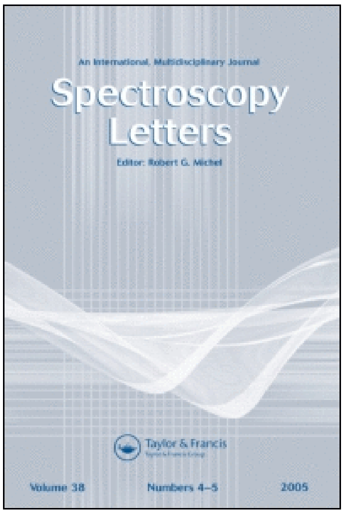

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

LUMINESCENCE PROPERTIES OF Eu^{3} DOPED ZnO-B_2O_3-SiO_2 GLASSES

N. Sooraj Hussain[a]; Y. Prabhakara Reddy[a]; S. Buddhudu[a]
[a] Department of Physics, Sri Venkateswara University, Tirupati, India

Online publication date: 13 June 2002

To cite this Article Hussain, N. Sooraj , Reddy, Y. Prabhakara and Buddhudu, S.(2002) 'LUMINESCENCE PROPERTIES OF Eu^{3} DOPED ZnO-B_2O_3-SiO_2 GLASSES', Spectroscopy Letters, 35: 2, 275 — 283
To link to this Article: DOI: 10.1081/SL-120003812
URL: http://dx.doi.org/10.1081/SL-120003812

SPECTROSCOPY LETTERS, 35(2), 275–283 (2002)

LUMINESCENCE PROPERTIES OF Eu^{3+} DOPED ZnO-B_2O_3-SiO_2 GLASSES

N. Sooraj Hussain,* Y. Prabhakara Reddy, and S. Buddhudu

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

ABSTRACT

This short paper summarizes the preparation and optical characterization of the Eu^{3+} (X = 0.2,0.5,1.0,1.5 & 2.0 mol%) doped 60ZnO+20B_2O_3+(20-X) SiO_2 glasses from the measurement of their excitation and luminescence spectra at the room temperature. Dependence of red emission performance upon the excitation wavelengths in the UV to near visible range has been investigated and it has been observed that these optical glasses display bright red emission at $\lambda_{ex} = 395$ nm with the three excitation wavelengths ($\lambda_{ex} =$ 395 nm, 380 nm and 362 nm) used. The concentration quenching phenomenon has been observed after a particular value of the dopant europium ions availability (beyond 1 mol%) in the glass matrices studied and hence the presence of 1 mol% of Eu^{3+} in the glass composition has been chosen as the ideal content for achieving brighter red fluorescence performance. Besides carrying out their luminescence study,

*Corresponding author: E-mail: nshussain72@yahoo.co.in

different physical properties such as refractive index, density, other related factors from these two quantities and also non-linearity properties of these glasses are reported in this paper.

Key Words: Luminescence properties; Europium; Silicate glasses

INTRODUCTION

The OH related capacitance voltage recovery effects in MOS capacitors passivated by fluoride containing zinc-boro-silicate glasses have been examined earlier[1]. Electrical and non-linear properties of such boro-silicate glasses have also been studied in literature[2,3]. It has been found that zinc-boro silicate glasses $60ZnO+20B_2O_3+20SiO_2$ doped with 0.2 mol% Tb_2O_3 exhibit phosphorescence after exciting with an UV source at 254 nm. This phosphorescence arises from f-f transitions of Tb^{3+} ions and is observable by the eye, in the dark up to one hour after stopping the UV-illumination. Electron spin resonance (ESR) measurement shows that electron-trapping centers, associated with Zn ions, are formed by the UV irradiation and the phosphorescent center decay after the irradiation stopped. It has been suggested that this UV induced center is the photo induced electron trap, which serves [effectively as an electron donor, in the dark[4]. A strongly enhanced luminescence efficiency of zinc-borate glasses and glass fibers doped with trivalent europium or terbium has been contemplated. Such enhancements have been attributed to a high content of direct gap ZnO nanocrystallites that operate as sensitizer for the rare-earth ions. The glasses have a low softening point and are designed to be compatible with the silicon technology[5] A strategy to create an oxide glass with long lasting phosphorescence (LLP) utilizing oxygen ion vacancy (V-O) associated with network modifying cations as electron traps has been proposed. LLP is a result of combination of V-O and multi-valent luminescent cations (Ln^{3+}). The LLP originates from a recombination of a photo oxidized luminescent ion (Ln^{3+}) with an electron thermally released from a V-O site. We found that oxide glasses exhibiting photo chromism based on photochemistry of V-O such as $ZnO+B_2O_3+SiO_2$ glasses[6]. As a preliminary work, we have earlier reported the emission properties of Cu^+ doped $ZnO+B_2O_3+SiO_2$ glasses[7]. According to Auzel and Pelle, emission performance of the luminescent materials could change depending upon the excitation wavelengths employed[8]. This paper reports briefly the red luminescent characteristics of Eu^{3+} doped $ZnO+B_2O_3+SiO_2$ glasses as function of excitation wavelengths: $^7F_0 \rightarrow {}^5L_6$ (395 nm); $^5L_7$ (380 nm), $^5L_8$ (362 nm).

