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Theoritical studies of Luminescence Emission in Europium Doped phosphate Compounds

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Abstract

This paper will discuss the experimental procedure of how the element of rare-earth is doped by phosphate compounds in the production of the industrial light. The interest in the use of rare-earth metals has tremendously increased due to their high industrial demand. The high demand is attributed to the luminescent properties of their Corresponding ions.The Europium is used to activate various compounds such as borates, and phosphates. Phosphates are widely used due to their application in the manufacture of various product such as display devices, visible luminophores, opticalfibers,optoelectronics etc. The transformation of phosphates in to other forms is achieved at elevated temperatures. These rare-earth doped phosphates are characterized by large specific surface area and high melting temperatures. Some of the commonly used rare-earth metals include lanthanum, Cerium, and Dysprosium among others. The Eu emission is intenseenough to find important industrial applications.

Keywords : Anneling, quantum efficiency, X-Ray Diffractometer, sphericalmorphology, Unit cell

INTRODUCTION:

The light plays a crucial role in our daily human lives, and it is an essential part of science in the 21st century. The light-based technologies have transformed various aspects of science and technology to a larger extent. Notable research efforts have been directed to explore for environmentally friendly, reliable and energy economic phosphor candidates for the application in the solid-state lighting devices [1-2]. The thrust of phosphor materials with improved luminescent properties in multidisciplinary areas has combined the research efforts in this field focused towards attaining superior material properties [3]. Rare earth (RE) ions are counted as leading activators luminescent centers in numerous inorganic host lattices and described by a partially filled 4f shell that is enclosed by 5s2 and 5p6 electrons hence, broadly integrated to produce phosphors with high quantum efficiency [4]. The incorporation of the small amount of RE ions into a host matrix came into existence as a promising method for regulating the optical and photoluminescence (PL) properties [4].

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 $Y_3Al_5O_{12}$: Ce^{3+}. 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 brightening 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 [5]. The phosphors mentioned above require very high absorption in the range near-Ultra Violet region[6-7] For this approach, the examined phosphors are $Ba_2MgSi_2O_7$: Eu^{2+}, β-SiAlON-+: Eu^{2+} and (Sr, Ba) $_2SiO_4$: Eu^{2+} for the green emitting component, $CaAlSiN_3$: Ce^{3+} and Sr_3SiO_5: Eu^{2+} for the orange / yellow-emitting component, and (Sr, Ca) $_2$ Si_5N_8: Eu^{2+} for the red-emitting component. [8]

Experiment and Materials

The desired molar ratios of Eu_2O_3Ca $(NO_3)_2$, $4H_2O$, and $LiNO_3$ were dissolved in a solution of dilute nitric acid. $(NH_4)2HPO_4$ which was then added to the mixture as the reagent for the PO_4^{3-}. Before the addition of the $(NH_4)_2HPO_4$, the pH for the mixtures was kept at a value less than two to prevent the occurrence of precipitation with the $LiNO_3$ and Ca $(NO_3)_2.4H_20$ [9]. The solution was then let to become transparent, after which citric acid ($C_6H_80_7.H_2O$) 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 N_2 and 5 percent H_2, 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 $LiCaPO_4$(Fig. 1) at 2θ = 32.81 degrees. However, Eu^{2+} (with x= 0.03) higher concentrations distorts the hexagonal structure with Ca_3 $(PO4)_2$ and Li_3PO_4 being the dominant phases showing increased peaks of 31.01 degrees for the Ca_3 $(PO_4)_2$and 33.89 degrees for Li_3PO_4. The X-Ray Diffractometer program estimated the amounts of Li_3PO_4, Ca_3 $(PO_4)_2$, and $LiCaPO_4$ to be 5 percent, 15 percent, and 80 percent respectively. The peak intensities for Li_3PO_4 and Ca_3 $(PO_4)^2$ increased with the increasing temperatures with 800°C being the optimal temperature of annealing.

The $Li(Ca_{0.99}Eu_{0.01})$ PO_4 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 (Fig. 4). The spectrum consisted of a strong, broad blue band that was centered about the 470 nm and this can be attributed to the Eu^{2+} allowed 5d to 4f transition [10]. The decrease is as a result of the presence of impurity phases within the powders[11]

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 (Fig 5-6). The powders that annealed at the 1150 degrees Celsius are the mixtures of the Li_3PO_4, Ca_3 $(PO_4)_2$, and $LiCaPO_4$. However, the products that re-annealed at the 800 degrees Celsius was $LiCaPO_4$ and a minuscule amount of the Li_3PO_4, Ca_3 $(PO_4)_2$at an about 5 percent. These results suggest that, during the process of re-annealing at 800 degrees Celsius, the impurity phases undergo reactions to form $LiCaPO_4$.

