Influence of Holmium Ions (Ho^{3+}) on the Physical and Optical Properties of Zinc Lithium Phosphate Glasses

Shwetha M[1,2] and B Eraiah[2,a)]

[1]Government First Grade College, Honnavar-581334, Uttara Kannada. Karnataka, India
[2]Department of Physics, Bangalore University, Bengaluru-560056, Karnataka, India
[a)]Corresponding author: eraiah@rediffmail.com

Abstract. Holmium doped zinc lithium phosphate glasses with formula xHo_2O_3-(15-x)Li_2O-45ZnO-40P_2O_5 (where x=0, 0.1, 0.3 and 0.5 mol%) are synthesized by conventional melt quenching method. The effect of Ho^{3+} ions on the physical and optical properties of these glasses has been investigated. Using Archimedes method densities of these glasses are measured and all the physical characteristics such as molar volume, oxygen packing density, polaron radius, interionic distance, and field strength are calculated. At room temperature, the optical absorption spectra in the UV-Visible region for all the glass samples was recorded to study the optical properties. Direct and indirect optical energy bandgap of all the prepared glass samples are calculated from Tauc plots. Refractive index of all the glasses are measured and using refractive index values molar refraction, molar polarizability of oxide ions, dielectric constant, reflection loss, and metallization criterion have been calculated.

INTRODUCTION

Phosphate glasses exhibit very good thermo-optical properties like low melting and transition temperature, high UV and IR transmission, high transparency and low dispersion[1-2]. They are also known for superior transparency, variety of compositions, easy production and good host materials for rare earth ions[3]. These glasses doped with lanthanide ions are of greater interest nowadays for their potential applications in development of laser hosts, multicolour phosphors, optical displays etc[4-6]. Among all the lanthanide ions holmium ion is one among the most important and attractive ions for the spectroscopic studies because of its favourable energy level structure i.e. it has many metastable levels which give rise to transitions in the UV-Visible region at different wavelengths[7]. In this glass matrix Li_2O as a glass modifier and ZnO as a former and also a modifier helps in decreasing the hygroscopic nature and also increasing the chemical durability of the glasses[8]. In the present work, holmium ions doped zinc lithium phosphate glasses have been characterised by absorption spectroscopy and the effect of holmium ions on the physical and optical properties of the glasses has been studied and reported.

EXPERIMENTAL

By melt quenching method, Ho^{3+} doped zinc lithium phosphate glasses having composition, xmol% Ho_2O_3 - 40mol% P_2O_5 -45mol% ZnO -(15-x)mol% Li_2O (where x=0, 0.1, 0.3 and 0.5 mol%) are prepared. Analar grade chemicals (Ho_2O_3, $LiOH.H_2O$, ZnO, and $NH_4H_2PO_4$) were weighed (about 8g per batch) and mixed thoroughly by grinding using agate mortar. The powdered mixture was then taken in porcelain crucibles and placed in a high temperature electric muffle furnace set to 1150°C temperature for 1 hr to get a homogenous liquid. The liquid was immediately quenched using preheated brass mould and blocks. The obtained glass samples were transparent, yellowish in colour and they were annealed at 300°C for 2 hrs to achieve thermal and structural stability. The glasses were then cut into suitable sizes, polished, named as PH0, PH01, PH03 and PH05. X-ray diffraction spectra was recorded using RIGAKU, ULTIMA IV, XRD operated at 40 kV and 30 mA, with Cu Kα radiation of wavelength λ=1.5406 Å. Archimedes'classic method of measuring the density was used at room temperature to measure density of the glasses. Optical absorption spectra from 200-1100 nm wavelength range at room temperature were recorded from Shimadzu spectrophotometer UV-1800 operated at 220V-240V. Refractive index values were measured using Abbe refractometer (digital) ATAGO at sodium wavelength 589.3 nm.

