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COMPOSITIONAL ANALYSIS OF PbPc and CuPc THIN

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Abstract: *The thin film of Lead Phthalocyanine (PbPc) and Copper Phthalocyanine (CuPc) on glass are prepared by Vacuum deposition method. Deposition of PbPc and CuPc on pre-cleaned glass substrates under the pressure of* 10^{-6} *Torr are achieved by slowly varying the current. The rate of evaporation is properly controlled and maintained constant during all the evaporations. The thicknesses of the films are 150 nm, 300 nm and 450 nm on glass substrate. The thickness of sample 450 nm annealed at 323 K and 373 K temperature. The sample has been analysed by Energy Dispersive Analysis using X-Rays (EDAX), Fourier Transform Infrared spectroscopy (FTIR) in order to get compositional analysis of the PbPc and CuPc thin film. The samples were evaluated by EDAX technique. The sample 450 nm is evaluated by Fourier Transform Infrared spectroscopy. The spectral pattern in 1000 – 1200* cm^{-1} *region depends strongly on the molecular structure of the complexes and its chemical structure for the central metal.*

Keywords: *Phthalocyanine, EDAX technique and Fourier Transform Infrared spectroscopy*.

I. INTRODUCTION

The search for materials suitable for low cost, versatile electronic devices has stimulated interest in organic thin film transistors [OTFTs] and sensors. It 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]. Photovoltaic devices made from organic pigments have reached power conversion efficiency of a few percent [19, 20] that is much lower than those of their inorganic combinations.

This paper deals with the structural and compositional studies of lead phthalocyanine and Copper phthalocyanine thin films prepared by vacuum evaporation technique. These materials are an organic semiconducting material which has various functional groups. So this paper deals with the Fourier transform infrared spectroscopy of functional group analysis.

II. 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 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. This procedure is used for preparing PbPc and 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 their various properties. The structures and composition of the films are examined by EDAX and FTIR.

III. RESULTS AND DISCUSSION

III.1. EDX Analysis

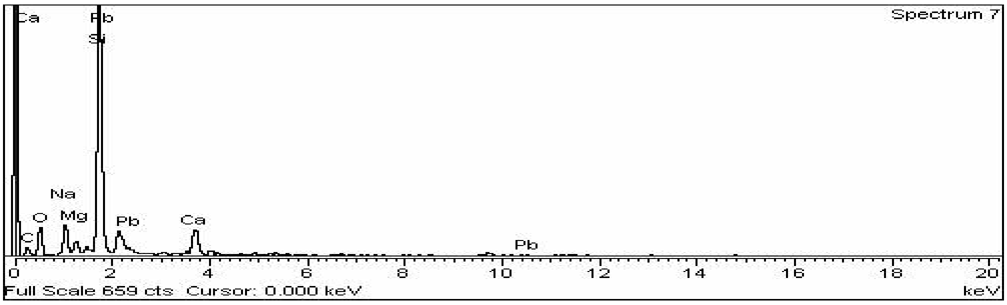
Energy dispersive analysis using X- ray (EDAX) helps us to determine the elemental contents in the specimen very accurately. A core level electron of a surface atom of PbPc is removed by an impinging electron or an X-ray photon. The excited atom decays to a lower energy state through an electronic rearrangement in which an additional electron from a higher level is knocked out leaving the atom in a doubly ionized state. The energy difference between the two states is given to the ejected electron, which will have kinetic energy characteristic of the atom.

III.1.1.Effect of thickness

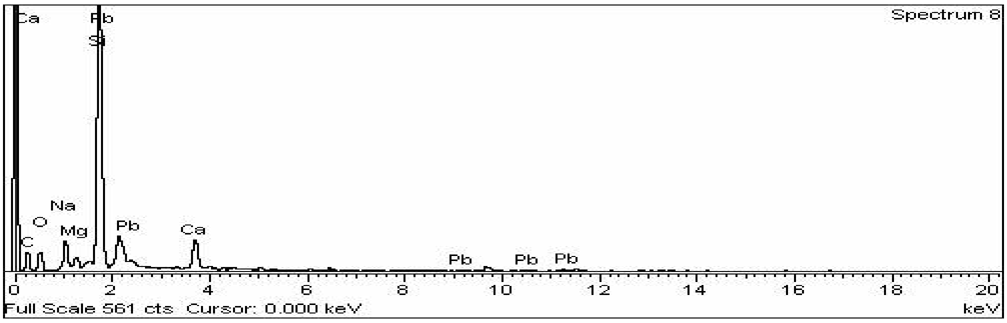
The elemental composition of the PbPc and CuPc films deposited at different thickness and annealed temperature were evaluated by EDAX technique. The Figure 1 & 2 (a, b and c) shows the EDAX spectrum of the PbPc and CuPc films respectively. The percentage of lead and copper increases with thickness in both PbPc and CuPc films respectively (0.77, 1.30 and 6.18 for 150, 300 and 450 nm of PbPc & 0.89, 1.93 and 8.78 for 150, 300 and 450 nm of CuPc respectively). The percentage of carbon increases with thickness (30.93, 50.47 and 62.00 for 150, 300 and 450 nm of PbPc & 38.34, 49.25 and 60.82 for 150, 300 and 450 nm of CuPc respectively). The nitrogen amount is very poor in both films. The film deposited at 303 K with different thickness has a uniform composition profile. However, the films deposited at 303 K with different thickness are required for the homogenization.

The peak corresponding to carbon, silicon, sodium and oxygen shows a transition from L to the K-shell which can be termed as a K-Alpha peak (Kα). The peaks corresponding to lead and Copper shows three types of transitions M-Alpha (Mα), M-beta (Mβ), M-Gamma (Mγ). These all transitions are shown in the EDAX patterns of PbPc and CuPc thin films of different thickness.

