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Citrate mediated synthesis of uniform monazite LnPO_4 ($\text{Ln} = \text{La}, \text{Ce}$) and $\text{Ln}:\text{LaPO}_4$ ($\text{Ln} = \text{Eu}, \text{Ce}, \text{Ce} + \text{Tb}$) spheres and their photoluminescence

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ABSTRACT

A simple method for the synthesis of spherical LaPO_4 (monazite) particles with narrow size distribution and tailored size in the 150–500 nm range is reported. The procedure is based on a homogeneous precipitation process at low temperature (120 °C) from solutions containing La^{3+} , citrate and phosphate ions under a very restrictive set of experimental conditions, which involves the use of La nitrate, citric acid and phosphoric acid as precursors and ethylene glycol as solvent. The growth mechanism of the spheres was investigated aiming at explaining the differences in particle size and shape observed when varying the experimental conditions. The applicability of this method for the synthesis of spherical particles of other lanthanide (Ce, Tb, Eu) phosphates is also analyzed. Finally, it is shown that the developed procedure can be used to dope the lanthanum phosphate particles with lanthanide cations, which resulted in spherical phosphors as illustrated for the Eu-doped, Ce-doped and Ce, Tb codoped systems, whose luminescent properties are also evaluated.

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1. Introduction

In the last years, lanthanide phosphates (LnPO_4) have attracted much attention due to their novel promising applications in several fields of science and technology. Thus, many papers have been recently published dealing with the use of these materials in biological imaging [1,2]. Other proposed applications include their use in oxygen sensing [3] or in plasma display panels [4]. Among the different LnPO_4 systems, lanthanum phosphate (LaPO_4) is perhaps the most studied one, in particular, its monoclinic polymorph (monazite). This material has been suggested as a good candidate for the immobilization of radioactive waste elements [5], as well as protective coating for ceramics [6]. Besides, it is one of the most commonly employed host matrices for the preparation of lanthanide-based phosphors. For example, fluorescent materials with tuned emission in the visible region and promising applications as biolabels are obtained when monazite nanoparticles are doped with some lanthanide (Ln) cations such as Eu, Ce, Tb or Dy [7]. It can be also mentioned that Ce, Tb codoped monazite is a well known green phosphor used in fluorescent lamps because of its high quantum yield and stability at high temperature [8]. Finally, near-infrared (NIR) emitting phosphors with potential applications in telecommunications have been prepared by doping monazite with Er, Nd or Pr [9]. For many of these applications, the availabil-

ity of powders consisting of uniform particles is highly required. Thus, for fluorescent lamps and PDP devices a spherical morphology is preferred, since it involves a high packing density of the phosphor particles [4] and an improved resolution [10]. Particle size distribution is also important since it also affects packing densities and brightness [8]. On the basis of these considerations, it has been established that the ideal phosphor for such applications must consist of non-agglomerated spherical particles with narrow size distribution in the micron size range ($<3 \mu\text{m}$) [10].

Several routes have been developed for the synthesis of monazite-based colloidal particles with controlled size and shape, conducting to anisometric [10–13] or almost equiaxed [14–18] morphologies, most of them in the nanometer size range. Fewer reports can be found dealing with the synthesis of monazite microspheres ($>0.1 \mu\text{m}$). In fact, up to our knowledge, monazite spheres of narrow size distribution ($\sim 0.3 \mu\text{m}$) have been only obtained by a hydrothermal process at 150 °C using phosphoric acid, La^{3+} salts and EDTA as quelating agent. However, this procedure yielded particles contaminated with organic species, which required further heating at $>250^\circ\text{C}$ for purification [19]. Monazite spheres have been also prepared by pyrolysis of aerosols at a very high reaction temperature ($<1000^\circ\text{C}$) but they presented a much broader size distribution [8]. Finally, Nishihama et al. [20] reported the synthesis of LaPO_4 microspheres through a microemulsion based method which led to the hexagonal phase (rhabdophane). These particles could be transformed into the monoclinic phase (monazite) by calcination at 1000 °C [20], which caused particle sintering, the spherical morphology being destroyed. Therefore,

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the development of new procedures for the direct synthesis of monazite microspheres is highly desirable.

Herein, we describe a facile method for the synthesis of LaPO_4 (monazite) spherical particles with rather narrow size distribution and tailored size in the 100–500 nm range. The procedure is based on a homogeneous precipitation process, which takes place through the controlled release under mild conditions (120 °C) of La^{3+} cations from lanthanide-citrate complexes in the presence of phosphoric acid using ethylene glycol (EG) as solvent. It should be noted that uniform particles with different morphologies of some LnPO_4 such as YPO_4 [21] and TbPO_4 [22] have been already synthesised in aqueous solutions using citrate ions as an organic additive to control particle size and shape. However, none of the reported procedures gave rise to spheres. In this paper, we demonstrate that the replacement of water by EG as solvent is essential to obtain spherical LaPO_4 particles of narrow size distribution with monazite structure. This requirement is justified on the basis of the mechanism of particle formation. The applicability of our procedure for the preparation of other lanthanide (Ln) phosphates (Ln = Ce, Eu, Tb) is also investigated. Finally, it is shown that our synthesis strategy can be extended to the preparation of luminescent monazite-based phosphors which is illustrated for the Eu-doped, Ce-doped and Ce, Tb codoped LaPO_4 systems whose luminescent properties are also evaluated.

