Influence of Pr^{3+} ions on Physical, Optical and Structural Properties of Lead borate Glasses and Effect of γ Irradiation

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ABSTRACT

The UV–Visible, Raman, Fourier transform infrared (FTIR) and Photoluminescence spectra of sodium lead calcium borate glasses doped with Pr^{3+}have been investigated. The same spectral measurements were repeated after gamma irradiation. The amorphous nature of the prepared glass samples was confirmed by analysis of the Powder X-Ray diffraction, before and even after gamma irradiation. The impact of pr^{3+} ions on absorption, Emission, Raman and FTIR spectra of the present glasses before and after γ irradiation were compared and discussed in detail. The UV-Visible absorption spectra after gamma irradiation show enhancement in the intensities of adsorption bands. FT infrared absorption spectra of the glasses samples reveal the characteristic vibrational bands arises from the sharing of modes due to triangular borate and tetrahedral borate groups. FTIR spectra have shown only minor effects on gamma irradiation but within the glass network due to the loose bonding, bands due to the water molecules was strongly affected by irradiation. Indicating the presence of Pr^{3+} ions in sodium lead calcium borate glass the Photoluminescence and Raman spectra were in compatibility with the UV–Visible and FTIR data. The CIE 1938 color chromaticity diagram has been used to demonstrate the color of the emission. With varied concentration of pr^{3+} ions the impact on physical properties of the glasses has been examined. Few physical parameters of the glasses like refractive index(n), density (ρ), Molecular weight(M.W), molar volume (V$_m$), polarizabilities (α$_m$), molar refractivity (R$_m$), concentration of rare earth ion (N$_i$), inter ionic distance (r$_i$), polaron radius (r$_p$), reflection loss (R$_L$%), field strength(F) and dielectric constant (ε) were calculated using standard formulae, before and after irradiation. The variable induced defects have been generated on synthesized samples which are clearly due to gamma irradiation. The gamma ray dose induced defects on the present glasses are interpreted and analyzed.

Graphical Abstract
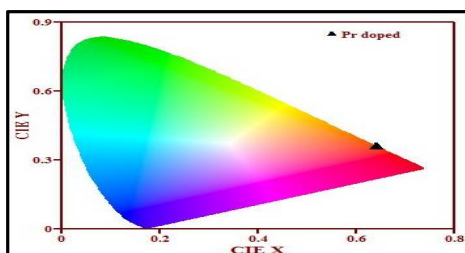
CIE of Pr^{3+} incorporated calcium sodium lead borate glasses after irradiation.

INTRODUCTION

Borate is one of the best and most well-known glass formers which have been extensively studied due to its several attractive features. Borate glasses are ease for preparation and forms high transparency and high stability glasses and inexpensive which the most important thing is. These glass are good host for alkali (such as Li, Na, K etc.) alkaline earth (like Mg, Ca, Sr, Ba etc.) and rare-earth ions (such as Sm, Dy, Ho, Pr, Er, Dy, Eu, L,Tb,Y, etc.) [1]. Moreover boron atom structural unit usually coordinates with three or either four oxygens forming trigonal $[BO_3]$ or tetrahedral $[BO_4]$ structural units. These structural units further arbitrarily can combined to form the different B_xO_y units such as diborate, triborate, tetraborate, pentaborate, metaborate and orthoborateetc [2, 3]. On addition of alkali oxide in borate glasses which leads to the shift in coordination number, there will be progressive conversion of three oxygen coordinated trigonal $[BO_3]$ units to four oxygen- coordinated tetrahedral $[BO_4]$ units. So particularly the structure of borate glasses are of great interest because of the anomalous nature of boron, variety of modification in skeleton and owing to influence of NBO. There are extensive fields of applications of glasses containing B_2O_3 which includes: gamma ray shielding [4], optical glasses [5], textile or continuous filament fiberglass [6], high capacity reversible electrodes [7] and even as bioactive material [8, 9] and inhibiting bacterial growth [10].

The improved resistance to ionizing irradiation has been observed by incorporation of heavy-metal ions having high atomic weight such as lead oxide or high bismuth oxide contents glasses are usually provides shielding from ionizing irradiations for example glass used as windows in hot cells, nuclear reactors and other different radiation environments.

It is well known that lead is one of best γ-rays shielding material and lead containing borate glasses have desirable excellent characteristics against gamma irradiation. Moreover these glasses are good host matrix for transition-metal oxide, rare-earths and due to their many promising applications in optoelectronic devices, photonics, luminescence materials, radiation shielding materials and in the fields of laser technology these glasses are of great importance. [11,12].

Further, calcium containing borate glasses due their potential as bioactive materials have received much attention. Bioactivity can be controlled by altering glass composition hence in bioactive glasses the level of bioactivity is completely composition dependent [13-15].

When the glass former (B_2O_3) are added with suitable modifiers (specifically such as PbO, Na_2O, CaO) and luminescence activators (rare-earths), it was observed that their physical and optical characteristics have been improved so that they can be used in glass laser technology. Praseodymium is the unique visible laser ion which offering blue, green and red laser transitions from same initial level. Pr^{3+} doped fiber amplifiers operating at 1.3 μm which is the zero-dispersion wavelength of optical fibers, have attracted a great deal of attention in research and industrial development [16, 17].

The investigations of radiation defects in glasses have become important since the lasers working particularly at increasingly shorter wave-lengths, stronger lamps have become more popular [18-20]. The effects cause due to interactions with radiation may be known by studying of the intrinsic damages or defects.

