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PHYSICAL, SPECTROSCOPIC PROPERTIES OF PBO – GEO_2 GLASSES DOPED WITH CR_2O_3

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Abstract:

The system of glass samples PbO- GeO_2 comprising dissimilar concentrations Cr_2O_3 (0.2 - 1.0 mol %) was composed. Experimental densities and refractive index are used to conjecture different physical parameters such as ion concentration (N_i), mean separation (r_i), Polaron radius (r_p), field strength (F_i), electronic polarizability (α_e), reflection loss & optical dielectric constant (ε_0). The samples were delineated by XRD and Optical absorption (OA) patterns. The optical absorption spectra bands observed at about 440 and 665 nm are assigned to $^4A_2 \rightarrow {}^4T_{1g}$ (F), $^4A_2 \rightarrow {}^2T_{1g}$ transitions respectively. Additionally, a pair of weak bands at 680 and 700 nm observed due to $^4A_2 \rightarrow {}^4T_{2g}$ (F) and $^4A_2 \rightarrow {}^2E_g$ (E) (spin and parity forbidden) transitions.

Key words: PbO-GeO_2 glasses, Physical properties, XRD, Optical absorption (OA)

I. INTRODUCTION

Coordination composites are built by transition metal ions (Cr_2O_3) which are in oxide glasses. The quantification of optical absorption spectra (OA) for the ions confers the state of the ligands, the structure of the glass, and the state of bonding. Glasses doped with Cr^{3+} ions are extremely engrossing owing to their intense and compliant emission. Over and above that, Cr^{3+} ions are useful for procuring information about the local environment in the amorphous vitreous material. The spectroscopic properties of Cr^{3+} ions are highly dependent on the crystal field strength, the nature of the local environment and the chemical bonding, which they establish with their ligands. In this manner, we can control the emission of these ions by making a convenient choice of the glass matrix. Conventionally, PbO is heavy metal oxide and has engrossing optical proprieties when used in the glasses. Due to their lofty atomic number, density of glasses is high. The structure of the glass material is transposed owing to its modifying nature. It has dual role in the glasses as modifier and glass former [1]. PbO glasses have high refractive index and relatively low melting points [2]. The imposing characteristic property of electrical conduction of the lead involve glasses with different formers is of great interest [3]. Germanium is typically found in the vitreous form and is one of the conventional glass formers possess superior optical properties like lofty refractive index (~2.14) and transmission in the NIR region [4]. GeO_2 glasses are used in the field of non-linear optics, fabrication of laser devices and for core of optical fiber [5]. In accordance with the structural aspects the germanium oxide comprises of GeO_4 and GeO_6 structural units [6]. GeO_2 glasses are used to make out solid electrolytes because of their high ionic conductivity [7]. When the modifier is added to GeO_2 network, it acts either as a network former or as a modifier; if Pb–O is ionic it acts as modifier or glass former if Pb–O is covalent. Covalent Pb–O bonds are formed due to high polarizability, Pb^{2+}

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ion strongly interacts with O^{2-} [8]. Lead germanate glasses are employed to make out high speed optical switches, optical amplifiers and many types of nonlinear optical devices. [9]. Chromium ions subsist in various valence positions in the samples. Among the different valence states of chromium ions, Cr^{3+} ions act like modifiers. These ions are in the form of CrO_6 structural frames in the glass whereas $Cr^{5+}$and Cr^{6+} ions infiltrate the glass system like network formers with CrO_4^{3-} and CrO_4^{2-} frames. The Cr^{3+} ion is a most stable ion. It is widely used as a luminescent material and luminescence sensitizer in different glasses [10]. The glasses integrated with chromium ions can be used as high pressure-calibrants, high-temperature sensors and solid-state lasers [11–13]. A possible disordered material for tunable lasers [14]. Fabrication &amp: erosion wear response of E-glass-epoxy based hybrid composites [15]. The present work deals with the role of oxidation states of Chromium ions in the PbO–GeO_2 glass network.

