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Spectroscopic Studies on Li_2O-Al_2O_3-P_2O_5Glasses Doped with Ho_2O_3

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Abstract: ***Li_2O-Al_2O_3-P_2O_5glasses mixed with Ho_2O_3have been prepared by melt quenching method and the systematic characterization like optical absorption behavior and physical parameters of Li_2O-Al_2O_3-P_2O_5 pure glass and Li_2O-Al_2O_3-P_2O_5 glass doped with 1.0 mol% of Ho_2O_3 systems have been carried out. The existence of Ho^{3+}in these glasses is expected to influence their physical properties to a large extent since these ions exist in different valence states. The optical absorption spectra of Li_2O-Al_2O_3-P_2O_5 glass doped with 1.0 mol% of Ho_2O_3 is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^5I_8$; these levels are assigned to the appropriate electronic transition.***

Keywords: Li_2O-Al_2O_3-P_2O_5, Melt quenching,Ho_2O_3 and Spectroscopic properties

1. Introduction

A glass is defined as an inorganic product of fusion which has been cooled to a rigid condition without crystallization. According to this definition, a glass is a non crystalline material obtained by a melt-quenching process [1]. The macroscopic properties of a glass such as optical transmission and absorption, refraction of light, thermal expansion, etc. are observed always equally in all directions, provided that the glass is free from stress and strain. 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 [2, 3].Interest in amorphous phosphates was stimulated by their use in a variety of industrial applications, including sequestering agents for hard water treatments and dispersants for clay processing and pigment manufacturing [4]. P_2O_5 glasses have several advantages over conventional silicate and borate glasses due to their superior physical properties such as high thermal expansion coefficients, low melting and softening temperatures and high ultra-violet transmission [5]. Certain compositions of these glasses have large rare-earth stimulated emission cross-sections and low thermo optical coefficients (compared with silicate glasses) and are the materials of choice particularly for high power laser applications [6].All the rare-earths exist in trivalent state and some occasionally in divalent and tetravalent states. These rare- earth ions are associated with the f-f and f-d transitions. Among these rare earth ions samarium (Ho^{3+}) is a good doping compound for improving the properties of prepared glass systems. C.K. Jayasankar et al. [7] have been preparedHo^{3+} doped lead phosphate (P_2O_5+K_2O+Al_2O_3+PbO+Na_2O+ Ho_2O_3) glasses by conventional melt quenching technique. The optical properties have been characterized through absorption, emission and gain spectra and decay rate analysis. The analysis indicates that these Ho^{3+} glasses exhibit relatively better properties for application in mid-infrared lasers at a wavelength of about 2.0 μm.Y.C. Ratnakaram et al. [8] studied the optical absorption and emission properties of Ho^{3+} doped mixed alkali phosphate glasses. Racah (E^1, E^2, E^3), spin–orbit (ξ_{4f}) and configuration interaction (α, β) parameters are calculated and these values are compared for different x values in the glass matrix. Judd–Ofelt intensity parameters (Ω_2, Ω_4, Ω_6) are calculated for all the Ho^{3+} doped mixed alkali phosphate glasses. From these parameters and from the spectral profiles of the hypersensitive transition structural studies have obtained. Radiative transition probabilities (A), radiative lifetimes (τ), branching ratios (β) and integrated absorption cross-sections (Σ) are obtained from the intensity parameters. Emission cross-sections (σ) are calculated for the two transitions, $^5F_4$, $^5S_2 \rightarrow {}^5I_8$ and $^5F_5 \rightarrow {}^5I_8$ of Ho^{3+} in these two mixed alkali phosphate glasses. Optical band gaps (E_{opt}) for both direct and indirect transitions are reported.M. Seshadri et al. have been studied the optical absorption and emission spectra of Ho^{3+} doped alkali, mixed alkali and calcium phosphate glasses. Variation of Judd–Ofelt intensity of parameters (Ω_λ), peak wavelengths of the hypersensitive transitions (λ_p), radiative transition probabilities (A_{rad}) and peak emission cross-sections (σ_p) with the variation of alkalis, mixed alkalis and calcium in the phosphate glass matrix has been studied. The shift in peak wavelength of the hypersensitive transition and Judd–Ofelt intensity parameter (Ω_2) are correlated with the structural changes in the host matrix. Radiative lifetimes (τ_R) are estimated for certain excited states of Ho^{3+} in these glass matrices. From the luminescence spectra, the emission cross-sections (σ_p) are evaluated for the two emission transitions of Ho^{3+} ion. G. Vijaya Prakash et al. [9] prepared the rare earth (Pr^{3+}, Nd^{3+}, Sm^{3+}, Dy^{3+}, Ho^{3+} and Er^{3+}) doped NASICON type phosphate glass and the optical absorption studies are carried out. The variation of Ω_2 values with *f* electrons shows a pronounced rise in the middle of the series arises due to the differences in the distribution of sites occupied by the rare earth ions in the present phosphate glass. The hypersensitive nature of absorption transitions of Nd^{3+}, Er^{3+} and Ho^{3+} are explained in the light of covalency and site asymmetry effects. Emission studies of Eu^{3+} and Dy^{3+} indicate that these rare earths are situated in highly distorted sites compared to other fluoride, phosphate and oxyfluoride glasses.T. Satyanarayana et al. [10] prepared and synthesized the glasses of the composition $(39-x)BaO–xAl_2O_3–60P_2O_5:1.0Ho_2O_3$ (in mol%) with x value ranging from 1.0 to 4.0 . The IR spectral studies of these glasses have indicated that there is a gradual transformation of Al^{3+} ions from tetrahedral to octahedral with increase in the concentration of Al_2O_3 up to 3.0 mol%. Optical absorption and fluorescence spectra (in the visible and NIR regions) of these glasses have been recorded at room temperature. The Judd–Ofelt theory could successfully be applied to characterize the absorption and luminescence spectra of Ho^{3+} ions in these glasses. From the luminescence spectra, various radiative properties like transition probability A, branching ratio β_r, the radiative lifetime τ_r and emission cross-section σ^E for various emission levels of these glasses have been evaluated. The radiative lifetime of the ${}^5S_2 \rightarrow {}^5I_8$ (green emission) transition has also been measured. The variations observed in these parameters have been discussed in the light of varying co-ordinations (tetrahedral and octahedral positions) of Al^{3+} ions in the glass network. The influence of hydroxyl groups on the luminescence efficiency of the transition ${}^5S_2 \rightarrow {}^5I_8$ has also been discussed. In the present investigation we have prepared Holmium(Ho_2O_3) doped$Li_2O–Al_2O_3–P_2O_5$ glass system and characterized by using different spectroscopic techniques.

