

Emission spectral studies of phthalocyanines in borate glass matrix

G. A. KUMAR, V. P. N. NAMPOORI, C. P. G. VALLABHAN

Solid State Electronics Division, International School of Photonics, Cochin University of Science & Technology, Kochi-682 022, India

G. JOSE, N. V. UNNIKRISHNAN

School of Pure & Applied Physics, Mahatma Gandhi University, Kottayam-686 560, India
E-mail: spapforum@vsnl.com

Organic semiconductors play a very important role in today's high technology applications viz. 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 the phthalocyanines (Pc), naphthalocyanines (Nc) and porphyrines (PP) are of special significance because of their inexpensiveness, thermal and environmental stability, non toxicity 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. Moreover, because of their excellent optical absorption efficiency in the red or NIR region they can be effectively utilized as a laser dye also. Most of the studies reported so far discuss the optical characterization of these organic semiconductors either in thin films, crystals, vapor or other solvents [4] whereas no work has been made to study the optical properties of these molecules in solid matrices especially work has been made to study the optical properties of these molecules in solid matrices especially a glassy matrix. Except for some studies in certain organic glassy matrices [5] only a limited amount of work has been done in organic matrices also. Recently our group has synthesized borate glassy matrices doped with metalated phthalocyanines and rare earth doped phthalocyanines and studied their optical absorption characteristics [6, 7] The purpose of the present communication which is a continuation of the earlier work is to study the stimulated emission characteristics of metalated phthalocyanine molecules in borate glass matrix with the intention of using them as efficient active media for solid state lasers.

All the glass samples were prepared by the well known rapid quenching technique [8]. Reagent grade boric acid (H_3BO_3) and doubly sublimed phthalocyanines have been used as the starting materials for the preparation of the glass samples. The weighed quantities of the starting materials for 18 gm of glass were mixed homogeneously using an agate mortar. The batch was then placed in a silica crucible and heated in an electric muffle furnace. A slow heating was initially maintained until the temperature reached $80^\circ C$ and decomposition of H_3BO_3 to B_2O_3 was complete. The temperature was then rapidly increased to $120^\circ C$ so

as to obtain a bluish melt. The melt 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 $60^\circ C$ and subsequently polished with water free lubricants. All the samples were obtained with very good transparency and appeared to be of good optical quality. Glass rods of length 8 cm, having diameter of 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 vapor originating as a result of the decomposition of H_3BO_3 a vacuum trap was provided in between the rotary inlet and the sample tube. The tube was kept in a 1 m long vertical heater, the temperature of which can be controlled externally. After melting, the heater was switched off and the melt allowed to cool to room temperature by keeping it inside the heater itself. Finally the tube was taken out and glass rod removed by breaking the glass tube.

The amorphous nature of the glass samples were confirmed by X-ray diffraction spectra recorded on a Shimadzu X-ray diffractometer with Ni filtered $Cu K_\alpha$ radiation. The absorption spectra were recorded in the UV-VIS-NIR region with a Hitachi U-2000 spectrophotometer. All the emission spectra were recorded at room temperature using a SPEX spectrofluorimeter with a wavelength resolution of ± 0.2 nm.

In all the fluorescence measurements the samples were excited at two wavelengths viz. 330 nm (corresponding to B band) and 700 nm (corresponding to Q band). Figs 1 to 8 show the fluorescence spectra of various Pc doped glassy matrices. All the other spectral data viz. emission wavelength, fluorescence bandwidth, relative fluorescence intensity, decay time and stimulated emission cross section are summarized in Table I. If we plot the absorption spectra of all these samples [6] and the corresponding emission spectra in the same plot it can be easily noted that the fluorescence spectra is almost the mirror image of the absorption lineshape as is observed in other matrices viz. crystals, vapors and other solvents [9–11]. Because of this "mirror image fluorescence" we can apply the Stickler-Berg formula [12] for evaluating the fluorescence decay time (τ) and the expression is given by

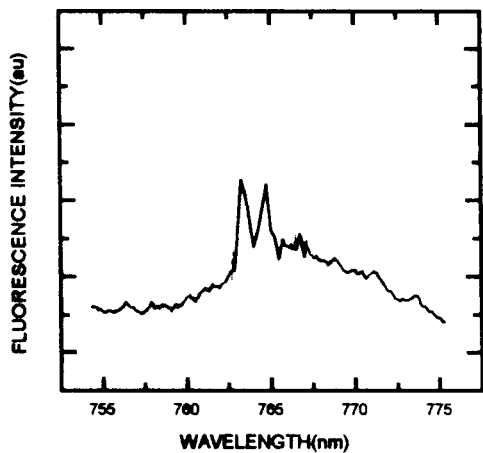


Figure 1 Fluorescence spectrum of H₂Pc doped borate glass.

