SPECTRAL INVESTIGATIONS OF TRIVALENT EUROPIUM (Eu³⁺) IONS DOPED ZnBiNaPSr OXYFLUORIDE GLASSES FOR VISIBLE PHOTONIC DEVICE APPLICATIONS

**D. Siva Raju^{1,2}, Megala Rajesh³, S. Hima Bindu⁴, J. Suresh Krishna¹,
V. Vinay Krishna⁵ B. Deva Prasad Raju³ and Ch. Linga Raju¹, ✉**

¹Department of Physics, Acharya Nagarjuna University, Guntur-522510, (A.P.) India

²Department of Physics, Indian Institute of Science Education and Research,
Tirupati-517507, (A.P.) India

³Department of Physics, Sri Venkateswara University, Tirupati-517507, (A.P.) India

⁴Department of Physics, National Institute of Technology, Warangal-506004, (Telangana) India

⁵Department of E & IT, Acharya Nagarjuna University, Guntur-522510, (A.P.) India

✉Corresponding Author: drchraj_phy@yahoo.com

ABSTRACT

Oxyfluoride (P₂O₅-Bi₂O₃-Na₂CO₃-SrCO₃-ZnF₂-Eu₂O₃) glasses of different dopant (Eu³⁺) 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 ⁷F₀→⁵L₆ transition. The covalency between the host environment and Eu³⁺ ion was noticed with the measured nephelauxetic ratios (β) and bonding parameters (δ). The energies of the energy band gaps (E_g) and Urbach (ΔE) 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 ⁵D₀→⁷F₂ characteristic transition of Eu³⁺ ion. The lasing (radiative) parameters of f-f transitions of the Eu³⁺ ion was evaluated using the Judd-Ofelt intensity parameters (Ω₂, Ω₄, and Ω₆). The higher magnitude of branching ratios (β_{exp}) suggests the suitability of the present glass. The decay profile for the ⁵D₀ 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.

RASAYAN J. Chem., Vol. 14, No.4, 2021

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.¹⁻³ 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 (Qⁱ, i=0-3), where n stands for the number of bridging oxygens for tetrahedron.⁴⁻⁶

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 Bi₂O₃ occupies both network building and modifying positions in oxides glasses when introduced in the network as BiO₆ units.^{7,8} Furthermore, the addition of ZnF₂, Na₂CO₃ and SrCO₃ 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.^{9,10}

Rasayan J. Chem., 14(4), 2392-2405(2021)

<http://doi.org/10.31788/RJC.2021.1446523>

This work is licensed under a CC BY 4.0 license.

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.¹¹ 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.¹² The europium ions with a narrow emission band (red light, $^5\text{D}_0 \rightarrow ^7\text{F}_2$) 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 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission transition. Under any site symmetry, the lower (ground) state ($^7\text{F}_0$) and immediate higher (excited) state ($^5\text{D}_0$) of Eu^{3+} ions are non-degenerate ($J=0$). Therefore, the local fields of Eu^{3+} ions depend only on the existing $^5\text{D}_0 \rightarrow ^7\text{F}_J$, $J=0-4$ transitions in the emission spectra.¹³ The asymmetry of the local crystal-field around Eu^{3+} ions were estimated using the luminescence intensity ratio between $^5\text{D}_0 \rightarrow ^7\text{F}_2(\text{ED})$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1(\text{MD})$ transitions.¹⁴⁻¹⁶

In the present work, Eu^{3+} doped ZnBiNaPSr ($\text{P}_2\text{O}_5\text{-Bi}_2\text{O}_3\text{-Na}_2\text{CO}_3\text{-SrCO}_3\text{-ZnF}_2$) 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 $(65-x) \text{P}_2\text{O}_5 + 15 \text{Bi}_2\text{O}_3 + 10 \text{Na}_2\text{CO}_3 + 5 \text{SrCO}_3 + 5 \text{ZnF}_2 + x \text{Eu}_2\text{O}_3$ (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 ($\text{NH}_4\text{H}_2\text{PO}_4$), zinc fluoride (ZnF_2), bismuth oxide (Bi_2O_3), strontium carbonate (SrCO_3), sodium carbonate (Na_2CO_3) and europium oxide (Eu_2O_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°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°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 $\text{ZnBiNaPSr:Eu}_{2.0}$ doped glasses exposed to UV light (392 nm), are shown in Fig.-1.

Fig.-1: (a) Photograph of the Prepared Glasses; Emission of (b) ZnBiNaPSr and (c) $\text{ZnBiNaPSr:Eu}_{2.0}$ Glass under UV (392 nm) Light.