2. Experimental section

2.1. Reagents

Lanthanum acetate ($\text{La}(\text{OAc})_3 \cdot x\text{H}_2\text{O}$, Aldrich, 99.9%), lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Fluka, 99.0%), europium (III) nitrate pentahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, Aldrich, 99.9%), terbium (III) nitrate hydrate ($\text{Tb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, Alfa Aesar, 99.9%) and cerium(III) nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Fluka, 99.0%), were selected as Ln precursors. Citric acid ($\text{C}_6\text{H}_8\text{O}_7$, Panreac, 99.5%) or ammonium citrate tribasic ($\text{C}_6\text{H}_{17}\text{N}_3\text{O}_7$, Fluka, 97%) were used as complexing agent and orthophosphoric acid (H_3PO_4 , Prolabo, 84–87%) or sodium diacid phosphate (NaH_2PO_4 , Aldrich, 99%), as phosphate sources. Ethylene glycol (EG, Fluka, <99.5%), diethylene glycol (DEG, Sigma–Aldrich, 99%), buthylene glycol (BG, Riedel-de Haën, 99%) and ethanol (Prolabo, absolute) were tested as solvents.

2.2. Synthesis of samples

The typical procedure for the synthesis of lanthanide phosphate samples was as follows. Weighted amounts of the desired lanthanide precursors were dissolved in the selected solvent under magnetic stirring. A proper amount of citrate anions was then dissolved in these solutions, keeping magnetic stirring, to form a Ln-citrate complex stable at room temperature. Finally, the desired amount of the phosphate precursor was admixed. After homogenization, the final solutions (total volume = 10 cm^3) were aged for 1.5 h in tightly closed test tubes using an oven preheated at the selected temperature. The resulting dispersions were cooled down to room temperature, centrifuged to remove the supernatants and washed, twice with ethanol and once with double distilled water. For some analyses, the powders were dried at room temperature.

2.3. Characterisation

The shape of the particles was examined by field emission scanning (FEGSEM, Hitachi S4800) and transmission (TEM, Philips 200CM) electron microscopy. Particle size distributions were obtained from the micrographs by counting several hundreds of particles.

The presence of the different Ln cations in the precipitated particles was tested by using energy dispersive X-ray analysis (EDX, Philips DX4) coupled to the TEM microscope.

The crystalline structure of the prepared particles was assessed by X-ray diffraction (XRD, Panalytical, X'Pert Pro). The crystallite size was estimated from the most intense XRD peaks by using the Scherrer method.

The infrared spectra for the powders diluted in KBr pellet were recorded in a Nicolet 510 Fourier transform spectrometer.

The excitation and emission spectra of the samples dispersed in water were measured in a Horiba Jobin Yvon spectrofluorimeter (Fluorolog fl3–11) operating with slits of 1 nm. The emission spectra were transformed to the CIE color coordinates system using a 2° observer.

To obtain the photographs of the phosphors fluorescence, powdered samples were deposited on Millipore filters and illuminated with ultraviolet radiation of $\lambda = 254$ nm, filtered from a Hg discharge a lamp.

3. Results and discussion

3.1. Undoped lanthanum and lanthanide (Ce, Eu, Tb) phosphates

It is well documented [23] that the formation of uniform particles in solution requires a homogeneous precipitation process, which can be achieved, for example, through a slow and controlled release of the corresponding precipitating anions or cations in the reaction medium [23]. To achieve such conditions in our system, we used citrate anions, which form Ln/citrate quelates stable at room temperature. However, these quelates can be decomposed by heating thus liberating the Ln cations, which in contact with phosphate anions precipitate as LnPO_4 [24]. It has been also reported that the synthesis of LaPO_4 in aqueous media at low temperature (<150°) usually yield the hydrated hexagonal phase (rhabdophane) [25,26], whereas in organic solvent the formation of the monoclinic phase (monazite) is favored [25]. For this, reason we selected EG as solvent in this study. It should be noted that polyols (DEG) have been already used as solvents for the preparation of monazite, although particles with irregular size and shape were obtained [27].

Under the above conditions, we first analyzed the effects of the nature of the La salt on the characteristics of the particles precipitated on aging the EG solutions at 120 °C, using citric acid (citrate/Ln mole ratio = 5) and phosphoric acid (0.15 mol dm^{-3}) as citrate and phosphate sources, respectively. We found that spherical particles (Fig. 1a) of a rather narrow size distribution (400 ± 52 nm, Table 1), consisting of monoclinic (JCPDS 84-0600) LaPO_4 (Fig. 2), resulted when using a La^{3+} concentration of 0.005 mol dm^{-3} and $\text{La}(\text{NO}_3)_3$ as precursor, whereas the change of the later by $\text{La}(\text{OAc})_3$ conducted to ill-defined precipitates consisting of tiny particles strongly aggregated.

The nature of the citrate and phosphate precursors and solvent was also found to be a key factor for the preparation of uniform spheres since the use of the citrate or phosphate salts instead of the corresponding acids also produced irregular particles similar to those obtained for the acetate system, whereas the use of other polyols (DEG or BG), ethanol or water as solvent gave rise to ill-defined precipitates.

It was also detected that the size of the spheres could altered by varying either the La^{3+} concentration or the amount of phosphoric acid added while keeping constant the other experimental conditions. Thus, for 0.15 mol dm^{-3} H_3PO_4 solutions, a particle diameter increase from 152 to 490 nm was observed when the lanthanum salt concentration was increased from 0.0005 to 0.01 mol dm^{-3} , whereas for solutions 0.005 mol dm^{-3} in La^{3+} , particle size

