SPECTROSCOPIC STUDIES OF COPPER DOPED PbO-Bi_2O_3-As_2O_3 GLASSES

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Received: Jan. 2020 Accepted: Feb. 2020 Published: Feb. 2020

Abstract: A study of the physical properties of the glasses is of considerable importance because of the insight it gives into the fundamental process-taking place in them. Such a study paved the way for the application of some of these glasses in technology. In fact, the physical properties of the glasses are to a large extent controlled by the structure, composition, and the nature of the bonds of the glasses. The investigation of the changes in the physical properties of glasses with controlled variation of chemical composition, doping etc., is of considerable interest in the application point of view. Investigations on the spectroscopic properties such as optical absorption, electron spin resonance can be used as probes to throw some light on the structural aspects of the glasses; Solid $As_2O_3$is interesting material in that, it exists in the crystalline state as both a molecular solid and as to polymers having an infinite layer structure. Addition of PbO to these glasses makes them to be relatively moisture resistant and also lowers the rate of crystallization, since PbO, has the ability to form stable glasses due to its dual role-one as modifier.

Keywords: X-Ray Diffraction, Optical absorption, Electron Spin Resonance (ESR).

Introduction: The transition metal ions such as copper dissolved in PbO-Bi_2O_3-As_2O_3 glass matrix even in very small quantities make these glasses colored and have strong influence over the insulating character and optical transmission of these glasses. Further, it is also expected that CuO form a single copper -arsenic-oxygen framework with the As_2O_3 structural units, strengthen its structure and raise the chemical resistance of the glass. Bi_2O_3 based glasses are known due to their optical transmission with long infrared cut off beyond 9µm, which is very high for oxide glasses. High non-linearity of these glasses makes them appealing candidates for ultra fast all optical switches.

In contrast to the conventional alkali / alkaline earth oxide modifiers PbO has the ability to form stable glasses due to its dual role; one as the modifier, if Pb-O is ionic and the other as the glass former if Pb-O is covalent. When Pb^{2+} ions are present in the glass as network formers they impart a three-dimensional character to the glass. This fact accounts for the ability of PbO to form glasses up to 90-mol%. Clearly this peculiar behavior, which distinguishes lead from alkali and alkaline earth metals, depends on the electronic structure of the Pb^{2+} ion. In fact the easily polarizable valence shell of the Pb^{2+} ion strongly interacts with also highly polarizable O^{2-} ion, giving rise to a rather covalent Pb-O bond. Thus PbO-Bi_2O_3-As_2O_3 glasses can be considered as relatively moisture resistant and to posses low rates of crystallization and are important materials for technological applications. Copper ions have strong bearing on optical and electrical properties of glasses. CuO containing oxide glasses are known as semi-

conducting glasses since a long time. These ions exist in different surroundings (ionic, covalent) in glass matrices. Cu^{2+} ions are well-known paramagnetic ions.The studies on physical properties of PbO-Bi_2O_3-As_2O_3: CuO glasses as such are very rare; however some of the latest reports available on the studies of certain other CuO doped glasses are mentioned below:

The compositions chosen for the present studies are: (30-x) PbO- 10 Bi_2O_3-60 As_2O_3: x CuO with 6 - values of x in the range $0 \leq x \leq 0.6$, in steps of 0.1.

The details are:

C_0 : 30 PbO- 10 Bi_2O_3-60 As_2O_3 (pure)
C_1 : 29.9 PbO- 10 Bi_2O_3-60 As_2O_3: 0.1 CuO
C_2 : 29.8 PbO-10 Bi_2O_3-60 As_2O_3: 0.2 CuO
C_3: 29.7 PbO-10 Bi_2O_3-60 As_2O_3: 0.3 CuO
C_4 : 29.6 PbO-10 Bi_2O_3-60 As_2O_3: 0.4 CuO
C_5 : 29.5 PbO-10 Bi_2O_3-60 As_2O_3: 0.5CuO
C_6 : 29.4 PbO-10 Bi_2O_3-60 As_2O_3: 0.6CuO

