Physical, Optical and Electron paramagnetic resonance studies of PbBr$_2$- PbO-B$_2$O$_3$ glasses containing Cu^{2+} ions

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Abstract. The glasses with the composition PbBr$_2$- PbO-B$_2$O$_3$ glasses containing Cu^{2+} ions were prepared by melt quenching technique. X-ray diffractograms revealed the amorphous nature of the glasses. Density and molar volume were determined. Density is found to decrease while the molar volume increases with increase of PbBr$_2$ content. The optical absorption spectra exhibited a broad band corresponding to the d-d transition of Cu^{2+} ion. From optical absorption spectra E$_{opt}$ and Urbach energies were determined. Electron Paramagnetic Resonance (EPR) studies were carried out by introducing Cu^{2+} as the spin probe. Glasses containing transition metal(TM) ions such as Cu^{2+} give the information about the structure and the site symmetry around the TM ions. EPR spectra of all the glass samples were recorded at X-band frequencies. From the EPR spectra spin-Hamiltonian parameters were evaluated. It was observed that g$_\parallel$ >g$_\perp$>g$_e$ (2.0023) and A$_\parallel$>A$_\perp$.From this values it is concluded that the ground state of Cu^{2+} is d$_{x2-y2}$ (^{2}B$_{1g}$) and the site symmetry around Cu^{2+} ion is tetragonally distorted octahedral. From the EPR and Optical data bonding co-efficients were evaluated. The in plane σ-bonding(α^2) is moderately ionic while out of plane π-bonding(β^2) and in plane π-bonding(β_1^2) are ionic nature

1. Introduction

Borate glasses itself have several advantages compared to its counterpart glass formers. Borate glasses have shown reduced thermal expansion, resistant to thermal shocks, enhanced toughness, chemical resistance and durability [**1, 2**]. On the other hand lead oxide has ability to enter into glass as network modifier or network former. The addition of lead oxide to these glasses increased the IR transparencies, refractive indices and the optical non linearities[**3**]. This made the PbO more choiced oxide for the researchers to probe in. The incorporation of PbO and PbX$_2$ (X=F, Cl and Br) into the borate glass matrix resulted in the creation of trigonal BO$_3$ and tetrahedral BO$_4$ units with further significant increase in IR transparencies, refractive indices and optical non linearities [**4, 5, 6**]. It is interesting to note that very few articles were published in EPR on these glasses. Since EPR is a

powerful technique to investigate the structure of the glasses, environment around the paramagnetic probe ion and its co ordination with ligands. Study of EPR and optical absorption of transition metal ion doped glasses have made it possible not only to interpret the energy levels involved in the observed transitions but to know the bonding coefficants like α^2(in plane σ-bonding, β^2 (in plane - σ bonding) and β_1^2 (out of plane π-bonding) [**7,8**]. The present study aims to understand about the influence of PbBr2 on the structure of $PbBr_2$- PbO-B_2O_3-CuO glasses by employing experimental techniques like physical, optical absorption and EPR studies.

2. Experimental

2.1. Sample Preparation
Glass samples with formula $xPbBr_2$-(30-x) PbO-$69B_2O_3$-$1CuO$ with $5 \leq x \leq 25$mole% were prepared by the melt quenching technique. Required quantities of analar grade $PbBr_2$, PbO, B_2O_3 and CuO were mixed together by grinding the mixture repeatedly to obtain a fine powder. The mixtures were melted in a porcelain crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 900^0c for 45minutes. The glasses are formed by quenching the melt on a pre heated stainless steel plate and annealed at temperature 200^0C below glass transition temperature. The glass compositions are given in **Table 1.**

2.2.Measurements

X-ray diffraction spectra were recorded to check the non- crystallinity of the glass samples using Philips Xpert Pro X Ray Difractometer. The density of the glass samples was determined using Archimedes technique by using xylene as immersion liquid. Optical absorption spectra of the glasses were recorded on JASCO V-670 UV-VIS spectrophotometer at room temperature. Electron Paramagnetic Resonance (EPR) spectra of the glass samples were recorded at room temperature using (BRUKER) EPR spectrometer operating at X-band frequency (9.7 GHz) with a modulating frequency of 100 KHz.

