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Physical and optical properties of phthalocyanine doped inorganic glasses

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Physical and optical properties of various free base and metallic phthalocyanine (Pc) doped glass matrix are reported for the first time. Absorption spectral measurements of H_2Pc, MnPc, NiPc, CoPc, CuPc, MoOPc, ZnPc and FePc doped borate glass matrix have been made in the 200–1100 nm region and the spectra obtained are analyzed in the 2.1–6.2 eV region to obtain the optical band gap (E_g) and the width of the band tail (E_t). Other important optical and physical parameters viz. refractive index (n), molar extinction coefficient (ε), density (ρ), glass transition temperature (T_g), molecular concentration (N), polaron radius (r_p), intermolecular separation (R), molar refractivity (R_m) are also reported.
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1. Introduction

Phthalocyanines are a class of organic compounds which have received considerable attention from scientists because of their potential applications in a variety of fields. Their unique properties include excellent semiconductivity, photoconductivity, chemical stability and optical absorption in the UV-VIS region. Some of the most important applications of these organic molecules are in the fabrication of solar cells, electronic displays, chemical sensors and also as efficient laser dyes . Most of the studies conducted so far on Pc-s are either in film, vapor or in any solvent medium, whereas only a limited amount of work has been reported in solid matrices which include some studies conducted by Lucia *et al.* [1] in thermoplastic media. In this report, we have determined some of the unique physical properties of free and metallated phthalocyanine doped borate glasses. It is recognized that the physical properties of phthalocyanines are affected by the metal ions and for glass science and technology, it is important to clarify the origin of the variation of these properties in glasses containing metal ions. Particularly, we focus our attention on the effect of metal ions on glass transition temperature, density, molar extinction coefficient, molecular concentration, intermolecular separation and polaron radius.

We have also extended our measurements to examine carefully the main optical absorption edge and the optical energy gap in the UV and visible spectral range. The optical absorption depends strongly on the electronic band structure and the same can be analyzed in terms of modern theoretical ideas of glassy materials. Thus it is quite desirable to study the nature of absorption edge and determine the energy gap of the present glassy systems. An attempt has also been made to see the effect of various metal ions on the absorption edge, optical energy gap and tailing of the band gap.

2. Experimental

All the glass samples were prepared by the well known rapid quenching technique [2]. Reagent grade boric acid (H_3BO_3) and doubly sublimed Pc-s have been used as the starting materials for the preparation of the glass samples. Weighed quantities of the starting materials for 18 g of glass are mixed homogeneously using an agate mortar. The batch was then placed in a silica crucible and heated in an electric furnace. To ensure that the metallophthalocyanines did not undergo thermal decomposition, the glass forming and processing temperatures were kept well below the thermal decomposition temperature ($\geq$450°C). A slow heating was initially maintained until the temperature reaches 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 minutes 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 well with water free lubricants. All

the samples have been obtained with very good transparency and appear to be of good optical quality.

The amorphous state of the prepared samples were confirmed by x-ray diffraction spectra recorded on a Shimadzu X-ray diffractometer with Ni filtered Cu K_α radiation. Densities were measured by Archemedes' method using xylene as the immersion liquid. The refractive index (n) was measured by the Brewster's angle method. The absorption spectra were recorded in the UV-VIS-NIR region with a Hitachi U-2000 spectrophotometer.

3. Results and discussion

A representative absorption spectrum corresponding to CuPc in the borate glass matrix is shown in Fig. 1. The sample concentrations were established through the Equation [3].

