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Infrared Spectral and EPR Studies of Mn^{2+} Ions Doped K_2O - CdO - B_2O_3 - SiO_2 (KCdBSi) glass system

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ABSTRACT: *K_2O - CdO - B_2O_3 – SiO_2glasses containing different concentrations of MnO_2 have been prepared. The Physical properties of the glasses are studied from their density. The studies have been analysed in the light of different oxidation states of manganese ion with the aid of the data on IR and EPR. The analysis shows that manganese ions exist mainly in Mn^{2+} state, occupy tetrahedral positions and increase the insulating strength of the glass if MnO_2 is present in smaller concentrations. However, if MnO_2 is present in higher concentrations in the glass matrix, the intensity and the half width of the EPR signal have been observed to decrease.*

KEY WORDS: *Borosilicate glass, Electron paramagnetic resonance,Infrared spectra, Manganese.*

I. INTRODUCTION

More recently, there has been a great deal of interest on the preparation and characterization of a wide variety of optical glasses comprising of oxides, silicates, borates, phosphates, fluorides etc., for their potential applications [1].Glasses based on borates and silicates have been identified as ideal optical systems because of their good glass forming ability, hardness, transparency and resistance towards moisture without any degradation on their surfaces.In order to improve the quality of glass and its optical performance from borosilicate glasses, suitable quantity (5 mol %) of CdO have been added separately as the network modifier (NWF).Transition metal ions are incorporated into these borosilicate glasses in order to characterize their optical behaviours. Glasses doped with transition metal ions exhibit interesting spectroscopic properties and hence are highly suitable for solid state lasers. Glasses containing transition metal ions have become the subject of interest owing to their potential applications [2]. Electronic and magnetic properties of these glasses depend on the relative proportion of different oxidation states of transition metal ions [3] and their near environments in the host. Electron Paramagnetic Resonance (EPR) spectroscopy and optical absorption techniques give rise to ligand field absorption energies, which sensitively reflect the distortion from cubic, octahedral and tetrahedral co-ordinations [4,5]. Amongst the paramagnetic compounds the divalent manganese are of particular interest, because the 3d electron shell responsible for the paramagnetic ion is just half filled by the five electrons of these ions, and the resultant orbital angular momentum is zero. Mn^{2+} ion, a d^5 configuration high-spin ion has found wide use as an extremely powerful probe in the study of structural as well as dynamic aspects of crystalline state, by incorporating it in diamagnetic and paramagnetic host crystals [6, 7]. The electron paramagnetic resonance (EPR) studies of Mn^{2+} ions in different crystalline materials have been reported by number of authors [8–17]. EPR spectrum of d^5 ion is particularly interesting when one is concerned with the local symmetry environment of the ion and a detailed study of d^5 ion in diamagnetic crystals gives the information about the environment around the paramagnetic ion.

In the present study, we have carried out electron paramagnetic resonance (EPR) and FT-IR studies in KCdBSi (K_2O - CdO - B_2O_3 – SiO_2) glasses doped with a small amount of paramagnetic impurity MnO_2.

II. EXPERIMENTAL STUDY

2.1. Glass preparation

The glass samples studied in the present work (Table 1) have been obtained by the classical melt quenching technique. They are prepared by mixing and grinding together appropriate amounts of K_2O , CdO , B_2O_3, SiO_2 and MnO_2 in an agate mortar before transferring to a silica crucible and heating in an electric furnace in air at 1280K for half an hour. The melt is then quenched at room temperature in air by pouring it onto a polished plate. Glasses obtained are with good optical quality and high transparency. The polished glasses are used for measurements.

Table 1: Glass compositions of Mn^{2+} ions in KCdBSi glass system

Glass system	K_2O (mol %)	CdO (mol %)	B_2O_3 (mol %)	SiO_2 (mol %)	MnO_2 (mol %)
Mn_o	20.0	5	60	15	-
Mn_1	19.9	5	60	15	0.1
Mn_2	19.8	5	60	15	0.2
Mn_3	19.7	5	60	15	0.3
Mn_4	19.6	5	60	15	0.4
Mn_5	19.5	5	60	15	0.5

2.2. Measurements

The EPR spectrum of (K_2O - CdO - B_2O_3 - SiO_2) glass sample recorded at room temperature using a JEOL–FE1X EPR spectrometer operating in the X-band frequency (9.205 GHz) with a field modulation frequency of 100 kHz. The magnetic field was scanned from 0 to 5000G and the microwave power used was 5mW. The IR transmittance spectra of the powdered glass samples are recorded using JASCO FT-IR 5300 spectrometer in the wave number range 400-4000cm^{-1} at room temperature. All the measurements were carried out at room temperature.