3. Results and Discussion.

3.1. X-Ray Diffraction.

X-ray diffraction spectrum of each glass system was examined, the absence of sharp characteristic peaks revealed the amorphous nature of the glasses. **Fig.1** presents the X-ray diffraction patterns of present glasses.
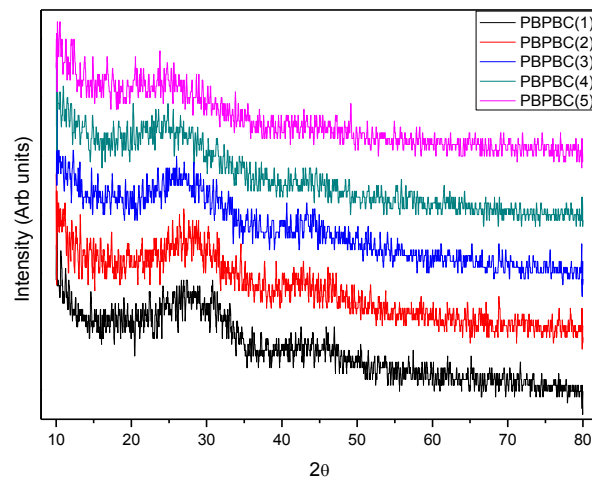
Fig.1 X-ray diffraction patterns of
$xPbBr_2$-(30-x) PbO-69B_2O_3-1CuO (where x=5, 10, 15, 20, & 25 mole %).

3.2. Density, molar volume.

Density is a useful parameter to measure when investigating changes in the structure of glasses, as it is affected by structural softening/compactness, changes in geometrical configuration, coordination number, cross-link density and the dimensions of interstitial spaces in the structure. The density (ρ) was determined using Archimedes principle

$$\rho_{exp} = \frac{W_a}{W_a - W_b} \rho_b \qquad (1)$$

Where W_a is the weight in air, W_b is the weight in xylene of the glass sample and ρ_b is the density of xylene (ρ_b =0.865 g/cm^3).

The molar volume (V_m) was calculated using the formula

$$V_m = M/\rho \qquad (2)$$

Where M in the total molecular weight of the multi-component glass and ρ being the density. The measured values of density (ρ) and calculated values of molar volume (V_m) are reported in **Table 1.** The effect of substitution of PbO by $PbBr_2$ on the density and molar volume of the present glasses shown in **Fig. 2**. The molar volume increases with increase of $PbBr_2$ concentration (equal concentration of PbO decreasing) while decreases with increase of $PbBr_2$ which is an expected result. The increase in V_m may be due to conversion of bridging oxygen atoms into non-bridging oxygen atoms.

Table1. Composition, Density(ρ gm/cc), Molar Volume(cm^3/mole), Optical Band Gap(eV), Urbach Energy(eV), refractive Index, Molar Refraction and Molar Electronic Polarizability of xPbBr$_2$-(30-x) PbO-69B$_2$O$_3$-1CuO (where x=5, 10, 15, 20, & 25 mole %) glasses

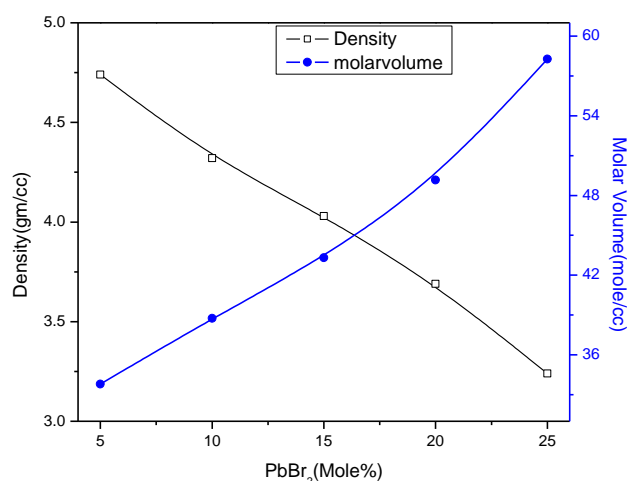| GLASS	Composition(Mole%)				ρ	M	E_{opt}(eV)	ΔE(eV)	n	R_m	α_m (10^{-24})
	PbBr$_2$	PbO	B2O3	CuO							
PBPBC-1	5	25	69	1	4.74	33.79	2.511	0.472	2.544	21.83	8.37
PBPBC-2	10	20	69	1	4.32	38.75	2.802	0.348	2.453	24.26	9.30
PBPBC-3	15	15	69	1	4.03	43.32	2.857	0.359	2.436	26.94	10.32
PBPBC-4	20	10	69	1	3.69	49.16	3.018	0.361	2.394	30.08	11.53
PBPBC-5	25	5	69	1	3.24	58.27	3.174	0.354	2.353	35.07	13.45

Fig 2. Variation of Density and molar Volume with PbBr$_2$ Concentration.

