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Optical Properties of Dysprosium (Dy^{3+}) doped Fluoroborate Glasses

Y Lakshmi Prasad Reddy[1]*, Mohammed Waaiz[2] , S Nisar Ahmed[3] and C.V Krishna Reddy[4]

[1] Department of Physics, Sri Krishnadevaraya University
Anantapur, Andhra Pradesh, India

[2] Department of Physics, Rayalaseema University,
Kurnool, Andhra Pradesh, India

[3] Department of Physics, Osmania College,
Kurnool, Andhra Pradesh, India

[4] Department of Physics, Rayalaseema University,
Kurnool, Andhra Pradesh, India

Abstract
Different concentrations of dysprosium doped sodium magnesium zinc fluro borate (NaMgZnFB) glasses were synthesized by the conventional melt quenching method and characterized through absorption, excitation, visible luminescence and Raman spectroscopies. These Dy^{3+} doped glasses are studied for their utility for white light emitting diodes. From the emission spectra, a strong yellow emission that corresponds to the transition, $^4F_{9/2}\rightarrow{}^6H_{13/2}$, was observed and it also shows combination of blue, yellow and red emission bands for these glasses. Dy^{3+} glasses has shown about eight absorption bands at 425, 452, 470, 749, 798, 896, 1085, 1264 and 1648 nm respectively. The decay curves have been plotted to evaluate their lifetimes and emission mechanism that arise in the glasses have been explained. Scanning Electron Microscopy (SEM) of the sample indicates the amorphous nature of the glass matrix and Energy Dispersive X-ray Spectrometry (EDS) gives information about the elements which are present in the investigated glass samples. Coexistence of trigonal BO_3 and tetrahedral BO_4 units was evidenced by Raman spectroscopy. These glasses are expected to give interesting application in the field of optics. Notable improvements of optical and structural properties due to the doping dysprosium ions are evidenced. Excellent features of our results suggest that these glasses are promising for lasers and other device applications.
Keywords: Rare earth ion, Dysprosium, Absorption, Luminescence, Emission, Life decay, Raman, glasses.

1.Introduction
Rare earth doped glasses properties have been extensively studied in recent years due to their interesting applications in the field of optical communications, sensors, and solid-state lasers. Spectroscopic transitions of any rare earth (RE) ion will be dissimilar in different host due to surrounding field effect (1). Glasses and crystals doped with various rare earth (RE) ions are important materials for making fluorescent display devices, optical detectors, laser, optical fibers, waveguides and fiber amplifiers (2-4). Oxy-flouro borate glasses have been identified as good glassy materials due to their good glass forming ability, hardness, transparency and resistance towards the moisture and with an extended IR transmission ability [5-7]. Rare-earth (Dy^{3+}) ions show narrow and intense absorption bands in the NIR region and interesting emissions in the blue/yellow colours under an UV excitation source.[8]

2. Materials and Methods:
Sodium Magnesium Zinc Fluoro Borate (NaMgZnFB) glasses (G1, G2, G3, G4) doped with 0.5, 1.0, 1.5, 2.0 mol% of Dysprosium (Dy^{3+}) were prepared using conventional melt quenching technique. In the present work the glasses with the following molar composition were investigated $65H_3BO_3$+MgF_2(20-X) + 10NaF+5ZnO + X Dy_2O_3 where (X= 0.5, 1.0, 1.5, and 2.0). High purity chemicals H_3BO_3, NaF, MgF_2, ZnO and Dy_2O_3 are used as starting materials. The above chemicals are weighed in the above mol % ratio, well mixed, grinded and heated in an electric furnace with platinum crucible for about 1hour at a temperature 1050^0C . It is then cooled quickly to 350^oC and annealed at this temperature for 5 hours for eliminating mechanical and thermal strains. The optical absorption spectrum in the wavelength region from 300 nm to 1700 nm was recorded using UV-VIS-NIR (UV-3600 plus) Spectrophotometer. The excitation and photoluminescence (PL) spectral profiles of the Dy^{3+} doped glass matrices were recorded using Fluorolog flourimeter. Life decay spectra were recorded by

