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Spectroscopic Studies on Cu^{2+}: B_2O_3 - Cdo - Pbo - AlF_3 Glass

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

ABSTRACT
This paper reports on the preparation and optical characterization of Cu^{2+} (0.5 mol %): (49.5)B_2O_3 - 10PbO - 30CdO -10AlF_3 (BPCA)glasses. Due to the homogeneous distribution of Cu^{2+} ions, the glasses are found to be in bright *blue* color has been noticed. From the XRD profile, amorphous nature the glass has been studied. Triogonal BO_3 units transformed into tetrahedral BO_4 units has evidenced from the FTIR spectrum of reference glass. From the measured absorption spectrum of the copper glass exhibits broad absorption band ($^2B_{1g}\rightarrow^2B_{1g}$) at 760 nm have been measured. Emission spectrum of Cu^{2+} (0.5 mol %): B_2O_3- CdO – PbO - AlF_3 glass has revealed a blue emission at 447 nm with an excitation wavelength 389 nm.
Keywords - absorption, Cu^{2+} : glass, emission, excitation, XRD

I. INTRODUCTION

In recent years, a great deal of work has been carried out on different rare earth ($4f^n$) ions and also transition metal ($3d^n$) ions in crystals and glassy matrices for various device and optical component development applications [1-10]. In order to improvise the glass quality and its optical performance from B_2O_3 glasses, suitable quantity (10mol%) of CdO have been added separately as the network modifiers[NWF] alongside other property improving network modifier like AlF_3. More interestingly, we have succeeded in developing these newly proposed glasses with an excellent transparency and UV and IR transmission ability. In order to verify their optical performance, we have undertaken to examine the optical absorption spectra of a simple transition metal (Cu^{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.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. Flouride glasses have low multiphonon rates(700cm^{-1}) compared to oxide,tellurite or chalcogenide glasses though they posses low thermal stability. 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]. 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. Transition metal ions doped glasses have become the subject of interest due to their potential applications. Bright blue colour could be found due to the presence of Cu^{2+} ions from the point of ligand fields theory. Recently, Cu^{2+} ions doped glasses have drawn a great attention because of their optical bistability [14-17]. Since there are no reports so far with regards to optical analysis of (49.5) B_2O_3 - 10PbO-30 CdO - 10AlF_3 glass, we have undertaken the present work.

II. EXPERIMENTAL

2.1 GLASS PREPARATION

The borate lead cadmium aluminum fluoride (BPCA) glasses in the following composition containing 0.5 mol% Cu^{2+} ions along with a host glass.

(i)50B_2O_3-10PbO-30CdO-10AlF_3:Host glass
(ii)(49.5)B_2O_3-10PbO-30CdO-10AlF_3: Cu^{2+}

The starting materials [H_3BO_3, PbO, CdO, AlF_3 and CuO] 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

Powder X-ray diffraction (XRD) spectrawere obtained on a Shimadzu XD3Adiffractometer with a Ni – filter and CuKα (=1.5418A^0) radiation with an applied voltage of 30kV and 20mA anode current calibrated with Si at the rate of 2^0/min. The FTIR spectrum (4000-450 cm^{-1}) was recorded on aPerkin Elmer spectrum1 spectrometer with KBr pellets. 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 SHIMADZURF 5301 spectrofluorometer with a slit width of 1.5 mm. **Fig.1a&.1b** present the photo graphs of the glasses studied in the present work.

III. RESULTS AND DISCUSSION

^2D is the free ion term for Cu^{2+} (d^9). In the presence of octahedral crystal field it splits into ^2E_g and $^2T_{2g}$ with ^2E_g being the lower level. ^2E_g generally splits due to Jahn –Teller effect. Therefore, Cu^{2+} is rarely found in regular octahedral site. Accordingly, in the present work, Cu^{2+} is taken to be octahedral co-ordinated by six oxygen atoms and the octahedron is tetragonally distorted. Therefore in the tetragonally distorted octahedral environment, the ^2E_g level splits into $^2A_1$ and $^2B_1$, and $^2T_{2g}$ levels into ^2E and $^2B_2$, the ground state being $^2B_1$.