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 spectrofluorometer (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) spectrofluorometer 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).

RESULTS AND DISCUSSION

Optical studies

The optical absorption spectra were recorded for ZnBiNaPSr: Eu³⁺ 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.

Fig.-2: Optical Absorption Spectra of ZnBiNaPSr and ZnBiNaPSr: Eu³⁺ Glasses

The obtained spectra contain six bands, ascribed to europium ion (4f⁶-4f⁶) characteristic transitions and which originate from the ⁷F₀ (ground) and ⁷F₁ (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 ⁷F₀→⁵D₄, ⁷F₀→⁵L₆, ⁷F₁→⁵D₃, ⁷F₀→⁵D₂, ⁷F₀→⁵D₁ and ⁷F₀→⁵D₀ transitions, respectively. The absorption bands consist of a small hump at a higher wavelength side for the transitions ⁵D₀, ⁵D₂, ⁵D₃, ⁵D₄, and ⁵L₆. The shoulders in the spectra are raised from thermally populated ground (⁷F₀) and next excited (⁷F₁) states, which are closely separated by order of kT (k: Boltzmann's constant and T: absolute temperature).¹⁷ The absorption band at 392 nm was assigned to ⁷F₀→⁵L₆ 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 ⁷F₀→⁵D₂ at 464 nm is higher than the magnetic dipole (MD) transition ⁷F₀→⁵D₁ at 527 nm. The transition, ⁷F₀→⁵D₃ has not been noticed as it is forbidden by a selection rule (ΔJ=3). All the observed bands corresponding to ⁷F_J→⁵D_J 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 Eu³⁺ content and the peaks are arising due to electronic transition between inner orbitals.¹⁸ The band assignments are observed to be similar and are in good agreement with europium doped glasses reported by Selvi et al.¹¹, Hima Bindu et al.¹³, babu et al.¹⁷ and Surendra babu et al.¹⁸

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-1.¹⁹ 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 (Eu³⁺) ion and its surrounding environment.²⁰

Table-1: Optical Band Position (cm⁻¹) and Bonding Parameters (δ, β) of Eu³⁺ Doped Oxyfluoride Glasses

Transition	ZnBiNaPSr:					Aqua ion [36]
	Eu0.1	Eu0.5	Eu1.0	Eu1.5	Eu2.0	
⁷ F ₀ → ⁵ D ₄	-----	-----	-----	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

${}^7F_0 \rightarrow {}^5D_1$	-----	-----	-----	19011	19011	19028
${}^7F_0 \rightarrow {}^5D_0$	17391	17391	17361	17271	17271	17277
N	3	3	3	6	6	
β	0.9988	0.9981	0.9975	0.9969	0.9953	
δ	0.1201	0.1903	0.2506	0.3109	0.4116	

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.^{19,21} The bandgap energies in the non-crystalline substances were calculated by Davis and Mott postulate.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 transitions²³ and are shown in Fig.-3.

Fig.-3: Tauc's Plots of (a) Direct and (b) Indirect Bandgap Energy of ZnBiNaPSr and ZnBiNaPSr: Eu³⁺ Glasses

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.²⁴ The Urbach energy (ΔE) was utilized to investigate the degeneracy of disorder and is estimated from the inverse slope of the plot drawn between $\ln \alpha$ 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.^{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 Eu³⁺ doped Lithium-Borosulphophosphate⁷, Lead boro-telluro-phosphate¹¹, Zincborophosphate¹³, Lead- fluorophosphate²³, Cadmium lithium aluminofluoroboro tellurite²⁵, Lead fluoro-chloro phosphate²⁶, Zinc Bismuth Borate²⁷, Lithium zinc phosphate²⁸, Bismuth Borate²⁹ glasses and are presented in Table-2.

Table-2: Optical Bandgaps of Direct ($n=1/2$), Indirect ($n=2$) allowed transitions and Urbach Energy (ΔE) of Eu³⁺ 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

ZnBiNaPSr: Eu1.5	4.174	3.630	0.718	P. work
ZnBiNaPSr: Eu2.0	4.125	3.537	0.725	P. work
LiBSP: Eu1.0	3.430	3.350	0.330	[7]
BPbTePZnBa: Eu2.0	3.080	2.900	0.336	[11]
ZBP: Eu0.9	4.300	3.690	0.510	[13]
PbFP: Eu2.0	3.380	--	0.510	[23]
TeBCdLiAl: Eu	2.582	--	0.299	[25]
PbP:Eu	3.180	--	0.014	[26]
CaZnBiB: Eu1.0	2.851	2.587	0.304	[27]
LiZnP: Eu0.5	3.350	2.220	--	[28]
BiBAg: Eu0.5	2.624	2.129	0.361	[29]

