

Article

Influence of Synthesis Conditions on the Monoclinic Structure Formation of $\text{Gd}_{0.85-y}\text{La}_y\text{PO}_4:15\%\text{Eu}$ and Luminescent Properties

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Abstract: In this study, nanoparticles with a monoclinic crystal structure of $\text{Gd}_{0.85-y}\text{La}_y\text{PO}_4:15\%\text{Eu}$ were synthesized through a hydrothermal method. Initial investigations focused on the influence of the precursor on the resulting structure of $\text{LaPO}_4:1\%\text{Eu}$, with variations in synthesis temperature. Various syntheses were conducted using ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) as PO_4^{3-} ion precursors, and the synthesis temperature ranged from room temperature to 200 °C. Based on the synthesis and analysis outcomes, diammonium hydrogen phosphate was selected as the precursor for PO_4^{3-} ions. Subsequent hydrothermal synthesis was performed at 180 °C to produce nanoparticles with a monoclinic crystal structure. After evaluating the synthesis and analysis results, the decision was made to increase the Eu^{3+} content from 1% to 15% by replacing La or Gd when a single-phase $\text{La}_{0.75}\text{Gd}_{0.24}\text{PO}_4:1\%\text{Eu}$ with a monoclinic crystal structure was achieved. These structural modifications were carried out in order to stabilize the anhydrous monoclinic structure and improve the luminescence properties of the phosphate. The synthesized samples were characterized using X-ray diffraction and scanning electron microscopy. Luminescence properties were meticulously measured and discussed. The emission intensity of monoclinic structure $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\%\text{Eu}$ was found to be almost twice as high as compared with $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\%\text{Eu}$. Additionally, magnetization dependence on the applied magnetic field strength was measured, revealing paramagnetic properties in the investigated samples.

Keywords: hydrothermal; monoclinic; GdPO_4 ; luminescence



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1. Introduction

Due to gadolinium's robust paramagnetic properties, Gd-based materials are widely employed in medicine, particularly as magnetic resonance contrast agents [1,2]. However, the high toxicity of Gd^{3+} ions, which poses a risk of release even in chelated form, is still a challenging issue [3,4]. Despite the effectiveness of magnetic resonance imaging (MRI) in medical diagnosis, ongoing efforts are directed towards improving imaging quality. Materials are being developed to obtain T1 and T2 MRI simultaneously, as single-mode MRI may not consistently provide sufficient image quality. In this pursuit, multimodal materials suitable for bioimaging and MRI, such as combining MRI with luminescence measurements, are being explored. GdPO_4 nanoparticles, considered nontoxic due to reduced Gd^{3+} ion release, are a notable example [5]. Lanthanoids, especially europium-

substituted GdPO_4 nanoparticles, are gaining attention as efficient single-phase multimodal nanoprobe with both luminescent and magnetic properties [6–8].

The concentration of the light-emitting substituent introduced into the crystal structure significantly impacts luminescence intensity. For europium, this concentration boundary varies based on the initial host matrix. Optimal substitution concentrations for intense photoluminescence and scintillation properties vary depending on the host matrix, such as 10% for single-crystalline scintillator $\text{Ca}_2\text{MgSi}_2\text{O}_7$ and 2–2.5% for $\text{LiCaAlF}_6\text{:Eu}$ single crystals [9,10]. In the case of Eu^{3+} -substituted GdPO_4 nanoparticles, the most intense luminescence occurs at a concentration range of 5–15% [11,12]. Luminescence intensity is also influenced by factors like particle size, length-to-width ratio, particle shape, and crystalline structure [13,14].

As mentioned before, the crystal structure and particle morphology of the host lattice are very important to obtain high-intensity luminescence. Recently, it has been reported that 5% Eu^{3+} -substituted GdPO_4 nanoparticles with monoclinic crystalline structures have better luminescence properties than nanoparticles with hexagonal or nanowires with monoclinic and hexagonal crystal structures [15]. Eu^{3+} -substituted GdPO_4 samples synthesized in a water medium all exhibited a hexagonal crystalline structure, which is stabilized by incorporating crystalline water. In contrast, the synthesis in an anhydrous medium yielded GdPO_4 nanoparticles with a monoclinic structure due to the absence of water. Samples synthesized in the anhydrous medium showed a more intense luminescence, which may have resulted from the difference in the crystal lattice. If the Eu^{3+} -substituted GdPO_4 nanoparticle with a hexagonal crystal structure is heated above 700 °C, water is removed, and the crystal structure changes to monoclinic, increasing luminescence intensity. However, in this case, not only is the crystal structure changed but most likely also the crystallinity and the size of the particles of the samples. It is difficult to attribute the improvement of luminescence properties to one of these phenomena, as they all can affect it [16]. Furthermore, in most cases, it is not desirable to anneal the samples, as it leads to particle size growth, and the preparation in anhydrous media can be complicated; as such, ways of changing the crystal structure are needed. Recent studies have further demonstrated that microwave-assisted synthesis offers significant advantages in producing highly crystalline GdPO_4 nanoparticles. By controlling reaction conditions, researchers have achieved enhanced luminescence and particle stability, particularly in Eu^{3+} doping ranges of 5–15% [17,18]. Moreover, nanoparticles synthesized under anhydrous conditions exhibit improved structural properties, leading to better luminescence and potential applications in dual-modal imaging [17]. Furthermore, scientists are engaged in the search for new structures that will yield optimal properties [19].

It is known that lanthanum phosphate can be obtained in two crystalline structures: a hydrated hexagonal rhabdophane type and a monoclinic monazite type [20]. The monazite-type Eu^{3+} , Tb^{3+} co-substituted $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods demonstrate higher photoluminescent efficiency than the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ rhabdophane-type nanorods co-substituted with the same amount of Eu^{3+} , Tb^{3+} [21]. It is known that the most common GdPO_4 nanoparticles are the hydrates; meanwhile, LaPO_4 is more commonly found in anhydrous form. With annealing at higher temperatures, the final products result in the anhydrous forms. Ullah et al. have demonstrated that monoclinic phase compounds of $\text{Gd}_x\text{La}_{1-x}\text{PO}_4\text{:5at.\%Eu}$ are obtained by co-precipitation synthesis under calcining at 1000 °C for 5 h in a muffle furnace [22].

The main objective of this work is to stabilize monoclinic anhydrous GdPO_4 by La^{3+} ions without additional annealing after synthesis.

2. Materials and Methods

The following materials were used for the synthesis of phosphates: $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Glenthams, Corsham, UK), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Alfa Aesar, Kandel, Germany), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Alfa Aesar, Kandel, Germany), ammonium dihydrogen phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ (99%, Reagent, Petrzalka, Slovakia), diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ (99%, Eurochemicals, Vilnius, Lithuania), citric acid $\text{C}_6\text{H}_8\text{O}_7$ (99.5% Eurochemicals, Vilnius, Lithuania), and concentrated HNO_3 (65.0%, Sigma-Aldrich, Steinheim, Germany). Firstly, required amounts of gadolinium, lanthanum, and europium nitrates are dissolved together in 5 mL of distilled water for about 0.5 mmol of the final product (around 0.1 g). Then, a 10 mL solution of citric acid, containing double the moles of citric acid as compared with the metals, is added to the europium and gadolinium solution and stirred for 10 min. Then, a 5 mL water solution of ammonium dihydrogen phosphate or diammonium hydrogen phosphate is added slowly. Then, the solution is diluted to the desired volume (25 mL). The final mixture is stirred for 30 min. Then, the solution is transferred to the Teflon-lined autoclave and left inside a furnace for 18 h. The obtained powders are centrifuged (7000 rpm, 10 min), washed with deionized water and ethanol 3 times, and then dried at 70 °C for 24 h and characterized.

