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# Journal of Non-Crystalline Solids

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# Raman and photoluminescence studies of europium doped zincfluorophosphate glasses for photonic applications



V.B. Sreedhar<sup>a,b</sup>, K. Venkata Krishnaiah<sup>b</sup>, S.K. Nayab Rasool<sup>b</sup>, V. Venkatramu<sup>c</sup>, C.K. Jayasankar<sup>a,\*</sup>

- <sup>a</sup> Department of Physics, Sri Venkateswara University, Tirupati 517501, India
- <sup>b</sup> Department of Physics, R.G.M. College of Engineering and Technology, Nandyal 518501, India
- <sup>c</sup> Department of Physics, Yogi Vemana University, Kadapa 516005, India

#### ARTICLE INFO

# Keywords: Europium Zinc-fluorophosphate glasses Electron-phonon coupling strength Judd-Ofelt parameters Radiative properties

#### ABSTRACT

Europium ( $Eu^{3+}$ )-doped zinc-fluorophosphate (PKAZfEu) glasses have been synthesized by usual meltquenching technique. Optical absorption, photoluminescence excitation, photoluminescence and decay curves of these glasses were measured at room temperature and investigated. The Judd-Ofelt (JO) parameters ( $\Omega_{\lambda}$ ,  $\lambda=2$  and 4) were determined from the measured emission spectra and used for quantifying the radiative parameters that include radiative transition probability ( $A_R$ ), radiative lifetime ( $\tau_R$ ), branching ratios ( $\beta_R$ ), effective bandwidths ( $\Delta \lambda_{eff}$ ) and peak stimulated emission cross-section ( $\sigma(\lambda_P)$ ) for the  $^5D_0$  luminescent state of  $Eu^{3+}$ . The electron-phonon coupling strength and phonon energy of the glasses were obtained from the phonon sideband spectrum. The chromaticity coordinates for different concentration of PKAZfEu glasses were evaluated by analyzing the emission spectra with Commission International de l'Eclairage (CIE) color diagram. Decay curves of  $Eu^{3+}$  ions for the  $^5D_0 \rightarrow ^7F_2$  transition have been obtained under 393 nm excitation. The decay curves exhibit a single exponential behavior for all the investigated glasses. Luminescence properties of  $Eu^{3+}$  ion for the  $^5D_0 \rightarrow ^7F_2$  transition indicate that the PKAZfEu glasses could be a suitable gain medium for visible red lasers and display devices.

# 1. Introduction

Development of novel lanthanide ( ${\rm Ln}^{3+}$ )-doped luminescent materials for photonic devices have drawn significant interest in the scientific and technological point of view [1–4]. These  ${\rm Ln}^{3+}$ -doped luminescent materials can find applications in diverse fields of photonics such as optical data storage, remote sensors, upconversion lasers, color displays, infrared laser viewers, indicators, optical printing, etc. Now-adays, phosphate glasses were also investigated due to their immense potential for bio-applications. However, these glasses alone do not have much chemical durability compared to multi component-phosphate glasses. These glasses modified with sodium, calcium, magnesium, and zinc were established abundance of interest.

Moreover, fluorophosphate glasses exhibit the combined advantages of fluoride and oxide matrices including good moisture resistance, relatively low refractive index, extended transparency from near ultraviolet (UV) to mid infrared (MIR) range, relatively low phonon energy, therefore, these are the suitable hosts for  ${\rm Ln}^{3+}$  ions [5,6]. However, ZnO plays a role of distribution of  ${\rm Ln}^{3+}$  ions through the matrix to prevent non-radiative relaxations which leads to enhance the

fluorescent emission [7]. It is challenging to reduce OH $^-$  groups in phosphate glasses, however, these can be minimized significantly in fluorophosphate glasses without the use of control atmosphere for making the glass. Further, with the addition of zincfluoride content to the glass matrix, which minimize the OH $^-$  groups and hence increases the radiative emission of the fluorescent level [8]. In the present host, Al $_2$ O $_3$  is introduced to the phosphate glasses to expand their mechanical properties.