2. Experimental

For the present study, the chosen composition is (30–x) $Li_2O–10Al_2O_3$- $60P_2O_5$: xHo_2O_3 with x = 1.0 mol%.
The details of the compositions are:
Ho_0: 30 Li_2O –$10Al_2O_3$- $60P_2O_5$
Ho_1: 29 Li_2O –$10Al_2O_3$- $60P_2O_5$:$1.0Ho_2O_3$
Analytical grade reagents of P_2O_5, Li_2CO_3 Al_2O_3 and Ho_2O_3 powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar, calcinated at about 400°C for 2 h in a platinum crucible and subsequently melted in the temperature range of 1000 to 1100°C in an automatic temperature microprocessor controlled furnace for about 30 minutes. The resultant bubble free melt was then poured in a pre-heated brass mould and annealed at 250°C in another furnace. The samples prepared were mechanically ground and optically polished to the dimensions of 1cm× 1cm× 0.2 cm (Fig. 1).

3. Characterization

The density of the glasses was determined to an accuracy of (± 0.0001) by the standard principle of Archimedes' using o–xylene (99.99% pure) as the buoyant liquid. The mass of the samples was measured to an accuracy of 0.1 mg using Ohaus digital balance Model AR2140 for evaluating the density. The optical absorption spectra of the glasses were recorded to a resolution of 0.1 nm at room temperature in the spectral wavelength range covering 250-900 nm using JASCO Model V-670 UV–VIS–NIR spectrophotometer.

