International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.6, pp 3276-3279, Aug-Sep 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Dy^{3+} doped oxy-fluoride phosphate glasses for laser materials: A photoluminescence study

S. Babu, A. Balakrishna, D. Rajesh, Y.C. Ratnakaram*

Department of Physics, S.V. University, Tirupati-517 502, Andhra Pradesh, India

***Corres.author: ratnakaramsvu@gmail.com**

Abstract: Spectroscopic properties of 0.5M Dy^{3+} embedded in $49.5P_2O_5$-$10AlF_3$-$10BaF_2$-$10SrF_2$-10PbO-10M (M = Li_2O, Na_2O, K_2O, ZnO and Bi_2O_3) fluoro-phosphate glasses (FP) were prepared by melt quenching technique and investigated through optical absorption, photoluminescence and CIE color co-ordinate mainly as function of different metal cations. Based on Judd-ofelt theory, three spectral intensity parameters Ω_λ (λ= 2, 4, 6) were calculated from absorption spectra. The variations of these parameters in different host glasses are discussed. These parameters are also used to determine radiative properties such as radiative transition probabilities (A_R), radiative lifetimes (τ_R), and branching ratios (β_R) of Dy^{3+} transitions from the excited state manifolds to corresponding lower laying multiplet manifolds. Luminescence spectra show two intense and one weak band due to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue), $^6H_{13/2}$ (yellow) and $^6H_{11/2}$ (red) transitions respectively. CIE chromaticity coordinates (x, y) are calculated for different glasses to evaluate the white light emission from luminescence spectra. Such luminescent glasses are expected as to find potential applications such as solid state white light systems.
Keywords: Absorption; Judd-Ofelt; Luminescence; White light emission.

1. Introduction and Experimental:

The 4f–4f electronic transitions of rare-earth ions play an important role in the applications like optical fiber amplifiers, solid state lasers, planar waveguides and compact microchip lasers (1). The present interest in the selection of fluoro-phosphate glasses is due to their high transparency in UV-NIR region and higher emission cross sections. Among the trivalent rare-earth ions, Dy^{3+} ($^4F_9$) is one of the interesting ion, because Dy^{3+} doped glasses have been considered as promising luminescent materials in the blue–yellow region ($^4F_{9/2}\rightarrow{}^6H_{15/2,13/2}$) (2). In the present work, syntheses of different FP glasses doped with dysprosium ions (Dy^{3+}) are reported. The optical absorption, photoluminescence and CIE color coordinates for these glasses have been characterized and analyzed. From the absorption spectra, Judd-Ofelt parameters were determined from which radiative parameters such as total radiative transition probabilities (A_T), radiative life times (τ_R) and branching ratios (β_R) are calculated. From luminescence spectra peak stimulated emission cross-sections (σ_p) and color co-ordinates (x,y) are calculated. To explore different metal cations on luminescence of FP glasses doped with Dy^{3+} in the system $49.5P_2O_5$-$10AlF_3$-$10BaF_2$-$10SrF_2$-10PbO-10M-$0.5Dy_2O_3$ (where M= Li_2O, Na_2O, K_2O, ZnO and Bi_2O_3) prepared by melt quenching technique and these glasses are labeled as G1, G2, G3, G4 and G5 respectively.

2. Results and Discussion:

The optical absorption spectra of Dy^{3+} doped different FP glasses recorded in the 320-1800 nm spectral region. Totally, ten transitions are observed. Among different FP glasses, sodium mixed FP glass has higher spectral intensity i.e. 18.90 X10^{-6} cm^2 for the transition $^6H_{15/2}\rightarrow$ $^6F_{11/2}+^6H_{9/2}$ and it is a hypersensitive transition of Dy^{3+} ion. When the environment of Dy^{3+} is of low symmetry, the field gradient imposed by ligand on the Dy^{3+} ion appears and the magnitude of induced f→ f transition is high, yielding high spectral intensity. Based on Judd-Ofelt theory (3), three spectral intensity parameters Ω_λ (λ= 2, 4, 6) were calculated from absorption spectra and presented in Table 1. The Ω_2 parameter is related to covalency of the rare earth ion site. While Ω_4 and Ω_6 are long range parameters related to rigidity and viscosity. Covalency found to be higher at sodium and lower at lithium mixed FP glasses. Rigidity and viscosity (Ω_6) found to be decrease in the order of Na→ Bi→ K→ Li→ Zn FP glass. It is noted that the predicted radiative transition probability for the transition $^4F_{9/2}\rightarrow^6H_{13/2}$ of Dy^{3+} doped sodium mixed FP glass is 2075 s^{-1}, which is higher than another kind of FP glasses. Among different FP glasses, zinc mixed glass matrix shows higher radiative lifetimes (τ_R) 2.394 ms and sodium mixed glass matrix shows lower τ_R 0.345 ms. Higher emission probability leads to faster decay of that emission level and hence shortening of the radiative lifetime.

