



EFFECT OF PH ON THE PHOTOLUMINESCENCE PROPERTIES OF LaPO₄ NANOPARTICLES DOPED WITH Tb³⁺ IONS

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Abstract:

LaPO₄ nanophosphors doped with Tb³⁺ were synthesized using a simple co-precipitation method in deionized water with NH₄H₂PO₄ and La(NO₃).5H₂O using Tb(NO₃) as the dopant at various pH values while maintaining a constant concentration. X-ray diffraction studies indicate a decrease in particle size with an increase in pH beyond pH 4. Photoluminescence (PL) studies reveal that PL intensity increases with rising pH and then decreases, likely due to changes in crystallinity. SEM and TEM images show that the synthesized nanoparticles have a nanorod structure. FTIR and EDX analyses were also conducted to determine the elemental composition of the nanoparticles.

Keywords: LaPO₄, nanophosphors, co-precipitation, pH variation, photoluminescence

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Introduction:

Rare-earth (RE) doped LaPO₄ nanophosphors, incorporating specific amounts of other RE elements into the lanthanum phosphate host structure, exhibit unique properties such as high luminescence, long lifetime, photostability, optical durability, insolubility, and high energy. These characteristics make them durable phosphors widely used in various fields [1-5]. LaPO₄ nanophosphors serve as excellent hosts for activators like Ln³⁺, enabling the emission of different colors [6-12]. Phosphate sources emit light upon absorbing ultraviolet radiation, a process arising from charge transfer between the oxygen (O²⁻) 2p shell and the partially filled 4f shell of lanthanides, which can be modified by doping with RE ions [13-14]. Lanthanides, being tripositive ions (Ln³⁺), can replace other lanthanides in the crystal lattice with minimal structural changes, while the doped ions exhibit luminescent properties [13-15]. The intense emission bands from 4f-4f and 5d-4f electronic transitions confer luminescence properties to LaPO₄. Various RE ions emit different colours: Eu³⁺ emits red, Tb³⁺ emits green, Sm³⁺ emits orange-red, and Tm³⁺ emits blue [11-12, 16-18].

In this study, LaPO₄ is doped with Terbium (Tb³⁺) which is less sensitive to vibrational quenching of luminescence, independent of the solvent, and luminescent in various chemical environments. This makes Tb³⁺ doped LaPO₄ suitable for diverse applications in telecommunications, lasers, displays, LEDs, luminescent materials, bioimaging, biosensors, and more [10,15,19-21].

Several synthesis methods for RE phosphates are reported in the literature, including solid-state reaction, urea hydrolysis, hydrothermal, sol-gel, co-precipitation, polyol, and spray pyrolysis methods [19-26]. The solid-state reaction requires high temperatures and lacks homogeneity. The hydrothermal method produces high yields but large particle sizes and requires complexing agents for uniformity. The sol-gel process involves expensive and sensitive to environmental conditions. In contrast, the co-precipitation method is low-cost, produces pure and homogeneous materials with high yield, does not require organic solvents, is simple and rapid, operates at low temperatures, and allows easy control of particle size. Therefore, co-precipitation is suitable for synthesizing LaPO₄ nanoparticles, and this study investigates the effect of pH on photoluminescence [27-29].

While numerous studies have synthesized LaPO₄ nanoparticles doped with Tb³⁺, few have explored the impact of pH on LaPO₄ [14, 30-32]. This investigation focuses on the influence of pH on photoluminescence in Tb³⁺ doped LaPO₄. Literature indicates varying trends: some report increased crystal size with higher pH [33-36], while others find stability and small crystals at both low and high pH [37]. Rani et al. observed that particle size decreases when pH exceeds 9 [38]. Changes in pH can significantly alter morphology [14, 39-41], with pH being a key factor affecting particle size and photoluminescence [40-42]. In this study, increasing pH initially leads to an increase in average size, followed by a decrease due to changes in crystallinity. This trend impacts photoluminescence, with intensity initially increasing but decreasing beyond pH4 as average size decreases. The variations in luminescence intensity are mainly due to protonation and deprotonation in acidic and alkaline conditions [43-47]. At low and high pH values, H⁺ and OH⁻ ions reduce luminescence intensity [40, 48]. This work presents the synthesis of LaPO₄ doped with Tb³⁺ at different pH values and their characterizations.

Reagents and Materials:

Lanthanum nitrate hexahydrate (La(NO₃)₃.6H₂O, 99.0%, Himedia), terbium nitrate pentahydrate (Tb(NO₃)₃.5H₂O, 99.9%, Sigma Aldrich), ammonium dihydrogen phosphate (NH₄H₂PO₄, 98.0%, Alfa Aesar), ethylene glycol, nitric acid, and sodium hydroxide were used without further purification. Deionized water was used for solution preparation.

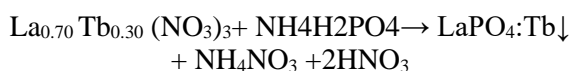
Preparation and Synthesis:

0.1M solutions of La(NO₃)₃.6H₂O and Tb(NO₃)₃.5H₂O were mixed in a beaker, with a few drops of dilute HNO₃ added to homogenize the solution. In another beaker, a 0.1M NH₄H₂PO₄ solution was prepared with deionized water.

