A Comparative Investigation of Eu^{3+}-Activated Self-Activated Vanadate Garnet Phosphor Obtained through Solid-State and Combustion Routes

Ganesh C. Vandile[1], Deoram V. Nandanwar[2], Satish G. Goswami[3], Amar K. Nandanwar[4], Bhupendra R. Walde[5]
[1,2,3,5]Shri Mathuradas Mohota College of Science, Nagpur-440009, India
[4]J. M. Patel Arts, Commerce & Science College, Bhandara-441904, India

***Abstract*—Garnet structured phosphor materials have gained considerable attention because of their stable crystal structure and promising optical characteristics, which make them useful for various photonic and lighting applications. In the present work, Eu^{3+}-activated $LiCa_3ZnV_3O_{12}$ (CLZVO) vanadate garnet phosphors were synthesized using two different preparation techniques, namely high-temperature solid-state reaction and conventional combustion synthesis, in order to examine the influence of the preparation route on their structural and luminescent behaviour. Phase formation and crystal structure of the prepared samples were verified through X-ray diffraction analysis with refinement of the cubic garnet structure. The optical response of the materials was investigated by photoluminescence excitation and emission measurements under ultraviolet excitation, where characteristic emissions from both the host lattice (VO_4^{3-} groups) and Eu^{3+} ions were observed. Surface morphology and particle distribution were examined using scanning electron microscopy, while compositional information were obtained through EDX studies. The comparative study indicates that the synthesis method influences crystallinity, particle morphology and emission intensity, while maintaining the typical garnet structure and Eu^{3+} luminescence transitions. Owing to their favourable optical characteristics, the prepared phosphors may serve as potential materials for applications in solid-state lighting devices, optical temperature sensors, cathode ray tubes and active media for solid-state lasers.**

***Index Terms*—Garnet phosphor; Eu^{3+}-doped vanadate garnet; Solid-state synthesis; Combustion method; Photoluminescence.**

I. INTRODUCTION

Garnet-structured phosphors have attracted considerable interest in optical materials because of their high chemical stability, structural flexibility and efficient luminescence behaviour. The general chemical formula of garnet compounds is $A_3B_2C_3O_{12}$, where A, B and C represent cations occupying dodecahedral, octahedral and tetrahedral coordination sites respectively. These materials usually crystallize in a cubic structure with space group Ia-3d, which allows various cation substitutions and results in tunable optical properties. Due to these advantages, garnet phosphors are widely studied for applications in solid-state lighting, display devices, lasers and optical sensing [1].

Vanadate-based garnets containing VO_4^{3-} groups are particularly interesting because they can absorb ultraviolet radiation and produce visible emission through charge-transfer transitions [2]. The vanadate group can also act as an efficient sensitizer for rare-earth activator ions. Among different activators, Eu^{3+} ions are widely used in phosphor materials because they provide sharp red emission arising from transitions between the $^5D_0$ excited state and the ^7F_J (J = 0–4) energy levels [3].

The garnet compound $LiCa_3ZnV_3O_{12}$ (LCZVO) is a suitable host lattice for Eu^{3+} doping due to the presence of vanadate units that enable energy transfer from the host to the activator ions [4]. As a result, the material can exhibit combined emission originating from both the VO_4^{3-} group and Eu^{3+} ions. Such phosphors are promising for applications in white light-emitting diodes, optical temperature sensors, cathode-ray tubes and solid-state laser materials [5].

Since the synthesis route can strongly influence particle morphology, crystallinity and luminescence efficiency, it is important to examine the effect of different preparation methods. In the present work, Eu^{3+}-activated $LiCa_3ZnV_3O_{12}$ phosphor was prepared using solid-state reaction and combustion synthesis methods, and their structural and photoluminescence properties were comparatively investigated.

II. MATERIALS AND PREPARATION

2.1 Materials

All chemicals used in this work were of analytical grade and used without further purification. The starting materials included lithium nitrate ($LiNO_3$), calcium nitrate tetrahydrate ($Ca(NO_3)_2\cdot 4H_2O$), zinc oxide (ZnO), vanadium pentoxide (V_2O_5), europium oxide (Eu_2O_3) and urea. For the solid-state synthesis route, lithium carbonate (Li_2CO_3), calcium carbonate ($CaCO_3$), zinc oxide (ZnO) and ammonium metavanadate (NH_4VO_3) were used as precursor materials. Europium ions were introduced into the host lattice with different concentrations to obtain $LiCa_3ZnV_3O_{12}$:xEu^{3+} phosphors.

2.2 Combustion Synthesis

In the combustion process, stoichiometric quantities of $LiNO_3$, $Ca(NO_3)_2\cdot 4H_2O$, ZnO and V_2O_5 were mixed thoroughly with urea, which served as a fuel. Europium oxide was first converted into europium nitrate by dissolving it in a small amount of nitric acid before adding it to the mixture to obtain compositions of $LiCa_3ZnV_3O_{12}$:xEu^{3+} (x = 0–5%). The homogeneous mixture was placed in a ceramic dish and introduced into a furnace preheated to about 500 °C. A rapid exothermic reaction occurred and producing a voluminous ash-like product within a short time. The obtained material was crushed to form a fine powder and then heated at 600 °C for about 30–40 minutes to improve crystallinity before cooling to room temperature [6].

