CHAPTER 6

OPTICAL PROPERTIES

6.1 INTRODUCTION

The theoretical and experimental investigation on the optical behaviour of thin films mainly deals with optical absorption, transmission, reflection and their relation to optical constants such as refractive index ($n$), absorption edge or extinction coefficient ($k_f$) and absorption coefficient ($\alpha$) (Goswami (1996), Chopra (1976)). These studies have led to the development of complex multilayer optical systems with remarkable reflection, anti-reflection, interference in optoelectronic device applications. The absorption studies are done by throwing light on the electronic structure of solids, their degeneracy, energy band gap, lattice bonding, optical transition that may be direct or indirect, allowed or forbidden and also the nature of solid materials.

Metal phthalocyanines (MPc) have been widely used as organic dye stuff because of their intense absorption of light in the visible and ultraviolet regions (Masafumi Sakata et al (2002), Leznoff and Lever (1996)). The optical constants have been evaluated in order to correlate the electronic band structure. Optical measurements provide information on the structure and topography of MPc films.

Considerable amount of work has been carried out on the various physical and chemical properties of metal phthalocyanines. It is necessary to study the optical properties of PbPc and CuPc thin films in order to obtain useful information such as optical band gap, transition, optical constants and oscillating parameters and the development of device technologies. Moreover the visible and near ultraviolet absorption spectra have been measured. The
fundamental and the onset energy gaps could also be estimated and discussed. This chapter deals with the optical properties of PbPc and CuPc thin films prepared by vacuum evaporation technique.

6.2 THEORY

6.2.1 Optical Absorption

Absorption of light by different material can induce various types of transitions such as band to band, between sub bands, resonance due to vibrational state of lattice and impurities. These led to the appearance of bands or absorption peaks in the spectra. Absorption has high values for material whereas it has low value for dielectrics. In order to produce films with absorption and reflection losses with high transparency, deposition procedure like purity, substrate cleaning, film contamination and thin film quality etc. must be carefully controlled.

6.2.2 Absorption Coefficient (α)

The absorption coefficient can be written in terms of incident radiation energy.

\[ \alpha \propto (h\nu - E_g)^p \]

\[ \alpha = A (h\nu - E_g)^p \]

(6.1)

where A is a constant, E_g, the band gap, \( \nu \), the frequency of incident radiation and h the Planck’s constant. The magnitude of the exponent p characteristics of the type of transition takes the value 1/2, 3/2, 2, 3 for direct allowed and direct forbidden, indirect allowed and indirect forbidden transition respectively.
When the material is free from any imperfection, only the direct but allowed transition can take value from valence to conduction band (Brooks (1995), Bardeen et al (1956), Dexter (1956)).

For direct allowed transition

\[ \alpha = A (h\nu - E_g)^{1/2} \]  \hspace{1cm} (6.2)

For direct forbidden transition

\[ \alpha = A (h\nu - E_g)^{3/2} \]  \hspace{1cm} (6.3)

When the material contains defects such as impurities, dislocation etc., one has to consider the perturbation of the system due to their presence and also their interaction with photons (Gray (1957)).

For direct allowed transition

\[ \alpha = A (h\nu - E_g)^{2} \]  \hspace{1cm} (6.4)

For direct forbidden transition

\[ \alpha = A (h\nu - E_g)^{3} \]  \hspace{1cm} (6.5)

6.2.2.1 Optical constants

Optical properties of the materials can be characterized by refractive index (n), absorption coefficient (\(\alpha\)) and extinction coefficient (k\(_d\)). The index of refraction ‘n’ is defined as the speed of light in vacuum(C) to its speed (v) of the medium

\[ n = \frac{C}{v} \]  \hspace{1cm} (6.6)

and is related to the velocity of the propagation of light in the material by
\[ v = \frac{C}{n} \] (6.7)

The refractive index and the extinction coefficient \((k_f)\) can be calculated from the real and imaginary of complex refractive index.

\[ N = \left( n - ik_f \right) \] (6.8)

In order to describe the fundamental absorption edge, the spectral dependence of absorption coefficient \((\alpha)\) is directly determined using the relation,

\[ \alpha = \frac{4\pi k_f}{\lambda} \] (6.9)

where \(\lambda\) is the wavelength of incident radiation.

