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Photoluminescence of lead phthalocyanine thin films

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The thin films of Lead Phthalocyanine (PbPc) on glass substrates were prepared by Vacuum deposition method. The thicknesses of the films were 150 nm, 300 nm and 450 nm. The thickness 450 nm sample is annealed in high vacuum at 303 K and 373 K temperature. The sample have been analysed by Photoluminescence, transmittance and absorption. Transmission and photoluminescence (PL) properties were measured in Lead Phthalocyanine (PbPc). A thin-film and a single crystal of PbPc were used for the measurements. These measured spectra were compared to theoretical values. The range of wavelengths used was different due to the different methodologies used for the measurements. It shows the variation of transmittance, absorption and Photoluminescence with wavelength of PbPc films for different thicknesses.

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Keywords: Lead, Phthalocyanine, Photoluminescence, Transmittance and absorption

1. Introduction

Photoluminescence (PL) is the spontaneous emission of light from a material under optical excitation. In recent years, a lot of effort has gone into the search of organic donor acceptor systems for providing an efficient light induced charge transfer (1). The large scale availability of organic semiconductors now enables technological photonic applications such as organic light emitting diodes (OLEDs) and organic solar cells [2–4]. One of the most attractive properties of organic semiconductors is the possibility to combine and chemically alter the materials to fit a specific application. Analysis of photoluminescence helps to understand the underlying physics of the recombination mechanism. In general, nonradiative process is associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus material quality can be measured by quantifying the amount of radiative recombination. When these states have radiative levels, they are readily identified in the PL spectrum, and the size of the associated PL peaks provides a relative measure of their presence in the sample. However, measuring the absolute density of these states is a far more formidable task and typically requires an exhaustive analysis of the excitation intensity dependence of the PL signal.

