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Spectroscopic properties of Dy^{3+} doped MgO-LiF-CdO-P_2O_5 glasses

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Spectroscopic properties of 60 P_2O_5 – 20 CdO – x MgO – (20-x) LiF – y Dy_2O_3+ x=5,10,15 and y = 0.01, 0.03, 0.05, 0.08 and 0.1 glasses were studied. Their characteristic bands were observed in optical absorption spectra from ground state $^6H_{15/2}$ to different excited states. By using Judd–Ofelt (J–O) intensity parameters Ω_λ (λ=2,4 and 6) various spectroscopic parameters have been evaluated to characterize the absorption and luminescence spectra of these glasses. For an excitation maximum at 348nm, emission spectra show three emission bands in visible region at 483nm, 573nm and 662nm corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and $^4F_{9/2} \rightarrow {}^6H_{11/2}$ transitions respectively which are shown by energy level diagram. The relative emission intensity ratio can be tuned by varying the concentrations of activator and/or composition of glass matrix.

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1. Introduction

The spectral properties of rare earth ions strongly depend on the ligand field originating from the surrounding environment of the host material. In order to improve the properties for a spectroscopic application and to understand the basic mechanism involved in the interaction between the rare earth ion and its surrounding host material, different rare earth ions have been investigated in a number of crystals [1–5]and glasses [6] at ambient temperature. Glasses with high nonlinear refractive indices have been widely investigated for the purpose of application to photonics, because they have high transparency, optical isotropy, good compatibility with the waveguide or fiber fabrication, and ultrafast response to optical signals. According to Miller's empirical rule [7], high refractive index glasses should have high nonlinear refractive indices. Because of the emission from ultraviolet to infrared region, rare earth ions have much attention in research for optical applications [8,9] in replacement of conventional lighting, white light emitting diodes plays a crucial role in recent years as an important class of lighting devices and shows high potential because of their long lifetime, higher reliability, environmental-friendly and low energy consumption nature [10].When compared to phosphors, used in the preparation of W-LED, luminescence glass has some such as lower production cost, simpler manufacture procedure, free of halo effect, etc. In order to know the local environment of the glass hosts [11] transitions metals are useful as probes. But in lower concentrations of Rare Earth ions as dopents may also significant to identify the surrounding environment.

In continuation of identifying the new optimized host for the W-LED applications [12,13], the present work emanates the novel luminescence glasses based on phosphate are studied, following the requirements of W-LED, that is, well absorbing the UV light of InGaN-based LED chip and converting it into white light. Besides, the dependence of luminescence property on the concentrations of REI activators and glass matrix compositions are examined in this paper to identify the luminescence glass as a replacement for phosphors in white light emission

2. Experimental

The present glasses were prepared with composition of 60P_2O_5 – 20 CdO – x MgO – (20-x) LiF – y Dy_2O_3 X=5,10,15 and y = 0.01, 0.03, 0.05, 0.08 and 0.1 respectively and were named as PG1 to PG15, each glass composition with label is represented in Table 1.

Table 1. Composition (in mol%) of present glass system studiedwith labels

Glass label	P_2O_5	CdO	MgO	LiF	Dy_2O_3
PG1	59.99	20	5	15	0.01
PG2	59.99	20	10	10	0.01
PG3	59.99	20	15	5	0.01
PG4	59.97	20	5	15	0.03
PG5	59.97	20	10	10	0.03
PG6	59.99	20	15	5	0.03
PG7	59.95	20	5	15	0.05
PG8	59.95	20	10	10	0.05
PG9	59.95	20	15	5	0.05
PG10	59.92	20	5	15	0.08
PG11	59.92	20	10	10	0.08
PG12	59.92	20	15	5	0.08
PG13	59.9	20	5	15	0.1
PG14	59.9	20	10	10	0.1
PG15	59.9	20	15	5	0.1