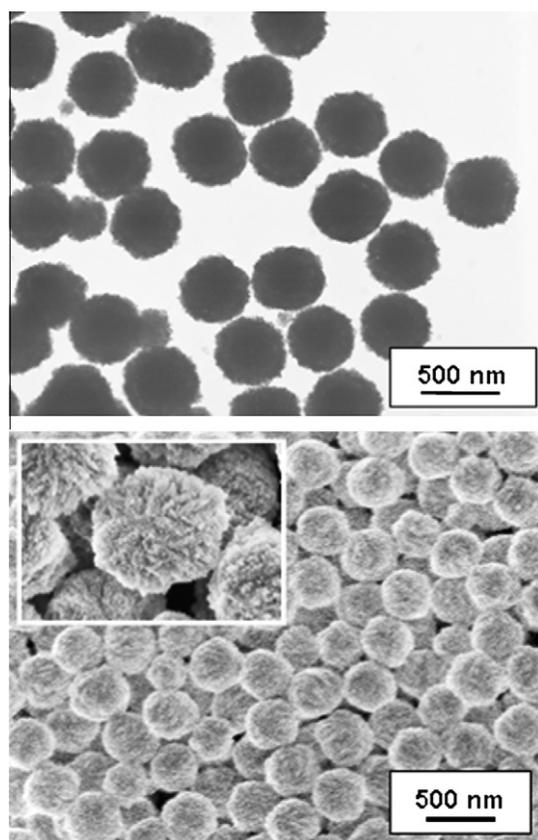


Fig. 1. TEM (top) and FEGSEM (bottom) micrographs of a LaPO_4 sample obtained by aging at 120°C for 90 min, 0.005 mol dm^{-3} $\text{Ln}(\text{NO}_3)_3$, 0.025 mol dm^{-3} citric acid and 0.15 mol dm^{-3} H_3PO_4 solutions in ethylene glycol.

decreased (from 400 to 100 nm) by lowering the H_3PO_4 concentration (from 0.15 to 0.01 mol dm^{-3}) (Table 1).

In order to explain these findings, some experiments were conducted to gain information on the mechanism of particle formation. First of all, it should be noted that a detailed observation of the spheres under the FEGSEM microscope (Fig. 1, inset) revealed a rough surface, which seems to suggest that they are formed by an ordered aggregation of smaller subunits. This behaviour was confirmed by following the evolution of particle size and shape with aging time for the sample shown in Fig. 1. As observed in Fig. 3, precipitation was very fast. In fact, after 3 min of aging, some spheres ($\sim 170\text{ nm}$) were already formed, although a certain amount of much smaller irregular and aggregated particles were

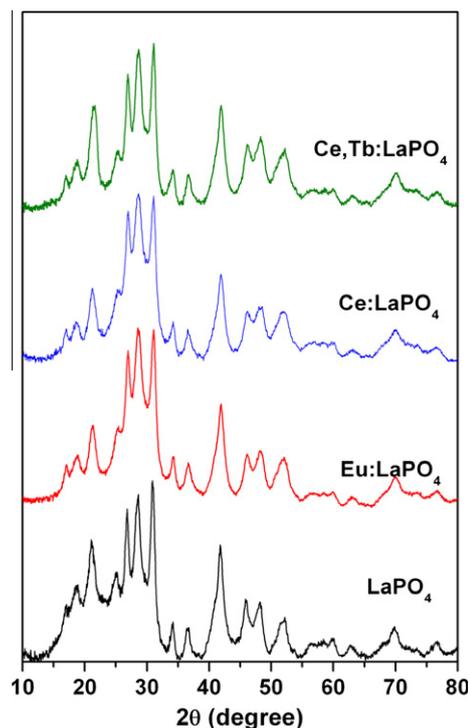


Fig. 2. X-ray diffraction patterns obtained for the LaPO_4 sample shown in Fig. 1 and for the Eu-doped, Ce-doped and Ce, Tb codoped LaPO_4 samples prepared as described in Table 2.

also present, which were consumed on prolonged aging as the spherical particles grew to their final size. The XRD pattern of this sample confirmed the polycrystalline nature of the spheres since the crystallite size (13 nm, Table 1) estimated by using the Scherrer method was much smaller than the size of the spheres (400 nm). A similar behaviour was also observed for all the other systems consisting of spherical particles. In all these cases, a crystallite size of about 13 nm was measured independent on the size of the spheres (Table 1), which indicates that the variations in particle size come from the aggregation of a different number of similar primary particles.

This mechanism of particle growth through an aggregation process has been previously observed for several solids obtained by homogeneous precipitation in different solvents [28] including polyols [30] and several theoretical approaches has been developed to explain the morphology of the aggregates and the size selection mechanism [29 and references therein]. Obviously, the

Table 1
Shape and size of the LaPO_4 particles precipitated by aging for 90 min solutions containing La^{3+} , citrate and phosphate ions under different experimental conditions keeping the citrate/La mol ratio = 5. The crystal size estimated from their XRD patterns is also included.

La source	$[\text{La}^{3+}]$ (mol dm^{-3})	Citrate source	Phosphate source	$[\text{Phosphate}]$ (mol dm^{-3})	Solvent	T ($^\circ\text{C}$)	Particle shape	Particle size (nm)	Crystal size (nm)
Nitrate	0.0005	Citric acid	H_3PO_4	0.15	EG	120	Spheres	152 (± 17)	10
Nitrate	0.002	Citric acid	H_3PO_4	0.15	EG	120	Spheres	300 (± 54)	13
Nitrate	0.005	Citric acid	H_3PO_4	0.15	EG	120	Spheres	400 (± 52)	13
Nitrate	0.010	Citric acid	H_3PO_4	0.15	EG	120	Spheres	490 (± 112)	13
Nitrate	0.005	Citric acid	H_3PO_4	0.01	EG	120	Spheres	100 (± 18)	11
Acetate	0.005	Citric acid	H_3PO_4	0.15	EG	120	Ill-defined		
Nitrate	0.005	Citric acid	NaH_2PO_4	0.15	EG	120	Ill-defined		
Nitrate	0.005	Ammonium citrate	H_3PO_4	0.15	EG	120	Ill-defined		
Nitrate	0.002	Citric acid	H_3PO_4	0.15	DEG	120	Ill-defined		
Nitrate	0.002	Citric acid	H_3PO_4	0.15	BG	120	Ill-defined		
Nitrate	0.005	Citric acid	H_3PO_4	0.15	Ethanol	120	Ill-defined		