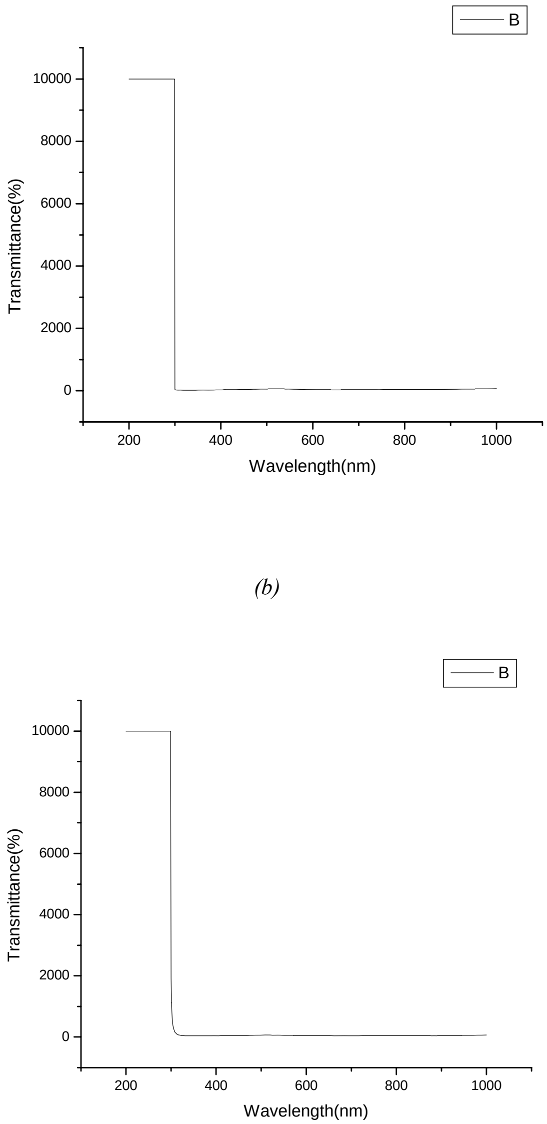
2. Experimental

The powder of lead phthalocyanine (80% dye, sigma Aldrich company, Bangalore, India) was kept in a molybdenum boat of 100 amps and heated with high current controlled by a transformer. The transformer is capable of supplying 150amps at 20volts is used to provide the accessory current for heating the molybdenum source which was used for the evaporation process. To prior evaporation, the evaporant material was carefully degassed at lower temperature for about 45 minutes with the shutter closed. Deposition of PbPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr was achieved by slowly varying the current. The rate of evaporation was properly controlled and maintained constant during all the evaporations. Rotary drive was employed to maintain uniformity in film thickness. The film thickness was controlled to be 150 nm, 300 nm and 450nm by Quartz crystal monitor. The adhesion of the films to the substrate seems to be extremely good.

3. Results and discussion

3.1 Transmittance and absorption coefficient

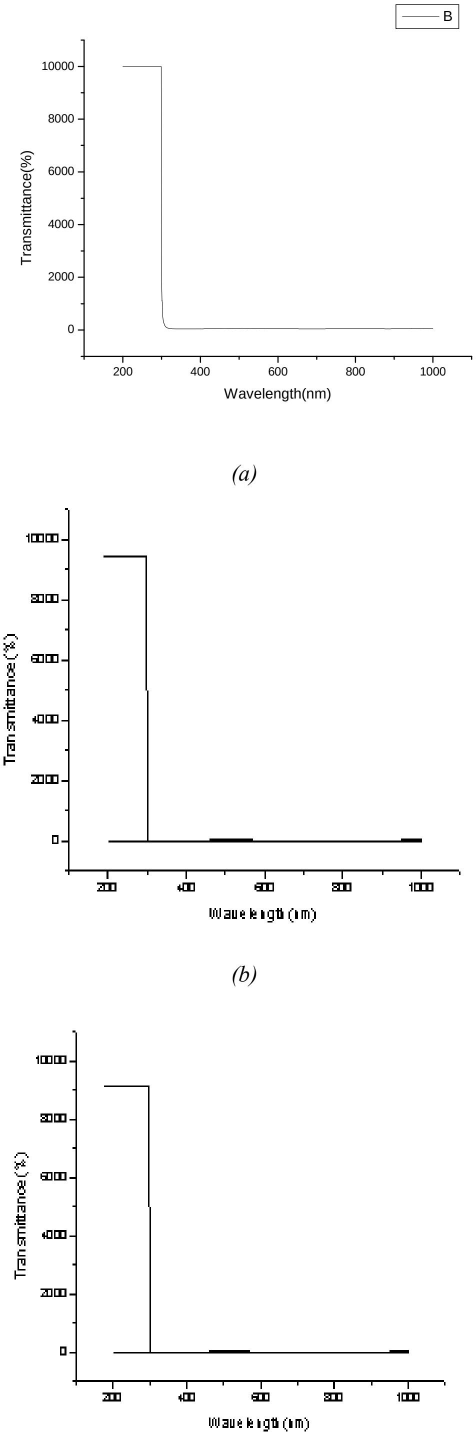
The transmittance of the thin-film for different wavelengths when plotted takes the form is shown in Fig. 1. It shows the variation of transmittance with wavelength of PbPc films for different thicknesses. It reveals that transmittance vary independently with film thickness. Fig. 2 shows the transmittance spectra of PbPc films for thickness 450 nm at different annealed temperatures. It is observed that transmittance decreases with increase in temperatures. The absorption edge energy decreases with increasing wavelength. All the samples show a absorption edge at 299 nm wavelength.



(b)

(c)

Fig. 1. Transmittance of PbPc Thin film for thickness.(a) 150 nm; (b) 300 nm; (c) 450 nm.



