ON THE EXISTENCE OF PYROPHOSPHATES OF TETRAVALENT METALS HAVING A LAYERED STRUCTURE

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ABSTRACT

After an accurate investigation of the thermal behaviour (TG and DTA curves) of several samples of α-Zr(HPO$_4$)$_2 \cdot$H$_2$O and α-Ti(HPO$_4$)$_2 \cdot$H$_2$O, prepared both by the refluxing and HF procedures, γ-Zr(HPO$_4$)$_2 \cdot$2 H$_2$O and γ-Ti(HPO$_4$)$_2 \cdot$2 H$_2$O, new pyrophosphate phases of tetravalent metals have been isolated.

The structure of these compounds, deduced from X-ray diffraction data, density measurements and considerations of bond length and angles, arises from the packing of layers of α and γ type, identical to those present in the starting materials and held together by P–O–P bridges.

These layered M(IV)P$_2$O$_7$ are obtained after the condensation process of the HPO$_4$ groups present in α and γ-M(IV)(HPO$_4$)$_2$ and are stable until the transition to the respective cubic pyrophosphates takes place.

The range of stability of these phases changes on going from the α to the γ phase and in part depends on the degree of crystallinity and/or the crystal size of the starting layered exchangers. The chemical implications of α- and γ-L-M(IV)P$_2$O$_7$ are examined and discussed.

INTRODUCTION

Cubic zirconium pyrophosphate is considered the prototype of the pyrophosphate of tetravalent metals, and its structure has been investigated by several authors [1]. This compound is generally obtained by heating (at 1000°C) the amorphous precipitates formed by mixing ammonium acid phosphate and a zirconyl salt [2], or by dissolution of a zirconium hydrate oxide in concentrated phosphoric acid at 240°C, and subsequent precipitation after slow cooling [3].

Cubic pyrophosphates of tetravalent metals are also obtained by the thermal decomposition of layered ion exchangers belonging to the class of

insoluble acid salts of tetravalent metals [4]. Cubic ZrP_2O_7 and TiP_2O_7 were in fact obtained by heating at high temperature either α-$Zr(HPO_4)_2 \cdot H_2O$ and γ-$Zr(HPO_4)_2 \cdot 2 H_2O$ or α-$Ti(HPO_4)_2 \cdot H_2O$ and γ-$Ti(HPO_4)_2 \cdot 2 H_2O$.

Various authors [5–9] have investigated the thermal behaviour of these exchangers, and their results may be summarised as follows.

(i) The thermoanalytical curves (TG, DTA) of a given compound may differ considerably from each other since they depend on the heating rates and on the method of preparation of the exchanger.

(ii) The condensation reaction of the $\equiv$POH groups sometimes occurs in two steps, the first of which leads to mixed phosphate–pyrophosphate phases [10].

(iii) Even when the condensation process is practically completed the cubic pyrophosphates are not directly obtained and other pyrophosphate phases, whose temperature of formation and range of stability strongly depend on the composition, structure and preparation methods of the starting materials, were detected.

It may be observed that the first maximum in the X-ray powder patterns of these phases has a value a little lower than the interlayer distance of the corresponding anhydrous acid phosphates, as if the layered structure is maintained also when the condensation process is practically completed. In several cases the transformation of these phases to cubic pyrophosphates occurs only by prolonged heating at higher temperatures.

It seemed of interest to re-examine the conditions for the formation of these new pyrophosphate phases and their stability range, as well as to make some hypotheses on their structure based on elaborations of X-ray diffraction and density data.

EXPERIMENTAL

Samples of α-$Zr(HPO_4)_2 \cdot H_2O$ and α-$Ti(HPO_4)_2 \cdot H_2O$ were prepared both by the method of slow decomposition of the Zr or Ti fluorocomplexes in the presence of phosphoric acid [11] and by the refluxing procedure [12].

Samples of γ-$Zr(HPO_4)_2 \cdot 2 H_2O$ and γ-$Ti(HPO_4)_2 \cdot 2 H_2O$ were prepared with the methods described in refs. 13 and 14, respectively.

DTA curves were obtained with a Netzsch 404 model apparatus, equipped with a Pt/Pt–10%Rh thermocouple, heating rate of 5°C min^{-1}. TG curves were obtained with a Stanton TG 750 thermobalance, heating rate 2°C min^{-1}. Simultaneous TG–DSC measurements were performed with a Mettler TA 2000°C apparatus, with heating rates of 5° min^{-1}.

