystalline specimens of $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ were obtained by slow evaporation of a solution containing a high concentration (10%) of NH_4HF_2 .

Results and discussion

Fluorination of scheelite

The interaction of scheelite with ammonium bifluoride begins even during their grinding together. Two compounds are formed: $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ (Fig. 1a). The former cannot be isolated in individual form. The second salt could be isolated by salting-out with ethanol or acetone from dilute solutions of ammonium oxofluorotungstates (40 g/l W). From more dilute solutions, salt mixtures salt out.

Table 1 Chemical analysis of the compounds isolated

Compound	Found / mass %			Calculated / mass %			<i>a</i> / Å
	NH ₄	F	W	NH ₄	F	W	
$(\text{NH}_4)_2\text{WO}_3\text{F}_2$	11.7	12.6	60.6	11.8	12.4	60.1	
$(\text{NH}_4)_3\text{WO}_2\text{F}_5$ (monocryst.)	14.7	24.8	49.4	14.8	26.0	50.4	5.98
$(\text{NH}_4)_{0.1}\text{WO}_{2.4}\text{F}_{0.6}$	0.92	3.20	78.0	0.77	3.23	78.3	3.79
$(\text{NH}_4)_{0.3}\text{WO}_{2.1}\text{F}_{0.9}$	2.45	7.12	76.6	2.23	7.13	76.1	3.83

Table 1 gives the chemical analysis of the salt with composition $(\text{NH}_4)_2\text{WO}_3\text{F}_2$. It is white, poorly soluble and decomposes in aqueous solution to $\text{NH}_4\text{WO}_3\text{F}$ and $(\text{NH}_4)_{1.8}\text{WO}_3\text{F}_{1.8}$ according to the scheme



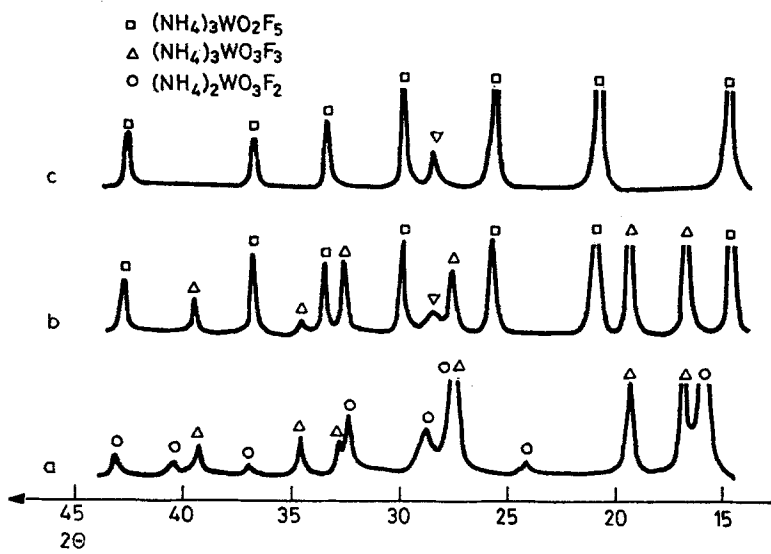


Fig. 1 X-ray patterns for products of scheelite and ammonium bifluoride interaction a) at room temperature, b) at 100°C, c) at 200°C

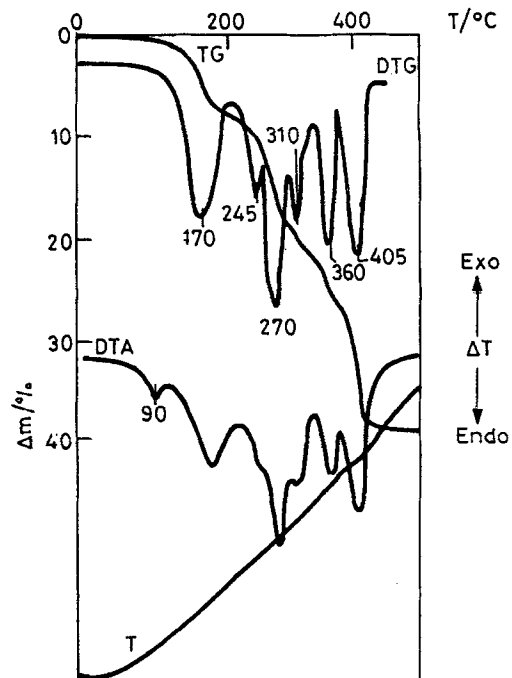


Fig. 2 TG, DTG and DTA curves of mixture of $\text{CaWO}_4 + 3.5\text{NH}_4\text{HF}_2$

The composition of the hydrolysis products was confirmed by chemical and X-ray data. $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ is isostructural with the analogous molybdenum complex [3] and $(\text{NH}_4)_{1.8}\text{WO}_3\text{F}_{1.8}$ reported in [4].

Thus, the interaction of scheelite with ammonium bifluoride at room temperature results in two complexes: $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ and the previously unknown $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ with the ratio $\text{NH}_4\text{F}:\text{WO}_3 = 2$ typical for the $\text{NH}_4\text{F}-\text{MoO}_3-\text{H}_2\text{O}$ system [5].