X-ray diffraction (XRD) analysis was performed using a Rigaku MiniFlex II (Rigaku Corporation, Akishima-shi, Japan). The source of the diffractometer radiation was Ni-filtered $\text{Cu K}\alpha 1$. At room temperature, measurements were performed in the 10–80° 2 θ range. A glass sample holder was used, on which the sample was placed.

Le Bail fitting was performed using the Match! (v. 3) software in conjunction with the FullProf Suite. Initial structural models for the refinement were based on $\text{BiPO}_4 \cdot 0.67\text{H}_2\text{O}$ (trigonal (hexagonal axis); 96–702–3719) or/and LaPO_4 (monoclinic structure; 96–153–0457 or 96–152–5731). During the fitting process, several parameters were refined to optimize the model, including the zero-shift, unit cell dimensions, background, profile shape, and the Caglioti half-width parameters (U, V, and W). This approach allowed for a more accurate representation of the experimental diffraction pattern and improved the reliability of the structural analysis. The Hitachi SU-70 scanning electron microscope (SEM) was used for particle morphology and size analyses. The sample was suspended in ethanol, and one drop of the prepared mixture was dropped on a carbon film. Then the SEM sample holder with the sample was dried by blowing with a stream of dry air. The microscope was adjusted, and the appropriate magnification ($\times 5$ –10 k) was selected. After that, the image was recorded. An open-access program, Fiji (v. 2.14.0), was used for image analysis.

The Edinburgh Instruments FLS980 spectrometer (Edinburgh Instruments Ltd., Livingston, UK) was used to investigate the luminescent properties. The spectrometer is equipped with double excitation and emission monochromators, a 450 W Xe arc lamp, a cooled (−20 °C) single-photon counting photomultiplier (Hamamatsu R928, Hamamatsu City, Japan), and lens optics for powder samples. For excitation and emission measurements, the step size was 0.5 nm, and the dwell time was 0.2 s. Excitation spectra were measured in the range from 250 to 585 nm. Emission spectra were measured in the range from 450 to 800 nm. The photoluminescence emission spectra were corrected using the correction file obtained from a tungsten incandescent lamp certified by NPL (National Physics Laboratory, Teddington, UK). Excitation wavelengths of 393.0 nm were selected, while the emission was monitored at 591 nm.

The magnetization of samples was recorded using a vibrating sample magnetometer consisting of the lock-in amplifier SR510 (Stanford Research Systems, Sunnyvale, CA, USA), the gauss/tesla meter FH-54 (Magnet Physics, Cologne, Germany), and the laboratory magnet supplied by the power source SM 330-AR-22 (Delta Elektronika, Zierikzee, The Netherlands).

3. Results and Discussion

To synthesize the monoclinic structure of $\text{Gd}_{0.85-y}\text{La}_y\text{PO}_4:15\%\text{Eu}$, it was decided to find out the conditions for the synthesis of $\text{LaPO}_4:1\%\text{Eu}$. It was decided to dope LaPO_4 with 1 percent of Eu^{3+} for economic reasons. First, it aimed to clarify the influence of PO_4^{3-} ions precursor and synthesis temperature on $\text{LaPO}_4:1\%\text{Eu}$ structure. XRD was performed in order to determine the crystal structure of the $\text{LaPO}_4:\text{Eu}$ synthesized in the hydrothermal reactor and to assess the purity of the phase. If diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ is used as a precursor of PO_4^{3-} ions, as shown in Figure 1, it is observed that at different synthesis temperatures, two different crystal structures of $\text{LaPO}_4:1\%\text{Eu}$ are formed.

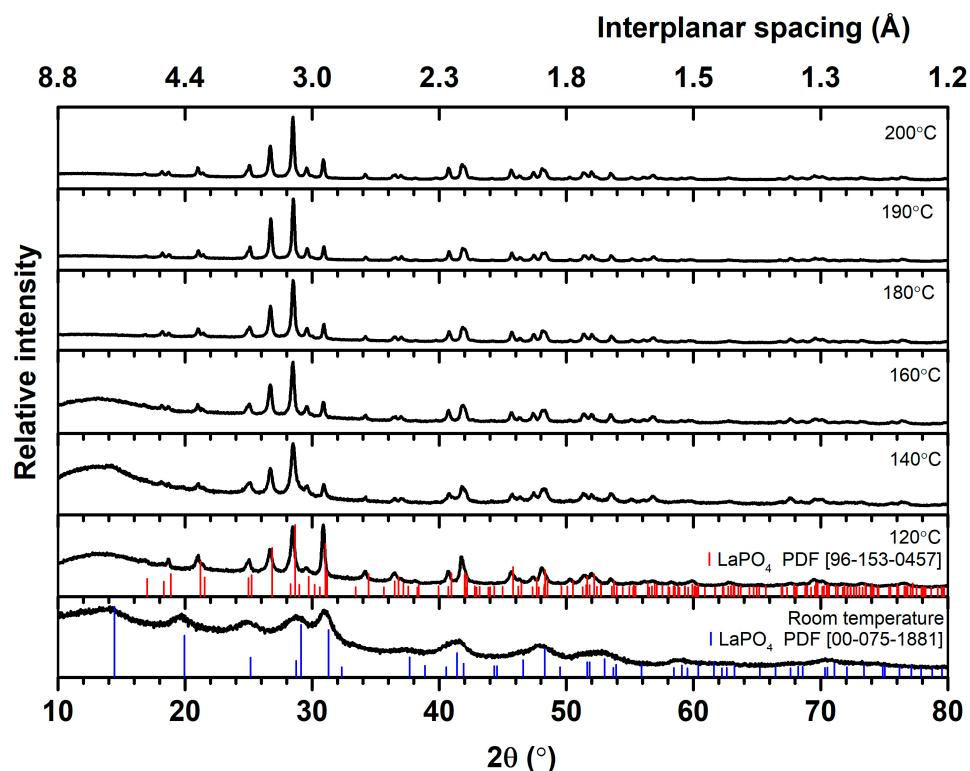


Figure 1. XRD patterns of $\text{LaPO}_4:1\%\text{Eu}$ samples synthesized using $(\text{NH}_4)_2\text{HPO}_4$ at different temperatures.

Analysis of the diffractograms and comparison of the data obtained with the reference in the database shows that at a synthesis temperature equal to or higher than 160°C , the peaks and their relative intensities of the experimental XRD data are in agreement with the standard data of the monoclinic LaPO_4 structure (PDF ICDD 96–153–0457) corresponding to $P12_1/n1$ space group. The single-phase $\text{LaPO}_4:1\%\text{Eu}$ with a monoclinic crystal structure is formed. At a lower synthesis temperature, 140°C and below, the peaks attributed to the monoclinic phase are still dominant; nevertheless, an observable peak at 14.4° characteristic of the hexagonal crystal structure ($P6_222$ space group) of LaPO_4 (PDF ICDD 00–075–1881) and the peak at 28.6° degrees is asymmetric and is broadened towards higher 2θ values, which can be explained by the same hexagonal structure of the peak at 29.1° . Therefore, it can be said that a two-phase crystal structure is formed, the hexagonal and monoclinic crystal structure of LaPO_4 . Meanwhile, a pure hexagonal phase with low crystallinity is obtained at room temperature. Notably, the synthesis performed at room temperature is not considered a hydrothermal synthesis but rather the $\text{LaPO}_4:1\%\text{Eu}$ obtained through the precipitation method.

