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THERMAL BEHAVIOUR OF ACIDIC SALTS OF MIXED TETRAVALENT METALS
III. Influence of gamma-radiation on the thermal decomposition of mixed zirconium-titanium phosphates

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Mixed zirconium-titanium phosphate samples were irradiated in a gamma-radiation facility with a Co-60 source. The adsorbed dose was 10^6 Gy. At this dose, a change in thermal bahaviour was found only for the samples intercalated with *n*-butylamine or *n*-propylamine. Further, it was found that the titanium catalysed the decomposition and the loss of organic molecules.

One of the promising fields of application of the inorganic ion-exchangers is radiochemical practice. From this point of view, it is important to know whether the material used changes its properties due to the radiation dose or not.

On the basis of earlier experience [1], various mixed zirconium-titanium phosphates and their intercalated forms were investigated; i.e. the change in thermal decomposition under a relatively high adsorbed dose was observed.

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Experimental

The samples were synthetised as described earlier [2]. The thermal analysis was carried out under the conditions given previously [3], with the exception that the curves were evaluated and drawn by a derivatograph C computer program. Measurements were made from 20° up to 1000° at a heating rate of 5 deg/min in air atmosphere, in a No 4 crucible, for a max. time of 200 min, with Al_2O_3 as reference material. Sample masses are given in Table 1.

Table 1 Survey of the investigated samples

Compound	Organic molecule	Treatment	Sample No.	Sample weight, mg
α-zirconium phosphate	EtOH	orig.	I	98.8
		irrad.	II	65.3
α-zirconium phosphate	n-butyl-amine	orig	III	88.1
		irrad.	IV	78.9
α-zirconium phosphate	n-propyl-amine	orig.	V	33.1
		irrad.	VI	21.7
α- titanium phosphate	n-butyl-amine	orig.	VII	38.2
		irrad.	VIII	36.6
α-titanium phosphate	ethylene-diamine	orig.	IX	35.3
		irrad	X	32.1
α-zirconium, titanium phosphate ($Zr_{0.1}$-$Ti_{0.9}$)	n-butyl-amine	orig.	XI	60.1
		irrad.	XII	62.9
α-zirconium, titanium phosphate ($Zr_{0.9}$=$Ti_{0.1}$)	ethylene-diamine	orig.	XIII	31.6
		irrad.	XIV	17.9

The dry materials were irradiated with gamma-photons in an irradiation facility having a Co-60 source, operating with a capacity of 3 x 10^4 Gy/hour. The samples were irradiated for 100 hours, during which the temperature did not exceed 40°.

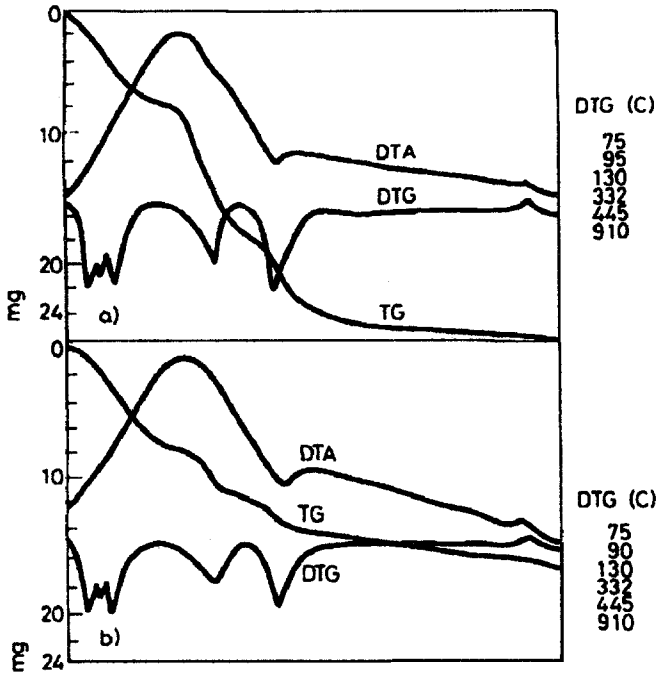

Fig. 1 TG, DTG and DTA curves of α-zirconium phosphate (α -ZP) intercalated with ethyl alcohol a - original; b - irradiated sample

Results and discussion

The samples were compared as shown in Table 1. The thermal processes occurring under the (irradiating) adsorbed dose are shown in the following Figures.

