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# Structural and Luminescence Properties in $Dy^{3+}$ Doped Antimony-Strontium-Magnesium-Oxyfluroborate Glasses

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**ABSTRACT** A series of glasses by melting quenching method fabricated for spectroscopic investigations of Dysprosium ($Dy^{3+}$) particle ions deposited on Antimony (Sb) - Magnesium (Mg) - Strontium (Sr) Oxyfluoroborate (BSbMgfSr) glasses. The structural and optical characterizations such as XRD, UV-VIS-NIR absorption spectroscopy, photoluminescence (PL) (excitation and emission) were accomplished to study the properties of prepared glasses. The transitions from lowest energy state to an excited state in $RE^{3+}$ ions were identified using optical UV-NIR absorption spectra. By the use of Judd-Ofelt theory the J-O intensity parameters $\Omega_\lambda$ ($\lambda$ = 2, 4, 6) have been evaluated utilizing the absorption spectra with the determination of experimental ($f_{exp}$) and calculated ($f_{cal}$) oscillator strengths. The emission of light from glass system was concluded through PL spectra (Excitation and emission) for $Dy^{3+}$ion. The radiative properties resembling radiative transition probability ($A_R$), radiative-lifetime ($\tau_R$), and branching-ratio ($\beta$) of the glasses have also estimated. Stimulated emission cross-section ($\sigma_{se}$) of the glasses also calculated for the feasibility of lasing applications. Experimental lifetime ($\tau_{exp}$) of the decay curves of the BSbMgfSrD glasses were also calculated upon excitation by suitable wavelengths of all various concentrations of the $RE^{3+}$ ions.

**KEYWORDS** Oxyfluoroborate glasses; optical; XRD; UV-NIR; Radioactive Properties

## INTRODUCTION

Now a day's research is growing to investigate the association, interface etc of rare earth ions with their respective host medium. The literature is very well known regarding different present deposited glass with esteemed rare-trivalent elements along with applications in various fields such as infrared boosters, solid-state lasers, industrial transparent filters, optical communication systems and various quantum computing. Due to the benefits of homogenous light emission, improved thermal stability, good chemical and mechanical strength, superior lanthanide ion solubility, lower manufacturing

costs, ease in manufacturing large samples, high doping capacity and straightforward fabricating processes (Plodinec M.J., 2000, Nageswara Raju, C. et al, 2014, Sudhakar Reddy, 2012) glasses became the host of promising materials for lanthanide ions making them very superior and superior (Kenyon, A.J, 2002, Juarez-Batalla, J. et al, 2016, Jaroszewski, K. et al, 2018, Eyring, L., 1966, Lira, A. et al., 2014).

In creation and production of future white light emitting devices (WLEDs), $Dy^{3+}$- doped glasses received great attention. It is well established that white light radiates with the correct yellow to blue strength of the $Dy^{3+}$ ions. The hardness is due to the two key transitions which depend on the choice of host and the coordination of the environment. The two strong bands of emissions at the yellow (470-500 nm) and blue (570-600 nm) regions related to the non-hypersensitive transitions between $^4F_{9/2} \rightarrow {}^6H_{3/2}$ and $^4F_{9/2} \rightarrow {}^6H_{15/2}$. The luminescent intensity ratio (Y/B) of these transformations therefore can be adjusted to emit white light from the triggered $Dy^{3+}$ -doped glasses.

This paper is aimed at improving the concentration of $Dy^{3+}$ ions with white-light light luminescence in antimony-magnesium-strontium-oxyfluoroborate (BSbMgfSrD) glasses. The structural properties of $Dy^{3+}$ -doped BSbMgfSr glasses were examined using the X-ray diffract meter (XRD), Varian Cary-5000 double beam absorption spectrometer and Edinburgh SpectroFluorometer-950 as well as the photoluminescence. The J-O intensity parameters obtained the radiographical characteristics, like the transition-probabilities ($A_R$), branching ratio $\beta_R$ ($\beta_{exp}$ & $\beta_{cal}$), emission of stimulated cross-sections ($\sigma_{se}$), the life-time $\tau_R$ (ms), gain bandwidth ($\Delta\lambda_{eff}$ x $\sigma_{se}$ respectively), and the optical gain ($\sigma_{se}$ x $\tau_R$).

