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COMPARISON OF OPTICAL PROPERTIES OF PbPc AND CuPc THIN FILMS

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Thermally evaporated lead phthalocyanine (PbPc) and copper phthalocyanine (CuPc) films are deposited on a glass substrate of film thicknesses 150 nm, 300 nm and 450 nm. Thickness of 450 nm thin films prepared at room temperature has been annealed at 323 and 373 K. The optical properties and spectral behavior of as deposited and annealed thin films of PbPc and CuPc are studied using spectrophotometric measurements of the transmissivity and reflectivity at normal incidence of light in the wavelength range 200–1400nm. The absorption index, k, Photon energy and α^2 are calculated and it is found that they are independent of film thickness. Indirect allowed transitions near the onset and fundamental absorption edges are observed. The optical absorption spectra of these films are studied.

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Keywords: Phthalocyanine, Transmissivity, Reflectivity,
Spectrophotometric measurements and extinction coefficient

1. Introduction

The search for materials suitable for low cost, versatile electronic devices has stimulated interest in organic thin film transistors[OTFTs] and sensors has led in recent years to an extensive investigation of a range of metal substituted phthalocyanines [1,2]. Application of OTFTs as chemical sensors has shown promise in the development of electronic noses and in nerve agent detection [3-5]. A key issue regarding the widespread production of OTFTs is the long term stability and device integrity in ambient operating conditions [6,7]. Among the small molecule based OTFTs, pentacene OTFTs have received significant attention regarding instability to ambient components such as oxygen and humidity [8-12]. Several mechanisms have been proposed to explain this instability in pentacene OTFTs, including water adsorption in grain boundaries [10,11] and oxygen generated impurities[13].

Phthalocyanines have potential applications in optical logic display devices, electrophotography, security printing, gas detectors [14], solar cells [15, 16], sensitisers and colour filters [17]. These materials are generally p-type semiconductors and have the advantage of being sufficiently stable towards chemicals and heat. They can be easily sublimed, resulting in high purity thin films without decomposition. The physicochemical properties can be altered by changing the metal ion. Film properties of this prototype organic semiconductor are dependent on the evaporation rate, substrate temperature and post-evaporation annealing [17, 18]. This paper deals with optical investigation on lead and copper phthalocyanine thin films.

2. Experiments

The powder of PbPc (80% dye, Sigma Aldrich company, Bangalore, India) is kept in a molybdenum boat (100 A current rating) heated with high current controlled by a transformer. The transformer is capable of supplying 150 amps at 20 volts which is used to provide the accessory

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current for heating the molybdenum source. It is used for the evaporation process. Prior to evaporation, the evaporant material is carefully degassed at lower temperature for about 45 minutes with the closed shutter. Thin films of PbPc are deposited at room temperature on pre-cleaned glass substrates under the pressure of 10^{-6} Torr using a (12 A 4D Hind Hivac, India) coating unit. The rate of evaporation is properly controlled and maintained constant during all the evaporations. Rotary drive is employed to maintain uniformity in film thickness. The thicknesses of the films are 150 nm, 300 nm and 450 nm. The thickness of the films is measured by Quartz crystal monitor. Thickness of 450 nm thin films prepared at room temperature has been annealed at 323 and 373 K for 1 h and the temperature is controlled by a programmable temperature controller. The similar procedure is used for preparing CuPc thin film on pre-cleaned glass substrate.The adhesion of the films to the substrate seems to be extremely good. The samples prepared in a similar environment are used for studying the optical properties. Optical measurement is done using Shimadzu 160 A spectrophotometer. Transmission spectra are recorded and the absorption edge is analysed to get the optical band gap. Optical band gap with annealed temperature are studied.

3. Results and discussion

3.1 Effect of Thickness

Fig. 1 and 2 shows the variation of transmittance with wavelength of PbPc and CuPc films for different thicknesses respectively. It reveals that transmittance vary independently with film thickness. Organic molecules of Phthalocyanine and their derivatives exhibit anomalous optical characteristics because of their unique aromatic molecular ring structure. It is well known that they posses two kinds of energy bands. One of them is called the Q band which is equivalent to α band in porphyrins and other one is called B band which is equivalent to the γ or soret band in porphyrins. The origins of the Q band and B band are an a_{1u} to e_g ($n \rightarrow \pi^*$) and an a_{2u} to e_g ($\pi \rightarrow \pi^*$) transition respectively [19]. The high energy peak of the Q-Band has been assigned to the first $\pi \rightarrow \pi^*$ transition on the phthalocyanine macrocycle [20]. The low energy peak of the Q-band has been variously explained as a second $\pi \rightarrow \pi^*$ transition [20].

