

SPECTROSCOPIC INVESTIGATIONS ON Dy³⁺, Pr³⁺ AND Sm³⁺ DOPED CdO-ZnO-P₂O₅ GLASSES FOR OPTICAL APPLICATIONS

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ABSTRACT

The present work deals with cadmium zinc phosphate glasses doped with different rare earth ions like Dy³⁺, Pr³⁺ and Sm³⁺. Optical absorption, emission, and excitation studies were carried out on these glasses at room temperature. All the corresponding rare earth doped glasses showed strong characteristic absorption bands from their ground states. Emission studies reveal that all these glasses exhibit visible emission for their respective excitation wavelengths. From these studies, it is found that the present host glass is suitable for white light emission as well as red emission. Therefore these Cd-Zn glasses are useful for lighting applications

Keywords: Phosphate Glass, Luminescence, White LEDs, Optical absorption.

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INTRODUCTION

Lanthanides are playing a key role in lighting applications in a different host. Phosphate glasses have a great interest in this particular area as with the great properties like low melting point, high transparency and greater accessibility of ions. It is well known that because of the variation in the composition of rare earth ions, there must be a definite change in its bond nature, local environment and the related properties for the optical applications.¹ The phosphate glasses are very important in their usage due to the low probability of energy back transfer and weak upconversion behavior. The present work deals with the cadmium zinc phosphate glasses doped with different rare earth ions like Dy³⁺, Pr³⁺ and Sm³⁺. Dy³⁺ ions have the importance in the generation of photo energy in both Visible and NIR regions. The transitions from the metastable state ⁴F_{9/2} to different lower levels ⁶H_{7/2}, ⁶H_{9/2}, ⁶H_{11/2}, ⁶H_{13/2} and ⁶H_{15/2} are the featured transitions². Particularly in yellow region, Dy³⁺ gives a strong emission line. In preparation of upconverters, optical amplifiers, optical fibers and UV-Vis-NIR lasers, Pr³⁺ has its own key role due to the close energy separation between its configuration.¹ Further, Pr³⁺ doped oxides and fluoride materials were useful for red emission applications and the emission processes are explained in the previous studies.³⁻¹⁰ In such studies, Pr³⁺ ions in solids emit more than one visible photon for each incident UV excitation photon.

Similarly, the Sm³⁺ (4f⁵) ion is an interesting Ln³⁺ ion which emits photo energy with high quantum efficiency from its metastable state ⁴G_{5/2}. level exhibits relatively high quantum efficiency. Moreover, the glasses doped with Sm³⁺ ions are very important in optical device manufacturing when compared to other rare earth ions in terms of undersea communications, high-density memory devices, solid state lasers and usual color displays.¹¹

EXPERIMENTAL

Cadmium Zinc phosphate glasses with different rare earth ions were prepared by using conventional melt quenching with different molar chemical compositions as:

CdPDy Glass:	70P ₂ O ₅ – 15CdO – 15ZnO – 0.5Dy ₂ O ₃
CdPPr Glass :	70P ₂ O ₅ – 15CdO – 15ZnO – 0.5Pr ₆ O ₁₁
CdPSm Glass:	70P ₂ O ₅ – 15CdO – 15ZnO – 0.5Sm ₂ O ₃

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°C for 1.5 hours. The melt was transferred to the clean surface of a preheated brass plate. Then it was annealed at 250 °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 (C₁₀H₇Br) 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

Absorption studies – CdPDy glass

Optical absorption spectra of Dy³⁺ (in the range of 300 nm –1800 nm) ions doped Cadmium zinc phosphate glass is shown in Figures-1 and 2. The absorption spectra shows nearly ten absorption bands analogous to the transition from its ground state ${}^6H_{15/2} \rightarrow {}^4I_{13/2}$, ${}^6H_{15/2} \rightarrow {}^4G_{11/2}$, ${}^6H_{15/2} \rightarrow {}^4I_{15/2}$, ${}^6H_{15/2} \rightarrow {}^4F_{9/2}$, ${}^6H_{15/2} \rightarrow {}^6F_{3/2}$, ${}^6H_{15/2} \rightarrow {}^6F_{5/2}$, ${}^6H_{15/2} \rightarrow {}^6F_{7/2}$, ${}^6H_{15/2} \rightarrow {}^6F_{9/2}$, ${}^6H_{15/2} \rightarrow {}^6F_{11/2}$ and ${}^6H_{15/2} \rightarrow {}^6H_{11/2}$. The absorption bands related to thermalization from the prime excited ${}^6H_{13/2}$ level are neglected because of the high energy gap ($\sim 3300\text{ cm}^{-1}$) between ${}^6H_{15/2}$ and ${}^6H_{13/2}$ levels.