Characterization:

X-ray Diffraction: As glassy or amorphous materials do not have long range order, a diffraction pattern containing sharp peaks is not expected as in crystalline materials. The X-ray diffraction pattern for some of the PbO-Bi_2O_3-As_2O_3: CuO glasses recorded in the range $10^O \leq 2\theta \leq 80^O$ is shown in Fig.1. The absence of sharp peaks in the pattern indicates the amorphous nature of the samples.

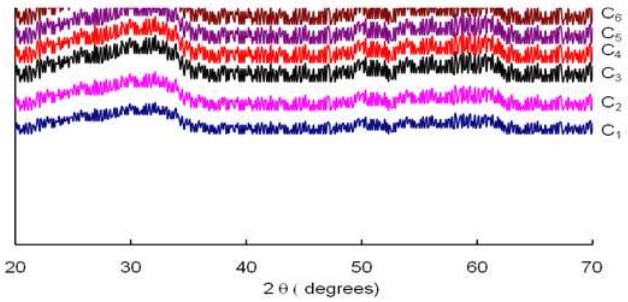

Fig.1: X-ray diffraction pattern of PbO-Bi_2O_3-As_2O_3: CuO glasses

Physical Parameters: Various physical parameters such as total copper (calculated as Cu^{2+} ions) ion concentration N_i, mean iron ion separation R_i, have been evaluated (using the conventional formulae]) with the measured values of density d and the calculated average molecular weight $\overline{M}$ for the present glasses and are presented in Table 1.

Table 1 Summary of Data on some Physical Parameters of PbO-Bi_2O_3-As_2O_3 CuO glasses

Glass	Conc. CuO (mol%)	Density	Avg. mol. wt (g/cm^3)	Conc. Cu ions N_i (x 10^{21} ions/cm^3)	Inter ionic distance of Cu ions r_i(A^0)
C_0	**0**	**5.4628**	**232.26**	**-----**	**------**
C_1	0.1	5.4611	232.11	1.417	8.920
C_2	0.2	5.4594	232.97	2.835	7.065
C_3	0.3	5.4577	232.82	4.253	6.171
C_4	0.4	5.4560	232.68	5.673	5.606
C_5	0.5	5.4538	232.54	7.093	5.204
C_6	0.6	5.4526	232.39	8.515	4.896

Table 2: Summary of data on Optical absorption spectra of PbO- Bi_2O_3-As_2O_3

Glass	Optical band gap E_0 (eV)	Cut-of wavelength (nm)	Position of $^2B_{1g} \rightarrow {}^2B_{2g}$ (nm)
C_0	***2.24***	***429***	***-----***
C_1	*2.20*	*451*	*810*
C_2	*2.16*	*466*	*821*
C_3	*2.08*	*486*	*838*
C_4	*2.40*	*395*	*755*
C_5	*2.44*	*375*	*744*
C_6	2.56	361	730

Optical Absorption Studies: Fig.2 represents the optical absorption spectra of PbO-Bi_2O_3-As_2O_3: CuO glasses recorded at room temperature in the wavelength region 300-1200 nm. The absorption edge observed at 429 nm for glass C_0 (pure glass) is observed to shift slightly to higher wavelength side with increase in the concentration of CuO up to 0.3 mol % and beyond this concentration the edge is observed to shift towards lower wavelength. The spectrum of glass C_4 has exhibited a broad absorption band at 755 nm corresponding to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition of Cu^{2+} ions [28-30]; with an increase in the concentration of CuO up to 0.3 mol %, the intensity of the band is found to increase with a shift in the peak position slightly towards higher wavelength. Beyond this concentration, the intensity of the band is noticed to decrease with the shifting of the peak position towards lower wavelength.