X-Ray powder spectra were taken on a Phillips diffractometer using the Ni filtered CuK_α radiation. X-Ray diffractograms at high temperature were

obtained with an Italstructure Model AF3 attachment.

The densities were measured pycnometrically at $20.0 \pm 0.1°C$, using CCl_4 as displacing liquid.

RESULTS AND DISCUSSION

Thermal behaviour

Figure 1 reports the TG and DTA curves of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ and several samples of α-$Zr(HPO_4)_2 \cdot H_2O$.

The phenomena occurring in the range 25–400°C, related to the dehydration process and to some phase transitions have been discussed in previous works [5,6,8,9].

Let us consider the thermal behaviour of the samples in the range of temperature in which the condensation of phosphate groups to pyrophosphate occurs (400–900°C).

For the α-zirconium phosphates the condensation process occurs in only one step for materials with a low degree of crystallinity, i.e. α-ZrP(10/100) *,
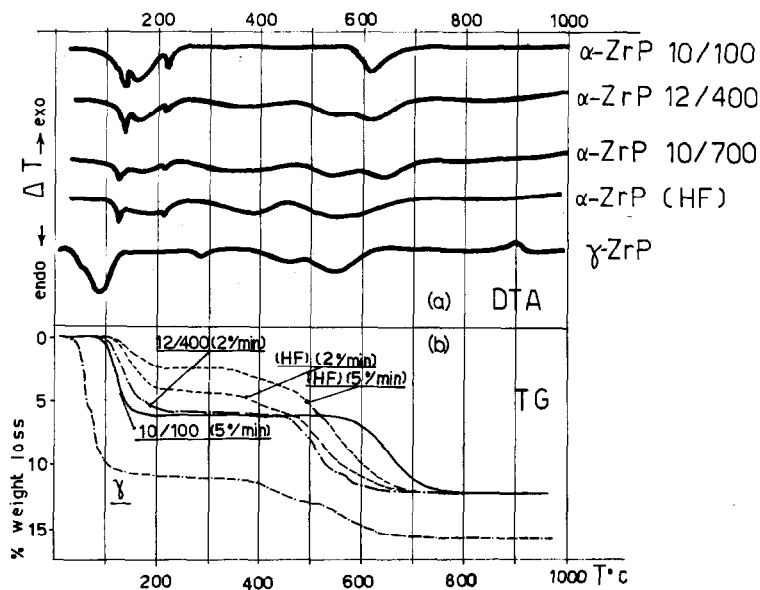

Fig. 1. DTA and TG curves of several samples of α-$Zr(HPO_4)_2 \cdot H_2O$ and of γ-$Zr(HPO_4)_2 \cdot 2H_2O$.

* The different phases will be hereafter indicated for sake of brevity as α- or γ-ZrP or TiP, where P corresponds to $(HPO_4)_2$ present in the exchangers.

while it seems to proceed in two stages for the samples refluxed for a longer time or prepared with the HF procedure.

The two-step process is generally more evident in DTA than in TG curves; if the heating rate is not sufficiently slow [8], as shown in Fig. 1(b), an overlap is noted between the dehydration and condensation processes. This is due to the fact that if the dehydration process is partially delayed at the higher temperatures the higher is the degree of crystallinity and/or the crystal size of the samples examined [8].

However, at 700–750°C the condensation process is practically completed for all the samples.

The characteristic peaks of the cubic ZrP_2O_7 were absent in the X-ray diffraction patterns of samples heated at 700°C.

All the α-ZrP samples show an X-ray pattern typical of a layered compound and the first reflection corresponds to the interlayer distance of 6.10 Å. It may be noted that phases with similar interlayer distance have been reported by Horsley and Nowell [6] and Clearfield and Pack [9], but in ref. 6 the conditions for the preparation are not reported, and in ref. 9 it seems that the phase reported had still to lose a further 0.2–0.3 H_2O of condensation.

