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Mode of thermal decomposition of diammonium lithium oxyfluoro vanadate (DALOFV) and diammonium rubidium oxyfluoro vanadate (DAROFV)

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Abstract

Diammonium lithium and diammonium rubidium oxyfluoro vanadates have been synthesised by solid state reactions at room temperature and their thermal decomposition mechanism determined by using simultaneous TG/DTA. The reaction intermediates have been synthesised separately and the residues identified by XRD to confirm the decomposition mechanism. In the case of the lithium compound, removal of two NH_4F molecules takes place in three steps, whereas in the case of the rubidium compound this takes place in two steps.

Keywords: Diammonium lithium oxyfluoro vanadate (DALOFV); Diammonium rubidium oxyfluoro vanadate (DAROFV); Synthesis; Thermal decomposition

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1. Introduction

The thermal decompositions of $(NH_4)_3VO_2F_4H_2O$ and its mono Na/K analogues have been described [1–3]. All three compounds show a reversible phase transition. In the triammonium compound, $(NH_4)_3VO_2F_4H_2O$, the three molecules of NH_4F are lost in two equal but different steps, indicating that two different crystallographically inequivalent ammonium ions exist. Of these, only one kind is responsible for the phase transition. Despite substitution with one equivalent of Na/K ions in the compound, the phase transition persists due to 0.5 NH_4^+ ions of this kind remaining in the structure.

In this paper, similar studies on the Li and Rb substituted products of $(NH_4)_3VO_2F_4H_2O$ are presented.

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2. Experimental

The chemicals used were AR grade Riedel-De Haen ammonium hydrogen fluoride, and lithium and rubidium vanadate. Both vanadates were synthesised by heating a 1:2 mixture of V_2O_5 and the respective carbonate for a few hours at 650°C and cooling to room temperature. The diammonium oxyfluoro compounds were synthesised as per the equation

$$MVO_3 + 2NH_4HF_2 \longrightarrow (NH_4)_2MVO_2F_4H_2O \qquad (1)$$

where M is Li or Rb.

Grinding of the reactants together at room temperature in a polythene bag for 15–20 min brought about the reaction as monitored by powder XRD. The absence of the lines due to the starting material was taken as an indication for completion of reaction. The course of thermal degradation of the product was studied by simultaneous TG/DTA on a Ulvac Sinku-Riko thermogravimetric analyser, RGD Model 7000 RHP. The rate of heating was 8–10 K min^{-1}, the sample size 30–40 mg in fine powder form, the atmosphere static air, the sample containers Pt, and the sensitivity 0.2 mg. A Philips PW 1710 automatic powder X-ray diffractometer with Ni-filtered Cu Kα radiation was used.

3. Results and discussion

Tables 1 and 2 give the fit of the powder XRD patterns of the compounds and Fig. 1 shows the simultaneous TG/DTA curves for the compounds.

3.1. Thermal decomposition of $(NH_4)_2LiVO_2F_4H_2O$

It can be seen from the figure that there is a single-step loss in weight between 200 and 400°C with a point of inflection at 220°C, while the DTA curve shows seven endothermic peaks at 80, 200, 270, 310, 375, 560 and 580°C. The endotherm at 80°C is not reversible and is attributed to loss of occluded moisture. Up to 220°C, the TG curve shows an estimated loss of 9% attributed to loss of half a molecule of NH_4F (calc. loss, 8%); hence the endotherm at 200°C could be attributed to loss of 0.5 NH_4F molecule. The other two endotherms at 270 and 310°C could be attributed to a combined loss of 1.5 molecules of NH_4F. The TG shows a loss of 28% up to 340°C against the calculated loss of 25% for 1.5 NH_4F molecules. The agreement is considered acceptable in view of overlap of the two steps in the TG. Thus although the TG does not suggest this, the DTA indicates that the two NH_4F molecules are lost in three different steps, suggesting that there are three crystallographically inequivalent NH_4^+ sites in the structure of this compound. The endotherm at 375°C is reversible and reappears on reheating the sample; the residue at 400°C is not a melt. Hence the peak at 375°C is attributed to a reversible phase transition of an intermediate, formed at 340°C on removal of two NH_4F molecules. This intermediate is inferred to be $LiVO_2F_2H_2O$. The endotherm at