Usually, most of the Ln ions present a single valence state in glasses, i.e. 3+ state, while europium exhibit both valence states, 2+ and 3+. Addition of europium (Eu<sup>3+</sup>) ion in these glasses brings a significant change in their optical, structural and magnetic behavior, which is useful in finding new applications. A detailed structural investigations of these glasses becomes highly essential. These Eu<sup>3+</sup>-doped glasses are mostly utilized for field emission technology as a red emitting phosphors because of their narrow emission at around 610 nm [9]. The Eu<sup>3+</sup>-doped glasses got a special attention due to the following reasons.

(i) At room temperature, persistent spectral hole burning has been applied to the  ${}^5D_0 \rightarrow {}^7F_0$  transition of Eu<sup>3+</sup> as it has a potential

E-mail address: ckjaya@yahoo.com (C.K. Jayasankar).

<sup>\*</sup> Corresponding author.

practice for high density optical data storage application [10].

- (ii) To estimate the local structure around the Ln ions, Eu<sup>3+</sup> ion is the most desirable one as its fluorescence is highly sensitive under the effect of environment as well as relatively modest energy level scheme [11].
- (iii) Magnetic-dipole transition,  ${}^5D_0 \rightarrow {}^7F_1$  (orange emission) of Eu<sup>3+</sup> is not influenced significantly by the site symmetry as it is parity allowed transition. On the other hand, the red emission (610–630 nm region) due to electric-dipole transition,  ${}^5D_0 \rightarrow {}^7F_2$ gains in intensity as there is a decrease of symmetry [12].

This paper reports the zinc-fluorophosphate glasses doped with varying Eu<sup>3+</sup> ion concentration. These glasses have been analyzed through X-ray diffraction (XRD), differential thermal analysis (DTA), Raman, absorption, photoluminescence and decay curves. The glass transition and crystallization temperatures were obtained from the DTA. Raman spectrum is used for identifying the various functional groups of the glass. Luminescence properties of the glass samples were evaluated and compared with reported Eu<sup>3+</sup>-doped systems.

# 2. Experimental techniques

# 2.1. Glass synthesis

The Eu3+-doped zinc-fluorophosphate glasses with the molar composition of  $44P_2O_5 + 17K_2O + 9Al_2O_3 + (30 - x) ZnF_2 + x Eu_2O_3$ (where x = 0.01, 0.05, 0.1, 0.5, 1.0, 2.0 and 3.0 mol% labeled as PKAZfEu0.01, PKAZfEu0.05, PKAZfEu0.1, PKAZfEu0.5, PKAZfEu1.0, PKAZfEu2.0 and PKAZfEu3.0, respectively) were synthesized by usual melt-quenching technique. About 20 g of glass composition was grinded carefully in an agate motor and taken in a platinum crucible. The crucible was heated at 1100 °C for 90 min. in an electric furnace. The melt was then casted onto a brass mold and subsequently annealed at 380 °C for 14 h for reducing the thermal strains. Usually, the glass samples were permitted to cool to room temperature and polished for different characterizations.

# 2.2. Characterizations

Thickness of the glass was assessed by a digital screw gauge. Density of the samples was estimated by the Archimedes' method with de-ionized water as dipping liquid. Abbe refractometer is used for measuring the index of refraction of the glasses at a wavelength of 589.3 nm with1bromonaphthalene ( $C_{10}H_7Br$ ) as adhesive liquid. Physical properties of the glasses were evaluated from the values of thickness, index of refraction, density and concentration using relevant expressions [13,14] and presented in Table 1. The experiments have been repeated to estimate errors. Therefore, all the above properties were measured for three times and are further used to compute mean and standard deviation using the expression [15].

Standard deviation ( $\sigma$ ) =  $\sqrt{\frac{\sum (x-y)^2}{N}}$  where x is the actual measurement reading, y is the mean reading and *N* is the number of measurements.

Table 1 Physical and optical properties of Eu3+: PKAZfEu1.0 glass.