Since the DTA curves do not show defined exothermic peaks relative to the transition to cubic ZrP_2O_7, in order to examine the stability of such pyrophosphates the samples of α-zirconium phosphate were heated in an
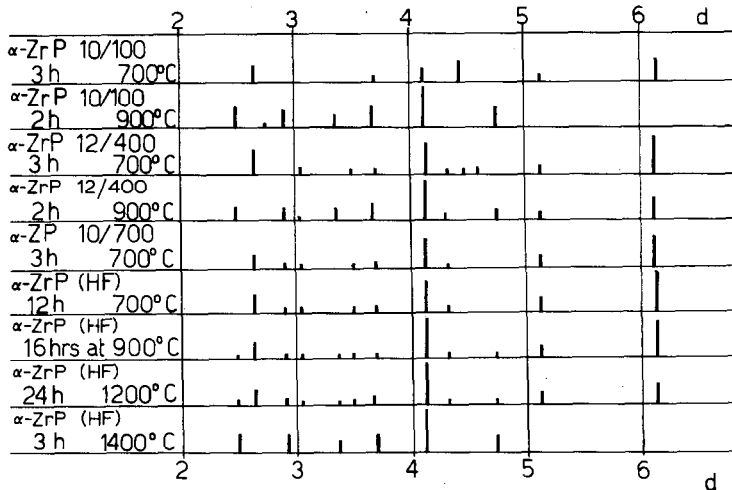

Fig. 2. X-Ray diffraction patterns of various samples of α-Zr(HPO$_4$)$_2 \cdot H_2O$ heated at the temperature and for the time indicated. The last spectrum may be taken as reference spectra of cubic ZrP_2O_7.

oven at different temperatures (700–1400°C) for several hours and their X-ray powder patterns recorded. From Fig. 2 it may be seen that while the samples refluxed for relatively short times are transformed into cubic ZrP_2O_7 after two hours at 900°C (see the X-ray powder pattern of ZrP10-100), those with a higher degree of crystallinity such as those obtained from the HF procedure show the presence of the phase with $d = 6.10$ Å even when they are heated at 1200°C for times as long as 24 h. For such a sample the complete conversion to cubic ZrP_2O_7 is achieved after heating for 3 h at 1400°C.

In the case of the γ-ZrP sample, the transition to cubic pyrophosphate occurs at 900°C and is indicated by a smooth exothermic peak, in the DTA curve. The TG curve shows a horizontal inflection point, during the weight loss related to the condensation of phosphate groups [15]. X-Ray diffractograms recorded with a high temperature camera at the temperature of this inflection revealed the presence of a phase with interlayer distance of 8.30 Å. This phase slightly transforms when the condensation process is completed at 700–750°C to a 8.26 phase (Table 2).

Similar experiments were performed with titanium hydrogen phosphates. Figure 3 shows the TG and DTA curves of γ-Ti$(HPO_4)_2 \cdot 2H_2O$ and of several samples of α-Ti$(HPO_4)_2 \cdot H_2O$, while the X-ray diffraction patterns of the samples heated at 650° are reported in Fig. 4.

From the thermal behaviour of α-TiP samples we can deduce the following.

(i) As observed for α-zirconium phosphates [7–9], the dehydration process occurs following different kinetics depending on the preparation methods of the materials and therefore on their degree of crystallinity. The less crystalline samples (i.e. TiP 12-50) lose their crystalline water below 300°C, and their DTA curves show a well evident endothermic peak due to the phase transition of the anhydrous TiP, (the interlayer distance changes from 7.33 to 7.10 Å) [8]. For samples with a higher crystallinity (i.e. TiP 12-500) the dehydration process begins at higher temperatures and is completed at 350–400°C. Moreover the kinetics seems slower and are furthermore slowed by the above-mentioned decrease in the interlayer distance.

(ii) The condensation processes beginning at 420–450°C occur in a single step, and not in two steps as observed in the case of and some α-ZrP samples.

(iii) The transition to cubic TiP_2O_7 occurs between 800 and 900°C, as indicated by the exothermic peak in the DTA curves.

In the case of γ-TiP the condensation of phosphate groups to pyrophosphate proceeds in two steps (see the TG curve) and the transition to cubic TiP_2O_7 occur at 850°C (see the DTA curve).

