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Synthesis and Luminescence Characteristics of Eu^{3+} activated $LiCa_4(BO_3)_3$ Phosphor for Photonic Applications

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ABSTRACT: Eu^{3+}- activated $LiCa_4(BO_3)_3$ phosphor were successfully synthesized by a modified solution combustion method using metal nitrates as oxidizers and urea as the fuel. The rapid combustion followed by annealing at 850°C yielded a fine, homogeneous phosphor powder. X-ray diffraction analysis confirmed the formation of a single-phase $LiCa_4(BO_3)_3$ host lattice with effective incorporation of Eu^{3+} ions. The photoluminescence excitation spectrum monitored at 614 nm exhibited a broad $O^{2-}\rightarrow Eu^{3+}$ charge-transfer band in the 210–310 nm region along with characteristic f–f transitions, with the most intense excitation peak at 395 nm corresponding to the $^7F_0\rightarrow{}^5L_6$ transition. Under 254 nm excitation, the phosphor displayed sharp emission bands associated with the $^5D_0\rightarrow{}^7F_J$ (J = 0,1,2,3,4) transitions of Eu^{3+}, dominated by an intense red emission at 615 nm ($^5D_0\rightarrow{}^7F_2$) indicating a non-centrosymmetric local environment around Eu^{3+}. The strong red luminescence and efficient energy transfer suggest that Eu^{3+}-doped $LiCa_4(BO_3)_3$ is a promising candidate for photonic and lighting applications.

KEYWORDS: Borate, Phosphor, PL, Eu^{3+} ion.

I. INTRODUCTION

In recent years, rare-earth-activated inorganic phosphors have attracted significant attention due to their exceptional optical properties and versatility in solid-state lighting, display technologies, scintillators, and photonic devices. Among various host lattices, borate-based materials have emerged as promising candidates because of their high thermal stability, wide band gap, low phonon energy, and ability to accommodate diverse rare-earth ions[1][2]. Borates also possess structural flexibility arising from the presence of BO_3 and BO_4 groups, enabling efficient energy transfer processes and enhanced luminescence performance. Among RE^{3+} ions, europium (Eu) ion is well-known RE activator, it generates the red luminescence from the $^5D_0\rightarrow{}^7F_{0\text{-}6}$ transition[3].The hypersensitive $^5D_0\rightarrow{}^7F_2$ transition near 612–620 nm makes Eu^{3+} an ideal dopant for developing red-emitting phosphors used in white light-emitting diodes (w-LEDs) and display devices[4][5]. The local environment around Eu^{3+} strongly influences the emission intensity and spectral characteristics, especially because the $^5D_0\rightarrow{}^7F_2$ transition is electric - dipole allowed and sensitive to site symmetry. $LiCa_4(BO_3)_3$ (LCB) is a borate compound with favorable optical properties, including a robust framework, good transparency, and low phonon energy conducive to efficient rare-earth emission. Its ability to host trivalent lanthanide ions without significant lattice distortion enhances its potential for photonic applications [6]. Recently reported LiCaBO3:Gd3+ phosphor by solid-state diffusion and reports the electron paramagnetic resonance (EPR) study of this phosphor[7].The current research focus is to explore novel red phosphors that can be effectively excited by near-UV with improved stability and with enhanced efficiency.

In the present study, Eu^{3+}-activated $LiCa_4(BO_3)_3$ phosphors were successfully synthesized using a modified solution combustion technique. This method offers several advantages, such as rapid reaction time, low energy consumption, and homogeneous mixing at the molecular level due to the use of metal nitrates as oxidizers and urea as the fuel [8]. The rapid combustion followed by annealing produced a fine, single-phase phosphor powder with uniform incorporation of Eu^{3+} ions.

