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Compositional dependence of red photoluminescence of Eu^{3+} ions in lead and bismuth containing borate glasses



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ABSTRACT

Herein, heavy metal borate glasses activated with different concertation of Eu_2O_3 were prepared via the melt quench method. The Eu^{3+} concentration effect on photoluminescence (PL) properties of prepared glasses was investigated and discussed in detail to understand their utility in solid-state lighting and other photonic applications. The present work explains the suitability of two heavy metal oxides such as PbO and Bi_2O_3 for Eu_2O_3 doping to develop the glassy materials for photonic applications. The PL intensity was increased with an increase in Eu^{3+} content in PbO framed borate glasses while in Bi_2O_3 containing borate glasses the PL intensity was decreased at higher concentration due to concentration quenching. The Judd–Ofelt parameters and the radiative properties suggest the heavy metal borate glass hosts activated with 1 mol % of Eu^{3+} were potential materials for red light-emitting devices under blue light excitations. The Lifetime values of the PbO framed glasses were greater compared to Bi_2O_3 framed borate glasses which suggest the borate glass host containing high PbO content is more precisely suitable than Bi_2O_3 containing borate glass for solid-state lighting applications under blue light excitation.

1. Introduction

Search for an efficient optical material for the solid–state lighting and laser applications has become growing interest from past decades to address the technological challenges in opto-electronics devices, display devices, optical amplifiers and many more. Recently, solid-state optical materials are used for spectral conversion such as wavelength up and down conversion processes etc. [1–4]. Interestingly, optical materials comprising of rare earth (RE)s were applied as light gain medium for near infrared solid state laser, optical amplifier, optical thermometry and many photonic devices [5–9]. In particular, the high power visible light emitting solid–state devices are crucial for pool lights, headlights and architecture lighting applications [10-12].

Among the different systems bearing relevant interest in photonics [13–16], the use of glasses as dielectric hosts for RE ions has some advantages over other systems, such as high transparency in selective electromagnetic fields, mechanical and chemical strength, possibility of production of devices on several shapes and the absence of metal–ligand interactions (causes quenching processes due to the high energy stretching vibrations) [17]. Especially, for the artificial lighting devices, moisture and heat resistant oxide glasses doped with RE ions are the excellent choice [18–20]. In view of this, the borate based glasses are of significant interest owing to their good optical transparency, chemical, thermal and mechanical, stability [21] along with low melting and

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processing temperatures. It is well known that, the local environment and its variation, as well as the concentration and distribution of the RE ion in the glass matrix influence the luminescence properties such as emission intensity, emission cross section, spectral line width and life time. Therefore, these properties play a vital role while selecting the RE doped glasses for photonic applications [22]. To this end also, the borate-based glasses are good choice as a host for the REs since they constituted with a wide range of compositions without the addition of any network modifiers. Nonetheless, the distinct structural units of borate glasses such as BO3 triangle and BO4 tetrahedra helps to improve the local crystal field around the RE³⁺ ions [23]. However, the borate glasses contain high energy phonons (1300–1500 cm^{-1}) [21], which negatively influence the photoluminescence (PL) of RE ions and hence limits the practical utility of borate glasses in photonic applications. To achieve the high PL intensity and related parameters of RE ions, it is desirable that the RE should locate in a low phonon energy environment, so that the probability of nonradiative transitions can be reduced, subsequently resulting to high PL intensity and hence improve the radiative properties [24]. It has been well reported that, the incorporation of heavy metal oxides (HMOs) such as Bi₂O₃, PbO, Sb₂O₃, CdO etc. reduces the phonon energy of the parent glass and thereby enhances the optical as well as spectroscopic properties RE activated glasses. In addition, the HMOs improves the transparency of the parent glass in the infrared regions [25-28].

Among all RE ions, trivalent europium ions (Eu³⁺) are of great importance as they exhibit efficient and intense red-orange emission originating from both electric dipole (ED, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$) and magnetic dipole (MD, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$) transitions with often high quantum efficiency. Also the Eu³⁺ is used in persistent spectral hole burning, luminescent devices and in high-density optical storage components [29,30]. Nonetheless, the band energy of the *f*-*f* transitions is generally not related to ligand field strength and, therefore, the host material, the ED allowed transition of Eu^{3+} : ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ strongly related to local symmetry. As a result, this ${}^{5}D_{0}$ \rightarrow ⁷ F₂ transition can be utilized to probe the local structure in the host material. For this, the relative PL intensity ratio of I_{02}/I_{01} transitions (often denoted as the asymmetry ratio, R) is widely employed to estimate the degree of non-centro symmetry of the Eu³⁺ site in a host material [31]. Normally, the absorption cross section of Eu^{3+} is very small in the ultra violet (UV) range due to parity-forbidden nature of Eu³⁺ absorption that result in low emission under the UV excitation and therefore, limits their versatility in many applications. Increasing the Eu^{3+} doping concentration in the host material is one way to overcome this problem, but which may causes the quenching of PL emission at higher concentrations [30]. However, the incorporation of glass modifiers and/or formers with higher concentration is an alternative way to overcome this problem. Nevertheless, Hirdesh et al. [32]. have observed the excitation dependence PL properties of Eu³⁺ activated in heavy metal oxide glasses. Yu et al. [33]. have further confirmed that the PL intensity of Eu³⁺ is maximum at the excitation of blue light than ultra--violet (UV) light in heavy metal oxide glasses. To this end, there are few reports are available in open literature on PL and spectroscopic properties of Eu³⁺ doped glasses excited at blue light. Furthermore, it is important to investigate the PL properties of Eu³⁺ doped heavy metal oxide containing glasses at both the excitations (UV and blue light) to demonstrate the glasses for device application more potentially. Therefore, in present study the PL properties of borate glasses containing high concentration of PbO and Bi2O3 activated with different concentration of Eu³⁺ ions are studied at dual excitations and discussed in detail for red solid-state lighting applications.

2. Experimental and characterization details

Eu₂O₃ varied series of glass samples with chemical formula $10La_2O_3-50HMO-(40-x)B_2O_3-xEu_2O_3$ (with x = 0, 0.5, 1 and 2 mol % and HMO = PbO, Bi₂O₃) were prepared through the process of melt-quenching using porcelain crucibles. The labels for the prepared

samples are LPb50BEux and LBi50BEux for the lead and bismuth containing samples respectively, here x indicates the concentration of Eu₂O₃ in the glass system. The Eu₂O₃ free samples are labelled as LPb50B and LBi50B for lead and bismuth containing glasses respectively. The starting reagents of 4 N (99.99%) purity oxides such as B₂O₃, Bi₂O₃, PbO, La2O3 and Eu2O3 were procured from SD Fine Chemicals Ltd. for glass preparation and same were used without additional purification. The weighted 15 gms of mixture of raw materials of glass composition was grinded thoroughly for homogenous. The well mixed glass mixture transferred to porcelain crucible and kept for melting using muffle furnace. The lead containing glass mixture was melted at 1050 °C and bismuth containing glass mixture was melted at 1030 °C. After 20 min of melting, molten mass was quenched on pre heated (200 °C) brass molds. The obtained glass samples were heat treated for 4 h at 450 °C to distress glass structure occurred while quenching. Later, the glass samples were finely polished using various grade emery sheets. The samples were optically homogeneous to naked eyes and free from strains occurred due to the high melt temperatures, large melting time, and low cooling rates.

