

Optical absorption studies of free (H₂Pc) and rare earth (RePc) phthalocyanine doped borate glasses

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Optical absorption studies of free base and rare earth incorporated phthalocyanine doped borate glass matrix are reported for the first time. The absorption spectra recorded in the UV-VIS region show two well defined absorption bands of phthalocyanine (Pc) molecule, namely the Soret band (B) and the Q band. The Q band always shows its characteristic splitting in all the doped glass matrices and the intensities of these components are found to vary from one Pc to another. Some of the important optical parameters, namely optical absorption coefficient (α), molar extinction coefficient (ϵ), absorption cross section (σ_a), oscillator strength (f), electric dipole strength (q^2), absorption half bandwidth ($\Delta\lambda$) of the principal optical transitions have also been evaluated. Moreover, the spectral dependence of refractive index (n) and thereby the optical dielectric constant (ϵ) on wavelength yielded values of carrier concentration to effective mass ratio (N/m^*) of the phthalocyanine molecule in the present glassy systems. Optical band gap (E_g) and width of the band tail (E_t) are computed and their variations among the prepared samples are also discussed.

Phthalocyanines are a class of organic semiconductors which have won considerable attention among scientists because of their potential applications in the pure and applied field. Their unique properties include excellent semiconductivity, photoconductivity, thermal and chemical stability and very good optical absorption in the UV-VIS region.⁽¹⁾ Some of the important applications of these organic molecules are in fabrication of solar cells, electronic displays and chemical sensors and also in photocopying processes.⁽²⁻⁴⁾ In addition to these applications,

being a very good absorber of light in the UV-VIS region they are widely used as excellent laser dyes capable of optical amplification in the red region.⁽⁵⁾ After the invention of phthalocyanine (Pc) in 1907 various attempts have been made by scientists to study the physical and chemical properties of the molecules in a variety of forms.⁽⁶⁻⁸⁾ Most of these studies are either in thin film form, vapour form or dissolved in a solvent medium whereas only a limited amount of work has been reported in solid matrices including some studies conducted by Lucia *et al*⁽⁹⁾ in thermoplastic medium. Recently, the authors of the present report conducted some studies on the physical and optical properties of various metal Pc doped borate glass which are considered to be the first of their kind.⁽¹⁰⁾ In that paper the authors conducted an elaborate study of the optical absorption spectra of various metal phthalocyanines (Cu, Zn, Ni, Co, Mo, etc) doped borate glass matrices with special emphasis on the splitting of the Q-band, red shift of the band and also on the origin of some extra bands. The rare earth dye doped inorganic glasses are found to be better candidates for exhibiting novel spectroscopic features relevant to optical amplification. To the authors knowledge no work has been performed on free and rare earth phthalocyanine doped solid media and hence investigations of the optical properties of these dopants in borate glass matrix assumes significance. In view of this we find it desirable to determine the relevant optical parameters and to study the variation of optical band gap, width of the band tail and optical dielectric constant with the rare earth ion substitution.

Theory

In evaluating the oscillator strength (f) and electric dipole strength (q^2), the two most important spectral parameters, the following mathematical expressions⁽¹¹⁾

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have been used.

$$f = 4.38 \times 10^{-9} \int \epsilon(\nu) d\nu \quad (1)$$

$$q^2 = (1/2500) \epsilon(\nu) \Delta\lambda / \lambda \quad (2)$$

where $\epsilon(\nu)$ is the molar extinction coefficient corresponding to the transition of frequency, ν and it can be evaluated using the expression

$$\epsilon(\nu) = A/Cl \quad (3)$$

where A is the absorbance, C concentration in mole/l and l the sample thickness. In Equation (1) $d\nu$ represents the absorption bandwidth which is usually taken as its full width at half maximum (FWHM).

The optical absorption coefficient $\alpha(\nu)$ at a given frequency (ν) is given by⁽¹²⁾

$$\alpha(\nu) = A \{h\nu - E_g\}^r / h\nu \quad (4)$$

where A and r are constants, $h\nu$ the photon energy and E_g the optical band gap. The width of the band tail (E_t) was calculated using Urbach's empirical relation.⁽¹³⁾

$$\ln(\alpha) = \ln B - (h\nu / E_t) \quad (5)$$

where B is a constant.

