Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 135–140

THERMOANALYTICAL INVESTIGATION OF CRYSTALLINE LAYERED HAFNIUM SALTS

L. Szirtes[*], *L. Riess and J. Megyeri*

Institute of Isotope CRC of the Hungarian Academy of Sciences H-1525 Budapest, PO Box 77, Hungary

Transition metal containing hafnium phosphates forms has layered monoclinic structure. In general these materials have similar route of thermal decomposition; i.e. they loss their crystal water first then at a higher temperature their structural one. At least the result HfP_2O_7 goes through phase change at about 1000 K. In detail among their thermal decomposition some differences occur. The Mn and Zn containing samples have similar behaviour as pure hafnium phosphate. The Cu and Ni containing materials have an additional exo-process connected with the transition metal oxide forms. In case of Co containing sample similar to that of Zn containing one (but very weak) processes were observed.

Keywords: *hafnium, phosphate, thermal analysis, transition metal*

Introduction

In the early fifties, in concerning with radiochemical processes, started the investigations on inorganic ion exchangers because of their good resistance against radiation. By the time widely was learning and used the zirconium phosphate having the best properties among the materials investigated.

Later, interest began to focus on investigation more about the behaviour of other metal salts having similar ion exchange property as the well-known zirconium phosphates. Among these materials, hafnium phosphate and related materials were learned [1–4]. Lately give rise interest to the investigations on nanoparticles [5] and transition metal salts [6, 7] used for catalytic and some other purposes. Data relating to the thermal behaviour of hafnium phosphate and related materials were presented earlier [8]. Partly these results, and partly the found electrical resistivity data [9] generated interest to investigate the thermal behaviour of the first-row transition metal containing hafnium phosphates too. Results of these investigations are presented here.

Experimental

Sample preparation

All chemicals used were of Merck analytical grade. To get hafnium phosphate [HfP] the following typical process was used: 2 g of $HfCl_4$ dissolved in 125 cm^3 of 3 M HF solution, then 500 cm^3 of 6 M H_3PO_4 was added, slowly during vigorous stirring. The solution was heated to 353 K and the fluor was evaporated trough 24 h. The precipitate was washed and dried over P_2O_5 [8].

Preparation of ion exchange forms

The freshly prepared hafnium phosphate (having α-crystalline form) was equilibrated with solutions of various first-row divalent transition metal ions, under the following conditions:

100 cm^3 of 0.1 M M(II)-acetate solution [where M(II)=Co, Ni, Mn, Cu and Zn, respectively] was added to 3 g of HfP. The mixtures were stirred and heated to 353 K and held at this temperature – with constant stirring and solution level – for 200 h, respectively. After the finish of equilibration the precipitate washed, filtered and air-dried.

The quantity of added solution was calculated taking into consideration the exchange capacity of hafnium phosphate (7.4 meq g^{-1} at pH=7; T=293 K). The supernatant liquid was stored for analytical determinations.

Analytical

The M(II) content both of the original and the residual solutions was checked, by spectrophotometric method described by Sandell [10], using a Spectromom 195D photometer and as coloured compound. The quantity of exchanged ions was calculated from the difference between the M(II) contents of the initial and the residual acetate solutions. The concentration values obtained are given in Table 1.

---

[*] Author for correspondence: szirtes@alpha.iki.kfki.hu

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hngary
Springer, Dordrecht, The Netherlands

Table 1 Analytical data

Solution	Co(II)/	Ni(II)/	Mn(II)/	Cu(II)/	Zn(II)/
	mM cm^{-3}				
Initial	0.08	0.10	0.10	0.10	0.1
Residual	0.04	0.048	0.039	0.068	0.045
ion uptake in %	40	52	61	32	55

The samples were subsequently checked by elemental (carbon) analysis to ascertain whether any acetate remained. The hafnium content was determined through an organic complex [11], while the phosphate, using a method described by Sandell [10].

Identification

The samples were identified by XRD method at the conditions described earlier [12] for zirconium salts.

