Spectroscopic Studies on RE^{3+} Doped Heavy Metal Oxide Glasses for Photonics Applications

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Abstract— Incorporation of rare earth (RE) ions into different host matrices is key to the development of photonic devices like optical amplifiers, solid state lasers and phosphors etc., that operate using intrashell or ''forced'' electric dipole transitions occurring within the 4f shell of RE ions. The local environment around the RE ions such as site symmetry, crystal field strength and electron-phonon interaction strength leads to differences in the spectral and lasing parameters. The RE ions in the glass host often interact with each other via multipolar process which gives information about the local field environment around the RE ions, energy transfer mechanism between RE ions and the host and energy transfer among the RE ions which are useful to design novel photonic devices. The Judd-Ofelt (JO) theory has been widely used to calculate the intensities of the 4f–4f electronic transitions which can be of electric dipole, electric quadruple and magnetic dipole in nature. The JO intensity parameters are highly influenced by the host matrices via change in local field/environment at the RE ion and provide a qualitative measure of asymmetry of the local crystal field around the RE ion. The decay time of the excited state of the RE ions in the glass matrices is an important parameter to evaluate the amplification properties that comprise the radiative and non-radiative transition rates. The radiative decay rate is highly influenced by the varying glass composition through the changes in the local crystal field symmetry around the RE ion site. The non-radiative decay rates depend upon the available phonon frequency in the host matrices which can couple with electron orbitals of the ion allowing the excited RE ions to decay non-radiatively. In this regard, the heavy metal oxide/oxyfluoride containing borate and telluroborate glasses have been chosen as a host for RE dopant to enhance the luminescence properties via decreasing the non-radiative transition.

Structural and luminescence behaviour of lead fluoroborate glasses prepared with the chemical composition $(50–x)B_2O_3+20PbO+20PbF_2+10ZnO +xEu_2O_3$ (where x=0.05, 0.1, 0.5, 1, 2 and 3 in wt%) have been studied by varying the trivalent europium ion content. Structural behaviour of the prepared glasses has been explored through XRD, FTIR and Raman spectral analysis. Optical characterization has been made using UV-Vis-NIR absorption, excitation, luminescence and decay curves of the present glasses. The PSB associated with the $^7F_0 \rightarrow {}^5D_2$ excitation transition is used to determine the electron–phonon coupling constant and the local structure of the Eu^{3+} ions with its surrounding ligands. Judd-Ofelt (JO) intensity parameters Ω_λ (λ=2,4,6) were obtained from the emission spectra and the same is used to estimate the transition probability (A), stimulated emission cross-section (σ_P^E) and branching ratios (β_R) for the excited levels of the Eu^{3+} ions. The higher values of A, σ_P^E and β_R corresponding to the $^5D_0 \rightarrow {}^7F_2$ emission level at 616 nm confirm the potentially of the present glasses as a red laser active medium.

The stimulation of white light from Dy^{3+} doped Lead tellurofluoroborate glasses have been analysed through luminescence measurement. The luminescence intensity increases with increasing Dy^{3+} ion concentration up to 0.5
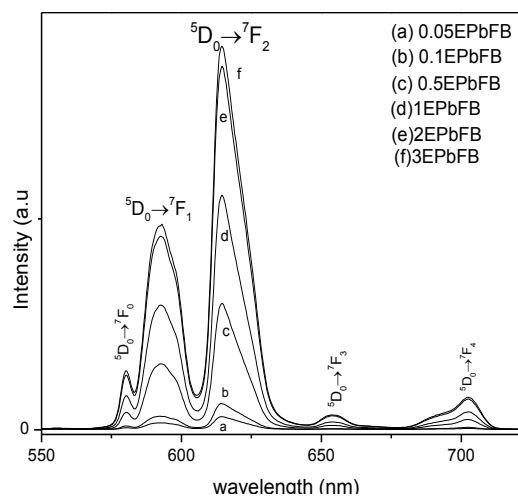

Fig. 1: Luminescence spectra of Eu^{3+} doped lead fluoroborate glasses

wt%, beyond that luminescence quenching is observed. The higher σ_P^E and β_R values of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions suggest the possible laser action in the visible region. The Y/B ratio, CIE chromaticity color coordinates (x,y) and Color correlated temperature (CCT) were also estimated from the luminescence spectra for different concentration as well as pumping wavelengths. The x,y chromaticity color coordinates fall within the white light region and the white light can be tuned by varying the excitation wavelengths. The lifetime