Table 1
Fit of powder XRD pattern

Line no.	NH_4HF_2 12–302[a]		$LiVO_3$ 33–835[a]		$(NH_4)_2LiVO_2F_4H_2O$ Orthorhombic[b]			
	d/Å	I/I_0	d/Å	I/I_0	d_{obs}/Å	d_{cal}/Å	I/I_0	hkl
1	5.86	5	6.32	6	5.193	5.193	100	020
2	4.08	15	4.76	100	4.564	4.564	20	120
3	3.68	35	4.22	15	4.431	4.431	31	022
4	3.35	5	3.35	10	3.179	3.177	31	204
5	2.93	25	3.15	16	3.134	3.134	18	301
6	2.77	85	3.07	19	3.001	3.001	15	311
7	2.73	100	2.97	45	2.583	2.585	11	134
8	2.65	70	2.75	7	2.331	2.331	17	410
9	2.62	30	2.69	6	2.292	2.292	21	143
10	2.60	15	2.10	8	2.216	2.216	14	044
11	2.59	40	1.92	8	2.013	2.013	5	340
12	2.29	25	1.86	20	1.773	1.773	8	047
13	2.19	7	1.57	10				
14	2.15	40						
15	2.12	30						
16	2.04	5						
17	1.96	5						
18	1.87	15						
19	1.84	25						

[a] ASTM card no.
[b] $a_0 = 9.568 \pm .003$Å; $b_0 = 10.366 \pm .002$Å; $c_0 = 17.003 \pm .003$Å.

560°C could be attributed to decomposition of this intermediate to give $LiVO_3$ and the endotherm at 580°C to melting of $LiVO_3$. The powder XRD pattern of the residue obtained at 900°C matches very well with the reported pattern for $LiVO_3$ in the ASTM data file. Hence the stepwise decomposition of the compound could be deduced as follows

$$(NH_4)_2LiVO_2F_4H_2O \xrightarrow{RT-200\ C} (NH_4)_{1.5}LiVO_2F_{3.5}H_2O + 0.5NH_4F \qquad (2)$$

$$(NH_4)_{1.5}LiVO_2F_{3.5}H_2O \xrightarrow{220-340\ C} LiVO_2F_2H_2O + 1.5NH_4F \qquad (3)$$

$$LiVO_2F_2H_2O(LT) \xrightarrow[PT]{375\ C} LiVO_2F_2H_2O(HT) \qquad (4)$$

$$LiVO_2F_2H_2O(HT) \xrightarrow{>400\ C} LiVO_3 \qquad (5)$$

Table 2
Fit of powder XRD pattern

Line no.	NH_4HF_2 12-302[a]		$RbVO_3$ 36-1213[a]		$(NH_4)_2RbVO_2F_4H_2O$ Orthorhombic[b]			
	d/Å	I/I_0	d/Å	I/I_0	d_{obs}/Å	d_{cal}/Å	I/I_0	hkl
1	5.86	5	6.95	5	5.181	5.179	50	010
2	4.08	15	5.70	5	4.559	4.558	12	111
3	3.68	35	3.87	20	4.440	4.439	10	211
4	3.35	5	3.66	10	3.601	3.600	8	012
5	2.93	25	3.20	100	3.531	3.532	10	710
6	2.77	85	3.09	10	3.476	3.476	12	702
7	2.73	100	2.85	65	3.175	3.177	100	512
8	2.65	70	2.71	10	3.113	3.112	35	811
9	2.62	30	2.63	15	3.005	3.005	20	902
10	2.60	15	2.55	20	2.590	2.589	30	020
11	2.59	40	2.51	25	2.476	2.476	10	420
12	2.29	25	2.34	10	2.322	2.324	25	1310
13	2.19	7	2.16	5	2.290	2.290	25	621
14	2.15	40	2.09	5	2.277	2.279	30	222
15	2.12	30	2.02	10	2.212	2.210	40	314
16	2.04	5	1.97	5	2.159	2.159	10	1013
17	1.96	5	1.94	10	2.094	2.093	10	614
18	1.87	15	1.91	5	1.884	1.884	10	723
19	1.84	25	1.83	10	1.836	1.835	15	1320
20			1.81	5	1.822	1.822	10	1612
21					1.809	1.810	10	805
22					1.586	1.586	15	532

[a] ASTM card no.
[b] $a_0 = 33.807 \pm .005$ Å; $b_0 = 5.179 \pm .003$ Å; $c_0 = 10.016 \pm .002$ Å.

3.2. Thermal decomposition of $(NH_4)_2RbVO_2F_4H_2O$

The TG/DTA curves for this compound are shown in Fig. 1. It can be seen that the decomposition starts at 50°C. The TG shows a sharp weight loss up to 350°C with a point of inflection at 245°C. The DTA shows four endothermic peaks at 70, 205, 290 and 390°C. The small irreversible endotherm at 70°C is due to removal of occluded moisture. The overall estimated weight loss up to 350°C is 25% as against the calculated weight loss of 25% for loss of two molecules of NH_4F. Up to the first point of inflection, i.e. 245°C, the compound loses approximately 1.5 molecules of NH_4F. The observed weight loss for this step is 17% against the calculated weight loss of 19%. A further 0.5 molecule of NH_4F is lost up to 300°C. Hence on loss of two NH_4F molecules, the product formed at 300°C is inferred to be $RbVO_2F_2H_2O$. The endotherm at 390°C is reversible and is probably due to melting of this product. This was confirmed by synthesising it independently by room temperature solid-state reaction between V_2O_5 and $RbHF_2$ and checking that it melts at the same temperature, i.e at