3.3. UV Measurements.

The optical absorption spectra for all the prepared glass samples shown in **Fig.3**. The optical absorption edge is not sharply defined which confirms the amorphous nature of the prepared glasses. It can be seen that on increasing PbBr$_2$ content the absorption edge shifts slightly towards shorter wavelengths. The absorption edge gives information about the width of the localized states in the band gap which arises due to disorder in the glass matrix. The optical band gap energy also provides information about the nature of chemical bonds and glass structure. The absorption coefficient, $\alpha(\nu)$ is determined near the absorption edge of different photon energies for all glasses and is given by the relation
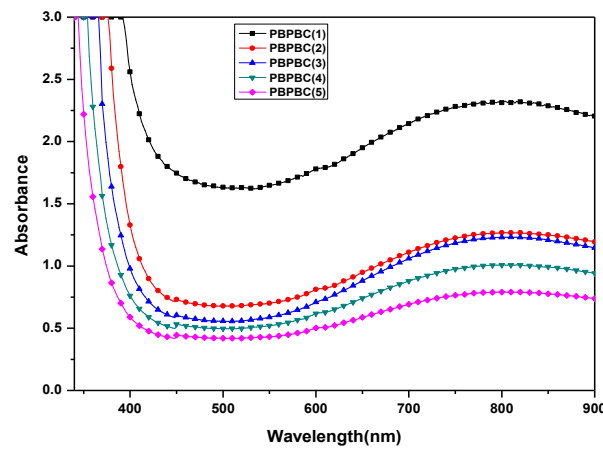
Fig 3 Optical absorption spectra of
$xPbBr_2$-(30-x) PbO-69B_2O_3-1CuO (where x=5, 10, 15, 20, & 25 mole %).

$$\alpha(\upsilon) = 2.303\frac{A}{d} \qquad\qquad (3)$$

Where 'A' is the absorbance and 'd' is the thickness of the sample Davis and Mott proposed the following relation for amorphous materials where the absorption co-efficient $\alpha(\upsilon)$ is a function of photon energy(hυ) for direct and indirect transitions [**9**].

$$(\alpha h\upsilon) = B^2(h\upsilon - E_g)^r \qquad\qquad (4)$$

Where E_g is the optical band gap, and r is the index which has different values (2, 3, ½ and 1/3) corresponding to indirect allowed, indirect forbidden, direct allowed and direct forbidden transitions, respectively. B is a constant called the band tailing parameter and hυ is the energy of incident photons. Here the optical band gap refers to photons assisting the electrons to move from valence band to conduction band [**10**]. The typical $(\alpha h\upsilon)^{1/2}$ versus photon energy(hυ) for indirect allowed transitions (called as Tauc's plot) have been plotted to find the values of optical band gap energy, E_g. The values of E_g are obtained by extrapolating the linear region of the curve to the (hυ) axis, i.e. $(\alpha h\upsilon)^{1/2}$=0 for indirect transitions and are presented in table **1**. The earlier structural investigations made on PbO-P_2O_5 glass system [**11**] suggested that introduction of every Pb^{2+} ion into the phosphate network in the form of PbO disrupts two bridging oxygens, or alternatively creates two non-bridging oxygens (NBOs). The increasing tendency of E_{opt} values for the samples in **Fig. 4** with increase in $PbBr_2$ content is attributed to the same reason. It is clear that E_{opt} value is strongly dependent on the composition. The origin of E_{opt} is attributed to phonon-assisted indirect transitions. The Urbach's energy, ΔE is defined as the energy gap between localized tail states in the forbidden band gap. It provides a measure of disorder in the amorphous and crystalline solids [**12, 13**]. The ΔE values are evaluated from the Urbach's plots of ln(α) versus(hυ) by taking the reciprocal of the slopes of the

linear portion of the curves and are listed in **Table. 1**. The variation Urbach energy (ΔE) with PbBr$_2$ concentration is shown in **Fig. 5.** Urbach energy is varying non- linearly with increase of PbBr$_2$ content.

3.4. Refractive index, molar refraction and molar polarizibility.

The refractive index, molar refraction and molar polarizibility of the glasses have been calculated by using the relation given by Dimitrova and Komatshu and Duffy [**14, 15**].

