ABSTRACT

Oxyfluoride glasses of different dopant (Eu$^{3+}$) ion concentrations were synthesized by the traditional melt quenching method. Optical absorption, luminescence and lifetime measurements were performed with UV-Vis and PL techniques. A total of six absorption bands were observed in the wavelength range 200-800 nm, including one intense high band at 392 nm was assigned to $^{7}F_{0} \rightarrow ^{5}L_{6}$ transition. The covalency between the host environment and Eu$^{3+}$ ion was noticed with the measured nephelauxetic ratios ($\beta$) and bonding parameters ($\delta$). The energies of the energy band gaps ($E_g$) and Urbach ($\Delta E$) were estimated from the Tauc’s plots, drawn from the absorption spectra. Luminescence spectra exhibited the prominent reddish-orange emission at 612 nm due to the $^{5}D_{0} \rightarrow ^{7}F_{2}$ characteristic transition of Eu$^{3+}$ ion. The lasing (radiative) parameters of f-f transitions of the Eu$^{3+}$ ion was evaluated using the Judd-Ofelt intensity parameters ($\Omega_{2}$, $\Omega_{4}$, and $\Omega_{6}$). The higher magnitude of branching ratios ($\beta_{exp}$) suggests the suitability of the present glass. The decay profile for the $^{5}D_{0}$ level of europium was recorded by monitoring the emission and excitation wavelengths 612 & 392 nm, respectively. The color temperature and purity were calculated using CIE 1931 color coordinates. The emission color band spectra have also been recorded.

Keywords: Bandgap Energy, Bonding Parameters, J-O Parameters, Decay Profile, Red Emission, Color Purity.

INTRODUCTION

Now a day, finding a suitable host for luminescent materials is a challenging task for scientists. Researchers have focused their attention on the development of efficient host material for the devices, including laser industry, optical amplifiers, IR to Vis up-converters, phosphor materials, display units, sensors, solar panels, waveguide lasers, memory devices, etc., for their requirement in various fields. Lanthanide (Ln) ions activated glasses made of multiple network modifiers utilized for the lasers are the current interesting topic. Phosphate glasses were identified as efficient host matrices than other oxide glasses due to their versatile properties such as low melting point, good transparency, superior conductivity, high optical energy storage capacity and high RE ion solubility (>1000 times). The oxygen to phosphorus (O/P) atomic ratio describes the tetrahedral assembly of the phosphate having various structural units ($Q_i$, $i=0-3$), where $n$ stands for the number of bridging oxygens for tetrahedron. However, the lower chemical durability can be enhanced by adding one or more metals that can form M-O-P (M=metal) bonds. It was noticed that Bi$_2$O$_3$ occupies both network building and modifying positions in oxides glasses when introduced in the network as B$_2$O$_3$ units. Furthermore, the addition of ZnF$_2$, Na$_2$CO$_3$ and SrCO$_3$ to the phosphate can increase the chemical durability, mechanical strength, fluorescence efficiency. The addition of heavy metals to the primary host can increase the disorderness of the glass network due to the formation of the nonbridging oxygen groups.

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RE ions doped oxyfluoride glasses will be played a significant role in the fabrication of high-efficiency photonic devices and solid-state lasers and have good optical properties from ultraviolet to near-infrared regions. Among the REIs, the trivalent europium (Eu$^{3+}$) was identified as an important ion and its structural information about the local environment can be found simply from the f-f spectral transitions. The europium ions with a narrow emission band (red light, $^5D_0 \rightarrow ^7F_2$) are good materials for producing light of a single wavelength and having a long lifetime in the active optical states. The Eu$^{3+}$ ion is an excellent initiator for an intense red-colored display device due to its dominant $^5D_0 \rightarrow ^7F_2$ emission transition. Under any site symmetry, the lower (ground) state ($^7F_0$) and immediate higher (excited) state ($^7D_0$) of Eu$^{3+}$ ions are non-degenerate ($J=0$). Therefore, the local fields of Eu$^{3+}$ ions depend only on the existing $^5D_0 \rightarrow ^7F_{J}$, $J=0-4$ transitions in the emission spectra. The asymmetry of the local crystal-field around Eu$^{3+}$ ions were estimated using the luminescence intensity ratio between $^5D_0 \rightarrow ^7F_2$ (ED) and $^5D_0 \rightarrow ^7F_1$ (MD) transitions.

In the present work, Eu$^{3+}$ doped ZnBiNaPSr (P$_2$O$_5$-Bi$_2$O$_3$-Na$_2$CO$_3$-SrCO$_3$-ZnF$_2$) glasses were synthesized by varying the europium content. A few spectroscopic studies such as optical, morphological, structural and luminescence characterizations were performed. This article reports an informative analysis of the optical and enhanced luminescent properties of the prepared glasses and their usefulness in photonic devices for intense red emission.