2.3 Solid-State Reaction Method

For comparison, $LiCa_3ZnV_3O_{12}$:xEu^{3+} phosphors were also synthesized using the conventional solid-state reaction technique. Appropriate amounts of Li_2CO_3, $CaCO_3$, ZnO and V2O5 were weighed according to the required stoichiometric ratios and mixed thoroughly using an agate mortar and pestle for about 30–40 minutes. The homogeneous mixture was then calcined in a muffle furnace in two steps: first at 650 °C for 2 hours and subsequently at 950 °C for 6 hours to ensure complete phase formation [7]. After sintering, the samples were ground again to obtain uniform fine powders suitable for further characterization.

2.4 Characterization Techniques

The crystal structure of the prepared phosphor samples was examined using an X-ray diffractometer (Rigaku Miniflex 600) operating with Cu Kα radiation ($\lambda = 1.54059$ Å). The diffraction patterns were recorded at a scanning rate of 4° per minute to identify the phase formation and structural characteristics of the materials. Photoluminescence measurements were carried out using a fluorescence spectrophotometer (F-7000 FL). Excitation and emission spectra were recorded using a 135 W xenon lamp as the excitation source with a spectral step interval of 0.2 nm. Surface morphology and elemental composition of the samples were analyzed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F). The instrument was operated with an accelerating voltage of about 25 kV between the anode and cathode to obtain detailed microstructural information.

Structural refinement of the diffraction data was performed using the FullProf Suite software to compare the observed and calculated diffraction intensities. In addition, particle size estimation from the SEM micrographs was carried out with the help of ImageJ and Origin software.

III. RESULT ANALYSIS

3.1 Structural Studies (XRD)

The crystal structure of the phosphor prepared by the combustion synthesis method was examined using X-ray diffraction analysis. The recorded diffraction pattern confirms the formation of a single-phase garnet structure corresponding to $LiCa_3ZnV_3O_{12}$. All the observed peaks are in good agreement with the standard reference pattern and indicating that the prepared material is pure phase without any detectable secondary phases. The incorporation of Eu^{3+} ions into the host lattice does not produce any significant change in the peak positions or pattern profile and suggesting that the dopant ions are successfully accommodated within the crystal lattice. The diffraction data were further analyzed through Rietveld refinement using the FullProf Suite software which provided good agreement between the calculated and observed patterns and confirming the formation of a cubic garnet structure with space group Ia-3d. The lattice consists of dodecahedral, octahedral and tetrahedral coordination sites corresponding to CaO_8, $(Li/Zn)O_6$ and VO_4 units, respectively. Figure 1 show the XRD pattern and refinement profile of the combustion-synthesized sample.

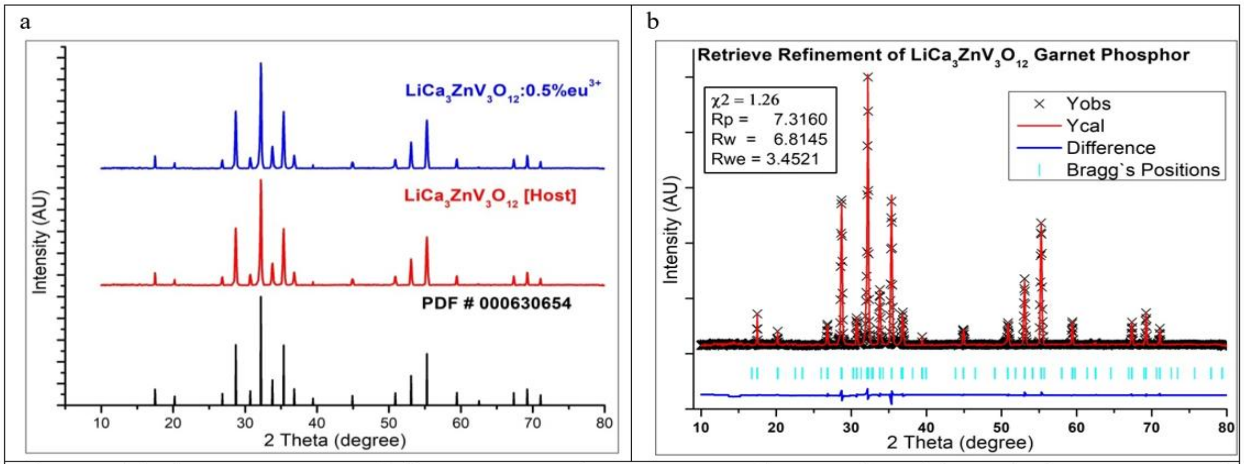


Figure 1 (a) The XRD patterns of $LiCa_3ZnV_3O_{12}$, $LiCa_3ZnV_3O_{12}$: Eu^{3+} comparing with standard XRD pattern of PDF #000630654. (b) Rietveld refinement of the vanadate garnet phosphor $LiCa_3ZnV_3O_{12}$ by combustion method.

