

## **THERMAL DECOMPOSITION OF HAFNIUM PHOSPHATE AND RELATED MATERIALS**

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### **Abstract**

The thermal decomposition of hafnium phosphate (both in amorphous and crystalline forms), molybdate and tungstate was investigated. Hafnium phosphate has a layered structure, that of molybdate and of tungstate are tetragonal one. On investigating these materials two main endothermic processes with mass loss were observed in the temperature range of 298–1023 K. These processes were identified as crystal and structural water loss of the materials. The total mass loss of hafnium phosphate, molybdate and tungstate was 11, 35 and 6.0%, respectively. In the case of mixed hafnium-titanium salts various crystal water quantities were found, depending on the titanium content of the sample.

**Keywords:** hafnium, molybdate, phosphate, thermal analysis, tungstate

### **Introduction**

In the field of inorganic ion exchange materials, a considerable time has been devoted to investigations of zirconium phosphate and related materials and their intercalates and/or organic derivatives. Most of the work in this field has been carried out by Clearfield [1]; similarly, Alberti [2] provided a very useful review. Later, interest began to focus on learning more about the behaviour of other metal salts having a similar structure and ion exchange properties as the well-known zirconium phosphates. Among these materials, hafnium phosphate and related materials were investigated [3–6]. Data relating to the thermal behaviour of these materials are presented here.

### **Experimental**

All chemicals used were of MERCK analytical grade.

### Preparation

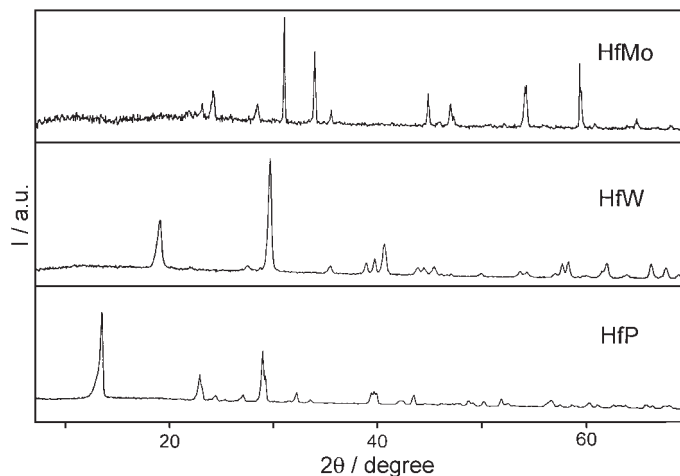
Amorphous hafnium phosphate (HfPa) was prepared as follows: 430 cm<sup>3</sup> of 0.3 M HfCl<sub>4</sub> in 4.5 M acetic acid (AcA) solution was mixed at 353 K with 460 cm<sup>3</sup> of 6 M H<sub>3</sub>PO<sub>4</sub> solution while vigorously stirring. The precipitate was then filtered, washed till pH≈4 and dried at room temperature in an exsiccator over P<sub>2</sub>O<sub>5</sub>. To obtain it in a crystalline form (HfP) we used another way. A typical process was: 2 g of HfCl<sub>4</sub> dissolved in 125 cm<sup>3</sup> of 3 M HF solution, then 500 cm<sup>3</sup> of 6 M H<sub>3</sub>PO<sub>4</sub> solution was added slowly during vigorous stirring. The solution was heated to 353 K and the HF was allowed to evaporate (about 24 h). The precipitate was treated in the same way as described for the amorphous sample. For the mixed hafnium-titanium phosphate (HfTiP) a typical way of preparation was as follows: 430 cm<sup>3</sup> of 0.32 M HfCl<sub>4</sub> (Aldrich anal. grade) in 4.5 M AcA solution was mixed with 135 cm<sup>3</sup> of 0.5 M TiCl<sub>4</sub> in 6 M AcA solution. To this mixture 430 cm<sup>3</sup> of 12% v/mass H<sub>3</sub>PO<sub>4</sub> solution was added slowly (over 14 h) with continuous stirring. The resulting gel was allowed to stand in the mother liquid for 96 h after which it was digested in the same way as crystalline pure hafnium phosphate. This procedure yielded a material of Hf<sub>0.67</sub>Ti<sub>0.33</sub>(HPO<sub>4</sub>)<sub>2</sub>·2.5H<sub>2</sub>O. The hafnium molybdate (HfMo) was synthesized as follows: to the aqueous solution of (NH<sub>4</sub>)Mo<sub>6</sub>O<sub>24</sub>·12H<sub>2</sub>O whose pH was first adjusted to 1.9 with 6 M solution of HCl during continuous vigorous stirring, the stoichiometric amount of HfCl<sub>4</sub> in 1 M solution of HCl was added dropwise. The precipitate (amorphous gel) was held in contact with its mother liquid for 96 h at 353 K. The product was filtered, washed with redistilled water till pH=4, and dried at room temperature in a vacuum desiccator over P<sub>2</sub>O<sub>5</sub>. The hafnium tungstate (HfW) was prepared in the same way as described above with the exception that (NH<sub>4</sub>)W<sub>7</sub>O<sub>24</sub>·12H<sub>2</sub>O solution was used as the starting material.

