Eu$^{3+}$ ions doped SrO-CaO-Li$_2$O.B$_2$O$_3$ glasses for optical display material application

A.R. Venugopal$^{a,*}$, J. Kaewkhao$^{b,c,**}$, Abhiram J $^b$, Rajashekara K M $^a$, R. Rajaramakrishna$^{b,c,*}$, N. G. Pramod$^b$, Chethan Rao $^d$

$^a$ Department of Physics, B.G.S R&D Centre, SJC Institute of Technology, Chikkaballapur, Karnataka, India
$^b$ Department of PG studies and research in physics, The National College, Jayanagar, Bangalore - 560070
$^c$ Center of Excellence in Glass Technology and Materials Science (CEGM), Nakhon Pathom Rajabhat University, Nakhon Pathom,73000, Thailand
$^d$ Department of Physics, SDM Institute of Technology, Belathangady, Ujire, Karnataka, India - 574240

*-Department of Physics, Brindavan College of Engineering, Bangalore, 560063, India

corresponding email: *r.rajaramakrishna@gmail.com, **mink110@hotmail.com

Abstract. The glass systems with composition 20SrO-5CaO-40Li$_2$O-(35-x) B$_2$O$_3$-x Eu$_2$O$_3$ (x = 0.3, 0.5 and 1 mol%) glasses were prepared by melt quenching technique to study absorption and luminescence properties and understand their lasing properties. The present work reports the studies on Physical, Optical and luminescence properties of the prepared glass systems. The photoluminescence (PL) intensity of the glass increases with increase in Eu$_2$O$_3$ content up to 1mol%. The increase in the density and decrease in molar volume reveals the close packing of glass network. For Eu$^{3+}$ emission the most intense red emission has been observed at the wavelength of 614 nm for the transitions $^5D_0 \rightarrow ^7F_2$. The phonon energy was measured from phonon side band spectra which showed 1280 cm$^{-1}$, typical value for the borate glasses. Luminescence intensity ratio and lifetime analysis has been measured and discussed in the present work. The present glasses are very near to reddish orange region and thus can be key entrant for optical display device applications.

1. Introduction

Borate glasses with suitable modifiers of alkali/alkali earth elements exhibits are good optical properties more ever these glasses doped with RE ions possess high transparency, low melting point, good thermal stability, and very good RE ion solubility [1]. The glass network of are composed of BO$_3$ triangles and BO$_4$ tetrahedral, which lead to the formation of the diborate, triborate, tetraborate, etc., with other co-present modifier oxides, this result in the formation of three-dimensional glass networks. Hence, the optical properties of the borate glasses could be modified with addition of glass modifier networks elements [2]. Borate glasses with common alkali (Li, Na and K) have nearly identical spectra with RE$^{3+}$ elements over the entire glass forming region [3]. Addition of alkaline-earth oxide element CaO into the glass matrix is expected to improve the resistance of the glasses to the moisture. The Li$^{2+}$ ions can occupy in glass network interstitial sites, and can alter the oxygen packing factor [4].
Li$_2$O is a modifier in B$_2$O$_3$ and is a good vacancy creator and forms a good borate network system by conversion of sp2 planar BO$_3$ groups to more stable sp3 tetrahedral BO$_4$ groups, which leads to formation of non-bridging oxygens [5]. The glasses are doped with several transition elements, so their optical and structural properties can be tailored [6]. The alkaline earth metal Sr$^{3+}$ modifies the borate glass network. Since, its ionic radii is very close to the lanthanide ions, as a result glass forming ability increases with good physical characteristics with increase in luminescence intensity [7, 8, 9].

The present work focused on NIR light emitting Eu$^{3+}$ doped glasses for the solid-state lasing material. In this work, the structural and fluorescence properties of 0.3, 0.5 and 1 mol% Eu$^{2+}$ doped quaternary glasses 20SrO-5CaO-40Li$_2$O-(35-x) B$_2$O$_3$-x Eu$_2$O$_3$ (x = 0.3, 0.5 and 1 mol%) have been studied and reported.

