RASĀYAN J. Chem.
Vol. 10 | No. 3 |771 - 777 | July - September | 2017
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

EFFECT OF LiF ON LUMINESCENCE PROPERTIES OF Dy^{3+} DOPED Cd-Zn PHOSPHATE GLASSES

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ABSTRACT

The present work deals with optical absorption, luminescence studies of the cadmium zinc phosphate glasses doped with Dy^{3+} ions. The effect of variation of LiF concentration in the host matrix cadmium-zinc phosphate glasses was established in this study. Optical absorption, luminescence studies reveals the emission of white light from the glass upon excitation. Characteristic nature of existence of Dy^{3+} ions in the host with absorption bands in absorption spectra, excitation and emission spectra with chromaticity coordinates in the white light region was described. These prepared glasses were useful in white light generation materials.

Keywords: Phosphate Glass, Luminescence, White LED's, Optical absorption.

INTRODUCTION

In applications of lasers, phosphors and display devices, rare earth or lanthanide doped glasses are playing important role in present research trends. The studies on such materials are also having an increase in interest. Phosphate glasses are one of the most important materials for the optical applications among the all other oxide glasses. In particular, multi-component glass systems have a considerable interest in different potential applications. High transparency, considerable refractive index and dispersion like properties create phosphate glasses into prominent materials for application oriented device manufacturing. Besides these advantages, phosphate glasses have a best thermo-optical performance with considerable chemical durability, high gain as with low energy back transfer and weak upconversion[1-5] and flexible to prepare in different concentrations with proper luminescent active ions.

Dy^{3+} ($4f^9$) are one of the attractive ions among rare earth for the present spectroscopic studies. The reason behind this is it exhibits near infrared region emission lines. The emissions are around 0.9, 1.1, 1.3, 1.7 and 3 μm and are very important in communication applications.[6,7] It is very important in considering the emissions from the $^4F_{9/2}$ state which will be in the visible region. However, Dy^{3+} exhibits different interesting optical characteristics in different hosts depending upon the concentration also.[8]

Therefore, it is well known that for efficient population inversion upon pumping, the resulting spectral region is narrow in between the absorption edge and the emitting state. Basically, Dy^{3+} ions doped hosts emit two strong emissions at blue and yellow regions and one feeble emission at the red region in the electromagnetic spectrum. At proper grouping of these emissions produces white light without the addition of any other rare earth ions[9-12] with proper excitation wavelength. Further Dy^{3+} has an another advantage of multiple excitation levels in between 340-480 nm allows the commercially available UV and Blue LEDs as additional excitation sources.

Finally, all the above emanates the improvement in the luminescence efficiency which is still a challenging task in a proper host. It is very clear that the nature of the bonds and the structural information of host glass matrix are known by the optical properties of the doped rare earth ions in the host are dependent on composition. Among different host matrices, metal phosphate glasses are quite prone with the advantages such as less hygroscopic, low non-linear refractive index, good physical and chemical stability and high transparency from near Ultra Violet to mid-Infrared region.[13-15] The addition of LiF is also an added advantage in improvement of luminescence efficiency with different concentration for optimization of the host matrix.

http://dx.doi.org/10.7324/RJC.2017.1031742

In this present paper, the preparation of transparent Dy^{3+} ions doped Cd-Zn phosphate glass via melt quenching method, optical and emission properties of the prepared glasses towards the application of white light emission have been reported.

