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THERMAL BEHAVIOUR OF ACIDIC SALTS OF MIXED TETRAVALENT METALS
IV. Thermal decomposition of crystalline zirconium-titanium phosphate prepared through the fluorine complex (HF method)

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The mixed metal phosphates were synthetized by the HF method, the resulting materials being crystalline. Thermal analysis revealed that they contain almost one mole of crystalline water per molecule unit. The mode of thermal decomposition of the samples was similar to those for crystalline phosphates containing only zirconium or titanium.

Keywords: complexes, mixed tetravalent metals

Introduction

Among the inorganic materials having ion-exchange properties, the samples containing a mixture of tetravalent metals (for exampe Zr+Ti) are of special interest.

The aim of the thermal analytical investigations was to learn whether these materials have unique thermal behaviour or whether their thermal decomposition is similar to that of phosphates containing only one kind of tetravalent metal, and whether it differs from that of phosphates prepared by the reflux method.

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Experimental

The sampes were prepared as described in a previous paper [2].

The contents of metal ions and phosphate were measured according to known methods [3–4].

The thermal behaviour of the samples was investigated by means of differential thermal analysis. The measurements were carried out with a MOM C thermobalance, allowing recording of the DTA, DTG and TG data in parallel. The main conditions of the determinations were:

Temperature range: 25-1000 °C
Heating rate: 10 deg/min
Sensitivity TG: 100
Standard: Al_2O_3
Atmosphere: air

The curves were evaluated via a computer program [5]. For the experiments, samples with metal contents of $Zr_{0.9}Ti_{0.1}$, $Zr_{0.8}Ti_{0.2}$, $Zr_{0.7}Ti_{0.3}$ and $Zr_{0.55}Ti_{0.45}$ were used. The crystallinity of the samples was controlled by X-ray diffraction using a DRON-2 diffractometer with a CuK_α Ni-filtered beam. The determinations were repeated at elevated temperature. As an example, the X-ray diffractograms of sample II are shown in Figs 1 and 2.

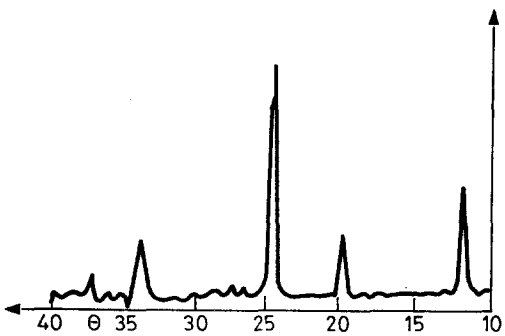

Fig. 1 X-ray diffractogram of the sample $(Zr_{0.8}Ti_{0.2})(HPO_4)_2 \cdot H_2O$

Results and discussion

The X-ray diffractogram of the sample with a metal content of $Zr_{0.8}Ti_{0.2}$ (II) is shown in Fig. 1 as an example. The curve showed that the examined material is crystalline, with a layered structure. Evaluation of the first peak using Bragg's equation yielded an interlayer distance (d_{001}) of 0.756 nm. By following the thermal decomposition with an X-ray diffraction technique, we found that the structure is changed as a result of thermal processes (Fig. 2).

After loss of the crystalline water, the interlayer distance was decreased to 0.715 nm. Following the destruction of phosphate groups, the structure was

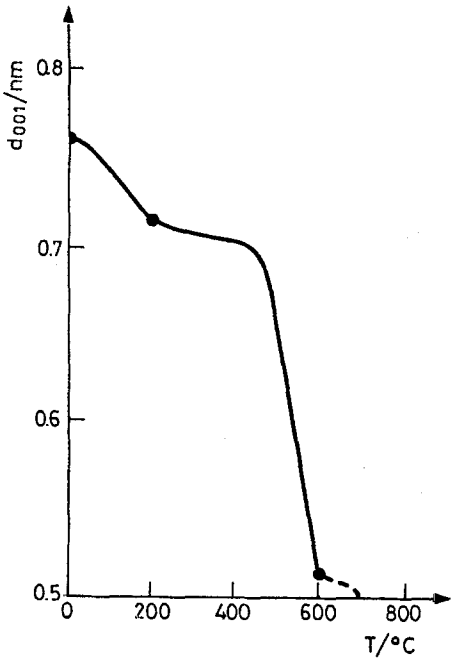

Fig. 2 Change of interlayer distance *vs.* temperature for sample $(Zr_{0.8}Ti_{0.2})(HPO_4)_2.H_2O$

