Optical properties of the Dy^{3+} doped Lead Calcium Zinc Borate glasses

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Abstract : PbO-CaO-ZnO-B_2O_3 (PCZB) glasses of Dy^{3+} ions are prepared by conventional melt quenching technique and investigated by X-ray diffraction and Optical absorption spectroscopic techniques. The XRD spectra of the glass samples reveal an amorphous nature with different compositions within the glass matrix. The Optical absorption spectra of these glasses are recorded at room temperature. Nephelauxetic ratios, bonding parameters, Urbach energies, direct and indirect band gaps are calculated. Various significant physical properties (Density, Ion concentration, Inter-ionic separation and Polaron radius) of these glass samples have been evaluated.

Index Terms **- Borate glasses; XRD; Optical absorption; Nephelauxetic ratio; bonding parameter; Urbach energy.**

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I. Introduction

In the new millennium, large numbers of research works are devoted to synthesize the rare-earth (RE) doped glasses, glass– ceramics and crystals which have promising applications in various fields of science and technology. Glasses doped with rare earth ions are of prime importance for the development of fibre lasers, optical amplifiers, lasers, sensors, energy upconverters and so on. In this direction, a great amount of investigation has been carried out to find/optimize new glass matrices containing rare earth ions. Optimization of new or improved optical quality glasses doped with rare earth ions have been characterized by absorption and emission transition probabilities which are influenced by the ligand field of the surrounding rare earth ions [1].
Among the trivalent RE ions, Nd^{3+}, Eu^{3+}, Er^{3+}, Sm^{3+} and Dy^{3+} show motivating emissions in a wide range of wavelengths from ultraviolet(UV) to infrared(IR) regions of the spectrum. Nd^{3+} and Er^{3+}doped crystals and glasses were previously fabricated as the laser sources and optical fibers [2]. Sm^{3+}, Eu^{3+} and Dy^{3+} ions emit intense blue, yellow, orange and redlines [2-4]. Due to the existence of two lines (red and yellow) in the emission spectrum of Dy^{3+}doped glasses, they are also nominated as potential materials to fabricate solid state lasers. However, the quantum efficiency and the gain of such systems still need to be improved. Furthermore, the choice of appropriate host is pre- required to optimize the quantum efficiency of favourable transitions. In order to optimise the efficiency of rare-earth doped glasses, the local environment around RE ions has to be changed by changing the glass composition or by changing the concentration of RE ions in a host glass. The ligand fields produced by a host matrix will have considerable influence on the absorption, emission and quantum efficiency of the doped ions. In general a host glass with low phonon energies decreases non-radiative relaxation rates and gives high quantum efficiencies useful for obtaining efficient lasers and optical fibre amplifiers [5].
It is well known that boric acid (B_2O_3) is one of the good glass formers and can form glass alone with good transparency, high chemical durability, thermal stability and good rare-earth ion solubility [6]. However a glass with B_2O_3 alone will possess high phonon energies (~1300 cm^{-1}) which cannot suppress the non- radiative decay process and hence rare-earth ion emissions are strongly reduced. Among different possibilities, the choice of the network former B_2O_3 ensures a wide glass-forming range allowing the incorporation of modifier constituents such as ZnO, PbO and CaO to tailor specific properties. Besides the usual suitable features of oxide glasses, such compositions present high density and high linear and nonlinear refractive indices, broad transmission window and low phonon energy enabling applications in several optoelectronic devices [7]. Presently the glassy (or vitreous) borate compounds with rare-earth ions are more promising in the technological point of view. In addition to that, Dy^{3+} doped glasses are found to be the suitable candidates for solid state lasers and broad band optical amplifier applications due to its distinct emission in the visible and near infrared (2.8 mm) regions respectively [8]. The optical spectra of RE ions in glasses provide important information about the effect of host–ion interaction on the electronic and vibration energy levels of the material, which are essential for the design of applications [9].
In this present work, the characteristics of Dy^{3+} ion doped PbO-CaO-ZnO- B_2O_3 glasses (PCZB) have been investigated through XRD and optical absorption spectral measurements.