EXPERIMENTAL STUDIES

Zinc borosilicate glasses with the following chemical composition of Eu^{3+}: $60ZnO+20B_2O_3+(20\text{-}X)SiO_2$ (X = 0.2,0.5,1.0,1.5 and 2.0 mol%) were prepared by employing quenching technique[9–11]. The raw chemicals (ZnO, H_3BO_3, SiO_2 and Eu_2O_3) of 99.99% purity used for this purpose were obtained from the Alfa Aesar of John Matthey Company, Ward Hill, USA. In each batch, about 10 g of the mixture was melt in a computer controlled electric furnace at 1300°C for three hours and quenched in between two flat stainless steel plates to obtain optical quality glasses in circular designs. These glasses were annealed at 550°C for an hour towards the prevention of air gaps if any and to ensure the uniform distribution of the dopant europium ions in the glass matrices studied. Besides the production of these five-europium glasses one reference glass in the composition of $60ZnO+20B_2O_3+20SiO_2$ was also prepared. These glasses were found to be good in transparency and transmission between 0.35 and 4.0 mm and resistant towards the moisture. For this reference glass, physical properties such as the refractive index (n_d) was obtained to be 1.7813 with a Na-vapor lamp at $\lambda_d = 589.3$ nm on a Abbe-refractometer. By employing the Archimede's principle with the xylene as an immersion liquid, glass density (d) was determined to be 4.0318 g/cm^{-3}. Both the excitation and luminescence spectral measurements of these europium glasses were carried out on a Spex Fluorolog-3 Spectroflurometer (Model FL3-21) and this system comes with a Xe-cw-source (450 W) and also a Xe-flash lamp as the excitation sources. This system comes with a room temperature R928 detector for signal detection. While measuring the lifetimes of the emission transitions, the fluorimeter was fitted with a 1934D phosphorimeter. This Spex system employs a Datamax software package in acquiring the spectral and lifetime data from the system in order to apply with the origin program in the analysis of the results. Under an UV source, these glasses have demonstrated a bright red luminescence lasting for more than half an hour even after the UV source was turned off. Thus these europium glasses could be identified as the red phosphorescent optical materials for potential applications as luminescent glasses.

RESULTS AND DISCUSSION

With the obtained values of glass density and refractive indices at three different wavelengths ($\lambda_c = 656.3$ nm, $\lambda_d = 589.3$ nm and $\lambda_F = 486.1$ nm), a few physical and non-linearity properties concerning the Eu^{3+} doped zinc boro-silicate glasses have been calculated by using the relevant expres-

Table 1. Physical Properties Such as Average Molecular Weight ($\overline{M}$) Density (d), Mean Atomic Volume (V), Molar Refractivity (R_M) Rare-Earth Ion Concentration (N), Electronic Polarizability (α_e), Dielectric Constant (ε), Reflection Losses (R%), Polaron Radius (r_p), Inter-ionic Distance (r_i) and Field Strength (F) of Eu^{3+}-Doped Zinc Boro-silicate Glass

Physical Properties	
$\overline{M}$ (gm)	76.12
d (gm/cm^3)	4.0318
V ($gm.cm^3$/atom)	0.0670
R_m (cm^{-3})	7.9311
N (10^{22} ions $/cm^3$)	3.1901
α_e (10^{-24} cm^{-3})	3.1436
ε	3.1730
R%	7.8911
r_p (Å)	1.2707
r_i (Å)	3.1531
F (10^{16} cm^{-2})	1.8580

Table 2. Non-linearity Properties Such as Refractive Indices n_C at $\lambda_C = 656.3$ nm, n_d at $\lambda_d = 589.3$ nm, and n_F at $\lambda_F = 486.1$ nm, Abbe Number (ν_d), Glass Dispersive Power (${\nu^{-1}}_d$) Non-linearity Refractive Index (n_2), Non-linearity Refractive Index Coefficient (γ), and Non-linearity Susceptibility ($\chi^{e(3)}_{111}$) of Eu^{3+}-Doped Zinc Boro-silicate Glass