The structural characteristics of the phosphor synthesized by the solid-state reaction (SSR) method were also investigated by X-ray diffraction. The obtained diffraction pattern reveals well-defined peaks that match with the characteristic reflections of the $LiCa_3ZnV_3O_{12}$ garnet phase and confirming the successful formation of the crystalline host lattice. Similar to the combustion-prepared sample, the introduction of Eu^{3+} ions does not lead to noticeable impurity peaks and indicating that the dopant ions are effectively incorporated into the structure without altering the phase purity. The cubic crystal structure with space group Ia-3d is maintained, where Ca^{2+} ions occupy the dodecahedral sites, Zn^{2+}/Li^{+} ions are located in octahedral positions, and V^{5+} ions form tetrahedral VO_4 units. Rietveld refinement of the diffraction data further supports the structural model and demonstrates a good fit between experimental and calculated patterns. Figure 2 present the XRD pattern of the SSR-prepared phosphor together with the corresponding refinement results.

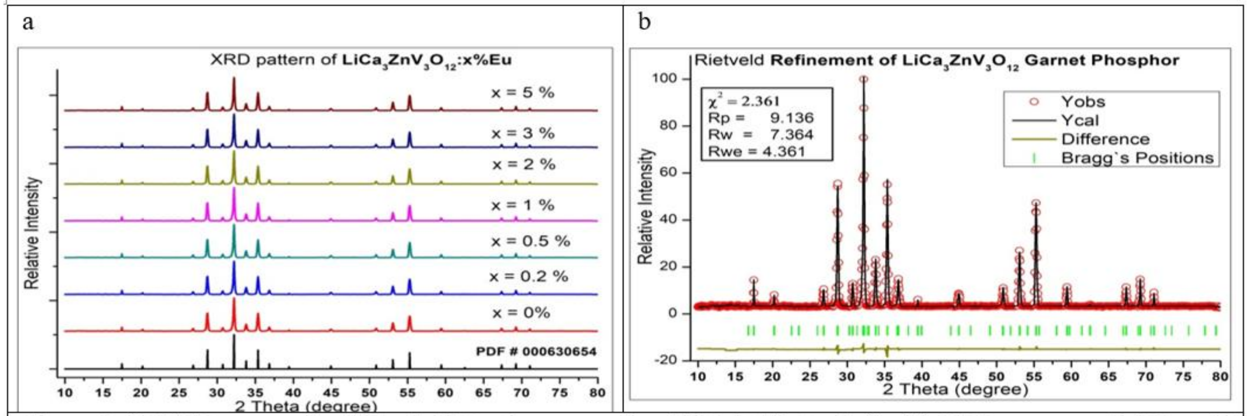


Figure 2 (a) XRD pattern for $LiCa_3ZnV_3O_{12}$ host as well as $LiCa_3ZnV_3O_{12}$:Eu^{3+}. (b) XRD pattern with Rietveld refinement of $LiCa_3ZnV_3O_{12}$ garnet phosphor by SSR method.

3.2. Morphology and EDX

The surface morphology of the Eu^{3+}-doped $LiCa_3ZnV_3O_{12}$ phosphor synthesized by the combustion method was examined using FE-SEM analysis. The microstructure reveals irregularly shaped granular particles with noticeable agglomeration, which is commonly observed in materials prepared through combustion synthesis due to the rapid exothermic reaction. Particle size distribution was analyzed using ImageJ software, showing grain sizes in the range of approximately 1–5 µm, with an average particle size of about 1.99 µm. The histogram representing the grain size distribution is presented in Figure 3 (b). To verify the elemental composition of the prepared phosphor, energy dispersive X-ray spectroscopy (EDS) analysis was performed. The EDS spectrum confirms the presence of the main constituent elements such as Ca, Zn, V, O and Eu, which correspond to the expected chemical composition of the garnet phosphor. Lithium is not visible in the spectrum due to its very low atomic mass and weak X-ray emission. The elemental weight percentages obtained from EDS analysis agree well with the theoretical composition of the synthesized material. Figure 3 (a, c) show the SEM micrograph and corresponding EDS spectrum of the combustion-prepared sample.

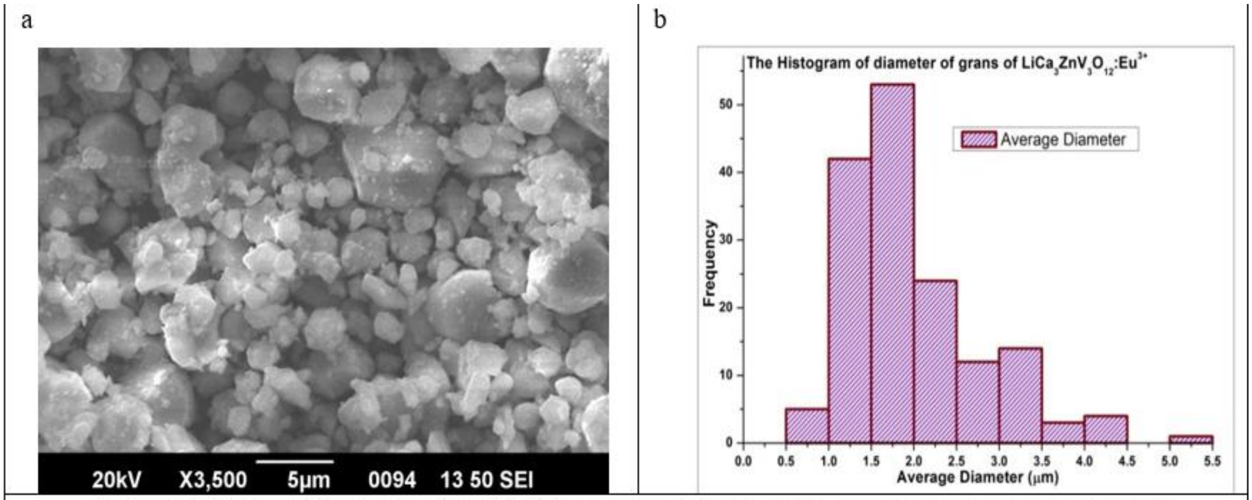


Figure (3) (a) The 35000X magnified SEM Image and (b) Histogram of average diameter of grans of $LiCa_3ZnV_3O_{12}:Eu^{3+}$ phosphor synthesized by a conventional combustion method.

