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X-ray diffraction and Ir-absorption characteristics of lanthanide orthophosphates obtained by crystallisation from phosphoric acid solution

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Powders of $LnPO_4 \cdot H_2O$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) prepared by crystallisation from boiling phosphoric acid (2 M H_3PO_4/1) solution were characterised by X-ray diffraction and FTIR-spectroscopy. Hexagonal $LnPO_4 \cdot H_2O$ (La → Tb), tetragonal (Ho → Lu and Y) and orthorombic $DyPO_4 \cdot H_2O$ crystalline modifications were identified. Ir-spectra of the hydrated hexagonal, anhydrous tetragonal $LnPO_4 \cdot H_2O$ (Dy, Ho, Er, Tm, Yb, Lu and Y) and anhydrous monoclinic (La → Tb) are consistent with those reported in the literature. However, the hydrated tetragonal $LnPO_4 \cdot H_2O$ (Ho, Er, Tm, Yb, Lu and Y) display a surplus band (625 cm^{-1}) in the region of ν_4, which was not reported in the literature. The band disappears after ignition at 950°C, while the tetragonal structure is still maintained, which may imply that it is attributed to hydrogen bonding of H_2O molecules to the phosphate oxygen in hydrated salts. Some of the phosphates, after ignition at 950°C, display additional $P_2O_7^{4-}$ band at 1265–1267 cm^{-1}. That may be resulted from HPO_4^{2-} for PO_4^{3-} substitution in the phosphates crystallised in acidic (2 M H_3PO_4/1) solution.

1. Introduction

Rare earth element phosphates display a variety of structures. They appear in hexagonal, tetragonal, orthorhombic and monoclinic modifications. The hydrated orthophosphates $LnPO_4 \cdot nH_2O$ exist in hexagonal (Ln = La → Dy) with the space group D_6^4, Z = 3, [1–5] or tetragonal (xenotime) (Ln = Ho → Lu and Y) forms [3–9]. The tetragonal is isomorphous with zircon which has the space group D_{4h}^{19} ($I4_1$/amd), Z = 4. $TbPO_4 \cdot nH_2O$ has been also reported as tetragonal [8], whereas $DyPO_4 \cdot H_2O$, besides the hexagonal, may be tetragonal or orthorombic [8–12]. The crystal structure of the series of synthetic $LnPO_4 \cdot nH_2O$ (Ln = La, Ce, Nd) was first established by Mooney [1, 13] and confirmed later by many other authors [2–12, 14–19].

There is an uncertainty about the number of H_2O molecules in the $LnPO_4 \cdot nH_2O$ and its role in the crystal structure. The H_2O is related to the specific structure of $LnPO_4 \cdot nH_2O$ [1, 20, 21]. There are large channels along the *c*-axes in the hexagonal and tetragonal crystal modifications. These channels accommodate nonstoichiometric water molecules. Mooney postulated different amount of water in the hexagonal $LnPO_4 \cdot nH_2O$ ranging in (*n*) from 0.5 to 1.5. That is probably why published data concerning the $LnPO_4 \cdot nH_2O$, obtained by different precipitation techniques, provide different (*n*) numbers, which may lead sometimes to confusing data.

On heating to 900°C the hexagonal modification transforms into monoclinic one with the space group C_{2h}^5 ($P2_1$/m), Z = 4 [4, 5, 7, 10, 14–17], while the tetragonal maintains its structure after dehydration upon ignition.

The aim of the present work was to characterise the powders of lanthanide phosphates obtained by crystallisation from boiling phosphoric acid solution containing 2 M/1 of H_3PO_4 and 0.02 M/1 Ln (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y). The method of preparation was described in a separate paper [22].

2. Materials and methods

All the investigated phosphates of $LnPO_4 \cdot nH_2O$, obtained by crystallisation from boiling phosphoric acid solution, contained water. The amount of water (*n*), determined by thermogravimetric method, was approximately equivalent to 1 molecule per formula unit.