From the absorption and transmission spectra the reflectance was calculated using the expression⁽¹²⁾

$$T = (1 - R)^2 \exp(-A) \quad (6)$$

where R is the reflectance, T the transmittance and A the absorbance.

The relation between optical dielectric constant ϵ , wavelength (λ) and refractive index (n) is given by⁽¹²⁾

$$\epsilon = n^2 = \{ (1 + \sqrt{R}) / (1 - \sqrt{R}) \}^2 = \epsilon_\infty - e^2 / \pi c^2 (N/m^*) \lambda^2 \quad (7)$$

when ϵ_∞ is the infinitely high frequency dielectric constant, e the electronic charge and (N/m^*) the ratio of carrier concentration to the effective mass.

Experimental

All the glass samples were prepared by the conventional rapid quenching technique.⁽¹⁴⁾ Reagent grade boric acid (H_3BO_3) and doubly sublimed phthalocyanines have been used as the starting materials for sample preparation. The weighed quantities of the starting materials for 18 g glass were mixed homogeneously using an agate mortar. The batch was then taken in a silica crucible and heated in an electric muffle furnace. Slow heating was initially maintained until the temperature reached 80°C and decomposition of H_3BO_3 to B_2O_3 is complete. The temperature was then rapidly increased to 120°C so as to obtain a bluish green melt. The melt was retained for about 10 min and then rapidly quenched by transferring between two well polished preheated brass plates so as to obtain glass discs of about 3 mm thickness and with a diameter of about 2 cm. The glass disc thus obtained was annealed at a temperature of about 60°C and subsequently polished well with water free lubricants. All the samples have been obtained with very good transparency and thus appear to be of good optical quality.

The amorphous nature of the glass samples obtained was confirmed by x-ray diffraction spectra recorded on

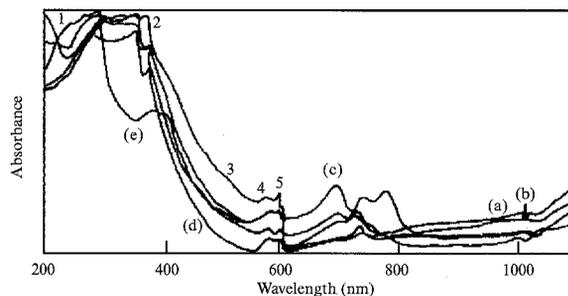


Figure 1. Optical absorption spectrum of various phthalocyanine doped borate glass: (a) H_2 -Pc; (b) La-Pc; (c) Eu-Pc; (d) Sm-Pc; (e) Nd-Pc

a Shimadzu x-ray diffractometer with Ni filtered $Cu K_\alpha$ radiation. The absorption spectra were recorded in the UV-VIS-NIR region with an Hitachi U2000 spectrophotometer. All the measurements were done at room temperature.

Results and discussion

Figure 1 shows the absorption spectra of free and rare earth metal incorporated Pc doped borate glasses. An intense absorption region in the ultraviolet region followed by a valley extending up to 550 nm characterises all the spectra. A close examination of the absorption band in the ultraviolet region reveals that it comprises three overlapping bands of which the most commonly

Table 1. Calculated spectral parameters of various phthalocyanine doped borate glass samples