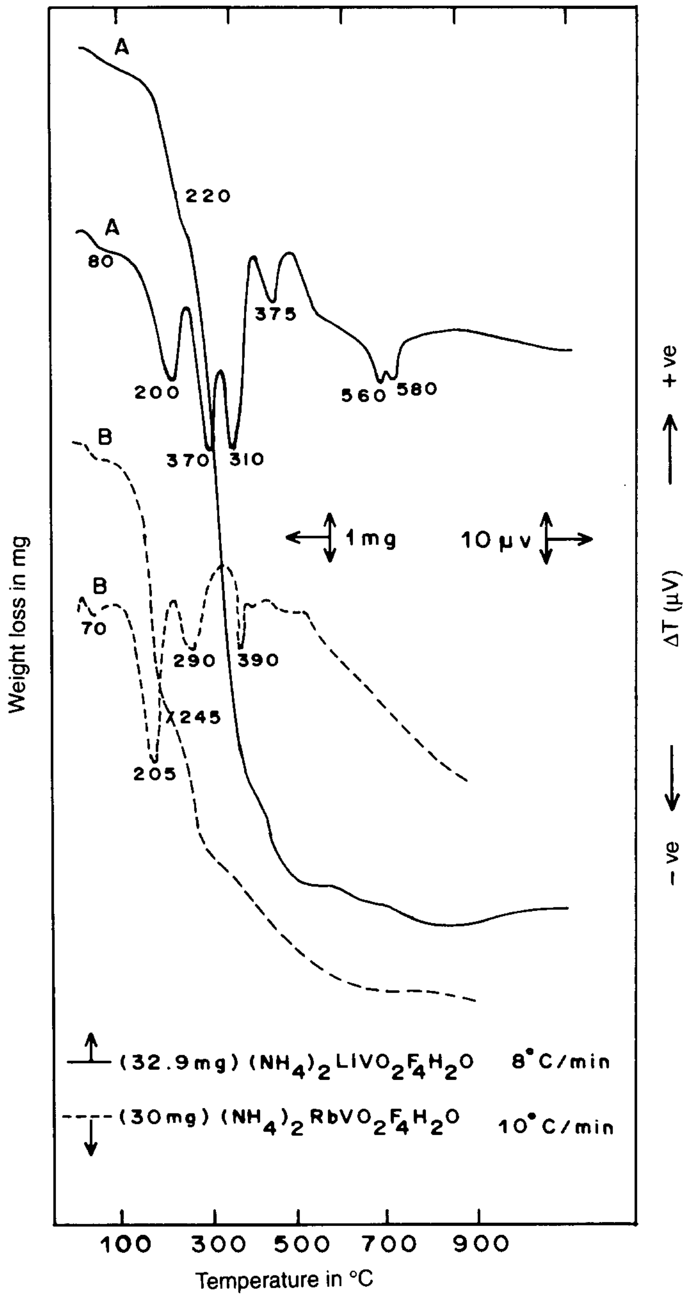

Fig. 1. Simultaneous TG/DTA curves of: A, $(NH_4)_2LiVO_2F_4H_2O$; B, $(NH_4)_2RbVO_2F_4H_2O$.

390°C. This compound decomposes immediately after melting as evidenced by a continuous loss of weight in TG up to 900°C, leaving $RbVO_3$ as the residue as confirmed by its powder XRD pattern. The overall thermal decomposition path of $(NH_4)_2RbVO_2F_4H_2O$ could be traced as follows

$$(NH_4)_2RbVO_2F_4H_2O \xrightarrow{\text{RT–245}^{\circ}\text{C}} (NH_4)_{0.5}RbVO_2F_{2.5}H_2O + 1.5NH_4F \qquad (6)$$

$$(NH_4)_{0.5}RbVO_2F_{2.5}H_2O \xrightarrow{245\text{–}350^{\circ}\text{C}} RbVO_2F_2H_2O + 0.5NH_4F \qquad (7)$$

$$RbVO_2F_2H_2O \xrightarrow[\text{melt}]{390^{\circ}\text{C}} RbVO_2F_2H_2O \qquad (8)$$

$$RbVO_2F_2H_2O \xrightarrow{>400^{\circ}\text{C}} RbVO_3 + 2HF \qquad (9)$$

4. Conclusion

In the case of the lithium compound, the two NH_4F molecules are lost in three different steps indicating that it contains three crystallographically inequivalent NH_4^+ sites. Similarly, it is concluded that the rubidium analogue contains two crystallographically inequivalent NH_4^+ sites.

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