**Optical absorption studies of Dy3+: LCZSFB glasses**

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**Abstract:** LCZSFB glasses doped with different Dy3+ ion concentrations have been prepared and characterized through optical absorption studies. The three phenomenological intensity parameters Ωλ (λ=2,4 and 6) have been determined from the absorption spectral intensities using the Judd-Ofelt (J-O) theory. The hypersensitivity of 6H15/2 $\rightarrow $ 6F11/2 transition based on the magnitude of Ω2 parameter has also been discussed. By using the J-O intensity parameters several radiative properties such as spontaneous transition probabilities (AR), radiative branching ratios (βR) and radiative lifetimes (τR) have been determined.

[[1]](#footnote-2) 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 RE3+ ions, the Dy3+ (4f9) ion is one of the best suitable candidates for analyzing the absorption and luminescence properties versus Dy3+ 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 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 the three dimensional network [6].

 Keeping in view of the advantages of fluoroborate glasses as well as technological importance of Dy3+ 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 Dy3+ doped LCZSFB glasses were determined by means of Judd-Ofelt theory [7, 8] and certain potential laser transitions are identified.

 Glass samples were prepared with chemical composition of 20PbO + 5CaO + 5ZnO + 10NaF + (60 - x) B2O3 + xDy2O3, (where x = 0.1, 0.25, 0.5, 1.0 and 2.0 mol %). Homogeneous mixture of reagent grade chemicals were melted in an electric furnace at 9500C in porcelain crucible for about one hour and subsequently annealed at 3600C for 8 hours to remove thermal strains. Absorption spectra of Dy3+ -doped LCZSFB glasses were recorded in the wavelength range 600- 1800 nm region using Varian Cary 5E UV-VIS-NIR spectrophotometer.

*Optical Absorption Spectra*

Optical absorption spectra of 1.0 mol% Dy3+ doped LCZSFB glass in the NIR region is shown in Fig. 3. The spectra totally consists of 6 peaks at 1682, 1273, 1094, 895, 800 and 752 nm corresponding to 6H15/2$\rightarrow $6H11/2, (6F11/2 + 6H9/2), (6F9/2 + 6H7/2), 6F7/2, 6F5/2 and 6F3/2 transitions respectively. The identification and assignment of energy levels has been done based on the 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 obeying the selection rules $\left|∆S\right|$= 0, $\left|∆L\right|$$\leq $ 2 and $\left|∆J\right|$$\leq $ 2 [12]. The hypersensitive transitions are associated with the large values of oscillator strengths as well as reduced matrix elements$ \left‖U^{λ}\right‖^{2}$. In case of Dy3+ ion the 6H15/2$\rightarrow $(6F11/2 + 6H9/2) is hypersensitive transition and the magnitude of measured oscillator strength ($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 ligand field or covalent bond of Dy3+ ion in the host [12].



**Fig. 1.** NIR absorption spectra of 1.0 mol% Dy3+ -doped LCZSFB glasses.

*J-O parameters and Radiative properties*

 The intensity of an absorption band is expressed in terms of its oscillator strength [13]. From the absorption spectra the experimental oscillator strengths (fexp) are determined by measuring the areas under the absorption bands. Calculated oscillator strengths (fcal) and J-O intensity parameters are determined by using least squares fit method and doubly reduced matrix elements$ \left‖U^{λ}\right‖^{2}$. The experimental and calculated oscillator strengths of observed absorption bands along with δrms deviation are tabulated in Table 1. The small δrms deviation of 0.55 $×$ 10-6 between the experimental and calculated oscillator strengths of the absorption bands indicates a good fit. The derived J-O parameters are *Ω*2 = 11.25 $×$ 10-20cm2, *Ω*4 = 2.45 $×$ 10-20 cm2, *Ω*6 = 5.16 $×$ 10-20 cm2. The tendency of the J-O parameters in the present glass is found to be in the order *Ω*2*> Ω*6 *> Ω*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. Table 2 presents the comparison of J-O intensity parameters, their trend and spectroscopic quality factors of Dy3+ ions in LCZSFB glass with different hosts.

In general, J-O intensity parameters provide an insight into the local structure and bonding in the vicinity of RE3+ ions. The magnitude of Ω2 parameter depends on the covalency of metal-ligand bond and also explains the symmetry of ion sites in the neighborhood of RE ions. In the present case the higher magnitude of Ω2 suggests that the bonding of the Dy3+ 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 comparison of Ω2 parameter values of Dy3+ ions in different borate hosts in Table 2 indicates that the Dy3+ ions in LCZSFB glasses are more covalently bonded than that of lead borate and LBTAF glass matrices and has less covalently bonded than that of L2FBD, NaZnBS glass matrices. The intensity parameter Ω6 is related to the rigidity of the host and also vibronic dependent [15]. The magnitude of Ω6 = 5.16$×$10-20 cm2 indicates the higher rigidity of present LCZSFB glass host than other reported systems [13, 16].