**EXPERIMENTAL**

**Material and Methods**

Concentration variation of europium (Eu$^{3+}$) ions doped oxyfluoride glasses with a chemical composition (65-x) P$_2$O$_5$ + 15 Bi$_2$O$_3$ + 10 Na$_2$CO$_3$ + 5 SrCO$_3$ + 5 ZnF$_2$ + x Eu$_2$O$_3$ (where x = 0, 0.1, 0.5, 1.0, 1.5 and 2.0 mol%) were synthesized by traditional melt quenching procedure. The raw materials used to prepare the samples are of high purity ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$), zinc fluoride (ZnF$_2$), bismuth oxide (Bi$_2$O$_3$), strontium carbonate (SrCO$_3$), sodium carbonate (Na$_2$CO$_3$) and europium oxide (Eu$_2$O$_3$). The glass samples of 15 g of each composition were amalgamated by manual grinding for about 30 min, then taken into silica crucible, melted at 1150 $^\circ$C for 1 hour in a programmable furnace. The molten was poured onto afore heated thick brass plate and pressurized against another brass plate to get coin-shaped samples. The acquired glasses were annealed at the glass transition temperature, i.e., 400 $^\circ$C for 8 h in an annealing furnace and slowly cooled to room temperature. Finally, obtained samples were polished mechanically and then cut into the required shape. The samples are kept in containers filled with paraffin liquid to prevent possible atmospheric moisture. The prepared samples, ZnBiNaPSr and ZnBiNaPSr: Eu2.0 doped glasses exposed to UV light (392 nm), are shown in Fig.-1.

**Instrumentation**

The absorption spectra were scanned with a spectrophotometer (Varian 5000) at room temperature in 200-800 nm spectral range of resolution 1.0 nm and maximum absorbance of 8 abs units. The luminescence spectra measurements were carried out with a high performance spectrophotometer (Jasco FP-8500) in the 250-550 nm and 550-800 nm range respectively. For both the measurements Xe arc lamp (150 W) was used as source and measurements were carried out with a resolution of 1.0 nm (at 546.1 nm), accuracy ±1.0 nm with silicon photodiode and photomultiplier tube used as a detector. The lifetimes were estimated using Horiba Jobin Yvon Fluorolog (FL3-11) spectrophotometer by monitoring the emission (612 nm) and excitation (392 nm) wavelength. The emission color bands were captured using a constant deviation spectrometer (Holmarc CD214S) with a resolution of 0.2 nm by varying the slit width (0-3mm).

Fig.-1: (a) Photograph of the Prepared Glasses; Emission of (b) ZnBiNaPSr and (c) ZnBiNaPSr: Eu2.0 Glass under UV (392 nm) Light.

Eu$^{3+}$ IONS DOPED ZnBiNaPSr OXYFLUORIDE GLASSES

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RESULTS AND DISCUSSION

Optical studies

The optical absorption spectra were recorded for ZnBiNaPSr: Eu\(^{3+}\) glasses, in the selected UV-Vis (200-800 nm) are shown in Fig.-2 and the spectra in the NIR region were not recorded due to the instrument limitations.

The obtained spectra contain six bands, ascribed to europium ion (4f\(^6\)-4f\(^6\)) characteristic transitions and which originate from the \(^7\)F\(_0\) (ground) and \(^7\)F\(_1\) (thermally populated) states to the higher excited levels. The bands were identified at 360, 392, 412, 464, 526 and 570 nm, which are assigned to the \(^7\)F\(_0\)→\(^5\)D\(_4\), \(^7\)F\(_0\)→\(^5\)L\(_6\), \(^7\)F\(_1\)→\(^5\)D\(_3\), \(^7\)F\(_0\)→\(^5\)D\(_2\), \(^7\)F\(_0\)→\(^4\)D\(_1\) and \(^7\)F\(_0\)→\(^4\)D\(_0\) transitions, respectively. The absorption bands consist of a small hump at a higher wavelength side for the transitions \(^5\)D\(_0\), \(^5\)D\(_2\), \(^5\)D\(_3\), \(^5\)D\(_4\), and \(^5\)L\(_6\). The shoulders in the spectra are raised from thermally populated ground (\(^7\)F\(_0\)) and next excited (\(^7\)F\(_1\)) states, which are closely separated by order of kT (k: Boltzmann’s constant and T: absolute temperature). The absorption band at 392 nm was assigned to \(^7\)F\(_0\)→\(^5\)L\(_6\) transition, which is allowed by ΔJ but forbidden by ΔS and ΔL selection rules (ΔS=ΔL=0 and ΔJ=0, ±1 but 0→0 is forbidden). The intensity of induced electric dipole (ED) allowed transition \(^7\)F\(_0\)→\(^5\)D\(_2\) at 464 nm is higher than the magnetic dipole (MD) transition \(^7\)F\(_0\)→\(^5\)D\(_1\) at 527 nm. The transition, \(^7\)F\(_0\)→\(^5\)D\(_3\) has not been noticed as it is forbidden by a selection rule (ΔJ=3). All the observed bands corresponding to \(^7\)F\(_0\)→\(^5\)D\(_2\) transitions have no sharp edges and less absorption intensity may be due to the amorphous nature. The slight shifting of optical bands towards the higher wavelengths may be attributed to the increasing structural disorder with Eu\(^{3+}\) content and the peaks are arising due to electronic transition between inner orbitals. The band assignments are observed to be similar and are in good agreement with europium doped glasses reported by Selvi et al., Hima Bindu et al., babu et al. and Surendra babu et al.

