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Research Article

Effect of heavy metal oxides on photoluminescence and spectroscopic attributes of ${\rm Eu}^{3+}$ activated borate glasses

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ABSTRACT

Influence of Heavy Metal Oxides (HMOs: PbO and Bi₂O₃) on structural and photoluminescence (PL) properties Eu^{3+} activated lanthanum borate glasses has been analyzed and discussed in thoroughly here. When the PbO is loaded more and more in the glass system, the luminesce intensity and lifetime values of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu^{3+} were improved for the excitation at 464 nm due to enhanced covalency of Eu-O bonds arose from the dual function of lead oxide in the structure of PbO varied glasses. The betterment in luminescence features are also attributed to the decrease of effective network phonon energy occurred because of the incorporation of lead oxide in the glass composition. On the other hand, the luminesce (emission intensity and lifetime values of 614 nm emission of Eu^{3+} under 464 nm excitation) results are completely upending as the Bi₂O₃ content increased gradually in the glass matrix. This reduction in luminescence properties are ascribed to the decrease of covalency of Eu-O and thus crystal field in the vicinity of Eu^{3+} site. The reduction of Covalent character of Eu-O is due to two facts, one being the newly generated NBOs owing to the generation of Bi₀O₀ linikages. The luminescence and spectroscopic attributes evidently reveal the lead varied borate glass hosts are more beneficial than Bi₂O₃ varied borate glass hosts for optoelectronic applications.

1. Introduction

For many photonic applications, including lasers, three–dimensional display systems, optical fibers, high–density optical storage, detectors and optical light guides, etc., glassy materials triggered with rare–earth (RE) ions have been investigated intensively for a long time by different

researchers across the globe [1,2]. The emission properties of numerous glasses activated with different RE ions have been extensively researched for the demonstration of vitreous materials for these applications. Due to the strong optical clarity, chemical, thermal and mechanical stability, low melting and processing temperatures [2], the borate–based glasses are of importance among the numerous glasses of

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being relevant interest. It is well established that the luminescence characteristics such as emission strength, quantum quality, emission cross section, spectral line width and life time are determined by the glass structure and its variance, the concentration and distribution of RE as an optically active ions in the glass system. These luminescence features are vital for choosing the RE doped glasses for the fabrications of display devices, solid state lasers and many other optoelectronic devices [3]. The borate glasses developed with a broad variety of compositions. Therefore, the borate glass hosts are an excellent option for REs doping. The different borate glass structural units such as BO₃ triangle and BO₄ tetrahedra also tend to boost the local crystal field around the RE³⁺ ions [4]. The borate glasses, however, possess high-energy phonons $(1300-1500 \text{ cm}^{-1})$ [2] that adversely affect the luminescence quantum performance of RE ions (results of non-radiative decay occurred because of multiphonic relaxation between the near-located energy level) and thus inhibit the functional usage of borate glasses in photonic and optoelectronic devise applications. In order to obtain the enhanced quantum photoluminescence (PL) yield of RE ions, the RE should be placed in a low phonononic energy structure which reduce the possibility of non-radiative transitions, resulting in high PL efficiency [5]. It has been well documented in literature that by incorporating heavy metal oxides (HMOs) such as Bi₂O₃, PbO, Sb₂O₃ CdO etc. into the glass compositions, the phonononic energy of the parent glass host can be minimized and thereby increase the optical and spectroscopic properties of activated RE glasses [6-9]. In addition, the presence of HMOs such as PbO and Bi₂O₃ in RE containing borate glasses resulted in an increase in RE-O covalence and revealed a rise in PL strength as a feature of HMOs, but consequently a decrease in higher concentrations. To this end, very few studies have a clear connection with the structure for observed active PL products at various HMO concentrations [7,10,11].

Of all the RE ions, the trivalent europium ions (Eu³⁺) are of considerable interest since the Eu³⁺ display efficient and bright red–orange emissions from both electric dipole and magnetic dipole transformations, sometimes with high quantum efficiency and thus useful in persistent spectral hole burning, optical storage components of high density and in many luminescent devices [11,12]. The electric dipole (ED) allowed the transition of Eu³⁺: ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ closely linked to local symmetry. For this reason, the relative PL strength ratio of transitions I₀₂/I₀₁ (often referred to as the asymmetry ratio, R) is commonly used to approximate the degree of non–center symmetry of the Eu³⁺ site in a host material since it depends on the symmetry of the ligand, covalence, and structural modifications that have occurred near the Eu³⁺ ion [13].

Due to the parity–forbidden existence of Eu^{3+} absorption, the absorption cross section of Eu^{3+} is usually very small in the ultra violet (UV) region, resulting in lower productivity emissions for UV light excitation and thus reducing their versatility in many industrial uses. One way to solve this issue is to raise the Eu^{3+} doping concentration in the host material, however this can trigger the concentration quenching of PL [11]. Varying the concentrations of glass modifiers and/or formers, is an alternate approach to overcome this issue effectively. To this end, very few studies are accessible in open literature [10,14,15] and structural differences have not been used by their authors to clarify the characteristics observed.

