

Spectral studies of naphthalocyanine (Nc) and rare earth phthalocyanine (RePc) molecules in an inorganic glassy borate matrix

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Optical absorption and emission spectral studies of free and metal naphthalocyanine doped borate glass matrix are reported for the first time. Absorption spectra recorded in the UV-VIS-NIR region show the characteristic absorption bands, namely, the B-band and Q-band of the naphthalocyanine (Nc) molecule. Some of the important spectral parameters, namely, the optical absorption coefficient (α), molar extinction coefficient (ϵ) and absorption cross section (σ_a) of the principal absorption transitions are determined. Optical band gap (E_g) of the materials evaluated from the functional dependence of absorption coefficient on photon energy lies in the range $1.6 \text{ eV} \leq E_g \leq 2.1 \text{ eV}$. All fluorescence spectra except that of EuNc consist of an intense band in the 765 nm region corresponding to the excitation of Q-band. In EuNc the maximum fluorescence intensity band is observed at 824 nm. The intensity of the principal fluorescence band is maximum in ZnNc, whereas it is minimum in H₂Nc. Radiative parameters of the principal fluorescence transitions corresponding to the Q-band excitation are also reported for the naphthalocyanine and phthalocyanine based matrices.

Organic semiconductors play a very important role in today's high technology applications, namely, optical imaging, optical switching, optical computing, data storage, photodynamic therapy, dynamic holography, frequency mixing, harmonic generation and optical communications.⁽¹⁻⁴⁾ Among the organic semiconductors phthalocyanines (Pc), naphthalocyanines (Nc) and porphyrins (PP) are of special significance because of their low cost, thermal and environmental stability, nontoxicity as well as excellent optical and electronic

properties. A combination of these features makes them an important class of photo-electronic materials for applications in various optoelectronic devices.⁽¹⁻⁴⁾ Moreover, because of their excellent optical absorption efficiency in the red and NIR region they can also be effectively utilised as a laser dye. Most of the studies reported so far discuss the optical characterisation of these organic semiconductors either in thin film, crystal, in vapour or other solvent forms whereas no effort has been made to study the optical properties of these molecules in solid matrices, especially the glassy matrix. Except for some studies in certain organic glassy matrices⁽⁵⁾ only a limited amount of work has been done in organic matrices. Recently, the authors of the present report have synthesised borate glassy matrices doped with phthalocyanines and porphyrins and studied their optical absorption and emission characteristics.⁽⁶⁻⁹⁾ The purpose of the present work is to study the optical absorption and stimulated emission characteristics of various naphthalocyanine molecules in borate glass matrix with the intention of using them as efficient active media in realising optical amplification.

Experimental

All glass samples were prepared by the well known rapid quenching technique.⁽⁸⁾ Reagent grade boric acid (H₃BO₃) and doubly sublimed naphthalocyanines were used as starting materials for the preparation of the glass samples. Weighed quantities of the starting materials for 18 g glass were mixed homogeneously using an agate mortar. The batch was then placed 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 H₃BO₃ to B₂O₃ was complete. The temperature was then rapidly increased to 120°C so as to obtain a bluish green melt. The melt

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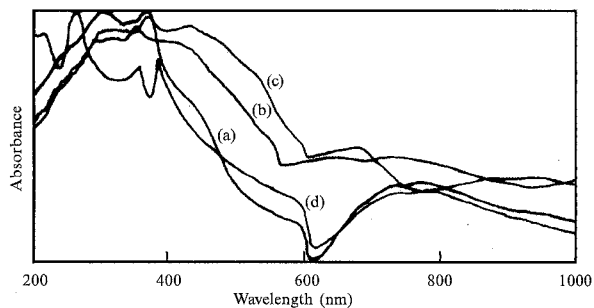


Figure 1. Absorption spectrum of (a) H_2Nc in borate glass; (b) $ZnNc$ in borate glass; (c) $EuNc$ in borate glass; and (d) $VoNc$ in borate glass

was retained for about 10 min and then rapidly quenched by placing in 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 discs thus obtained were annealed at a temperature of about 60°C and subsequently polished with water free lubricants. All samples have been obtained with very good transparency and appear to be of good optical quality.