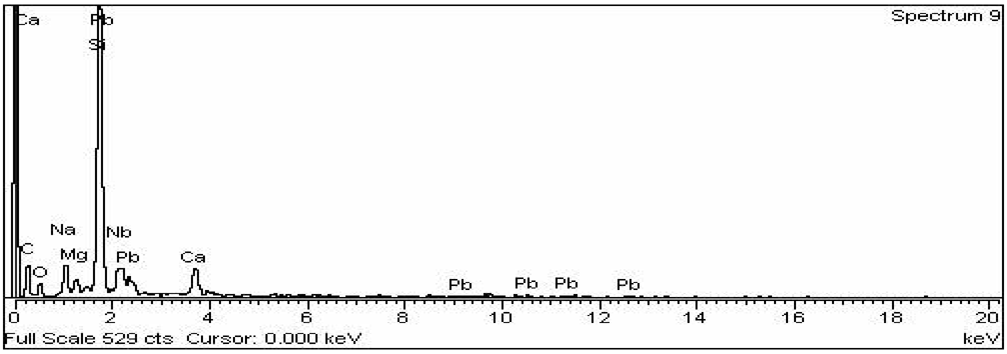
Figure 1. EDAX Patterns of PbPc Films for thicknesses



(a) 150 nm

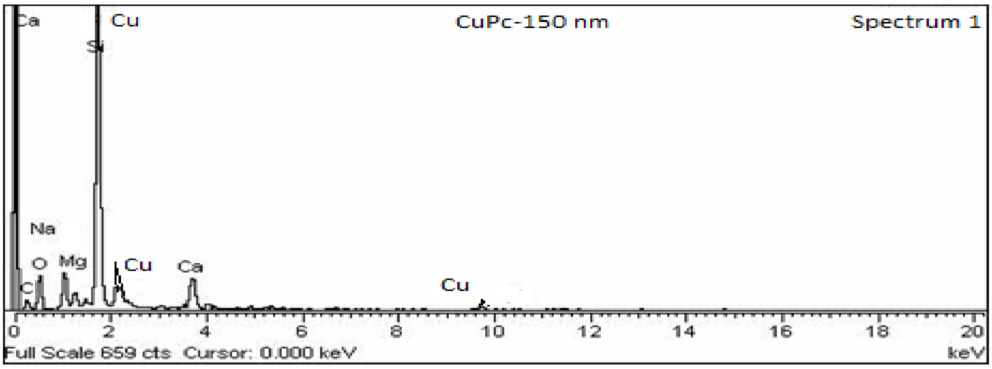


(b) 300 nm

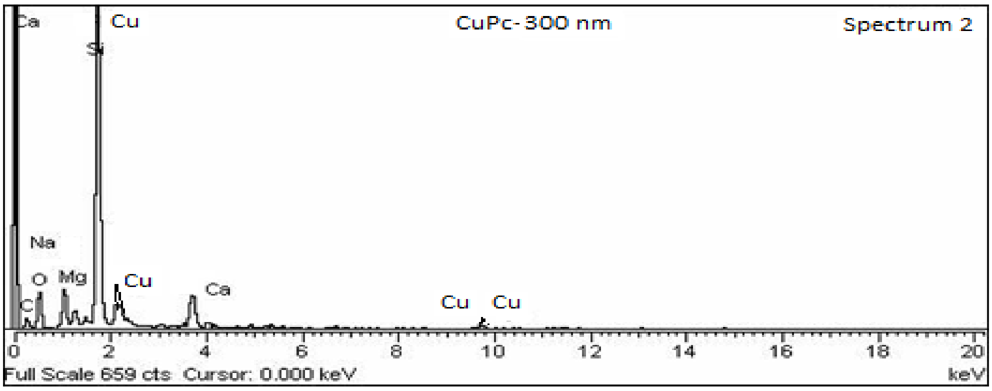


(c) 450 nm

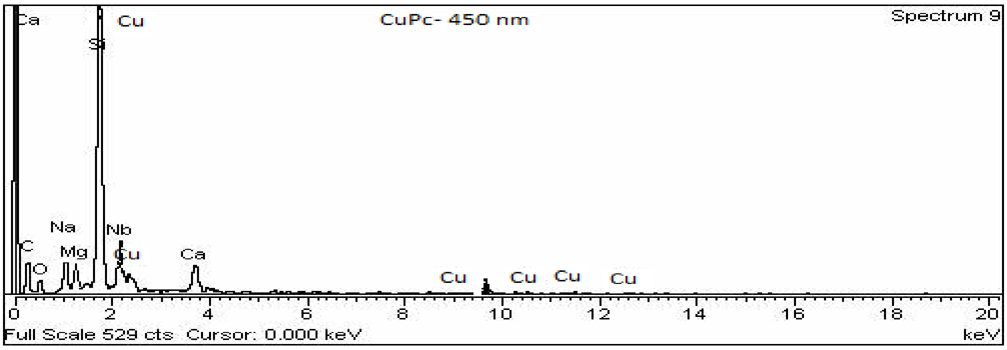
Figure 2. EDAX Patterns of CuPc Films for thicknesses



(a) 150 nm



(b) 300 nm



(c) 450 nm

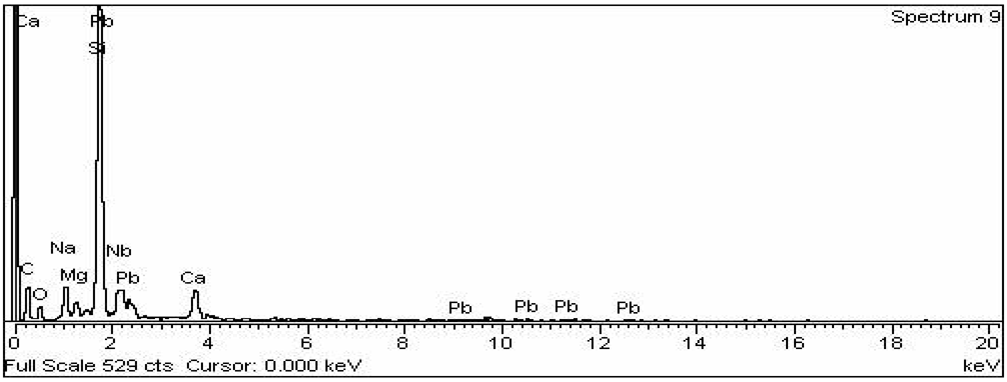
III.1.2.Effect of temperature

Figure 3 & 4 (a, b and c) shows the EDAX patterns of PbPc and CuPc thin films of thickness 450 nm at room temperature (303 K) and annealed at 323 K and 373 K temperature. The percentage of lead and Copper are same in both cases and its amount is low. The percentage of carbon is increased from 62 to 84.81 for Lead and from 60 to 80 for Copper when annealed at high temperature (373 K). The nitrogen amount is very poor. Generally elements of low atomic number are difficult to detect by EDAX. So, in the cases of PbPc and CuPc films hydrogen is difficult to detect.