Basically, structures and consequently compositions determine the optical attributes in glasses. However, the dependence of the local structure on compositions and the structure effects on optical parameters are not well known, although they are significant in the configuration of the compositions of the glass and the tuning of the attributes of luminescence. Nevertheless, relatively few studies are accessible in which the structural effects on optical properties have been explored [7, 9,16–19]. What much of the local structure did was to speculate on the local structure of RE ions based on the theory of Judd–Ofelt (JO) or by studying the optical absorption and luminescence spectra [15,20,21] that are insufficient for a detailed comprehension of glass structures. In view of exploring the effect of glass compositions and their structure

modification by incorporating the HMOs for B₂O₃ on PL properties of Eu³⁺, series of glasses with composition (mol %) $10La_2O_2-xHMO-(89-x)B_2O_3-1Eu_2O_3$, (HMO = PbO and Bi₂O₃, $30 \le x \le 50$, insteps of 10 mol %) are prepared and PL properties are correlated with structural modifications occurred. The present investigation has been taken up in view of achieving the improved PL intensity of RE (here is Eu³⁺) ion through higher concentration of HMOs.

2. Experimental protocols

2.1. Synthesis of glass samples

Nominal composition line glasses (mol percent) 10La2O3•xHMO• $(89-x)B_2O_3 \bullet 1Eu_2O_3$ (30 < x < 50, x is insteps of 10 mol % and HMO = PbO, Bi₂O₃) were synthesized using a resistive furnace open to the atmosphere by melt-quenching technique in porcelain crucibles following the process mentioned elsewhere [22]. The prepared glasses are labelled as LPbxBEu and LBixBEu for the glasses containing PbO and Bi₂O₃ respectively, in which the x represent the concentration of PbO and Bi₂O₃ in corresponding compositions. The starting reagents La₂O₃ (purity 99.98%), PbO (purity >99.9%) Bi₂O₃ (purity 99.99%), H₃BO₃ (purity 99.98%), Eu₂O₃ (99.99%), all from SD Fine, were used without further purification. Depending on the composition, 15 gms of homogeneous mixtures of precursors were melted about 750-820 °C about 30-40 min and cooled rapidly by pouring the melts into a pre-heated brass molds (200 °C). The glass samples prepared were annealed at 450 °C for around 4 h to eliminate the residual stresses that existed during high temperature quenching.

2.2. Characterization

The glasses samples used in the current analysis were verified by subjecting the samples to X-Ray Diffraction (XRD) measurements for the amorphous nature. XRD profiles were registered using a Rigaku Ultima–IV X–Ray diffractometer with \pm 0.01 $^{\circ}$ resolution. Using the PerkinElmer Lambda-35 Ultra Violet-Visible (UV-Vis) spectrometer fitted with a deuterium lamp and halogen lamp to produce the light in 200-1100 nm wavelength range, the room temperature (RT) absorption spectra of all glass samples were obtained with a resolution of ± 1 nm. A PerkinElmer Spectrometer (Spectrum 1000) was utilized for recording the Fourier transform infrared (FTIR) transmission spectra of all prepared glasses in the 400–4000 cm⁻¹ range with a resolution of 4 cm–1, the KBr pellet technique was used to collect the FTIR spectral results of the samples. Using Yvon Fluorolog 3 spectrofluorimeter fitted with a 450 W Xenon flash lamp as the light source, PL excitation and emission spectrums were obtained. Using the same device under the Xe flash lamp under 464 nm excitation, lifetime tests were carried out by monitoring the emission wavelength at 614 nm.

3. Results and discussion

3.1. XRD results

The XRD profiles of glasses containing 30 and 50 mol % of HMOs (HMOs = PbO and Bi₂O₃) are presented in Fig. 1. The presence of broad halo between 25° and 45° and absence of distinct diffraction peaks suggest the amorphous nature of the samples.

3.2. Optical absorption properties

The UV–Vis linear absorption spectra for the LPbxBEu and LBixBEu glass series are illustrated in Fig. 2 (a) and (b) respectively. Examined glasses are optically translucent and show a transparency window for wavelengths greater than 500 nm. Fig. 2 shows the UV absorption edge red shifted with successive insertion of HMOs in the glass system. The incorporation of PbO from 30 to 50 mol % for B₂O₃ in the glass



Fig. 1. XRD features of investigated glasses.



Fig. 2. Linear optical absorption spectra of studied glasses: (a) LPbxBEu glasses, and (b) LBixBEu glasses.

composition shifts the band edge from ~ 429 nm–461 nm. While the addition of Bi₂O₃ shifts the band edge from ~451 nm–486 nm. In the prepared samples, as a result of the red shift in the UV absorption band tip, the darkening of the yellowish color tinge was found to rise with an increase in HMO content in the glass compositions. The existence of Pb²⁺ and Bi³⁺ in LPbxBEu and LBixBEu glasses respectively responsible for this red shift of the optical band edge and the identification of just only two absorption peaks attributable to $^{7}F_{0}\rightarrow^{5}L_{6}$ and $^{7}F_{0}\rightarrow^{5}D_{2}$ transitions of Eu³⁺ ions located at 393 nm and 464 nm respectively, as shown in Fig. 2 [23].

3.3. Structural elucidation by FTIR spectroscopy

The apprehension of the infrared (IR) spectra of the glasses under study would be helpful in analysing the influence of HMOs on the glass structure. Thus, the IR spectra of all the investigated glasses were recorded in the wave number range 400–4000 cm⁻¹ and are depicted in Fig. 3 (a) and (b) for PbO and Bi₂O₃ loaded glasses respectively.