The synthesis of lanthanum phosphate via the co-precipitation method proceeded as follows [16, 24-51]:

- 1) 25 ml of the La(NO₃)₃ and Tb(NO₃)₃ solution was added dropwise to 25 ml of NH₄H₂PO₄ solution. The mixture was stirred at 60°C for 30 minutes with a magnetic stirrer, resulting in a white cloudy solution.
- 2) The pH of the solution was adjusted to 1.06 by adding NaOH solution.

- 3) The nanoparticle solutions were sonicated for 30 minutes, purified through centrifugation using a Remi cooling centrifuge, washed with distilled water and acetone, and then dried at 60°C for 16 hours in a vacuum oven.
- 4) The dried samples were powdered by grinding in an agate mortar.
- 5) The entire synthesis procedure was repeated for solutions with pH values of 3.10, 4.06, 6.04, and 8.99 by adjusting with NaOH solution.
- 6) All samples were heated in a muffle furnace at 700°C. The reaction between lanthanum phosphate and ammonium dihydrogen phosphate is as follows:



The prepared samples were sent for XRD, IR, SEM, TEM, EDAX, PL study etc.

Characterization:

To predict the crystalline size and structure, X-ray powder diffraction (XRD) was performed using an Xpert Pro with a scanning rate of 0.02°/min over a 2θ range from 10° to 80°. The measurement utilized nickel-filtered CuKα radiation with a wavelength of 0.15405 nm. The X-ray tube operated at a current of 30 mA and a voltage of 40 kV. Fourier transform infrared (FTIR) spectra were recorded on an IR Affinity-1S spectrometer to identify functional groups and trace species present in the LaPO₄ preparation. The morphology and size of the samples were examined using scanning electron microscopy

(SEM) and transmission electron microscopy (TEM). Elemental composition was determined from energy-dispersive X-ray (EDX) spectra. Photoluminescence (PL) measurements were conducted using an F-7000 Hitachi spectrometer.

Results and Discussion:

X-ray Diffraction: The X-ray diffraction patterns of LaPO₄ doped with Terbium at different pH levels (1.03, 3.1, 4.06, 6.04, and 8.99) are shown in Figure 1. All samples exhibited intense peaks characteristic of the monoclinic phase at 14.60°, 20.30°, 25.20°, 29.03°, 31.04°, 38.30°, 41.40°, and 48.30°. These patterns matched the standard JCPDS file no. 04-0635, which has a space group of P21/n, with the main peak at 31.40°. The sharp peaks observed indicate good crystallinity of the prepared samples.

The average crystalline size was calculated using the Scherrer equation:

$$D = k\lambda/\beta\cos\theta$$

where, k=0.94, D= the crystal size, λ= wavelength of CuKα radiation 0.154nm, and β=half-width at full maximum.

The calculated average crystal sizes were 18.65 nm, 21.80 nm, 33.16 nm, 28.32 nm, and 21.47 nm for the samples with pH values of 1.03, 3.1, 4.06, 6.04, and 8.99, respectively. These results indicate that the average crystallite size increased with pH up to a point and then decreased (Table - 1), a trend also reported in previous studies [32, 36].

Table - 1: pH value and the average size

pH	1.06	3.1	4.06	6.04	8.99
Average size	18.65	21.80	33.16	28.32	21.47

The samples prepared at different pH levels showed an increase in intensity up to pH4, followed by a decrease. This trend may be attributed to an increase in crystallinity up to pH4, which then diminishes beyond this point [52-54]. According to Leirina Aparecida P.G. et al. (2020), the nanoparticle size was found to be

small at both low and high pH values. This smaller nanoparticle size observed at extreme pH levels may be due to the repulsion between nanoparticles caused by the accumulation of excess charges (H⁺ at low pH and OH⁻ at high pH) on the surface of the nanophosphors [32,55].

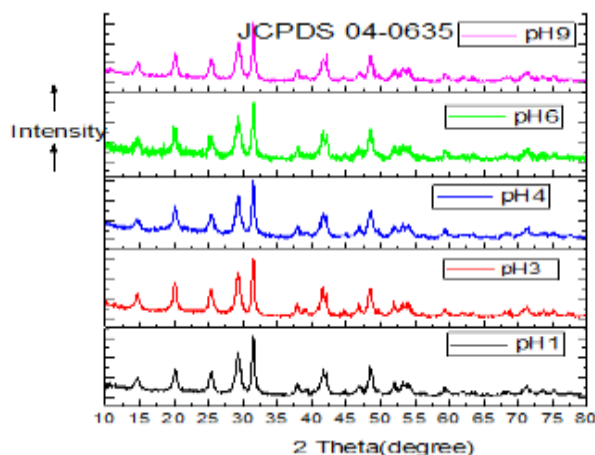


Figure - 1: XRD graph for pH 1,pH 3,pH 4,pH6 and pH9

FTIR Spectra:

Figure - 3 presents the FTIR spectra of the prepared samples at pH levels 1, 3, 4, 6, and 9, within the range of 500 to 4000 cm⁻¹. The spectra for pH 1.6, 3.04, 4.06, 6.04, and 8.99 all exhibit identical peaks at 538.18, 615.29, 991.41, 1051.20, 1312.28, 1620.34, 3340.70, and 2353.98 cm⁻¹. Detailed information on the IR bands of LaPO₄ doped with Terbium is provided in Table - 2. The IR spectra of these samples reveal eight distinct peaks. The peaks at 538 cm⁻¹ and 615.29 cm⁻¹ correspond to the bending

vibrations of the PO₄³⁻ group. The absorption bands at 991.41 cm⁻¹ and 1051.20 cm⁻¹ are attributed to the stretching vibrations of the PO₄³⁻ group. Additionally, the peaks at 1620 cm⁻¹ and 3340.70 cm⁻¹ are associated with the bending and stretching vibrations of the O-H bonds in water molecules. The IR spectra of lanthanum phosphate doped with Tb³⁺ at different pH are found to be identical and their spectra are shown in Figure - 2. These experimental observations are consistent with the findings reported by the previous finding too [10].