### Analytical

From HfP hafnium was determined through an organic complex [7], while the phosphorus colorimetrically [8]. In the case of HfMo 0.2 g was dissolved in 10 cm<sup>3</sup> of hot conc. sulphuric acid and the solution was diluted to 200 cm<sup>3</sup>. The molybdenum was precipitated with 5% silver nitrate solution. After ignition the MoO<sub>3</sub> was determined gravimetrically. In case of HfW, 0.2 g of it was dissolved in 10 cm<sup>3</sup> of concentrated sulphuric acid solution and then diluted to 200 cm<sup>3</sup>. Tungsten was determined using the method described by Heyne [9], the Hf as described above.

### Identification

The samples were identified by XRD method, using a computer controlled DRON-2 type diffractometer under the conditions described earlier [10]. The diffractograms were evaluated by a so-called 'search' program [11]. A fragment of each of the diffractograms is shown in Fig. 1.



**Fig. 1** A fragment of each of the X-ray diffractograms

#### *Thermal analysis*

Thermal analysis was carried out using a computer controlled Mettler TA1-HT type thermobalance giving DTA and TG data in parallel. The conditions of the measurements were the same as presented earlier [12].

### **Result and discussion**

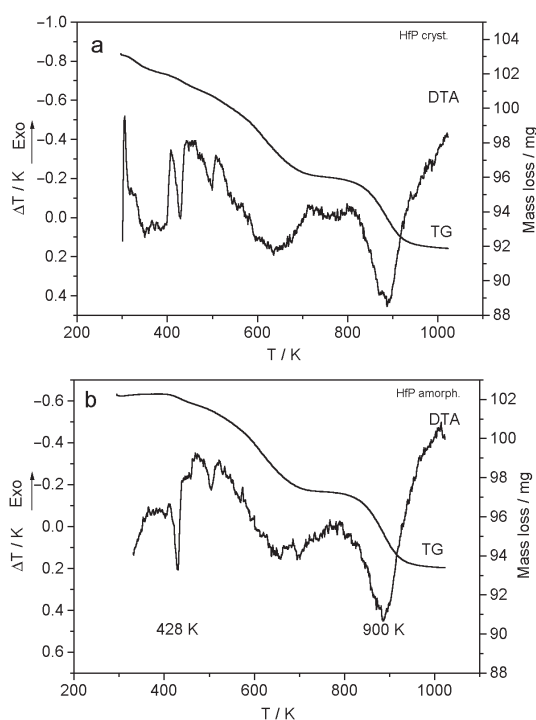
Based on the analytical data, for the prepared samples the stoichiometric ratio of  $Me/Hf=2$  (with the exception of the amorphous sample) was found, where  $Me=P$ ,  $Mo$  and  $W$ , respectively. XRD analysis was utilized to identify the prepared materials. Their possible structure and some main crystallographic data were determined and calculated in each case based on 45 peaks of the given diffractogram. The calculated data were accepted only if the results simulated using CaRine W 3.1 program were concordant with them. The most informative fragment (in reduced form) of the given diffractograms is shown on Fig. 1.