Density and refractive index measurement of the prepared glasses carried out by utilising Archimedes' principle (comprising of analytical balance and toluene as immersion liquid) and Abbe's refractometer (measured at 589.3 nm) respectively. Optical absorption spectra of all the prepared glass samples were recorded using PerkinElmer Lambda–35 UV–Vis spectrometer. The identification of structural groups formed in the glass network (in Eu³⁺ free samples) was carriedout through the Fourier transform infrared (FTIR) transmission and Raman scattering measurement using home-made setup described elsewhere [34–36]. The Raman spectra of samples were recorded at the excitation of 532 nm. PL excitation and emission spectra were collected using an YvonFluorolog 3 spectrofluorimeter having a 450 W Xenon flash lamp as the exiting source.

3. Result and discussion

3.1. Physical properties

The prepared glass samples were checked for glassy nature using X–Ray Diffractometer (XRD). The XRD profiles of the Eu free samples and samples containing 1 mol % of Eu^{3+} are shown Fig. 1. The samples were demonstrated a broad hump with absence of sharp crystalline peaks suggest the investigated glass samples are amorphous in nature. The glass becomes luminescent material when it contains optically active ions such as Eu^{3+} in its network. The oxide form of Eu_2O_3 has



Fig. 1. XRD profiles of prepared LPb50B and LBi50B glasses, and respective glasses containing 1 mol % of Eu_2O_3 .

been taken to dope the Eu³⁺ ion in the PbO and Bi₂O₃ borate glass network. The doping process carried out by replacing the B_2O_3 by 0.5, 1 and 2 mol % Eu₂O₃. The Eu³⁺ ion is differed by its ionic radii, molar mass and electro–negativity compared to B^{3+} and thereby affect the bonding of the glass network. Thus, physical properties of the glass such as density, refractive index are measured and other properties were calculated using the equations mentioned in the references [36,37].

The undoped glasses are heavily dense compared to respective RE doped glasses. From Table 1 it is evident that density values of LPb50BEux and LBi50BEux glasses are decreased as Eu³⁺ doping level increased from 0.5 to 2 mol %. The refractive index and molar volume of the glasses are increased as Eu^{3+} ions entered the network and it is highest for 2 mol % Eu³⁺ doped glasses. The other properties of the glasses such as dielectric constant, molar refractivity and electronic polarizability of the glasses increased with doping concentration of Eu³⁺ ion. Meanwhile, inter-ionic distance between the Eu³⁺ ions is decreased in lead as well as in bismuth lanthanum borate glass. These changes are attributed to the structural re–arrangement occurred in the Eu³⁺ doped PbO and Bi₂O₃ containing borate glasses. The increase in refractive index and polarizability values shows the enhancement in the light interaction with the glassy structure. These changes are due to decrease of bridging oxygen's over non-bridging oxygen's (NBO's). The NBO's in the network provides more scope for light-matter interaction through its less bounded excited electrons [38]. Further, the bismuth containing samples are highly dense compared lead comprising samples which is due to the greater atomic mass of Bi2O3 (465.96 amu) compared to PbO (223.2 amu). Also, the molar volume values of the LBi50BEux glasses are greater compared to those of LP50BEux, this is because the Bi-O (ranges from 2.08 to 2.80 Å) bond lengths are higher compared to Pb–O (in the range of 2.18–2.49 Å) bond lengths [39].

3.2. Structural properties

3.2.1. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of LPb50B and LBi50B glasses are shown in Fig. 2 (a). There are three main bands in the figure which are in agreement with those found in Ref. [40–42] but of better resolution that allows assignments of the various bands. It was greatly accepted that the broad band around $1100-1500 \text{ cm}^{-1}$ is ascribed to stretching vibration of B–O bonds of trigonal (BO₃)^{3–} groups in metaborate, pyroborate and orthoborates [40,44], whereas the band around 750–1100 cm⁻¹ is attributed to stretching vibration of B–O bonds in tetrahedral (BO₄)[–] groups [43]. The transmission band at around 690–700 cm⁻¹ is due to the bending vibrations of the B–O linkages in the borate network [40]. The weak band or the kink at 621 cm⁻¹ observed in lead containing glass was attributed to bending vibration of O–B–O bonds of borate units [44]. Nevertheless, the IR analysis of the Bi₂O₃ containing glasses demonstrated a weak bands in low frequency region extended between 500 and 600 cm⁻¹

Table 1

Physical properties of the un-doped and Eu³⁺doped PbO and Bi₂O₃ lanthanum borate glasses.

which are attributed to bending vibrations of Bi-O-Bi bonds in highly distorted BiO₆ octahedral units [45,46]. By the keen observation of IR spectra, it was evident that, the centres of the 750–1100 cm^{-1} and 1150–1500 cm⁻¹ bands in bismuth containing glass were slightly shifted to lower wave number with reduced width compared to lead containing sample. It has been reported that, the centre of the band around $750-1100 \text{ cm}^{-1}$ shifted to lower wave number indicating an increase in NBOs, and a longer bond length of BO₄ structural unit. While, the center of the same band shifted to higher wave number indicating a decrease in NBOs and a shortening in the bond length of BO₄ [48]. Therefore, the shift of 760–1100 cm^{-1} band to lower wave number is attributed to increase in NBOs and a lengthening in the bond length of BO4 when Bi₂O₃ incorporated in the place of PbO. Further, the shift of 1150–1500 cm⁻¹ band towards the lower wave number in Bi₂O₃ containing sample may be due to the fact that, the new bridging bond of Bi–O–B is formed by the inducement of strongly polarizing Bi³⁺ ions. Since the stretching force constant of Bi-O bonding is substantially lower than that of the Pb–O, hence the stretching frequency of Bi–O–B might trend to be lower [47,49,50].