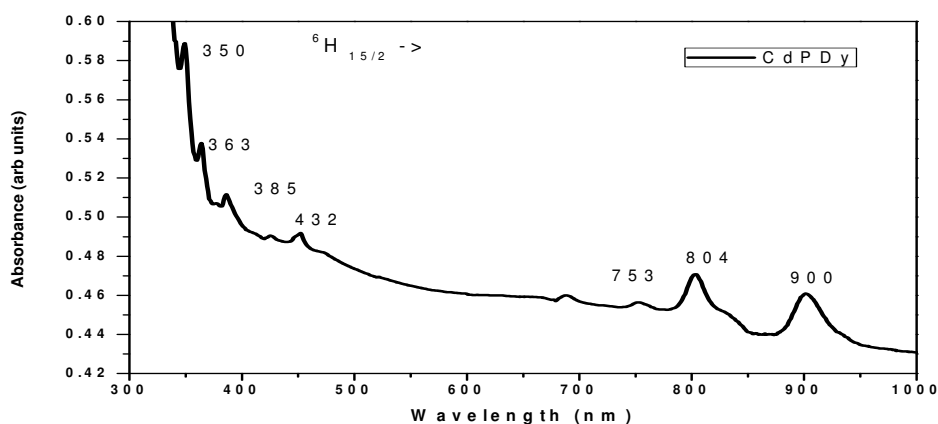


Fig.-1: Optical absorption spectrum of Dy³⁺ doped CdPDy glass (UV-Visible region)

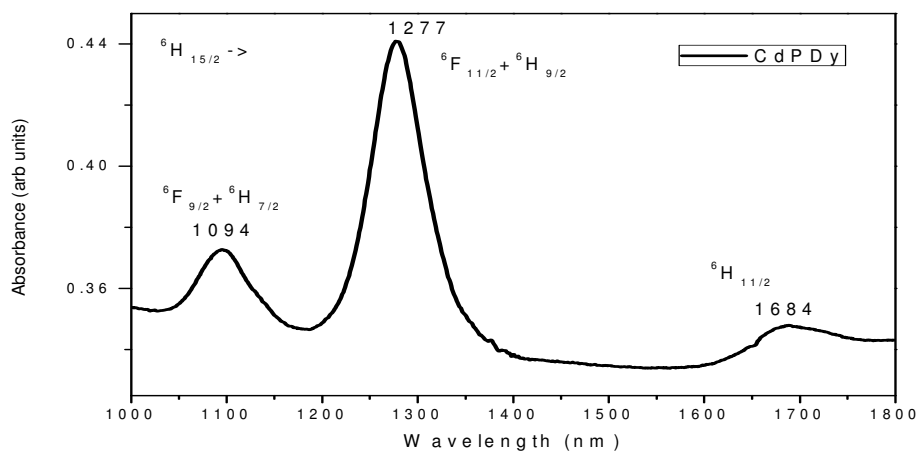


Fig.-2: Absorption spectrum of Dy³⁺ ions doped CdPDy glass (NIR region)

By applying the J-O theory to the observed absorption bands, the intensity parameters Ω_k ($k = 2, 4, 6$) were evaluated with the help of the oscillator strengths^{12,13} and particularly, with the Ω_2 parameters, it is possible to explain the covalency of metal-ligand bond and the symmetry of local environment surrounded by the rare earth ions. The higher value of Ω_2 parameters in this work specifies the enhancement in covalent bonding and implies higher site asymmetry of the Dy^{3+} ions in Cd-Zn phosphate glass matrix. The Ω_6 parameters are well-known for the rigidity of the host and also vibronic dependent.¹⁴ The hypersensitive transitions observed in the absorption spectra are defined as the transitions which are very sensitive to the host matrix and dopant concentration because of inhomogeneity of the surrounded ligand environment.

Absorption Studies - CdPPr glass

The recorded absorption spectrum at room-temperature for CdPPr phosphate glass is given in Fig.-3 and Fig.-4 as in UV-Vis region and NIR regions respectively. From the spectrum, absorption bands at 444, 467, 479, 590, 1014, 1527 and 1942 nm are assigned to characteristic Pr^{3+} transitions from its ground state 3H_4 to different excited states, such that 3P_2 , $^3P_1+^1I_6$, 3P_0 , 1D_2 , 1G_4 , $^3F_4+^3F_3$ and 3F_2 .¹⁵

