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Spectroscopic investigations of copper doped MB_4O_7(M=Zn, Cd) glasses

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EPR and optical absorption investigations are carried out at room temperature on copper-doped MB_4O_7 (M = Zn, Cd) glasses. The results indicate that the copper ions (Cu^{2+}) enter the glass matrix into a tetragonally elongated octahedral site. Crystal field and spin-Hamiltonian parameters are evaluated. The bonding parameters suggest that bonding between the metal ion and ligands is partially covalent.

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1. Introduction

Glasses with high heavy metal contents are potential materials for use in the field of nonlinear optics [1,2]. Glasses have been used for matrices of rare earth ion/transition metal ion doped lasers. They have many advantages over single crystals such as mass production at low cost fibers [3]. Fritted glasses with various compositions, some of them containing boric oxide are recommended for this use. Most suitable for this purpose are heavy metal oxide glasses containing lithium, zinc, cadmium and bismuth oxides [4]. Zinc borate glasses are also used for decoration as crystalline, reactive, flow smear, crackle and opaque with transparent spots [5]. The study of oxide glasses has received considerable attention due to their structural peculiarities. In borate glasses, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size, smaller heat of fusion and valency (= 3) of B. In borate glasses, B^{3+} ions, triangularly coordinated by oxygen, form glasses very easily [6]. The studies of transition metal ions in glasses by EPR and optical absorption techniques give information on the structure of the glass. The changes in the composition of the glass may change the local environment of the transition metal ion incorporated into the glass, leading to ligand field changes, which may be reflected in the EPR and optical absorption spectra. In different glasses, copper can exist as a monovalent (Cu^+) ion or as a divalent (Cu^{2+}) ion. The stability of both Cu^+ and Cu^{2+} ions could be found to be sensitive to the glass environment. It has been reported earlier that the valence state of copper modifies not only chemical and physical properties, but also the glass forming ability [7].The multianvil-synthesis of the new oxoborate β-ZnB_4O_7 under extreme high-pressure/high temperature conditions was reported for new non-linear optical crystals [8]. The coordi-nation of one oxygen atom (O2) is enhanced from two to three and the coordination of the Zn^{2+}-cations in β-ZnB_4O_7 is square-pyramidal by five oxygen atoms in contrast to all other zinc borates exhibiting Zn^{2+} ion is fourfold coordination [8]. Recently spectroscopic investigations of transition metal ions doped tetraborates glasses are reported [9-11]. It has been observed very recently that MB_4O_7 (M = Mn, Ni and Cu) single crystals have very similar lattice parameters analogous to β-ZnB_4O_7. It has been reported that copper is in a square-planar coordination in CuB_2O_3, whereas it is in a square, square-pyramidal and octahedral coordi-nation in $Cu_3B_2O_6$ (also known as $Cu_{15}[(B_2O_5)_2(BO_3)_6O_2]$) [12]. The aim of the present spectroscopic investigations on CuO doped in MB_4O_7 (M = Zn, Cd) glasses is to give comprehensive view about the site symmetry, bonding nature, oxidation states and possible environment of copper ions.

2. Experimental

The starting materials used in the present study are Analar grade ZnO (99.9%)/ CdO (99.9%) and B_2O_3 (99.9%). The host glass composition is taken in the ratio 1:4 in order to get MB_4O_7 glass (M = Zn, Cd). For transition metal doping, 0.1 mol% of CuO is added to starting materials. These mixtures are sintered at 700 K and melted in an electric furnace in silica crucible at 1200 K for nearly 1h. The melt is then quenched at room temperature in air to form a glass. The glasses so formed are annealed at 550 K for about 1/2 h. EPR recordings are made at room temperature for polycrystalline samples of copper doped MB_4O_7 glasses (M= Zn, Cd) on JEOL FE 100 EPR spectrometer and optical absorption spectra are recorded at room temperature on JASCO V550 spectrophotometer in 200 - 900 nm.

3. Theory

Divalent copper has an electronic configuration (Ar) $3d^9$. In an octahedral crystal field the corresponding ground state electronic configuration is $t^6_{2g}e^3_g$ and yields ^2E_g, state. On excitation, one of the electrons in the t_{2g} orbital is promoted to the e_g orbital and configuration

$t^5_{2g}e^4_g$ gives $^2T_{2g}$ state. Thus, only one single electron transition $^2E_g \rightarrow {}^2T_{2g}$ is expected for Cu^{2+} in regular octahedral symmetry. The ground state, ^2E_g is Jahn-Teller unstable in regular octahedral field. Generally the degeneracy of the ground state ^2E_g, is lifted by descent in symmetry. The degeneracy of ^2E_g cannot be lifted in trigonal fields. Hence, the site symmetry can either be tetragonal or rhombic.