To characterise the crystallised solids X-ray powder diffraction patterns (XRD) were acquired using Philips Xpert XRD equipment furnished with graphite monochromator PW 1752/00, with radiation Cu K_α, Ni filter, 2Θ from 10 to 60 degrees at 30 kV, 30 mA. For the unit cell parameters determination program Unit Cell (Tim Holland and Simon Redfern) was applied. The Ir

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spectra were recorded using spectrometer FTIR - FTS 175 (Bio-Rad).

3. Results and discussion

3.1. Powder X-ray diffraction

Three different types of crystalline powders of the hydrated phosphates have been identified. They were hexagonal $LnPO_4 \cdot H_2O$ (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb), (Fig. 1), tetragonal $LnPO_4 \cdot H_2O$ (Ho, Er, Tm, Yb, Lu) isostructural with YPO_4, (Fig. 2) and orthorhombic $DyPO_4 \cdot H_2O$. XRD analyses showed shifts in the positions of diffraction peaks reflecting the contraction of the ionic radii of the lanthanides.

The unit cell dimentions obtained are in fair agreement with those in literature. The lattice parameters, plotted against the revised crystal (CR) ionic radii of the eight-coordinated lanthanide three-valent cations [23] are presented in Fig. 3A and B.

It has to be noted, that there were some problems with identification of the $DyPO_4 \cdot H_2O$ crystal modification. According to literature it may crystallise in the hexagonal, tetragonal or orthorombic form. Although its XRD pattern (Fig. 1) is very similar to that of the hexagonal, it cannot be indexed in this modification. Instead, the XRD of $DyPO_4 \cdot H_2O$ has been fit to the orthorhombic system with the unit cell parameters:

$a = 0.69528 \pm 0.00288$ nm, $b = 1.37126 \pm 0.00645$ nm, and $c = 0.90927 \pm 0.00343$. However, the error on the level of 95% confidence is large in comparison to the error of the a- and c-axes of the rest of the $LnPO_4 \cdot H_2O$ in the hexagonal or the tetragonal crystallographic forms, which was ranging from 0.00009 to 0.00037 nm. Difficulties with the identification of the $DyPO_4 \cdot H_2O$ structure were also reported by Hezel and Ross [20], who pointed out that some XRD lines were at the intermediate positions of the reported structures.

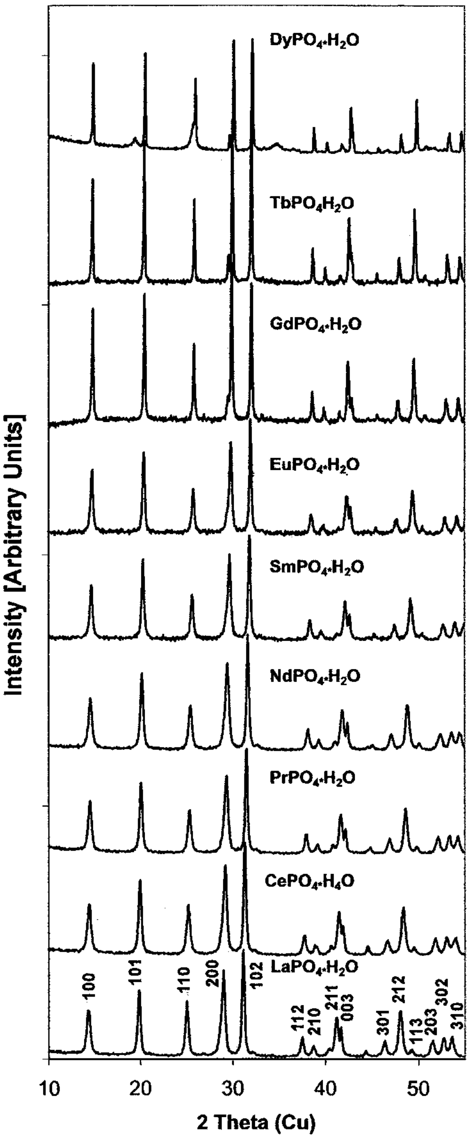

Figure 1 X-ray diffraction pattern of hexagonal (La → Tb)$PO_4 \cdot H_2O$ and orthorhombic $DyPO_4 \cdot H_2O$.