The α-zirconium phosphate and the other phosphates contained 10, 33 and 50% of zirconium besides titanium. Neither those containing only crystal water nor those with intercalated ethanol changed their thermal behaviour under the adsorbed dose of 3 x 10^6 Gy. As an example, the curves

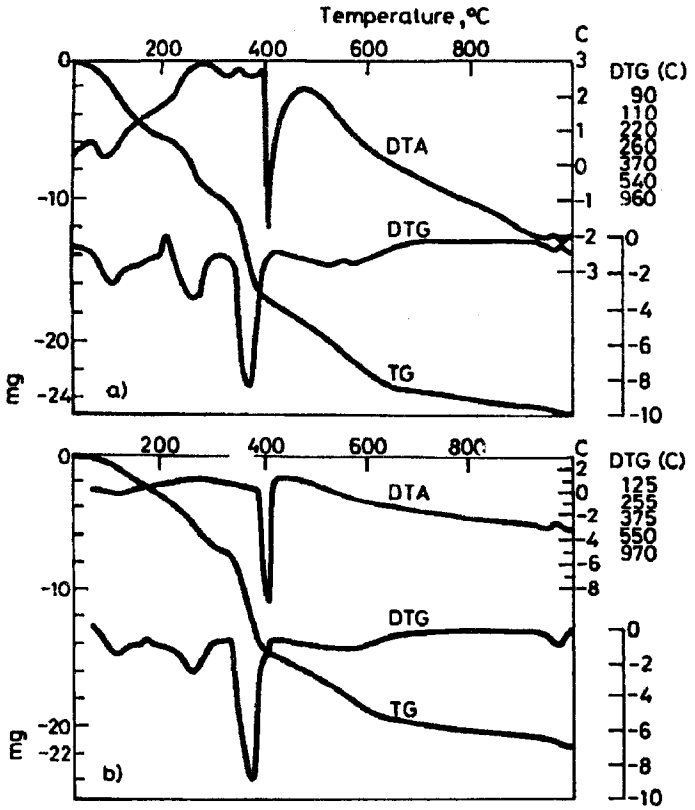

Fig. 2 TG, DTG and DTA curves of α--ZP intercalated with n-butyl-amine a - original; b - irradiated samples

for α-zirconium phosphate intercalated with ethanol are shown in Fig. 1. The thermal decomposition curves of α-zirconium phosphate intercalated with n-butylamine and n-propylamine, respectively, are shown in Figs 2 and 3, while Figs 4-5 depict the thermal decomposition curves of α-titanium phosphate intercalated with n-butylamine and n-propylamine, respectively.

The thermal behaviour of mixed zirconium-titanium ($Zr_{0.1}$-$Ti_{0.9}$) phosphate intercalated with n-butylamine and of the phosphate ($Zr_{0.9}$-$Ti_{0.1}$) intercalated with ethylenediamine presented in Figs 6-7. Similarly as for the samples intercalated with ethanol α-titanium phosphate intercalated with n-propylamine and the mixed metal ($Zr_{0.1}$-$Ti_{0.9}$) phosphate intercalated with n-butylamine did not change their thermal behaviour under the maximum possible radiation dose.