When glasses are subjected to high energy ionizing radiations such as gamma ray it acquires radiation-induced defects. The principle effects of irradiation occurs are almost from purely electronic processes and these effects are specifically occurs if the incident energy is greater than the energy band gap, electrons are initially excited from the valence band to conduction band and then the excess energy will be converted into kinetic energy and these electrons will travel through glass network,

they will either become trapped or recombine with positively charged holes [21-23]. The removal or addition of one or more electrons from impurity centers or defects particularly results in formation of the color centers which can absorb light.

The Radiation damage in the glass can be classified into three basic processes, the first one is charge trapping and ionization and second is due to atomic displacement by momentum and charge transfer and third one is photochemical effect or radiolytic [24]. These all the three radiation damage under some condition can be active concurrently.

The glass deviates from ideal network structure and since it contains preexisting defects such as impurities, non-bridging oxygen's, vacancies etc. This structural defect assumed to occur mainly due to free energy which is minimized by admitting certain amount of the disorder into structure. The rare-earth ions and transition metal ions are able to trap positive holes or electrons when irradiated. This multivalent impurity is accepted to compete with intrinsic defects which are already present in the glass to trap the holes and electrons produced by irradiation. Depending on nature and concentration of rare-earth ions or transition metal ion and even on type and state of host glass the capturing or trapping process takes place [25, 26].

The studies have indicated that some transition metal ions show shielding behavior towards gamma irradiation but in this present paper we have investigate rare-earth ions(Pr^{3+}) instead of transition metal ions. Hence the present work explores the role of Pr_2O_3 on Optical, structural and physical properties in Na_2O-PbO-CaO-B_2O_3 glasses and even the effect of gamma irradiation in glass system which has been studied in detail.

The objective of the present work is to study collective spectroscopic measurements such as UV–Visible, Fourier transform infrared (FTIR), Raman and Photoluminescence spectrum have been employed to investigate the effect of Pr^{3+} ions with varied concentrations on calcium sodium lead borate glasses. After gamma irradiation all the spectrums were re-measured and studied in detail to know the structural changes and optical properties of the present glass. It is expected that this study can clarify the radiation induced defects which are generated by gamma irradiation and the effect of Pr^{3+} on the process of defects generation. The study extended to the role of gamma irradiation doses in the variation of the optical energy gap, FTIR and Raman spectra for the prepared glasses.

MATERIALS AND METHODS

Preparation of the Glasses: The glass samples having nominal composition $20Na_2O$-$10PbO$-$10CaO$–$(60-x)B_2O_3$-xPr_2O_3) (where, x=0, 0.1, 0.3, 0.5 mol% of Pr^{3+}) is here after named as C,C01, C03,C05 (after gamma irradiation as C-G,C01-G,C03-G,C05-G) were prepared by melt quenching technique. The mixture of analytical grade of sodium carbonate(Na_2CO_3), lead oxide(PbO), calcium carbonate ($CaCO_3$), boric acid (H_3BO_3) and praseodymium trioxide (Pr_2O_3) (99.99%) weighed by using an electronic balance having an accuracy of 0.001 g. The chemicals were then mixed homogeneously in agate and motor for 30 min. This composition is taken in an open porcelain crucible and kept in high temperature furnace. Initially the glass batches were maintained at about 450–500°C for 30 min for the decarburization of Na_2CO_3 and the decomposition H_3BO_3, and then the temperature was raised and maintained at 1000-1080°C for 30 min. The crucibles were stirred frequently many times for a homogeneous mixing of all the constituents. After the complete melting, the melts were quickly poured on a preheated brass moulds to get pellet form samples which were polished and powdered for further characterization. The glasses so obtained are transparent and non-hydroscopic. The Pr^{3+} doped glasses are light green in color which is mainly due to the uniform distribution of the dopant rare earth ions in the glasses.

Characterizations

X-ray diffraction: XRD measurements (Rigaku Ultima IV) using the Cu-Ka radiations (λ=1.54 Å) with copper filters operating at 40 kV and 100 mA by using this glassy nature of samples was confirmed. The 2θ range was 0°–80° with step size of 0.20 and a resolution of 0.01°.

UV–VIS optical spectroscopy: The optical absorption spectra for polished samples have been recorded using Pekin Elmer lambda-35 UV-Vis spectrometer in the wavelength range 400nm -800nm at room temperature.

Fourier transform infrared (FTIR): FTIR measurements in the range of 400-4000 cm^{-1} were carried out by a Thermo Nicolet, Avatar 370 spectrometer with resolution of 4 cm^{-1} using KBr pellet technique.

Raman spectroscopy: At room temperature using an integrated FRA 106 Raman module, the Raman spectra have been recorded.

Photoluminescence spectra: The luminescence spectrum has been recorded by Spectroflourometer, Horiba JobinYvon Fluorolog-3, 450W Xenon source with excitation 450 nm.

CIE Diagram: The Commission International deI'Eclairage (CIE) chromacity coordinates are determined for estimation the emission color of the Pr^{3+} incorporated sodium lead calcium borate glasses.

Gamma Irradiation Facility: A ^{60}Co gamma cell (2000 Ci) has been used as the gamma ray source with the dose rate of 1.5 Gy/s (150 rad s^{-1}) at a temperature of 30°C. All the glass was subjected into a dose of 30 KGy for 3h 31min.

RESULTS AND DISCUSSION

Physical Properties: Physical parameters like refractive index(n), density (ρ), Molecular weight (M.W), molar volume (V_m), polarizabilities ($α_m$), molar refractivity (R_m), concentration of rare earth ion (N_i), inter ionic distance (r_i), polaron radius (r_p), reflection loss (R_L%), field strength(F) and dielectric constant (ε) have been calculated to characterize the optical efficiencies of the glasses. The physical parameters of non-irradiated and irradiated glass samples presented in table 1.