The research grade raw materials were taken in an agate mortar and powdered well to obtain homogenous mixtures. At a temperature range of 950-1050 ^{0}C by using melt quenching technique, the samples were prepared and annealed at 250^{o}C for 4 hours to remove the irregularities with the composition. The optical absorption spectra were obtained using JASCO UV-Vis spectrophotometer for the polished glass samples at room temperature. The Emission and Excitation spectra had been done by using Thermo fluorescence spectrometer in visible region with excitation wave length, 443 nm. The refractive indices of the samples were determined with an Abbe refractometer using monobromonaphthalene as an adhesive coating and the density measurements were made using Archemedes principle with kerosene as immersion liquid. Some physical properties for present glass system were evaluated and presented in Table 2.

Table 2. Some physical properties of present cadmium phosphate glasses

Glass label	Refractive Index (n) at 589.3 nm	Ion Concentration N (x 10^{22} ions)/cm^3	Optical dielectric Constant $p\partial t/\partial p$	Reflection Loss R (%)	Interionic Distance r_i (Å)	Molecular Electronic Polarizability α (x 10^{-23} cm^3)	Dielectric Constant $\in$
PG1	1.532	0.188	1.538	5.230	8.107	4.311	2.538
PG2	1.499	0.378	1.554	5.298	6.420	2.155	2.554
PG3	1.5	0.571	1.547	5.271	5.595	1.423	2.547
PG4	1.467	0.562	1.550	5.285	5.624	1.447	2.550
PG5	1.523	0.566	1.550	5.285	5.611	1.437	2.550
PG6	1.53	0.570	1.557	5.312	5.598	1.431	2.557
PG7	1.435	0.562	1.541	5.244	5.626	1.443	2.541
PG8	1.55	0.754	1.544	5.257	5.100	1.076	2.544
PG9	1.48	0.949	1.550	5.285	4.723	0.857	2.550
PG10	1.536	0.187	1.557	5.312	8.119	4.366	2.557
PG11	1.489	0.188	1.595	5.476	8.100	4.405	2.595
PG12	1.498	0.189	1.550	5.285	8.082	4.294	2.550
PG13	1.543	0.187	1.586	5.435	8.123	4.424	2.586
PG14	1.522	0.188	1.544	5.257	8.104	4.317	2.544
PG15	1.523	0.189	1.550	5.285	8.085	4.299	2.550

3. Results and discussion

The optical absorption spectrum of PG8 cadmium phosphate glass is presented in (Fig. 1 and Fig. 2) in UV-visible region and NIR region respectively because of the same absorption bands.

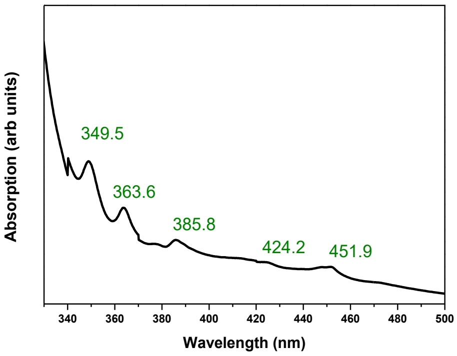

Fig. 1. Optical absorption spectra in Visible Range

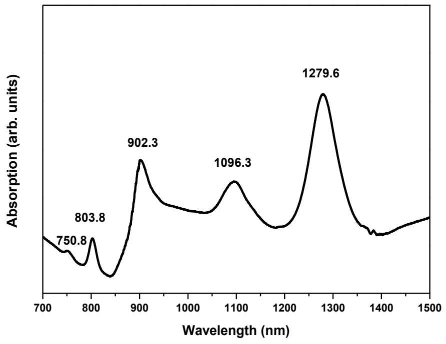

Fig. 2. Optical absorption spectra in NIR region

The 10 observed bands were assigned to different transitions from $^6H_{15/2}$ to as 349.5 - $^6P_{7/2}$, 363.6-($^4M_{19/2}$+$^4D_{3/2}$+$^6P_{5/2}$),385.8($^4M_{21/2}$+$^4K_{17/2}$+$^4F_{7/2}$+$^4I_{13/2}$), 424.2 - $^4G_{11/2}$ + $^4I_{15/2}$, 451.9 - $^4F_{9/2}$, 760.8 – $^6F_{3/2}$, 803.8 – $^6F_{5/2}$, 902.3 – $^6F_{7/2}$, 1096.3 – ($^6F_{9/2}$+$^6H_{7/2}$), 1279.6 - ($^6F_{11/2}$+$^6H_{9/2}$) respectively. The assignment of absorption transitions has been done based on the earlier literature [14].