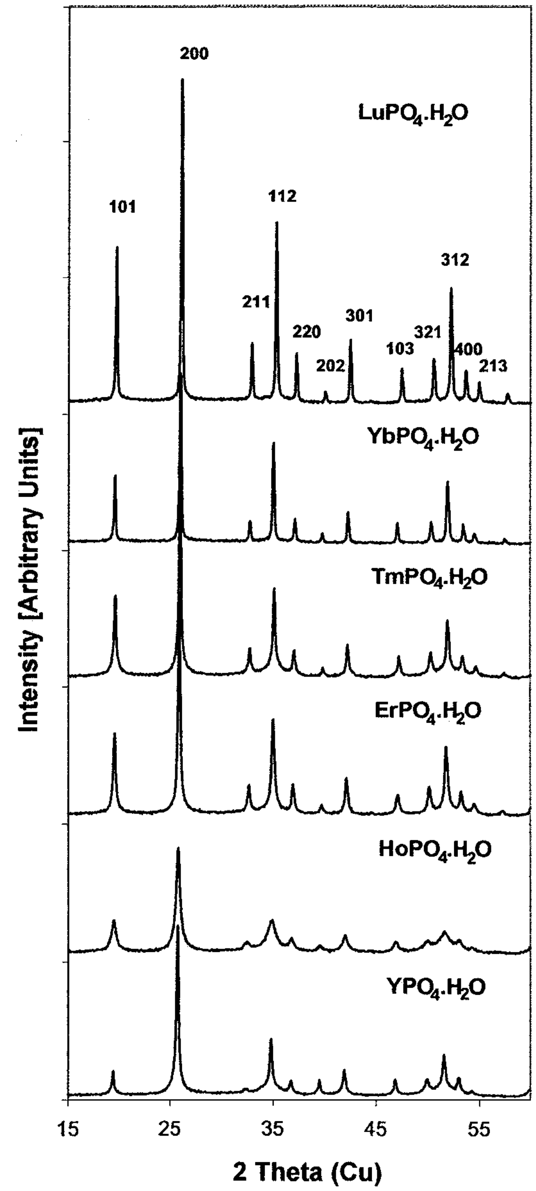

Figure 2 X-ray diffraction pattern of tetragonal (Ho → Lu, Y) $PO_4 \cdot H_2O$.

3.2. IR-spectra

Ir spectra of rare earth element and Y phosphates have been extensively discussed by Hezel and Ross [20]. Data concerning some individual elements in question were reported later by other authors [6, 21, 24–26].