Thermal analysis

The measurements were carried out with a Mettler TA-1-HT computer controlled thermobalance that simultaneously provided DTA and TG data. The heating rate was chosen 278 K min^{-1}. The temperature range was 298–1100 K, the reference material was Al_2O_3, ambience: air, the experiments were carried out in a Pt crucible. The data were evaluated by means of a computer program, and they are collected in Table 2 and showed on Figs 2–7.

Result and discussion

Analysis

The measured values of hafnium and phosphate give a ratio of 1:2. The elemental (carbon) analysis showed no carbon (acetate) in the investigated samples. Evaluating the analytical data (Table 1) we found that during 200 h equilibration 40; 52, 61, 32, and 55% of Co(II), Ni(II), Mn(II), Cu(II) and Zn(II) were exchanged for, respectively. During the shorter contacting time these quantities are strongly decreased. At the end of the process the ion uptake became slower and slower and the total (100%) change of hydrogen to transition metal ions could not be achieved under the given experimental conditions (Fig. 1). Taking these data into consideration the following Hf/*M*(II) molar ratios could be calculated: 1/0.40, 1/0.52, 1/0.61, 1/0.32 and1/0.55 for Co, Ni, Mn, Cu, and Zn containing samples, respectively.

In consequence the following compositions are suggested for the samples:

Table 2 Data of thermal decomposition of transition metal containing hafnium phosphate

Ion exchanged form	Temperature range/K	Mass loss/%	DTG$_{max}$/K endo	DTG$_{max}$/K exo	DTA$_{max}$/K
Zn(II)	till 450	11.8	11.8/710	–	–5.75/400
	570–710				
	above 1100				
Mn(II)	till 360	12.8	12.6/685	–	–4.85/610
	365–485				
	485–685				
	above 1100				
Co(II)	370–405	10.3	10/1000	–	–4.0/980
	405–610				
	above 1100				
Ni(II)	till 570	10.2	10.1/1010	–	–1.25/595
	575–580				
	580–950			1.8/500	
	above 1100				
Cu(II)	till 455	14.1	12.0/780	–	–1.7/590
	455–565			2.1/560	
	770–1010				
	above 1100				

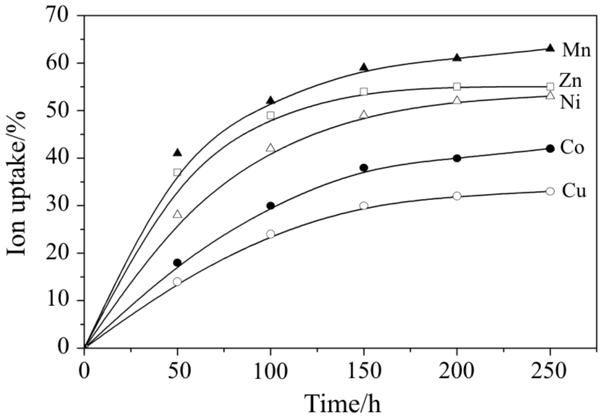

Fig. 1 Ion uptake (exchange) *vs*. equilibrium time =Co(II); =Ni(II); =Mn(II); =Cu(II); =Zn(II)