Fig.-4: Urbach Energy of ZnBiNaPSr and ZnBiNaPSr: Eu³⁺ Glasses

Luminescent Studies

Excitation Spectra

The excitation spectra of the Eu³⁺ doped ZnBiNaPSr glasses, emission monitored at 612 nm of ⁵D₀→⁷F₂ 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 ⁷F₀ and ⁷F₁ 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 Eu³⁺ to O²⁻ electron transition. A group of obtained narrowed 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 ⁷F₀→⁵I₈, ⁷F₀→⁵F₂, ⁷F₁→⁵F₃, ⁷F₀→⁵H₄, ⁷F₁→⁵H₃, ⁷F₀→⁵D₄, ⁷F₁→⁵D₄, ⁷F₀→⁵G₂, ⁷F₁→⁵L₇, ⁷F₀→⁵L₆, ⁷F₁→⁵D₃, ⁷F₀→⁵D₂, ⁷F₀→⁵D₁, and ⁷F₁→⁵D₁ are corresponding to the wavelengths of 286, 296, 302, 317, 326, 361, 365, 374, 381, 392, 414, 464, 525 and 534 nm respectively.²⁵⁻²⁹ 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 ⁷F₀→⁵L₆ at 392 nm is high intense and very sharper than other bands and this excitation wavelength gives us good emission with high intensity.³⁰ All the obtained transitions are intrinsic f-f transitions of europium and are ascribed to electronic transitions from the ground levels ⁷F₀ and ⁷F₁. The transition ⁷F₁→⁵D₁ at 534 nm exhibits the characteristic doublet nature. Two intense transitions, the one associated with ⁷F₀→⁵L₆ are because of direct excitation into 4f⁶ levels of Eu³⁺ ions and the other ⁷F₀→⁵D₂ is due to the electronic dipole (ED) transition. The less intense transition ⁷F₀→⁵D₁, 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.^{1-5,31}

Emission Spectra

The recorded emission spectra (550-750 nm) of Eu³⁺ doped ZnBiNaPSr glass samples, excitation wavelength monitored at 392 nm of ⁷F₀→⁵L₆ 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.²³

Fig.-5: Excitation Spectra ($\lambda_{em}=612$ nm) of ZnBiNaPSr: Eu³⁺ Glasses

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 ($^5D_0 \rightarrow ^7F_2$) ED transition strongly depends on the site symmetry of the host matrix because of its allowed nature ($|\Delta L| \leq 6$ and $|\Delta J| = 2, 4, \text{ or } 6$). The ($^5D_0 \rightarrow ^7F_1$) MD transition intensity may not be affected because it is partially allowed ($|\Delta J|$ 0 or 1 but not $J = 0, J' = 0$).²⁻⁵ The emission intensity of forced electric dipole (ED) transition was influenced by the crystal field of ligand atoms because of its hypersensitive nature.

Fig.-6: Emission Spectra ($\lambda_{ex}=392$ nm) of ZnBiNaPSr: Eu³⁺ Glasses and inset shows the intensity ratio variation with Europium Concentration

The partial energy level diagram of the obtained luminescent transitions of titled glasses is shown in Fig.-7. 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 ($^5D_0 \rightarrow ^7F_2$) ED transition strongly depends on the site symmetry of the host matrix because of its allowed nature ($|\Delta L| \leq 6$ and $|\Delta J| = 2, 4, \text{ or } 6$). The ($^5D_0 \rightarrow ^7F_1$) MD transition intensity may not be affected because it is partially allowed ($|\Delta J|$ 0 or 1 but not $J = 0, J' = 0$).²⁻⁵ 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.⁶

Therefore, the relative intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to $^5\text{D}_0 \rightarrow ^7\text{F}_1$ 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 $^5\text{D}_0 \rightarrow ^7\text{F}_0$ is not allowed because switching between $J=0$ levels is strictly forbidden. But the possible existence of low intense $^5\text{D}_0 \rightarrow ^7\text{F}_0$ 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 ($^5\text{D}_J$, $J=0, 1$ and 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 $^5\text{D}_0 \rightarrow ^7\text{F}_0$ 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 $^5\text{D}_0 \rightarrow ^7\text{F}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 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^- . 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^{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 (Ω_2 and Ω_4) from the transitions $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ were estimated using the squared values of the reduced matrix obtained from carnal et al.³⁶ and are listed in Table-3. The parameter Ω_6 value cannot be determined because the emission transition $^5\text{D}_0 \rightarrow ^7\text{F}_6$ was not

found in the present study. The greater magnitudes of Ω_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 Ω_4 and Ω_6 are accountable for the long-range effects such as viscosity, bulk modulus and dielectric constant.