The extinction coefficient is defined as,

\[ k_f = \frac{2.303\log_{10}\left( \frac{1}{T} \right)\lambda}{4\pi d} \] (6.10)

where \(d\) is the film thickness.

6.2.2.2 Determination of band gap

For incident photon energy greater than the band gap and above, the exponential tail and the optical absorption follow a power law.

\[ \alpha = A (h\nu - E_g)^n \]
The optical energy band gap for different film thickness is obtained by extrapolating the straight line portion of $\alpha^2$ vs $h\nu$ curves. The line touching the point on X axis will be the band gap for the material.

6.3 MEASUREMENTS

Spectrophotometric method is used for estimating the optical parameters in the present study. Spectrophotometer consists of light source, monochromatic slits and detectors. A sample beam instrument uses a single light path for the interference and wavelength. Advantage of double beam spectrophotometers are speed of operation, automatic compensation for variation in lamp output, changes in detector sensitivity and spectra scan. Most instruments have various options and selections that can be made during an analysis. The two major choices are absorbance (a log amplifier convert’s transmittance to absorbance) and transmittance.

Double beam spectrophotometers are generally of recording type. The instrument composes automatic sample beam energy with reference beam energy. The ratio of two would be transmittance of the sample. This procedure is followed over a sequence of wavelength. A graph is plotted with transmittance (absorbance) as ordinate and wavelength as abscissa given in the transmittance spectrum of the sample under analysis.

The optical transmittance and absorption studies were made in the UV-VIS-NIR region at normal incidence by using (JASCO-V 570 UV-VIS-NIR) double beam spectrometer, whose wavelength ranges from 300 to 2500 nm with an accuracy of ± 0.3 nm. Since the spectrophotometer is interfaced with computer, the recorded spectrum is obtained directly from the computer.
6.4 RESULTS AND DISCUSSION

6.4.1 Effect of Thickness

Figures 6.1 and 6.2 show 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→π*) and an a_{2u} to e_g (π→π*) transition respectively (Pakhmov G.L (2005)). The high energy peak of the Q-Band has been assigned to the first π→π* transition on the phthalocyanine macrocycle (Leznoff and Lever (1993)). The low energy peak of the Q-band has been variously explained as a second π→π* transition (Leznoff and Lever (1993)).

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 (π→π*) and Q-band a_{1u} to e_g (n→π*) transitions (Seoudi R et al (2006)).
Figure 6.1 Variation of transmittance with wavelength of PbPc films for different thicknesses

Figure 6.2 Variation of transmittance with wavelength of CuPc films for different thicknesses

The variation of absorbance and extinction coefficient with wavelength of PbPc films for different thicknesses is shown in Figures 6.3 and 6.5. The variation of absorbance and extinction coefficient with wavelength of CuPc...
films for different thicknesses is shown in Figures 6.4 and 6.6. 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 nm-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 excitation formation (Fielding and Gutmann (1957)) and a new band appeared at about 440 nm (Collin and Belgachi (1989)).

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

![Absorbance vs Wavelength](image)

**Figure 6.3** Variation of absorbance with wavelength of PbPc films for different thicknesses
Figure 6.4 Variation of absorbance with wavelength of CuPc films for different thicknesses

Figure 6.5 Variation of extinction coefficient ($k_f$) with wavelength of PbPc films for different thicknesses
Figure 6.6  Variation of extinction coefficient ($k_f$) with wavelength of CuPc films for different thicknesses

Figure 6.7 and 6.8 shows the photon energy dependence of $\alpha^2$ 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.

In PbPc the absorption has been confirmed for many phthalocyanine complexes and is related to the formation of single excitation (Day P. and Williams R.J.P (1962), Anwar M. and Hogarth C.A. (1982)). The monoclinic structure shows a doublet at 1.86eV and 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 (Anwar M. and Hogarth C.A. (1982), Darby J. E et al (1991)).

In CuPc the absorption has been confirmed for many phthalocyanine complexes and is related to the formation of single excitation (Ambily.S et al (1999), Anwar and Hogarth (1982)). The monoclinic structure shows a doublet at 1.86eV and 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 (Ambily.S et al (1999)).