Table - 2: IR band of LaPO₄ doped with terbium

Peak position (cm ⁻¹)	Functional groups	Mode of vibration
1) 538.13	O-P-O	Bending
2) 615.29	O=P-O	Bending
3) 991.41	P-O	Stretching
4) 1051.20	P=O	Stretching
5) 1312.20	HNO ₃	
6) 1620.34	O-H	Bending
7) 3340.70	O-H	Stretching

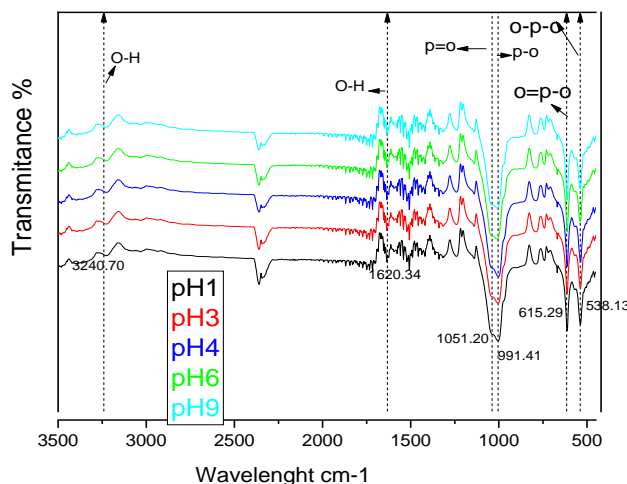


Figure - 2: IR spectra of pH 1,3,4,6 and 9.

SEM and EDX Study

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) analyses were conducted. Figure 3 displays SEM images of samples prepared at different pH levels. Although the rod-shaped particles are visible, the images lack sharpness due to low magnification. However, high magnification Transmission Electron Microscopy (TEM) images confirm the rod-shaped structure of the

prepared nanoparticles. The EDX spectra for all samples are identical, indicating the incorporation of dopant ions into the host matrix. Elements such as La, Tb, P, and O were detected, as shown in Figure 4. The intensity of the light element oxygen is not clearly observed in the EDX pattern, likely due to the increasing difficulty in ionizing atoms with lower atomic numbers to generate X-rays [56, 57].

EDAX ZAF Quantification (Standardless)

Element Normalized SEC Table: Default

Elem	Wt %	At %
O K	0.90	4.62
P K	18.64	49.50
LaL	56.95	33.72
TbL	23.52	12.17
Total	100.00	100.00

