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Luminescence efficiency of Dy^{3+} ions in zinc aluminum phosphate glasses

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Abstract

We have synthesized ZnO–Al_2O_3–P_2O_5 glasses doped with different concentrations of Dy_2O_3. Their emission and decay characteristics were investigated as a function of Dy_2O_3 concentration. The emission spectra exhibited three principal emission bands in the visible region corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (478 nm), $^6H_{13/2}$ (562 nm) and $^6H_{11/2}$ (671 nm) transitions. With increase in the concentration of Dy_2O_3 a considerable increase in the intensity of these bands is observed, quenching of PL output is observed. Using emission spectra various radiative parameters were evaluated and all these parameters are found to increase with increase of Dy_2O_3. The Y /B integral emission intensity ratio of Dy^{3+} ions evaluated from these spectra exhibited a decreasing trend with increase in the concentration of Dy_2O_3. The quenching of lumeniscence observed in case of the glasses doped with 1.0 mol% is attributed to clustering of Dy^{3+} ions.

Keywords: Y/B ratio; Luminescence

1.0 Introduction

Among different glasses ZnO based glasses are important materials. These materials are direct wide band gap semiconductors with large exciton binding energy and hence find many technological applications, for example, in gas sensors, catalysis, solar cells, transducers, varistors, in optoelectronic devices such as light-emitting and laser diodes [1, 2].

Aluminum glasses are used in electrical and optical memories. Alumina is one of the best ion conducting hard refractory materials[3].

Phosphate glasses are technologically important materials, because of their relatively large thermal expansion coefficients, low optical dispersions and low glass transition temperatures. They have found important applications in glass-to-metal seals, laser hosts and biocompatible materials [4].

Zinc phosphate glasses are well known due to their response to femto second (fs) laser irradiation and for their applications in three dimensional structures for integrated optical devices [5].

Dysprosium ions (Dy^{3+}) mixed glasses and phosphors are being extensively used as white light luminescent materials. These ions are well known due to their prominent emission transitions viz., $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (forced electric dipole transition) in the blue region and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (magnetic dipole transition) in the yellow region. The ratio of intensities of these two emissions viz., (Y/B) of Dy^{3+} ion differs from material to material and plays a crucial role in the white light emission of this ion [6].

The objective of this study is to investigate the Dy^{3+} ion concentration dependence on its luminescence efficiency and *Y/B* fluorescence integral intensity ratio in zinc aluminum phosphate glasses.

2. 0 Experimental

The details of composition of the samples used for the present study are as follows:

D_0: 20 ZnO–05 Al_2O_3–75 P_2O_5 (Pure)
D_1: 20 ZnO–05 Al_2O_3–74.9 P_2O_5 :0.1 Dy_2O_3
D_3: 20 ZnO–05 Al_2O_3–74.7 P_2O_5 :0.3 Dy_2O_3
D_5: 20 ZnO–05 Al_2O_3–74.5 P_2O_5 :0.5 Dy_2O_3
D_8: 20 ZnO–05 Al_2O_3–74.2 P_2O_5 :0.8 Dy_2O_3
D_{10}: 20 ZnO–05 Al_2O_3–74.0 P_2O_5 :1.0 Dy_2O_3

Analytical-grade reagents of ZnO, Al_2O_3,P_2O_5 and Dy_2O_3 powders in appropriate amounts were thoroughly mixed in an agate mortar and melted in silica crucible at about 1000 °C in a PID temperature–controlled furnace for about 1 h. The resultant bubble-free melt was then poured in a brass mould and subsequently annealed at 300 °C. The amorphous nature of the samples was confirmed by X–ray diffraction. Afterwards, the samples were ground and optically polished to the average dimensions of 1.0 cm x 1.0 cm x 0.2 cm.