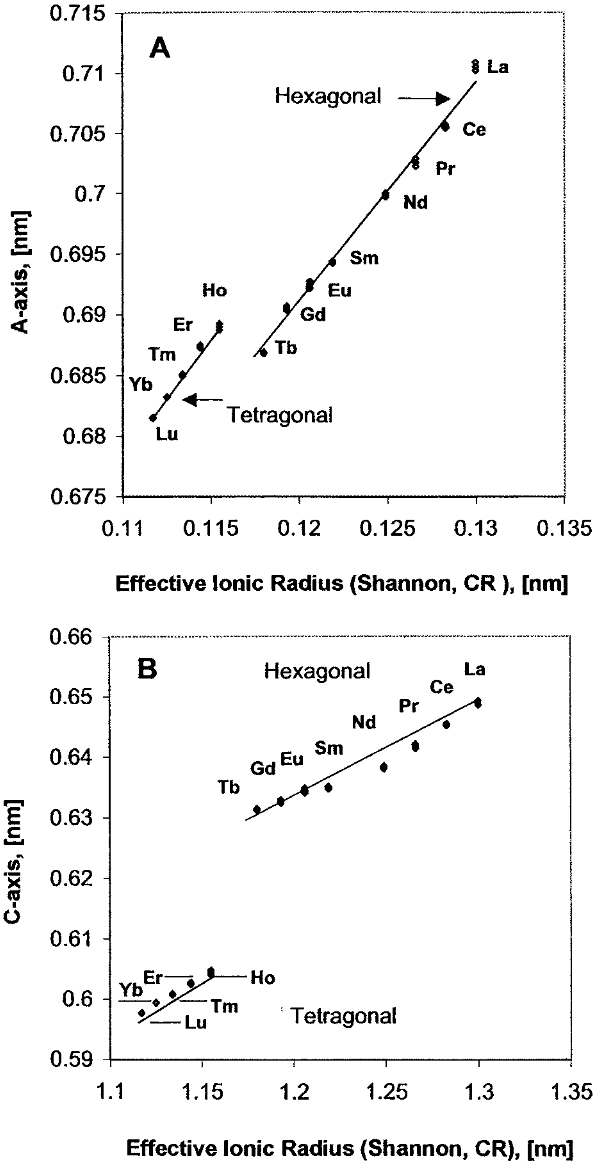

Figure 3 (A) *a*-axis, (B) c-axis of the hexagonal and tetragonal $LnPO_4 \cdot H_2O$ unit cell plotted against ionic radii of the lanthanide.

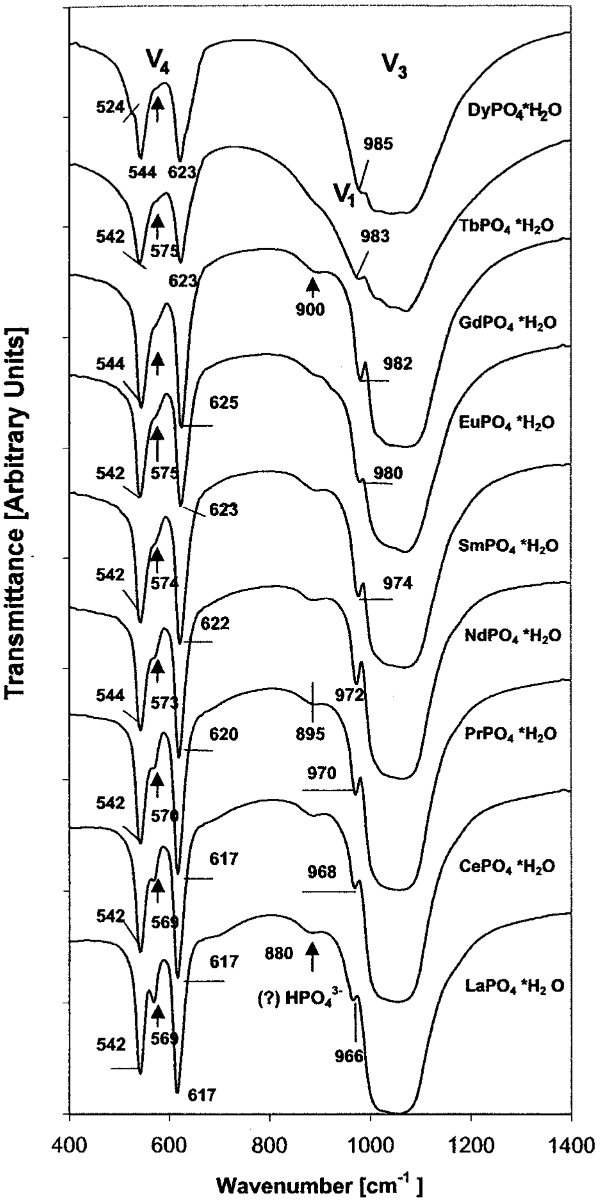

Figure 4 Ir-spectra of the hexagonal (La → Tb)$PO_4 \cdot H_2O$ and orthorombic $DyPO_4 \cdot H_2O$.

