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OPTICAL INVESTIGATIONS ON EUZNNABIB GLASSES

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Abstract: A new family of novel optical glasses $10ZnO$-$5Na_2CO_3$-$10Bi_2O_3$–(75-x) B_2O_3–xEu_2O_3 (x =0, 0.1, 0.5, 1, 1.5, 2, 3 mol %), are synthesized by melt quench technique. Optical properties were investigated for their luminescence behavior through various spectroscopic techniques such as UV-Vis –NIR absorption, excitation, emission, decay profiles and color measurements at room temperature. Judd –Ofelt intensity parameters [Ω_2, Ω_4] estimated form PL spectra were used to predict the lasing properties of the glasses like total radiative life time, branching ratio, emission cross-section and optical gain. From the measured values of emission cross-sections, branching ratios, and strong photoluminescence features, 0.5mol% of Eu^{3+} ions doped ZnNaBiB glasses showed optimum performance and are potential novel optical luminescent material for red light generation at 613 nm.

Keywords: Europium doped, Optical absorption, Photoluminescence

Introduction:

In recent years, glasses doped with Rare-Earth ions (RE^{3+}) have drawn much attention due to their potential applications in solid state lasers, optical amplifiers, three-dimensional displays, planar wave guides, field emission displays, white light emitting diodes, optoelectronic devices such as short wavelength (visible) lasers, and high density frequency domain optical data storage [1-8]. The radiative properties of these glasses depend on the concentration of the (RE^{3+}) ions as well as the chemical environment of the host material and the nature of neighbouring ion if more than one type of (rare earth) ion is present [7]. These glasses have proved to be luminescence materials as they have high emission efficiencies. These emissions correspond to 4f-4f and 4f-5d electronic transitions in the RE^{n+} [6]. The 4f-4f transition gives an especially sharp fluorescence pattern from the UV-VIS to the infrared region (NIR) [4,6]. This is due to shielding effects of the outer 5s and 5p orbitals on the 4f electrons [6]. Luminescent properties of these rare earth (which is decided by the chemical composition of the host) ions like emission cross section and radiative life time dependent on the phonon energy of the host glassy system [9]. Among the given rare earths, triply ionized europium ions has got technological importance due to the prominent red and orange emission peak around 600 nm, used in various field emission displays as well as red light emitting diodes[7,9,15,16]. In the present paper, we have explored a new family of novel optical glasses based on ZnO-Na_2CO_3-Bi_2O_3–B_2O_3–Eu_2O_3 with different concentrations of europium.

Experimental:

Sample Preparation:

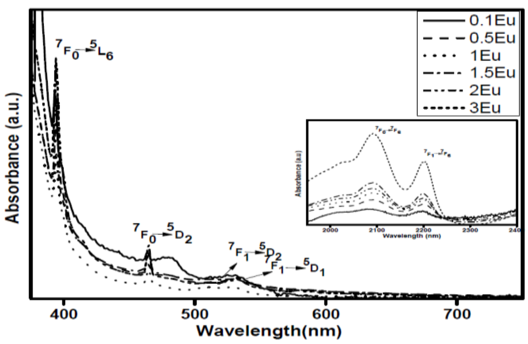
Europium doped multi-component 10 ZnO – 5 Na_2CO_3 – 10 Bi_2O_3 – (75 – x) B_2O_3 – x Eu_2O_3 (x =0.1, 0.5, 1, 1.5, 2, 3 mol %) ZnNaBiB glasses have been prepared by melt quench technique. Required amount of host chemicals weighed and grounded thoroughly using an agate mortar and pestle. The fine powder thus formed was transferred to a porcelain crucible and melted at 950 ^{0}C for 2 hour in a temperature controlled electric furnace. After the retirement of the melting period, the molten mass was quenched on a preheated rectangular stainless steel mould. The raw glasses thus prepared were annealed at glass transition temperature for 3 hours to remove the thermal stresses induced in the glass matrix due to the rapid quenching process. Different grain size emery sheets were used to polish the glasses to get transparent bubble free europium doped glasses for further characterization. UV-Vis-NIR absorption spectra of the samples were recorded using Perkin Elmer Lambda -750 spectrophotometer with 1nm resolution, in the wavelength region 250 to 2500 nm. Photoluminescence [excitation and emission spectra] and life time decay measurements were done using Edinnburg Spectro Fluorimeter-950 with xenon flash lamp and pulsed laser as excitation sources. Emission spectra of ZnNaBiBEu glasses were recorded in 520 to 750 nm spectral region and optical properties of the glasses monitored at 613 nm.

