THE PHYSICAL AND LUMINESCENT PROPERTIES OF DY^{3+} DOPED PHOSPHATE GLASSES FOR SOLID STATES LIGHTING APPLICATIONS

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Abstract

Oxyfluoride phosphate glass samples doped with Dy^{3+} ions were prepared by melt quenching technique and study through physical, optical and luminescent characterization. The density and refractive index increase with Dy_2O_3 concentration while molar volume decreases. The UV-Vis-NIR absorption spectra were recorded in the 200 to 2,000 nm wavelength range. Eight clear absorption peaks were observed in UV-Vis-NIR spectra. Photoluminescence excitation and emission spectra have been recorded under 573 and 350 nm wavelength respectively. The intensity of the peaks in the excitation and emission spectra increase with increasing concentration of Dy^{3+} ions up to 1mol% and then decrease. The JO theory is applied to find the JO intensity parameters $\Omega_\lambda(\lambda=2,4,6)$ and radiative properties JO intensity Parameters show $\Omega_2>\Omega_4$ Ω_6 trend. The. The decay time, CIE coordinates and CCT values were also investigated.

Keywords: Phosphate glass, JO theory, transition probability, branching ratio

Introduction

The solid-state lighting (SSL) particularly WLEDs are the potential alternate for the incandescent fluorescent lamps (Zulfiqar, *et al.*, 2013). The WLEDs have the advantages such as long lifetime, lower energy consumption, and higher reliability (Xiaoluan *et al.*, 2008, Chaofeng *et al.*, 2015). In recent years luminescent glasses for light emitting

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diodes (LEDs) based lighting applications have attracted significant research interest (Babu *et al.,* 2011; Chaofeng *et al*., 2015).

The oxide glasses commonly have good chemical durability, mechanical strength and thermal stability (Chenggang *et al.,* 2011), but at same time have high phonon energy compare to fluoride glasses which affect the emission ability of luminescent glasses. While fluoride glasses have low phonon energy and wide optical (UV-NIR) transparency as compare to the oxide's glasses (Haritha *et al*., 2017; Srihari *et al*., 2017). So, the oxyfluoride glasses might have the good mechanical properties and low phonon energy characteristics (Barbara *et al.,* 2010).

Phosphate glass has many exceptional properties, in particular high transparency, low dispersion, high thermal stability, low melting point, high gain density and high solubility for RE ions (Reddy *et al*., 2011; Prathyusha *et al.,* 2017). As far oxyfluoride glasses are consider, the fluorophosphate glasses catch huge attention because of its high optical quality, low melting temperature and relatively high density (Kesavulu *et al.,* 2011).

Dy^{3+} is an interesting rare earth ion because it is a promising luminescent source for blue-yellow region ($^4F_{9/2}\rightarrow{}^6H_{15/2,\ 13/2}$). By tuning a suitable ratio of yellow and blue light, the CIE diagram coordinates of Dy^{3+} doped glass systems can be positioned in the weight light region because the line joining the yellow and blue region pass through the weight light region (Babu *et al.,* 2015).

In majority of glasses, Gd^{3+} just acts as sensitizer ion (Chunmei *et al.,* 2015). In this study we used Gd_2O_3 in our composition to improve the emission efficiency of Dy ions.

The aim of present work is to report a detailed study on effect of different concentration of Dy^{3+} ions on physical and luminescence properties of fluorophosphates glasses for solid state lighting applications.

Experiment and Measurements

The Oxyfluoride phosphates glasses with chemical composition of $17Li_2O$-$17GdF_3$-(66-x) P_2O_5-xDy_2O_3 where x = 0.0, 0.05, 0.1, 0.5, 1.0, 2.0 mol% were prepared through melt quenching technique. The glass samples referred as LF0.0, LF0.05, LF0.1, LF0.5, LF1.0, and LF2.0 respectively in subsequent sections. The raw materials Li_2O, GdF_3, P_2O_5, and Dy_2O_3 99.99% pure, weighted according to the chemical composition and mixed thoroughly and melt in an electric furnace at 1,500°C. After annealing at 400°C to remove the internal stresses, the samples were cut and polish for further process.