II. RELATED WORK

Borate hosts activated with Eu^{3+} have been widely studied as effective red-emitting phosphors, where the hypersensitive $^5D_0\rightarrow{}^7F_2$ transition is significantly affected by the surrounding crystal field environment. Lithium calcium borate matrices are recognized for their ability to incorporate trivalent lanthanide ions with minimal lattice distortion, resulting

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in improved emission efficiency. In this regard, $LiCa_4(BO_3)_3:Gd^{3+}$ phosphors produced through a solid-state diffusion method exhibited strong and narrow UV-B emission at 314 nm when excited at 275 nm, demonstrating the optical suitability of this host lattice[9]. Various synthesis methods have been investigated to enhance phase purity and luminescence properties. Despite previous investigations, there is a lack of comprehensive studies on Eu^{3+}-doped $LiCa_4(BO_3)_3$ phosphors synthesized using solution combustion techniques, which is the focus of the current research.

III. METHODS AND MATERIALS

Synthesis of Phosphor: The phosphor LiCa4 (BO3)3 doped with Eu^{3+} was prepared by modified Solution Combustion Synthesis method. The stoichiometric amounts of high purity (Analytical Reagent) starting materials Lithium Nitrate (LiNO3), Calcium Nitrate (Ca(NO3)2), Europium Nitrate (Eu(NO3)3) (99.99% purity), Boric Acid (H3BO3),Urea [NH2-CO-NH2] have been used for preparation of phosphors. The precursors were mixed with a small amount of double-distilled water to form a homogeneous solution and heated at **90 °C** to remove excess water. The resulting thick paste was transferred to a preheated furnace at **700 °C**, where the nitrates acted as oxidizers and urea served as the fuel. The mixture ignited spontaneously, completing combustion within **5 minutes.** After cooling for 10 minutes, the product was ground and annealed in a muffle furnace at **850 °C for 3 hours**, then quenched to room temperature. The final phosphor powder was characterized using **XRD** and a **F-7000 fluorescence spectrophotometer**. The corresponding chemical reaction and molar ratios are given below.

Chemical Reaction :

$LiNO_3 + 4(1\text{-}x)[Ca(NO_3)_2] + x\,[Eu(NO_3)_3] + 3(H_3BO_3) + CO(NH_2)_2 \rightarrow LiCa_{4(1\text{-}x)}(BO_3)_3\text{: } x\,Eu^{3+}$ + Gaseous Products (H_2O, NH_3, NO_Y)

Table 1.

Synthesized Phosphor	**$LiCa_{4\text{-}x}(BO_3)_3 : x\,Eu^{3+}$ x = 0.03**				
Precursors	$LiNO_3$	$Ca(NO_3)_2$	H_3BO_3	$CO(NH_2)_2$	Eu_2O_3
Molar ratio	1	3.88	3	7.4	0.03
Weight in gm	1.5238	22.9066	4.8692	12.1892	0.1320

Molar Ratio and Stoichiometric amounts of ingredients

IV. RESULTS AND DISCUSSION

The prepared material were characterized by powder XRD and PL. Powder X-ray diffraction measurements were taken on a Rigaku Mini flex II 600 X-ray diffractometer and compared with JCPDS PDF card no.9007607. PL and PLE measurements at room temperature were performed on a F-7000 FL spectrophotometer.

XRD: The powder X-ray diffraction (XRD) pattern of the synthesized $LiCa_4(BO_3)_3$:xEu phosphor shown in Fig.1 displays sharp, well-defined diffraction peaks in the 2θ range 10 - 90°, demonstrating a high degree of crystallinity. The major reflections located near 2θ equals to 30.58°, 32.38°,33.94°, 35.86°, 41.76°, 47.94° and 59.62°. The absence of additional peaks attributable to secondary phases indicates that Eu^{3+} ions were successfully incorporated into the host lattice without forming detectable impurity phases. The $LiCa_4(BO_3)_3$:xEu phosphor crystallizes in a trigonal-type unit cell a = b = 8.6377 Å, c = 11.8490 Å and α = β = 90°, γ = 120° with unit-cell volume 765.612 Å^3.The average crystallite size was estimated from the most intense diffraction peak (2θ=30.65°) using the Debye–Scherrer equation:

$$D = \frac{k\lambda}{\beta\cos\,\theta}$$

where $k = 0.9$, $\lambda = 1.5406$ (Cu Kα), the observed FWHM $(\beta) = 0.156^\circ = 0.00272$ rad , and $\theta = 15.5^\circ$. The calculated average crystallite size is D ≈53 nm indicating the formation of well-crystallized, nano-sized grains favorable

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for efficient luminescence. The XRD pattern of $LiCa_4(BO_3)_3:Eu^{3+}$ is found to be good agreement with the XRD pattern of $LiCa_4(BO_3)_3:Gd^{3+}$[9] reported in the literature.