From the optical absorption spectra, the oscillator strengths and the related intensity parameters Ω_λ (λ= 2,4,6) were calculated using least squares fit method and the theory specified elsewhere [14]. The intensity parameters calculated were presented in Table 3.

Table 3. J-O intensity parameters from optical absorption spectra

Glass	Ω_2 x10^{-21}	Ω_4 x10^{-21}	Ω_6 x10^{-21}	Trend	Ref
PG1	1.04	0.114	0.16	Ω_2> Ω_4> Ω_6	Present Work
PG2	0.96	0.05	0.162		
PG3	1.38	0.549	0.547		
PG4	0.715	0.079	0.029		
PG5	0.942	0.126	0.0504		
PG6	0.65	0.146	0.0539		
PG7	0.869	0.169	0.015		
PG8	0.61	0.0555	0.0665		
PG9	0.742	0.245	0.0158		
PG10	0.743	0.158	0.0619		
PG11	0.637	0.172	0.0721		
PG12	0.843	0.154	0.0346		
PG13	0.619	0.287	0.0153		
PG14	0.435	0.231	0.00513		
PG15	0.375	0.201	0.00977		
SrZnPbPD10	2.15	0.04	0.82	Ω_2>Ω_6>Ω_4	[12]
Phosphate glass	9.72	3.08	1.66	Ω_2>Ω_4>Ω_6	[15]
PPbZdy	4.63	0.77	0.79	Ω_2>Ω_6>Ω_4	[16]
ZnP glass	2.23	0.14	0.41	Ω_2>Ω_6>Ω_4	[17]
PbPKANDy10 glass	11.74	2.64	2.86	Ω_2>Ω_6>Ω_4	[18]

In the present glass system, the intensity parameter follows the pattern that is Ω_2>Ω_4> Ω_6. The trend of the J-O intensity parameters were compared with phosphate glass systems also represented in the Table 3. The higher magnitude of Ω_2 in the present work indicates the increase of covalent bonding and suggests that the Dy^{3+} ion posses higher site asymmetry in cadmium phosphate glass host.

The variation of Ω_2 with modifier content has been attributed to changes in the asymmetry of the ligand field at the rare earth ion site and to the changes in their rare earth-oxygen (R-O) covalence. The Ω_6 is related to the rigidity of the host and also vibronic dependent [19] and the variation of Ω_6 strongly depends on nephlauxetic effect.

Excitation and emission spectra were shown in (Fig. 2 and Fig. 3) respectively. (Fig. 2) exemplifies the excitation spectrum of Dy^{3+} ions in phosphate glasses (0.1 mol%), with emission atλ = 573 nm of $^4F_{9/2} \rightarrow {}^6H_{13/2}$. As can be seen from the figure there are several excitation bands situating between300 and 500 nm, suggesting the suitable wavelength to excite the Dy^{3+} ions with UV or violet/blue lasers. 348 nm wavelength is chosen as the excitation wavelength for the present emission studies.

