



Thermal decomposition of lanthanide orthophosphates synthesized through crystallisation from phosphoric acid solution

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Abstract

Thermal decomposition characteristics of lanthanide phosphates $\text{LnPO}_4 \cdot \text{H}_2\text{O}$ (Ln: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) prepared by crystallisation from boiling phosphoric acid solution has been presented. On the basis of the effects observed on DTA and DTG curves, while heated up to 1000°C , the phosphates can be divided into two groups: (a) the first group includes hexagonal (La \rightarrow Tb), and orthorhombic Dy phosphates, (b) the second group consists of tetragonal (Ho \rightarrow Lu) and Y phosphates. The group (a) is characterised by two endotherms below 300°C , associated with dehydration, and one exotherm above 700°C , associated with transformation of the hexagonal/orthorhombic into monoclinic modification. The temperature of the polymorphic transformation is increasing with the increase of the atomic number of the lanthanide from $<750^\circ\text{C}$ (La, Ce) to $>900^\circ\text{C}$ (Tb, Dy). The group (b) dehydrates within a wide temperature range ($100\text{--}600^\circ\text{C}$) and maintains the tetragonal crystal structure even after heating at 950°C . However, an increased crystallinity, contraction of the *a*- and *c*-axes, and difference in IR spectra suggests topotactical structural changes in (Ho \rightarrow Lu) and Y phosphates.

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1. Introduction

Rare earth element phosphates have not been thoroughly investigated compounds. They are usually obtained by direct precipitation from aqueous solutions of their salts. The precipitate obtained tends to be gelatinous, very often unfiltrable and is contaminated with foreign ions derived from the precipitant [1–9]. Syntheses of crystals in nano- or micro-meter size were achieved by other than direct precipitation; hydrolysis of pyrophosphate or hydrothermal methods [10–12].

Data reported in literature indicate that the rare earth element phosphates display a variety of structures. They appear in hexagonal, tetragonal, orthorhombic and monoclinic modifications [13–33]. Thermal decomposition of some individual lanthanide phosphates have been sporadically investigated [18,25,33–36] except the rhabdophane crystal group (La–Dy) reported by Jansen and Vance [37].

Recently, a preparation method, based on crystallisation of pure crystalline lanthanide phosphates from phosphoric acid solution, has been developed in our laboratory [38].

The phosphates of the elements (La \rightarrow Tb) obtained by that method crystallised in hexagonal modification, $\text{DyPO}_4 \cdot \text{H}_2\text{O}$ in orthorhombic, while the

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phosphates of the elements (Ho → Lu and Y) were in tetragonal form [39].

The aim of the present work was to investigate systematically thermal decomposition of the phosphates obtained by crystallisation from phosphoric acid solution throughout the group of the lanthanides and Y.

2. Experimental

2.1. Materials and methods

The investigated phosphates $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ (Ln: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), where n was ≈ 1 , were prepared by crystallisation from boiling phosphoric acid solution, containing 2 M l^{-1} of H_3PO_4 and 0.02 M l^{-1} of Ln. The preparation method was described in [38].

Thermal decomposition was investigated using TGA–DTA fully automated system of the Universal V2.3C TA Instruments. The sample of 30–40 mg in size was heated in a Pt crucible with a heating rate of $20^\circ\text{C min}^{-1}$ from room temperature to 1000°C using air ($100 \text{ cm}^3 \text{ min}^{-1}$) as a purge gas. Al_2O_3 was employed as reference material. To characterise the solids before and after ignition X-ray powder diffraction (XRD) and IR spectra methods were applied. The XRD patterns were acquired using Philips X'pert XRD equipment furnished with graphite monochromator PW 1752/00, with radiation Cu $\text{K}\alpha$, Ni filter, 2θ from 10 to 60° at 30 kV, 30 mA. For the unit cell parameters determination program Unit Cell (Tim Holland and Simon Redfern) was applied. A Fourier transform IR spectrometer FTIR-FTS 175 (Bio-Rad) was used to record IR spectra of the samples in KBr pressed pellets covering the wavenumbers $400\text{--}4000 \text{ cm}^{-1}$.