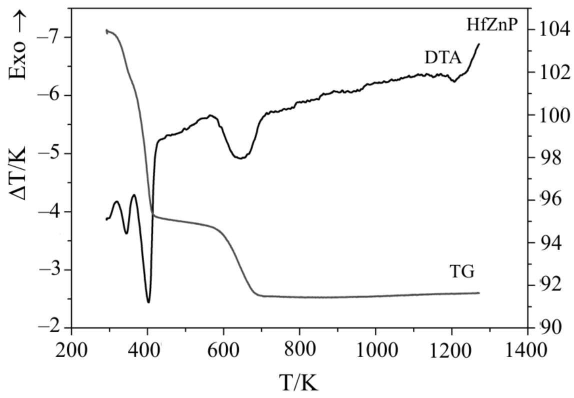

Fig 2 DTA and TG curves of zinc containing hafnium phosphate

$HfCo_{0.40}H_{1.20}(PO_4)_2{\cdot}xH_2O$

$HFNi_{0.52}H_{0.96}(PO_4)_2{\cdot}xH_2O$

$HfMn_{0.61}H_{0.78}(PO_4)_2{\cdot}xH_2O$

$HfCu_{0.32}H_{1.36}(PO_4)_2{\cdot}xH_2O$ and

$HfZn_{0.55}H_{0.90}(PO_4)_2{\cdot}xH_2O$

Based on these data the following selectivity order was found: Cu<Co<Ni<Zn<Mn, which is in good correlation with found selectivity sequence of hafnium phosphate [13].

XRD analysis was utilised to identify the prepared materials. Their possible structure and some main crystallographic data were determined [14] and calculated in each case base on 50 peaks of the given diffractograms. The calculated data were accepted only if the results simulated using Ca Rine W 3.1 program was concordant with them.

In such a way was found that the investigated samples have monoclinic layered structure and they are from crystallographic point of view a two-phase system.

During the thermal treatment the various first-row transition metal containing hafnium phosphates have different behaviour, against the consequent zirconium- and titanium salts investigated earlier [15, 16]. Generally the manganese and zinc containing samples showed similar behaviour as pure hafnium phosphate. In case of nickel and copper containing materials an addition exothermic process connected with oxygen loss was found, while the curve of sample containing cobalt showed the same processes as it was found for zinc and manganese containing samples, but they are very weak.

As it can be seen on the thermogram of zinc containing sample (Fig. 2) three endothermic processes with mass loss appear. Based on the data of earlier work [14] among them the first two connected with crystal water (till 450 K), while the third one with the structural water (result of the decomposition of hydrogen phosphate part) loss between 570–710 K. In addition an exothermic process without mass loss was found (started at about 1200 K), correspond to the phase transition – from monoclinic to cubic – of result hafnium oxide. During the treatment 11.8% total mass loss was found.

Taking into consideration the analytical and thermal data the following way of thermal degradation of the original molecule can be proposed:

$$[HfZn_{0.55}H_{0.9}(PO_4)_2]{\cdot}2.2H_2O \xrightarrow{-\ 2.2H_2O}$$

$$[HfZn_{0.55}H_{0{\cdot}9}(PO_4)_2] \xrightarrow{-\ 0.45H_2O}$$

$$HfP_2O_7{\cdot}0.55ZnO \xrightarrow{\text{phase trans.}}$$

$$HfO_2{\cdot}0.55ZnO{\cdot}P_2O_5$$

On the Fig. 3 are shown the DTA and TG curves of manganese containing sample. During the thermal treatment four endothermic processes with mass loss and an exothermic one without mass loss occurred. They result a total mass loss of 12.8%.

The endothermic processes cover both of the crystal- and structural water loss (the crystal water loss in two near equal steps), while the exothermic process adequate with the phase transition of hafnium oxide [HfO_2] (from monoclinic to cubic). Based on the data the following way of thermal decomposition can be proposed:

$$[HfMn_{0.61}H_{0.78}(PO_4)_2]{\cdot}2.41H_2O \xrightarrow{-\ 0.045H_2O^*}$$

$$[HfMn_{0.61}H_{0.78}(PO_4)_2]{\cdot}2.41H_2O \xrightarrow{-\ 0.41H_2O}$$

$$[HfMn_{0.61}H_{0{\cdot}78}(PO_4)_2 \xrightarrow{-\ 0.39H_2O}$$

$$HfP_2O_7{\cdot}0.61MnO \xrightarrow{\text{phase trans.}}$$

$$HfO_2{\cdot}0.61MnO{\cdot}P_2O_5$$

[*] adsorbed on the surface.