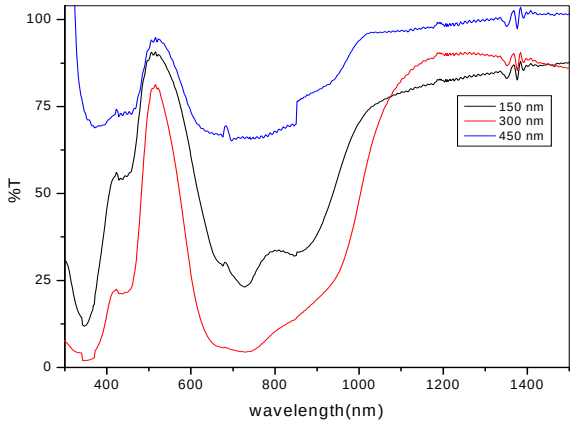

Fig. 1. Variation of transmittance with wavelength of PbPc films for different thicknesses

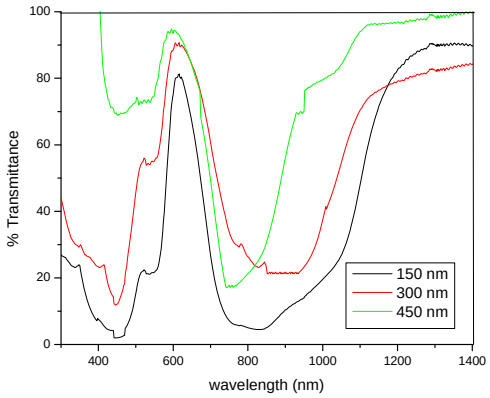

Fig. 2. Variation of transmittance with wavelength of CuPc films for different thicknesses.

The transmittance graph of PbPc shows that B (soret) band is less than 400 nm and Q band is in between 570-750 nm. The wavelength region above 800 nm seems to be transparent for transmission spectroscopy. The transmittance graph of CuPc shows that B (soret) band is less than 450 nm and Q band is in between 550-650 nm. The wavelength region above 700 nm seems to be transparent for transmission spectroscopy. They are observed on close examination that the B or soret band is due to a_{2u} to e_g ($\pi \rightarrow \pi^*$) and Q-band a_{1u} to e_g ($n \rightarrow \pi^*$) transitions [21].

The variation of absorbance and extinction coefficient with wavelength of PbPc films for different thicknesses is shown in Figures3 and 5. The variation of absorbance and extinction coefficient with wavelength of CuPc films for different thicknesses is shown in Figures 4 and 6. Similar trend is observed for both spectrums. It is observed from the above Figures that absorbance and extinction coefficient vary independently with film thickness.

It is observed in both PbPc and CuPc from the absorbance peak that in the near UV, B or the soret band appear below 450 nm where $\pi \rightarrow \pi^*$ transition takes place. The Q-band $n \rightarrow \pi^*$ transition appeared in the visible at about 550-650 nm. . The B-band and Q-band transition appeared in the visible at about 570 nm and 600 nm. This band has a doublet for all samples associated with exciton formation [22] and a new band appeared at about 440 nm [23].

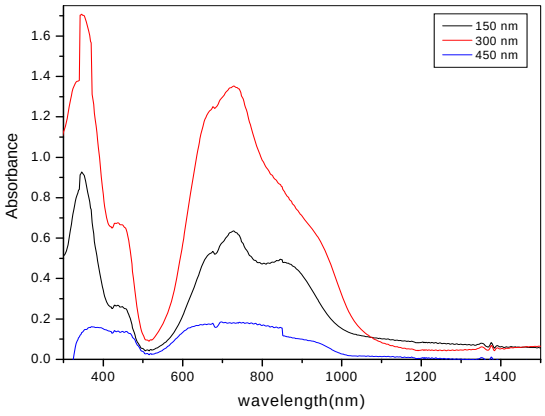

Fig. 3. Variation of absorbance with wavelength of PbPc films for different thicknesses

