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# ON THE PREPARATION AND THERMAL STABILITY OF $(NH_4)_3VOF_6.1.5H_2O$ AND $(NH_4)_3NbOF_6.1.5H_2O$

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## SUMMARY

$(NH_4)_3VOF_6$ and $(NH_4)_3NbOF_6$ were prepared by a simple solid state route and their thermolysis studied. It is concluded that both these compounds have water of hydration, their structures are different and they show first order phase transitions.

## INTRODUCTION

The compound $(NH_4)_3NbOF_6$ was prepared by Baker and Haendler [1] by brominating the metal in methanol and then precipitating the oxyfluoride by addition of ammonium fluoride. The X-ray powder pattern of this compound was indexed with an f.c.c. lattice of a=9.31A. In this communication we describe alternate and simpler route for the preparation of the niobium as well as its vanadium analogue.

In our earlier communications [2,3] we used $NH_4HF_2$ for preparing several oxyfluoride compounds. By intimately mixing together at room temperature $NH_4HF_2$ and $NH_4VO_3$ in 2:1 ratio, we obtained $(NH_4)_3VO_2F_4.0.5H_2O$. [2]. Starting from $NH_4HF_2$ we were also able

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to prepare by solid state synthesis $(NH_4)_2VO_2F_3.0.5H_2O$, $(NH_4)_3V_2O_4F_5.H_2O$ and $NH_4VO_2F_2.0.5H_2O$ [3]. It was our aim to prepare the title compounds starting from the ammonium bifluoride and $[Nb/V]_2O_5$ as per the following scheme:

$$6NH_4HF_2+[Nb/V]_2O_5 \rightarrow 2\ [NH_4]_3(Nb/V)OF_6.n\ H_2O+(1.5-n)H_2O$$

## RESULTS AND DISCUSSION

Mixing at room temperature of $V_2O_5$ and $NH_4HF_2$ in 1:6 mole ratio did result in a reaction as was inferred from the absence of reflections due to the reactants in the X-ray pattern of the mixture. However, similar mixing at room temperature of $Nb_2O_5$ and $NH_4HF_2$ did not bring about the reaction. Heating the mixture to 126°C (i.e. the melting point of $NH_4HF_2$) and cooling back to room temperature showed the formation of a product, the X-ray powder pattern of which matched well with that reported for $(NH_4)_3NbOF_6$[1]. Alternatively we obtained the hexafluoro oxyniobate by repeated digestion of niobium pentoxide and $NH_4HF_2$ (1:6) mixture with aqueous HF, heating to dryness over a water bath and storing over NaOH pellets to remove the last traces of HF. The vanadium and niobium compounds so prepared were studied using thermal analysis techniques.

Figure 1 shows the TG patterns of these compounds. Both these compounds degrade thermally in air in one single step while the corresponding DTA runs, given in Fig. 2, exhibit endotherms as well as exotherms. The thermal data are arranged in Table I.

The DTA of the vanadium compound exhibits five well-resolved endotherms along with a shoulder and an exotherm. The X-ray powder pattern of the residue of thermolysis at 350°C cooled to room temperature showed it to be $V_2O_5$. The exotherm at 450°C in the DTA is characteristic of $V_2O_5$ [2] and the reversible endotherm at 720°C is due to melting of $V_2O_5$. Hence the product

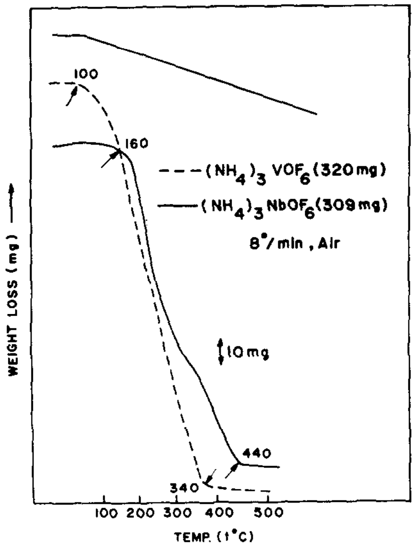

Fig. 1. TG curves of $(NH_4)_3VOF_6 \cdot 1.5H_2O$ and $(NH_4)_3NbOF_6 \cdot 1.5H_2O$

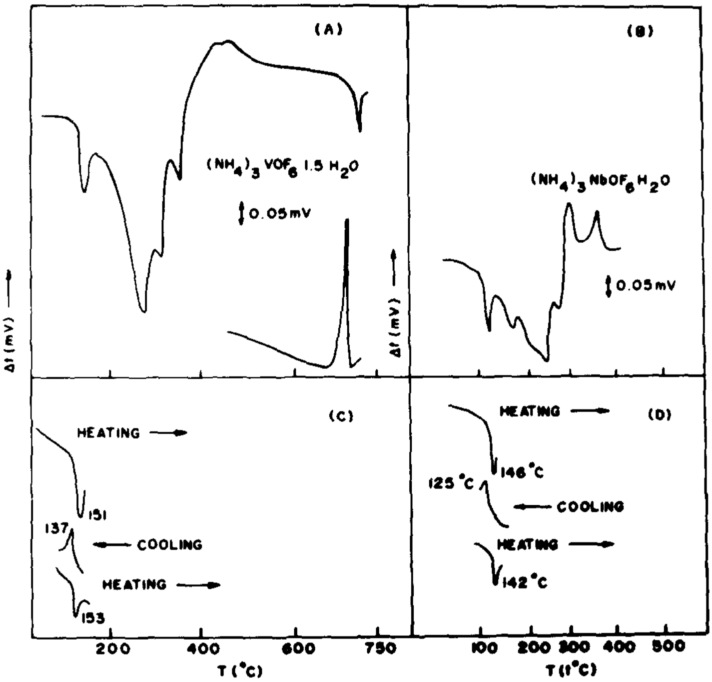

Fig. 2. DTA curves of (a) vanadium compound (b) niobium compound (c) reversibility of phase transition in vanadium compound and (d) reversibility of phase transition in niobium compound.