The X-ray diffraction spectrum of the $50B_2O_3$ - 10PbO - 30CdO-$10AlF_3$ host (BPCA) glass is given in **Fig.2**, which confirms the amorphous nature of the glass. The UV optical absorption spectrum of undoped $50B_2O_3$ - 10PbO - 30CdO -$10AlF_3$ (BPCA) glass is shown in **Fig.3**, and from this spectrum, it is also observed that reference glass has shown UV transmitting ability which is extended up to 330nm. The FT-IR spectrum of undoped (BPCA) glass is shown in **Fig 4.** The structure of borate based glasses consists of a random network of BO_3 triangles with certain fraction of boroxol (six – membered) rings [18]. In the infrared spectral region, the vibrational modes of the borate network have three regions [19-20]. The 1200-1600cm^{-1} band is the first region, which is due to asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units. The second region is located between 800 -1200 cm^{-1} and is due to the B-O bond stretching of tetrahedral BO_4 units, and the last band around 700cm^{-1} is due to the bending of B-O-B linkages in the borate network. Thus, the band around 1340 cm^{-1} is due to B-O stretching vibrations of $(BO_3)^{3-}$ unit in metaborate chain and orthoborates. The peak observed at 987 cm^{-1} is attributed to the B-O bond stretching of BO_4 units. The absorption band at 702 cm^{-1} indicates the B-O-B bending vibrations. The peak at 457 cm^{-1} could be due to lose BO_4 units [21]. In general, the IR absorption band at 806 cm^{-1} is assigned to the boroxol ring in the borate glass network. In the present study, the peak at 806 cm^{-1} is found missing, which indicates the absence of boroxol ring in the glass network. Similarly, the band in the region of 3200-3600cm^{-1} is ascribed to the hydroxyl (or) water groups. **Fig.5** presents the Vis-NIR absorption spectrum of (0.5mol %) Cu^{2+} doped glass. From this a broad absorption band near 760nm ($^2B_{1g\rightarrow}$ $^2B_{2g}$) is due to Cu^{2+} ion in octahedral co-ordination with a strong tetragonal distortion [22-24]. The optical absorption studies confirm the presence of Cu^{2+} ions in the (49.5) B_2O_3-10PbO-30CdO-$10AlF_3$: $0.5Cu^{2+}$glasses. **Fig.6** reveals the excitation spectrum of 0.5 mol% CuO doped (49.5) B_2O_3-10PbO - 30CdO -$10AlF_3$ glass. According to ligand field theory [35], oxide based glasses could show charge transfer bands in the UV region due to the absorption by the oxygen ligands around the cations.Accordingly, for the 0.5 mol% of CuO doped (49.5) B_2O_3-10PbO - 30CdO - $10AlF_3$ glass, one excitation band 389 nm have been observed. This band is due to charge transfer phenomena caused by O^{2-} with an UV radiation exposure. **Fig.6** shows emission spectrum of 0.5 mol% CuO doped (49.5) B_2O_3-10PbO - 30CdO - $10AlF_3$ glass with an excitation at 389 nm, and one emission peak at 447 nm this is due to Cu^{2+} ions in the glass. However, according to an earlier report [36], emission at 447 nm arises due to localized excitation of isolated Cu^{2+} ions.

IV. CONCLUSION

It could be concluded that, we have developed transparent, moisture resistant and more stable optical glasses based on the chemical composition of (0.5 mol%) Cu^{2+}: (49.5) B_2O_3-10PbO-30CdO-$10AlF_3$ .Keeping in view of these encouraging optical properties, host glasses have been selected to examine its amorphous nature through XRD spectrum. Absorption spectrum has revealed the presence of Cu^{2+} ions, in the glass investigated. Emission spectrum of Cu^{2+} (0.5 mol %): B_2O_3- CdO – PbO - AlF_3 glass has revealed a blue emission at 447 nm with an excitation wavelength 389 nm. Based on the spectral results, we suggest that, the Cu^{2+} glass have potential applications to carry on further research work with several other transition metal ions. 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. Photograph of (a)Host glass and (b) 49.5B_2O_3-10PbO-30CdO-10AlF_3: 0.5Cu^{2+}glass

Fig.2. XRD spectrum of 50B_2O_3-10PbO-30CdO-10AlF_3 glass

Fig.3. UV Absorption transmission spectrum of 50B_2O_3-10PbO-30CdO-10AlF_3 glass

Fig.4. FTIR profile of 50B_2O_3-10PbO-30CdO-10AlF_3 glass

Fig.5. Absorption spectrum of (49.5) B_2O_3-10PbO-30CdO-10AlF_3: 0.5Cu^{2+}glass

Fig.6. Excitation spectrum of (49.5) B_2O_3-10PbO-30CdO-10AlF_3: 0.5Cu^{2+}glass

Fig.7.Emission spectrum of (49.5) B_2O_3-10PbO-30CdO-10AlF_3: 0.5Cu^{2+}glass

(a) Host glass **(b) Cu^{2+} glass**

Fig.1.

