

## PHASE TRANSITIONS IN AMMONIUM OXYFLUORO VANADATES

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### ABSTRACT

Due to their potential as ferroelectric materials, we investigated the occurrence of phase transitions in several ammonium vanadium oxyfluoride compounds. In all the compounds studied two phase transitions, viz. one below and one above ambient temperature, were observed. The low-temperature transition is believed to be associated with electric dipoles.

### INTRODUCTION

The variety of oxyfluoride compounds of Group V and VI elements of the Periodic Table offer an extensive proving ground for testing the theories of stereochemistry. However, one is handicapped by the non-availability of single crystals of the majority of these compounds for directly obtaining structural information. Solution crystallisation normally yields a polycrystalline material while melt growth is not feasible due to their thermal degradation at temperatures much below their melting points. Hence, one has to resort to employing other techniques for obtaining structural information indirectly. Recently, we [1,2] studied a number of oxyfluoride compounds of vanadium, such as  $(\text{NH}_4)_3\text{VO}_2\text{F}_4 \cdot 0.5 \text{H}_2\text{O}$ ,  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{VO}_2\text{F}_3 \cdot \text{H}_2\text{O}$ , etc., using different techniques, such as TG, DTA, DSC and EPR. It is believed that in most of these compounds the central atom, viz. vanadium, is surrounded octahedrally by oxygen and fluorine atoms with bridging of an appropriate number of these atoms with neighbouring vanadium giving the required stoichiometry. In most cases this bridging is supposed to extend to form polymeric units. A previous study [3] indicated that in some of these compounds discrete anions exist and a fraction of these anions are rotating while the rest of them are static. This rules out the possibility of the anions sharing either corners or edges of the octahedron around the central atom. There are reports in the literature [4] based on powder X-ray diffraction data that some of these compounds have an elpasolite structure similar to the perovskite structure. Thus, there is a strong possibility that these compounds might turn out to be ferroelectric

materials. Besides, in our EPR study of the triammonium compound at low temperature [3], the  $Q$  value of the cavity was disturbed, indicating a phase transition involving electric dipoles. It is the aim of this communication to search thoroughly for the phase transitions, if any, in these compounds in the temperature range  $500 \text{ K} > T > 100 \text{ K}$ .

## EXPERIMENTAL

$(\text{NH}_4)_3\text{VO}_2\text{F}_4$ ,  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4$  and  $(\text{NH}_4)_2\text{VO}_2\text{F}_3$  were prepared by solid-state reaction at room temperature [1,2]. A commercial Perkin-Elmer DSC 2C with a sample size of a few milligrams was used. The aluminium pans were crimped. The DSC curves were recorded in flowing dry argon. Two ranges of temperature were scanned, one from 300 to 500 K in the high-temperature mode, the other from 100 to 300 K in the low-temperature mode of the DSC instrument. Heating/cooling rate was  $10\text{--}40 \text{ K min}^{-1}$  and the sensitivity was varied from 1 to  $16 \text{ mcal s}^{-1}$ . Each compound was thermally cycled 10–15 times and the observations were confirmed by employing a fresh sample each time.

## RESULTS AND DISCUSSION

Figure 1 shows the DSC scan of  $(\text{NH}_4)_3\text{VO}_2\text{F}_4 \cdot 0.5 \text{ H}_2\text{O}$ . It shows a first-order, reversible phase transition at 412 K with a temperature hysteresis of about 16 K. A similar transition was observed for  $(\text{NH}_4)_2\text{VO}_2\text{F}_3 \cdot \text{H}_2\text{O}$  at 423 K but with a much larger temperature hysteresis of 21 K. The heats of these transitions are given in Table 1. Figure 2 shows the low-temperature DSC scans of the same two compounds. Both show very weak transitions

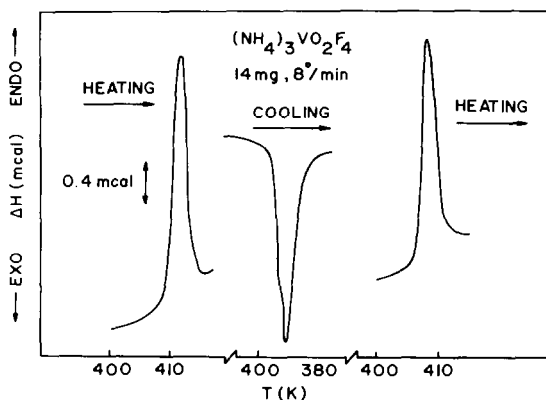


Fig. 1. DSC scan in the high-temperature mode of  $(\text{NH}_4)_3\text{VO}_2\text{F}_4 \cdot 0.5 \text{ H}_2\text{O}$ .

