Chapter 3

3. OPTICAL STUDIES ON TTBPc, ZnTTBPc AND CuTTBPc THIN FILMS

3.1. Introduction

Metal phthalocyanines, with excellent thermal and chemical stability and strong absorption in the region of visible to near infrared regions, has become one of the main recording media for optical disc with the operating laser wavelength of 780-830 nm. (Gan, 1999). In recent years they have received particular attention in nonlinear optical systems, specifically in the field of optical limiting (Shirk and Hanack, 2000). These studies distinguish whether the valence band and conduction band extremes occur at the same or different points in the K-space knowing the frequency dependence of the absorption processes such as fundamental absorption, free carrier absorption, excitonic absorption and impurity absorption. Electrons can be excited from the valence band to the conduction band with the absorption of a photon of energy equal to the band gap of the material.

Optical absorption spectroscopy is used to characterize predominant phases of various Pc's (Campbell and Collins, 1995). Pcs exhibit strong non-linear optical properties due to their spatially extended π electron system (Fang and Maruyama, 1993). Each carbon atom in a conjugated system has three nearest neighbours with which it forms 3 equivalent σ bonds made from the SP^2 hybridisation of 3 valence atomic orbitals of the carbon atom:
2S,2Pₓ and 2Pᵧ. For such an hybridization state, the fourth orbital 2P₂ lies perpendicular to the bond plane. It is the lateral overlap of these out of plane 2Pₓ atomic orbitals, which \( \pi \) gives rise to the \( \pi \)-bonds (Nunzi, 2002). The range of interest for optical limiting is the high transmission region between 420nm and 600 nm, i.e., between the two intense Q and B bands in most of the Pcs. Gu et al. (Gu and Xu, 1998) show that the broad absorption in the wavelength region 580-850 nm could be used for optical recording in the organic Pcs.

The MPcs belong to the \( D_{4h} \) symmetry group having 10e₉, 4a₁u, 6a₂u, 5b₁u, and 5b₂u \( \pi \) orbitals. The scheme of the energy levels in MPcs and the various allowed transitions, Q,LMCT (ligand to metal charge transfer), MLCT (Metal to Ligand charge transfer) bands are shown in Figure 3.1.1.

![Figure 3.1.1: The schematic diagram of energy levels in metal phthalocyanine and the various allowed transitions](image)

Since most of the Pcs are found to exhibit very good optical absorption and emission in the 600-700nm regions, they can be considered as suitable candidates for optical application in this region (Kumar and Nampoori, 2003). The peaks in the absorption spectra...
are due to overlapping π electron orbitals created by the conjugated double bonds within
the crystal structure of the film. These electrons are able to transfer energy throughout the
structure (Brown, 1980).

3.2. Theory

Optical absorption studies are very useful method to determine the band structure in semi-
conductors. A careful and systematic analysis of optical data can give a large amount of
information regarding the material (Guyon and Her, 1998), (Wang and Liu, 1999), (Caglar
and Caglar, 2007). We can determine the band gap energy of a material using this method.
The direct and indirect method are the two types of transitions. The functional depend-
ence of the absorption coefficient of photon energy near a transition determines whether
the transition is allowed or forbidden. The nature of the transition can give information
about the electronic state from which the transition takes place and this in turn helps to
identify the band structure of the semiconducting material (Collins and Mohammed, 1987).
Thus the electronic transitions between the valance and the conduction bands can be direct
or indirect. In both cases it can be allowed as permitted by the transition probability or
forbidden when no such possibility exists. The transition probability is related to α by the
relation (Goswami, 1996)

\[ \alpha = (Ah\nu - E_g) \]  

(3.2.1)

where \( E_g \) is the energy gap and \( p \) has discrete values like \( \frac{1}{2}, \frac{2}{3}, 2, 3 \) or more depending on
whether the transition is direct or indirect or allowed or forbidden. In the direct and allowed
cases the index \( P = \frac{1}{2} \) where as for the direct but forbidden transition \( p \) is \( 3/2 \). But for the
indirect and allowed cases $p = \frac{1}{2}$ and for the indirect forbidden cases it will be 3 or more. Thus a linear graph when $\alpha^2$ is drawn against $h\nu$, will suggest a direct allowed transition, where as a linear one with $\alpha^{\frac{1}{2}}$ against $h\nu$ indicates an indirect allowed transition. The magnitude of $P$ can also be estimated from the slope of the graph of log $\alpha$ versus log $h\nu$ and hence can suggest the type of mechanism. By extrapolating the linear portion of the graph to $\alpha = 0$, one can obtain the energy band gap of a material.

