

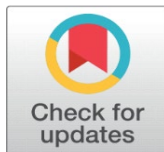
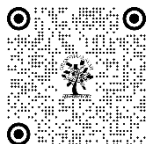
THE OPTICAL AND STRUCTURAL CHARACTERISTICS OF THE SERIES OF EU+3 – DOPED SELF-ACTIVATED VANADATE GARNET PHOSPHORS

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ABSTRACT

The Garnet phosphors have always earned extensive attraction due to their optical and structural properties. The garnet materials have a wide range of applications. CLZVO: Eu3+ prepared by conventional combustion method. The emission color of the prepared sample can be easily controlled by the different compositions of the sensitizer. The materials were excited by ultraviolet energy. The as-prepared sample has undergone various investigations like XRD, Photoluminescence excitation, emission and SEM and for color chromaticity. The materials can be used to prepare LEDs, optical temperature sensors, active powder in solid-state laser and CRT.

Keywords: Photoluminescence, Solid State Reaction, Garnet Phosphor, Temperature Sensor

1. INTRODUCTION

Nowadays, the garnet structure phosphors play a vital role in optics. Due to their high tunability, effective structure flexibility and optimum efficiency, the researchers are paying attention to them. The universal formula for garnet structure nanomaterials is $A_3B_2C_3O_{12}$. Where A is for the dodecahedral coordinated site, B is for the octahedral and C is for the tetrahedral coordinated sites of the structure. In the standard formula, the B & C either may be the same or different group/s also B and C point to 8 and 6 coordinated cationic sites. The large trivalent cations taken by A sites and smaller trivalent cations taken by B sites. The garnet structure can be represented by the cubic unit cell containing 160 atoms. An atom takes up 24 places within the 8-fold dodecahedral coordination and B atoms take up 16 places within the 6-fold octahedral coordination whereas C atoms take up 24 places within the 4-fold tetrahedral coordination [1]. The

space group is Ia-3d for the garnet-structured phosphors. The structure of garnet material is depicted as shown in figure (1).

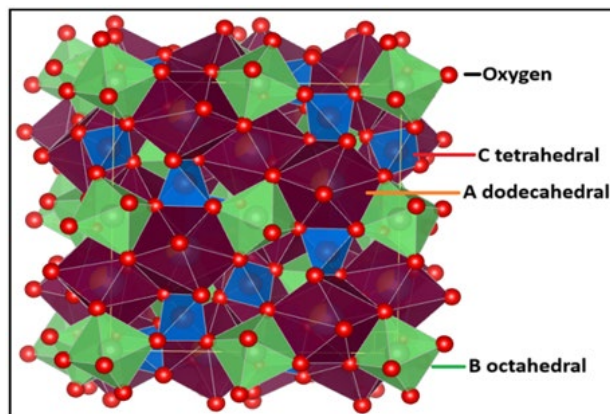


Figure 1 The polyhedral structure of garnet phosphor A₃B₂C₃O₁₂ by mentioning A, B and C as dodecahedral, octahedral and tetrahedral coordinated sites respectively.

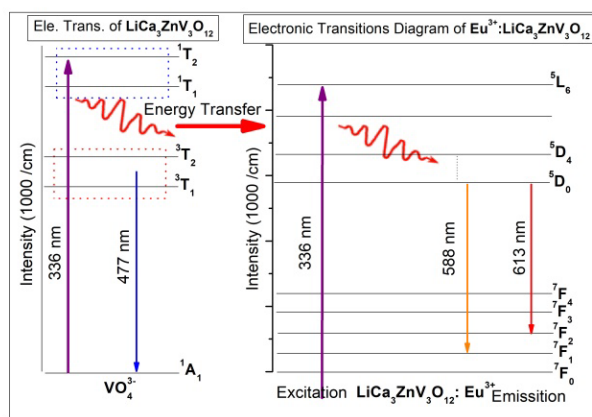


Figure 2 Energy level diagram of Eu³⁺ with absorption and emission lines of transitions in the LiCa₃ZnV₃O₁₂:Eu³⁺ garnet crystal

The word 'Garnet' comes from the Latin word 'Granatum' meaning "many grains" which is related to the pomegranate fruit. This fruit has a lot of Red Seeds that look like some dark-red garnet gemstones in both structure and color. Garnets (gemstones) have been used since time of the Bronze Age, which is a really long time ago. For thousands of years garnets have served as Abrasives (i.e. means abrasives are materials used for grinding, cutting and polishing other materials by rubbing or wearing them away through friction). Due to their toughness and as gemstones corresponding has their high refractive index and vibrant colors. The rare earth nanoparticles have great thermal Stability [2].