Glass rods (having length 8 cm and diameter 2 cm) were also developed by heating the starting chemicals in 75 cm long borosil glass tubes after providing the necessary vacuum using a rotary pump. To remove the water vapour originating as a result of the decomposition of H_3BO_3 , a vacuum trap was provided in between the rotary inlet and sample tube. The tube was kept in a 1 m long vertical heater the temperature of which could be controlled externally. After melting, the heater was switched off and allowed the melt to cool to room temperature by keeping inside the heater itself. Finally, the tube was taken out and glass rod was removed by breaking the glass tube.

The amorphous nature of the glass samples was confirmed by x-ray diffraction spectra recorded on a Shimadzu x-ray diffractometer with Ni filtered CuK_{α} radiation. Absorption spectra were recorded in the UV-VIS-NIR region with a Hitachi U-2000 spectrophotometer. All emission spectra were recorded at room temperature using a SPEX spectrofluorimeter with a wavelength resolution of ± 0.2 nm.

Results and discussion

Figures 1(a–d) show the absorption spectra of the various Nc doped borate glass matrices. All spectra are characterised by an intense broad band in the ultraviolet region followed by a valley. A close examination of the absorption band in the ultraviolet region reveals that it comprises several bands of which the most com-

Table 1. Calculated optical constants of the absorption bands of various Nc-S in borate glass matrix

Nc-S	Bands				Q λ (nm)	α (cm^{-1})	ϵ^*	σ $\times 10^{24} cm^2$
	λ (nm)	α (cm^{-1})	ϵ^*	σ $\times 10^{24} cm^2$				
H_2Nc	307	5.8	2900	6.7	763	1.3	652	1.5
$ZnNc$	321	2.8	1406	3.0	678	0.37	678	0.3
$EuNc$	321	5.5	2750	2.8	691	2.5	125	1.3
$VoNc$	272	4.5	2250	4.8	739	2.4	1215	2.5

* ($mol l^{-1}cm^{-1}$)⁻¹

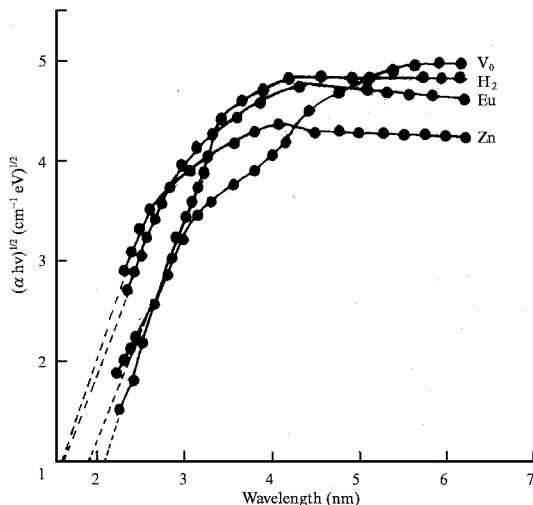


Figure 2. Plot of $(\alpha hv)^{1/2}$ versus hv for the four glass samples prepared

monly known is the Soret band or B-band arising out of the molecular transition $b_{2u}(\pi) \rightarrow e_g(\pi^*)$. The broad absorption band in the ultraviolet region is preceded by the ultraviolet absorption edge of the glassy matrix. The other well known band of the Nc molecule, namely, the Q-band appears in the region between 670–763 nm. The important spectral parameters, such as absorption coefficient, absorption cross section and molar extinction coefficient which are evaluated for the four samples are collected in Table 1. The absorption cross section of the B-band is found to be maximum for H_2Nc , whereas in $EuNc$ it is the least.