Table 4. Radiative lifetimes of highest intensity transition

Sample name	State/transition	τ_R (m sec)
PG1	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.12
PG2	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.13
PG3	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.08
PG4	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.21
PG5	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.14
PG6	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.18
PG7	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.19
PG8	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.19
PG9	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.20
PG10	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.16
PG11	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.19
PG12	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.16
PG13	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.18
PG14	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.28
PG15	$^4F_{9/2} \rightarrow {}^6H_{13/2}$	0.33

It is well known that, from the emission spectra the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition is hypersensitive ($\Delta L = 2$ and $\Delta J = 2$) and therefore, its intensity strongly depends on the host, whereas intensity of the $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{11/2}$ transitions are less sensitive to the host and are also shown (Fig. 4) (inset shows the emission spectra of all the glass samples) and the energy level diagram of excitation and emission mechanisms are given in (Fig. 5) with some non-radiative transitions. The radiative lifetimes of the transition from $^4F_{9/2} \rightarrow {}^6H_{13/2}$ for all the glasses are given in Table 4.

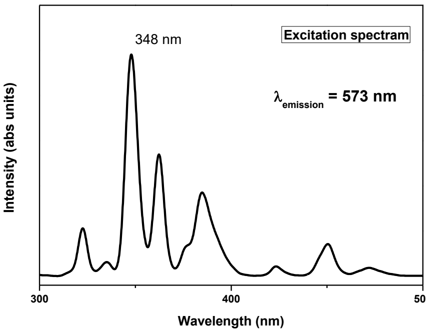

Fig. 3. Excitation spectra of Cadmium phosphate glass (0.1mol%)

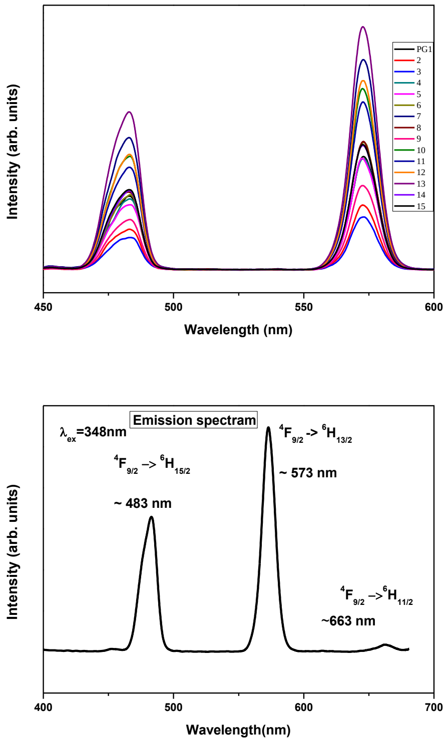

Fig. 4. Emission spectra of cadmium phosphate glass (a) all Samples (b) sample (PG13)0.1mol%

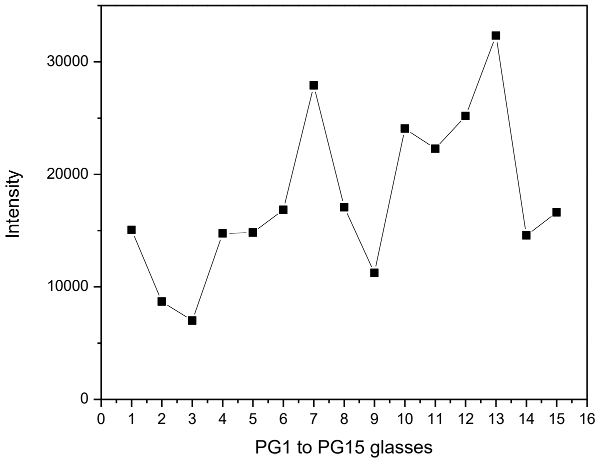

Fig. 4a. Emission Intensity variations in present glasses (PG1 to PG15)

From the emission spectra it can be clearly seen that the highest intensity of the emission is for the PG13 and the lowest intensity is for PG3 glasses which have high concentration of LiF (15 mol%) as well as Dy_2O_3 (0.1 mol %) for PG13 glass and low concentration of LiF (5 mol%) and Dy_2O_3 (0.01 mol %) respectively. Therefore concentration variation in the composition is playing a key role in higher emissions. Further it is important to notice that all other glasses are also showing considerable intensity variations in between and is shown in below Fig. 4a. The results in intensity variation show that MgO and LiF are acting as intermediates in influencing the cadmium phosphate network. For constant dopent concentrations, the variation in the intensities supports the same. So, in case of higher concentration of LiF (15 mol %), the non symmetric electric field acting on Dy^{3+} ions is relatively higher when compared to 5 mol% and 10 mol% of LiF glasses.