(a)

(b)

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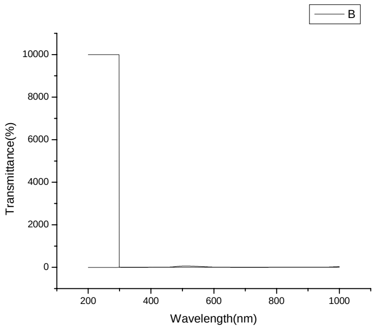
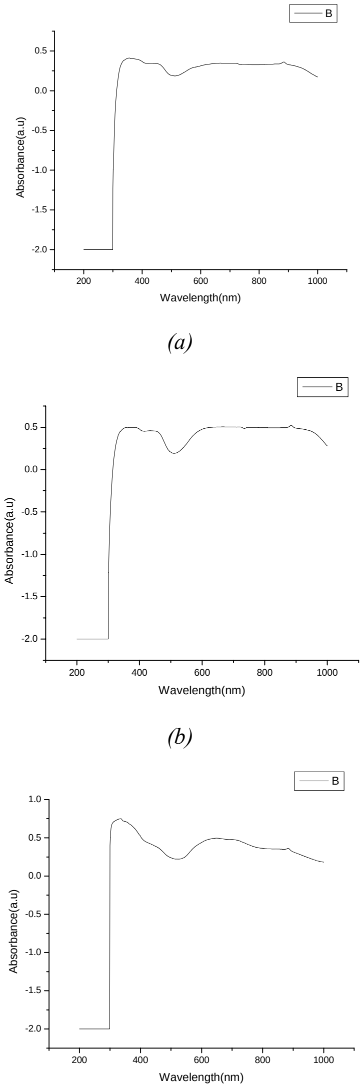
Fig. 2. Transmittance of PbPc Thin film for thickness 450 nm at annealed temperatures: (a) 303; (b) 323 K; (c) 373 K.

The variation of absorbance with wavelength of PbPc films for different thicknesses is shown in Fig. 3. It is observed from the above figures that absorbance vary independently with film thickness. The variation of absorbance with wavelength of PbPc films at different annealed temperatures are shown in Fig. 4.





(a)

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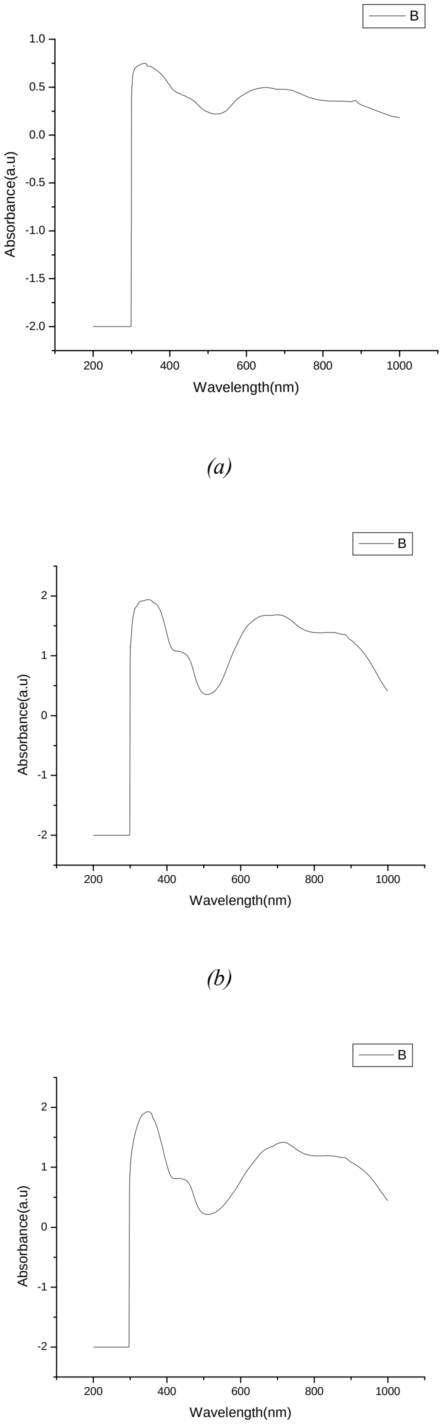
Fig. 3. Absorbance of PbPc Thin film for thickness: (a) 150 nm; (b) 300 nm; (c) 450 nm.



