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Spectroscopic studies on Mn^{2+} ions doped Cadmium Aluminum Fluoro Lead Borate Glass

K.Nagamuni Reddy*, B. Sudhakar Reddy**
[*](Department of Chemistry, S.V. Degree College, Kadapa-516003, India)
[**](Department of Physics, S.V. Degree College, Kadapa-516003, India)

ABSTRACT
This article reports on optical properties of Mn^{2+} (0.5 mol%): 49.5 B_2O_3 - 10PbO - 30CdO -10AlF_3 glasses. Optical absorption spectrum of the manganese ions doped glass exhibits broad absorption band at 473 nm. Photoluminescence spectrum of Mn^{2+} (0.5 mol %): 49.5B_2O_3- 30CdO – 10PbO - 10AlF_3 glass has revealed a red emission at 618 nm with an excitation wavelength 467 nm.
Key words: XRD, emission, excitation, absorption

I. INTRODUCTION

Over the past several years, a great deal of research work has been carried out on different rare earth ($4f^n$) ions and also transition metal ($3d^n$) ions in glassy matrices for various optical device applications [1-10]. B_2O_3 is a glass forming oxide, AlF_3 is a conditional glass former and with these two chemicals in the glass matrix a low rate of crystallization, moisture resistance, stable and transparent glasses have been achieved. To improvise the lead borate glass quality and its optical performance suitable quantity (30 mol%) of CdO have been added separately as the network modifiers[NWF] alongside other property improving network modifier like (30 mol%) AlF_3. Interestingly, we have successfully developed these newly glasses with good transparency and UV and IR transmission ability. Oxide glasses are more appropriate for practical applications, due to their high chemical durability and good thermal stability compared to fluoride, chalcogenide and chloride glasses. But oxide glasses have a high multiphonon relaxation rate (1400 cm-1) which causes for the high non-radiative energy losses that are caused in the decrement of the emission efficiency in glasses. Mixing of oxide and fluoride ions in the preparation of glasses will combine the properties of both these ions i.e.,Oxyflouride glasses will exhibits good thermal stability, moisture resistance and low multiphonon rates which have the value in between oxide and fluoride based glasses for the better emission efficiency [11-13]. Transition metal ions doped glasses have become the subject of interest due to their potential applications.In order to check their optical performance; we have undertaken to examine the optical absorption spectra of a transition metal (Mn^{2+}) ion with $3d^9$ as electronic configuration. Cd belongs to the group IIB transition elements. The element (Cd) of IIB transition elements and have significantly improved the transmission ability and moisture resistance and transparency in the UV and IR wavelength regions for their utilization as optical materials of potential importance with the suitable dopant ions in those matrices for their applications. Among the transition metal ions, Mn^{2+} is a typical luminescent ion with potential applications. It has been studied in various inorganic hosts covering a wide range of emissions from blue to red. Fluorescence mechanism usually involves both parity and spin forbidden transitions and hence the intensity of the emission is relatively weak . Recently, Mn^{2+} ions doped glasses have drawn a great attention because of their optical bistability. In the present work, our main objective is to investigate the optical properties of newly developed transition metal ions such as Mn^{2+} ions doped (49.5) B_2O_3 - 10PbO-30 CdO - 10AlF_3 glass, we have undertaken the present work to study optical properties.

II. EXPERIMENTAL

2.1 GLASS PREPARATION

0.5 mol% Mn^{2+} ions doped borate lead cadmium aluminum fluoride glass has been prepared in the following chemical composition.

(49.5)B_2O_3-10PbO-30CdO-10AlF_3: 0.5Mn^{2+}

The starting materials [H_3BO_3, PbO, CdO, AlF_3 and MnO] were purchased from Sigma Aldrich and employed for subsequent procedures without any further purification. All the weighed chemicals were finely powdered and then mixed thoroughly before each of batches (10g) was melt by using alumina crucibles in an electric furnace at 980^0C for an hour. These melts were quenched in between two brass plates and thus obtained 2-3 cm diameter optical glasses with a uniform thickness 0.3 cm and these glasses were annealed at 200^0C for an hour in order to remove thermal strains if any in them soon after the glasses production.

2.2. MEASUREMENTS

The optical absorption spectra (350-1500 nm) for all glasses were measured on a Varian - Cary win spectrometer. The excitation and emission spectra were obtained on a in the wavelength range of 200–700 nm is recorded using a SHIMADZU RF5301 spectrofluoro meter with a slit width of 1.5 mm.

III. RESULTS AND DISCUSSION

In a cubic crystalline field of low to moderate strength, the five d electrons of Mn^{2+} ion are distributed in the t_{2g} and e.g. orbitals, with three in the former and two in the latter. Thus, the ground state configuration is $(t_{2g})^3 (e_g)^2$. This configuration gives rise to the electronic states, $^6A_{1g}$, $^4A_{1g}$, ^4E_g, $^4T_{1g}$, $^4T_{2g}$ and to a number of doublet states of which $^6A_{1g}$ is the lowest according to Hund's rule. The free ion levels of Mn^{2+} in the order of an energy increasing are ^6S, ^4G, ^4P, ^4D and ^4F etc. The energy level for Mn^{2+} ion in octahedral environment (CN=6) are $^6A_{1g}$ (^6S), $^4T_{1g}$ (^4G), $^4T_{2g}$ (^4G), ^4E_g - $^4A_{1g}$ (^4G), $^4T_{2g}$ (^4D) and ^4E_g (^4D). The ^4E_g - $^4A_{1g}$ (^4G) and ^4E_g (^4D) levels have relatively less influence compared to the other levels by crystal field. It means that the relative sharp lines can be expected in the absorption or excitation spectrum, which is the criterion for assignments of levels for Mn^{2+} ion. Since all the excited states of Mn^{2+} ion ($3d^5$) will be either quartets or doublets, the optical absorption spectra of Mn^{2+} ions will have only spin forbidden transitions.

