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THERMAL BEHAVIOUR OF ACIDIC SALTS OF MIXED TETRAVALENT METALS
V. Thermal decomposition of amorphous glassy-type zirconium–titanium phosphate

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The mixed amorphous glassy-type zirconium–titanium phosphates contain various quantities of adsorbed water per molecule unit. Pure zirconium phosphate lost the structural water in two steps. This character disappeared with increasing titanium content. However, glassy titanium phosphate lost its water in two steps at lower temperature in comparison with glassy zirconium phosphate.

Keywords: amorphous glassy-type zirconium–titanium phosphates

Introduction

The behaviour of the phosphates of tetravalent metals, and particularly zirconium and titanium phosphates, is well known. To establish whether the mixing of metal ions changes the features of these materials or not, a series of samples in crystalline, amorphous and glassy form were synthetized.

The results concerning the thermal decomposition of crystalline mixed zirconium-titanium phosphates were presented in a previous paper [1], and the corresponding data on the amorphous glassy-type materials are reported here.

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Experimental

A typical mode of preparation of glassy-type mixed metal phosphates was described earlier [2].

The metal content was determined colorimetrically by using well-known methods [3], while the phosphate content was determined by the method described by Bernhardt and Wreath [4].

The crystallinity of the samples was controlled by means of an X-ray powder diffraction method, using a DRON-2 diffractometer with a CuK_α (Ni-filtered) beam. As an example, the diffractogram of glassy-type pure zirconium phosphate (sample I) is shown in Fig. 1.

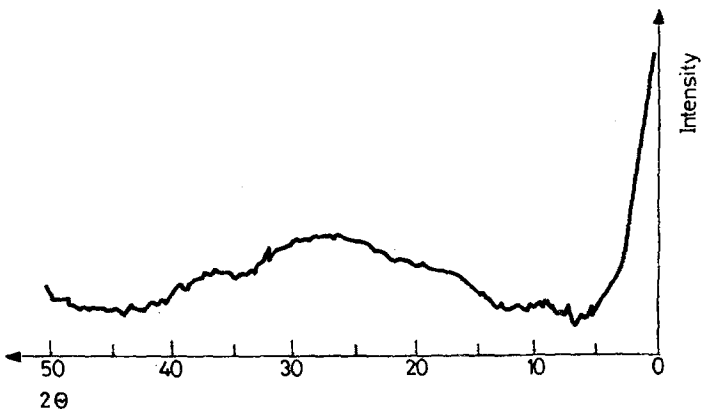

Fig. 1 X-ray diffractogram of zirconium phosphate (ZrP)

The thermal decomposition of the samples was investigated by differential thermal analysis. The measurements were carried out on a MOM-C thermobalance under the conditions described previously [1]. The curves were evaluated by a computer program [5].

The sample conditions and weight loss data are compiled in Table 1.

Results and discussion

The X-ray diffractogram (Fig. 1) exhibited no peaks characteristic of an amorphous material. For all samples, the visual microscope showed a glassy character.

The thermoanalytical curves of the investigated samples are shown in Figs 2–8. The curves indicated endothermic processes with weight loss, and an exothermic one without weight loss. The endoprocesses characterize the loss of various water

Table 1

Sample	Sample composition		Initial weight /	Total weight loss /	Adsorbed water content/
	Me^{4+}	Me^{4+}/PO_4 ratio	mg	mg	mole
I.	Zr	1:2	223.5	42.5	3.0
II.	$Zr_{0.9}Ti_{0.1}$	1:2	325.5	49.5	2.0
III.	$Zr_{0.66}Ti_{0.33}$	1:2	360.7	65.3	2.5
IV.	$Zr_{0.5}Ti_{0.5}$	1:2	235.2	40.8	2.2
V.	$Zr_{0.33}Ti_{0.66}$	1:2	360.0	55.5	2.0
VI.	$Zr_{0.1}Ti_{0.9}$	1:2	247.0	45.2	2.3
VII.	Ti	1:2	179.7	38.0	3.0

I. endo processes with peak at 100°, 480° and 560°C
exo processes with peak at 900°C

II. endo processes with peak at 100°, 420° and 510°C
exo processes with peak at 890°C

III. endo processes with peak at 100° and 400°C
exo processes with peak at 800°C

IV. endo processes with peak at 100° and 380°C
exo processes with peak at 750°C

V. endo processes with peak at 110° and 350°C
exo processes with peak at 720°C

VI. endo processes with peak at 200° and 310°C
exo processes with peak at 790°C

VII. endo processes with peak at 150°C
exo processes with peak at 720°C

molecules, i.e. the chemical decomposition of the investigated materials, while the exo process (generally at high temperature) is connected with change in the crystalline form of the resulting metal oxides [6].