From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Urbach plot. Fig.3 represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap (E_o) obtained from the extrapolation of these curves are presented in Table 2. The value of E_o is found to decrease with the increase in concentration of CuO up to 0.3 mol % and after the E_o is found to increase.

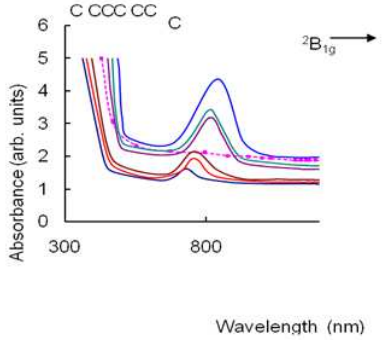

Fig.2: Optical absorption spectra of PbO-Bi_2O_3-As_2O_3:

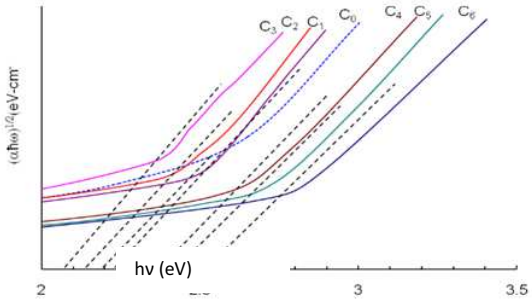

Fig.3: Urbach plots of all these glasses

Electron Spin Resonance Studies: ESR spectra of PbO-Bi_2O_3-As_2O_3 glasses containing different concentrations of CuO recorded at room temperature are shown in the Fig. 4. The structure and the intensity of the signal are observed to be strongly dependent on the concentration of CuO. The spectra of the glass C_2 exhibited an asymmetric signal with a hyperfine structure partially resolved with a value of $g_\perp = 2.018$ and a shallow quadruplet at $g_\parallel = 2.372$. As the concentration of CuO increases in the glass matrix (up to about 0.3 mol %), the perpendicular spectrum broadened progressively and the hyperfine structure smeared and exhibited a broad absorption at $g_\perp = 2.057$. The hyperfine parallel components of the spectra have also exhibited a similar behaviour. When the concentration of CuO is increased beyond 0.3 mol %, the intensity and the line width of both the parallel and perpendicular hyperfine peaks are observed to decrease. The pertinent data corresponding to the ESR spectra of PbO-Bi_2O_3-As_2O_3: CuO glasses are presented in the Table 3.

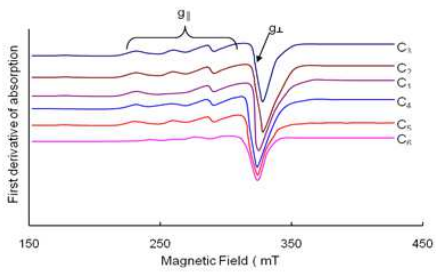

Fig.4: ESR Spectra of PbO-Bi2O3-As2O3: CuO glasses

Glass	$g_\parallel$	$g_\perp$	α^2	β_1^2
C_2	2.372	2.018	0.759	0.631
C_3	2.366	2.041	0.773	0.608
C_4	2.360	2.048	0.779	0.591
C_5	2.342	2.050	0.785	0.579
C_6	2.318	2.057	0.791	0.568

Table :3 Data on ESR Spectra of PbO- Bi2O3-As2O3: CuO glasses.