3.3.1. FTIR spectra of lead containing borate glasses

From Fig. 3 (a) it can be seen that there are three major bands that are in harmony with those alluded to in Refs. [24-26] but of finer firmness that enables the numerous bands to be allocated. It is generally agreed that the band about 1200-1500 cm⁻¹ is attributed to the stretching vibration of trigonal B–O bonds of (BO3)3- groups found in various borate groups such as metaborate, pyroborate and orthoborates [24], whereas the band between 760 and 1100 cm^{-1} attributed to the stretching vibration of tetrahedral B-O bonds of (BO₄) groups [27]. The bending vibrations in the borate network of the B-O linkages culminated in the band about 690–700 cm⁻¹ [24]. The unstable band or the kink at 621 cm⁻¹ ascribed to the O–B–O bonds vibration of borate unit in bending configuration [28]. Upon the introduction of PbO, improvements in the glass framework could be accomplished by the creation of the structural groups of PbO4. The evolution of the PbO4 structural groups of PbO needed an additional oxygen atom or two independently bound oxygen ions [29]. The transition from [BO₃] to [BO₄] tetrahedra involves one oxygen atom that can be generated by sharing the structural units of the bridging oxygen atoms between BO₄ and PbO₄. The existence of positively charged structural faults in the PbO network is indicated by neutralization of the excess negative charge on BO₄ units. Therefore, as the PbO concentration rises in the composition, the region of the band observed at 1200–1500 cm⁻¹ decreases and the core shifts



Fig. 3. FTIR spectra of glasses used in the current study: **(a)** LPbxBEu glasses, and **(b)** LBixBEu glasses.

towards the low–wavenumber, as shown in Fig. 3 3 (a). This activity has been due to an improvement in both N_4 and the destruction of BO_3 into asymmetric BO_4 structural units associated with non–bridging oxygens (NBOs) [29]. This is synonymous with replacing weaker Pb–O bonds (low bond strength) rather than stronger B–O bonds (high bond strength).

[30]. Since the Pb^{2+} ions will inhabit the boron–oxygen voids, and when all voids in the glass network are filled, the "surplus" Pb^{2+} ions facilitate the depolymerization of the glass structure by creating independent structural groups of BO₄. The change of the band observed at 800–1100 cm–1 to lower wavenumbers, as seen in Fig. 3 (a) [29,31] was reflected by this depolymerisation. Nevertheless, it was understood that the rise in the concentration of PbO in the composition of the glass would be followed by an increase in the degree of ionic bonding in the glass, which would increase atomic anharmonic vibrations. Thus, through B-O-Pb bonding, lead oxide has been progressively added to the borate glass matrix. Since the Pb-O bonding stretching force constant is slightly lower than that of the B–O, the Pb–O–B stretching frequency in the glass matrix may appear to be lower [29,32]. From Fig. 3 (a), it can also be observed that when the PbO content in the glass composition is raised, the bands below 620 cm⁻¹ become sharp and high intensities that can be correlated with vibrations attributable to [PbO₄]²⁻ groups [28]. The band displayed a small change towards a

larger wavenumber at about 690–700 cm⁻¹ with a decreased band diameter to raise the concentration of PbO in the composition. The electrostatic field of the extremely polarizing Pb²⁺ ions might be the reason for this change towards greater wavenumber, which may help to raise the wave number of B–O–B bending vibration [32]. Overall, it can be inferred that as PbO is integrated into the glass framework for B₂O₃, the PbO modifies the glass structure by converting from the BO₃ to the BO₄ units. The PbO₄ classes preferentially bridge the groups of BO₃ rather than those of BO₄. The infrared band strength correlated with the BO₄ group is therefore rising.

3.3.2. FTIR spectra of bismuth containing borate glasses

The LBixBEu glass samples also displayed systematic improvements in the IR spectra as seen in Fig. 3 (b). At about $690-700 \text{ cm}^{-1}$, 760-1100 cm^{-1} and 1150–1500 cm^{-1} , the spectra reveals the existence of three major wide bands. On the other hand, the Bi₂O₃ containing glasses IR analysis shows a poor band extended from 500 to 600 cm^{-1} in the low frequency area, which is due to bending vibrations of Bi-O-Bi bonds in highly twisted octahedral BiO6 structures [33,34]. The keen observation of IR spectra indicates that the centers of the vibrational bands about $690-710 \text{ cm}^{-1}$ and $760-1100 \text{ cm}^{-1}$ have been moved to longer wavenumbers as the bismuth content rises in the glass matrix. Whereas the middle of the band was moved to a lower wavenumber with a decreased amplitude about 1150–1500 cm⁻¹ (or with reduced width). The electrostatic field of the extremely polarizing Bi³⁺ ions will introduce the change of the middle of the band about $690-710 \text{ cm}^{-1}$ to a greater wavenumber. The improvement in the concentration of Bi2O3 in the composition of the glass results in an increase in the intensity of the electron cloud across the oxygen of the [BO3] unit, thereby leading to an increase in the roll-torque of the B-O-B band and consequently contribute to the shift of the rolling vibration of the B-O-B band to a greater wavenumber [33,35]. It has been stated that the 760–1100 cm⁻¹ band center moved to a lower wavenumber suggests an improvement in NBOs, and a longer bond lengths in the structural units of BO₄. The middle of the same band, meanwhile, moved to a higher wavenumber, signalling a decrease in NBOs and a shortening of the bond lengths in BO_4 units [34]. The change from 760 to 1100 cm⁻¹ band to longer wavenumber was thus due to a decrease in NBOs and a shortening of bond lengths in BO₄ units. Nonetheless, in the BiO₃ pyramidal units, the band at 880 cm⁻¹ attributed to the symmetric vibrations of the Bi-O bond in stretching mode that can be superimposed on the stretching vibrations of the B–O bond from diborate groups of the BO₄ groups [36]. The change of the 760–1100 cm^{-1} band to the lower wavenumber further suggests that in the glass network BiO₃ units are declining. Consequently, only BiO₆ units in LBixBEu glasses are predicted to influence the borate structure. In addition, the change of the 1150-1500 cm⁻¹ band to the lower wavenumber with a rise in Bi₂O₃ content may be attributed to the assumption that the induction of highly polarizing Bi³⁺ ions results in the formation of the new Bi-O-B bridging bond in the glass network. As the Bi-O bond stretching force constant is slightly lower than that of the B–O, the Bi–O–B stretching frequency could also appear to be lower [33].