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Fluorolog-3 spectrophotometer. The Fluoroscence spectra in the range of 400-700nm were recorded with FL920 Edinburg using Xenon flash lamp as exciting source. Raman spectrum was performed by Raman Spectrophotometer (LabRAM HR800). The SEM with EDS images were recorded with Carl Zeiss EVO MA15 with EDS (Oxford INCA Penta FETX3) has been employed to investigate the morphological studies of the prepared glass samples. All the measurements are done at room temperature.

3. RESULTS AND DISCUSSION

3.1 Optical absorption

The absorption spectra of Dy^{3+} ions doped NaMgZnFB glasses in Visible and Near IR regions with varied concentration of 0.5, 1.0, 1.5 and 2.0 mol% is shown in figure-1. It is observed from the figure that, the absorption spectra exhibit nine absorption bands around 425, 452,470, 749, 798, 896, 1085, 1264 and 1648 nm due to the 4f9 electronic transition of the Dy^{3+} ions from the $^6H_{15/2}$ ground level to the various excited states such as $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, ($^6F_{11/2}$+$^6H_{9/2}$) and $^6H_{11/2}$ respectively[9]. Most of the absorption transitions of Dy^{3+} originate based on the selection rules of $|\Delta L| \geq 0$, $|\Delta J| \geq 0$ and $|\Delta S| = 0$. The high intense transitions in the infrared region are spin allowed ($\Delta S = 0$) and the transitions in the visible region are spin-forbidden [10-15].

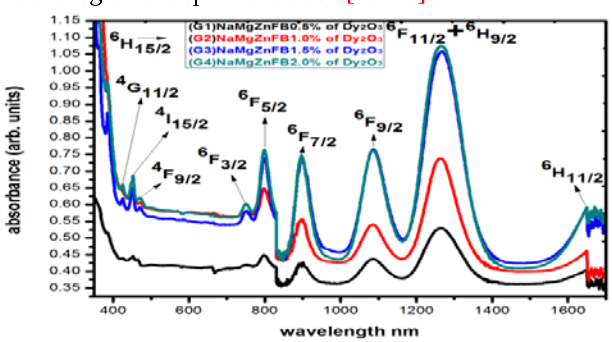

Figure 1: Absorption spectra of Dy^{3+}doped NaMgZnFB glasses.

3.2 Excitation spectra

The excitation spectrum of Dy^{3+} doped NaMgZnFB glasses is shown in Fig 2. It has the following seven excitation bands: $^6H_{15/2} \rightarrow {}^4M_{17/2}$ (323 nm), $^6H_{15/2} \rightarrow (^6P_{7/2} + {}^4M_{7/2})$ (350 nm), $^6H_{15/2} \rightarrow {}^4I_{11/2}$(364 nm), $^6H_{15/2} \rightarrow (^4F_{7/2} + {}^4I_{13/2})$ (387 nm), $^6H_{15/2} \rightarrow {}^4G_{11/2}$ (425 nm), $^6H_{15/2} \rightarrow {}^4I_{15/2}$ (452 nm), and $^6H_{15/2} \rightarrow {}^4F_{9/2}$ (471 nm). An intense excitation band possessed at $^6H_{15/2} \rightarrow {}^4I_{15/2}$ (450 nm) has been selected of Dy^{3+} glass for the measurement of emission spectrum because in the visible region it is having the highest OD value (1.45).