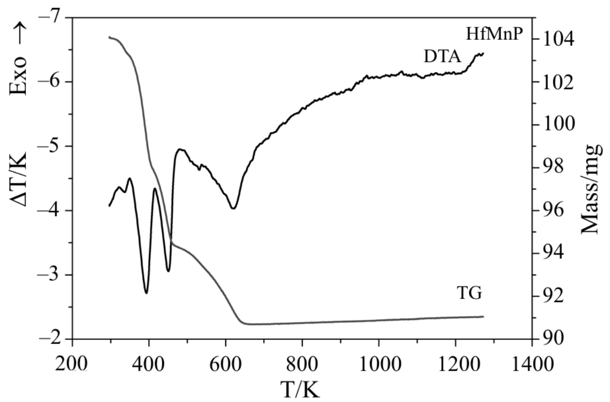

Fig. 3 DTA and TG curves of manganese containing hafnium phosphate

On the next figure (Fig. 4) are presented data concerned to the cobalt containing sample. As can be seen on the DTA curve also four endothermic processes with mass loss appeared. From them the first two was identified as crystal water loss, while the other two as structural water loss. In this case also was found an exothermic process about 1200 K, belongs to the phase transition of hafnium oxide. They are very weak in comparison with that one written above.

During the above processes a total mass loss of 10.3% was found. Taking into consideration the analytical data the following way of thermal decomposition is proposed:

$$[HfCo_{0.4}H_{1.2}(PO_4)_2{\cdot}1.64H_2O] \xrightarrow{-\ 1.64H_2O}$$

$$[HfCo_{0.4}H_{1.2}(PO_4)_2] \xrightarrow{-\ 0.6H_2O}$$

$$HfO_2{\cdot}0.4CoO{\cdot}P_2O_5$$

In case of nickel and copper containing samples (Figs 5–6) four endothermic- and an exothermic processes with mass loss were found. In addition appear at 1200 K an exothermic process (without mass loss) cover the phase transition of hafnium oxide. Two endothermic processes form the four can be ordered to the crystal water loss, while the other two to the structural water loss. The exothermic process, exist at 450–650 K temperature interval, cover the oxygen loss result of the transition of *M*O to M_2O. The reverse of this process goes very fast at about 1000–1100 K. This presumption is in good correlation with that of made by Viano *et al.* [17]. Based on the above mentioned the following way of thermal decomposition is proposed:

$$[HfNi_{0.58}H_{0.96}(PO_4)_2{\cdot}0.58H_2O] \xrightarrow{-\ 0.58H_2O}$$

$$[HfNi_{0.58}H_{0.96}(PO_4)_2] \xrightarrow{-\ 0.26O\uparrow}$$

$$[HfPO_4{\cdot}PO_3{\cdot}0.26Ni_2O{\cdot}0.48H_2O] \xrightarrow{-\ 0.48H_2O}$$

$$HfO_2{\cdot}0.52NiO{\cdot}P_2O_5$$

The above processes result a total mass loss of 12.8%.

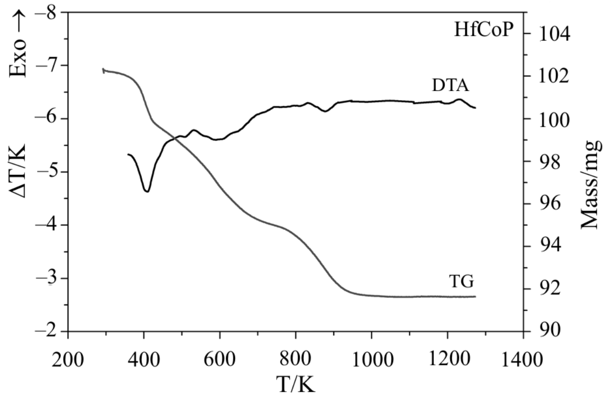

Fig. 4 DTA and TG curves of cobalt containing hafnium phosphate

The copper containing sample different from the earlier one only in the speed of the processes. The crystal water loss goes in two nearly equal steps at relatively low temperature. It immediately followed by