A broad band ranging from 10° to 20° is also observed. This may be due to the amorphous nature of the synthesized material or the influence of the amorphous glass tray on which the research material was placed. The diffractograms show that the band from 10° to 20° disappears when the synthesis temperature exceeds 180 °C. All materials were prepared in the same way during the XRD analysis. Therefore, the material's amorphousness itself influences it. In conclusion, a temperature of 120 °C is sufficient to obtain the dominant monoclinic LaPO₄:1%Eu phase. Still, the pure monoclinic crystal structure phase is only achieved at 180 °C and higher temperatures when using diammonium hydrogen phosphate ((NH₄)₂HPO₄) as a precursor of PO₄^{3−} ions. The observations are confirmed by Le Bail fitting of all XRD patterns. The results are presented in Table 1, where lattice parameters of monoclinic and/or trigonal (hexagonal axis) structure product(s) are given. Note that lattice parameter values are very close to those used as a reference. The values of global user-weighted χ^2 (Bragg contrib.) vary from 0.729 to 2.08, indicating good matching between calculated and experimental data.

Table 1. The values of cell parameters and χ^2 of XRD patterns' Le Bail fitting.

T (Annealing), °C	Phase 1: Monoclinic (<i>P12₁/n1</i>)			Phase 2: Trigonal (Hexagonal Axes; <i>P3₁21</i>)			χ^2
	a ₁ , Å	b ₁ , Å	c ₁ , Å	a ₂ , Å	b ₂ , Å	c ₂ , Å	
No annealing	—	—	—	7.063 (3)	7.063 (3)	6.473 (3)	0.730
120	6.8376 (7)	7.0733 (7)	6.5014 (6)	7.104 (7)	7.104 (7)	6.469 (8)	1.04
140	6.8447 (7)	7.0727 (5)	6.5019 (6)	7.119 (1)	7.119 (1)	6.285 (2)	0.729
160	6.8343 (4)	7.0702 (3)	6.4981 (3)	6.968 (12)	6.968 (12)	6.428 (27)	0.850
180	6.8382 (2)	7.0717 (2)	6.5016 (3)	—	—	—	1.23
190	6.8287 (4)	7.0653 (3)	6.4954 (3)	—	—	—	2.08
200	6.8366 (2)	7.0702 (2)	6.5015 (2)	—	—	—	1.47
Ref. 96–153–0457	6.82500	7.05700	6.48200	—	—	—	—
Ref. 96–152–5731	6.84130	7.07800	6.51530	—	—	—	—
Ref. 96–702–3719	—	—	—	6.97930	6.97930	6.47430	—

A hydrothermal reactor performed a series of syntheses with ammonium dihydrogen phosphate (NH₄H₂PO₄) as a precursor of PO₄^{3−} ions. Figure 2 presents the diffractograms of the XRD analysis. The diffractograms show that only at the synthesis temperature of 200 °C, a single-phase of LaPO₄:1%Eu with a monoclinic crystal structure is obtained. There are no additional peaks in this diffractogram. At a synthesis temperature lower than 200 °C, a low-intensity peak corresponding to the hexagonal crystal structure of LaPO₄ (PDF ICDD 00–075–1881) is visible at 14.4°, and the asymmetry of the peak at 29.1° is also observed. At the synthesis temperature of 140 °C, the peak at 14.4° becomes more prominent, and the peak at 29.1° starts to separate. Therefore, it can be stated that two-phase LaPO₄:1%Eu is obtained at a lower synthesis temperature than 200 °C. Similar to the previously synthesized LaPO₄:1%Eu series, a broad peak is observed at 10° to 20° at temperatures of 180 °C and below, which may indicate the amorphous nature of the synthesized material.

Therefore, by comparing the diffractograms of the first series synthesis using diammonium hydrogen phosphate as the PO₄^{3−} ion precursor and the second series synthesis using ammonium dihydrogen phosphate as the PO₄^{3−} ion precursor, it can be concluded that the ion precursor has an effect on the temperature at which the pure monoclinic crystal structure of the synthesized LaPO₄:1%Eu product is formed. The pure monoclinic phase is formed at a lower temperature of 180 °C when using (NH₄)₂HPO₄. However, when using NH₄H₂PO₄, the pure monoclinic phase is only formed at the synthesis temperature of 200 °C, and a hexagonal phase impurity is visible at lower temperatures. The results are

additionally confirmed by Le Bail fitting analysis. The calculated values of lattice parameters and χ^2 are presented in Table 2. Again, the calculated values of lattice parameters are close to the reference, and χ^2 values are very low, indicating a good match between calculated and experimental data.

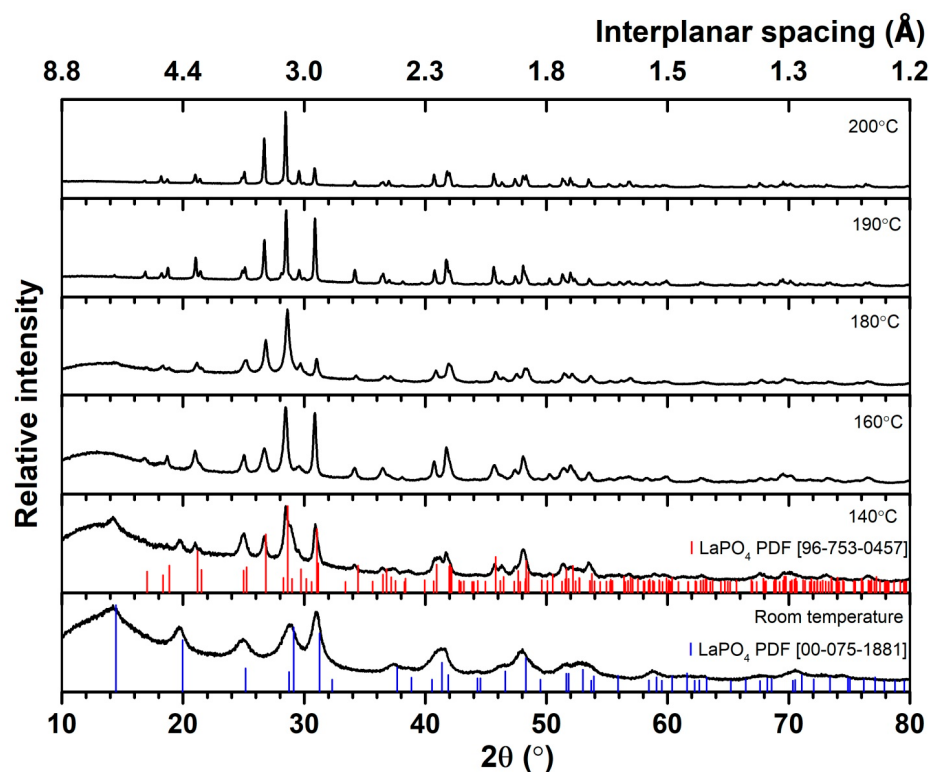


Figure 2. XRD patterns of $\text{LaPO}_4\text{:1\%Eu}$ samples were synthesized using $\text{NH}_4\text{H}_2\text{PO}_4$ at different temperatures: from room temperature to 200 °C. The red and blue sticks are the data of references.

Table 2. The values of cell parameters and χ^2 of XRD patterns' Le Bail fitting.