II. Experimental

2.1 Composite Preparation

Within the glass-forming region of Lead-Calcium-Zinc-Borate glass system, the composition (15-x) Pbo-10Cao-5Zno-70B_2O_3: xDy_2O_3, 0≤x≤ 2 (all composition in mol %) was prepared. Appropriate amounts of reagent grade of PbO, CaO, ZnO, H_3BO_3 and Dy_2O_3 powders were thoroughly mixed in an agate mortar and melted in a porcelain crucible in air at 950^0c for 30 min until a bubble free liquid was formed. The resultant melt was then poured on a polished brass slab and quenched to room

temperature in air. Care should be taken to obtain glasses of uniform thickness for recording Optical absorption spectra. After polishing, good quality glasses were obtained for optical measurements. Good quality glasses were obtained for optical measurements.

2.2 Characterization techniques

The amorphous nature of the glasses was confirmed by X- ray diffraction studies carried out by XRD-6100 SHIMADZU X-Ray diffractometer in the scanning range of 10-70^0 (2θ) using CuKα radiation having a wavelength of 1.5406 Å at room temperature. The density (ρ) of the glass samples was determined to an accuracy of ±0.0001, by standard principle of Archimedes using o-Xylene (99.9% pure) as the buoyant liquid. Average molecular weight (M), various physical parameters such as manganese ion concentration (N_i), mean manganese ion separation (r_i), the polaron radius (r_p) and optical basicity (Λ_{th}) are evaluated. The optical UV-Visible absorption spectra of prepared glass samples are recorded using JASCO V-670 UV-Vis-NIR Spectrophotometer in the wavelength region of 200-2000 nm.

III .Results and discussion

3.1. XRD

Fig.1 shows the typical X-ray diffraction patterns for all PCZB glass samples. The X- ray diffraction spectra show no sharp peaks, indicating that all the prepared PCZB glass samples are amorphous.

3.2. Physical parameters

To understand the physical properties of PCZB glasses, various parameters are calculated. Using conventional formulae [10], practically measured glass density 'ρ' and calculated average molecular weight (M) of the PCZB glass samples various physical parameters such as Manganese ion concentration (N_i), mean Manganese ion separation (r_i) and the polaron radius (r_p) are evaluated and the values have been furnished in Table 1. Density is a useful parameter to measure the change in the structure of glasses, as it is affected by structural softening/compactness, changes in geometrical configuration, co-ordination number, cross-link density and the dimensions

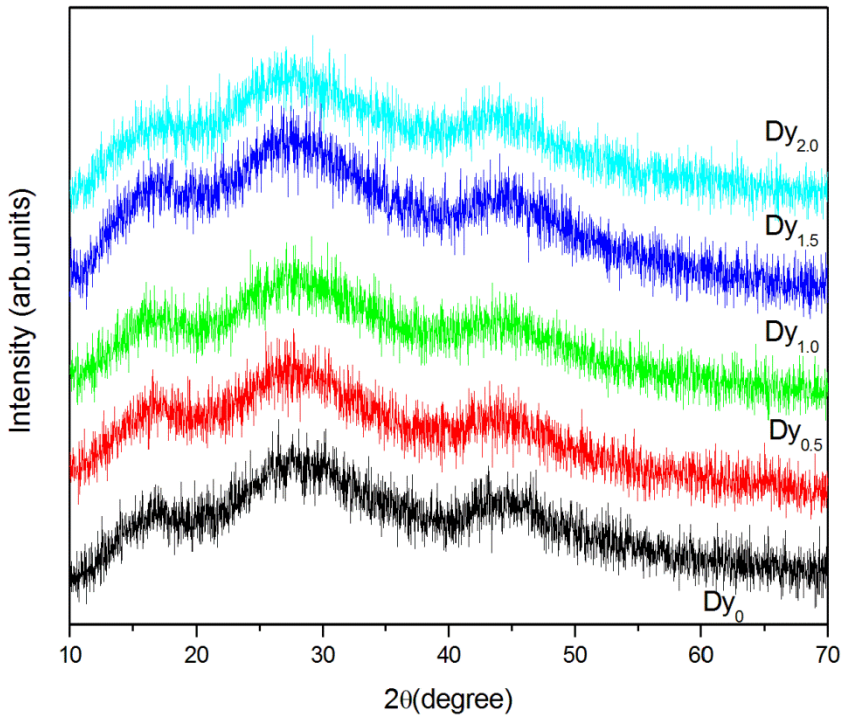

Fig.1. X-ray diffraction pattern of Dy_2O_3 doped PCZB glasses.