Table 1

Sign	Sample composition Me^{4+}	Me/PO_4	initial weight / mg	total weight loss / mg
I.	$Zr_{0.9}Ti_{0.1}$	1:2	96.0	13.0
II.	$Zr_{0.8}Ti_{0.2}$	1:2	183.1	25.0
III.	$Zr_{0.7}Ti_{0.3}$	1:2	98.1	13.7
IV.	$Zr_{0.55}Ti_{0.45}$	1:2	98.8	14.2

I.	endo processes with peak of 175° and 585°C exo processes with peak of 920°C
II.	endo processes with peak of 180° and 595°C exo processes with peak of 890°C
III.	endo processes with peak of 180° and 550°C exo processes with peak of 890°C
IV.	endo processes with peak of 170° and 545°C exo processes with peak of 895°C

changed. The values measured above ~700°C relate to the pyrophosphates and metal oxides. Figures 3–6 show the TG, DTG and DTA curves of samples with various metal-ion ratios.

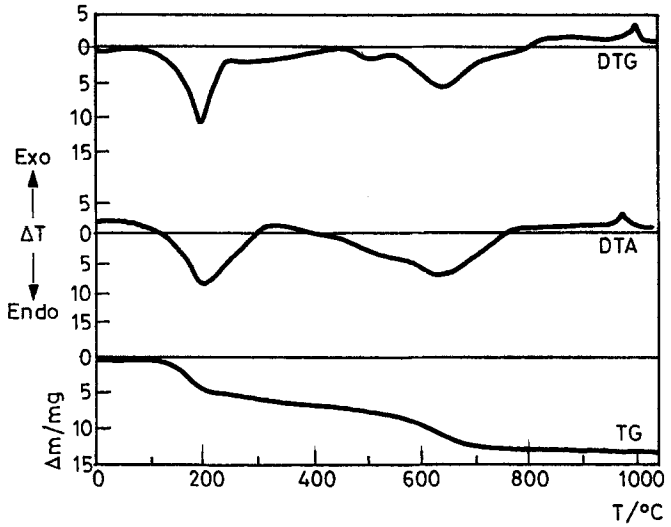

Fig. 3 TG, DTG and DTA curves of the sample $(Zr_{0.8}Ti_{0.2})(HPO_4)_2 \cdot H_2O$

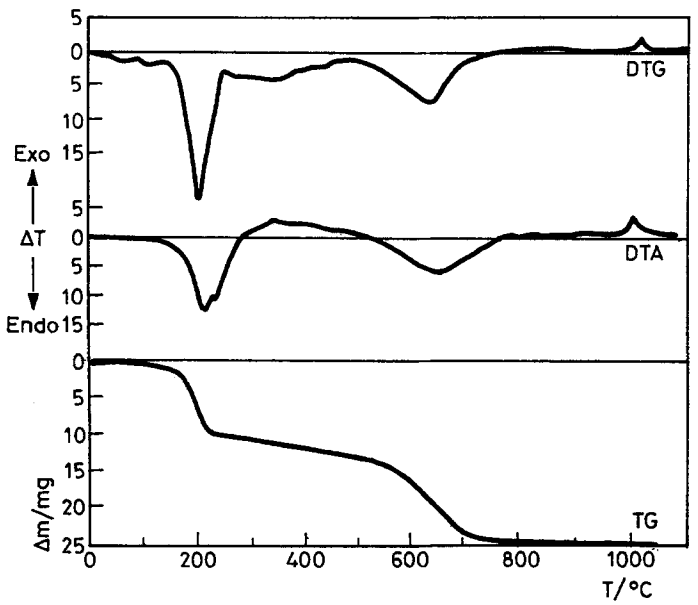

Fig. 4 TG, DTG and DTA curves of the sample $(Zr_{0.7}Ti_{0.3})(HPO_4)_2 \cdot H_2O$

Evaluation of the curves demonstrated endothermic processes with weight loss peaking at about 180° and 600°C. There was also an exothermic process without weight loss, having a peak at about 890°C. The total weight loss of the samples was found to be 13–14% in all cases.