Results and Discussion

Optical Properties:

Absorption Spectroscopy

Overlaid UV-Visible -NIR absorption spectra of Eu^{3+} doped ZnNaBiB glass is shown in figure 1 (a). Absorption bands in the figure 1 (a) were attributed to the 4f-4f intra band electronic transitions, takes place from ground state $^7F_0$ andthermally populated first excited state $^7F_1$ to next excited $^5L_6$, $^5D_2$, $^5D_1$ and $^7F_6$ state [7,9]. Each absorption spectrum showed a maximum of 6 transitions attributed to $^7F_0 \rightarrow (^5L_6,\ ^5D_1,\ ^5D_2)$, $^7F_1 \rightarrow {}^5D_1$ in UV-Vis region and two transitions ($^7F_0 \rightarrow {}^7F_6$ and $^7F_1 \rightarrow {}^7F_6$) in NIR region at wavelengths 394, 465, 526, 534, 2097, 2207nm respectively. Intensity of each absorption peak increased as Eu^{3+} concentration increased in the base of ZnNaBiB glass matrix. The plot between (αhυ) and energy (hυ) known as Tauc plot [7] used to calculate the band gap energy [E_g] is shown in Fig 1 (b).The value of (hυ) at the point where $(\alpha h\upsilon)^{(1/2)}$ becomes zero yields a directmeasure of the optical band gap energy [7].



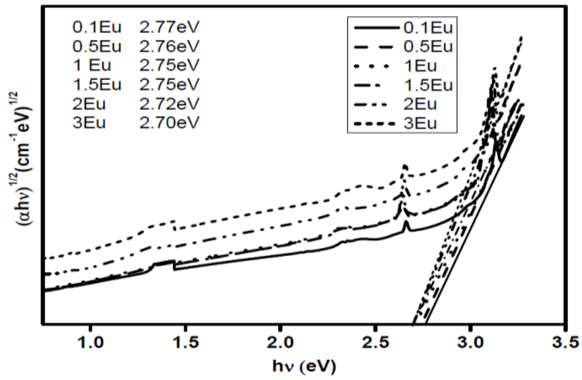


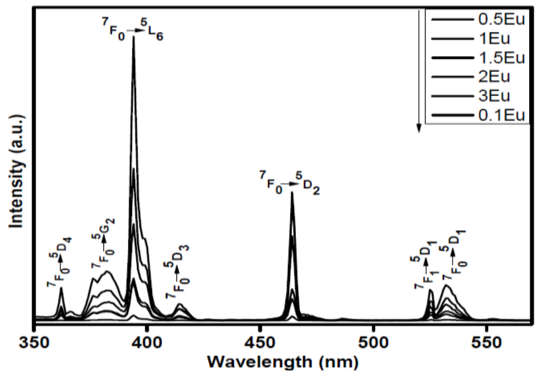
Fig.-1. (a) Overlaid absorbance spectra in UV-Vis-NIR region (b) Tauc's plot of Eu^{3+} doped ZnNaBiB glasses.

Overlaid Tauc's plot of Eu^{3+} doped ZnNaBiB glasses is shown in Figure 1b). Band energy gap [E_g] values measured through Tauc's plot were found to be 2.65, 2.66, 2.64, 2.69, 2.69, 2.69 respectively correspond to 0.1, 0.5, 1.0, 1.5, 2.0, 3.0 Eu^{3+} doped ZnNaBiB glasses. These values once again confirmed the insulating nature of the glasses and are almost same for all Eu^3doped glasses.

Photoluminescence Spectroscopy

*Excitation spectra, Emission spectra, J-O analysis and R*adiative parameters

The excitation spectra [PLE] of Eu^{3+} doped ZnNaBiB glasses monitoring emission at 613 nm are shown in a figure 2 (a). Each PL spectrum comprises five emission bands at 580, 590, 613, 646, 702 nm respectively correspond to the $^5D_0$ to $^7F_0$, $^7F_1$, $^7F_2$,$^7F_3$,$^7F_4$ transitions. Intensity of emission band increased with increase in Eu^{3+} concentration up to 0.5 mol% and intensity quenching was observed with further increase in europium content in the glass network.



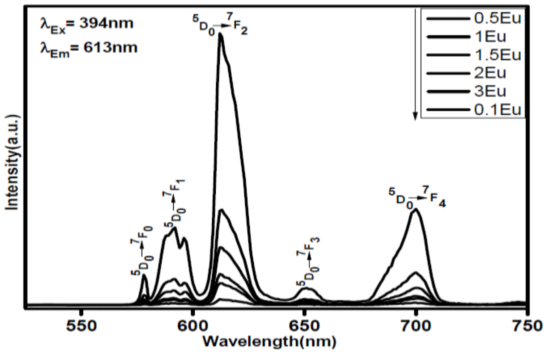


Fig.-2.(a) Overlaid (a) excitation and (b) emission spectra of Eu^{3+} doped ZnNaBiB glasses.

The decrease in peak intensity may be due to the self-quenching of excited Eu^{3+} ions when the concentration is more than the 0.5 mol %. Judd-Ofelt [J-O] intensity parameters [9,16] of Eu^{3+} doped ZnNaBiB glasses are obtained from the PL emission spectra. In J-O analysis, electric induced dipole transitions [$^5D_0$ to ^7F_j (j = 2, 4, 6)] to host independent magnetic dipole transition [$^5D_0$ to $^7F_1$] will be used to estimate the J-O intensity parameters Ω_λ (λ = 2, 4, 6) [9, 16].

