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THERMAL BEHAVIOUR OF MIXED TETRAVALENT METAL SALTS

I. Thermal decompositions of mixed zirconium–titanium phosphates

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In contrast with the well-known zirconium and titanium phosphates, products containing these metal ions together are unknown. To investigate the thermal behaviour of such materials, samples were synthetized with various ratios of the two metal ions. The samples were identified by means of X-ray diffraction. Their thermal behaviour was investigated in the temperature interval 25–1000 °C via simultaneous TG, DTG and DTA measurements. The data obtained are presented in this paper.

During the past 20 years, synthetic inorganic materials with ion-exchange properties have been investigated in detail. The best known of them is zirconium phosphate, the thermal behaviour of which was investigated earlier [1]. The thermal decompositions of various titanium phosphates have also been investigated [2].

In contrast, the thermal behaviour of materials containing both these metal ions is not known.

In this paper we present results on the thermal decompositions of materials containing zirconium and titanium ions together in various ratios.

Experimental

The mixed acidic salts of the given metal ions were synthetized as follows. The amorphous gel was prepared as described earlier [10], then aged for 48 hours in the mother liquor. It was next filtered off and the residue was washed (once) with

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Table 1 Conditions of synthesis

Sample no.	Method	Drying temp., °C	Washing agent	Final pH	Zr/Ti ratio	Gnion
1				4.0	9:1	
2				4.1	2:1	
3	HF	60	water	3.8	1:1	PO_4^{3-}
4				4.0	1:2	
5				4.0	1:9	

distilled water. Subsequently, the semicrystalline materials was refluxed in 12 *M* H_3PO_3 for 100 h [3–4].

The conditions of the syntheses are given in Table 1.

The final samples were stored at room temperature over saturated NaCl solution (p/p_0 = 75%). The metal and anion contents were determined in conventional ways: the metal ions colorimetrically [5] and the phosphate content photometrically [6].

The samples were identified by means of X-ray diffraction with a DRON diffractometer, with a CuK_α (Ni-filtered) beam.

The thermoanalytical experiments were carried out with a Paulik–Paulik–Erdey (MOM, Budapest) derivatograph [7], which is capable of recording TG, DTG and DTA curves simultaneously. Given quantities of the samples were heated in a quartz crucible in the temperature range 25–1000°. The measurements were performed in air, with alumina (α-Al_2O_3) as reference material (Table 2).

Results and discussion

The synthetized samples were shown by X-ray diffraction measurements to be crystalline (layered) materials.

Table 2 Conditions of thermal analysis

Sample no.	Weight, mg	Sensitivity				Time, min	Heating rate, deg/min
		T, °C	TG, °C	DTG	DTA		
1	42.0						
2	62.2						
3	115.6	1000	100	1/5	1/5	100	10
4	56.4						
5	183.4						

Table 3 Compositions of investigated samples

Sample no.	Metal content		$\sum Me^{4+}/PO_4^{3-}$ ratio
	Zr	Ti	
1	0.90	0.10	
2	0.67	0.33	
3	0.50	0.50	2.0
4	0.33	0.67	
5	0.10	0.90	

The analytical data indicated the compositions shown in Table 3.

The results of thermoanalytical investigations are to be seen in Figs 1–5.

Sample 1, containing about 10% of titanium (Fig. 1), revealed three endothermic processes with weight loss. The first two, nearly equal peaks at 160° and 270° are smaller than that at 610°, but the weight loss associated with the latter is similar to that of the first two.

At higher temperatures, a very small and a more considerable exothermic process, without weight loss, were observed at 880° and 910°, respectively.

Further, 0.36 mol of water adsorbed on the surface was lost up to 40°.

At about 850°, α'-TiP_2O_7 changes into cubic TiP_2O_7, and at above 900° monoclinic α-ZrO_2 changes to tetragonal β-ZrO_2 [8–9]. These phenomena could be followed via X-ray diffraction [11].