The garnet phosphor has been used in a wide range of lighting devices based on its spectrum. LiCa₃ZnV₃O₁₂:xEu³⁺ (x = 0%, 0.5%, 1%, 2%, 3% and 5%) were prepared by conventional combustion method pre-heat at 500°C. We used urea as the burning fuel. The vanadate-rich garnet phosphor LiCa₃ZnV₃O₁₂ can show an emission spectrum at 484 nm (bluish) [3]. We doped europium ions (Eu³⁺) in the vanadate-rich garnet structure phosphor to increase the luminescence efficiency [4].

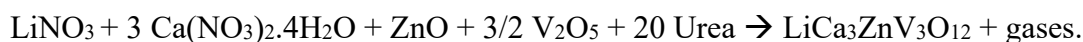
The europium ions (Eu³⁺) have taken the site of calcium. The europium-rich phosphors are applicable in solid-state laser and pure white LEDs due to their optical properties [5-7]. The absorbance coefficient is low as suitable due to narrow excitation in the transition from 7F₀ to 5L₆ and emission 5D₀ to 7F_i (i=0,1,2,3,4) as shown in figure (2) [8].

The garnet structured phosphor materials LiCa₃ZnV₃O₁₂ was given lanthanide free emission which is very cost effective. It is purely inorganic phosphor involving pentavalent vanadate. LCZVO: Eu³⁺ emits red phosphors because it has high efficiency in converting energy into light, strong absorption properties and long-term stability. It is used in

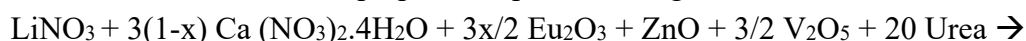
cathode ray tubes, fluorescence thermometry optical properties change with temperature. To enhance colour accuracy of light, we're considering using a mix of red and green phosphors [9].

2. MATERIALS AND PREPARATION

The raw materials in analytical reagent grade were used to prepare $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$. We used the combustion method to prepare this material. We used Lithium nitrate (LiNO_3 99.995 MERCK), Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ACS MERCK), Zinc oxide (ZnO ACS MERCK), Vanadium pentoxide (V_2O_5 MERCK), Europium oxide (Eu_2O_3 99+ MERCK) and Urea as fuel. $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ was prepared by the following reaction;



$\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{xEu}^{3+}$ were prepared as per following reaction;



$\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{xEu}^{3+} + \text{gases.}$ To prepare $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{xEu}^{3+}$ ($\text{x} = 0\%, 0.5\%, 1\%, 2\%, 3\%$ and 5%), first we weighed europium oxide for all concentrations and then added nitric acid by dropper as dropwise and was reaction took place and europium nitrate was formed. According to stoichiometric ratios, we first weighed all raw materials by a four-decimal electric digital balance and then transferred them into a china disc of four inches. The raw materials were mixed uniformly by pastel. Combustion reaction (method) exothermic reaction that means when we mixed the materials then metal nitrate works as oxidizing while urea works as deducing agents. This china disc burst in an electric furnace at pre-heated at 500°C . The final product was prepared after bursting for a few seconds.

The burst ash of the product was crushed by pastel in the same china disc to form a fine powder. There is some gel in the product due to vanadate, so we heated it at 600°C for 30-40 minutes to increase crystallinity and provide a quenching process to cool at room temperature. Left them for some time to cool and then again crushed them until product materials were converted into fine powder. The fine powder was transferred in a centrifuge bottle and then sent for further characterization. The whole process is shown in Figure (3).