TABLE 1

Heats of transition (K) for the compounds studied

Compound	High-temp. mode		$\Delta H$ (kJ mol <sup>-1</sup> )	Low-temp. mode	
	heating	cooling		heating	cooling
(NH <sub>4</sub> ) <sub>3</sub> VO <sub>2</sub> F <sub>4</sub>	412	396	2.5 ± 0.4 <sup>a</sup>	210	205
Na(NH <sub>4</sub> ) <sub>2</sub> VO <sub>2</sub> F <sub>4</sub>	366 <sup>b</sup>	346 <sup>b</sup>	–	244	232
	383	366	11 ± 2 <sup>a</sup>	–	–
(NH <sub>4</sub> ) <sub>2</sub> VO <sub>2</sub> F <sub>3</sub>	442	400	0.9 ± 0.2 <sup>a</sup>	210	200

<sup>a</sup> Evaluated from the first heating run.<sup>b</sup> Broad and weak.

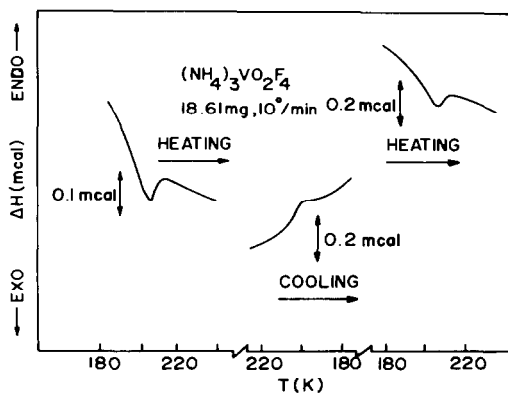
with negligible heat of transition but with hysteresis. This is reminiscent of the occurrence of first-order transitions in KMnF<sub>3</sub> and TlMnF<sub>3</sub>, again with a negligible heat of transition as reported earlier [5]. These transitions in KMnF<sub>3</sub> and TlMnF<sub>3</sub> arise out of distortion of the cubic lattice into a tetragonal one. This distortion is so weak that it was missed by most of the techniques used. These weak transitions in our vanadium compounds are highly reproducible.

Figure 3 shows the transitions observed in the case of Na(NH<sub>4</sub>)<sub>2</sub>VO<sub>2</sub>F<sub>4</sub> · H<sub>2</sub>O. The relevant observations are summarised as follows.

(1) In the high-temperature mode a strong first-order peak at 383 K was observed along with a shallow, broad peak around 366 K. The combined heat of transition is given in Table 1.

(2) On cooling from 400 K to room temperature, both peaks were obtained with a temperature hysteresis of about 17 K.

(3) During further thermal cyclings through the transitions, however, the peaks were obtained with progressively lower heats of transition.

Fig. 2. DSC scan in the low-temperature mode of (NH<sub>4</sub>)<sub>3</sub>VO<sub>2</sub>F<sub>4</sub> · 0.5 H<sub>2</sub>O.

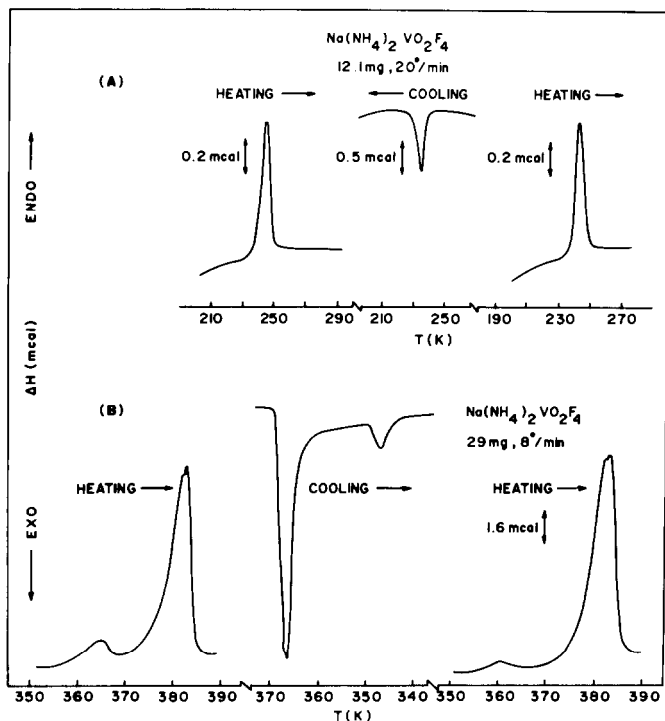


Fig. 3. DSC scan in both modes of  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4 \cdot \text{H}_2\text{O}$ .