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of the $^4F_{9/2}$ excited state were measured and is found to decrease with increasing Dy^{3+} ion content. The non-exponential behaviour is predominant in higher Dy^{3+} ion content glasses and is due to the efficient energy transfer between Dy^{3+}–Dy^{3+} ions. The decay curves were fitted to the Inokuti–Hirayama (IH) model to understand the nature of energy transfer.
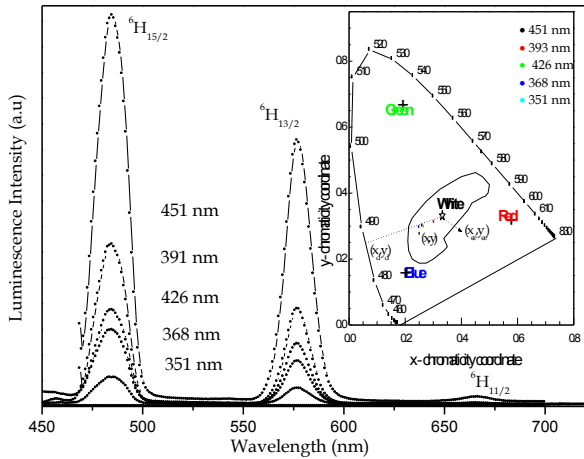

Fig. 2: Luminescence spectra of Dy^{3+} ions doped 0.5DPTFB lead tellurofluoroborate glass
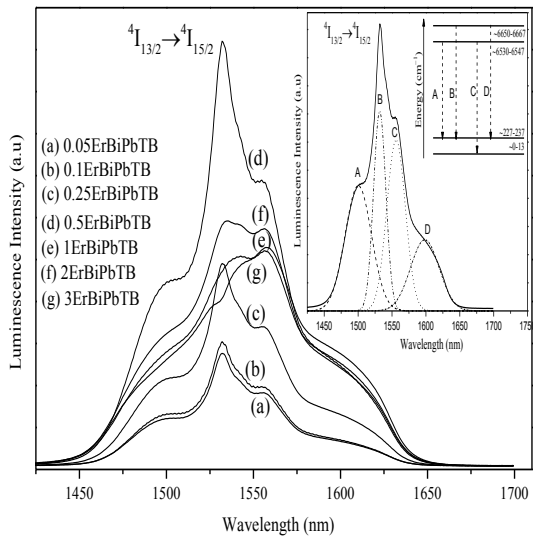

Fig. 3: NIR emission spectra of Er^{3+} doped xErBiPbTB glass

The development of 1.532 μm amplification in Er^{3+} doped bismuth leadtelluroborate glasses with the composition $25TeO_2+10H_3BO_3+30PbO+$ $(25-x)Bi_2O_3+10CdO+$

xEr$_2$O$_3$ were studied and reported. The absorption and emission cross-section for the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition (1.532 μm) were calculated using McCumbar theory and compared with the reported Er^{3+} doped glasses. Further, the results obtained from the McCumbar theory also found to be in good agreement with the results obtained from JO theory. The Gain coefficient (G) of the 1.532 μm emission band also calculated using absorption and emission cross-sections to explore the suitability of the prepared glasses for broad band amplification.
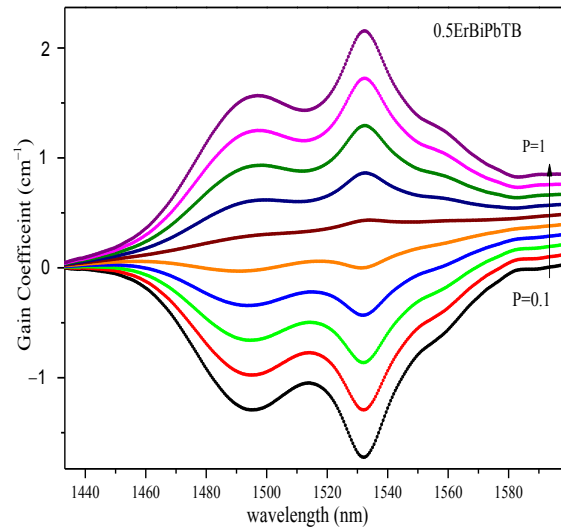

Fig. 4: Gain coefficient of the $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition as a function of population inversion parameter for 0.5ErBiPbTB glass

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