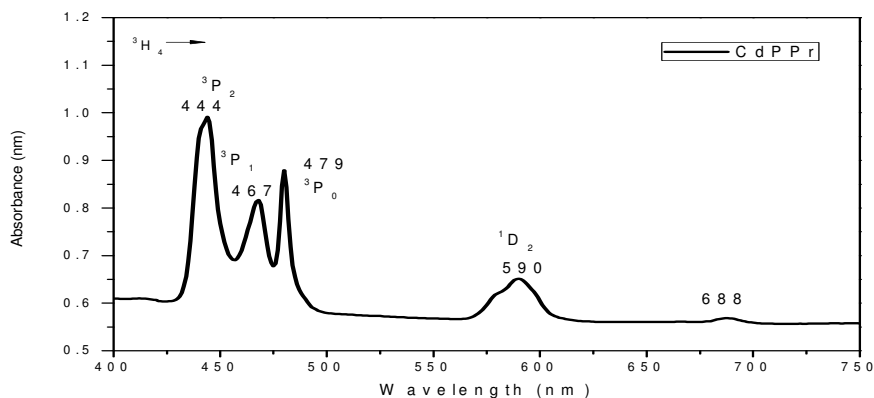


Fig.-3: Absorption spectrum of Pr^{3+} ions doped CdPPr glass (UV-Vis region)

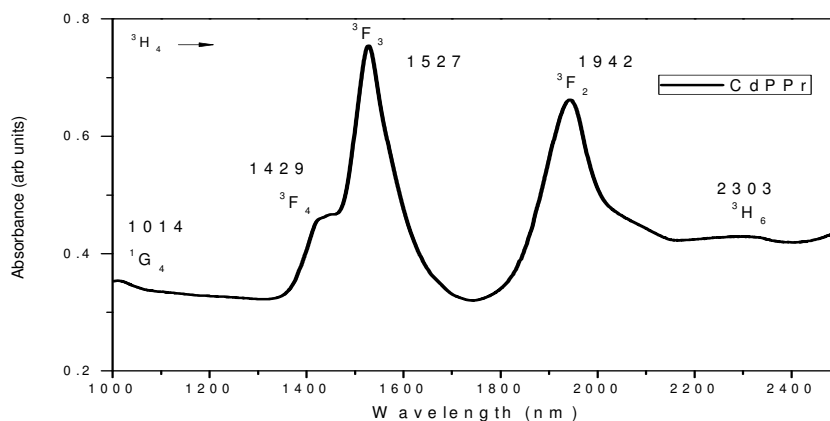


Fig.-4: Absorption spectrum of Pr^{3+} ions doped CdPPr glass (NIR region)

As said above all transitions observed are start from the 3H_4 ground state and these bands are due to the $4f^2$ -intra-configurational electric dipole (ED) transitions to different excited states $^3P_{J=0,1,2}$ and 1D_2 . The

band widths of the absorption bands are because of the addition of both unresolved Stark splitting and inhomogeneous broadening.

Absorption Studies - CdPSm Glass

In the present Cd-Zn phosphate glasses, the obtained optical absorption spectrum is shown in Fig.-5 and Fig.-6 for UV-VIS and NIR regions respectively. The observed transitions are from the ${}^6\text{H}_{5/2}$ ground state to different excited states. These characteristic transitions of Sm^{3+} are intra-configuration (f-f) transitions. For the present study the eight absorption bands obtained are centered at 360 nm, 373 nm, 401 nm, 473 nm, 949 nm, 1081 nm, 1232 nm, 1383 nm, 1486 nm, 1551 nm and 1590 nm are assigned to various transitions from ground state to excited states - ${}^4\text{F}_{9/2}$, ${}^6\text{P}_{7/2}$, ${}^4\text{F}_{7/2}$, ${}^4\text{I}_{11/2}$, ${}^6\text{F}_{11/2}$, ${}^6\text{F}_{9/2}$, ${}^6\text{F}_{7/2}$, ${}^6\text{F}_{5/2}$, ${}^6\text{F}_{3/2}$, ${}^6\text{H}_{15/2}$ and ${}^6\text{F}_{1/2}$ respectively¹⁶.

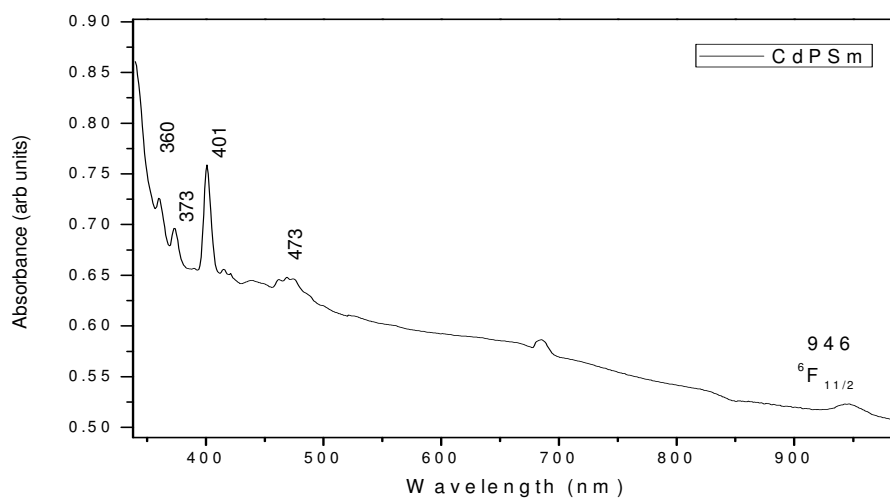


Fig.-5: Optical absorption spectrum of Sm^{3+} doped CdPSm glass (UV-Vis region)