In order to evaluate the optical band gap (E_g) the following mathematical expression is employed⁽⁸⁾

$$\alpha(v) = Ahv\{hv - E_g\}^r \tag{1}$$

where A and r are constants, hv the photon energy and E_g the optical band gap.

The dependence of $(\alpha hv)^r$ on 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 and corresponds to Tauc equation.^(10,11) Figure 2 shows the functional dependence of $(\alpha hv)^{1/2}$ on hv for all 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 are 2.1, 1.6, 1.6 and 1.9 eV, respectively, for H_2Nc , $ZnNc$, $EuNc$ and $VoNc$ (Vanadyl Nc) which is almost similar to the band gap values of phthalocyanine molecules in borate glass matrix.^(7,8)

The fluorescence spectra obtained corresponding to the Q-band excitation are presented in Figures 3(a–d) and the calculated spectral parameters are collected in Table 2. All samples except $EuNc$ show intense fluores-

Table 2. Radiative parameters of emission bands of various Nc-S in borate glass matrix

Nc-S	λ_{ex} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	I_p	τ (μs)	σ_e $\times 10^{18} cm^2$
H_2Nc	700	765.2	1.77	0.13	36	2.47
$EuNc$	700	824.57	2.6	0.23	74	1.10
$ZnNc$	700	765.17	1.87	1.0	117	0.71
$VoNc$	700	765.0	2.15	0.18	16	4.57

