Optical absorption and photoluminescence studies of Dy^{3+}: LCZSFB glasses

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Abstract-Lead containing calcium zinc sodium fluoroborate [LCZSFB] glasses doped with different Dy^{3+} ion concentrations have been prepared and characterized through optical absorption and photoluminescence studies. The three phenomenological intensity parametersΩ_λ (λ=2,4 and 6) have been determined from the absorption spectral intensities using the Judd-Ofelt (J-O) theory. The hypersensitivity of $^6H_{15/2} \rightarrow {}^6F_{11/2}$ transition based on the magnitude ofΩ_2 parameter has also been discussed. By using the J-O intensity parameters several radiative properties such as spontaneous transition probabilities (A_R), radiative branching ratios (β_R) and radiative lifetimes (τ_R) have been determined. The effect of Dy^{3+} ion concentration on emission intensities has also been reported and stimulated emission cross section (σ_e) of emission transitions is also reported.

Glasses doped with rare earth (RE) ions are good laser materials as they emit intense radiations in the visible (VIS), near infrared (NIR) and infrared (IR) spectral regions under suitable excitation conditions. Optical absorption and fluorescence studies of rare earth ions doped glasses found wide applications in the field of lasers and telecommunications. Among RE^{3+} ions, the Dy^{3+} ($4f^9$) ion is one of the best suitable candidates for analyzing the absorption and luminescence properties versus Dy^{3+} ion concentration along with different host glass compositions.

Borate glasses are important hosts for RE ions because they exhibit lower thermal expansion coefficients, higher densities, stronger bonding and denser packing [1]. Fluoride based glasses are promising host materials for applications in photonics such as frequency up converters, optical amplifiers [2, 3]. The modifiers such as alkali fluorides (NaF) have got the ability to form stable glasses due to the dual role of PbO as a glass modifier and former [4, 5]. The present interest in the selection of fluoroborate glasses is due to their high ionic conductivity, short range order around network forming borons, anomalous dependence of their structure on the molar fraction of oxide modifiers and special role of the fluorine ions in the formation of a three dimensional network [6].

Keeping in view the advantages of fluoroborate glasses as well as technological importance of Dy^{3+} ions luminescence in glasses, this study mainly includes the optical absorption studies of LCZSFB glasses in order to know their utility for solid state laser devices. From the absorption spectra recorded in the NIR region, the oscillator strengths, intensity parameters, branching ratios and radiative lifetimes for the excited fluorescent levels of Dy^{3+} doped LCZSFB glasses were determined by means of the Judd-Ofelt theory [7, 8] and certain potential laser transitions are identified.

Glass samples were prepared with a chemical composition of 20PbO + 5CaO + 5ZnO + 10NaF + (60 - x) B_2O_3 + xDy_2O_3, (where x = 0.1, 0.25, 0.5, 1.0 and 2.0 mol %). A homogeneous mixture of reagent grade chemicals was melted in an electric furnace at 950^0C in a porcelain crucible for about one hour and subsequently annealed at 360^0C for 8 hours to remove thermal strains. Absorption spectra of Dy^{3+} -doped LCZSFB glasses were recorded in the wavelength range of 600- 1800 nm using a Varian Cary 5E UV-VIS-NIR spectrophotometer.

Optical absorption spectra of 1.0 mol% Dy^{3+} doped LCZSFB glass in the NIR region are shown in Fig. 3. The spectra totally consist of 6 peaks at 1682, 1273, 1094, 895, 800 and 752 nm corresponding to $^6H_{15/2} \rightarrow {}^6H_{11/2}$, ($^6F_{11/2}$ + $^6H_{9/2}$), ($^6F_{9/2}$ + $^6H_{7/2}$), $^6F_{7/2}$, $^6F_{5/2}$ and $^6F_{3/2}$ transitions, respectively. The identification and assignment of energy levels has been based on earlier literature [9, 10]. Certain absorption transitions of each rare earth ion are very sensitive to the host environment and ion concentration due to the inhomogenity of the ligand environment [11]. Such transitions are known as hypersensitive transitions. Hypersensitive transitions are associated with the large values of oscillator strengths as well as reduced matrix elements $\|U^{\lambda}\|^2$. In the case of Dy^{3+} ion the $^6H_{15/2}\rightarrow(^6F_{11/2} + {}^6H_{9/2})$ is a hypersensitive transition and the magnitude of measured oscillator strength (f_{exp}) is high for this transition, which is solely dependent on the magnitude of Ω_2 and also sensitive to the local symmetry of a ligand field or covalent bond of Dy^{3+} ion in the host [12].