EDAX Table showing composition LaPO₄:Tb³⁺

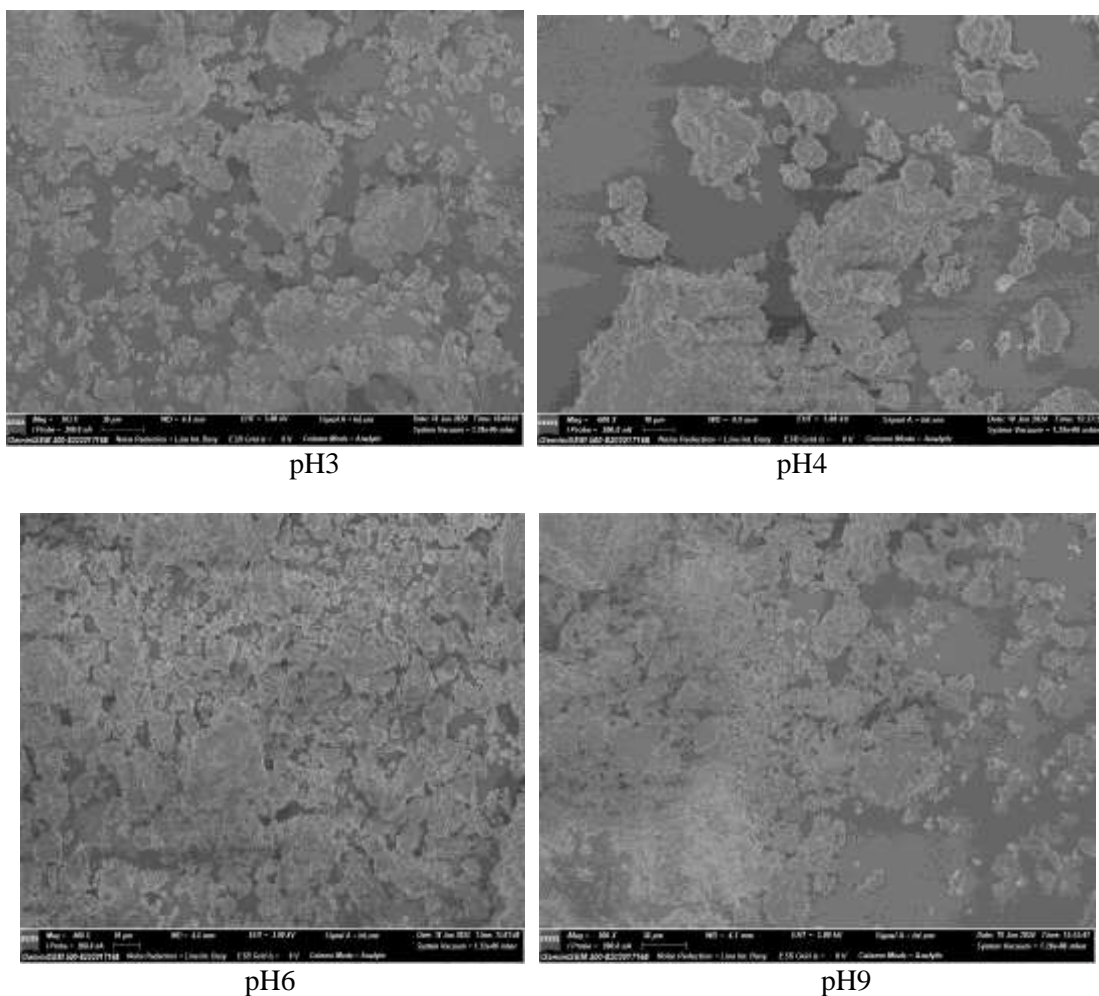


Figure - 3: SEM Images of pH 3,4,6 and9 at 30 μm.

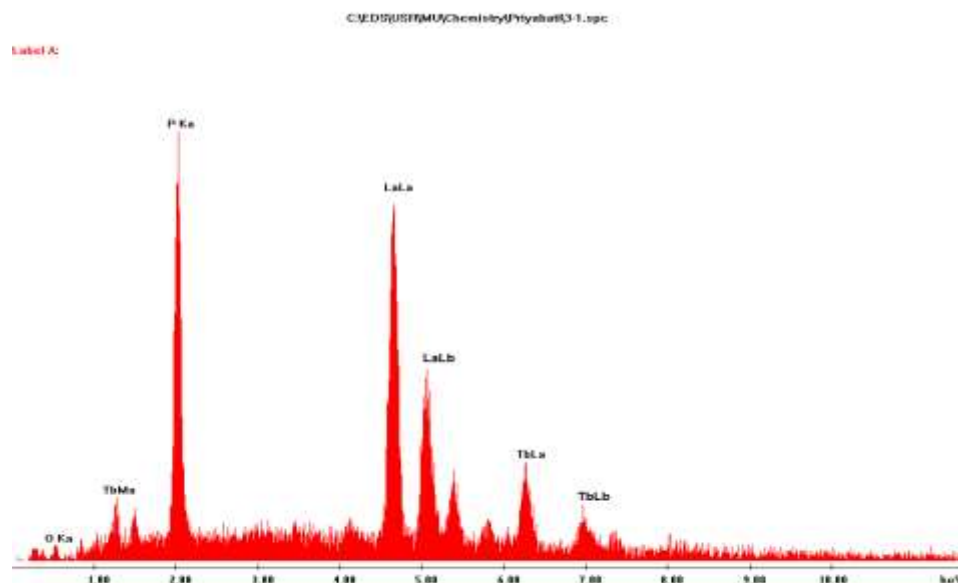


Figure - 4: EDX spectra of pH9

Transmission Electron Microscopy (TEM)

TEM images of samples at pH4 and pH6 are shown in Figure - 5. These images reveal a mixture of large and small rod-shaped nanoparticles. The average lengths of the nanorods are approximately 32.6 nm and 28.48 nm, respectively, closely matching the X-ray

diffraction (XRD) patterns. The Selected Area Electron Diffraction (SAED) pattern for pH4 exhibits a regular pattern of bright spots, indicating higher crystallinity compared to pH6. The ring pattern indices suggest that the LaPO₄ nanophosphors have a monoclinic phase, which is consistent with the XRD results.