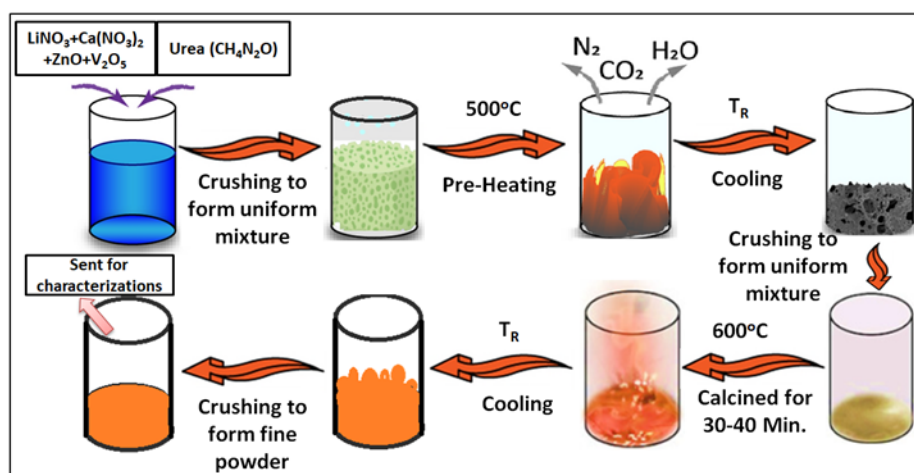


Figure 3 Detailed process to synthesize the garnet structure phosphor by conventional combustion method.

3. CHARACTERIZATION: INSTRUMENTS AND SOFTWARE CONFIGURATIONS

The structural properties were studied by an X-ray diffractometer Rigaku Miniflex 600 of wavelength $\lambda = 1.54059 \text{ \AA}$ with Cu $\text{K}\alpha$ source of radiation at scanning rate $4^\circ/\text{min}$. The luminescence properties were studied by Spectrophotometer (F-7000 FL, 1914-024, Version-5J14000 03) for photoluminescence. The emission and excitation are recoated at a step of 0.2 nm by a 135 W Xe lamp. The morphological and compositional characterizations were optimized by FE-SEM JEOL, JSM-6500F with 80 W Xe light source of 25 kV high tension voltage between anode to cathode electron accelerating voltage.

4. RESULT ANALYSIS

1) Structural studies (XRD):

The single-phase garnet-structured phosphor $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ was cauterized by XRD for structural studies and densification of phases. Figure 4(a) shows the comparison between XRD patterns of $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$, $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$ and the standard XRD pattern of PDF number 000630654. All peaks of $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ matches with a standard pattern. There is no affecting on the XRD pattern due to doping of europium in host garnet.

Figure 4(b) depicts the XRD data which simulated via Rietveld refinement by FullProf_Suite software. The value of chi square is 1.26 which is very good agreement with the standard file. The R and R_w values gave agreed results. The garnet structure $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ is described as a cubic structure with translational lattice parameters ($a = b = c = 10.8962$ Å). The prepared material is garnet structured material having space group Ia-3d with space group international number 230 [15]. This cubic structure has a dodecahedral coordinated site (A with O₈), octahedral coordinated site (B with O₆) and tetrahedral coordinated site (C with O₄) as shown in fig. (1). The dodecahedral coordinated site (A) contains Ca^{2+} ions and formed CaO_8 similarly, octahedral coordinated site (B) contains Li^+ & Zn^{2+} ions and formed ZnO_6 - Li^+ due to their ionic radii [16] and tetrahedral coordinated site (C) contains V^{5+} ions and formed VO_4 . The Wyckoff symbols are given in Table 1.

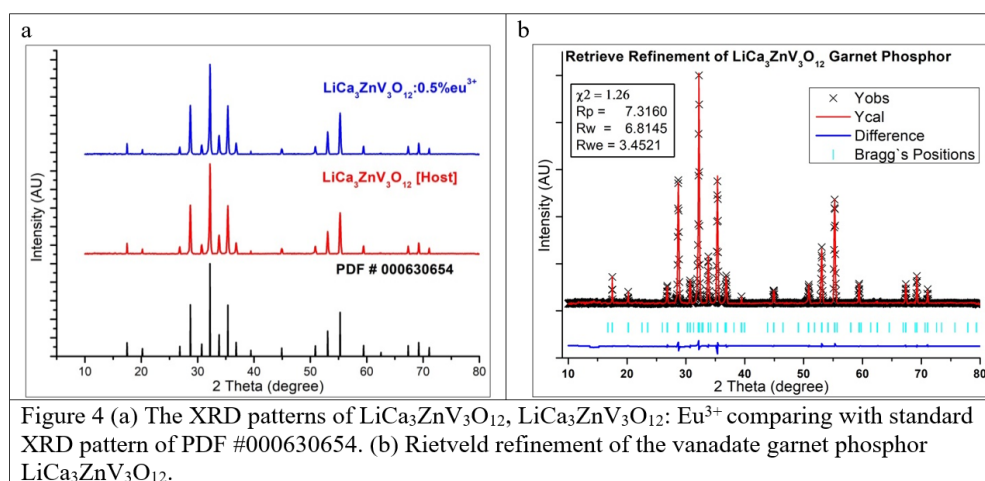


Figure 4 (a) The XRD patterns of $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$, $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$ comparing with standard XRD pattern of PDF #000630654. (b) Rietveld refinement of the vanadate garnet phosphor $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$.