Refractive index, n	1.55 ( ± 0.01)
Density, d (gm/cc)	$3.149 (\pm 0.002 \mathrm{g/cc})$
Optical path length, <i>l</i> (mm)	1.72 ( ± 0.01 mm)
Concentration, C (10 <sup>20</sup> ions/c.c)	3.126 ( ± 0.002 ions/cc)
Inter nuclear distance, r <sub>i</sub> (Å)	14.73 ( ± 0.001 A°)
Dielectric constant, $\varepsilon$	2.403 ( ± 0.021)
Reflection losses, R (%)	4.652 ( ± 2%)
Molecular refractivity, R <sub>m</sub> (cc)	12.28 ( ± 0.03)
Molecular electron polarization factor, α	$2.44 \times 10^{-22}$
Polaron radius, r <sub>p</sub> (Å)	$5.9 (\pm 0.01A^{\circ})$

The XRD profile of the glass was obtained using the X-ray diffractometer (RIGAKU; Miniflex-600) under CuKα1 (1.5406 Å) rays excitation. Thermal behavior of the glasses was obtained in the temperature range of 30–1300 °C using DTA (Model: Exstar TG/DTA 6300). About 11.30 mg of the glass sample in the form of powder was taken in an alumina pan of DTA setup and was then examined at the heating rate of 5 °C/min under nitrogen atmosphere with a flow rate of 200 ml/min.

Raman spectrum of the glass sample was recorded by using Raman spectrometer (Lab Ram HR800) under the wavelength of 514 nm (Ar + laser) excitation and the signal was collected under the geometry of back scattering. The absorption spectrum of glass sample was measured by using JASCO UV (V-670) spectrophotometer in the wavelength range of 200-2300 nm. The JOBIN YVON fluorolog-3 spectrofluorometer with xenon lamp an excitation source has been used for measuring the photoluminescence, photoluminescence excitation and decay profiles.

#### 3. Results and discussion

# 3.1. X-ray diffraction spectrum

The X-ray diffraction (XRD) technique is used to recognize the structure of the materials. XRD profile of PKAZfEu1.0 glass is shown in the Fig. 1 that displays a broad hump at lower diffraction angles (pronounced structure), confirms the amorphous nature of the PKAZfEu1.0 glass.

#### 3.2. Differential thermal analysis

Differential thermal analysis (DTA) profile of PKAZfEu1.0 glass is shown in Fig. 2. Thermal analysis explores the glass transition (T<sub>o</sub>, 638 °C,  $\pm 2/$  °C), crystallization (T<sub>c</sub>, 926 °C,  $\pm 2/$  °C) and melting (T<sub>m</sub>, 1100 °C,  $\pm$  2/°C) temperatures of the PKAZfEu1.0 glass. The factor of glass stability ( $\Delta T = T_x - T_g$ ) and the Hruby's parameter (H) of PKAZfEu1.0 glass were found to be 288 °C and 1.65, respectively. The high value of  $\Delta T = 288$  °C,  $\pm 2/$  °C, evidences that the present glass found to be suitable as a potential candidate for fiber drawing ability. A large value of Tg is essential to reduce the thermal damage of the sample which can be used in high power lasers [16,17]. Glass with relative stability and durability could be designated for laser applications.

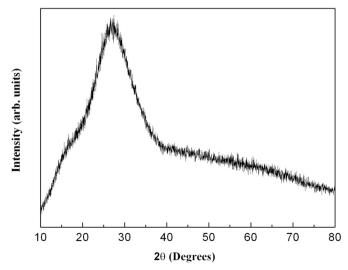


Fig. 1. XRD pattern of PKAZfEu1.0 glass.

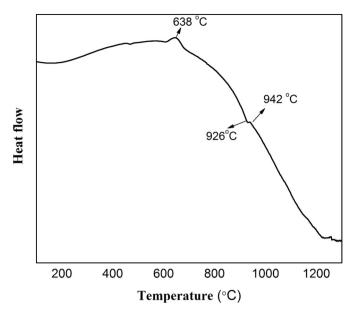


Fig. 2. Differential thermal profile of PKAZfEu1.0 glass.

# 3.3. Raman spectrum

Raman spectrum of PKAZfEu1.0 glass is shown in Fig. 3, reveals seven characteristic bands at 358, 530, 637, 755, 930, 1091 and  $1144\,\mathrm{cm}^{-1}$  that are associated to the vibrations of phosphate groups [18]. Raman modes of the phosphate glass network can be analyzed in the spectral regions including modes of non-bridging oxygen ( $\sim$ 905–1140 cm $^{-1}$ ), bridging oxygen ( $\sim$ 700–900 cm $^{-1}$ ) and deformation ( $\sim$ 500 cm $^{-1}$ ).