3. Results and discussion

3.1. Thermal decomposition

Fig. 1 displays the thermal decomposition of the lanthanide phosphates. This decomposition is structure dependent. According to thermal analysis patterns the phosphates can be divided into two groups.

The first group includes hexagonal $\text{LnPO}_4 \cdot \text{H}_2\text{O}$ (Ln: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) (Fig. 1A–H) and orthorhombic $\text{DyPO}_4 \cdot \text{H}_2\text{O}$ (Fig. 1I) phosphates. The group is characterised by two phenomena described below.

- (a) Double endothermic effect below 300°C accompanied by a loss of water of about 6–8 wt.%.
- (b) An exotherm recorded at temperatures higher than 700°C without any weight change. It is associated with polymorphic transformation. The transformation is illustrated by X-ray diffraction patterns (Fig. 2) and IR spectra (Fig. 3). The XRD patterns show a change in crystal structure from hexagonal (not ignited) to monoclinic (ignited at 950°C). This is supported by the observation of additional infrared bands in IR spectra of the monoclinic, less symmetrical LnPO_4 (Fig. 3C and D), which is consistent with literature values [40]. The temperature of the polymorphic transformation is increasing with the increase of the atomic number of the element from below 750°C (La, Ce) to above 900°C (Tb, Dy) (Fig. 1A–I).

The second group consists of tetragonal $\text{LnPO}_4 \cdot \text{H}_2\text{O}$ (Ln: Ho, Er, Tm, Yb, Lu and Y) phosphates (Fig. 1J–P). These phosphates dehydrate within a wide temperature range ($100\text{--}600^\circ\text{C}$) without major structural changes. Fig. 4 demonstrates that the tetragonal phosphate, which initially was in hydrated form, maintained the same crystal structure after ignition at 950°C except that the crystallinity increased. Analysis of XRD data and IR spectra revealed two phenomena not previously reported.

- (1) Dimensions of the unit cell of the tetragonal modification after ignition at 950°C became smaller (Fig. 5). The differences (average 0.0016 nm) in the unit cell parameters were larger than the error. On the level of 95% confidence the errors of a - and c -axes of the ignited phosphates were ranging from 0.00002 to 0.000092 nm , while the errors of not ignited were ranging from 0.00004 to 0.00037 nm .
- (2) In contrast to Hezel and Ross [40], IR spectra of the hydrated tetragonal form have shown three (instead of two) bands in the region of ν_4 (example in Fig. 6). An additional band in the region of