3.2.2. Raman spectroscopy

The Raman spectra of Eu³⁺ free LPb50B and LBi50B glasses are shown in Fig. 2 (b). The spectra of both hosts evidenced the absence of the boroxol characteristic band at $\sim 805 \text{ cm}^{-1}$ [42], which represents the glasses under study are not containing any boroxol rings. The broad Raman signal observed at around $\sim 1252 \text{ cm}^{-1}$ was attributed to the pyroborate structural units $(B_2O_5^{4-})$ [51,52]. This band is slightly shifted to lower wavenumber in Bi2O3 containing glass system. This shift suggest an increasing depolymerization and an increasing number of NBOs sites in bismuth containing glass sample [53]. The Raman lines appeared at $\sim 935 \text{ cm}^{-1}$ and at $\sim 900 \text{ cm}^{-1}$ (present in lead containing sample only) were attributed to symmetric stretching vibration of the planar orthoborate units (BO $_3^{3-}$) units [54]. The weak bands appeared at ~ 628 cm⁻¹ in lead containing sample was attributed to ring type metaborate groups [42]. The Raman bands observed at \sim 710 (\sim 718 cm⁻¹ in bismuth containing host) and $\sim 731 \text{ cm}^{-1}$ were ascribed to chain type metaborate units [42]. The identified weak peak at \sim 761 cm⁻¹ in lead containing host reveals the presence of a BO₄ structural groups units, probably in diborate groups [55]. The Raman band present at ~ 490 cm⁻¹ in PbO comprising glass host was ascribed to loose' diborate groups and 'loose' BO₄ group [56]. The band observed at \sim 595 cm⁻¹ in LPb50B glasses was ascribed to isolated diborate units [55]. Finally, the weak intense band developed at ~ 240 and ~ 315 cm⁻¹ in lead containing sample could be ascribed to the vibrational mode of Pb²⁺ in fourfold coordination [53]. This developed Raman bands at low frequency region is also indicate the gradual growth of a PbOn pseudo phase within the glass matrix; for high PbO concentration this may take the form of PbO₄ square-pyramidal structures with considerable degree

Properties (\pm error limits)	LPb50B	LPb50BEu0.5	LPb50BEu1	LPb50BEu2	LBi50B	LBi50BEu0.5	LBi50BEu1	LBi50BEu2
Physical Properties								
Average Molecular Weight, M (gmol ⁻¹)	156.67	158.08	159.49	162.32	293.41	294.82	296.233	299.056
Density, ρ (gcm ⁻³)(±0.002)	5.393	5.36	5.103	5.043	6.812	6.795	5.808	5.940
Molar Volume, $V_m (cm^3 mol^{-1})(\pm 0.001)$	29.05	29.45	31.25	32.18	43.071	43.387	50.996	50.339
Refractive index, $n(\pm 0.001)$	1.79	1.80	1.81	1.83	2.084	2.089	2.142	2.171
Dielectric constant, $\varepsilon(\pm 0.001)$	3.23	3.24	3.28	3.37	4.343	4.363	4.588	4.713
Molar Refractivity, R_M (cm ⁻³)(±0.002)	12.40	12.60	13.50	14.20	22.700	22.934	27.774	27.843
Electronic Polarizability, $\alpha_e(\times 10^{-24} \text{ cm}^3)(\pm 0.001)$	4.91	4.99	5.35	5.63	8.996	9.089	11.00	11.03
Optical Properties								
Direct optical band gap, E_g^{dir} (eV) (±0.002)	2.867	-	-	-	2.503	-	-	-
Indirect band gap, E_g^{indir} (eV) (±0.002)	2.265	-	-	-	2.374	-	-	-
Inter- ionic Properties								
Concentration of Eu2O3 (mol %)	0	0.5	1	2	0	0.5	1	2
Eu ³⁺ concentration, N ($ imes 10^{22}$ ions/cm ³) (±0.0001)	-	1.92	2.022	3.74	-	0.694	1.181	2.392
Eu–Eu Interionic spacing, d _{Eu-Eu} (Å) (±0.0001)	-	4.68	3.79	3.04	-	5.331	4.466	3.041



Fig. 2. FTIR spectra (a) and Raman spectra (b) of Eu free LPb50B and LBi50B glasses.

of covalent Pb–O bonding [57]. The Raman band appeared at ~ 790 cm⁻¹ in LBi50B glass could be assigned to the vibration of planar six membered borate rings with one BO₄ tetrahedron [42]. The band observed at ~ 432 cm⁻¹ in bismuth containing sample assigned to stretching vibrations of Bi–O–Bi linkages of BiO₆ octahedron [58]. The peak developed at ~ 263 cm⁻¹ in LBi50B glass could be assigned for vibration of Bi–O bond in [BiO₃] structural unit [59]. No clear assignment of the weak Raman line appeared at ~ 680 cm⁻¹ in bismuth containing glass sample. Because, the formation of [B Θ 2O₂^{2–}] tetrahedra was evidenced due to the presence of the 680, 395 and 350 cm⁻¹ bands in Raman spectra the Raman signals at 395 and at 350 cm⁻¹ are not evidenced. Hence, we cannot readily assign the 680 cm⁻¹ Raman signal for B Θ 2O₂^{2–} tetrahedra.

3.3. Optical absorption study

The absorption characteristics of the Eu³⁺ ion in the PbO and Bi₂O₃ lanthanum borate glasses were measured in the UV–Vis region and the resulted spectra is shown in Fig. 3 (a) and (b) respectively. The LPb50Eux and LBi50BEux glasses are exhibited strong UV absorption and good transmission for visible radiation. In both the spectra, 0.5 mol % of Eu³⁺–doped glass is exhibit a single absorption due to ${}^{7}F_{0}\rightarrow{}^{5}D_{2}$ transition at 464 nm [61]. An additional absorption peak at 393 nm corresponding to ${}^{7}F_{0}\rightarrow{}^{5}L_{6}$ transition appeared in the lead containing samples for higher Eu³⁺ concentration [61]. The absorption intensity of absorption peaks are increased with Eu³⁺ content and highest for 2 mol % doped glasses. From Fig. 3 it can be seen that among different characteristic absorption peaks of Eu³⁺, most of absorption bands of Eu³⁺ ion in the UV and visible region are masked due to strong absorption of the host glass [25]. The presence of heavy metal cations such as Pb²⁺



Fig. 3. Optical absorption spectra of LPb50BEux (a) and LBi50BEux (b) glasses. In set of Fig. (a) represent the plots of $(\alpha h\nu)^2 v/s h\nu$ for direct bandgap measurement for Eu³⁺ free LPb50B and LBi50B glasses and inset of Fig. (b) represents the plots of $(\alpha h\nu)^{1/2} v/s h\nu$ for indirect bandgap measurements for LPb50B and LBi50B glasses.

 Bi^{3+} in LPb50BEux and LBi50BEux glasses respectively might be responsible for the strong absorption of the glasses.