## EXPERIMENTAL TECHNIQUES

### Synthesis

BSbMgfSrD glass matrices doped with $Dy^{3+}$ ion were synthesized using the famous glass composition melt quenching method $(70\text{-}x)B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3 + xDy_2O_3$, where x =0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%, and tagged as BSbMgfSrD01, BSbMgfSrD05, BSbMgfSrD10, BSbMgfSrD15, BSbMgfSrD20 and BSbMgfSrD25 respectively. A mixture of glass composition of approximately 15 g was weighed by microbalance and pulverized in an agate mortar for high homogeneity. The grounded mixture of various formulations has been converted into a vessel sink and heated in a muffled furnace at 1200°C for around 90 minutes. Afterwards, the molded liquid compound was decantated on the brass mould and then cooled at temperature of 350°C for 15 hours, thus eliminating the internal stress of the glass, enhancing its thermal and mechanical strength, and the glass specimens were cooled up to room temperature.

A. $70B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3$ (Host: BSbMgfSr)
B. $69.9B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3 + 0.1Dy_2O_3$ (BSbMgfSrD01)
C. $69.5B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3 + 0.5Dy_2O_3$ (BSbMgfSrD05)
D. $69B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3 + 1.0Dy_2O_3$ (BSbMgfSrDy10)
E. $68.5B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3 + 1.5Dy_2O_3$ (BSbMgfSrD15)
F. $68B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3 + 2.0Dy_2O_3$ (BSbMgfSrD20)
G. $67.5B_2O_3 + 10MgF_2 + 15SrO + 5Sb_2O_3 + 2.5Dy_2O_3$ (BSbMgfSrD25)

### Analysis

Bruker-$D_8$ X-ray Spectrophoto diffractometer (XRD) has recorded the structure of the fused glass material (BSbMgfSr) without the use of dopant. Ultraviolet (UV)-near infrared (NIR) spectrometer Varian Carry-5000 was used to test the absorption spectra of the BSbMgfSr01 glass matrix. Photoluminescence spectrums were examined for all synthesized matrices using Edinburgh SpectroFluorometer-950 with continuous lamp Xenon (Xe) as an excitation source in the 452 nm wavelength between 550-750 nm of spectrum. By tracking the emission wavelength at 575 nm, decay profiles were obtained using that instrument. Measurements of the refractive index from the ellipsometer, in particular, the characterizations were exercised at a laboratory room temperature.

## RESULTS AND DISCUSSION

### Physical properties

Table 1 displays the investigated Glass Matrix, BSbMgfSrD01 density, refractive index, concentration, average molecular weight, polar radius, field strength, reflective loss, optical dielectric constant, electronic polarizability. The smaller field strength in present glasses indicates the greater solubility of RE ion. Smaller field strength shows the larger solubility of RE ion in present glasses. The smaller electronic polarizability makes the glass more stable (Rao, A.S. et al., 1998).

**Table 1: Physical properties of BSbMgfSrD01 glass**

| Physical parameters | BSbMgfSrD01 |
|---|---|
| Concentration N( $\times 10^{22} ions/cm^3$) | 0.144 |
| Avg molecular weight ($g/mol$) | 132.62 |
| Refractive index ($n_d$) | 1.578 |
| Polar radius $r_p$ (A°) | 1.65 |
| Density ($g/cm^3$) | 3.17 |
| Inter ionic distance $r_i$ (A°) | 4.09 |
| Field strength F ( $\times 10^{16} cm^2$) | 1.06 |
| Dielectric constant Ɛ | 1.62 |
| The molar refractivity $R_M(cm^3)$ | 7.14 |
| The reflection loss R (%) | 0.014 |
| Optical dielectric constant | 0.62 |
| The electronic polarizability $\alpha_e$ ($10^{-23} cm^3$) | 0.28 |

### XRD analysis

The undoped BSbMgfSr powder glass samples XRD intensities profile identified at 2θ values between 6 ° and 80 ° is shown in figure 1. Rather than sharp tops in the XRD profile, expansive protuberances were observed. Such big XRD humps were attributed to the unstructured existence of the investigated glass and also XRD pattern then verified the amorphous nature.