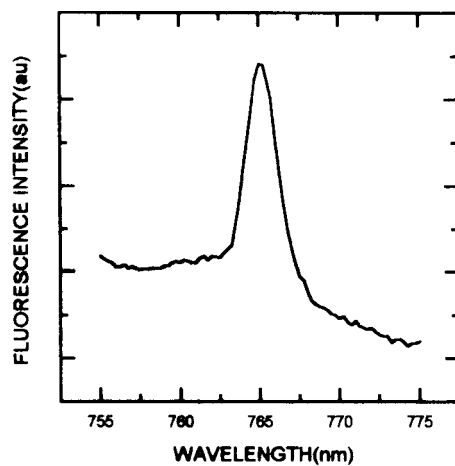


Figure 4 Fluorescence spectrum of NiPc doped borate glass.

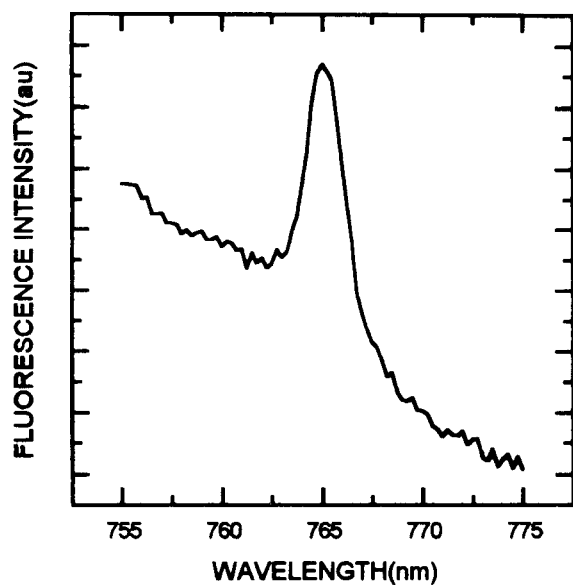


Figure 2 Fluorescence spectrum of MnPc doped borate glass.

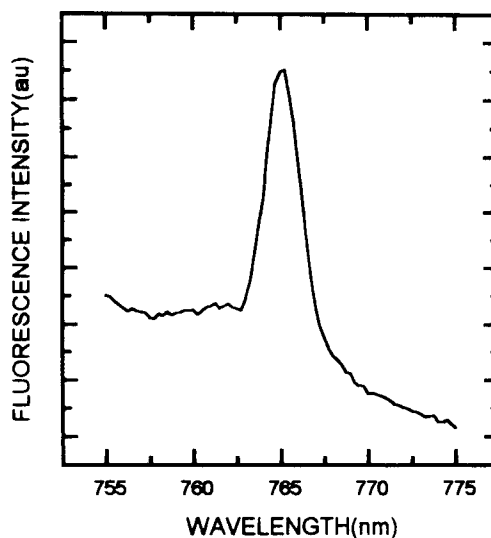


Figure 5 Fluorescence spectrum of CoPc doped borate glass.

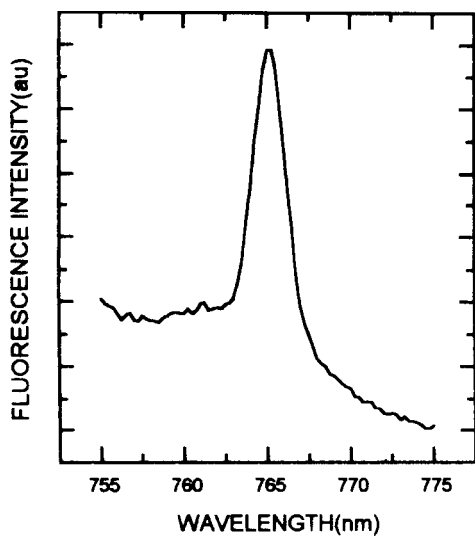


Figure 3 Fluorescence spectrum of FePc doped borate glass.