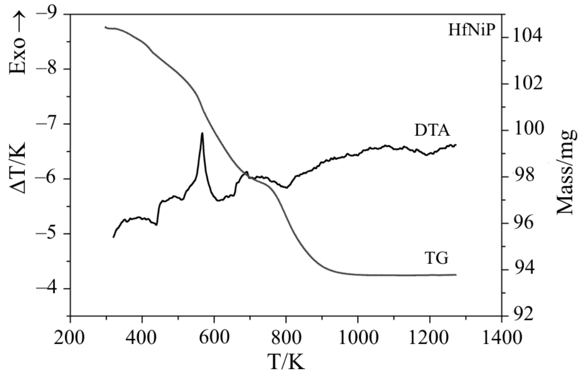

Fig. 5 DTA and TG curves of nickel containing hafnium phosphate

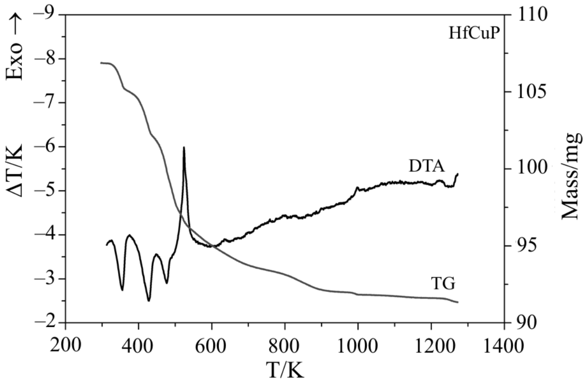

Fig. 6 DTA and TG curves of copper containing hafnium phosphate

the transition of metal oxide form and the loss of structural water. During these processes a total mass loss of 14.11% was registered. Based on the analytical data the following way of thermal decomposition is proposed:

$$[\mathrm{HfCu_{0.32}H_{1.36}(PO_4)_2{\cdot}2.3H_2O}] \xrightarrow{-\ 2.3\mathrm{H_2O}}$$

$$[\mathrm{HfCu_{0.32}H_{1.36}(PO_4)_2}] \xrightarrow{-\ 0.16\mathrm{O}\uparrow}$$

$$[\mathrm{HfPO_4(PO_3){\cdot}0.16Cu_2O{\cdot}0.34H_2O}] \xrightarrow{-\ 0.34\mathrm{H_2O};\ \text{phase trans.}}$$

$$\mathrm{HfO_2{\cdot}0.32CuO{\cdot}P_2O_5}$$

Taking into consideration of the above written results and the structural data of the investigated materials we conclude that in case of copper and nickel containing samples the transition metal ions exist in oxide form after the loss of crystal water. These oxide forms also have a low symmetry monoclinic structure [15], possible goes through on a rapid phase transition, indicate an exothermic peak. As an example is shown the DTA curves of pure copper oxide and copper containing hafnium phosphate (Fig. 7). Based on these curves and the given calculations we presumed that exotherm process exists at about 500–600 K temperature interval cover the CuO–Cu_2O phase transition followed with oxygen loss. The reverse process is going above 1000 K as is written by Viano [17]. Rightfully arose the question why only these two metal have such behaviour, and why not the others? In this moment we only supposed that the presence of hafnium and/or phosphate influenced them in this way. Perhaps this idea must be supported with further detailed investigations (they are in advance).

In case of other samples the thermal degradation has similar route than that was found for the transition metal containing zirconium and/or titanium phosphates.

