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THERMAL BEHAVIOUR OF ACIDIC SALTS OF MIXED TETRAVALENT METALS

II. Thermal decomposition of various intercalated mixed zirconium–titanium phosphates

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The results of investigations on intercalated crystalline zirconium phosphate are described in the literature. The behaviour of crystalline phosphates containing both zirconium and titanium metal ions has not been investigated previously. Within these investigations, the thermal behaviour of such materials has been studied in the temperature interval 25–1000 °C by simultaneous recording of TG, DTG and DTA curves. The results are presented in this paper.

Investigations on intercalated crystalline tetravalent metal salts, and primarily α-zirconium bis-monohydrogenphosphate started about ten years ago. The results of this work are collected in the monographs of Costantino [1] and Alberti [2]. We recently started to investigate the intercalation of various organic molecules by acidic salts containing both zirconium and titanium metal ions.

As part of the work, the thermal stability and thermal decomposition of mixed zirconium–titanium phosphate intercalated with ethyl alcohol, *n*-butylamine, *n*-propylamine or ethylenediamine were studied.

The results are described in this paper.

Experimental

The synthetized (as described earlier [3, 4]) samples were intercalated with ethyl alcohol, *n*-propylamine, *n*-butylamine, or ethylenediamine, from 0.1 M solution at

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pH = 6, adjusted with NaOH solution. The materials were identified by X-ray diffraction and analytical methods. The thermoanalytical experiments were carried out with, a MOM–C (MOM, Budapest, Hungary) thermobalance, capable of recording TG, DTG and DTA curves simultaneously.

The given quantity of sample was heated in a quartz crucible in the temperature range 25–1000°. The measurements were performed in air, and alumina (α-Al_2O_3) was used as reference material (see Table 1). The results were evaluated by means of a computer program.

Table 1 Conditions of thermal analysis

Sample no.	Weight, mg	Sensitivity				Time, min	Heating rate, deg/min
		T, °C	TG, °C	DTG	DTA		
I	198.8						
II	65.3	1000	100	1/5	1/5	100	10
III	44.5						
IV	21.7						
V	88.1						
VI	66.2	1000	100	1/5	1/5	100	10
VII	38.2						
VIII	30.2						
IX	60.1						
X	27.1						
XI	35.3	1000	100	1/5	1/5	100	10
XII	31.6						

Results and discussion

Via X-ray diffraction, the samples were identified as crystalline (with layered structure) materials. The analytical data, indicated the compositions given in Table 2. The results of thermoanalytical investigations are illustrated in the following Figures.

Sample I (Fig. 1) reveals four endothermic processes with weight loss, and one exothermic process without weight loss. In agreement with the literature data [5], the exothermic peak relates to the change of α-ZrO_2 to β-ZrO_2 (monoclinic to tetragonal structure).

In two steps up to 140°, it lost 8.67% of the total weight. Additional endothermic processes took place, with peaks at 338° and 445°. The final weight and the analytical data on the processes during the thermal decomposition indicated that

Table 2 Compositions of investigated samples

Sample no	Metal cont.		M/PO_4^{3-} ratio	R, mmole/g	R
	Zr	Ti			
I	1.0	0		0.66	
II	0.5	0.5	2.0	0.56	EtOH
III	0.1	0.9		10.84	
IV	1.0	0	2.0	0.63	*n*-PA
V	1.0	0		0.65	
VI	0.9	0.1		0.82	
VII	0.67	0.33	2.0		*n*-BA
VIII	0.5	0.5		0.56	
IX	0.1	0.9		0.85	
X	1.0	0		0.62	
XI	0	1.0	2.0	0.63	EDA
XII	0.9	0.1		0.86	