Then optical parameters of phthalocyanine thin films can be calculated from the absorption and reflectivity data. The transmittance $T$ of a thin film on a transparent substrate is given by (Araghi-Azim and Krier, 1997)

$$T = \frac{A(1 - R)(1 - R^1)(1 + \frac{k^2}{n^2})}{exp(\alpha t) + R R^1 exp(-\alpha t) - 2(R R^1)^{\frac{1}{2}} cos(2\gamma + \Psi + \Psi^1)}$$  \hspace{1cm} (3.2.2)

Where $\Psi^1 = \tan^{-1}(\frac{2n_1^{\frac{1}{2}} k}{n^2 + n_1^2 + k^2})$

$\gamma = \frac{2\pi n t}{\lambda}$

$\Psi = \tan^{-1}(\frac{2k}{n^2 + k^2 - 1})$

and $k = \frac{2\alpha}{\lambda}$

Here $R$ and $R^1$ are air film and film substrate reflections respectively and $A$ is a constant. The parameters $\alpha, k, t$ and $\lambda$ are the absorption coefficient, extinction coefficient, thickness and wavelength of the incident light used. The cosine term in equation is the interference term.

The parameters, $n$ and $n^1$ are the refractive indices of the film and substrate respectively.

In the region of inter band transition in the optical spectrum the absorption is so large that $\exp (\alpha t) \gg R R^1 \exp (-\alpha t)$

$k^2/n^2 \ll 1$ and the interference term is very small. Then equation can be written as

$$T = A(1 - R)(1 - R^1)exp(-\alpha t)$$  \hspace{1cm} (3.2.3)
The reflectivity of an absorbing medium of indices \( n \) and \( k \) in air for normal incidence is given by (Araghi-Azim and Krier, 1997)

\[
R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]  

(3.2.4)

The optical properties of the medium are characterized by a complex refractive index (\( N = n - ik \)) and complex dielectric constant (\( \varepsilon = \varepsilon_1 - i\varepsilon_2 \)). The real part \( \varepsilon_1 \) generally relates to dispersion, while the imaginary part \( \varepsilon_2 \) provides a measure of the dissipative rate of the wave in the medium.

3.3. Experiment

Thin film of TTBPc, ZnTTBPc and CuTTBPc are deposited onto optically flat glass substrates using a Hind Hivac 12A4D coating unit by thermal evaporation technique as per the procedure described in section 2.3 of chapter 2. Cleaned glass slides of dimensions 40mm X 12mm X 1.3mm is used as substrates. The substrates are cleaned as stated in the procedure described in section 2.7 of chapter 2. Evaporation of the material is performed at a base pressure of \( 1.3 \times 10^{-3} \) Pa from a molybdenum boat of dimensions 2.9cm X 1.2cm X 0.5cm which is used as the resistive heating element. Several films are prepared in the same experimental condition by arranging a series of substrates horizontally and keeping the evaporating sources to one-side but well below the specimen plane. Thickness of the film are determined using the procedure described in section 2.10 of chapter 2. The films deposited at room temperature are further annealed in air and in vacuum at various temperatures.

UV-VIS absorption and reflection spectra of TTBPc, ZnTTBPc, CuTTBPc thin films are recorded using the JASCO Corp;V-550 Spectrophotometer. The Spectrophotometer consists
of a ’Spex Minimate’ monochromator containing deuteruim and halogen lamps illuminating a diffraction grating of 900 lines(nm) inferred to a computer, which can record the spectrum from 200nm to 900nm. Absorption and reflection spectra of the film are analyzed to obtain the energy band gap and optical constants.

3.4. Results and Discussion

3.4.1. Optical constants

Visible ultra-violet and near infrared absorption spectra of TTBPc, ZnTTBPc,CuTTBPc thin films on glass substrates are recorded and band gaps are investigated. In the absorption spectra Q and B bands are obtained for the three materials and their optical band gaps are found varying with increase in thickness, annealing temperatures and substrate temperatures. It is reported that the absorbance spectrum shows a sharp increase in absorption at wavelength near to the absorption edge of the threshold wavelength. The energy corresponds to this determines the band gap of the material(Raji and Ramachandran, 2005). In general, all spectra display the existence of strong absorption bands in the range of 300 to 900nm caused by the $\pi - \pi^*$ transitions of the conjugated macrocycle of 18$\pi$ electrons.(James and Silve, 1992). The splitting of Q-band was explained by the aggregation of the molecules or molecular distortion (Mi and Qian, 2003), (Tian and Sasabe, 1998),(Terasaki and Kobayashi, 1992),(Mizuguchi and Karfunkel, 1995).