of interstitial spaces in the structure. The densities of all PCZB glasses are given in Table 1. For the sample with x = 2.0 mol% the density attains a maximum value. Polaron radius (r_p) values are found consistently less than that of inter ionic distance (r_i) in all PCZB glasses. Further, the values of r_p and r_i gradually decreased with increasing concentration of Dy_2O_3.

Table.1. Various physical properties of Dy_2O_3 doped PCZB glasses

Glass sample	Dy_0	$Dy_{0.5}$	$Dy_{1.0}$	$Dy_{1.5}$	$Dy_{2.0}$
Concentration of Dy_2O_3 (mol%)	0	0.5	1.0	1.5	2.0
Average molecular weight, M (g/mol)	91.890	92.639	93.388	94.137	94.886
Density, ρ (g/cc) (±0.0001)	3.4865	3.4186	3.4360	3.4707	3.5112
Ion concentration, N_i (x 10^{20}ions/cm^3) (±0.001)	_	1.111	2.216	3.330	4.457
Inter ionic separation, r_i (A^0) (±0.001)	_	20.799	16.525	14.426	13.090
Polaron radius, r_p (A^0) (±0.001)	_	8.383	6.660	5.814	5.276

3.3. Optical absorption studies

The absorption spectrum of PCZB glasses doped with Dy^{3+} are recorded in the spectral region 300-2000 nm is shown in Fig. 2. The spectrum exhibit ten inhomogeneously broadened absorption bands cantered at around 348, 364, 385, 425, 451, 797, 894, 1086, 1266 and 1676 nm corresponds to the transitions which originates from the $^6H_{15/2}$ ground state to the various excited states $^6P_{7/2}$, $^6P_{5/2,}$ $^6I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^6F_{5/2}$, $^6F_{7/2}$, $^6H_{7/2}$, $^6F_{11/2}$ and $^6H_{11/2}$ respectively. The absorption band at around 1266 nm corresponds to the hypersensitive transition ($^6H_{15/2}\rightarrow{}^6F_{11/2}$) which possess higher intensity compared to the other transitions and obey the selection rules $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$. The observed band positions for all the prepared glasses were presented in Table 2 along with the aqua ion values and their assignments were made referring the reported literature [11].

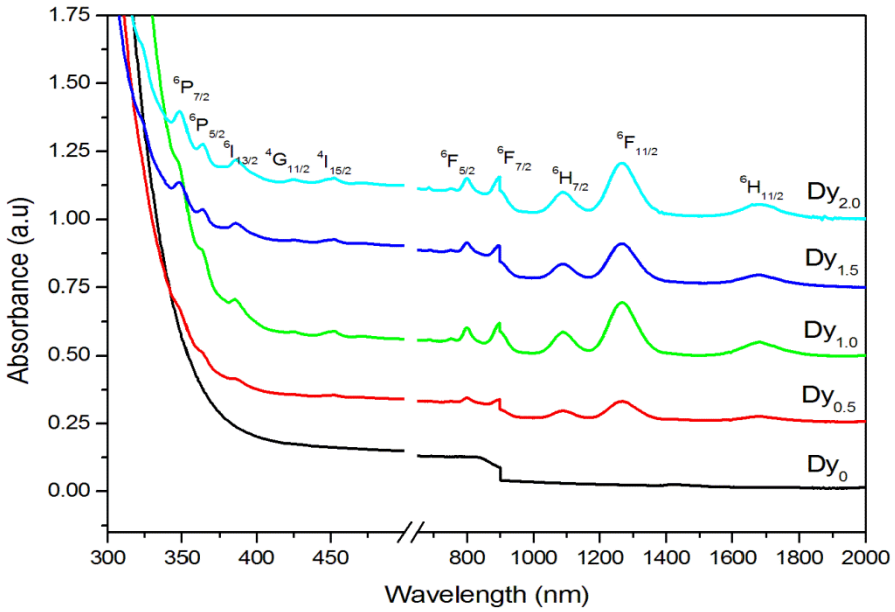

Fig.2. Optical absorption spectra of Dy_2O_3 doped PCZB glasses at room temperature.