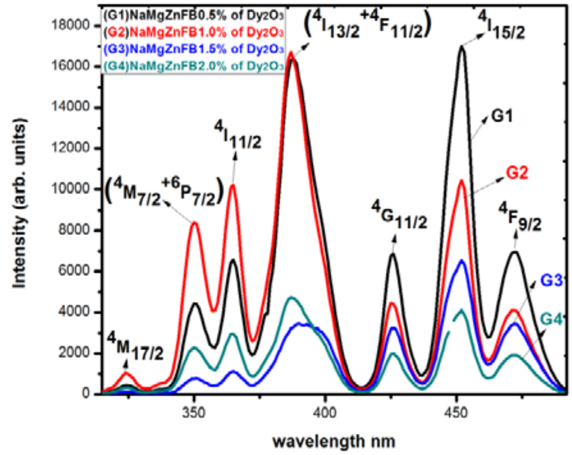

Figure 2: Excitation spectrum of Dy^{3+} doped NaMgZnFB glasses

3.3 Fluorescence properties

At an excitation of 410nm Dy^{3+} glasses shows three bands at 467 nm, 560 nm and 650 nm, which equivalent to the transitions of $^4F_{9/2} \rightarrow {}^6H_{15/2}$,$^4F_{9/2} \rightarrow {}^6H_{13/2}$ and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ respectively shown in Figure 3. The highest intensity is obtained at wavelength of 560nm corresponding to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. At 467 nm (blue), 560 nm (yellow) and 650 nm (red) are observed. It is observed that as the concentration of dysprosium increases, the emission intensity decreases from 0.5 mol % to 2.0 mol %. 0.5 mol% of dysprosium has been identified as optimized concentration. It is likely to be effect of concentration quenching. Among the three emission bands, the band at $^4F_{9/2} \rightarrow {}^6H_{13/2}$ is magnetic dipole (MD) transition possessing the most intense, $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition possessing moderate intensity, which is related to electric dipole (ED) transition, and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transition possessing the lowest intensity[16-18].

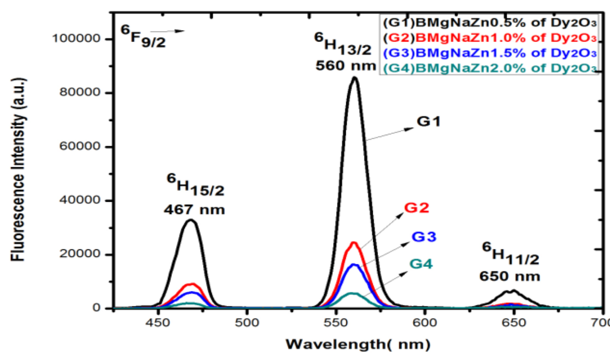

Figure 3: Fluorescence spectra of Dy^{3+} doped NaMgZnFB glasses.

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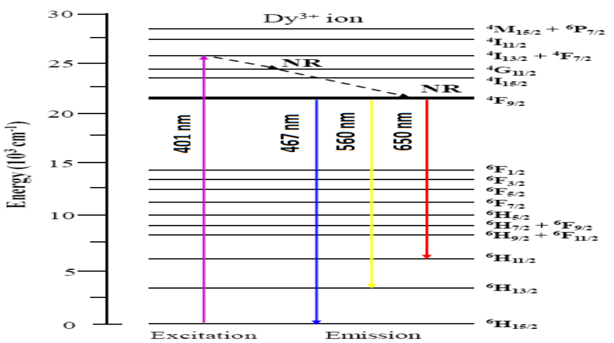

Figure 4: The partial energy level diagram of Dy^{3+} ions showing the possible emission transitions and non-radiative (NR) decay in Dy^{3+} doped NaMgZnFB glasses.

3.4 Decay lifetime

For all the sample glasses (G1,G2,G3,G4) with different concentrations the lifetime of the $^6F_{9/2}$ level of Dy^{3+} ions was measured under the excitation of 401 nm. By monitoring the florescence decay of $^6F_{9/2} \rightarrow {}^6H_{13/2}$ transition at room temperature the characteristic decay curves have been obtained for glass samples with 0.5, 1.0, 1.5, and 2.0 mol% of Dy^{3+} concentrations which are displayed in figure 5. Energy transfer process resulting in luminescence quenching is due to two different mechanisms. The first one is due to cross-relaxation between pairs of Dy^{3+} ions and another one is due to the migration of excitation energy which can accelerate the decay by energy transfer to the structural defects acting as energy sinks [19]. The life time has been found to be 207.46 ns for 0.5 mol%, 279.1 ns for 1.0 mol%, 355.63 ns for 1.5 mol%, and 498.49 ns for 2.0 mol% Dy^{3+} doped NaMgZnFB glasses.