TABLE I

Thermal data of $(NH_4)_3VOF_6 \cdot 1.5\ H_2O$ and $(NH_4)_3NbOF_6 \cdot 1.5H_2O$

| S NO | NAME OF THE COMPOUND | PRODUCT OF THERMOLYSIS | WEIGHT LOSS % | | DTA peak Temp °C | | DSC ΔH data | |
|---|---|---|---|---|---|---|---|---|
| | | | obsd | expected | Endos | Exos | Peak temp °C | ΔH in $kJ.M^{-1}$ |
| 1 | $(NH_4)_3VOF_6 \cdot 1.5H_2O$ | $V_2O_5$ | 61 | 65 | 151,187<br>284,322,<br>358 | 450,720 | 121 | 20.6 + 0.4 |
| 2 | $(NH_4)_3NbOF_6 \cdot 1.5H_2O$ | $NbO_2F$ | 47 | 51 | 146,202,<br>232,270,<br>303 | 330,390 | 124 | 18.9 + 0.4 |

hysteresis of about 30°C at $16^{\circ}.min^{-1}$ rate of heating/cooling

hysteresis of about $16^{\circ}C$ at $16^{\circ}.min^{-1}$ rate of heating/cooling of thermolysis of $(NH_4)_3VOF_6$ at T ⩾ 350°C is vanadium pentoxide. The first endotherm at 151°C is found to be reversible (Fig. 1b) although thermal degradation of the compound had already set in by 110°C (TG).

The DTA of the niobium compound exhibits four endotherms and two exotherms. The X-ray powder pattern of the residue obtained by heating the niobium compound to 450°C and cooling back to room temperature showed it to be $NbO_2F$ [4]. Figure 2d demonstrat the reversibility of the 146°C endotherm. Just as in the case of the vanadium compound, this first endotherm is attributed to a crystallographic phase transition. The only difference is that in the niobium compound the thermal degradation sets in after the phase transition. DSC patterns of the two compounds are similar and that of the niobium compound is given in Fig. 3. The ΔH for the transition was obtained from the DSC scans during first heating only. No other transition was observed in either case in the temperature range -173°C to 27°C.

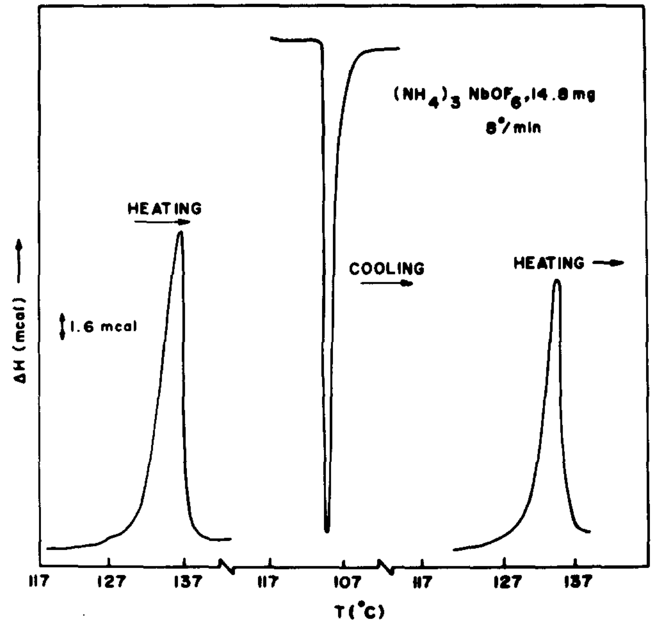

Fig. 3. DSC of niobium compound.

If there is no water of hydration in either $(NH_4)_3VOF_6$ or in $(NH_4)_3NbOF_6$, as has been assumed so in the latter case in earlier report [1], it is not possible to satisfactorily explain their residues of thermolysis of $V_2O_5$ and $NbO_2F$ respectively. Such a difficulty did arise in the case of $(NH_4)_3VO_2F_4$ also where we were able to explain all the features of thermal degradation by assuming the presence of one half of a molecule of water.

The infrared spectra of both the compounds taken with KBr pellet quickly after preparation of the pellets showed the bands characteristic of lattice water at 1600 $cm^{-1}$ and 3500 $cm^{-1}$. In the present case also, since the TG of the mechanical mixture of $Nb_2O_5$ and $NH_4HF_2$ in 1:6 ratio does not show any weight loss up to 160°C and the formation of the compound is complete even at 126°C, we ascribe a value of 1.5 for n for the niobium compound in the above equation. By analogy, a similar situation could be assumed for the vanadium compound also. In that case the overall thermal degradation of the two compounds can be formulated as follows:

$$2\ (NH_4)_3\ VOF_6\ 1.5\ H_2O \rightarrow 6\ NH_4F + V_2O_5 + 6\ HF$$

$$2\ (NH_4)_3NbOF_6 1.5\ H_2O \rightarrow 3NH_4F + NbO_2F + 2\ HF + 0.5\ H_2O$$

Then the expected loss in weight for the vanadium and niobium compounds are 65% and 51% while the observed ones are 61% and 47% respectively.

Attempts to index the observed X-ray powder pattern of the vanadium compound based on the f.c.c. lattice did not succeed showing that its structure is different from that of the niobium compound. This is consistent with totally different products of thermolysis of the two otherwise stoichiometrically similar compounds. With the present data it is not possible to account individually for several endo- and exo- therms in the DTA of both these compounds. Further work to resolve this problem is in progress.

## ACKNOWLEDGEMENT

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