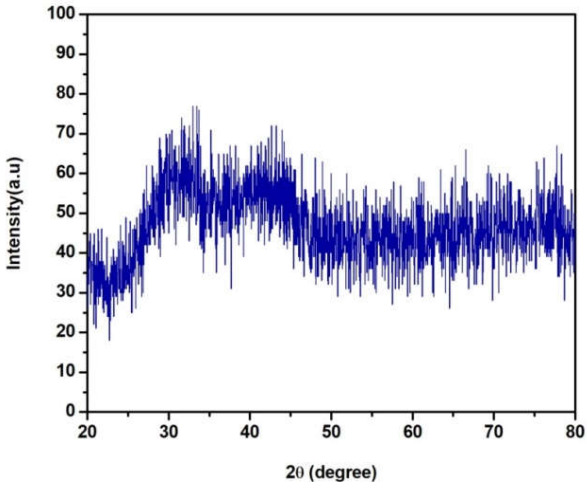


**Figure 1: XRD pattern of undoped BSbMgfSr glass between 2θ = 20° - 80°.**

### Absorption spectra

Figure 2 indicates a continuum of optical absorption of 1.00 mole % BSbMgfSr glass sample of $Dy^{3+}$ - deposited in the range of 300-2000 nm. Table 2 includes absorption bands collected from the soil stage of $^6H_{15/2}$ to various excited rates including high wavelength, energy and their spectral words. In the absorption range, a few small bands in the UV visible area were not detected because of the

absorption edge of the host compound matrix. For both transformations the transformation $^6H_{15/2} \rightarrow {}^6F_{11/2}$ based at 1262 nm are considered a hypersensitive transfer that corresponds with the selection rules $\Delta J = \pm 2$ or $\Delta J \leq 2$, $\Delta L = \pm 2$ or $\Delta L \leq 2$ and $\Delta S = 0$ and found that the transition is most sensitive in the case of the investigated $Dy^{3+}$ host (Mahamuda, S. K. et al., 2014, Thulasiramudu A et al., 2007) ion.

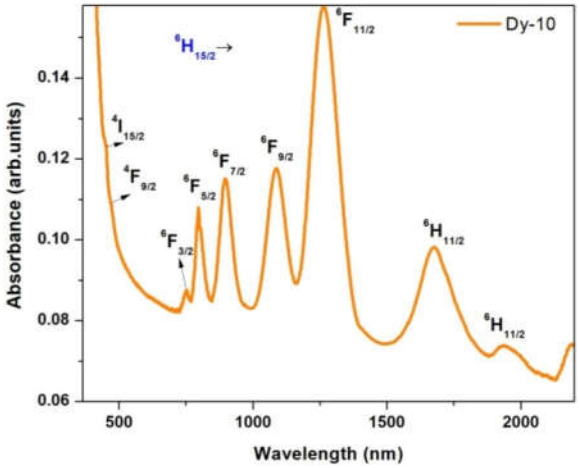


**Figure 2: $Dy^{3+}$- deposited BSbMgfSr glass absorption spectrum at 1.00 mole % in the VIS-NIR regions.**

**Table 2: Transition, peak wavelength (nm), Energy ($cm^{-1}$) Experimental ($f_{exp}$ in micron) and calculated ($f_{cal}$ in micron) oscillator strengths of 1.00 mole % $Dy^{3+}$ deposited BSbMgfSrD01 glasses.**

| Transition $^6H_{15/2}\rightarrow$ | $\lambda_p$ (nm) | E ($cm^{-1}$) | $f_{exp}$ | $f_{cal}$ | $\lvert\Delta f\rvert$ |
|---|---|---|---|---|---|
| $^4I_{15/2}$ | 456 | 21929 | 0.033 | 0.324 | 0.291 |
| $^4F_{9/2}$ | 472 | 21186 | 0.201 | 0.123 | 0.078 |
| $^6F_{3/2}$ | 753 | 13280 | 0.180 | 0.147 | 0.33 |
| $^6F_{5/2}$ | 796 | 12562 | 0.875 | 0.785 | 0.090 |
| $^6F_{7/2}$ | 895 | 11173 | 1.441 | 1.601 | 0.156 |
| $^6F_{9/2}$ | 1087 | 9199 | 1.581 | 1.555 | 0.034 |
| $^6F_{11/2}$ | 1262 | 7923 | 3.783 | 3.791 | 0.008 |
| $^6H_{11/2}$ | 1674 | 5973 | 0.963 | 0.900 | 0.628 |
| $\delta_{rms} = 0.128 \times 10^{-6}$ | | | | | |

The intensities of transitions obtained for BSbMgfSrD01 absorption spectra are resolved and expressed in the form of oscillator strengths ($f_{exp}$, $f_{cal}$). The values of $f_{exp}$ and $f_{cal}$ along with wavelengths, energies of absorption spectra of BSbMgfSrDy01 glass are unveiled in Table.2. The smaller $\delta_{rms}$ shows a significant adjustment between $f_{experimental}$ and $f_{calculated}$ values and the reliability of the J-O theory. The three parameters referred to as J-O intensity parameters $\Omega_\lambda$ (where $\lambda$ = 2, 4, 6) may provide a significant study of the rare earth ion bonding (RE ion covalency), locale structure, symmetrical environment in the RE-ion, viscosity and glass rigidity. These are calculated by using the principle of Judd-Ofelt (Swapna, K. et al., 2013) to experimentally test oscillator strengths. In this paper, the measured J-O parameters of BSbMgfSrD01 glass are shown in the Table 3. The values of $\Omega_\lambda$ (where $\lambda$ = 2, 4, 6) obtained suggest that $\Omega_2$ is stronger than $\Omega_4$ and $\Omega_6$ and this is followed the trend $\Omega_2 > \Omega_4 > \Omega_6$ relation. The phenomenon supports $Dy^{3+}$'s strong covalence with ligands and a more asymmetric environment around the host rare earth ion (Kiran, N, et al., 2013).