Figure 4 shows that the α-TiP samples, heated in an oven at 650°C, a temperature at which the condensation process is completed, give rise to a
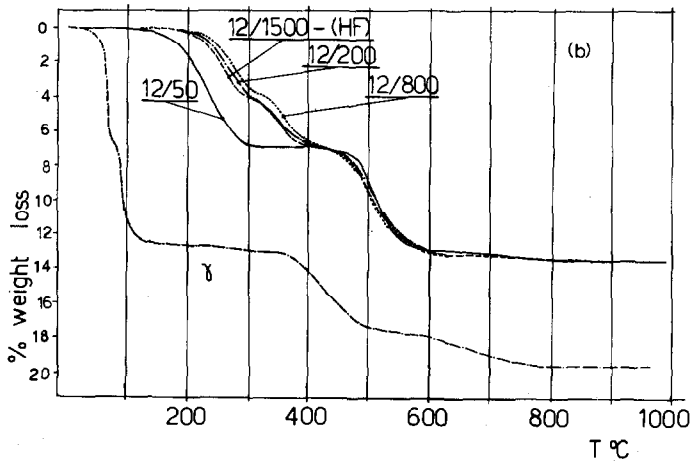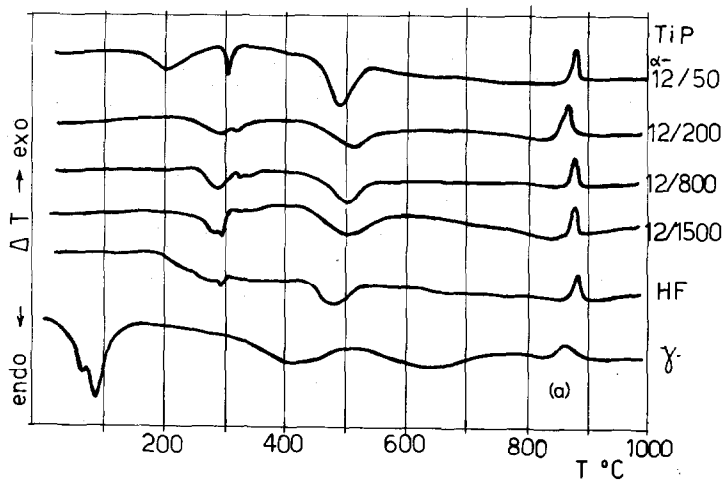
Fig. 3. DTA and TG curves of several samples of α-Ti(HPO$_4$)$_2 \cdot$H$_2$O and of γ-Ti(HPO$_4$)$_2 \cdot$ 2 H$_2$O.
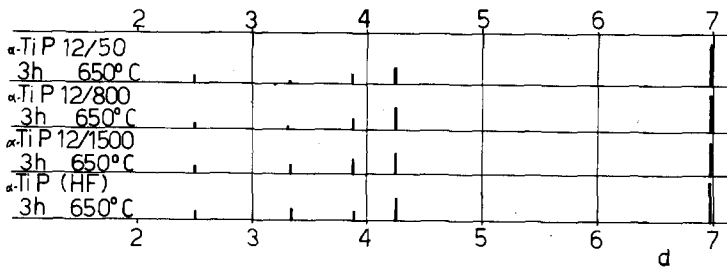

Fig. 4. X-Ray diffraction patterns of various samples of α-Ti(HPO$_4$)$_2 \cdot$H$_2$O heated at the temperature and for the time indicated.

phase having a first *d* value of 6.94 Å. We believe that this phase, like that derived from the γ-TiP (8.3 phase) could be pyrophosphate phases of a layered type.

Structural considerations

From the series of results obtained by examining the thermal analytical curves, IR spectra and X-ray diffraction patterns of several samples of titanium and zirconium acid phosphate (α- and γ-forms) after the condensation processes, we may suppose that the phosphate condensation leads initially to pyrophosphate phases having layered structures similar to those of the starting materials. The formation of P–O–P bridges in these samples is supported by the presence of bands at ~740 cm^{-1} in their IR spectra.

Since single crystals of these phases, to work out the structure, are not yet available to give further support to the previous hypothesis, the method developed by Alberti and co-workers [16] was applied. This method allows one to check if during the ion exchange or hydration processes of layered acid salts of tetravalent metals, the structure of the $[M_n^{IV}(PO_4)_{2n}]^{2n-}$ macro-anions, constituting the layers, changes or not. In particular it was found that the parameter $n = \rho(d/M)$ (where d, ρ and M are respectively the interlayer distance (cm), the density (g cm^{-3}) and the formula weight of a given ionic form) does not appreciably change if the structure of the layers of the acid salt remains practically unaffected irrespective of the water and the nature of the counter-ions placed between them. The n-value which has the physical meaning of the number of formula weights per square centimeter of layer, depends in fact on the structure of the planar macroanions and it is characteristic of a given acid salt.