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_{opt}}{20}} \qquad (5)$$

$$R_M = \frac{n^2-1}{n^2+2} * V_m \qquad (6)$$

$$\alpha_m = \left(\frac{3}{4\Pi N_A}\right) * R_m \qquad (7)$$

Where n, E$_{opt}$, R$_m$, N$_A$ and α$_m$ are the refractive index, optical band gap, molar refraction, Avogadro number and polarizibility respectively. The calculated values of refractive index, molar refraction and molar polarizibility of the glasses have been given in **Table 1** which shows that refractive index decreases progressively and molar refraction and molar polarizibility correspondingly increases by following the band gap of the glasses.
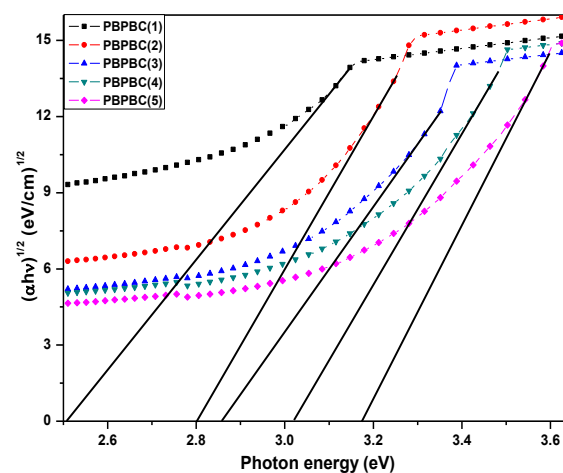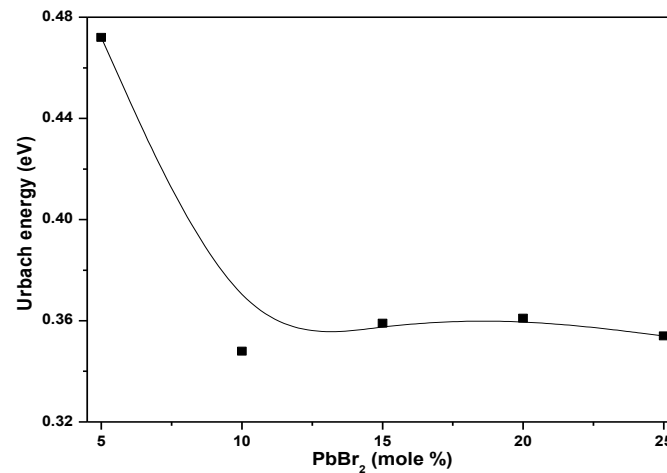

Fig 4. Photan Energy Vs (αhν)$^{1/2}$

Fig 5. Variation of Urbach Energy with $PbBr_2$ concentration.

3.5. EPR Spectra.

Fig 6 shows EPR spectra of present glass system. When Cu^{2+} ions introduced into the glasses, the EPR spectra exhibited absorption lines. The Cu^{2+} ion, with effective spin S=1/2, has a nuclear spin I=3/2 for both ^{63}Cu and ^{65}Cu. Hence, (2I+1) i.e. four parallel and four perpendicular hyperfine (hf) components were expected. In the present work, three parallel components were observed in the lower field region and fourth parallel component was overlapped with the perpendicular component. The EPR spectra can be analyzed by spin-Hamiltonian [**16**] given by the following equation.

$$\mathcal{H} = \beta[g_\parallel H_Z S_Z + g_\perp(H_X S_X + H_Y S_Y)] + A_\parallel I_z S_Z + A_\perp(I_X S_X + I_Y S_Y) \qquad (8)$$

where Z is the symmetry axes of the individual copper centers and other symbols have usual notation. In the analysis of the spectra nuclear quadrupole interaction is neglected. The solution of spin-Hamiltonian gives the expressions for the peak positions related to the principal '*g*' and '*A*' tensors [**17**] for the parallel and perpendicular hyperfine peaks respectively.

$$hv = g_\parallel \beta H + m A_\parallel + \left(\frac{15}{4} - m^2\right)\frac{A_\perp^2}{2g_\parallel \beta H} \qquad (9)$$