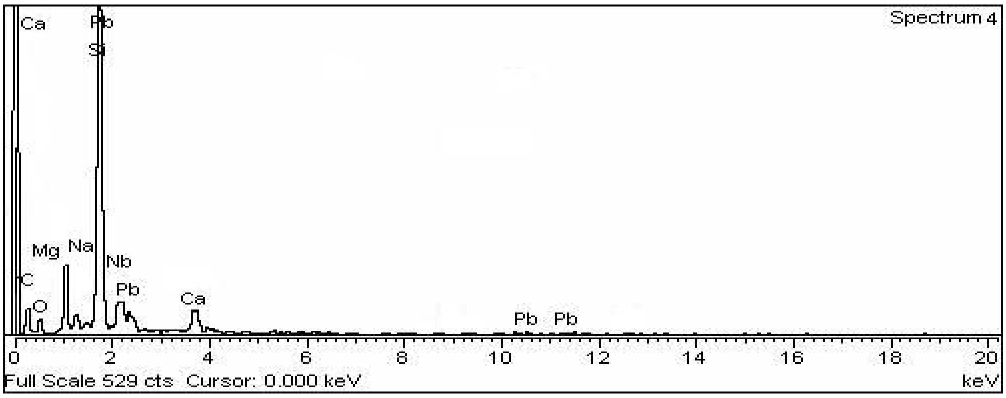
The presence of Silicon, Sodium and Oxygen peaks are due to the glass substrates [21]. The composition of the films deposited at higher thickness and annealed temperatures are found to be more in percentage. It is observed that the deposited annealed films of 373 K slightly deviation from stoichiometry and the film deposited at 303 K has a uniform composition profile. However, the film deposited at 303 K is required for the homogenization. The films deposited and annealed at 373 K only, the thermodynamically stable phase are present and it exhibited a microcrystalline structure with a uniform composition at the micrometer. From this analysis, it is found that the film possess PbPc and CuPc stoichiometry. The small deviation for the stoichiometry may be attributing to surface oxidation.

The peak corresponding to carbon, nitrogen, silicon, sodium and oxygen shows a transition from L to the K-shell which can be termed as a K-Alpha peak (Kα). The peaks corresponding to lead and Copper shows three types of transitions – M-Alpha (Mα), M-beta (Mβ), M-Gamma (Mγ).All these transitions are shown in the EDAX patterns of PbPc and CuPc thin films.

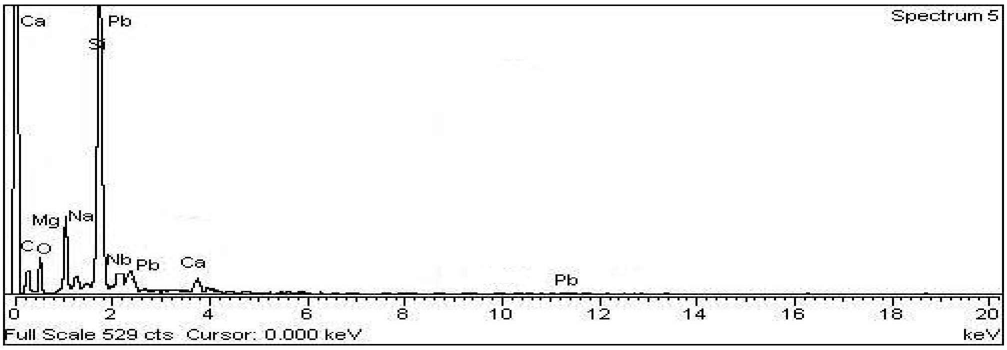
Figure 3 **EDAX patterns of PbPc films for thickness 450 nm at annealed temperature**