3.0 Results

From the measured values of density *d* and calculated average molecular weight $\overline{M}$ of ZnO– –Al_2O_3–

P_2O_5: Dy_2O_3 glasses, various physical parameters such as Dy^{3+} ion concentration N_i and mean Dy^{3+} ion separation r_i are evaluated using the conventional formulae [7] and are presented in Table 1.

Table 1 Physical parameters of $ZnO–Al_2O_3–P_2O_5$:Dy_2O_3 glasses.

Glass	Avg.Mol. Wt M	Density d (g/cm^3)	Dy^{3+} ion con. N_i (10^{19}/ cm^3)	Inter ionic distance of Dy^{3+} ions R_i (nm)
D_1	190.21	3.52	1.12	4.13
D_3	191.72	3.64	3.52	2.98
D_5	192.46	3.83	6.05	2.46
D_8	193.54	3.91	9.64	2.15
D_{10}	194.63	3.98	11.37	2.04

The optical absorption spectra of the titled glasses Figs.1 and 2 have exhibited the bands due to the following transitions of Dy^{3+} ions:

$^6H_{15/2} \longrightarrow {}^4G_{11/2} + {}^4M_{21/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{1/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$ $^6F_{11/2}+{}^6H_{9/2}$ and $^6H_{11/2}$

Out of these, the last three bands *viz.*, $^6H_{15/2} \longrightarrow {}^6F_{9/2}$ $^6F_{11/2}+{}^6H_{9/2}$ and $^6H_{11/2}$ are found to be in the NIR region and the rest of them are in visible range. With increase in the concentration of Dy_2O_3 an increase in the absorption of all the bands is observed.

Fig. 1 Optical absorption spectra of $ZnO–Al_2O_3–P_2O_5$:Dy_2O_3 glasses recorded in the visible region.

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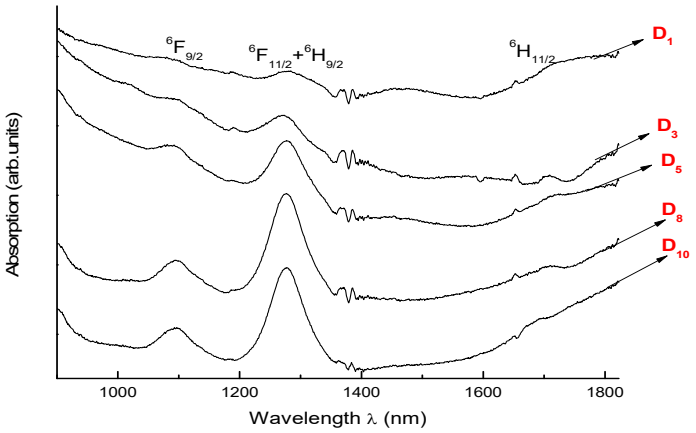
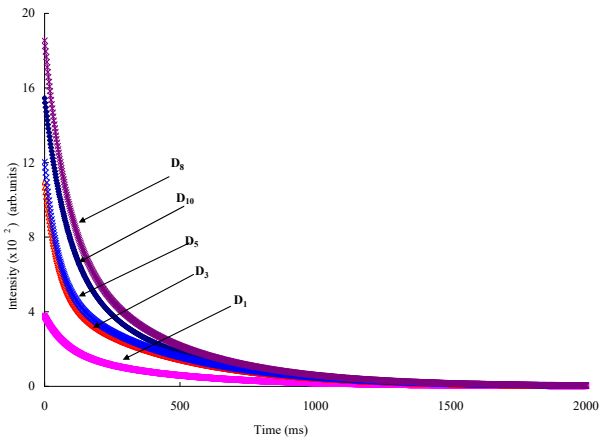