3.4.2. Optical studies of as deposited TTBPc thin film

A possible reason for the differences in the optical spectra is the change in thickness of the films. Absorption spectrum of as deposited TTBPc thin film is given in Figure 3.4.1.
generally been interpreted in terms of $\pi - \pi^*$ excitation between bonding and antibonding molecular orbitals (El-Nahass and Asiri, 2004), (Davidson, 1982). In order to find the various optical constants, it is necessary to know the variations in reflection spectra of TTBPC thin films shown in figures 3.4.1 and 3.4.2.

Figure 3.4.1: Plot of optical absorption spectrum for TTBPC thin films as a function of wavelength

![Absorption Spectrum](image)

Figure 3.4.2: Plot of reflection spectrum of TTBPC thin films as a function of wavelength.

![Reflection Spectrum](image)

The fundamental absorption edge can provide information about direct or indirect interband transactions. The absorption coefficient $\alpha \geq 10^4 \text{cm}^{-1}$ is related to direct band
transitions and \( \alpha \leq 10^4 \text{cm}^{-1} \) is related to indirect interband transitions (Collins and Abass, 1993), (S. Ambily and Menon, 1999), (Rajesh and Menon, 2005), (El-Nahass and Harbi, 2001). The absorption edge at the higher energy side can be related to the onset of the fundamental absorption.

The absorption at the lower energy side is ascribed as excitation absorption and related to the formation of singlet excations (Collins, Krier and Abass, 1993).

![Figure 3.4.3: Plots of \( \propto \) versus \( h\nu \) for TTBPc thin film of thickness 285nm.](image)

Plot of \( \alpha^2 \) versus \( h\nu \) corresponding to fundamental absorption, is given in figure 3.4.3

For TTBPc thin film of thickness 285nm. The fundamental band gap is estimated to be \( 3.23 \pm 0.01 \text{ eV} \).
From the reflectance spectrum maximum reflectance is shown at around 356 nm. In TTBPc thin film, the reflectance in the lower wavelength region is in between 300 nm-500nm.

![Plot of real and imaginary parts of the dielectric constants with photon energy for TTBPc thin film.](image1)

From the absorption coefficient the extinction coefficient ($k$) can be found out and from reflectance, the refractive Index can be determined. Figure 3.4.4 shows the plots of refractive Index $n$ and extinction coefficient $k$ against photon energy for TTBPc thin films. The highest value of $k$ corresponds to 0.14 at 2eV and the refractive index $n$ has a maximum value of 74.

![Plot of real and imaginary parts of the dielectric constants with photon energy for TTBPc thin film.](image2)

Figure 3.4.5: Plot of real and imaginary parts of the dielectric constants with photon energy of TTBPc thin film.

From the absorption coefficient the extinction coefficient ($k$) can be found out and from reflectance, the refractive Index can be determined. Figure 3.4.4 shows the plots of refractive Index $n$ and extinction coefficient $k$ against photon energy for TTBPc thin films. The highest value of $k$ corresponds to 0.14 at 2eV and the refractive index $n$ has a maximum value of
3.44 at 3.12eV. Variation of real and imaginary parts of the dielectric constants with photon energy of TTBPc thin film is show in figure 3.4.5.

3.4.2.1 Effect of thickness In addition to 285nm, thickness has been varied to study the optical properties. Optical absorption spectra of TTBPc thin films having thicknesses 150nm and 200nm are shown in figures 3.4.6 and 3.4.7 respectively.

A possible reason for the difference in the optical spectra is the change in thickness of the film. Hsieh et al. (Hsieh and Ju, 1998) has stated that the characteristic of vacuum sublimed organic films varies with deposition parameters. In solid state, Pc molecules are aggregated and Q-band becomes much broader than that of the monomer in solution due to strong intermolecular interactions resulting in exciton coupling effect (including the Davydov splitting) of the allowed transitions or the lift of the degeneracy of two LUMO orbits induced by molecular distortion (Mi and Qian, 2003)

![Figure 3.4.6: Plot of optical absorption spectra of TTBPc thin films having thickness 150nm.](image)

Figure 3.4.6: Plot of optical absorption spectra of TTBPc thin films having thickness 150nm.
Figure 3.4.7: Plot of optical absorption spectra of TTBPc thin films having thickness 200nm

Present study shows the Q and B bands in the absorption of TTBPc thin films. It is observed that the high intensity peak of absorption maximum of Q band observed at 615nm.