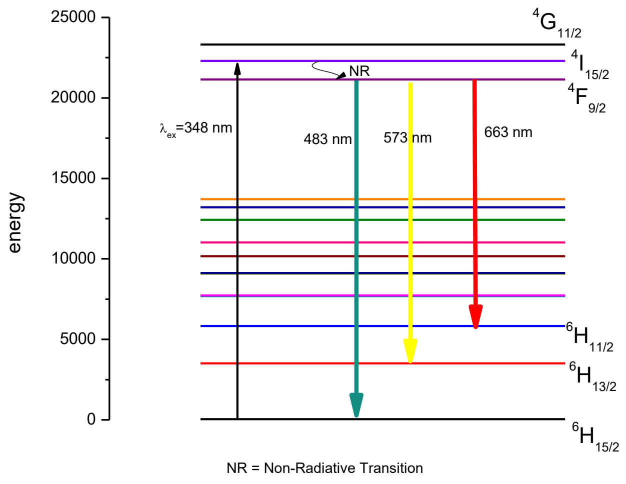

Fig. 5. Energy level diagram for Dy3+ doped Alkali Earth Cadmium Phosphate Glasses

The Y/B ratios of all the Dy^{3+}doped phosphate glasses are in the range 1.53 – 1.64. These Y/B ratios are comparable to those obtained for Dy^{3+}-doped considerably equal to obtained for other phosphate glasses [20].

The Y/B ratio is nearly equal for all the Dy^{3+}-doped phosphate glasses that is though there is decrease in emission intensity with the increase in concentration, the local environment around Dy^{3+} is invariant with varying concentration. Comparatively larger Y/B ratios suggest the pronounced nature of covalency and asymmetry effects [21]. The feasibility of generation of white light in the Dy^{3+}-doped cadmium phosphate glass is high as the Y/B ratios are in visible region.Thechromaticity color coordinates for Dy^{3+}-doped cadmium phosphate glasseswith various concentration were calculatedand obtained as averagely x=0.39, y=0.35and the corresponding CIEx–y chromaticity diagram are also presented in (Fig. 6). TheCIE coordinates of all investigated glasses, excited with348 nm, lies within the white region, though they are faraway from the ideal equal energy white light illumination.

Further studieson simulation of white light for these Dy^{3+}-doped present phosphateglasses are necessary by both adjusting the glass compositionsand enhancing the red emission part by co-doping.