$$N = \frac{A}{\varepsilon l} \tag{1}$$

with known values of the absorbance A and the molar extinction coefficient ε obtained from the absorption spectra, and the sample thickness l. The molecular separation, polaron radius and the molecular refractivity are defined through the following expressions [3, 4]

$$R = (1/N)^{1/3} \tag{2}$$

$$r_p = 1/2(\pi/6N)^{1/3} \tag{3}$$

$$R_m = M/\rho(n^2 - 1/n^2 + 2) \tag{4}$$

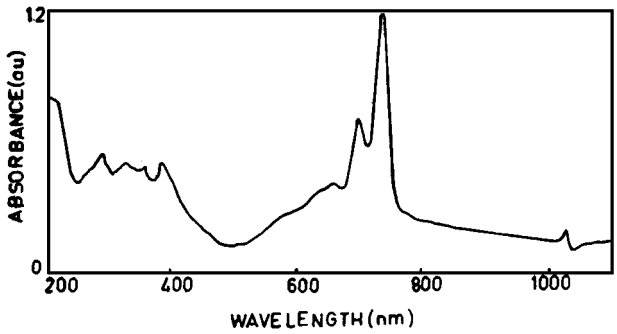

Figure 1 Typical absorption spectrum of CuPc doped borate glass.

where N is the molecular concentration, M the molecular weight, ρ the density, and n the refractive index.

The calculated values of the physical and optical parameters are summerised in Table I. Among the eight glass samples prepared MoOPc doped sample is found to have maximum density (2.2 g/cm^3) while minimum for NiPc doped sample (1.55 g/cm^3). The glass transition temperature (T_g) is found to be unaffected by the change of metal ions whereas the refractive index shows some variations in the range 2.6–1.58. Since the high dopant concentration is found to affect the glass transparency considerably we have fixed the dopant concentration as 0.002 g in all the cases. Hence, as expected the molecular concentration do not show wide variation among the eight samples studied. The same is the case with the other two parameters viz. polaron radius and intermolecular separation. The polaron radius, r_p in all cases is less than the corresponding intermolecular separation, which is in accordance with the usual prediction of polaron theory that the polaron radius should be smaller than the site separation and greater than the radius of the ion in which the electron is localised. The molar refractivity values do not show a definite dependance with the metal atoms as one goes from the free base to various metallated matrices with increasing order of molecular weight.

In many amorphous materials in general and oxide glasses in particular, it is usual to analyse the optical absorption at the fundamental edge in terms of a theoretical treatment given in general form by Davis *et al.* [5] and Demichelis *et al.* [6]. In this treatment the absorption data follow a power law

$$\alpha h\omega = A\{h\omega - E_g\}^n \tag{5}$$

and yield values of the optical energy (E_g). Here A is a constant and n is an index which can assume values of 1, 2, 1/2 or 3/2 depending on the nature of the band to band electronic transitions and the profile of the electron density in the valance and conduction bands. The experimental data have been fitted with the theoretical Equation 5 with different values of n using the ORIGIN software package. As expected, the best fit was obtained for $n = 2$ which is the characteristic behaviour of indirect transitions in non-crystalline materials. In

TABLE I Physical and optical properties of Pc doped borate glasses

Pc-s	ρ (g/cm^3)	n	ε 10^{-4} (l/mol cm)$^{-1}$	T_g (°C)	N (10^{18} mol/cm^3)	r_p (nm)	R (nm)	R_m (cm^3)	E_g (eV)	E_t (eV)
H_2Pc	1.83	2.41	5.80	240	2.34	3.03	7.53	173	1.88	0.52
MnPc	1.77	2.61	6.81	240	2.18	3.10	7.71	211	2.16	0.48
FePc	1.76	1.99	3.96	240	2.11	3.14	7.79	93	2.11	0.52
NiPc	1.56	2.47	6.10	240	2.01	3.19	7.92	231	1.73	0.62
CoPc	1.76	1.62	2.62	240	2.09	3.15	7.82	113	2.14	0.54
CuPc	1.74	1.58	2.49	240	2.09	3.15	7.82	110	2.23	0.55
ZnPc	1.90	2.43	5.90	240	2.08	3.15	7.83	189	1.76	0.53
MoOPc	2.20	2.60	6.76	240	1.92	3.24	8.04	187	2.04	0.52

ρ the density; n the refractive index; ε the molar extinction coefficient; T_g the glass transition temperature; N the molecular concentration; r_p the polaron radius; R the intermolecular separation; R_m the molar refractivity; E_g the optical band gap; E_t the Urbach bandwidth.