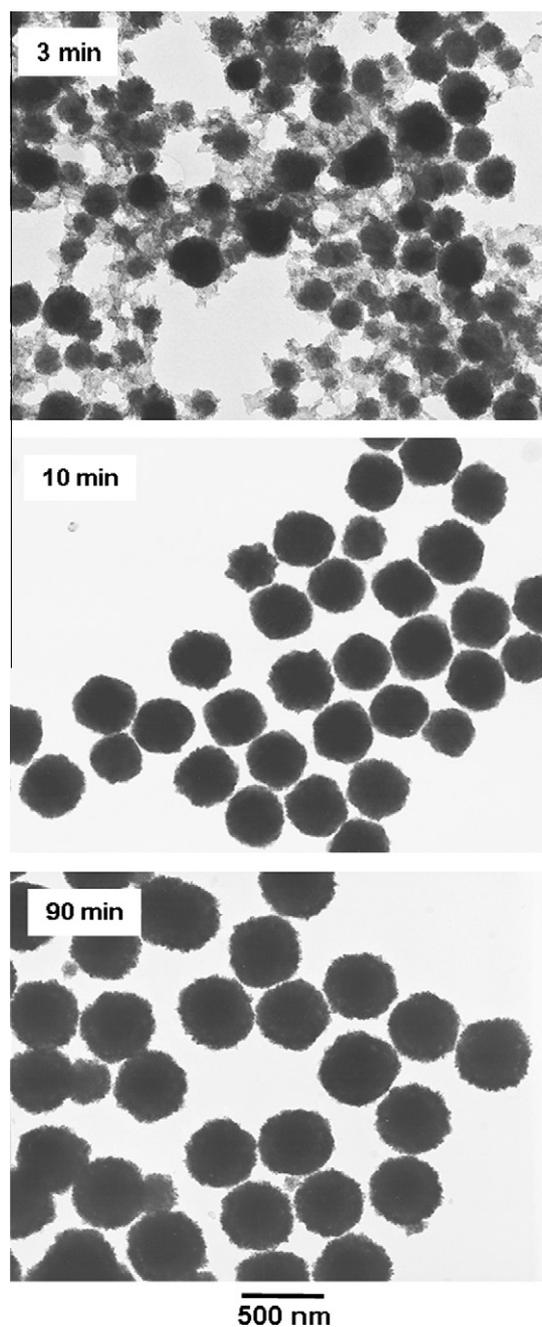


Fig. 3. TEM images for the LaPO₄ sample obtained from 0.005 mol dm⁻³ Ln(NO₃)₃, 0.025 mol dm⁻³ citric acid and 0.15 mol dm⁻³ H₃PO₄ solutions in ethylene glycol after aging at 120 °C for different periods of time.

formation of uniform particles by aggregation requires the surface potential to be low so that the attractive interaction between primary particles predominates over the repulsive interparticle forces [28], whose magnitude is governed, among other factors, by acidity, ionic strength and the dielectric constant of the solvent [29]. It has been also accepted that the growth of secondary particles is a diffusion controlled process [29] so that the viscosity of the solvent also affects the kinetic of aggregation. Therefore, the aggregation behaviour in our system must be strongly affected by the acidity, the total ions concentration and the nature of the solvent, thus justifying, at least qualitatively, the different morphological characteristics (size and shape) of the precipitated particles. It should be noted that owing to the well known complexing ability

of polyols [31,32], they could also be adsorbed onto the particle surfaces, which would also have a strong influence on the aggregation process. However, such possibility must be disregarded in our case since the IR spectrum of our spheres (Fig. 4) only displayed bands corresponding to adsorbed water (3440 and 1640 cm⁻¹) and LaPO₄ (<1200 cm⁻¹) [33].

Finally, to explain the important effect of the nature of the starting lanthanum salt on the mechanism of particle formation, we must take into account that one of the most important factors governing the process of particle formation is the nature of the soluble complexes precursors to precipitation, which determine their reactivity towards nucleation [34]. In our case, it seems reasonable to assume that the ability of acetate anions to form complexes with lanthanum cations through the carboxyl group is much higher than that of nitrates [32], which would have an important effect on the nucleation and aggregation processes and therefore on the size and shape of the precipitated particles.

Before proceeding to the preparation of luminescent LaPO₄-based spheres, we explored the applicability of our procedure for the synthesis of pure phosphates of the doping cations (Eu³⁺, Ce³⁺, Tb³⁺). For this purpose, La(NO₃)₃ was replaced by the nitrates of the other lanthanides, keeping the experimental conditions (reagent concentrations, temperature, aging time) similar to those used for the sample shown in Fig. 1. It was found that for the Ce system, almost spherical particles of narrow size distribution and a mean size (368 ± 25 nm), slightly lower than that of the LaPO₄ sample (400 nm), were formed (Fig. 5). As shown in Fig. 6, they also crystallized into the monazite structure (JCPDS 32-0199). In this case, the estimated crystallite size was also much lower (20 nm) (Table 2) than particle size (368 ± 25 nm) indicating the polycrystalline nature of the CePO₄ spheres. It should be noted that a detailed observation of the TEM picture obtained for these Ce(PO₄) particles (Fig. 5, inset) seems to suggest that most of them were hollow and porous. Up to our knowledge, there are very few bibliographic antecedents for such a kind of hollow CePO₄ structures, which have potential applications in several fields as drug delivery, chemical storage and catalysis [35,36]. In the previous reports, the spheres presented a broad size distribution [36] and/or were much larger (5–10 μm) than those here obtained [35].