EXPERIMENTAL

Dy^{3+} doped Cadmium zinc phosphate glasses with different molar concentrations of LiF were prepared by using well-known melt quenching method with the following chemical compositions: (70-x)P_2O_5 – 15CdO – 15ZnO – x LiF - 0.5Dy_2O_3 for x = 1,3,5 and 10 mol% (referred as LCdP1, LCdP2, LCdP3 and LCdP4 respectively). About 15 g of the total batch composition taken and was thoroughly mixed in an agate mortar. The resulting homogeneous powder was poured into a porcelain crucible and heated in a muffle furnace at a temperature of 1050^{0}C for 1.5 hours. The melt was transferred to the clean surface of a preheated brass plate. Then it was annealed at 250 ^{0}C for about 4 h to remove sudden breaks due to thermal strains. The resulting transparent glass samples were cooled to room temperature (RT). The as-prepared samples were polished for the clear surface for optical studies. By using Abbe refractometer, the refractive index of all the samples was measured at 589.3 nm (1-bromonaphthalin ($C_{10}H_7Br$) is used as contact liquid). The density is also measured at room temperature by using Archimede's principle. For this measurement distilled water is used as the immersion liquid. Emission and excitation measurements were done at Room Temperature by using Thermo Lumina Fluorescence Spectrophotometer (200-900nm) with Xenon lamp as the excitation source.

RESULTS AND DISCUSSION

The amorphous character that is no such definite sharp peaks of the present glasses were confirmed by the obtained X-Ray diffraction pattern for all the samples and one (LCdP4) among is shown in Fig.-1. The halo pattern represents the typical nature of the amorphous state.

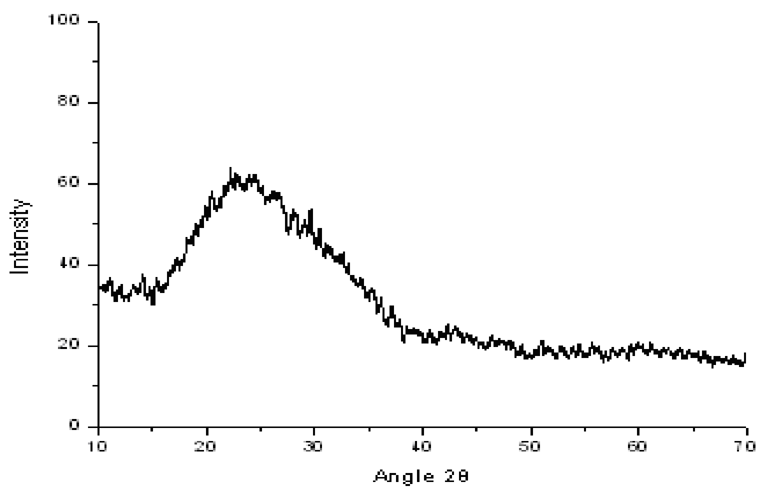

Fig.-1: XRD pattern image of LCdP4 glass

The absorption band positions for the various concentrations of LiF-doped LCdP glasses takes place at round about the similar wavelength and is shown in Fig.-2 and Fig.-3 for visible and infrared regions respectively in the wavelength range 300-1800 nm at room temperature. It is clear from the Fig. 2 and Fig 3 that the identification and assignment are very critical in UV-Vis regions due to the overlap of different $^{2S+1}L_J$ levels. Further the levels in the near infrared region are most significant and intense for the Dy^{3+} ions.

The absorption spectra consists the absorption bands equivalent to the transitions from ground state $^6H_{15/2}$ to different excited states like - $^6P_{7/2}$ (349 nm), -($^4M_{19/2}$+$^4D_{3/2}$+$^6P_{5/2}$) (363 nm), -($^4M_{21/2}$+$^4K_{17/2}$+$^4F_{7/2}$+$^4I_{13/2}$) (385 nm), - $^4F_{9/2}$ (452 nm), – $^6F_{5/2}$ (802 nm), – $^6F_{7/2}$ (902 nm), – ($^6F_{9/2}$+$^6H_{7/2}$) (1096 nm), - ($^6F_{11/2}$+$^6H_{9/2}$)

(1277 nm), -$^6H_{11/2}$ (1683 nm) respectively. Due to the powerful absorption of the network in the ultraviolet region, the bands at 385 nm and 452 nm are weak. By using observed absorption bands at various positions due to the transitions, using the relations from previous literature,[16] spectral intensity parameters or Judd-Ofelt (J-O) parameters were evaluated and presented in Table-1.