T (Annealing), °C	Phase 1: Monoclinic ($P12_1/n1$)			Phase 2: Trigonal (Hexagonal Axes; $P3_121$)			χ^2
	a_1 , Å	b_1 , Å	c_1 , Å	a_2 , Å	b_2 , Å	c_2 , Å	
No annealing	—	—	—	7.095 (1)	7.095 (1)	6.486 (1)	0.854
140	6.8453 (9)	7.0714 (7)	6.5006 (6)	7.187 (169)	7.187 (169)	6.030 (453)	1.20
160	6.8347 (4)	7.0731 (3)	6.5020 (2)	6.988 (13)	6.988 (13)	6.462 (20)	1.93
180	6.8395 (5)	7.0740 (5)	6.5021 (6)	7.207 (2)	7.207 (2)	6.137 (3)	1.49
190	6.8348 (4)	7.0732 (3)	6.5015 (5)	6.966 (8)	6.966 (8)	6.424 (21)	1.10
200	6.8338 (1)	7.0704 (1)	6.5004 (1)	—	—	—	2.06

Scanning electron microscopy (SEM) was used to investigate the morphological characteristics of $\text{LaPO}_4\text{:1\%Eu}$ particles synthesized at different temperatures using two different phosphate precursors: diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). The resulting morphologies are shown in Figure 3A,B. At room temperature, both precursor systems gave irregular, agglomerated particles with generally spherical or ill-defined shapes. These morphologies are attributed to limited crystallization and particle growth due to insufficient thermal energy. As the synthesis temperature increased, significant morphological changes were observed. In both systems, particle shapes gradually evolved from irregular shapes to more defined, elongated structures resembling nanorods—particularly noticeable at temperatures above 160 °C. However, the degree of particle uniformity and size varied significantly depending on

the precursor used. Samples synthesized with $(\text{NH}_4)_2\text{HPO}_4$ produced more diminutive and more uniform particles across all temperatures compared with those synthesized with $\text{NH}_4\text{H}_2\text{PO}_4$. For example, at 200 °C, the average length and width of particles synthesized with $(\text{NH}_4)_2\text{HPO}_4$ were 1227 nm and 224 nm, respectively, whereas those synthesized with $\text{NH}_4\text{H}_2\text{PO}_4$ reached 2652 nm in length and 609 nm in width—more than twice the size (Tables 3 and 4). This highlights the remarkable influence of precursor type on particle growth and final morphology. The aspect ratio (length to width) also reflected this trend. The highest aspect ratio of 17.1 was observed for the sample synthesized at 120 °C using $(\text{NH}_4)_2\text{HPO}_4$, indicating a brief regime favoring rapid axial growth before further thermal input altered the balance between longitudinal and radial crystal development. In contrast, $\text{NH}_4\text{H}_2\text{PO}_4$ -based samples exhibited more significant but less consistent aspect ratios, with a maximum of 13.6 at 180 °C. These observations suggest that thermal energy plays a key role in controlling anisotropic growth, while the chemical environment provided by the phosphate precursor further governs particle size distribution and morphological uniformity.

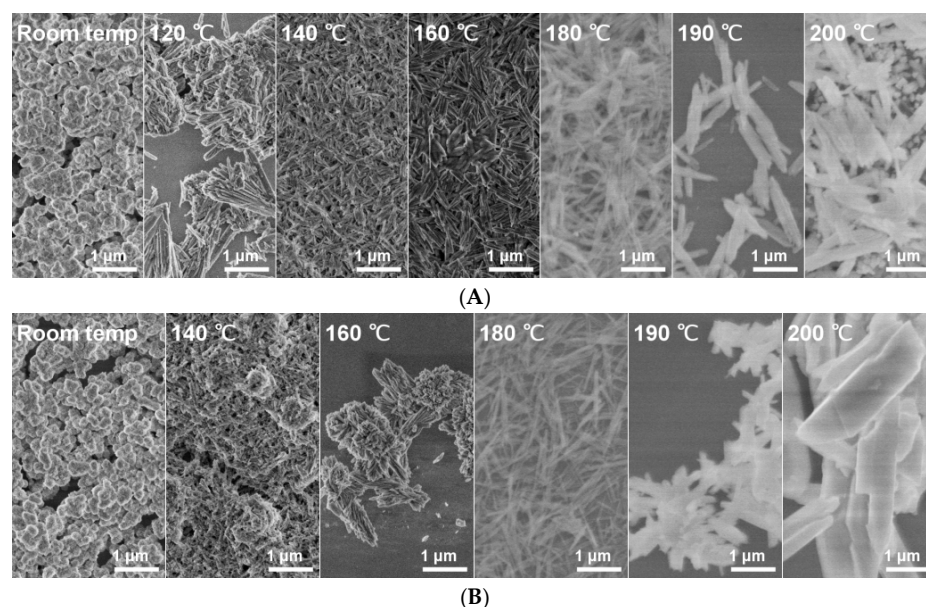


Figure 3. (A) SEM images of $\text{LaPO}_4\text{:1\%Eu}$ samples were synthesized using $(\text{NH}_4)_2\text{HPO}_4$ at different temperatures: from room temperature to 200 °C (from left to right). (B) SEM images of $\text{LaPO}_4\text{:1\%Eu}$ samples were synthesized using $\text{NH}_4\text{H}_2\text{PO}_4$ at different temperatures.

Table 3. The measured particle size of $\text{LaPO}_4\text{:1\%Eu}$ samples was synthesized using $(\text{NH}_4)_2\text{HPO}_4$ at different temperatures.

Sample	Length, nm	Standard Deviation, nm	Width, nm	Standard Deviation, nm	Length-to-Width Ratio
t = room temp.	740	202	385	62	1.9
t = 120 °C	1508	1005	88	33	17.1
t = 140 °C	286	83	36	7	7.9
t = 160 °C	486	89	77	20	6.3
t = 180 °C	737	921	76	20	9.7
t = 190 °C	1162	223	179	48	6.5
t = 200 °C	1227	143	224	92	5.5

Table 4. Measured particle sizes of $\text{LaPO}_4\text{:1\%Eu}$ samples were synthesized using $\text{NH}_4\text{H}_2\text{PO}_4$ at different temperatures.

Sample	Length, nm	Standard Deviation, nm	Width, nm	Standard Deviation, nm	Length-to-Width Ratio
t = room temp.	525	99	319	27	1.6
t = 140 °C	271	57	65	15	4.2
t = 160 °C	826	253	205	86	4.0
t = 180 °C	800	379	59	29	13.6
t = 190 °C	1324	235	210	59	6.3
t = 200 °C	2652	728	609	218	4.4

In conclusion, SEM analysis shows that both synthesis temperature and phosphate precursor significantly influence the size, shape, and uniformity of $\text{LaPO}_4\text{:1\%Eu}$ particles. Higher synthesis temperatures promote nanorod formation, with this effect becoming more pronounced above 160 °C. $(\text{NH}_4)_2\text{HPO}_4$ results in more uniform and smaller particles, making it preferable when controlled morphology is desired. Conversely, $\text{NH}_4\text{H}_2\text{PO}_4$ tends to produce larger and more variable structures, which may be advantageous in applications where higher surface area or specific aspect ratios are desirable.

Diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ was chosen as the precursor of PO_4^{3-} ions based on these synthesis and analysis results. Monoclinic crystal structure particles were synthesized through hydrothermal synthesis at 180 °C. A series of $\text{La}_x\text{Gd}_{1-x}\text{PO}_4\text{:1\%Eu}$ synthesis was performed where $x = 1, 0.75, 0.5, 0.25$, and 0. The XRD analysis results are presented in Figure 4. The diffractogram shows that the material's crystal structure obtained at $x = 0.5, 0.25$, and 0 is hexagonal, corresponding to the reference data of hexagonal Gadolinium Phosphate Hydrate (PDF ICDD 00–039–0232). Meanwhile, $\text{La}_{0.75}\text{Gd}_{0.24}\text{PO}_4\text{:1\%Eu}$ is a mixture of monoclinic and hexagonal phases. The $\text{LaPO}_4\text{:1\%Eu}$ sample exhibits only a monoclinic structure, contributing to the Lanthanum Phosphate (PDF ICDD 96–153–0457) reference. Furthermore, Rodriguez–Liviano et al. show that GdPO_4 can be a tetragonal system with space group $I4_1/amd$ [19]. In the present case, however, the tetragonal phase is not observed because the characteristic peaks at 19.5° (the third most intensive peak) or 35.1° 2θ (the second most intensive peak) are missing. In addition, Le Bail fitting was applied for all XRD patterns, confirming the interpretation that only monoclinic and/or tetragonal (with hexagonal axis) ones are formed under the given synthesis conditions. The cell parameter values, which are close to the reference, and the χ^2 values are given in Table 5.