Table-3: J-O Parameters and their trend of Eu^{3+} Doped Oxyfluoride Glasses

Glass sample	Ω_2	Ω_4	Ω_6	Trend of Ω_λ	References
	(x10 ⁻²⁰), cm ⁻²				
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]
LLiFB: 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	5.62	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 Ω_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.³⁷ The estimated J-O parameters and measured refractive indices were used in the calculation of radiative parameters such as radiative transition probability (A_T), lifetime (τ_R), branching ratio (β_R), stimulated emission cross-section (σ_e), non-radiative relaxation rates (W_{NR}), quantum efficiency (η), optical gain parameter ($\sigma_e \times \tau_R$) and optical gain bandwidth ($\sigma_e \times \Delta\lambda_p$) of the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0-4$) emission transitions. The radiative parameters have been calculated for all the concentrations of Eu^{3+} doped oxyfluoride using the equations⁶ and obtained values are reported in Table-4. The increment in A_T and Ω_2 values and decrement in the τ_r values with Eu^{3+} concentration indicates the higher covalency at higher concentrations. The magnitude of radiative properties of emission transitions follows the $^5\text{D}_0 \rightarrow ^7\text{F}_2 > ^7\text{F}_1 > ^7\text{F}_4 > ^7\text{F}_3 > ^7\text{F}_0$ order. The high intense transition with a β_R value of more than 50% is found to be a suitable host material for the devices in lasing applications.³⁸ The value of σ_e could explain the rate of energy extraction from the lasing material and its value is more for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, which will be used to develop and fabricate the low threshold and high gain laser applications.³⁹ The experimental and calculated β_R values are found to be 67% and 80% respectively for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 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 fluorophosphate¹, Lead fluorophosphate²³, Lead borotellurophosphate¹¹, Zincborophosphate¹³, Calcium phosphate¹⁴ glasses.

Table-4: The emission band position (λ_p , nm), effective bandwidth ($\Delta\lambda_p$, nm), radiative transition probability (A_R , s^{-1}), stimulated emission cross-section (σ_e , $\times 10^{-22} \text{ cm}^2$), experimental (β_{exp}) and calculated (β_{cal}) branching ratios of the $^5\text{D}_J \rightarrow ^7\text{F}_J$ ($J=0-4$) transitions, optical gain ($\sigma_e \times \tau_{\text{exp}}$, $\times 10^{-25} \text{ cm}^2 \text{ s}$) and optical gain bandwidth ($\sigma_e \times \Delta\lambda_p$, $\times 10^{-28} \text{ cm}^3$) of Eu^{3+} doped oxyfluoride glasses

Transition	Parameters	ZnBiNaPSr: Eu					[1]	[4]	[11]	[13]	[14]	[23]
		0.1	0.5	1.0	1.5	2.0						
$^5\text{D}_0 \rightarrow$	λ_p	579	579	579	579	579	579	576	572	578	581	579