The absorbance spectrum shows sharp increase in absorption at wavelength near the absorption edge of the threshold wavelength. The energy corresponds to this determines the optical band gap of the material.

Figure 3.4.8: The plot $\alpha^2$ Vs. $hv$ for TTBPc thin films with thickness 150nm.
Figure 3.4.9: The plot $\alpha^2$ Vs. $h\nu$ for TTBPc thin films with thickness 200nm.

The optical band gap of TTBPc thin films with thickness 150nm and 200nm is as shown in the figures 3.4.8 and 3.4.9. The direct electronic transitions from $\pi - \pi^*$ orbitals in the 300 to 400 nm region results in an intense band called the sortet band, which gives the absorption edge. Variation of both intrinsic and extrinsic band gap energy for different thicknesses of TTBPc thin films are shown in table 3.4.1

Table 3.4.1: Band gap energy of TTBPc thin films for various thicknesses

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>Band gap energy (Eg ±0.01eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>3.16</td>
</tr>
<tr>
<td>200</td>
<td>3.14</td>
</tr>
<tr>
<td>285</td>
<td>3.20</td>
</tr>
</tbody>
</table>

From the above table, it is found that the band gap energy slightly decreases up to 200 nm then increases.

3.4.2.2 **Effect of substrate heating.** Figures 3.4.10, 3.4.11, 3.4.12 show the absorption spectra of TTBPc thin films of thickness 285 nm deposited at substrate temperatures 323 K, 373 K and 523 K respectively. B band in absorption spectra for all substrate heated TTBPc
thin films is near 320 nm and Q band is near at 606 nm.

Figure 3.4.10: Plot of absorption spectra of TTBPc thin films of thickness 285 nm as a function of wave length deposited at substrate temperature 323K.

Figure 3.4.11: Plot of absorption spectra of TTBPc thin films of thickness 285 nm as a function of wave length deposited at substrate temperature 373K.
Figure 3.4.12: Plot of absorption spectra of TTBPc thin films of thickness 285 nm as a function of wave length deposited at substrate temperature 523k.

Figure 3.4.13: The plot $\alpha^2$ Vs. $h\nu$ for TTBPc thin films with thickness 285nm substrate heated at 323K.
Figure 3.4.14: The plot $\alpha^2$ Vs. $h\nu$ for TTBPc thin films with thickness 285nm substrate heated at 373K.

Figure 3.4.15: The plot $\alpha^2$ Vs. $h\nu$ for TTBPc thin films with thickness 285nm substrate heated 523K.

Table 3.4.2: Band gap energy of TTBPc thin films for different substrate temperatures

<table>
<thead>
<tr>
<th>Substrate temperature(K)</th>
<th>Band gap energy($E_g \pm 0.01$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>3.16</td>
</tr>
<tr>
<td>373</td>
<td>3.20</td>
</tr>
<tr>
<td>523</td>
<td>3.25</td>
</tr>
</tbody>
</table>

The fundamental optical band gaps are tabulated in table 3.4.2. The optical band gap
of TTBPc thin film decreases with substrate temperature.

### 3.4.2.3 Effect of annealing temperature

Figures 3.4.16, 3.4.17, 3.4.18 shows the absorption spectra of TTBPc thin films of thickness 285 nm annealed in air for, one hour at 323K, 373K and 423K. In the absorption spectrum, B band occurs near at 332 nm and Q band at 620 nm.

![Figure 3.4.16](image)

**Figure 3.4.16:** Plot of absorption spectra of TTBPc thin films of thickness 285 nm annealed in air at 323k.

![Figure 3.4.17](image)

**Figure 3.4.17:** Plot of absorption spectra of TTBPc thin films of thickness 285nm annealed in air at 373K.
Figure 3.4.18: Plot of absorption spectra of TTBPc thin films of thickness 285nm annealed in air at 423k.

Figure 3.4.19: Plot of $\alpha^2$ Vs photon energy of TTBPc thin film at various annealing temperatures.