Non-linearity Properties	
n_C (656.3 nm)	1.7711
n_d (589.3 nm)	1.7813
n_F (486.1 nm)	1.7819
ν_d	72
${\nu_d}^{-1}$	0.0139
n_2 (10^{13} esu)	1.9902
γ(10^{15} cm^2 /w)	4.6831
$\chi^{e(3)}_{111}$ (10^{15} esu)	9.4038

sions[12–16] and the results are presented in Tables 1 and 2. From these results it is observed that based on the Abbe number of the Eu^{3+} glass this material could be suggested as a good optical material[14]. The visible excitation spectrum of Eu^{3+} doped zinc boro-silicate glass has been shown in Fig. 1, revealing excitation bands of $^7F_0 \rightarrow {}^5L_6$ (395 nm), $^7F_0 \rightarrow {}^5L_7$ (380 nm),

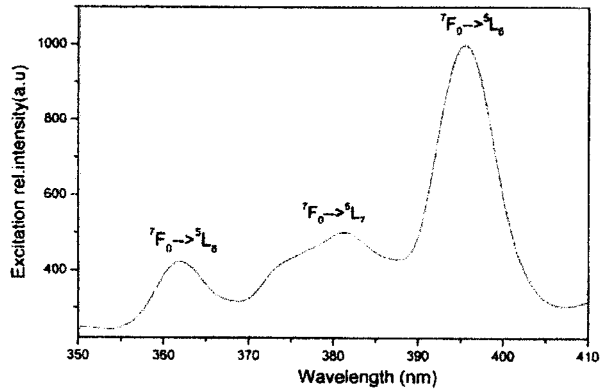

Figure 1. Visible excitation spectrum of Eu^{3+}(1 mol%): $60ZnO$-$20B_2O_3$-$19SiO_2$ glass.

$^7F_0 \rightarrow ^5L_8$ (362 nm). Among these, a stronger excitation peak at 395 nm has been chosen as monitoring wavelength in recording the emission spectra of Zinc boro-silicate glass doped with europium in different (0.2, 0.5, 1.0, 1.5 and 2.0 mol%) concentrations in order to examine the concentration effect. All these glasses have displayed the following four emission peaks: $^5D_0 \rightarrow ^7F_1$ (593 nm); $^7F_2$ (612 nm); $^7F_3$ (652 nm); $^7F_4$ (697 nm). Bright reddish-orange color has been observed from all these samples since the spectra are dominated by two main emission transitions ($^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$) at 593 nm and 612 nm wavelengths respectively as it is evidenced from Fig. 2. From

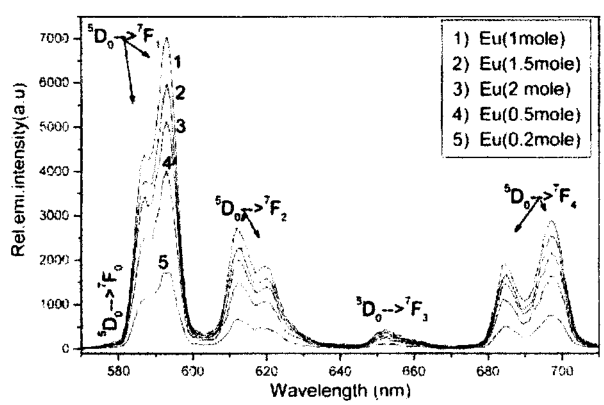

Figure 2. Luminescence spectra of Eu^{3+} (x = 0.2, 0.5, 1.0, 1.5, and 2.0 mol%) doped $60ZnO$-$20B_2O_3$-$19SiO_2$ glasses.

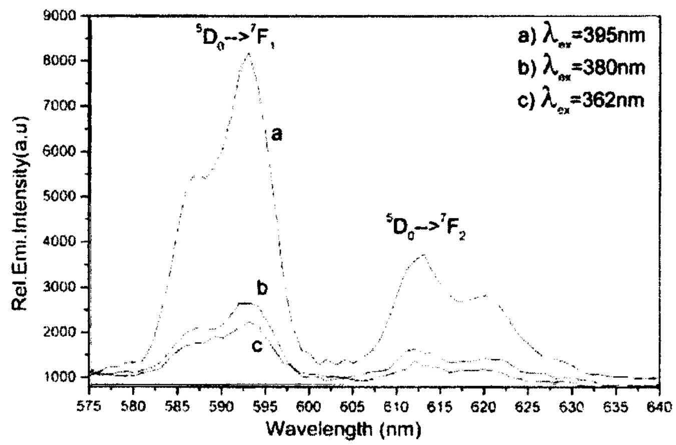

Figure 3. Luminescence spectra of Eu^{3+}(1 mol%): 60ZnO-20B_2O_3-19SiO_2 glass at different visible excitation wavelengths.