The calculated bonding parameter and nephelauxetic ratios range from 0.9988 to 0.9953 and 0.1201 to 0.4116 respectively and are displayed in Table-1. The trends showed the nephelauxetic ratios (β) decrease whereas the values of bonding parameter (δ) increase with europium content in the ZnBiNaPSr glasses. The obtained values with positive signs indicated the existence of predominant covalency between europium (Eu\(^{3+}\)) ion and its surrounding environment.

Table-1: Optical Band Position (cm\(^{-1}\)) and Bonding Parameters (δ, β) of Eu\(^{3+}\) Doped Oxyfluoride Glasses

| Transition     | ZnBiNaPSr: | Aqua ion |
|----------------|------------|----------|
|                | Eu0.1      | Eu0.5    | Eu1.0 | Eu1.5 | Eu2.0 | [36]   |
| \(^7\)F\(_0\)→\(^5\)D\(_4\) | -----      | -----    | 27473 | 27473 | 27473 | 27670  |
| \(^7\)F\(_0\)→\(^5\)L\(_6\) | 25380      | 25380   | 25380 | 25380 | 25380 | 25400  |
| \(^7\)F\(_1\)→\(^5\)D\(_3\) | -----      | -----    | 24096 | 23923 | 24038 |        |
| \(^7\)F\(_0\)→\(^5\)D\(_2\) | 21322      | 21277   | 21277 | 21277 | 21277 | 21519  |
The direct and indirect transitions are expected as electromagnetic wave interacts with the electrons in the valance band and electrons are upraising to the conduction band by overcoming the fundamental bandgap. The existed anions and cations in the material can play a remarkable role in the conduction band.\textsuperscript{19,21} The bandgap energies in the non-crystalline substances were calculated by Davis and Mott postulate.\textsuperscript{22} The energy gap was estimated by extrapolating the linear part of the plots to the zero absorption at $(\alpha h\nu)^{1/2} = 0$ for direct allowed and $(\alpha h\nu)^2 = 0$ for indirectly allowed transitions\textsuperscript{23} and are shown in Fig.-3.

The estimated band gap values vary from 4.282 to 4.125 eV and 3.886 to 3.537 eV, respectively, with europium content. The decreasing trend in the bandgap accounts for the formation of more non-bridging oxygens and localized states in the energy gap.\textsuperscript{24} The Urbach energy ($\Delta E$) was utilized to investigate the degeneracy of disorder and is estimated from the inverse slope of the plot drawn between In$\alpha$ and $h\nu$ is shown in Fig.-4. This energy is used to categorize the degree of disorders and higher value may have an enormous trend to change the weak bonds into defects.\textsuperscript{22,23} The Urbach energies measured to be from 0.709 to 0.725 eV. The obtained optical band gaps and Urbach energy values are found to be similar to the others reported for Eu$^{3+}$ doped Lithium-Borosulphophosphate,\textsuperscript{7} Lead boro-telluro-phosphate,\textsuperscript{11} Zincborophosphate,\textsuperscript{13} Lead- fluorophosphate,\textsuperscript{22} Cadmium lithium aluminofluoroboro tellurite,\textsuperscript{25} Lead fluoro-chloro phosphate,\textsuperscript{26} Zinc Bismuth Borate,\textsuperscript{27} Lithium zinc phosphate,\textsuperscript{28} Bismuth Borate glasses and are presented in Table-2.

Table-2: Optical Bandgaps of Direct (n=1/2), Indirect (n=2) allowed transitions and Urbach Energy ($\Delta E$) of Eu$^{3+}$ Doped Oxyfluoride Glasses

| Glass sample         | Bandgap Energy (eV) | References |
|----------------------|---------------------|------------|
|                      | Direct | Indirect | Urbach   |             |
| ZnBiNaPSr            | 4.385  | 3.984    | 0.703    | P. work    |
| ZnBiNaPSr: Eu0.1     | 4.282  | 3.886    | 0.709    | P. work    |
| ZnBiNaPSr: Eu0.5     | 4.252  | 3.783    | 0.711    | P. work    |
| ZnBiNaPSr: Eu1.0     | 4.218  | 3.694    | 0.716    | P. work    |

\begin{tabular}{|c|c|c|c|}
\hline
$^7F_0\rightarrow^5D_1$ & $^7F_0\rightarrow^5D_0$ & \multicolumn{2}{c|}{References} \\
\hline
17391 & 17391 & 17361 & 17271 & 17271 & 17277 \ 
\hline
N & 3 & 3 & 3 & 6 & 6 \ 
\hline
\beta & 0.9988 & 0.9981 & 0.9975 & 0.9969 & 0.9953 \ 
\hline
\delta & 0.1201 & 0.1903 & 0.2506 & 0.3109 & 0.4116 \ 
\hline
\end{tabular}
Luminescent Studies