(a) 303 K

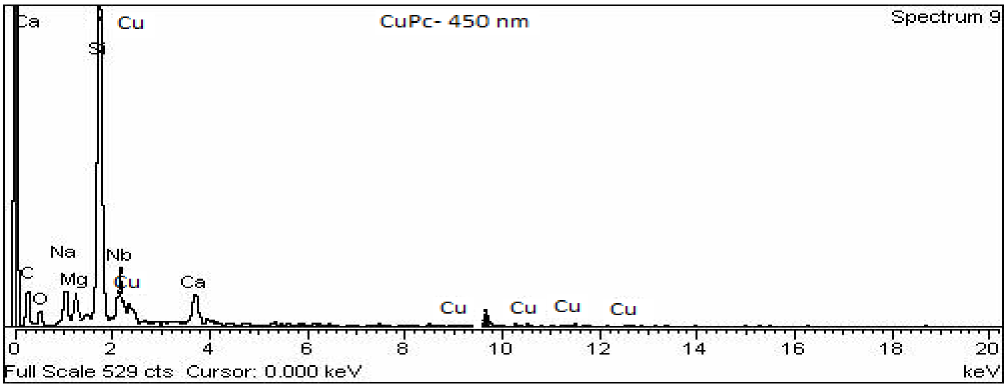


(b) 323 K

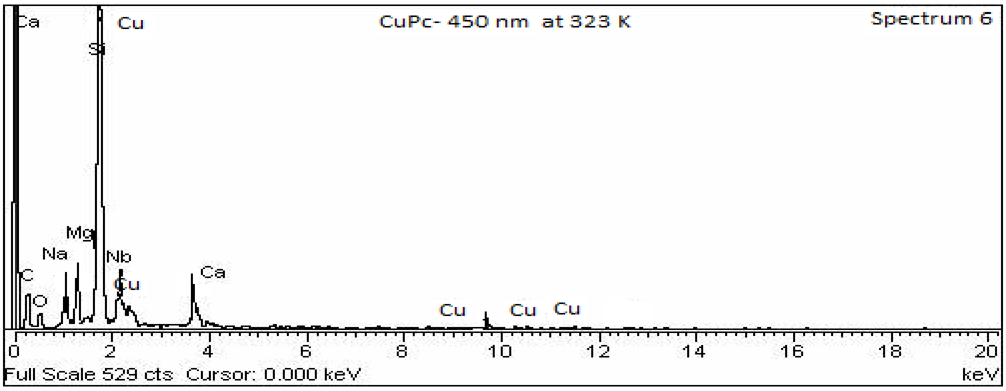


(c) 373 K

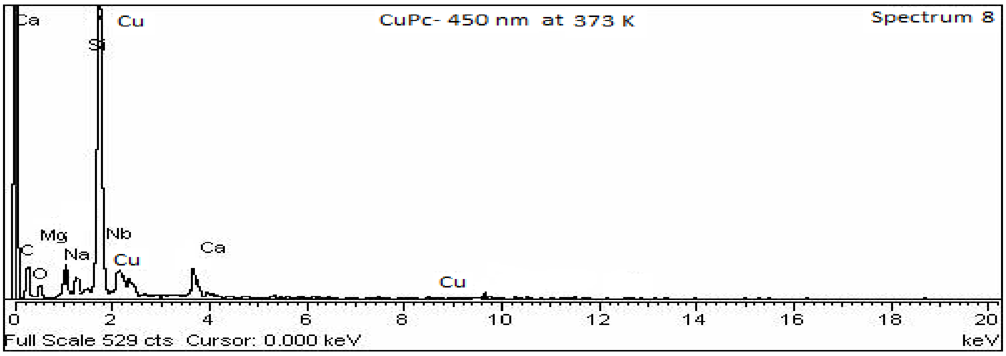
Figure 4 **EDAX patterns of CuPc films for thickness 450 nm at annealed temperature**



(a) 303 K



(b) 323 K



(c) 373 K

III.2.FT-IR Analysis

Figures 5 to 14 shows the infrared spectrum of PbPc and CuPc thin film of 150 nm, 300 nm and 450 nm thickness prepared at room temperature and 450 nm annealed at 323 K and 373 K temperature. The main peak at 725.23±4 cm^{-1} is attributed to non-planar deformation vibrations of the C–H bonds of benzene rings [22, 23] and the C–H in plane bonding at 1112.93±4 cm^{-1} [22, 24]. A medium band at 771.53±4 cm^{-1} also corresponds to non-planar vibrations (Out-of-plane-bonding) of the C–H bonds [22, 25]. The following assignments can be made for the other ligand bands, the 3049.46±4 cm^{-1} band to aromatic C–H symmetric stretching vibrations and the 1606.70±4 and 1479.40±4 cm^{-1} band to C–C benzene ring skeletal stretching vibrations [22, 26, 27]. So it is expected to be intense compared to the C–N stretching at 1078.21±4 cm^{-1}.

One strong intensity band at 881.47±4 cm^{-1} indicates the extraordinary stability of the metal phthalocyanines due to the strong bonding between the metal ion and the four surrounding nitrogen atoms in the pyrrole rings [22, 28]. The peaks in the 700-400 cm^{-1} interval originate most probably from vibrations in the benzene ring in interaction with the pyrrole ring [22].

The band at 1332 ± 6 cm^{-1} is assigned to the C–C stretching in isoindole. The bands appearing at 882 ± 10 and 728 ± 5 cm^{-1} are assigned to the C–H bonding out of plane deformations. The bands appearing at 1284 ± 6 and 1162 ± 4 cm^{-1} is assigned to the C–N in isoindole and in plane band stretching vibration [29].

3.2.1Effect of thickness

Figures 5 to 7 shows the referred spectrum of PbPc thin film of 150 nm, 300 nm and 450 nm respectively. The peaks are formed at 439.77±4, 495.71±4 and 605.65±4 cm^{-1} due to vibrates in the benzene ring in interaction with the byrrole ring. The intensity of the peak increases with increase in the thickness of the films. The strong intensity band at 881.47±4 cm^{-1} decreases with increase in the thickness indicates the stability of the metal Phthalocyanines due to the strong bonding. The intensity of the peak at 3049.46±4 cm^{-1} for aromatic C-H symmetric stretching vibration and peak at 2536.39±4 cm^{-1} decreases with increase in the thickness. The peaks at 1606.70±4 cm^{-1}, 1479.40±4 cm^{-1} and 1330.88± 4 cm^{-1} bands to C-C benzene ring skeletal stretching vibrations. The C-C and C-H benzene ring peak intensities increase with thickness. The intensity of C-N stretching at 1078.21±4 cm^{-1} decreases with increase the thickness of the film. The absence of the band at 1006-1008 cm^{-1} and 1539±4 cm^{-1} suggest that the sample does not contain any metal free phthalocyanine. The peaks are at 1078.21±4 cm^{-1}, 1112.93±4 cm^{-1} and 1159.22±4 cm^{-1} depends on the molecular structure of the complexes and its chemical structure for the central metal.

Figures 8 to 10 shows the spectrum of CuPc thin film of 150 nm, 300 nm and 450 nm respectively. In a metal phthalocyanine, spectrum have a band at 1003 cm$^{−1}$ originates from N–H bending vibration. This band is absent in metal phthalocyanine. This is because in copper phthalocyanine, metal is replaced by metal cation. Metal ligand vibration band is observed in both copper and lead phthalocyanine at 940 and 960 cm$^{−1}$. The peaks are formed at 495.85±4 and 581.4571±4 cm^{-1} due to vibrates in the benzene ring in interaction with the byrrole ring. The intensity of the peak increases with increase in the thickness of the films. The strong intensity band at 771.50±4 cm^{-1} decreases with increase in the thickness indicates the stability of the metal Phthalocyanines due to the strong bonding. The intensity of the peak at 3038.90±4 cm^{-1} for aromatic C-

H symmetric stretching vibration and peak at 2678.89±4 cm^{-1} was decreases with increase the thickness of the film. The peaks at 1391.09±4 cm^{-1}, 1490.00±4 cm^{-1} and 1900.25± 4 cm^{-1} bands to C-C benzene ring skeletal stretching vibrations. The C-C and C-H benzene ring peaks intensities increases with thickness. The intensity of C-N stretching at 1091.34±4 cm^{-1} was decreases with increase the thickness of the film. The absence of the band at 1006-1008 cm^{-1} and 1539±4 cm^{-1} suggests that the sample does not contain any metal free phthalocyanine. The peaks are at 1091.34±4 cm^{-1}, 1391.09±4 cm^{-1} and 1491.22±4 cm^{-1} depends on the molecular structure of the complexes and its chemical structure for the central metal.

