

## THERMAL STABILITY OF $K_2U(SO_4)_3 \cdot H_2O$ , A NEW DOUBLE SALT

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### ABSTRACT

$K_2U(SO_4)_3 \cdot H_2O$  was synthesized and investigated by elemental analysis, X-ray powder diffraction, IR, TG and DTA techniques. By comparing its behaviour with that of its constituents, viz.  $K_2SO_4$  and  $U(SO_4)_2$ , it was inferred to be a double sulphate.

### INTRODUCTION

The thermal stability of  $U(SO_4)_2 \cdot n H_2O$  was investigated by Rode and Golovlea [1]. The aim of this study is to investigate the effect on the thermal stability of  $U(SO_4)_2$  of forming the double sulphate with  $K_2SO_4$ . We report in this communication the preparation, chemical analysis, X-ray powder pattern, IR spectrum, TG and DTA studies of the double salt  $K_2U(SO_4)_3 \cdot H_2O$ .

### EXPERIMENTAL

A known amount of nuclear grade uranium metal, dissolved in concentrated HCl, was heated to dryness over a sand bath. The residue was fumed with  $H_2SO_4$  until it was free from  $Cl^-$ . A dark green solution of  $U(SO_4)_2$  was thus obtained [2]. A visible spectrum of this solution showed no absorption at 430 nm of U(VI). A calculated amount of solid  $K_2SO_4$  was added to this U(IV) solution and kept at room temperature under a cover of argon gas. In about 3–4 days green crystals separated out. After filtering and washing with ethanol, they were dried in a vacuum desiccator over  $P_2O_5$ . The product was found to be both moisture and air sensitive.

For chemical analysis of the sulphate, the double salt was dissolved in 3–4 N HCl and by adding  $BaCl_2$ , the sulphate was precipitated which, after

incineration, was weighed as such. For uranium content, it was precipitated under appropriate conditions as  $(\text{NH}_4)_2\text{U}_2\text{O}_7$ , ignited and weighed as  $\text{U}_3\text{O}_8$  [3].

The IR spectra of the compound were recorded using the KBr pellet method. A Stanton TG setup with a sample size of  $\sim 400$  mg and a heating rate of  $4^\circ\text{C min}^{-1}$  was employed. The DTA apparatus used has been described elsewhere [4]. The heating rate was  $10^\circ\text{C min}^{-1}$  and the sample size varied between 60 and 200 mg.

## RESULTS AND DISCUSSION

The results of chemical analysis of the double sulphate are shown in Table 1. The double salt was found to be insoluble in DMF, DMSO and even in 2 M  $\text{H}_2\text{SO}_4$  at room temperature.

The X-ray powder pattern of the double sulphate along with those of related compounds is given in Fig. 1. The double salt is crystalline and its pattern differs from those of the starting materials.

Figure 2 shows the IR spectra of the solid at room temperature between 400 and  $3000\text{ cm}^{-1}$ . Basic and neutral sulphates containing U(IV) and alkali ions were investigated by Perez et al. [5] using IR spectroscopy. They observed in all basic salts containing U(IV) two distinct bands at  $840\text{ cm}^{-1}$  and  $455\text{ cm}^{-1}$  attributable to U–O–H vibrations. In the IR pattern of the present compound, the conspicuous absence of the  $840\text{ cm}^{-1}$  absorption indicates the absence of basic U–O–H linkage. For a  $C_{2v}$  symmetry of the sulphate group, if the degeneracy is completely lifted, a maximum of nine local modes is expected [ $\nu_1(1)$ ,  $\nu_2(2)$ ,  $\nu_3(3)$  and  $\nu_4(3)$ ]. The multiplicity of bands observed for the double salt in the region anticipated for these vibrations, viz.  $\nu_1$  ( $1010$  and  $1020\text{ cm}^{-1}$ ),  $\nu_2$  ( $425$ ,  $455$  and  $495\text{ cm}^{-1}$ ),  $\nu_3$  ( $1035$ ,  $1145$  and  $1210\text{ cm}^{-1}$ ) and  $\nu_4$  ( $590$ ,  $650$  and  $660\text{ cm}^{-1}$ ), exceeding the

TABLE 1  
Chemical analysis of  $\text{K}_2\text{U}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$

	Uranium content		Sulphate content	
	%	Deduced M.W.	%	Deduced M.W.
Calculated	38.3	622	46.3	622
Found	38.6	624	46.7	617

