

Synthesis and Characterization of Luminescence Emission in Blue Emitting Li (Ca_{1-x}Eu_x) PO₄ (X=0.005, 0.01, 0.03) Phosphors

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Abstract

Over the past decades, the common approach to the production of the white Light Emitting Diodes in the lighting industry has been the use of a blue InGaN Light Emitting Diode together with a color correction' red emitting phosphor and yellow-emitting phosphor Y₃Al₅O₁₂: Ce³⁺. However, white Light Emitting Diodes near the Ultra Violet Light Emitting Diode can be combined with the red, green, and blue phosphors. Their combination is due to their improved binging and less the Ultra Violet Light Emitting Diode's current droop, as well as a better control of the color temperature and color rendering index through the phosphor blends manipulation (Kang 79). The phosphors mentioned above require very high absorption in the range near-Ultra Violet region (Thakur et al. 42). The strong absorption can be obtained from the dipole-allowed 4f and 5d transitions in the rare earth activated ions, such as the Eu²⁺ and the Ce³⁺, in a suitable host (Brown and Shand 73). For this approach, the examined phosphors are Ba₂MgSi₂O₇: Eu²⁺, β-Si AlON-+: Eu²⁺ and (Sr, Ba)₂SiO₄: Eu²⁺ for the green emitting component, CaAl₂SiN₃: Ce³⁺ and Sr₃SiO₅: Eu²⁺ for the orange/ yellow-emitting component, and (Sr, Ca)₂Si₃N₈: Eu²⁺ for the red-emitting component.

Keywords: Spectroscopic condition; Electro vibronic; Wavelength; Yellow; Green blue range

Introduction

Globally phosphate compounds are widely used since they tend to be paramount material in the overall utility and development in the scientific progress. It is as a result of their unwavering characteristics such as, their thermal capabilities, charges stabilities that they display, environmental friendliness, low cost that gets associated with them and their availability in naturally. Solid-state luminescence is getting preferred to gas discharge in various capacities and measurements. Therefore it is of adamant to comprehend the mechanism of the transfer of energy and the behavior of the photoluminescence typically of phosphate and th0e phosphors. This paper gives a review on the synthesis and characterization of luminescence emission in rare earth elements with activated phosphate compound for the lamp industry.

In recent times, materials for inorganic luminescent are highly on the use of the quotation equipment on the studies based on the spectroscopic conduction, acquisition and in applications of the substances. The orthophosphates as a result of their mixed properties and their rarity on earth are known to be a critical class of the host lattices acting as ions of activators as a result of their physical energy thus giving the phosphors their capabilities to be used, and when compared to other elements comparatively, they are more durable. The materials have also been known to induce excitabilities in places with ultraviolet radiations This experimental research on phosphors needs a diversified combination of interdisciplinary strategies and techniques. Phosphate compounds doped with Dy is based on physical and inorganic chemistry, with the luminescence mechanism being interpreted and elucidated dependent of solid state physics. The ability gives them an upper hand in fluorescent lamps that do not use mercury. Consequently, mercury is being reduced in its application since it is hazardous to the environment. They are also employed in cathode-ray tubes, television projections, and the field emission displays. Currently, emphasis and intensive research are getting conducted on different phosphor material to unravel their properties of luminescence together with their display devices and mechanisms [1]. When inorganic compounds get doped with some rare ions, they produce fascinating attributes such as softly emitted colors with