Table 2 Lattice parameters of tetragonal $(\text{NH}_4)_3\text{WO}_2\text{F}_5$

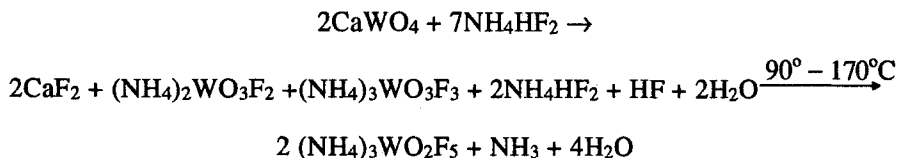
$d \cdot 10^{-1} / \text{nm}$	I/I_0	hkl
5.965	71	100
5.91	48	001
4.24	100	101
3.45	38	111
3.01	13	200
2.97	6	002
2.68	8	201
2.67	6	102
2.45	17	211
2.13	5	220
2.12	9	202
2.01	6	221
1.985	2	003
1.905	6	301
1.888	5	103
1.817	10	311
1.734	5	222
1.673	2	320
1.660	2	203
1.610	5	321
1.607	5	312
1.509	1	400
1.491	1	004
1.463	2	410
1.460	1	401

Tetragonal system: $a = b = 6.03(3) \text{ \AA}$, $c = 5.95(9) \text{ \AA}$; $V = 216.91 \text{ \AA}^3$

The ^{19}F and ^1H NMR data showed that free HF is isolated in the reaction $\text{CaWO}_4 + 3.5\text{NH}_4\text{HF}$ at room temperature, and the following process could be

regarded as further fluorination of the compound formed, to give $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ (Fig. 2). The first step, at 90°C , is $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ fluorination (Fig. 1b) and the second one, at 170°C , is the fluorination of $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ (Fig. 1c). This could be confirmed by fluorination of pure $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ with ammonium bifluoride. In the interval $90^\circ\text{--}110^\circ\text{C}$, the compound obtained is $(\text{NH}_4)_3\text{WO}_3\text{F}_5$.

The stoichiometry of this interaction can be expressed by the following scheme:



The thermal decomposition of $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ accompanied by nonstoichiometric tungsten oxyfluoride formation has been well studied [6].

It is known that $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ has cubic symmetry [7]. Our monocrystal X-ray data showed that the cubic $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ modification is metastable and underwent a lattice transformation at room temperature to a more stable tetragonal

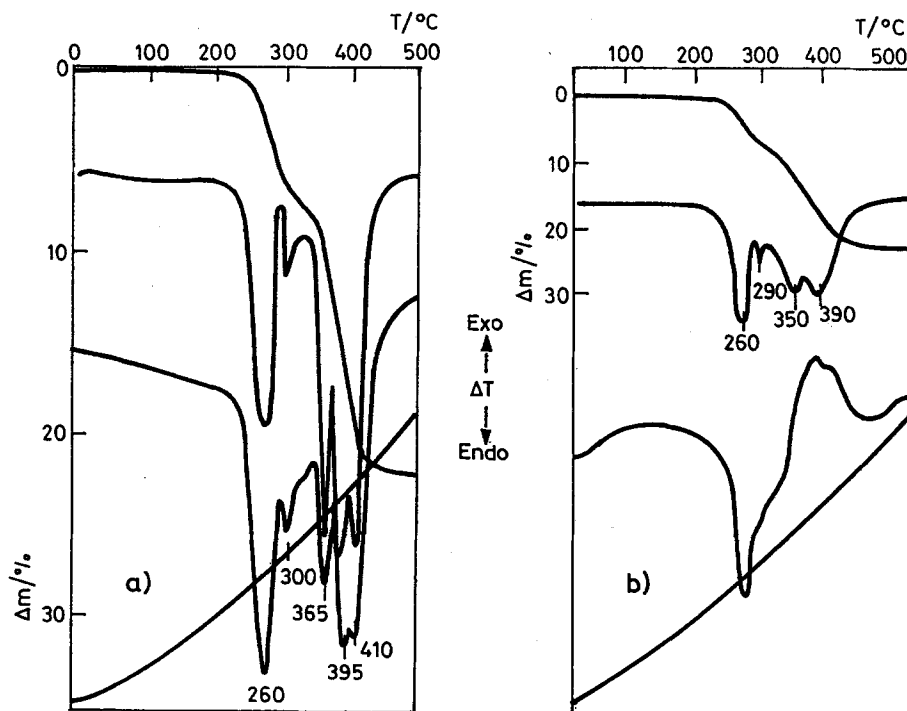


Fig. 3 TG, DTG and DTA curves of $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ a) in labyrinth crucible; b) in air

modification. This compound displays a reverse lattice transformation from tetragonal to cubic at about 140°C. The X-ray data obtained are given in Table 2.