Table 5. The values of cell parameters and χ^2 of XRD patterns' Le Bail fitting.

Comound	Phase 1: Monoclinic ($P12_1/n1$)			Phase 2: Trigonal (Hexagonal Axes; $P3_121$)			χ^2
	$a_1, \text{\AA}$	$b_1, \text{\AA}$	$c_1, \text{\AA}$	$a_2, \text{\AA}$	$b_2, \text{\AA}$	$c_2, \text{\AA}$	
$\text{GdPO}_4\text{:1\%Eu}$	–	–	–	6.8961 (2)	6.8961 (2)	6.3116 (2)	1.24
$\text{La}_{0.25}\text{Gd}_{0.74}\text{PO}_4\text{:1\%Eu}$	–	–	–	6.9470 (4)	6.9470 (4)	6.3597 (4)	0.888
$\text{La}_{0.50}\text{Gd}_{0.49}\text{PO}_4\text{:1\%Eu}$	–	–	–	6.9969 (7)	6.9969 (7)	6.4059 (7)	0.955
$\text{La}_{0.75}\text{Gd}_{0.24}\text{PO}_4\text{:1\%Eu}$	6.830 (2)	7.040 (2)	6.452 (2)	7.0468 (14)	7.0468 (14)	6.4520 (17)	1.45
$\text{LaGdPO}_4\text{:1\%Eu}$	6.871 (2)	7.063 (2)	6.504 (2)	–	–	–	1.83

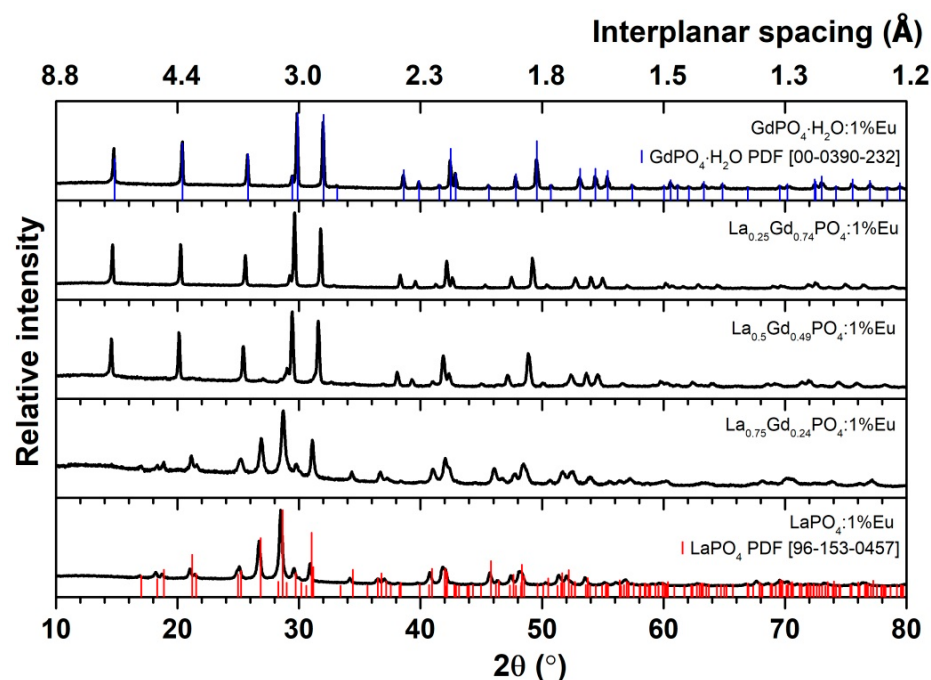


Figure 4. XRD of $\text{La}_x\text{Gd}_{1-x}\text{PO}_4:1\%\text{Eu}$ containing different content of lanthanum synthesized at 180°C . The red and blue sticks are the data of LaPO_4 and $\text{GdPO}_4\cdot\text{H}_2\text{O}$ references, respectively.

A slight increase in the intensity of the background line is observed between 10° and 20° when $x = 0.50$ and 0.75 , indicating the amorphous nature of the synthesized material or the influence of the amorphous glass tray on which the research material was placed. Due to the constant annealing temperature of all samples, it is difficult to determine whether the phase elementary composition or sample preparation gives this effect.

SEM was used to examine the materials obtained during the syntheses. The SEM images of $\text{La}_x\text{Gd}_{1-x}\text{PO}_4:1\%\text{Eu}$ obtained at a synthesis temperature of 180°C reflect the morphology of the particles. The shape and size of the synthesized particles vary depending on the product composition. The sintered $\text{LaPO}_4:1\%\text{Eu}$ particles (Figure 5A) have a similar shape, resembling nanorods, with an average length of 727 nm and an average width of 80 nm. The particles of $\text{La}_{0.75}\text{Gd}_{0.25}\text{PO}_4:1\%\text{Eu}$ (Figure 5B) can be described as a precursor to nanorods, but they are shorter than the pure lanthanum phosphate particles mentioned earlier. The average particle length is 216 nm, and the average width is 58 nm. When gadolinium is present in the synthesized phosphate in equal or greater amounts than lanthanum, the particles lose their nanorod shape and become irregular, unevenly sized, cohesive polygons. These can no longer be classified as nanoparticles but rather as microstructures with a size of up to $5\ \mu\text{m}$, as shown in Figure 5D. The average particle length is $2.7\ \mu\text{m}$ and $5\text{E}—1.6\ \mu\text{m}$.

Our previous study showed that GdPO_4 exhibits the best luminescence properties when the sample is substituted with 15% europium [12]. Therefore, after evaluating the previously described synthesis and analysis results, we decided to increase the Eu^{3+} concentration from 1% to 15% by replacing La or Gd, resulting in a single-phase $\text{La}_{0.75}\text{Gd}_{0.25}\text{PO}_4:15\%\text{Eu}$ with a monoclinic crystal structure. An XRD study evaluated the crystal structure, phase composition, and sample purity. XRD analyses of both samples have shown that a uniform phase composition was achieved, as shown in Figure 6. The XRD patterns of the samples correspond to the reference data of monoclinic Lanthanum Phosphate (PDF ICDD 96–153–0457), indicating a pure monoclinic phase. The Le Bail fitting analysis confirms the monoclinic structure. The calculated values of cell parameters are given in Table 6.