Excitation Spectra

The excitation spectra of the Eu$^{3+}$ doped ZnBiNaPSr glasses, emission monitored at 612 nm of $^5D_0 \rightarrow ^7F_2$ transition have been recorded in 255-550 nm wavelength regions are shown in Fig.-5. The obtained spectra consist of a few well resolved transitions originated from $^7F_0$ and $^7F_1$ states which are closely separated with the energy gap of 240 cm$^{-1}$ from the free-ion energy level structure with the electric and magnetic dipole moments. A very low intense broadband, observed to be a charge transfer band (CTB) nearly centered at 265 nm is attributed Eu$^{3+}$ to O$^{2-}$ electron transition. A group of obtained narrower sharp lines in 275 to 550 nm spectral range arises due to the transitions from both the ground and thermally populated states ($^7F_J=0,1$) to the higher energy states. The observed transitions $^7F_0 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5L_7$, $^7F_0 \rightarrow ^5L_8$, $^7F_0 \rightarrow ^5D_2$, $^7F_0 \rightarrow ^5D_3$, $^7F_0 \rightarrow ^5D_4$, and $^7F_1 \rightarrow ^5D_1$, are corresponding to the wavelengths of 286, 296, 302, 317, 326, 361, 365, 374, 381, 392, 414, 464, 525 and 534 nm respectively. The assignment of band positions for the high energy transitions was made by considering the electric and magnetic dipole line strengths in the J-O analysis. Among all these transitions, the transition $^7F_0 \rightarrow ^4L_6$ at 392 nm is high intense and very sharper than other bands and this excitation wavelength gives us good emission with high intensity. All the obtained transitions are intrinsic f-f transitions of europium and are ascribed to electronic transitions from the ground levels $^7F_0$ and $^7F_1$. The transition $^7F_1 \rightarrow ^5D_1$ at 534 nm exhibits the characteristic doublet nature. Two intense transitions, the one associated with $^7F_0 \rightarrow ^4L_6$, are because of direct excitation into 4f$^6$ levels of Eu$^{3+}$ ions and the other $^7F_0 \rightarrow ^4D_2$, is due to the electronic dipole (ED) transition. The less intense transition $^7F_0 \rightarrow ^4D_1$, observed at 525 nm owing to the magnetic dipole (MD) transition. It is assumed that two high intense bands excited by near-ultraviolet (392 nm) and blue light (465 nm) emitting diodes are effective pumping sources to attain reddish-orange emission.

Emission Spectra

The recorded emission spectra (550-750 nm) of Eu$^{3+}$ doped ZnBiNaPSr glass samples, excitation wavelength monitored at 392 nm of $^7F_0 \rightarrow ^4L_6$ transition is shown in Fig.-6. The acquired spectra have 5
bands at 579, 592, 612, 652 and 701 nm are attributed to $^5D_0 \rightarrow ^7F_0$ (Yellow), $^5D_0 \rightarrow ^7F_1$ (Orange), $^5D_0 \rightarrow ^7F_2$ (Red-Orange), $^5D_0 \rightarrow ^7F_3$ (Red) and $^5D_0 \rightarrow ^7F_4$ (deep-Red) transitions respectively.  

The obtained f-f transitions in europium ion may be due to both ED or MD interactions and f electrons intensity depends on the local environment site symmetry of the rare earth ions (J-O theory). The intensity of ($^3D_0 \rightarrow ^7F_2$) ED transition strongly depends on the site symmetry of the host matrix because of its allowed nature ($|\Delta L| \leq 6$ and $|\Delta J| = 2, 4, or 6$). The ($^3D_0 \rightarrow ^7F_1$) MD transition intensity may not be affected because it is partially allowed ($|\Delta J| = 0$ or $J'$ but not $J = 0, J' = 0$). The emission intensity of forced electric dipole (ED) transition was influenced by the crystal field of ligand atoms because of its hypersensitive nature.
Fig.-7: Possible Energy Level Diagram of the ZnBiNaPSr: Eu 2.0 Glass