![Figure 6.7 Photon energy dependence of $\alpha^2$ of PbPc films for different thicknesses](image)

**Figure 6.7 Photon energy dependence of $\alpha^2$ of PbPc films for different thicknesses**
The band gap energies for different thickness films of PbPc and CuPc are shown in Table 6.1 and 6.2 respectively. It is 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 (Prabahar S and Dhanam M (2005), Pakhmov G.L. (2005)).

**Table 6.1 Band gap energies of PbPc films for different thicknesses**

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Band gap energy (eV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Eg₁</td>
</tr>
<tr>
<td>1500</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>4500</td>
<td>1.14</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6.2 Band gap energies of CuPc films for different thicknesses**

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>Band gap energy (eV)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Eg₁</td>
</tr>
<tr>
<td>1500</td>
<td>1.24</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>4500</td>
<td>1.16</td>
<td></td>
</tr>
</tbody>
</table>
6.4.2 Effect of Temperature

Figures 6.9 and 6.10 show the transmittance spectra of PbPc and CuPc films of thickness 450 nm at different annealed temperatures. It is observed that transmittance decreases with increase in temperature. The present observation of similar structure of CuPc 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 (Leznoff and Lever (1993)).

![Figure 6.9 Optical transmittance spectra of PbPc films at different annealed temperatures](image)

**Figure 6.9** Optical transmittance spectra of PbPc films at different annealed temperatures
Figure 6.10 Optical transmittance spectra of CuPc films at different annealed temperatures

The variation of absorbance and extinction coefficient ($k_l$) with wavelength of PbPc films at different annealed temperatures are shown in Figures 6.11 and 6.12. The variation of absorbance and extinction coefficient ($k_l$) with wavelength of CuPc films at different annealed temperatures are shown in Figures 6.13 and 6.14. The spectrum reveals that both the absorbance and $k_l$ increases with increase in annealed temperature.

Figures 6.15 and 6.16 show the photon energy dependence of $\alpha^2$ of PbPc and CuPc thin films of thickness 450 nm at different annealed temperatures. Extrapolation of this plot to $\alpha^2 = 0$ determines the optical band gap energy.
Figure 6.11 Optical absorbance spectra of PbPc films at different annealed temperatures

Figure 6.12 Wavelength dependence on extinction coefficient ($k_f$) of PbPc films at different annealed temperatures
Figure 6.13 Optical absorbance spectra of CuPc films at different annealed temperatures

Figure 6.14 Wavelength dependence on extinction coefficient ($k_f$) of CuPc films at different annealed temperatures
Table 6.3 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 (Anwar M. and Hogarth C.A. (1982), Darby J. E et al (1991)) and it is observed that band gap increases with increase in annealed temperature.
It can be due to the decrease of localized states in band gap (Kanefusa S. and Nitta M. (1992), Parlak M. (1998), El-Sayed S.M. (2004)).

Table 6.3  Band gap energies of PbPc film of thickness 450 nm at different annealed temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Band gap energy (eV)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eₙ₁</td>
<td>Eₙ₂</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>1.14</td>
<td>2.40</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>1.18</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>1.20</td>
<td>2.50</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4  Band gap energies of CuPc film of thickness 450 nm at different annealed temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Band gap energy (eV)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eₙ₁</td>
<td>Eₙ₂</td>
<td></td>
</tr>
<tr>
<td>303</td>
<td>1.16</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>323</td>
<td>1.22</td>
<td>2.42</td>
<td></td>
</tr>
<tr>
<td>373</td>
<td>1.26</td>
<td>2.24</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4 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 (Leznoff and Lever (1993)) and it is observed that band gap decrease with increase in annealed temperature. It can be due to the reduction in the number of unsaturated defects (Leznoff and Lever (1993)).

Generally phthalocyanines absorb light on either side of the blue - green region and hence it is used as photoconductors and colour filters (Seoudi R et al (2006)). The optical analysis of PbPc and CuPc confirms the above result.
6.5 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 and CuPc films shows the existence of two absorption bands at low energies less than 2.4 eV and 2.46 eV and high energies greater than 2.4 eV and 2.46 eV. It is observed from the spectra that the lowest band gap is about 1.2 eV and 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 exhibited 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 which is shifted towards high energy side of spectra. The variation 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 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 it is observed that band gap decreases with increase in annealed temperature due to the reduction in the number of unsaturated defects.