3.4. Nephelauxetic ratio and the bonding parameter

The Nephelauxetic ratios (β) and the bonding parameters (δ) are calculated from the absorption spectra to investigate the bonding nature of the metal - ligand bond in the studied glasses. Nephelauxetic ratio (β) is a measure of covalency of the metal - ligand bond and is directly proportional to the hypersensitivity of a particular transition. The Nephelauxetic ratio can be expressed as

$$\beta = \upsilon_c / \upsilon_a \qquad (1)$$

where, υ_c is the observed band position (in cm^{-1}) of a particular transition of the RE ion in the chosen glass material and υ_a is the observed band position (in cm^{-1}) correspond to the aquo-ion transition. The bonding parameter (δ) can be calculated using the following relation [12],

$$\delta = \frac{1-\bar{\beta}}{\bar{\beta}} \times 100 \qquad (2)$$

where, $\bar{\beta}$ is the average value of the Nephelauxetic ratios. The Dy^{3+} metal -ligand bond may be covalent or ionic depending upon positive or negative sign of the d value. The $\bar{\beta}$ and δ values of the prepared glasses have been calculated and presented in Table 2. The negative sign of the δ value specify the fact that the Dy-metal ligand bond is of ionic in nature. The iconicity decreases (or covelancy increases) monotonically with the increase in Dy_2O_3 content in the prepared glasses.

Table 2 The empirical energy levels (in cm^{-1}) and bonding parameters ($\bar{\beta}$, δ) of the Dy_2O_3 doped PCZB glasses.

Transitions	$Dy_{0.5}$ cm^{-1}	$Dy_{1.0}$ cm^{-1}	$Dy_{1.5}$ cm^{-1}	$Dy_{2.0}$ cm^{-1}	Aqua ion
$^6P_{7/2}$	28623	28747	28711	28659	28551
$^6P_{5/2}$	27464	27464	27497	27481	27503
$^4I_{13/2}$	25985	25956	25899	25885	25919
$^4G_{11/2}$	23553	23529	23529	23565	23321
$^4I_{15/2}$	22127	22127	22172	22159	22293
$^6F_{5/2}$	12534	12534	12534	12565	12432
$^6F_{7/2}$	11149	11149	11184	11220	11025
$^6H_{7/2}$	9186	9202	9202	9202	9115
$^6F_{11/2}$	7893	7893	7893	7905	7730
$^6H_{11/2}$	5963	5963	5963	5980	5833
$\bar{\beta}$	1.0157	1.0141	1.0091	1.0087	-
δ	-1.5491	-1.3933	-0.9105	-0.8305	-

3.5. Band gap and Urbach's energy

The optical band gap (Eg) for the prepared PCZB samples is evaluated by Urbach theory. The theory shows the relation between energy band gap (eV) and αE for n = 0.5 (direct band gap) and n = 2 (indirect band gap). The Direct Band Gaps for the current glasses are observed within close limits around (3.97–4.15) eV as shown in Fig. 3. In Fig. 4, the Indirect Band Gaps for PCZB glasses doped Dy^{3+} ions are observed around (3.97–4.18) eV. Along with these direct and indirect optical band gaps, the theoretical optical band gap energy is also calculated using the equation E= hc/ λ_0 where h is Planck's constant, c is the velocity of light and λ_0 is cut-off wavelength respectively.