As a result of the evaluation we found that all (with the exception of the amorphous sample) prepared materials were crystalline; hafnium molybdate and tungstate had a tetragonal structure, the hafnium phosphate and the various mixed hafnium-titanium phosphates have monoclinic one. The crystal dimensions of hafnium molybdate and tungstate were found:  $a=1.1771\pm 0.0001$  nm,  $c=1.2742\pm 0.0001$  nm and  $a=1.1073\pm 0.0001$  nm,  $c=1.0667\pm 0.0001$  nm, respectively. The space groups are  $I4c, d$ . The unit cell dimensions of hafnium phosphate in space groups  $P2_1/n$  are:  $a=0.8182\pm 0.0001$  nm,  $b=0.5526\pm 0.0001$  nm,  $c=1.6731\pm 0.0001$  nm and  $\beta=110.8$ . (For mixed metal phosphate samples practically the same parameters were calculated.) The interlayer distance 1.18 nm was found. If compare these data with those found by Clearfield and Troup [13] for  $\gamma$ -zirconium phosphate a considerable similarity could be

found between their structures so we suggest that hafnium phosphate is also a layered material. Because the mixed metal phosphates have practically the same parameters as the hafnium phosphate we believe that this suggestion is also valid for them.

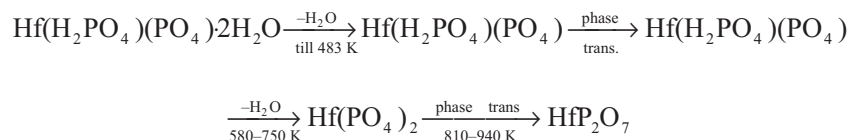
On evaluating the thermal analytical data we found the following:

For crystalline hafnium phosphate 11% total mass loss was found (Fig. 2a). On the DTA curve four endothermic processes were observed. The second is practically without mass loss. At a relatively low temperature some adsorbed water is lost. This is followed by a reversible solid phase transition (it was identified by XRD method from the back-titrated sample), and the loss of crystal-, and structural water, the latter which arose during the decomposition of the phosphate groups.



**Fig. 2** TG and DTA curves of hafnium phosphate; a – crystalline; b – amorphous

Taking into consideration the mass loss together with the analytical data the following way of thermal decomposition can be proposed for the crystalline hafnium phosphate:



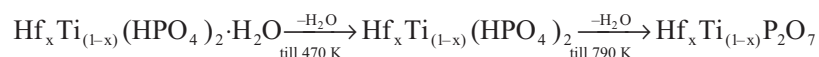
In contrast to the crystalline form the amorphous hafnium phosphate (Fig. 2b) lost one mole of structural water released at a relatively high temperature (the process is finished at ~920 K) and 11% total mass loss was found. From the mixed titanium-hafnium phosphates the sample having a hafnium content near to the pure phosphate (0.9%) has practically identical thermal behaviour with them. No differences were found between the amorphous and crystalline materials. The other compositions, are different as demonstrated by the mass loss and crystal water content data in Table 1.

**Table 1** Mass loss and crystal water content of mixed metal containing phosphate

Metal content	Total mass loss/%	Crystal water cont./ mole/molecular unit	Ratio Me/PO <sub>4</sub>
Hf	11.2	2.0	1:2
Hf <sub>0.9</sub> Ti <sub>0.1</sub>	11.2	2.1	1:2
Hf <sub>0.67</sub> Ti <sub>0.33</sub>	10.0	2.5	1:2
Hf <sub>0.5</sub> Ti <sub>0.5</sub>	9.6	1.0	1:2
Hf <sub>0.33</sub> Ti <sub>0.67</sub>	17.3	2.3	1:2
Hf <sub>0.1</sub> Ti <sub>0.9</sub>	20.0	2.1	1:2
Ti	20.6	2.0	1.2