this figure it could also be seen that, the intensities of the emission transitions are increasing gradually from 0.2 to 1.0 mol% and beyond this concentration the emission intensities are diminishing due to the concentration quenching process. According to Auzel[17] and Meijeriak & Blasse[18] the decrease in emission intensity after reaching a critical concentration of the dopant ion is because of the formation of dopant ion clusters at higher concentrations. Hence an optimum concentration of the europium glasses

Table 3. Effective Band Width ($\Delta\lambda p$ nm) and Stimulated Cross Section ($\sigma^{P}{}_{E}$ X10^{21}) and Lifetimes (τ_m) of the Emission Transitions ($^5D_0 \rightarrow {}^7F_{1\&2}$) at 593 nm and 612 nm Respectively of Eu^{3+}-Doped (1 mol%): 60ZnO-20B_2O_3 -19SiO_2 Glass upon Different Excitation Wavelengths

	Emission Transitions					
	$^5D_0 \rightarrow {}^7F_1$ at 593			$^5D_0 \rightarrow {}^7F_2$ at 612		
	Excitation Wavelengths (λ_{ex})			Excitation Wavelengths (λ_{ex})		
Property	395 nm	380 nm	362 nm	395 nm	380 nm	362 nm
$\Delta\lambda p$	4	4	4	4	4	4
σ_p^E	5.99	6.22	9.04	7.33	7.45	7.48
τ_m	3.42	3.30	2.26	3.17	3.12	3.10

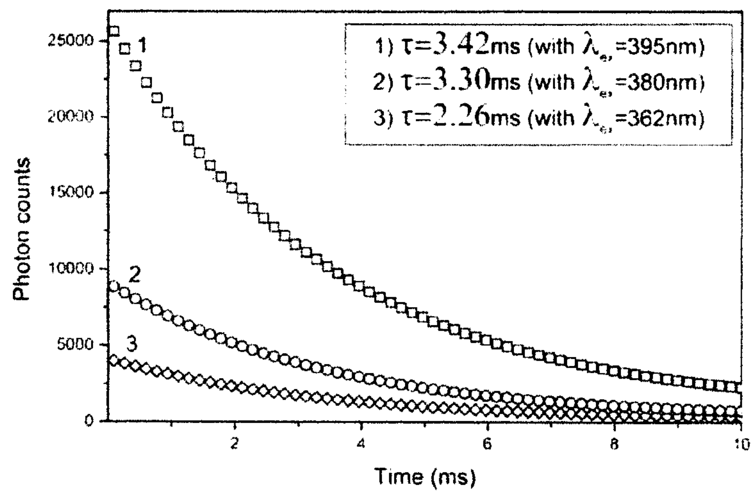

Figure 4. Decay curves of the emission transition (593 nm) of Eu^{3+} (1 mol%): 60ZnO-20B_2O_3-19SiO_2 glass at different excitation wavelengths.

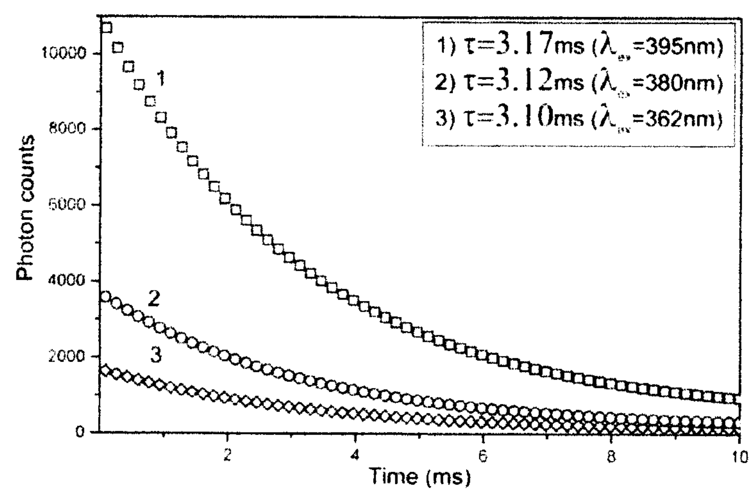

Figure 5. Decay curves of the emission transition (612 nm) of Eu^{3+}(1 mol%): 62ZnO-20B_2O_3-19SiO_2 glass at different excitation wavelengths.