II. EXPERIMENTAL

The chemical compositions of the synthesized glasses used in the present study as follows

Cr_2 :40 PbO–59.8 GeO_2: 0.2 Cr_2O_3
Cr_4 :40 PbO–59.6 GeO_2: 0.4 Cr_2O_3
Cr_6 :40 PbO–59.4 GeO_2: 0.6 Cr_2O_3
Cr_8 :40 PbO–59.2 GeO_2:0.8 Cr_2O_3
Cr_{10} :40 PbO–59.0 GeO_2: 1.0 Cr_2O_3

Analytical grade reagents of PbO, GeO_2 and Cr_2O_3 powders in suitable proportion are well grounded, homogenized mixtures were melted in silica crucible at 1300ºC in PID controlled furnace. After 1hour bubble free liquid was found then poured in a bras mold and subsequently annealed at another furnace operated at 430°C to avoid cracks then finally required glasses are formed. The X-ray diffraction pattern of the samples were recorded with Philips expert system using the step scan method with Cu–Kα radiation (λ = 1.5406 Å), to infer the amorphous nature of the glasses. Density measurements were taken by programmable VIBRA HT kit by means of Archimedes principle with O-xylene as buoyant liquid. The samples were then optically polished. The final dimensions of the samples used for the present measurements were about 1.0cm x 1.0cm x 0.1cm. The optical absorption spectra of the samples were recorded in the wavelength range of 400 to 900 nm up to resolution of 0.1nm using JASCO V–670 UV–Vis NIR spectrophotometer.

III. RESULTS AND DISCUSSIONS

A. Physical Parameters

Density and refractive index are important physical parameters of the glasses, more over these are useful to estimate other important physical parameters such as Cr^{3+} ion concentration (N_i), mean separation (r_i), Polaron radius (r_p), field strength (F_i), electronic polarizability (α_e), reflection loss as well as optical dielectric constant (ε_0) in the present glass network. The predictable formulae [16] used for the estimation of these parameters. With increasing of mol % density increased, molar volume decreased as shown in Fig.1. With increasing of mol % polaron radius decreased, Field strength increased as shown in Fig.2. With increasing of mol % density increased, refractive index decreased as shown in Fig.3.

The density of the prepared glass samples at room temperature is measured by the traditional famous standard principle of Archimedes' using O-xylene as the buoyant liquid. The density is calculated to the known formula

- Density $(D) = \frac{W_1}{W_1 - W_2} \times 0.86$
- The Cr^{3+} ion concentration $(N_i) = \frac{N_A M(mol\%) D}{\overline{M}}$
- Inter ionic distance (r_i) in A° $= \left[\frac{1}{N_i}\right]^{1/3}$

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- Polaron radius (r_p) in A° $= \frac{1}{2}\left[\frac{\pi}{6N_i}\right]^{1/3}$
- Field strength (F_i) in $cm^{-2} = \frac{Z}{{r_p}^2}$
- Electronic polarizability $(\alpha_e) = \frac{3(\mu^2-1)}{4\pi N_i(\mu^2+2)}$
- Fresnel's formula for reflection loss $(R) = \frac{(\mu^2-1)}{(\mu^2+2)}$
- The molar reflectivity $(R_M) = \frac{M(\mu^2-1)}{D(\mu^2-1)}$

Table 1: Various physical parameters of PbO-GeO_2 glasses doped with Cr_2O_3

Glass	0.2	0.4	0.6	0.8	1.0
Density d (g/cm^3)	5.447	5.50	5.515	5.530	5.585
Avg. Mol. Weight $\overline{M}$	151.9	151.76	151.61	151.47	151.33
Conc. of Cr^{3+} ions(N_i) ($10^{21}/cm^3$)	4.31	8.73	13.14	17.59	22.22
Inter ionic distance r_i (A°)	6.14	4.85	4.23	3.84	3.55
Polaron radius r_p (A°)	2.47	1.95	1.70	1.54	1.43
Field strength F, ($x10^{15}$ cm^{-2})	4.9	7.84	10.29	12.5	14.6
Refractive index(n)	1.472	1.468	1.459	1.443	1.439
Reflection loss	0.28	0.277	0.273	0.265	0.263
Molar volume (V_m)	27.88	27.59	27.49	27.39	27.09
Molar refraction (R_m)	7.8064	7.642	7.5102	7.261	7.125
Molar electronic polarizability(α_m) $(A°)^3$	3.09	3.03	2.97	2.87	2.82

