CHARACTERIZATION OF Pr6O11 DOPED ZINC FLUOROBORATE GLASS

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Abstract

Pr^{3+} doped zinc fluoroborate glasses with the chemical composition [(mol %) $30ZnF_2 – 20\ TeO_2 – (50\text{-}x)\ B_2O_3 – xPr_6O_{11}$] (where x = 0.0, 0.1, 0.5, 1.0 and 1.5 mol %) of different concentration of rare earth element praseodymium (Pr^{3+}) have been prepared by conventional melt quench technique. The physical parameters like density, refractive index, number density, molar refraction, molar electronic polarizability, electronic polarizability, dielectric constant, polaron radius, inter–ionic separation, molar volume and oscillator strength of these glasses were calculated as a function of dopant concentration. The densities and refractive indices of these glasses were found to be in the range 2.0 g/cm^3 - 2.67 g/cm^3 and 1.644 – 1.73 respectively. Stability of the glass doped with 1.0 mol % Pr^{3+} was found to be 120.

Keywords: Praseodymium doped glasses, oscillator strength, optical energy gap, absorption spectrum, electronic polarizability

Introduction

Glass doped with various rare earth ions are attracting attention since they are seen as promising materials for high power lasers. The properties of doped glasses depend on the concentration of the dopant ions as well as the chemical environment of the host material. Glasses with different host material doped with ions in different proportion are therefore being developed and their suitability as laser material is tested by measurement of their optical properties. Incorporated in glassy matrices, the rare earth

element praseodymium (Pr^{3+}) shows efficient luminescence only when it is in its triply ionized state. The observed electric dipole transitions of Pr^{3+} involve primarily the excited states ^3P_j (j=0,1,2) and $^1D_2$ and the ground state $^3H_4$ or the other low lying states of the $4f^2$ configuration. Compared to the intraconfigurational ($4f^n$) optical transitions of the other rare earth ions, the electric dipole transition $^3P_1$ $^3H_4$ of Pr^{3+} exhibits a shorter decay time. In many technical applications scintillators with fast luminescence decay are required, and Pr^{3+} is used as a dopant in the X– ray conversion detectors used for modern X- ray computer tomography experiments. Transitions from the $^3P_{0,\ 1,\ 2}$ levels of Pr^{3+} are also used in phosphors. The other prominent transition of Pr^{3+} is $^1D_2$. $^3H_4$ which has a much longer decay time and lasing has been observed for this transition. The optical properties of Pr^{3+} in various glass hosts are, however, still not as thoroughly investigated, as for the other rare earth ions due to difficulties in the preparation of these glasses. In the present paper, we report physical as well as optical properties of Pr^{3+} doped zinc fluoride glass (Mahato,1999).

Material and Methods

The chemical composition used to develop Pr^{3+} doped zinc fluoride glasses is

$$30\ ZnF_2 – 20\ TeO_2 – (50 – x)\ B_2O_3 – x\ Pr_6O_{11}$$

Where x = 0, 0.1, 0.5, 1.0 and 1.5 mol % of Pr_6O_{11}. All the ingredients with a reported purity of 99.99% were used, imported from Sigma Aldrich. A mixture of these compounds was powdered in a ceramic mortar and was made a homogeneous mixture. This mixture was taken in a ceramic boat and heated in Muffle furnace up to 1000 ˚C for 2 hours. Then the melt was poured onto a metal plate and pressed with another metal plate which resulted into a transparent glass (Mahato,1999).

Results and Discussion

Physical Properties

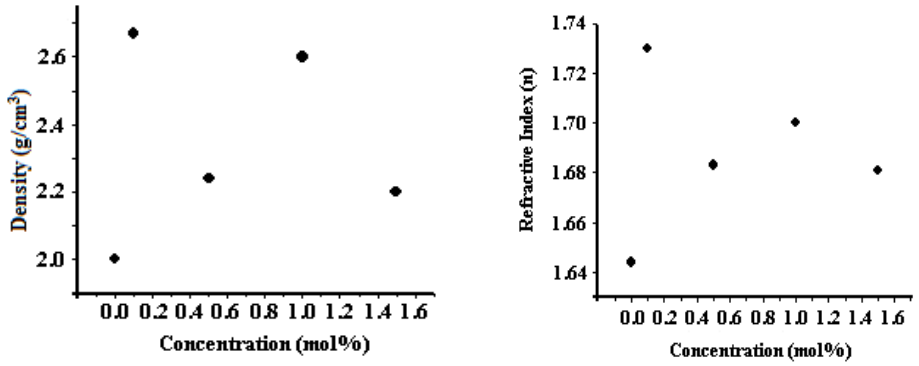

Fig.1: The variation of (a) density (b) refractive index of the glass samples with a change in the Pr_6O_{11} concentration.