The absorption coefficient α(ν) near the absorption band edge exhibits an exponential behaviour on the photon energy(hν) and obeys the Urbach empirical relation $\alpha(\nu)=\alpha_0 \exp(h\nu/\Delta E)$, where α_0 is a constant and ΔE is the Urbach energy corresponds to the optical transition between the localized tail states adjacent to the valance band and the conduction band which extend into the band gap [13]. From Fig. 5 the Urbach energy values of the prepared glasses are found to be in the range 0.23–0.25eV. In the present glasses $Dy_{1.5}$ possess lower Urbach energy suggesting the possibility of long range order locally arising from the minimum number of defects [14]. Further it is observed that, the Urbach energy value changes inversely with the optical band gap values. The Urbach energy is indicative of degree of disorderness in the materials. The changes in the Urbach energy values are due to the formation of defects in the glasses [15-17]. These defects produce localized states in the glasses causing the decrease in the width of the localized states in the optical band gap which in turn increases the optical band gap values. Table 3 shows the summary of the data on optical band gaps and Urbach energy of Dy^{3+} doped PCZB glasses.

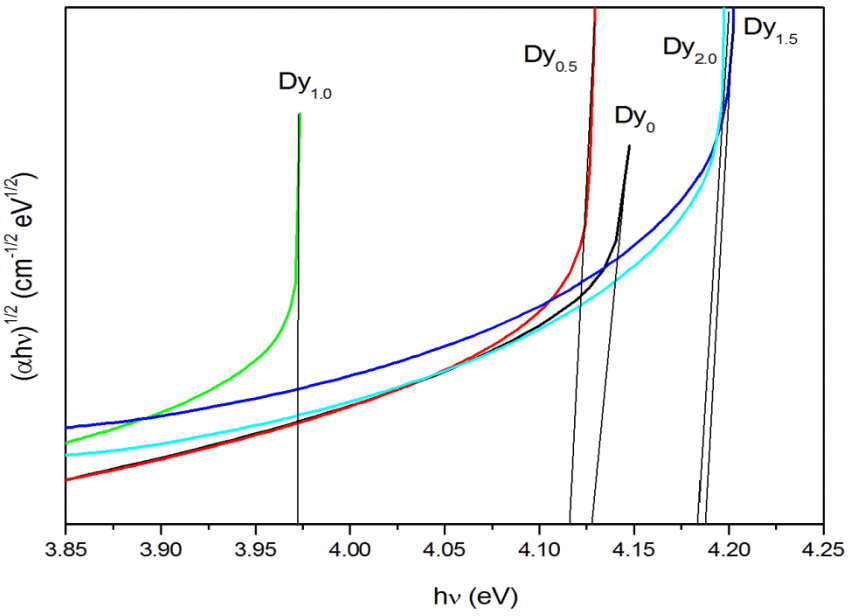

Fig. 3 Tauc plots to evaluate direct band gap of Dy_2O_3 doped PCZB glasses.

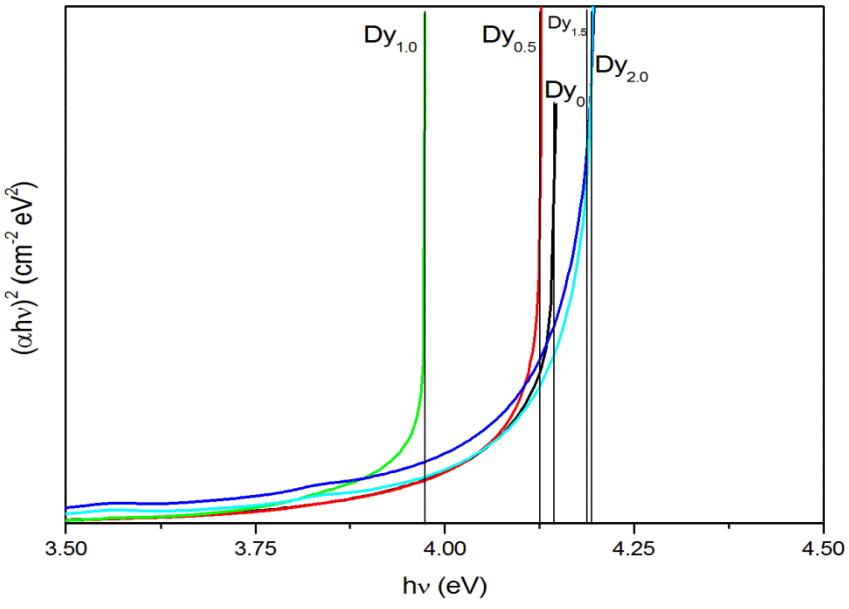

Fig. 4 Tauc plots to evaluate indirect band gap of Dy_2O_3 doped PCZB glasses.