The presence of bands at 712 and 739 $cm^{−1}$ suggests the presence of α-phase and the presence of bands at 730 and 752 $cm^{−1}$ suggests that β -phase is also present in CuPc. The FTIR spectroscopic analysis of PbPc and CuPc suggest that these metal phthalocyanines contain both α- and β -phases. The presence of band at 771 $cm^{−1}$ in CuPc spectrum suggests presence of β phase.

Figure 5 FTIR Spectrum of PbPc film of thickness 150 nm prepared at room temperature

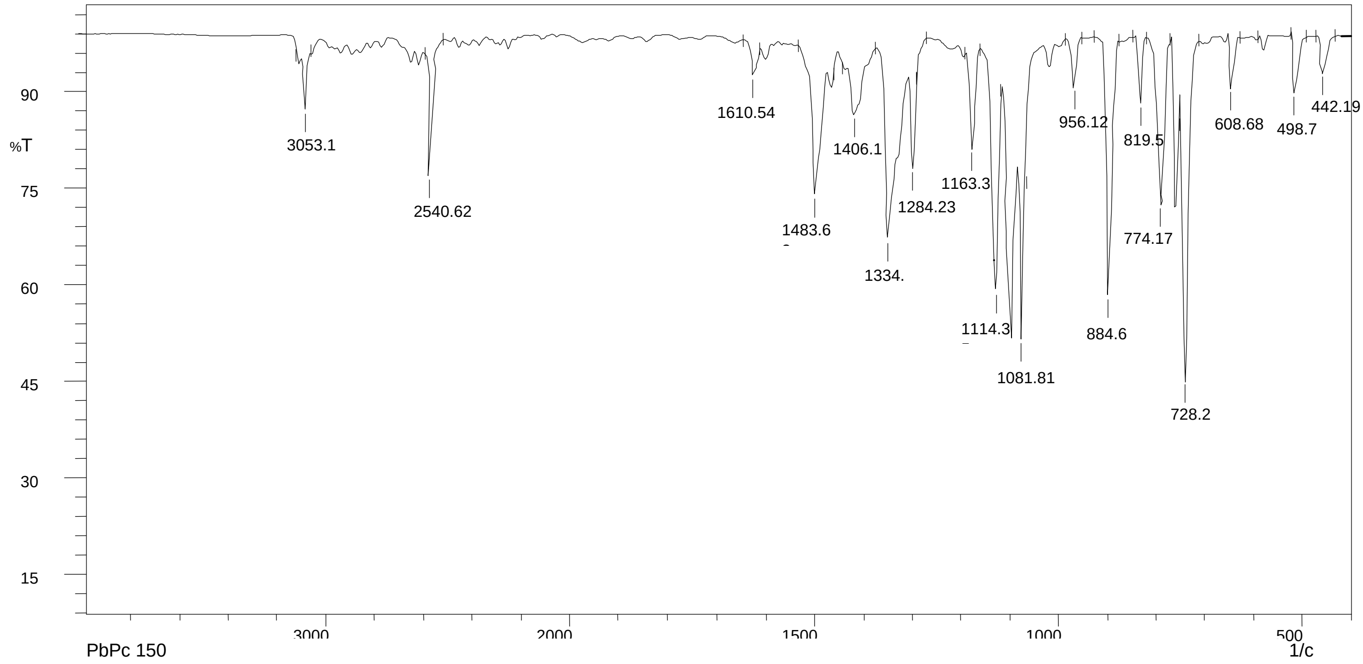


Figure 6. FTIR Spectrum of PbPc film of thickness 300 nm prepared at room temperature