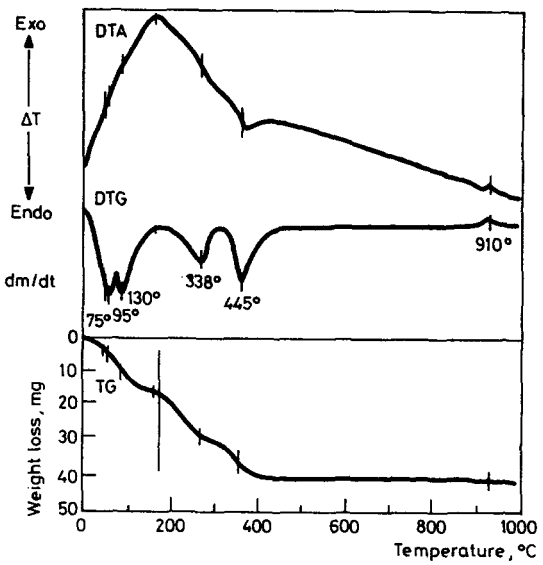

Fig. 1 Thermogram of α-zirconium phosphate intercalated with ethyl alcohol

0.66 mole of ethyl alcohol, one mole of crystalwater and one mole of structural water were lost. Thus, the complex process can be described as follows:

$$[Zr(HPO_4)_2 \cdot 0.66\,EtOH] \cdot H_2O \xrightarrow[-EtOH]{\text{up to } 140^\circ} Zr(HPO_4)_2 \cdot H_2O \rightarrow$$

$$\xrightarrow[-H_2O]{140^\circ-380^\circ} Zr(HPO_4)_2 \xrightarrow[-H_2O]{380^\circ-600^\circ} ZrP_2O_7 \xrightarrow{\text{above } 900^\circ} \beta\text{-}ZrO_2 \cdot P_2O_5$$

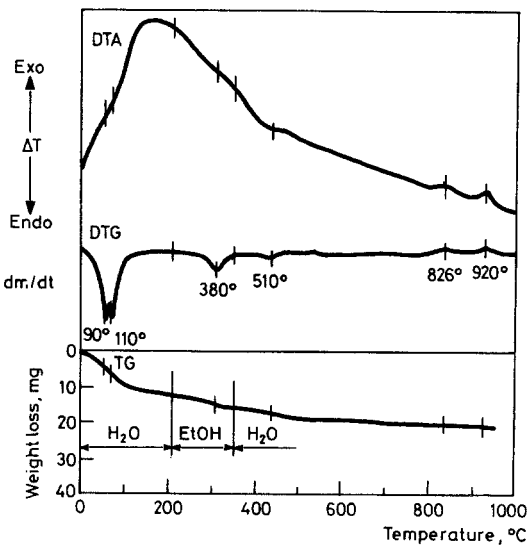

Fig. 2 Thermogram of α-$Zr_{0.5}Ti_{0.5}$ phosphate intercalated with ethyl alcohol

Sample II (Fig. 2) also exhibits four endothermic processes with weight loss. The first two proceeded up to 180°. The other two processes gave peaks at 380° and 510°. Comparison of the curves for samples I and II shows a new exothermic process without weight loss at about 850° in the latter. From the literature data [6], the process can be identified as the change of α-TiP_2O_7 into cubic three-dimensional TiP_2O_7. The thermal decomposition for this sample can be described as follows:

$$[(Zr_{0.5}Ti_{0.5})(HPO_4)_2 \cdot 0.56\,EtOH] \cdot 0.5H_2O \xrightarrow[-EtOH]{\text{up to } 180^\circ}$$

$$(Zr_{0.5}Ti_{0.5})(HPO_4)_2 \cdot 0.5H_2O \xrightarrow[-0.5H_2O]{180^\circ-465^\circ} (Zr_{0.5}Ti_{0.5})(HPO_4)_2$$

$$\xrightarrow[-H_2O]{465^\circ-570^\circ} 0.5ZrO_2 \cdot 0.5TiP_2O_7$$

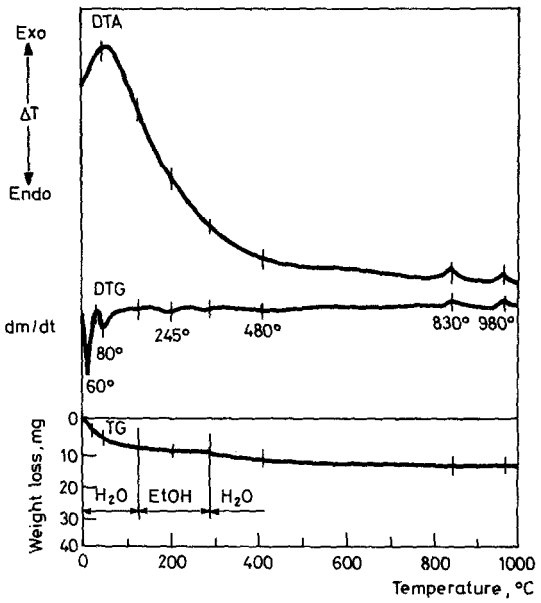

Fig. 3 Thermogram of α-$Zr_{0.1}Ti_{0.9}$ phosphate intercalated with ethyl alcohol