2. Experimental

2.1. Preparation of glass Samples

Glasses with composition (mol%) of 20SrO-5CaO-40Li$_2$O-(35-x) B$_2$O$_3$-x Eu$_2$O$_3$ (x = 0.3, 0.5 and 1 mol%) are prepared using conventional melt quenching method using porcelain crucibles in air at 1100 °C for 2 hours in muffle furnace. The melts were poured onto preheated polished thick brass block for required dimensions approximately 0.5cm thickness glasses. The obtained glass samples were optically transparent. The prepared glasses samples are polished and grinded into fine powder for further characterization. The chemical composition details and identity names are listed in Table 1.

| Code | Li$_2$O | SrO | B$_2$O$_3$ | CaO | Eu$_2$O$_3$ |
|------|--------|-----|-----------|-----|------------|
| 5T-3 | 40     | 20  | 34.7      | 5   | 0.3        |
| 5T-5 | 40     | 20  | 34.5      | 5   | 0.5        |
| 5T-10| 40     | 20  | 34        | 5   | 1          |

2.2. Measurement techniques

To investigate the physical properties, the density of the samples was measured by Archimedes principle using digital balance, both in water and air. The UV-VIS-NIR absorption spectra is performed in the wavelength range 400-2400nm on polished glass samples using Shimadzu, UV-3600 spectrophotometer. The Photoluminescence excitation or emission spectra of the glasses and life time measurements were obtained using fluorescence spectrophotometer (Agilent Technologies, Cary Eclipse) with xenon lamp as a light source.

3. Results and discussions

3.1 Physical Properties

The Physical properties are studied; all the measurements are made at room temperature such as density ($\rho$) obtained by Archimedes method with toluene as the immersing liquid using Equation (1) [10]. The molar volume ($V_m$) is calculated using Equation (2) [11], and are listed in the Table. 2.

$$\rho (\text{gm/cm}^3) = \frac{W_a}{W_a - W_L} \times (\rho_L) \quad \text{(1)}$$

Where $W_a$ is the glass sample weight in air, $W_L$ is glass sample weight in water and $\rho_L$ is the density of immersion liquid i.e., toluene (0.867 gm/cm$^3$).

$$V_m (\text{cm}^3/\text{mol}) = \frac{M}{\rho} \quad \text{(2)}$$

Where M is the total molar weight and $\rho$ is the density of the glass sample. It is observed that the density $\rho$ increases linearly with increase in Eu$_2$O$_3$ content and decreases molar volume
simultaneously. Such trend is observed because of increase in its compactness in the structure making the glass more rigid structure. The increase in the density is due to heavier molecular weight (351.92 g/mol) of Eu$_2$O$_3$ is replaced by lower molecular weight (69.63 g/mol) of B$_2$O$_3$. In this case, the increase in the Eu$^{3+}$ ions must have created more bridging oxygens (BOs) due to which more tetrahedral BO$_4$ units produced in the matrix than trigonal BO$_3$ units. Furthermore, Eu$^{3+}$ ions caused BO$_4$ triangles have been converted into tetrahedral BO$_3$ units and acted as 'network modifier' by increasing the boron–oxygen coordination number. As the asymmetric BO$_4$ units are denser than symmetric BO$_3$ units, the glass structure is thus continuously compacted with progressive increase in Eu$^{3+}$ concentration and hence the molar volume decreases. Thus, the modifier ions have modified the structure, thereby changing the physical/optical properties. The Eu$^{3+}$ ion concentration N in the prepared glasses is calculated using Equation (3).

$$N \text{ (ions/cm}^3) = \frac{x \rho N_A}{M}$$

Where x is the molar fraction of the RE oxide present in glass matrix, N$_A$ is the Avogadro’s number. The Physical properties such as, inter ionic distance, r$_i$ (Å), and Polaron radius, r$_p$ (Å) are determined using the following equations listed below [14,15,16].

$$\text{Inter ionic distance } r_i(\text{Å}) = 1 \frac{\sqrt{\pi}}{N}$$

$$\text{Polaron radius } r_p(\text{Å}) = 2 \frac{\sqrt{\pi}}{6N}$$

$$\text{Mean spacing } R(x) = 3 \sqrt{\frac{4\pi N}{3}}$$

The concentration (N) of Eu$^{3+}$ ions increase with increase in Eu$_2$O$_3$ content, hence their mean spacing (R), inter-ionic radius (r$_i$) and polaron radius (r$_p$) decreases due to congestion in their atomic separation. The polaron radius (r$_p$) is greater than the radius of the atom, on which the electron is localized, but less than the distance r, separating these sites. The decrease in the molar refraction ($R_m$) is accompanied by a decrease of molar polarizability ($\alpha_m$) was observed in the present glass.