For the TbPO₄ system, uniform spheres also resulted, but they were smaller (243 ± 13 nm) than those obtained for the La or Ce systems (Table 2), and appeared interconnected forming hard agglomerates (Fig. 5). The XRD pattern of this sample (Fig. 6) showed very broad reflections corresponding to the tetragonal TbPO₄ phase (JCPDS 32-1292). Such a large peak broadening involved a crystallite size of ~2 nm (Table 2). Finally, the EuPO₄

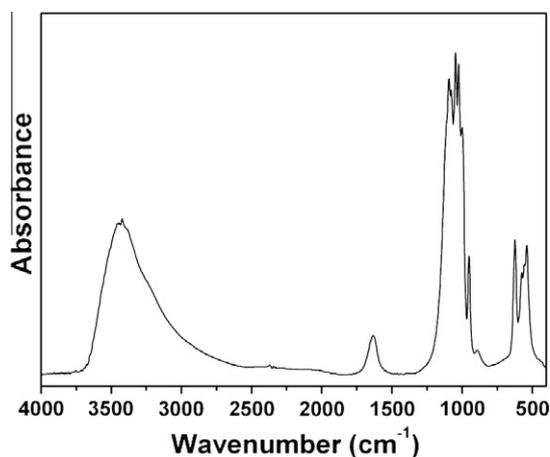


Fig. 4. Infrared spectrum of the LaPO₄ sample shown in Fig. 1.

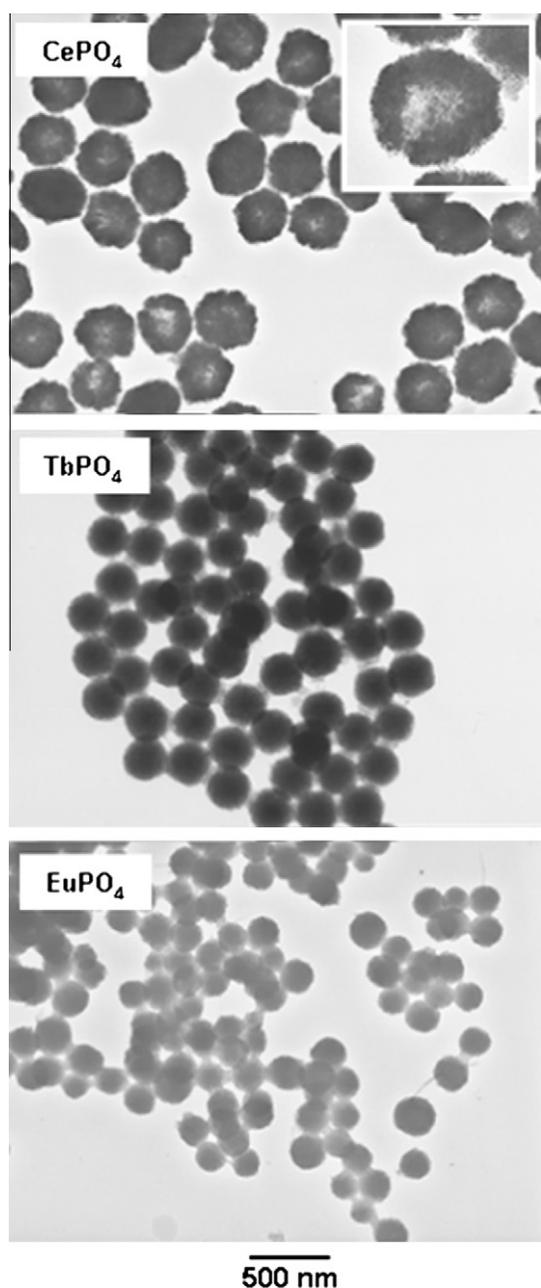


Fig. 5. TEM images for the LnPO₄ samples obtained under the conditions described in Table 2.

particles obtained were very similar to those of TbPO₄ (Fig. 5) although slightly smaller (203 ± 23 nm). The XRD pattern of these spheres (Fig. 6) also consisted of very broad peaks (crystallite size of ~ 2 nm), which could not be indexed according to any JCPDS file reported for EuPO₄. However, such pattern was very similar to that of the TbPO₄ sample (Fig. 6), which, as mentioned above, consisted of a tetragonal phase. Therefore, on the basis of this similitude, it could be reasonably assumed that the crystal structure of the EuPO₄ sample is also tetragonal.

As in our case, the size and shape of the LnPO₄ particles precipitated under identical conditions have been previously observed to depend on the nature of the Ln cation [37,12]. The reason for this behaviour has been associated to the different crystalline phase obtained in each case, as a consequence of the gradual contraction of the Ln ionic radius [12].

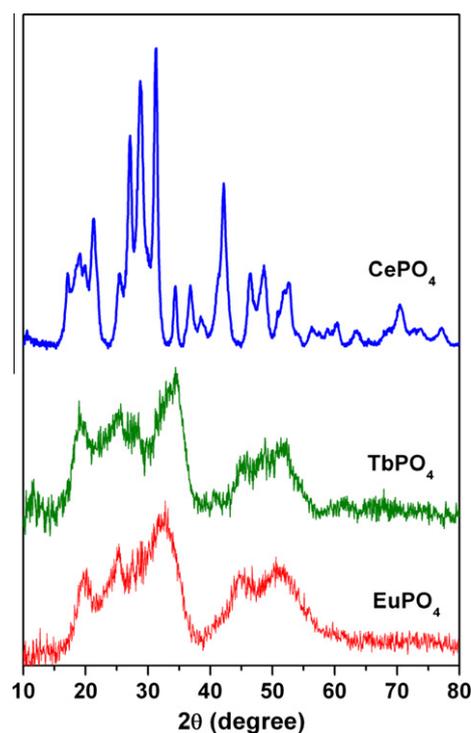


Fig. 6. X-ray diffraction patterns obtained for the LnPO₄ samples shown in Fig. 5.