7F_0	$\Delta\lambda_p$	3.0	3.0	3.0	3.0	3.0	2.0	2.96	4.13	2.70	2.02	2.97
	A_R	0	0	0	0	0	0	0	0	0	0	0
	σ_c	0	0	0	0	0	0	0	0	0	0	0
	β_{exp}	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0	0.02	0.01	0.01
	β_{cal}	0	0	0	0	0	0	0	0	0	0	0
	$\sigma_c \times \tau_{exp}$	0	0	0	0	0	0	0	0	0	0	0
	$\sigma_c \times \Delta\lambda_p$	0	0	0	0	0	0	0	0	0	0	0
${}^5D_0 \rightarrow {}^7F_1$	λ_p	592	592	592	592	592	592	590	592	591	594	592
	$\Delta\lambda_p$	10.0	10.0	11.0	11.0	12.0	11.4	11.5	17.8	10.6	9.68	11.1
	A_R	63.6	64.1	65.7	66.3	67.0	52.0	50.0	80.2	52.0	48.8	62.0
	σ_c	2.28	2.41	2.57	2.76	2.84	0.31	3.17	2.25	3.20	3.61	3.39
	β_{exp}	0.20	0.20	0.20	0.21	0.21	0.15	0.19	0.45	0.20	0.18	0.17
	β_{cal}	0.23	0.25	0.27	0.28	0.32	0.28	0.20	0.26	0.09	0.19	0.28
	$\sigma_c \times \tau_{exp}$	4.83	5.20	5.60	6.10	6.40	0.87	7.92	3.10	7.42	9.42	7.76
	$\sigma_c \times \Delta\lambda_p$	2.28	2.41	2.82	3.03	3.40	3.53	3.66	4.00	2.46	3.49	3.79
${}^5D_0 \rightarrow {}^7F_2$	λ_p	612	6126	612	612	612	611	609	616	613	614	613
	$\Delta\lambda_p$	12.0	12.0	12.0	12.0	13.0	10.0	10.3	13.2	8.54	10.1	10.9
	A_R	188	194	201	210	219	203	187	223	220	180	199
	σ_c	7.95	8.21	9.28	10.1	12.3	10.5	12.8	10.6	19.6	14.5	12.7
	β_{exp}	0.61	0.62	0.63	0.65	0.67	0.58	0.69	0.55	0.72	0.65	0.53
	β_{cal}	0.71	0.73	0.75	0.78	0.80	0.66	0.75	0.72	0.73	0.69	0.65
	$\sigma_c \times \tau_{exp}$	16.8	17.7	20.2	23.4	27.6	4.47	32.0	14.6	51.9	37.8	29.2
	$\sigma_c \times \Delta\lambda_p$	9.54	9.85	11.1	12.7	15.9	10.5	13.2	13.9	45.5	14.6	14.0
${}^5D_0 \rightarrow {}^7F_3$	λ_p	653	653	653	653	653	653	651	653	654	655	654
	$\Delta\lambda_p$	8.0	8.0	8.0	8.0	8.0	7.0	8.54	7.70	6.30	9.41	6.30
	A_R	0	0	0	0	0	0	0	0	0	0	0
	σ_c	0	0	0	0	0	0	0	0	0	0	0
	β_{exp}	0.02	0.02	0.03	0.03	0.03	0.01	0.02	0.03	0.01	0.04	0.01
	β_{cal}	0	0	0	0	0	0	0	0	0	0	0
	$\sigma_c \times \tau_{exp}$	0	0	0	0	0	0	0	0	0	0	0
	$\sigma_c \times \Delta\lambda_p$	0	0	0	0	0	0	0	0	0	0	0
${}^5D_0 \rightarrow {}^7F_4$	λ_p	701	701	701	701	701	701	698	704	701	703	701
	$\Delta\lambda_p$	6.0	6.0	6.0	6.0	6.0	15.0	7.0	7.1	11.8	6.78	14.5
	A_R	23.1	25.6	26.9	27.8	30.2	97	13	21.9	40	31.2	114
	σ_c	1.02	1.11	1.16	1.22	1.29	0.87	0.19	0.43	4.39	4.65	9.46
	β_{exp}	0.12	0.12	0.13	0.13	0.14	0.04	0.05	0.02	0.14	0.11	0.05
	β_{cal}	0.03	0.04	0.04	0.49	0.05	0.27	0.08	0.30	0.27	0.12	0.30
	$\sigma_c \times \tau_{exp}$	2.16	2.39	2.52	2.69	2.90	2.46	0.47	0.59	10.18	12.3	21.6
	$\sigma_c \times \Delta\lambda_p$	0.61	0.66	0.69	0.73	0.77	1.35	0.13	0.30	5.18	3.15	13.7

Decay Studies

The fluorescence decay profile of the titled glasses for the ${}^5D_0 \rightarrow {}^7F_2$ 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,⁶ the obtained average lifetimes (τ_{exp}) are 2.25, 2.21, 2.18, 2.16 and 2.12 ms and the lifetimes (τ_{exp}) from J-O theory are found to be comparable with the lifetime determined experimentally. The value of non-radiative decay rate (W_{NR}, s^{-1})⁴⁰ i.e., the deviation between τ_{rad} and τ_{exp} for the 5D_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

and the values are higher than others reported for europium doped LCZSFB², Lead-fluoroborate³, Zinc-phosphate⁶, Lead-fluorophosphate⁸, Lead-telluro-phosphate¹¹, Zincborophosphate¹³, Phosphate¹⁴, Lead-borophosphate¹⁶, Fluoroborate⁴¹ and Zinc-phosphate⁴² glasses and are presented in Table-5.

Fig.-8: Decay curves of 5D_0 level of ZnBiNaPSr: Eu glasses.