(a)

(b)

(c)

Fig. 4. Absorbance of PbPc Thin film for thickness 450 nm at annealed temperatures: (a) 303 K; (b) 323 K; (c) 373 K.

The spectrums reveal that the absorbance increases with increase in annealed temperatures. Apart from these two measurements, a set of data was recorded to measure the reflection coefficient *R*. the result obtained from the above experiment are given in the table (Table 1). The absorption spectrum of the evaporated film of PbPc measured against a clean glass slide as reference shows a strongly broadened Q-band in the red and near infrared part of the spectrum. This is due to a π–π interaction of the PbPc molecules in a close packed film that leads to a Davydov splitting and broadening of the absorption peak. The antireflection effect of the thin PbPc film on the glass slide leads to the negative values for the extinction around 350 nm.

Table 1. Result of the reflectance measurement.

S. No.	Input signal (mA)	Reflected signal (mA)	Average input (mA)	Average Reflected (mA)	Reflectance	% of R
1	0.396	0.062	0.397	0.08946	0.2253	22.53
2	0.375	0.093				
3	0.398	0.0983				
4	0.409	0.109				
5	0.407	0.085				

3.2 Photoluminescence excitation

Fig. 5 shows the excitation spectra of PbPc thin films. The principle of PL measurements is to create carriers by optical excitation with photon energy above the band gap of the films (2.4eV and 3.3 eV). Electrons and holes relax to their respective ground states in the conduction and valence band. They can then recombine radiatively as most free carrier of excitons.

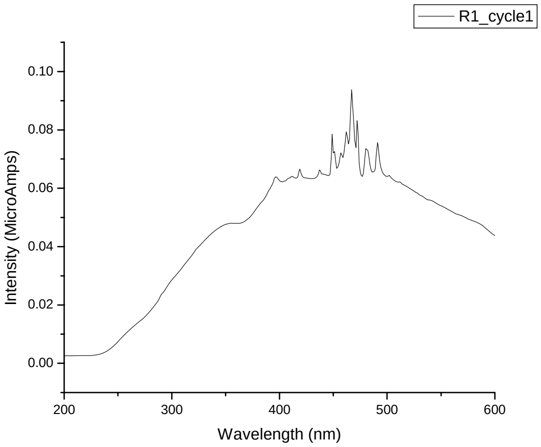


Fig. 5. Excitation spectra of PbPc thin film.

When light energy input is applied to the film there is an electronic transition between two energy levels, E_1 & E_2 (E_2>E_1) with the emission of wavelength λ , where

$$\frac{hc}{\lambda} = E_2 - E_1$$

Invariably E_1 and E_2 are part of two groups of energy levels so that instead of a single emission wavelength a band of wavelength is observed [5].

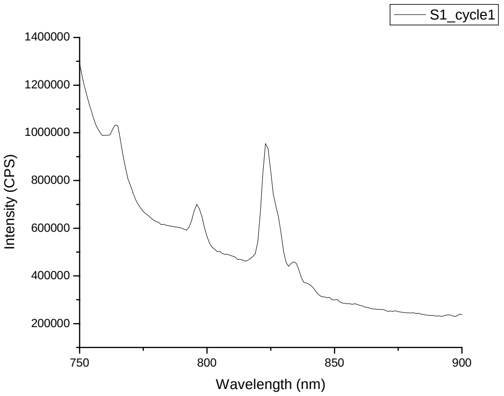


Fig. 6. Photoluminescence spectra of PbPc Thin film for thickness 450 nm.