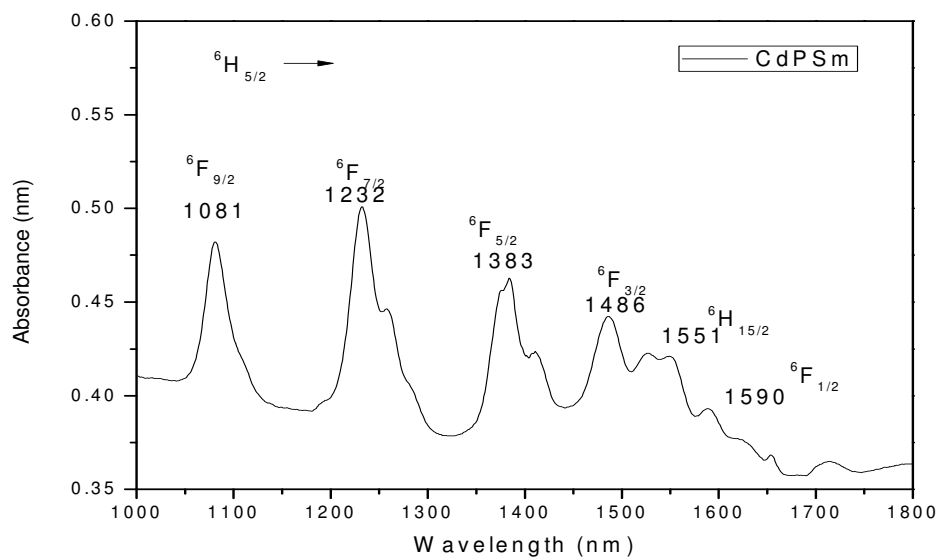


Fig.-6: Absorption spectrum of Sm^{3+} doped CdPSm glass (NIR region)

The absorption bands of Sm^{3+} ion is separated into low energy and higher energy groups such that the transitions up to 935 nm and the transitions from 570 nm to 313 nm respectively.

The evaluated J-O intensity parameters shows the trend, $\Omega_2 < \Omega_6 < \Omega_4$. These parameters are very useful in determining both the bonding nature and local environment surrounded by the doped rare earth ions. A Large value of the J-O parameter (Ω_2) enunciates the high covalency nature of the ion-ligand bond (Sm-O) and also the high occupancy of asymmetry sites by Sm^{3+} ions in the present host. Different trends of J-O parameters are also observed from the literature¹⁷. The large spectral intensities are due to the high mixing of the opposite parity electronic configurations.

Excitation and Emission Studies: CdPDy glass

The excitation spectrum of the Dy^{3+} ions doped Cd-Zn phosphate glasses obtained is shown in Fig.-7. The highest level at 348 nm is selected as the excitation wavelength for the recording of the emission spectrum.

The emission spectrum of Dy^{3+} -doped Cd-Zn phosphate glasses in the visible region (400–700 nm) upon 348 nm excitation is shown in Fig.-8. The spectrum consists of three characteristic emission peaks. The first two intense emission bands obtained at 483 nm and 574 nm are assigned to the transition from meta stable state $^4\text{F}_{9/2}$ to lower energy states as $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$. The other remaining feeble emission band at 663 nm is assigned to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{11/2}$ transition. The transitions observed from the emission spectra are similar to the recent studies on bismuth based alkali phosphate glasses².

In any host matrix, for a proper yellow to blue (Y/B) ratio of emission transitions, the Dy^{3+} ions shows white light emission. In the present study of Dy^{3+} -doped Cd-Zn phosphate glass the (Y/B) ratio ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) (yellow) / ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) (blue) is 1.56. The emitting photo luminescence of the present sample upon 348 nm excitation has been characterized by the CIE 1931 chromaticity diagram.^{18,19}

The color coordinates (x, y) for chromaticity diagram are evaluated as (0.32, 0.36) for the present Cd-Zn glass. The falling of these coordinates takes place in the white light region of CIE 1931 chromaticity diagram which is built by the MATLAB module and is shown in Fig.-13. So, this result suggests that the studied Cd-Zn phosphate glass doped Dy^{3+} ions emit white light upon 348 nm excitation.