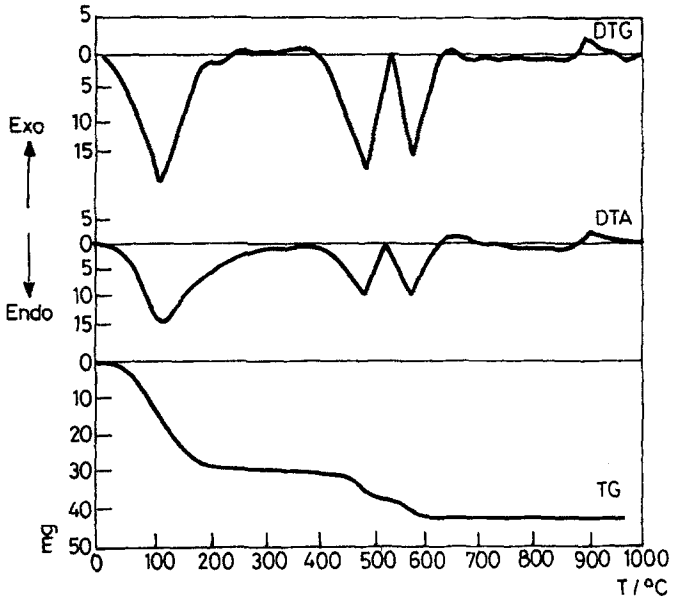

Fig. 2 Thermoanalytical curves of zirconium phosphate (I)

As can be seen in Fig. 2, three endothermic processes with weight loss, and one exothermic process without weight loss were found. The first endothermic process can be assigned to the loss of adsorbed water, while the second and third processes, closely following each other, characterize the loss of structural water originating from the decomposition of phosphate groups. The exothermic process may be connected with the crystalline change of zirconium oxide [6].

It can be proposed that 3 mol of adsorbed water are lost from glassy zirconium phosphate below 200°C (Fig. 2).

At higher temperatures, a two-stage condensation of hydrogenphosphate groups occurs. The first is accompanied by the loss of half of the water at about 470°–500°C, followed by the second loss between 500° and 650°C, resulting in zirconium pyrophosphate.

The loss of structural water on condensation of the phosphate groups is similar to that noted for the thermal behaviour of the γ-form of crystalline zirconium phosphate [7].

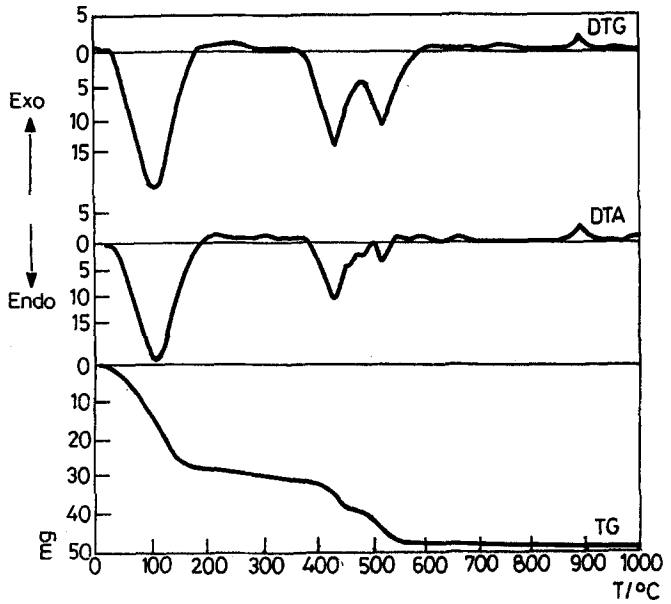

Fig. 3 Thermoanalytical curves of $Zr_{0.9}Ti_{0.1}P$ (II)