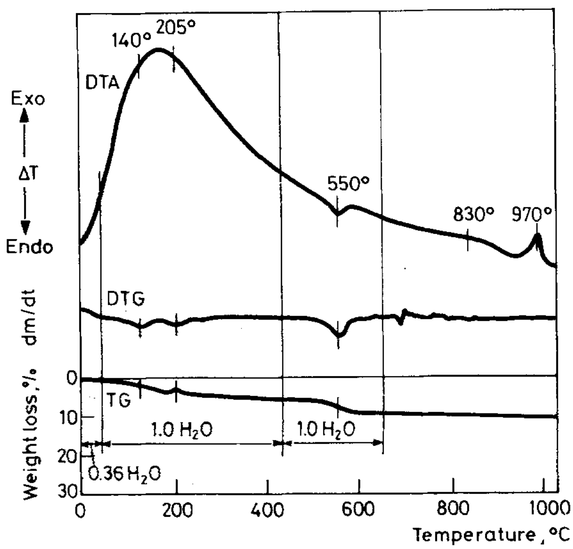

Fig. 1 Thermal curves of sample 1

Taking into consideration the analytical data, the thermal decomposition of sample 1 may be described as follows:

$$Zr_xTi_{1-x}(HPO_4)_2 \cdot H_2O \xrightarrow[-H_2O]{40\text{–}400^\circ} Zr_xTi_{1-x}(HPO_4)_2$$

$$\xrightarrow[-H_2O]{400\text{–}650^\circ} Zr_x\text{-}Ti_{1-x}P_2O_7 \xrightarrow{\text{above } 900^\circ} (ZrO_2)_x \cdot (TiP_2O_7)_{1-x}$$

where $x = 0.9$.

For sample 2 (Fig. 2), a weight loss was found up to 45°, which corresponds to the water adsorbed on the surface.

Additionally, two endothermic processes (nearly equal sharp peaks) with weight loss were observed. At higher temperatures, there was a very small peak (800°) and a more pronounced (895°) exothermic peak, without weight loss. The thermal decomposition of sample 2 can be described as follows:

$$Zr_xTi_{1-x}(HPO_4)_2 \cdot 2\,H_2O \xrightarrow[-H_2O]{45\text{–}400^\circ} Zr_xTi_{1-x}(HPO_4)_2 \cdot H_2O$$

$$\xrightarrow[-H_2O]{400\text{–}660^\circ} Zr_xTi_{1-x}P_2O_7 \xrightarrow{\sim 900^\circ} (ZrO_2)_x(TiP_2O_7)_{1-x}$$

where $x = 0.66$.