Similar curves were found for sample III (Fig. 3) on which basis the thermal decomposition is characterized as:

$$[(Zr_{0.1}Ti_{0.9})(HPO_4)_2 \cdot 0.84EtOH] \cdot H_2O \xrightarrow[-EtOH]{\text{up to } 145^\circ}$$

$$(Zr_{0.1}Ti_{0.9})(HPO_4)_2 \cdot H_2O \xrightarrow[-H_2O]{145^\circ\text{–}365^\circ} (Zr_{0.1}Ti_{0.9})(HPO_4)_2$$

$$\xrightarrow[-H_2O]{365^\circ\text{–}610^\circ} 0.1ZrO_2 \cdot 0.9TiP_2O_7$$

The following two Figures depict the thermal decomposition of α-zirconium bis-monohydrogenphosphate intercalated with *n*-propylamine and *n*-butylamine, respectively. In Fig. 4, the endothermic peaks with weight loss can be seen. The first, small peak at 50° represents the water adsorbed on the surface. The following two peaks relate to the crystal water, while the peak at 260° is due to the decomposition or loss of organic molecules. Finally, the process with peak at 540° can be assigned to the loss of structural water. The exothermic process (with peak above 900°) without weight loss is assigned to the crystalline transformation of ZrO_2.

In comparison, the thermal decomposition of the sample containing *n*-butylamine (Fig. 5) seems to be more complicated. The water adsorbed on the

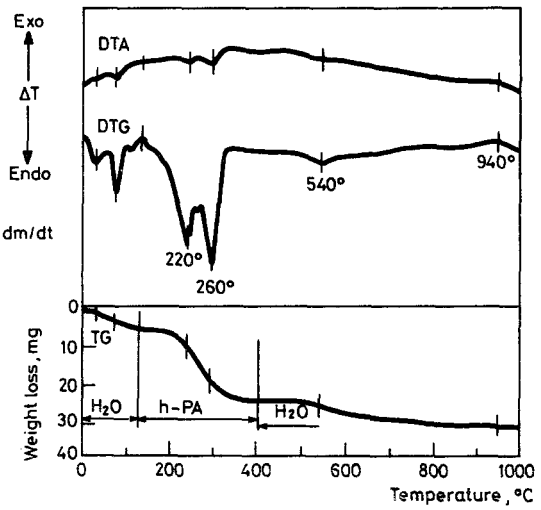

Fig. 4 Thermogram of α-zirconium phosphate intercalated with *n*-propylamine

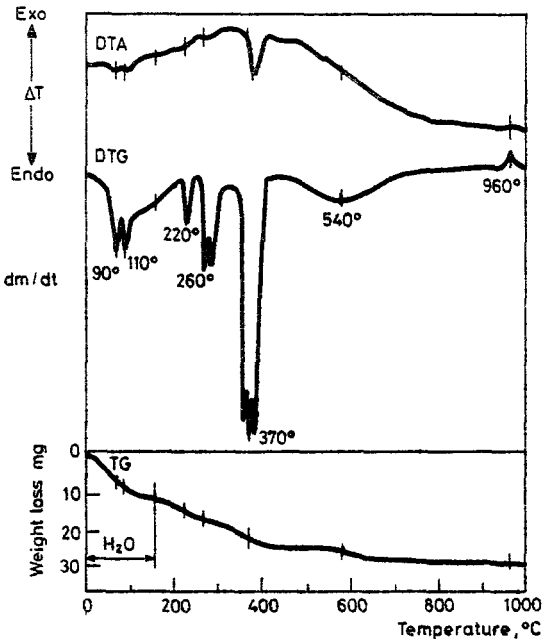

Fig. 5 Thermogram of α-zirconium phosphate intercalated with *n*-buthylamine

surface, and the crystal water, were lost at higher temperature (peaks at 90°, 110° and 260°).