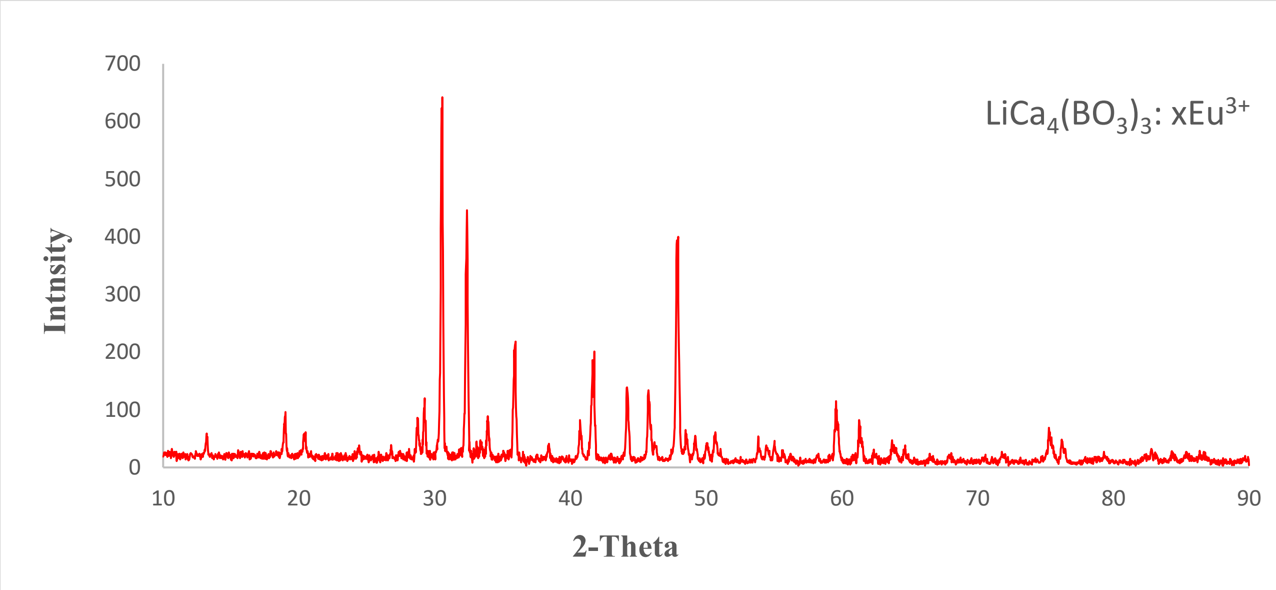

Fig.1: ***XRD pattern of $LiCa_{3.88}(BO_3)_3:0.03Eu^{3+}$ agrees with Takedaite type reference of JCPDS PDF card no. 9007607.***

PL Study: Eu^{3+}doped $LiCa_4(BO_3)_3$ phosphor shows red emission Fig.2 Shows the PL excitation and emission spectra of $LiCa_{3.88}(BO_3)_3:0.03Eu^{3+}$.The photoluminescence excitation spectrum of $LiCa_{3.88}(BO_3)_3:0.03Eu^{3+}$ monitored at 614 nm shows a broad band between 210–310 nm due to the $O \rightarrow Eu^{3+}$ charge-transfer transition, along with several sharp f–f transitions in the 320 - 400 nm range. The strongest excitation peak at 395 nm corresponds to the $^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+}. The emission spectrum displays characteristic Eu^{3+} emissions from 570–700 nm arising from the $^5D_0 \rightarrow {}^7F_j$ (J = 0,1,2,3,4) transitions, with the most intense red emission at 615 nm attributed to the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition, while the 597 nm peak is due to the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition. Under 254 nm excitation, similar Eu^{3+} emissions are observed at 587, 597, (615, 626), 659 and 692 nm, corresponding to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, $^5D_0 \rightarrow {}^7F_4$ transitions[10]. The excitation spectrum (λ_{em} = 614 nm) exhibits a broad CT band near 267 nm along with sharp f–f absorption peaks. The intense emission at 615 nm confirms that the red transition dominates the PL behavior of Eu^{3+}-activated $LiCa_4(BO_3)_3$ phosphor, resulting in strong red luminescence[11].