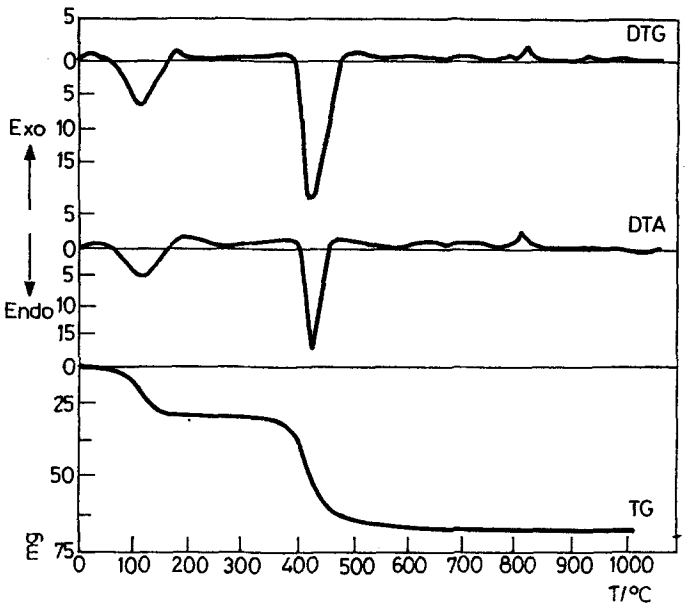

Fig. 4 Thermoanalytical curves of $Zr_{0.66}Ti_{0.33}P$(III)

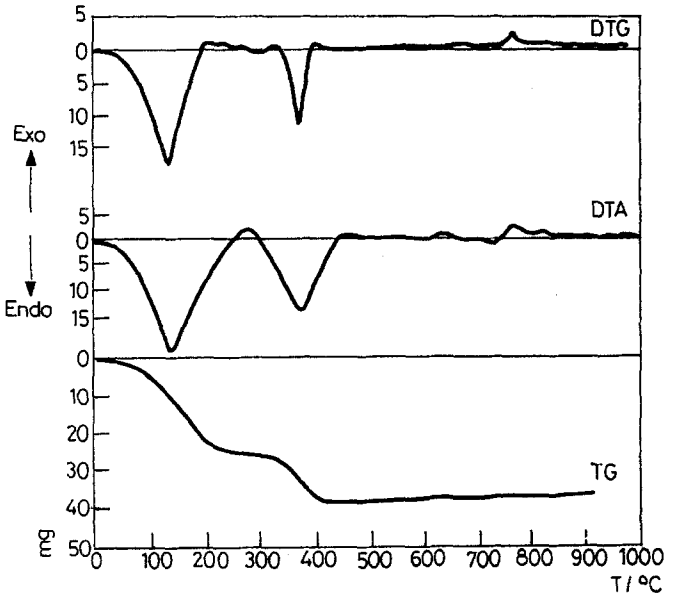

Fig. 5 Thermoanalytical curves of $Zr_{0.5}Ti_{0.5}P$ (IV)

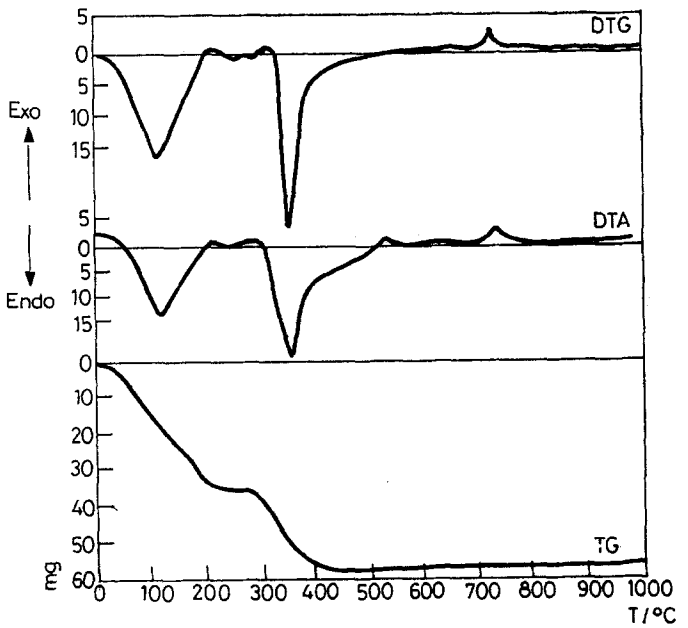

Fig. 6 Thermoanalytical curves of $Zr_{0.33}Ti_{0.66}P$ (V)