quite a good number of activators, incredible chemical stability and promising efficiency in luminescence. Phosphate based compounds are crucial hosts in delivering large crystal field situations that get forced on outflow centers, and also the doped phosphates with ions of rare earth are known to have adamant thermal stability. Phosphors that get incorporated in phosphates have also been studied. When they get activated with EU3+ ions for diodes, they emit white light [2]. When all there is integrated into the mind, the ability of the doped EU material in the solid-state and the stable luminescent characteristic displayed within limited periods or time is what has triggered most scientists to establish the application of the concept specifically in the industry [3]. Ce3+ ground state is split (2F5/2, 2F7/2), these are the only levels possible for 4f configuration. f-f transitions in Ce3+ are in IR region. At RT, they occur as unresolved bands with maximum at about 2200- 2300 cm⁻¹ and half – width 250-300 cm⁻¹. At low temperature, the band splits into some lines, which are due to f-f transitions and electro-vibronic transitions 1, 2, 3, 4, 5. The excited states above 2F7/2 level belong to 5d configuration in the form of broad bands. Most commonly observed emission is characteristics of 5d (4f transition). Both absorption and emission have usually a broad band character this experimental research on phosphors needs a diversified combination of interdisciplinary strategies and techniques. Phosphate compounds doped with Dy is based on physical and inorganic chemistry, with the luminescence mechanism being interpreted and elucidated dependent of solid state physics Typically two types of luminescence are; incandescence, which refers to the glowing of light when some material are heated leading to the production of bright light. Secondly, we have luminescence which

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encompasses a group of phenomena where materials provide light without any substantial heating. There are also 17 rare earth elements of vital importance, which are found unevenly distributed worldwide. Exploitation, understanding, manipulation and utilization of these substances give the basis of this case study experiment.

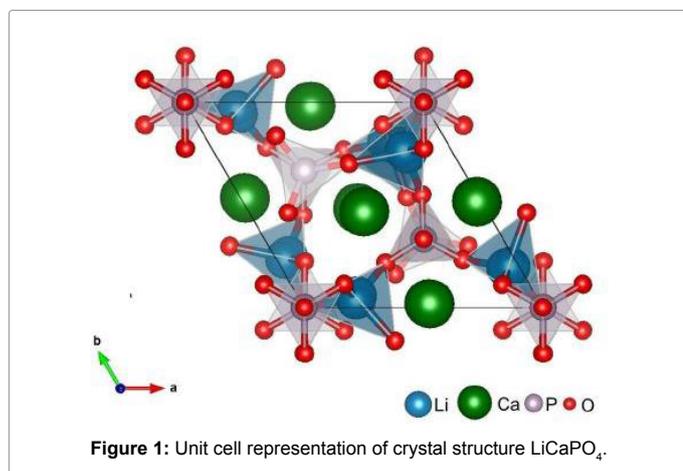
Experiment and Materials

The desired molar ratios of Eu₂ (99.999 percent Alfa Aesar), Ca (NO₃)₂·4H₂O (99.99 percent Mallinckrodt Chemicals), and LiNO₃ (99 percent Alfa Aesar) were dissolved in a solution of dilute nitric acid. (NH₄)₂HPO₄ which is one of the Emanuel Merck Darmstadt chemicals was then added to the mixture as the reagent for the PO₄³⁻. Before the addition of the (NH₄)₂HPO₄, the pH for the mixtures was kept at a value less than two to prevent the occurrence of precipitation with the LiNO₃ and Ca (NO₃)₂·4H₂O (Gregorkiewicz, 52). The solution was then let to become transparent, after which citric acid (C₆H₈O₇·H₂O, Emanuel Merck Darmstadt Chemicals) was added to act as the chelating agent for the metal ions. Ethylene glycol was also added. Polyethylene glycol weighing at 1.0 grams was added to the aqueous solution as a cross-linking agent and the mixture stirred well to bring about uniformity. It was then placed in a water-bath of 80 degrees Celsius for the purpose of hydrolyzing it into a solution and, consequently, a gel.

The gel was then subjected to heat at 800 degrees Celsius for an hour in the air, so that the organic material and carbon would be successfully removed. Then in a slightly reducing atmosphere, achieved through a mixture of 95 percent N₂ and 5 percent H₂, the gel was annealed at a temperature of between 800-1150 degrees Celsius. The particle size and morphology measurement was carried out through the field emission scanning electron microscope, while the X-ray diffraction identified the annealed powders' crystalline phases. The phases' percentages and peak were determined through the use of the X-Ray Diffractometer analysis program. The spectrum one charge-coupled device detection systems and the Jobin-Yvon Triax 180 monochromator were used in taking the photoluminescence measurements with the excitation source being a 450 W Xe lamp. A 400 nm laser diode excitation source was used in taking the Quantum Efficiency (QE) measurements.