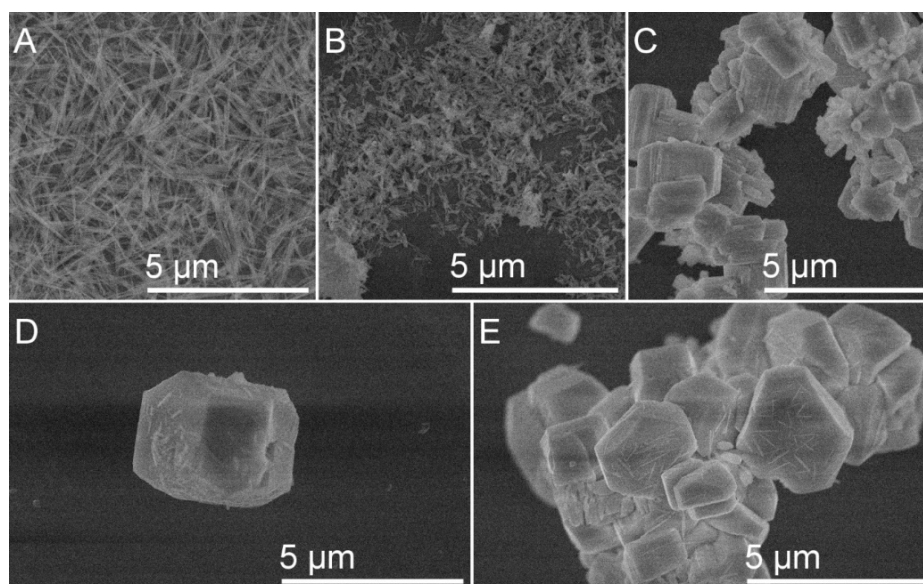


Figure 5. SEM images of $\text{La}_x\text{Gd}_{1-x}\text{PO}_4:1\% \text{Eu}$ $x = 1$ (A); 0.75 (B); 0.5 (C); 0.25 (D); 0 (E).

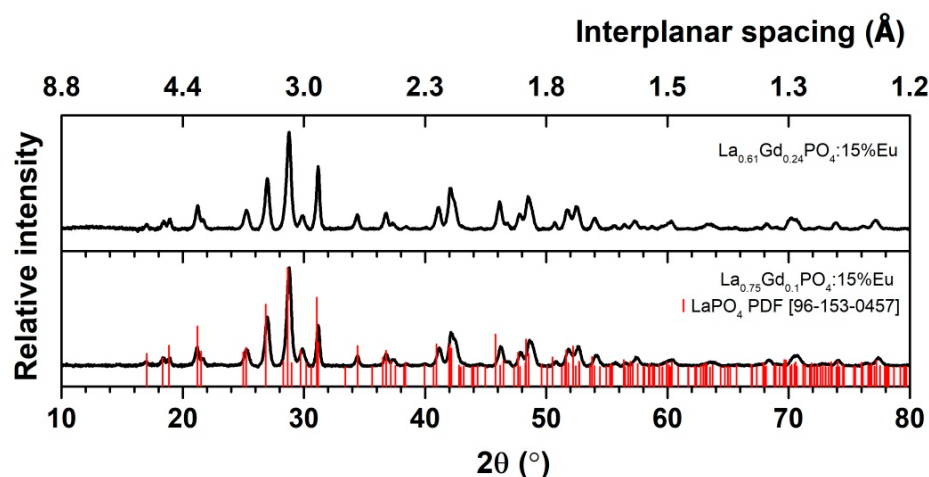


Figure 6. XRD of $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\% \text{Eu}$ and $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\% \text{Eu}$ synthesized at 180°C . The red sticks indicate data of LaPO_4 reference.

Table 6. The values of cell parameters and χ^2 of XRD patterns' Le Bail fitting.

Compound	Monoclinic Phase ($P12_1/n1$)			
	$a_1, \text{\AA}$	$b_1, \text{\AA}$	$c_1, \text{\AA}$	χ^2
$\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\% \text{Eu}$	6.7695 (8)	6.9890 (7)	6.4397 (7)	1.92
$\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\% \text{Eu}$	6.7768 (4)	6.9990 (4)	6.4462 (4)	1.77

SEM analysis was conducted to investigate the morphology and particle size of the materials obtained by hydrothermal synthesis. Nanorod-shaped particles were synthesized in both samples. However, the particles were not uniform in size or shape in either sample, with some particles adhering to one another (see Figure 7). In sample A ($\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\% \text{Eu}$), the particles were slightly shorter and thicker than in sample B ($\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\% \text{Eu}$). The length of $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\% \text{Eu}$ particles range from 45 nm to 150 nm, with very few smaller particles. The particle thickness ranges from 13 nm to 35 nm without measuring agglomerated particles. Sample B synthesized particles have a measured length ranging from 120 nm to 250 nm and a thickness ranging from 10 nm to

40 nm. The particles formed in sample A are slightly shorter but slightly thicker than those in sample B.

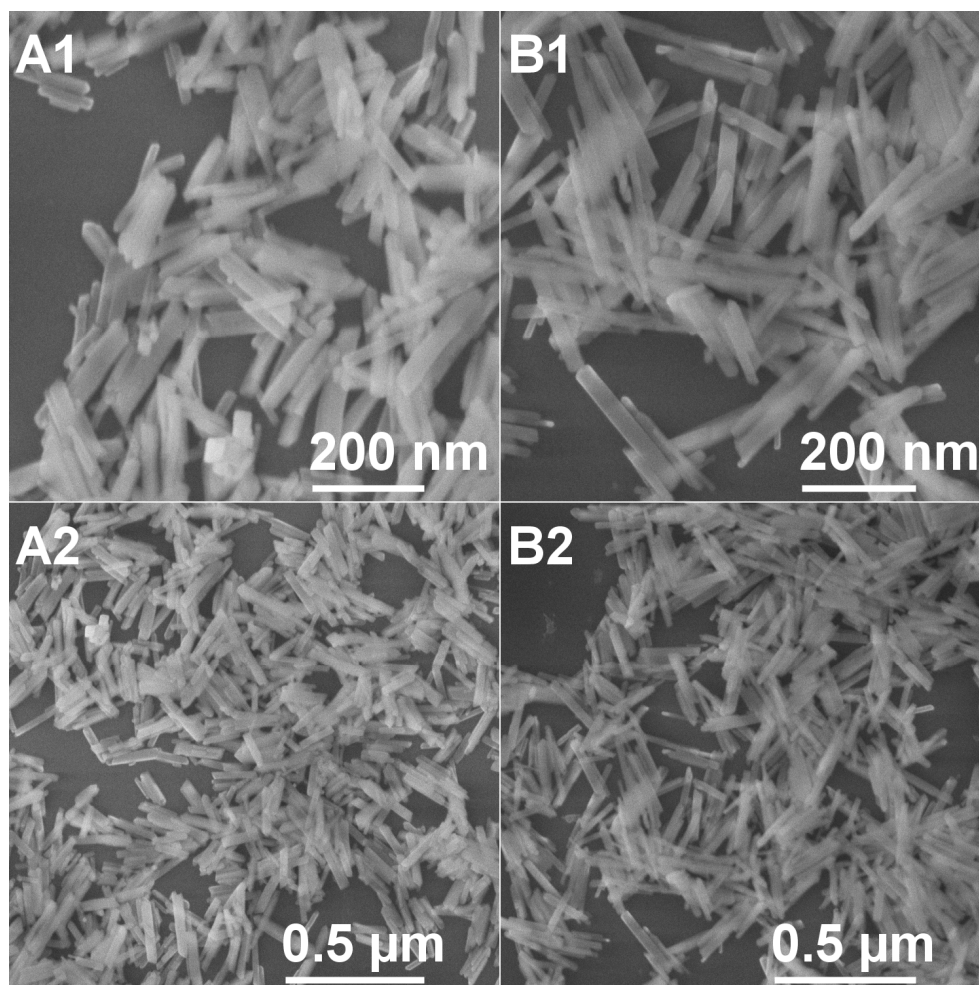


Figure 7. SEM images of $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\%\text{Eu}$ (A1,A2) and $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\%\text{Eu}$ (B1,B2) under different magnifications.