In Table 1 the values of n, and of the parameters necessary for its calculation, for the hydrated, anhydrous α and γ-titanium and zirconium phosphates as well as for the corresponding pyrophosphates, are reported. It can be seen that the n-values of the pyrophosphate phases are very similar to those obtained for the hydrated and anhydrous forms of the corresponding exchangers. Thus, the structure of these pyrophosphates arise from the packing of layers similar to those present in the acid salts from which they are derived. These phases will be indicated as α- or γ-L-pyrophosphates. An idealized structure of the α-L-ZrP$_2$O$_7$ (with $d_{002} = 6.10$ Å), obtained only by allowing the α-$[Zr_n(PO_4)_{2n}]^{2n-}$ macroanions to approach one another until the formation of P–O–P bonds (revealed by the presence of the band at 740 cm^{-1} in the IR spectra of samples heated at 600–700°C) is depicted in Fig. 5.

The structure is very similar to that of α-Zr(HPO$_4$)$_2$ in which the ≥POH groups belonging to two adjacent layers have condensed to P–O–P groups

TABLE 1

Values of n for hydrated, anhydrous and L-pyrophosphate phases of α and γ zirconium and titanium phosphates

Compound	Formula weight	Inter-layer distance $(cm \times 10^8)$	Density $(g\ cm^{-3})$	n (moles $cm^{-2} \times 10^{10}$)
α-Zr(HPO$_4$)$_2 \cdot$H$_2$O	301.2	7.56	2.72	6.8
α-Zr(HPO$_4$)$_2$	283.2	7.41	2.62	6.8
ZrP$_2$O$_7$	265.2	6.1	2.86	6.6
γ-Zr(HPO$_4$)$_2 \cdot$2 H$_2$O	319.2	12.2	2.43	9.3
γ-Zr(HPO$_4$)$_2$	283.2	9.4	2.79	9.3
ZrP$_2$O$_7$	265.2	8.26	2.99	9.3
α-Ti(HPO$_4$)$_2 \cdot$2 H$_2$O	257.8	7.56	2.61	7.7
α-Ti(HPO$_4$)$_2$	239.8	7.33	2.44	7.5
TiP$_2$O$_7$	221.8	6.94	2.46	7.7
γ-Ti(HPO$_4$)$_2 \cdot$2 H$_2$O	275.8	11.6	2.37	10.0
γ-Ti(HPO$_4$)$_2$	239.8	9.1	2.60	9.9
TiP$_2$O$_7$	221.8	8.11	2.77	10.1

and the value 6.10 Å corresponding to the first reflection in the X-ray diffractogram, is due to the distance between two adjacent planes of the zirconium atom. It is known that the distance between the mean plane of zirconium atoms and the mean plane of a phosphorus atom of the $\geqslant$POH groups belonging to the same layer in α-Zr(HPO$_4$)$_2 \cdot$ H$_2$O is 1.64 Å [17] and that the distance between the phosphorus atoms in the P–O–P groups is
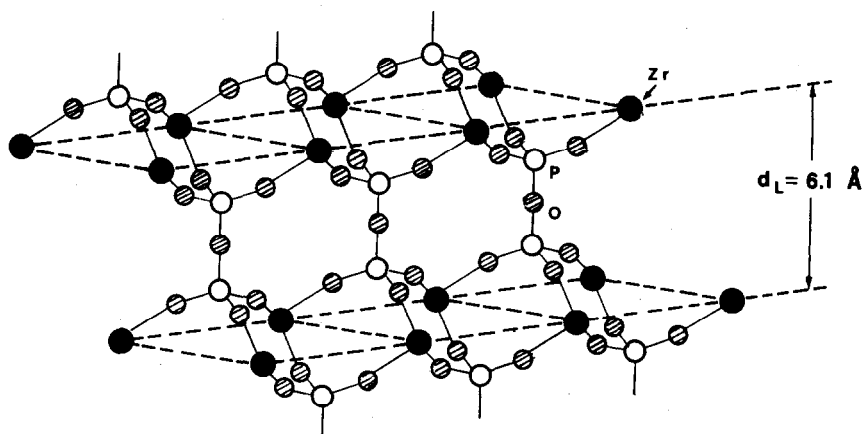

Fig. 5. Idealized structure of α-L-ZrP$_2$O$_7$.

estimated to be 2.96 Å, when the P–O–P angle is equal to 180° [1]. Thus, if the structure of the layers remains practically unchanged, the interlayer distance in α-L-ZrP$_2$O$_7$ must be $(1.64 \times 2 + 2.96) = 6.16$ Å.