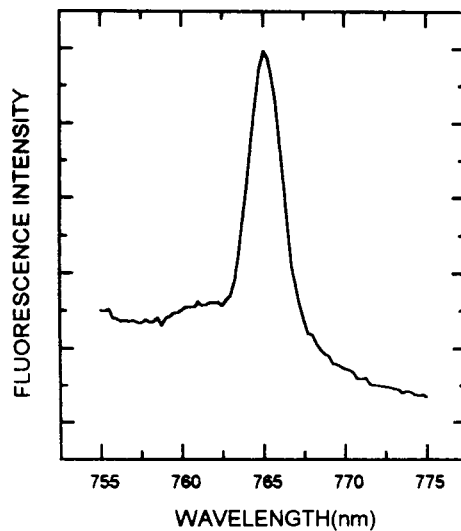


Figure 6 Fluorescence spectrum of CuPc doped borate glass.

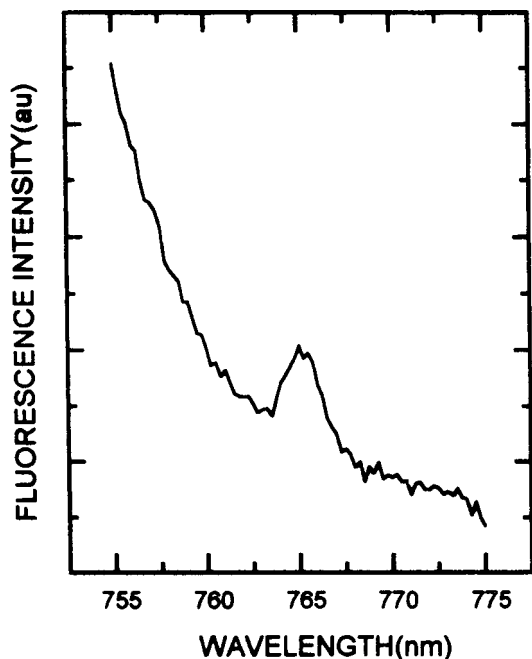


Figure 7 Fluorescence spectrum of ZnPc doped borate glass.

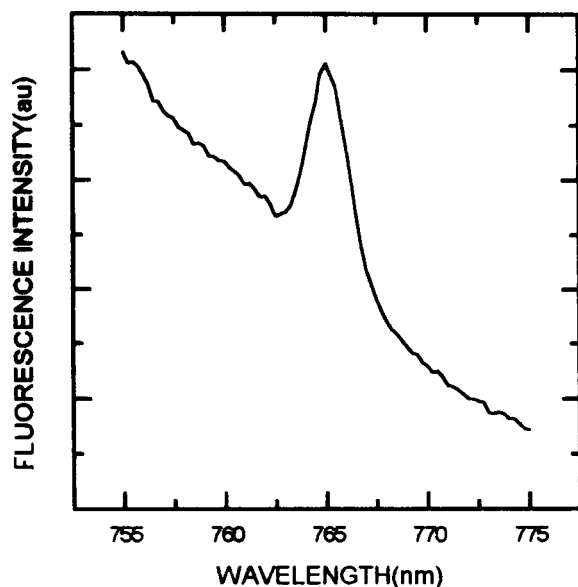


Figure 8 Fluorescence spectrum of MoOPc doped borate glass.

$$\frac{1}{\tau} = 2.88 \times 10^9 n^2 v^2 \frac{\int_{em} F(\nu) d\nu \int_{abs} \varepsilon(\nu) d\nu}{\int_{em} F(\nu) d\nu} \quad (1)$$

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

$$\sigma_E = \frac{\lambda^4}{8\pi c n^2 \tau \Delta\lambda} \quad (2)$$

Knowing the decay time and the fluorescence linewidth the stimulated emission cross-section (σ_c) can be evaluated using the equation [13].

According to Kasha [14] 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. Consequently, the radiative

TABLE I Radiative parameters of various phthalocyanine doped borate glass matrices

Pc-S	λ_{ex} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	I_p	τ (ns)	$\sigma_c \times 10^{14} \text{cm}^2$
H ₂ Pc	330	762.5	—	0.00014	4.7	3.3
	700	763.4	—	0.00012		
MnPc	330	765.3	1.99	0.07	2.36	4.13
	700	765.0	1.61	0.05		
FePc	330	765.4	2.13	0.43	1.22	6.02
	700	765.2	2.15	0.16		
NiPc	330	763.1	3.23	0.22	1.66	2.04
	700	765.0	4.63	0.09		
CoPc	330	765.1	2.15	0.48	0.69	10.6
	700	765.2	2.15	0.19		
CuPc	330	765.2	2.05	0.11	0.15	48.3
	700	765.1	2.17	0.06		
ZnPc	330	765.3	1.87	0.03	0.60	15.1
	700	765.2	1.73	0.29		
MoOPc	330	764.9	2.15	0.57	8.9	0.34
	700	765.0	5.19	0.22		