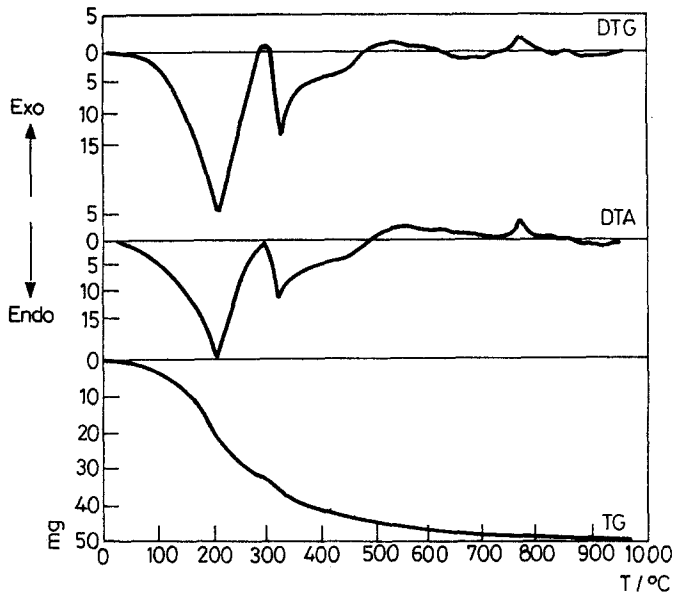

Fig. 7 Thermoanalytical curves of $Zr_{0.1}Ti_{0.9}P$ (VI)

The structure of crystalline γ-titanium phosphate was recently proposed [8] as $(Ti(H_2PO_4)(PO_4)\cdot 2H_2O$, and it was also proposed that the γ-crystalline form of zirconium phosphate must have a similar structure. Thus glassy zirconium phosphate can also be formulated as $Zr(H_2PO_4)(PO_4)\cdot 3H_2O$ on the basis of its similar thermal behaviour to that of the γ-crystalline form materials.

Taking into consideration the data of thermal and analytical investigations on glassy zirconium phosphate, its thermal decomposition can be described as

$$Zr(H_2PO_4)(PO_4)\cdot 3H_2O \xrightarrow[\text{up to } 180°C]{-3H_2O} Zr(H_2PO_4)(PO_4) \xrightarrow[400°-700°C]{-H_2O}$$

$$\rightarrow ZrP_2O_7 \rightarrow ZrO_2\cdot P_2O_5\,;\quad \alpha - ZrO_2 \xrightarrow{900°C} \beta - ZrO_2$$

The same picture was found for the sample containing 10% of titanium (sample II), which can also consist of dihydrogen phosphate groups as in glassy zirconium phosphate.

Further, with increase of the titanium content in the material, the phenomenon disappears, perhaps because of the influence of the titanium.

As compared with the pure glassy-type zirconium phosphate and sample II (10% Ti), the mixed zirconium-titanium phosphates display the following thermal features (Figs 4–7):

– the structural water is lost in one step,

– with increase of the titanium content, the second endothermic process (loss of structural water) starts at lower temperature; as can be seen in Fig. 8, an almost linear dependence was found between the titanium content and the starting temperature.