Fig.1presents the Vis-NIR absorption spectrum of (0.5mol %) Mn^{2+} doped glass. From this a broad absorption band near 453 nm and 470 nm has been observed. The optical absorption studies confirm the presence of Mn^{2+} ions in the (49.5) B_2O_3-10PbO-30CdO-10AlF_3: 0.5Mn^{2+}glasses. **Fig.2** reveals the excitation spectrum of 0.5 mol% MnO doped (49.5) B_2O_3-10PbO - 30CdO -10AlF_3 glass. In the case of Mn^{2+} ions, it is difficult to pump the d-d absorption transitions because these are spin and parity forbidden to electric dipole radiation in octahedral symmetry. From the excitation spectrum, two excitation bands are observed at 467 nm and 492 nm. From Mn^{2+}: glasses, red colour has been observed when the co-ordination number of Mn^{2+} in the glass host is 6 and it emits green light if it is tetrahedrally co-ordinated (CN=4). **Fig.3.** shows the emission spectrum of (0.5 mol %) Mn^{2+}: CLBT glass with an excitation wavelength 497 nm. From the emission spectrum, a broad red emission band at 618 nm is observed and is assigned to the $^4T_{1g}$ (G) → $^6A_{1g}$ (S) transition of Mn^{2+} ions in octahedral symmetry

IV. CONCLUSION

It is concluded that, we have developed transparent, moisture resistant and more stable optical glasses based on the chemical composition of (0.5 mol %) Mn^{2+}: (49.5) B_2O_3-10PbO-30CdO-10AlF_3 by using melt quenching technique. Absorption spectrum has revealed the presence of Mn^{2+} ions, in the glass investigated. Photoluminescence spectrum of Mn^{2+} (0.5 mol %): (49.5) B_2O_3-10PbO-30CdO-10AlF_3 glass has revealed a red emission at 618 nm with an excitation wavelength 497 nm. Based on the spectral results, we suggest that, the Mn^{2+} glass have potential applications and such novel glasses are considered as potential optical systems. It is strongly contemplated for further development in future as laser materials doping with suitable lasing ions.

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Caption of Figures

Fig.1. Absorption spectrum of (49.5) B_2O_3-10PbO-30CdO-10AlF_3: 0.5Mn^{2+}glass

Fig.2. Excitation spectrum of (49.5) B_2O_3-10PbO-30CdO-10AlF_3: 0.5Mn^{2+}glass

Fig.3.Emission spectrum of (49.5) B_2O_3-10PbO-30CdO-10AlF_3: 0.5Mn^{2+}glass

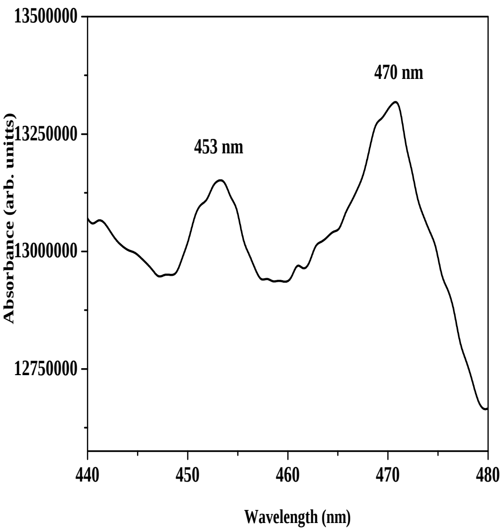

Fig.1

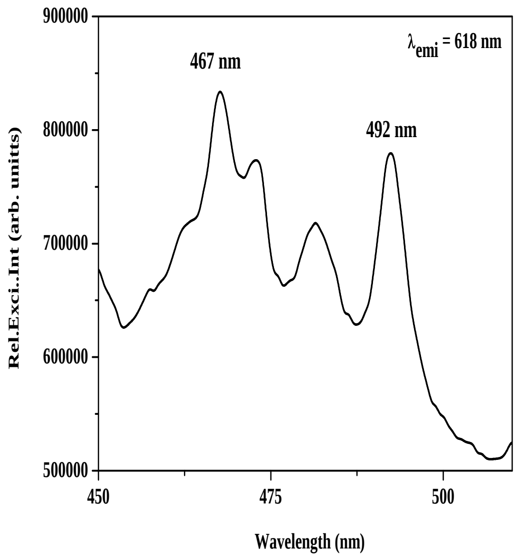

Fig.2

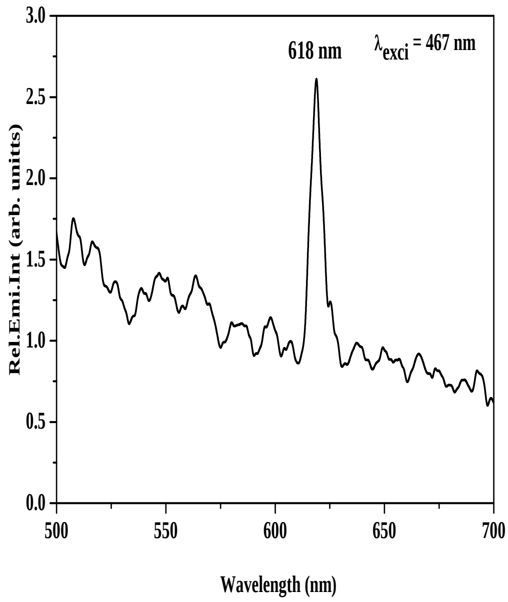

Fig.3