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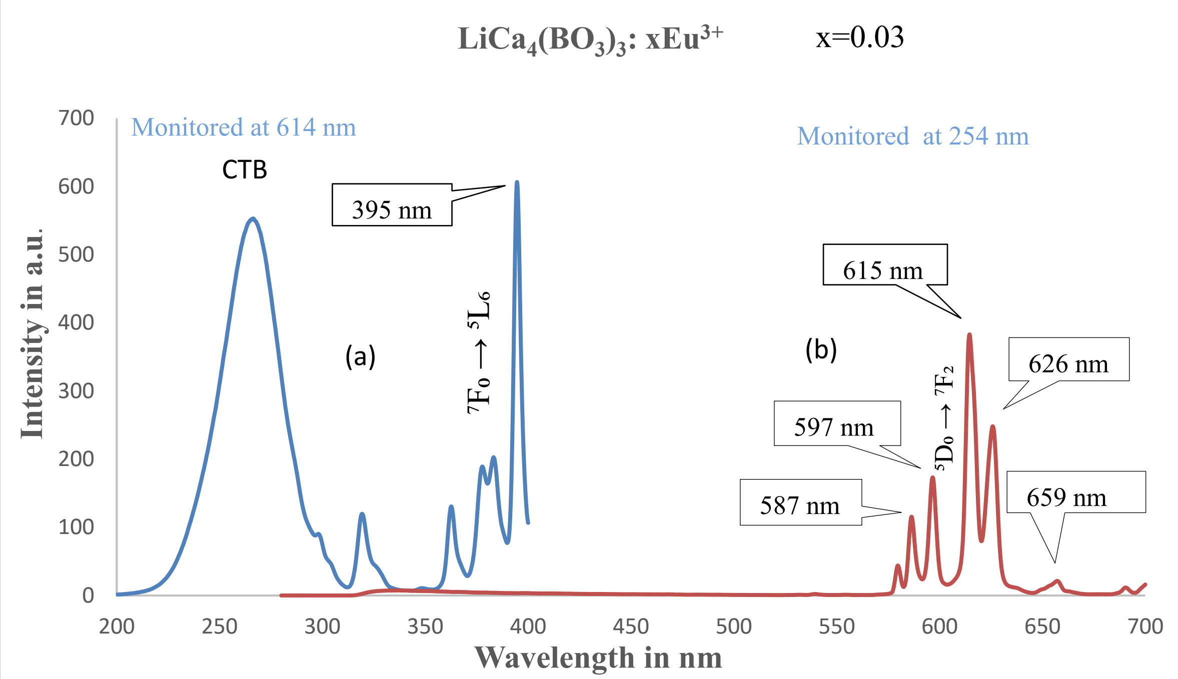

Fig.2: ***Excitation (a) and emission (b) spectra of the luminescence of $LiCa_{3.88}(BO_3)_3$: $0.03Eu^{3+}$.***

CIE Chromaticity: Fig.3 shows the Commission International del Eclairage (CIE) chromaticity diagram of the $LiCa_{3.88}(BO_3)_3$: $0.03Eu^{3+}$ phosphor at 615 nm. CIE values for the phosphor $LiCa_{3.88}(BO_3)_3$:$0.03Eu^{3+}$ are calculated using Zirqle LuxaLight CIE converter and diagram is drawn using GO-CIE software[12].

