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An Emission Analysis of A Novel Trivalent Eu^{3+} Ion-Doped Zinc Phosphate Glass for Photonic Applications

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Abstract. The popularity of inorganic glasses is growing due to their wide range of applications. Therefore, this study focuses on creating a new type of zinc phosphate glasses (ZnP) that contain Eu^{3+} ions by using the melt-quenching method. The glasses were made in the following composition: (60-x)P_2O_5-20ZnO-10SrO-10LiF-xEu_2O_3, with x ranging from 0.1 to 2.0%. The XRD profiles of the fabricated glasses revealed their amorphous nature, and the photoluminescence spectra of the prepared glasses displayed five distinct emission bands at an excitation wavelength of 394 nm. Judd-Ofelt (JO) parameters were calculated from the photoluminescence spectra and showed a trend $\Omega_2 > \Omega_4$. The radiative total transition probabilities (A_T), stimulated emission cross-sections (σ), and quantum efficiencies (η) were also calculated. The $^5D_0 \rightarrow {}^7F_2$ transition at 612 nm exhibits high intensity. The characteristic color emission of the ZnP glasses was determined by means of the Commission International de l'éclairage (CIE) 1931 chromaticity coordinates (x, y) and lies in the red region. These glasses exhibited strong red luminescence. Zinc phosphate glasses (ZnP) doped with Eu^{3+} ions have potential applications as red lighting components.

INTRODUCTION

Rare earth (RE)-doped hosts have been the subject of research for many decades and have potential applications in various optical devices including solid-state lighting, optical temperature sensors, lasers, color displays, and optical communications [1-2]. Trivalent rare-earth ions have gained increasing importance in modern optical technology because of their rich color emissions from either 5d-4f or 4f-4f transitions [3]. Glass formers, such as phosphate-based oxide glasses, have been used, but their limitations have led to the addition of network modifiers, such as ZnO, SrO, and LiF [4]. LiF was added to maintain transparency[5]. Fluorides have been added to increase luminescence intensity, which is particularly important for W-LEDs[6]. Eu^{3+} is an efficient luminescence center among trivalent rare-earth ions owing to its energy-level configuration and excellent luminescence efficiency[7]. The trivalent europium ion (Eu^{3+}) is widely used as a dopant for inorganic structures and as a red light-emitting center for display devices because of its $^5D_0 \rightarrow {}^7F_2$ electronic transition[8]. Eu^{3+} ions are often employed as activators for blue (Eu^{2+}) and red (Eu^{3+}) emissions in phosphate glasses, depending on the preparation environment[3]. Recently, researchers have conducted thorough investigations into diverse glass matrices infused with Eu^{3+} ions. Dhavamurthy et al., recently delved into the optical features of Eu^{3+} doped alumino borophosphate glass which encompasses Al^{3+}, Zn^{2+}, Li^{2+}, Sr^{2+}, and Ba^{2+} ions[3]. Priya et al., conducted a thorough investigation into the incorporation of Eu^{3+} ions in borate and boro-phosphate glasses, analysing their optical characteristics, radiative spectroscopic properties, and colour emission and resulting glasses displayed a distinct reddish-orange light emission, making them a viable candidate for laser applications [9]. The main objective of this study is to assess the practicability of ZnP glasses containing Eu^{3+} ions by evaluating their photoluminescence properties. The purpose of this study was to determine its suitability for use in applications that require red light emission.

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EXPERIMENTAL METHODS

The glasses were fabricated using a traditional melt-quenching method[10], which involved employing high-purity raw materials such as LiF, SrO, ZnO, P_2O_5, and Eu_2O_3. The glass compositions are expressed as (60-x)P_2O_5-20ZnO-10SrO-10LiF-xEu_2O_3, where x varied from 0.1 to 2.0%. A detailed explanation of the preparation of the glass is given elsewhere [4]. The prepared glass samples were labelled ZnP01Eu, ZnP05Eu, ZnP10Eu, ZnP15Eu, and ZnP20Eu, respectively. To determine whether the Eu^{3+} ion-doped ZnP glasses were crystalline or amorphous, a RIGAKU bench top Mini flex 600 X-ray diffractometer operated at 40 kV and 15 mA was used[11]. To perform excitation and emission studies, a Horiba Jobin Yvon Fluorolog FL3-11 spectrofluorometer was used with a 450 W xenon lamp and a UV-visible source[11].

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The XRD profiles of the Eu^{3+} ions doped ZnP glasses are depicted in Fig. 1. The profiles indicate that there are no crystalline peaks present, which confirms the amorphous nature of the synthesized ZnP glasses[12]. Additionally, the XRD spectra reveal that the amorphous nature of the ZnP glasses is maintained even after the incorporation of Eu^{3+} ions.