Due to stark splitting, the MD transition further split into two bands. The dominated intensity of ED transition than MD transition proposed the local symmetry of europium ion is without an inversion center. The forbidden forced electric transition becomes parity allowed because of the odd parity component of the crystal field. The parity allowed transition accounts for best color purity and brightness and which makes Eu$^{3+}$ ion becomes an excellent activator for red luminescent materials. Therefore, the relative intensity of the $^5D_0$→$^7F_2$ to $^5D_0$→$^7F_1$ transitions, represented by fluorescence intensity ratio (R$_{21}$) allows one to estimate the variation from the site symmetries of Eu$^{3+}$ ions. As per the JO postulate, the transition $^5D_0$→$^7F_0$ is not allowed because switching between J=0 levels is strictly forbidden. But the possible existence of low intense $^5D_0$→$^7F_0$ transition may be due to one of the reasons i.e., (i) “breakage of the closure approximation in JO theory” (ii) “either due to parity mixing (d-f mixing) or J-J mixing due to the thermal population at ground (F$_J$, J=0 to 4) state or the excited state ($^5D_J$, J=0,1and 3).” Because of the large energy gap between d and f states, the parity (d-f) mixing is not workable. Anyway, the possibility of J-J mixing at ground state (F$_J$, J=0 to 4) is due to thermal population and probably the $^5D_0$→$^7F_0$ transition occurred between J=0 and 2 because of low energy difference compared to J=0 and J=4, 6,32,33 The emission intensity ratio (R$_{02}$) between the $^5D_0$→$^7F_0$ and $^5D_0$→$^7F_2$ transitions has also been calculated. From the magnitude of intensity ratios (R$_{21}$ and R$_{02}$), it is observed that the interaction between the dopant ion and glass matrix is strong for europium 2.0 mol% concentration. When europium ions are embedded into a host matrix, Eu$^{3+}$ ions cannot be dispersed in the host network but become Eu$^{3+}$-Eu$^{3+}$ ion pair closer at a high concentration which leads to quenching of fluorescence intensity. The measured values fluorescence intensity ratio (R$_{21}$) is observed that the value is higher for 2.0 mol% doped oxyfluoride glass matrix which indicates the red color emission is high intense than compared to orange color emission. The higher value of R$_{21}$ indicates the 2.0 mol% concentration suggests the higher distortion of site symmetry and dominated covalency of the chemical bond between Eu$^{3+}$ and O$^\text{2-}$. The obtained intensity of red to orange asymmetric ratios (R$_{21}$) are 2.072, 2.178, 2.238, 2.278 and 2.368 and the highest value indicates a lower symmetry of Eu$^{3+}$ ions and a higher Eu$^{3+}$-O$^\text{2-}$ covalence.34,35 The measured intensity ratio (R$_{02}$) values are 0.070, 0.046, 0.045, 0.044 and 0.042, due to lower J-J mixing. The increasing trend in the intensity ratios of R$_{21}$ and the decreasing trend in intensity ratios of R$_{02}$ indicate the increasing red emission with europium ion concentration.1-6,23 The obtained PL spectra are found to be similar to the other reports for Eu$^{3+}$ doped glasses by Madhukar Reddy et al.2, Deva Prasad Raju et al. (2012)3, Hatefi et al. (2011)31, Parchur et al. (2012)32 and Wen et al. (2010).33

Judd-Ofelt and Radiative Properties

The magnitudes of the JO intensity parameters ($\Omega_2$ and $\Omega_4$) from the transitions $^5D_0$→$^7F_2$ and $^5D_0$→$^7F_4$ were estimated using the squared values of the reduced matrix obtained from carnal et al.36 and are listed in Table-3. The parameter $\Omega_6$ value cannot be determined because the emission transition $^5D_0$→$^7F_6$ was not
found in the present study. The greater magnitudes of $\Omega_2$ indicate a higher degree of asymmetry, evidence for high Eu$^{3+}$-O$^2-$ covalency and structural variations in the vicinity of europium ions. The $\Omega_1$ and $\Omega_6$ are accountable for the long-range effects such as viscosity, bulk modulus and dielectric constant.

| Glass sample       | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | Trend of $\Omega_6$ | References |
|-------------------|------------|------------|------------|--------------------|------------|
| ZnBiNaPsr: Eu0.1  | 3.12       | 0.37       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | P. work   |
| ZnBiNaPsr: Eu0.5  | 3.27       | 0.39       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | P. work   |
| ZnBiNaPsr: Eu1.0  | 3.44       | 0.43       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | P. work   |
| ZnBiNaPsr: Eu1.5  | 3.57       | 0.45       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | P. work   |
| ZnBiNaPsr: Eu2.0  | 3.69       | 0.49       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | P. work   |
| LCZSFB: Eu1.0     | 3.62       | 1.43       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [2]       |
| LiFB: Eu1.0       | 3.62       | 1.19       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [3]       |
| ZPBT1: Eu1.0      | 2.42       | 1.02       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [6]       |
| LBTP: Eu1.0       | 3.12       | 0.08       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [11]      |
| ZBP: Eu0.9        | 5.42       | 2.55       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [13]      |
| PKMgNa: Eu1.0     | 5.62       | 2.05       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [14]      |
| NaPbB: Eu2.0      | 3.03       | 0.38       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [16]      |
| PbFP: Eu1.0       | 3.51       | 0.47       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [23]      |
| BLNE: Eu1.0       | 3.56       | 2.05       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [41]      |
| PZBaNa: Eu1.0     | 3.47       | 0.50       | 0          | $\Omega_2 > \Omega_4 > \Omega_6$ | [42]      |

