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Optical and Physical Properties of Sodium Calcium Lead fluoro Borate Glasses Incorporated with Praseodymium Ion

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Abstract : In the present paper, the glass composition $20Na_2O$ -$10CaO$-$10PbF_2$ -$60B_2O_3$ doped with varied concentrations of Pr^{3+} have been prepared using muffle furnace by the conventional melt quenching technique and the impact of Praseodymium ions concentration on optical and physical properties of present glasses have been examined. The densities (ρ) of the glass samples were measured using Archimede's principle with toluene as an immersion liquid. Refractive indices (n) of samples were measured at 589.3 nm using an Abbe's refractometer with mono-bromonaphthalene as the contact liquid and few physical parameters of the glasses like, molar volume (V_m), molar refractivity (R_m), polarizabilities (α_m), concentration of rare earth ion (N_i) , polaron radius (r_p) , inter ionic distance (r_i), field strength(F), reflection loss (R_L%) and dielectric constant (ε), energy band gap and urbach energy are also calculated and tabulated. The Powder X-Ray diffraction analysis of the prepared samples confirms the amorphous nature of the samples. The optical absorption spectra of polished samples have been recorded at room temperature in the wavelength range 400nm -800nm using Perkin Elmer lambda-35 UV-Vis spectrometer. Direct and Indirect band gaps are calculated using Tauc's plot.
Keywords : Sodium Borate Glasses, Optical Band Gap, X Ray Diffraction, UV/Visible Spectroscopy.

Introduction

Among various optical glasses available, borates are the most important glassy systems owing to their peculiarities such as low melting point, high optical transparency, high chemical stability and good rare earth ion solubility. They are also found to be robust and inexpensive[1-4]. But the addition of alkali/alkaline earth oxide/fluoride converts the boron coordination and the structural groups from one to another depending on the type and concentration of the alkali/alkaline earth oxide/fluoride. On the other hand, the high phonon energies (~1300-1500 cm-1) possessed by borate glasses encourage non radiative emission process very much and

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cannot acts as good laser host[5-8]. From this point of view, the fluoride compounds have less phonon energies (300–600 cm^{-1}) added to borate host as network modifiers, can strongly reduce the phonon energies of borates to a relatively lower values and even increases their mechanical strength [9]. Moreover, the solubility of RE ions is also larger in the fluoride medium than in the oxide [10] and the fluoride compounds present in borates helps in reacting and removing the –OH group from the borate glass. Over and above, the fluoride compounds in a glass can reduce scattering and dispersion losses which are very much required for the construction of LEDs.

Praseodymium doped glasses find variety of practical applications such as solid lasers, fibre amplifiers in 1.3 μm region, optical fibres, up-converters [11]. Laser action in visible spectral region has been observed for the transition $^1D_2 \rightarrow {}^3H_4$ of the Pr^{3+} ion. Laser transition $^1G_4 \rightarrow {}^3H_5$ observed at ~1.3 μm in Pr^{3+} doped glass fibres has been found to be very promising transition for developing fibre amplifier for communication in the second telecom window[12]. In the present work an attempt is been made to observe the optical properties upon the Pr^{3+} ions incorporated to sodium lead fluoro borate glasses.

Experimental Methods

Oxide glasses with composition $20Na_2O$ -$10PbF_2$-10CaO -$60B_2O_3$ -XPr_2O_3 with X=0, 0.1,0.3,0.5 mol% were prepared using electric furnace by the conventional melt quenching technique and designated as FC, FC01, FC03, FC05, respectively. 10g batch chemical compositions were weighted more accurately, mixed and grinded in an agate mortar. Then compositions were taken in porcelain crucible melted in an electric furnace in the temperature range of at 1030-1050 ^{0}C for 45 minutes (stirred for homogeneous mixing) and quickly poured on a preheated brass moulds to get pellet form samples. The amorphous nature of samples was confirmed by XRD measurements (Rigaku Ultima IV) using Cu-Ka radiations (λ = 1.54 Å) with copper filters at 40 kV and 100 mA. The densities of the glass samples are measured at room temperature by using Archimedes principles, with toluene as the immersion liquid of density (0.866 g/cm^3). The refractive indices measurements were made by the Abbe's refractometer with mono-bromonaphthalene as the contact liquid**.** The optical absorption coefficient α (λ) of the samples was calculated by using the following equation [13] $\alpha(\lambda) = 2.303 \left(\frac{A}{d}\right)$ Where A is absorbance and d is thickness of the sample respectively. The optical bandgap Eopt, defines the direct and indirect energy difference between valence and conduction band of glasses, is obtained from the equation [8, 14] $\alpha h\nu = B\left(h\nu - E_{opt}\right)^n$ Where α is the absorption coefficient, hν is the incident photon energy, B is the electronic transition constant and the index n values are 1/2 and 2 for direct and indirect allowed transitions respectively. The absorption coefficient α (υ), in amorphous materials, in the optical region near the absorption edge at particular temperature, obeys empirical relation known as, Urbach rule [15] given by $\alpha(\vartheta) = \alpha_0 \exp(h\vartheta/E_U)$, Where, hυ is photon energy, a_0 is a constant and E_U is the Urbach energy. The physical properties were determined using standard formulae [16] were also calculated and tabulated.