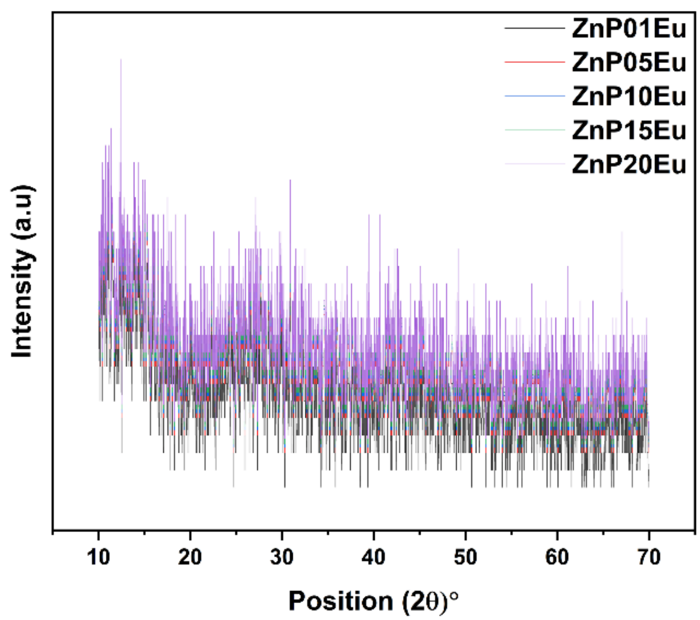

FIGURE 1. XRD profiles of ZnP glasses doped with Eu^{3+} ions

Photoluminescence Analysis

The excitation spectra of ZnP20Eu glass are depicted in Fig. 2(a) at an emission wavelength of 612 nm. Despite the intensity fluctuations, the remaining glasses have shapes similar to those of the ZnP20Eu glass. The spectra reveal Seven excitation bands were observed at wavelengths of 362, 383, 394, 414, 464, 525, and 532 nm, corresponding to the $^7F_0 \rightarrow {}^5D_4$, $^7F_0 \rightarrow {}^5G_2$, $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_3$, $^7F_0 \rightarrow {}^5D_2$, $^7F_1 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_1$ transitions, respectively [6]. Of all the detected transitions, the transition detected as $^7F_0 \rightarrow {}^5L_6$ at 394 nm had the highest intensity and was therefore a good candidate for monitoring the emission profiles of the prepared Eu^{3+} ion-doped ZnP glasses[13].

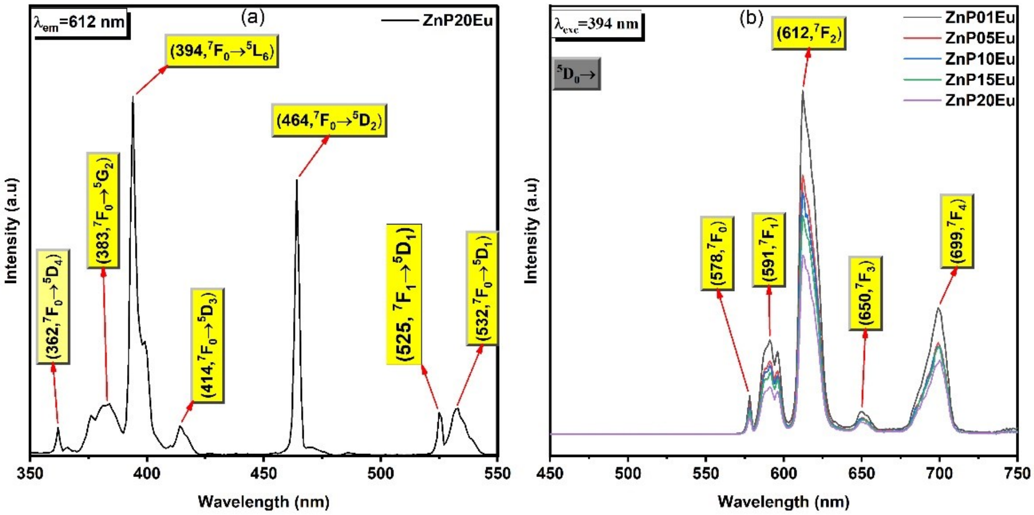

FIGURE 2 (a) Representative excitation spectra of 2.0 mol% of Eu^{3+} ion doped ZnP glass (b) Photoluminescence spectra of Eu^{3+} ion doped ZnP glass.