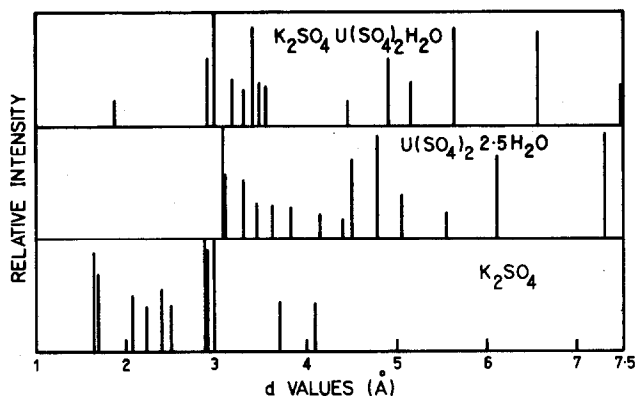


Fig. 1. X-Ray powder diffraction pattern of the double salt and starting material.

maximum expected number of nine, indicates a  $C_{2v}$  local symmetry for the sulphate. It could either be a chelating or bridging type of  $C_{2v}$  for the sulphate. The fact that the S–O stretching frequencies are slightly on the higher side favours a chelating sulphate group with  $C_{2v}$  symmetry [5].

Figures 3, 4 and 5 show the TG runs on  $UO_2SO_4 \cdot 3H_2O$ ,  $U(SO_4)_2 \cdot 2.5H_2O$  and the double salt  $K_2U(SO_4)_3 \cdot H_2O$ .  $UO_2SO_4 \cdot 3H_2O$  is included here because it can be one of the decomposition products of the other two compounds;  $U(SO_4)_2 \cdot 2.5H_2O$  is included because it is the starting material for the preparation of the double salt, besides, we wish to compare the thermal stability of the double salt with that of  $U(SO_4)_2 \cdot 2.5H_2O$ .

$UO_2SO_4 \cdot 3H_2O$  (BDH AR grade) starts to lose weight at 433 K and levels off at 573 K (Fig. 3). This loss is due to the removal of water of

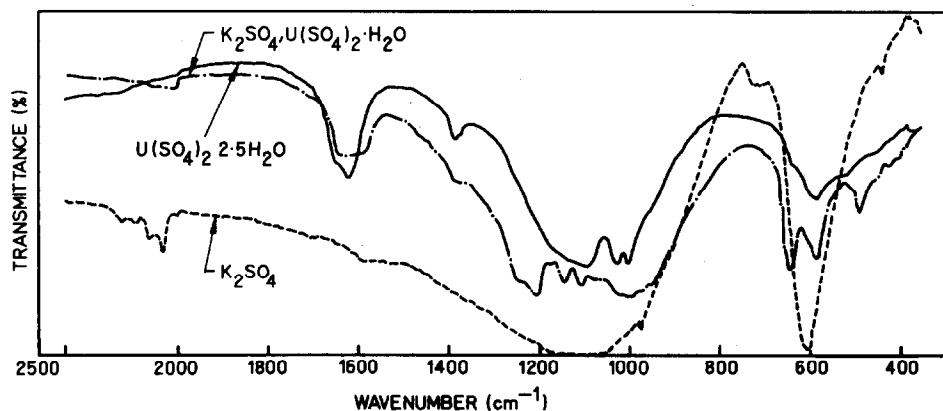


Fig. 2. IR pattern of the double salt and starting material.