RESULTS AND DISCUSSION

Physical Properties

XRD Analysis

Figure 1 shows typical X-ray diffraction pattern obtained for the prepared glass samples. A broad hump due to the scattering of X-rays instead of any sharp peaks is observed between 15° and 35°, which confirms the amorphous nature of the glasses prepared.

Density, Molar Volume and Oxygen Packing Density

All the physical parameters which are determined and evaluated have been listed in Table 1. It is found that, density of the glass system is increasing from 3.161 to 3.262 g/cm^3 and molar volume is decreasing from 30.96 to 30.540 g/mol on adding Ho_2O_3 to the matrix. The variation of density and molar volume with Ho_2O_3 is shown in Fig 2. The molecular weight of Ho_2O_3 is 377.86 g/mol which is very much higher than the molecular weight of any other compounds present in the matrix and so the glass is becoming denser on adding Ho^{3+} to the network. Oxygen packing density is calculated using the appropriate formula[9]. It is found that the oxygen packing density is increasing with increasing Ho^{3+}content indicating the increase of non-bridging oxygen in the network. The relationship betweenoxygen packing density andconcentration of Ho_2O_3 is shown in Fig 3.

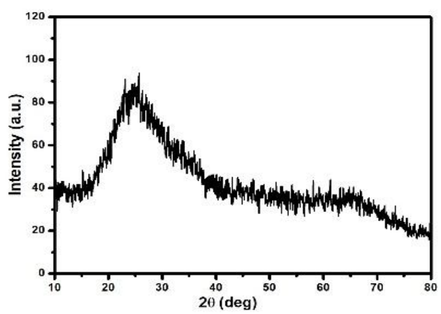

FIGURE 1. Typical XRD pattern of holmium doped lithium zinc phosphate glass.

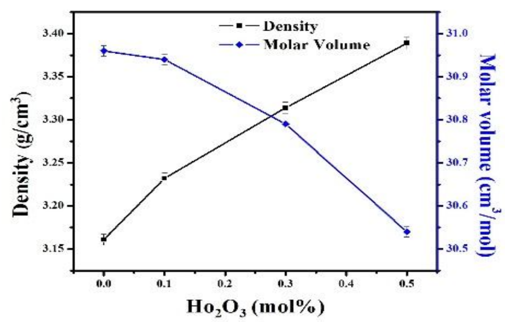

FIGURE 2. Variation of density (ρ) and molar volume (V_m)wrt Ho_2O_3content(mol%).

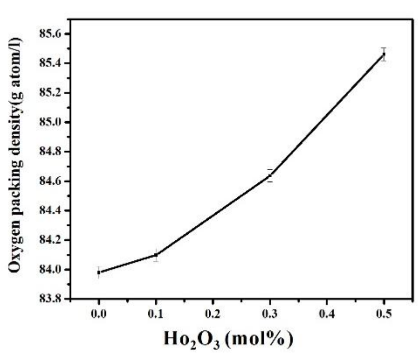

FIGURE 3. Variation of oxygen packing density (OPD) with concentration of Ho_2O_3 (mol%).

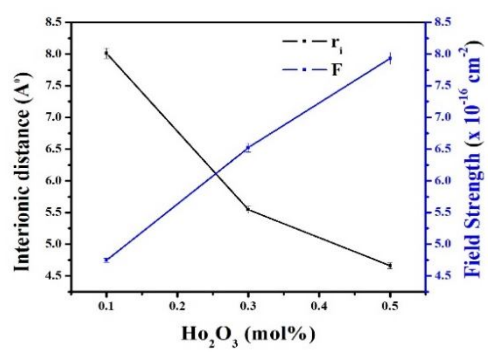

FIGURE 4. Variation of interionic distance (r_p) and field strength (F) wrt Ho_2O_3content(mol%).