This value is very near to that experimentally observed. The assumption that the P–O–P bridge is linear results from the fact that the terminal phosphate groups should be in a parallel configuration as required by the layered structure. The presence of linear pyrophosphate anions is unusual, it has been observed in a variety of cubic ZrP$_2$O$_7$ [1] and thus further investigations are needed to confirm our hypothesis.

The estimate of the d_{002} of the γ-L-ZrP$_2$O$_7$ cannot be made owing to the lack of knowledge of the structure of γ-layers.

On the other hand, if the P–O–P angle is 180°, the value of the interlayer distance of γ-L-M(IV)P$_2$O$_7$ can be assumed to be equal to the thickness of the γ-$[M_n^{(IV)}(PO_4)_{2n}]^{2n-}$ macroanion, considering this to be the distance

TABLE 2

X-Ray powder patterns of layered Ti and Zr pyrophosphates

α-L-ZrP$_2$O$_7$ from α-ZrP at 700°C		γ-L-ZrP$_2$O$_7$ from γ-ZrP at 700°C	
d	i	d	i
6.10	vs	8.26	mw
5.12	mw	5.11	m
4.31	w	3.83	s
4.12	s	3.29	ms
3.69	w	2.68	mw
3.50	w	2.58	mw
3.05	vw	2.50	mw
2.92	vw	2.12	w
2.64	m		
α-L-TiP$_2$O$_7$ From α-TiP at 650°C		γ-L-TiP$_2$O$_7$ from γ-TiP at 700°C	
d	i	d	i
6.94	s	8.11	s
4.24	ms	5.21	vw
3.90	m	4.06	vw
2.50	mw	3.73	m
		3.69	ms
		2.70	mw

between the planes passing through the baricentres of the fixed charges (O^-) present on the two surfaces of the γ-layers.

Since the condensation process occurs between ⩾P–OH groups belonging to adjacent layers, it seems likely that the ⩾P–OH groups present on the surface of the microcrystals and distant from each other by 5.0–5.3 Å and 4.4–4.6 Å in the α- and γ-phases respectively, will undergo the condensation only when the compounds are converted into the respective cubic pyrophosphates. Thus, the α- and γ-L-M(IV)P$_2$O$_7$ should possess surface exchangeable protons at very high temperatures.

Finally, it may be observed that the α- and γ-L-M(IV)P$_2$O$_7$ cannot undergo uni-dimensional swelling without hydrolyzing the P–O–P bond. Such a process seems very slow since a sample of α-L-ZrP$_2$O$_7$ refluxed in diluted H$_3$PO$_4$ solution did not convert to α-Zr(HPO$_4$)$_2$ even after 24 h.

The X-ray powder patterns of the α and γ-L-M(IV)P$_2$O$_7$ are reported in Table 2.

CONCLUSIONS

The main result of the present work lies in the isolation and characterization of new pyrophosphates of tetravalent metals in which adjacent layers of α- or γ-type are covalently joined by P–O–P bridges.

These compounds are obtained after the condensation process of the HPO$_4$ groups of the α- and γ-M(IV)(HPO$_4$)$_2$ layered exchangers and they persist until the transformation to the cubic pyrophosphates is obtained. This phase transition, clearly evident in the DTA curves of α- and γ-TiP and γ-ZrP samples, occurs very slowly for α-ZrP samples so that the heat of this transition, spread out over a broad temperature range, cannot give evident exothermic peaks in the DTA curve. However, the static experiments showed that the transformation occurs, only after prolonged heatings, at temperatures higher than 900°C.

This datum and those obtained from the DTA curves results in the temperatures of transition to cubic pyrophosphates of the α-phases being higher than those of the corresponding γ-ones and, in turn, those of zirconium salts being higher than those of the corresponding titanium ones. Nevertheless, in preparing an L-pyrophosphate, care must be taken of the crystallinity and of the crystal size of the starting material since these factors may influence both the temperature at which condensation is complete and that of transition to the cubic phase.

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