III. RESULTS AND ANALYSIS

3.1 EPR:

Figure 1, shows the EPR spectra of 0.1 to 0.5 mol% of Mn^{2+} ions in the present glass samples observed at room temperature. All the glass samples doped with manganese ions show a broad resonance at g ~ 2.0 with six line hyperfine pattern, which is a characteristic of Mn^{2+} ions with a nuclear spin I=5/2. The evaluated g values and hyperfine splitting (A) parameters are shown in Table 2. It is observed that the Mn^{2+} ions in KCBSi glasses are quite ionic in nature [10, 11]. The spectra at a concentration of MnO_2; 0.1, 0.3 and 0.5 mol% exhibited a predominant broad band around 500 nm. This absorption band is assigned to a single allowed transition $^5E_g \rightarrow {}^5T_{2g}$, due to Mn^{3+} ions being in octahedral symmetry. Furthermore, this band was asymmetric, indicating that the octahedral ligand field had suffered a tetrahedral deformation by the Jahn-Teller effect. The most common manganese ions found in oxide glass are Mn^{2+} and Mn^{3+}ions. However, the Mn^{2+}ions could not be observed as they had a lower intensity than the Mn^{3+} ions and in addition, the Mn^{2+} ion had a $3d^5$ configuration and all transitions are spin forbidden.

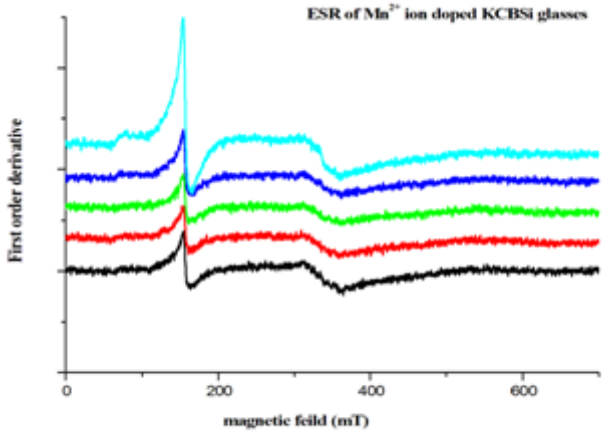

Fig: 1EPR Spectrum of Mn^{2+} ion doped KCdBSiglass system

Table 2: g-values of Mn^{2+} ions doped KCdBSi glass system

Glass system	g-value
Mn_1	2.023
Mn_2	1.982
Mn_3	1.974
Mn_4	1.980
Mn_5	2.020

3.2 FT-IR

Recollecting the data on IR spectra, with the raise in the concentration of MnO_2, the intensity of the bands due to BO_3 structural units has been observed to decrease at the expense of the bands due to BO_4 units up to 0.5 mol %. This observation suggests a gradual increase in the concentration of divalent manganese ions in the glass network that acts as modifiers; improved the tetrahedral sites in the glass matrix at this concentration
The infrared absorption spectrum is the most useful technique to identify the functional groups and to know the molecular structure. Fig. 2 represents the FTIR spectra of all the glasses in the wave number region 400-2000 cm^{-1}. In the present investigations, the observed bands and their corresponding assignments are presented in Table 3. The IR spectrum of MnO_2 free glass sample has bands at 1470, 1320, 1120, 750, 562 cm^{-1}. Two feeble bands are also observed at 526 and 474 cm^{-1}. Generally KCBSi glasses are active in the mid IR region.K_2O,CdO enters into the glass network by converting BO_3 into BO_4 and also creates non bridging oxygens. These units act as defects in the glass network and modify the boro silicates glass structure.