3.4. Photo-physical properties

The evaluation of excitation and emission properties of luminescent materials such as RE doped glasses are essential for demonstrating the glasses for optoelectronic and photonic applications. Thus, in current study, PL properties were carried–out on lead and bismuth varied samples. In order to formalise the optimal Eu_2O_3 concentration, we initially prepared the lead and bismuth containing glasses with different Eu_2O_3 concentrations and recorded the emission spectra under 464 nm excitation. The spectra showed, the Eu_3^{3+} emission intensity first increases and then decreases with elevating Eu_2O_3 content and presented the highest luminescence at the 1 mol % of Eu_2O_3 . Thus, 1 mol % Eu_2O_3 doping level is selected for understanding the efficacy of PbO and Bi_2O_3



Fig. 4. Room temperature PL excitation spectra of LPb30BEu and LBi30BEu glasses collected by monitoring the emission at 614 nm ($\lambda_{emi} = 614$ nm).

on PL attributes of Eu³⁺ ions. Fig. 4 shows the excitation spectra of LPb30BEu and LBi30BEu glasses. Typical excitation bands of Eu³⁺ ions were observed with unequal intensity in the recorded emission spectra monitored at 614 nm. It signifies excitation transitions of the Eu³⁺ ion is not equally probable/populated and it varies according to the selection rule. The band assignments were done by referring to the previous reports [22,37]. Among all, the peak positioned at 464 nm due to $^7F_0 \rightarrow ^5D_2$ transition has highest intensity and hence it was chosen as excitation wavelength for photo–emission studies.

Red emission from Eu³⁺-doped glasses are most appreciable for enhancement of colour rendering index for tri colour white light emitting diodes (WLEDs) as well as red colour solid state lasers. Even in present study the red emitting bands related to Eu³⁺ ion are observed in the PL emission spectra of glass samples under the excitation at blue light. Fig. 5 (a) and (b) are depicts the PL emission spectra of LPbxBEu and LBixBEu glasses respectively. The four emission bands with corresponding band assignments [38] are depicted in Fig. 5. The observed emission lines of Eu³⁺ ions are due to both magnetic and electronic dipole transitions of electrons. The emission line at 592 nm originated due to magnetic dipole transition between ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ states. While, the transition at 614 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) arise because of electric dipole transition [11,39]. According to $\Delta S = 0$, $\Delta L \leq 2$ and $\Delta J \leq 2$ quantum mechanical selection rule the intense electric dipole transitions are allowed. Emission intensity of the Eu³⁺ ion remarkably varied with HMO content in the glass system.

3.4.1. Photo-physical properties of lead containing borate glasses

In these glasses, the enhancement in the Eu³⁺ emission as the PbO concentration elevated from 30 to 50 mol % has been observed as evidenced from Fig. 5(a). To our experience, the RE–O bond covalency is a vital determinant that influences the emission decorum of luminescence RE ions. The electrons from oxygen ligands are likely to coordinate substantially with RE ions as the RE-O bond covalence is greater. Consequently, this contributes to a rise in the O^{2-} ligand crystal field around the site of RE ions and allows the strong separation of f-f transitions [7]. The deviation in the covalency of Eu–O bond occurred due to the addition of PbO for B₂O₃ in the glass matrix can be analysed by evaluating the Judd–Ofelt (JO) [40,41] intensity variables Ω_t (t = 2, 4) via JO theory. Normally, if the Ω_2 is larger in magnitude, which means that both the RE-O bond covalence and the asymmetric habitat around the RE ion sites are stronger because the JO factor Ω_2 is heavily contingent on the atmosphere around the RE ions [42]. As seen in Table 1, the magnitude of Ω_2 steadily increased with the rise in the concentration of PbO in the glass framework, the increase in covalence



Fig. 5. Room temperature PL emission spectra of LPbxBEu (a) and LBixBEu (b) glasses, collected under the excitation of 464 nm ($\lambda_{ex} = 464$ nm).

Table 1

Judd–Ofelt parameters Ω_2 & Ω_4 (\times $10^{-20})$ and R values of Eu_2O_3–doped glasses.

| Glass Code | Ω_2 | Ω_4 | R | References |
|------------|------------|------------|-------|--------------|
| LPb30BEu | 6.57 | 3.7 | 4.31 | Present work |
| LPb40BEu | 6.50 | 3.75 | 5.16 | Present work |
| LPb50BEu | 7.06 | 3.86 | 5.60 | Present work |
| LBi30BEu | 6.48 | 3.31 | 5.14 | Present work |
| LBi40BEu | 3.34 | 2.86 | 2.88 | Present work |
| LBi50BEu | 3.18 | 2.81 | 2.52 | Present work |
| LGBiBEu40 | 2.334 | 3.434 | 3.07 | [51] |
| LPbABE3 | 2.04 | 0.15 | 2.024 | [52] |
| BBFBEu1 | 6.69 | 4.82 | 3.60 | [53] |
| TBLFE | 3.64 | 0.39 | 1.08 | [54] |
| BTPAE | 3.53 | 5.54 | 1.08 | [4] |
| ZnAlBiB | 2.19 | 1.49 | 2.66 | [58] |
| ZNBBE | 5.14 | 4.17 | 3.98 | [37] |
| LBTAF | 4.71 | 0.48 | 4.77 | [59] |
| LBTPE | 3.12 | 0.08 | 1.44 | [57] |