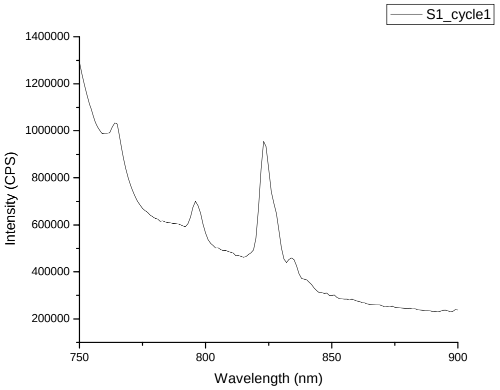


Fig. 7. Photoluminescence spectra of PbPc Thin film for thickness 450 nm at 373 K annealed temperature.

The variation of intensity with wavelength of PbPc films for 450 nm is shown in Fig. 6. The variation of intensity with wavelength of PbPc films at 373 K annealed temperature is shown in Fig. 7.

The excitation energy and intensity will have profound effects on the PL signal. Although the excitation conditions must be considered carefully, the strength of the PL technique relies heavily on the flexibility. Because the absorption of most materials depends on energy, the penetration depth of the incident light will depend on the excitation wavelength. The excitation intensity will influence the result of any PL experiment. The excitation intensity controls the density of photo excited electrons and holes, which governs the behavior of these carriers. Each electron–hole recombination mechanism has a distinct functional dependence on carrier density.

3.3 Penetration depth and Stoke's shift

The absorption of a material depends strongly on the energy of the incident light. In the analysis of surfaces, it is useful to describe this wavelength-dependent absorption by a penetration depth, which is a measure of the thickness of the layer that is probed. In PbPc, above-bandgap excitation has a penetration depth of the order of 1 µm. Hence, PL with above-gap excitation is very sensitive to surface effects. In direct-bandgap material with sub-bandgap excitation, absorption is weaker and the light penetrates deeper into the sample. Here, the PL is dominated by bulk recombination. If multiple excitation wavelengths are available, this property of PL can be used to distinguish surface and bulk contributions. Stoke's shift has been found that the absorption peaks occur at wavelength 350 and 710 nm (Figs. 3 and 4) and emission peak is found at 764 and 822 nm (Figs. 6 and 7). The emission peak occurs at a higher wavelength than that of the absorption peaks. In fact the peak emission wavelength is invariably shifted towards red end of the spectrum compared to the peak of the absorption spectrum. This phenomenon is known as the Stokes shift.

3.4 Effect of excitation power

The excitation energy of the incident light controls a critical property of the PL experiment the density of photo excited electrons and holes. When the carrier density is low, the measurement is dominated by discrete defect and impurity sites at the interfaces and within the bulk of the material. Recombination at these energetically favored sites is frequently referred to as Shockley–Read–Hall (SRH) recombination. The SRH rate is proportional to the dominant carrier density *n*. The dominant carrier density is the greater of two quantities: the equilibrium carrier concentration and the photo excited carrier concentration.

Various excitation powers allow for varying penetration depths into the material and thus varying levels of volume excitation. It can be clearly seen that for low excitation intensity (2.4eV) (Fig 8) the relative intensities of the low energy peaks (1, 2, 3) in the spectrum are larger while the relative intensities of high energy peaks (5, 6, 7, 8) decrease with excitation intensity or pump power (3.3eV) (Fig.9). Energy peaks 1, 2 and 3 result from transitions between excited states. This should require complete filling of the electron and hole ground states and partially filling of the excited states, which is unlikely at the low excitation intensity. The lowest excitation energy peak 1 corresponds to ground state transitions. PL spectra (Fig. 8) consist of 5 bands for the excitation energy is 2.4 eV whereas the spectrum (Fig. 9) has 6 bands for the pump power has been increased to 3.3 eV. Moreover the relative intensity of the peak 3 (IR Emission (IR) band of PbPc) is larger, When the excitation is large. With the increase in intensity of IR band. The lower energy peak often saturates with increasing excitation because of state filling. In this case, the saturation intensity can be used to estimate the size of interface islands in the quantum well where the lower energy PL is believed to originate [6].