Figure 2(b) shows the Photoluminescence spectra of ZnP glasses infused with varying concentrations of Eu^{3+} ions upon excitation at a wavelength of 394 nm. The spectra showed five distinct bands, comprising three principal and two minor bands, at wavelengths of 578, 591, 612, 650, and 699 nm. These bands correspond to the transitions $^5D_0 \rightarrow {}^7F_P$ (P=0,1,2,3,4)[14]. All transitions are electric dipole transitions, except for the $^5D_0 \rightarrow {}^7F_1$ transition. Among the five transitions, the electric dipole transition from $^5D_0 \rightarrow {}^7F_2$, which adheres to the selection rule of $\Delta S = 0$, $\Delta L \leq 2$, and $\Delta J \leq 2$ [15], is responsible for emitting the most concentrated and prominent red emission with a center wavelength of 612 nm in the Eu^{3+} ion. This is in contrast to the magnetic dipole transition from $^5D_0 \rightarrow {}^7F_1$, which occurs at 591 nm. The $^5D_0 \rightarrow {}^7F_2$ transition is widely known as the hypersensitive transition (HST)[16].

Analysis of Judd-Ofelt (JO) & Laser Properties

The emission spectra were analyzed using refractive indices and the JOES application software to calculate the Judd-Ofelt (JO) intensity parameters and various laser parameters[17], which are presented in Table 1. The results show that for all ZnP glasses, the trend $\Omega_2 > \Omega_4$ indicates the covalency and asymmetric nature of the glasses. Specifically, Ω_2 describes the covalency and asymmetry of the ligand field surrounding the RE ion site, whereas Ω_4 and Ω_6 describe bulk properties such as stiffness, viscosity, and basicity associated with long-range coordination effects [1]. The study reveals that as the concentration of Eu^{3+} ions increased from 0.1 mol % to 1.0 mol %, the covalency and asymmetric nature decreased but further increased with an increase in Eu^{3+} ion concentration. Among all the prepared ZnP glasses, the ZnP20Eu glass shows high magnitudes of (Ω_2:6.046 and Ω_4:5.747) $\times 10^{-20}$ cm^2, respectively, and a high total transition probability (A_T:423.27 s^{-1}).

TABLE 1. Refractive index (n), JO parameters (Ω_2, $\Omega_4 \times 10^{-20}$, cm^2), and radiative total transition probability (A_T,s^{-1}) of the ZnP glasses doped with different concentrations of Eu^{3+} ions.

	ZnP01Eu	**ZnP01Eu**	**ZnP01Eu**	**ZnP01Eu**	**ZnP01Eu**
n	1.651	1.653	1.653	1.654	1.654
Ω_2	5.742	5.343	4.935	5.489	5.747
Ω_4	5.197	4.649	4.687	5.412	6.046
A_T	403.71	377.59	361.13	399.76	423.27

From the analysis of the emission spectra, laser parameters were calculated and results are presented in Table 2. Notably, the stimulated emission cross section (σ) is the most critical parameter that determines the lasing characteristics of the prepared glasses [1]. Among the three transitions examined, the $^5D_0 \rightarrow {}^7F_2$ transition displayed high branching ratios (β) and stimulated emission cross sections (σ) for all glass samples[18]. Notably, ZnP20Eu glass exhibited the highest magnitude of stimulated emission cross section (σ) for the $^5D_0 \rightarrow {}^7F_2$ transition among all the glass samples tested. Furthermore, the ZnP20Eu glass demonstrated the highest PL quantum efficiency (η) of 77.51% among all glass samples. The results obtained suggest that ZnP20Eu glass, with its high stimulated emission cross section (σ) and PL quantum efficiency (η) values, is a potential candidate for applications in red emission laser technology.

TABLE 2. Spontaneous emission transition rates (A_R, s^{-1}), experimental branching ratios (β, %), stimulated emission cross-sections (σ, cm^2), and PL Quantum efficiency (η, %).

	A_R	β	σ	η
ZnP01Eu				75.03
$^5D_0 \rightarrow {}^7F_1$	65.406	0.162	1.516	
$^7F_2$	233.224	0.577	6.305	
$^7F_4$	105.084	0.261	3.958	
ZnP05Eu				70.14
$^5D_0 \rightarrow {}^7F_1$	65.424	0.173	1.440	
$^7F_2$	217.722	0.576	5.812	
$^7F_4$	94.449	0.251	3.507	
ZnP10Eu				
$^5D_0 \rightarrow {}^7F_1$	65.164	0.181	1.401	66.86
$^7F_2$	200.73	0.555	5.506	
$^7F_4$	95.236	0.264	3.458	
ZnP15Eu				73.20
$^5D_0 \rightarrow {}^7F_1$	65.679	0.164	1.504	
$^7F_2$	223.989	0.560	6.108	
$^7F_4$	110.098	0.276	4.182	
ZnP20Eu				77.51
$^5D_0 \rightarrow {}^7F_1$	65.663	0.155	1.473	
$^7F_2$	234.646	0.554	6.344	
$^7F_4$	122.964	0.291	4.516	