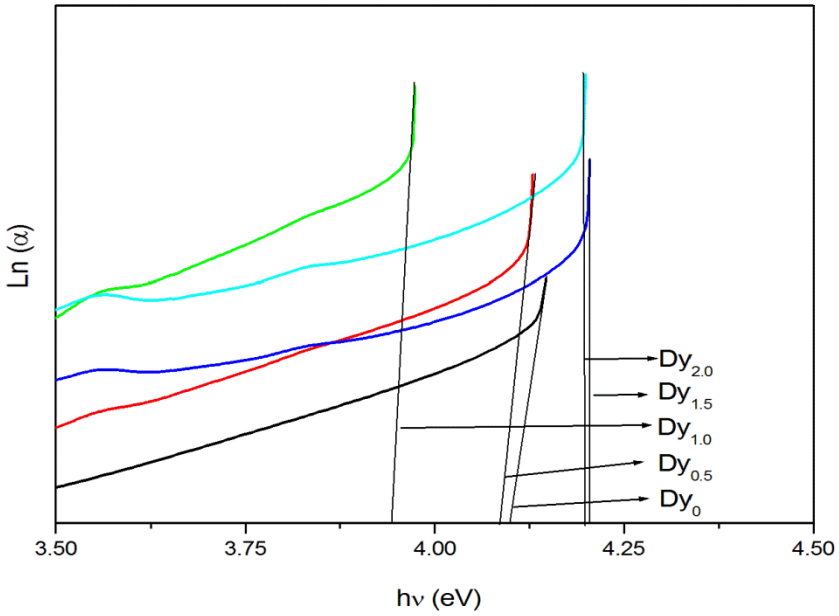

Fig.5. Plots between ln (α) and hν for Dy_2O_3 doped PCZB glasses.

Table 3 Summary of the data on optical band gaps and Urbach energy and of Dy_2O_3 doped PCZB glasses.

Glass sample	Cut-off Wavelength λ_c (nm) (±0.1)	Theoritical band gap (eV)	Direct band gap E_g (eV) (±0.001)	Indirect band gap E_g (eV) (±0.001)	Urbach energy ΔE_g (eV) (±0.001)
Dy_0	299.5	4.147	4.135	4.113	0.241
$Dy_{0.5}$	300.8	4.129	4.125	4.116	0.244
$Dy_{1.0}$	312.6	3.973	3.971	3.972	0.253
$Dy_{1.5}$	295.4	4.205	4.146	4.187	0.237
$Dy_{2.0}$	295.8	4.199	4.155	4.183	0.238

IV. Conclusion

1. Lead-Calcium-Zinc-Borate glasses (PCZB) with good optical quality at different compositions of Dy^{3+} ions are prepared by the conventional melt quenching technique.
2. The amorphous nature of prepared glass samples is confirmed by XRD.
3. Density, Ion concentration, Inter-ionic separation and Polaron radius of these glass samples have been evaluated.
4. The room temperature absorption spectra of Dy^{3+} ions doped PCZB glasses are recorded and the respective band assignments are given.
5. Covalent character of Dy^{3+} ions with its surrounding ligands has been confirmed through optical spectra.
6. The direct, indirect and Urbach energies of PCZB glasses are evaluated.
7. Urbach energy value changes inversely with the optical band gap values, and shows the degree of disorderness in the materials.

V. Acknowledgment

The authors would like to acknowledge **DST-FIST**, New Delhi; and DRS for sanctioning equipment to the Department of Physics, Acharya Nagarjuna University to carry out the present research work.

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