In any host, the three important J-O intensity parameters Ω_2, Ω_4 and Ω_6 determines the covalency nature between the rare earth and ligand oxygen ions. Further, these parameters reveal the coordination environment around the luminescent center. Here Ω_2 parameters characterize Dy-O covalency in the surrounding of Dy^{3+} ions. Ω_4 and Ω_6 correspond to the relation between Dy^{3+} ions and ligand ions, dielectric nature, rigidity and viscosity of the host glass matrix.

From Table-1, it is observed that the asymmetry of crystal field at the Dy^{3+} ions site is higher at LCdP3 because of highest value (1.38 x 10^{-21}), and is lower at LCdP2 because of low value (0.96 x 10^{-21}) in the present work. So it is clear that LCdP3 Glass experiences relatively higher covalency and asymmetry than the other LCdP phosphate glasses. According to the J-O parameter Ω_6 , high viscosity and low viscosity applies to LCdP4 and LCdp1 respectively depending on their values. The overall intensity parameters trend in the present host glasses is as $\Omega_2>\Omega_6>\Omega_4$. Therefore, the existence of higher magnitude of Ω_2 represents the presence of Dy-O bonding as an increase in covalency in the present glass system.

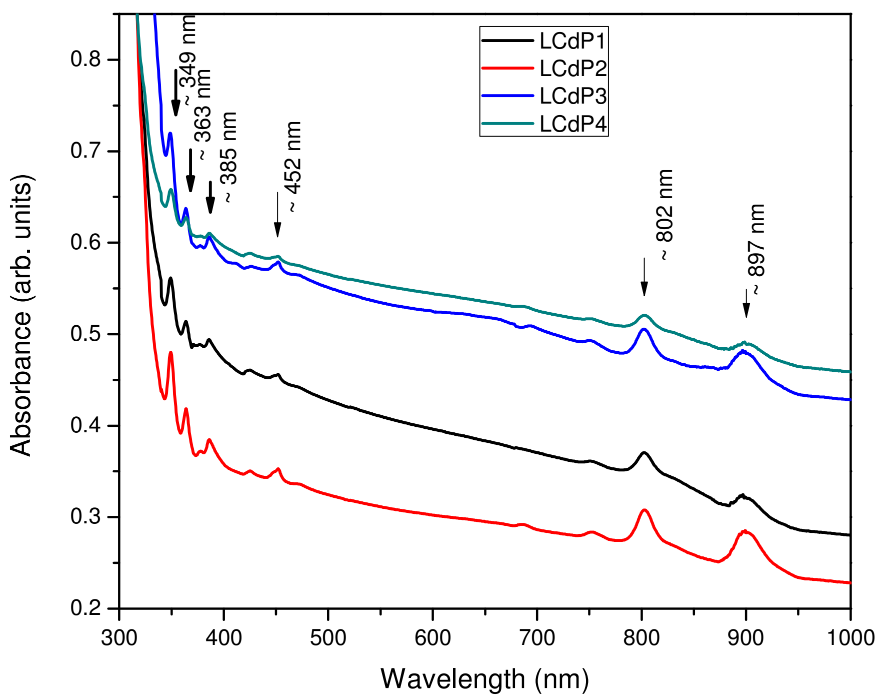

Fig.-2: Optical absorption spectra of LiF Metal Phosphate Glasses in Visible region

Table-1: J-O intensity parameters for the present Cd-Zn phosphate glasses

Glass	Ω_2 x10^{-21}	Ω_4 x10^{-21}	Ω_6 x10^{-21}	Trend	Reference
LCdP1	1.04	0.114	0.16	$\Omega_2>\Omega_6>\Omega_4$	Present Work
LCdP2	0.96	0.05	0.162	$\Omega_2>\Omega_6>\Omega_4$	Present Work
LCdP3	1.38	0.542	0.547	$\Omega_2>\Omega_6>\Omega_4$	Present Work