The increment in $\Omega_2$ values with the Eu$^{3+}$ ion content is in good agreement with the emission intensity ratio ($R_{21}$) and the samples exhibit the lower symmetry and higher Eu-O covalence around Eu$^{3+}$ ions. The estimated J-O parameters and measured refractive indices were used in the calculation of radiative parameters such as radiative transition probability ($A_1$), lifetime ($\tau_R$), branching ratio ($\beta_R$), stimulated emission cross-section ($\sigma_e$), non-radiative relaxation rates ($W_{NR}$), quantum efficiency ($\eta$), optical gain parameter ($\sigma_o x \tau_R$) and optical gain bandwidth ($\sigma_o x \Delta \lambda_p$) of the $^5D_0 \rightarrow ^7F_j$ ($J=0$–$4$) emission transitions. The radiative parameters have been calculated for all the concentrations of Eu$^{3+}$ doped oxyfluoride using the equations and obtained values are reported in Table-4. The increment in $A_1$ and $\Omega_2$ values and decrement in the $\tau_R$ values with Eu$^{3+}$ concentration indicates the higher covalency at higher concentrations. The magnitude of radiative properties of emission transitions follows the $^5D_0 \rightarrow ^7F_2 > ^7F_3 > ^7F_4 > ^7F_5 > ^7F_6$ order. The high intense transition with a $\beta_R$ value of more than 50% is found to be a suitable host material for the devices in lasing applications. The value of $\sigma_e$ could explain the rate of energy extraction from the lasing material and its value is more for the $^5D_0 \rightarrow ^7F_2$ transition, which will be used to develop and fabricate the low threshold and high gain laser applications. The experimental and calculated $\beta_R$ values are found to be 67% and 80% respectively for the $^5D_0 \rightarrow ^7F_2$ transition in ZnBiNaPsr: Eu2.0 glass and are identified to be a suitable lasing material for red luminescence. The measured radiative properties are listed in Table-4 and observed to be in good agreement, specified by the others reported for europium doped Zinc fluorophosphate, Lead fluorophosphate, Lead borotellurophosphate, Zincborophosphate, Calcium phosphate glasses.

| Transition | Parameters | $\lambda_p$ (nm) | ZnBiNaPsr: Eu | References |
|------------|------------|------------------|---------------|------------|
| $^5D_0 \rightarrow ^7F_j$ (J=0–4) | $\lambda_p$ | 0.1 0.5 1.0 1.5 2.0 | [1] [4] [11] [13] [14] [23] | [16] |
Decay Studies

The fluorescence decay profile of the titled glasses for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition was recorded at an excitation wavelength of 392 nm and emission wavelength monitored 612 nm is shown in Fig.-8. The decay plots were suitably fitted with a bi-exponential equation, the obtained average lifetimes ($\tau_{\text{exp}}$) are 2.25, 2.21, 2.18, 2.16 and 2.12 ms and the lifetimes ($\tau_{\text{exp}}$) from J-O theory are found to be comparable with the lifetime determined experimentally. The value of non-radiative decay rate ($W_{\text{NR}}$, s$^{-1}$) i.e., the deviation between $\tau_{\text{rad}}$ and $\tau_{\text{exp}}$ for the $^5\text{D}_0$ level is found to be 118, 99, 90, 69 and 41 s$^{-1}$. The quantum efficiency values for the sample are obtained to be 75, 78, 80, 85 and 91% with europium concentration.

| Transition  | $\Delta\lambda_P$ | $A_R$ | $\sigma_e$ | $\beta_{\text{exp}}$ | $\beta_{\text{cal}}$ | $\sigma_{x\lambda}\Delta\lambda_P$ | $\sigma_{x\lambda\lambda}\Delta\lambda_P$ |
|-------------|-------------------|-------|-----------|---------------------|----------------------|-------------------------------|-----------------------------------|
| $^7\text{F}_0 \rightarrow ^5\text{D}_0$ | 3.0 | 3.0 | 3.0 | 3.0 | 2.0 | 2.96 | 4.13 | 2.70 | 2.02 | 2.97 |
| $^5\text{D}_0 \rightarrow ^7\text{F}_1$ | 10.0 | 10.0 | 11.0 | 11.0 | 12.0 | 11.4 | 11.5 | 17.8 | 10.6 | 9.68 | 11.1 |
| $^5\text{D}_0 \rightarrow ^7\text{F}_2$ | 63.6 | 64.1 | 65.7 | 66.3 | 67.0 | 52.0 | 50.0 | 80.2 | 52.0 | 48.8 | 62.0 |
| $^5\text{D}_0 \rightarrow ^7\text{F}_3$ | 7.95 | 8.21 | 9.28 | 10.1 | 12.3 | 10.5 | 12.8 | 10.6 | 19.6 | 14.5 | 12.7 |
| $^5\text{D}_0 \rightarrow ^7\text{F}_4$ | 12.0 | 12.0 | 12.0 | 12.0 | 13.0 | 10.3 | 13.2 | 13.9 | 45.5 | 14.6 | 14.0 |

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and the values are higher than others reported for europium doped LCZSFB\(^2\), Lead-fluoroborate\(^3\), Zinc-phosphate\(^6\), Lead-fluorophosphate\(^8\), Lead-telluro-phosphate\(^11\), Zincborophosphate\(^13\), Phosphate\(^14\), Lead-borophosphate\(^16\), Fluoroborate\(^41\) and Zinc-phosphate\(^42\) glasses and are presented in Table-5.