Table1. Refractive index(n), Density (ρ) gm cm^{3-1}, Molar volume(V_m)g cm^{3-1}, Molar refractivity(R_m) cm^{-3}, Electronic polarizability (αe) ×$10^{-24}cm^3$, Reflection loss(R_L)%, Dielectric constant(ε), Concentration(N_i)×10^{19} ions/cc, Polaron radius(r_p)nm, Inter ionic distance(r_i)nm, Field strength(F) ×$10^{15}cm^2$

Glasses	Non irradiation				Irradiation			
	C	C01	C03	C05	C-G	C01-G	C03-G	C05-G
Physical Properties								
Refractive index (n)	2.416	2.363	2.62	2.717	2.763	2.744	2.843	2.848
Density (ρ, gcm^{-3})	3.36	3.06	3.404	3.308	3.341	2.86	3.25	3.18
Average Molecular Weight (M, $gmol^{-1}$)	82.498	82.425	82.085	82.744	82.498	82.425	82.085	82.744
Molar Volume (Vm, cm^3mol^{-1})	24.56	26.93	24.41	25.31	24.69	28.82	25.56	26.33
Molar Refractivity (Rm, cm^{-3})	15.155	16.281	16.147	17.220	17.003	19.747	17.958	18.521
Electronic Polarizability (αe, x 10^{-24} cm^3)	6.007	6.453	6.401	6.826	6.749	7.827	7.118	7.341
Reflection loss, R(%)	17.182	16.426	20.026	21.338	21.950	21.698	22.999	23.063
Dielectric constant (ε)	5.837	5.584	6.864	7.383	7.634	7.529	8.082	8.111
Inter-ionic properties								
RE ion concentration, N (x10^{20})ions cm^{-3}	-	0.321	1.063	1.710	-	0.299	1.014	1.643
Polaron radius, r_p (nm)	-	2.773	1.860	1.588	-	2.836	1.889	1.610
Inter-ionic radius, r_i (nm)	-	6.880	4.615	3.939	-	7.037	4.686	3.992
Filed strength, F (x10^{15} cm^{-2})	-	0.399	0.866	1.189	-	0.373	0.841	1.158

The density (ρ) is calculated using (W_a) weight of the glass sample in air, (W_b) weight of the sample when immersed in toluene of density ($\rho_l = 0.8669 \text{gcm}^{-3}$),

$$\rho = \frac{W_a}{W_a - W_b} \times \rho_l \qquad (1)$$

The molar volume (V_m) is calculated using the expression molecular weight of the sample(M) and density of the glass sample(ρ),

$$V_m = \frac{M}{\rho} \qquad (2)$$

The molar refractivity (R_m) can be expressed in terms of refractive index and molar volume V_m,

$$R_m = \frac{n^2 - 1}{n^2 + 2}[V_m] \qquad (3)$$

The polarizabilities (α_m) can be calculated using molar refractivity (R_m) and Avogadro's number(N_A),

$$\alpha_m = \frac{3}{4\pi N_A}(R_m) \qquad (4)$$

The concentration of rare earth can be calculated by (x) weight of rare earth ion (Pr^{3+}), (ρ) density of the glass, (N_A) Avogadro's number, (y) molecular weight of Rare earth ion (Pr^{3+}) and (b) total batch weight.,

$$N_i = \frac{x \, \rho N_A}{y \, b} \qquad (5)$$

Polaron radius was calculated using concentration of Rare earth ion N_i from the expression,

$$r_p = \frac{1}{2}\left[\frac{\pi}{6N_i}\right]^{\frac{1}{3}} \qquad (6)$$

Inter - ionic distance of Pr^{3+} ions was calculated from the equation,

$$r_i = \left[\frac{1}{N_i}\right]^{\frac{1}{3}} \qquad (7)$$

Dielectric constant which is a square of refractive index of the glass (n) calculated from,

$$\varepsilon = n^2 \qquad (8)$$

Reflection loss in the samples was obtained from the expression,

$$R(\%) = \left(\frac{n-1}{n+1}\right)^2 \times 100 \qquad (9)$$

The field strength of Pr^{3+} ions was obtained by,

$$F = \left(\frac{z}{r_p^2}\right) \qquad (10)$$

Where, Z will be charge of rare earth ion.

Using Lorentz-Lorenz formula the refractive indexes have been calculated

$$\frac{n^2-1}{n^2+1} = 1 - \sqrt{\frac{Eg}{20}} \qquad (11)$$

Density is very useful parameter to investigate the degree of structure compactness, changes or modification in the coordination and geometrical configurations and variation of the dimensions of the glass network. As expected that molar volume and density shows opposite behaviour, variation of molar volume and density of present glasses doped with different concentration of Pr_2O_3 is shown in fig 1. How tightly atomic groups and atoms in a glass network placed together is mainly related to molar volume and density. On addition of rare earth ions in the studied glasses there is decrease in the density it can be attributed to the conversion of BO_4tetrahedrals into BO_3 triangles which means that on incorporating Pr_2O_3 in borate glasses leads to formation of nonbridgingoxygens (NBO) which opens up the glass network and also causes increase in molar volume [**27, 28**].
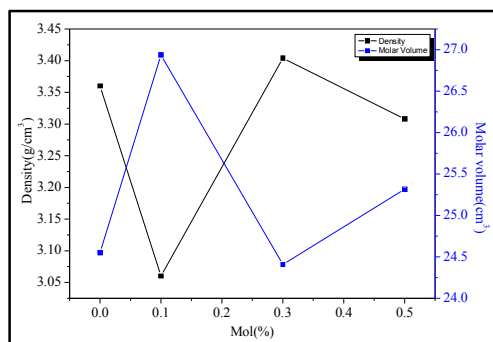
Figure 1. Density v/s molar volume variation of glasses.