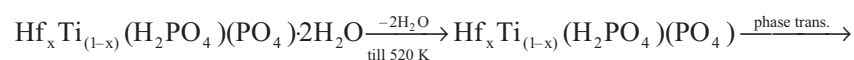
In the case of these samples no additional processes in comparison with those for pure phosphate were observed. At the same time a dependence on the titanium content was found for the peak temperature. Based on the data the following thermal decompositions are proposed:

a) amorphous



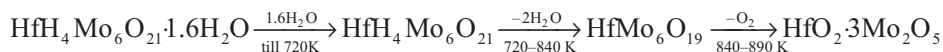
and

b) crystalline



In the case of hafnium molybdate (Fig. 3) on the DTA curve endothermic processes were found in the temperature ranges of 720–780, 780–840 and 840–890 K, respectively. All these processes were accompanied by mass loss. In addition, there was a slow, continuous, but not significant mass loss between 298 and 720 K. This means that a small amount of crystal water was lost monotonously until high temperature was reached. This process was immediately followed by the decomposition of the molecule in three steps. Judging from the analytical and thermal decomposition

data the initial material has the composition  $\text{HfH}_4\text{Mo}_6\text{O}_{21}\cdot 1.6\text{H}_2\text{O}$  and the final product consists of a mixture of oxides of  $\text{HfO}_2\cdot 3\text{Mo}_2\text{O}_5$ . Taking into consideration these data the following mode of thermal decomposition is proposed:



For hafnium tungstate (Fig. 4), endothermic processes were found in the temperature ranges of 430–560 and at 670–760 K, respectively. Both are followed by mass loss. Of these two processes the first covers the crystal water loss whereas the second is connected with the decomposition of the anionic part of the molecule. Judging from the analytical and thermal analytical data the initial material had the composition  $\text{HfH}_2\text{W}_7\text{O}_{24}\cdot 6.7\text{H}_2\text{O}$  while the final product consists of a mixture of oxides of  $\text{HfO}_2\cdot 7\text{WO}_3$ .

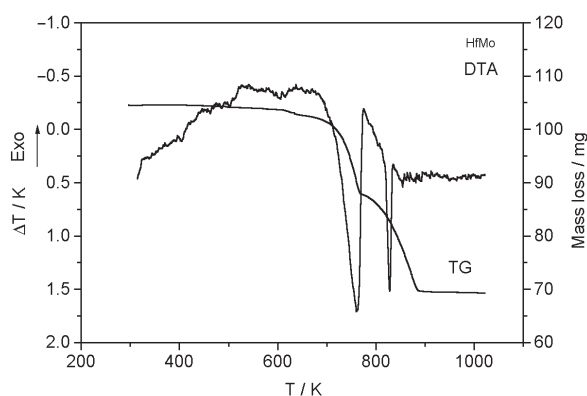


Fig. 3 TG and DTA curves of hafnium molybdate

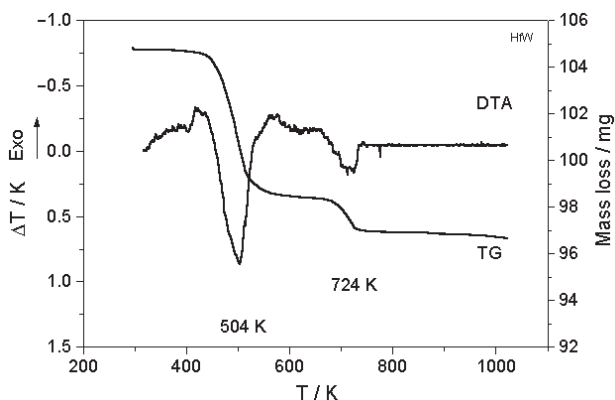
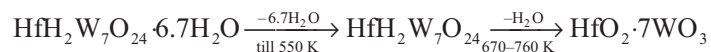


Fig. 4 TG and DTA curves of hafnium tungstate

Bearing these data in mind the following mode of thermal decomposition can be proposed:



Disregarding the similar crystalline structure, hafnium tungstate has a more simple way of thermal decomposition than hafnium molybdate, and in addition, the endothermic processes were found at a lower temperature.

## Conclusions

Of the materials investigated the phosphate and the mixed metal phosphates have a different crystalline structure from that of the molybdate and tungstate.

Bearing in mind this difference, generally speaking the thermal behaviour of these materials was quite similar. All the given materials lost their crystal water in the first step, characterized by a well defined endothermic process, with the exception of molybdate which lost its crystal water during a slow, continuous process until high temperature was reached. The structural water of the materials was lost in one step, with the exception of molybdate: molybdate lost its structural water in two steps. These phenomena probably arose from the oxidation state of molybdenum within the molecule.

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