Excitation and Emission Studies: CdPPr glass

The excitation spectrum of the Pr^{3+} doped phosphate glass, monitoring emission at 607 nm. Three excitation bands at 441 nm ($^3\text{H}_4 \rightarrow ^3\text{P}_2$), 465 nm ($^3\text{H}_4 \rightarrow ^3\text{P}_1, ^1\text{I}_6$) and 480 nm ($^3\text{H}_4 \rightarrow ^3\text{P}_0$) respectively were observed from this spectrum and is shown in Fig.-9.

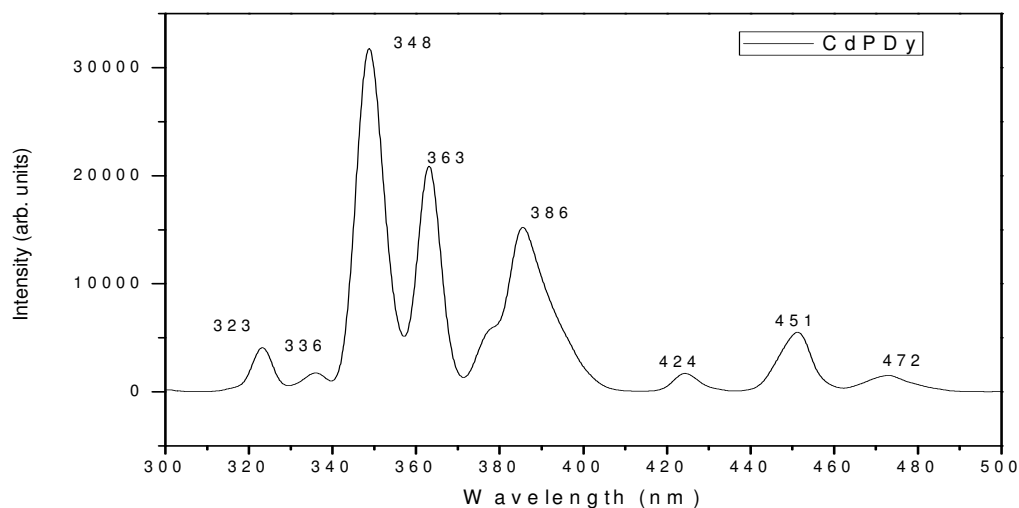


Fig.-7: Excitation spectrum of Dy^{3+} doped CdPDy glass ($\lambda_{\text{em}} = 573 \text{ nm}$)

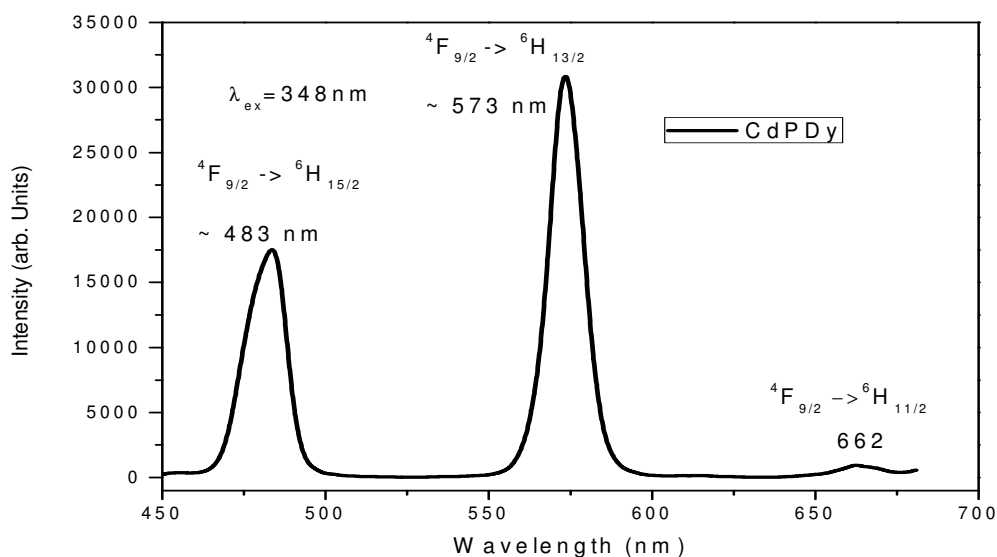


Fig.-8: Emission spectrum of Dy^{3+} doped CdPDy glass ($\lambda_{\text{ex}} = 348 \text{ nm}$)