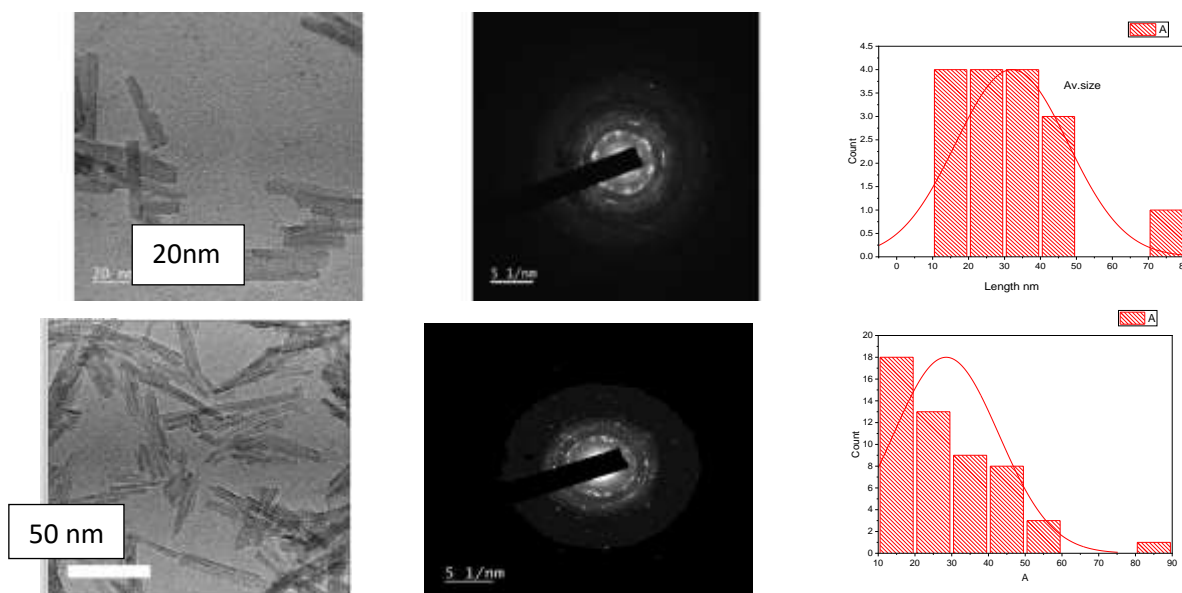


Figure - 5: Images of pH4 and pH6 HRTEM, SAED, Histogram for calculation of size

Photoluminescence Study:

The excitation and emission spectra of Tb³⁺ doped LaPO₄ samples at various pH values are shown in Figures 6 and 7. The excitation spectra, monitored at an emission wavelength of 546 nm, display a broad band from 200 nm to 400 nm, highest peak at 276 nm. This broad band includes several peaks at approximately 228 nm, 261 nm,

276 nm, 319 nm, 340 nm, 350 nm, and 368 nm. The strongest band at 276 nm corresponds to the charge transfer band (CTB), resulting from electron delocalization from the filled 2p shell of O²⁻ to the partially filled 4f shell of Tb³⁺. The peaks at 228 nm and 261 nm are attributed to transitions within the host LaPO₄, while the peaks at 319 nm, 340 nm, 350 nm, and 368 nm

are associated with the $4f^8-4f^75d^1$ transition of Tb³⁺.

Upon excitation at 276 nm, the emission peaks are observed at 490 nm, 545 nm, 586 nm, and 622 nm, corresponding to the transitions $^5D_4 \rightarrow ^7F_6$, $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_4$, and $^5D_4 \rightarrow ^7F_3$ of Tb³⁺ ions, respectively. The strongest emission peak at 545 nm is responsible for green emission. As the pH of the samples increases, the emission intensity also increases up to pH 4, after which it decreases. This behaviour suggests that the crystallinity increases with pH up to 4, enhancing the emission intensity, and decreases beyond

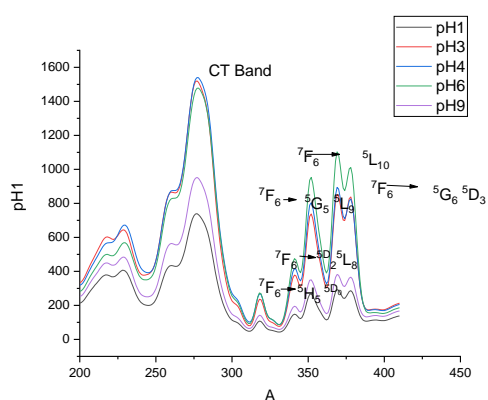


Figure - 6: Excitation spectra of LaPO₄: Tb

Conclusion:

In this study, Tb³⁺ doped LaPO₄ nanoparticles were synthesized using the co-precipitation method at different pH values to determine the effect of pH on photoluminescence. The average size of the nanoparticles varied with pH, as revealed by XRD and confirmed by TEM. The XRD patterns indicated that as pH increased, the average particle size and crystallinity also increased, reaching a peak at pH 4 before decreasing. FTIR spectra identified the structural bonding of different functional groups within the nanophosphors. SEM and TEM analyses confirmed that the particles were crystalline nanorods, which was further supported by XRD results. The influence of pH on nanoparticle size and crystallinity, and their impact on photoluminescence, can be summarized as follows: as pH increases, crystallinity increases up to pH 4 and then decreases. The high-intensity green emission from LaPO₄ doped with Tb³⁺ makes these nanoparticles suitable for various lighting applications.

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pH4. The photoluminescence intensity, as well as the size and crystallinity of the nanoparticles, are influenced by the concentration of H⁺ and OH⁻ ions, which is consistent with the XRD patterns. The lower intensity observed in the emission spectra of LaPO₄ at high H⁺ ion concentrations may be due to protonation of the nanoparticles. Similarly, increased OH⁻ concentration at higher pH levels also results in reduced emission intensity. Thus, an increase in the average crystallite size enhances the crystallinity and consequently the luminescence intensity of the complex.

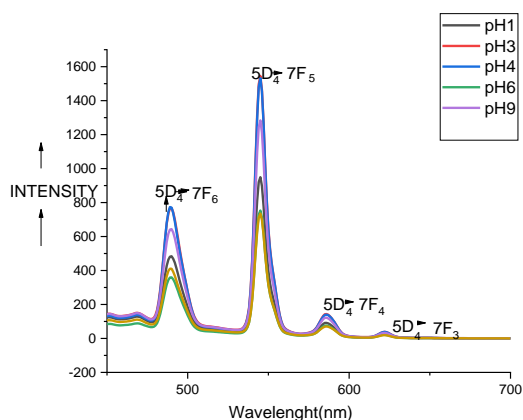


Figure - 7: Emission spectra of LaPO₄: Tb³⁺

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References:

1. Priya, R., Mariappair, R., Karthikaya, A., Palani, E., Krishnamoorthy, E., & Gowrisanker, G. Review on rare earth metal doped LaPO₄ for optoelectronic application. *Solid State Communications*. 2021 Nov; 339:114457.
2. al-Wahish, A., al Binni, U., Tetrat, L., Bridge, C. A., Günaydın-Şen, Ö., Huq, A., Musfeldt, J. L., Paranthaman, M. P., & Mandrus, D. Structure and Dynamics Investigations of Sr/Ca-Doped LaPO₄ Proton Conductors. *Journal of Physical Chemistry C*. 2017; 121(22): 11991-12002.
3. Ansari, A. A, Khan, M.A. M. Synthesis, characterization, and optical properties of lanthanide-doped nanomaterials. *Bulletin of Materials Science*. 2014; 37(5):1085-1092.
4. Runowski, M., Dąbrowska, K., Grzyb, T., Miernikiewicz, P., & Lis, S. Core/shell-type nanorods of Tb³⁺-doped LaPO₄, modified

- with amine groups, revealing reduced cytotoxicity. *Journal of Nanoparticle Research*. 2013; 15:2068.
5. Phaomei, G., Singh, W. R., Shanta Singh, N., Ningthoujam, R. S. Luminescence properties of Ce³⁺ co-activated LaPO₄ nanorods prepared in different solvents and tunable blue to white light emission from Eu³⁺ co-activated LaPO₄,Ce³⁺. *Journal of Luminescence*. 2013; 134: 649-656.
 6. Zheng, Y., Tian, Y., Tian, Y., Ma, H. L., Qu, Y., Wang, Z., An, D., Guan, S., & Gao, X. Synthesis and performance study of zinc borate nanowhiskers. *Journal of Colloids and Surface A: Physicochemical and Engineering Aspects*. 2009; 339:178-184.
 7. Singh, L. P., Ningthoujam, R. S., Srivastava, S. K., & Misra, R. Multifunctional Hybrid Nanomaterials from Water Dispersible CaF₂, Eu³⁺, Mn²⁺, and Fe₂O₃ for Luminescence and Hyperthermia Application. *Journal of Physical Chemistry C*. 2014; 118:18087-18096.
 8. Hera, P., & Shanmugam, S. Nanoparticles Characterization of Application. *International Journal of Current Microbiology and Applied Sciences*. 2015; 4(8): 379-386.
 9. Wang, G. Reng, & LiY. Lanthanide doped nanocrystal Synthesis, Optical, Magnetic properties and Application. *Journal of Chemical Research*. 2011; 44(5).
 10. Luo, W., Huayan, P., Rubiao, C. H., Dong, L., Hong, Z., Ye, S., Yanghui, L., & Le, W. Effect of the solution pH value changes on fluorescence intensity of magnetic luminescence of Fe₃O₄@ Gd₂O₃ nanoparticles. *Journal of Rare Earths*. 2016; 34(1):71-76.
 11. Singh, L. Peter, Sorodhoni Devi, P., Rishikanta Sharma, A., Priyabati Devi, L., Singh, W. R., & Laishram, Raju. Room Temperature Synthesis of Highly Luminescence Eu³⁺ and Tb³⁺ doped hexagonal-phase YPO₄ Nanoparticle with tunable Emission. *New Journal of Chemistry*. 2024. DOI:10.1039/D3NJ05219B.
 12. Phaomei, G., Ningthoujam, R. S., Singh, W. R., Singh, N. S., Luwang, M. N., Singh, R. S., Luwang, M. N., Tewari, R., & Vatsa, R. K. Low temperature synthesis and luminescence properties of re-dispersible Eu³⁺ doped LaPO₄ nanorods by ethylene glycol route. *Optical Materials*. 2010; 32: 616-622.
 13. Pimpalshende, D. M., & Dhoble, S. J. Stability of Luminescence in LaPO₄(3+)(RE=Dy, Eu) nanophosphors. *Luminescence*. 2015 Mar; 30(2):144-54.
 14. Santosh Gupta, K., Ghosh, P. S., Sahu, M., Bhattacharyya, K., Tewari, R., & Natarajan, V. Intense red emitting monoclinic LaPO₄ nanoparticles: Host-dopant energy transfer dynamics and photoluminescence properties. *RSC Advances*. 2015; 5(72).
 15. Sarah, B. "The Effect of pH and Counterion on the Size Distribution and Luminescence Lifetime of Terbium-Doped Lanthanum Nanocrystals" (2014). Undergraduate Honors Theses. 14. Retrieved from: https://digital.sandiego.edu/honors_theses/14.
 16. Nan, S., Hong, F., Xu, H., Dou, J., Liu, G., Dong, X., Liu, J. G., Wang, J., & Yu, W. Luminescence properties and energy transfer of Tb³⁺, Eu³⁺ co-doped YTaO₄ phosphors obtained via sol-gel combustion process. *Journal of Materials in Electronics*. 2020; 31:13688-13695.
 17. de Sousa Filho, P. C., & Serra, O. A. Red, green, and blue lanthanum phosphate phosphors obtained via surfactant-controlled hydrothermal synthesis. *Journal of Luminescence*. 2009 Dec; 129(12): 1664-1668.
 18. Li, C., Hou, Z., Zhang, C., Yang, P., Li, G., Xu, Z., Fan, Y., Lin, J. Controlled Synthesis of Ln³⁺ (Ln = Tb, Eu, Dy) and V⁵⁺ Ion-Doped YPO₄ Nano-/Microstructures with Tunable Luminescent Colors. *Chemistry of Materials*. 2009; 21(19): 4598-4607.
 19. Fang, Y. P., Xu, A. W., Song, R. Q., & Zhang, H. X. Systematic Synthesis and Characterization of Single-Crystal Lanthanide Orthophosphate Nanowires. *Journal of the American Chemical Society*. 2003; 125(51): 16025-16034.
 20. Rao, S. K., Indira, P., & Murthy, K. V. R. Rare Earth doped LaPO₄ Phosphor Synthesis and Characterization. *International Journal of Scientific & Engineering Research*. 2013 Dec; 4(12): 1032.
 21. Pan, B., Zhou, Y., Su, W., & Wang, X. Self-assembly synthesis of LaPO₄ hierarchical hollow spheres with enhanced photocatalytic CO₂-reduction performance. *Nano Research*. 2017; 10:534-545.
 22. Colomer, M. T., Zur, L., Ferrari, M., & Ortiz, A. L. Structural-microstructural characterization and optical properties of Eu³⁺, Tb³⁺ -codoped LaPO₄·nH₂O and LaPO₄ nanorods hydrothermally synthesized with microwaves. *Ceramics International*. 2018; 44: 11993-12001.