**Table 3: Judd - Ofelt values $\Omega_\lambda$ ($10^{-20}$ $cm^2$) and $\chi$ ($\Omega_4/\Omega_6$) of BSbMgfSrD01 glasses**

| Glass | $\Omega_2$ | $\Omega_4$ | $\Omega_6$ | $\chi$ | Trend |
|---|---|---|---|---|---|
| BSbMgfSrD01 | 4.27 | 0.87 | 2.33 | 0.37 | $\Omega_2 > \Omega_6 > \Omega_4$ |
| OFBD1.0 [ 18] | 27.9 | 11.2 | 0.97 | - | **$\Omega_2 > \Omega_4 > \Omega_6$** |
| PNABSDy10 [19] | 14.49 | 1.26 | 2.23 | **0.56** | **$\Omega_2 > \Omega_6 > \Omega_4$** |
| LSPDY10 [20] | 6.37 | 0.34 | 2.16 | **0.15** | **$\Omega_2 > \Omega_6 > \Omega_4$** |
| TBPDy10 [21] | 7.74 | 2.31 | 2.70 | **0.85** | **$\Omega_2 > \Omega_6 > \Omega_4$** |
| ZTWDy10 [22] | 6.91 | 0.99 | 1.01 | **0.89** | **$\Omega_2 > \Omega_6 > \Omega_4$** |
| Glass C [23] | 4.89 | 2.73 | 3.62 | **0.75** | **$\Omega_2 > \Omega_6 > \Omega_4$** |
| Glass D [23] | 4.18 | 1.65 | 3.03 | **0.55** | **$\Omega_2 > \Omega_6 > \Omega_4$** |

**Radiative Properties**

Table 4 gives band emission wavelength ($\lambda_p$ nm), effective bandwidth ($\Delta\lambda_{eff}$), energy (E $cm^{-1}$) and radiative properties, such as probabilities of radiative-transition ($A_R$) ($s^{-1}$), branching-ratio ($\beta_{exp}$ & $\beta_{cal}$), stimulated cross-sections of emission ($\sigma_{se}$) (x $10^{-22}$), radiative-lifetime $\tau_R$ (ms), band-width gain $\Delta\lambda_{eff}$ x $\sigma_{se}$ (x $10^{-28}$ $cm^3$) and $\sigma_{se}$ x $\tau_R$ (x $10^{-25}$ s) for the prominent transition emission. To measure radiative properties, the J-O factors $\Omega_\lambda$ (where $\lambda$ = 2, 4, 6) and the refractive index were used. The capacity for induced pollution in laser media is defined by a ratio $\beta_R$ ($\beta_{exp}$ & $\beta_{cal}$) and should be greater than or equivalent to 50% in a strong laser media. The present branching ratio of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is over 50% (0.55). For transformation n $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow) the maximum readings of $A_R$, $\beta_R$ and $\beta$se were obtained. Thus, the correct mechanism for lasing operation was considered. The band-width gain ($\Delta\lambda_{eff}$ x $\sigma_{se}$) and the optical-gain ($\sigma_{se}$ x $\tau_R$) for BSbMgfSrDy01 were found to be wide and this suggests that BSbMgfSrD01 glasses were ideal for the optical amplifier (Rao A.S. et al., 1998, Mahamuda S.K. et al., 2014, Thulasiramudu A et al., 2007). A comparison of $\lambda_p$, $\Delta\lambda_{eff}$, $A_R$, $\beta_R$ and $\sigma_{se}$ of yellow transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ for BSbMgfSrD01 emission spectra with literature reported for PNABSD, PKANbDy, DyPPbBi, BZABiD05, ZDTBF (Thulasiramudu A et al., 2007, Swapna K. et al., 2013) has been presented in Table.5.