The densities of the samples were measure with the Archimedes principle using water as immersion liquid at room temperature. The Abbe refractometer has used to measure refractive index (n), with a sodium-vapor lamp as a light source and mono bromo-naphthalene ($C_{10}H_7Br$) as a contact liquid. The UV-Vis-NIR absorption spectra were recorded with UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600). The excitation, emission spectra and decay time were recorded with fluorescence spectrophotometer (Agilent Technologies, Cary Eclipse) with xenon lamp as a light source. The CIE 1931chromaticity diagram was used to characterize the emission color of our samples in the electromagnetic visible spectrum.

The f-f transitions for our glass samples were study through JO theory. The experimental and the calculated oscillator strength, JO intensity parameters and radiative properties of the present glasses calculated with references (Praveena *et al.,* 2008; Babu *et al.,* 2009; Kesavulu *et al.,* 2011).

Results and Discussions

Physical Properties

The measure values of density, molar volume and refractive index are presented in Table 1. The Figure 1 shows the density of the glass samples. The density increases while the molar volume decreases with increasing concentration of Dy_2O_3. The possible reason for increase in density is that the Dy_2O_3 have more molecular weight as compare to P_2O_3 so when we replace P_2O_5 by Dy_2O_3 the density of the system increases. The refractive index listed in Table 2 show increases increasing value with increasing concentration of the Dy_2O_3 increase. Increase of refractive index is due to the fact that the density of the glass and refractive index has direct relation, so as the density increase the refractive index also increases.

Absorption Spectra

The Figure 2(a) present the UV-Vis-NIR absorption spectra recorded in the wave length range of 200-2,500 nm. Eight characteristic Dy^{3+} peaks observed. These peaks centered at 382, 449, 748, 805, 896, 1,084, 1,266, and 1,667 nm and correspond to $^6H_{15}\rightarrow{}^4F_{7/2}$, $^4I_{13/2}$,

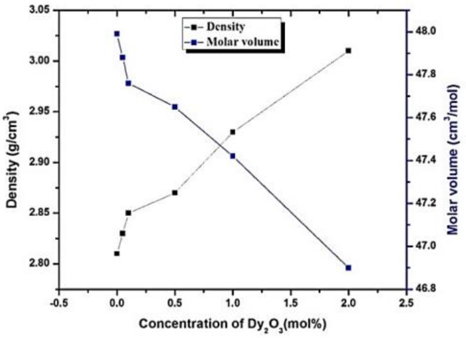

Figure 1. **Density of present glasses and molar volume Vs Dy_2O_3 concentrations**

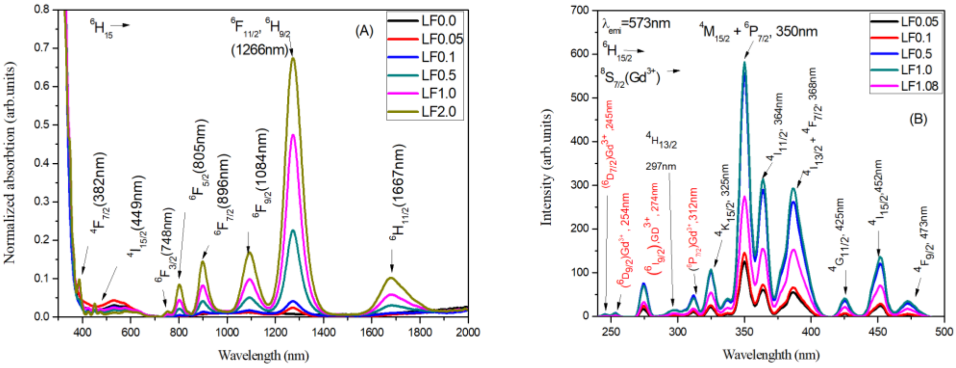

Figure 2. A) Absorption; and B) excitation spectra for GdF3 based glass

Table 1. **Physical properties Vs concentration of Dy_2O_3 contents**

Doping Mol%	LF0.0	LF0.05	LF0.1	LF0.5	LF1.0	LF2.0
Density, ρ (g/cm^3)	2.8164	2.83	2.85	2.89	2.93	3.01
Refractive index, nd (589.3 nm)	1.47	1.524	1.533	1.545	1.580	1.611
Molar volume, V_M (cm^3/mol)	47.99	47.80	47.76	47.65	47.42	46.90