Table-5: Emission intensity of forced ED ($^5D_0 \rightarrow ^7F_2$), MD ($^5D_0 \rightarrow ^7F_1$) and ($^5D_0 \rightarrow ^7F_0$) transitions, luminescence intensity ratios (R_{21} and R_{02}), experimental (τ_{exp} , ms) and calculated (τ_{cal} , ms) lifetimes, non-radiative relaxation rates (W_{NR} , s^{-1}), Quantum efficiency (%) and total radiative transition (A_T , s^{-1}) of Eu^{3+} doped oxyfluoride glasses

sample	$^5D_0 \rightarrow ^7F_2$	$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_0$	(R_{21})	(R_{02})	τ_{exp} (ms)	τ_{cal} (ms)	W_{NR} (s^{-1})	η (%)	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.^{43,44} 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.

Fig.-9: (a) CIE 1931; (b) CIE 1976 Color Coordinate Diagrams with Dominant Wavelength.

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

sample	λ_{exc} (nm)	λ_{d} (nm)	Coordinates		CCT (K)	Emission Color	Color Purity (%)	Ref.
			CIE 1931 (x, y)	CIE 1976 (u' , v')				
ZnBiNaPSr								
Eu0.1	392	616	(0.582, 0.334)	(0.399, 0.514)	2102	Red-Orange	82.4	P. work
Eu0.5	392	616	(0.599, 0.342)	(0.405, 0.521)	2125	Red-Orange	87.7	P. work
Eu1.0	392	615	(0.610, 0.342)	(0.414, 0.523)	2232	Red-Orange	91.0	P. work
Eu1.5	392	615	(0.621, 0.347)	(0.419, 0.527)	2265	Red-Orange	94.4	P. work
Eu2.0	392	615	(0.635, 0.349)	(0.428, 0.531)	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)	(0.300, 0.550)	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.⁴⁵⁻⁴⁷ 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.^{48,49} 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.⁵⁰ In the present

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 LCZSFB², Lead-fluoroborate³, 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 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 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 $\Omega_2 > \Omega_4 > \Omega_6$ and a higher value of Ω_2 confirms the hypersensitive nature of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 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 $^5\text{D}_0$ 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 (12.3×10^{-22}), branching ratios ($\beta_{\text{exp}}=0.67$, $\beta_{\text{cal}}=0.80$), optical gain bandwidth (15.99×10^{-25}), optical gain (27.67×10^{-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.

ACKNOWLEDGMENT

One of the authors (D. Siva Raju) wants to thank UGC for providing financial assistance in the form of RGNF (2016-17).

REFERENCES

1. N. Vijaya and C.K. Jayasankar, *Journal of Molecular Structure*, **1036**, 42(2012), <https://doi.org/10.1016/j.molstruc.2012.09.037>
2. C. Madhukar Reddy, B. Deva Prasad Raju, N. John Sushma, N.S. Dhoble and S.J. Dhoble, *Renewable and Sustainable Energy Reviews*, **51(C)**, 566(2015), <https://doi.org/10.1016/j.rser.2015.06.025>
3. B. Deva Prasad Raju and C. Madhukar Reddy, *Optical Materials*, **34(8)**, 125(2012), <https://doi.org/10.1016/j.optmat.2012.01.027>