The band gap of the glass is related to the variation in the glass structure. Usually band gap of the glass shifts to higher wavelength side due to locally created energy levels near the band edge. Therefore, in the present investigation the band gap of the glasses is determined using Davis and Mott relation [37] which is derived from absorption edge given by

$$\alpha h \nu = B \left(h \nu - E_g \right)^n \tag{1}$$

where *B* is the constant called as band tailing factor, E_g is the optical band gap between the valence band and conduction band, $h\nu$ is the photon energy of the incident radiation, *n* is an index of phonon assisted direct and indirect allowed transition equal to $\frac{1}{2}$ and 2 respectively, and α be the absorption coefficient. The absorption coefficient (α) of the investigated glasses has been estimated using the following relation [62].

$$\alpha(\lambda) = 2.303 \quad \left(\frac{A}{d}\right) \tag{2}$$

where, A and d are the absorbance and the thickness of the glass samples, respectively. Further, the Tauc's plots used to estimate the optical bandgaps of glasses using equation (1) are shown in insets of Fig. 3. In set of Fig. 3 (a) represent the plots for direct bandgap measurement for Eu^{3+} free LPb50B and LBi50B glasses and inset of Fig. 3 (b) represents the plots for indirect bandgap measurements for LPb50B and LBi50B glasses. By extrapolating the linear part of *ahv vs hv* curve is intersected at different values of E (*hv*) axis. The direct band gap values of Eu^{3+} free glasses are listed in Table 1 from which it is clear that the band gap for PbO borate glass is higher than Bi₂O₃ contain glasses.

3.4. Photoluminescence properties

The heavy metal borate glasses are transparent to optical radiations in the visible to near infrared (NIR) region. But, the RE doped glasses are optically active and exhibits strong absorption and luminescence in the visible to NIR region of electromagnetic spectrum [1]. This versatile behaviour attributed to intra-band 4f–4f and 4f–5d electronic transition of triply ionized RE ions [61]. In the PL phenomenon, light is used to excite the RE ions to record the resultant emission (spectrum). The peak

position and emission intensity of the Eu^{3+} ion rely on the host glass chemical composition and its concentration. Thus, in the present study, excitation spectra of the Eu^{3+} in the PbO and Bi_2O_3 containing lanthanum borate glasses are recorded by monitoring the emission at 614 nm. Fig. 4 (a) and (b) shows the recorded PL excitation spectra of the LPb50BEux and LBi50BEux glasses respectively. The excitation spectra in both glass hosts shows several peaks, the observed peaks are assigned as shown in Fig. 4 using the references [63,64]. The intensity of the excitation peaks are enhanced as Eu³⁺ doping increased in PbO containing glasses while the Bi2O3 comprising glass host demonstrated the concentration dependency. The excitation peaks at 393 nm and 464 nm is equally high intense among other transitions in the PbO contained glasses. But, in bismuth contained glasses, excitation peak at 464 nm is highest compared to 393 nm. Thus, the PL spectra of the glass hosts were recorded at both 393 nm and at 464 nm excitations to demonstrate the studied glasses for lighting applications more potentially and their suitability.

The PL emission spectra of LP50BEux and LBi50BEux glass hosts at excitation of 393 nm are shown in Fig. 5 (a) and (b) respectively and the corresponding PL spectra at 464 excitation are depicted in Fig. 5 (c) and (d) for lead and bismuth containing glasses. The Eu^{3+} ion exhibited its characteristic emission wavelengths in visible region of spectrum in both hosts. The emission peaks at 579, 593, 614, 653 and 702 nm are assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ electric and magnetic dipole transitions of the Eu³⁺ ion allowed by $\Delta J = 2$ and 1 selection rules. The band at 614 nm is peaked highest among other transitions. Interestingly, emission at 702 nm is considerably intense compared to band at 593 nm and other heavy metal borate host glasses [54,63]. The Eu³⁺ ion emission intensity of PbO hosted borate glass is dependent on ion concentration and independent to the excitation wavelengths. Whereas, the bismuthate glasses emission shown concentration dependency and intensity quenched at 2 mol % Eu³⁺ doping. Thus, emission intensity is highest at the excitation of 464 nm compared to 393 nm in the LBi50BEux glasses. In LPb50BEux glasses, the luminescence intensity significantly increased at 1 mol % compared to 0.5 mol % of Eu³⁺ and intensity further slightly increased for 2 mol% of Eu³⁺ ions. But in the case of LBi50BEux glasses, emission intensity for Eu³⁺ at 1 mol% enhanced noticeably compared to 0.5 and at 2 mol % Eu^{3+} the bismuth containing glasses exhibited decrease in PL intensity due to concentration quenching. The overall emission intensity of lead and bismuth containing glasses shown in Fig. 5 clearly proves composition dependency of luminescence properties of Eu^{3+} ion. Further, it has been



Fig. 4. PL excitation spectra of Eu³⁺ doped LPb50BEux (a) and LBi50BEux (b) glasses.



Fig. 5. PL emission spectra of LPb50BEux (a) and LBi50BEux (b) glasses at 393 nm excitation. PL emission spectra of LP50BEux (c) and LBi50BEux (d) glasses at the excitation of 464 nm.

reported that the intensity of 702 nm transition of Eu³⁺ was enhanced greatly along with 614 nm transition due to high polarizability of the glasses [65]. In Fig. 5 it can clearly identified that with increase in Eu₂O₃ content in the glasses, 702 nm transition of Eu³⁺ is improved along with 614 nm transition (not at equal rate) which is attributed to the high polarizability of the studied glasses attained due to the highly polarizable PbO and Bi₂O₃ oxides. The energy level diagram depicted in Fig. 6 demonstrating the different transitions occurred under the excitation of 464 nm [66,67]. The multiphonon relaxation process effects the relaxation of Eu³⁺ ion from ${}^{5}D_{2} \rightarrow {}^{5}D_{0}$ lower state by low level lattice vibration. Later, stimulated electronic transition between ⁵D₀ to lower ⁷F_{1,2,3}, 4 states results in red light at various wavelengths in the emission spectra. Furthermore, PL emission intensity ratio's (R) of orange to red band (electric to magnetic dipole transition) infers local asymmetry around the Eu³⁺ ion offered by surrounding ligands and it also infer the chemical bond strengths of Eu–O [63]. The calculated intensity ratio (R) values at the excitation of 393 nm and 464 nm are provided in Tables 2 and 3 respectively. The R values are highest for LPb50BEux glass over LBi50BEux glasses suggests Eu³⁺ ion centered at highly asymmetric site and possess higher Eu-O covalence in the PbO framed borate glass network compared to Bi₂O₃ framed borate glass [68]. Nonetheless, the R values higher than the unity for all the investigated glass samples suggest the Eu^{3+} ions are situated in acentric sites [65]. On the contrary, a large diversity of low-symmetry sites in the present glass samples can be corroborated by large R values and the inhomogeneous line broadening observed from the emission spectra [65].

