Characterization of Mn^{2+} ion Doped KCdBSi (K_2O - CdO - B_2O_3 – SiO_2) Glasses on the Basis of Optical and Physical Properties

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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 from optical absorption. 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.***

Keywords: Boro silicate glass, density, optical basicity, optical absorption.

1. 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 (5mol %) 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 containing transition metal ions have become the subject of interest owing to their potential applications [2], exhibit interesting spectroscopic properties and hence are highly suitable for solid state lasers. 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.

In the present study, we have calculated the physical properties and optical properties of KCdBSi (K_2O - CdO - B_2O_3 – SiO_2) glasses doped with a small amount of paramagnetic impurity MnO_2.

2. Glass preparation and measurements

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 hourThe 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.

The physical properties are calculated by measuring density of the glasses.The density of glass samples is determined by using Archimedes' principle with Xylene as an inert buoyant liquid. Optical absorption spectra are recorded at room temperature on JASCO V-670 Spectrophotometer with 200-900 nm.

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

Glass system	*K_2O (mol %)*	*CdO (mol %)*	*B_2O_3 (mol %)*	*SiO_2 (mol %)*	*MnO_2 (mol %)*
Mn_o	20	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

3. Results and Analysis

3.1. Physical Properties

From the measured values of density D, and calculated average molecular weight *M*, various physical parameters such as manganese ion concentration N_i and mean manganese ion separation r_i for these glasses are determined using the conventional expressions and are presented in Table 1

The density of the glasses is found to increase considerably with the concentration of MnO_2. The increase of structural compactness, the modification of the geometrical configuration of the glassy network, changes in the coordination of the glass forming ions are the some of the factors that are responsible for the observed increase in the density.

3.2 Optical basicity of the glass (Λ_{th})

The theoretical optical basicity (Λ_{th}) is expressed in terms of the electron density carried by oxygen. Simultaneously, an intrinsic relationship exists between the electronic

polarizability of the oxide ions and the optical basicity of the oxide medium. An increase in the oxide ion polarizability shows stronger electron donor ability of the oxide ions and vice - versa. The theoretical values of optical basicity (Λ_{th}) of the glass can be estimated by using the formula.

$$\Lambda_{th} = \sum_{i=1}^{n} \frac{z_i}{2\gamma_i} \quad (1)$$

where n is the total number of cations present, Z_i is the oxidation number of the i^{th} cation, r_i is the ratio of number of i^{th} cations to the number of oxides present and γ_i is the basicity moderating parameter where n is the total number of cations present, Z_i is the oxidation number of the i^{th} cation, r_i is the ratio of number of i^{th} cations to the number of oxides present and γ_i is the basicity moderating parameter of the i^{th} cation. of the i^{th} cation. $\gamma_i$can be calculated from the following equation.

$$\gamma_i = 1.36(x_i - 0.26) \quad (2)$$

where x_i is the Pauling electronegativity of the cation. The optical basicity can be used to classify the covalent/ionic character of the glasses since an increasing Λ_{th} indicates decreasing covalence. The theoretical values of optical basicity (Λ_{th}) were calculated for all the glass samples and are presented in Table 2.

3.3 Optical Absorption Studies

The UV- visible absorption spectra of manganese doped KCdBSi glass samples in the wavelength region 350-900 nm is shown in Fig.1. It's observed that, two bands are formed at 720 and 450 nm. The bands observed at 720 and 450 nm are assigned to the transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}$ (G) and $^6A_{1g}(S) \rightarrow {}^4T_{2g}$ (G). 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. It shows a strong broad band centered at around 450 nm [3], [4, [5], and another weak band at 720nm. In general the optical spectra have been analysed in the framework of crystal field theory [6], [7]. The excited quartet states ^4G, ^4P, ^4D and ^4F of Mn^{2+} ions in the octahedral crystal field are situated above the ground ^6S state and the trigonal crystal field splits the four levels into ten sublevels. Hence, all the transitions from the ground sextet ^6S to the excited levels are spin-forbidden, the intensity of optical absorption lines of Mn^{2+} are weak and in addition, the Mn^{2+} ion had a $3d^5$ configuration. The broad absorption band with the maximum at around 450 nm is assigned to spin-allowed $^5E_g \rightarrow {}^5T_{2g}$ transition of Mn^{3+} ($3d^4$, $^5D_0$) ions in the octahedral sites of host glass. 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+}.