Table 1 Details of phase identification of XDR data with Rietveld refinement

Parameters	$\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ Garnet
Crystal lattices	Cubic
Space group	Ia-3d
Z	8
Translational lattice parameters ($a = b = c$) in nm	1.08962 nm
Volume of unit cell (nm^3) ³	1.29367 nm^3
Chi ²	1.26
R	7.3160
R_w	6.8145
Expected R_w	3.4521
Wyckoff symbols	
Ca^{2+}	24c
Zn^{2+}	16a
Li^+	16a
V^{5+}	24d
O (for Ia-3d)	96h

2) Morphological study (by Scanning Electron Microscope):

The SEM image of europium-doped vanadate garnet phosphor is shown in Figure 5(a). This image depicts the surface of the prepared materials which is irregular granules. The image is studied by ImageJ software and the particle sizes are in the range of 1 μm to 5 μm and the average grain size was determined at 1.988781 μm . The histogram of the average diameter of grains is shown in figure 5(b). As per J.B. Gruber et al, the morphology is the same when increasing temperature [13]. The particle size of materials containing zinc changes randomly.

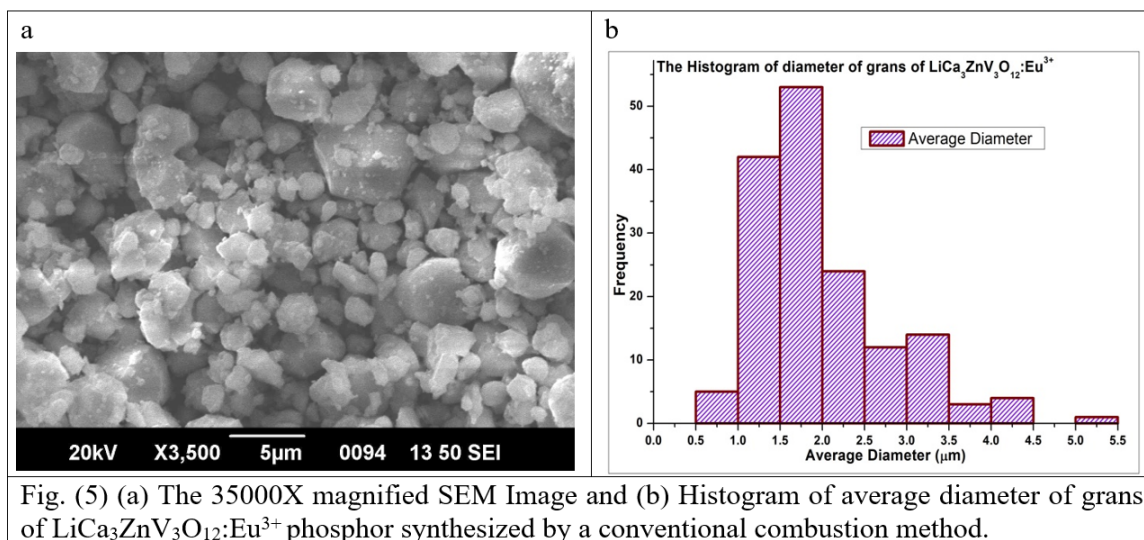


Fig. (5) (a) The 35000X magnified SEM Image and (b) Histogram of average diameter of grains of $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$ phosphor synthesized by a conventional combustion method.