Pc	λ (nm)	Band	α (cm^{-1})	ϵ (10^6) ($mol^{-1} cm^{-1}$)	$\sigma_a \times 10^{18}$ (cm^2)	f	$\Delta\lambda$ (nm)	q ($^\circ A$) ²
H ₂ -Pc	282.6	N	2.99	0.27	1.27	*	-	-
	358.4	-	3.01	0.77	1.28	*	-	-
	382.5	-	2.47	0.63	1.05	*	-	-
	493.0	-	0.59	0.15	0.25	0.94	-	6.7
	579.1	-	0.56	0.14	0.23	0.39	-	2.0
	600.0	-	0.63	0.16	0.26	0.27	-	1.4
	737.8	Q	0.27	0.07	0.11	0.15	21.12	1.03
	730.9	Q _s	0.038	0.022	0.036	0.36	20.49	0.24
La-Pc	303.3	B	3.2	1.87	3.09	*	-	-
	358.4	-	3.2	1.87	3.09	*	-	-
	382.5	-	2.8	1.63	2.7	*	-	-
	496.4	-	0.67	0.39	0.64	-	-	-
	579.1	-	0.62	0.36	0.59	-	-	-
	600.0	-	0.67	0.39	0.64	-	-	-
	696.4	Q _y	0.21	0.12	0.20	-	-	-
	730.9	Q _s	0.038	0.022	0.036	0.36	20.49	0.24
Eu-Pc	303.3	B	3.09	1.82	3.02	*	-	-
	351.5	-	3.09	1.82	3.02	*	-	-
	379.1	-	2.77	1.63	2.71	*	-	-
	493.0	-	0.27	0.15	0.26	-	-	-
	579.0	-	0.21	0.12	0.20	-	-	-
	600.0	-	0.21	0.12	0.20	-	-	-
	696.4	-	0.40	0.23	0.39	-	-	-
	741.2	Q _y	0.76	0.44	0.74	1.81	51.7	12.27
Sm-Pc	779.14	Q _s	0.86	0.50	0.84	1.73	48.5	12.44
	310.2	B	3.04	1.79	3.0	*	-	-
	351.5	-	3.04	1.79	3.0	*	-	-
	379.1	-	3.04	1.79	3.0	*	-	-
	496.4	-	0.97	0.57	0.56	-	-	-
	579.1	-	0.59	0.34	0.33	-	-	-
	600.0	-	0.65	0.38	0.37	-	-	-
	689.5	Q _y	0.81	0.47	0.46	2.68	62.01	16.9
730.9	Q _s	0.40	0.23	0.42	-	-	-	
Nd-Pc	293	B	1.55	0.91	1.5	*	-	-
	395	-	0.85	0.50	0.82	*	-	-
	420	-	-	-	-	*	-	-
	692	Q _s	0.22	0.12	0.21	0.21	20.0	1.38
	754	Q _y	0.19	0.11	0.18	0.18	10	0.58

* Since the bands are all overlapping in this region, f is not evaluated

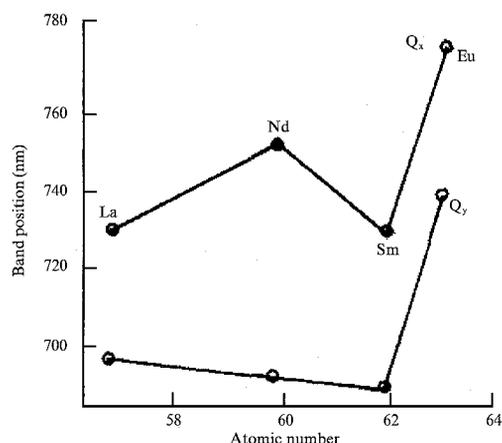


Figure 2. Variation of Q band position with atomic number of the central metal atom. Q_x and Q_y are the components of the Q band

known is the Soret or B band arising out of the molecular transition $b_{2u}(\pi) \rightarrow e_g(\pi^*)$.⁽⁸⁾ The broad absorption band in the ultraviolet region is preceded by the ultraviolet absorption band edge of the glassy matrix. The other well known band of the Pc molecule, namely Q band appears in the region between 600–800 nm. It can also be noticed that this band always shows the characteristic splitting (Davidov splitting) in all the samples studied. As noticed in all other Pc based systems here also the Q band appears with intensities which are comparatively smaller than that of the B band. The important spectral parameters, namely absorption coefficient, absorption cross section, oscillator strength, electric dipole line strength and FWHM which are evaluated for the five samples are collected in Table 1. A comparison of these results shows that the oscillator strength of the Q band varies in the sequence $Sm > Eu > Nd > La > H_2$ whereas the bandwidth variation is in the sequence $Sm > Eu > H_2 > La > Nd$. In phthalocyanine molecule (free base or metallated) oscillator strength of an absorption band is a measure of the extent of interaction between the central metal atom (the metal atom is positioned at the centre of the Pc ring) and the Pc ring. Hence, it can be inferred from the results that there is a strong interaction between metal ion and Pc- π system for Sm Pc while for H_2 Pc the interaction is not quite strong. Absorption cross section of the B band is found to be maximum for LaPc whereas for H_2 Pc it is the least.