Density is an effective tool to explore the degree of structural compactness modification of the geometrical configurations of the glass network. The density, ρ, of the glass samples were measured at room temperature (300 K) according to Archimedes Method using distilled water as the immersion liquid using Sartorius BSA series electronic analytical and precision balance. The density of distilled water at the experimental temperature was taken to be 0.999 g/cm^3. The density of glass was calculated according to the formula:

$$\rho = [W_A / (W_A – W_B)] * 0.999$$

Where W_A is the weight of the sample in air and W_B is the weight of the sample in distilled water (Eraiah, 2006). Plot of density versus different concentration of Pr^{3+} doped in glass matrix is shown in Fig.1 (a).

Refractive index is one of the most important properties in optical glasses. Therefore, a large number of researchers have carried out investigations to ascertain the relation between refractive index and glass composition. Refractive Index, n, of each sample was measured using the portable jewel Refractometer at single line sodium wavelength of 589.3 nm and sensitivity of 0.01. Plot of refractive index versus different concentration of Pr^{3+} doped in glass matrix is shown in Fig.1 (b).

The number density of rare – earth ions (N) were determined using the formula given in equation. Thus the number density (N) of Pr^{3+} ions can be calculated by

$$N = [(\rho / M_{total}) * M_C * 2 * A_v]$$

where ρ is the glass density, M_C is the molar percent concentration of rare – earth element, M_{total} is the sum of molecular weights in rare- earth borate glass and A_v is Avogadro's number [$A_v = 6.022 * 10^{23}$] (Hai Lin,2005).

The molar refraction, (R_m) of the glass samples were calculated using the formula which is well known as Volf and Lorentz - Lorenz formula,

$$R_m = \{[(n^2 – 1)/ (n^2 + 2)] * [M/ \rho]$$

Where n is the refractive index of the glass sample, ρ is the density and M is the molecular weight of the glass samples. M / ρ is called the molar volume, (V_m)

The molar refraction is related to the structure of the glass and it is proportion to the molar electronic polarizability of the material (α_m) according to the relation, (Kaewwiset, 2009).

$$\alpha_m = [3 / (4* \pi * A_v)] * R_m$$

The reflection loss from the glass surface was computed from the refractive index using Fresnel's formula,

$$R = [(n^2 – 1) / (n^2 + 2)]$$

Where n is the refractive index.

The dielectric constant (ε) was calculated using refractive index of the glass,

$$\varepsilon = n^2$$

Where n is the refractive index.

The electronic polarizability (α_e) was calculated using the formula,

$$\alpha_e = [3 * (n^2 - 1) / [4 * \pi (n^2 + 2)]$$

Where N is the number of praseodymium ions per unit volume and n is the refractive index.

The polaron radius (r_p) was calculated using the formula,

$$r_p = (1/2) *[(\pi / (6 * N))]^{(1/3)}$$

Where N is the number of praseodymium ions per unit volume.

The inter – ionic separation (r_i) was calculated using the formula

$$r_i = [\frac{1}{N}]^{(1/3)}$$

Where N is the number of praseodymium ions per unit volume (Raghavendra, 2011).

Based on the determined density and refractive index, the various physical properties of the glass studied are present in Table 1.

Table 1: The physical property of Pr_6O_{11} doped zinc fluoroborate glass.