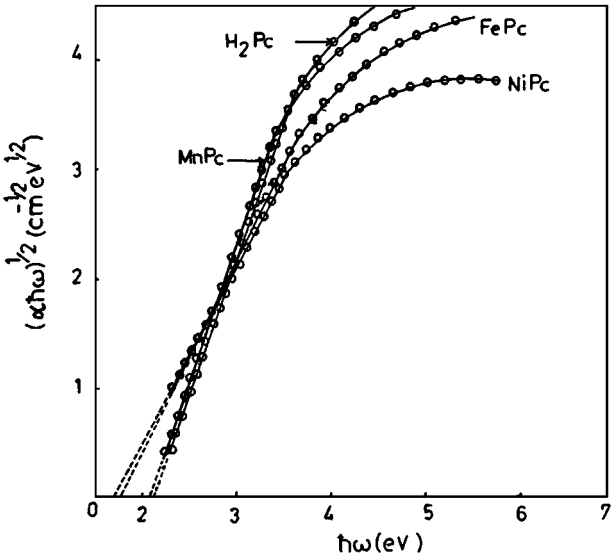

Figure 2 $(\alpha h\omega)^{1/2}$ against photon energy for MnPc, FePc, NiPc and H_2Pc doped borate glasses.

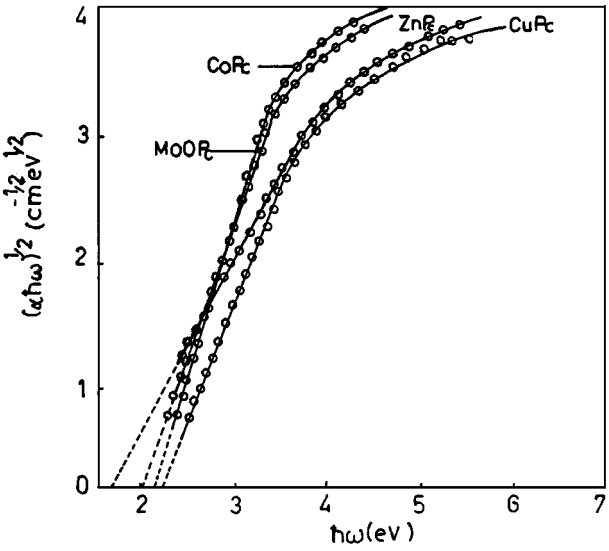

Figure 3 $(\alpha h\omega)^{1/2}$ against photon energy for MoOPc, CoPc, CuPc and ZnPc doped borate glasses.

the context of indirect transitions, the lowest minimum of the conduction band and the highest maximum of the valance band lie in different regions of k-space and the observed indirect transitions may be associated with transitions from the top of the valance band to the bottom of the conduction band.

Figs 2 and 3 show the functional dependence of $(\alpha h\omega)^{1/2}$ on $h\omega$ for all the samples investigated. The extrapolation of the absorption curve $(\alpha h\omega)^{1/2}$ vs $h\omega$ to the value $(\alpha h\omega)^{1/2} = 0$ yields the value of E_g. The magnitudes of E_g obtained from these curves are listed in Table I. The band gaps show a nearly steady value of $\approx$2 eV throughout the glass samples which points to the fact that it is unaffected by the nature of the central metal atom of the Pc ring. The optical band gap is closely related to the energy gap between valance band and conduction band. In glasses the latter is strongly influenced by the anions [7]. The s and p orbitals of B^{3+} and s orbitals of O^{2-} interact with each other to form bonding and antibonding states which contribute to valence band and conduction band, respectively. Since in the present case the amount of B_2O_3 is always fixed the bonding and antibonding states remain the same and hence will not affect the band gap.