The spectra have been discussed with reference to crystal class, space symmetry and anion site symmetry. Mooney postulated that the space group of the hexagonal form of the $LnPO_4 \cdot H_2O$ was D_6^4 ($C6_22$) with $Z = 3$. The author considered also a departure from D_6^4 into a lower symmetry D_3^4 ($C3_12$) but the deviations were too small to be detected [1]. The above space group provides sets of threefold sites with point symmetry D_2 for the metal and phosphate ions, and sixfold sites with point symmetry C_2 for phosphate [1, 25, 27]. Following the correlation table (Table I) for site symmetries and activities of the vibrations of tetrahedral ion, if the PO_4^{3-} anion occupied D_2 sites the ν_1 and ν_2 would be Ir-inactive [20]. According to Hezel *et al.* [20], and Petrov [25] who investigated Ir spetra of $LnPO_4$, their spectra were consistent with the C_2 site symmetry.

TABLE I Correlation between selected site symmetries and Ir-activities of the vibrations (ν) of tetrahedral PO_4^{3-} anion [20]

Site symmetry	ν_1	ν_2	ν_3	ν_4
T_d	A_1 (inactive)	E (inactive)	F_2 (active)	F_2 (active)
D_{2d}	A_1 (inactive)	$A_1 + B_1$ (inactive)	$B_2 + E$ (active)	$B_2 + E$ (active)
D_2	A (inactive)	2A (inactive)	$B_1 + B_2 + B_3$ (active)	$B_1 + B_2 + B_3$ (active)
C_2	A (active)	2A (active)	A + 2B (active)	A + 2B (active)

Our Ir-spectra can be classified in four groups:

1. hydrated hexagonal $LnPO_4 \cdot H_2O$ (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) and orthorhombic $DyPO_4 \cdot H_2O$ (Fig. 4),
2. hydrated tetragonal $LnPO_4 \cdot H_2O$ (Ho, Er, Tm, Yb, Lu and Y) (Fig. 5),
3. anhydrous tetragonal $LnPO_4$ (Dy, Ho, Er, Tm, Yb, Lu, and Y) (Fig. 6),
4. anhydrous monoclinic $LnPO_4$ (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb) (Fig. 7).

(1) and (2) are the original (not ignited) samples prepared by crystallisation from boiling phosphoric acid (2 M/1 H_3PO_4) solution, while (3) and (4) are obtained upon ignition at 950°C.

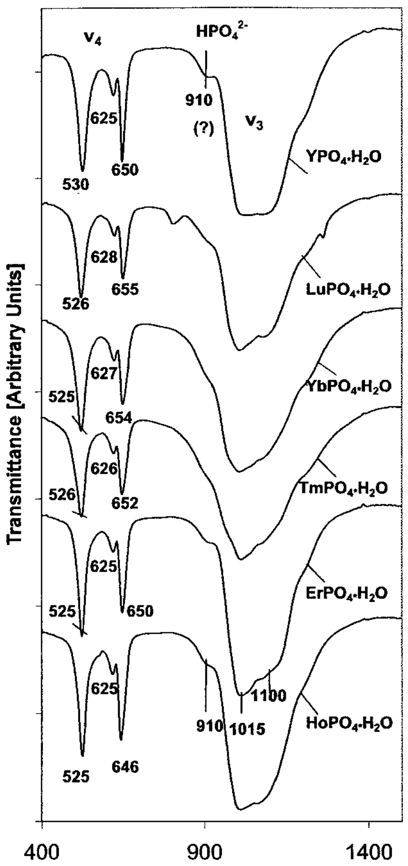

Figure 5 Ir-spectra of the hydrated tetragonal (Ho → Lu, Y)$PO_4 \cdot H_2O$.

3.2.1. Ir-spectra of hydrated hexagonal and the orthorombic phosphates

Except ν_3, which is broad and incompletely resolved, the spectra are consistent with the C_2 anion site symmetry reported by Hezel and Ross [20], assuming that ν_2 is too weak to be recorded. The ν_1 band (966 cm^{-1} for La) is systematically shifting into higher frequency (985 cm^{-1} for Dy) (Fig. 4). That systematic shift was also observed by Hezel and Ross [20]. Ir of the Tb and Dy phosphates exhibits lower resolution in the region of ν_1.