As the effect gamma irradiation slight changes are produced in the molar volume and density on rare earth doped glasses which may be due to the number of NBOs stability in glass. It is expected that radiation compaction may cause many effects which includes displacements, electronic defects and permitting the structure for recreation or to relax and in oxygen and boron atoms interconnected network, filling the large interstices. This type behaviour is retarded mainly due to the presence of heavy metal ions such as PbO in the present studied glasses hence these glass are capable to shield the effect of gamma irradiation [**29, 30**]

The refractive index of the present glass matrix is higher which are suitable for optical fibre glass. The observed results of glasses express that as the concentration increased the inter-ionic distance decreases which results in increase in field strength of the Pr^{3+} ion in host matrix. This variation in inter-ionic, polar on radius and field strength is clearly represented in fig. 2. The increment in molar refractivity from 15.155 cm^{-3} to 17.220 cm^{-3} is proportional to the polarizability of the glass samples.
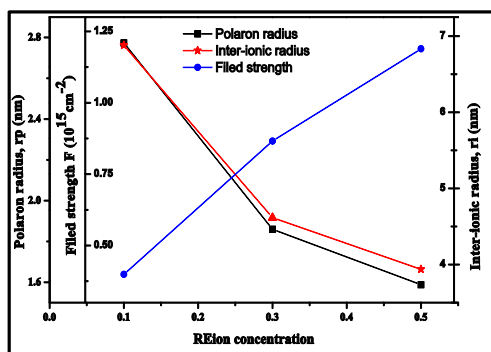

Figure 2. Polar on radius, Inter ionic distance v/s Field strength of glasses.

There is no noticeable change in the Physical parameters of irradiated glass samples since there is only slight change in density and refractive index of glasses because remaining parameters mainly depends on these two parameters.

XRD measurements: XRD profiles of C-G are gamma Irradiated and C is Non-Irradiated glasses shown in the fig.3. Without any sharp crystallization peak and presence of a broad hump confirms the glassy nature of samples. The amorphous structure did not change by the effect of irradiation process. The XRD features of all samples are nearly the same.
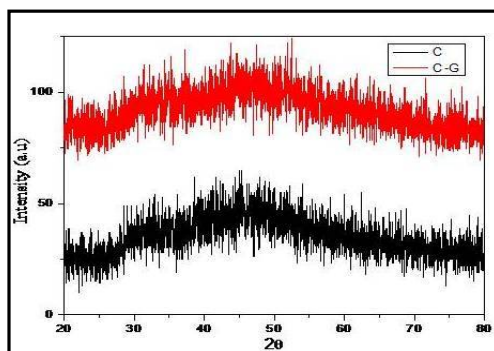
Figure 3. XRD patterns of gamma Irradiated and Non-Irradiated base glass samples.

Fourier Transform Infrared Spectroscopy (FTIR): Infrared spectroscopy is a powerful and very sensitive probe of the glass structure. Since it can be used to identify even very low concentration impurities such as hydroxyl ions and water in glass [31]. Moreover, the FTIR spectra can also be used to identify the defect groups' presence in glass or the radiation-induced defects [32] within the glass. Fourier transform infrared (FTIR) transmission spectral curves were measurements in the range of 400-4000 cm^{-1} for the glass samples before and after irradiation are illustrated in fig. 4 and fig. 5 respectively. FTIR spectra of present C, C01, C03, C05 glasses from shows 5 prominent bands at ~600-770cm^{-1}, ~770-1180cm^{-1}, ~1180-1600cm^{-1}, ~2300cm^{-1} ~2730cm^{-1} and ~3465cm^{-1}. A weak band ~480cm^{-1} is also observed, the band at < 600cm^{-1} can be assigned to cage vibrations of metal ions such as Pb^{2+}.
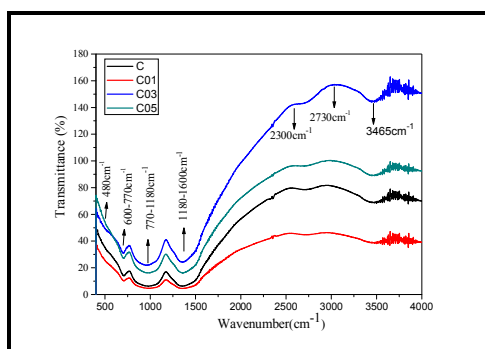

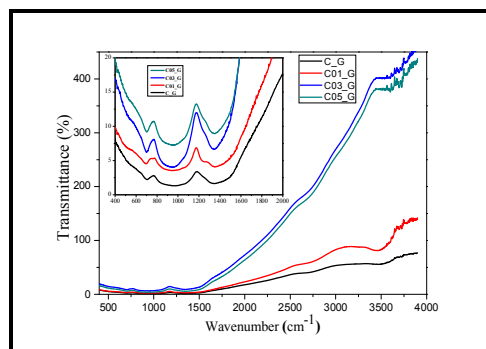**Figure 4.** FTIR spectra of Pr3+ incorporated glasses.   **Figure 5**. FTIR spectra of Pr3+ incorporated glasses after irradiation.