The Judd–Ofelt (JO) [69,70] theory access the quantitative luminescence properties such as branching ratio, radiation transition probability, emission cross-section and total radiative lifetime of Eu^{3+} ions in the given host [71,72]. The JO intensity parameters of the host medium

used to predict the above mentioned radiative properties of the prepared glasses. The JO parameters related to LPb50BEux and LBi50BEux glasses were calculated using emission spectrum and using corresponding relations mentioned in Refs. [37]. The JO parameters, Ω_2 varies according to the strength of Eu–O covalence and short range structural rearrangement around the Eu³⁺ ion, where as Ω_4 and Ω_6 parameters are attributed to the glass rigidity and viscosity [73]. The calculated values of JO parameters at the excitation of 393 nm and at 464 nm are furnished in Tables 2 and 3 respectively. Since the PL intensity and JO parameters are better at 464 nm excitation and hence the JO parameters (obtained at excitation of 464 nm) are compared with other heavy metal borate glasses [23,37,68,74,75]. The value Ω_2 and Ω_4 of LPb50BEux glasses are more compared to LBi50BEux glass shows strength of covalent bonding of Eu³⁺ to O⁻ in PbO framed B₂O₃ glass network is much higher.

The lasing properties of the investigated glasses calculated using JO parameters with the relations found in previously mentioned reference. The calculated radiative parameters of the LPb50BEux and LBi50BEux glass are listed in Tables 4 and 5 respectively for 393 and 464 nm excitations. The deciding factor for lasing transition such as branching ratio is should be more than 0.5 for given emission transition. Among all emission peaks, $^{7}F_{0} \rightarrow ^{5}D_{2}$ transition of Eu³⁺ ion is exhibited such potentiality and both the glass host containing 1 mol % of Eu³⁺ yielded highest branching ratio compared to other prepared glasses. The RE doped glass is useful as optical gain material for solid state laser and it is dependent on stimulated emission cross–section of particular transition [76,77]. Interestingly, $^{5}D_{0}\rightarrow ^{7}F_{4}$ transition has gain slightly large stimulated cross–section compared to $^{5}D_{0}\rightarrow ^{7}F_{2}$ emission band. But, this transition has shortage of required branching ratio to achieve necessary population inversion. The reciprocal of the total transition probability



Fig. 6. Schematic energy-level diagram Eu3+ ion in studied glasses.

Table 2

JO parameters Ω_2 and Ω_4 (x 10^{-20}) and Intensity ratio (R) values of Eu₂O₃ doped glasses at the excitation of 393 nm.

Glass Code	Ω_2	Ω_4	R	References
LPb50BEu0.5 LPb50BEu1 LPb50BEu2 LBi50BEu0.5 LBi50BEu1 LBi50BEu2	3.30 4.73 4.22 3.02 3.95 3.94	4.20 4.48 4.03 5.15 4.66 4.83	2.61 3.75 3.35 2.4 3.12 3.14	Present work Present work Present work Present work Present work

Table 3

JO parameters Ω_2 and Ω_4 (x $10^{-20})$ and Intensity ratio (R) values of Eu_2O_3 doped glasses at 464 nm.

Glass Code	Ω_2	Ω_4	R	References
LPb50BEu0.5	4.69	5.15	8.75	Present work
LPb50BEu1	6.86	6.75	5.45	Present work
LPb50BEu2	5.98	6.87	4.75	Present work
LBi50BEu0.5	3.55	4.46	2	Present work
LBi50BEu1	5.33	4.6	4.23	Present work
LBi50BEu2	5.57	4.96	4.2	Present work
BTPAE	3.53	5.54	1.08	[22]
ZnAlBiB	2.19	1.49	2.66	[73]
ZNBBE	5.14	4.17	3.98	[38]
LBTAF	4.71	0.48	4.77	[74]
LBTPE	3.12	3.12	0.08	[75]

gives metastable life of excited state ${}^{5}D_{0}$ state and calculated values decreased as increase in number density of Eu $^{3+}$ ion in the glass network. The actual lifetime of metastable state can be determined by decay curve analysis. The recoded decay curves at the excitation of 464 nm of LPb50BEux and LBi50BEux glasses are shown in Fig. 7. The single exponential function is well fitted to observed decay curves [37]. The

obtained lifetime of ${}^{5}D_{0}$ state is 1.29, 1.27, 1.24 ms and 1.01, 0.96, 0.90 ms for LPb50BEux and LBi50BEux (x = 0.5, 1 and 2 mol %) glasses respectively. The LPb50BEu1 and LBi50BEu1 glasses has gained optimum stimulated emission cross–section and optical gain values for ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 614 nm compared to other studied glasses, suggesting that the heavy metal borate glasses containing 1 mol % of Eu³⁺ are potential photonic materials. Further, obtained quantum efficiency (τ_{mea}/τ_{cal}) of the lead containing glass is 85% compared with 50% of bismuth hosted glass signifies LPb50BEu1 glasses [37]. The emission intensity and radiative properties and also the life time values of studied glasses are greater while the JO parameters and R values are lesser compared to Eu³⁺ doped red emitting phosphor materials [73,74]. Further, the PL emission peaks are broad in the studied glasses compared to the phosphor materials.

The colour chromaticity profile is an important parameter to evaluate the colour purity of the glass. The emission spectra of the glass have wavelengths at different position such as orange, red and deep red region of the spectrum. Sometime more than one emission bands helps in modulating the total emission colour of the glass. To evaluate the colour index of the glass, 1931 CIE chromaticity theory has been adopted [78–80]. The emission spectra of the glasses were used to calculate the x, y using the equations

$$x = \frac{X}{X + Y + Z} \tag{3}$$

$$y = \frac{Y}{X + Y + Z} \tag{4}$$

where X, Y and Z are the tristimulus values used to get the stimulation (i. e. power) for each of the three primary colours such as red, green and blue colours required to match the colour $P(\lambda)$. The stimulant values for given wavelength calculated by

$$X = \int_{\lambda} \overline{X}(\lambda) P(\lambda) d\lambda$$
(5)

$$Y = \int_{\lambda}^{\lambda} \overline{Y}(\lambda) P(\lambda) d\lambda$$
(6)

$$Z = \int_{\lambda}^{1} \overline{Z}(\lambda) P(\lambda) d\lambda$$
⁽⁷⁾

where $\overline{X}(\lambda)$, $\overline{Y}(\lambda)$ and $Z(\lambda)$ is colour matching functions, $P(\lambda)$ is spectral density.

Fig. 8 (a) and (b) shows the CIE chromaticity diagram of the LPb50BEux and LBi50BEux glasses for which the PL emission spectra recorded at 464 excitation was utilized. From the figure it is evident that the chromaticity co-ordinates (x, y) travels in the red region in both the glass hosts. However, the glasses containing 1 mol % of Eu^{3+} lies very close to ideal red region which suggest that studied glasses containing 1 mol % of Eu^{3+} are much suitable for red light solid state lighting applications or red LEDs under blue light excitations.