ν_4 appears as a triplet. It is characteristic for the triplet that the intensity of one of the ν_4 band (569 cm^{-1} for La) of the triplet is decreasing when the atomic number of the element is increasing (Fig. 4, arrow). It is still recorded as a very weak shoulder (575 cm^{-1}) in $TbPO_4 \cdot H_2O$, while becomes absent in the spectra of $DyPO_4 \cdot H_2O$. Instead, the $DyPO_4 \cdot H_2O$ shows a shoulder of a new band at wave number 524 cm^{-1}, at the same position as the strong one (525 cm^{-1}), characteristic to the tetragonal (Ho → Lu and Y) phosphates (Figs 5 and 6).

3.2.2. Ir-spectra of tetragonal phosphates

Referring to Hezel and Ross [20] the PO_4^{3-} tetrahedron in the tetragonal $LnPO_4 \cdot H_2O$ (xenotime structures) with the D_4^{19} space group should occupy D_{2d} sites. Under such symmetry ν_1 and ν_2 are inactive, while ν_3 and ν_4 are each split into two components (Table I). In their spectra, which were consistent with the D_{2d} site symmetry, there were no differences in the hydrated and not-hydrated Ir-spectra of the tetragonal lanthanide phosphates.

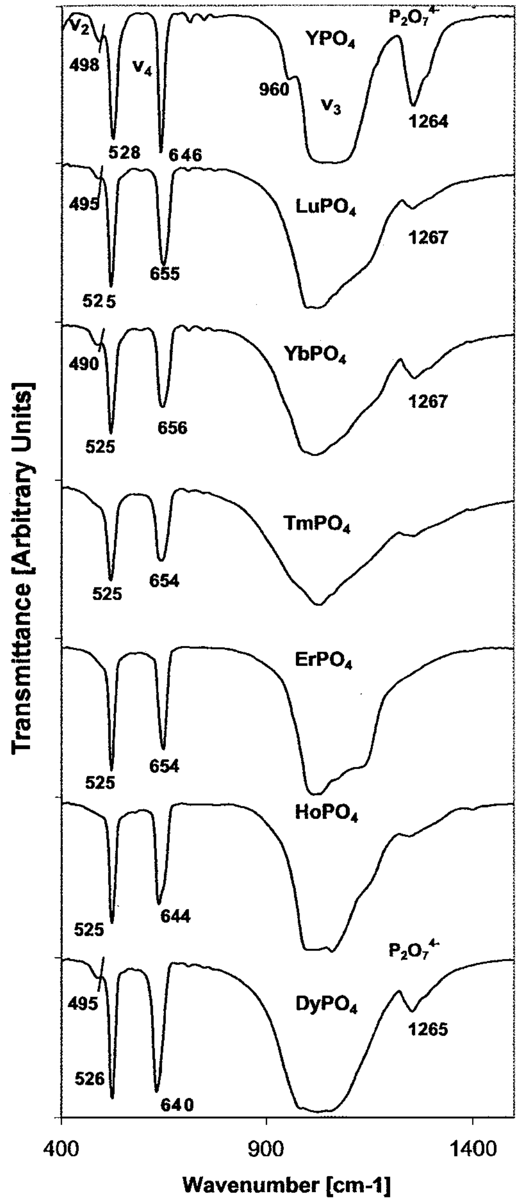

Figure 6 Ir-spectra of the dehydrated tetragonal (Dy → Lu, Y)PO_4.

In our case, there is a different number of the ν_4 bands in Ir-spectra of the (a) hydrated and (b) dehydrated (ignited at 950°C) phosphates of the tetragonal form (Figs 5 and 6)

(a) Ir-spectra of the hydrated tetragonal $LnPO_4 \cdot H_2O$ (Ho, Er, Tm, Yb, Lu and Y), is not showing the bands attributed to ν_1 and ν_2 (Fig. 5). That may imply that the anions in this structure occupy D_{2d} sites (Table I). However, there are three (instead of two) bands in the region of ν_4. Two of the bands correspond with Hezel and Ross while a surplus band appears at wave number position (625–628 cm^{-1}) similar to that which was observed in the hexagonal hydrated forms.