parameters corresponding to the Q-band excitation are evaluated. (Table I). The results clearly show that all the samples give intense fluorescence in the 765 nm region irrespective of the exciting wavelength. The relative fluorescence intensity is found to be a maximum in a MoOPc doped matrix whereas it is observed to be a minimum in the H₂Pc doped matrix. Variations of the relative fluorescence intensity among the metal substituted phthalocyanines can be accounted for in terms of the effect of spin-orbit interaction, electronegativity and ionic radius of the central metal ion. Fig. 9 shows the variation of the fluorescence band intensities (corresponding to B band and Q-band excitation) with the atomic number of the central ion. The effect of the spin-orbit interaction is to reduce the fluorescence intensity by intersystem crossing whereby the phosphorescence intensity is considerably enhanced [15]. The spin-orbit interaction is found to increase with atomic number of the central metal atom. In the present case the decrease in the fluorescence intensity from Co to Zn can be accounted for based on this effect whereas in the case of other metals the result is contrary to spin-orbit effect. For H₂Pc the fluorescence intensity

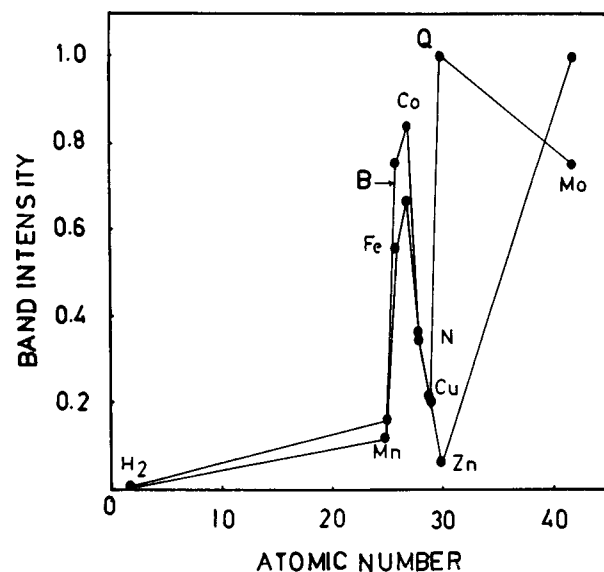


Figure 9 Variation of fluorescence intensity with atomic number.

is found to be the least and this can be accounted for in terms of the electronegativity and ionic radius effects. For H₂ electronegativity as well as ionic radius are found to be maximum and the variations are in the sequence Mn < Zn < Ni = Co = Mo = Fe < Cu < H₂ (electronegativity), Mo < Ni < Zn = Fe < Mn < Co = Cu < H₂ (ionic radius). Because of this there should be greater overlap between the pyrole nitrogen orbitals and those of H₂ ion. This would tend to perturb the charge cloud even more with a consequent increase in spin-orbit perturbation. Even though these are some of the reasons for the variations in the fluorescence intensity among the various metal phthalocyanines, the exact reasons for the arbitrariness in the variation of fluorescence intensities with atomic number, ionic radius and electronegativity need further investigations.

The emission cross-section was calculated to be a maximum in CuPo ($48.3 \times 10^{-14} \text{ cm}^2$) whereas it is a minimum in NiPc ($2.04 \times 10^{-14} \text{ cm}^2$). This is extremely high compared to the emission cross-section of all the laser dyes reported so far [16] and hence the present dye doped borate matrix can be effectively considered as an efficient solid state active medium capable of optical amplification in the 765 nm region.

In this letter, fluorescence spectral analysis of various phthalocyanines doped borate glasses have been reported for the first time. Irrespective of the excitation wavelength almost all the samples show intense fluorescence in the 765 nm region. However, the emission intensity, fluorescence bandwidth, decay time and emission cross section are found to be varying from one to another. Even though the fluorescence intensity variation among the various Pc-s can be accounted for to some extent by considering the effect of spin-orbit interaction, electronegativity and ionic radius of the central metal atom, the exact reason for the arbitrariness is unknown. Emission cross sections of these newly developed glasses is found to be many times larger than other dye doped glass systems which make them good candidates for application in a typical glass laser system.

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