4. K. Linganna and C.K. Jayasankar, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **97**, 788(2012), <https://doi.org/10.1016/j.saa.2012.07.031>
5. M. Reza Dousti, G.Y. Poirier and A.S.Strucchi de Camargo, *Optical Materials*, **45**, 185(2015), <https://doi.org/10.1016/j.optmat.2015.03.033>
6. K. Jha and M. Jayasimhadri, *Journal of the American Ceramic Society*, **100** (4), 1402(2017), <https://doi.org/10.1016/j.jrser.2015.06.025>
7. B.M. Isah, M.E. Garba, R. Hussian and S.A. Dalhatu, *Nigerian Journal of Technology and Development*, **15** (4), 121(2018), <https://doi.org/10.4314/njtd.v15i4.3>
8. N.A Young Hoon, Nam Jin KIM, Sang Hyeok IM, Jae Min CHA and Ki RYU, *Journal of the Ceramic Society of Japan*, **117** (11), 1273(2009), <https://doi.org/10.2109/jcersj2.117.1273>
9. M.A. Marzouk, F.H. ElBatal and H.A. ElBatal, *Silicon Springer Science*, **10**(2), 615(2018), <https://link.springer.com/article/10.1007/s12633-016-9503-z>
10. D. Shajan, P. Murugasen and S.Sagadevan, *Optik*, **136**, 165(2017), <https://doi.org/10.1016/j.ijleo.2017.02.013>
11. S. Selvi, K. Marimuthu, N. SuriyaMurthy, G. Muralidharan, *Journal of Molecular Structure*, **1119**, 276(2016), <https://doi.org/10.1016/j.molstruc.2016.04.073>
12. G.Galleani, S.H.Satagneli, YounesMessaddeq, Marcos de Oliveira Jr, and Hellmut Eckert, *Physical Chemistry and Chemical Physics*, **19** (32), 21612(2017), <https://doi.org/10.1039/C7CP03927A>
13. S. Hima Bindu, D. Siva Raju, V. Vinay Krishna, T. Rajavardhana Rao, K. Veerabrahmam and Ch. Linga Raju, *Optical Materials*, **62**, 655(2016), <https://doi.org/10.1016/j.optmat.2016.10.055>
14. Ch.Srinivasa Rao, K. Upendra Kuma and C.K. Jayasankar, *Solid State Sciences*, **13**(6), 1309(2011), <https://doi.org/10.1016/j.solidstatesciences.2011.03.027Get>
15. K. Upendra Kumar, S. Surendra Babu, Ch. Srinivasa Rao and C.K. Jayasankar, *Optical Communications*, **284** (12), 2909(2011), <https://doi.org/10.1016/j.optcom.2011.02.033>
16. N. Kiran, *Journal of Molecular Structure*, **1065**, 93(2014), <https://doi.org/10.1016/j.molstruc.2014.02.047>
17. S. Surendra Babu, P. Babu, C.K. Jayasankar, W. Sievers, Th. Troster and G. Wortmann, *Journal of Luminescence*, **126**(1), 109(2007), <https://doi.org/10.1016/j.jlumin.2006.05.010>
18. P. Babu and C.K. Jayasankar, *Physica B: Condensed Mater*, **279**(4), 262(2000), [https://doi.org/10.1016/S0921-4526\(99\)00876-5](https://doi.org/10.1016/S0921-4526(99)00876-5)
19. M. Rajesh, M. Reddi Babu, N. John Sushma and B. Deva Prasad Raju, *Journal of Non-Crystalline Solids*, **528**, 119728(2020), <https://doi.org/10.1016/j.jnoncrysol.2019.119732>
20. M. Rajesh, G. R. Reddy, N. J. Sushma, G. Devarajulu and B. D. P Raju, *Optical Materials*, **107**, 110038(2020), <https://doi.org/10.1016/j.optmat.2020.110038>
21. S. Rani, S. Sanghi, A. Agarwal, V.P. Seth, *Spectrochimica Acta PartA: Molecular and Biomolecular Spectroscopy*, **74**(3), 673(2009), <https://doi.org/10.1016/j.saa.2009.07.023>
22. E.A. Davis and N.F. Mott, *The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics*, **22**, 903(1970), <https://doi.org/10.1080/14786437008221061>
23. C.R. Kesavulu, K. Kiran Kumar, N. Vijaya, Ki-Soo Lim and C.K. Jayasankar, *Materials Chemistry and Physics*, **141**(2-3), 903(2013), <https://doi.org/10.1016/j.matchemphys.2013.06.021>
24. Y.D. Siva Prasad, A. Veerabadra Rao, K. Srikanth and K.A. Emmanuel, *Rasayan Journal of Chemistry*, **4**(2), 358(2011), <http://rasayanjournal.co.in/vol-4/issue-2/19.pdf>
25. K. Vemasevana Raju, S. Sailaja, C. Nageswara Raju and B. Sudhakar Reddy *Spectrochimica Acta PartA: Molecular and Biomolecular Spectroscopy*, **79**(1), 87(2011), <https://doi.org/10.1016/j.saa.2011.02.009>
26. G. Vijaya Prakash and R. Jagannathan, *Spectrochimica Acta PartA: Molecular and Biomolecular Spectroscopy*, **55**, 1799(1999), [https://doi.org/10.1016/S1386-1425\(99\)00005-0](https://doi.org/10.1016/S1386-1425(99)00005-0)
27. B. Ramesh, G. Srinivas, D. Komaraish, Md. Shareefuddin, M.N. Chary and R. Sayanna, *International Journal of Innovative Research in Science and Engineering Technology*, **7**, 27(2015), <https://dx.doi.org/10.15680/IJRSET.2015.0408047>
28. M. Shwetha and B. Eraiah, *IOP Conference Series: Materials Science and Engineering*, **310**, 0120333(2018).