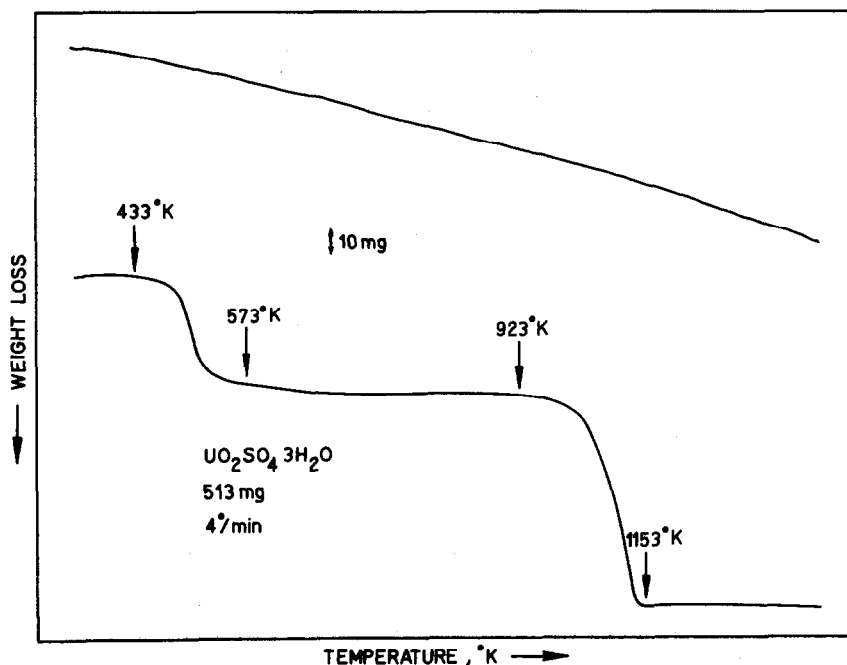


Fig. 3. TG of  $\text{UO}_2\text{SO}_4 \cdot 3 \text{H}_2\text{O}$ .

hydration and the product is anhydrous  $\text{UO}_2\text{SO}_4$ . Between 573 K and 903 K the product is anhydrous  $\text{UO}_2\text{SO}_4$ . Between 923 K and 1153 K  $\text{UO}_2\text{SO}_4$  loses  $\text{SO}_2$  to give an oxide of uranium of uncertain composition,  $\text{UO}_x$ . Here we observed the loss in weight to be  $\sim 16.5\%$ . The weight loss in this step depends very sensitively on the sample amount, particle size, atmosphere, and rate of heating, as was reported by Notz and Jaffe [6].

Figure 4 gives the TG of  $\text{U}(\text{SO}_4)_2 \cdot n \text{H}_2\text{O}$ . In this compound  $n$  varies according to the mode of preparation. Under the conditions used in the present preparation,  $n$  was 2.5. This is inferred from the 8.9% weight loss observed by us in the first step in TG, compared with an expected loss of 9.4%. This loss was observed between 450 and 550 K, in agreement with the results reported by Rode and Golovlea [1]. In the following two steps, viz., between 710 and 995 K and 1010 and 1153 K, the weight loss was 13.5% and 15.1%, respectively, starting from the anhydrous salt. Although both steps involve the loss of one molecule of  $\text{SO}_2$  in each step, individual fits are not good. However, the overall loss in both the steps was 28.6%, while that expected for the loss of two molecules of  $\text{SO}_2$  stands at 29.8%. This is also in agreement with the results of Russian workers [1]. The plateau region between 995 and 1010 K does not correspond exactly to the composition of