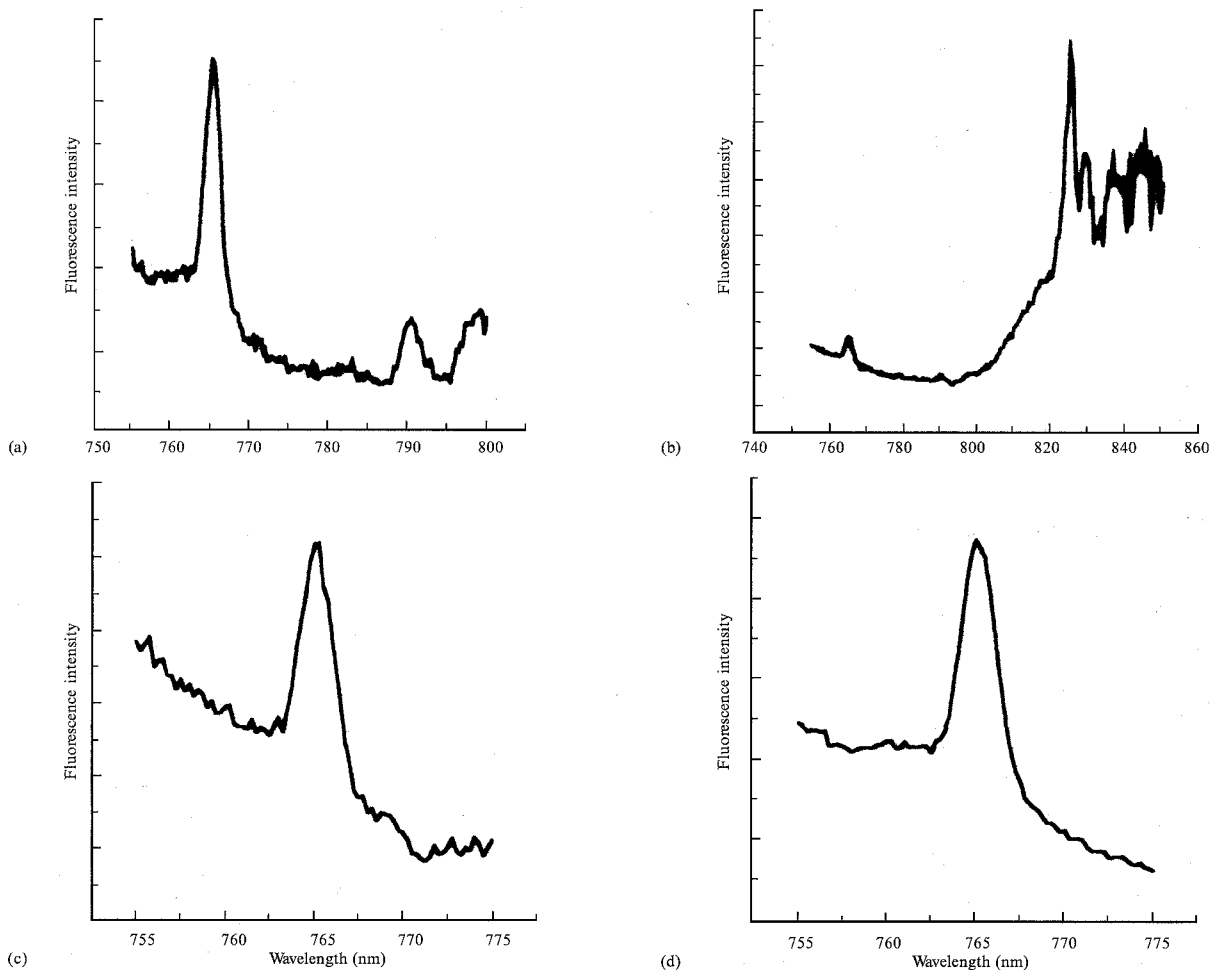


Figure 3. Fluorescence spectrum of (a) H_2Nc ; (b) $EuNc$ (c) $ZnNc$; and (d) $VoNc$

cence in the 765 nm region. In the case of $EuNc$ fluorescence, transition is observed in the 824 nm region. The observed fluorescence intensity is found to be maximum in $ZnNc$ whereas it is minimum in H_2Nc .

The spectra of H_2Nc and $EuNc$ are characterised by some other weaker transitions in the 765 and 790 nm regions. These may be the vibrational levels characteristic of the molecular ground state. The emission cross

section of the fluorescence transition varies in the range 0.71 to $4.57 \times 10^{-18} \text{ cm}^2$ whereas the maximum value is observed in $VoNc$. Optical gain is also found to be highest in the $VoNc$ doped glass (6.2 dB/cm) whereas for $ZnNc$ it is the least (-1.8 dB/cm). Because of high op-