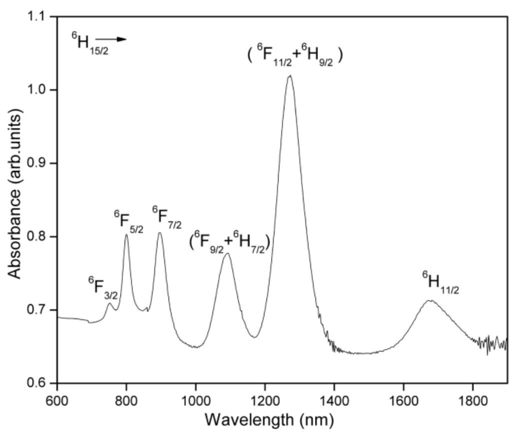

Fig. 1. NIR absorption spectra of 1.0 mol% Dy^{3+} -doped LCZSFB glasses.

From the observed absorption spectrum, experimental oscillator strengths (f_{exp}) are determined by measuring the areas under the absorption bands using $f_{exp}=4.318\times10^{-9}\int\varepsilon(\nu)d\nu$. Calculated oscillator strengths (f_{cal}) and J-O intensity parameters are determined by using the least squares fit method and doubly reduced matrix elements $\|U^{\lambda}\|^2$. The experimental and calculated oscillator strengths of observed absorption bands along with δ_{rms} deviation are tabulated in Table 1. The small δ_{rms} deviation of 0.55×10^{-6} between the experimental and calculated oscillator strengths of the absorption bands indicates a good fit. The calculated J-O parameters are $\Omega_2 = 11.25\times10^{-20}$cm^2, $\Omega_4 = 2.45\times10^{-20}$ cm^2, $\Omega_6 = 5.16\times10^{-20}$ cm^2. The tendency of the J-O parameters in the present glass is found to be in the order $\Omega_2 > \Omega_6 > \Omega_4$. These J-O parameters are host dependent and are important for the investigation of glass structure, transition rates of rare-earth ion energy levels and bonding in the vicinity of RE ions.

In the present case the higher magnitude of Ω_2 suggests that the bonding of the Dy^{3+} ions with the ligand is of covalent nature [14] and suggests that the rare-earth ion site has lower asymmetry in LCZSFB glass host. The Ω_2 parameter values of Dy^{3+} ions of LCZSFB glasses are compared with different host matrices containing Dy^{3+} ions and are presented in Table 2. The comparison of Ω_2 parameter values of Dy^{3+} ions in different borate hosts of Table 2 indicates that the Dy^{3+} ions in LCZSFB glasses are more covalently bonded than those of lead borate and LBTAF glass matrices and are less covalently bonded than those of L2FBD, NaZnBS glass matrices. The intensity parameter Ω_4 is related to the bulk properties and Ω_6 is inversely related to the rigidity of the host and also vibronic dependent [15]. The magnitude of $\Omega_6 = 5.16\times10^{-20}$ cm^2 indicates higher rigidity of present LCZSFB glass host than other reported systems [13, 16]. The high value of spectroscopic quality factor X= $\Omega_4/\ \Omega_6$ = 0.48, predicts efficient stimulated emission in the present host [17].

Transition $^6H_{15/2}\rightarrow$	Energy (cm^{-1})	f_{exp}	f_{cal}
$^6H_{11/2}$	5945	1.93	2.56
$^6F_{11/2} + {}^6H_{9/2}$	7856	11.29	11.22
$^6F_{9/2} + {}^6H_{7/2}$	9140	4.54	4.73
$^6F_{7/2}$	11173	4.90	4.34
$^6F_{5/2}$	12500	3.65	2.16
$^6F_{3/2}$	13298	0.99	0.40
$\delta_{rms} = \pm 0.55\times10^{-6}$			

Table 1: Experimental and calculated oscillator strengths ($\times10^{-6}$) for 1.0 mol% Dy^{3+} -doped LCZSFB glass.

Glass system	Ω_2	Ω_4	Ω_6	X
LCZSFB[Pre.work]	11.25	2.45	5.16	0.47
LBTAF [9]	7.05	1.22	1.91	0.63
Leadborate [13]	3.59	3.50	5.26	0.67
NaZnBS [16]	16.82	9.45	6.50	1.45
L2FBD [18]	11.32	2.54	3.78	0.67

Table 2: Comparison of J-O intensity parameters ($\times10^{-20}$ cm^2), their trends and spectroscopic quality factors ($X = \Omega_4/\ \Omega_6$) for Dy^{3+} ions in LCZSFB glass with different glass hosts.