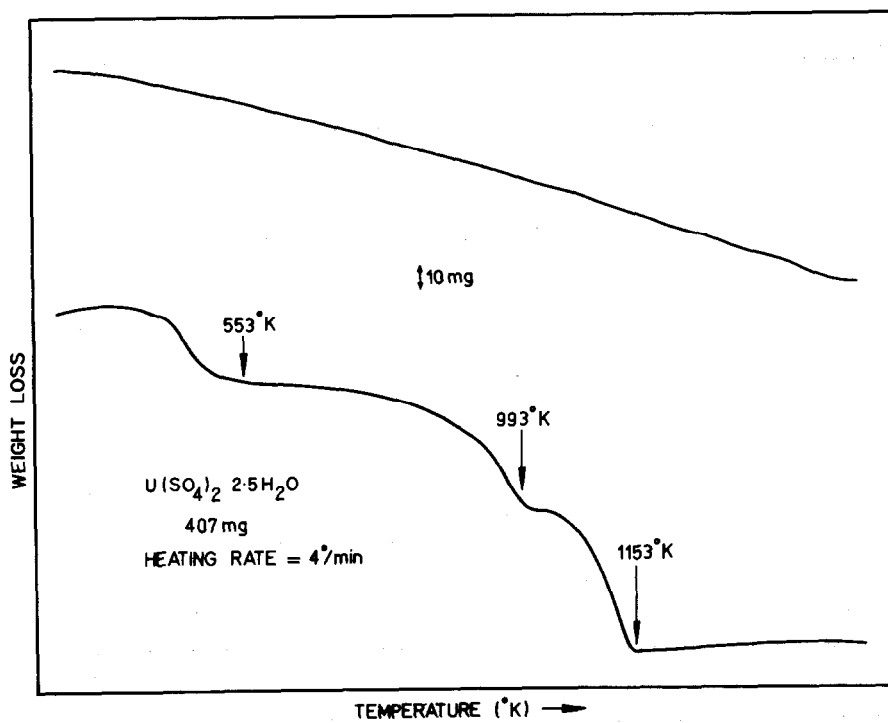
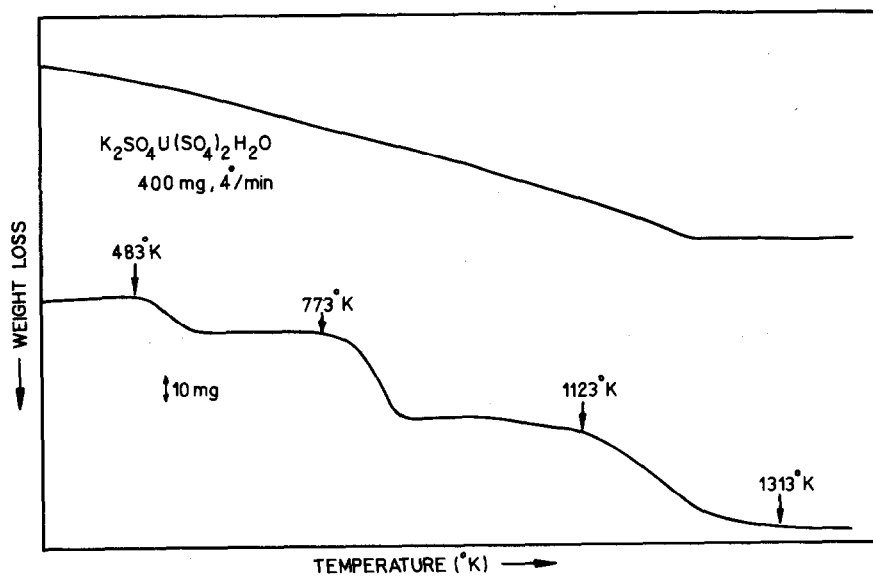
Fig. 4. TG of U(SO<sub>4</sub>)<sub>2</sub>·2.5 H<sub>2</sub>O.

Fig. 5. TG of the double salt.

$\text{UO}_2\text{SO}_4$ , although is the expected intermediate. This is possibly due to overlapping decomposition processes of the predecessor and the product [7].

Figure 5 depicts the TG pattern of the double salt  $\text{K}_2\text{U}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ . The water of hydration was lost in the first step between 480 and 575 K. The observed loss of 3% in this step is in agreement with that of 2.9% expected for the loss of one molecule of water. The anhydrous double salt was found to be stable up to 793 K, as against up to 710 K for  $\text{U}(\text{SO}_4)_2$  (Fig. 4). It is known that  $\text{K}_2\text{SO}_4$  is stable up to its melting point of 1340 K. The only part of the double salt which is susceptible to thermal degradation is the actinide sulphate moiety. Thus, by forming the double sulphate, the thermal stability region of U(IV) sulphate is enhanced by  $\sim 80$  K. But at the same time it is also worth noting that the first decomposition step is completed in the double salt at 890 K, almost 100 K ahead of that in  $\text{U}(\text{SO}_4)_2$ . The observed weight loss in the double salt in this step is 8.9%, as against 10.6% based on  $\text{SO}_2$  loss. The product at this stage is supposed to be  $\text{K}_2\text{SO}_4 \cdot \text{UO}_2\text{SO}_4$ . The stability range of pure  $\text{UO}_2\text{SO}_4$  according to Fig. 3 is 995–1010 K, while in the double salt it is wider, i.e. 880–1060 K. The most important feature of thermolysis of the double salt is that the next weight loss goes on and on, even at 1300 K, in contrast to pure  $\text{UO}_2\text{SO}_4$  wherein an almost plateau region was observed beyond 910 K (Fig. 3).