The introduction of rare earth metals into the Pc molecule has a variable effect on the intensity and spacing but does not alter the general type. If the position of the Q bands of each Pc in borate glass is plotted against the atomic number of the metal it is found that the values fall on almost a smooth curve (Figure 2). A similar tendency of the bands has already been reported by Anderson *et al* in chloronaphthalene.⁽¹⁵⁾ The shift of the Q band position to the higher wavelength side is comparatively larger for Eu-Pc. Such a shift could be explained on the basis of the strength of interaction of the central metal atom with the Pc ring. The strength of this coordinate bond and thereby the tendency of formation of the molecule is found to increase with the

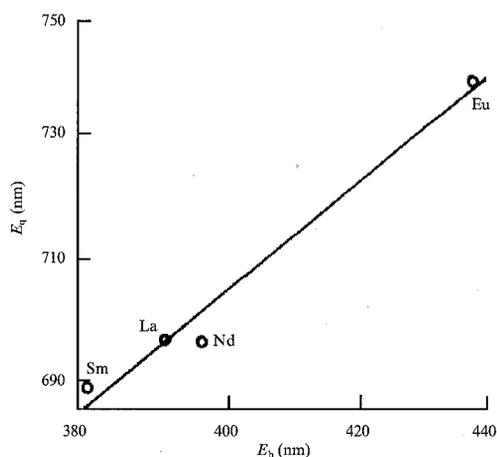


Figure 3. Plot of B band energy (E_B) versus Q band energy (E_Q)

decrease in size of the central metal atom. This is because of the fact that when the size of the central metal atom decreases the probability of occupancy of the atom within the central position of the Pc ring increases. In view of the fact that the tendency to form planar four coordinate compounds reaching the maximum with Eu, it is possible that the magnitude of the shift in the absorption spectrum can be correlated with the strength of the coordinate links of the central metal ion.

Analysis of absorption spectrum clearly shows the fact that except for some minor changes the positions of B and Q bands are almost similar irrespective of the rare earth substitution. In Figure 3 the variations of B band versus Q band energies are graphically shown for all samples studied. The points fit reasonably well to a straight line of slope ~ 1 which implies that the energy difference between B and Q bands is necessarily a constant and is estimated to be about 402–32 nm.

The amount of Q band splitting (Davidov splitting) of various Pc doped glassy systems is graphically shown in Figure 4. The graph does not show any linear relationship of the D-splitting with the atomic number of the rare earth ion. From the graph it can be seen that the Davidov splitting is maximum for Nd-Pc (62 nm)

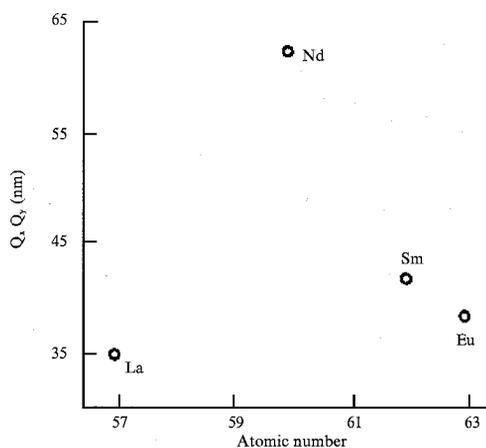


Figure 4. Variation of Q band splitting with atomic number of the central metal atom

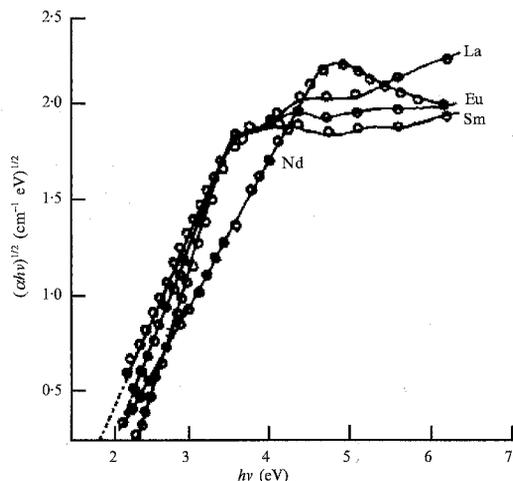


Figure 5. Plot of $(\alpha hv)^{1/2}$ against the photon energy, hv , for La-Pc, Nd-Pc, Eu-Pc and Sm-Pc doped borate glasses

whereas it is minimum in La-Pc (34.5 nm). A comparison of the Davidov splitting with other reported matrices⁽¹⁶⁾ clearly shows that the splitting in glassy matrices is considerably reduced.