Usually, phosphate network is developed from the corner sharing of tetrahedral units of PO<sub>4</sub> [19]. The band centered at 1144 cm<sup>-1</sup> relates the symmetric stretching vibration of O-P-O groups in the Q<sup>1</sup> tetrahedra of metaphosphate glass [20,21]. Band centered at 1091 cm<sup>-1</sup> governs the mode of asymmetric stretching of P-O-P groups that are linked with metaphosphate groups [22–24]. A band positioned at 930 cm<sup>-1</sup> relates the mode of P-O symmetric stretching vibrations (it relates to the non-bridging oxygens on the Q<sup>0</sup> tetrahedral groups). The reason to increase Q<sup>0</sup> groups might be due to the rupture of phosphate chains [25]. Raman band at 755 cm<sup>-1</sup> is related to the symmetric stretching vibrational

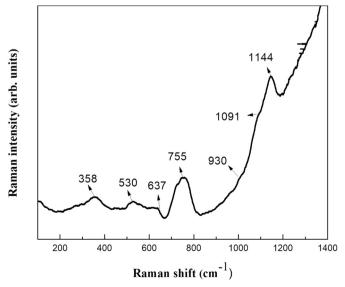


Fig. 3. Raman spectrum of PKAZfEu1.0 glass.

mode of P-O-P bridging bond in Q $^1$  structure [26-29]. This indicates further rupture of phosphate groups. The weak band positioned at 637 cm $^{-1}$  belongs to the vibration modes of Al $_2$ O $_3$  [18,30]. A band centered at 530 cm $^{-1}$  corresponds to twisting vibrations of O-P-O and PO $_2$  modes. Raman band at 358 cm $^{-1}$  relays about the skeletal deformation vibrations of various phosphate chains and PO $_3$  deformation [31,32]. From the Raman analysis, phonon energy of PKAZfEu1.0 is found to be 1144 cm $^{-1}$  that plays a vital character on the photoluminescence properties of Eu $^{3+}$  ions.

# 3.4. Optical absorption and excitation spectra

Fig. 4. (a) and (b) displays the optical absorption profile of 1.0 mol% Eu<sub>2</sub>O<sub>3</sub>-doped zinc-fluorophosphate glass in the UV-visible and NIR regions. These bands are ascribed due to a typical  $4f^6-4f^6$  optical transition of Eu³+ ions from both the ground  $(^7F_0)$  and excited  $(^7F_1)$  states. Absorption bands in the UV-visible region are centered at 362, 376, 382, 393, 465, and 525 nm are ascribed to the  $^7F_0 \rightarrow ^5D_4$ ,  $^5G_3$ ,  $^5G_2$ ,  $^5L_6$ ,  $^5D_2$ , and  $^5D_1$  transitions, respectively. In addition, some of the transitions centered at 413 and 535 nm are assigned to  $^7F_1 \rightarrow ^5D_3$  and  $^5D_1$ . Absorption bands in NIR region are correspond to  $^7F_0 \rightarrow ^7F_6$  (2087 nm) and  $^7F_1 \rightarrow ^7F_6$  (2208 nm) transitions. The absorption transition,  $^7F_0 \rightarrow ^5L_6$  is more intense although it do not followed by the selection rules ( $\Delta S$  and  $\Delta L$ ), however it is followed by  $\Delta J$  rule. The  $^7F_0 \rightarrow ^5D_2$  transition is allowed transition of induced electric-dipole and it is hypersensitive to the environment about the Eu³+ ions and the  $^7F_0 \rightarrow ^5D_1$  transition is allowed transition of magnetic-dipole.

The photoluminescence (PL) excitation spectrum of PKAZfEu1.0 glass was obtained by screening a red emission at 610 nm is shown in Fig. 5. The spectrum comprises of characteristic excitation bands of Eu³+ ion centered at 362 nm (27,624 cm³-1,  $^7F_0 \rightarrow ^5D_4$ ), 376 nm (26,595 cm³-1,  $^7F_0 \rightarrow ^5G_3$ ), 382 nm (26,178 cm³-1,  $^7F_0 \rightarrow ^5G_2$ ), 394 nm (25,380 cm³-1,  $^7F_0 \rightarrow ^5L_6$ ), 415 nm (24,096 cm³-1,  $^7F_1 \rightarrow ^5D_3$ ), 465 nm (21,505 cm³-1,  $^7F_1 \rightarrow ^5D_2$ ), 526 nm (19,011 cm³-1,  $^7F_0 \rightarrow ^5D_1$ ) and 534 nm (18,726 cm³-1,  $^7F_1 \rightarrow ^5D_1$ ). More intense absorption bands are observed in the excitation spectrum that is centered at 394 nm and 465 nm corresponds to the  $^7F_0 \rightarrow ^5L_6$  and  $^7F_0 \rightarrow ^5D_2$  transitions. It is remarkable that the excitation bands in the wavelength range of 380–480 nm, are much stronger for utilizing these glasses for different device applications.