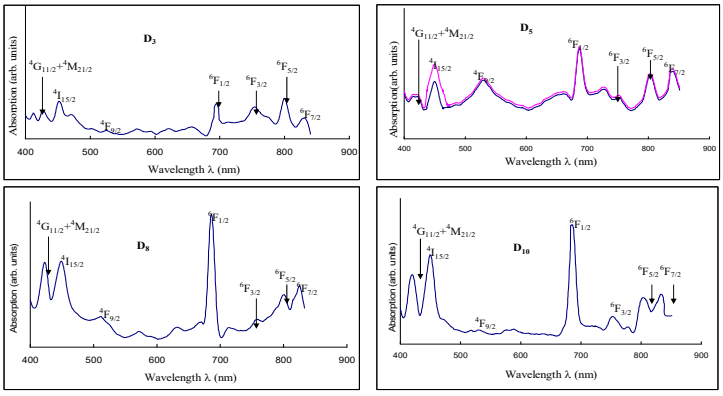
Fig.2 Optical absorption spectra of $ZnO–Al_2O_3–P_2O_5$:Dy_2O_3 glasses recorded in the NIR region

Excitation spectra for all the glasses were recorded (monitored at the wavelength of 562 nm) for all the glasses (Fig. 3 (a)). The spectra exhibited a strong band at 354 nm. The same was used for recording photoluminescence (PL) spectra. The PL spectra (Fig. 3 (b)) exhibited the following emission bands originated from $^4F_{9/2}$ excited level:

$^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$, $^6H_{11/2}$

Out of these, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, yellow emission transition (with $\Delta L=2$, $\Delta J=2$) is observed to be hypersensitive. With increase of Dy_2O_3 a considerable increase





in the intensity of this band is observed and beyond this concentration, quenching of emission is visualized.

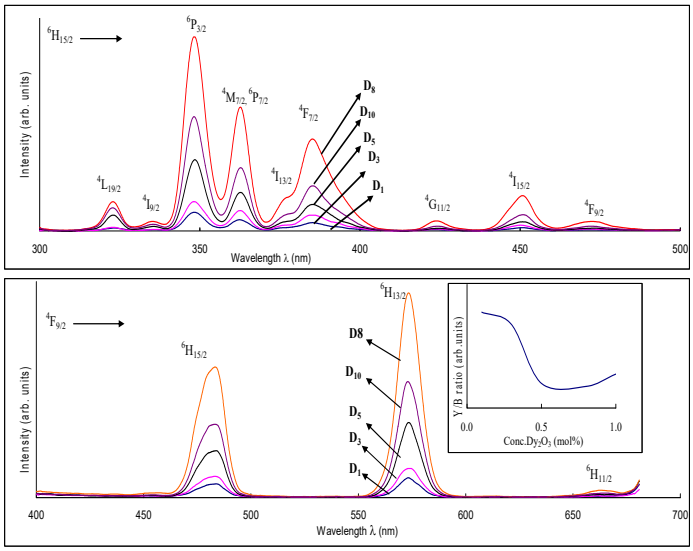


Fig.3 (a) Excitation (λ_{emi} = 562 nm) and (b) Emission (λ_{exc} = 354 nm) spectra of Dy^{3+} doped $ZnO–Al_2O_3–P_2O_5$ glass system. Inset of Fig. 3 (b) represents variation of integral Y/B intensity ratio with the concentration of Dy_2O_3.

We have recorded the decay profiles of the $^4F_{9/2}$ excited level of Dy^{3+} ions for the titled glasses and presented in Fig. 4. The decay curves though appeared to be double exponential the faster decay component seems to be too smaller < 10 %. The life times (τ_{mes}) evaluated from slow decay part of these curves are presented in Table 2. The value of τ_{mes} is observed to increase significantly with increase in the concentration of Dy_2O_3.