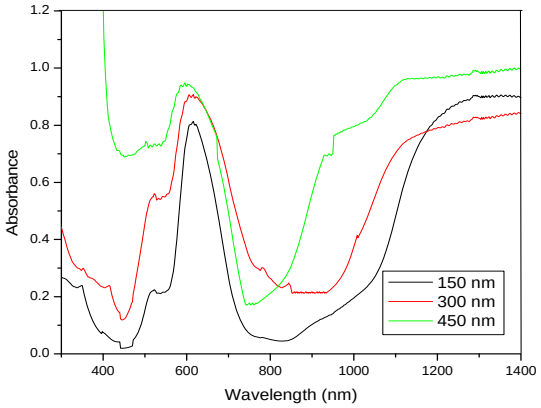

Fig. 4. Variation of absorbance with wavelength of CuPc films for different thicknesses.

The stability in the peak positions in transmission and reflection spectra in absorbing region showed the stability of the structure of CuPc. The refractive indexes as well as the absorption index are practically independent on the film thickness.

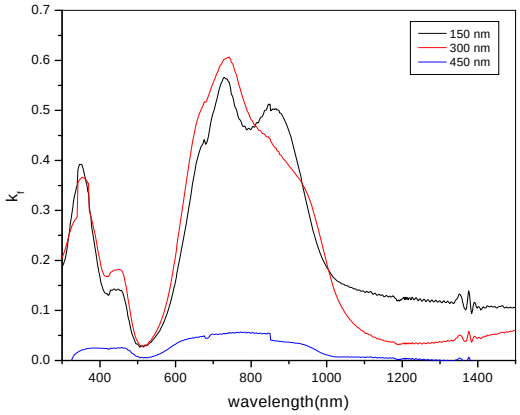

Fig. 5. Variation of extinction coefficient (k_f) with wavelength of PbPc films for different thicknesses

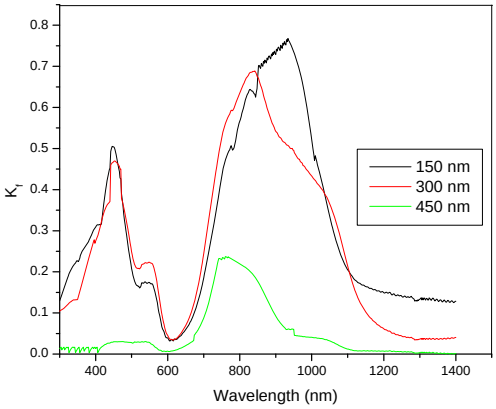

Fig. 6. Variation of extinction coefficient (k_f) with wavelength of CuPc films for different thicknesses.

Fig. 7 and 8 shows the photon energy dependence of α^2 of PbPc films for different thicknesses of PbPc and CuPc thin films respectively. Extrapolation of this plot to $\alpha^2 = 0$ determines the optical band gap energy. The transparent band shows that the absorption decreases slowly with increasing photon energy for triclinic and decreasing more sharply with photon energy for the monoclinic films.

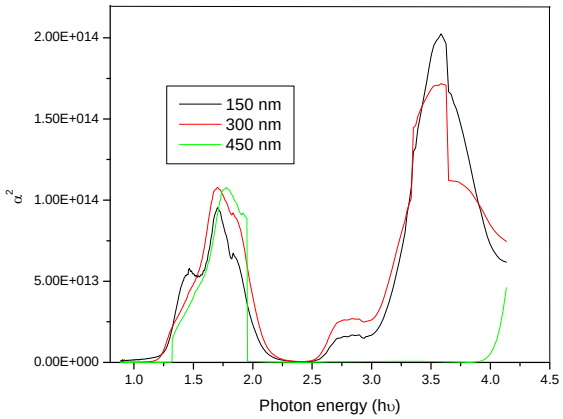

Fig. 7. Photon energy dependence of α^2 of PbPc films for thicknesses.