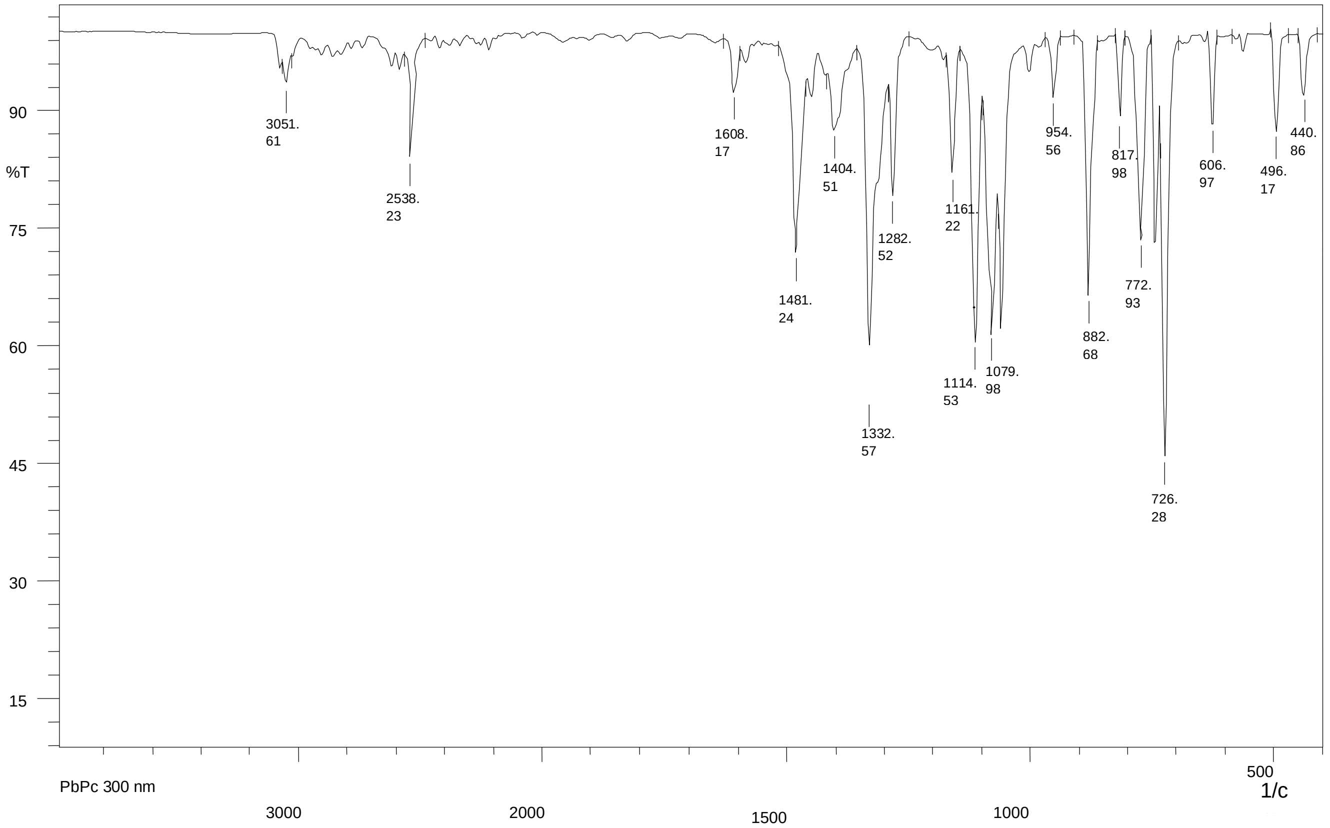


Figure 7: FTIR Spectrum of PbPc film of thickness 450 nm prepared at room temperature

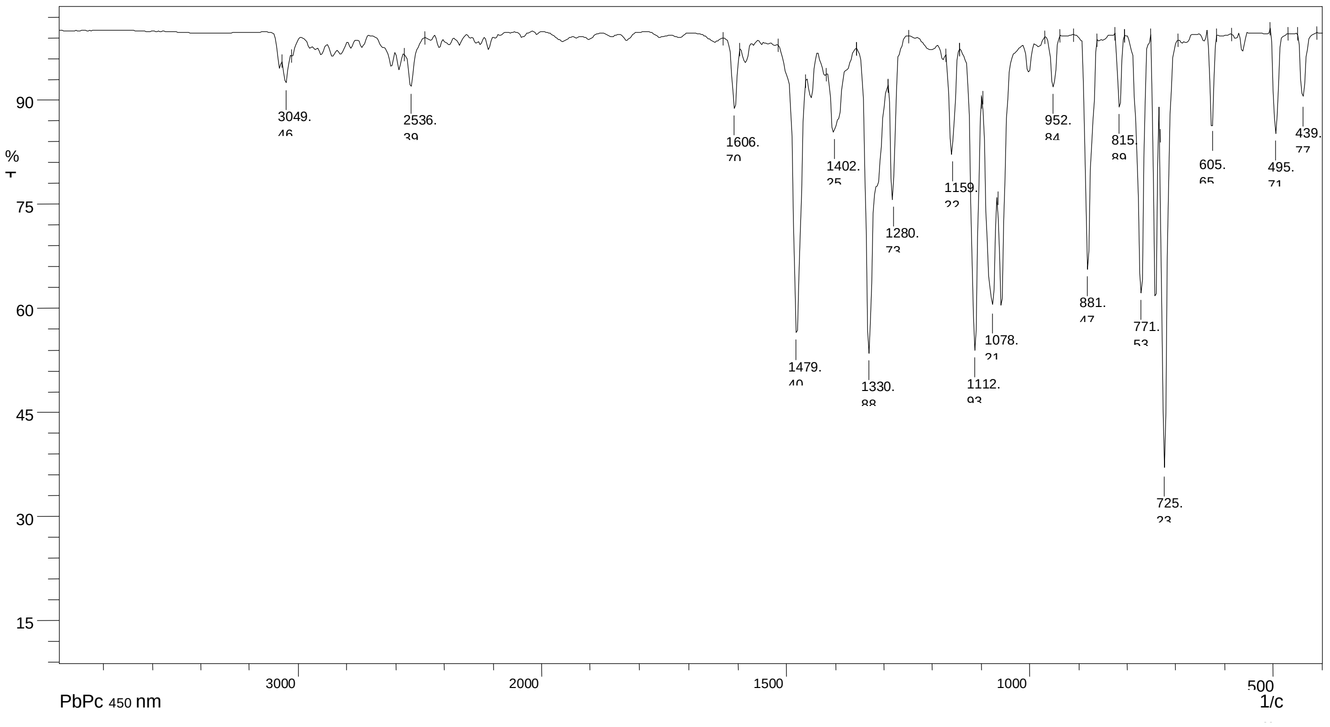


Figure 8 FTIR Spectrum of CuPc film of thickness 150 nm prepared at room temperature

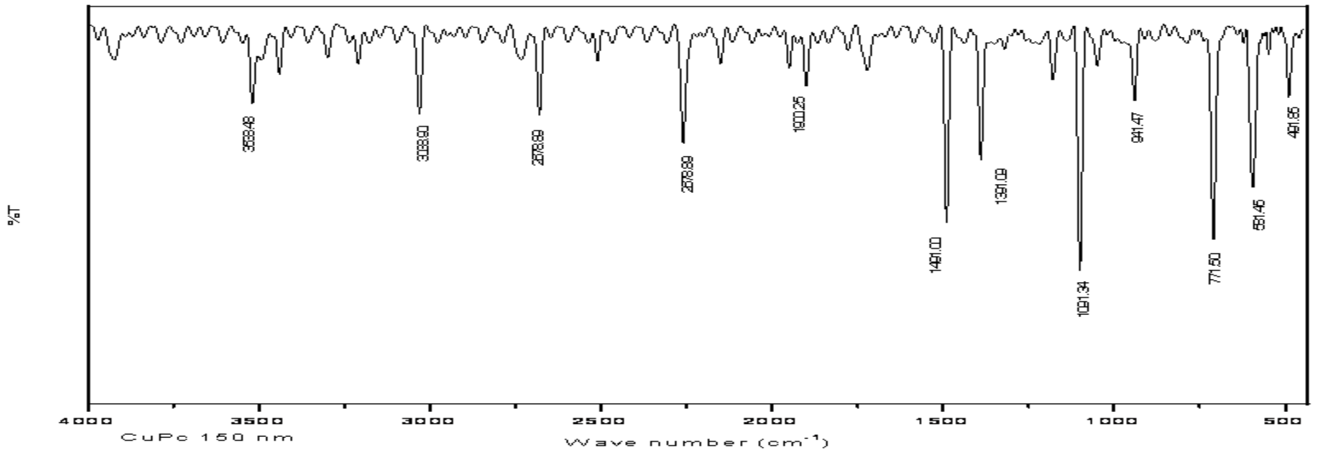


Figure 9 FTIR Spectrum of CuPc film of thickness 300 nm prepared at room temperature