of Eu–O bond as the PbO content raised in the glass system is probable reason for enhancement of Ω_2 . This allows the PL emission rate to rise by rising the percentage of PbO mol in the glass matrix. To further validate this, the relative intensity ratio (R) values have been evaluated using the procedure mentioned in the references [38,43]. The R values are demonstrated increasing trend from 4.31 to 5.60 as the PbO concentration raised from 30 to 50 mol %, which further confirms the improvement in the Eu-O bond covalency and asymmetry around the $^+$ site. This results in the increase of crystal field of the O^{2-} around En³ Eu^{3+} site, causes an increase of stark splitting of *f*-*f* transitions and hence triggering the PL emission intensity to greater extent as PbO loaded in the glass composition. It has been highlighted that, for small concentration of PbO, Pb was found to probe the glass system as a network modifier with the creation of non-bridging oxygens (NBOs). Whereas, for higher content the PbO it engages with the dual roles such as the glass former as well as structure modifier [44]. The FTIR spectra of PbO containing glasses showed that different types of borates groups such as pyroborate, metaborate groups coexist. Therefore, in the meta-borate compositional range the PbO engage as a structure changer (glass modifier) while in the pyro-borate groups, PbO participates in the glass network as a glass former. The dual function of PbO is attributed to the bonding properties between the ions of Pb^{2+} and O^{2-} . Pb is octahedrally organized and Pb–O is ionic when PbO serves as the network modifier. Whereas, when PbO behaves as glass former, the structural units of PbO₄ are formed in the system and Pb-O is covalent [45]. The covalent structure of PbO is possibly attributed to the excellent association with the strongly polarizable O^{2-} ions of freely polarizable valence shells of Pb²⁺ ions. It is understood that the strength ratio of R decreases with increased PbO content in the glass host when PbO is engaged as a glass modifier, owing to decreased covalence and asymmetry of the local atmosphere around the Eu³⁺ ions. Nevertheless, when PbO behaves as a glass former, due to enhanced covalent bonding between the Eu³⁺ ions and the surrounding ligands, factor R increases with increasing PbO content. The spectral findings of the FTIR indicated that the PbO serves a dual function as a network modifier as well as the network former and showed an improvement in the former role of the network with an increase in PbO content contributing to increased covalence of Eu-O and asymmetry across the Eu³⁺ site and hence an increase in the PL emission strength of Eu³⁺ ions in the glass system. Therefore, owing to the reduced phononic energy glass host, the enhanced optical properties for Eu^{3+} were obtained with the replacement of PbO for B₂O₃ in the glass device.

Furthermore, it is well known that, incorporation of HMO reduces the phononic energy of the glass host. Therefore, the effect of PbO on phonon energy of the glass host cannot be ruled out. According to Jayasankar et al. [46] the luminescence lifetimes of RE ions are strongly contingent on the phononic energy of the glass host. In fact, the multi–phononic approach relies exponentially on the phononic energy [7], therefore, the lower phonic energy of the glass matrix allows more phonons to cross the energy difference between the 5D_0 and next lower lying $^7F_{1-6}$ states of Eu $^{3+}$, as the separation between the 5D_0 state and the next lower lying 7F_6 state of Eu $^{3+}$ is $\Delta E = 12,500$ cm $^{-1}$ [46]. Consequently, the chance of non–radiative transfer decreases, resulting in an increase in lifetime values of the 5D_0 state of Eu $^{3+}$ and an increase in the emission of Eu $^{3+}$ as seen in Fig. 6 (a). Therefore, the improved optical properties have been attained for Eu $^{3+}$ with substitution of PbO for B₂O₃ in the glass system due to the decreased phononic energy of the glass host.

3.4.2. Photo-physical properties of bismuth containing borate glasses

In LBixBEu glasses, the PL emission intensity is reduced as Bi_2O_3 increased from 30 to 50 mol % in the glass composition as evidenced from Fig. 5(b). Further, the measured lifetime values of ${}^{5}D_0$ state of Eu³⁺ are also followed same trend (decreased as the function of Bi_2O_3 content) as evidenced in Fig. 6 (b). This decrease in emission and decay properties is attributed to the change of glass structure occurred due to the incorporation of Bi_2O_3 for B_2O_3 . The FTIR spectral results are showed that the glass network has a great change toward depolymerization as the concentration of Bi_2O_3 increased in the glass composition. As the concentration of Bi_2O_3 improved in the glass matrix, the FTIR spectral findings indicate that the glass network has a significant shift



Fig. 6. Decay profiles for the 614 nm emission at the excitation of 464 nm fitted to single exponential function: (a) LPbxBEu glasses, and (b) LBix-BEu glasses.