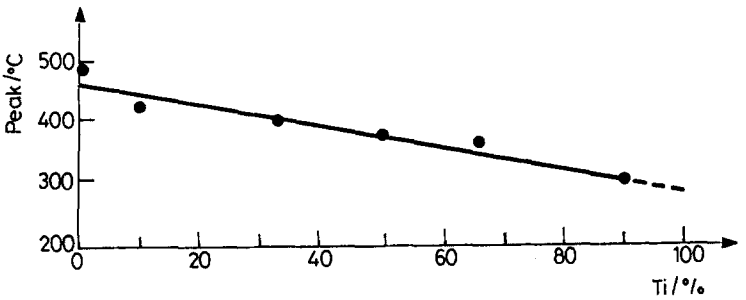

Fig. 8 Change of peak temperature *versus* Ti content

Pure glassy-type titanium phosphate (Fig. 9) lost both its adsorbed and its structural water up to 400°C.

The conventional calculations revealed 3 mol of adsorbed water and 1 mol of structural water per molecule unit.

The character of the second endothermic process for samples containing a mixture of tetravalent metals permitted the suggestion that in these the phosphate groups exist in the monohydrogen form, with the exception of the sample with 10% of Ti.

On the other hand, with increase of the titanium content, the acidity of the material increases, which facilitates chemical decomposition of the sample; it is evident that the thermal decomposition (loss of structural water) starts at a lower temperature as a function of the titanium content of the investigated samples.

The general character of the thermal decomposition of mixed zirconium-titanium phosphate samples and of pure titanium phosphate leads us to propose that the adsorbed water is more significant in the compactibility of these glassy-type molecules than for pure glassy zirconium phosphate.

Accordingly, the thermal decomposition of samples of III-VII can be described as follows:

$$[Zr_xTi_{(1-x)}(HPO_4)_2 \cdot nH_2O] \xrightarrow[\text{up to } 150^\circ C]{-nH_2O} [Zr_xTi_{(1-x)}(HPO_4)_2]$$

$$\xrightarrow[\text{up to } 550^\circ C]{-H_2O} [Zr_xTi_{(1-x)}]P_2O_7 \longrightarrow xZrO_2 \cdot (1-x)TiO_2 \cdot P_2O_5$$

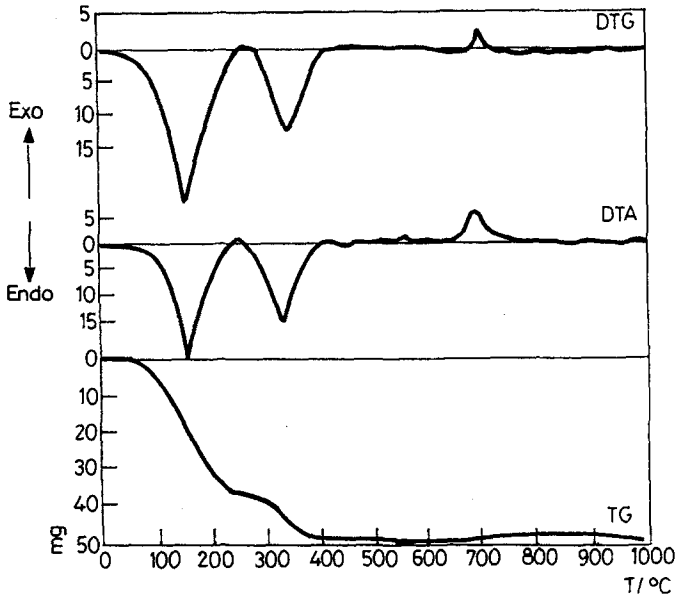

Fig. 9 Thermoanalytical curves of titanium phosphate (TiP) (VII)

The clear stepwise water losses from the investigated samples showed characteristic thermal behaviour typical of crystalline rather than amorphous materials, which are characterized by the continuous loss of both their adsorbed and structural water content.

* * *

The thermal analysis data provide information on the chemical features of these mixed glassy materials and also shed light on their ion-exchange properties.

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Zusammenfassung — Das gemischte amorphe Zirkonium-Titan-Phosphat enthält pro Molekülеinheit verschiedene Mengen adsorbierten Wassers. Reines Zirkoniumphosphat verliert das strukturelle Wasser in zwei Schritten. Diese Eigenschaft verschwindet mit zunehmenden Titangehalt. Amorphes Titanphosphat verliert sein Wasser in zwei Schritten bei niedriger Temperatur im Vergleich zu amorphem Zirkoniumphosphat.