Physical Properties	Glass Code				
	P_1	P_2	P_3	P_4	P_5
Concentration of Pr_6O_{11} (mol %)	0	0.1	0.5	1.0	1.5
Molecular Weight (M) (g /mol)	4.88	4.92	5.11	5.35	5.58
Density (ρ) (g/cm^3)	2.0	2.67	2.24	2.6	2.2
Refractive Index (n)	1.644	1.73	1.683	1.7	1.681
Number Density (N) $*10^{22}/cm^3$)	0	6.536	5.279	0.585	0.712
Molar Refraction (R_m) (cm^3 /mol)	0.883	0.735	0.865	0.795	0.959
Molar Electronic Polariability (α_m) ($*10^{24}$/ cm^3)	-	2.686	3.911	32.438	32.15

Electronic Polrizability (α_e) ($*10^{24}$ ions / cm^3)	-	2.452	2.588	15.764	12.68
Dielectric Constant (ε)	2.702	2.992	2.832	2.89	2.825
Reflection Loss	0.362	0.399	0.379	0.386	0.378
Inter-Ionic Distance (r_i) (A^o)	-	0.0248	0.0266	0.0119	0.0111
Polaron Radius (r_p) (A^o)	-	0.01	0.01	0.4817	0.4512

The corresponding molar volume (V_m) was calculated using the relation,

$$V_m = M_T / \rho,$$

Where MT is the total molecular weight of the multi-component glass system by

$$M_T = x_{TeO2}\, Z_{TeO2} + x_{B2O3}\, Z_{B2O3} + x_{Pr6O11}\, Z_{Pr6O11}$$

Where, x_{TeO2} ,x_{B2O3} and x_{Pr6O11} = the mole fractions of the constituents oxides.

Z_{TeO2} , Z_{B2O3} and Z_{Pr6O11} = the molecular weights of the constituents oxides.

Using this formula molar volume for glass doped with 1.0 mol % concentration was calculated. Table 2 determines molar volume with different Pr_6O_{11} concentration (% mol).

Table 2: Variation of molar volume with different concentration.

Concentration (mol %)	Molar Volume (cm^3, mol^{-3})
0.0	33.365
0.1	25.348
0.5	31.91
1.0	29.323
1.5	36.818

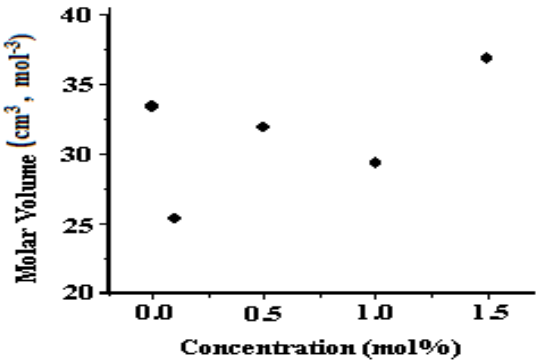

Fig. 2 illustrates molar volume as the function of Pr_6O_{11} concentration (% mol).

The behaviour of molar volume mainly depends upon the density of glasses (Eraiah, 2006). Fig. 2: Molar volume of [30 ZnF_2 – 20 TeO_2 – (50 – x) B_2O_3 – x Pr_6O_{11}] glass system.

Optical Properties

Absorption Spectrum

Optical absorption in solids occurs by various mechanisms, in all of which the photon energy will be absorbed by either the lattice or by electrons where the transferred energy is covered. The lattice (or phonon) absorption will give information about atomic vibrations involved and this absorption of radiation normally occurs in the UV-Visible region of the spectrum. Optical absorption is a useful method for investigating optically induced transitions and for getting information about the band structure and energy gap of non-crystalline materials. The principle of this technique is that a photon with energy greater than the band gap energy will be absorbed. To study the optical properties like optical energy gap, oscillator strengths of different transitions possible in praseodymium doped glasses, we recorded absorption spectra of these glasses using an Ocean Optics CHEMUSB4-UV-VIS single beam spectrophotometer shown in Fig.3. The CHEMUSB4-UV-VIS consists of a USB4000 Spectrometer with a combination of deuterium tungsten halogen light source and 1 cm cuvette holder with high-speed electronics. The spectrophotometer covers 210 to 880 nm range, has optical resolution of 1.0 nm (FWHM) and captures 3648 wavelengths in less than 1 second. It sees changes as small as 0.01 Absorbance Units. The light source (far right) sends light via an input fiber into a cuvette in a cuvette holder (bottom center). The light interacts with the sample. The output fiber carries light from the sample to the spectrometer (top center) connected to the computer (far left).