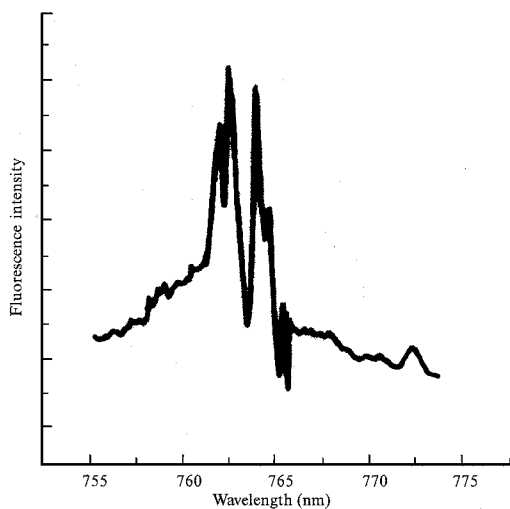


Figure 4. Fluorescence spectrum of H_2Pc doped borate glass

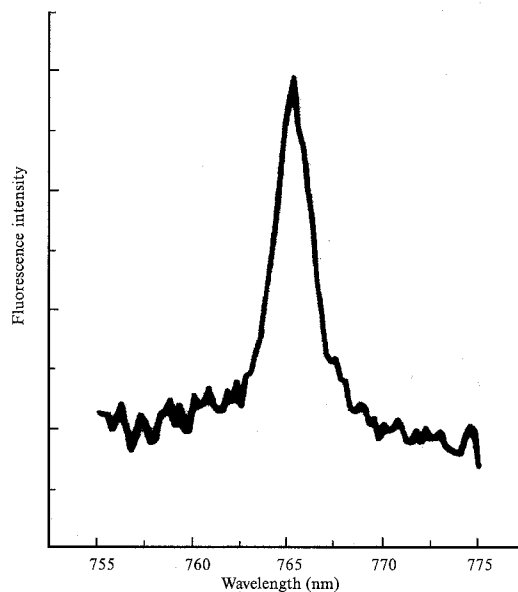


Figure 5. Fluorescence spectrum of $NdPc$ doped borate glass

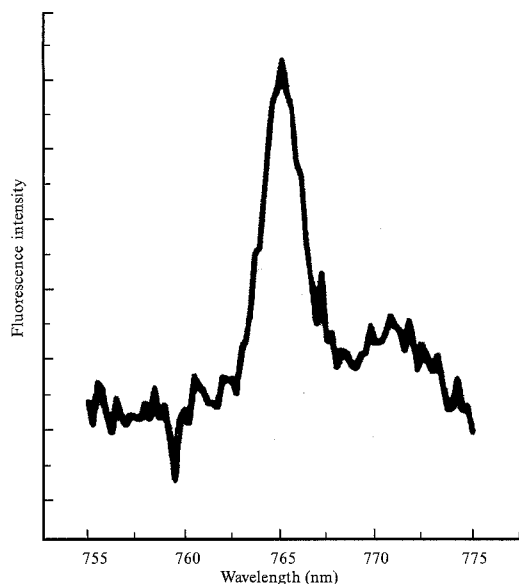


Figure 6. Fluorescence spectrum of SmPc doped borate glass

tical gain and stimulated emission cross section the present VoNc doped borate glass matrix can be effectively utilised in the development of new solid state laser amplifiers capable of producing optical amplification in the NIR region.

For fluorescence measurements all the RePc samples were excited at two wavelengths: 330 nm (corresponding to the B-band) and 700 nm (corresponding to the Q-band). Figures 4–8 show the fluorescence spectra of various Pc doped glassy matrices. All the other spectral data, i.e. emission wavelength, fluorescence bandwidth, relative fluorescence intensity, decay time, stimulated emission cross section and optical gain are summarised in Table 3. If we plot the absorption spectra of all these samples⁽⁸⁾ and the corresponding emission spectra in the same plot it can be easily noted that the shapes of the fluorescence bands are almost the mirror image of the absorption lineshapes as is observed in other matrices, namely, crystals, vapours and

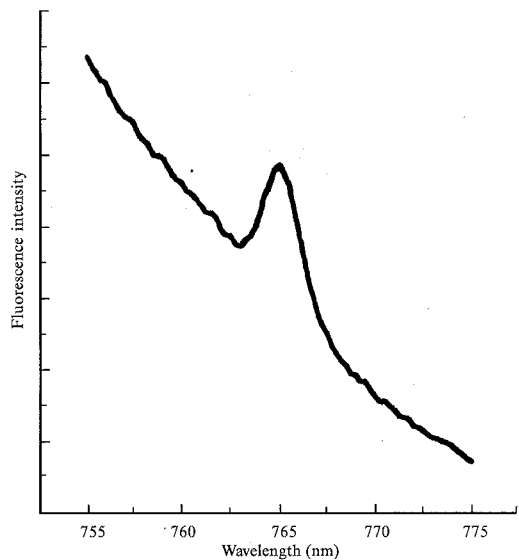


Figure 7. Fluorescence spectrum of LaPc doped borate glass

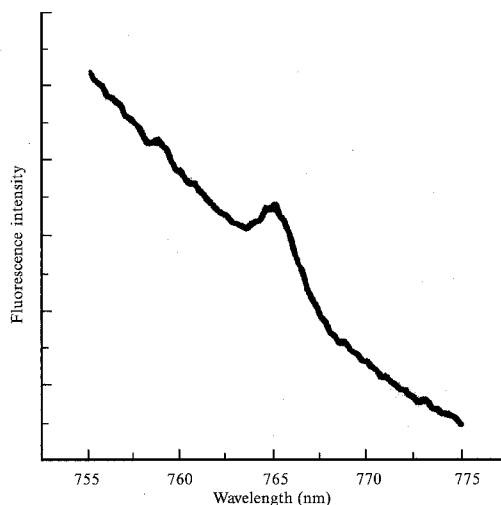


Figure 8. Fluorescence spectrum of EuPc doped borate glass

other solvents.^(9–14) Because of this ‘mirror image fluorescence’ we can apply the Stickler–Berg formula⁽¹⁵⁾ for evaluating the fluorescence decay time (τ). The expression is