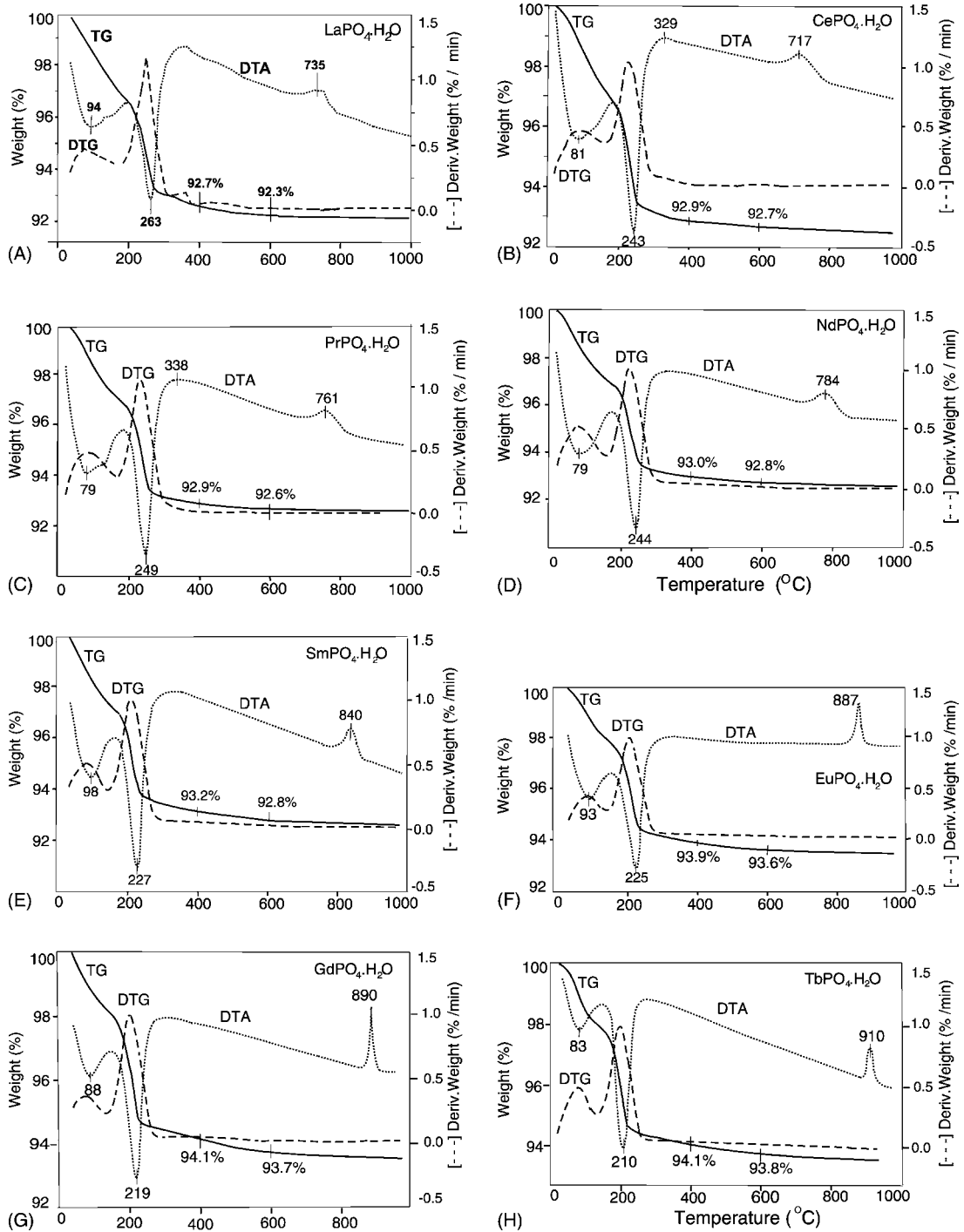


Fig. 1. Thermal decomposition of the phosphates prepared by crystallisation from boiling phosphoric acid solution: (A–H) hexagonal LnPO₄·H₂O (Ln = La → Tb); (I) orthorhombic DyPO₄·H₂O; (J–N) tetragonal LnPO₄·H₂O (Ln = Ho → Lu); (P) represents tetragonal YPO₄·H₂O.