**Table 1** Experimental and calculated oscillator strengths ($×$10-6) for 1.0 mol% Dy3+ -doped LCZSFB glass.

|  |  |  |  |
| --- | --- | --- | --- |
| Transition 6H15/2$\rightarrow $ | Energy (cm-1) | $$f\_{exp}$$ | $$f\_{cal}$$ |
| 6H11/2 | 5945 | 1.93 | 2.56 |
| 6F11/2 + 6H9/2 | 7856 | 11.29 | 11.22 |
| 6F9/2 + 6H7/2 | 9140 | 4.54 | 4.73 |
|  6F7/2 | 11173 | 4.90 | 4.34 |
| 6F5/2 | 12500 | 3.65 | 2.16 |
|  6F3/2 | 13298 | 0.99 | 0.40 |
| $δ\_{rms}$ = ± 0.55 $×$10-6 |  |  |  |

The spectroscopic quality factor X=Ω4/Ω6, is one of the important lasing characteristic parameter for predicting the stimulated emission in any active medium. Dy3+ ion doped glass hosts having the range of spectroscopic quality factors 0.42 – 1.92 are the good candidates for laser active media [17]. The reasonably high value of spectroscopic quality factor X= 0.48, predicts efficient stimulated emission in the present host.

**Table 2** Comparison of J-O intensity parameters ($×$10-20 cm2), their trends and spectroscopic quality factors ($X= Ω\_{4}/ Ω\_{6}$) for Dy3+ ions in LCZSFB glass with different glass hosts.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| 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 |

 Once the values of Ωλ are obtained, the other radiative parameters such as electric dipole line strength (Sed), magnetic dipole line strength (Smd), spontaneous transition probabilities (AR), total transition probability (AT), radiative lifetime(τR) and branching ratios (βR) corresponding to different emission channels from 4F9/2 level have also been calculated and are presented in Table 3. The radiative transition rates (AR) and branching ratios (βR) have been determined for the 4F9/2 level of 1.0 mol% Dy3+ -doped LCZSFB glass, and are presented in Table 3. From the values of radiative transition probabilities of Table 3, it is noted that 4F9/2→ 6H13/2 transition has 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 AR values. The levels having the relatively large values of AR, βR and energy gap to the next lower level may exhibit laser action. The contribution of these transitions to the total branching ratio is nearly 95%, thereby suggesting that these transitions have the most potential for visible laser action for 1.0 mol% Dy3+ ions in LCZSFB glass.

**Table 3** Radiative properties such as peak emission wavelength ($λ\_{P}$) electric ($S\_{ed}$, $×$10-22 cm2) and magnetic ($S\_{md}$, $×$10-22 cm2) dipole line strengths, radiative transition probabilities ($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% Sm3+ -doped LCZSFB glass.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Transition 4F9/2$\rightarrow $ | $λ\_{P}$ (nm) | $$S\_{ed}$$ | $S\_{md}$  | $$A\_{R}$$ | $$β\_{R}$$ |
| 6F5/2 | - |  7.38 | 0 | 13.00 | 0.007 |
| 6F7/2 | - |  2.77 | 1.93 | 7.63 | 0.004 |
| 6H5/2 | - |  1.43 | 0 | 4.92 | 0.003 |
| 6H7/2 | - |  6.30 | 0.66 | 28.60 | 0.016 |
| 6F9/2 | - |  2.34 | 1.14 | 10.80 | 0.006 |
| 6F11/2 | - |  5.62 | 7.58 | 35.30 | 0.019 |
| 6H9/2 | - |  4.60 | 0.44 | 29.16 | 0.016 |
| 6H11/2 | 664 | 12.60 | 1.16 | 113.00 | 0.062 |
| 6H13/2 | 576 | 87.26 | 0 | 1205.00 | 0.660 |
| 6H15/2 | 484 | 16.20 | 0 | 383.80 | 0.210 |
| $A\_{T}$ = 1833, $τ\_{R}$ = 0.55 |  |

 In conclusion, the optical absorption studies of Dy3+ ions doped in LCZSFB glasses have been studied. From the analysis of optical absorption the oscillator strengths, the J-O intensity parameters, radiative transition rates, branching ratios and radiative lifetimes are calculated and are found to be comparable with other reported values. Usually, a good material for a laser emission should have high radiative transition rates and high branching ratios. Based on the physical and optical properties such as strong visible emissions and high branching ratios, it is concluded that 1.0 mol% Dy3+ ions doped LCZSFB glass may be used as luminescent novel optical materials for the development of lasers and photonic devices operating in the visible region.

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