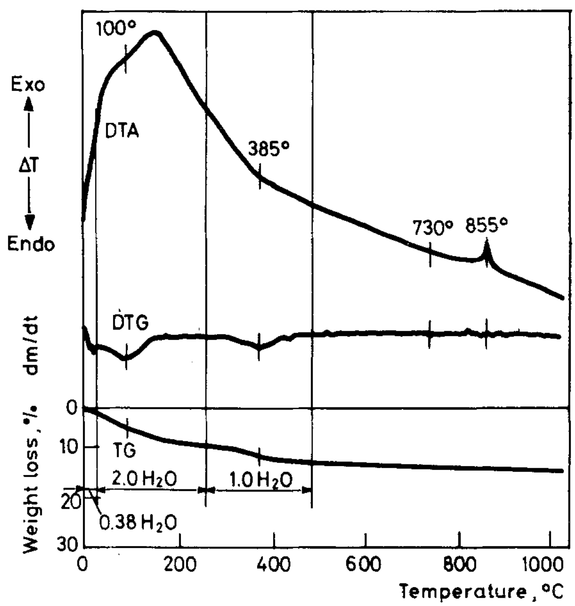

Fig. 2 Thermal curves of sample 2

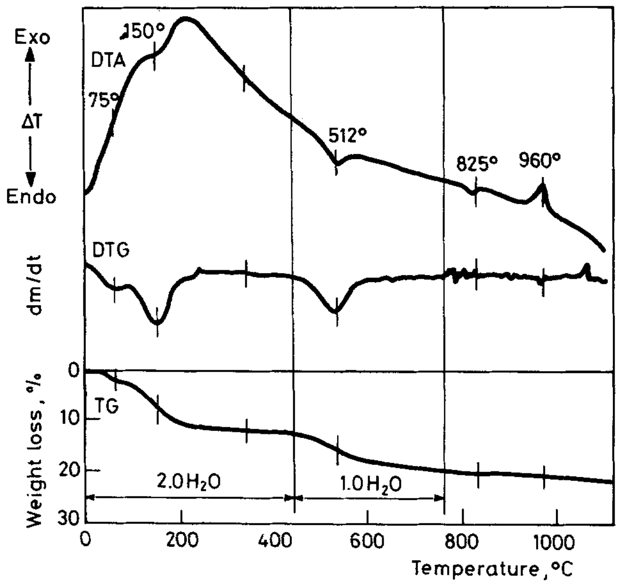

Fig. 3 Thermal curves of sample 3

For sample 3 (Fig. 3), 0.05 mol of water (adsorbed on the surface) was lost up to 50°.

Two endothermic processes with weight loss were found, with peaks at 170° and 570°. Exothermic processes relating to the transformation of the crystal forms were found at higher temperature.

The thermal decomposition of sample 3 can be described as follows:

$$Zr_xTi_{1-x}(HPO_4)_2\cdot 2H_2O \xrightarrow[-H_2O]{45-120^\circ} Zr_xTi_{1-x}(HPO_4)_2\cdot H_2O$$

$$\xrightarrow[-H_2O]{120-400^\circ} Zr_xTi_{1-x}(HPO_4)_2 \xrightarrow[-H_2O]{400-680^\circ} Zr_xTi_{1-x}P_2O_7$$

$$\xrightarrow{\text{above } 900^\circ} (ZrO_2)_x\cdot(TiP_2O_7)_{1-x}$$

where $x=0.5$.

For sample 4 (Fig. 4), 0.05 mol of surface water was adsorbed and two endothermic processes with weight loss were found. The first revealed about twice as high a weight loss as the second one.

Further, the same exothermic processes without weight loss take place at higher temperature.

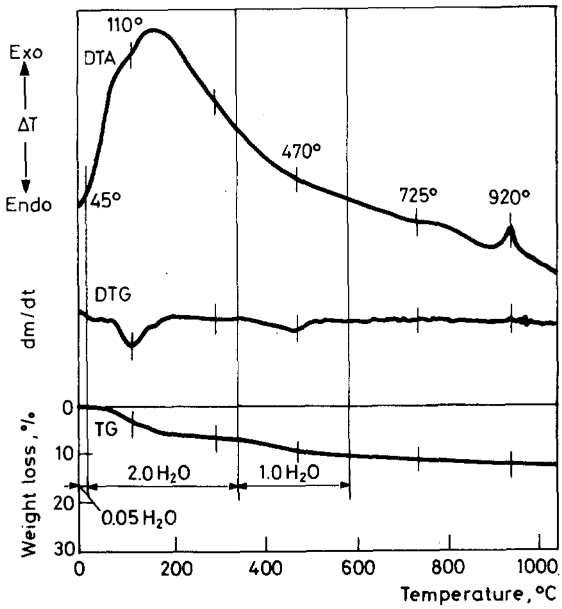

Fig. 4 Thermal curves of sample 4

The following thermal decomposition of sample 4 may be assumed:

$$Zr_xTi_{1-x}(HPO_4)_2\cdot 2H_2O \xrightarrow[-2H_2O]{40\text{–}400^\circ} Zr_xTi_{1-x}(HPO_4)_2$$

$$\xrightarrow[-H_2O]{400\text{–}680^\circ} Zr_xTi_{1-x}P_2O_7 \xrightarrow{\text{above } 900^\circ} (ZrO_2)_x\cdot(TiP_2O_7)_{1-x}$$

where $x=0.33$

Sample 5 (Fig. 5) also contains 0.05 mol of adsorbed surface water. A further two endothermic processes with weight loss were found, with peaks at 240° and 535°. The exothermic processes without weight loss were found at higher temperature. These results, combined with the X-ray data, suggest that the thermal decomposition of sample 5 can be described as follows:

$$Zr_xTi_{1-x}(HPO_4)_2\cdot H_2O \xrightarrow[-H_2O]{45\text{–}440^\circ} Zr_xTi_{1-x}(HPO_4)_2$$

$$\xrightarrow[-H_2O]{440\text{–}650^\circ} Zr_xTi_{1-x}P_2O_7 \xrightarrow{\text{above } 900^\circ} (ZrO_2)_x\cdot(TiP_2O_7)_{1-x}$$

where $x=0.1$.