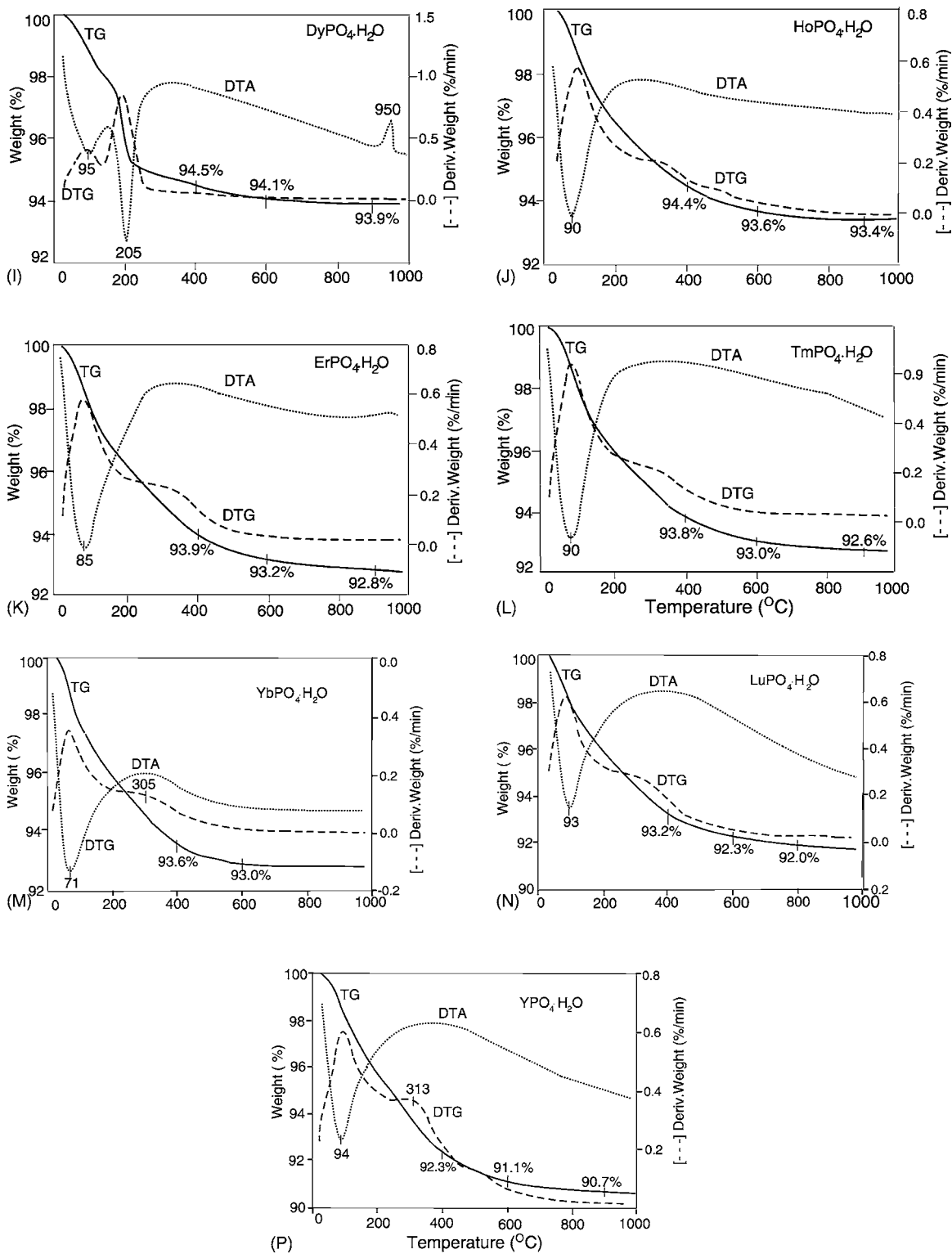


Fig. 1. (Continued).

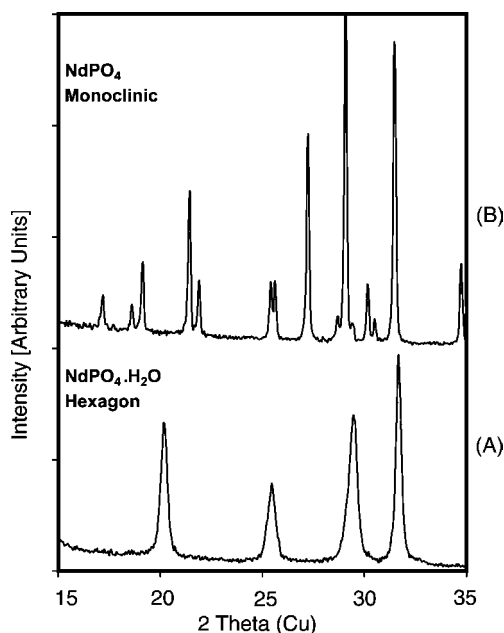


Fig. 2. X-ray diffraction patterns of neodymium phosphate: (A) hexagonal, prepared by crystallisation from phosphoric acid solution; (B) monoclinic, obtained after ignition of (A) at 950 °C.