The most important information resulting from the analysis of optical spectra is the increase of absorption band intensity depends on the host glass basicity (Table 2). This concludes that the structural factor plays an important role in the formation of valence and coordination state of manganese ions in host glass system.

Table 2: Physical parameters of Mn^{2+} ion in KCdBSi glass system

Density	2.478	2.584	2.587	2.57	2.58	2.548
Manganese ion concentratio(N_i) (10^{19}ions/cm^3) (±0.015)	-	1.88	3.88	5.51	7.47	9.71
Interionic distance (r_i) A^0 (±0.005)	-	37.6	29.58	26.27	23.74	21.76
Polaron radius A^0 (±0.005)	-	15.15	11.92	10.58	9.56	8.77
Optical basicity	-	0.432	0.432	0.432	0.432	0.432
Avg.mol Wt.(M)	80.17	80.12	80.07	80.01	79.97	79.96

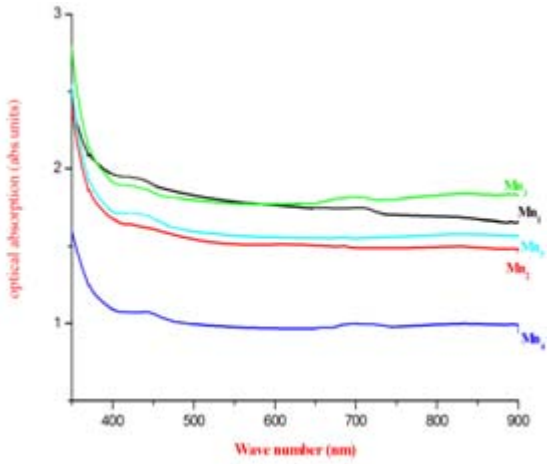

Figure 1: Optical absorption bands ofMn^{2+} ion doped KCBSi glass system.

3.4. Optical band gap (E_g) and Urbach energy (ΔE)

The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transitions and electronic band structure in both crystalline and non-crystalline materials. The principle of this technique is that a photon with energy greater than the band gap energy will be absorbed [8]. It is calculated by extrapolating the linear region of the graph towards X-axis.

The optical band gap of all the glass samples were obtained from their ultraviolet absorption edges by plotting$(\alpha h\nu)^2$, $(\alpha h\nu)^{1/2}$, as a function of photon energy hν as shown in Figs.2,3.The values have been calculated by extrapolating the linear region of the graph towards X-axis.

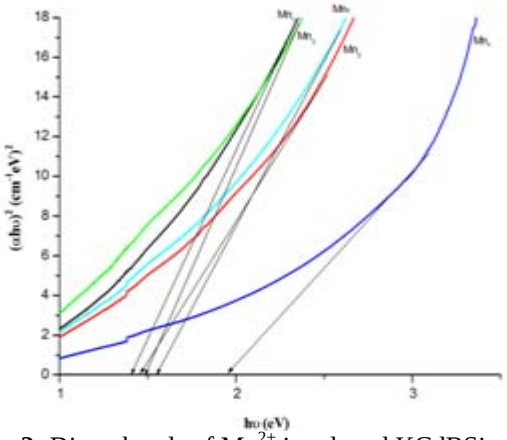

Figure 2: Direct bands of Mn^{2+} ion doped KCdBSi glass system

The absorption coefficients in Urbach's tail region have been given as a function of photon energy by the equation [3]

$$\alpha = \alpha_0 \exp\left(\frac{h\upsilon}{\Delta E}\right)^{1/2} \qquad (3)$$

Where α_o is a constant, ΔE is the Urbach energy interpreted as the energy gap between localized tails in the forbidden region.