The bonding of B-O-B linkages (diborate linkage) can be assigned at ~600-770cm^{-1} [**33-36**]. Incorporation of lead oxide in borate glasses can result in creation of three and four coordinated boron's which attributes to a Pb-O-B bending, resulting in [PbO$_{4/2}$]$^{2-}$ or pyramidal units of metal ions overlaps with [BO$_3$] triangles [37]. The broad band ~770-1180 cm^{-1} can be assigned to B-O bond

stretching of tetrahedral BO_4 units from tri-,tetra- and penta-borate groups due to stretching vibration of B-O-M linkage(M represents metal ion), It may be due to vibrations of some boron atoms attached to the non bridging oxygen in form of BO_4 vibrations [38-39]. Also we can expect stretching vibrations of the B-O bonds in BO_3 units from meta- and ortho- borate groups. The B-O stretching vibrations of $(BO_3)^{3-}$ unit in meta borate and ortho- borate chains due to some B-O stretching of BO_3 unit we may expect the shift in band due to asymmetric stretching vibrations of B-O bonds in BO_3 units [40]. The bands at~2300 cm^{-1}, ~2730 cm^{-1} and ~3465 cm^{-1} can be assigned to Hydrogen bonding, molecular water and –OH bonding respectively [41]. Absence of the absorption peak at ~ 806 cm^{-1} indicates that absence of boroxol ring which means that glass structure consists of BO_3 and BO_4 groups [42-45]. In the all the present glasses, borate network are showing typical type of characteristic modes of vibrations that are observed and reported in borate based glasses [46-49].

Effect of gamma irradiation on FTIR spectra: The changes in bond length and/or bond angles generally generated as the effect of gamma irradiation induced defects within the structural building units. For the present Pr^{3+} doped sodium lead calcium borate glass samples, experimental IR data reveal almost the same FTIR spectral bands as previously observed in the non-irradiated samples. So it is obvious that gamma irradiation has not causes major changes in the IR spectra especially concerning the position or number of the vibrational bands. But the gamma irradiation samples have higher intensity than the non-irradiated ones and causes only very minor changes or shifting the peak position. Further near-IR broad band centered at 3465 cm^{-1} is highly increased with increased Pr^{3+} content in the glass sample.

The main observed change in the IR band can be interpreted as loose bonding of OH groups or water within the glass network [50, 51] and the vibrations due to water, OH related groups, gamma irradiation is effective while the vibrations due to bending boron groups remain prominent. These types of similar results are previous reported in the literatures by several authors assuming that it is the stability of the glass network which makes vibrational bands unaffected by the radiation. This is an evident that synthesized samples have by some shielding behavior [52-57].

Raman Spectroscopy: The Raman spectrum of the investigated glass was recorded in the region of 200– 2000 cm^{-1}. The structure proposed by FT-IR results confirms by Raman bands assignments form the obtained data. The Raman spectrum of the base glasses before and after irradiation is shown in fig. 6. The bands in the low-wavenumber region below 400 cm^{-1} occur due to the vibrations of PbO. Since in the region 400-1600 cm^{-1} all the observed bands are mainly occur due to borate structure i.e. associated to the vibrations of complex borate units [58]. The weak bands also presented at 1061 cm^{-1}, 1094 cm^{-1}, 1194 cm^{-1} assigned to the normal vibrations tri-, tetra- and penta-borate groups which are due to the B-O stretching vibrations of the BO_4 tetrahedral units; presence of diborate groups [59].
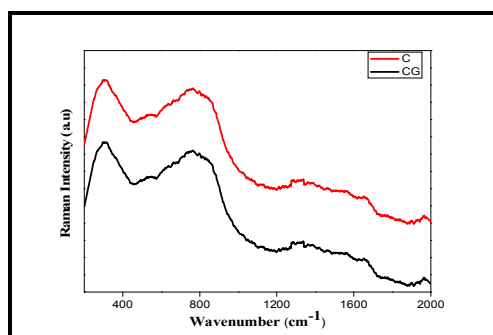

Figure 6. Raman spectra of C and C-G glasses.

The band observed at 1202-1257 cm^{-1} is associated with the Stretching vibrations B-O− bonds of pyroborate this is mainly due to the vibrations $BO_2O−$ triangles linked with BO units. The bands

observed at 1358–1453 cm^{-1} are attributed to the B-O− stretching vibrations involving NBO's in various borate groups, stretching vibrations of B-O− bonds and stretching vibrations of O_3B-O-BO_4 bonds in BO_3 pyramidal units, B-O− stretching in metaborate rings and chains and stretching vibrations of B-O-B bonds in pyramidal BO_3 units.

There is no much significant changes in structural groupings in the present glasses each series which remained almost the same as those obtained for sodium lead calcium borate glasses doped with Pr^{3+} and even after gamma irradiated.

Absorption Spectra: Spectra in visible region for Pr^{3+} doped glasses as shown in fig. 7. We can clearly observe inhomogeneous prominent 4 peaks due to 4f transitions of Pr^{3+} ions. The 4 peaks at 443 nm, 470 nm, 482 nm and 592 nm 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 in the glasses [60]. These bands correspond to the $4f^2$-intra-configurational electric dipole(ED) transitions from the ground state $^3H_4$ to the excited states $^3P_{J(J=2,1,0)}$ and $^1D_2$ [61] and the combination of unresolved Stark splitting and in homogeneous broadening leads to band widths.

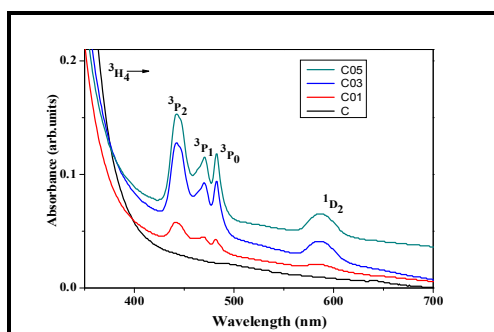**Figure 7.** Absorption spectra of Praseodymium incorporated glasses.