(b) The spectra of the dehydrated tetragonal orthophosphates $LnPO_4$ (Dy, Ho, Er, Tm, Yb, Lu, and Y) are presented in Fig. 6. As predicted from the correlation Table I there are only two bands in the region of ν_4; one at a steady position (525 cm^{-1}), and another one which position is shifting along the group of the elements from Dy (640 cm^{-1}) to Lu (655 cm^{-1}). The band at 625–628 cm^{-1}, which was present in the

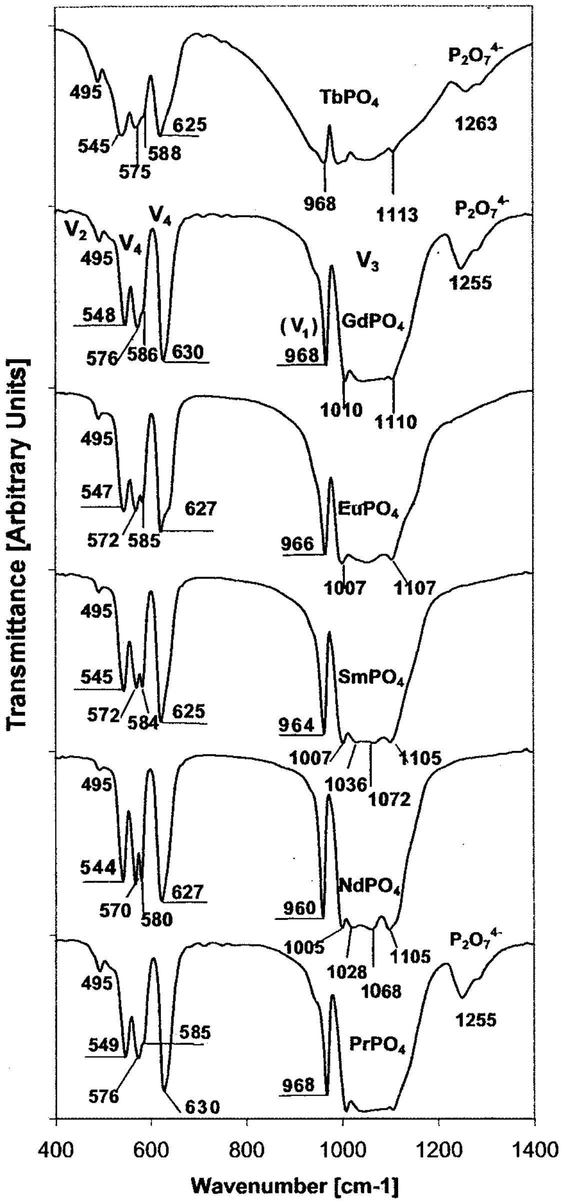

Figure 7 Ir-spectra of the monoclinic (anhydrous) lanthanide phosphates.

hydrated tetragonal $LnPO_4 \cdot H_2O$ (Fig. 5), disappeared after ignition, resulting in Ir-spectra similar to those of Hezel and Ross, consistent with the D_{2d} site symmetry, reported by those authors [20].

In some ignited tetragonal samples pyrophosphate band appeared at about 1250 cm^{-1}. In those cases a weak band of ν_2 at 494–498 cm^{-1} was recorded, which may imply that pyrophosphate ion lowers symmetry, which deviates from the D_{2d}.

At the present stage of investigation only some speculative reasoning can be introduced. Based on it the differences in Ir-spectra between the hydrated and anhydrous tetragonal phosphates might be explained in terms of hydrogen bonding of H_2O molecules to the phosphate oxygen in hydrated salts. The interaction may lower point symmetry of the anion PO_4^{3-} into D_2, in which ν_1 and ν_2 are still inactive while ν_4 have three components (Table I). If so, the hydrogen bonding would contribute to the Ir-spectra giving rise to an extra frequency.