Discussion: The observed $g_{\parallel}$ and $g_{\perp}$ values (Table 3.) in the ESR spectra of PbO-Bi_2O_3-As_2O_3: CuO glasses are the characteristic of Cu^{2+} ions coordinated by six ligands which from an octahedron elongated along the z- axis. Because $g_{\parallel} > g_{\perp} > 2.0023$, the ground state for the paramagnetic electron is the $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state). The ESR and optical absorption spectral data can be correlated to understand the environment of Cu^{2+} ions in PbO-Bi_2O_3-As_2O_3: CuO glass network as follows:

$$g_{\parallel} = 2.0023 \left[1 - \frac{4\lambda\alpha^2\beta_1^2}{E(^2B_{2g})} \right] \longrightarrow \quad (1) \text{ and}$$

$$g_{\perp} = 2.0023 \left[1 - \frac{\lambda\alpha^2\beta^2}{E(^2E_g)} \right], \longrightarrow \quad (2)$$

where λ is the spin-orbit coupling coefficients and the bonding coefficients α^2 , β_1^2 and β^2 (=1.00) characterize, respectively, in –plane σ bonding, in –plane π bonding and out of –plane π bonding of the Cu(II) complexes. Their values lie between 0.5 and 1, the limits of pure covalent and pure ionic bonding . The value of β^2 may be expected to lie sufficiently close to unity as to be indistinguishable from unity in the bonding coefficients calculations . Since only one absorption band corresponding to the transition, $^2B_{1g} \rightarrow {}^2B_{2g}$ has been observed; the position of the second band has been estimated using the equation

$$E\ (^2B_{1g} \rightarrow {}^2E_g) = \frac{2k_{\perp}^2\lambda}{2.0023 - g_{\perp}} \longrightarrow \quad (3)$$

where $k_{\perp}$ is the orbital reduction factor ($k^2_{\perp}$ = 0.77) and λ the spin–orbit coupling constant (= -828 cm^{-1})

The values of α^2 and β_1^2 obtained using eqns. (1) and (2) are furnished in Table.3 . α^2 given in the equations is the bonding coefficient due to covalency of the σ bonds with the equatorial ligands that measures the electron density delocalized on ligand ions and β_1^2 accounts for the covalency of π bonding between ligands and $^2B_{2g}$ excited state. The values of α^2 and β_1^2 show an increasing trend towards unity; these observations indicate a gradual adaptation of Cu^{2+} ions from covalent environment to ionic environment in PbO - Bi_2O_3 - As_2O_3: CuO glass network.

The optical absorption spectra of CuO doped PbO-Bi_2O_3-As_2O_3 glasses exhibited a broad absorption band at about 800 nm. This is the characteristic of distorted octahedral symmetry. Thus the band can be assigned to $^2B_{1g}$ $^2B_{2g}$ transition. When the concentration of CuO is increased beyond 0.3 mol %, a gradual decrease in the intensity of optical absorption band and also the ESR signal are observed. These observations indicate a gradual decrease in the concentration of Cu^{2+} ions that take modifier positions in the glass network. In this concentration range of CuO. The lower the concentration of modifying Cu^{2+} ions, the lower is the concentration of NBO's in the glass matrix leading to a decrease of the disorder in the glass network. Such a decrease of disorder in the network results an increase in the optical band gap and shifts the absorption edge towards low wavelength side as observed (Figs:2 and 3) for the glasses C_3 to C_6.

When the concentration of CuO is more than 0.3 mol % in these glasses, we have observed the dielectric constant and loss to decrease; this is vividly due to the decrease in the concentration of Cu^{2+} ions that take modifying positions or due to increase in the concentration of Cu^{+} ions that take network forming positions.

Conclusion: The optical absorption and ESR measurements on these glasses indicate the presence of copper ions mostly in octahedral distorted tetragonally positions. The analysis of these data further indicates with an increase in the concentration of CuO, a gradual adaptation of Cu^{2+} ions from ionic environment to covalent environment.The analysis of the results of various studies viz. optical absorption, ESR, of PbO-Bi_2O_3-As_2O_3: CuO glasses indicates that there is a possibility of conversion of a part of Cu^{2+} ions into Cu^{+} ions, leading to decrease in the total concentration of Cu^{2+} ions (that take part

in modifying positions). As a result an increase the rigidity of the glass network may be achieved when the content of CuO is greater than 0.3 mol % in the glass matrix.

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