LCdP4	1.23	0.329	0.621	$\Omega_2 > \Omega_6 > \Omega_4$	Present Work
Phosphate glass	9.72	3.08	1.66	$\Omega_2 > \Omega_4 > \Omega_6$	17
ZnP glass	2.23	0.14	0.41	$\Omega_2 > \Omega_6 > \Omega_4$	18
PPbZdy	4.63	0.77	0.79	$\Omega_2 > \Omega_6 > \Omega_4$	19
SrZnPbPD10	2.15	0.04	0.82	$\Omega_2 > \Omega_6 > \Omega_4$	20

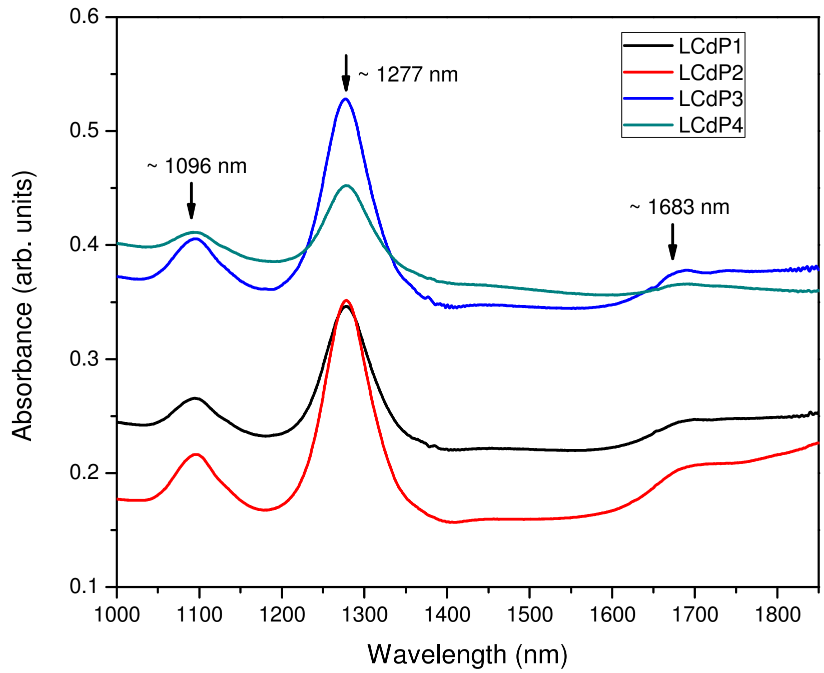

Fig.-3: Optical absorption spectra of LiF Metal Phosphate Glasses in NIR region

Excitation and emission spectra were recorded to understand the luminescence properties of the present LCdP glasses. The excitation spectra are shown in Fig.4 and the bands observed are assigned to various levels. The highest absorption level in the present glass systems is $^6P_{7/2}$ and is at 348 nm. So, this is to be chosen as excitation wavelength for these cadmium zinc phosphate glasses.

The emission spectra for the presently prepared glasses with different molar concentrations of LiF-doped with Dysprosium ions were recorded in the spectral range of 450 – 700 nm at RT with an excitation of 348 nm is shown in Fig 5. The obtained spectra show the emission lines originated from the luminescent $^4F_{9/2}$ level to the ground ^6H_J (J = 11/2, 13/2 and 15/2) multiplets. The obtained emission spectra of these presently studied glasses are similar and are comparable. All these transitions are in different regions as the transitions from $^4F_{9/2} \rightarrow ^6H_{15/2}$ at 473 nm related to the blue colored region, $^4F_{9/2} \rightarrow ^6H_{13/2}$ at 573 nm related to the yellow colored region, $^4F_{9/2} \rightarrow ^6H_{11/2}$ at 663 nm related to the red colored region as a feeble transition. The resultant emission will appear as white light.

By the comparison of the emission intensities of the all the glasses, the trend in intensities is as LCdP4 > P2 >P1 >P3. Therefore the highest concentration of the Lithium Fluoride is exhibiting the highest white light emission. So, all these glasses were useful for white light emission applications. The chromaticity coordinates were calculated with the help of emission spectra and chromaticity diagram is also drawn.