23. Phaomei, G., & Yaiphaba, N. Ce³⁺ sensitize RE³⁺ (RE=Dy, Tb, Eu, Sm) doped LaPO₄ nanophosphor with white emission tenability. *Advances in Nano Research*. 2015; 3(2): 55-66.
24. Zainurul, A. Z., Husairi, F. S., Rusop, M., & Abdullah, S. Preparation of nanostructures LaPO₄ films by sol-gel reaction with different annealing temperature. *International Journal of Materials Engineering Innovation*. 2013; 5(1):01211.
25. Lenggoro, W., Xia, B., Mizushima, H., Okuyama, K., & Kijima, N. Synthesis of LaPO₄Tb phosphor particles by spray pyrolysis. *Journal of Crystal Growth*. 2001 Aug; 50(2-3): 92-96.
26. Ramunujam, P., Vaidhyanathan, B., Binner, J., ANshumar, A., & Spacie, C. A comparative study of the synthesis of nanocrystalline YAG using sol-gel and coprecipitation method. *Ceramics International*. 2014; 40(3): 4179-4186.
27. Patil, Y. S., Chaudhari, K. G., Poornachandra Rao, N. V., & Murthy, K. V. R. Synthesis & Photoluminescence study of LaPO₄: Eu, Tb Phosphor. *Archives of Physics Research*. 2011; 2(3):110-115.
28. Brown, S. S., Im, H. J., Rondinone, A. J., & Dai, S. Facile, alternative synthesis of lanthanum phosphate nanocrystals by ultrasonication. *Journal of Colloid and Interface Science*. 2005; 292(1): 127-132.
29. Abdulrahman, A. F., Ahmed, S. M., Hamad, S. M., Almessiere, M. A., & Ahmed, N. M. Effect of different pH values on growth solutions for the ZnO nanostructures. *Chinese Journal of Physics*. 2021; 71: 175-189.
30. Chithra, M. J., Sathya, M., & Pushpanathan, K. Effect of pH on the crystal size and photoluminescence properties prepared by chemical precipitation method. *Acta Metallurgica Sinica (English Letters)*. 2015; 28(3): 394-404.
31. Wang, H. X., Zhango, L., Zhang, Z., Wang, X., & Zhang, Z. Effects of pH value on growth morphology of LaPO₄ nanocrystals: investigated from experiment and theoretical calculations. *Applied Physics A*. 2016; 122:508.
32. Ahmadzadeh, M. A., Chini, S. F., & Sadeghi, A. Size and shape tailored sol-gel synthesis and characterization of lanthanum phosphate (LaPO₄) nanoparticles. *Materials & Design*. 2019; 181:108058.
33. Yan, S. Q. Effect of pH on the microstructure and luminescence of Eu³⁺ doped BiPO₄ phosphors. *Journal of Materials in Electronics*. 2015; issue6.
34. Umar, S., Sulaiman, F., Abdullah, N., & Mohamad, S. N. Investigation of the Effect of pH Adjustment on The Stability of Nanofluid. *AIP Conference Proceedings*. 2018; 2031:020031(1-5).
35. Sridevi, D. V., RamyaDevi, K. T., Jayakumar, N., & Murthy, K. V. R. pH dependent synthesis of TiO₂ nanoparticles exerts its effect on bacterial growth inhibition and osteoblasts proliferation. *AIP Advances*. 2020; 10: 095119.
36. Al-Gebory, L., & Mengüç, M. P. The effect of pH on particle agglomeration and optical properties of nanoparticle suspensions. *Journal of Quantitative Spectroscopy and Radiative Transfer*. 2018; 219: 46-60.
37. Gurubasavaraj, M. P., Anigol, L. B., Charantimath, J. S., & Gurubasavaraj, P. M. Effect of Concentration and pH on the Size of Silver Nanoparticles Synthesized by Green Chemistry. *Research Article*. Vol. 3 Issue 5- September.
38. Rani, S., Suri, P., Shishodia, P. K., & Mehra, R. M. Synthesis of nanocrystalline ZnO powder via sol-gel route for dye-sensitized solar cells. *Solar Energy Materials and Solar Cells*. 2018; 92(12):1639-1645.
39. Wang, X., Zhang, L., Zhang, Z., & Wang, X. Effects of pH value on growth morphology of LaPO₄ nanocrystals: investigated from experiment and theoretical calculations. *Applied Physics A*. 2016; 122:508.
40. Ningombam, G. S., & Nongmaithem, R. S. Morphology and photoluminescence of self-assembled CaWO₄+ microspheres: effect of pH and surfactant concentration. *International Nano Letters*. 2017; 7:133-140.
41. Krishna, P. H., & Ramrakhiani, M. Nano Particle Size Effect on Photo-Luminescence. *International Journal of Nanotechnology and Applications*. ISSN 0973-63.
42. Yang, K. S., Wu, A. P., Zhao, X., Yan, Y., Guo, X. Y., Bian, Y. L., Bao, J. R., Li, W. X., & Zhu, X. W. Controlled synthesis of EuPO₄ nano/microstructures and coreshell SiO₂@ EuPO₄ nanostructures with improved photoluminescence. *RSC Advances*. 2017; 7:52238-52244.
43. Liu, C., Zhang, F., Hu, J., Gao, W., & Zhang, M. A Mini Review on pH-Sensitive Photoluminescence in Carbon Nanodots. *Frontiers in Chemistry*. 2021; 8:2020.