Holmium Ion Concentration, Polaron Radius, Interionic Distance and Field Strength

Holmium ion concentration, polaron radius, interionic distance and field strength are calculated using appropriate formulae. It is observed that with increasing concentration of Ho^{3+} ions, polaron radius and interionic is decreasing which means Ho-O distance is decreasing causing an increase in the Ho-O bond strength and producing stronger field strength around Ho^{3+} ions[10]. Correlation of interionic distance and field strength with Ho_2O_3 content is shown in Fig. 4.

TABLE 1. Density (ρ), molar volume (V_m), oxygen packing density (OPD), holmium ion concentration (N_{RE}), polaron radius (r_p), interionic distance (r_i) and field strength (F) of holmium doped lithium zinc phosphate glasses.

Glass code	ρ (g/cm^3)	V_m(cm^3/mol)	OPD (g atom/l)	N_{RE}x10^{21}(atoms/cm^3)	r_p(Å)	r_i(Å)	Fx10^{15}(cm^{-2})
PH0	3.161	30.96	4.23	3.02	1.568	4.016	2.458
PH01	3.174	30.94	4.74	3.67	1.570	4.076	2.464
PH03	3.212	30.79	4.59	3.62	1.572	4.087	2.471
PH05	3.262	30.54	4.56	3.54	1.575	4.094	2.480

Optical Properties

Optical Absorption, Energy band gap, Refractive index, Molar refraction and molar polarizability

The optical absorption spectra of holmium doped zinc lithiumphosphate glass with 0.5 mol% of Ho_2O_3 concentration is shown in Fig. 5. Six prominent absorption peaks centred at 416, 450, 472, 484, 537 and 642 nm corresponding to the transitions $^5I_8 \rightarrow ^5G_5$, $^5I_8 \rightarrow ^5G_6$, $^5I_8 \rightarrow ^5F_2$, $^5I_8 \rightarrow ^5F_3$, $^5I_8 \rightarrow ^5F_4$ and $^5I_8 \rightarrow ^5F_5$ respectively[11] are observed between 200-1100 nm wavelength for all the three glass samples. All the observed absorption peaks are accredited to the 4f-4f transitions of holmium ions from the ground level to various excited levels. It is observed that the type of absorption spectra obtained for all the three glasses is the same but the intensity has slightly changed. We can see that the transitions $^5I_8 \rightarrow ^5G_6$ (450 nm), $^5I_8 \rightarrow ^5F_4$ (537 nm) and $^5I_8 \rightarrow ^5F_5$ (642 nm) are more sharp and intense compared to the other transitions. $^5I_8 \rightarrow ^5G_6$ (450 nm) is a hypersensitive transition whose intensity is sensitive to even a small change in the environment and the transitions obey $\Delta S = 0$, $\Delta L \leq 0$ and $\Delta J \leq 0$ selection rules[12]. The optical energy bandgap gives the information about the nature and structure of the glass network. Direct and indirect bandgaps are determined from Tauc's plots as shown in Fig. 6 and Fig. 7. The values obtained are listed in Table 2. It is found that, both direct and indirect optical energy band gaps are decreasing with increasing Ho_2O_3. This decrease is due to the negative charge on the non-bridging oxygen atoms which is helping in excitation of electrons to the conduction band.

TABLE 2. Direct (E_{dir}) bandgap, indirect (E_{ind}) bandgap, refractive index (n), polarizability (α), dielectric constant (ε), reflection loss (R_L) and metallization criterion of holmium doped lithium zinc phosphate glasses.

Glass	E_{dir} (eV)	E_{ind}(eV)	n	R_m(cm^3/mol)	α_m (Å^3)	ε	R_L (%)	M
PH0	4.23	3.02	1.568	10.128	4.019	2.458	4.89	0.672
PH01	3.14	2.69	1.589	10.282	4.08	2.493	5.04	0.667
PH03	3.24	2.63	1.592	10.318	4.094	2.512	5.121	0.664
PH05	2.98	2.27	1.597	10.363	4.112	2.540	5.243	0.66