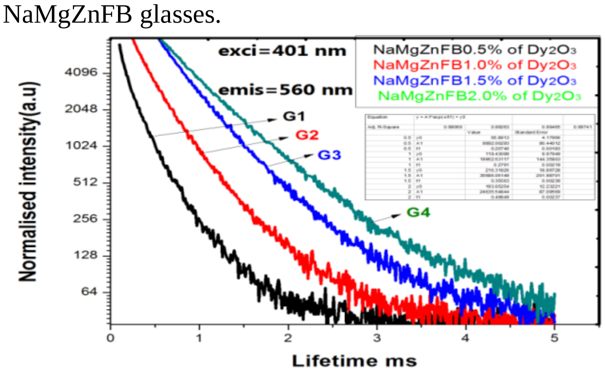

Figure: 5 Decay life time of Dy^{3+}: NaMgZnFB glasses

3.5 Raman spectra

Raman spectra of Dy^{3+} doped NaMgZnFB glass is shown in Fig. 6 and the absorption bands are listed in Table 1. In the present work, Raman spectrum shows different peaks at 101 cm^{-1} ,~ 473 cm^{-1} ,~ 779 cm^{-1} ,~ 986 cm^{-1} , ~1488 cm^{-1} , ~1728 cm^{-1},~2034 cm^{-1} and ~2426 cm^{-1} shown in Figure 6. From the Raman spectrum, it is observed that one high intensity band at 101 cm^{-1}, is related to the heavy metal Zn vibrations. The broad band at 355 cm^{-1} is assigned to vibrations of Zn–O–Zn band of ZnO_6 octahedral units [20–22]. The intense band at 585 cm^{-1} may be due to both vibrations of Zn–O stretching in ZnO_6 units and vibrations of ring type metaborate groups. The bands at 727 cm^{-1}, 727 cm^{-1}, 833 cm^{-1} and 917 cm^{-1} are owing to vibrations of different borate groups such as metaborate, pyroborate and orthoborate, respectively [23–26]. At 1170 cm^{-1}, the spectra consist of a band due to the symmetric stretching vibrations of terminal B–O$^-$ bands in pyroborate groups [27]. The bands centered at 1304 cm^{-1} and 1586 cm^{-1} correspond to the B–O stretching vibrations in various borate groups [28-29].

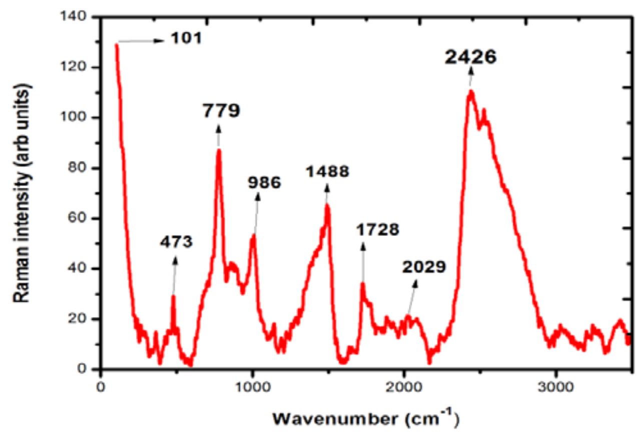

Figure 6: Raman spectra of Dy^{3+} doped NaMgZnFB glass matrics

Table 1

S.No	Wave number (cm^{-1})	Raman assignment
1	101	Metal Zn^{3+} vibrations
2	473	Zn-o-Zn stretching vibrations of Zno_6 of units
3	779	Both Zn-o$^-$ stretching vibrations of Zno_6 of units and rig type metaborate vibrations.
4	986	Vibrations of chain type metaborate groups
5	1488	Vibrations of pyroborate groups
6	1728	Vibrations of orthoborate groups
7	2034	Symmetric stretching vibrations of B–O bands in pyroborate groups
8	2426	B–O stretching vibrations involving non bridging oxygen (NBO) in various borate groups