The optical absorption coefficient α (λ) of the samples was calculated by using the following equation [62]

$$\alpha(\lambda) = 2.303\,(A/d) \qquad (12)$$

Where, A is absorbance and d is thickness of sample respectively. The optical band gap Eopt, defines the direct and indirect energy difference between valence band and conduction band of glasses is obtained from the equation [63].

$$\alpha h\upsilon = B(h\upsilon - E_{opt})^n \qquad (13)$$

Where, hν is the incident photon energy, α is the absorption coefficient, , 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 [64] given by,

$$\alpha(\upsilon) = \alpha_0 \exp(h\upsilon/E_U) \qquad (14)$$

Where, a_0 is a constant, hν is photon energy and E_U is known as the Urbach energy, which is interpreted as width of the localized state in normally forbidden band gap.

Using equation (13) indirect, direct band gap and from the equation (14) urbach energy is calculated as shown in figures.8 (a), (b) and (c) respectively. Direct(E_D) and indirect band gap (E_{In}) shows decreasing in nature as concentration of Pr^{3+} ions is increased in C,C01,C03,C05 glasses. This

is clearly indicates that the NBO ion content increases with the increasing Pr_2O_3 concentration which lead to a decrease in the E_{opt} values there by shifts the band edge to lower energie. The urbach energy E_U is found using Good Square linear fit Urbach energy is increase with Pr^{3+} concentration therefore weak bonds are converted into defects. Values of E_D, E_{In} and E_U are estimated and tabulated in the table 2.
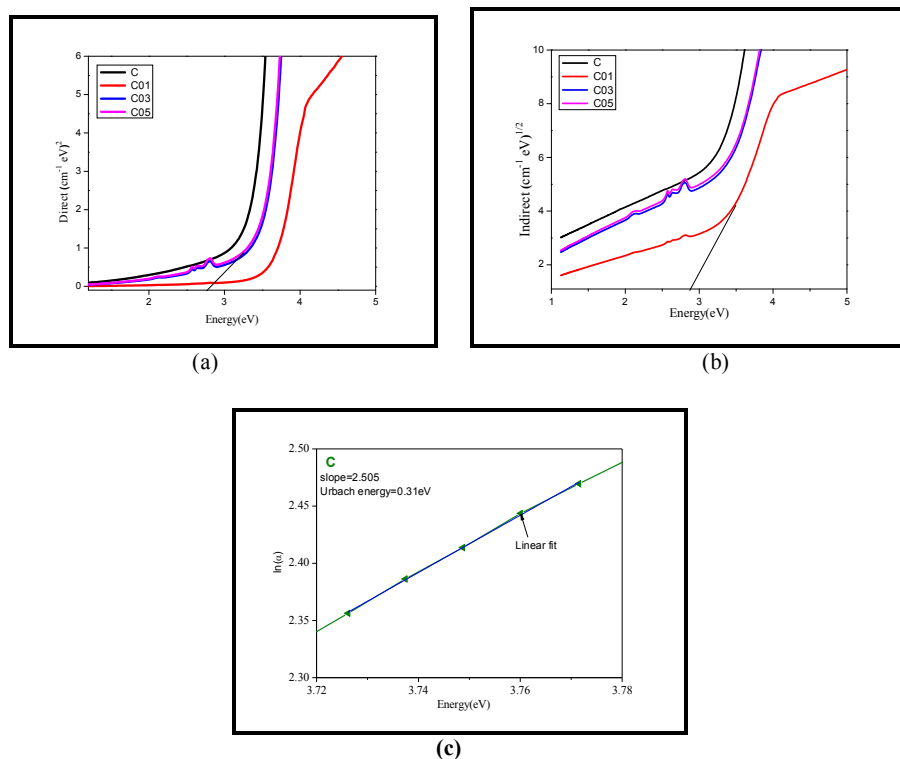

(a)   (b)

(c)

Figure 8. (a) Direct energy band gap, (b) Indirect energy band gap, (c) Urbach energy.

Table 2. Direct(E_D), Indirect(E_{In}) band gap and Urbach energy(E_U) for all glasses.

Glasses	Direct band gap (eV)		Indirect band gap (eV)		Urbach energy	
	Irradiated	Non-Irradiated	Irradiated	Non-Irradiated	Irradiated	Non-Irradiated
C, C-G	1.94	2.93	0.95	2.9	0.97	0.31
C01,C01-G	1.98	3.13	0.99	2.16	0.98	0.9
C03,C03-G	1.77	2.29	0.35	1.63	2.4	1.35
C05,C05-G	1.76	2.04	0.23	1.34	2.08	1.66

Gamma irradiation effect on Absorption spectra: Generally radiation causes displacement of the lattice atoms or electron defects which involve changes in impurity atoms or valence state of lattice. Due to ionizing radiation the electron-hole pairs are produces in the glass structure this develops a new optical absorption bands**.** These changes in absorptions are associated with either excess oxygen or oxygen deficiency in glass network [65].

The colors of Pr^{3+} ions doped glasses before gamma irradiation were light green in color and after irradiation all glasses exhibited deep brownish colors. The change in color from clear to brown accompanied optical changes in the visible range [66]. Glass has random nature because this the radiation-induced absorption are generally consists of overlapping absorption bands rather than the discrete bands which are formed in ionic crystals. This is radiation-induced activation of color centers (color change) due to non-crystalline structure of glasses [67].