4. Conclusion

The Eu^{3+} activated heavy metal borate glasses were prepared and the effect of Eu^{3+} ions on optical absorption, optical band gap and PL properties were analysed. The XRD profiles were confirmed the glassy nature of prepared glasses. The optical band gap values were demonstrated decreasing trend with increase in Eu_2O_3 concertation due to the decrease of bridging oxygen's over non-bridging oxygen's (NBO's). These NBO's in the glass network provides more scope for light–matter interaction through its less bounded excited electrons. The PL emission

Table 4

Emission peak wavelength (λ_p , nm), effective bandwidth ($\Delta \lambda_p$, nm), Radiative transition probabilities (A, s^{-1}), Total radiative transition probabilities (A_T , s^{-1}), stimulated emission cross section ($\sigma_{se} \times 10^{-22} \text{ cm}^2$), experimental branching ratios (β_{exp}), gain bandwidth ($\sigma_{se} \Delta \lambda_p$) ($x \ 10^{-28}, \text{cm}^3$) and life time values (τ) (ms) of the Eu₂O₃-doped glasses at the excitation of 393 nm.

Transitions ${}^{5}D_{0} \rightarrow$	Parameters	LPb50BEu0.5	LPb50BEu1	LPb50BEu2	LBi50BEu0.5	LBi50BEu1	LBi50BEu2
7 _{F1}	λ_p	593	593	593	593	593	593
	$\Delta \lambda_p$	13	15.1	15.1	12.9	14.2	12.9
	A	73.11	73.11	73.11	73.11	73.11	73.11
	σ_{se}	2.73	2.35	2.35	2.35	2.36	2.36
	β_R	0.18	0.15	0.16	0.16	0.16	0.16
	$\sigma_{se} x \Delta \lambda_p$	3.54	3.54	3.54	3.03	3.35	3.04
7_							
′F ₂	λ_p	614	614	614	614	614	614
	$\Delta \lambda_p$	13	14	14	12.7	12.9	12.8
	Α	195	280	250	233	234	234
	σ_{se}	8.33	11.1	9.90	7.63	9.97	10.8
	β_R	0.50	0.58	0.57	0.52	0.53	0.53
	$\sigma_{se} \Delta \lambda_p$	10.8	15.54	13.86	9.69	12.86	13.82
	A _T	387	497	436	397	438	442
	$ au_{cal}$	2.58	2.05	2.28	2.51	2.28	2.22
_							
⁷ F ₄	λ_p	702	702	702	702	702	702
	$\Delta \lambda_p$	10	11.33	11.7	10.1	12	10.2
	A	118	126	113	145	131	136
	σ_{se}	11.4	11.1	9.32	13.9	10.5	13.1
	β_R	0.30	0.26	0.26	0.36	0.29	0.30
	$\sigma_{se} \Delta \lambda_p$	11.4	12.54	10.90	14.03	12.6	13.36

Table 5

Emission peak wavelength (λ_{p} , nm), effective bandwidth ($\Delta \lambda_{p}$, nm), Radiative transition probabilities (A, s^{-1}), Total radiative transition probabilities (A_{τ} , s^{-1}), stimulated emission cross section ($\sigma_{se} \times 10^{-22} \text{ cm}^2$), experimental branching ratios (β_{exp}), gain bandwidth ($\sigma_{se} \Delta \lambda_p$) ($x \times 10^{-28}, \text{cm}^3$) and life time values (τ) (ms) of the Eu₂O₃ doped glasses at the excitation of 464 nm.

Transitions ${}^{5}D_{0} \rightarrow$	Parameters	LPb50BEu0.5	LPb50BEu1	LPb50BEu2	LBi50BEu0.5	LBi50BEu1	LBi50BEu2
⁷ F ₁	λ_p	593	593	593	593	593	593
	$\Delta \lambda_p$	15	15.2	15.2	15	15.1	15.1
	A	73.11	73.11	73.11	73.11	73.11	73.11
	σ_{se}	2.33	2.32	2.33	2.36	2.35	2.35
	β_R	0.14	0.10	0.11	0.20	0.14	0.13
	$\sigma_{se} \Delta \lambda_p$	3.49	3.59	3.54	3.54	3.54	3.54
7 _{E2}	۵_	614	614	614	614	614	614
12	$\Lambda \lambda_{-}$	13.84	13.81	13.80	13.9	13.21	14.07
	A	277.88	406.45	354.31	151.08	315.11	330.02
	σ _{co}	12.20	14.6	14.2	8.96	14.6	13.52
	βp	0.55	0.60	0.57	0.43	0.60	0.60
	$\sigma_{se} \Delta \lambda_{p}$	18.3	25.25	24.56	12.45	19.28	19.02
	A_T	496.314	670.0338	621.2799	350.0494	518.7146	543.0927
	τ_{cal}	2.01	1.49	1.61	2.83	1.94	1.84
	$ au_{mea}$	1.29	1.27	1.24	1.01	0.96	0.90
7 _E	1	700	702	702	700	702	702
F4	λ_p	11 50	11 50	11 56	702	12.04	10.7
	$\Delta \lambda_p$	11.59	11.59	11.50	9.9	12.04	10.7
	A	145.51	190.40	193.85	125.64	129.79	139.95
	σ_{se}	12.20	17.0	15.8	11.4	12.7	10.4
	PR	0.29	0.28	10.06	0.35	0.200	0.23/
	$\sigma_{se} \Delta \Lambda_p$	14.19	20.39	18.20	11.28	15.29	11.12

properties were analysed under UV and blue light excitations. The PL intensity was increased with increase in Eu³⁺ content in lead containing glass samples whereas it was decreased at 2 mol % of Eu³⁺ in bismuth framed glasses. The JO parameters and radiative properties clearly suggest the investigated glasses containing 1 mol % of Eu³⁺ were competing materials for red light solid state lighting application under blue light excitations. Further, the life time and quantum efficiency values of lead containing glass significantly high compared to bismuth containing borate glass. Therefore, the PbO framed borate glass host is more precisely suitable than Bi₂O₃ containing borate glass for solid state lighting applications under blue light excitations.

Credit author statement

P. Ramesh: Carried the materials synthesis, characterization, Vinod Hegde: Recorded the absorption spectra, A.G. Pramod: Collected the XRD profiles, B. Eraiah: Helped in collecting the FTIR spectra, G. Jagannath: Completed the JO parameters calculations and analysis, D. A. Agarkov and G.M. Eliseeva: Recorded the Raman spectra and contributed in structural analysis, K. Annapurna: Contributed to concept discussion and in paper writing. M.K. Pandey: Helped in PL analysis, concept discussion and in paper writing. M.K. Kokila: Mainly supervised the whole research from content to final analysis.



Fig. 7. The decay curves for ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (614 nm) emission of Eu³⁺ ions in LPb50BEux (a) and LBi50BEux (b) glasses when excited at 464 nm.