The appearance of the general Q and B bands is a typical feature of the Pc absorption spectrum. The basic features in the absorption spectrum of many differently substituted Pc's are quite similar. Major difference in the spectra between various matrices is attributed to the effect of the surrounding matrix upon the energy levels of the Pc molecules. In our observations we have noticed a number of such 'extra' bands in the entire UV-VIS region and are designated by numbers 1–5 in Figure 1. The appearance of such extra bands has already been noticed in vapour spectra also.⁽¹⁶⁾ Our experimental result shows except for the 600 nm band all other extra bands are matrix dependent. Molecular orbital calculations show the presence of some $\sigma \rightarrow \pi$ transitions in the 300–700 nm region. Some of the identified transitions are $e'_u(\sigma) \rightarrow 6e_g(\pi)$ (at ~579 nm), $e''_u(\sigma) \rightarrow 6e_g(\pi)$ (at ~480 nm) and $a_{1u}(\sigma) \rightarrow 6e_g(\pi)$ (at ~355 nm) Even though these are forbidden transitions, the ligand field surrounding the Pc molecules can mix these

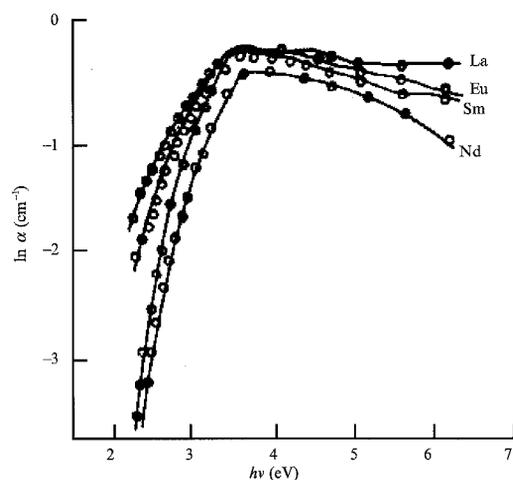


Figure 6. Plot of $\ln(\alpha)$ against the photon energy, hv for La-Pc, Nd-Pc, Eu-Pc and Sm-Pc doped borate glasses

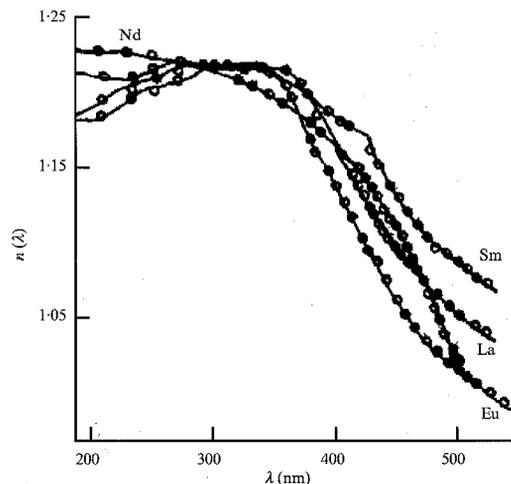


Figure 7. Variation of refractive index with wavelength for the four glass samples studied

transitions with the nearby allowed transitions and thereby relax the forbiddenness of the $\sigma \rightarrow \pi$ transitions. These transitions could account for the bands at ~579, 490 and 350 nm of the present glassy system. Interpretation of the other 'extra' bands require further molecular orbital calculations on the particular Pc.