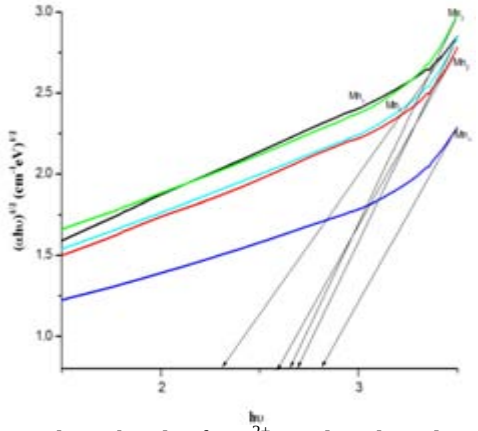

Figure 3: Indirect bands of Mn^{2+} ion doped KCdBSi glass system

The Urbach energy has been calculated for all the glass samples by taking the reciprocal of the slope of the linear region in the plot drawn between lnα vs hν as shown in Fig.4.The values of the optical energy gap and Urbach energy calculated in the present work for all the glass samples are of the same order reported in the literature for borate glasses [3], [9], [10], and are given in Table 3.

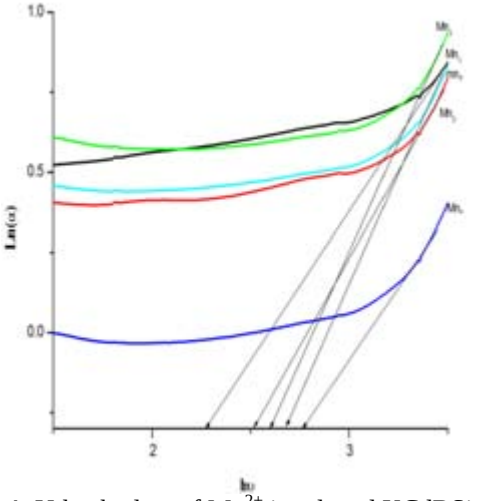

Figure 4: Urbach plots of Mn^{2+} ion doped KCdBSi glass system

From the table, it is observed that the decrease in optical band gap (E_g) and increase in Urbach energy (ΔE) with increase of manganese content. This is due to the shift of UV absorption band to longer wavelengths corresponds to transitions from the non-bridging oxygen which bind an excited electron less tightly than a bridging one. The KCdBSi: Mn_0 sample has the least Urbach energy (0.18 eV). This suggests that defects in these glasses are at a minimum.

Table 3: Observed band positions, optical band gap and Urbach energies for Mn^{2+} ions in KCdBSi glass system

Glass	*Cut off Wave length*	*Band positions*		*Optical band gap (eV)*		*Urbach energies*
		$^6A_{1g}(S\rightarrow{}^4T_{1g})$ *(G)*	$^6A_{1g}(S\rightarrow{}^4T_{2g})$ *(G)*	*Direct*	*Indirect*	
Mn_1	360	450	692	1.39	2.31	0.447
Mn_2	362	445	685	1.44	2.57	0.395
Mn_3	354	448	680	1.49	2.64	0.384
Mn_4	362	439	685	1.56	2.69	0.373
Mn_5	356	457	678	196	2.81	0.361

4. Conclusions

1. The physical parameter - density shows a small increase and decrease in its value by the introduction of MnO_2 into the KCdBSi glasses.
2. The optical basicity remains the same for all the glasses.
3. The Optical band gap energy and the Urbach energy (ΔE) are found to be dependent upon the variation of manganese content.
4. From the results of Optical absorption spectra of Mn^{2+} ions in the above glasses, it is concluded that the site symmetry of the Mn^{2+} ion is tetragonally distorted octahedral.

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Author Profile

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