Upon subjecting glasses to the gamma irradiation a new spectrum is observed as shown in fig. 9. It should be noted that no significant peak can be observed and with the higher intensity than the non-irradiated sample. The increases in intensity of induced visible absorption are attributed to photochemical reactions. This increase in intensity can be related to the presence of impurities and lattice defects in the glass before irradiation.
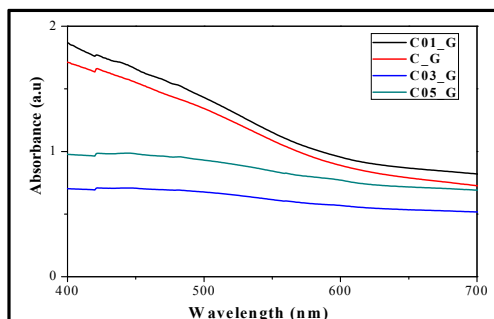

Figure 9. Absorption spectra of gamma irradiated.

After gamma irradiation both the optical band gap data reveal prominent changes to lower values than the non-irradiated samples which is an expected result due to the formation of induced defect centers between conduction and valence bands. So the optical photons may induce transitions between the valence band and defect levels or from defect levels to excited states or the conduction band [**68, 69**]. E_D, E_{In} and E_U is calculated as shown in figures.10 (a), (b) and (c) As concentration of Pr^{3+} ions is increased in host matrix of irradiated and non-irradiated glasses in both the samples, direct(E_D) and indirect band gap (E_{In}) shows decreasing in nature and the Urbach energy (E_U) increases. Values of E_D, E_{In} and E_U of present glasses are estimated and tabulated in table 2.
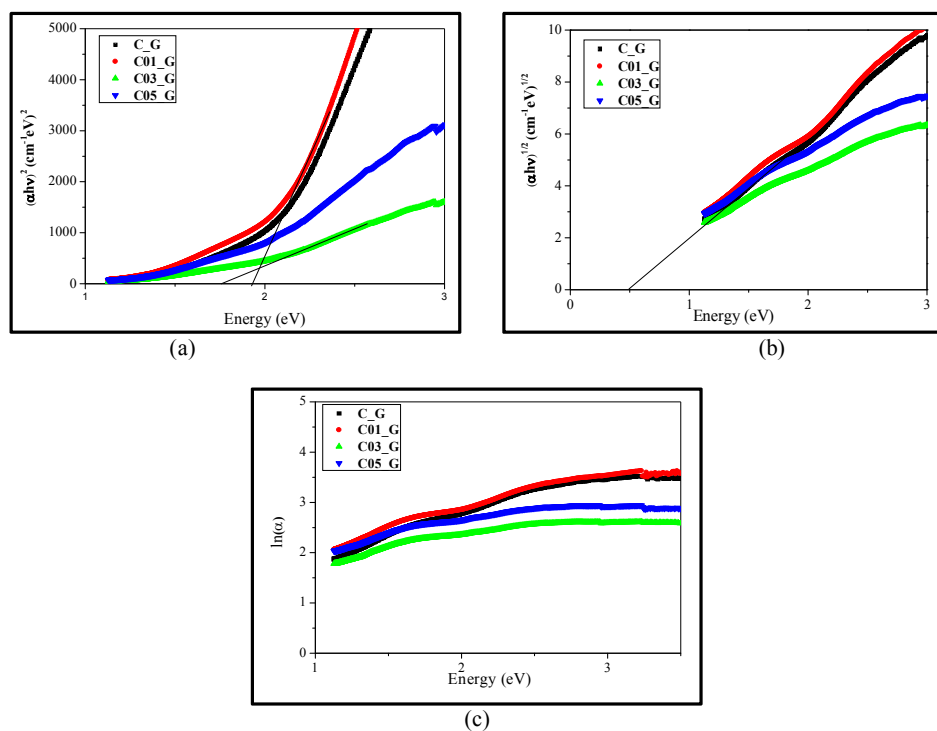

Figure 10. (a) Direct energy band gap, (b) Indirect energy band gap, (c) Urbach energy of irradiated C-G series.

Emission spectra: The luminescence spectra of Pr^{3+} incorporated sodium lead calcium borate non irradiated glasses is recorded by monitoring an excitation at 402 nm and are shown in fig. 11. The luminescence spectra of the present glasses are recorded in the wavelength range 450-750nm wavelength. For the excitation of 450nm, the emission bands corresponding to $^3P_0{\rightarrow}^3H_4$ and $^3P_0{\rightarrow}^3F_4$, we have observed two prominent band transitions at 494 nm and 739 nm. Transition band at 603nm and 612 nm is almost merged and overlapped refers to $^3P_0{\rightarrow}^3H_6$ and $^3P_0{\rightarrow}^3F_2$. Also very weak bands are seen at 526 nm and 557 nm for the transition $^3P_1{\rightarrow}^3H_5$ and $^3P_0{\rightarrow}^3H_5$ respectively [70-74]. With 0.5 mol% Pr^{3+} doped glasses is more intense camped to other glasses.For the excitation of 450nm the non-irradiated glasses are exhibiting lasing emission at 494 nm and 611 nm which proves us that present glasses can be used for multi lasing material. Using the proper optimization method we can make use of these two lasers for photonic applications.
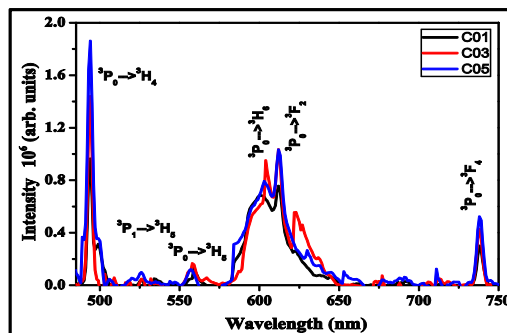

Figure 11. Emission spectra of Pr^{3+} incorporated calcium sodium lead borate glasses.