Fig. 8. The CIE chromaticity diagram of LPb50BEux (a) and LBi50BEux (b) glasses under the excitation of 464 nm. In Left figure, (A) = LPb50BEu0.5, (B) = LPb50BEu1 and (C) = LPb50BEu2. In Right figure (A) = LBi50BEu0.5, (B) = LBi50BEu1 and (C) = LBi50BEu2.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

- A.S. Kuznetsov, V.K. Tikhomirov, M.V. Shestakov, V.V. Moshchalkov, Nanoscale 5 (2013) 10065–10075.
- [2] K. Linganna, R. Narro-García, H. Desirena, E. De La Rosa, C. Basavapoornima,
- V. Venkatramu, C.K. Jayasankar, J. Alloys Compd. 684 (2016) 322–327.
 [3] K. Haladejová, A. Prnová, R. Klement, W.H. Tuan, S.J. Shih, D. Galusek, J. Eur. Ceram. Soc. 36 (2016) 2969–2973.
- [4] G. Ji, G. joon Hong, C. hyuck Bae, P. Babu, K.S. Lim, Appl. Surf. Sci. 478 (2019) 412–416.
- [5] F. Steudel, S. Loos, B. Ahrens, S. Schweizer, J. Lumin. 170 (2016) 770-777.
- [6] F. Zaman, J. Kaewkhao, G. Rooh, N. Srisittipokakun, H.J. Kim, J. Alloys Compd. 676 (2016) 275–285.
- [7] X. Zhang, L. Huang, F. Pan, M. Wu, J. Wang, Y. Chen, Q. Su, ACS Appl. Mater. Interfaces 6 (2014) 2709–2717.
- [8] X. Zhang, J. Wang, L. Huang, F. Pan, Y. Chen, B. Lei, M. Peng, M. Wu, ACS Appl. Mater. Interfaces 7 (2015) 10044–10054.
- [9] S. Tabanli, G. Eryurek, Sens. Actuators, A Phys. 285 (2019) 448-455.
- [10] J.S. Zhong, H.B. Gao, Y.J. Yuan, L.F. Chen, D.Q. Chen, Z.G. Ji, J. Alloys Compd. 735 (2018) 2303–2310.
- [11] P. Zheng, S. Li, L. Wang, T.-L. Zhou, S. You, T. Takeda, N. Hirosaki, R.-J. Xie, ACS Appl. Mater. Interfaces 10 (2018) 14930–14940.
- [12] F. Zaman, G. Rooh, N. Srisittipokakun, T. Ahmad, I. Khan, M. Shoaib, Ataullah, J. Rajagukguk, J. Kaewkhao, Solid State Sci. 89 (2019) 50–56.
- [13] P. Cai, X. Wang, H.J. Seo, Phys. Chem. Chem. Phys. 20 (2018) 2028–2035.
- [14] M. Gong, Q. Liu, B. Cook, B. Kattel, T. Wang, W.-L. Chan, D. Ewing, M. Casper,
- A. Stramel, J.Z. Wu, ACS Nano 11 (2017) 4114–4123.
 [15] X. Wang, Y. Wang, Y. Bu, X. Yan, J. Wang, P. Cai, T. Vu, H.J. Seo, Sci. Rep. 7
- (2017). [16] X. Chen, W. Xu, L. Zhang, X. Bai, S. Cui, D. Zhou, Z. Yin, H. Song, D.-H. Kim, Adv.
- Funct. Mater. 25 (2015) 5462–5471.
 [17] D.F. Franco, A.C. Sant'Ana, L.F.C. De Oliveira, M.A.P. Silva, J. Mater. Chem. C 3 (2015) 3803–3808.
- [18] T.A. Lodi, N.F. Dantas, T.S. Gonçalves, A.S.S. de Camargo, F. Pedrochi, A. Steimacher, J. Lumin. 207 (2019) 378–385.
- [19] V. Hegde, C.S.D. Viswanath, K.K. Mahato, S.D. Kamath, Mater. Chem. Phys. 234
- (2019) 369–377.[20] A.U. Trápala-Ramírez, J.L.N. Gálvez-Sandoval, A. Lira, I. Camarillo, E. Alvarez-
- Ramos, A.N. Meza-Rocha, U. Caldiño, J. Lumin. 215 (2019). [21] S. Selvi, K. Marimuthu, G. Muralidharan, J. Non-Cryst. Solids 461 (2017) 35–46.
- [22] W.A. Pisarski, T. Goryczka, J. Pisarska, W. Ryba-Romanowski, J. Phys. Chem. B 111 (2007) 2427–2430.
- [23] S. Pravinraj, M. Vijayakumar, K. Marimuthu, Phys. B Condens. Matter 509 (2017) 84–93.
- [24] X. Huang, S. Han, W. Huang, X. Liu, Chem. Soc. Rev. 42 (2013) 173–201.
- [25] B.C. Jamalaiah, L.R. Moorthy, H.J. Seo, J. Non-Cryst. Solids 358 (2012) 204–209.
 [26] Y. Wang, J. Cao, X. Li, J. Li, L. Tan, S. Xu, M. Peng, J. Am. Ceram. Soc. 102 (4) (2018) 1694–1702, jace.16067.
- [27] K. Ouannes, K. Lebbou, B.M. Walsh, M. Poulain, G. Alombert-Goget, Y. Guyot, J. Alloys Compd. 649 (2015) 564–572.
- [28] C. Doerenkamp, E. Carvajal, C.J. Magon, W.J.G.J. Faria, J.P. Donoso, Y. Galvão Gobato, A.S.S. de Camargo, H. Eckert, J. Phys. Chem. C 123 (2019) 22478–22490.
- [29] M. Haouari, F. Ben Slimen, A. Maaoui, N. Gaumer, J. Alloys Compd. 743 (2018) 586–596.
- [30] G. Gao, J. Wei, Y. Shen, M. Peng, L. Wondraczek, J. Mater. Chem. C 2 (2014) 8678–8682.
- [31] H. Wen, G. Jia, C.K. Duan, P.A. Tanner, Phys. Chem. Chem. Phys. 12 (2010) 9933–9937.
- [32] A. Khanna Hirdesh, J. Lumin. 204 (2018) 319–326.
- [33] C. Yu, Z. Yang, J. Qiu, Z. Song, Z. Dacheng, J. Am. Ceram. Soc. 101 (2018) 612–623.
- [34] I. Burmistrov, D. Agarkov, I. Tartakovskii, V. Kharton, S. Bredikhin, ECS Trans. 68 (2015) 1265–1274.
- [35] D.A. Agarkov, I.N. Burmistrov, F.M. Tsybrov, I.I. Tartakovskii, V.V. Kharton, S. I. Bredikhin, Russ. J. Electrochem. 52 (2016) 600–605.