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 $(Ca_{1-x}Eu_x)$ PO_4 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 $(Ca_{1-x}Eu_x)$ PO_4 stands a chance as a blue emitter for applications in the white-emitting Ultra Violet Light Emitting Diodes.

Conclusion

The preparation of the single-phase powders of the blue emitting phosphors Li $(Ca_{1-x}Eux)$ PO_4, for x= 0.005, 0.01, and 0.03 was done through the method of sol-gel.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 Violetregion and Deep Ultra Violet region (370nm-410nm). They also show a strong blue emission band that is centered near the 470nm. Therefore, a conclusion can be reached that Li $(Ca_{1-x}Eu_x)$ PO_4 blue phosphors stand as a potential candidate that can be applied in the lighting industry for the white-emitting Ultra Violet Light Emitting Diodes

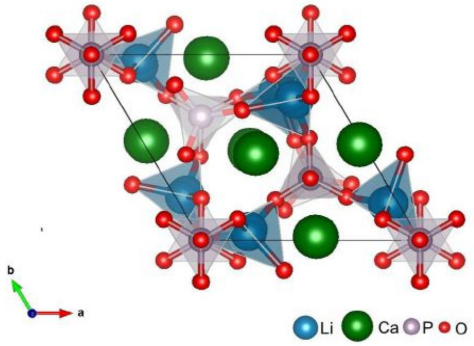

Figure 1.Unit cell representation of crystal structure $LiCaPO_4$

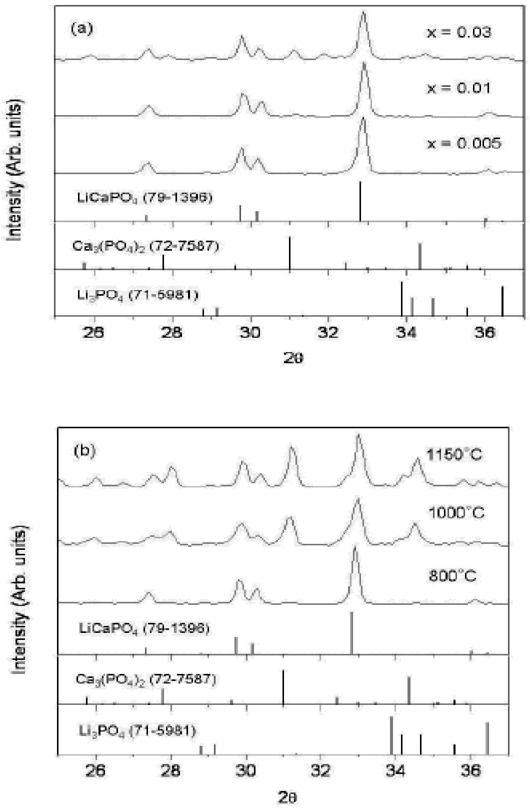

Figure .2. XRD patterns of (a) Li($Ca_{1-x}EU_x$)PO_4 (x =0.005, 0.01, 0.03) phosphors and (b) Li($Ca_{1-x}EU_x$)PO_4 (x =0.01) at various post synthetic annealing temperatures

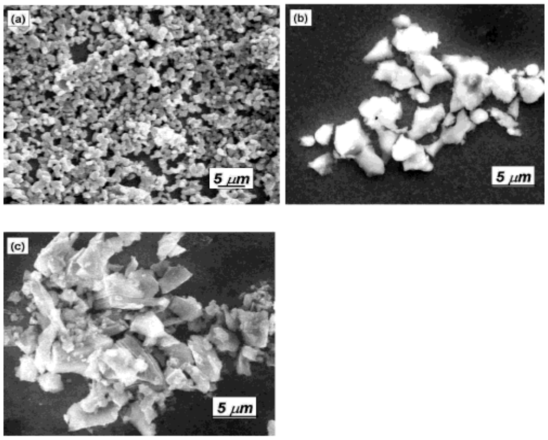

Figure 3. scanning electron microscopic image of (SEM) micrographs of Li($Ca_{0.99}Eu_{0.03}$)PO_4 annealed at (a) 800°C, (b) 1000°C, and (c) 1150°C.