Once the values of Ω_λ are obtained, the other radiative parameters such as electric dipole line strength (S_{ed}), magnetic dipole line strength (S_{md}), spontaneous transition probabilities (A_R), total transition probability (A_T), radiative lifetime (τ_R) and branching ratios (β_R) corresponding to different emission channels from $^4F_{9/2}$ level are also calculated for 1.0 mol% Dy^{3+} -doped LCZSFB glass, and are presented in Table 3. From the values of radiative transition probabilities of Table 3, it is noted that $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition has the highest radiative transition rate compared to other transitions. Hence, this transition is very useful for laser emission. The predicted branching ratios are found to be high for those transitions having maximum A_R values. The levels having relatively large values of A_R and β_R may exhibit laser action. The contribution of these transitions to the total branching ratio is nearly 95%, thereby suggesting that these transitions have the greatest potential for visible laser action for 1.0 mol% Dy^{3+} ions in LCZSFB glass.

Transition $F_{9/2}$→	λ_P (nm)	S_{ed}	S_{md}	A_R	β_R
$^6F_{5/2}$	-	7.38	0	13.00	0.007
$^6F_{7/2}$	-	2.77	1.93	7.63	0.004
$^6H_{5/2}$	-	1.43	0	4.92	0.003
$^6H_{7/2}$	-	6.30	0.66	28.60	0.016
$^6F_{9/2}$	-	2.34	1.14	10.80	0.006
$^6F_{11/2}$	-	5.62	7.58	35.30	0.019
$^6H_{9/2}$	-	4.60	0.44	29.16	0.016
$^6H_{11/2}$	664	12.60	1.16	113.00	0.062
$^6H_{13/2}$	576	87.26	0	1205.00	0.660
$^6H_{15/2}$	484	16.20	0	383.80	0.210
A_T = 1833, τ_R = 0.55					

Table 3: Radiative properties such as peak emission wavelength (λ_P) electric (S_{ed}, $\times10^{-22}$ cm^2) and magnetic (S_{md}, $\times10^{-22}$ cm^2) dipole line strengths, radiative transition probabilities (A_R, s^{-1}), total radiative transition probability (A_T, s^{-1}), radiative lifetimes (τ_R, ms) and branching ratios (β_R) for 1.0 mol% Sm^{3+} -doped LCZSFB glass.

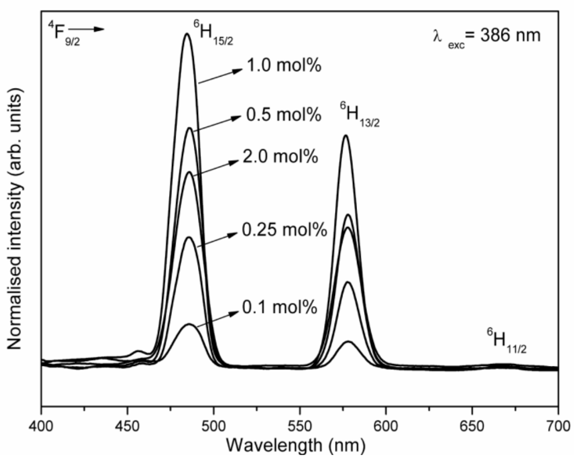

Fig. 2. Photoluminescence spectra for different concentrations of Dy^{3+}-doped LCZSFB glasses.

Figure 2 represents photoluminescence spectra of LCZSFB glasses recorded as a function of Dy^{3+} concentration. Three peaks observed at 484, 576 and 664 nm, corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ transitions, respectively. The intensity of peaks increases with the increase of concentration of Dy^{3+} ions up to 1.0 mol % and then decreases. The variation of luminescence intensity of transitions with Dy^{3+} ion concentration suggests that the LCZSFB glasses doped with 1.0 mol % Dy^{3+} ions can generate intense luminescence at 386nm excitation. The stimulated emission cross section of emission transition (σ_e) is one of the important parameters used to identify a laser active medium. The measured values of stimulated emission cross sections (σ_e) for 1.0 mol % Dy^{3+} concentration are found to be 5.83×10^{-22} cm^2, 42.60×10^{-22} cm^2, 6.0×10^{-22} cm^2 for $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ transitions respectively. The radiative transition probability, branching ratios and stimulated emission cross sections are higher for $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition compared to other transitions. High radiative transition rates (A_R), branching ratios (β_R) and stimulated emission cross sections (σ_e) suggest that $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition has the greatest potential for lasing action.

In conclusion, optical absorption and photoluminescence studies of Dy^{3+} ions doped in LCZSFB glasses have been done. From the analysis of optical absorption oscillator strengths, J-O intensity parameters, radiative transition rates, branching ratios and radiative lifetimes are calculated and found to be comparable with other reported values. Usually, a good material for laser emission should have high radiative transition rates and high branching ratios. Based on optical properties such as strong visible emissions and high branching ratios , it is concluded that 1.0 mol% Dy^{3+} ions doped LCZSFB glass may be used as a luminescent novel optical material for the development of lasers and photonic devices operating in the visible region.

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