![Decay curves of \(^{2}\)D\(_{0}\) level of ZnBiNaPSr: Eu\(^{3+}\) glasses.](image)

**Table-5:** Emission intensity of forced ED (\(^{5}\)D\(_{0}\)→\(^{7}\)F\(_{2}\)), MD (\(^{5}\)D\(_{0}\)→\(^{7}\)F\(_{1}\)) and (\(^{5}\)D\(_{0}\)→\(^{7}\)F\(_{0}\)) transitions, luminescence intensity ratios (R\(_{21}\) and R\(_{02}\)), experimental (\(\tau_{\text{exp}}\), ms) and calculated (\(\tau_{\text{cal}}\), ms) lifetimes, non-radiative relaxation rates (\(W_{\text{NR}}\), s\(^{-1}\)), Quantum efficiency (%) and total radiative transition (\(A_{T}\), s\(^{-1}\)) of Eu\(^{3+}\) doped oxyfluoride glasses

| sample       | \(^{5}\)D\(_{0}\)→\(^{7}\)F\(_{2}\) | \(^{5}\)D\(_{0}\)→\(^{7}\)F\(_{1}\) | \(^{5}\)D\(_{0}\)→\(^{7}\)F\(_{0}\) | (R\(_{21}\)) | (R\(_{02}\)) | \(\tau_{\text{exp}}\) (ms) | \(\tau_{\text{cal}}\) (ms) | \(W_{\text{NR}}\) (s\(^{-1}\)) | \(\eta\) (%) | \(A_{T}\) (s\(^{-1}\)) | Ref.      |
|--------------|-----------------|-----------------|-----------------|------------|------------|-----------------|-----------------|-----------------|------------|-----------------|----------|
| ZnBiNaPSr    |                 |                 |                 |            |            |                 |                 |                 |            |                 |          |
| Eu0.1        | 92              | 44              | 7               | 2.072      | 0.070      | 2.25            | 2.98            | 109             | 75         | 275             | P. work  |
| Eu0.5        | 474             | 218             | 22              | 2.178      | 0.046      | 2.21            | 2.85            | 102             | 77         | 284             | P. work  |
| Eu1.0        | 951             | 425             | 43              | 2.238      | 0.045      | 2.18            | 2.71            | 90              | 80         | 294             | P. work  |
| Eu1.5        | 1352            | 593             | 60              | 2.279      | 0.044      | 2.16            | 2.55            | 71              | 85         | 304             | P. work  |
| Eu2.0        | 2000            | 844             | 85              | 2.368      | 0.042      | 2.12            | 2.33            | 43              | 91         | 317             | P. work  |
| LCZSFB       | --              | --              | --              | 2.38       | --         | 1.37            | 1.70            | 142             | 80         | 534             | [2]      |
| LLiFB        | --              | --              | --              | 2.32       | --         | 1.34            | 1.75            | 175             | 77         | 570             | [3]      |
| ZPBT1        | --              | --              | --              | 2.20       | --         | 2.22            | 5.28            | 261             | 42         | 220             | [6]      |
| LBTP         | --              | --              | --              | 1.44       | --         | 1.37            | 3.40            | 431             | 41         | 306             | [11]     |
| ZBP          | --              | --              | --              | 3.65       | --         | 2.22            | 3.20            | 138             | 72         | 315             | [13]     |
| PKMgNa       | --              | --              | --              | 3.68       | --         | 2.61            | 3.85            | 123             | 68         | 260             | [14]     |
| NaPbB        | --              | --              | --              | 2.15       | --         | 2.30            | 2.56            | 44              | 90         | 264             | [16]     |
| PbFP         | --              | --              | --              | 2.36       | --         | 2.29            | 2.69            | 66              | 86         | 372             | [23]     |
| BLNE         | --              | --              | --              | 3.89       | --         | 1.76            | 2.70            | 197             | 65         | 315             | [41]     |
| PZBaNa       | --              | --              | --              | 2.29       | --         | 2.49            | 3.17            | 86              | 78         | 275             | [42]     |

**CIE 1931 and CIE 1976 Chromaticity Diagrams**

The expected characteristic emission (color) wavelength of the present samples was perfectly identified with Commission International de l’Eclairage (1931 and 1976) chromaticity (x, y and u’, v’) coordinate diagrams and is shown in Fig.-9.

According to National Television Standard Committee (NTSC), the standard values of x and y coordinates for red phosphor are 0.670 and 0.330, respectively.\(^{33,44}\) The obtained chromaticity coordinates for CIE 1931 are (x=0.5829, y=0.3340), (x=0.5979, y=0.3426), (x=0.6101, y=0.3429), (x=0.6219, y=0.3479) and
(x=0.6353, y=0.3496) and CIE 1976 are (u’=0.399, v’=0.514), (u’=0.405, v’=0.521), (u’=0.414, v’=0.523), (u’=0.419, v’=0.527) and (u’=0.428, v’=0.531) for the selected concentrations of Eu$^{3+}$ ions doped ZnBiNaPSr glass system. The CIE coordinates shift towards the strongest reddish-orange region with increasing the europium concentration. The chromaticity coordinates of ZnBiNaPSr: Eu2.0 glass is identified to be closer to the reference values of red phosphor and it can have the strongest reddish-orange emission and are reported in Table-6.