Luminescence spectral profiles of different FP glasses for Dy^{3+} ion exited at 387 nm is presented in Fig.1. Two bands corresponding with the transitions $^4F_{9/2}\rightarrow$ $^6H_{15/2}$ (blue) and $^4F_{9/2}\rightarrow^6H_{13/2}$ (yellow) are considerably more intensive than the third weak band related to $^4F_{9/2}\rightarrow^6H_{11/2}$ (red) transition. Intensities of these bands are strongly influenced by the kind of metal cations which is noticed from the Fig. 1. In the present work, highest luminescence intensity is observed for sodium mixed FP glass. The transition $^4F_{9/2}\rightarrow^6H_{13/2}$ is purely electric dipole (ED) where as the transition $^4F_{9/2}\rightarrow^6H_{15/2}$ is magnetic dipole (MD) allowed one. In the present work, intensity of ED transition is greater than MD transition in all FP glasses evident more asymmetry of Dy^{3+} ions. In the present work, Yellow/Blue ratio values as 1.106, 1.176, 1.108, 1.113 and 1.005 corresponding to Li, Na, K, Zn and Bi FP glasses. Higher value of Y/B in sodium mixed FP glass indicates higher degree of covalency between Dy^{3+} and oxygen ions and lowering of symmetry. This assumption is also consistence with the higher Ω_2 J-O intensity parameter. Various luminescence properties are presented in Table 2. The experimental branching ratios β_{exp} for all glasses are found to be in the order of $^4F_{9/2}\rightarrow^6H_{13/2}$ >$^6H_{15/2}$ >$^6H_{11/2}$. Branching ratios of yellow emission transition is found to be the highest one and considered as luminescent transition. Further, comparison of β_{exp} values for all FP glasses, higher magnitude for the glass mixed with sodium (52%) is more appropriate modifying monovalent cation. A good luminescent transition can have a large emission cross section (σ_p). It is observed that the transition, $^4F_{9/2}\rightarrow^6H_{13/2}$ shows higher σ_p i.e. 4.08 X 10^{-21} cm^2 at λ_p= 576 nm in sodium mixed FP glass. To obtain near-white emission, the Y/B ratio of Dy^{3+} ions needs to be close to 1. It can be seen that all FP glasses have close to 1, but the emission intensity is different one. For all Dy^{3+} doped FP glasses, the color coordinates are located nearer to white light region. The color coordinates (x,y) calculated for sodium mixed FP glass and found to be (0.37, 0.31) as indicated in Fig.2. Due to simultaneous emissions of Dy^{3+} in the blue, yellow and red ranges, dysprosium ion possess the unique prospect of realizing white light (4).

Table 1 Judd-Ofelt parameters (Ω_λ,x10^{-20} cm^{-2}) of Dy^{3+} doped fluoro-phosphate glass matrix with different metal cations.

S.No	Glass	Ω_2	Ω_4	Ω_6	Trend
1	**G1**	06.83	3.14	1.60	Ω_2>Ω_4>Ω_6
2	**G2**	20.45	3.15	4.27	Ω_2>Ω_6>Ω_4
3	**G3**	14.27	1.58	2.78	Ω_2>Ω_6>Ω_4
4	**G4**	06.89	1.15	1.33	Ω_2>Ω_6>Ω_4
5	**G5**	11.21	1.63	3.12	Ω_2>Ω_6>Ω_4

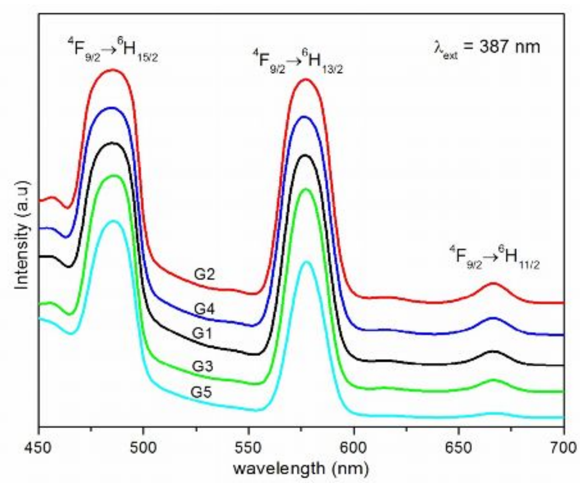

Fig.1 luminescence spectra of Dy^{3+} doped fluoro-phosphote glass matrix with different metal cations