**Table 2. Physical Properties of 20SrO-5CaO-40Li$_2$O-(35-x) B$_2$O$_3$-x Eu$_2$O$_3$ (x = 0.3, 0.5 and 1 mol%)**

| Physical Properties | 5T-3 | 5T-5 | 5T-10 |
|---------------------|------|------|-------|
| Density of sample (gm/cc) | 3.340 | 3.561 | 3.762 |
| Molar volume "Vm" (cm$^3$ mol$^{-1}$) | 22.808 | 21.599 | 20.902 |
| Eu$^{3+}$ Ion Concentration "N" (×10$^{21}$/cc) | 1.43 | 2.51 | 5.2 |
| Molar refractivity, $R_m$ (cm$^3$) | 60.062 | 56.858 | 55.042 |
| Molar polarizability, $\alpha_m$ (cm$^3$) | 2.38 | 2.26 | 2.18 |
| Inter ionic distance, r$_i$ (Å) | 10.9 | 9.08 | 7.14 |
| Polaron Radius, r$_p$ (Å) | 3.66 | 3.03 | 2.38 |
| Mean Spacing , R (Å) | 5.63 | 4.66 | 3.66 |

### 3.2. UV-VIS-NIR Spectra

Figure 1, shows the Optical absorption spectrum of 20SrO – 5CaO – 40 Li$_2$O – (35-x) B$_2$O$_3$ – x Eu$_2$O$_3$ (x = 0.3, 0.5 and 1 mol%) glasses were recorded in the wavelength range of 1600 nm to 2500nm at room temperature. From Fig. 1(a) four peaks are observed for Eu$^{3+}$ ions, corresponding from ground
state $^7F_0$ to excited states of 364 nm ($^7D_4$), 394 nm ($^7L_6$), 464 nm ($^7D_3$), 526 nm ($^7D_1$), and 2095 nm ($^7F_6$). Whereas other three peaks originate from $^7F_1$ states to 415 nm ($^7D_3$), 534 nm ($^7D_1$), and 2209 nm ($^7F_6$). The absorption peaks were obtained at each peak were similar at various concentration of Eu$_2$O$_3$ content in the glasses. The intensity of absorption peak observed to be increased and found maximum for the higher concentration of Eu$^{3+}$ ions (1 mol%) [10, 15].

![Figure 1](image1.png)

**Figure 1.** The absorption spectra of the 5T-3, 5T-5 and 5T-10 glasses. (a) UV-Vis region (b) NIR region

### 3.3. Photo-luminescence spectra

Photoluminescence excitation spectra were measured at 614 nm emission wavelength for 5T-3, 5T-5 and 5T-10 glasses respectively as presented in Fig. 2. All the excited peaks correspond from ground state $^7F_0$ to excited levels of 320 nm ($^5H_4$), 363 nm ($^5D_4$), 383 nm ($^5L_7$), 394 nm ($^5L_6$), 415 nm ($^5D_3$), 465 nm ($^5D_2$), 534 nm ($^5D_1$) respectively. It is also worth to note that these glasses show broad absorption peak corresponding to charge transfer band (CTB) around 228 nm in ultraviolet region, such existence of broad peak is due to ligand-to-metal charge transfer (LMCT) bands could be seen due to divalent cationic content (such as Sr$^{2+}$, Ca$^{2+}$, Eu$^{2+}$). They are very intense compared to f-f transitions, since the transitions are allowed by the Laporte selection rule which was first observed by Ryan and Jørgensen [16]. The photoluminescence emission spectra are recorded by exciting 394 nm of Eu$^{3+}$ ions and recording the spectra between the wavelength range of 550 to 750 nm as shown in the Fig. 3. These wavelengths are due to the transition of the Eu$^{3+}$ ion during the de-excitation process from the state excited lower state of $^5D_0$ to higher ground states of (579 nm) $^7F_0$, (590 nm) $^7F_1$, (614 nm) $^7F_2$, (652 nm) $^7F_3$, (701 nm) $^7F_4$ [17-19] respectively as presented in energy level diagram (Fig. 4). The intensity of the emission peak increases with increase in Eu$^{3+}$ concentration. The maximum emission intensity is observed at the wavelength 614 nm is due to transition of $^5D_0 \rightarrow ^7F_2$ [20, 21]. The non-existence of emission from the excited higher states of $^5D_1$, $^5D_2$, $^5D_3$, $^5D_4$ to $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ levels indicate the non-radiative transitions through multiphonon relaxation (MPR) process as displayed in Fig. 4. The energy level diagram of excitation and emission transitions of Eu$^{3+}$ doped 5T3, 5T5 and 5T10 glass matrix is shown in figure 5. When excited with 395 nm, Eu$^{3+}$ ions are excited from its ground state $^7F_0$ to the higher excited state $^7L_6$. The population of the $^7L_6$ level relaxes non-radiatively to the lower excited state of $^5D_2$, and successively decays to the lower states as $^5D_2 \rightarrow ^5D_1 \rightarrow ^5D_0$ through non-radiative relaxation process.
The luminescence excitation spectra of the Eu$^{3+}$ doped 20SrO – 5CaO – 40 Li$_2$O – 35 B$_2$O$_3$ glasses recorded on excitation with 613 nm in the spectral region 310–550 nm at room temperature have been shown in figure 04. The intensity of the peaks increases with the increase in Eu$^{3+}$ concentration and is large for 1 mol %. This is due to the multiphonon relaxation in the adjacent $^7$F$_1$ levels. There is a maximum energy transfer for the $^7$F$_0$ to $^5$L$_6$ energy state, this further results in the de-excitation of $^5$D$_0$ to $^7$F$_2$. Therefore the glass 5T-10 has been identified as a potential for lasing applications [22]. Due to limited range of experimental facilities, the $^5$D$_0$ → $^7$F$_6$ transition is believed to present in the IR region and could not be observed in the present case. The appearance of the faint narrow band in the emission spectra is due to the shielding effect of 4f$^6$ electrons by 5s and 5p electrons in the outer shells of the Eu$^{3+}$ ion.
3.4 Phonon Side Band (PSB) Spectra