(4) If, during the first heating cycle, the run is terminated at 372 K, i.e., the shallow peak is traversed but not the sharp one, and the sample is cooled to room temperature, the 346 K peak is obtained without the sharp peak at 366 K. Thus, a one-to-one correspondence between the peaks during heating and cooling is established.

(5) In the low-temperature mode a single, sharp peak was observed at 244 K during heating. The temperature hysteresis of this peak was about 12 K.

(6) During subsequent heating and cooling cycles the heat of transition remains the same for this transition in the low-temperature mode.

In the case of  $(\text{NH}_4)_3\text{VO}_2\text{F}_4 \cdot 0.5 \text{H}_2\text{O}$ , DTG [1] showed that half of the ammonium ions are chemically different from the other half. It was argued [1] that the phase transition at 412 K was brought about by the onset of complete rotation of all the anions in the compound by the breaking of all hydrogen bonds between one half of the cations and the fluorine atoms of the anion [2,3]. However, in our EPR experiments, we experienced difficulty in studying the triammonium salt at low temperature [3] due to disturbance in the  $Q$  value of the microwave cavity. Thus, we can conclude that the transition at 210 K mentioned above, observed in the triammonium salt, is involved with ordering of electric dipoles in the compound.

In the case of  $(\text{NH}_4)_2\text{VO}_2\text{F}_3 \cdot \text{H}_2\text{O}$ , again a preliminary EPR study [6]

indicated the presence of rotating as well as rigid anions simultaneously at room temperature. In this compound also, just as in the case of the triammonium salt [2], there are two kinds of ammonium ions but with different relative abundances (0.5 and 1.5). Again the high-temperature phase transition at 442 K in this compound is believed to be triggered by the complete breaking off of the hydrogen bonds. This is borne out by the fact that in two related compounds,  $(\text{NH}_4)_3\text{V}_2\text{O}_4\text{F}_5$  and  $\text{NH}_4\text{VO}_2\text{F}_2$ , where again preliminary EPR data [6] show no rotation of the anions, these high-temperature transitions are absent. The most important observation in this context is the absence of this high-temperature transition in  $\text{Na}_3\text{VO}_2\text{F}_4$ , where there is no scope for hydrogen bonding. Although the two salts, viz. triammonium and diammonium, give the high-temperature transition at different temperatures, it is interesting to note that they show the low-temperature transition at essentially the same temperature with a negligible heat of transition. However, there is a definite hysteresis, showing a first-order nature. This transition in the diammonium compound may also be involved with the ordering of electric dipoles, as in the case of the triammonium salt.

In the case of  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4 \cdot \text{H}_2\text{O}$  in the high-temperature mode, the DSC shows two consecutive, reversible phase transitions. One is associated with the  $\text{NH}_4$  ions, as in the case of both the above-mentioned ammonium compounds. This also, like the diammonium salt, has two kinds of anions, one having 0.5 ions and the other 1.5 ions. The only important difference between all the above-mentioned ammonium compounds and this mono-sodium compound is the occurrence of a very strong first-order transition in the low-temperature mode in the latter at a higher temperature compared to the former ones. Compared to the large  $\text{NH}_4$  ion, the Na ion is more polarising and, hence, stabilises the electric dipoles and orders them. This may be the cause of the transition occurring at higher temperatures compared to all the ammonium compounds.

## CONCLUSIONS

We conclude that the three compounds,  $(\text{NH}_4)_3\text{VO}_2\text{F}_4$ ,  $\text{Na}(\text{NH}_4)_2\text{VO}_2\text{F}_4$  and  $(\text{NH}_4)_2\text{VO}_2\text{F}_3$ , show one phase transition each in both the high-temperature and low-temperature modes. In the ammonium compounds the transitions are rather close, while in the case of the mono-sodium compound the transitions are well separated and at the same time the low-temperature transition is much stronger in terms of the heat of transition.

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