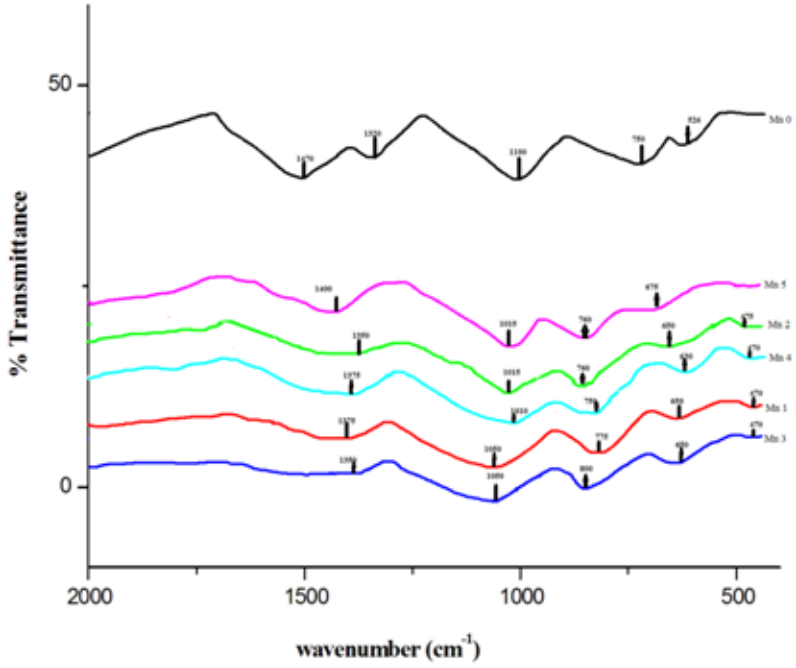

Fig:2 FT-IR Spectrum of Mn^{2+} ion doped KCdBSi glass system

The vibration modes of such modified glasses are found to be active in three IR spectral regions [14, 18-20] as follows (i) from 600-800 cm^{-1} is due to the bending vibrations of various borate groups. (ii) From 800-1150 cm^{-1} is attributed to the B-O stretching vibrations of BO_4 units and (iii) 1150-1550 cm^{-1} are due to the B-O and B-O^- stretching vibrations of BO_3 and SiO_2-O^- units respectively. In addition, to these, a small band is also observed at about 467 cm^{-1} and is assigned to the angles modification of the B-O-B linkages [21]. With initial 0.1 % doping of MnO_2 ions, all the band intensities are slightly decreased and shifted along with intensification of the band at 562 cm^{-1}. It is difficult to attribute the vibrational modes below 600 cm^{-1}, as they may be due to angle modifications of B-O-B linkages or Mn-O stretching of MnO_2 units [22-24]. An absorption band 650 cm^{-1} is observed only in low concentration of dopant and is disappeared with $x \geq 0.5$ wt% of MnO_2. This disappear might be due to the rupture of boron ring structure with higher MnO content. Also suggests the formation of BO_3 units at the expense of BO_4 units. Further additions of MnO_2upto 0.5 wt%, the peaks are broadened with shift of the bands at 1400 and 1050 cm^{-1} to 760 and 675cm^{-1} respectively. This is due to the formation of new bridging bonds like B-O-Mn in the glass network. However a reverse trend is observed beyond 0.5 wt% of Mn^{2+} ions and the band around 460 cm^{-1} is nearly disappeared. In compliance with the decrease of spin concentration inferred from EPR studies, the observed reverse trend can be explained by the decrease of Mn^{2+} ions and formation of Mn^{3+} ions (Since MnO % is increased). At higher concentrations of dopant, Mn^{2+} ions are oxidizing to Mn^{3+} ions by taking oxygens from the surroundings as follows:

$$2Mn^{2+} + O_2 \rightarrow 2Mn^{3+} + 2O^{2-}$$

This is the reason for increase of non-bridging oxygens and decreases the energy band gaps at higher concentrations of MnO.

Table 3: FT-IR spectral data of Mn^{2+} ions doped KCdBSi glass system

Mn_o	Mn_1	Mn_2	Mn_3	Mn_4	Mn_5	Assignment
1470	1375	1350	1350	1375	1400	B-O $^-$ bonds stretching Vibrations in BO_3 units
1300	1050	1015	1050	1010	1015	B-O $^-$ bonds stretching vibrations in BO_4 units
1100	775	760	800	760	760	asymmetric stretching vibrations of Si-O-Si groups
750	650	650	650	630	675	Si-O-Si symmetric vibrations
526	650	650	650	630	675	Si-O-Si rocking motion SiO_4 structural unit/covalent bond of B_2O_3
-	475	475	470	475	-	Octahedral structural units of Mn-O

IV. CONCLUSION

1) From the results of Electron Paramagnetic Resonance and optical absorption spectra of Mn^{2+} ions in the above glasses, it is concluded that the site symmetry of the Mn^{2+} ion is distorted octahedral.
2) The analysis of FT-IR results suggests that the glass consists of BO_3, BO_4, Si-O and Mn-O bridge bands forming a large glass network. It has also been observed that MnO_2 content help in converting BO_3 group to BO_4 units. This reveals that these ions also enter the glass structure as a network modifier.
3) In the investigated glass system the four-fold boron atoms are dominated compared with the three- fold ones.

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