towards depolymerization. RE ions are liable to form the cluster in the loose glass network according to the network topology condition, which will improve the cross relaxation rates between RE ions [7]. Therefore, due to the depolymerization of glass structure, the emission intensity and measured decay lifetime values of ⁵D₀ state Eu³⁺ present an obvious reduce trend. Thus, the optical properties of Eu^{3+} with the insertion of Bi₂O₃ for B₂O₃ are reduced. Nevertheless, it was well known that the covalency of RE-O and ligand field around the RE strongly influences the PL emission and lifetime values. To validate this, the JO intensity factor Ω_2 was estimated and the values demonstrated decrement trend as the Bi_2O_3 content elevated from 30 to 50 mol %. This result means that, the covalency of Eu-O decreases thereby the reduces the crystal field of the O²⁻ around Eu³⁺ site which results in decrease of PL emission and lifetime values of ${}^{5}D_{0}$ state of Eu³⁺. This might be due to the fact that, the NBOs are generated as the more and more Bi₂O₃ loaded in the glass system. Further, the FTIR spectral analysis revealed that, the BiO₆ structural groups are forming at higher concentration of Bi₂O₃. This result means that the generated NBOs are utilised in the formation of BiO₆ network units, and B–O–Bi and Bi–O–Bi bonds thereby the covalency of Eu-O decreased as the Bi2O3 content increased in the glass matrix. In order to ascertain further, the R values are demonstrated

decreasing trend from 5.14 to 2.52 as the Bi₂O₃ content increased from 30 to 50 mol %. This decrement trend of R values as a function of Bi₂O₃ content further confirm the decrease in the covalency of Eu–O bond and asymmetry around the Eu³⁺ site. In lead varied glasses the R values showed increase trend with increase in PbO content while in bismuth varied glasses the R values demonstrated reduced trend as the function of Bi₂O₃. At initial concentrations of HMOs (30 mol %) the R value is greater for Bi₂O₃ containing glass compared to PbO containing glass which means that the Eu–O bond covalency and asymmetry around the Eu³⁺ site is greater in Bi₂O₃ containing glasses than lead comprising glasses. Whereas at higher concentrations (at 50 mol %) the R value is greater for PbO containing glass compared to Bi₂O₃ containing glass which means that the Eu–O bond covalency and asymmetry around the Eu³⁺ site is greater in Bi₂O₃ containing glass compared to Bi₂O₃ containing glass which means that the Eu–O bond covalency and asymmetry around the Eu³⁺ site is greater in PbO containing glass compared to Bi₂O₃ containing glass which means that the Eu–O bond covalency and asymmetry around the Eu³⁺ site is greater in PbO containing glasses than Bi₂O₃ comprising glasses.

The decrease in Ω_2 and R values with respect to Bi_2O_3 may also be attributed to the fact that the LBixBEu glasses have a lower electrostatic attraction between Bi^+ and anion (O^{2-}) relative to the B^+ and O^{2-} anions as incorporating Bi_2O_3 for B_2O_3 in the systems, resulting in a lower magnitude of Ω_2 factor [2]. Furthermore, Bi^{3+} (117 pm) (for Bi^{5+} , 90 pm) is greater in size than B^{3+} (41 pm) [47] and raises the average Eu–O bond distance. A weaker field around Eu $^{3+}$ ions is created by such an increase in bond lengths. This may contribute to a lower value of Ω_2 [2] in the glass–containing bismuth and hence a decrease in the intensity of PL emission strength and therefore a lifetime of 5D_0 state of trivalent europium. The decrease in PL emission intensity is also due to the undesirable absorption of excitation energy by host with the more red shift of UV band edge as Bi_2O_3 content elevated from 30 to 50 mol % as described below.

However, the dual role of Bi₂O₃ cannot be ruled out completely since the Bi₂O₃ is also well known glass former and modifier as well similar to PbO. Therefore, the decrease of covalency of Eu–O with respect to Bi₂O₃ content is not alone the possible reason. The other plausible reason for decrease of luminesce intensity of Eu³⁺ ions is as follows; Basically, the Bi³⁺ ion possess the 6s² electronic configuration with the ground state ¹S₀ and four excited states ³P₀, ³P₁, ³P₂ and ¹P₁ as shown in the energy level diagram of Bi³⁺ provided in Fig. 7. The existence of absorption bands of Bi³⁺ greatly depends on the matrix of the host. Two absorption bands which belong to the ¹S₀→³P₁ and ¹P₁ transitions have been

recorded in several hosts. The later band is in the high–energy UV field, which tends to be comparatively lower in energy [48] than the former [48]. Due to its potential overlap with the fundamental absorption edge of the glass hosts, no Bi³⁺ bands have been found in the ongoing inquiry. As shown in Fig. 7 the energy levels of Bi³⁺ are very close to that of Eu³⁺ ions. Also, with respect to Bi₂O₃ concentration the optical band gap values showed decrease trend, hence the host absorption in the UV–Vis region is masking the Eu³⁺ energy levels which are extended to localized conduction band in the Bi₂O₃ comprising glasses. Because of this host abortion no efficient pumping is happening to Eu³⁺ ions in Bi₂O₃ containing glasses thereby the luminescence intensity and hence spectroscopic properties are weakened in the Bi₂O₃ containing glasses.

The calculated JO parameters of trivalent europium activated PbO and Bi₂O₃ framed glasses and recently reported other heavy metal borate glasses are shown in Table 1. The evaluation of radiative features of the glass signifies the potentiality of the lasing transition among emission peaks. Moreover, it helps in quantification of qualitative emission peaks of RE including Eu³⁺ ion. The vital factors such as total transition probability, branching ratio, radiative lifetime and stimulated cross-section of the glass samples are calculated and tabulated in Table 2. In comparison with the intensity of the emission peaks, intense ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition gained larger radiative values among other transitions. For the same transition, branching ratio crossed more than 50% suggests it can be tuned for lasing action. The stimulated emission cross-section along with total transition probability values of all transitions are listed in Table 2 and it is high for transition peaked at 614 nm. The parameters for PbO based glass increased and decreased for bismuth containing glasses. Among synthesised glasses, LPb50BEu glass is usable for red lighting applications.