The optical band gap energy are estimated and are given in table. 3.4.3

Table 3.4.3: The band gap energy of TTBPc thin films with various annealing temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature (K)</th>
<th>Band Gap Energy ($E_g \pm 0.01$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>3.21</td>
</tr>
<tr>
<td>373</td>
<td>3.25</td>
</tr>
<tr>
<td>423</td>
<td>3.27</td>
</tr>
</tbody>
</table>
3.4.3. Optical studies of As deposited ZnTTBPc thin film

ZnTTBPc thin film is prepared for a thickness of 285nm. Absorption and reflection spectra are taken and give in figures 3.4.20 and 3.4.21 respectively. Figure 3.4.20 shows the absorbance versus wavelength spectra for ZnTTBPc thin films.

![Absorbance versus wavelength for ZnTTBPc thin films](image.png)

Figure 3.4.20: Plot of absorbance versus wavelength for ZnTTBPc thin films with thickness 285 nm.

The absorption spectra exhibit two main bands B and Q. The Q band, which exists in the visible region of the spectrum, is split out to two distinct peaks. The higher energy peak is connected with the first $\pi - \pi^* (a_{1u} \text{ to } e_g)$ transition on the phthalocyanine macrocycle, while the lower energy peak has been attributed to the excitonic transition (El-Nahass and El-Ghamaz, 2004) or vibrational interval (Sathyamoorthy and Mathew, 2004). The intrinsic band (soret band) at 335nm and the Q band is at 618 and 683nm respectively.
Figure 3.4.21: Reflection spectra for ZnTTBPc thin films with thickness 285nm as a function of wavelength.

Figure 3.4.22 represents such a plot for ZnTTBPc thin films. The intrinsic band gap energy for ZnTTBPc thin film is found to be 3.09 eV.

Figure 3.4.22: Plot of $\alpha^2$ vs photon energy of ZnTTBPc thin film.

Figure 3.4.23 represents the refractive index, n and extinction coefficient, k as a function
of photon energy and the corresponding maximum values are 2.3 at 2.78 eV and 2.2 at 1.8eV respectively.

Figure 3.4.23: Plot of refraction index, n and extinction coefficient k as a function of photon energy for ZnTTBPc

Figure 3.4.24: Variation of the real and imaginary parts of dielectric constant as a function of photon energy of ZnTTBPc.

3.4.3.1 Effect of thickness ZnTTBPc thin film of different thicknesses 180nm, 370nm and 240nm are also prepared. The absorbance of ZnTTBPc thin films of different thicknesses are shown in figures 3.4.25, 3.4.26 and 3.4.27. The absorption spectra of ZnTTBPc thin
film also shows two bands, the Q and B. Also a sharp splitting of Q band is observed in the absorption spectra. It is observed that the high intensity of peak of absorption maximum of a band observed at 333nm becomes prominent with increasing thickness. Variation of band gap energy with thickness is narrated through figures 3.4.28, 3.4.29, 3.4.30 and the respective values are enlisted in table 3.4.4. From the table it is found that as the thickness of the film increases, the band gap energy decreases. The size effect on quantum can be coupled with the decrease of band gap energy and is a favourable factor for homogenous layer by layer deposition.

Figure 3.4.25: Plot of absorbance Vs wavelength of ZnTTBPc thin films with thickness 180nm.
The absorption spectra of ZnTTBPc thin film also shows two bands, Q and B. A sharp splitting of Q band is observed in the absorption spectra. It is observed that the high intensity peak of absorption maximum of a band observed at 333nm becomes prominent with increasing thickness.
The absorption maximum of low energy peak of Q band observed at 620 nm becomes
prominent with increasing thickness. Kumar et al. (Kumar and Nampoori, 2003) have studied NiPc absorption spectrum and showed two intense bands in the 600-800nm region, which are Qx and Qy bands.

Table 3.4.4: Band gap energy of ZnTTBPc thin films with different thickness.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Band gap energy (Eg±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180nm</td>
<td>3.25</td>
</tr>
<tr>
<td>240nm</td>
<td>3.20</td>
</tr>
<tr>
<td>370nm</td>
<td>3.26</td>
</tr>
</tbody>
</table>

It is observed that the band gap energy is found almost same and no significant differences observed, which can be seen in Table 3.4.4. These films are identified to be of α-form (Jungyoon, 2003), (Lee and Maa, 2001). The phase separation could be responsible for the degradation of the optical properties (Herrera and Garcia, 2004).