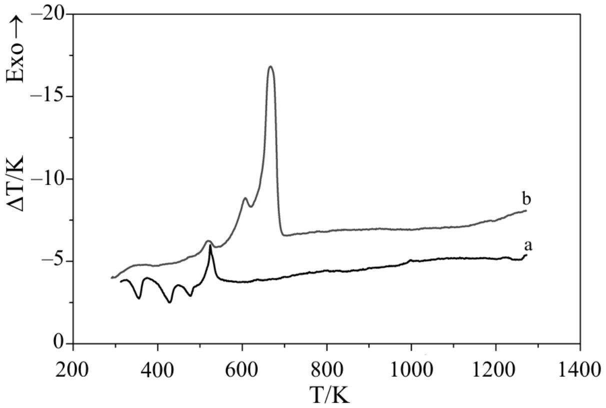

Fig. 7 DTA curves of copper containing a – hafnium phosphate and b – copper oxide

Conclusions

The zinc and manganese containing hafnium phosphates have the same way of thermal degradation as was found for pure hafnium phosphate.

Similar processes were found in case of cobalt containing sample. The found processes had lower intensity. Presumable this phenomenon is in connection with the low degree of crystallinity of this material.

In case of nickel and copper containing hafnium phosphates beyond the endothermic processes an exothermic one (with mass loss) exists. Based on mass loss and DTA data assumed that the mentioned exotherm process characterises the *M*O–M_2O phase transition.

Acknowledgements

The support from OTKA (M-027367) is greatly appreciated. The authors would like to express thanks to Mrs. A. Vashegyi for performing the analytical measurements, and to Dr. E. Kuzmann for making X-ray analysis.

References

1 Y. Elmismari, A. Dehair, L. Szirtes and S. K. Shakshooki, J. Radioanal. Nucl. Chem. Art., 158 (1992) 3.
2 S. K. Shakshooki, N. Naqvi, J. Kowalczyk, S. Khalil, M. Rais and F. Tarish, React. Polym., 7 (1988) 221.
3 S. K. Shakshooki, N. Naqvi, S. Khalil, M. Mostaq and L. Szirtes, J. Radioanal. Nucl. Chem. Art., 121 (1988) 195.
4 S. K. Shakshooki, F. Masaodi, A Dehair, L. Szirtes and J. Kowalczyk, J. Radioanal. Nucl. Chem. Art., 132 (1989) 251.
5 G. C. Hadjipanayis and R. W. Siegel (Eds), Nanophase Materials: Synthesis, Properties, Applications, Kluwer, Dordrecht,1994 and references herein.
6 K. Mészáros-Szécsényi, V. M. Leovac, Z. K. Jacimovic and G. Pokol, J. Therm. Anal. Cal., 74 (2003) 943.
7 V. Logvinenko, L. Yudanova, N. Yudanov and G. Chekhova, J. Therm. Anal. Cal., 74 (2003) 395.
8 L. Szirtes, J. Megyeri, L. Riess and E. Kuzmann, J. Therm. Anal. Cal., 65 (2001) 975.
9 L. Szirtes, J. Megyeri and E. Kuzmann, Solid State Ionics in press.
10 E. B. Sandell (ed.), Colorimetric Determination of Traces of Metals, Intersci. Publ. Inc. N.Y. 1959.
11 E. Schulek and Z. Szabó, Theory and methods of quantitative analysis, Tankönyvkiadó, Budapest 1971, p. 418 (in Hungarian).
12 L. Szirtes, J. Megyeri, L. Riess and E. Kuzmann, J. Therm. Anal. Cal., 63 (2001) 117.
13 S. K. Shakshooki, A. Dehair, L. Szirtes and Yu.V. Yakovlev, J. Radioanal. Nucl. Chem. Lett., 154 (1991) 23.
14 L. Szirtes, J. Megyeri and E. Kuzmann, J. Crystallogr. to be published.
15 L. Szirtes, J. Megyeri, E. Kuzmann and Z. Klencsár, Solid State Ionics, 145 (2001) 257.

16 L. Szirtes, L. Riess and J. Megyeri, J. Therm. Anal. Cal., 73 (2003) 209.
17 S. Viano, R. Mishra, J. Lloyd, T. Losby and T. Gheyi, J. Non-Cryst. Solids, 325 (2003) IBNLFASSI16.

Received: March 25, 2004
In revised form: May 20, 2004