3.2. Ln-doped lanthanum phosphates

To obtain spherical Ln-doped LaPO₄ phosphors, we proceeded as described above for the case of pure LaPO₄ system but incorporating the desired amount of the doping cations to the starting La(NO₃)₃ solution. The total Ln concentration ($0.005 \text{ mol dm}^{-3}$) and the citric acid/Ln mol ratio (5) were kept constant (Table 2).

For the Eu-doped case, we chose a doping level (Eu/La mol ratio = 0.1) within the range usually employed for this system [12]. We found that the addition of this Eu(III) amount to the raw La(III) solution did not affect neither the crystalline structure (Fig. 1) nor the morphology of the precipitated particles (Fig. 7), although a decrease of their mean size from $400 (\pm 52)$ to $297 (\pm 48)$ nm was detected (Table 2) in agreement with the smaller size of the particles obtained for the EuPO₄ system (Fig. 5). The incorporation of the Eu³⁺ cations to the LaPO₄ particles was confirmed by the EDX spectra recorded for several single particles of this sample, in which, the peaks corresponding to the Eu cations were always detected in addition to those of La, O and P (Fig. 8).

A further evidence of the success of the doping procedure was given by the luminescence behaviour of this sample. It is well known that the Eu³⁺ emission properties are sensible to the environment of the Eu³⁺ cations so that they can be used as a probe of the localisation of the dopant in the host matrix [38]. The excitation spectrum monitored at the most intense Eu³⁺ emission wavelength (590 nm) (Fig. 9, top) is in agreement with those previously reported for the Eu-doped LaPO₄ system. As observed, it consists of several sharp lines due to the direct excitation of the Eu³⁺ cations from the ground state to higher levels of the 4f-manifold [38]. The emission spectrum of the Eu:LaPO₄ spheres obtained using the most intense excitation line ($\lambda_{\text{exc}} = 393$ nm) displayed the bands associated to the $^5D_0 \rightarrow ^7F_J$ ($J = 1, 2$ and 4) electronic transitions characteristic of the Eu³⁺ cations at a position and with a relative intensity (Fig. 9, bottom) very similar to those reported for Eu-doped monazite [15,16,38] confirming the location of the Eu cations in the phosphate matrix. The most intense emissions

Table 2

Shape and size of the LnPO_4 and Ln-doped LaPO_4 particles precipitated by aging at 120 °C for 90 min, $\text{Ln}(\text{NO}_3)_3$, citric acid (citrate/Ln mol ratio = 5) and H_3PO_4 (0.15 mol dm^{-3}) solutions in ethylene glycol. The crystal size estimated from their XRD patterns and the C.I.E. chromatic coordinates of the emissions (X, Y) are also included.

$[\text{La}^{3+}]$ (mol dm^{-3})	$[\text{Eu}^{3+}]$ (mol dm^{-3})	$[\text{Ce}^{3+}]$ (mol dm^{-3})	$[\text{Tb}^{3+}]$ (mol dm^{-3})	Particle shape	Particle size (nm)	Crystal size (nm)	X	Y
		0.005		Spheres	368 (± 25)	20		
	0.005		0.005	Agglomerated spheres	240 (± 13)	2		
0.00450	0.0005			Agglomerated spheres	203 (± 23)	2		
0.00335		0.00165		Spheres	297 (± 48)		0.49	0.50
0.0040		0.00075	0.00025	Spheres	417 (± 33)		0.15	0.08
				Spheres	443 (± 68)		0.24	0.41

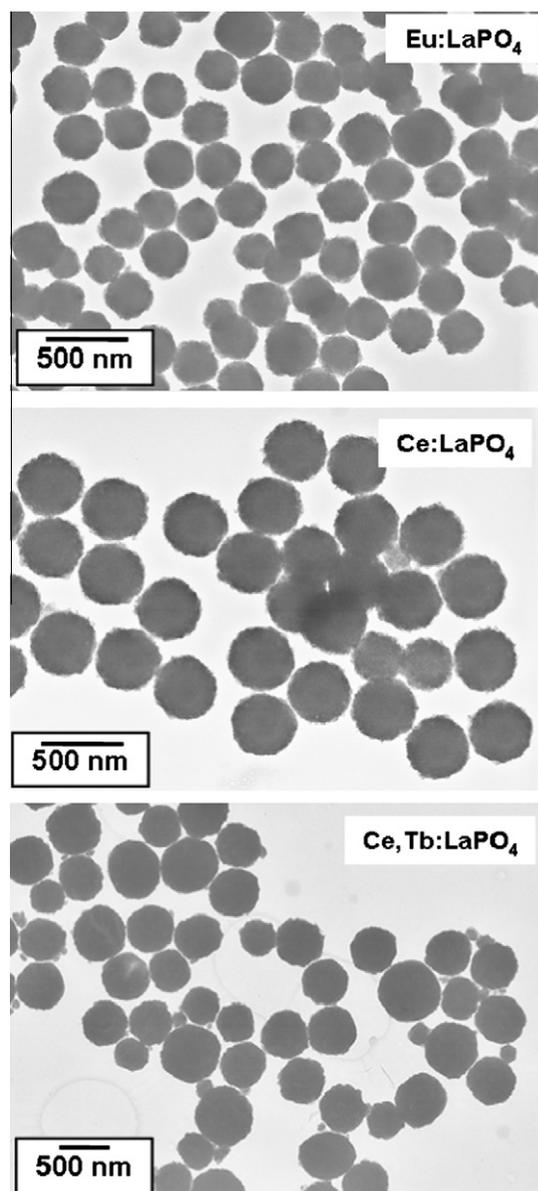


Fig. 7. TEM images of the Ln-doped LaPO_4 samples obtained under the conditions described in Table 2.

appearing in the 580–620 nm region are responsible for the strong orange–red luminescence observed for this sample (Fig. 10) whose CIE colour coordinates are shown in Table 2.