$$hv = g_\perp \beta H + m A_\perp + \left(\frac{15}{4} - m^2\right)\frac{A_\parallel^2 + A_\perp^2}{4g_\parallel \beta H} \qquad (10)$$
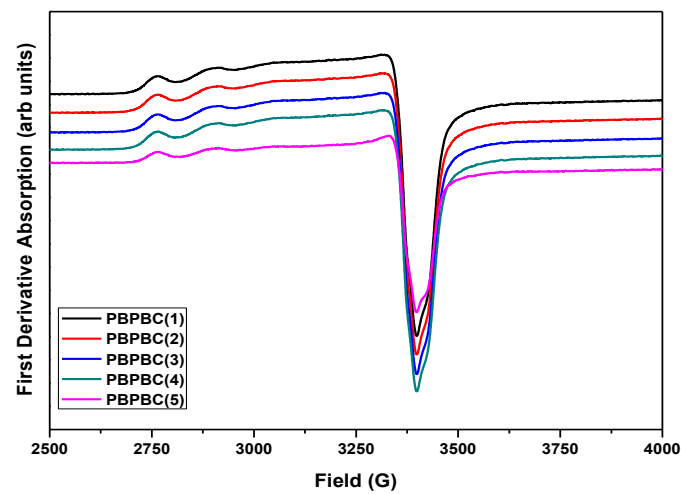
Fig 6. EPR Spectra of
$xPbBr_2$-(30-x) PbO-$69B_2O_3$-$1CuO$ (where x=5, 10, 15, 20, & 25 mole %).

TABLE 2. Spin - Hamiltonian parameters, number of spins and bonding parameters of $xPbBr_2$-(30-x) PbO-$69B_2O_3$-$1CuO$
(where x=5, 10, 15, 20, & 25 mole %) glasses

GLASS	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ $(10^{-4}cm^{-1})$	$A_{\perp}$ $(10^{-4}cm^{-1})$	ΔE_{xy} (cm^{-1})	$N(10^{21})$ Per Kg	α^2	β^2	β_1^2
PBPBC-1	2.351	2.060	131	35	12894	6.426	0.783	0.982	0.865
PBPBC-2	2.352	2.060	134	32	12817	6.781	0.793	0.969	0.854
PBPBC-3	2.344	2.060	138	35	12971	5.809	0.792	0.970	0.843
PBPBC-4	2.465	2.061	129	36	12817	5.955	0.890	0.864	0.998
PBPBC-5	2.354	2.061	132	34	12852	6.025	0.786	0.975	0.891

The calculated spin-Hamiltonian parameters, the number of spins (*N*) participating in resonance at room temperature are calculated and are given in **Table 2**. The optical absorption spectra of Cu^{2+} ions in glass system exhibited only one broad absorption band. **Table 2** contains the peak position (ΔE_{xy}) of optical absorption spectra. The observed 'g' and 'A' values and shape of the EPR spectra suggest that the CuO in all the glasses is existing as Cu^{2+} ion with $3d^9$ configuration. In the present work it was observed that $g_{\parallel} > g_{\perp} > g_e$ (g_e= 2.0023) and $A_{\parallel} > A_{\perp}$ from these results it can be concluded that the ground state of Cu^{2+} ion is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state), the Cu^{2+} ions being located in tetragonally distorted octahedral sites[8]. The variation $g_{\parallel}$ and $A_{\parallel}$ with $PbBr_2$ content was found to be non-linear which suggest that there is a change in the tetragonal distortion of Cu^{2+} ion. The values of *N* depend on the glass composition value and they vary in a non-linear manner with the composition $PbBr_2$. For all glass samples a single asymmetric broad band near IR region was observed which is shown in **Fig 3**. This band can be identified as d-d transition band due to Cu^{2+} ion. In the present investigation the observed optical absorption band can be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition

(ΔE_{xy}).The EPR and Optical data was used for the calculation of covalency parameters ($\alpha^2, \beta^2 and \beta_1^2$) which describe the bonding between the Cu^{2+} ion and its ligands. The bonding parameters are given **Table 2**. α^2 represents in plane σ-bonding between ligands and copper $d_{x^2-y^2}$ orbital which seems to be moderately ionic for these glasses. While β^2 represents out of plane π-bonding which is due to bonding between ligands and copper $d_{xz,yz}$ orbital and it is found ionic for these glasses. Whereas in plane π-bonding represented by β_1^2 is due to the bonding between ligands and copper d_{xy} orbital and for these it is from table mostly ionic in nature.

4. Conclusions.

It was noticed that the density is decreasing and molar volume is increasing with increase in $PbBr_2$ content. Non linear increase in optical band gap energy was observed with increase in $PbBr_2$ content. From the EPR spectra it was concluded that the ground state of Cu^{2+} ion is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state), the Cu^{2+} ions being located in tetragonally distorted octahedral sites. The variation $g_\parallel$ and $A_\parallel$ with $PbBr_2$ content was found to be non-linear which suggest that there is a change in the tetragonal distortion of Cu^{2+}ion. The values of N depend on the glass composition value and they vary in a non-linear manner with the composition $PbBr_2$. The observed optical absorption band can be assigned to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition (ΔE_{xy}).

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