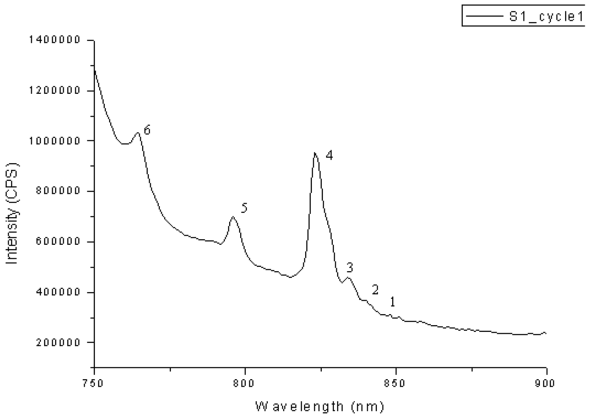


Fig. 8. Photoluminescence spectra of PbPc Thin film (excitation energy 2.4 eV).

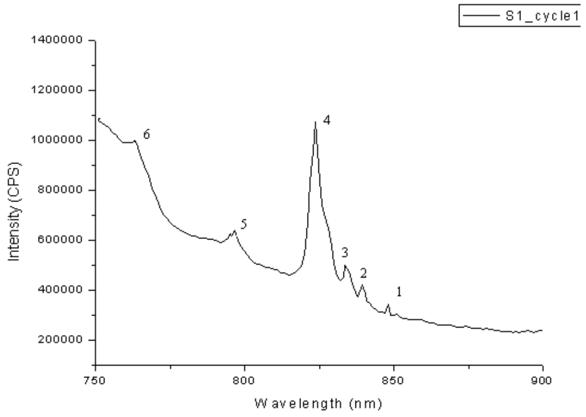


Fig. 9. Photoluminescence spectra of PbPc Thin film (Excitation energy 3.3 eV).

The disappearance of YE (yellow emission) band confirms the improvement of crystalline quality decreasing the density of native defects in the lattice and on increasing the grain size and hence diminishing the total grain boundary surface. The emitted blue radiation may have an appreciable amount of the radiant energy in the ultraviolet region. The ultraviolet radiation may be converted into useful radiation there by the luminous efficiency can be increased. We propose that this concept of coordination between donor-acceptor moieties might also be applied in the production of other organic optoelectronic devices to improve their performance.

4. Conclusions

The transmittance of the thin-film for different wavelengths varies independently with film thickness. Transmittance decreases with increase in annealed temperatures. The absorption edge energy decreases with increasing wavelength. All the samples show an absorption edge at 299 nm wavelength. The absorbance increases with increase in annealed temperatures. Intensity varies independently with film thickness and annealed temperature. Stoke's shift has been found that the absorption peaks occur at wavelength 350 and 710 nm and emission peak is found at 764 and 822 nm. The emission peak occurs at a higher wavelength than that of the absorption peaks. PL spectra consist of 5 bands for the excitation energy is 2.4 eV whereas the spectrum has 6 bands for the pump power has been increased to 3.3 eV. Moreover the relative intensity of the peak 3 (IR Emission band of PbPc) is larger, when the excitation is large.

4.1 Evidence for good polycrystalline quality of the deposited films

The band 4 which is localized approximately at 2.4 eV of green emission (GE) band is due to electronic transitions from the conduction band to an acceptor level due to interstitial sulfur [7]. The bands 5 to 9 localized in the energy region 2.56 to 2.92 eV are attributed to bound excitation [8]. The band 1 to 3 in the energy range 2.19 to 2.28 eV is due to radioactive transitions from donor levels arising in interstitial sites to the valence band [9].The origin of GE band may be due to the recombination of free electrons with trapped holes [10].

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