ν_4 appears at 625 cm^{-1} wave number position. This band disappears after ignition and the spectra showing two bands at 525 and 652 cm^{-1} (Fig. 6B), comes to an agreement with those reported in the literature [40].

In some ignited samples pyrophosphate band at about 1250 cm^{-1} (Fig. 3D) was observed. The presence of $\text{P}_2\text{O}_7^{4-}$ band may result from the presence of HPO_4^{2-} in the lanthanide phosphates. The phosphates crystallised in the acid solution where HPO_4^{2-} for PO_4^{3-} substitution was quite possible. If the HPO_4^{2-} is built in the crystal structure it should be decomposed upon ignition at higher than $500\text{ }^\circ\text{C}$ and according to the reaction:

$2\text{HPO}_4^{2-} \rightarrow \text{P}_2\text{O}_7^{4-} + \text{H}_2\text{O}$ the pyrophosphate ion is possible to appear [42,43].

3.2. The nature of H_2O in lanthanide phosphates?

There is an uncertainty about the number of H_2O molecules in $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ and its role in the crystal structure. The H_2O is reported to be of zeolitic nature

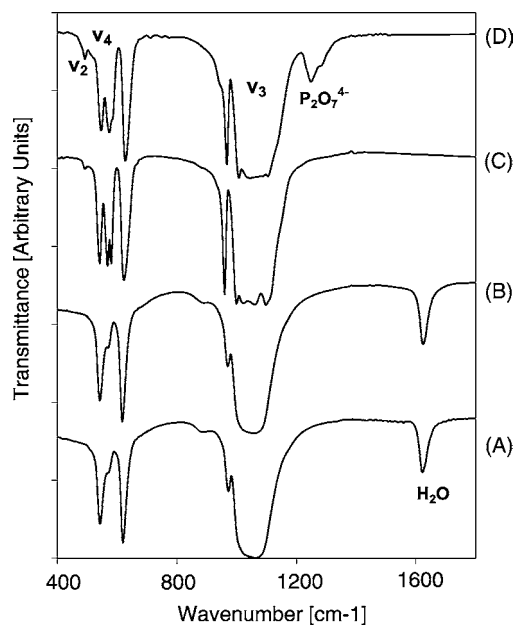


Fig. 3. IR spectra of the phosphates: (A and B) hexagonal $\text{NdPO}_4 \cdot \text{H}_2\text{O}$ and $\text{PrPO}_4 \cdot \text{H}_2\text{O}$ prepared by crystallisation; (C and D) anhydrous monoclinic NdPO_4 and PrPO_4 obtained after ignition of A and B at 950 °C.

and is related to the specific structure of $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ [14,32,36]. According to Mooney [14] who was first to describe the hexagonal crystal structure of the La, Ce, Nd, Pr phosphates, the open channels along the c -axis