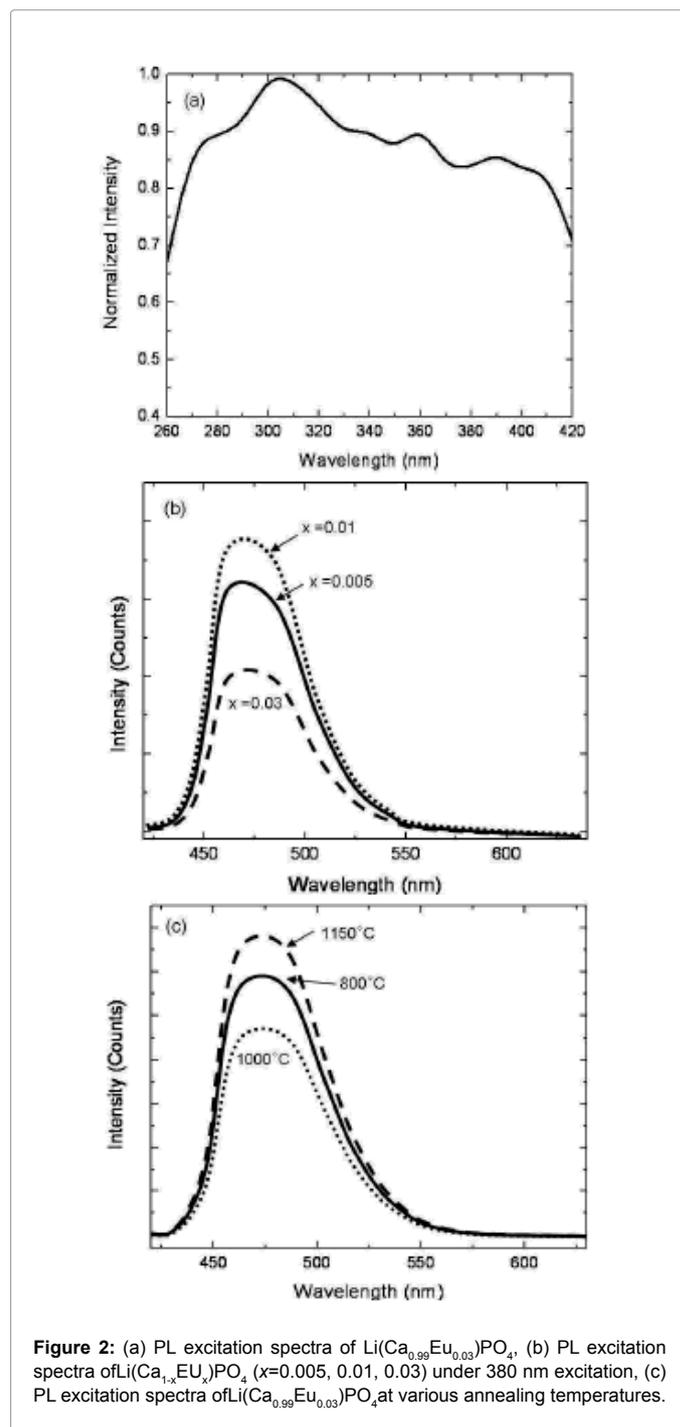
Results and Discussion

All the samples demonstrated the central peak of the LiCaPO₄ (Figure 1) at 2θ=32.81 degrees. However, Eu²⁺ (with x=0.03) higher concentrations distorts the hexagonal structure with Ca₃(PO₄)₂ and Li₃PO₄ being the dominant phases showing increased peaks of 31.01 degrees for the Ca₃(PO₄)₂ and 33.89 degrees for Li₃PO₄. The X-Ray



Diffractometer program estimated the amounts of Li₃PO₄, Ca₃(PO₄)₂, and LiCaPO₄ to be 5 percent, 15 percent, and 80 percent respectively. The peak intensities for Li₃PO₄ and Ca₃(PO₄)₂ increased with the increasing temperatures with 800°C being the optimal temperature of annealing.