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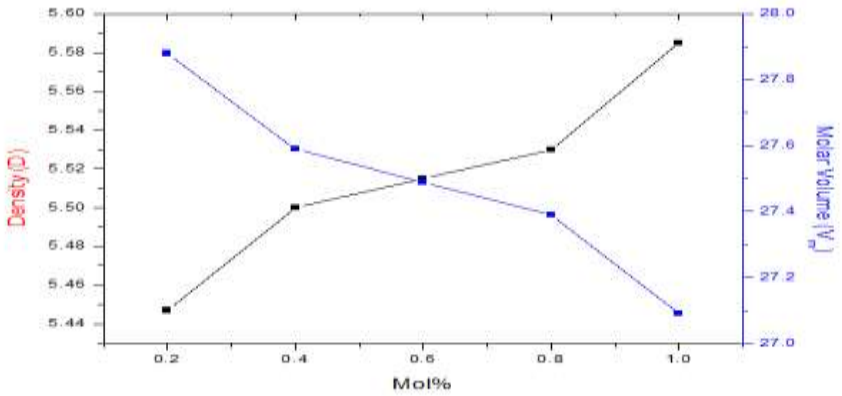

Fig.1.Mol % Vs Density and Molar Volume

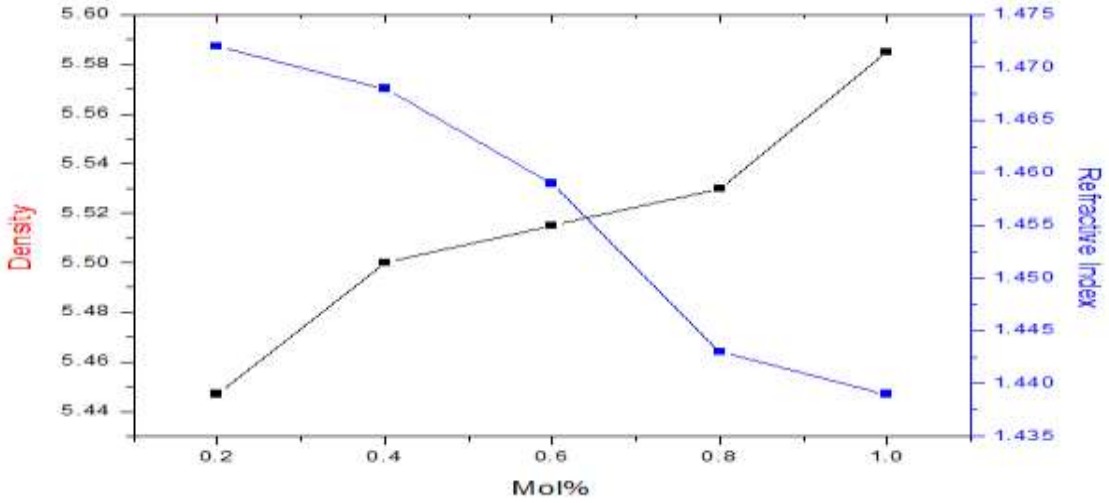

Fig.2.Mol % Vs Density and Refractive Index

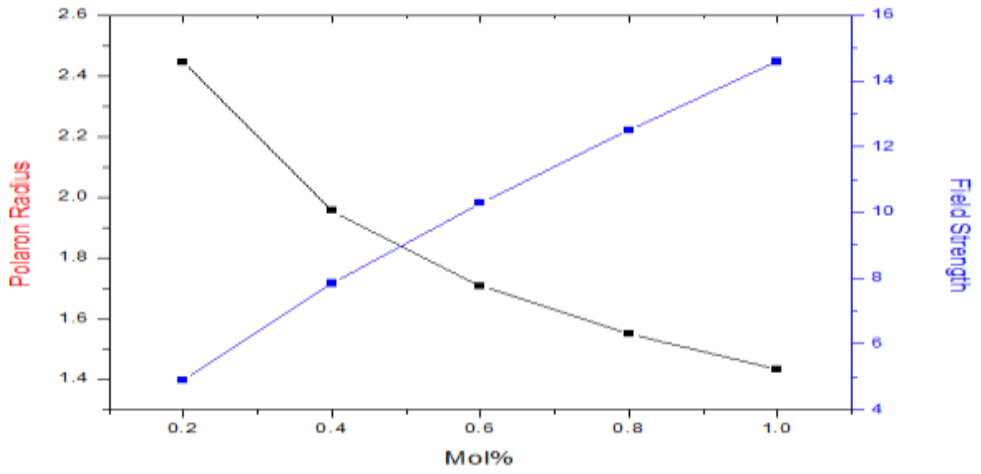

Fig.3.Mol % Vs Polaron Radius and Field Strength

B. X-Ray Diffraction

Fig. 4. shows X-ray diffraction pattern of some of the glass samples. The pattern shows absence of sharp Bragg peaks confirming the amorphous nature of the prepared samples. It confirms

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the irregular atomic arrangement of the atoms in the present glass system. All glasses samples are analyzed as shown in Fig.4.