Colorimetry

The characteristic color emission of ZnP glasses was determined using CIE 1931 chromaticity coordinates, as depicted in Fig. 3. The CIE diagram allows for the evaluation of the color of the light perceived by the human eye. The CCT (K) was calculated using McCamy's approximation [19-20]. Table 3 displays the CIE x and y coordinates, correlated colour temperature CCT (K), and colour purity CP (%) for the ZnP glasses that were obtained. These color coordinates lie in the red region of the CIE 1931 color chart, which corresponds to red emission. Furthermore, these coordinates were located near the locus line. The sample ZnP20Eu exhibits a color purity of approximately 99.3%. This result suggests that ZnP glasses doped with Eu^{3+} have the potential to be utilized as promising candidates for red light-emitting applications.

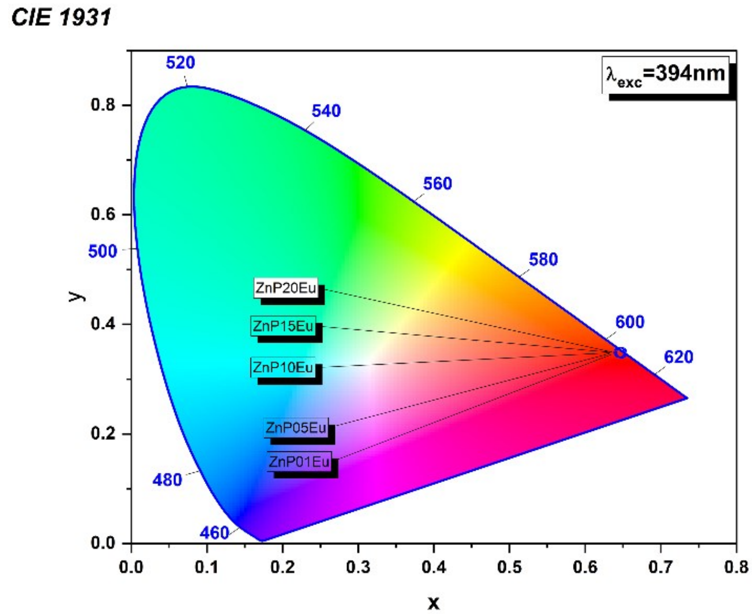

FIGURE 3. 1931 CIE color chart of Eu^{3+} ions infused ZnP glasses

TABLE 3. 1931 CIE colour coordinates (x, y), correlated colour temperature (CCT, K) and colour purity (CP, %) of ZnP glasses infused with Eu^{3+} ions.

Glass Sample	Color Coordinates		Correlated color temperature (K)	Color Purity (%)
	x	y	CCT	CP
ZnP01Eu	0. 64451	0. 34868	1047	98.1
ZnP05Eu	0. 64574	0. 34834	1041	98.3
ZnP10Eu	0. 64682	0. 34823	1036	98.6
ZnP15Eu	0. 64817	0. 34737	1028	98.8
ZnP20Eu	0. 64846	0. 34893	1033	99.3

CONCLUSION

Using the melt-quenching method, different concentrations of Eu^{3+} ion-doped ZnP glasses were prepared, each with a different composition of (60-x)P_2O_5-20ZnO-10SrO-10LiF-xEu_2O_3, where x varied from 0.1 to 2.0%. The amorphous nature of the ZnP glasses was verified using XRD profiles. The JOES application software was employed to examine the photoluminescence spectra and determine the JO intensity parameters and various laser parameters. The JO intensity parameters for all synthesized Eu^{3+} ion-doped ZnP glasses exhibited a consistent trend of $\Omega_2>\Omega_4$. Glass ZnP20Eu is particularly noteworthy because of its strong covalency and asymmetrical properties within the ligand field, particularly in the vicinity of the Eu^{3+} ion location. Among all the prepared ZnP glasses doped with Eu^{3+} ions, the ZnP20Eu glass demonstrated high A_R, σ, and η values, indicating its potential as a candidate for visible laser applications. The CIE color coordinates and CCT obtained fell within the red region, with the ZnP20Dy glass exhibiting a high CP value of 93.7%, thus confirming the suitability of ZnP glasses doped with varying concentrations of Eu^{3+} ions for red light applications.

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