Phonon sideband spectra of 5T-3, 5T-5 and 5T-10 glasses are presented in Fig. 5. The PSB spectra ranges between 420 − 480 nm corresponding to the $^7F_0$−$^5D_2$ transition (464 nm) of pure electronic band (PEB) and towards lower wavelength region corresponding to phonon side band. The centers of the one phonon lines located at about 438 nm and 428 nm associated to phonon energy of 1280 cm$^{-1}$ and 1813 cm$^{-1}$ respectively. The present glasses show phonon energy are well within around 1300 cm$^{-1}$ due to borate content.

3.5 Luminescence intensity ratio

Luminescence intensity ratio ($I_{R/O}$) is evaluated using electric dipole transition to the magnetic dipole transition ($I_{R/O}$) = $I(^{5}D_{0} \rightarrow ^{7}F_{2}) / I(^{5}D_{0} \rightarrow ^{7}F_{1})$, is asensitive function of the local asymmetry around the optically activedopant and the degree of covalent bonds. In present glasses luminescence intensity ratios ($I_{R/O}$) were calculated at 394 nm excitation and found to be 2.574, 2.588 and 1.417 for 5T-3, 5T-5
and 5T-10 glasses respectively. From the obtained data it is clear that the asymmetry around the active dopant (Eu$^{3+}$ ions) and its nature around it seems to more ionic in nature for 5T-10 glass than other concentration of Eu$_2$O$_3$ content.

3.6Lifetime analysis

The luminescence exponential decay curve obtained by at 394 nm excitation wavelength and 614 nm emission wavelength at room temperature for 5T-3, 5T-5 and 5T-10 as presented in Fig.6. The lifetime of the $^5\text{D}_0$ level for 0.3, 0.5 and 1 mol% are found to be as 2.82, 2.79 and 2.71 ms respectively. The lifetime values decrease with increase in Eu$_2$O$_3$ content.

![Figure 6.Lifetime decay graph of 5T-3, 5T-5 and 5T-10 glasses.](image)

4. Conclusion

The 5T-3, 5T-5 and 5T-10 glasses were synthesized by melt quenching technique. These glasses showed highest emission at 1.0 mol% Eu$_2$O$_3$. It is observed from the results of Eu$^{3+}$ doped glasses 5T-3, 5T-5 and 5T-10 yields an intense red emission for the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 614 nm when excited at 394 nm. These glasses show charge transfer band at ultra violet region. Non-existence of emission from $^5\text{D}_J$ (where $J = 1, 2, 3, 4$) to ground state is due to multiphonon relaxation process. The phonon energy was located at about 438 nm and 428 nm associated to phonon energies of 1280 cm$^{-1}$ and 1813 cm$^{-1}$ respectively. Luminescence intensity ratios ($I_{R}/I_{O}$) were measured and found to be 2.574, 2.588 and 1.417 for 5T-3, 5T-5 and 5T-10 glasses respectively. The decay life time’s values were obtained for 0.3, 0.5 and 1 mol% Eu$_2$O$_3$ content are found to be as 2.82, 2.79 and 2.71 ms respectively. The optical studies show 5T-3 and 5T-10 glasses are the optimal candidate for a laser working at 614 nm red emission.

Acknowledgement

The Authors would like to thank National Research Council of Thailand (NRCT), Nakhon Pathom Rajabhat University (NPRU) and Department of PG studies and research in physics The National college, Jayanagar, Bangalore, India for support to conduct the research.

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