Results and Discussion

I. Physical Properties

The idea about the physical properties is necessary to analyze the changes in the structure of the glass systems. The calculated physical parameters of glass samples are enlisted in Table 1.The refractive index of the present glass matrix is higher (~1.65). From the literature it is found that, the glass higher density are rigid in nature [17]. Also glass containing higher average molecular weight will have lesser in inter ionic distance values [18]. The decrease in inter ionic distance in the present glasses with increase in Pr3+ content indicates that the atoms are more tightly packed.

Table.1.Physical parameters of the glasses: Refractive index(n), density (ρ), molar volume (V_m), molar refractivity (R_m), polarizabilities (α_m), concentration of Rare earth ion (N_i) , polaron radius (r_p) , inter ionic distance (r_i), Field strength(F), Reflection loss (R_L%) and Dielectric constant (ε).

Glass	n	ρ(g/cm^3)	M.W(g)	V_m (cm^3)	R_m (cm^{-3})	α_m (×10^-24)cm^3	N_i(×10^20) ions/cm^3	r_p (nm)	r_i (nm)	F (×10^15)cm^{-2}	R_L(%)	ε
FC	1.624	3.315	89.04	26.86	9.48	3.759	--	--	--	--	5.655	2.637
FC01	1.654	3.363	89.37	26.57	9.74	3.863	3.176	1.292	3.205	1.797	6.079	2.737
FC03	1.653	3.384	90.03	26.60	9.74	3.860	9.678	8.915	2.211	3.774	6.058	2.732
FC05	1.653	3.314	90.69	27.36	10.02	3.973	1.573	7.582	1.881	5.217	6.065	2.734

II. XRD Measurements

XRD profiles of glasses scanned at the rate of 20/min. for the 2θ values between 10^0 and 80^0 which is shown in Fig.1. The presence of a broad hump between 40^0 and 55^0 without any sharp crystallization peak confirms the amorphous nature of the prepared samples.

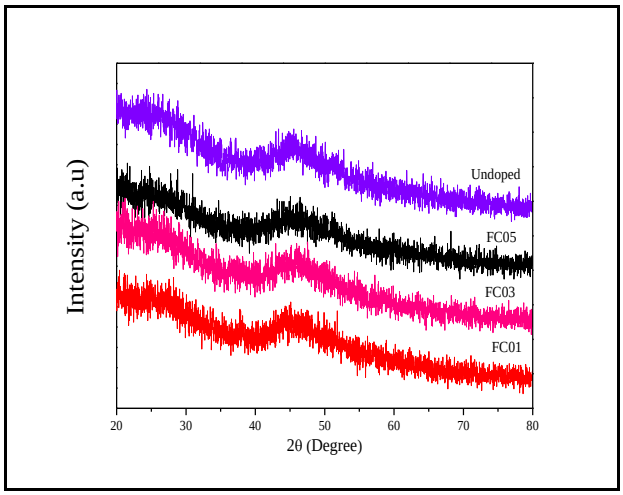


Fig 1. XRD spectra of glasses.