- [36] D.A. Agarkov, I.N. Burmistrov, F.M. Tsybrov, I.I. Tartakovskii, V.V. Kharton, S. I. Bredikhin, Solid State Ionics 302 (2017) 133–137.
- [37] V. Hegde, C.S.D. Viswanath, V. Upadhyaya, K.K. Mahato, S.D. Kamath, Phys. B Condens. Matter 527 (2017) 35–43.
- [38] G. Jagannath, B. Eraiah, K. NagaKrishnakanth, S. Venugopal Rao, J. Non-Cryst. Solids 482 (2018) 160–169.
- [39] G. Upender, S. Ramesh, M. Prasad, V.G. Sathe, V.C. Mouli, J. Alloys Compd. 504 (2010) 468–474.
- [40] Y.G. Choi, K.H. Kim, V.A. Chernov, J. Heo, J. Non-Cryst. Solids 259 (1999) 205–211.
- [41] P. Limkitjaroenporn, J. Kaewkhao, P. Limsuwan, W. Chewpraditkul, J. Phys. Chem. Solid. 72 (2011) 245–251.
- [42] E.I. Kamitsos, M.A. Karakassides, G.D. Chryssikos, J. Phys. Chem. 91 (1987) 1073–1079.
- [43] B.V.R. Chowdari, Z. Rong, Solid State Ionics 90 (1996) 151-160.
- [44] I. Khan, G. Rooh, R. Rajaramakrishna, N. Sirsittapokakun, H.J. Kim, J. Kaewkhao, K. Kirdsiri, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 210 (2019) 21–29.
 [45] E.I. Kamitsos, A.P. Patsis, M.A. Karakassides, G.D. Chryssikos, J. Non-Cryst. Solids
- [40] L. Kalinkov, A.F. Fatsis, M.A. Katakassides, G.D. Chryssikov, J. Hon-Cryst. Joints 126 (1990) 52–67.
 [46] I. Kashif, A. Abd El-Maboud, R. El-Said, E.M. Sakr, A.A. Soliman, J. Alloys Compd.
- [46] I. Kashir, A. Abd El-Maboud, R. El-Said, E.M. Sakr, A.A. Soliman, J. Alloys Compo 539 (2012) 124–128.
- [47] Y. Cheng, H. Xiao, W. Guo, W. Guo, Thermochim. Acta 444 (2006) 173-178.
- [48] Y.B. Saddeek, M.S. Gaafar, Mater. Chem. Phys. 115 (2009) 280-286.
- [49] Y.B. Saddeek, M.S. Gaafar, S.A. Bashier, J. Non-Cryst. Solids 356 (2010) 1089–1095.
- [50] Y. Cheng, H. Xiao, W. Guo, W. Guo, Ceram. Int. 33 (2007) 1341–1347.
- [51] D. Maniua, T. Iliescu, I. Ardelean, S. Cinta-Pinzaru, N. Tarcea, W. Kiefer, J. Mol. Struct. 651–653 (2003) 485–488.
- [52] B.N. Meera, A.K. Sood, N. Chandrabhas, J. Ramakrishna, J. Non-Cryst. Solids 126 (1990) 224–230.
- [53] H.A. Othman, A. Herrmann, D. Möncke, Int. J. Appl. Glass Sci. 10 (2019) 339–348.
 [54] B. Shanmugavelu, V.V.R.K. Kumar, R. Kuladeep, D.N. Rao, J. Appl. Phys. 114
- (2013).
- [55] W.L. Konijnendijk, J.M. Stevels, J. Non-Cryst. Solids 18 (1975) 307-331.
- [56] B.N. Meera, J. Ramakrishna, J. Non-Cryst. Solids 159 (1993) 1–21.
- [57] Z.Y. Yao, D. Möncke, E.I. Kamitsos, P. Houizot, F. Célarié, T. Rouxel, L. Wondraczek, J. Non-Cryst. Solids 435 (2016) 55–68.
- [58] M. Dogra, K.J. Singh, K. Kaur, V. Anand, P. Kaur, P. Singh, B.S. Bajwa, Radiat. Phys. Chem. 144 (2018) 171–179.
- [59] K. Chen, L. Fang, T. Zhang, S.P. Jiang, J. Mater. Chem. 2 (2014) 18655-18665.
- [60] E.I. Kamitsos, G.D. Chryssikos, J. Mol. Struct. 247 (1991) 1-16.
- [61] W.T. Carnall, P.R. Fields, K. Rajnak, J. Chem. Phys. 49 (1968) 4424-4442.
- [62] E.A. Davis, N.F. Mott, Philos. Mag. A 22 (1970) 903-922.
- [63] S. Balaji, P. Abdul Azeem, R.R. Reddy, Phys. B Condens. Matter 394 (2007) 62–68.
 [64] C.S. Dwaraka Viswanath, K. Venkata Krishnaiah, C.K. Jayasankar, Opt. Mater. 83 (2018) 348–355.
- [65] G. Jagannath, B. Eraiah, K. Jayanthi, S.R. Keshri, S. Som, G. Vinitha, A.G. Pramod, K.N. Krishnakanth, G. Devarajulu, S. Balaji, S. Venugopal Rao, K. Annapurna, S. Das, A.R. Allu, Phys. Chem. Chem. Phys. 22 (2020) 2019–2032.
- [66] I. Khan, G. Rooh, R. Rajaramakrishna, N. Sirsittipokakun, H.J. Kim, C. Wongdeeying, J. Kaewkhao, J. Lumin. 203 (2018) 515–524.
- [67] R. Rajaramakrishna, P. Nijapai, P. Kidkhunthod, H.J. Kim, J. Kaewkhao, Y. Ruangtaweep, J. Alloys Compd. 813 (2020) 151914.
- [68] K. Swapna, S. Mahamuda, A.S. Rao, T. Sasikala, P. Packiyaraj, L.R. Moorthy, G. V. Prakash, J. Lumin. 156 (2014) 80–86.
- [69] B.R. Judd, Phys. Rev. 127 (1962) 750-761.
- [70] G.S. Ofelt, J. Chem. Phys. 37 (1962) 511-520.
- [71] B.R. Judd, J. Math. Phys. 3 (1962) 557–563.
- [72] G.S. Ofelt, J. Chem. Phys. 38 (1963) 2171–2180.
- [73] C.B. Annapurna Devi, S. Mahamuda, K. Swapna, M. Venkateswarlu, A. Srinivasa Rao, G. Vijaya Prakash, Opt. Mater. 73 (2017) 260–267.
- [74] B.C. Jamalaiah, J.S. Kumar, A.M. Babu, L.R. Moorthy, J. Alloys Compd. 478 (2009) 63–67
- [75] S. Selvi, K. Marimuthu, N. Suriya Murthy, G. Muralidharan, J. Mol. Struct. 1119 (2016) 276–285.
- [76] C. Görller-Walrand, S. De Jaegere, Spectrochim. Acta 28 (1972) 257-268.
- [77] P. Paufler, Cryst. Res. Technol. 30 (1995), 926–926.
- [78] W.D. Wright, Trans. Opt. Soc. 30 (1929) 141.
- [79] R.J. Mortimer, T.S. Varley, Displays 32 (2011) 35-44.
- [80] S. Ravangvong, N. Chanthima, R. Rajaramakrishna, H.J. Kim, J. Kaewkhao, J. Lumin. 219 (2020) 116950.