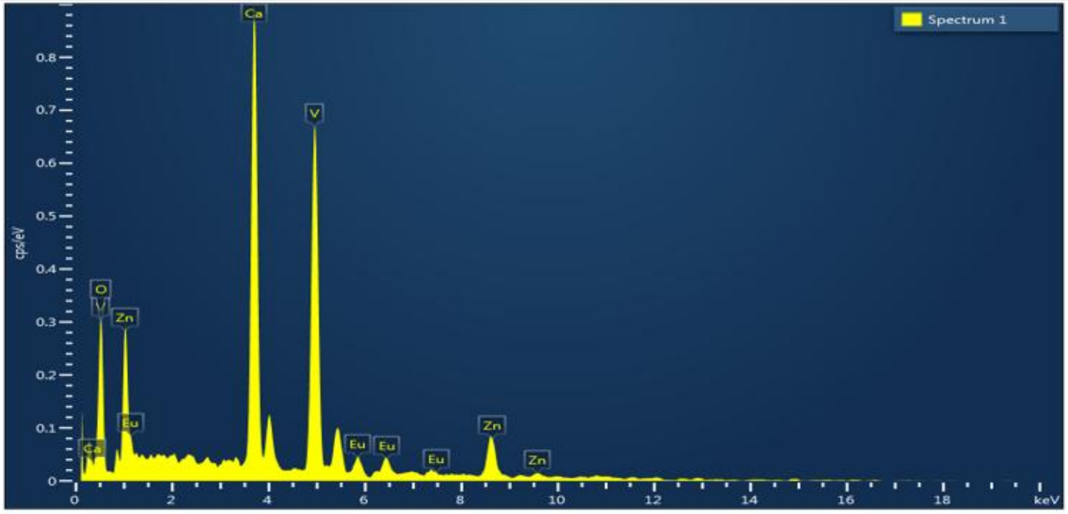


Figure 3 (c). The Energy Dispersive X-ray Spectrometry (EDS) spectra of $LiCa_3ZnV_3O_{12}:Eu^{3+}$ phosphor synthesized by a conventional combustion method.

The morphology of the LiCa$_3$ZnV$_3$O$_{12}$:Eu^{3+} phosphor prepared by the solid-state reaction (SSR) method was also investigated using FE-SEM. The micrographs reveal comparatively larger grains with relatively dense and compact particle distribution, which is typical for materials synthesized through high-temperature solid-state processing. The SEM images provide valuable information about grain formation and surface characteristics of the phosphor particles. Elemental composition of the sample was further analyzed using EDX spectroscopy and confirming the presence of Ca, Zn, V, O and Eu elements in the host lattice. The obtained spectral peaks indicate that the dopant ions are successfully incorporated into the garnet structure without introducing additional impurity elements. Similar to the combustion-prepared sample, lithium could not be detected in the spectrum because of its very low atomic weight. The SEM and EDS results together confirm the successful formation of Eu^{3+}-activated vanadate garnet phosphor. Figure 4 presents the SEM images and EDS spectrum of the sample synthesized by the SSR method.