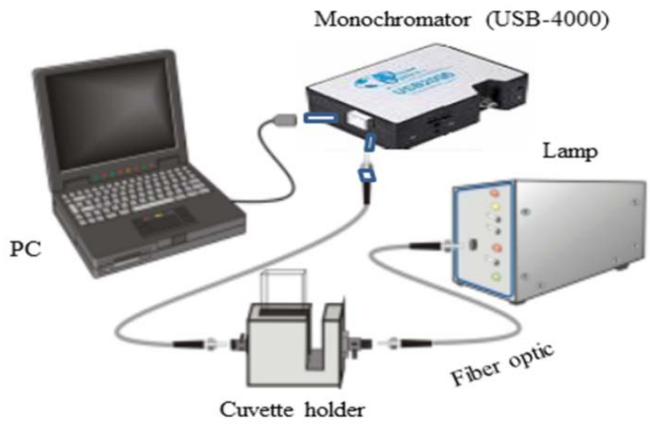

Fig.3: Ocean Optics CHEMUSB4-UV-VIS single beam spectrophotometer used for recording absorbance spectra of Pr_6O_{11} doped zinc fluoroborate glasses.

The absorption spectrums of the glasses were recorded in a Ocean Optics USB4000-UV-VIS single beam spectrometer in both the UV and visible spectral region ranging from 200 nm to 700 nm. The spectra's were obtained using software called Spectra Suite. Absorption spectra of zinc fluoroborate glasses recorded at temperature 300 K with 1.0 mol % Pr_6O_{11} concentration are shown in Fig.4. The high phonon energy in borate glass is not detrimental to Sm^{3+} and Pr^{3+} normal 4f transition emissions, and sometimes it can accelerate the relaxation processes, which is necessary and beneficial for visible emissions. The absorption spectrum in visible region of 1.0 mol% of Pr_6O_{11} doped borate glass demonstrates the suitability of borate glasses as a suitable host for Pr^{3+} .

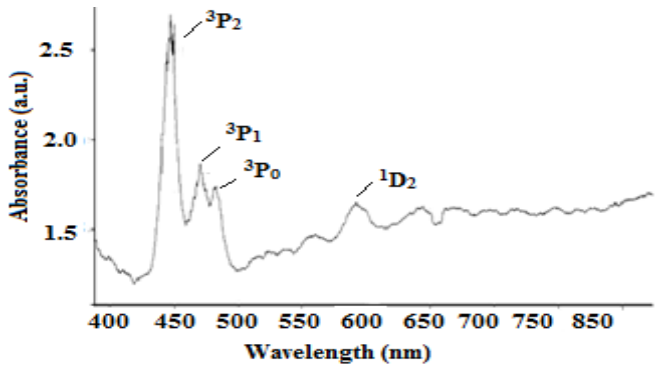

Fig. 4 : Absorption spectrum of zinc fluoride glass doped with 1.0 mol % doped Pr^{3+}.

The observed electric dipole transitions of Pr^{3+} involve primarily the excited states ^3P_j (j=0, 1, 2) and $^1D_2$ (Sharma, 2005).

Oscillator Strength

The assignment of the lines, their frequencies and the spectral oscillator strength (f x $10^{-6)}$ are given in Table 3.The oscillator strength (f) corresponding to the different transitions was obtained by integrating the intensities of the absorption bands. It is given as

$$f = \frac{mc^2}{\pi N e^2}\int \alpha(\gamma^{|})d\gamma^{|} \qquad where\ \ \alpha(\overline{\gamma}) = \frac{\ln\left[\frac{I_0(\bar{\gamma})}{I(\bar{\gamma})}\right]}{t} = 2.303\, E(\overline{\gamma})/t$$

where m is the mass of electron, N is the number of rare earth ions, c is the speed of light, $\bar{\gamma}$ is the wavenumber, $\alpha\,(\overline{\gamma})$ is the absorbance, and t is the sample thickness. The oscillator strength is thus obtained (Hai Lin, 2005).