# 3.5. Fluorescence spectra and Judd-Ofelt analysis

Emission spectra of PKAZfEu glasses are shown in Fig. 6. The spectra display five bands centered at 579 nm (17,271 cm<sup>-1</sup>,  ${}^5D_0 \rightarrow {}^7F_0$ ), 585 nm (17,094 cm<sup>-1</sup>,  ${}^5D_0 \rightarrow {}^7F_1$ ), 612 nm (16,339 cm<sup>-1</sup>,  ${}^5D_0 \rightarrow {}^7F_2$ ), 654 nm (15,290 cm<sup>-1</sup>,  ${}^5D_0 \rightarrow {}^7F_3$ ) and 702 nm (13,888 cm<sup>-1</sup>,  ${}^5D_0 \rightarrow {}^7F_3$ ) <sup>7</sup>F<sub>4</sub>). Red emission centered at 610 nm is the strongest among the other transitions. The intensity of emission of the electric-dipole transition,  $^{5}D_{0} \rightarrow ^{7}F_{2}$  depends significantly on the native symmetry about the Eu<sup>3+</sup> ion. On the other hand, the intensity of the magnetic-dipole transition,  $^{5}D_{0} \rightarrow ^{7}F_{1}$  is liberated of the native symmetry. It is observed that no significant difference in the profiles and peak positions but their emission intensities increase slightly with increasing Eu<sup>3+</sup>concentration.

The Judd-Ofelt (JO) parameters,  $\Omega_2$  and  $\Omega_4$  were determined using the measured emission spectra by considering the intensity ratios of the  ${}^5D_0 \rightarrow {}^7F_{2,\ 4}$  and  ${}^5D_0 \rightarrow {}^7F_1$  transitions. JO intensity parameters follow the tendency as  $\Omega_2 > \Omega_4$  and matched to other reported Eu<sup>3+</sup>: glasses [33–38] as shown in Table 2. However, the  $\Omega_6$  parameter is not attained because of the non-appearance of  ${}^5D_0 \rightarrow {}^7F_6$  transition. Consequently, the  $\Omega_6$  parameter is considered as zero for evaluating the radiative parameters. The parameter,  $\Omega_2$  indicates the nature of the bond (covalent bond) and/or the structural variations in the locality of the Eu<sup>3+</sup> ions. On the other hand, viscosity and stiffness of the glass can be explained by the parameters,  $\Omega_4$  and  $\Omega_6$ . The asymmetric ratio 'R' (ratio

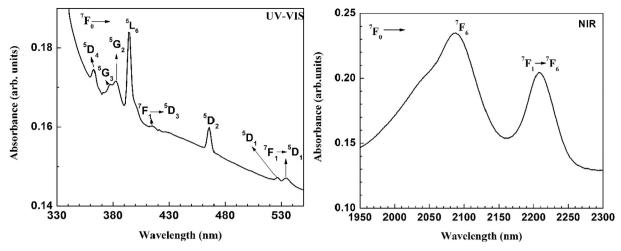


Fig. 4. Optical absorption spectra of PKAZfEu1.0 glass in the UV-Visible and NIR regions.

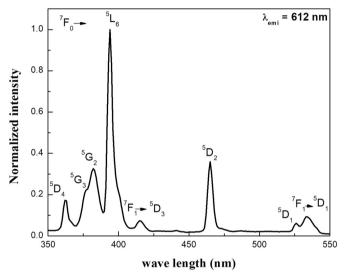
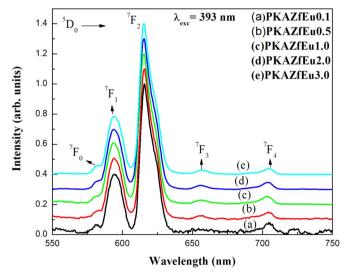


Fig. 5. Excitation spectrum of PKAZfEu1.0 glass.