29. D.R. Patwari and B. Eraiah, *AIP Conference Proceedings*, **1951**, 030017(2018), <https://aip.scitation.org/doi/abs/10.1063/1.5031743>
30. S. Hussain, X. Chen, W.T.A. Harrison, M.R.J. Elsegood, S. Ahmad, S. Li, S. Muhammad and D. Awoyelu, *Frontiers in Chemistry*, **7**, 728 (2019), <https://doi.org/10.3389/fchem.2019.00728>
31. Y. Hatefi, N. Shahtahmasebi, A. Moghimi and E. Attaran, *Journal of Luminescence*, **131(1)**, 114(2011), <https://doi.org/10.1016/j.jlumin.2010.09.029>
32. A.K. Parchur and R.S. Ningthoujam, *RSC Advances*, **2**, 10859(2012), <https://doi.org/10.1039/C2RA22144F>
33. H. Wen, G. Jia, C.K.Duan and P.A. Tanner, *Physical Chemistry Chemical Physics*, **12**, 9933 (2010), <https://doi.org/10.1039/C0CP00206B>
34. P.A. Azeem, M. Kalidasan, K. Ramagopal, R.R. Reddy, *Journal of Alloys Compounds*, **474(1-2)**, 536(2009), <https://doi.org/10.1016/j.jallcom.2008.06.134>
35. G. Gao, J. Wei, Y. Shen, M. Peng and L. Wondraczek, *Journal of Materials Chemistry C*, **2**, 8678(2014), <https://doi.org/10.1039/C4TC01447B>
36. W.T. Carnall, P.R. Fields and Rajnak, *Journal of Chemical Physics*, **49**, 4450(1986), <https://doi.org/10.1063/1.1669896>
37. A.N. Meza-Rocha, A. Speghini, J. Franchini, R. Lozada-Morales and U. Caldino, *Journal of Materials Science: Materials in Electronics*, **28**, 10854 (2017), <https://doi.org/10.1007/s10854-017-6830-9>
38. C.S. McCamy, *Color Research and Application*, **17**, 142(1992), <https://doi.org/10.1002/col.5080170211>
39. N. Chanthima, Y. Tariwong, H.J. Kim, J. Kaewkhao and N. Sangwarantee, *Key Engineering Materials*, **766**, 122(2018), <https://doi.org/10.4028/www.scientific.net/KEM.766.122>
40. K. Mariselvam, R. Arun Kumar and S. Karthik, *Chemical Physics*, **525**, 110379 (2019), <https://doi.org/10.1016/j.chemphys.2019.05.006>
41. K. Marimuthu, R.T. Karunakaran, S. Surendra Babu, S. Arumugam and C.K. Jayasankar, *Solid State Science*, **11(7)**, 1297(2009), <https://doi.org/10.1016/j.solidstatesciences.2009.04.011>
42. Y.C. Ratnakaram, V. Reddy Prasad, S. Babu and V.V. Ravikanth Kumar, *Bulletin Material Science*, **39(4)**, 1065(2016)
43. S. Pravinraj, M. Vijayakumar and K. Marimuttu, *Physica B: Condensed Matter*, **509**, 84(2017), <https://doi.org/10.1016/j.physb.2017.01.008>
44. J. Schanda, *Encyclopedia of Color Science and Technolog*, (2016), <https://www.springer.com/gp/book/9781441980700>
45. V.A. Pratyusha and D. Punyaseshudu, *Rasayan Journal of Chemistry*, **10(3)**, 881(2017), <https://doi.org/10.1364/OE.20.012658>
46. F. Zaman, G. Rooh, N. Sristittipokakun, C. Wongdeeying, H.J. Kim and J. Kaewkhao, *Solid State Science*, **80**, 161(2018), <https://doi.org/10.1016/j.solidstatesciences.2018.04.010>
47. V.A. Pratyusha and D. Punyaseshudu, *Rasayan Journal of Chemistry*, **10(3)**, 7711(2017), <http://dx.doi.org/10.7324/RJC.2017.1031742>
48. MelisGokce, *Journal of Non-Crystalline Solids*, **505**, 272(2019), <https://doi.org/10.1016/j.jnoncrysol.2018.11.011>
49. Mithun De, Subash Sharma and Samar Jana, *Physica B*, **556**, 131(2019), <https://doi.org/10.1016/j.physb.2018.12.020>
50. S.M. Lima, L.H.da.C. Andrade, J.R. Silva, A.C. Bento, M.L. Baesso, J.A. Sampaio, L.A.de.O. Nunes, Y. Guyot and G. Boulons, *Optics Express*, **20(12)**, 12658(2012), <https://doi.org/10.1364/OE.20.012658>

[RJC-6523/2021]