In literature, there are very few reports dedicated in studying the impact of HMOs on PL properties of RE ions. Among them, Srivastava et al. [49] have observed the changes in luminescence attributes of Dy^{3+} ions in borate glasses with addition of PbO (15–40 mol %) in the glass composition. They have observed enhancement of PL emission strength with the changes of glass network into BO₄ groups due to glass modifier role of PbO in the glass network. However, excess addition of PbO (50–60 mol %) quenched the luminescence strength due to disappearance of BO₄ group around the vicinity of Eu³⁺ ions. Udaya Kumar et al. [50] have studied the effect of Bi₂O₃ on luminescence features of Sm₂O₃



Fig. 7. Partial energy level diagrams of Bi³⁺ and Eu³⁺ in glasses showing the different transitions at 464 nm excitation.

Table 2

| | 000 0000000 (0 3E 00 - 0 | | | 0, 8 | se | | -F 9 |
|------------------------------------|--|----------|----------|----------|----------|----------|----------|
| Transitions $^5D_0\!\!\rightarrow$ | Parameters | LPb30BEu | LPb40BEu | LPb50BEu | LBi30BEu | LBi40BEu | LBi50BEu |
| | λ_p | 592 | 592 | 592 | 592 | 592 | 592 |
| ⁷ F ₁ | $\Delta \lambda_p$ | 10.5 | 11 | 11 | 11 | 12 | 12.2 |
| | A | 75.1 | 75.11 | 75.11 | 75.11 | 75.11 | 75.11 |
| | σ_{se} | 3.22 | 3.22 | 3.22 | 3.22 | 3.22 | 3.22 |
| | β_R | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 | 0.12 |
| | $\sigma_{se} 	imes \Delta \Lambda_{p}$ | 3.38 | 3.54 | 3.54 | 3.54 | 3.54 | 3.54 |
| | λ_p | 612 | 612 | 612 | 612 | 612 | 612 |
| | $\Delta \lambda_p$ | 13.4 | 13.8 | 13.8 | 12.2 | 12.3 | 12.3 |
| ⁷ F ₂ | Α | 389 | 385 | 418 | 383 | 215 | 188 |
| | σ_{se} | 16.1 | 15.9 | 16.8 | 15.4 | 9.4 | 8.51 |
| | β_R | 0.68 | 0.68 | 0.70 | 0.68 | 0.59 | 0.55 |
| | $\sigma_{se} 	imes \Delta \Lambda_{p}$ | 21.57 | 21.94 | 23.18 | 18.78 | 11.56 | 10.26 |
| | λ_p | 701 | 701 | 701 | 701 | 701 | 701 |
| | $\Delta \lambda_p$ | 11 | 11.2 | 11.2 | 11 | 11.1 | 11.15 |
| ⁷ F ₄ | Α | 104 | 106 | 102 | 93 | 80 | 73 |
| | σ_{se} | 9.1 | 9.16 | 8.75 | 8.13 | 7.04 | 6.91 |
| | β_R | 0.18 | 0.18 | 0.17 | 0.16 | 0.19 | 0.21 |
| | $\sigma_{se} 	imes \Delta \Lambda_{p}$ | 10.01 | 10.25 | 9.8 | 8.94 | 7.81 | 7.70 |
| | A_T | 565 | 566 | 593 | 550 | 369 | 340 |

Emission peak wavelength (Λ_p , nm), effective bandwidth ($\Delta \Lambda_p$, nm), Radiative transition probabilities (A, s^{-1}), Total radiative transition probabilities (A_r , s^{-1}), stimulated emission cross section ($\sigma_{cr} \times 10^{-22} \text{ cm}^2$), experimental branching ratios (β_p), gain band width ($\sigma_{cr} \times \Delta \Lambda_p$) ($\times 10^{-28} \text{ cm}^3$) of the Eu₂O₂-doped glasses.

Table 3

Measured and calculated lifetime values of Eu^{3+} doped PbO and $\mathrm{Bi}_2\mathrm{O}_3$ comprised glasses.

| Sample Code | Calculated Lifetime (ms) | Measured Lifetime (ms) | Reference |
|-------------|-----------------------------|---------------------------|--------------|
| LPb30BEu | 1.76 | 1.22 | Present work |
| LPb40BEu | 1.76 | 1.29 | Present work |
| LPb50BEu | 1.68 | 1.31 | Present work |
| LBi30BEu | 1.81 | 1.06 | Present work |
| LBi40BEu | 2.71 | 0.92 | Present work |
| LBi50BEu | 2.94 | 0.88 | Present work |
| LGBiBEu40 | 2.28 | 1.50 | [51] |
| LPbABE3 | 4.23 | 2.46 | [52] |
| BBFBEu1 | 3.15 | 1.72 | [53] |
| TBLFE | 3.5 | 1.13 | [54] |
| B1-0.5Eu | 1.72 | 1.69 | [9] |
| BBCE1 | 1.62 | 0.81 | [55] |
| SLABSE1 | - | 1.57 | [60] |
| ZBBE1 | - | 1.03 | [56] |
| LBTPE1 | - | 1.37 | [57] |
| PbPGE1 | | 1.70 | [45] |

ions activated in borate glasses. The increment of Bi_2O_3 increased the symmetry around Sm^{3+} ions as well as covalency between Sm^{3+} to O^{2-} ions. This change resulted in decrement of emission intensity of Sm^{3+} ions in bismuth concentrated glasses. Further, Atul et al. [48] have doped the Bi^{3+} (0.1–2 mol %) ions into Eu^{3+} doped borate glasses. At low level doping of Bi^{3+} (0.1–1 mol %) ions in glass network enhanced the PL intensity of Eu^{3+} ions. At 346 nm excitation, Bi^{3+} ion successively transferred its energy to Eu^{3+} ions and thereby emission intensity of the glass increased. But when doping level of Bi^{3+} ions reached more than 1 mol% PL intensity got saturated due to energy transfer among the Bi^{3+} ions rather than Bi^{3+} to Eu^{3+} .