The second part of the crystal water was lost in three steps that followed each other very quickly. The *n*-butylamine was lost in a very fast process, which is indicated by the large, sharp peak at 370°. The further decomposition of the material followed the conventional pattern i.e. it lost the structural water (peak at 540°) and underwent the crystalline transformation of ZrO_2 at 960°.

The comparison of these and the analytical data suggests the following thermal decompositions:

$$[Zr(HPO_4)_2 \cdot n\text{Pa}] \cdot H_2O \xrightarrow[-H_2O]{\text{up to } 240^\circ} [Zr(HPO_4)_2 \cdot n\text{Pa}]$$

$$\xrightarrow[-n\text{Pa}]{240^\circ\text{–}325^\circ} Zr(HPO_4)_2 \xrightarrow[-H_2O]{325^\circ\text{–}700^\circ} ZrP_2O_7 \xrightarrow{\text{above } 900^\circ} \alpha\text{-}ZrO_2 \rightarrow$$

$$\rightarrow \beta\text{-}ZrO_2 \cdot P_2O_5$$

and

$$[Zr(HPO_4)_2 \cdot n\text{BA}] \cdot H_2O \xrightarrow[-H_2O]{\text{up to } 325^\circ} [Zr(HPO_4)_2 \cdot n\text{BA}]$$

$$\xrightarrow[-n\text{BA}]{325^\circ\text{–}445^\circ} Zr(HPO_4)_2 \xrightarrow[-H_2O]{445^\circ\text{–}680^\circ} ZrP_2O_7 \xrightarrow{\text{above } 900^\circ} \alpha\text{-}ZrO_2 \rightarrow$$

$$\rightarrow \beta\text{-}ZrO_2 \cdot P_2O_5$$

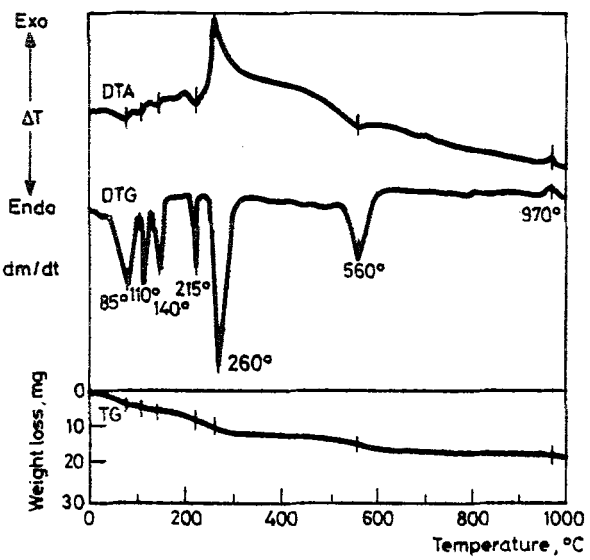

Fig. 6 Thermogram of α-$Zr_{0.9}Ti_{0.1}$ phosphate intercalated with *n*-buthylamine

In samples containing Zr and Ti metal ions in various ratios and intercalated with *n*-butylamine (Figs 6–9) some interesting phenomena were found as compared with the thermal decomposition of the sample containing only Zr atoms and intercalated with *n*-butylamine (Fig. 5). For the sample containing 10% of Ti ions (Fig. 6), a new