C. Optical absorption studies

Fig. 5. Illustrates the optical absorption spectra of PbO-GeO_2: Cr_2O_3 glass samples at room temperature between the wavelength range 300–900 nm. In the spectrum of glass samples (0.2 to 1.0 mol% of Cr_2O_3). The optical absorption spectra bands observed at about 440 and 665 nm are assigned to $^4A_2 \rightarrow {}^4T_{1g}$ (F), $^4A_2 \rightarrow {}^2T_{1g}$ transitions respectively. Additionally, a pair of weak bands at 680 and 700 nm observed due to $^4A_2 \rightarrow {}^4T_{2g}$ (F) and $^4A_2 \rightarrow {}^2E_g$ (E) (spin and parity forbidden) transitions as shown in below Fig.5. In order to exhibit tauc plot as shown in belowFig.6. The highest mol% of Cr_2O_3 glass band gap is very less.

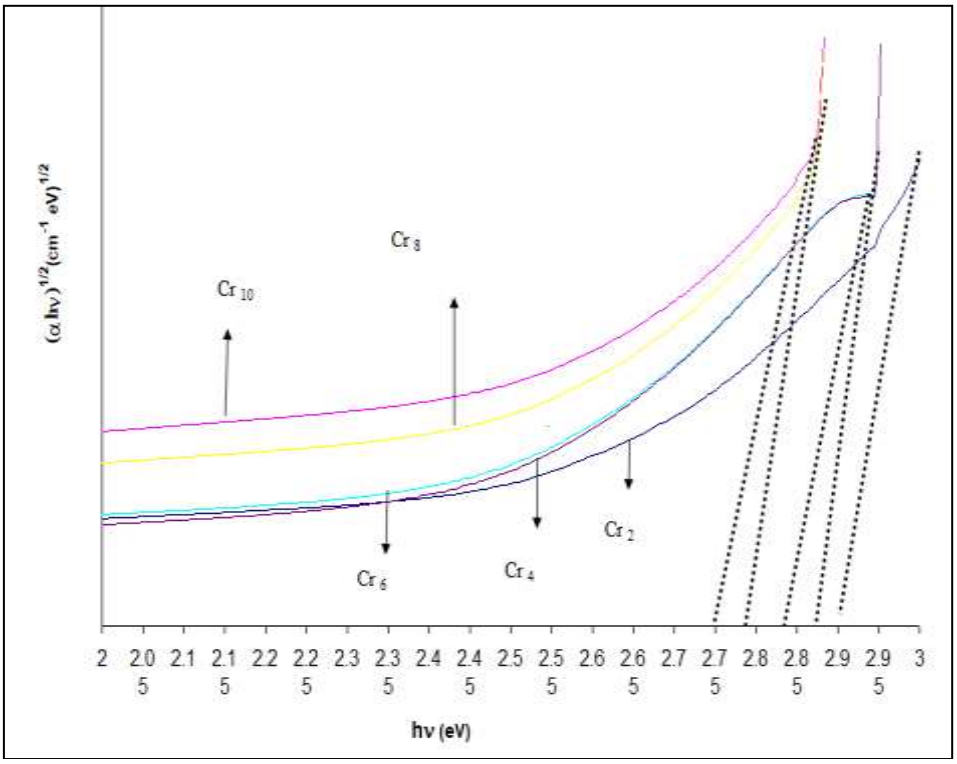

Fig.4.XRD Pattern of PbO-GeO_2: Cr_2O_3 glasses

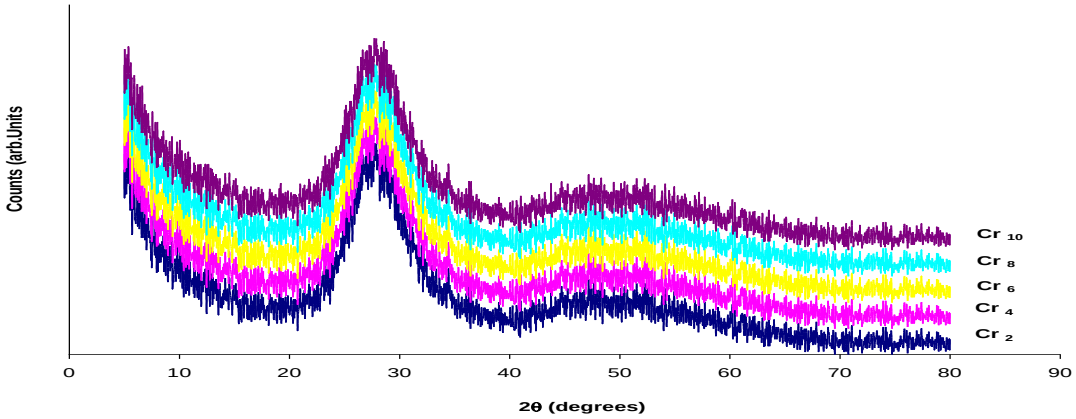