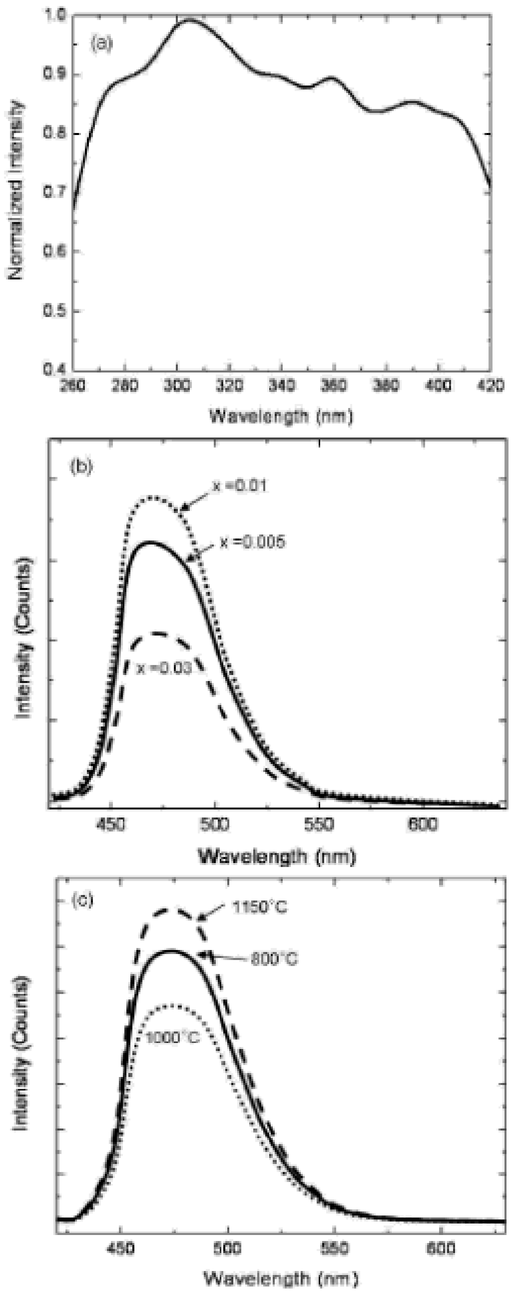

Figure 4. (a)PL spectra of Li(Ca 0.99Eu 0.003) PO_4 (b) PL excitation spectra ofLi($Ca_{1-x}EU_x$)PO_4 (x =0.005, 0.01, 0.03) excited at 380 NO (c)

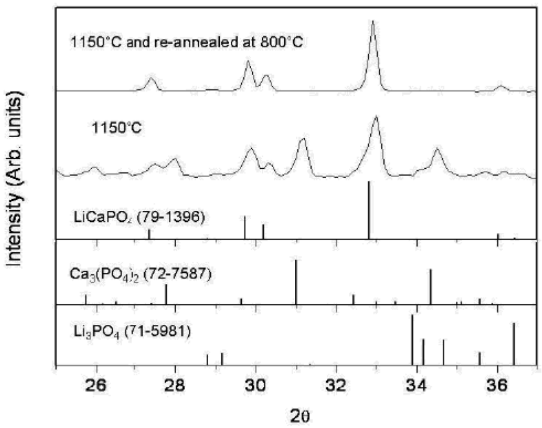

Figure 5. XRD patterns of Li(Ca$_{0.99}$Eu$_{0.03}$)PO$_4$annealed at 1150^{0}C and re-annealed at 800^{0}C (Liu et al. 82).

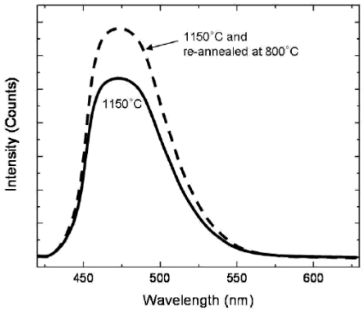

Figure 6. PL spectra of Li(Ca$_{0.99}$Eu$_{0.03}$)PO$_4$ annealed at 1150^{0}C and re-annealed at 800^{0}C under 380 nm excitation

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