In glasses and amorphous materials the disorder phonon assisted processes are associated with the tailing into the normally forbidden energy band gap of the density of states curve. The origin of this band tailing is still a matter of conjecture but according to Dow and Redfield [8] it arises from the random fluctuations of the internal fields associated with structural disorder which are considerable in many amorphous solids. The amount of tailing can be estimated to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [9] and which has been applied to many glassy materials. The absorption edge of non metallic materials gives a measure of the energy band gap and the exponential dependence of the absorption coefficient α on photon energy $h\omega$ is found to hold over several decades for a glassy material and takes the form

$$Ln(\alpha) = Ln(B) - (h\omega/E_t) \qquad (6)$$

where B is a constant and E_t is interpreted as the width of the tail of localized states in the forbidden band gap. Figs 4 and 5 represent the linear dependence of the natural logarithm of absorption coefficient, Ln(α) on the photon energy $h\omega$ for all the samples studied.

The reciprocal of the slope of each line yields the magnitude of E_t and are collected in Table I. This also shows almost a steady average value of 0.54 eV irrespective of the change in the central metal atom. This value is more in line with the range of values reported in many oxide glasses. This suggests that the bonding in these materials is more like that of typical borate glasses.

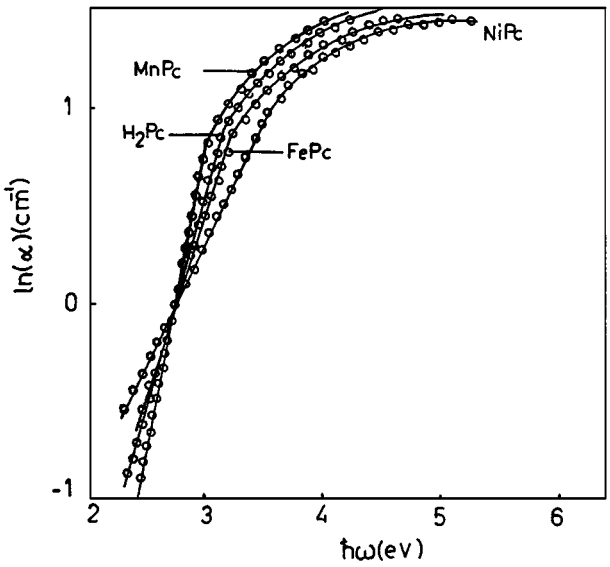

Figure 4 Ln (α) against photon energy ($h\omega$) for MnPc, FePc, NiPc and H_2Pc doped borate glasses.

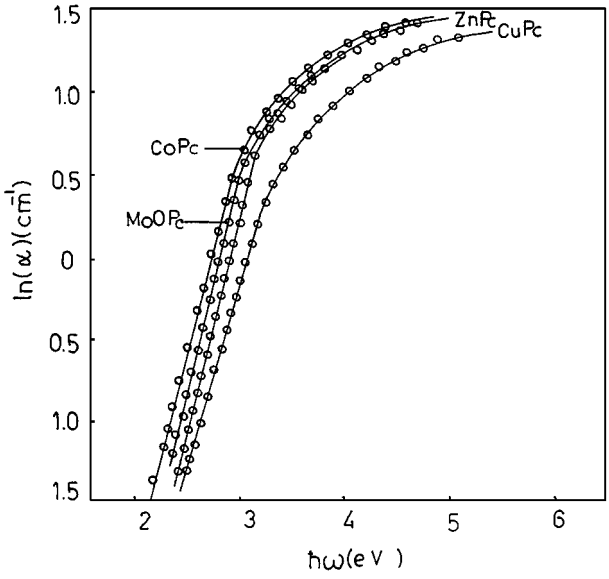

Figure 5 Ln (α) against photon energy ($h\omega$) for MoOPc, CoPc, CuPc and ZnPc doped borate glasses.

4. Conclusions

The preparation of Pc doped borate glass is reported for the first time. The recorded optical absorption spectra show very good absorption in the UV-VIS-NIR region. In general, the measured parameters viz. refractive index, molar extinction coefficient, density, glass transition temperature, optical band gap and width of the band tail of the Pc doped glasses do not show wide variation among the samples. The tailing of the bands is found to be responsible for the phonon assisted indirect electronic transitions. It is observed that the substituent metal atoms can modify the energy band gap of free base phthalocyanine doped borate matrices while these atoms have no significant effect on the width of the band tail.

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