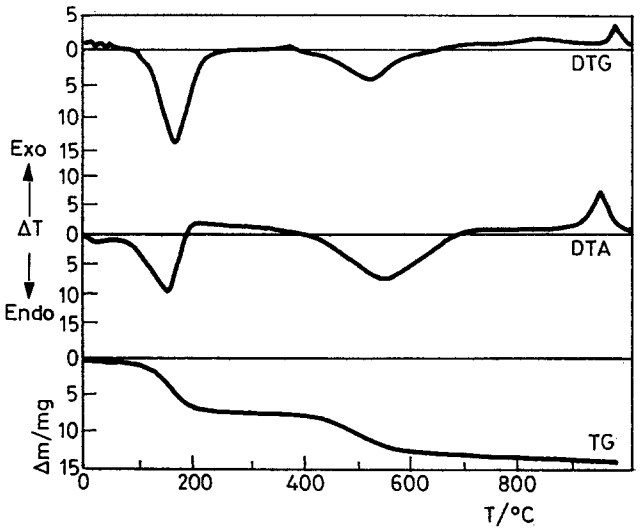

Fig. 5 TG, DTG and DTA curves of the sample $(Zr_{0.55}Ti_{0.45})(HPO_4)_2 \cdot H_2O$

The first endothermic process relates to the loss of crystalline water, while the second stems from the loss of structural water.

The exotermic process covered the crystalline change of zirconium oxide (α–$ZrO_2 \xrightarrow[900°C]{}$ β–ZrO_2).

From a consideration of the analytical data and the total weight loss, the decreases in weight in the individual processes were calculated. On the basis of these results, the thermal decomposition of the samples may in general be described as follows:

$$[Zr_xTi_{(1-x)}(HPO_4)_2] \cdot nH_2O \xrightarrow[\text{till } 200°C]{-H_2O} [Zr_xTi_{(1-x)}(HPO_4)_2]$$

$$(Zr_xTi_{(1-x)})P_2O_7 \xrightarrow[\text{till } 690°C]{-H_2O} x\,ZrO_2 \cdot (1-x)\,TiO_2 \cdot P_2O_5$$

where $x = 0.9, 0.8, 0.7$ or 0.55.

Further, the curves showed no significant differences i.e. the investigated samples have similar thermal decomposition mechanisms, consisting of the following stages:

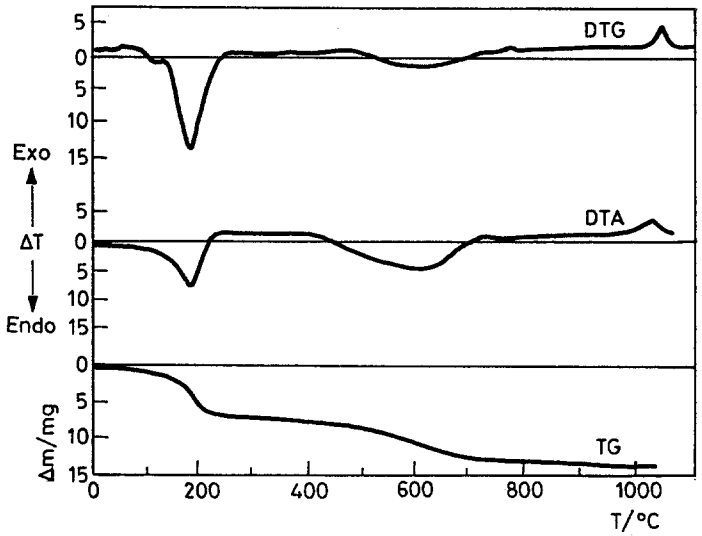

Fig. 6 TG, DTG and DTA curves of the sample $(Zr_{0.9}Ti_{0.1})(HPO_4)_2 \cdot H_2O$

– loss of crystalline water (at a relatively high temperature)

– loss of structural water (resulting from the destruction of hydrogenphosphate groups)

– formation of metal pyrophosphates and oxides

– change of crystalline state of metal oxides (~900°C).

On comparison of these results with those for phosphates containing only zirconium or titanium ions, no considerable difference was found.

A comparison of these findings with those on mixed crystalline zirconium-titanium phosphates prepared by the reflux method and dried in air or above P_2O_5 [1] revealed their similar thermal behaviour.

References

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Zusammenfassung — Die Mischmetallphosphate wurden mit der HF-Methode hergestellt, wobei man kristalline Substanzen erhielt. Die Thermoanalyse zeigte, daß sie fast ein Molekül Kristallwasser pro Moleküleinheit besitzen. Die Art der thermischen Zersetzung der Proben ähnelt der Zersetzung von kristallinen Phosphaten von nur Zirkonium oder nur Titan.