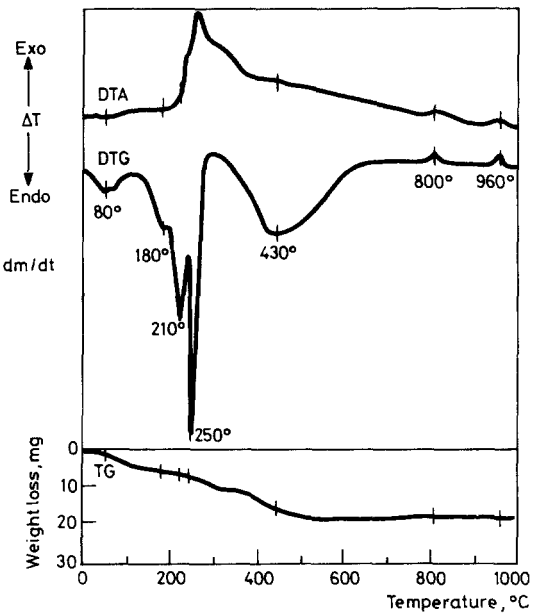

Fig. 7 Thermogram of α-$Zr_{0.67}Ti_{0.33}$ phosphate intercalated with *n*-buthylamine

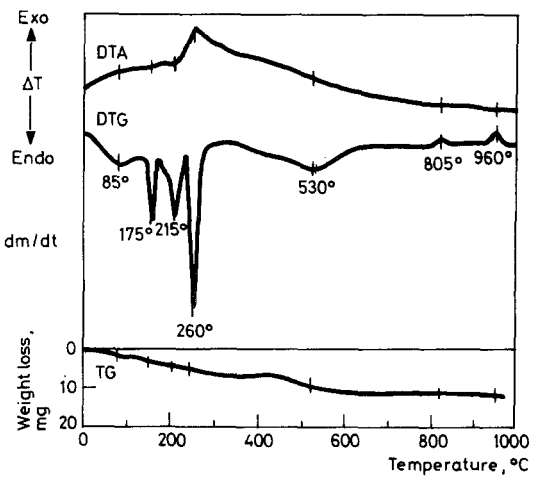

Fig. 8 Thermogram of α-$Zr_{0.5}Ti_{0.5}$ phosphate intercalated with *n*-buthylamine

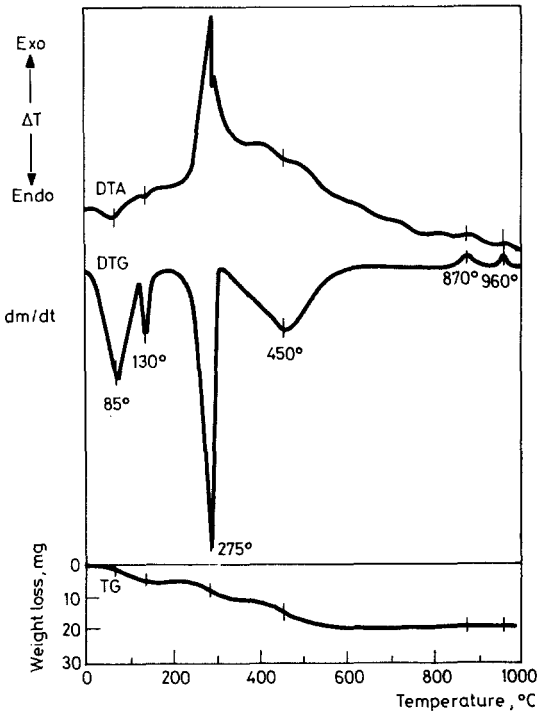

Fig. 9 Thermogram of α-$Zr_{0.1}Ti_{0.9}$ phosphate intercalated with *n*-buthylamine

endothermic process with a peak temperature of 140° was observed and another with maximum at 370°.

Another characteristic feature was found for these samples: besides the endothermic process with maximum at about 260° and simultaneous weight loss, there is an exothermic process, too.

For the sample with 33% of Ti ions (Fig. 7), the endothermic peaks at 110° and 140° disappeared, and instead a very weak process was found with maximum at 180°. For sample VII (Zr : Ti = 1) the same curves were found as in the previous case (Fig. 8).

For the sample containing 10% of Zr ions (Fig. 9), the endothermic is processes at low temperature overlapped and the structural water was lost at a lower temperature (450°) than for the other samples (the corresponding peak appeared at 560°).