In PbPc the absorption has been confirmed for many phthalocyanine complexes and is related to the formation of single excitation [24,25].The monoclinic structure shows a doublet at 1.86eV & 1.74eV and triclinic shows a high intensity band at 1.61 eV. The plot shows two absorption bands, identified as Q band or exciton absorption at low energies (below 2.4 eV) and fundamental absorption at higher energies (greater than 2.4 eV). A direct allowed band gap is found to exist at this energy 2.4 eV. It is observed from the graph that the lowest band gap is about 1.2 eV. This band gap energy is estimated as the onset of absorption spectrum. These values are confirmed from the previous literature works [25,26].

In CuPc the absorption has been confirmed for many phthalocyanine complexes and is related to the formation of single excitation [25, 27]. The monoclinic structure shows a doublet at 1.86eV & 1.74eV and triclinic shows a high intensity band at 1.61 eV. The plot shows two absorption bands, identified as Q band or exciton absorption at low energies (below 2.46 eV) and fundamental absorption at higher energies (greater than 2.46 eV). A direct allowed band gap is found to exist at this energy 2.46 eV. It is observed from the graph that the lowest band gap is about 1.24 eV. This band gap energy is estimated as the onset of absorption spectrum [27].

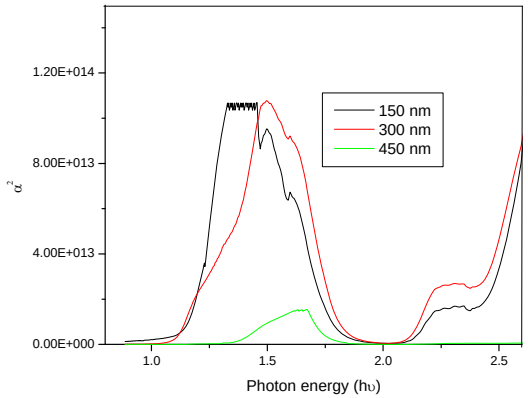

Fig. 8 Photon energy dependence of α^2 of CuPc films for thicknesses.

The band gap energies for different thicknesses PbPc and CuPc are shown in Table 1 and 2. They are seen that band gap decreases with the increase in film thickness. It may be due to the increase in grain size and a decrease of strain or due to the action of atmospheric oxygen or the presence of impurity electronic levels on the surface of the films which produces an acceptor level in the forbidden band [28,19].

Table 1 Band gap energies of PbPc films for different thicknesses.

Thickness (Å)	Band gap energy (eV)	
	Eg_1	Eg_2
1500	1.20	2.50
3000	1.18	2.48
4500	1.14	2.40

Table 2 Band gap energies of CuPc films for different thicknesses.

Thickness (Å)	Band gap energy (eV)	
	Eg_1	Eg_2
1500	1.24	2.61
3000	1.20	2.52
4500	1.16	2.46

3.2 Effect of Temperature

Fig. 9 and 10 shows the transmittance spectra of PbPc and CuPc films for thickness 450 nm at different annealed temperatures. They are observed that transmittance decreases with increase in temperature. In both films similar structure are observed before and after annealing on the visible and Soret bands is taken as supporting evidence for explanation of structure in terms of a molecular vibrations [20]. The results showed no effect of the annealing on the optical properties of the films.

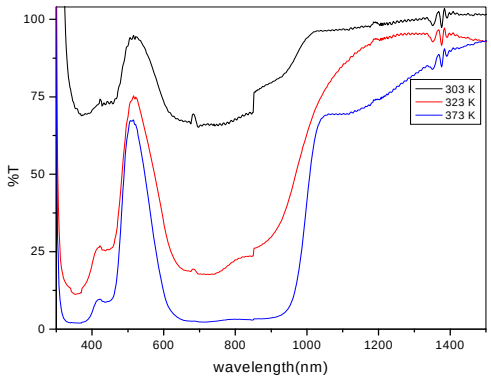

Fig. 9. Optical transmittance spectra of PbPc films at different annealed temperatures

Annealing at 323 K and 373 K increases absorbance of films in comparison with absorbance of as deposited ones and shifts peak positions of all bands towards low energy side of spectra except the peak position of N-band is shifted towards high energy side of spectra.