The Li(Ca_{0.99}Eu_{0.01}) PO₄ excitation spectrum covers the wavelength range from the visible region to the Ultra Violet region with the phosphorous exciting efficiently in the regions between 280 nm to 410 nm (Figure 2). The spectrum consisted of a strong, broad blue band that was centered about the 470 nm and this can be attributed to the



Eu²⁺ allowed 5d to 4f transition (Righini et al. 78) [4]. The intensity of the emission increases with an increase in x showing a maximum at x=0.01, besides recording a decrease at x=0.03 (Figure 3). The decrease is as a result of the presence of impurity phases within the powders (Liu et al. 82).

For the purpose of increasing the crystallinity and the emission intensity of the powders, higher annealing temperatures are required (Figure 4) (Liu et al. 82) [5]. However, the impurity phases form at temperatures beyond the 800 degrees Celsius. In this regard, the powders were re-annealed at the 800 degrees Celsius (Figures 5 and 6). The powders that annealed at the 1150 degrees Celsius are the mixtures of the Li₃PO₄, Ca₃(PO₄)₂, and LiCaPO₄. However, the products that re-annealed at the 800 degrees Celsius was LiCaPO₄ and a minuscule amount of the Li₃PO₄, Ca₃(PO₄)₂ at about 5 percent. These results suggest that, during the process of re-annealing at 800 degrees Celsius, the impurity phases undergo reactions to form LiCaPO₄ [6].

The re-annealed powders' emission intensity proved higher compared to that of the powder annealed at the 1150 degrees Celsius. Additionally, the re-annealed powder's quantum efficiency increased from 62 percent to 73 percent. The results also demonstrate that the phase purity of the Li (Ca_{1-x}Eu_x) PO₄ carries out a vital role in the improvement of its luminescence properties. However, the high values of the quantum efficiency show that the phase Li (Ca_{1-x}Eu_x) PO₄ stands a chance as a blue emitter for applications in the white-emitting Ultra Violet Light Emitting Diodes.

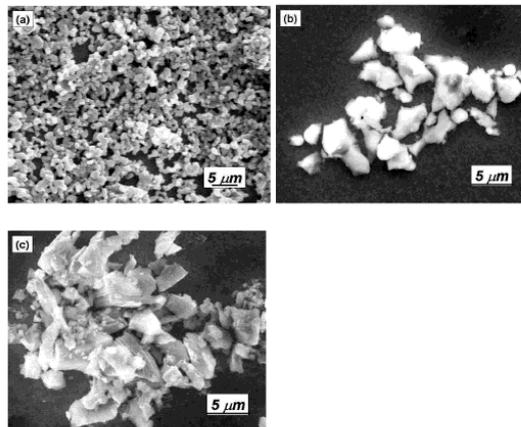


Figure 4: SEM micrographs of Li(Ca_{0.99}Eu_{0.03})PO₄ annealed at (a) 800°C, (b) 1000°C, and (c) 1150°C.