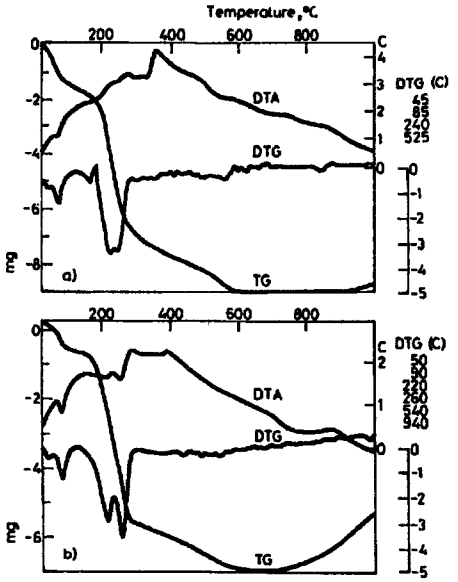

Fig. 3 TG, DTG and DTA curves of α- ZP intercalated with n-propyl-amine

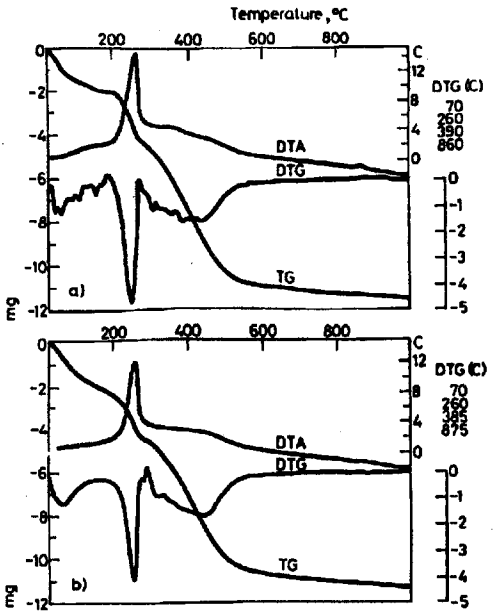

Fig. 4 TG, DTG and DTA curves of α- titanium phosphate (α-TP) intercalated with n-butyl-amine a - original; b - irradiated samples

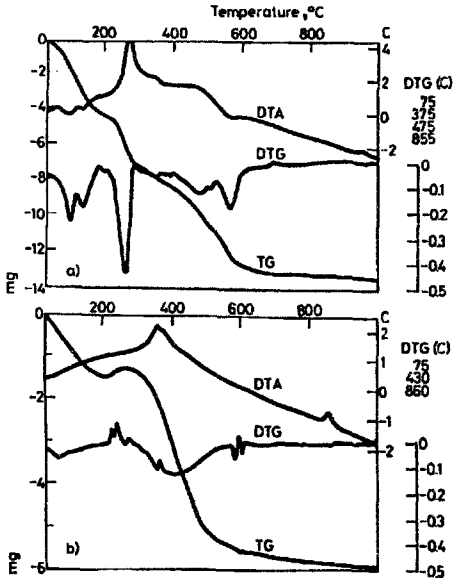

Fig. 5 TG, DTG and DTA curves of α TP intercalated with ethylene-diamine a - original; b - irradiated samples

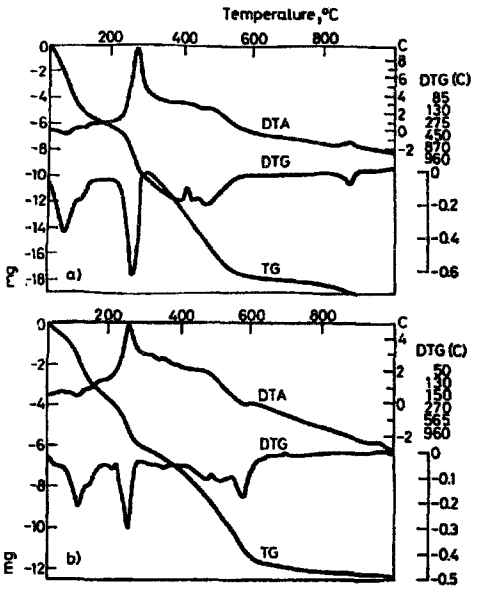

Fig. 6 TG, DTG and DTA curves of α -zirconium-titanium phosphate $Zr_{0.1} - Ti_{0.9}$ intercalated with n-butyl-amine a - original; b - irradiated samples

Due to irradiation of α-zirconium phosphate intercalated with *n*-butylamine (IV), all endothermic processes became clearer and the crystal water was lost in one step; in the other samples it was lost in two steps. For the same phosphate intercalated with *n*-propylamine (VI), the endothermic process of decomposition and loss of organic molecules became more pronounced. For α-titanium phosphate intercalated with ethylenediamine (X), smoother curves were found. For zirconium-titanium ($Zr_{0.9}$-$Ti_{0.1}$) phosphate intercalated with ethylenediamine (XIV), only the peaks relating to