3.4.3.2 Effect of substrate temperature In vacuum deposition the substrate temperature is an important factor that controls properties of vacuum deposited films. In MPcs the central metal atom is in a position of nearest approach to nitrogen atoms in parallel molecules and this increases the orbital overlap between parallel pairs of molecules. Hence any crystal phase change would affect the energy gap between conduction and valence bands. The variation in the ambient, like substrate temperatures, induces changes in the crystal structures by rearrangement of molecules and that causes changes in the band gap energies and thus different trap levels are found. The effects of substrate temperature on the properties of various thin films of phthalocyanine compounds including CuPc, NiPc, VOPc and PbPc was conducted by Lee (Lee and Maa, 2001), Yamashita A (A. Yamashita, 1993) et al. have also observed that the Q band absorption shifts towards longer wave lengths when deposi-
tion temperature are increased. It is increasing substrate temperature due to phase change activity from $\alpha$ to $\beta$.

Figure 3.4.31: Plot of absorbance vs wavelength of ZnTTBPc thin films for substrate temperature 320K.

Figure 3.4.32: Plot of absorbance vs wavelength of ZnTTBPc thin films for substrate temperature 355K.
Figure 3.4.33: Plot of absorbance vs wavelength of ZnTTBPc thin films for substrate temperature 418K.

Figures 3.4.31, 3.4.32 and 3.4.33 are the absorbance versus wavelength plot for ZnTTBPc thin films prepared at temperature 320K, 355 K and 418K respectively. The thickness of the films is 285nm. The tensile stress produced due to the constraint imposed by substrate temperature affects the electronic structure and thereby results in new absorption spectra. It is observed that the Q-band shifts by 4nm, towards longer wavelength for the variation of substrate temperature from 355 to 418K. The absorption maxima are same for all substrate temperatures. Absorption spectra reveal there is no remarkable Q splitting.
Figure 3.4.34: Plot of $\alpha^2$ Vs photon energy of ZnTTBPc thin film with substrate temperature 320K.

Figure 3.4.35: Plot of $\alpha^2$ Vs photon energy of ZnTTBPc thin films with substrate temperature 355K.
The plots of $\alpha^2$ versus $h\nu$ for ZnTTBPc thin films deposited at substrate temperatures 320K, 355K and 418K are given in figures 3.4.34, 3.4.35 and 3.4.36. The extrapolation of the linear portion to $\alpha^2 = 0$ near the absorption edge gives the band gap energy. The energy gap and trap level for different temperatures are shown in table 3.4.5.

Table 3.4.5: Band gap energy of ZnTTBPc thin films for various substrate temperatures

<table>
<thead>
<tr>
<th>Substrate Temperature(K)</th>
<th>Band gap energy (Eg±0.01)</th>
<th>Trap levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>3.20</td>
<td>1.61</td>
</tr>
<tr>
<td>355</td>
<td>3.18</td>
<td>1.62</td>
</tr>
<tr>
<td>418</td>
<td>3.36</td>
<td>1.50</td>
</tr>
</tbody>
</table>

It is observed that when substrate temperature increases from 320K to 355K the band gap energy first decreases and then increases when substrate temperature is increased to 418K.

Campell and Collins (Campbell and Collins, 1995) have shown a narrowing of the band gap by forming trap levels above the valence band. The trap level remains constant up to 355K and then decreases slightly (Agarwal and Reddy, 2005). Gutman and Lyons (Gutman
and Lyous, 1999) reported that traps normally are associated with crystal imperfections, dislocations, grain boundaries and surface of the material. The band gap shows a drastic change for the film deposited at 473K for H\textsubscript{2}Pc and is attributed to the phase transition from \( \alpha \) to \( \beta \).

### 3.4.3.3 Effect of annealing temperature

Figures 3.4.37, 3.4.38, and 3.4.39 shows the absorption spectra of ZnTTBPc thin film of thickness 285nm annealed in air for one hour at 323K, 373K, 423K. Q-splitting is observed in all the annealed samples. Moreover, the magnitude of Q-splitting increases with increase in annealing temperature. There exists a correlation between the Central metal ion to form out of plane bonding and the magnitude of Q-splitting (Kumar and Nampoori, 2003).

![Plot of absorbance Vs wavelength of ZnTTBPc thin films for annealing temperature 323K.](image)

Figure 3.4.37: Plot of absorbance Vs wavelength of ZnTTBPc thin films for annealing temperature 323K.
Figure 3.4.38: Plot of absorbance Vs wavelength of ZnTTBPc thin films for annealing temperature 373K.

Figure 3.4.39: Plot of absorbance Vs wavelength of ZnTTBPc thin films for annealing temperature 423K.