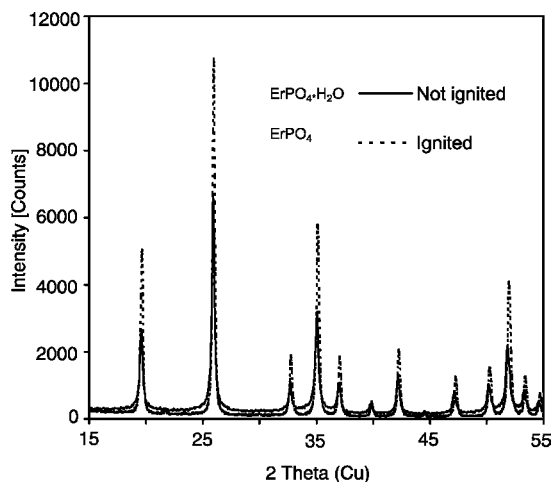
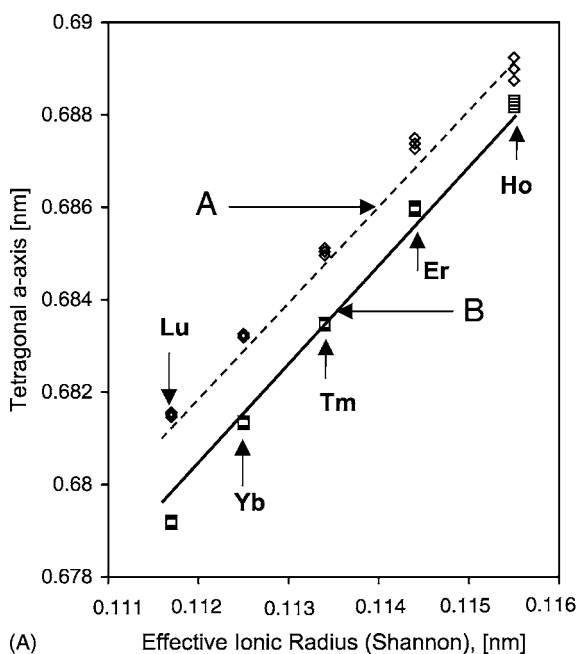
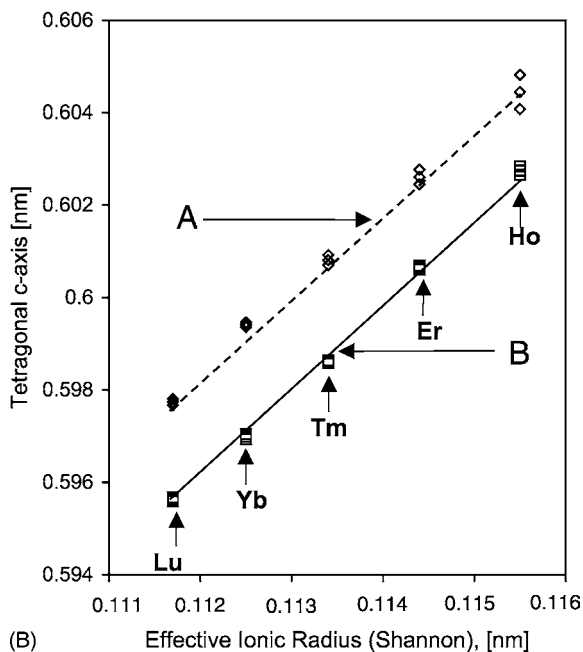


Fig. 4. X-ray diffraction patterns of tetragonal erbium phosphate: (—) tetragonal $\text{ErPO}_4 \cdot \text{H}_2\text{O}$ prepared by crystallisation; (···) anhydrous tetragonal ErPO_4 , after ignition at 950 °C.



(A)



(B)

Fig. 5. *a*- and *c*-axes of the tetragonal unit cell of the phosphates plotted against Shannon [41] ionic radii of the eight-coordinated lanthanide three-valent cations: (A) $\text{LnPO}_4 \cdot \text{H}_2\text{O}$ prepared by crystallisation; (B) anhydrous LnPO_4 ($\text{Ln} = \text{Ho} \rightarrow \text{Lu}$) obtained by ignition of A at 950°C .