Table 2 Transition probabilities (A) (s^{-1}), peak stimulated emission cross-sections (σ_P, $x10^{-21}cm^2$), experimental branching ratios (β_{exp}, %) of $^4F_{9/2}$ state of Dy^{3+} doped fluoro-phosphate glass matrix with different metal cations.

Glass	$^4F_{9/2}\rightarrow$	A	σ_P	β_{exp}	Color co-ordinates (x, y)
G1	$^6H_{15/2}$	170	0.16	46	
	$^6H_{13/2}$	764	1.87	51	(0.31, 0.27)
	$^6H_{11/2}$	79	0.35	3	
G2	$^6H_{15/2}$	397	0.32	45	
	$^6H_{13/2}$	2075	4.08	52	(0.37, 0.31)
	$^6H_{11/2}$	222	1.44	3	
G3	$^6H_{15/2}$	247	0.23	46	
	$^6H_{13/2}$	1415	3.13	51	(0.28, 0.30)
	$^6H_{11/2}$	154	0.76	3	
G4	$^6H_{15/2}$	128	0.11	46	
	$^6H_{13/2}$	693	1.54	51	(0.27, 0.27)
	$^6H_{11/2}$	75	0.39	3	
G5	$^6H_{15/2}$	281	0.30	49	
	$^6H_{13/2}$	1206	2.91	49	(0.35, 0.27)
	$^6H_{11/2}$	125	0.53	2	

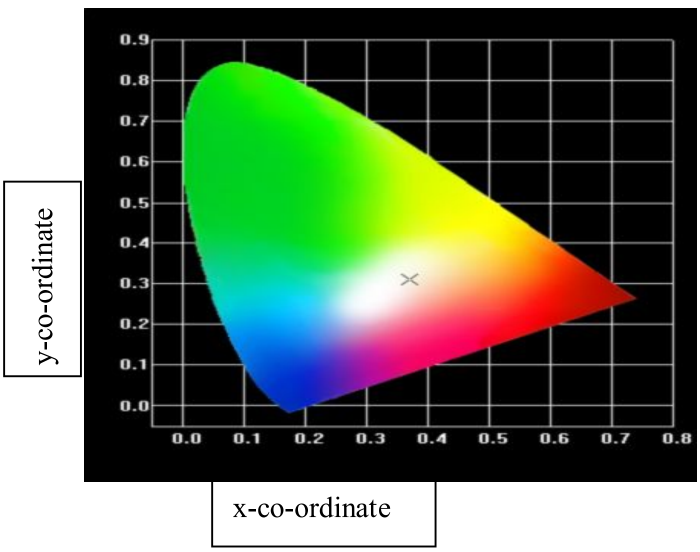

Fig.2. shows color chromaticity diagram of Dy^{3+} doped sodium mixed fluoro-phosphate glass.

Acknowledgment:

The author YCR expresses his thanks to UGC, New Delhi for providing financial support in the form of MRP Project. One of the authors S. Babu would like to thank UGC for the sanction of JRF under Research Fellowship in Sciences for Meritorious students (RFSMS) scheme.

References:

1. Vijaya Kumar M.V., Jamalaiah B.C., Rama Gopal K, Reddy R. R, Optical absorption and fluorescence studies of Dy^{3+}-doped lead telluroborate glasses. J Lumin 2012, 132, 86–90.
2. Raja J Amjad, Sahar M. R, Ghoshal S. K, Dousti M. R, Arifin R, Synthesis and characterization of Dy^{3+} doped zinc–lead-phosphate glass. Opt Mater 2013, 35, 1103-1108.
3. Suresh Kumar J, Pavani K , Mohan Babu A, Neeraj Kumar Giri, Rai SB, Rama Moorthy L, Fluorescence characteristics of Dy^{3+} ions in calcium fluoroborate glasses. J Lumin 2010,130, 1916–1923.
4. Liu S, Zhao G, Lin X, Ying H, Liu J, Wang J, Han G. White luminescence of Tm–Dy ions co-doped aluminoborosilicate glasses under UV light excitation. J Solid State Chem 2008, 181, 2725–2730.

*****