Table 2. **Oscillator strength parameters for LF1.0 glass sample**

Transitions $^6H_{15}\rightarrow$	f_{ext} (10^{-6})	f_{cal} (10^{-6})
$^4F_{7/2}+{}^4I_{15/2}$	1.9266	1.2032
$^4I_{15/2}$	0.8026	0.6917
$^6F_{3/2}$	0.1151	0.2442
$^6F_{5/2}$	1.5520	1.2887
$^6F_{7/2}$	3.3820	3.2856
$^6F_{9/2}$	4.7860	4.8129
$^6H_{9/2}+{}^6F_{11/2}$	15.0630	15.0465
$^6H_{11/2}$	1.9600	2.1027
	RMS=0.286	

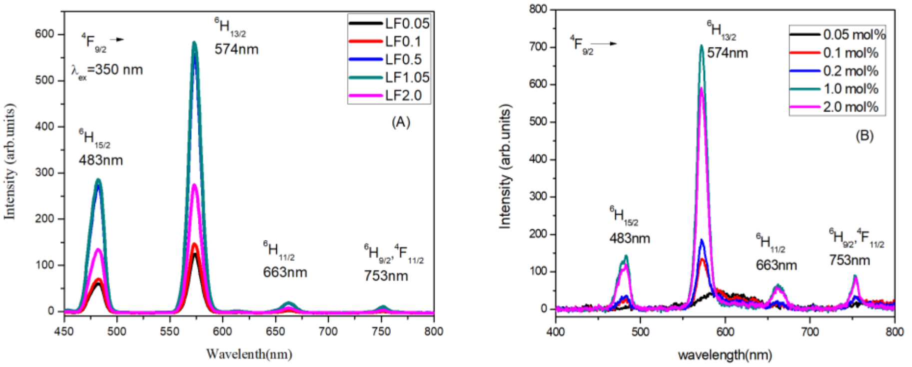

Figure 3. A) Photoluminescence emission; and B) XEL spectra for present glasses

Table 3. JO parameters (10^{-20}) of present glasses compared to the reported values

Glass	$\Omega_2(10^{-20})$	$\Omega_4(10^{-20})$	$\Omega_6(10^{-20})$	Trends
This work (LF1.0)	15.91	5.79	3.19	$\Omega_2>\Omega_4>\Omega_6$
PKBAD (Babu *et al*., 2009)	9.72	3.08	1.66	$\Omega_2>\Omega_4>\Omega_6$
Dy^{3+} doped Li phosphate glass (Praveena *et al*., 2008)	12.60	7.06	2.52	$\Omega_2>\Omega_4>\Omega_6$
Sodium zinc phosphate glass (Vijaya *et al*., 2013)	2.69	0.29	0.12	$\Omega_2>\Omega_4>\Omega_6$
PKBAFD10 (Basavapoornima *et al*., 2009)	12.36	2.67	2.30	$\Omega_2>\Omega_4>\Omega_6$
$20La_2O_3$:10CaO:$69P_2O_5$:$1Dy_2O_3$ (Jayasankar *et al*., 1997)	14.83	4.01	2.87	$\Omega_2>\Omega_4>\Omega_6$
PKAZLFDy10 (Jayasankar *et al*., 2004)	7.05	1.43	1.15	$\Omega_2>\Omega_4>\Omega_6$
BPA0.05D (Vijayakumar *et al*., 2014)	7.3378	2.7885	0 .7285	$\Omega_2>\Omega_4>\Omega_6$
LGBiBDy1.0 (Zaman *et al*., 2016)	10.64	6.10	5.86	$\Omega_2>\Omega_4>\Omega_6$

$^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$, $^6F_{11/2}+^6H_{9/2}$, $^6H_{11/2}$ transitions, respectively (Kaewkhao *et al*., 2016, Luewarasirikul *et al*., 2017). The transition $^6H_{15}\rightarrow{}^6F_{11/2}+^6H_{9/2}$ show greater intensity than the other transitions.