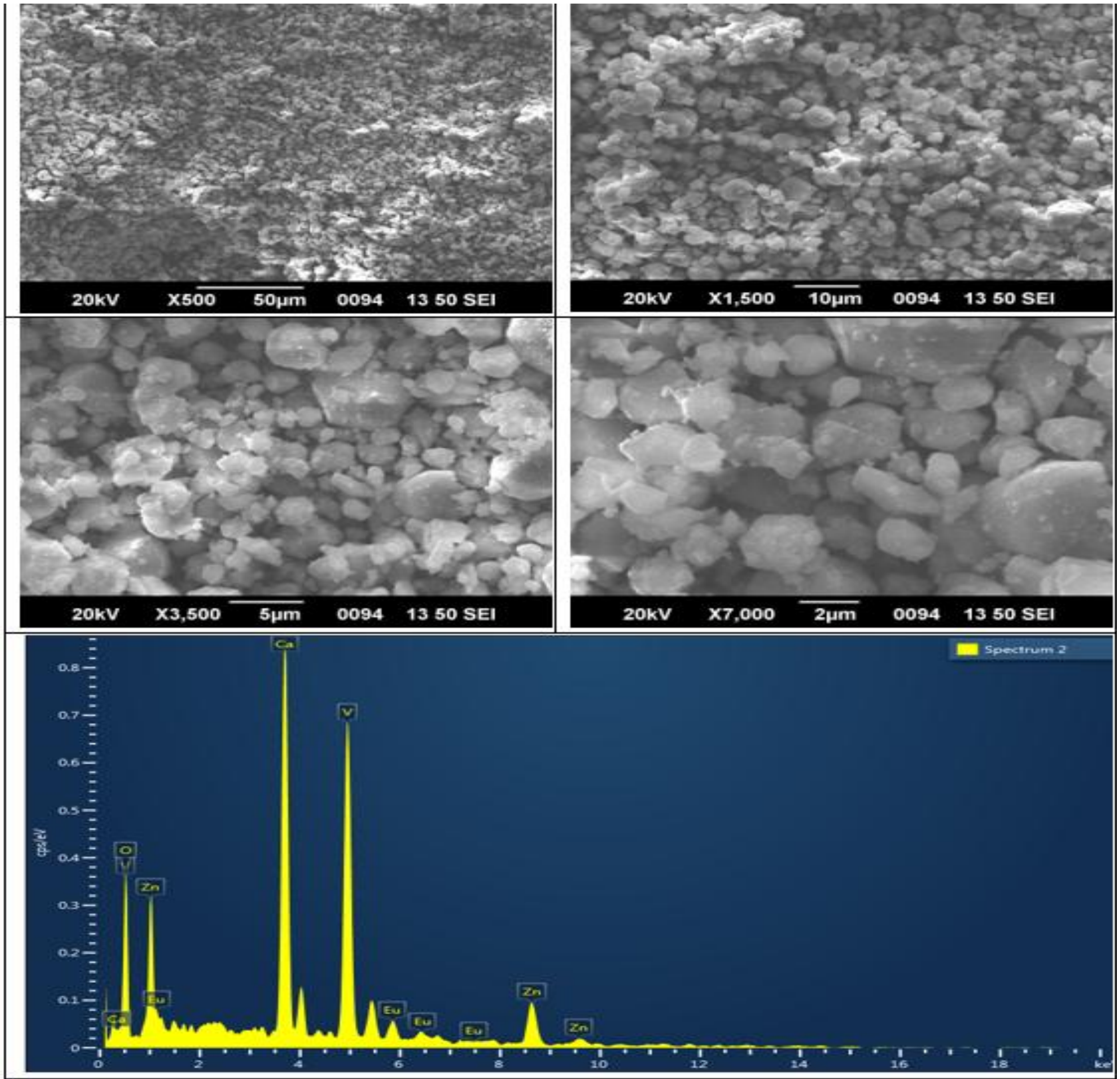


Figure 4: SEM images of LiCa$_3$ZnV$_3$O$_{12}$:2%Eu^{3+} garnet phosphor and Energy Dispersive X-ray Spectrum of LiCa$_3$ZnV$_3$O$_{12}$:2%Eu^{3+} garnet phosphor.

3.3 Photoluminescence (PL):

The photoluminescence behaviour of $LiCa_3ZnV_3O_{12}$:xEu^{3+} phosphors prepared by the combustion method was investigated through excitation and emission spectroscopy. The emission spectra recorded under ultraviolet excitation show a broad blue emission band around 477 nm, which originates from the electronic transition of the VO_4^{3-} group from $^3T_1$, $^3T_2$ to $^1A_1$. In addition to the host emission, the introduction of Eu^{3+} ions produces characteristic narrow emission peaks in the red region. These peaks appear mainly at 588 nm and 613 nm, corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions of Eu^{3+} ions, where the $^5D_0 \rightarrow {}^7F_2$ transition near 613 nm exhibits the strongest intensity. The presence of both host and dopant emissions indicates an effective energy transfer process from the VO_4^{3-} groups to Eu^{3+} ions [8]. The excitation spectra monitored at the emission wavelengths also display a broad absorption band in the ultraviolet region associated with transitions within the vanadate group. The variation of emission intensity with increasing Eu^{3+} concentration reveals an optimum luminescence intensity before the onset of concentration quenching. Figure 5 show the emission spectra and corresponding excitation behaviour of the combustion-synthesized phosphor samples.