Table-1. Judd-Ofelt parameters $\Omega_{\boldsymbol{\lambda}}$ ($\boldsymbol{\lambda}$ = 2, 4) (x 10^{-20}) calculated from PL spectral and red to orange ratio [R/O = ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) of Eu^{3+} ions in ZnNaBiB glasses.

Glass Code	Ω_2	Ω_4	Ω_6
Eu 0.1	4.12	3.28	-
Eu 0.5	4.23	3.32	-
Eu 1	4.01	3.53	-
Eu 1.5	3.87	3.32	-
Eu 2.0	3.80	3.26	-
Eu 3.0	3.71	3.22	-

The calculated values of J-O intensity parameters Ω_2, Ω_4, are presented in Table 1. J-O parameters $\Omega_2 > \Omega_4$ shown inTable 1 confirms the covalence nature of Eu-O in the glass. The essential radiative properties of the Eu^{3+} doped ZnNaBiB glasses were determined using J-O intensity parameters. Radiative properties like, transition probability (A), total transition probability (A_T), radiative life time ($\boldsymbol{\tau_R}$) and branching ratio ($\boldsymbol{\beta}$) will decide the lasing properties of prepared gasses [9-16]. Total radiative transition probability [A_T] estimated by adding the individual radiative transition probabilityA**:** $A_T = \sum A$

Lasing power of an emission transition is characterized by the branching ratio (β) if its value is >0.50. Branching ratio (β) which decides the potentiality of the lasing action of the lasing glass was calculated by: $\beta = \frac{A}{A_T}$

Ability of the host in lasing emission determined by calculating the stimulated emission cross-section for $^5D_0$ excited state to lower state $^7F_{1,2,4}$ given by: $\sigma_{se} = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_p} A$

Where λ_p represents peak emission wavelength, $\Delta\lambda_p$ effective band width, σ_{se} peak stimulated emission cross-section, $\sigma_{se} x \Delta\lambda_p$ gain bandwidth, c speed of light and n refractive index of the glass. The measured and calculated values of

$\lambda_p, \Delta\lambda_p, \sigma_{se}, \sigma_{se}x\, \Delta\lambda_p$ and β for 0.5 europium doped glass are included i

All these values were found to be significantly high for the prominent transition $^5D_0$-$^7F_2$ and also for 0.5 mol% Eu^{3+} doped ZnNaBiB glass [As our main focus is on developing good luminescent/lasing material, the optical/radiative parameters studied based on PL spectra are included only for 0.5 mol% glass, as it showed optimal performance compared to other Eu^{3+} doped ZnNaBiB glasses explored in this study].

Table-2.Emission peak wavelength $\boldsymbol{\lambda}_p$ (nm), effective bandwidth ($\Delta\boldsymbol{\lambda}_p$), experimental branching ratios (β_{exp}), stimulated emission cross section (σ_{se} x 10^{-22}) (cm^2), gain band width (σ_{se} x $\Delta\boldsymbol{\lambda}_p$) (x 10^{-28}) (cm^3) and optical gain (σ_{se} x $\boldsymbol{\tau_R}$) (x 10^{-24}) (s) for the emission transitions of ZnNaBiB 0.5Eu glass.

Transition $^5D_0 \rightarrow$	$\boldsymbol{\lambda}_p$	$\Delta\boldsymbol{\lambda}_p$	β	σ_{se}	σ_{se} x $\Delta\boldsymbol{\lambda}_p$	σ_{se}x τ_R
$^7F_0$	579	2.63	0	0	0	0
$^7F_1$	591	12.03	0.16	1.52	1.81	0.49
$^7F_2$	613	12.22	**0**.59	9.73	12.1	3.15
$^7F_3$	646	6.66	0	0	0	0
$^7F_4$	701	15.1	0.22	5.2	7.85	2.54

Considering the values of all spectroscopic parameters [A, σ_{se}, σ_{se}x $\Delta\lambda_p$, β] studied on

PL spectra, 0.5 mol% Eu^{3+} doped ZnNaBiB glass showed better performance. Hence, 0.5 Eu^{3+} doped ZnNaBiB glass could be used as an active medium for lasing action and also suitable for high red light generating luminescent material at 613 nm.

Conclusion:

We have developed a new family of novel optical glasses based on ZnO-Na_2CO_3-Bi_2O_3–B_2O_3–Eu_2O_3 using melt quench technique. Calculated values of radiative parameters using JO analysis like transition probability (A_T), stimulated emission cross-section σ_{se}, gain bandwidth [$\sigma_{se} x \Delta\lambda_p$], branching ratio [β] and quantum efficiency [η]showed competitive results. Among various emission transitions, $^5D_0$-$^7F_2$ transition possessed maximum J–O parameter (Ω_2) and stimulated emission cross-section (σ_{se}) indicating abundance of red color in present glasses. From the measured emission cross-sections, branching ratios, life times, strong photoluminescence features, 0.5 mol% doped ZnNaBiB glass showed optimum performance, are potential novel optical luminescent material for red light generation at 613 nm.

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