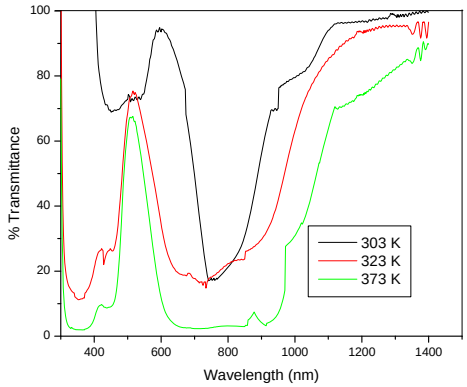

Fig. 10. Optical transmittance spectra of CuPc films at different annealed temperatures

The variation of absorbance and extinction coefficient (k_f) with wavelength of PbPc films at different annealed temperatures are shown in Figures11 and 13. The variation of absorbance and extinction coefficient (k_f) with wavelength of CuPc films at different annealed temperatures are shown in Figures 12 and 14. The spectrum reveals that both the absorbance and k_f increases with increase in annealed temperature.

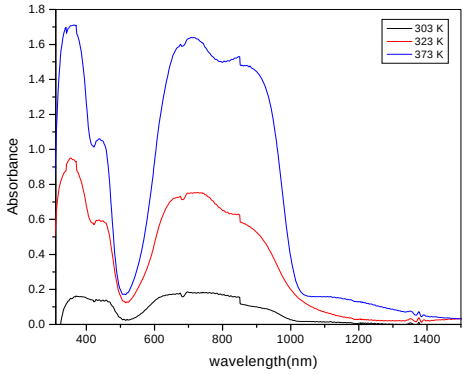

Fig. 11. Optical absorbance spectra of PbPc films at different annealed temperatures

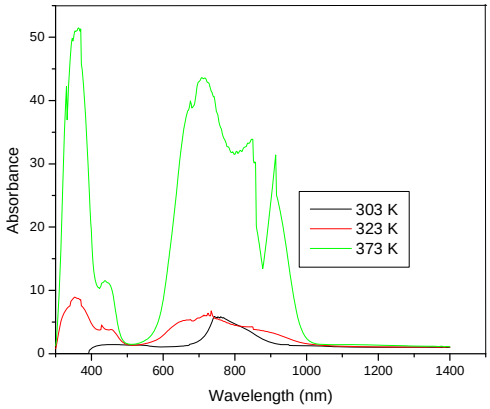

Fig. 12. Optical absorbance spectra of CuPc films at different annealed temperatures

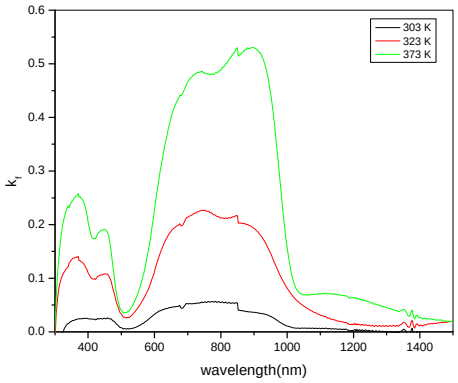

Fig. 13. Wavelength dependence on extinction coefficient (k_f) of PbPc films at different annealed temperatures

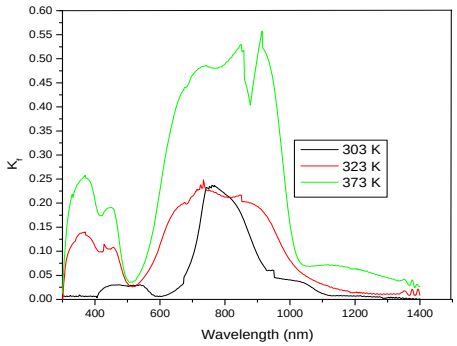

Fig. 14. Wavelength dependence on extinction coefficient (k_f) of CuPc films at different annealed temperatures

Figure 15 and 16 shows the photon energy dependence of α^2 of PbPc and CuPc thin films for thickness 450 nm at different annealed temperatures. Extrapolation of this plot to $\alpha^2 = 0$ determines the optical band gap energy.