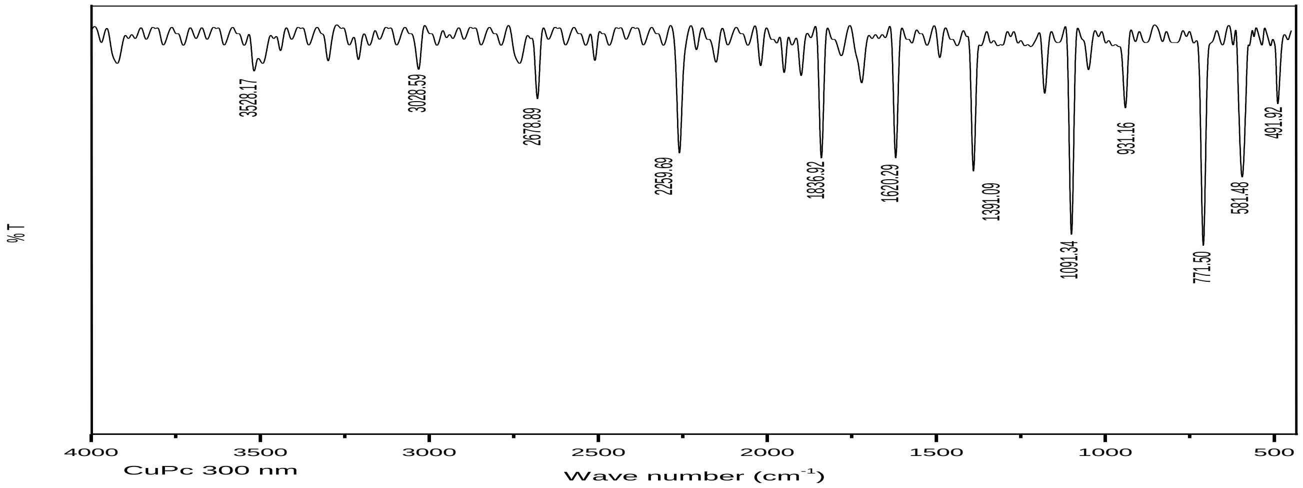
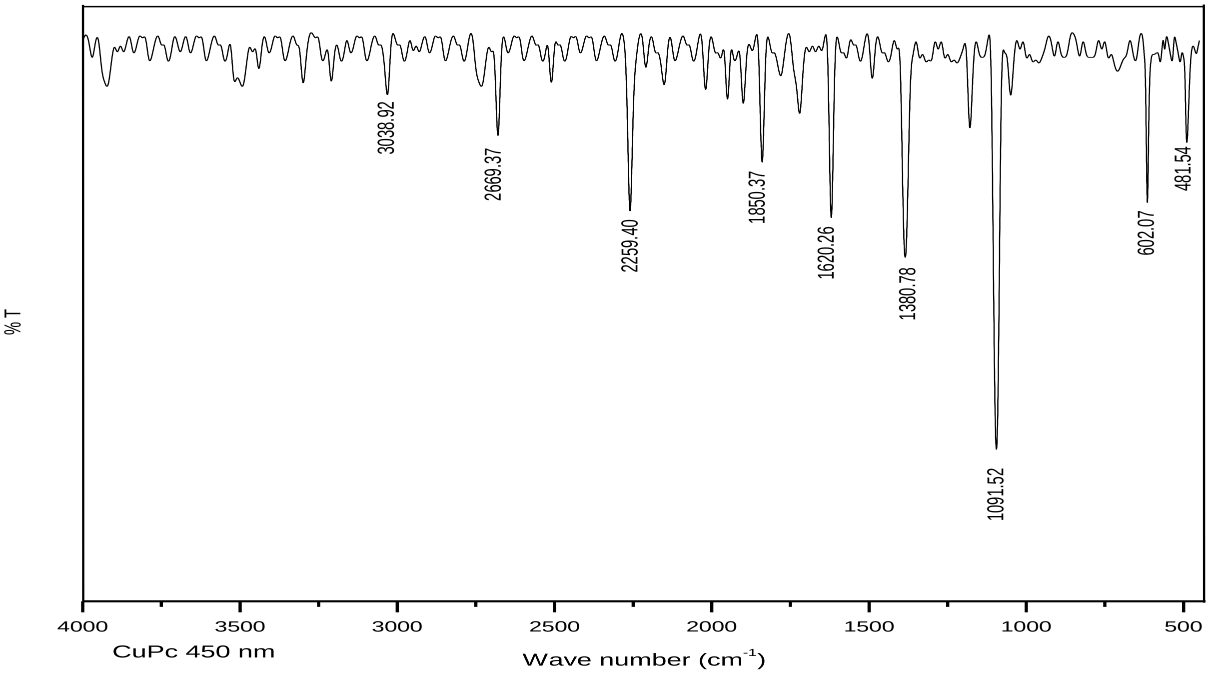


Figure 10: FTIR Spectrum of CuPc film of thickness 450 nm prepared at room temperature.



The Reflectance (R) / Transmission (T) ratios for drop casting films over glass substrate are shown in Table 1. The *R*/*T is* found to be around 1.0 in case of PbPc films, which suggests that in drop casting PbPc films have their molecular plane oriented closer to parallel to plane of the glass substrate. In case of CuPc drop casting films, *R*/*T*value is around 1.8, which suggests that CuPc molecules have similar preferential orientation as PbPc drop casting films.