The plots of $\alpha^2$ versus $h\nu$ for ZnTTBPc thin films annealed in air are given in figures 3.4.40, 3.4.41 and 3.4.42.
Figure 3.4.40: Plot of $\alpha^2$ Vs photon energy of ZnTTBPC thin films with annealing temperature 323K.

Figure 3.4.41: Plot of $\alpha^2$ Vs photon energy of ZnTTBPC thin films with annealing temperature 373K.
Figure 3.4.42: Plot of $\alpha^2$ Vs photon energy of ZnTTBPc thin films with annealing temperature 423K.

The fundamental energy gaps are determined and are collected in table 3.4.7. Band gap energy does not vary even if different annealing temperatures possess different intrinsic band gap energy as that of many phthalocyanines (Kaplan and Schmidt, 1966)

Table 3.4.6: Band gap and trap level values of ZnTTBPc thin films for different annealing temperatures.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>Band gap energy (E_g±0.01)</th>
<th>Trap levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>323 K</td>
<td>2.95</td>
<td>1.70</td>
</tr>
<tr>
<td>373 K</td>
<td>3.10</td>
<td>1.60</td>
</tr>
<tr>
<td>423 K</td>
<td>3.10</td>
<td>1.80</td>
</tr>
</tbody>
</table>
3.4.4. Optical Properties of As Deposited CuTTBPC Thin Films

Figure 3.4.43: Plot of absorbance Vs wavelength of CuTTBPC thin films with thickness 285nm

Figure 3.4.43 shows the optical absorption spectrum of CuTTBPC thin films. In absorption spectra B band appears at 339nm and Q band at 620nm

Figure 3.4.44: Plot of $\alpha^2$ Vs photon energy of CuTTBPC thin film with thickness 285nm.

98
Figure 3.4.45: Plots of n,k Vs photon energy of CuTTBPc thin film

Figure 3.4.45 shows the n,k versus photon energy of CuTTBPc thin film. The maximum value of n is 2.9 at 2.67eV.

Figure 3.4.46: Plot of $\varepsilon_1$ and $\varepsilon_2$ Vs photon energy of CuTTBPc thin film

3.4.4.1 Effect of thickness Optical absorption is measured using UV - Visible Spectrophotometer. Figures 3.4.47, 3.4.48 and 3.4.49 shows the absorption spectra of CuTTBPc thin film of thicknesses 150nm, 200nm and 300nm respectively. The absorption spectra of CuTTBPc thin films also showed two bands, the Q and B bands. James et al. (James and Silve, 1992) also observed, all spectra display the existence of strong absorption bands.
caused by the $\pi - \pi^*$ transitions of the conjugated macrocycle of 18$\pi$ electrons. Again it is reported that the spectra originate from the orbitals within the aromatic 18$\pi$ electron system and from overlapping orbitals of the central metal atom.

Figure 3.4.47: Plot of absorbance Vs wavelength of CuTTBPC thin films with thickness 150nm

Figure 3.4.48: Plot of absorbance Vs wavelength of CuTTBPC thin films with thickness 200nm
Figure 3.4.49: Plot of absorbance Vs wavelength of CuTTBPc thin films with thickness 300nm

Variation of band gap energy with thickness of CuTTBPc thin films are shown in Figures 3.4.50, 3.4.51, and 3.4.52. The values obtained from graph are listed in Table 3.4.7.

Figure 3.4.50: Plot of $\alpha^2$ Vs photon energy of CuTTBPc thin film with thickness 150nm.
Figure 3.4.51: Plot of $\alpha^2$ Vs photon energy of CuTTBPc thin film with thickness 200nm.

Figure 3.4.52: Plot of $\alpha^2$ Vs photon energy of CuTTBPc thin film with thickness 300nm.

Table 3.4.7: Band gap value of CuTTBPc thin films with different thickness.

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>Band gap energy (E_g±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>3.18</td>
</tr>
<tr>
<td>200</td>
<td>3.16</td>
</tr>
<tr>
<td>300</td>
<td>3.15</td>
</tr>
</tbody>
</table>

From the table, it is found that the band gap energy slightly decreases when thickness of the film increases.
3.4.4.2 **Effect of substrate temperature** CuTTBPc thin films of thickness 285nm are deposited with a substrate temperature 323K, 473K and 523K. The absorption spectra for different CuTTBPc samples are given in figures 3.4.53, 3.4.54 and 3.4.55.