Ho_0Ho_1

Figure 1: Images of pure and doped glasses of the Li_2O-Al_2O_3-P_2O_5 glass system

4. Results and Discussion

The composition of $Li_2O – Al_2O_3 – P_2O_5$: Ho_2O_3 glass system is an admixture of glass formers, modifiers and intermediates. P_2O_5 is a strong glass forming oxide, participates in the glass network with PO_4 structural clusters. The PO_4 tetrahedra are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross-bonding between the metal cation and two non-bridging oxygen atoms of each PO_4 tetrahedron. The presence of such PO_4 units in the titled glass samples is evident from the IR spectral studies [9, 10]. Among various rare earth ions, Ho^{3+} doped glasses that give rich emission in the ultraviolet, visible and near infrared region (at ~2.0 µm). The introduction of Neodymium ions in the glass network will create bond defects liberating non bridging oxygen atoms (NBOs) and also suitable cations for giving rich emission. So these glasses are best candidates for lazing materials.From the measured values of the density and average molecular weight M of the samples, various other physical parameters such as rare earth ion concentration Ni, mean rare earth ion separation R_i and molar volume for all the glass samples were evaluated and presented in Table 1.

Table 1 Physical parameters of $Li_2O–Al_2O_3–P_2O_5$ glasses doped with Ho_2O_3

Glass	Density (g/cm^3)	Avg. Mol. Wt. (g)	Mol. Vol (cm^3/ mol)	r_i (Å)	r_p (Å)	N_i (10^{21}, ions/ cm^3)	Field Strength (10^{15})	band gap (eV)
Ho_0	2.515	104.32	41.49	--	--	--	--	4.35
Ho_1	2.544	107.80	42.37	18.9	7.60	0.15	0.52	4.80

The study of optical absorption, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of the materials. It is possible to determine whether the optically induced transition is direct or indirect and allowed or forbidden by analysis of the absorption edge. The optical absorbance of glass system has been studied in the vicinity of the fundamental absorption edge.The optical absorption spectra of $Li_2O – Al_2O_3 – P_2O_5$pure glass recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands (Fig. 2).

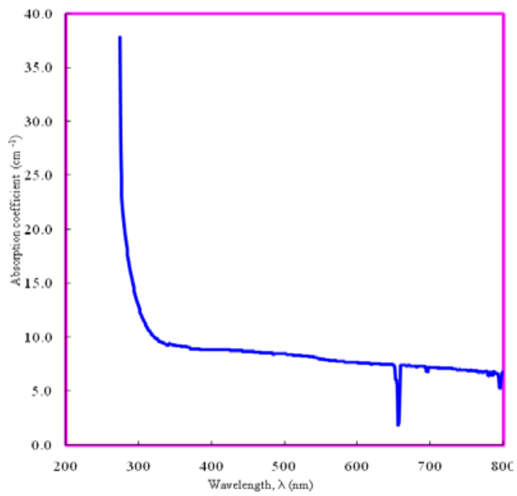

Figure 2: Optical absorption spectra of $Li_2O–Al_2O_3–P_2O_5$ glassrecorded at room temperature

The optical absorption spectra of $Li_2O– Al_2O_3–P_2O_5$glass doped with 1.0 mol% of Ho_2O_3 is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^5I_8$ (Fig. 3&Fig. 4); these levels are assigned to the following appropriate electronic transition [11,12]:

$^5I_8 \rightarrow {}^3H_5, {}^3H_6, {}^3K_7$,(near UV region)

$^5I_8 \rightarrow {}^5G_5, {}^5G_6, {}^5F_1, {}^5F_3, {}^3K_8\, {}^5F_2, {}^5F_3, {}^5F_4, {}^5S_2, {}^5F_5$ (in the Visible region)

$^5I_8 \rightarrow {}^5I_6, {}^5I_7$ (in the NIR region)

From the observed absorption edges, we have evaluated the optical band gaps (E_o) of these glasses by drawing Tauc plot between $(\alpha \hbar \omega)^{1/2}$ and $\hbar \omega$ as per the equation:

$$\alpha(\omega) \hbar \omega = C (\hbar \omega - E_o)^2 \text{----------} (1)$$

Fig. 5 represents the Tau plot of this glass in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap (E_0) obtained for $Li_2O – Al_2O_3 – P_2O_5$glass is presented in Table 1.