**Fig. 6.** Luminescence spectra of PKAZfEu glasses. Lines are shifted vertically for better comparison.

between integrated intensities of  ${}^5D_0 \rightarrow {}^7F_2$  and  ${}^5D_0 \rightarrow {}^7F_1$  transition) allows one to estimate the covalent nature around the Eu³+ ions and the centro-symmetric modification of Eu³+ ion site. As the 'R' value increases, the symmetry about the Eu³+ ions decreases and the Eu-O covalency increases and vice versa [39,40]. The value of 'R' is found to be 2.39 which is lower than those of the other reported glasses [33–38] as shown in the Table 2.

Table 3 presents the radiative properties of luminescent levels of Eu³+ ion in PKAZfEu1.0 glass that can be determined using JO intensity parameters. From the Table 3, ' $A_R$ ' is found to be  $128\,s^{-1}$  which is significantly higher in magnitude for the  ${}^5D_0 \rightarrow {}^7F_2$  transition. Both, the derived and experimental branching ratios are comparable to each other for  ${}^5D_0 \rightarrow {}^7F_J$  transitions of Eu³+ ion. It is evidenced that any emission transition whose branching ratio is bigger than 0.50, could be suitable for an efficient laser emission [41]. However, the  $\beta_{\rm exp}$  for the  ${}^5D_0 \rightarrow {}^7F_2$  transition is found to be 0.63. Effective bandwidth ( $\Delta\lambda_{\rm eff}$ ) and stimulated emission cross-section ( $\sigma(\lambda_p)$ ) for  ${}^5D_0 \rightarrow {}^7F_J$  (J = 0, 1, 2, 3 and 4) transitions of Eu³+ ion were calculated [11,42,43] and presented in Table 3. The  $\sigma(\lambda_p)$  is also a significant one which expects the laser emission of the material. The large value of  $\sigma(\lambda_p)$  of Eu³+ ions for  ${}^5D_0 \rightarrow {}^7F_2$  transition indicates that the PKAZfEu glass is a promising material for the development of optical devices around at 615.5 nm.

# 3.6. Phonon sideband spectra

Phonon sideband spectroscopy is a suitable technique to explore the local structure around the Ln ions [44]. Absorption bands are due to the interaction of incident photon with the lattice in the form of phonons around the Ln ions [45,46]. Phonon energy (h $\omega$ ) and strength of electron-phonon coupling (g) of the host matrix were estimated, which alter the multi-phonon relaxation processes significantly. The influence of the fluoride component reduces the phonon energy of the glass matrix. Fig. 7 shows the phonon side band (PSB) and pure electronic transition (PET) of the Eu³+:  $^7F_0 \rightarrow ^5D_2$  transition. This PET,  $^7F_0 \rightarrow ^5D_2$  is situated at 465 nm while the PSB (joined to PET) is observed at 441 nm. The contrast between the peak positions of PSB and PET signifies the phonon energy of the glass matrix [44] which was found to be 1171 cm $^{-1}$  for the investigated glass. Phonon energy of the PKAZfEu1.0 glass obtained from both Raman spectrum and PSB spectrum are in good agreement.

In fluorophosphate glasses, interactions are mainly due to the contribution of multi-phonon relaxation and value of 'g' of phonon sideband that connected with the phosphate (PO<sub>2</sub>) groups. The 'g' is the comparative amount of PSB line-strength and it can be evaluated by  $g = \int I_{\rm PSB} dv/\int I_{\rm PET} dv$ , where  $I_{\rm PSB}$  is the intensity of phonon sideband and  $I_{\rm PET}$  is the intensity of the pure electronic transition. The value of 'g' is

Table 2 Glass lables, intensity ratios of  ${}^5D_0 \rightarrow {}^7F_2$  to  ${}^5D_0 \rightarrow {}^7F_1$  (R(2/1)) transitions, Judd-Ofelt parameters ( $\Omega_{\lambda}$ , × 10<sup>-20</sup> cm<sup>2</sup>), refractive index (n), experimental  $\tau_{exp}$  (ms) and calculated  $\tau_{cal}$  (ms) lifetimes and quantum efficiency (η %) for  ${}^5D_0$  level of Eu<sup>3+</sup>-doped glasses.