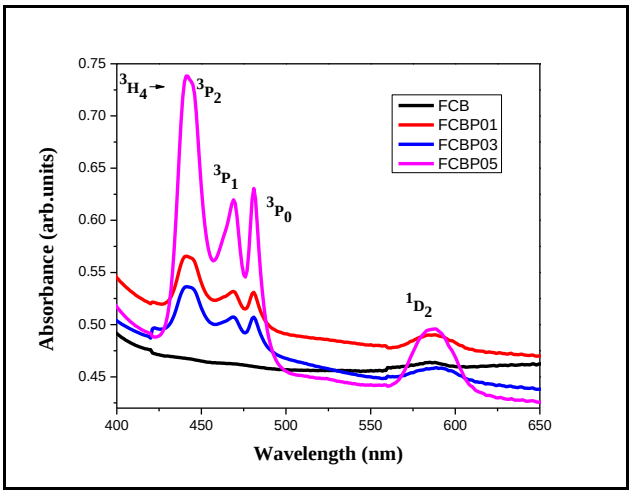
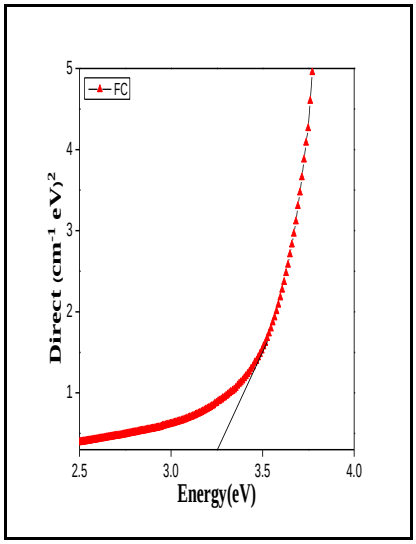
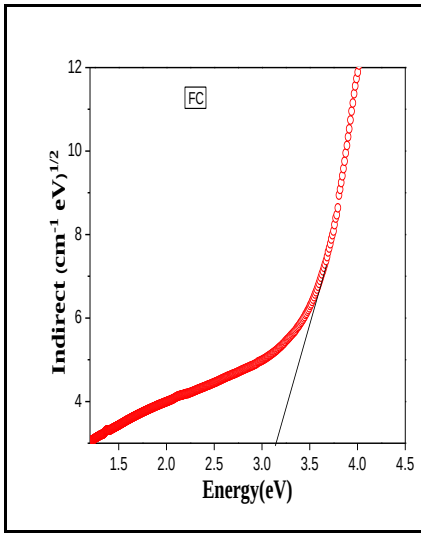


Fig.2. Absorption spectra in visible region of glasses.

III. Absorption spectra:

The spectra in visible region are as shown in Fig.2. For Pr^{3+} doped NPCB glasses. We can clearly observe inhomogeneous prominent 4 peaks due to 4f transitions of Pr^{3+} ions. The 4 peaks at 443nm, 470nm, 482nm and 592nm are due to $^3P_2$,$^3P_1$,$^3P_0$ and $^1D_2$ respectively from $^3H_4$ ground state of Pr^{3+}ions. As the Pr^{3+} ions are increased the intensity of the peak also increasing of FC glasses.





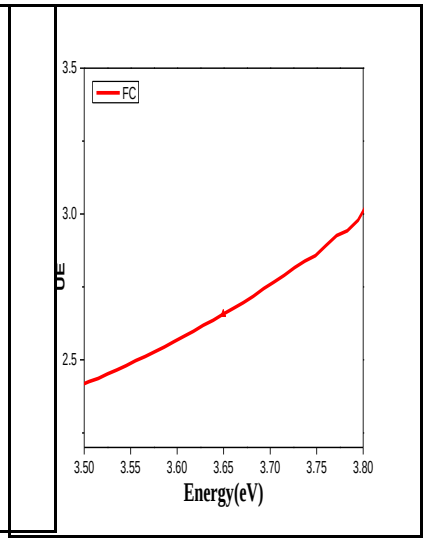


Fig.3.Direct energy band gap **Fig.4. Indirect energy band gap** **Fig.5. Urbach energy**

Table 2: Optical Properties of glasses at different concentration of Pr^{3+}			
Glasses	Direct bandgap energy, E_D(eV))	Indirect bandgap energy, E_{In}(eV)	Urbach energy, E_U(eV)
FC	3.24	3.27	0.44
FC01	3.15	3.19	0.95
FC03	3.10	3.09	1.05
FC05	3.04	3.01	1.33

Direct(E_D) and indirect band gap (E_{In}) shows decreasing in nature as concentration of Pr^{3+} ions is increased in glasses. The E_U is found to be increasing indicates that weak bonds is converted into defects as Pr^{3+} ions concentration is increased. This suggests that the non-bridging oxygen ion content increases with increasing Pr_2O_3 content and there by shifts the band edge to lower energies and in-turn lead to have a decrease in the E_{opt} values. The direct, indirect band gap and urbach energy is calculated as shown in Fig.3,4 and 5 reported in Table.2.

Conclusions

In the present work, Pr^{3+} doped FC glasses optical properties were analysed and few physical properties are also calculated. We can observe the 4 transition peaks of Pr^{3+} ions in glasses in UV-Vis region have increasing intensity of peaks as the concentration is increased. The Tau's plot results the direct and indirect band gap to be decreased as the concentration of Pr^{3+} ions is increased which concludes that the non-bridging oxygen ion content increases with increasing Pr_2O_3 content and there by shifts the band edge to lower energies and in-turn lead to have a decrease in the E_{opt} values. These glasses have increase in Urbach energy therefore weak bonds are converted into defects as Pr^{3+} ions concentration is increased. Few physical parameters like density ,molar volume ,molar polarizbility and RI are also reported.

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