It was assumed that the crystal water was lost in several steps up to 150°, followed by decomposition of the organic molecules (simultaneous oxidation and loss) and finally the samples lost their structural water in the interval 500–600°, with the exception of the material having Zr : Ti = 2 : 1. In this case the difference may have

appeared as a result of the low stability of the crystalline structure of such materials. Accordingly the thermal decompositions of these samples can be described as follows:

$$[(Zr_xTi_{1-x})(HPO_4)_2 \cdot n\text{BA}] \cdot zH_2O \xrightarrow[-zH_2O]{\text{up to } 150^\circ} [(Zr_xTi_{1-x})(HPO_4)_2 \cdot n\text{BA}]$$

$$\xrightarrow[-n\text{BA}]{150^\circ\text{–}350^\circ} (Zr_xTi_{1-x})(HPO_4)_2 \xrightarrow[-H_2O]{350^\circ\text{–}600^\circ} (xZrO_2 \cdot 1-xTi)P_2O_7$$

$$\xrightarrow{\text{up to } 900^\circ} x(ZrO_2 \cdot P_2O_5) \cdot (1-x)TiP_2O_7$$

The samples intercalated with ethylenediamine showed different pictures. Zirconium phosphate (sample X, Fig. 10) decomposed by losing the crystal water in

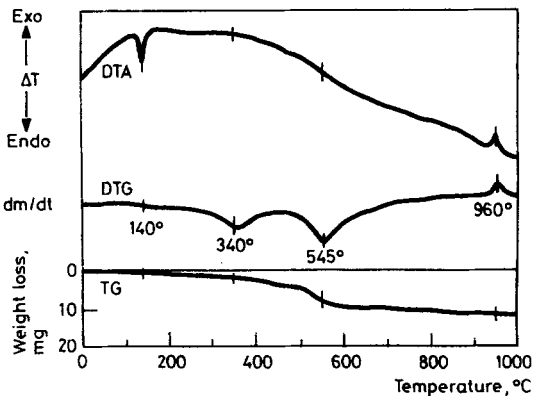

Fig. 10 Thermogram of α-zirconium phosphate intercalated with ethylenediamine

a long continuous process, combined with the loss of the organic molecules, while the structural water was lost in a relatively fast process with peak at about 550°.

Titanium phosphate (sample XI, Fig. 11) yielded endothermic peaks at 75°, 375° and 475°. With the exception of the first process, the DTG curve showed a very strong, long exothermic process, with peak at 375°.

The last sample, investigated with composition $Zr_{0.9}Ti_{0.1}$ (Fig. 12), underwent thermal decomposition similar to that of α-zirconium bis-monohydrogenphosphate intercalated with *n*-BA, except that the loss of the organic molecules was followed by a strong exothermic process.

The results indicate the following thermal decomposition of the samples with intercalated ethylenediamine:

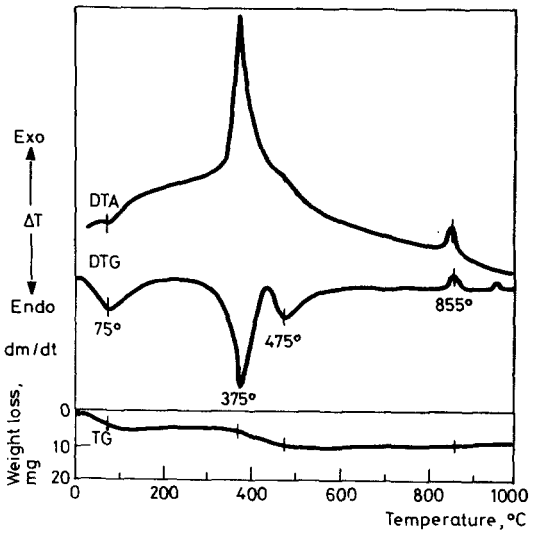

Fig. 11 Thermogram of α-titanium phosphate intercalated with ethylenediamine

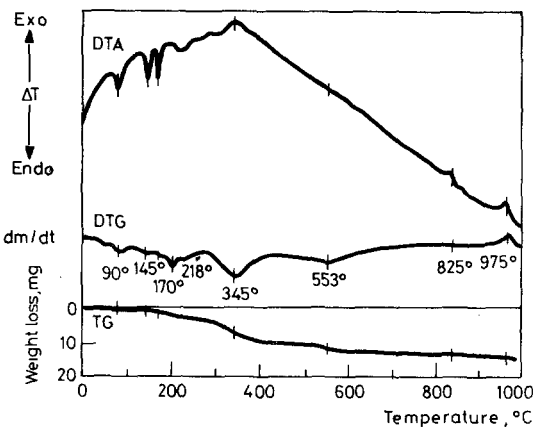

Fig. 12 Thermogram of α-$Zr_{0.9}Ti_{0.1}$ phosphate intercalated with ethylenediamine