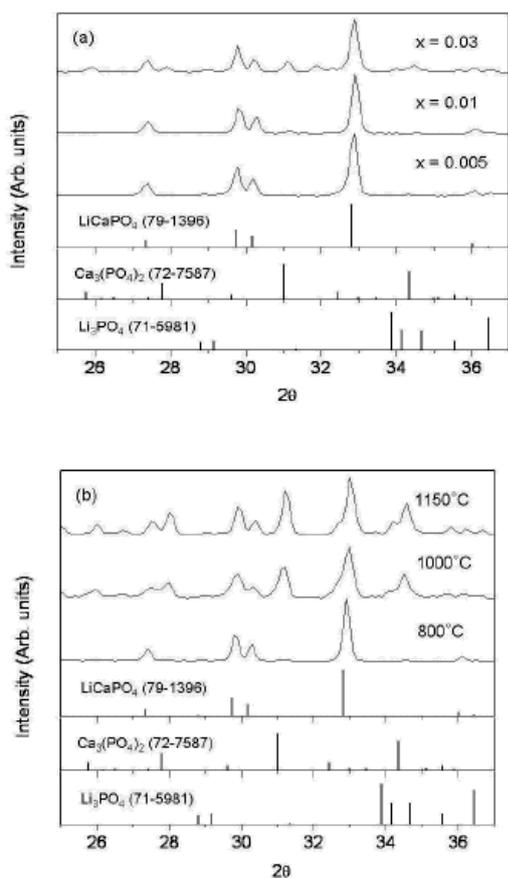


Figure 3: XRD patterns of (a) Li(Ca_{1-x}Eu_x)PO₄ (x=0.005, 0.01, 0.03) phosphors and (b) Li(Ca_{1-x}Eu_x)PO₄ (x=0.01) at various post synthetic annealing temperatures.

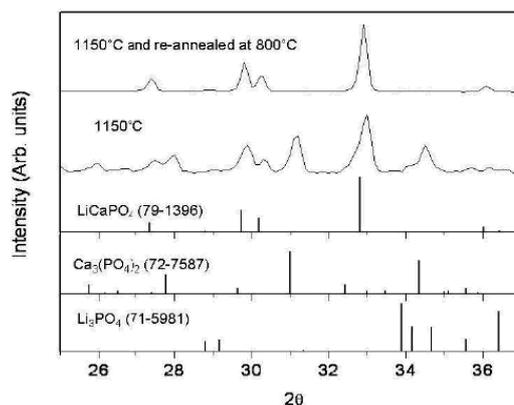


Figure 5: XRD patterns of Li(Ca_{0.99}Eu_{0.03})PO₄ annealed at 1150°C and re-annealed at 800°C.

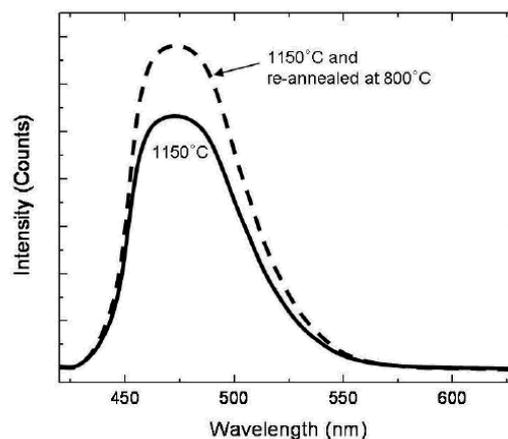


Figure 6: XRD patterns of Li(Ca_{0.99}Eu_{0.03})PO₄ annealed at 1150°C and re-annealed at 800°C under 380 nm excitation (Liu et al. 82).

Conclusion

The preparation of the single-phase powders of the blue emitting phosphors Li (Ca_{1-x}Eu_x) PO₄ for x=0.005, 0.01, and 0.03 was done

through the method of sol-gel/Pechini. The method is simpler and faster than the solid state reaction. The impurity phases were discovered at higher temperature of annealing that is greater than 800 degrees Celsius. At these temperatures, the spherical morphology of the substance transforms into irregular shapes. The phosphors are efficiently excited in the near Ultra Violet region and Deep Ultra Violet region (370 nm-410 nm). They also show a strong blue emission band that is centered near the 470 nm. Re-annealing of powders at higher temperatures results in the production of higher emission intensity single phase powder besides an increase in the quantum efficiency. Therefore, a conclusion can be reached that Li (Ca_{1-x}Eu_x) PO₄ blue phosphors stand as a potential candidate that can be applied in the lighting industry for the white-emitting Ultra Violet Light Emitting Diodes.

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