![Figure 3.4.53](chart1.png)

**Figure 3.4.53**: Plot of absorbance Vs wavelength of CuTTBPc thin films of substrate temperature 323K

![Figure 3.4.54](chart2.png)

**Figure 3.4.54**: Plot of absorbance Vs wavelength of CuTTBPc thin films of substrate temperature 473K
Figure 3.4.55: plot of absorbance versus wavelength of CuTTBPc thin films of substrate temperature 523K

Variation of band gap energy with substrate heating temperature are shown in Figures 3.4.56, 3.4.57, 3.4.58

Figure 3.4.56: plot of $\alpha^2$ versus photon energy of CuTTBPc thin films of substrate temperature 323K
Table 3.4.8: Variation of band gap energy with different substrate temperature.

<table>
<thead>
<tr>
<th>Substrate temperature (K)</th>
<th>Band gap energy (Eg_0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>3.35</td>
</tr>
<tr>
<td>473</td>
<td>3.25</td>
</tr>
<tr>
<td>523</td>
<td>3.21</td>
</tr>
</tbody>
</table>

**Figure 3.4.57**: plot of $\alpha^2$ versus photon energy of CuTTBPc thin films of substrate temperature 473K

**Figure 3.4.58**: plot of $\alpha^2$ versus photon energy of CuTTBPc thin films of substrate temperature 523K

The values of band gap energy enlisted in table 3.4.8

From the table it is found that substrate temperature increases band gap energy
decreases.

3.4.4.3 Effect of annealing temperature  In addition to the thickness of thin film and substrate temperature, the changes in the optical spectra of CuTTBPC thin films are studied after post deposition annealing. It is reported that thermal annealing improves film quality of organic MPcs (Song and Zhu, 2005). Annealing produced additive effects in films of organic Pcs, the annealed film showed lower absorption, increased resistance and formation of rather gross and closely packed grains. Heat annealing causes slight grain growth and partial structural change in the film. Optical absorption spectrum is shown in figures 3.4.59, 3.4.60 and 3.4.61. Optical absorption spectrum consists of B band near 339nm and Q band near 620nm.

Figure 3.4.59: Plot of absorbance Vs wavelength of CuTTBPC thin film with annealing temperature 323K.
Variation of band gap energy with different annealing temperature is shown in Figures 3.4.62, 3.4.63 and 3.4.64. The band gap energy obtained from the graphs are collected in table 3.4.9. Band gap energy does not vary much by air annealing even if different annealing temperature possess different intrinsic band gap energy as that of many phthalocyanines (Ambily and Menon, 1996).
Figure 3.4.62: Plot of $\alpha^2$ Vs photon energy of CuTTBPc thin films with annealing temperature 323K.

Figure 3.4.63: Plot of $\alpha^2$ Vs photon energy of CuTTBPc thin films with annealing temperature 373K.
Figure 3.4.64: Plot of $\alpha^2$ vs photon energy of CuTTB Pc thin films with annealing temperature 473K

Table 3.4.9: Band gap energy of CuTTB Pc thin films for different annealing temperatures

<table>
<thead>
<tr>
<th>Annealing temperature(K)</th>
<th>Band gap energy (Eg±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>3.27</td>
</tr>
<tr>
<td>373</td>
<td>3.26</td>
</tr>
<tr>
<td>473</td>
<td>3.25</td>
</tr>
</tbody>
</table>

3.5. Conclusions

The optical properties of TTBPc,ZnTTBPc and CuTTBPc thin films, annealed and deposited at different substrate temperatures have been studied in the spectral range 300nm-900nm. The occurrence of the Q band and B (soret) band are ascribed to the transition from the two upper filled $\pi$ orbitals to $e_g(\pi^*)$. Both the fundamental and excitonic energy gaps of the materials are determined and the effects of growth parameters on the band gaps are studied. Variation is observed in the energy gaps of all the three materials on varying substrate temperature. The slight decrease in the band gap energy on the thickness variation may be attributed to the quantum confinement effects where the particle size of individual
grain increases with the decrease of band gap energy by varying the thickness of thin films.

The photon energy dependence of the absorption coefficient in the fundamental absorption region confirms the transition as direct band to band type, in all the three materials. The dependence of refractive index $n$ and extinction coefficient $k$ on photon energies is plotted. The variations in the real and imaginary parts of the dielectric constant ($\varepsilon_1$ and $\varepsilon_2$ respectively) with the photon energy are also plotted.
References


Gan F 1999 Physics 28 323.