$$a) \quad [M(HPO_4)_2 \cdot x\text{EDA}] \cdot yH_2O \xrightarrow[-yH_2O]{\text{up to } 260^\circ} [M(HPO_4)_2 \cdot x\text{EDA}]$$

$$\xrightarrow[-x\text{EDA}]{260^\circ\text{–}425^\circ} M(HPO_4)_2 \xrightarrow[-H_2O]{425^\circ\text{–}550^\circ} MP_2O_7 \xrightarrow[900^\circ]{\text{above}} MO_2 \cdot P_2O_5$$

where M = Zr or Ti.

b)

$$[(Zr_xTi_{1-x})(HPO_4)_2 \cdot yEDA] \cdot zH_2O \xrightarrow[-\text{ads. } H_2O]{\text{up to } 100^\circ}$$

$$[(Zr_xTi_{1-x})(HPO_4)_2 \cdot yEDA] \cdot zH_2O \xrightarrow[-zH_2O]{100^\circ-190^\circ}$$

$$[(Zr_xTi_{1-x})(HPO_4)_2 \cdot yEDA] \xrightarrow[-yEDA]{190^\circ-425^\circ} (Zr_xTi_{1-x})(HPO_4)_2$$

$$\xrightarrow[-H_2O]{425^\circ-650^\circ} x(ZrO_2 \cdot P_2O_5) \cdot (1-x)TiP_2O_7 \xrightarrow[900^\circ]{\text{above}}$$

$$x(\beta\text{-}ZrO_2 \cdot P_2O_5) \cdot (1-x)TiP_2O_7$$

The results of thermal analysis demonstrated the original compositions of the investigated materials, with various metal ratios and various intercalated organic molecules. These materials lost their crystal water in several steps. This was followed by decomposition of the organic molecules. The structural water was lost at higher temperatures in all cases; this is due to the stability of the crystalline structure of these materials. The abnormality of the decomposition of the organic molecules when the original Ti ions content was sufficiently high was ascribed to the catalytic effect of titanium on the decomposition of various amines.

References

1 U. Costantino, Inorganic Ion Exchange Materials, CRC Press, Boca-Raton, FL, 1982.

2 G. Alberti and U. Costantino, Intercalation Chemistry, Academic Press, Paris, 1982, p. 5.

3 J. Környei, L. Szirtes and U. Costantino, J. Radioanal. Nucl. Chem. Art., 89 (1985) 331.

4 L. Szirtes, J. Környei and Z. Pokó, Reactive Polymers, 7 (1988) 185.

5 W. B. Blumenthal, The Chemical Behaviour of Zirconium Van Nostrand, Princeton, 1958, p. 159.

6 A. Clearfield (Ed.), Inorganic Ion Exchange Materials CRC Press, Boca-Raton, FL, 1982, p. 82.

Zusammenfassung — Ergebnisse über Untersuchungen an in Schichten eingelagerten kristallinen Zirkoniumphosphat sind in der Literatur beschrieben. Das Verhalten kristalliner Phosphate, die sowohl Zirkonium- als auch Titanmetallionen enthalten, wurde bis jetzt nicht untersucht. Als Teil dieser Untersuchungen wurde das thermische Verhalten solcher Materialien im Temperaturbereich 25–1000 °C durch simultanes Registrieren der TG-, DTG- und DTA-Kurven näher bestimmt, dessen Ergebnisse hier dargelegt werden.

Резюме — Результаты исследований интеркалированного кристаллического фосфата циркония описаны в литературе. До настоящего времени не исследованы кристаллические фосфаты, содержащие иона циркония и титана. Неполно представлено термическое поведение таких материалов, изученных совмещенным методом ТГ, ДТГ и ДТА в температурном интервале 25–1000°. Представлены полученные данные.