Doping levels of Ce^{3+} as high as 33% (Ce/La mol ratio) could be incorporated to the LaPO_4 particles without significantly altering particle shape, size ($417 \pm 33 \text{ nm}$) or monodispersity (Fig. 7). The presence of Ce cations in the LaPO_4 spheres was corroborated by

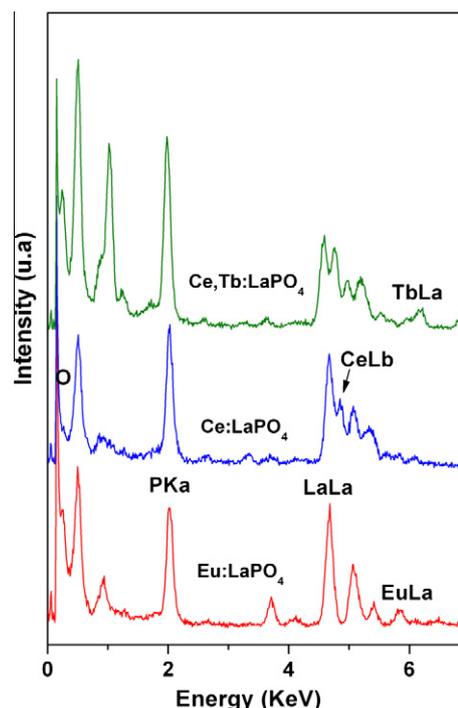


Fig. 8. EDX spectra of the Ln-doped LaPO_4 samples obtained under the conditions described in Table 2. The most intense peak for each element has been labelled.

the existence of Ce peaks accompanying those of P, O and La in the EDX spectrum recorded for a single particle (Fig. 8). XRD measurements indicated that the Ce-doped LaPO_4 spheres also consisted of monazite (Fig. 2). The excitation and emission spectra of the Ce-doped LaPO_4 sample are shown in Fig. 11. As observed, both spectra displayed very broad bands (centred at 295 and 358 nm for the excitation and emission spectra, respectively) corresponding to the $4f \rightarrow 5d$ transition of cerium, which was in agreement with the spectra previously reported for this system [33,38], thus confirming the efficiency of the doping procedure. Such broadening, larger than that of the Eu bands, has been explained by the fact that the 5d-electrons involved in the cerium transition couple more strongly to lattice phonons than the well shielded f-electrons of the excited state of europium [38]. The CIE coordinates corresponding to the blue colour¹ of the fluorescence coming from the emission band centered at 358 nm (Fig. 10) have been included in Table 2.

Finally, we also addressed the preparation of Ce, Tb codoped LaPO_4 , which is the most popular green emitting phosphor [8 and references therein]. By using synthesis conditions similar to those involved in the other doped systems studied, monoclinic

¹ For interpretation of color in Fig. 10, the reader is referred to the web version of this article.

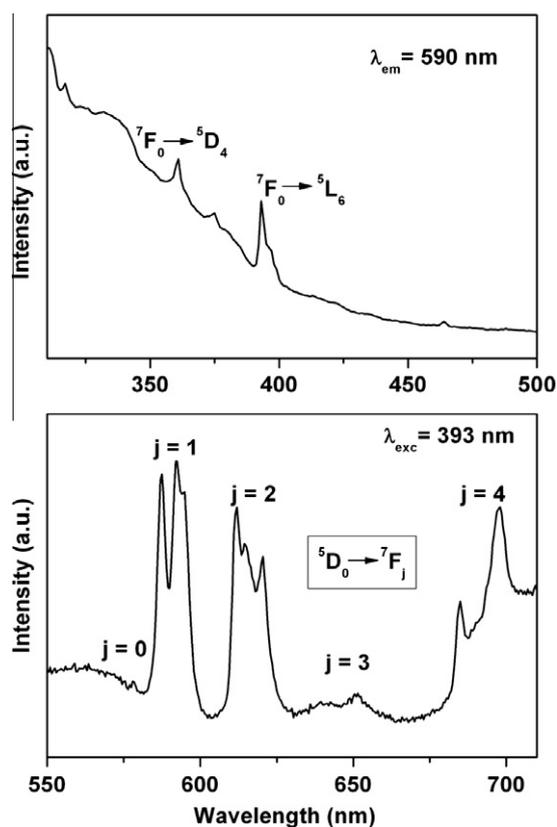


Fig. 9. Emission (bottom) and excitation (top) spectra obtained for the Eu^{3+} -doped LaPO_4 sample shown in Fig. 7.

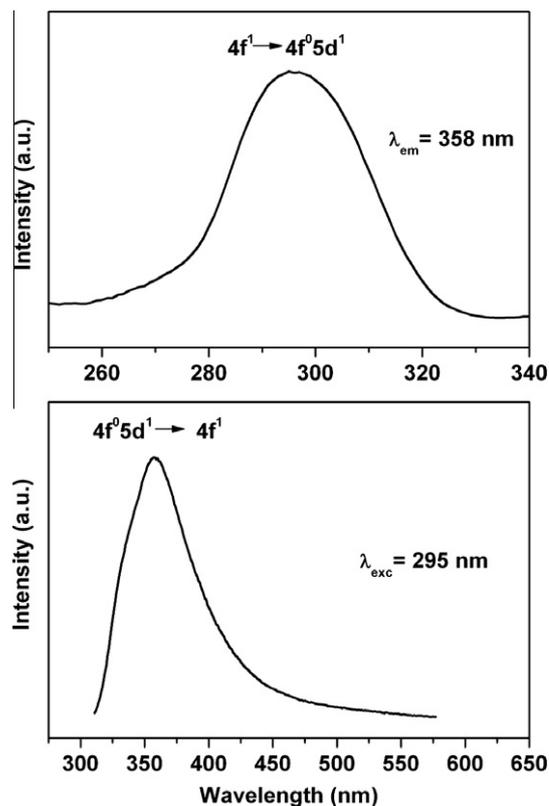


Fig. 11. Emission (bottom) and excitation (top) spectra obtained for the Ce^{3+} -doped LaPO_4 sample shown in Fig. 7.