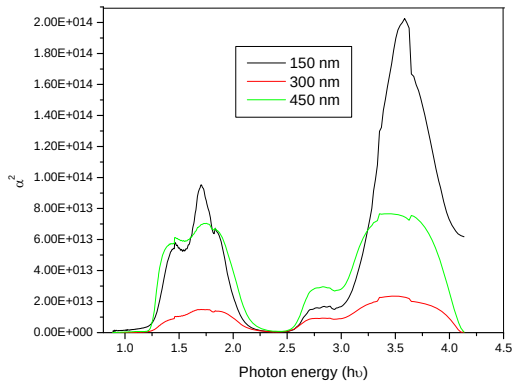

Fig. 15. Photon energy dependence of α^2 of PbPc films for thickness 450 nm at annealed temperatures

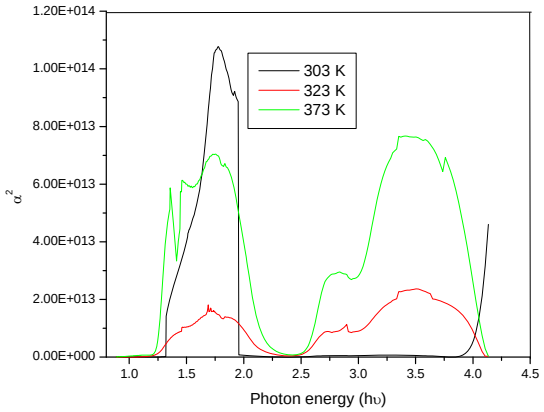

Fig. 16. Photon energy dependence of α^2 of CuPc films for thickness 450 nm at annealed temperatures

Table 3 shows the band gap energies of PbPc film. From the plots and table it is concluded that this material exhibits only the direct allowed transition [25,26]and is observed that band gap increases with increase in annealed temperature. It can be due to the decrease of localized states in band gap [29,30,31].

Table 3. Band gap energies of PbPc films of thickness 450 nm at different annealed temperatures.

Temperature (K)	**Band gap energy (eV)**	
	Eg_1	**Eg_2**
303	1.14	2.40
323	1.18	2.42
373	1.20	2.50

Table 4. Band gap energies of CuPc films of thickness 450 nm at different annealed temperatures.

Temperature (K)	**Band gap energy (eV)**	
	Eg_1	**Eg_2**
303	1.16	2.46
323	1.22	2.42
373	1.26	2.24

Table 4 shows the band gap energies of CuPc film. From the plots and table it is concluded that this material exhibits only the direct allowed transition [20] and is observed that band gap decrease with increase in annealed temperature. It can be due to the reduction in the number of unsaturated defects [20].

Generally phthalocyanines absorbs light on either side of the blue - green region and can be used as photoconductors and colour filters [32]. The optical analysis of PbPc and CuPc confirms the above result.

4. Conclusion

Optical analysis confirms a direct allowed transition. The variation of transmittance, absorbance and extinction coefficient with wavelength has been reported for both PbPc and CuPc films. Optical studies of PbPc & Cupc films shows the existence of two absorption bands at low energies less than 2.4 eV & 2.46 eV and high energies greater than 2.4 eV & 2.46 eV. It is observed from the graph that the lowest band gap is about 1.2 eV & 1.24 eV. This band gap energy is estimated as the onset of absorption spectrum. The stability in the peak positions in transmission and reflection spectra in absorbing region showed the stability of the structure of the films.

Annealing at 323 K and 373 K increases absorbance of films in comparison with absorbance of deposited ones and shifts peak positions of all bands towards low energy side of spectra except the peak position of N-band is shifted towards high energy side of spectra. The variations of transmittance, absorbance and extinction coefficient with wavelength of PbPc and Cupc films for different thicknesses are studied. It is observed that absorbance and extinction coefficient vary independently with film thickness. The spectra reveal that both the absorbance and extinction coefficient increases with increase in annealed temperature.

The band gap of PbPc and Cupc decreases with the increase in film thickness. It may be due to the increase in grain size and a decrease of strain or due to the action of atmospheric oxygen or the presence of impurity electronic level on the surface of the films which produces an acceptor level in the forbidden band. The band gap energy of PbPc increases with increase in annealed temperature which is due to the decrease of localized states in band gap. But in CuPc is observed that band gap decrease with increase in annealed temperature which is due to the reduction in the number of unsaturated defects.

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