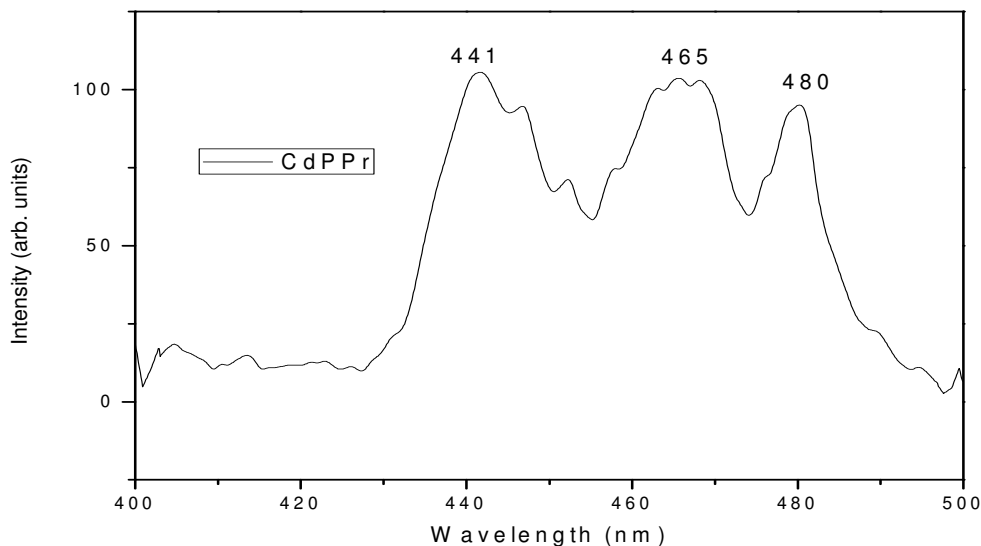


Fig.-9: Excitation spectrum of Pr^{3+} ions doped CdPPr glass ($\lambda_{\text{em}} = 607 \text{ nm}$)

By the excitation at room temperature with 441 nm as excitation wavelength to the Pr^{3+} doped CdPPr glass, the obtained emission spectrum is shown in Fig.-10.

Four characteristic emission bands were observed at different barry centers and were assigned to different transitions as 481 nm to the transition ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6 + {}^1\text{D}_2 \rightarrow {}^3\text{H}_4$, at 522 nm to the transition ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$, at 607 nm to the transition ${}^3\text{P}_0 \rightarrow {}^3\text{F}_3$ and at 637 nm to the transition ${}^3\text{P}_0 \rightarrow {}^3\text{F}_4$ respectively. The emission bands belong to the transitions ${}^3\text{P}_0 \rightarrow {}^3\text{H}_6 + {}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ and ${}^3\text{P}_0 \rightarrow {}^3\text{F}_3$ are more intense when compared to other observed transitions. Upon the modification of glass composition, the local crystal field splits the $4f^15d^1$ state. So the $4f^15d^1 \rightarrow 4f^2$ transition is more prominent in the emission spectra. Further, it is also

important that the local environment at the Pr^{3+} ions surroundings in the glass materials are relatively different when compared to the crystalline materials²⁰.

All the transitions are in the visible region and exhibiting different colors. But in this present case, the transition at 607 nm is more intense and is emitting a red color. So the present glass is useful for the making of red colored laser materials with good efficiency. By using CIE chromaticity diagram, the evaluated color coordinates from the emission spectrum are $x = 0.52$ and $y = 0.26$ and are fall at the orange red region in the CIE diagram and is also shown in Fig.-13.

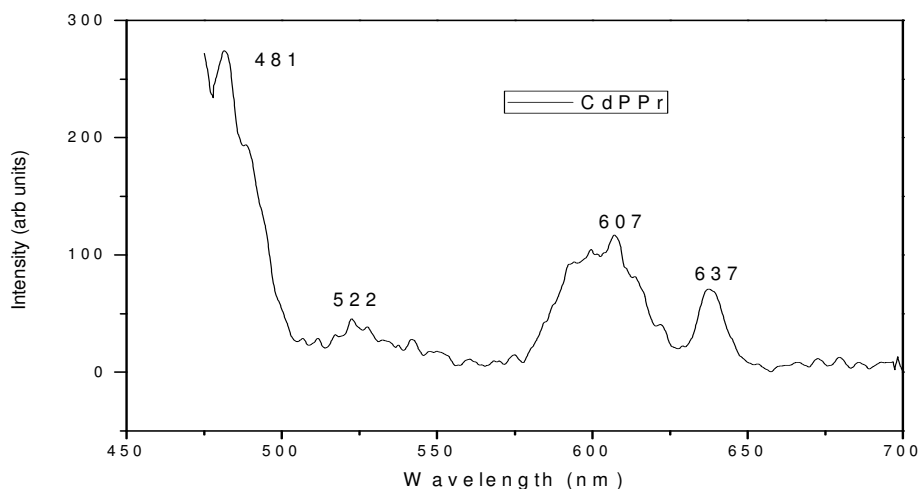


Fig.-10: Emission spectrum of Pr^{3+} ions doped CdPPr glass ($\lambda_{\text{ex}} = 441 \text{ nm}$)