Photoluminescence Analysis

The Figure 2(b) show the excitation spectra recorded at 573 nm emission wavelength in the range of 200 to 500 nm. Eight excitation peaks of Dy^{3+} observed along with the four peaks belong to the Gd^{3+} excitation. The emission spectra shown in Figure 3(a), measure in the range of 400 to 800 nm. Total four clear peaks observed in emission spectra at 483, 574, 663 and 753 nm wavelength. These peaks correspond to the transitions $^4F_{9/2}\rightarrow{}^6H_{15/2}$, $^4F_{9/2}\rightarrow{}^6H_{13/2}$, $^4F_{9/2}\rightarrow{}^6H_{11/2}$ and $^4F_{9/2}\rightarrow{}^6H_{9/2}+^4F_{11/2}$ respectively. The peak at 574 nm has greater intensity as compare to the other peaks. In the emission spectra the intensity of the emission increases up to the 1.0 mol% concentration of Dy_2O_3 and then decrease due to the energy transfer among the Dy^{3+} ions through cross relaxation channels.

X-rays Induced Luminescence Spectra

The Figure 3(b) shows the X-rays induced emission spectra of the prepared samples. The samples were irradiated with X-ray at 50 Kv and 30 mA. These spectra also show us four clear peaks at the wavelength of 483, 574, 663, and 753 nm. Same as in photoluminescence emission spectra, in X-ray induced luminescent the intensity of the emission increase with the increase of the Dy_2O_3 concentration up to 1.0 mol% of Dy_2O_3.

JO Analyses

Table 2 present the experimental and calculated oscillator strength for the transition bands observed in the absorption spectra. The experimental and calculated oscillator strength values show good agreement with each other, some transition have little disagreements but

Table 4. Radiative properties i.e. radiative transition probability (A_R (s^{-1})), stimulated emission cross section (σ (10^{-21}) cm^2) and branching ratio (β_R (%)) of present LF1.0 glasses

S/No	Transitions	Ar	σ (10^{-23})	Br_{exp}	Br_{cal}
1	$^6H_{15/2}$	50.75	3.23	0.35	0.13
2	$^6H_{13/2}$	619.38	37.9	0.59	0.67
3	$^6H_{11/2}$	509.38	5.56	0.03	0.07
4	$^6H_{9/2}$	161.64	6.4	0.02	0.04

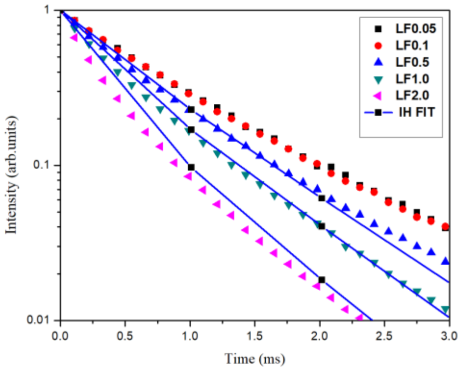

Figure 4. Decay curve of glass samples with IH fit

with an overall RMS value of 0.286. The JO intensity parameters Ω_λ(λ = 2,4,6) find from the experimental oscillator strength are given in the Table 3, together with the prior reported values. Trend observed for JO intensity parameters is $\Omega_2>\Omega_4>\Omega_6$ which is similar to other samples shown in Table 3. The parameter Ω_2 is related to the local structure symmetry and bonding nature around the Dy^{3+} ions. So, the larger value of Ω_2 is a sign that our samples have highly asymmetric structure around the RE ions and high degree of covalency for metal-ligand bond. The parameters Ω_4, Ω_6 are structure dependent, these parameters characterized the rigidity of glass samples.