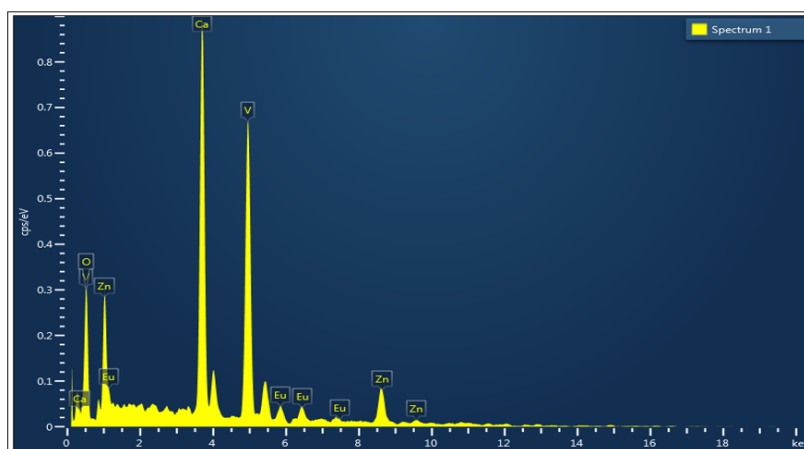


Fig. (6). The Energy Dispersive X-ray Spectrometry (EDS) spectra of $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$ phosphor synthesized by a conventional combustion method.

3) Chemical Compositions (by Energy Dispersive X-ray Spectrometry):

To confirm the chemical compositions, Figure (6) shows the spectrum of EDS analysis. The energy-dispersive X-ray spectrometry data gave simplified & the concentration ratio of the existing elements in the prepared phosphor. The EDS spectrum shows the peaks of containing elements. The lithium is not shown in the result (both in Figure (6) as well as in Table 2 for EDS calculation) due to its relatively smaller molecular weight [14]. The chemical composition has been determined by peaks of Calcium, Zinc, Vanadate, Oxygen and Europium. The agreement of the result with the prepared garnet phosphor is shown by the EDS spectrum. The weight percentage of the existing elements is given in Table 2 contains observed data (EDS Calculation) and synthesis calculated data from the chemical composition of prepared garnet phosphor $\text{LiCa}(3-x)\text{ZnV}_3\text{O}_{12}:x\text{Eu}^{3+}$ where $x = 5\%$.

Table 2. Weight percentage of elements is presented in LiCa₃ZnV₃O₁₂:Eu³⁺ and comparison with observed data and calculated data.

Elements	O	Ca	V	Zn	Eu	Li	Total Wt%
EDS Calculation	31.94%	19.42%	28.94%	14.19%	5.51%	0%	100%
Synthesis Calculations	31.51%	19.12%	28.26%	15.02%	5.19%	0.9%	100%

4) Photoluminescence (PL):

Figure 7(a, b, c) depicts the emission spectrum of LiCa₃ZnV₃O₁₂:xEu³⁺ ($x = 0\%$, 0.5% , 1% , 2% and 3% and 5%) vanadate garnet and europium doped garnet phosphors and three-dimensional view respectively. The emission spectrum is stimulated by 336 nm of radiation. The emission peak is obtained at wavelengths 477 nm for VO₄³⁻ in the transition from 3T₁, 3T₂ to 1A₁ [10]. More emission peaks are obtained at wavelengths 588 and 613 nm for Eu³⁺ in the transition from 5D₀ to 7F_j ($j = 0, 1, 2, 3, 4$) [11], but the more intense peak is at 613 nm with the electronic transition from 5D₀ to 7F₂. All the emission peaks are shown in the energy level diagram Figure (2). The energy transformation is done from VO₄³⁻ to Eu³⁺ [12].

Figure (7) (d) depicts the excitation spectrum of LiCa₃ZnV₃O₁₂:xEu³⁺ ($x = 0\%$, 0.5% , 1% , 2% , 3% and 5%) vanadate garnet and europium doped garnet phosphors. The excitation spectrum is stimulated by 477 nm for VO₄³⁻ and 613 nm for Eu³⁺. The dark blue line depicts that the electronic transition is taken place from 1A₁ to 1T₁, 1T₂ for vanadate garnet phosphor.