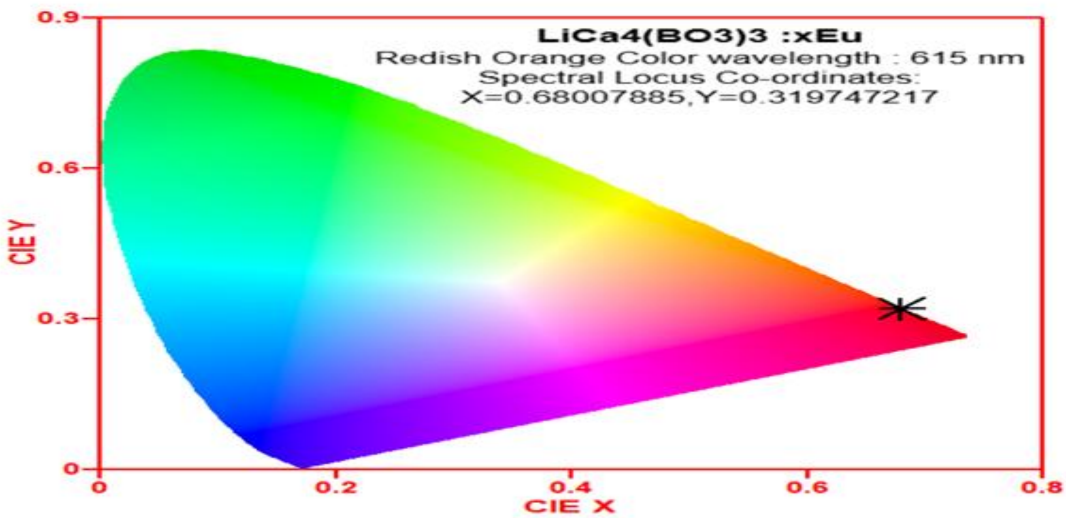

Fig.3: ***CIE chromaticity coordinates diagram of $LiCa_{3.88}(BO_3)_3$:$0.03Eu^{3+}$ phosphor at 615 nm***

In $LiCa_{3.88}(BO_3)_3$: $0.03Eu^{3+}$ for six hundred fifteen[615nm] emission wavelength chromaticity co-ordinates are X = 0.6801, Y = 0.3197. The color coordinates are close to the standard red color of NTSC (0.67, 0.33). This indicates that europium activated $LiCa_4(BO_3)_3$ is a promising candidate with red emission when excited in the near UV region[13]. It lies in the red region of the spectrum and is shown by black star in the figure. By using online CCT calculator Correlated Color Temperature of $LiCa_{3.88}(BO_3)_3$:$0.03Eu^{3+}$ was found to be 4340 ^{0}K from CIE 1931 xy co-ordinates. From CCT equals to 4340^{0}K we conclude that $LiCa_{3.88}(BO_3)_3$:$0.03Eu^{3+}$ is "natural" white or "neutral" phosphor.

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Table 2

Comparison of CIE co-ordinates and CCT values of $LiCa_4(BO_3)_3:Eu^{3+}$ with various Eu^{3+} doped phosphor materials

Phosphor	CIE color co-ordinates		CCT ºk	Ref.
	X	Y		
$LiCa_4(BO_3)_3:Eu^{3+}$	0.6801	0.3197	4340	Present Work
$YCa_4O(BO_3)_3:Eu^{3+}$	0.67	0.32	4098	[11]
KSr4(BO3)3: Eu^{3+}	0.64	0.35	2433	[14]
$Li_6Gd(BO_3)_3:Eu^{3+}$	0.57	0.34	1899	[13]
$NaSrB_5O_9:Eu^{3+}$	0.63	0.37	1992	[15]
$Li_2Al_2B_2O_7:Eu^{3+}$	0.68	0.32	4320	[16]
$Ba_2Lu_5B_5O_{17}:Eu^{3+}$	0.643	0.356	2228	[17]