have been evaluated as 1 mol% for the brighter emission performance from these phosphorescent glasses. The glass with an optimum concentration (1mol%) has been excited with all the three recorded excitation bands in order to study their effects on the fluorescence intensities and decay-times as well. Figure 3 shows the recorded emission spectra of Eu^{3+}(1 mol%) doped zinc boro-silicate glass in the wavelength range from 575 nm to 640 nm with three different wavelengths. It is clear from this figure that, the measured emission transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ show changes in their intensities depending upon the excitation. The evaluated values of effective bandwidths ($\Delta\lambda_p$ nm) and stimulated emission cross-sections ($\sigma_p{}^E$) for these two emission peaks have been listed for comparison in Table 3. The same table gives the lifetime data of these emission peaks obtained from the measured decay curves. The decay curve profiles are presented in Figs. 4 and 5. From these figures and Table 3, notable dependence of excitation wavelengths on the lifetimes of emission transitions has clearly been evidenced.

CONCLUSIONS

The glasses in the chemical composition $60ZnO+20B_2O_3+(20-X)SiO_2+X\ Eu_2O_3$ (X = 0.2, 0.5, 1.0, 1.5 and 2.0 mol%) were prepared in order to study the concentration effects and dependence of excitation wavelengths on the emission properties of the dopant Eu^{3+} ion. The intensities of the emission transitions are observed to be increasing gradually from 0.2 to 1.0 mol% of Eu^{3+} content and beyond this concentration, the emission intensities are diminishing due to the concentration quenching process. Hence 1.0 mol% dopant ion concentration has been taken as an optimum for a bright emission performance. The zinc boro silicate glass with 1mole% of europium ion displayed the significant changes in their relative fluorescence intensities and lifetimes. Important physical and non-linearity properties have been evaluated with the measured glass density and determined refractive indices and these results suggest that this Eu^{3+} doped zinc boro-silicate glass could be used as a strong red-luminescent glass.

REFERENCES

1. Kobayashi, K. J Solid State Chem. **1995**, *118*, 212.
2. Lee, Y.S.; Tseng,T.Y. J Mater. Sci. Mater. El. **1997**, *8* (2), 115.
3. Lee, Y.S.; Tseng, T.Y. J Mater. Sci. Mater. El. **1998**, *9*, 65.

4. Yamazaki, M.; Yamakoto, Y.; Nagahama, S.; Mizuguchi, M.; Hosono, H. J Non Crystal Solids **1998**, *241* (1), 71.
5. Ruter, D.; Bauhofer, W. Appl. Phys. Lett. **1996**, *69* (7), 892.
6. Kinoshita, T.; Hosono, H. J. Non-Crystal. Solids **2000**, *274* (1–3), 257.
7. Annapurna, K.; Anil Kumar.; Dwivedi, R.N.; Sooraj Hussain, N.; Buddhudu, S. Mater. Lett. **2000**, *45*, 23.
8. Auzel, F.; Pelle, F. J Lumin. **1996**, *69* (5/6), 249.
9. Nasu, H.; Sugimoto, S.; Matsuoka, J.; Kamiya, K. J Non-Crystal.-Solids **1995**, *182*, 321.
10. Shen, Z.J.; Ekstrom, T.; Nygrem, M. J Am Ceram Soc. **1996**, *79*, 721.
11. Thomas, S.; Philips, J. Phys Status Solid **1997**, *B200* (2), 359.
12. Shankar, A.; Dasgupta, A.; Basu, B.; Paul, A. J Mater. Sci. Lett. **1978**, *4*, 679.
13. Ahmed, M.M.; Hogarth, E.A.; Khan, M.N. J Mater Sci. **1984**, *19*, 4041.
14. Boiling, N.L.; Glass, A.J. IEEE J Quantum Electron. **1978**, *14*, 601.
15. Kim, S H.; Yoko, T.; Sakka S. J Am Cermaic Soc. **1993**, *76*, 865.
16. Annapurna, K.; Buddhudu, S. J Solid State Chem. **1991**, *93*, 454.
17. Auzel, F.E. Upconversion by Energy Transfer (World Scientific) Singapore, 1985.
18. Meijerink, A.; Blasse, G. J Lumin. **1989**, *43*, 283.

Received January 17, 2001
Accepted November 15, 2001