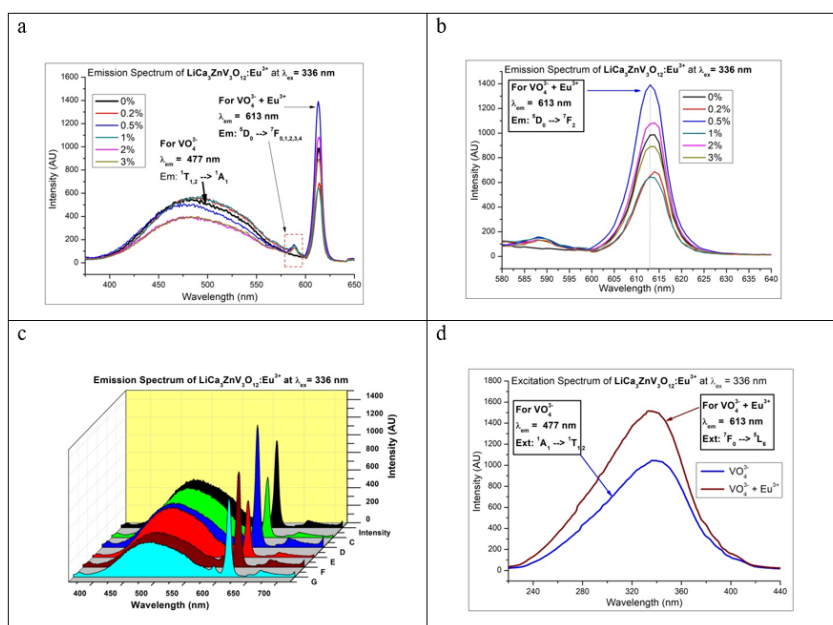


Figure (7) (a) The emission spectrum of LiCa₃ZnV₃O₁₂:xEu³⁺ prepared by combustion method was monitored at 336 nm and we got emission wavelengths at 477 nm due to only vanadate and 613 nm due to europium doped garnet phosphor. (b) The emission spectrum of europium doped garnet phosphor. (c) A three-dimensional view of the emission spectrum are showing effect of doping concentrations. (d) The excitation spectrum of LiCa₃ZnV₃O₁₂:xEu³⁺ were simulated at 477 nm for vanadate and at 613 nm for europium-doped garnet phosphor by exciting at 336 nm.

5) Color Chromaticity/CIE Parameters:

Figure (8) shows the colour chromaticity CIE diagram of lanthanide-free vanadate garnet and europium-rich vanadate garnet phosphors. The CIE chromaticity diagram gives information about hue (color) and saturation (colour purity). This is a digital photograph of the prepared garnet structured phosphor under irradiation by 356 nm and 6 watts

of light. The color coordinates of the entire range of wavelength of the prepared garnets are $(x,y) = (0.238, 0.325)$ for VO_4^{3-} at the emission wavelength and $(x,y) = (0.571, 0.331)$ for Eu^{3+} at an emission wavelength [17].

The colour coordinates $(x,y) = (0.238, 0.325)$ for VO_4^{3-} shows bluish-white color while colour coordinates $(x,y) = (0.571, 0.331)$ for Eu^{3+} shows orange-red color of emission. The $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ can be used as blue color sources of vanadate garnet structured phosphor. The colour correlated temperatures (CCT) are calculated by Mc-Camy empirical equation (1) [18] and found to be 11924 K and 2028.5 K for VO_4^{3-} and Eu^{3+} respectively. The colour purity (in %) and average lifetime (in ns) are mentioned in table (1) which are calculated by equations (2) and (3) respectively.

Table (2) CIE Chromaticity Parameters of $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ and $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$

Sr. No.	Compositions	Activators	CIE Coordinates		CCT (K)	Colour Purity (%)	Average Life Time (ns)
			x	y			
1.	$\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$	VO_4^{3-}	0.238	0.325	11924 K	72.12%	513.6515
2.	$\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$	Eu^{3+}	0.571	0.331	2028.5 K	81.23%	520.0315

$$(A) \text{ CCT (K)} = -437r^3 + 3601r^2 - 6861r + 5514.31 \quad \text{----- (1)}$$

Where, $r = \frac{(x-x_e)}{(y-y_e)}$ and $x_e = 0.3320$ & $y_e = 0.1858$ are chromaticity epicenters.