The excitation spectra of the investigated 0.5% Pr-doped glass sample C05-G after successive gamma irradiation is shown in fig.12. It is obvious that after exposed to gamma irradiation, the excited spectra show decrease in intensity and appearance peak only at about 611 nm. Moreover, PL measurements showed this result only for high content of pr3+ ions i.e for 0.5%. For low concentration of Pr^{3+} doesn't show any prominent band transitions. Hence present glass is selected for the laser amplification with transition $^3P_0{\rightarrow}^3H_6$.The glass matrices are good laser active media that has been indicate by the high values of emission cross-sections.
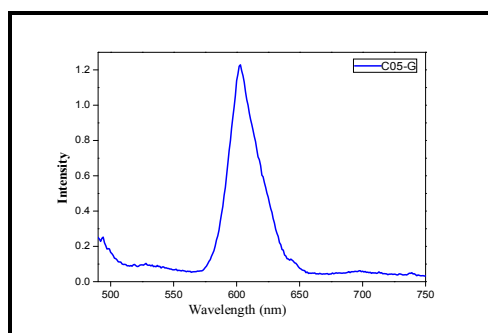

Figure 12. Emission spectra gamma irradiated of Pr^{3+} incorporated calcium sodium lead borate glasses.

Chromaticity diagram and coordinates: Pr^{3+} incorporated sodium lead calcium borate glasses were excited with 450 nm expecting the transitions of primary colors. Those emissions were analyzed in CIE-1938 chromaticity diagram [75]. Interesting think is for the samples depending upon the excitation the emission can tuned to obtain required LED applications. Upon the excitation of 450 nm blue, red emission is obtained as shown in the fig.13. Variation in coordinates upon 450 nm excitation

is observed for varied concentration of Pr^{3+} ions are, they obtained coordinate values (x, y) from CIE diagram are tabulated in table 2.
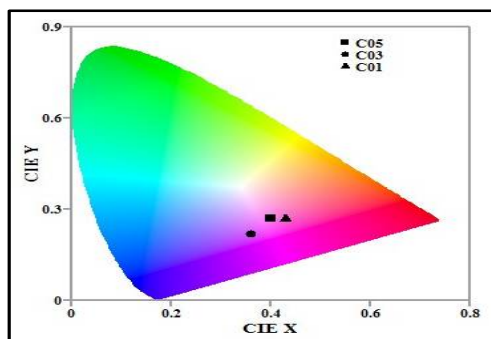

Figure 13. CIE of Pr^{3+} incorporated calcium sodium lead borate glasses for 450 nm.

The irradiation 0.5% Pr^{3+} incorporated sodium lead calcium borate glass samplewere also excited with 450 nm wavelength emit red emission is obtained as shown in the fig.14. Variation in coordinates upon 450 nm excitation is observed for 0.5% concentration of Pr^{3+} ions are, they obtained coordinate values (x, y) from CIE diagram are tabulated in table 3.
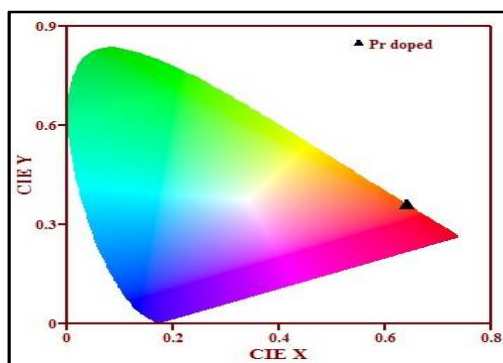

Figure 14. CIE of Pr^{3+} incorporated calcium sodium lead borate glasses after irradiation.

Table 3. The table summarizes color co-ordinates calculated.

Sample code	Color co-ordinates(x, y) upon 450nm excited	
	Non irradiation	Irradiation
0.1% Pr^{3+}	(0.43,0.27)	-
0.3% Pr^{3+}	(0.36,0.22)	-
0.5% Pr^{3+}	(0.40,0.27)	(0.64,0.36)

APPLICATION

The present study of glass has shielding properties and can be utilized as radiation shielding materials.

CONCLUSIONS

In the present work, the physical, structural and optical properties of sodium lead calcium borate glasses doped with different concentration Pr^{3+} have been studied in detail and to know the effect of

gamma irradiation on prepared samples all the above said properties were reinvestigated. The amorphous nature of the samples is confirmed by X-ray diffraction technique, before and even after gamma irradiation. To study the optical behavior absorption and photoluminescence is carried out. Due to the presence of Pr^{3+}ions, $^3P_2$, $^3P_1$, $^3P_0$ and $^1D_2$ transition band is observed from $^3H_4$ ground state in glasses. For the excitation of 450 nm of C01-C05 glasses are exhibiting lasing emission at 494 nm, 611 nm and for irradiated C05-G glass are exhibiting lasing emission at 603 nm. These emissions were analyzed in CIE-1938 chromaticity diagram. Above results evidence us to prove, present glasses can be used for multi lasing material.

The fundamental stretching vibrations in the synthesized glasses were investigated using Raman and FTIR spectroscopy. Results indicate that the appearances of characteristic vibrational bands are mainly due to Boron groups. FTIR data revels that gamma irradiation has causes minor effects on the spectra and because of loose bonding of water molecules within the glass network, strongly affected. So it can be recommended that the present glass has shielding properties and can be utilized as radiation shielding materials.

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