In tetragonal symmetry ^2E_g level splits into $^2B_{1g}$ ($d_{x^2-y^2}$) and $^2A_{1g}$ (d_{z^2}) levels. The upper state $^2T_{2g}$ splits into $^2B_{2g}$, (d_{xy}) and ^2E_g, (d_{xz}, d_{yz}) levels, the ground state being $^2B_{1g}$. In rhombic field (D_{2h}) the lower state ^2E_g splits into $^2A_{1g}$ ($d_{x^2-y^2}$) and $^2A_{2g}$ (d_{z^2}) whereas the upper level $^2T_{2g}$ splits into $^2B_{1g}$ (d_{xy}), $^2B_{2g}$, (d_{xz}) and $^2B_{3g}$ (d_{yz}) states [13]. The number of bands expected for Cu^{2+} ion is four in rhombic and three in tetragonal fields respectively. The three bands are expected [14] for the following transitions in the tetragonal field:

$^2B_{1g} \rightarrow {}^2A_{1g}$: 4 Ds + 5Dt
$^2B_{1g} \rightarrow {}^2B_{2g}$: 10 Dq
$^2B_{1g} \rightarrow {}^2E_g$: 10 Dq + 3 Ds - 4 Dt

where Dq, Ds and Dt are crystal field (Dq) and tetragonal field (Ds and Dt) parameters. Octahedral molecules involve the lowering of symmetry (O_h to D_{4h}) due to the result of lengthening or shortening two transition metal ligand bonds with respect to the other four. Either in octahedron or in tetragonally distorted octahedron, the ligands are treated as point charges surrounding the central metal ion. Here Dq, Ds and Dt are defined as

$$Dq = (1/6)2e^2(\acute{r}^4/a^5)$$
$$Dt = (2/21)Ze^2\,\acute{r}^4\,(1/a^5 - 1/b^5)$$
$$Ds = (2/7)Ze2\,\acute{r}^2\,(1/a^3 - 1/b^3)$$

where $\acute{r}^2$ and $\acute{r}^4$ are interpreted as mean square and mean fourth power radii of the metal orbitals. *a* and *b* are represented in terms of bond length differences for axial and equatorial bonds [15]. Here Dq is the cubic crystal field parameter and is a measure of the separation between the t_{2g} and e_g orbitals. Actually 10 Dq gives the magnitude of the splitting.

When the cubic symmetry of the ligand environment is distorted tetragonally to specify the amount of distortion, two parameters Ds and Dt are used. Dt and Dq will have the same sign in the case of axial elongation and opposite sign in the case of axial contraction.

4. Results and discussion

4.1Optical absorption spectra of Cu^{2+}doped MB_4O_7 M= Zn, Cd) glasses

The optical absorption spectra of copper doped MB_4O_7 glasses (M= Zn, Cd) are shown in Fig. 1 and Fig. 2. The broad band observed at 785 nm for ZnB_4O_7 glass (here after called ZnB glass) and 775 nm for CdB_4O_7 glass (here after called CdB glass) is characteristic of distorted octahedral symmetry [2, 9-11, 16-18]. Thus these broad bands are assigned to $^2B_1 \rightarrow {}^2B_2$ transition.

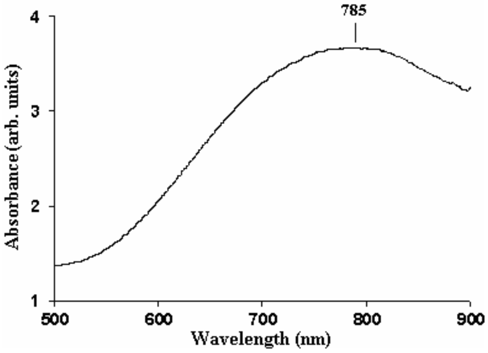

Fig. 1. Optical absorption spectrum of Cu^{2+} doped ZnB_4O_7 glass.

