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Note

THERMAL BEHAVIOUR OF $Na_2WO_2F_4$: OCCURRENCE OF PHASE TRANSITIONS

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Tungsten (VI) is known to form many oxyhalides and oxyhalide anions [1,2] but they have not been studied in detail. These molecules and ions offer a very wide testing arena for stereochemical predictions based on different theories such as the VSEPR theory [3]. It would therefore be interesting as a prelude to prepare and study their thermophysical properties. Among the oxyfluoride species, anionic salts of general formulae M_3WO_4F, $M_2WO_3F_2$, $M_2WO_2F_4$, MWO_2F_3 and $MWOF_5$, where M = alkali metal, are known [4]. One such salt, $Na_2WO_2F_4$, has been studied and this short note describes its preparation, chemical analysis, X-ray powder patterns at different temperatures, TG and DTA scans.

$Na_2WO_4 \cdot 2\,H_2O$ was dissolved in 40% HF, the solution was evaporated to dryness and the process was repeated till a greenish white non-hygroscopic solid was obtained. The product was powdered and kept over NaOH pellets under vacuum in a desiccator to remove traces of HF. For chemical analysis, the salt was dissolved in concentrated sulfuric acid, evaporated to dryness and the process repeated until all fluoride was driven off as HF. The residue was dissolved in distilled water and tungsten was precipitated as the oxinate and weighed as such after drying [5]. The percentage of tungsten observed was 54.3% compared with the expected value of 54.4% for $Na_2WO_2F_4$. The X-ray powder pattern was taken with Cu-K_α radiation. A Stanton TG apparatus in static air was used for TG studies. The homemade DTA apparatus employed here was described elsewhere [6].

The salt was found to be crystalline as was inferred from the sharp lines in its X-ray powder pattern (Table 1). The TG and DTA patterns are given in Figs. 1 and 2, respectively. Between room temperature and 823 K, the loss in weight is less than 1% of the starting amount showing that it is thermally stable at least up to 823 K. Even at 1370 K, the loss does not level off. The weight loss behaviour in the whole temperature interval appears to be that of slow evaporation in the static air atmosphere of the TG set-up. The DTA run from room temperature up to 1100 K during first heating, shown in Fig. 2(a), is highly reproducible. It exhibits five endotherms at 749, 814, 823,

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TABLE 1

X-Ray powder patterns of different polymorphs of $Na_2WO_2F_4$

300 K		779 K		889 K	
d(Å)	I [a]	d(Å)	I [a]	d(Å)	I [a]
3.14	87	3.24	61	5.11	34
3.03	72	3.00	40	3.20	100
2.95	27	2.84	25	3.11	17
2.64	14	2.77	92	2.80	24
2.28	19	2.11	36	2.56	38
2.22	18	1.88	100	2.24	47
2.13	51	1.81	83	2.00	30
2.10	100	1.66	92	1.94	29
2.00	17	1.58	56	1.71	40
1.88	32			1.61	26
1.83	27			1.60	29
1.71	13				
1.64	16				
1.58	16				

[a] I = relative intensity.

942 and 1104 K. A sample heated beyond 1190 K and cooled showed that it had melted. The first cooling DTA run of a sample heated to 950 K is shown in Fig. 2(b). This shows a very strong exotherm at 900 K and a semblance of two weak exotherms, both broad, at lower temperatures. On

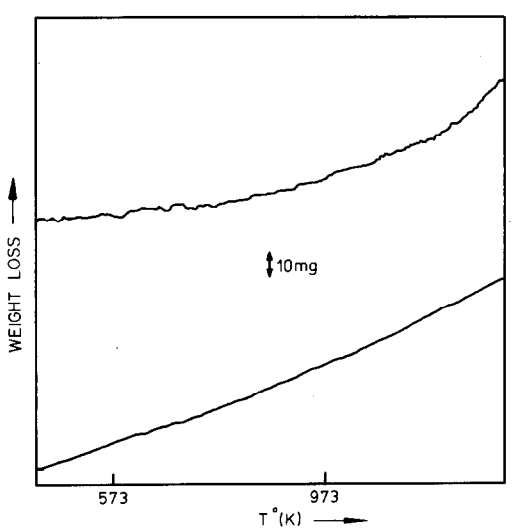

Fig. 1. TG run of $Na_2WO_2F_4$.

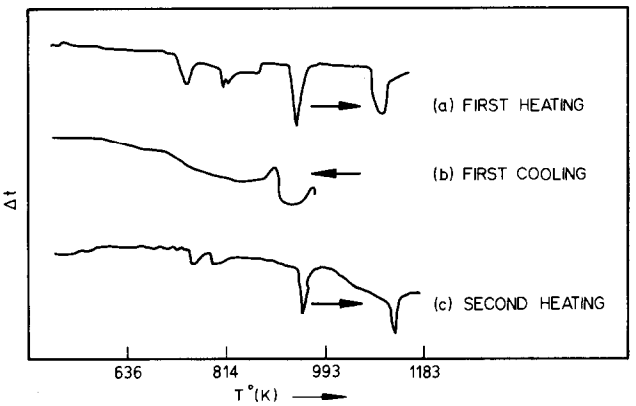

Fig. 2. DTA runs of $Na_2WO_2F_4$ and its thermal cycling behaviour.

reheating this sample from room temperature, all three endotherms are seen again [Fig. 2(c)], although with less intensity and an upward shift in temperature compared with the first heating run. It shows that all the endotherms represent reversible first-order phase transitions in this compound.

The X-ray powder pattern of $Na_2WO_2F_4$ at selected temperatures were recorded using an MRC model X-86-N3 high temperature X-ray diffractometer attachment described elsewhere [7]. The data are given in Table 1. These patterns support the earlier contention, based on DTA results, that the sample does undergo phase transitions and that these X-ray patterns represent those of different polymorphs of $Na_2WO_2F_4$. The X-ray pattern at 980 K did not show any diffraction peaks. However, a sample heated to 1190 K and immediately cooled back to room temperature gives the original room temperature X-ray pattern.

From their ^{19}F NMR studies of $[WO_2F_4]^{2-}$ in the solid state at various temperatures, Chuvaev et al. [8] concluded that the anions are in a state of rotation at room temperature. From the recent EPR studies on γ-irradiated $(NH_4)_3VO_2F_4$, evidence was obtained [9] for the simultaneous existence of static and dynamic forms of $[VO_2F_4]^{2-}$ units at room temperature and also for the existence of a first-order phase transition at 412 K. All these compounds have elpasolyth-related structures and are expected to show polymorphs with minor distortions at various temperatures. Thus, in the present case of $Na_2WO_2F_4$ also the polymorphism is exhibited.

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