Glass lable	R (2/1)	$\Omega_2$	$\Omega_4$	n	$ au_{exp}$	$ au_{ m rad}$	$\eta = \tau_{exp}/\tau_{rad}$
PKAZfEu1.0 [present]	2.39 ( ± 0.03)	3.73	0.33	1.55 ( ± 0.02)	2.35 ( ± 0.04)	5.36 ( ± 0.10)	43.84 ( ± 5%)
ZFPEu10 [33]	2.48	3.62	0.41	1.54	2.47	5.55	44.50
NaBE [34]	4.32	5.56	1.85	1.58	2.13	3.23	65.90
PKSAEu [35]	4.43	5.78	0.79	1.524	2.50	3.99	62.65
PKBAEu [36]	4.55	6.91	5.01	_	2.51	2.64	95.00
PKBFAEu [37]	4.69	7.13	5.18	-	2.52	2.60	97.00
PKBAFEu [37]	5.29	8.12	5.79	-	2.46	2.35	105.00
Lithium borate [38]	3.73	6.14	5.04	1.573	1.89	2.68	70.50

found to be  $1.4 \times 10^{-2}$ . The ' $\hbar\omega$ ' and 'g' are compared with the other reported glasses [33,47,48] as shown in Table 4.

#### 3.7. Chromaticity color co-ordinates

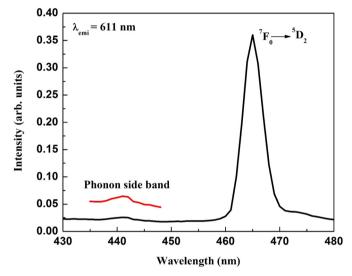
To reflect the color of luminescence of the investigated glasses it is essential to represent the color coordinates on the standard chromaticity diagram. The color coordinates have been calculated based on the Commission International del'Eclairge (CIE) 1931 standard diagram using the emission spectra [49]. CIE 1931 chromaticity coordinates of PKAZfEu glasses under 393 nm excitation are shown in Fig. 8. All the color coordinates of PKAZfEu are located in the intense red region. CIE coordinates are considerably stable with increase of Eu<sup>3+</sup> ion concentration. Here the chromaticity coordinates are closer to the standard equal energy red light illumination, therefore, they exhibit intense red region in the diagram of chromaticity. Hence, the PKAZfEu glasses could be used as a potential candidate for the red emitting devices applications.

# 3.8. Decay analysis

Decay curves of Eu³+ ion for the  $^5D_0$  level as a function of Eu³+ concentration under a wavelength of 393 nm excitation by screening the  $^5D_0 \rightarrow ^7F_2$  transition are shown in Fig. 9, which reveal a single exponential behavior. The  $\tau_{exp}$  of  $^5D_0$  level is found to be 2.23, 2.40, 2.59, 2.35, 2.34 and 2.37 ms for PKAZfEu0.05, PKAZfEu0.1, PKAZfEu0.5, PKAZfEu1.0, PKAZfEu2.0 and PKAZfEu3.0 glasses, respectively. The lifetime increased slightly from 0.05 to 0.5 mol% and thereafter decreases slightly from 0.5 to 3.0 mol% concentration. This directs the non-radiative energy transfer process is vanishes among the Eu³+ ions. Lifetime of  $^5D_0$  level of Eu³+ ions in the PKAZfEu glasses is shown in Table 2 and it is matched with those of other reported Eu³+ doped glasses [33–38]. It is observed that the lifetime is higher than those of NaBE [34] and lithium borate [38] glasses.