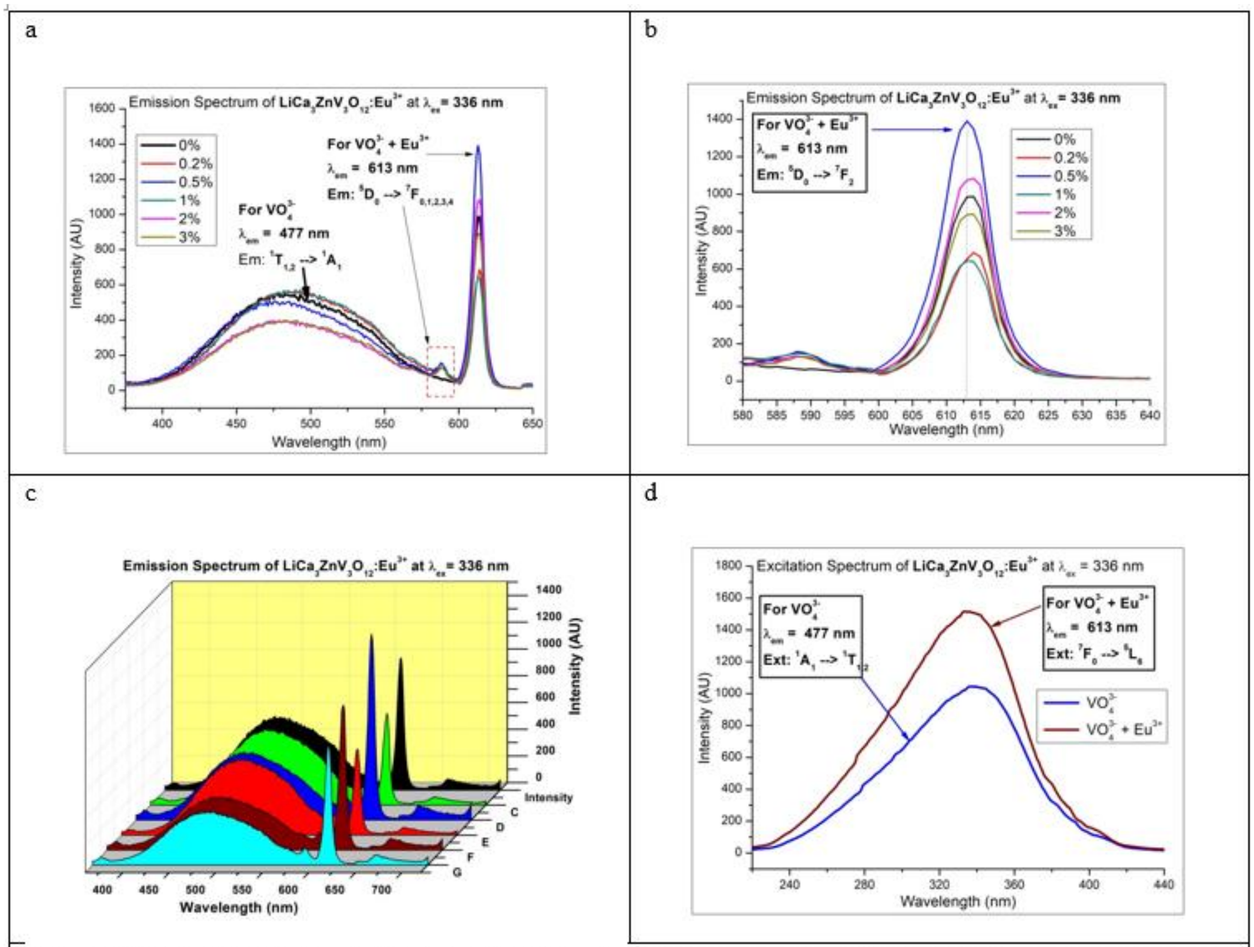
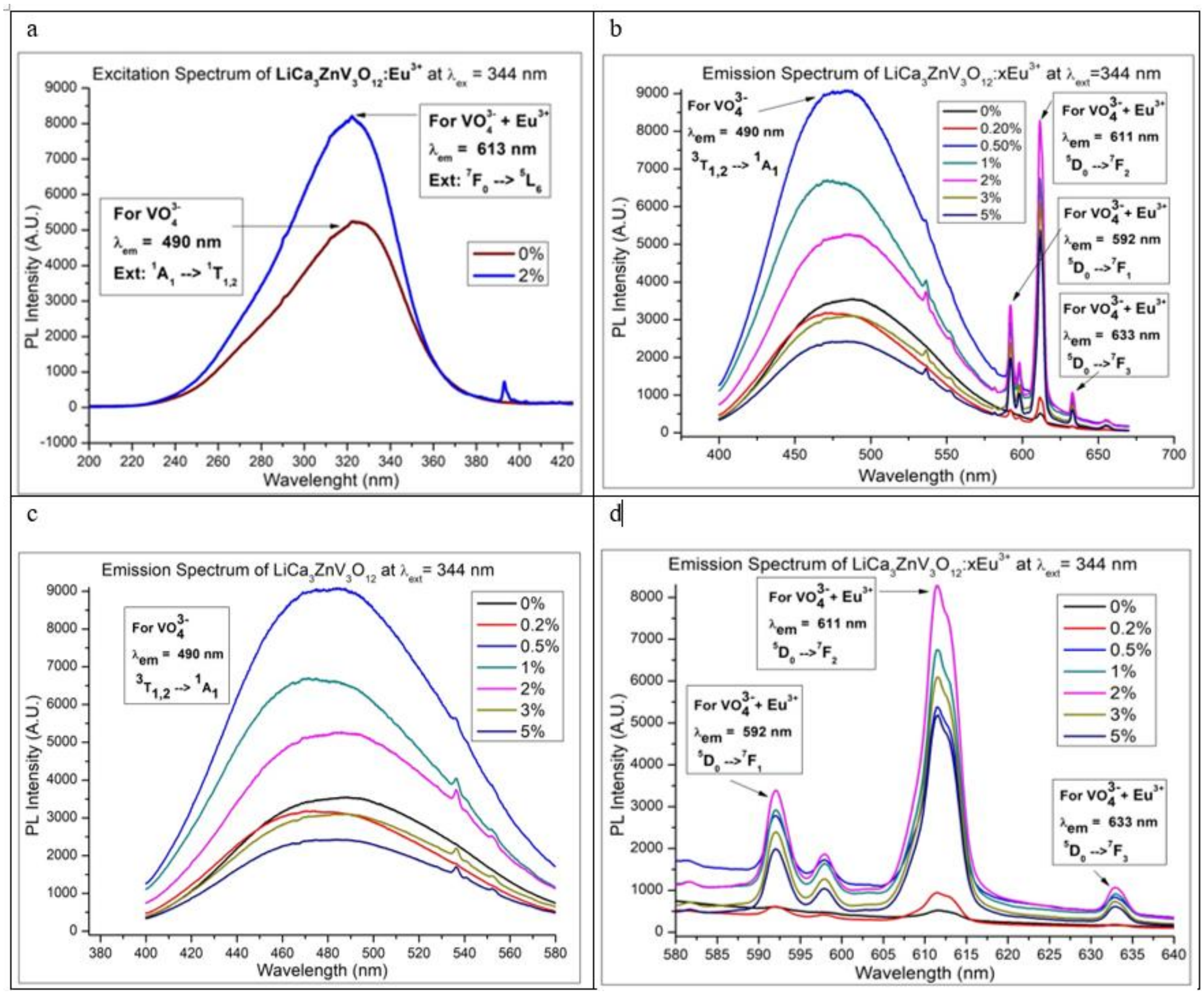