Excitation and Emission Studies: CdPSm glass

At 597 nm – emission wavelength, the excitation spectrum observed for the present studying CdPSm glass is recorded at room temperature is shown in Fig.-11. Nearly, seven excitation bands were observed in the excitation spectra and were assigned to different transitions such as the peak at 400 nm to ${}^6\text{H}_{5/2} \rightarrow {}^4\text{F}_{7/2}$ transition, at 413 nm to ${}^6\text{H}_{5/2} \rightarrow ({}^6\text{P}, {}^4\text{P})_{5/2}$, at 468 nm to ${}^6\text{H}_{5/2} \rightarrow {}^4\text{G}_{9/2}$ transition and so on.

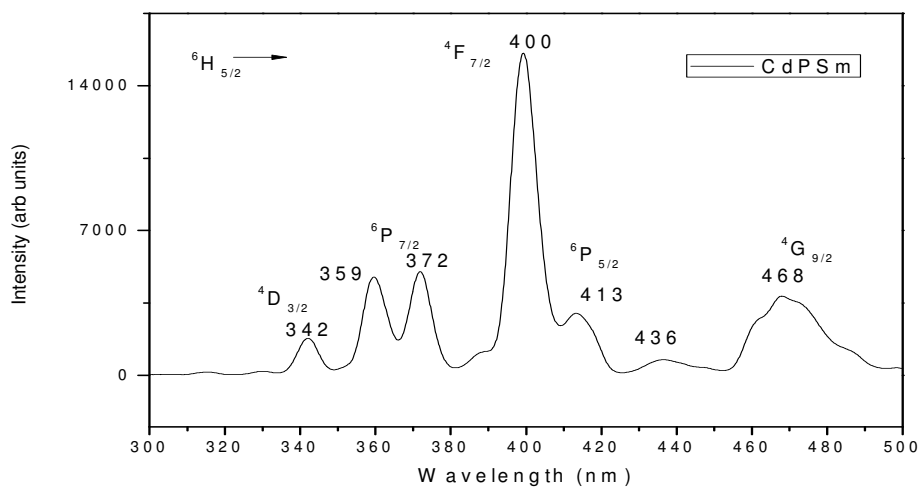


Fig.-11: Excitation spectrum of Sm^{3+} ions doped CdPSm glass ($\lambda_{\text{em}} = 597 \text{ nm}$)

From the excitation spectrum it is clear that most of the population resides at the ${}^4\text{F}_{7/2}$ level, so when this level is exciting, most of the population relaxes at lower ${}^4\text{G}_{5/2}$ level with various known radiative

transitions in between ${}^4F_{7/2}$ and ${}^4G_{5/2}$ levels. So, finally ${}^4G_{5/2}$ level becomes as a metastable state which originates the emission spectrum for Sm^{3+} ions.

The emission spectrum which is shown in Fig.-12, exhibited three characteristic emission bands, which are attributed to the center at 562 nm to the transition ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$, at 597 nm to the transition ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ and at 643 nm to the transition ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ respectively. The transition ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ observed at 597 nm shows a strong orange luminescence. The emission lines which are observed for the present host is similar to the previous works on Sm^{3+} ions doped materials²¹⁻²⁶.

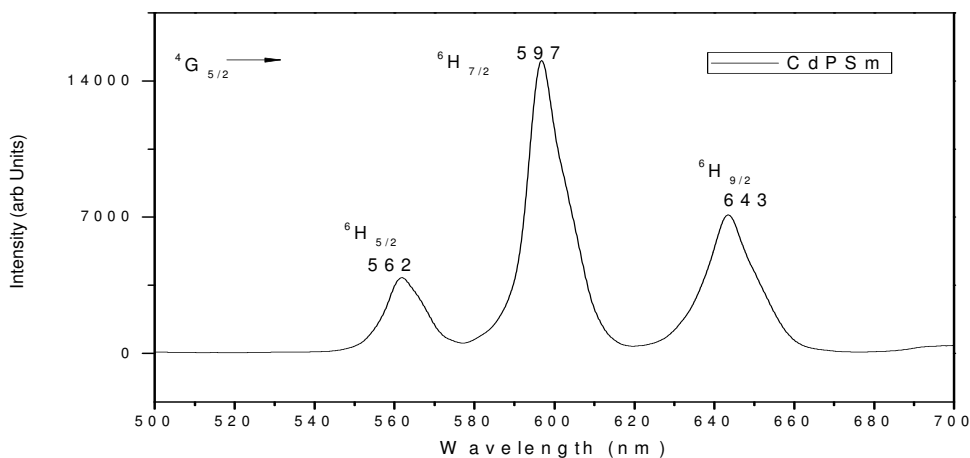


Fig.-12: Emission spectrum of Sm^{3+} doped CdPSm glass ($\lambda_{\text{ex}} = 400 \text{ nm}$)