The dependence of $(\alpha hv)^r$ on the photon energy, hv was plotted for different values of r . The best fit was obtained for $r=2$. This is the characteristic behaviour of indirect transitions in noncrystalline materials.⁽¹⁷⁾ Figure 5 shows the functional dependence of $(\alpha hv)^{1/2}$ on hv for all the glass samples studied. The extrapolation of the absorption curve $(\alpha hv)^{1/2}$ versus hv to the value $(\alpha hv)^{1/2}=0$ yields the value of the optical band gap E_g . The magnitude of E_g obtained and also the values of the constant A of Equation (4) are listed in Table 2. The band gap shows a nearly steady value of ~2.1 eV throughout the glass samples which point out the fact that it is unaltered by the nature of the central metal ion of the Pc ring. Our earlier observation⁽¹⁰⁾ also shows a band gap of ~2.1 eV for other metal-Pc compounds, namely Ni, Cd, Co, Cu, Zn, H₂, Mo and Fe doped borate glasses. The optical band gap is closely related to the energy gap between the valance and conduction bands. In glasses the latter is strongly influenced by the anions.⁽¹⁸⁾ The s and p orbital of B³⁺ and s orbital of O²⁻ interact with each other to form bonding and antibonding states which contribute to valance band and conduction band respectively. Since in the present case the amount of B₂O₃ is always fixed the bonding and antibonding states remain the same and hence will not alter the optical band gap.

Table 2. Calculated values of the optical band gap (E_g), band tailing (E_t), constants (A), (B), infinitely high dielectric constant (ϵ_∞) and ratio of carrier concentration to effective mass in various phthalocyanines

Pc	E_g (eV)	E_t (eV)	A (cm ² eV)	B	ϵ_∞	$(N/m^*) / (10^{20} \text{ cm}^{-3})^{-1/2}$
H ₂ Pc				1.52	4.60	
LaPc	2.1	0.56	1.33	1.46	1.53	4.75
EuPc	2.3	0.35	1.52	1.52	1.53	4.21
SmPc	1.9	0.67	1.15	1.20	1.52	4.80
NdPc	2.13	0.61	1.03	1.21	1.54	4.50

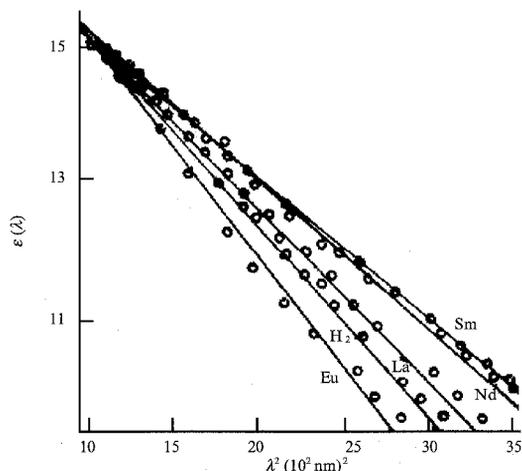


Figure 8. Plot of optical dielectric constant ϵ with λ^2 for the four glass samples studied

Figure 6 shows the linear dependence of the natural logarithm of the absorption coefficient on the photon energy for all the samples studied. The reciprocal of the slopes of each line yields the magnitude of E_t and is collected in Table 2. This also shows a steady average value of ~ 0.54 eV in agreement with our earlier reported value.⁽¹⁰⁾ The width of the tail of the localised states is attributed to the phonon assisted indirect electronic transitions.⁽¹³⁾

Figure 7 shows the variation of the refractive index of the Pc doped glass samples with the wavelength of the radiation. In agreement with the dispersion relation⁽¹⁹⁾ refractive index shows its maximum value in the ultraviolet region whereas it drops to its minimum value in the visible region.

The dielectric constant ϵ versus λ^2 plots shown in Figure 8 are all linear verifying Equation (7). Values of ϵ and (N/m^*) determined from the extrapolation of these plots to $\lambda^2=0$ and from the slopes of the graph are listed in Table 2. It has been observed that these parameters do not show noticeable variation from one matrix to another; the average value remains 1.53 and $4.56 \times 10^{20} \text{ cm}^{-3}$ respectively for ϵ_∞ and (N/m^*) .

Conclusions

The newly synthesised Re-Pc doped borate glasses show good optical absorption in the UV-VIS region. In addition to the prominent B and Q bands appearance of some 'extra' bands is a characteristic feature of the present matrix. Optical band gap, E_g , width of the band tail, E_t and the ratio of carrier concentration to effective mass (N/m^*) do not show remarkable variation among the samples prepared. To conclude one can say that they are necessarily constants irrespective of the change of the central metal ion.

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