![Graph showing CIE 1931 and 1976 color coordinate diagrams with dominant wavelength](image)

**Table-6**: Excitation wavelength ($\lambda_{exc}$, nm), dominant wavelength ($\lambda_{d}$, nm), CIE 1931 and CIE 1976 chromaticity coordinates, color temperature (CCT, K), color purity (%) of Eu$^{3+}$ doped oxyfluoride glasses

| sample      | $\lambda_{exc}$ (nm) | $\lambda_{d}$ (nm) | Coordinates             | CCT (K) | Emission Color | Color Purity (%) | Ref. |
|-------------|-----------------------|--------------------|-------------------------|---------|----------------|------------------|------|
| ZnBiNaPSr   |                       |                    |                         |         |                |                  |      |
| Eu0.1       | 392                   | 616                | (0.582, 0.334)          | 2102    | Red-Orange     | 82.4             | P. work |
| Eu0.5       | 392                   | 616                | (0.599, 0.342)          | 2125    | Red-Orange     | 87.7             | P. work |
| Eu1.0       | 392                   | 615                | (0.610, 0.342)          | 2232    | Red-Orange     | 91.0             | P. work |
| Eu1.5       | 392                   | 615                | (0.621, 0.347)          | 2265    | Red-Orange     | 94.4             | P. work |
| Eu2.0       | 392                   | 615                | (0.635, 0.349)          | 2385    | Red-Orange     | 98.7             | P. work |
| KZP         | 392                   | --                 | (0.637, 0.351)          | 2117    | Red-Orange     | 96.8             | [37]  |
| LGBiB       | 394                   | --                 | (0.646, 0.304)          | 2171    | Red-Orange     | --               | [46]  |
| BGE         | 393                   | --                 | (0.644, 0.350)          | 2205    | Red-Orange     | --               | [48]  |
| PbNaP       | 393                   | --                 | (0.634, 0.346)          | 2180    | Red-Orange     | --               | [49]  |
| LSCAS       | 394                   | --                 | (0.550, 0.430)          | 2000    | Red-Orange     | 50               | [51]  |

**CCT, Dominant Wavelength and Color Purity Studies**

The correlated color temperature (CCT) values varying from 2000 K to 12500 K have been estimated using McCamy’s formula with CIE 1931 color coordinates. The CCT values of the present glass system related to the CIE chromaticity values are found to be 2102K, 2125K, 2232K, 2265K and 2385K and estimated CCT values less than 4000 K are desirable for the better red light emitting materials. The materials having the highest percentage of color purity and the CIE chromaticity values closure to the standard values may be useful for the development of display devices and solid-state lasers.
study the obtained percentage of color purity are 82.4%, 87.7%, 91%, 94.4% and 98.7%, which is better than the others reported for europium doped LCZSF2, Lead-fluoroborate1, Zinc-phosphate6, Lead-fluorophosphate23, Lead-telluro-phosphate11, Zincborophosphate13, Phosphate14, Lead-borophosphate16, Fluoroborate41, Zinc-phosphate42, glasses and are listed in Table-6. The obtained color band images with the wavelength accuracy ± 1 nm, resolution 0.2 nm and exposure time of 100 ms are shown in Fig.-10.

Fig.-10: (a) Dark Data Subtracted Emission Spectra; (b) Color Bands of ZnBiNaPSr: Eu2.0 mol Glass and Inset set shows the Dark (Raw) Data

CONCLUSION

A very less intense absorption bands were observed in the optical spectra and optical band gap energies (E_g) and Urbach (ΔE) energies were measured. The obtained values of bonding parameters showed the existence of predominant covalency between the Eu^{3+} ion and its surrounding environment. The decreasing trend in optical band gaps was observed due to the existence of structural changes and Eu-O weaker bond strength leads to the formation of more NBOs. The photoluminescence spectra were recorded at 392 nm excitation wavelength and an intense emission peak was observed at 612 nm corresponding to 5D_0→7F_2 transition is a characteristic peak of red-light emission. No concentration quenching effect was observed in the titled glass series and the luminescence intensity ratio confirmed that the 2.0 mol% Eu^{3+} doped sample showed high asymmetry and covalent nature. The JO parameters followed the trend Ω_2 > Ω_4 > Ω_6 and a higher value of Ω_2 confirms the hypersensitive nature of the 5D_0→7F_2 transition. The magnitudes of radiative parameters are indicative of the suitability of the ZnBiNaPSr: Eu^{3+} glasses for visible photonic applications. The decreasing lifetime with europium content in the decay profile for the 5D_0 level is evidence for small nonradiative relaxation rates. The color chromaticity coordinates from CIE are lying in the strong reddish-orange region and the color purity was obtained by 98.7%. The stimulated emission cross-section (12.3x10^{-22}), branching ratios (β_{exp}=0.67, β_{cal}=0.80), optical gain bandwidth (15.99x10^{-25}), optical gain (27.67x10^{-28}), efficiency (91%) and color purity (98.7%) are found to be maximum for ZnBiNaPSr: Eu2.0 glass which might be a potential and prominent for reddish-orange (612 nm) emission.

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