Table 2 Summary of the data on life time measurements of $^4F_{9/2}$ excited level (λ_{exc}= 354 nm and λ_{em} = 562 nm)

Glass	Measured (μ sec) (τ_{mes})	Calculated (μ sec) (τ_R)	Quantum efficiency (η %)
D_1	349	438	78.12
D_3	359	442	79.26
D_5	398	491	80.35
D_8	415	507	81.76
D_{10}	424	512	82.64

Fig. 4 Decay profiles of Dy^{3+} doped $ZnO–Al_2O_3–P_2O_5$ glasses recorded at room temperature

4.0 Discussion

$ZnO–Al_2O_3–P_2O_5$: Dy_2O_3 glass system is an admixture of network formers, modifiers and intermediates. P_2O_5 is a strong glass forming oxide, participates in the glass network with PO_4 structural units. Among the three J-O parameters Ω_2 is mainly due to non-centro symmetric potential arises because of occupancy of rare earth ions in different coordination sites. Sometimes even with similar coordination there may be re-distribution in the crystal field due to the differences in the distortion at the sites of the rare earth ions. Such distortions may also contribute to Ω_2. The other two parameters *viz.*, Ω_4 and Ω_6 are connected with the vibrational levels of the bondings of central rare earth ions bound with the ligand atoms. The Dy^{3+} ion concentration dependence of Ω_2 parameter indicates a gradual decrease with increase of Dy_2O_3. Such decrease suggests that there is an increase in the degree of disorder in the glass network. Such de-polymerization produces weaker field around Dy^{3+} ions and causes to decrease the value of Ω_2. Further, the average Dy–O distance is expected to be relatively larger in the glass sample containing Dy_2O_3 in this concentration range and the concentration of probable Dy^{3+} clusters that hinders PL emission is also small. Normally, rare earth ions including Dy^{3+} in amorphous glass systems form aggregates or clusters in which cross relaxation can give rise to non-radiative de-excitation resulting in short lifetimes [8].

Low PL intensity and short emission lifetime exhibited by the glass D_{10} indicates possible presence of larger concentration of Dy^{3+} ion clusters that may cause luminescence quenching. We have observed a gradual decay in the intensity ratio of bands related to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ (Y) $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (B) to decrease with the increase of Dy_2O_3 concentration up to 0.8 mol%. In fact, Y/B ratio is dependent on site asymmetry or environmental variations in the vicinity of the Dy^{3+} ion and also covalency of the bonds with the oxygen ions [9]. The observed higher values of Y/B ratio for the glasses D_1 to $D_{1.0}$ indicates larger concentration of dissociated Dy^{3+} ions from Dy–O–Dy bonds.

5.0 . Conclusions

zinc aluminum phosphate glasses doped with different concentrations of Dy_2O_3 (from 0.1 to 1.0 mol %) were prepared. Optical absorption, photoluminescence and luminescence decay studies have been carried out. The optical absorption spectra of these glasses exhibited bands

due to $^6H_{15/2} \longrightarrow {}^4G_{11/2}+{}^4M_{21/2}$, $^4I_{15/2}$, $^4F_{9/2}$, $^6F_{1/2}$, $^6F_{3/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6F_{9/2}$ $^6F_{11/2}+{}^6H_{9/2}$ and $^6H_{11/2}$ transitions of Dy^{3+} ions. These spectra were analyzed using JO theory and a reasonable matching between experimental and theoretical oscillator strengths could be achieved. The luminescence spectra of these glasses were recorded at an excitation wavelength of 354 nm. The spectra exhibited bands due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue), $^6H_{13/2}$ (yellow), $^6H_{11/2}$ transitions of Dy^{3+} ions. The PL output and consequential radiative parameters including emission cross section have been observed to increase with increase in the concentration of Dy_2O_3 upto 1.0 mol%. However, the integral Y/B emission intensity ratio is found to decrease with increase in the concentration of Dy_2O_3. The enhanced PL output is attributed to (i) increase of Dy_2O_3 concentration and (ii) the concentration of clusters of Dy^{3+} ions is relatively lower in the glasses D_1 to $D_{1.0}$.The observed low PL intensity and short emission lifetime exhibited by the glass $D_{1.0}$ are ascribed to be possible presence of larger concentration of Dy^{3+} ion clusters that may cause luminescence quenching due to cross relaxation.

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