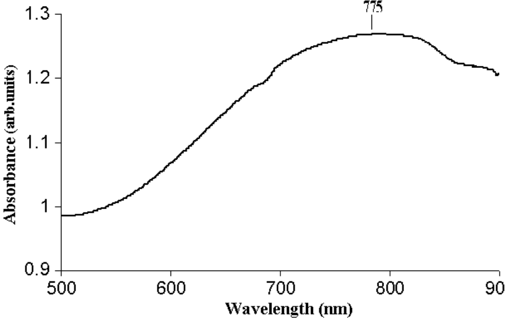

Fig. 2. Optical absorption spectrum of Cu^{2+} doped CdB_4O_7 glass.

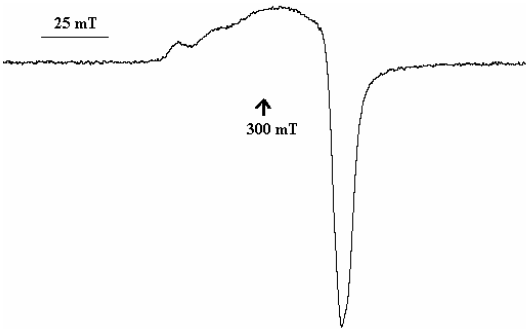

Fig. 3. Polycrystalline EPR spectrum of Cu^{2+} doped ZnB_4O_7 glass ($\nu = 9.445$ GHz).

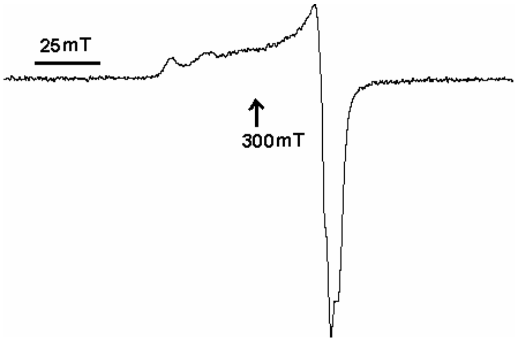

Fig. 4. Polycrystalline EPR spectrum of Cu^{2+} doped CdB_4O_7 glass ($\nu = 9.444$ GHz).

4.2 EPR spectra of Cu^{2+} doped MB_4O_7 (M= Zn, Cd) glasses

No EPR signal was detected in the spectra of un-doped glasses. When Cu^{2+} ions are introduced into the MB_4O_7 (M = Zn, Cd) glasses, the glasses show resonance lines. The EPR spectra are analyzed using the spin-Hamiltonian

$$H = g_{\parallel}\, \beta H_zS_z + g_{\perp}\beta\, (H_xS_x + H_yS_y) + A_{\parallel}I_zS_z + A_{\perp}(I_xS_x + I_yS_y) \quad (1)$$

where the symbols have their usual meanings [19]. The hyperfine peak positions are related to the principal values of *g* and *A* tensors by the solutions of the spin-Hamiltonian. The parallel hyperfine peaks are resolved in the present glasses and perpendicular hyperfine peaks are unresolved. Three hyperfine lines are observed on the parallel features of the spectrum. EPR spectra of Cu^{2+} ion doped MB_4O_7 (M = Zn, Cd) glasses are shown in Fig. 3 and Fig. 4 respectively. From the spectrum, the spin-Hamiltonian and hyperfine splitting values evaluated for ZnB_4O_7 and CdB_4O_7 glasses are:

$g_{\parallel}=2.355$, $g_{\perp}=2.079$, $A_{\parallel}= 48 \times 10^{-4}\ cm^{-1}$, $A_{\perp}=28 \times 10^{-4}\ cm^{-1}$ for ZnB_4O_7

$g_{\parallel}=2.345$, $g_{\perp}=2.060$, $A_{\parallel}=148 \times 10^{-4} cm^{-1}$, $A_{\perp}=30 \times 10^{-4}\ cm^{-1}$ for CdB_4O_7

These spin-Hamiltonian values are in good agreement with those reported for borate glasses [9-11, 16, 20-28] and they are given in Table 1. The fact that $g_{\parallel} > g_{\perp}$ suggests that Cu^{2+} ions are subjected to tetragonally elongated distortion. Based on charge compensation and size of the impurity, it can be assumed that the paramagnetic impurity might have entered the zinc/cadmium location in these glasses. Similar observations have been reported with copper and zinc crystals [12]. From the spin-Hamiltonian parameters, the dipolar term (P) and the Fermi-contact term (κ) are calculated using the following expressions [29, 30].

$$P = 2\, \gamma_{Cu}\, \beta_o\, \beta_N \langle r^{-3} \rangle = 0.036\ cm^{-1} \quad (2)$$

$$\kappa = (A_o/P) + \Delta g_o \quad (3)$$

Table 2. Comparison of spin-Hamiltonian parameters of Cu^{2+} in different glass systems.