Figure 5 (a) The emission spectrum of $LiCa_3ZnV_3O_{12}$:xEu^{3+} prepared by combustion method was monitored at 336 nm and we got emission wavelengths at 477 nm due to only vanadate and 613 nm due to europium doped garnet phosphor. (b) The emission spectrum of europium doped garnet phosphor. (c) A three-dimensional view of the emission spectrum are showing effect of doping concentrations. (d) The excitation spectrum of $LiCa_3ZnV_3O_{12}$:xEu^{3+} were simulated at 477 nm for vanadate and at 613 nm for europium-doped garnet phosphor by exciting at 336 nm by combustion method.

The photoluminescence properties of $LiCa_3ZnV_3O_{12}:xEu^{3+}$ phosphors synthesized by the solid-state reaction (SSR) method were also examined to understand the optical response of the material. The excitation spectra monitored in the visible region show a broad band between 200 and 400 nm, which is mainly attributed to the charge transfer transitions within the VO_4^{3-} tetrahedral groups [9]. In Eu^{3+}-doped samples, an additional excitation feature appears due to the Eu–O charge transfer band, indicating that absorbed energy from the host lattice can be efficiently transferred to Eu^{3+} ions. When excited in the ultraviolet region, the phosphors exhibit a wide emission band in the blue region arising from VO_4^{3-} transitions ($^3T_{1,2} \rightarrow {}^1A_1$) along with sharp red emission lines of Eu^{3+} located near 592 nm, 611 nm and 633 nm corresponding to $^5D_0 \rightarrow {}^7F_J$ transitions. Among these, the emission around 611 nm remains dominant, confirming the strong red luminescence of the Eu^{3+} activator. The intensity of the emission peaks increases with Eu^{3+} concentration until an optimum doping level is reached, after which concentration quenching occurs due to non-radiative energy transfer between neighbouring activator ions. Figure 6 illustrate the excitation and emission spectra of the phosphor synthesized by the SSR method.



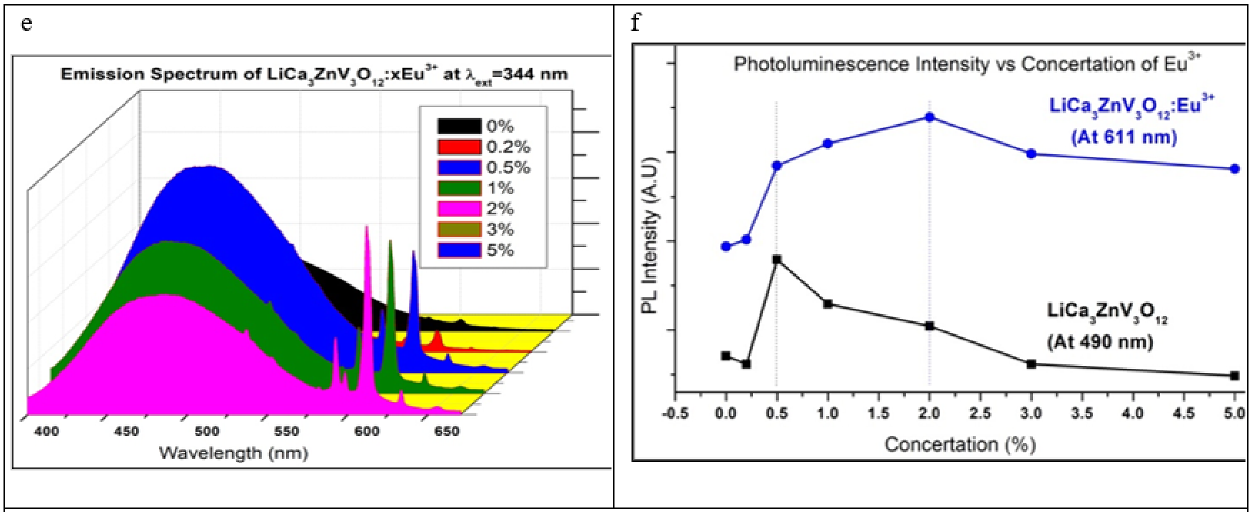


Figure 6 (a): Excitation spectra of $LiCa_3ZnV_3O_{12}$ and $LiCa_3ZnV_3O_{12}:Eu^{3+}$. (b) Emission spectra of $LiCa_3ZnV_3O_{12}:Eu^{3+}$. (c) Emission spectra due to VO_4^{3-}. (d) Emission spectra due to Eu^{3+}. (e) 3D view of emission spectra with concentrations of Eu^{3+}. (f) Variation of PL intensity due to concentrations of Eu^{3+} by SSR.