Table 3: The assignment of the lines, their frequencies and the spectral oscillator strength (f X10^{-6}) are given in table.

Wavelength (nm)	Energy (cm^{-1})	Assignment	Oscillator Strength (*10^{-6})
438	22831.05	$^3P_2$	7.67
464	21551.72	$^3P_1$	3.99
476	21008.40	$^3P_0$	2.31
584	17123.28	$^1D_2$	9.13

The points shown in the Table 3 are specified in Fig.4 and we have found that the peak at wavelength 584 nm have maximum oscillator strength. This means that, the $^1D_2$ transition has higher energy and this can be used to build lasers.

Optical Band Energy Gap:

The experimental value of the absorption coefficient □ (□) is calculated by using the equation,

$$\alpha(\omega) = (2.303 * A) / d$$

Theoretically, the optical band gap energy for indirect allowed optical transitions can be calculated. The quantity ($^{1/2}$ i$) plotted as a function of the photon energy (ħf) for glass sample doped with 1.0 mol % is as shown in the Fig.5. The straight portion of the graph is then extrapolated to intersect with x axis. The value of ħf at the point where ($^{1/2}$ b$) becomes zero yields a direct measure of the optical band gap energy (Altaf,2005). The optical band gap energy was found to be 2.83eV.

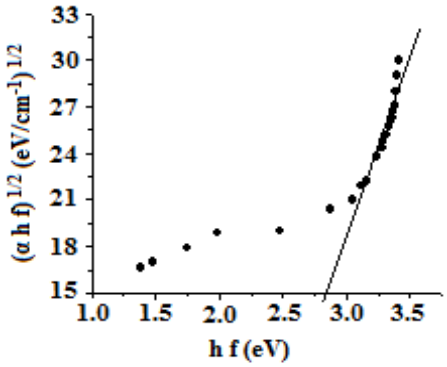

Fig.5: A representative plot of the quantity $(\alpha\hbar f)^{½}$ as a function of the photon energy (ħf).

Glass Stability

The stability of the glass was measured by using Differential Scanning Calorimeter (DSC). Here glass stability was calculated by taking the difference of crystalline temperature (T_c) and glass transition temperature (T_g). Higher the value, higher is the glass stability. The stability of the glass doped with 1.0 mol % was found to be 120 and for undoped glass it is 50.

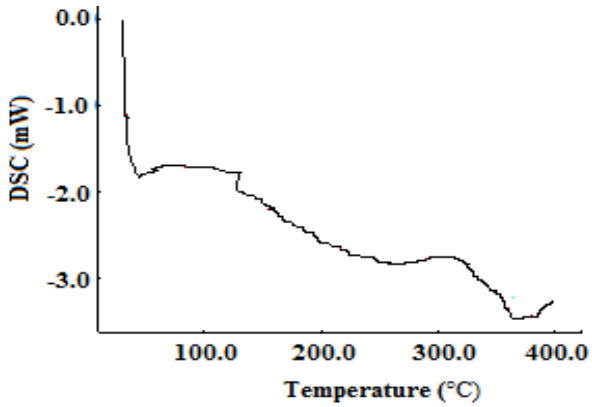

Fig.6: DSC plots of 1.0 mol % Pr^{3+} doped zinc fluoride glass.

Conclusion

In the present study, the glass samples of composition [30 ZnF_2 – 20 TeO_2 – (50 – x) B_2O_3 – x Pr_6O_{11}] (where, x = 0.0, 0.1, 0.5, 1.0 and 1.5 mol %) have been synthesized by normal melt-quench technique. The density and refractive index results show unusual behaviour with no particular trend in either increase or decrease of the outcomes. This might be because of the substitution of B_2O_3 oxides into Te_2O_3 where B_2O_3 plays a dual nature, it acts as network modifier and network former position for different concentrations of the dopant. The electronic polarizability for 1.0 mol% was found to be maximum compared to other glass samples [Table 1]. Stability of the 1.0 mol % doped glass was measured to be 120. The energy band gap of the doped glass mentioned above was found to be 2.83 eV. The absorption spectrum, gave the strength of $^1D_2$ line to be maximum. In the present work, the glasses with more than 30% of zinc have been built which finds its applications in both photonics and optoelectronics fields.

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