All the measured and calculated optical parameters are listed in Table 2. Refractive index is one of the important optical parameters of any material. It is found that the refractive index is increasing with increasing Ho_2O_3 concentration which may be because Ho_2O_3 is acting as a modifier causing an increase in the non-bridging oxygen and also its coordination number which is higher than any other compounds present in the matrix may be causing the increase in refractive index followed by increased molar refraction and molar polarizability. Dielectric constant (ε) and reflection loss (R_L) of all the prepared glass samples are calculated from the corresponding refractive index values and using the appropriate relations. Correlation of refractive index and polarizability of oxide ions with Ho_2O_3 concentration is shown in Fig. 8. Metallization criterion, M is also calculated and since $R_m < V_m$ we can say that all the prepared glass samples show insulating nature.

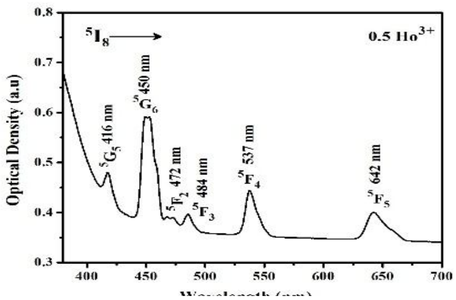

FIGURE 5. Optical absorption spectrum of the Ho^{3+} doped zinc lithium phosphate glass.

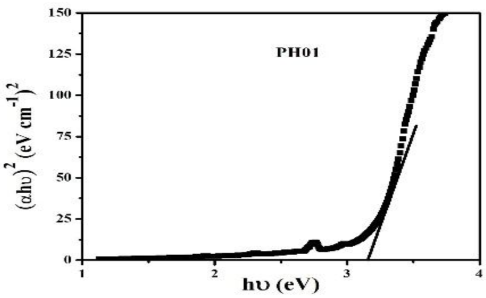

FIGURE 6. Plot of $(\alpha h\nu)^2$*vs. hν*.

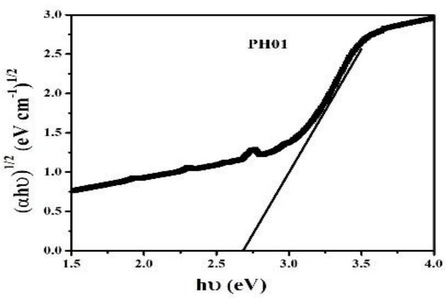

FIGURE 7. Plot of $(\alpha h\nu)^{1/2}$*vs. hν*.

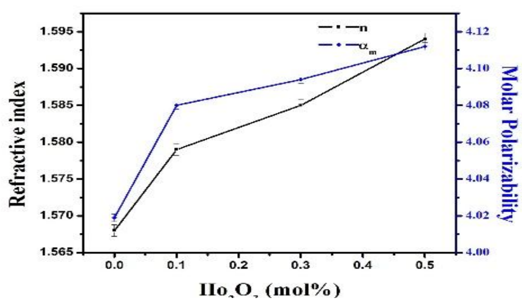

FIGURE 8. Variation of refractive index and molar polarizability wrt Ho_2O_3 concentration.

CONCLUSION

From the study of Ho_2O_3 -P_2O_5 -ZnO -Li_2O glass matrix the following conclusions can be made,

- Glass samplesprepared are amorphous which is confirmed by the obtained X-ray diffraction spectra.
- The density of the glasses is increasing with holmium ion concentration due to its larger molecular weight and the non-bridging oxygen formed and also increase in the oxygen packing density.
- Both direct and indirect optical energy band gap values are decreasing with increasing Ho_2O_3 concentration and the optical absorption edge shifts towards longer wavelength.
- Ho_2O_3 in the glass matrix acts as a glass modifier leading to the increase in non-bridging oxygen bonds inside the matrix. Higher coordination number of Ho^{3+} ion in the matrix may be the reason for increasing refractive index, molar refraction and molar polarizability of oxide ions on increasing Ho^{3+} concentration.

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