The luminescent characteristics of $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\%\text{Eu}$ and $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\%\text{Eu}$ samples were examined and are shown in Figures 8 and 9. As the samples appeared pure white, they were expected to exhibit minimal or no absorption within the visible spectrum. The excitation spectra were recorded from 250 nm to 585 nm, with an emission wavelength of $\lambda_{\text{em}} = 591$ nm. The excitation spectra demonstrated broadband at higher energy (ranging from 250 nm to 270 nm), attributable to charge transfer resulting from electron transfer from O^{2-} to Eu^{3+} . The $^8\text{S}_{7/2} \rightarrow ^6\text{P}_j$ transitions of the Gd^{3+} ions were assigned to the narrow peaks at ~ 298 nm. The presence of these Gd^{3+} excitation lines in the excitation spectra monitored for Eu^{3+} ion indicated $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer. The remaining excitation peaks were attributed to the Eu^{3+} ion. The peaks at ~ 318 nm were associated with the $^7\text{F}_0 \rightarrow ^5\text{H}_j$ transitions, while a cluster of several peaks was visible in the range of 370 nm to 390 nm, ascribed to the $^7\text{F}_0 \rightarrow ^5\text{D}_4$, $^7\text{F}_0 \rightarrow ^5\text{G}_j$, $^7\text{F}_0 \rightarrow ^5\text{G}_j$; $^5\text{L}_7$ transitions. The most intense peak at 393 nm was related to the transition $^7\text{F}_0 \rightarrow ^5\text{L}_6$. The small peaks at ~ 415 nm, ~ 463 nm, and ~ 527 nm were assigned to the transitions of $^7\text{F}_0 \rightarrow ^5\text{D}_3$, $^7\text{F}_0 \rightarrow ^5\text{D}_2$, and $^7\text{F}_0 \rightarrow ^5\text{D}_1$, respectively.

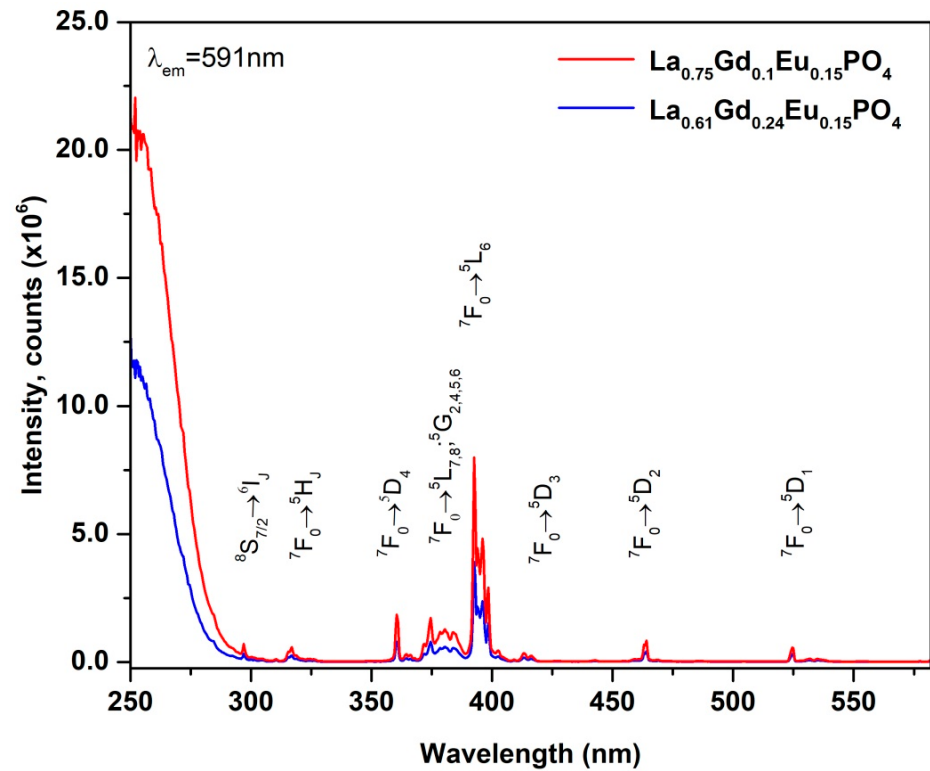


Figure 8. Excitation spectra of $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\%\text{Eu}$ and $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\%\text{Eu}$ for 591 nm emission wavelength.

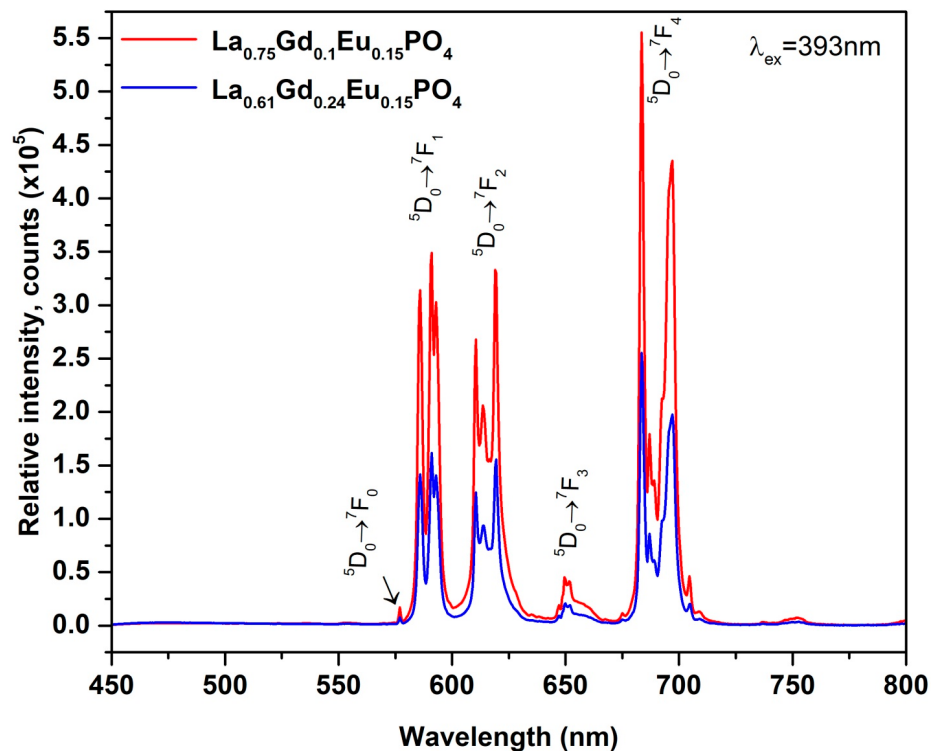


Figure 9. Emission spectra of $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\%\text{Eu}$ and $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\%\text{Eu}$ under 393 nm excitation.

Figures 8 and 9 show the luminescent characteristics of $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4:15\%\text{Eu}$ and $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4:15\%\text{Eu}$ samples. Since the samples were pure white, it was expected that they would exhibit minimal or no absorption within the visible spectrum. Excitation spectra were recorded from 250 nm to 585 nm, with an emission wavelength of $\lambda_{\text{em}} = 591$ nm. The

excitation spectra show a broadband at higher energy (ranging from 250 nm to 270 nm), attributable to charge transfer resulting from electron transfer from O^{2-} to Eu^{3+} . The narrow peaks at ~298 nm were assigned to the $^8S_{7/2} \rightarrow ^6P_J$ transitions of the Gd^{3+} ion. These Gd^{3+} excitation lines in the excitation spectra monitored for Eu^{3+} ion indicate $Gd^{3+} \rightarrow Eu^{3+}$ energy transfer. The remaining excitation peaks were attributed to the Eu^{3+} ion. The peaks at approximately 318 nm are associated with the $^7F_0 \rightarrow ^5H_J$ transitions, while a cluster of several peaks is visible in the range of 370 nm to 390 nm, ascribed to the $^7F_0 \rightarrow ^5D_4$, $^7F_0 \rightarrow ^5G_J$, $^7F_0 \rightarrow ^5G_J$; 5L_7 transitions. The most intense peak at 393 nm is related to the transition $^7F_0 \rightarrow ^5L_6$. The small peaks at approximately 415 nm, 463 nm, and 527 nm are assigned to the transitions of $^7F_0 \rightarrow ^5D_3$, $^7F_0 \rightarrow ^5D_2$, and $^7F_0 \rightarrow ^5D_1$, respectively.