Fig.5.Optical absorption of PbO-GeO_2: Cr_2O_3 glasses

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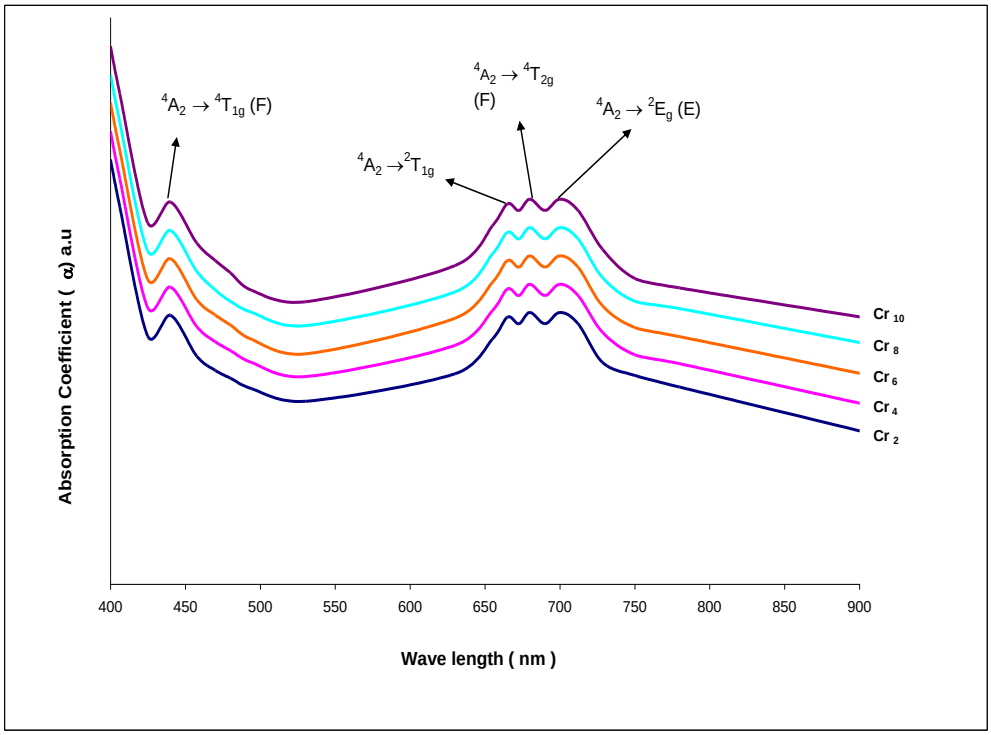

Fig.6. Tauc plot of PbO-GeO$_2$: Cr$_2$O$_3$ glasses

IV. CONCLUSIONS

PbO-GeO$_2$: xCr$_2$O$_3$ (x: 0.2, 0.4, 0.6, 0.8, 1.0) (mol %) glasses were prepared by adopting melt-quenching technique, Various physical parameters are estimated with the help of experimental densities and refractive index. The optical absorption spectra bands observed at about 440 and 665 nm are assigned to $^4A_2 \rightarrow {}^4T_{1g}$ (F), $^4A_2 \rightarrow {}^2T_{1g}$ transitions respectively. Additionally, a pair of weak bands at 680 and 700 nm observed due to $^4A_2 \rightarrow {}^4T_{2g}$ (F) and $^4A_2 \rightarrow {}^2E_g$ (E) (spin and parity forbidden). optical band gaps are calculated from the absorption edges.

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