The coordinates obtained are x = 0.39, y = 0.36 and are placed in the white region as shown in Fig.-6. The Yellow to Blue (Y/B) ratio for all the metal phosphate glasses is in the range of 1.53 to 1.64.

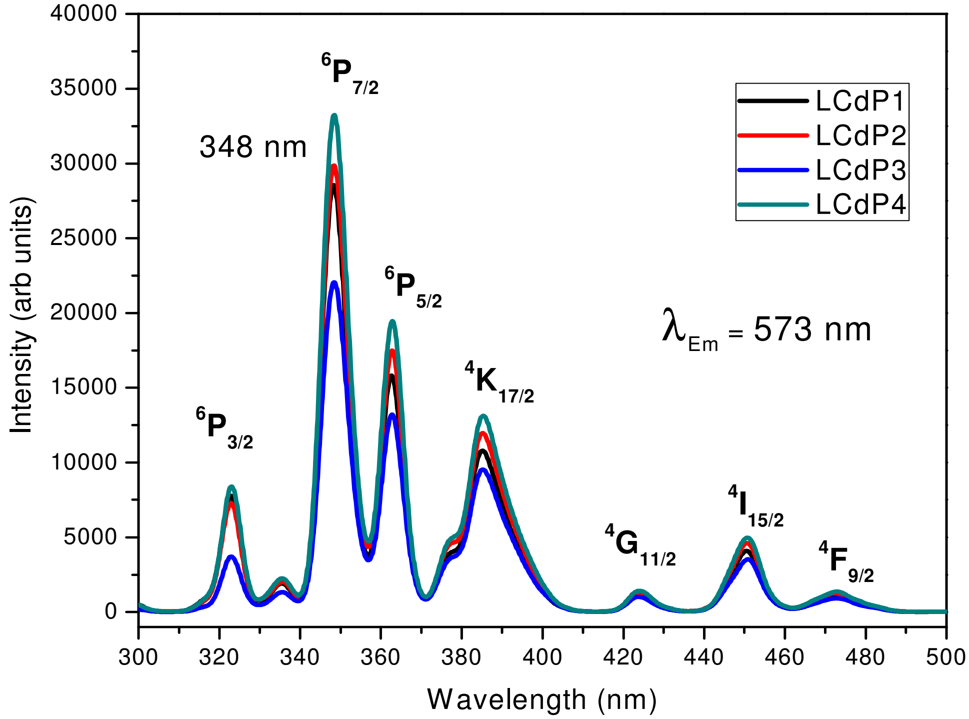

Fig.-4: Excitation spectra of LiF Metal Phosphate Glasses in Visible region

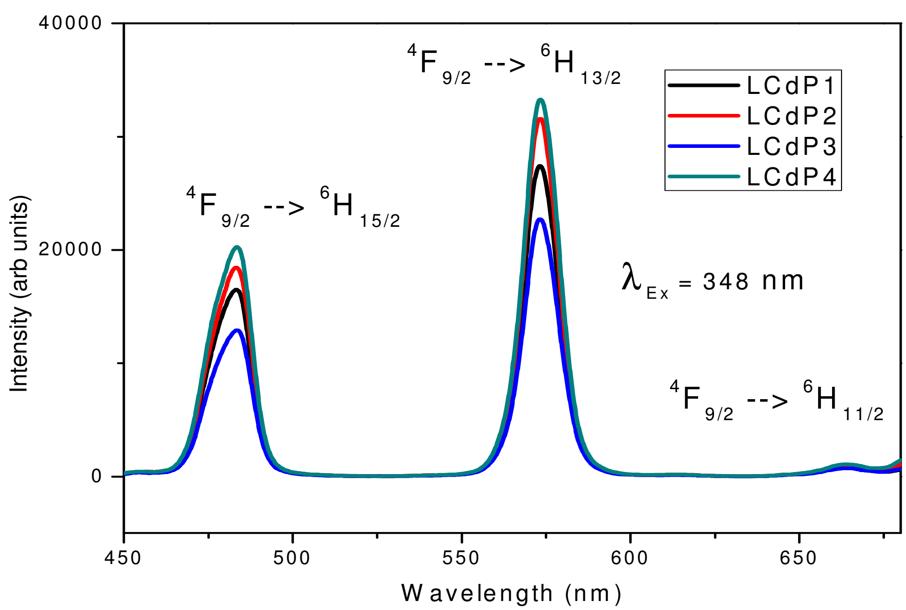

Fig.-5: Emission spectra of LiF Metal Phosphate Glasses in Visible region

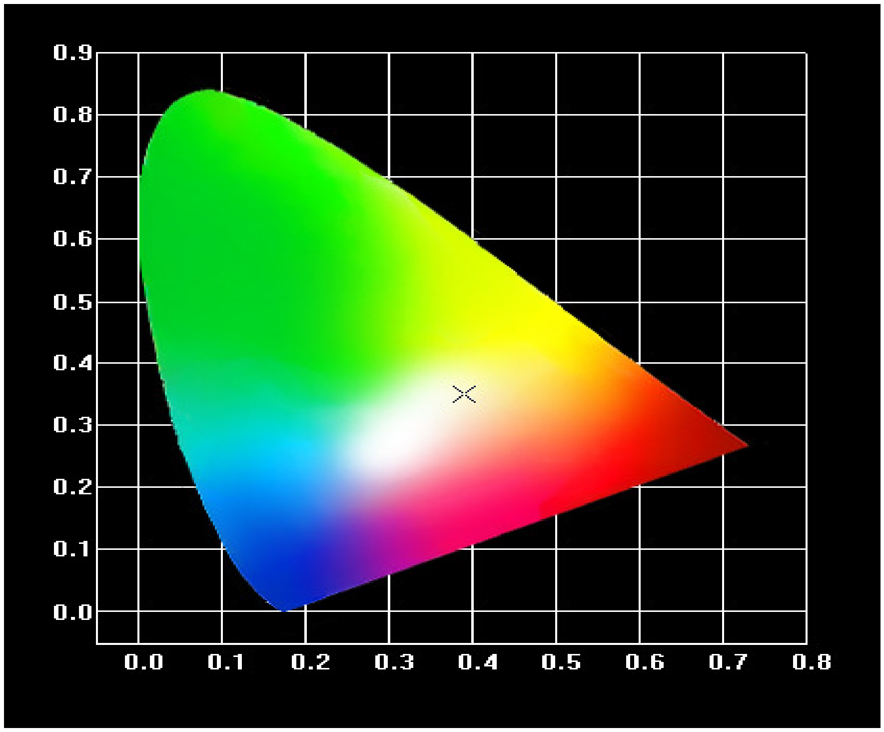

Fig.-6: Chromaticity diagram for dy3+ doped Cd-Zn phosphate glasses

CONCLUSION

The characteristic nature of Dy^{3+} ions in present LiF varied Cd-Zn phosphates glasses has been deduced from absorption spectra. By using Judd-Offeld theory, the absorption spectra is analyzed and dependency of these parameters on different transitions is also discussed. There is a clear agreement in experimental and theoretical values of different radiative properties in the current studied glasses. The Y/B ratios of all the Dy^{3+} doped phosphate glasses are in the range 1.53 – 1.64. The chromaticity color coordinates are obtained in the white region suggests that these cadmium zinc phosphate glasses with Dy^{3+} ions are useful for white light emission applications. The influence of LiF is also clear that the emission intensity is as LCdP4 > LCdP2 > LCdP1 > LCdP3. That is a higher concentration of LiF the emission intensity is very high and it is also observed that there is no linearity with concentration. So LiF is not only acting as intermediate but also it is acting as a modifier in the present glass system.

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[RJC-1742/2017]