# 4. Conclusions

Spectroscopic features of Eu³+-doped zinc-fluorophosphate glasses were investigated as a function of Eu³+ concentration. The JO parameters were derived for PKAZfEu1.0 glass from the emission spectrum. A high value of  $\Omega_2$  intensity parameter reflects that the Eu³+ ions



**Fig. 7.** Phonon side band (PSB) and pure electronic transition (PET) of PKAZfEu1.0 glass.

Table 4 Comparison of phonon energy ( $\hbar\omega$ , cm $^{-1}$ ) and coupling strength (g) of Eu $^{3+}$ :

Glass	$\hbar\omega$ (cm <sup>-1</sup> )	g (10 <sup>-2</sup> )
PKAZfEu1.0 [Present glass]	1171	1.4
ZFPEu10 [33]	1130	2.4
Lithium fluoroborate [47]	1675	2.1
Phosphate [48]	1200-1350	1.2
Borate [48]	1340-1480	1.8
Fluoride [48]	500–600	1500-3500

situated at a highly polarized environment. Radiative parameters of the emitting level,  ${}^5D_0$  of  $Eu^{3+}$  ions were evaluated by using the Judd-Ofelt parameters. The color coordinates of  $Eu^{3+}$ -doped glasses appear within the red light region. Photoluminescence intensity of  $Eu^{3+}$  ions increased with increasing concentration and no concentration quenching was witnessed for the range of concentrations. Decay curves of  ${}^5D_0$  level of  $Eu^{3+}$  unveil a mono-exponential nature for the investigated samples.

Table 3
Emission band positions ( $\lambda_p$ , nm), effective band widths ( $\Delta\lambda_{eff}$ , nm), radiative transition probability ( $A_R$ ,  $s^{-1}$ ), peak stimulated emission cross-section ( $\sigma(\lambda p)$ , ×  $10^{-22}$  cm<sup>2</sup>), experimental and calculated branching ratios ( $\beta_R$ ) for  ${}^5D_0$  level of Eu<sup>3+</sup>:PKAZfEu glasses.

Transition $^5D_0 \rightarrow$	$\lambda_p~(~\pm~1)$	$\Delta\lambda_{eff}$ ( $\pm~0.01$ )	$A_R$	$\sigma(\lambda_p)~(~\pm~0.01)$	$(\beta_R)_{\rm exp}~(~\pm~0.0002)$	$(\beta_R)_{cal}$
<sup>7</sup> F <sub>0</sub>	581.5	4.86	0.0 ( ± 0.0)	0.00	0.0234	0.00
$^{7}F_{1}$	594	12.35	$53.0 (\pm 0.1)$	2.95	0.2630	0.285
$^{7}F_{2}$	615.5	12.23	$128.0 \ (\pm 1.0)$	8.27	0.6300	0.68
<sup>7</sup> F <sub>3</sub>	655.5	8.432	$0.0 (\pm 0.0)$	0.00	0.0157	0.00
$^{7}F_{4}$	703.5	8.918	$6.0 (\pm 0.1)$	0.858	0.0300	0.0304

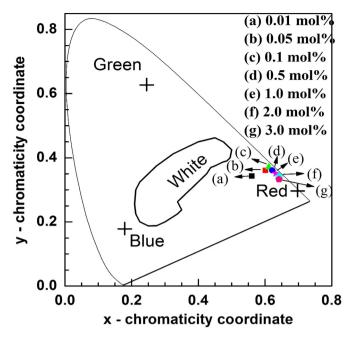


Fig. 8. CIE color coordinates of PKAZfEu glasses with different  $\mathrm{Eu_2O_3}$  concentrations.

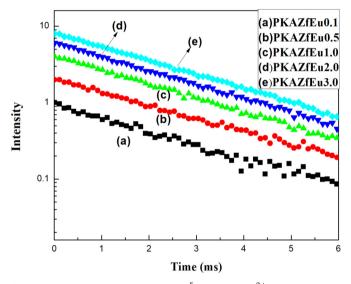


Fig. 9. Fluorescence decay curves of the  $^5D_0$  level of  $Eu^{3+}$  ions in PKAZfEu glasses. Lines are shifted vertically for better comparison.

A slight variation in the lifetime of the  $^5D_0$  level with increasing  $Eu^{3\,+}$  concentration which signifies the non-existence of energy transfer among the  $Eu^{3\,+}$  ions. The results reveal that the present zinc-fluor-ophosphate glasses could be an appropriate candidate for visible optical device applications.

# Acknowledgements

One of the authors (CKJ) is grateful to DAE-BRNS, Govt. of India for the award of research project (No.2009/34/36/BRNS/3174) under MoU between Sri Venkateswara University, Tirupati, RRCAT, Indore and BARC, Mumbai. Dr. KVK is thankful to SERB-DST, Govt. of India, New Delhi for the award of a major research project (File No: EMR/2017/000009).

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