From the results described above, the following conclusions can be drawn:

1. All samples contain a small quantity of adsorbed surface water, which is lost up to 50°.

2. The samples contain different quantities of crystalline water, which is lost up to 450°. These quantities are related to the metal ratio; in samples 1 and 5, which have compositions near those of the pure one-metal phosphates, 1 mol of crystalline water was found, the same as in the one-metal phosphates: α-$Zr(HPO_4)_2 \cdot H_2O$ and α-$Ti(HPO_4)_2 \cdot H_2O$. In accord with the modification of the crystal structure [11], at intermediate metal ion ratios (samples 2–4) 2 mol of crystalline water was found.

3. The following phenomena were identified: the known transformation

$$\alpha'\text{-}TiP_2O_7 \text{ (with } \equiv P\text{—}O\text{—}P\equiv \text{ structure)} \xrightarrow{\text{above } 850^\circ} \text{cubic } TiP_2O_7$$

and α-$ZrO_2 \xrightarrow{\text{above } 900^\circ} \beta$-$ZrO_2$ (monoclinic to tetragonal).

4. On the basis of the above data, the thermal decompositions of the samples can be described as follows:

$$Zr_xTi_{1-x}(HPO_4)_2 \cdot 2H_2O \xrightarrow[-2H_2O]{50\text{–}400^\circ} Zr_xTi_{1-x}(H_2PO_4)_2$$

$$\xrightarrow[-H_2O]{400\text{–}680^\circ} Zr_xTi_{1-x}P_2O_7 \xrightarrow{\text{above } 900^\circ} (ZrO_2)_x \cdot (TiP_2O_7)_{1-x}$$

where $(x+y) = 1$

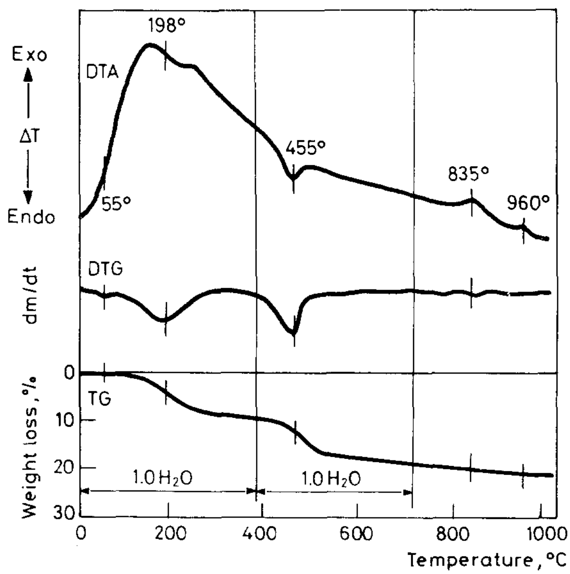

Fig. 5 Thermal curves of sample 5

To summarize, the thermal decompositions of samples containing various amounts of the two tetravalent metals are similar to those of the original materials containing only zirconium or titanium metal ions. This behaviour may be of interest from the aspect of evaluation of the ion-exchange properties of these materials.

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Zusammenfassung — Im Gegensatz zu den wohlbekannten Zirkonium- und Titanphosphaten sind beide Metallionen gleichzeitig enthaltende Produkte unbekannt. Zur Untersuchung solcher Substanzen wurden Proben mit unterschiedlichen Mengen der beiden Metallionen gefertigt und mittels Röntgendiffraktion identifiziert. Die Proben wurden im Temperaturbereich 25–1000 °C mittels simultaner TG-, DTG- und DTA-Messungen untersucht. Die Ergebnisse werden in dieser Arbeit mitgeteilt.

Резюме — В противоположность хорошо известным фосфатам циркония и титана, смешанные фосфаты обоих металлов неизвестны. С целью исследования термического поведения таких соединений они были синтезированы при различном соотношении обоих металлов. Полученные таким путем образцы были идентифированы рентгено-диффракционным методом, а термическое поведение их было изучено совмещенными методами ТГ, ДТГ и ДТА в интервале температур 25–1000°. Представлены полученные данные.