In determining the symmetric nature of the host glass, both electric dipole transitions and magnetic dipole transitions play an important role. Here the transitions ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ and ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ are electric dipole transitions but the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition is also a magnetic dipole allowed transition with a selection rule $\Delta J = \pm 1$. But the second transition is purely electric dipole transition²⁷. In fact; to estimate the symmetry of the vicinity of the rare earth ions, the ratio of the electric dipole to magnetic dipole transitions plays a key role. The high intensity of electric dipole transition indicates higher asymmetry nature. In the present study, ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (MD) transition of Sm^{3+} ions in the host is high intensity when compared to ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ (ED) transition showing the asymmetric nature of the present CdPSm glass host.

For the luminescence evaluation of the Sm^{3+} ions doped Cd-Zn phosphate glass, CIE chromaticity diagram is drawn and the obtained coordinates $x = 0.56$ and $y = 0.23$ lies in the red region and is shown in Fig.-13. So the Cd-Zn phosphate glass host is feasible for red emission laser materials.

CONCLUSION

These present Cd-Zn phosphate glasses are base glasses with different rare earth ions and have no Alkali fluoride elements in it. X-ray diffraction studies on these present glasses confirm the amorphous nature. Optical absorption studies on Dy^{3+} ions exhibiting the Characteristic absorption bands and were assigned to various transitions. The emission spectra show three intense emission bands upon excitation of 348 nm. The chromaticity diagram represents the white light emission in this host.

The studies on Pr^{3+} ions in the present host have very interesting results. Characteristic absorption bands observed are assigned to various transitions from its ground state to different excited states. The emission spectra show four characteristic emission bands in the present host.

Upon Sm^{3+} ion doping in the Cd-Zn phosphate host, it is also showing its characteristic features in absorption spectra and as well as in emission spectra. It is observed that intense red emission is exhibiting in this host glass matrix.

These studies by doping the Pr^{3+} and Sm^{3+} ions into the Cd-Zn phosphate glasses exhibits intense red emission and it is clear that the host is able to accept the other rare earth ions also.

So, the present work shows a new way to establish other optical applications also with both concentration variations and as well as with different modifiers.

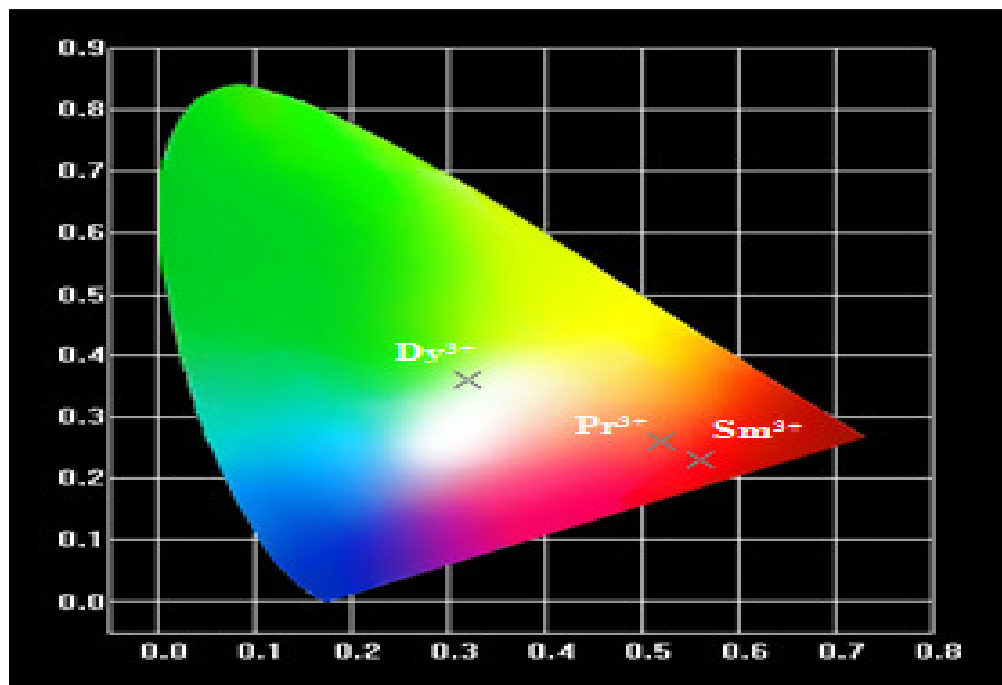


Fig.-13: CIE chromaticity diagram indicating the emission region of Cd-Zn phosphate glasses doped with Dy^{3+} , Pr^{3+} and Sm^{3+} ions

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