(1) For $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$:

$$x = 0.238 \text{ \& } y = 0.325$$

$$r = \frac{(x-x_e)}{(y-y_e)} = \frac{(0.238-0.3320)}{(0.325-0.1858)} = -0.67529 \text{ put in equation(1)}$$

$$\therefore \text{ CCT (K)} = -437 \times (-0.67529)^3 + 3601 \times (-0.67529)^2 - 6861 \times (-0.67529) + 5514.31$$

$$\therefore \text{ CCT (K)} = 11924 \text{ K}$$

(2) $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$:

$$x = 0.571 \text{ \& } y = 0.331$$

$$r = \frac{(x-x_e)}{(y-y_e)} = \frac{(0.571-0.3320)}{(0.331-0.1858)} = 1.646 \text{ put in equation(1)}$$

$$\therefore \text{ CCT (K)} = -437 \times (1.646)^3 + 3601 \times (1.646)^2 - 6861 \times (1.646) + 5514.31$$

$$\therefore \text{ CCT (K)} = 2028.5 \text{ K}$$

$$(B) \text{ Colour Purity} = \sqrt{\frac{(x-x_s)^2 + (y-y_s)^2}{(x_d-x_s)^2 + (y_d-y_s)^2}} \times 100 \quad \text{----- (2)}$$

Where, (x,y) are CIE coordinates of sample (entire wavelength)

(x_s, y_s) are Coordinates of UV Sours lamp for illuminant the sample (356 nm, 6W)

(x_d, y_d) are dominant coordinates of sample (at peak wavelength)

$$(C) \text{ Average Life Time } (\tau) = \frac{\int t \times i(t) dt}{\int i(t) dt} \quad \text{----- (3)}$$

Where, $i(t)$ is intensity count of the function of time t .

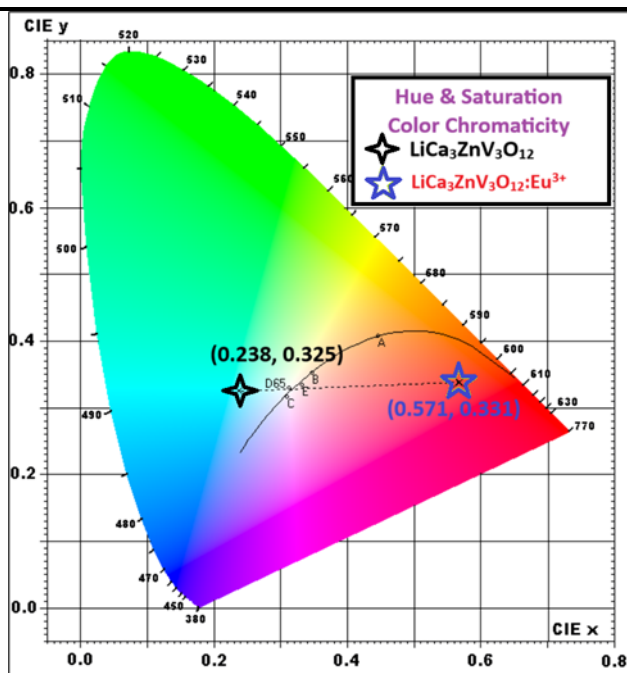


Figure 8 Colour chromaticity of emission $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}$ and $\text{LiCa}_3\text{ZnV}_3\text{O}_{12}:\text{Eu}^{3+}$ under 356 nm and 6 W radiations.

5. CONCLUSION

A vanadate garnet-type phosphor activated by europium trivalent ions was prepared by combustion method at 500°C pre-heated and then cancelled the materials at 650°C. The prepared garnet phosphor was investigated by various characterizations techniques to confirm the materials desirable application. The phase identifications was studied by an X-ray diffractometer and the materials as a cubic crystal structure of lattice constant 10.8962 Å and this XRD data was refined by retrieve refinement software and it was refined in proper way upto value of chi square 1.26. The morphology and composition were done by SEM and EDS respectively. The average gran size was calculated by ImageJ software is 1.988781 µm and it was found in the range of 1 µm to 5 µm. The exiting elements were investigated by EDS.

The photoluminescence properties of the garnet-type phosphor were studied by exciting the materials at 336 nm for both vanadate and europium-rich garnet phosphor. The excitation spectrum was monitored at 477 nm for VO_4^{3-} and 613 nm for Eu^{3+} as emissive wavelengths. The emission spectrum was recorded at 336 nm and emission peaks were obtained at 477 nm for vanadate and dominant peak at 613 nm for vanadate garnet-structure activated by europium ions. Color chromaticity coordinated were obtained (0.238, 0.325) for VO_4^{3-} and (0.571, 0.331) for Eu^{3+} by CIE digital diagram. By these results, the prepared garnet phosphor is the best material for red LEDs. The garnet containing zinc is much used for cutting process.

CONFLICT OF INTERESTS

None.

ACKNOWLEDGMENTS

None.

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