Glass System	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ $x10^{-4}\ cm^{-1}$	$A_{\perp}$ $x10^{-4}\ cm^{-1}$	$g_{\parallel}/A_{\parallel}$ cm	Ref.
$Li_2O–B_2O_3$	2.328	2.050	157	24.9	148.28	[20]
$Na_2O–B_2O_3$	2.327	2.065	150	26.0	155.13	[21]
$Na_2O-K_2O–B_2O_3$	2.338	2.046	135	23.7	173.31	[22]
$Li_2O–Na_2O–B_2O_3$	2.382	2.061	162	22.5	147.03	[23]
$Li_2O–Na_2O–B_2O_3–As_2O_3$	2.348	2.071	135	--	173.92	[18]
$SrO–B_2O_3$	2.308	2.044	153	--	150.85	[24]
$ZnO–B_2O_3$	2.321	2.039	159	--	145.97	[25]
$PbO–B_2O_3$	2.323	2.042	152	--	152.83	[25]
$CdSO_4–B_2O_3$	2.422	2.084	77	--	314.54	[26]
$Li_2SO_4–CdSO_4–B_2O_3$	2.421	2.089	77	--	314.41	[26]
$Na_2SO_4–CdSO_4–B_2O_3$	2.420	2.086	77	--	314.28	[26]
$K_2SO_4–CdSO_4–B_2O_3$	2.420	2.089	77	--	314.28	[26]
$Cs_2SO_4–CdSO_4–B_2O_3$	2.421	2.086	77	--	314.41	[26]
$Li_2CO_3–BaCO_3–H_3BO_3$	2.284	2.053	131	25	174.35	[27]
$Na_2CO_3–BaCO_3–H_3BO_3$	2.262	2.049	137	24	165.11	[27]
$K_2CO_3–BaCO_3–H_3BO_3$	2.259	2.048	114	24	198.16	[27]
$Li_2B_4O_7–PbO–TeO_2$	2.323	2.067	129	22	180.80	[28]
$Na_2B_4O_7–PbO–TeO_2$	2.293	2.056	136	23	168.60	[28]
$Li_2B_4O_7–TeO_2$	2.310	2.063	117	26	197.44	[28]
$Na_2B_4O_7–TeO_2$	2.303	2.060	122	24	188.77	[28]
$K_2B_4O_7–TeO_2$	2.294	2.056	129	25	177.83	[28]
$LiRbB_4O_7$	2.445	2.056	158	30	154.75	[09]
$NaRbB_4O_7$	2.443	2.051	162	27	150.80	[10]
$KRbB_4O_7$	2.422	2.059	181	27	134.18	[10]
SrB_4O_7	2.316	2.043	139	49	166.64	[11]
ZnB_4O_7	2.355	2.079	148	28	159.12	Present
CdB_4O_7	2.345	2.060	148	30	158.45	study

Here γ_{Cu} is the magnetic moment of copper, β_o is the Bohr magneton, β_N is the nuclear magneton and r is the distance from the central nucleus to the electron. $A_o = (A_\parallel + 2A_\perp)/3$, where $A_\parallel$ and $A_\perp$ are the hyperfine coupling constants in the parallel and perpendicular directions to the field. $g_\parallel$ and $g_\perp$ are the g-values parallel and perpendicular to the field and $\Delta g_o = g_o - g_e$, where $g_o = (g_\parallel + 2g_\perp)/3$ and g_e is the free ion g-value (2.0023). The Fermi contact term k is a measure of the polarization produced by the uneven distribution of d-electron density on the inner core s-electron. The evaluated k values 0.358 for ZnB_4O_7 and 0.346 for CdB_4O_7 are in tune with the general order of k [31]. The covalency parameter for the in plane σ - bonding is evaluated from the expression [32].