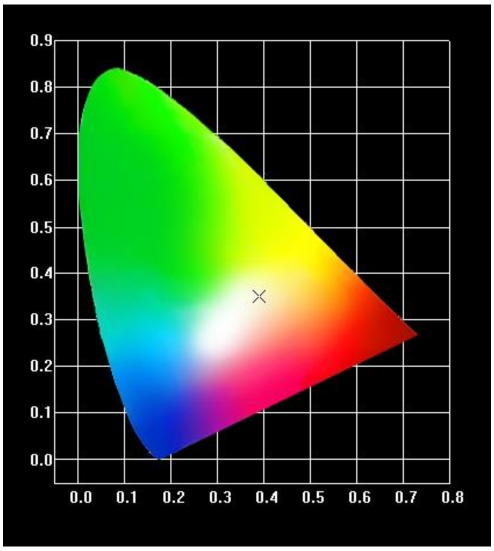

Fig. 6. CIE chromaticity diagram

4. Conclusions

In summary, Cadmium Phosphate glasses were synthesized with different concentrations of Dy^{3+} ions by using the melt quenching technique. The absorption spectra were analyzed by using the JO theory, from the integrated intensities of various absorption bands. The JO parameter Ω_2 value indicates that these doped glasses are more covalent in nature. Strong yellow and blue emissions were observed upon the 348 nm excitation wavelengths, thus realizing the generation of the white light emission under UV excitation. The emission intensity ratio's of yellow and blue transitions, Y/B, of Dy^{3+} ions indicate the strong covalent nature and dependence on the local environment in which the RE ions are occupied. These results also show the possibility of obtaining white light from the present glasses.These Mg-based phosphate glasses are highly transparent and capable to accommodate larger concentrations of RE ions; therefore, these glasses are of particular interest for developing optical amplifier based devices and suitable for white light generation because of its broad excitation band area. Energy level diagram shows the luminescence mechanism and the CIE co-ordinates also stays in white light region.

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References

[1] W. T. Carnall, G. L. Goodman, K. Rajnak, R. S. Rana, J. Chem. Phys. **90**(7), 3443 (1989).

[2] P. A. Tanner, V. R. K. Kumar, C. K. Jayasankar, M. F. Reid, J. Alloy. Compd. **215**(1-2), 349 (1994).

[3] K. W. Krämer, H. U. Güdel, R. N. Schwartz, Phys. Rev. B **56**(21), (1997).

[4] V. J. Pugh, F. S. Richardson, J. B. Gruber, M. D. Seltzer, J. Phys. Chem. Solids **58**(1), 85 (1997).

[5] E. Antic-Fidancev, M. Lemaitre-Blaise, M. Latroche, P. Porcher, J. Coutures, J. P. Coutures, J. Alloy. Compd. **250**(1-2), 342 (1997).

[6] C. Gorller-Walrand, K. Binnemans, North-Holland, Amst. **25**, 101 (1998).

[7] C. C. Wang, Phys. Rev. B **2**(6), (1970).

[8] P. I. Paulose, G. Jose, V. Thomas, N. V. Unnikrishnan, M. K. R. Warrier, J. Phys. Chem. Solids **64**(5), 841 (2003).

[9] M. Nogami, T. Enomoto, T. Hayakawa, J. Lumin. **97**(3-4), 147 (2002).

[10] C. Zhu, Y. Yang, X. Liang, S. Yuan, G. Chen, J. Lumin. **126**(2), 707 (2007).

[11] G. Giridhar, M. Rangacharyulu, P. R. V. S. S. N. Ravi Kumar, Electron. Adv. Mater. Rapid Commun. **2**, (2008).

[12] V. R. Kumar, G. Giridhar, N. Veeraiah, Luminescence **32**(1), 71 (2017).

[13] V. Ravi Kumar, G. Giridhar, N. Veeraiah, Opt. Mater. **60**, 594 (2016).

[14] J. S. Kumar, K. Pavani, A. M. Babu, N. K. Giri, S. B. Rai, L. R. Moorthy, J. Lumin. **130**(10), 1916 (2010).

[15] S. P. Jamison, R. J. Reeves, Phys. Rev. B**67**(11), 115110 (2003).

[16] R. J. Amjad, M. R. Sahar S. K. Ghoshal, M. R. Dousti, R. Arifin, Opt. Mater. **35**(5), 1103 (2013).

[17] V. Reddy Prasad, S. Babu, Y.C. Ratnakaram, Ind. J. Phys. **90**(10), 1173 (2016).

[18] K. Linganna, Ch. Srinivasa Rao, C. K. Jayasankar, J. Quan. Spec. & Rad. Trans. **118**, 40 (2013).

[19] C. K. Jørgensen, R. Reisfeld, J. Less Common Met. **93**(1), 107 (1983).

[20] M. Jayasimhadri, K. Jang, H. S. Lee, B. Chen, S.-S. Yi, J.-H. Jeong, J. Appl. Phys. **106**(1), 013105 (2009).

[21] K. Seneschal, F. Smektala, S. Jiang, T. Luo, B. Bureau, J. Lucas, N. Peyghambarian, J. Non-Crystalline Solids **324**(1-2), 179 (2003).

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