Time resolved luminescence characterization of the RE doped glass is gives out the radiative and non-radiative decay rates of excited rare earth ion. This measurement calculates the lifetime of excited metastable state of RE ions. The pulsed mode of light has been used to excite the Eu^{3+} ion and after, the number of decayed photon (light) were measured to obtain the decay curve. The excited Eu^{3+} ion loses its excited energy via multiphonon relaxation and majorly through non-radiative relaxation processes. This type of relaxation prominent in high phonon energy glass matrix and results in more phonons than photons during de-excitation. In this case, energy gap of the transition states of RE ions easily bridges by the phonons of the host matrix glass.

In the current analysis, an excitation pulse of 464 nm was used to excite the Eu³⁺ from $^7F_0 \rightarrow ^5D_2$ state. The relaxation of Eu³⁺ ions from $^5D_2 \rightarrow ^5D_0$ lower state by low level lattice vibration is caused by the multiphonon relaxation mechanism and is shown in Fig. 7.

Later, the electrical transition between 5D_0 to lower ${}^7F_{1,2,3,4}$ states results in the emission of light at various wavelengths with prominent emission of red light as evident from emission spectra. The lifetime of Eu^{3+} ion is time taken for reduction of number of electrons to 1/e times after excitation at 5D_0 meta state. The recorded decay curves of Eu^{3+} ion in PbO and Bi_2O_3 containing glasses are shown in Fig. 6 (a) and (b) respectively. The single exponential decay function has been fitted to decay curves for determination of lifetime.

The experimental lifetime values of the lead borate and bismuth borate glasses are shown in Table 3 with other Eu³⁺ doped LGBi-BEu40:50Li₂O-15Gd₂O₃-5Bi₂O₃-29B₂O₃-1Eu₂O₃ [51], LPbABE3:10-Li₂O-10PbO-7Al₂O₃-70B₂O₃-3Eu₂O₃ [52], BBFBEu1:69B₂O₃-5Bi₂O₃-10 BaCO₃-7.5CaF₂-7.5ZnO-1Eu₂O₃ [53], TBLFE:29TeO₂-30B2O₃-20PbO-20PbF₂-1Eu₂O₃ [54], B10.5Eu:49.5B₂O₃-40PbO-10PbF₂-0.5EuF₃ [9], BBCE1:42B₂O₃-49Bi₂O₃-8CaO-1Eu₂O₃ [55], SLABSE1: 20SrO-19 La₂O₃-10 Al₂O₃-40 B₂O₃-10 SiO₂-1Eu₂O₃ [11], ZBBE1:59-B₂O₃-30Bi₂O₃-10ZnO-1Eu₂O₃ [56], LBTPE:30B₂O₃-19PbO-15TeO₂-10P₂O₅-10ZnO-15BaO-Eu₂O₃ [57] and PbPGE1:45PbO-45P₂O₅-9Ga₂O₃-1Eu₂O₃ [45] glasses. The lifetime of the Eu³⁺ ion is comparatively more for PbO containing glasses than bismuth containing ones. The higher measured lifetime of the prepared LPb50BEu glass suggest that, the required necessary population inversion can be easily achieved for lasing action of 5D0 \rightarrow ⁷F₂ transition at 614 nm in LPb50BEu glass.

4. Conclusion

Series of glasses with varied concentration of HMOs (PbO and Bi₂O₃) were prepared through the melt–quench process. Influence of HMOs on PL properties has been evaluated and discussed in detail. In lead containing glasses, both the PL emission intensity and lifetime values of ${}^{5}D_{0}$ state of Eu^{3+} showed increase trend as a function of PbO content. These improvements are attributed to enhancement in covalency of Eu–O bonds caused due to dual role of PbO in the glass network. The improvement in properties are also attributed to decrease of maximal phonon energy resulted due to incorporation of PbO for B₂O₃ in the glass composition. While, the bismuth containing glasses demonstrated a decreased PL emission intensity along with lifetime values. This reduction in PL properties are ascribed to the decrease of covalency of Eu–O

and crystal filed around the Eu³⁺ site. The decrease in covalency is probably owing to the fact that, the newly generated NBOs due to the incorporation Bi₂O₃ in the glass matrix utilised in the formation of BiO₆ structural groups and Bi–O–Bi and Bi–O–B bonds. The PL, lifetime and radiative features evidently reveal that the PbO containing glasses are more advantage over Bi₂O₃ comprising glasses. In particular the glasses comprising 50 mol % of PbO are beneficial for the fabrication of lighting and electro–optic devices.

Credit author statement

P. Ramesh: Carried the materials synthesis, characterization and drafted the manuscript, Jagannath Gangareddy: Supervised the whole research and involved in drafting, K.N. Sathish: Contributed to concept discussion and editing, A.G. Pramod: Recorded the XRD and the absorption profiles, and did the formal analysis of PL data, Vinod Hegde: Contributed to the JO parameters calculations and involved in drafting, U. Mahaboob Pasha: Contributed to concept discussion and editing, Sultan Khan: Helped in collecting the PL spectra and analysis, K. Annapurna: Contributed to concept discussion and editing, M.I. Sayyed: Contributed to concept discussion and editing, M.I. Sayyed: Contributed to concept discussion and editing, A.G. Pramot: Contributed to FTIR spectral measurements and editing, and M.K. Kokila: Supervised the whole research and involved in review.

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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