$$1/\tau = 2 \cdot 88 \times 10^{-9} n^2 v_{em}^2 \frac{\int F(\nu) d\nu \int \epsilon(\nu) d\nu}{\int F(\nu) d\nu} \quad (2)$$

where $F(\nu)$ is the fluorescence lineshape function and $\epsilon(\nu)$ the molar extinction coefficient.

Knowing the decay time (t) and fluorescence linewidth ($\Delta\lambda$) the stimulated emission cross section (σ_e) can be evaluated using the equation⁽¹⁶⁾

$$\sigma_e = \lambda^4 / 8\pi c n^2 \tau \Delta\lambda \quad (3)$$

The results summarised in Table 3 clearly show that all samples give intense fluorescence in the 765 nm region irrespective of exciting wavelength. According to Kasha⁽¹⁷⁾ transitions involving emission in condensed organic molecules always take place from the lowest excited electronic level independently of the order of levels to which the molecules were excited upon absorption of light. The relative fluorescence intensity is found to be maximum in SmPc doped matrix, whereas it is observed to be minimum in the H₂Pc doped matrix. Emission cross section is calculated to be maximum in EuPc ($9 \cdot 29 \times 10^{-14} \text{ cm}^2$) whereas it is minimum in LaPc

Table 3. Radiative parameters of various phthalocyanine doped borate glass matrices

Pc-S	λ_{ex} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	I_p	τ (ns)	σ $\times 10^{14} \text{ cm}^2$	G (dB/cm)
H ₂ Pc	330	762.5	—	0.00014	4.7	3.3	35.1
	700	763.4	—	0.00012			
NdPc	330	765.1	2.31	0.43	1.6	4.0	17.8
	700	764.8	2.15	0.16			
SmPc	330	765.3	2.41	1.0	1.15	4.43	19.4
	700	765.3	3.09	0.99			
LaPc	330	765.1	1.87	0.77	8.55	1.25	5.6
	700	765.0	1.47	0.36			
EuPc	330	765.2	1.33	0.08	1.78	9.29	41.1
	700	764.9	0.95	0.05			

($1.25 \times 10^{-14} \text{ cm}^2$). This is extremely high compared to the emission cross section of all the laser dyes reported so far.⁽¹⁸⁾ The calculated optical gain values (G) vary in the sequence EuPc > H₂Pc > SmPc > NdPc > LaPc. Because of the high optical gain and stimulated emission cross section, the present EuPc doped borate matrix can be effectively considered as an efficient solid state active medium capable of optical amplification in the 765 nm region. The results also show that the metal ion Eu favours optical amplification processes while Sm, Nd and La ions hinder these processes in H₂Pc matrices.

Conclusions

The preparation of naphthalocyanine doped borate glasses is reported for the first time. Optical absorption parameters of these glasses show a strong dependence on the nature of the central metal atom of the Nc ring. Optical band gap energies of these glasses lie in the range $1.6 \text{ eV} \leq E_g \leq 2.1 \text{ eV}$. All samples except EuNc are found to be intensely fluorescing in the 765 nm region with the emission cross section lying in the range $0.71 \times 10^{-18} \text{ cm}^2$ to $4.57 \times 10^{-18} \text{ cm}^2$. Out of all the samples studied the VoNc doped sample is found to have the maximum optical gain. It is also observed that among the phthalocyanine based matrices the EuPc matrix is a better candidate in realising optical amplification.

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