It is worth to point out, that dysprosium phosphate as $DyPO_4 \cdot H_2O$ hydrate crystallised in orthorombic form with Ir-spectra similar to those of the hexagonal form, then, during ignition at 950°C transformed into anhydrous tetragonal form with Ir-spectra characteristic to those of the xenotime structure.

3.2.3. Ir-spectra of the monoclinic phosphates

According to Hezel *et al.* the PO_4^{3-} site symmetry in the monoclinic (monazite) $LnPO_4$ structure should be C_1. Under such symmetry no selection rules operate and all possible combinations of fundamental vibrations would be Ir active. They also reported that in the ν_4 region four bands appeared as two doublets; the upper doublet split about 45 cm^{-1} and the lower doublet by 25 cm^{-1}.

Ir-spectra of our monoclinic $LnPO_4$ obtained by ignition of the hexagonal La → Tb phosphates at 950°C is presented in Fig. 7. The spectra display an increased resolution in the region of ν_3, four bands in the region of ν_4, and the presence of ν_2 around 495 cm^{-1}. The ν_4 appeared as two doublets, for example, $NdPO_4$ shows a doublet at 580 cm^{-1}, 627 cm^{-1} (difference 47 cm^{-1}) and a doublet at 544 cm^{-1}, 570 cm^{-1} (difference 26 cm^{-1}). However, when pyrophosphate band (1255–1263 cm^{-1}) appeared, which happened in some cases, the resolution of the doublets was lower. That may be a result of some interference of the pyrophosphate ion with orthophosphate vibrations. The presence of $P_2O_7^{4-}$ band in some ignited samples may be resulted from the presence of HPO_4^{2-} in the lanthanide phosphates crystallised from acidic solution (2 M H_3PO_4/1) where HPO_4^{2-} for PO_4^{3-} substitution is possible. The weak P—O—H band due to the presence HPO_4^{2-} at about 850–880 cm^{-1} is usually observed in other phosphates like hydroxyapatite [28, 29]. In the investigated phosphates a very weak band at 880–900 cm^{-1} (Fig. 4) and a shoulder at 910 cm^{-1} (Fig. 5) has also been recorded. If the HPO_4^{2-} is present it should be decomposed upon ignition at higher than 500°C and according to the reaction: $2\ HPO_4^{2-} \rightarrow P_2O_7^{4-} + H_2O$ the pyrophosphate ion is possible to appear.

4. Conclusion

Three different types of hydrated lanthanide phosphates crystallised from 2 M/1 H_3PO_4 boiling phosphoric acid solution containing 0.02 M/1 of Ln. They were hexagonal $LnPO_4 \cdot H_2O$ (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb), (Fig. 1), tetragonal $LnPO_4 \cdot H_2O$ (Ho, Er, Tm, Yb, Lu) isostructural with YPO_4, (Fig. 2) and orthorhombic $DyPO_4 \cdot H_2O$.

Ir-spectra indicate that the hydrated hexagonal, anhydrous tetragonal $LnPO_4 \cdot H_2O$ (Ho, Er, Tm, Yb, Lu and Y) and anhydrous monoclinic are consistent with those reported in the literature.

As opposed to the anhydrous tetragonal, hydrated tetragonal $LnPO_4 \cdot H_2O$ (Ho, Er, Tm, Yb, Lu) display a surplus band (625 cm^{-1}) in the region of ν_4, which was not reported in the literature. The band disappears after ignition at 950°C, while the tetragonal structure is still maintained. That may imply that the extra (625 cm^{-1}) band is attributed to hydrogen bonding of

H_2O molecules to the phosphate oxygen in hydrated salts.

Some of the phosphates after ignition at 950°C display additional $P_2O_7^{4-}$ band at 1265–1267 cm^{-1}. In such cases the ν_2 (forbidden for D_{2d}) becomes active and the band is recorded at 490–498 cm^{-1} (Fig. 6). The presence of $P_2O_7^{4-}$ band may be resulted from the presence of HPO_4^{2-} in the lanthanide phosphates crystallised from acidic solution ($2MH_3PO_4/1$) where HPO_4^{2-} for PO_4^{3-} substitution is possible.

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