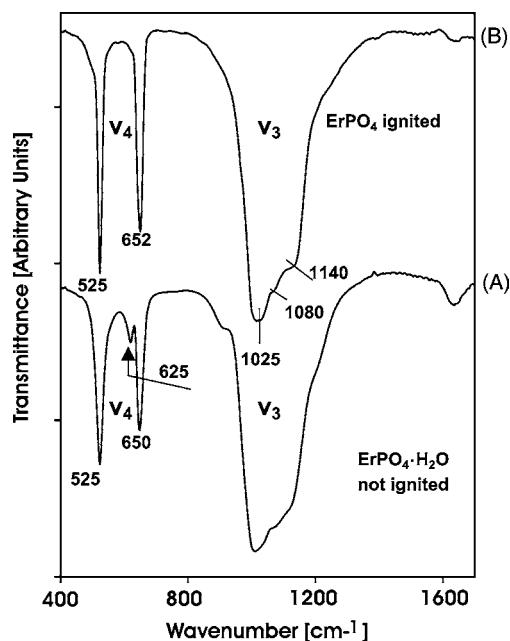


Fig. 6. IR spectra of the tetragonal phosphates: (A) $\text{ErPO}_4 \cdot \text{H}_2\text{O}$ prepared by crystallisation; (B) anhydrous ErPO_4 obtained by ignition of A at 950°C .

can accommodate up to 1.5 molecules of water per unit cell. Therefore, with three molecules of LnPO_4 in the unit cell of the hexagonal structure, it should be no more than 0.5 H_2O per Ln atom. Shao-Long Tie also reported a possibility of accommodation of water or of chain-shaped molecules such as NaPO_3 in the channels of the tetragonal dysprosium phosphate [32].

All the phosphates described in the present paper were in well crystallised hydrated form and their thermal dehydration was related to the crystal modification. The dehydration of the tetragonal phosphates, expressed on TG curves was observed within a wide temperature range (Fig. 1J–P), as for zeolitic water could have been expected, however XRD and FTIR analysis showed considerable structure changes after thermal treatment. The contraction in *a*- and *c*-axes, after dehydration (Fig. 5) may suggest, that the crystal structure of the tetragonal lanthanide phosphates is affected in some way by the presence of the molecules of water in question. The differences in IR spectra (Fig. 6), between the hydrated and anhydrous tetragonal phosphates may be linked to some hydrogen bonding of H_2O molecules to the phosphate oxygen

in the hydrated salts. It is possible that an interactions between the water molecules and the PO_4^{3-} tetrahedron lowers site symmetry of the anion PO_4^{3-} and contribute to the IR spectra giving rise to an additional frequency.

As opposed to the tetragonal, the dehydration of the hexagonal/orthorhombic form was performing within a very narrow temperature range (Fig. 1A–I), and subsequent recrystallisation into monoclinic modification may suggest that the water could be of different than zeolitic nature.

Different authors reported different amount of water in the hexagonal $\text{LnPO}_4 \cdot n\text{H}_2\text{O}$ ranging in (n) from 0.5 to 1.5. If the water is of zeolitic nature that wide range of water molecules uptake may be resulted from different precipitation techniques.

On the basis of the TG curves presented in Fig. 1, the total amount of water (6–8 wt.%) could be approximated to $\text{LnPO}_4 \cdot \text{H}_2\text{O}$ formula whether the hexagonal or tetragonal lanthanide phosphates are considered. However, the number (n approximated to 1) of H_2O molecules determined in the present paper has to be treated as the one attributed to these particular phosphates, obtained under these particular conditions without distinction between surface and zeolitic or crystal water. The nature of the water in the lanthanide phosphates seems to be still open for discussion.

4. Conclusions

Thermal dehydration of lanthanide phosphates prepared by crystallisation from boiling phosphoric acid solution is structure dependent.

The hexagonal (La \rightarrow Tb), and orthorhombic Dy phosphates dehydrate below 300 °C and transform into monoclinic form at temperatures higher than 700 °C.

The tetragonal (Ho \rightarrow Lu) and Y phosphates dehydrate within a wide temperature range (100–600 °C). An increased crystallinity (Fig. 4), contraction of the a - and c -axes (Fig. 5), and difference in IR spectra (Fig. 6) gave some experimental evidence that thermal dehydration caused some minimal rearrangement of the atoms in the crystal. The maintenance of the tetragonal crystal lattice after ignition at 950 °C suggests that the phase change of the phosphates proceeds topotactically within the initial crystal lattice, however,

detailed crystal structure investigations are required to gain knowledge on the mechanism of the process.

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