3.6 SEM

The SEM micrograph of the Dy^{3+} doped NaMgZnFB glasses is shown in Fig.7, respectively. In SEM micrograph shows that it is nearly perfect homogeneous and unsolved particles are not seen. Doping Dy_2O_3 of Sodium Magnesium Flouroborate glasses has got a fine surface feature.

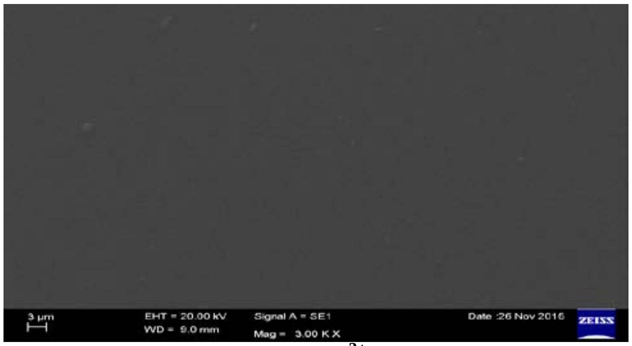

Figure 7: SEM image of Dy^{3+} doped NaMgZnFB glasses

3.7 EDS

The spectroscopy (EDS) is a standard procedure for identifying and quantifying elemental composition with the standard element .The elemental analysis has been carried out from the EDS spectral profile as shown in Figure 8. The deficiency of F may be due to its low melting temperature and there by evaporating after 250°C which is clearly visible in the EDS spectrum in figure 8. The spectrum gives the information about the elements which are present in the investigated glass samples. EDS spectra clearly show elemental composition for optimum sample.

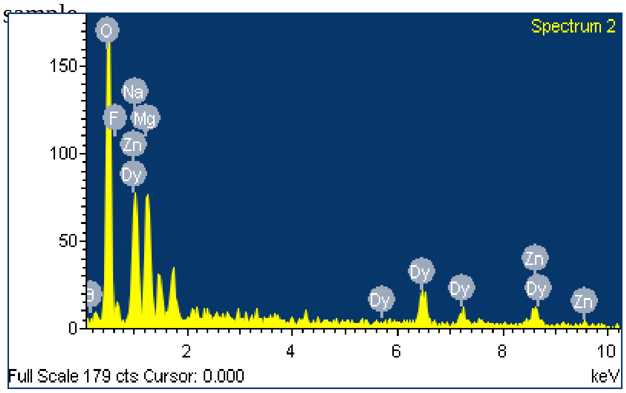

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Figure 8: EDS of Dy^{3+} doped NaMgZnFB glasses

4. CONCLUSIONS

From the absorption spectra, various absorption transitions are assigned. From these transitions, one transition is chosen for excitation of dysprosium ions and emission spectra are recorded. From emission spectra, four luminescence transitions are observed. Among these transitions, emission transition at 560 nm has high in intensity. With the increases of content of Dysprosium, concentration quenching is observed. Decay curves of the visible emissions have been plotted to measure life times. The structural, morphological and compositional analysis of host glass has been demonstrated by RAMAN shift, SEM and EDS spectroscopic studies. From the EDS confirmed the presence of all elements in Dy^{3+} doped fluoroborate glass matrices. From the results of these investigations, it is concluded that the 0.5 mol% of Dy^{3+} doped fluoroborate glass is more useful for wavelength nearly at 467 nm(blue),560 nm (yellow) and 650 nm (red) are observed, luminescent photonic device applications. It was found suitable for wide range of applications in the field of spectral hole burning process, photovoltaic cells and other laser applications.

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