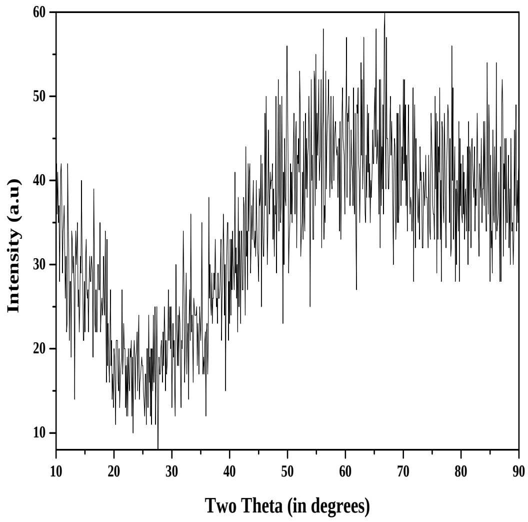

Fig.2

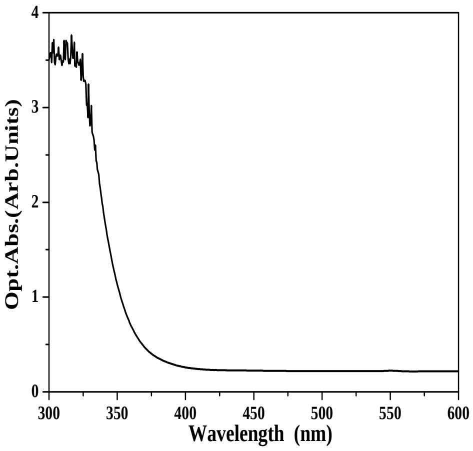

Fig.3

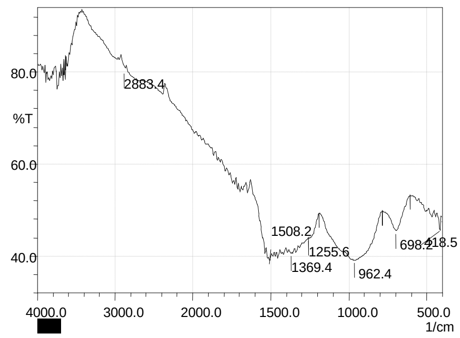

Fig.4

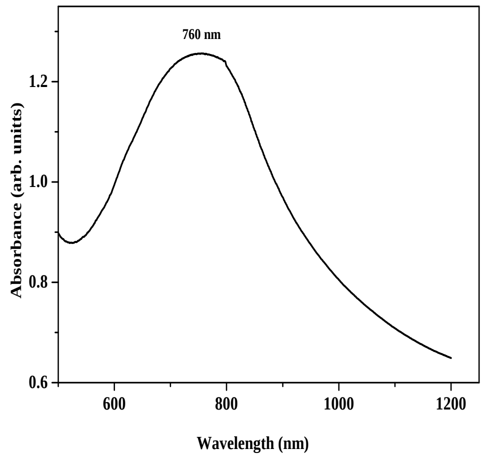

Fig.5

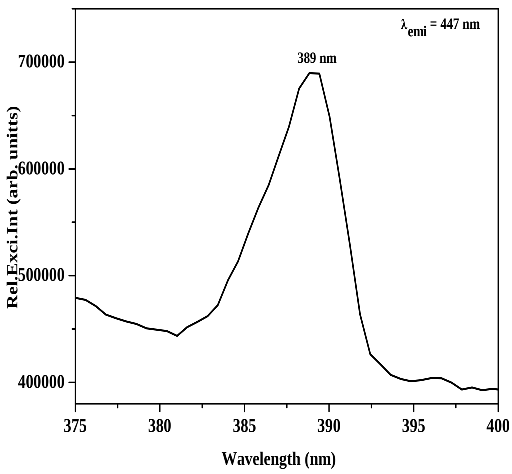

Fig.6

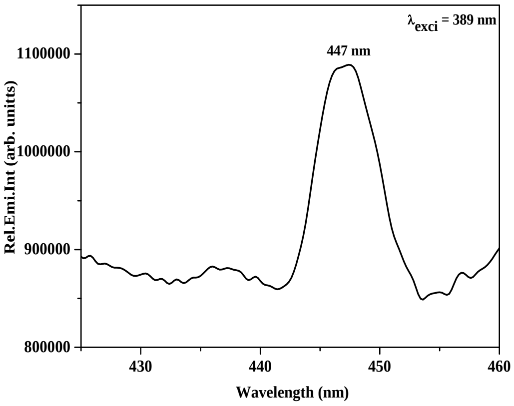
λ_{exci} = 389 nm
447 nm
1100000
1000000
900000
800000
Rel.Emi.Int (arb. unitts)
430
440
450
460
Wavelength (nm)

Fig.7