FTIR Spectra : The FTIR spectrum of the $LiCa_{3.88}(BO_3)_3:0.03Eu^{3+}$shows several characteristic vibrational bands that confirm the presence of borate groups and other functional units typically observed in rare-earth-doped borate materials[7]. The bands at 4627 cm⁻¹ and 3902 cm⁻¹ these weak bands generally arise from O–H vibrations. Their presence indicates trace moisture or surface-adsorbed hydroxyl groups. The strongest and most characteristic borate vibrations occur between 1450–1200 cm^{-1}, corresponding to asymmetric stretching of triangular BO_3 units. The band at 1009 –929 cm^{-1} corresponds to symmetric stretching of BO_3 groups. The bands at 771 cm^{-1} and 699 cm^{-1} represent in-plane and out-of-plane bending vibrations of BO_3 triangles, confirming the presence of trigonal borate units. The peaks at 502 cm^{-1} and 417 cm^{-1} correspond to B–O–B linkage bending and lattice vibrations attributed to the metal–oxygen framework in the borate matrix.

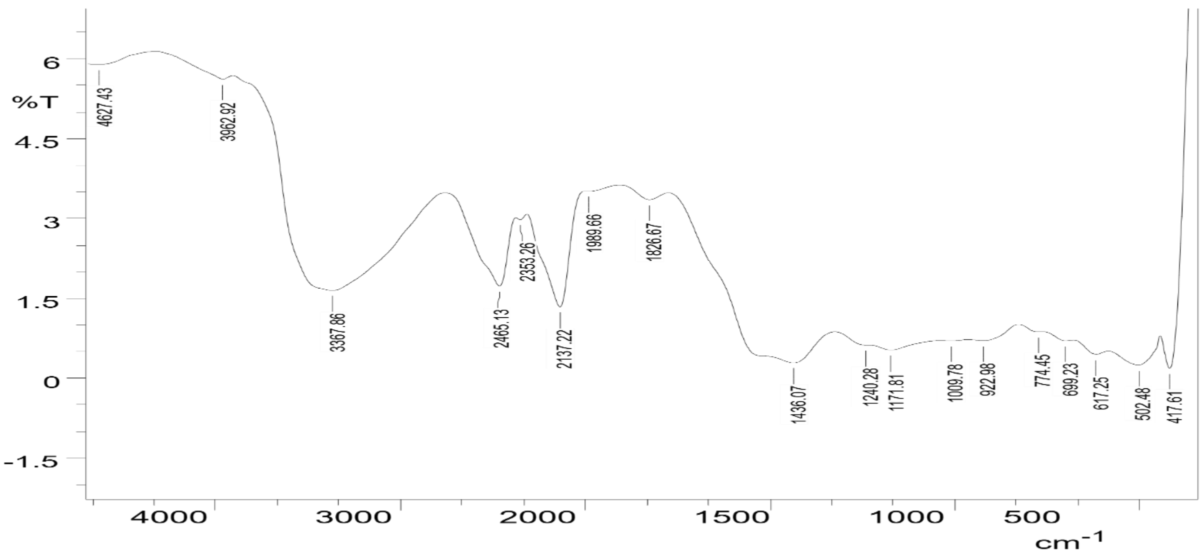

Fig.4 : ***FTIR Spectra of*** $LiCa_{3.88}(BO_3)_3:0.03Eu^{3+}$

V. CONCLUSION

The $LiCa_{3.88}(BO_3)_3:0.03Eu^{3+}$ phosphor prepared by solution combustion synthesis method exhibits strong red luminescence dominated by the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition at 615 nm. The excitation spectrum reveals both a broad $O \rightarrow Eu^{3+}$ charge-transfer band and sharp Eu^{3+} f–f transitions, confirming efficient energy absorption. CIE chromaticity coordinates X = 0.6801, Y= 0.3197 giving redish orange color

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which place the phosphor in the deep-red region of the color space and a correlated color temperature of 4340 ^{0}K suggests that the emission corresponds to a neutral or natural white category. Overall, the Eu^{3+}-activated $LiCa_4(BO_3)_3$ phosphor demonstrates excellent red-emitting potential for advanced photonic applications.

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