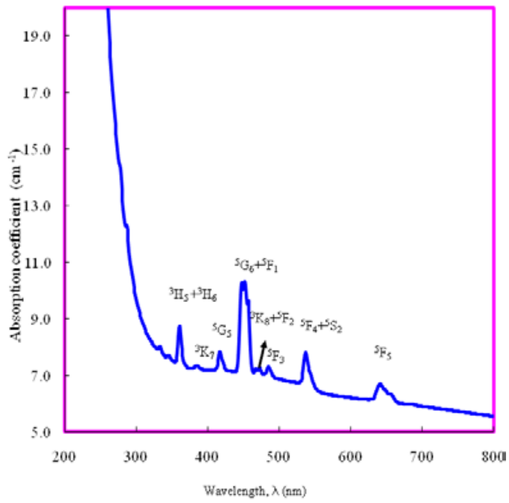

Figure 3: Optical absorption spectra of $Li_2O–Al_2O_3– P_2O_5$ glasses doped with1.0 mol % of Ho^{3+}recorded at room temperature in the visible region.

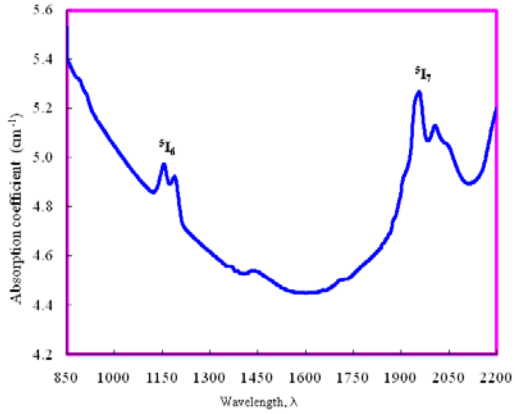

Figure 4: Optical absorption spectra of $Li_2O–Al_2O_3– P_2O_5$ glasses doped with 1.0 mol % of Ho^{3+} recorded at room temperature in the NIR region

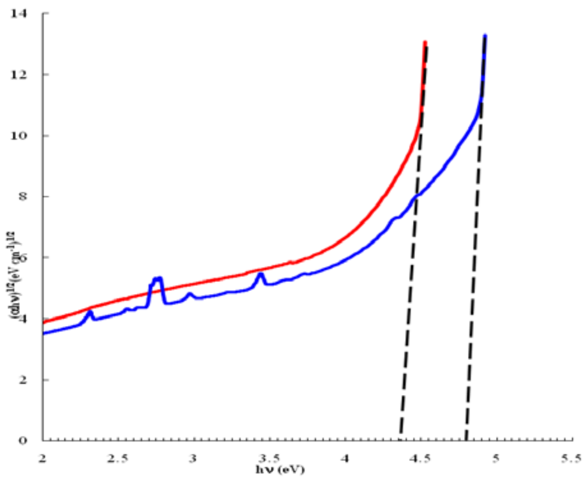

Figure 5: Tauc plots for evaluating the optical band gap of $Li_2O–Al_2O_3–P_2O_5$ glasses doped with Ho^{3+} ions

5. Conclusion

$Li_2O–Al_2O_3–P_2O_5$pure glass and $Li_2O–Al_2O_3–P_2O_5$glass doped with 1.0 mol% of Ho_2O_3 systems are prepared by melt quenching method. The systematic studies like physical parameters evaluation and optical absorption behavior of $Li_2O–Al_2O_3–P_2O_5$pure glass and$Li_2O–Al_2O_3–P_2O_5$glass doped with 1.0 mol% of Ho_2O_3 systems have been carried out. The optical absorption spectra of $Li_2O–Al_2O_3–P_2O_5$pure glass recorded at room temperature in the wavelength region 300-2000 nm exhibited no absorption bands. From the observed absorption edges, we have evaluated the optical band gap. The optical absorption spectra of $Li_2O–Al_2O_3–P_2O_5$glass doped with 1.0 mol% of Ho_2O_3 is recorded at room temperature in the wavelength region 300-2000 nm exhibited all from the ground state $^5I_8$; these levels are assigned to the appropriate electronic transition. Summing up the entire work presented in this project it is felt that the study of various physical and spectroscopic properties of $Li_2O–Al_2O_3–P_2O_5$glasses doped with Ho_2O_3 have yielded some valuable information which will be useful for the practical applications of these materials in the laser industry.

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