Radiative Properties

The radiative Properties, radiative transition probability (Ar), stimulated emission cross section (σ) and branching ratio (Br) are presented in Table 4. The "Ar" show larger value 619.38 for $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition. The total "A_T" is estimated to be 2064 by summing all radiative rates "Ar" for each $^4F_{9/2}\rightarrow{}^6H_j$. Similarly, the Branching ratio and stimulated cross section also show greater values for same transition $^4F_{9/2}\rightarrow{}^6H_{13/2}$. The branching ratio is important because it characterized the lasing power of emission transition. The branching ratio have value more than 50% for good lasing transition so in our case the emission transition $^4F_{9/2}\rightarrow{}^6H_{13/2}$ have branching ratio of 59 % and 67 % experimental and calculated values respectively. These values offer that this transition can be a good contestant for lasing action.

Decay Time

The decay profiles of glass samples are shown in the Figure 4. At low concentration (0.05 and 0.1 mol%) the decay curves are single exponential but when the concentration of optically active RE ions increase (0.5, 1.0, and 2.0 mol%) the curve deviate from the single exponential. It is due to the fact that at low concentration the optically active ions interaction with each other is very low but when the concentration of these ions increases then their interaction also increase and the curve cannot fit with single exponential fitting. At high concentration the curves are fit in the frame of Inokuti-Hirayama (IH) model to find the energy transfer parameters (Jayasankar *et al.*, 2004, Vijayakumar *et al.*, 2014). The decay time, energy transfer parameter (Q), CIE coordinates and CCT values measure for prepared samples and are presented in Table 5. It is clear from the Table 5 that the decay time decrease when the concentration of Dy^{3+} ions increase and at same time the energy transfer parameter(Q) increase with increase concentration of Dy^3. The Figure 5 presenting the CIE coordinates of class samples studied in this work and the values are (0.37, 0.42). These coordinated are positioned in the weight region of CIE diagram and agree with reported studies in literature (Zaman *et al.*, 2016).

Table 5: Decay time (ms) , energy transfer parameter (Q), CIE coordinates and CCT values

Samples (%)	Decay time	Q	(x,y)	CCT
LF0.05	0.842	--	(0.380, 0.42)	4265.00
LF0.1	0.832	--	(0.379,0.42)	4288.82
LF 0.5	0.689	0.0.2567	(0.379,0.42)	4288.82
LF 1.0	0.545	0.52666	(0.378, 0.42)	44407.00
LF 2.0	0.356	1.0389	(0.360, 0.42)	4753.95

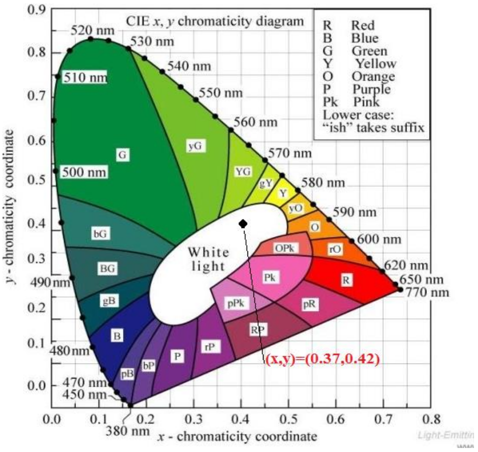

Figure 5. CIE diagram for LF1.0 glass

Conclusions

In present work we study the effect of different Dy^{3+} ions on physical and luminescent properties of fluorophosphates glass. The absorption, excitation and emission spectra were study in detail and it is found that the excitation and emission band intensity increase with increase in Dy^{3+} ions up to 1mole%. The radiative rates work out from the JO calculation as well as the concentration dependencies of the $^4F_{9/2}$ measured lifetimes have been reported. The JO intensity parameters show $\Omega_2>\Omega_4>\Omega_6$, and from JO intensity parameters it is concluded that the present glass have asymmetric and high covalency nature around RE elements. The other radiative properties like transition probability (Ar), stimulated cross section and branching ratio have been measured. These properties show higher values for $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition. The branching ratio more than 50% for $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition indicates that these glasses can be used for the laser action. It is clear from this study that the present glass can be a good candidate for many optical applications including lasing solid stat lighting applications.

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