Thermal decomposition of $(\text{NH}_4)_2\text{WO}_3\text{F}_2$

Figure 3 shows the results obtained in a DTA investigation of $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ in its own steam (a) and in air (b). It can be seen that the salt is stable up to 210°-220 °C and then decomposes in four steps. The X-ray and chemical data confirm that the decomposition of $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ begins with ammonia release. The loss of ammonia in the initial stage (260°C) is 4.3%, while that of fluorine is only 1.5%. This doesn't accord with the thermal decomposition scheme to be found in [2, 6]. $\text{NH}_4\text{WO}_3\text{F}$, the main product of decomposition, is stable up to 380°C (Fig. 4). The other phase (phases) was not determined from the X-ray data, but its thermal decomposition resembles that of $(\text{NH}_4)_2\text{WO}_2\text{F}_4$ to yield $(\text{NH}_4)_3\text{W}_2\text{O}_4\text{F}_7$ and $\text{NH}_4\text{WO}_2\text{F}_3$. The endothermic peaks at 395° and 410°C represent $\text{NH}_4\text{WO}_3\text{F}$ and $\text{NH}_4\text{WO}_2\text{F}_3$ decomposition. The cubic oxyfluoride $(\text{NH}_4)_{0.1}\text{WO}_{2.6}\text{F}_{0.4}$ is the final product.

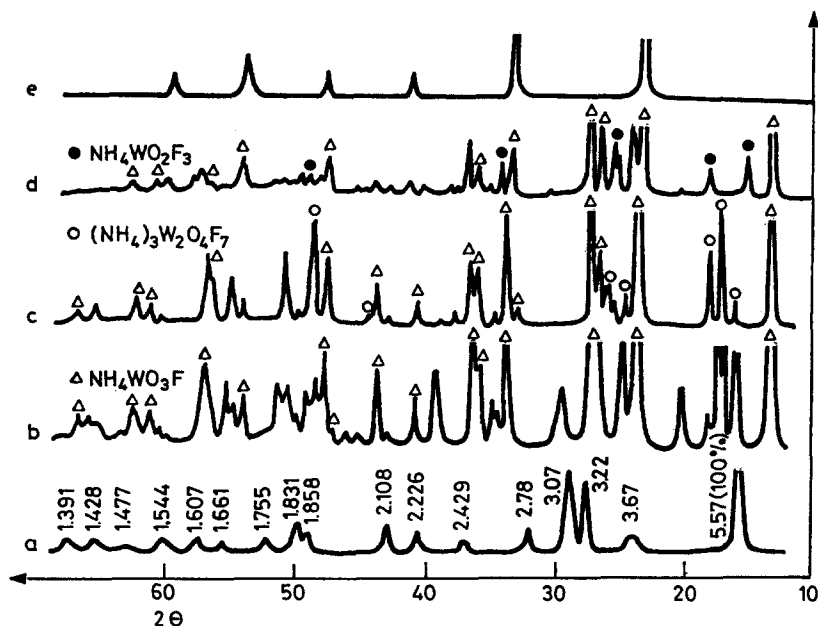
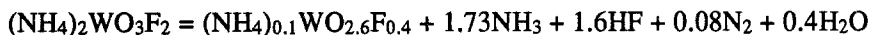


Fig. 4 X-ray patterns of products of thermal decomposition of $(\text{NH}_4)_2\text{WO}_3\text{F}_2$: a) original $(\text{NH}_4)_2\text{WO}_3\text{F}_2$; b) at 270 °C; c) at 310 °C; d) at 370 °C; e) at 500 °C – tungsten oxyfluoride

The scheme of this process can be expressed as:



In air, $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ decomposes to WO_3 .

It is interesting that the thermal decomposition of monocrystalline $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ yields the cubic oxyfluoride $(\text{NH}_4)_{0.3}\text{WO}_{2.1}\text{FO}_{0.9}$.

Thus, the region of ammonium tungsten oxyfluoride formation is expanded in comparison with that described in [7].

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Zusammenfassung— Es wird die Wechselwirkung von Scheelit und Ammoniumhydrogenfluorid untersucht. Im Gegensatz zu Wolframoxid und anderen Wolframverbindungen geht Scheelit mit Ammoniumhydrogenfluorid bei Raumtemperatur eine chemische Reaktion ein, wobei zwei verschiedene Komplexe gebildet werden: $(\text{NH}_4)_3\text{WO}_3\text{F}_3$ und der bisher unbekannte Komplex $(\text{NH}_4)_2\text{WO}_3\text{F}_2$. Die erhaltenen Verbindungen werden zu $(\text{NH}_4)_3\text{WO}_2\text{F}_5$ fluoriert (endotherme Peaks bei 170° bzw. 90°C).

Man erhält die kubischen Einkristalle $(\text{NH}_4)_3\text{WO}_2\text{F}_5$. Die instabile kubische Form wandelte sich bei Raumtemperatur in die stabilere tetragonale Form um, die bei 140°C reversibel wieder in die kubische Form überführt werden kann.

Es wird weiterhin die thermische Zersetzung von $(\text{NH}_4)_2\text{WO}_3\text{F}_2$ untersucht.