IV. CONCLUSION

In this work, Eu^{3+}-activated $LiCa_3ZnV_3O_{12}$ vanadate garnet phosphors were successfully synthesized using both combustion and solid-state reaction (SSR) methods in order to examine the influence of the preparation route on their structural and optical properties. X-ray diffraction analysis confirmed the formation of a single-phase garnet structure with cubic symmetry belonging to the Ia-3d space group. The refined lattice parameter was found to be approximately 10.89 Å, indicating good agreement with the standard garnet structure. The refinement results showed a satisfactory fit between observed and calculated diffraction patterns and confirming the structural stability of the prepared materials.

The surface morphology observed through FE-SEM analysis revealed irregular granular particles with sizes in the micrometer range and the average grain size was determined to be about 1–5 µm. Elemental composition analysis using EDS confirmed the presence of Ca, Zn, V, O and Eu elements, which corresponds well with the expected chemical composition of the phosphor material. Photoluminescence studies showed that the host lattice exhibits a broad blue emission around 477–490 nm due to the VO_4^{3-} groups, while Eu^{3+} doping introduces characteristic red emission peaks near ~592 nm and 611–613 nm corresponding to the $^5D_0 \rightarrow {}^7F_J$ transitions. The dominant red emission peak around 611–613 nm indicates efficient energy transfer from the VO_4^{3-} sensitizer groups to Eu^{3+} activator ions and confirming its potential for color-tunable optical applications.

REFERNCES

[1] Berezovskaya, I. V., Z. A. Khapko, A. S. Voloshinovskii, N. P. Efryushina, S. S. Smola, and V. P. Dotsenko. "The effects of temperature and impurity phases on the luminescent properties of Ce3+-doped Ca3Sc2Si3O12 garnet." Journal of Luminescence 195 (2018): 24-30. https://doi.org/10.1016/j.jlumin.2017.11.002.

[2] Vandile, Ganesh, Deoram Nandanwar, and Amar Nandanwar. 2023. "A Review Synthesis and Luminescence Characterize of Emitting Phosphor of Garnet Structure With Effect of Heating Time". Journal of Condensed Matter 1 (02):5-9. https://doi.org/10.61343/jcm.v1i02.19.

[3] Bharat, L. Krishna, Soo-Kun Jeon, Kurugundla Gopi Krishna, and Jae Su Yu. "Rare-earth free self-luminescent Ca2KZn2 (VO4) 3 phosphors for intense white light-emitting diodes." Scientific Reports 7, no. 1 (2017): 42348. https://doi.org/10.1038/srep42348.

[4] G. Gundiah, Y. Shimomura, N. Kijima, A.K. Cheetham, Novel red phosphors based on vanadate garnets for solid state lighting applications, Chem. Phys. Lett. 455 (2008) 279–283, https://doi.org/10.1016/j.cplett.2008.02.083.

[5] T. Hasegawa, Y. Abe, A. Koizumi, T. Ueda, K. Toda, M. Sato, Bluish-White Luminescence in Rare-Earth-Free Vanadate Garnet Phosphors: Structural Characterization of LiCa3MV3O12 (M =Zn and Mg, Inorg. Chem. 57 (2018) 857–866, https://doi.org/10.1021/acs.inorgchem.7b02820.

[6] R. Cao, T. Chen, Y. Ren, C. Liao, Z. Luo, Y. Ye, Y. Guo, Tunable emission of LiCa3MgV3O12: Bi3+via energy transfer and changing excitation wavelength, Mater. Res. Bull. 111 (2019) 87–92, https://doi.org/10.1016/j.materresbull.2018.11.011.

[7] Ganesh C. Vandile, Deoram V. Nandanwar, Amar K. Nandanwar and Bhupendra R. Walde. “Synthesis and Photoluminescence of the Self-Activated Garnet Phosphor Triggered by Eu^{3+} for Blue-Red Luminescence”, Letters in High Energy Physics, 2(7), 2024, 7888- 7898. https://doi.org/10.31526/lhep.2024.

[8] P. Dang, S. Liang, G. Li, Y. Wei, Z. Cheng, H. Lian, J. Lin, Full color luminescence tuning in Bi3+/Eu3+-doped LiCa3MgV3O12 garnet phosphors based on local lattice distortion and multiple energy transfers, Inorg. Chem. 57 (2018) 9251–9259, https://doi.org/10.1021/acs.inorgchem.8b01271.

[9] Mihóková, E., V. Babin, V. Jarý, L. Havlák, M. Buryi, and M. Nikl. "Defect states and temperature stability of Eu2+ center in Eu-doped yttrium aluminum garnet." Journal of Luminescence 190 (2017): 309-313. https://doi.org/10.1016/j.jlumin.2017.05.065.