44. Benilor, A., Chenko, C., Benilova, I., Skryshevsky, V., & Cabrera, M. Influence of pH solution on photoluminescence of porous silicon. *Sensors and Actuators A*. 2007; 137: 345-349.
45. Karaba, P. The Effect of pH on the Photoluminescent Properties of Silicon Nanoparticles. University Honors Theses. 2016; Paper 337. <https://doi.org/10.15760/honors.32>.
46. Fernando, I., & Zhou, Y. Impact of pH on the stability, dissolution and aggregation kinetics of silver nanoparticles. *Chemosphere*. 2019; 216: 297-305. doi:10.1016/j.chemosphere.2018.10.122.
47. Mendoud, A., Guerbous, L., Boukerika, A., Boudine, B., & Benrekaa, N. Effect of pH value on structural and photoluminescence properties of Tb³⁺-doped Lu₂O₃ nanopowders synthesized by sol-gel route. *Optical Materials*. 2018; 75:802-808.
48. Gorshkov, O. N., Dmitryuk, A., & Kaminy, V. A. Luminescence quenching in erbium doped phosphate glass film irradiated with hydrogen ions. *Technical Physics Letters*. 2013; 30(4):325-327.
49. Jarosewich, E., & Boatner, L. A. Synthesis and characterization of lanthanum phosphate sol for fibre. *Geostandards Newsletter*. 1991; 15:397.
50. Hernandez, A. G. Synthesis by hydrothermal process of lanthanide orthophosphates for optical applications. Université Blaise Pascal - Clermont-Ferrand II. 2015. English. NNT: 2015CLF22564.
51. Majeed, S. M., Bashir, M., & Shivashankar, S. A. Dispersible crystalline nanobundles of YPO₄ and Ln (Eu, Tb)-doped YPO₄: rapid synthesis, optical properties and bio-probe applications. *Journal of Nanoparticle Research*. 2015; 17:1-15.
52. Wang, X., S, L., Su, R., Wendt, S., Hald, P., Mamakhel, A., Yang, C., Huang, Y., Iversen, B. B., & Besenbacher, F. The influence of crystallite size and crystallinity of anatase nanoparticles on the photo-degradation of phenol. *Journal of Catalysis*. 2014 Feb; 310:100-108.
53. Hindeleh, M., & Johnson, D. J. Crystallinity and crystallite size measurement in polyamide and polyester fibres. Vol 9 Issue 1. 1978; p27-32.
54. Matsushima, N., & Hikichi, K. Age changes in the crystallinity of bone mineral and in the disorder of its crystal. *Biochim Biophys Acta*. 1989; 18; 992(2):155-9.
55. Aparecida P.G., L. Raphael, & Ferrani, T. L. pH effect on the synthesis of different size silver nanoparticles evaluated by DLS and their size dependent antimicrobial activity. *Materia (Rio J)*. 2020; 25(4).
56. Konopa, J. Options for Quantitative Analysis of Light Elements by SEM/EDS. Thermo Fisher Scientific, Madison, WI USA. 2013.
57. Heslop-Harrison, J. S. Energy Dispersive and X-ray Analysis. *Physical Methods in Plant Science*. 1990; Vol 11. ISBN 978-3-642-83613-8.
58. Groeneveld, M., Catalan, N., Einarsdottir, K., Bravo, A. G., & Kothawala, D. N. The influence of pH on dissolved organic matter fluorescence in inland waters. *Journal of Analytical Methods*. 2022; Issue 13.
59. Hiramoto, R., Juran, J., & Hamin, M. The effect of Hydrogen ion concentration of fluorescent labelled antibodies.
60. Yan, Y. C., Faber, A. J., de Waal, H. W., Luminescence quenching by OH⁻ groups in highly Er-doped phosphate glasses. *Journal of Non-Crystalline Solids*. 1994; 181(3):283-290.
61. Wu, M., Park, H., Lee, E. G., Lee, S., Hong, Y. J., & Choi, S. Luminescence Quenching behavior of hydrothermally Grown YVO₄: Eu³⁺ Nanophosphor excited under Low temperature and vacuum ultraviolet discharge. *Materials (Basel)*. 2020; 13(15):3270.