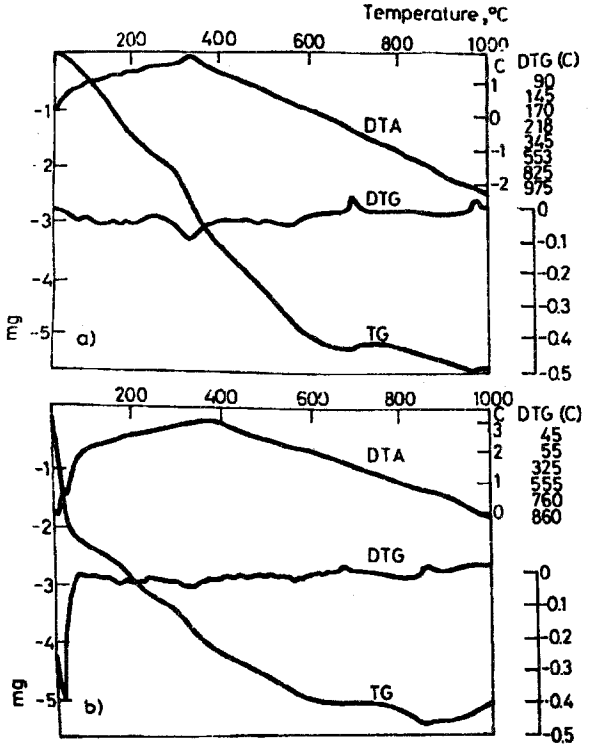

Fig. 7 TG, DTG and DTA curves of α-zirconium-titanium phosphate $Zr_{0.9}$ - $Ti_{0.1}$ intercalated with ethylene-diamine a - original; b - irradiated samples

the loss of surface-adsorbed water and the crystalline transformation of TiO_2 were found. For the samples containing titanium, independently of their status (irradiated or not), in parallel with an endothermic process (in the temperature interval 270-340°), a sharp exothermic peak was observed in the DTA curve (Fig. 6):

Table 2 Change of interlayer distance with the temperature

Compound	Org. molecule	T, °C	d, nm
α-zirconium	EtOH	25	1.42
phosphate		400	0.76
		600	0.52
	n-butyl-	25	1.86
	amine	390	0.76
		600	0.52
	n-propyl-	25	1.73
	amine	400	0.76
α-titanium	n-butyl-	25	1.88
phosphate	amine	400	0.76
		600	0.508
	ethylene-	25	1.07
	diamine	400	0.76
		600	0.508
α-zirconium,	n-butyl-	25	1.90
titanium phosphate	amine	400	0.74
($Zr_{0.1}$ - $Ti_{0.9}$)		600	0.495
α-zirconium,	ethylene-	25	1.11
titanium phosphate	diamine	400	0.74
($Zr_{0.9}$ - $Ti_{0.1}$)		600	0.50

A comparison of the thermoanalytical and analytical data suggests that the thermal decomposition of the intercalated materials proceeds in general as follows:

$$[M(HPO_4)_2 \cdot R] \cdot nH_2O \xrightarrow[-n\,H_2O]{\text{up to } 150^\circ} [M(HPO_4)_2 \cdot R \xrightarrow[-R]{\text{up to } 380^\circ}$$

$$M(HPO_4)_2 \xrightarrow[-H_2O]{\text{up to } 580^\circ} MP_2O_7 \xrightarrow[\text{with cryst. transition}]{\text{up to } 1000^\circ} MO_2 \cdot P_2O_5$$

where M = Zr or Ti or a mixture of them (Zr + Ti = 1)

R = *n*-butylamine, *n*-propylamine, ethylenediamine or ethanol.The X-ray diffraction data [4] demonstrated a good correlation between the change in crystalline structure and the thermal decomposition. The sharp exothermic process accompanying the decomposition of the organic molecules is explained as due to the catalytic effect of titanium on the oxidation of organic substances [5].

A comparison of the thermoanalytical data on the original and irradiated samples showed that the radiation has a considerable effect only on zirconium-titanium ($Zr_{0.9}$-$Ti_{0.1}$) phosphate intercalated with ethylenediamine, since the missing processes (after irradiation) point to the destruction of the crystalline structure. The other materials are practically resistant against radiation (up to the limit of the investigated dose) and as a result their thermal behaviour did not change during irradiation with gamma-photons.

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Zusammenfassung - Gemischte Zirkonium-Titanphosphatproben wurden in einer Gammabestrahlungskammer mit einer Co-60-Quelle bestrahlt. Die adsorbierte Dosis betrug 10^6 Gy. Bei dieser Dosis konnte eine Veränderung im thermischen Verhalten nur für Proben mit eingelagertem *n*-Butylamin oder n-Propylamin festgestellt werden. Weiterhin wurde gefunden, daß Titan die Zersetzung und die Abgabe der organischen Moleküle katalysiert.