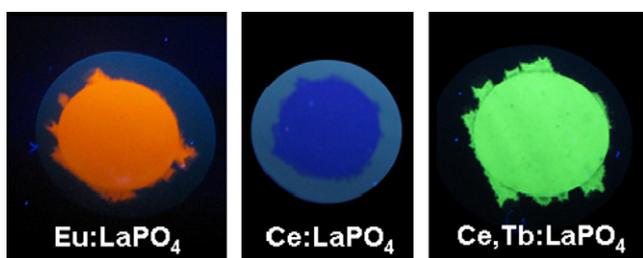


Fig. 10. Color resulting from the emission of the Ln-doped LaPO_4 samples shown in Fig. 7.

(Fig. 1) lanthanum phosphate spheres of rather narrow size distribution (Fig. 7) doped with a 15% of Ce and a 5% of Tb (Table 2), could be synthesised, having a mean size (Table 2) slightly higher (443 ± 68) than that of the undoped LaPO_4 spheres (400 nm, Table 1). The presence of Ce and Tb cations in these spheres was confirmed by EDX analyses (Fig. 8).

The luminescent properties of these Ce, Tb: LaPO_4 spheres were in agreement with those reported for this system [14,17,33,38]. Thus, the excitation spectrum monitored at the main Tb emission line at 543 nm [14] displayed a broad band centred at 295 nm (Fig. 12, top) very similar to that obtained for $\text{Ce}:\text{LaPO}_4$ (Fig. 11), confirming the energy transfer from excited Ce^{3+} to Tb^{3+} , which causes the Tb emissions in this phosphor [14,17,38]. Such emissions, corresponding to the $\text{Tb}^{5}\text{D}_4\text{-}^7\text{F}_j$ ($j = 4, 5$ and 6) electronic transitions [14,38], can be clearly observed at 489, 543 and 584 nm in the luminescence spectrum obtained for this sample upon excitation at 295 nm (Fig. 12, bottom), which also displayed a band at about 370 nm coming from the cerium $4f \rightarrow 5d$ transition. As a result of the most intense Tb emission band at 543 nm,

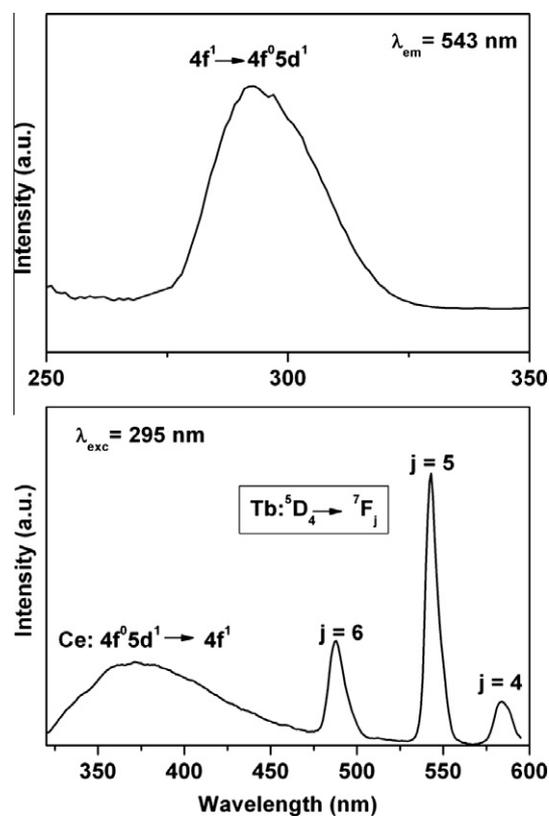


Fig. 12. Emission (bottom) and excitation (top) spectra obtained for the Ce^{3+} , Tb^{3+} -codoped LaPO_4 sample shown in Fig. 7.

the colour of the fluorescence observed for this phosphor was green (Fig. 10), having the C.I.E. coordinates shown in Table 2.

4. Conclusions

A simple method for the synthesis of spherical particles with narrow size distribution consisting of monoclinic LaPO_4 (monazite) has been developed. The procedure is based on a homogeneous precipitation process at low temperature (120 °C) from solutions containing La^{3+} , citrate and phosphate ions in appropriated concentrations. The citrate anions are used to form a lanthanum-citrate complex, which prevents sudden precipitation on phosphate addition and acts as a reservoir for the controlled release of the La cations to the reaction medium. An essential requisite for the precipitation of spherical particles by this procedure is the use of La^{3+} nitrate, citric acid and phosphoric acid as precursors and ethylene glycol as solvent, since the change of the nature of these reagents or the solvent led to ill-defined precipitates. It has also been shown that the mean size of the spheres could be tailored in the 150–500 nm range by changing the lanthanum nitrate and phosphoric acid concentrations in the starting solutions. In all cases, the spheres were formed by an ordered aggregation of smaller subunits, which explains the differences in particle size and shape observed when varying the experimental conditions.

This method can be extended to the preparation of well dispersed monoclinic CePO_4 spherical particles, although it failed when applied to the Eu or Tb phosphate systems since, in these cases, agglomerated spheres with tetragonal crystal structure were formed. Finally, the procedure herein presented has been used to synthesize LaPO_4 particles doped with lanthanide (Eu, Ce, or Ce + Tb) cations, which resulted in spherical phosphors with strong orange-red (Eu-doped), blue (Ce-doped) or green (Ce, Tb) luminescence.

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