Figure 6 gives the DTA traces of all related compounds pertinent to this study:  $\text{K}_2\text{SO}_4$  (A);  $\text{UO}_2\text{SO}_4 \cdot 3 \text{H}_2\text{O}$  (B);  $\text{U}(\text{SO}_4)_2 \cdot 2.5 \text{H}_2\text{O}$  (C); and  $\text{K}_2\text{U}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$  (D). Pure  $\text{K}_2\text{SO}_4$  shows the presence of a phase transition at 885 K, in agreement with the literature [8]; it is known to melt at 1340 K.  $\text{UO}_2\text{SO}_4 \cdot 3 \text{H}_2\text{O}$  exhibits two endotherms, one at 499 K and the other at 1100 K. The first corresponds to the dehydration step in TG (Fig. 3) while the second corresponds to the loss of  $\text{SO}_2$  which is the second step in TG.

The DTA of  $\text{U}(\text{SO}_4)_2 \cdot 2.5 \text{H}_2\text{O}$  exhibits two endotherms, one at 495 K and the other, a broad one, at 1100 K. In addition, there is a weak exotherm at 1015 K, the origin of which is not clear at the moment. The first endotherm at 495 K has a noticeable shoulder at 518 K and these two are attributed to the loss of water of hydration in distinct, though overlapping, steps. However, no such resolution was evident in the TG curve. It was inferred by Notz [9] that all water molecules are not held equally strongly in a related compound,  $\text{UO}_2\text{SO}_4 \cdot 3 \text{H}_2\text{O}$  the DTA of which shows three endotherms attributed to stepwise dehydration. The high temperature endotherm at 1100 K in  $\text{U}(\text{SO}_4)_2 \cdot 2.5 \text{H}_2\text{O}$  is attributed to the loss of the second molecule of  $\text{SO}_2$ , as in the case of  $\text{UO}_2\text{SO}_4 \cdot 3 \text{H}_2\text{O}$ .

Lastly, the DTA of  $\text{K}_2\text{U}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$  shows several endotherms: at 570 K, a closely spaced doublet at 886 and 899 K, and a last one at 1052 K. The 570 K endotherm represents the dehydration process, in agreement with its TG result given earlier. The doublet is highly reproducible and reversible,

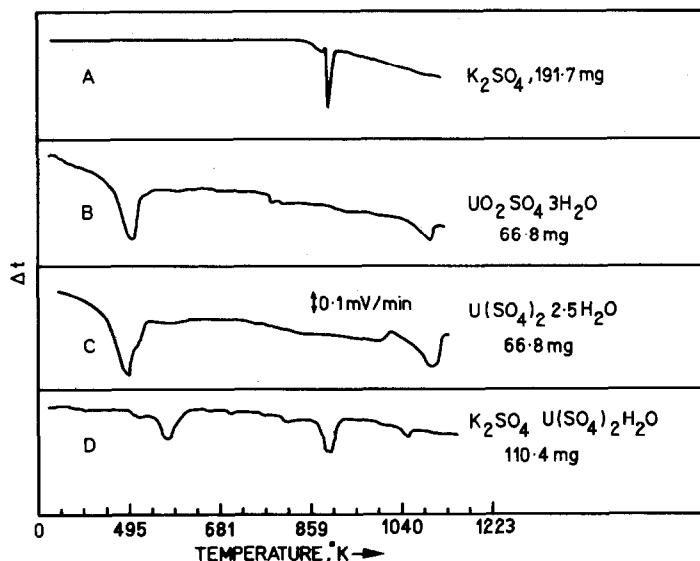


Fig. 6. DTA of the double salt and related compounds.

and is attributed to a crystallographic phase transition in the double salt, akin to that exhibited by pure  $\text{K}_2\text{SO}_4$  while going over to a high temperature  $\alpha$ -phase. At this stage, it is tempting to attribute the 1052 K endotherm to the loss of the second molecule of  $\text{SO}_2$  to give  $\text{UO}_x$  residue. But such an endotherm is conspicuously absent in the DTA of  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{U}(\text{SO}_4)_2 \cdot 2.5\text{H}_2\text{O}$  which also lose  $\text{SO}_2$  to give  $\text{UO}_x$ . In the latter two compounds,  $\text{SO}_2$  loss possibly takes place over a broad temperature interval, thereby spreading the heat effect over this interval. But the corresponding TG studies give an illusion of a clear-cut step for the loss of  $\text{SO}_2$ . The presence of the 1052 K endotherm in the double salt and its absence in the other two sulphates can be understood if the TG of the double salt is examined more critically. In the double salt, the step representing the loss of the second molecule of  $\text{SO}_2$  starts much later than in the other two compounds, and the loss continues without tapering off even at 1300 K, the highest temperature recorded by us in this TG. This proves that the loss of  $\text{SO}_2$  in the first step of the double salt does not yield  $\text{UO}_2\text{SO}_4$ . If it did, it would have followed the same course of degradation as in the other compounds, levelling off the loss at  $\sim 1150$  K. Instead, the presence of  $\text{K}_2\text{SO}_4$  influenced the subsequent degradation of  $\text{UO}_2\text{SO}_4$ . Conversely, the presence of  $\text{UO}_2\text{SO}_4$  has a noticeable effect on the phase transition of  $\text{K}_2\text{SO}_4$ . In place of a single sharp peak in pure  $\text{K}_2\text{SO}_4$ , the double salt exhibits two closely spaced doublets for the phase transition. Thus the fact