$$\alpha^2 = \frac{A_\parallel}{0.036} + (g_\parallel - g_e) + \frac{3}{7}(g_\perp - g_e) + 0.04 \qquad (4)$$

The value of α^2 thus evaluated is 0.84 for ZnB_4O_7 glass and 0.82 for CdB_4O_7 glass. By correlating EPR and optical absorption data, the bonding parameter β_1 is calculated using the formula

$$g_\parallel = 2.0023 - 8\rho[\alpha\beta_1 - (1/2)\alpha'(1-\beta_1^2)^{1/2}T(n)] \qquad (5)$$

where $\rho = (\lambda_o\alpha\beta_1/\Delta E)$ and T(n) is a function involving metal ligand hybridization constant and the effective nuclear charges for the ligand 2s, 2p orbitals and the metal 3d orbitals and is equal to 0.220. ΔE is the transition energy between the $^2B_1 \rightarrow {}^2B_2$ and λ_o is the spin-orbit coupling constant (-828 cm^{-1}), **α'** can be evaluated from the normalisation conditions on the ground state b_1 orbital as

$$\alpha' = (1 - \alpha^2)^{1/2} + \alpha S \qquad (6)$$

In the above equation S is the overlap integral between $d_{x^2-y^2}$ orbital and normalised ligand orbital. A value of S equal to 0.076 will be used if the ligands are oxygens. In the present case, the atom surrounding the copper ion is oxygen and hence S = 0.076. Accordingly the parameters evaluated for the β_1^2 values are 0.83 and 0.92 for ZnB_4O_7 glass and CdB_4O_7 glass respectively. The values of **α'** are 0.473 for ZnB_4O_7 glass and 0.493 for CdB_4O_7 glass respectively.

From the calculated parameters α^2, β_1^2 of investigated glass systems and using value of S (=0.076) in oxide ligands, two more variables that give an idea about the basicity of the oxide ion can be calculated. α^2 refers to the covalency of the in-plane s-bonding between copper and its ligands. α' is a parameter for normalization of b1 orbital and indicates the extent of overlap between $d_{x^2-y^2}$ orbital of the central metal ion and the normalized ligand orbital. This intermediate parameter is used to evaluate another important parameter β_1^2 which is a direct measure of the covalency of the in-plane π-bonding between copper and its ligands. The β_1^2 is more sensitive to variations in covalency than α^2 and is therefore better indicator of the covalent character.

The normalized covalency of Cu^{2+}–O in-plane bonding of σ or π symmetry is expressed as [33]

$$\Gamma_\sigma = 200(1-S)(1-\alpha^2)/(1-2S \;\% \text{ and } \Gamma_\pi = 200(1-\beta_1^2) \;..(7)$$

Here, the normalized covalency (Γ_π) of Cu^{2+}–O bonding of π symmetry indicates the basicity of the oxide ion. Generally the covalency of the in-plane σ bonding (Γ_σ) decreases, while the covalency of in-plane π-bonding (Γ_π) increases. The evaluated values are for Γ_σ = 35.5%, 39.2% and Γ_π = 33.4%, 16% with respect to ZnB_4O_7 and CdB_4O_7 glasses respectively. Since only one band is observed in optical absorption spectrum of both the glasses, the nature of the out of plane π-bonding could not be inferred.

5. Conclusions

From the EPR and optical absorption studies of Cu^{2+} doped ZnB_4O_7 and CdB_4O_7 glasses, the following conclusions are drawn:

The analysis of the optical absorption spectra confirms the tetragonally distorted octahedral coordination of Cu^{2+} ions in the host lattices. From the EPR spectral studies, the evaluated spin-Hamiltonian and hyperfine splitting parameters are in tune with the other reported borate glass systems. The g-values ($g_\parallel > g_\perp$) indicates tetragonally elongated octahedral site for Cu^{2+} ion in both these glass systems. One can assume the substitution of Cu^{2+} ions in place of Zn^{2+}/Cd^{2+} ions. The values of $g_\parallel/A_\parallel$ of the present glass systems indicate that site symmetry of Cu^{2+} ions is distorted octahedron.

By correlating EPR and optical results, the evaluated parameters indicate the partial covalency of in-plane σ (α^2) and in-plane-π bonding (β_1^2) between copper ions and its ligands. The parameters Γ_σ and Γ_π are in accordance with the complexes expected that of basicity character.

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