The luminescence properties of $La_{0.61}Gd_{0.24}PO_4:15\%Eu$ and $La_{0.75}Gd_{0.1}PO_4:15\%Eu$ samples were investigated by exciting them with a wavelength of 393 nm and measuring their emission spectra. The emitted radiation was found to be in the red color range, and the emission peaks were attributed to various transitions between energy levels of the Eu^{3+} ion. The emission spectral peaks at ~577 nm, ~590 nm, ~615 nm, ~650 nm and ~690 nm attributed to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$, and $^5D_0 \rightarrow ^7F_4$ transitions, respectively. The peak with the highest intensity was observed at 690 nm, which is typical for Eu^{3+} -substituted orthophosphates. As expected, and aimed for, the emission intensity of $La_{0.75}Gd_{0.1}PO_4:15\%Eu$ is significantly higher and reaches 5.5×10^5 counts compared with the previously synthesized and discussed samples with a hexagonal crystal system, where the maximum emission intensity is 5.5×10^5 counts.

It is interesting to note that, despite both $La_{0.61}Gd_{0.24}PO_4:15\%Eu$ and $La_{0.75}Gd_{0.1}PO_4:15\%Eu$ samples exhibiting the same monoclinic crystalline structure, there is a high degree of similarity in terms of particle size ($La_{0.75}Gd_{0.1}PO_4:15\%Eu$ particles are marginally larger). However, it has been demonstrated that emission can be strongly influenced by the luminescent center environment. Previous studies have shown that $^5D_0 \rightarrow ^7F_4$ emission increases with increasing electronegativity [23]. In this instance, further detailed studies are required, and neutron diffraction studies would be particularly valuable in explaining the structure–emission relationship in greater detail.

Figure 10 shows the dependence of magnetization on the strength of the applied magnetic field. For paramagnets, the magnetization is proportional to the applied magnetic field strength, given by $M = \chi H$, where the volume magnetic susceptibility χ is determined by the Curie–Weiss law

$$\chi = \frac{N}{3k_B} \cdot \frac{\mu_{eff}^2}{T + \Theta}. \quad (1)$$

Here, N represents the number of paramagnetic atoms per unit volume, k_B is the Boltzmann constant, and Θ is the Weiss constant. The effective magnetic moment of a paramagnetic atom is given by the formula $\mu_{eff} = g\sqrt{J(J+1)}\mu_B$, where J is the angular momentum quantum number and μ_B is the Bohr magneton. Although $J = 0$ for the main state of Eu^{3+} , its first excited state is close to it at room temperature, causing Eu^{3+} to also contribute to the paramagnetism of the samples [24]. However, the effective magnetic moment is larger for the Gd^{3+} ion with $J = 7/2$ and a g -factor of 2. Although magnetic susceptibility depends on the Weiss constant and deviations from the Curie–Weiss law are possible, due to the fact that the $GdPO_4$ magnetic ordering temperature T_N is quite close to room temperature at 225 K [25]. As La^{3+} is diamagnetic, the susceptibility differences for samples can mainly be explained by different amounts of Gd^{3+} .

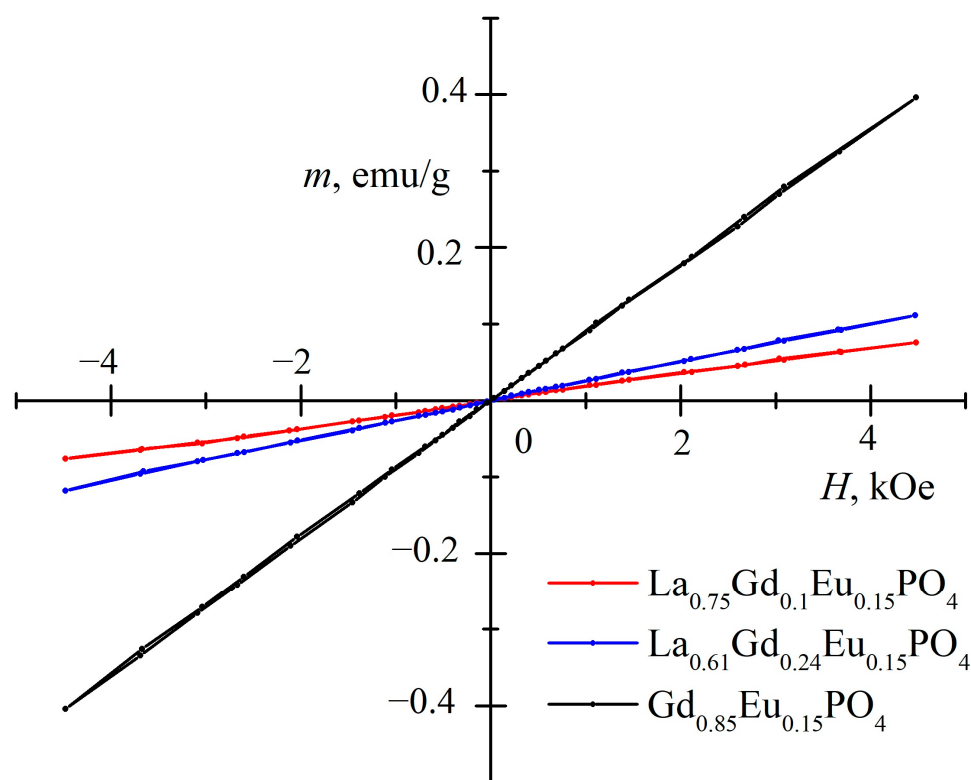


Figure 10. Dependence of magnetization (m , emu/g) on magnetic field strength (H , kOe) at room temperature.

All three investigated samples exhibited paramagnetic properties and could potentially be used as contrast in magnetic resonance imaging (MRI). However, based on the luminescence measurements of the samples, $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4\text{:}15\%\text{Eu}$ monoclinic nanorods showed the highest emission intensity and could potentially be used for multimodal imaging combining magnetic resonance imaging (MRI) and luminescence measurements.

4. Conclusions

The crystal structure of $\text{LaPO}_4\text{:}1\%\text{Eu}$ was significantly influenced by the choice of the precursor of PO_4^{3-} ions. The use of $(\text{NH}_4)_2\text{HPO}_4$ precursor resulted in distinct crystal structures at lower temperatures compared with $\text{NH}_4\text{H}_2\text{PO}_4$. A higher concentration of lanthanum in the $\text{La}_x\text{Gd}_{1-x}\text{PO}_4\text{:}1\%\text{Eu}$ compound led to the formation of a monoclinic phase.

The luminescence emission was enhanced in $\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4\text{:}15\%\text{Eu}$ and $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4\text{:}15\%\text{Eu}$ samples with an increased Eu^{3+} content. The emission spectra showed clear peaks that corresponded to Eu^{3+} transitions. The $\text{La}_{0.75}\text{Gd}_{0.1}\text{PO}_4\text{:}15\%\text{Eu}$ samples exhibited superior emission intensity compared with the hexagonal counterparts.

The magnetization studies indicated paramagnetic behavior in the synthesized samples, which was influenced by the Gd^{3+} ions content.

$\text{La}_{0.61}\text{Gd}_{0.24}\text{PO}_4\text{:}15\%\text{Eu}$ monoclinic nanorods exhibit paramagnetism and high luminescence emission intensity. This sample has potential for multimodal imaging through the combination of magnetic resonance imaging (MRI) and luminescence measurements.

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