**Table 4: Emission band wavelength ($\lambda_p$ nm), effective band width ($\Delta\lambda_{eff}$), energy (E $cm^{-1}$) radiative transition probabilities ($A_R$) ($s^{-1}$), branching-ratio ($\beta_{exp}$& $\beta_{cal}$ ), stimulated emission cross-sections ($\sigma_{se}$) (x $10^{-22}$), radiative-lifetime $\tau_R$ (ms), band-width gain $\Delta\lambda_{eff}$ x $\sigma_{se}$ (x $10^{-28}$ $cm^3$) and optical-gain $\sigma_{se}$ x $\tau_R$ (x $10^{-25}$ s) for the prominent emission transitions of BSbMgfSrD01 glass matrix.**

| Transition $^4F_{9/2} \rightarrow$ | $\lambda_p$ | E | $\Delta\lambda_{eff}$ | $A_R$ | Branching ratio($\beta_R$) | | $\sigma_{se}$ | $\Delta\lambda_{eff}$ x $\sigma_{se}$ | $\sigma_{se}$ x $\tau_R$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | $\beta_{exp}$ | $\beta_{cal}$ | | | |
| $^6H_{15/2}$ | 480 | 20796 | 17.42 | 95 | 0.15 | 0.23 | 2.3 | 4.0 | 5.71 |
| **$^6H_{13/2}$** | **573** | **17429** | **18.92** | **262** | **0.49** | **0.55** | **13.7** | **25.9** | **32.61** |
| $^6H_{11/2}$ | 663 | 15060 | 16.91 | 63 | 0.14 | 0.18 | 5.30 | 8.96 | 21.32 |
| $\tau_R$ = 2.38 | | | | | | | | | |

**Table 5: Emission band wavelength ($\lambda_p$ nm), energy (E $cm^{-1}$), effective band width ($\Delta\lambda_{eff}$), radiative transition probabilities ($A_R$) ($s^{-1}$), branching-ratio ($\beta_{exp}$ & $\beta_{cal}$ ), stimulated emission cross-sections ($\sigma_{se}$) (x $10^{-22}$), radiative-lifetime $\tau_R$ (ms) for $^4F_{9/2}\rightarrow{}^6H_{13/2}$ level of BSbMgfSrD01 glass matrix with various $Dy^{3+}$ doped glasses.**

| Glass | $\lambda_p$ | E | $\Delta\lambda_{eff}$ | $A_R$ | Branching ratio | | $\sigma_{se}$ |
|---|---|---|---|---|---|---|---|
| | | | | | $\beta_{exp}$ | $\beta_{cal}$ | |
| **BSbMgfSrD01** | **573** | **17429** | **18.92** | **262** | **0.49** | **0.55** | **13.7** |
| PNABSD [19] | 575 | 17391 | 17.19 | 955 | 0.71 | 0.77 | 2.92 |
| PKANbDy [27] | 575 | 17391 | 18.59 | 2245 | 0.55 | 0.72 | 6.40 |
| DyPPbBi [28] | 573 | 17429 | 14.3 | 1135 | - | 0.66 | 3.88 |
| BZABiD05 [29] | 577 | 17331 | 15.25 | 1225 | 0.47 | 0.62 | 36.25 |
| ZDTBF [30] | 574 | 17421 | 7.220 | 539 | 0.46 | 0.51 | 6.01 |

## CONCLUSION

For the present analysis the traditional melt-quenching technique for synthesizing the antimony-magnesium-strontium-oxyfluoroborate glass (BSbMgfSrD) doped dysprosium ($Dy^{3+}$) was used and the future laser applications are examined. The amorphous existence of these glasses was verified by XRD. The measurements of the J-O strength parameters $\Omega_\lambda$ (where $\lambda$ = 2, 4, 6) have been completed for BSbMgfSrD01 with the value $f_{exp}$ and $f_{cal}$. Higher value of $\Omega_2$ in the present glass device demonstrated strong covalence in the vicinity of the $Dy^{3+}$ molecule. A strong emission peak has observed at 575 nm below the wavelength of 425 nm excitation that corresponds to the transition of the $^4F_{9/2}\rightarrow{}^6H_{13/2}$ alleviation (Yellow) of the $Dy^{3+}$ ion. The radiative property of transitional transformation $^4F_{9/2}\rightarrow{}^6H_{13/2}$ in BSbMgfSrD01 such as branching ratio, transfer likelihood and stimulated emissions cross section has been found to be small, suggesting that the BSbMgfSrD01 gauzes are appropriate for yellow laser emission. These results show that BSbMgfSr glass 0.5 mole % $Dy^{3+}$ deposited which can be provide a medium of the emission of white light and laser applications at approximately 575 nm at a surge of 425 nm.

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