that the loss continues even at and beyond 1300 K shows that  $\text{UO}_2\text{SO}_4$  is stabilized by the presence of  $\text{K}_2\text{SO}_4$ . Thus the intermediate should also be a double salt,  $\text{K}_2\text{UO}_2(\text{SO}_4)_2$ . It should be added here that  $\text{UO}_2\text{SO}_4$  is reported to go through a crystallographic phase transition at 1028 K [9] while undergoing decomposition. As such, the 1052 K peak in the double salt can be attributed to the phase transition akin to what pure  $\text{UO}_2\text{SO}_4$  exhibits at 1028 K. The direct and unambiguous proof for this contention is given by the DTA heating run up to 1183 K followed immediately by a cooling run down to room temperature of the double sulphate. The heating run as usual shows the 1052 K endotherm, while the cooling run gives an exotherm at 1020 K, proving the reversibility of the process taking place at 1052 K during heating. Thus it cannot be due to decomposition, but rather it is due to a reversible phase transformation. Such reversible phase transitions, concomitant with decomposition, were reported by us in  $\text{CsH}_2\text{PO}_4$  [10] and  $(\text{NH}_4)_3\text{VO}_2\text{F}_4$  [11].

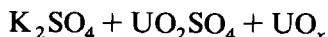
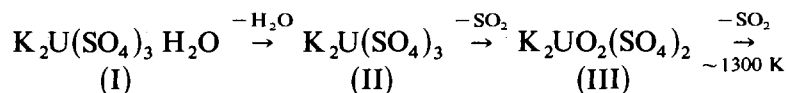
It is worth mentioning here that although in  $\text{UO}_2\text{SO}_4 \cdot 3 \text{H}_2\text{O}$  and  $\text{U}(\text{SO}_4)_2 \cdot 2.5 \text{H}_2\text{O}$ , the TG gives an impression of a clear-cut step for the loss of the first molecule of  $\text{SO}_2$ , their DTA does not indicate any corresponding heat effect. The TG result indeed is an artefact of the technique and is not a true picture, as evidenced from our recent combined TG studies with various sample sizes on the one hand and micro TG studies on the other [12]. Thus the TG results should be accepted with reservation unless corroborated by other independent evidence.

## CONCLUSIONS

From the present study the following conclusions can be made.

$\text{K}_2\text{U}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  appears to be a double sulphate with no basic U-O-H linkage and the sulphate groups find themselves in a  $C_{2v}$  local symmetry in the solid.

The decomposition pattern appears to be



Intermediate (II) is thermally more stable than  $\text{U}(\text{SO}_4)_2$ . In (III) the  $\text{UO}_2\text{SO}_4$  part does not decompose completely even at 1300 K while pure  $\text{UO}_2\text{SO}_4$  decomposes completely by 910 K. The presence of  $\text{K}_2\text{SO}_4$  is responsible for stabilizing (III) thermally. Intermediate (II) exhibits a phase transition akin



to that shown by pure  $K_2SO_4$  but with a double hump. Further, (III) gives a reversible phase transition at  $\sim 1052$  K similar to that shown by pure  $UO_2SO_4$ . Hence (II) and (III) are shown as double sulphates rather than mechanical mixtures of their respective constituent sulphates.

In both  $U(SO_4)_2 \cdot 2.5 H_2O$  and  $K_2U(SO_4)_3 \cdot H_2O$ , the DTA does not show a heat effect corresponding to the removal of the first molecule of  $SO_2$ , while their TGs appear to exhibit a clear step. Thus the TG result appears to be an artefact of the technique and hence is suspect in this case.

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