Table 2 Comparison of reflectance spectra of films with transmission

MPc	Reflectance (*R*)	Transmission (*T*)	*R*/*T*
PbPc	0.78	0.79	1.0
CuPc	2.42	1.34	1.8

III.2.2Effect of temperature

The FT-IR patterns of PbPc and CuPc thin films for thickness 450 nm at different annealed temperatures are shown in the Figures 11 to 14. The benzene ring peaks in the 700 - 400 cm^{-1} interval have increased the intensity with increase in the temperature. The main peaks at 725.23±4 cm^{-1} and 771.53±4 cm^{-1} attributed to non-planar deformation vibrations of the C-H bonds. There is no change in this peak due to annealing. The strong bonding between the metal ion and the four surrounding nitrogen atom in the pyrrole ring peak at 881.47±4 cm^{-1} indicates increasing intensity with annealing temperature. The C-H in-plane bonding at 1112.93±4 cm^{-1} peaks intensity increase with temperature. The spectral pattern in this region 1200-1000 cm^{-1} depends strongly on the molecular structure of the complexes and its chemical structure for the central metal. The middle peak originates from the vibration mode of a pyrrole ring and other two peaks are assigned to the in- plane deformation vibration of C-H bonding in the ring. The middle band has the highest intensity among the three peaks in the usual MPc's with D_4 molecular symmetry; however, the band shows lowest intensity in to the case of PbPC and CuPc. This should be attributed to the molecular structure of PbPc and CuPc [29, 30, 31]. Due increase the temperature, the absence of the band at 3049.46±4 and 2536.39±4 cm^{-1} in the phthalocyanine complexes results in the replacement of hydrogen by metal cation [29].

Figure 11 FTIR Spectrum of PbPc film of thickness 450 nm annealed at 323 K

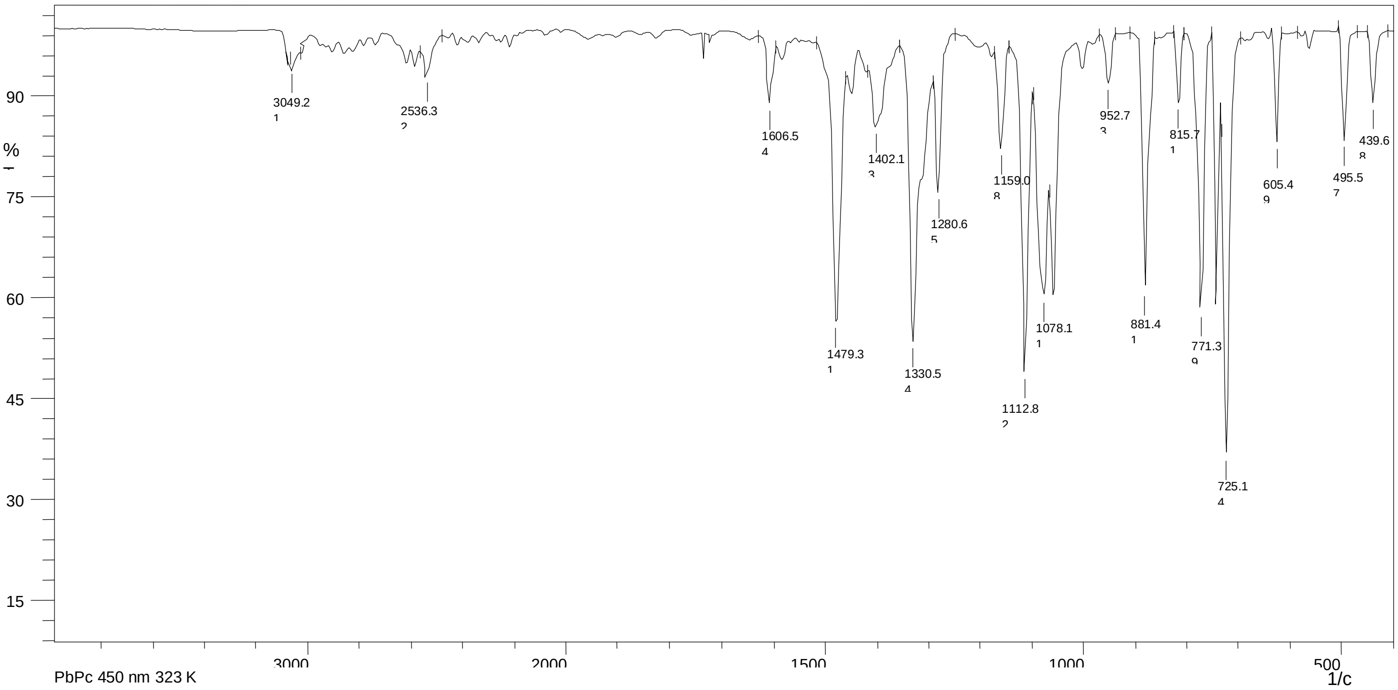


Figure 12 FTIR Spectrum of PbPc film of thickness 450 nm annealed at 373 K

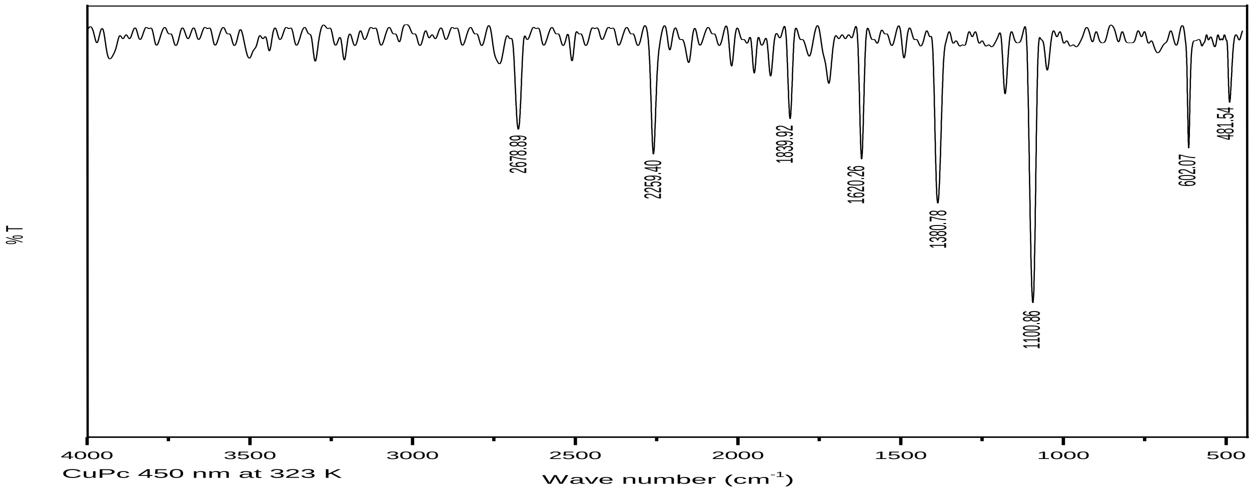


Figure 13 FTIR Spectrum of CuPc film of thickness 450 nm annealed at 323 K

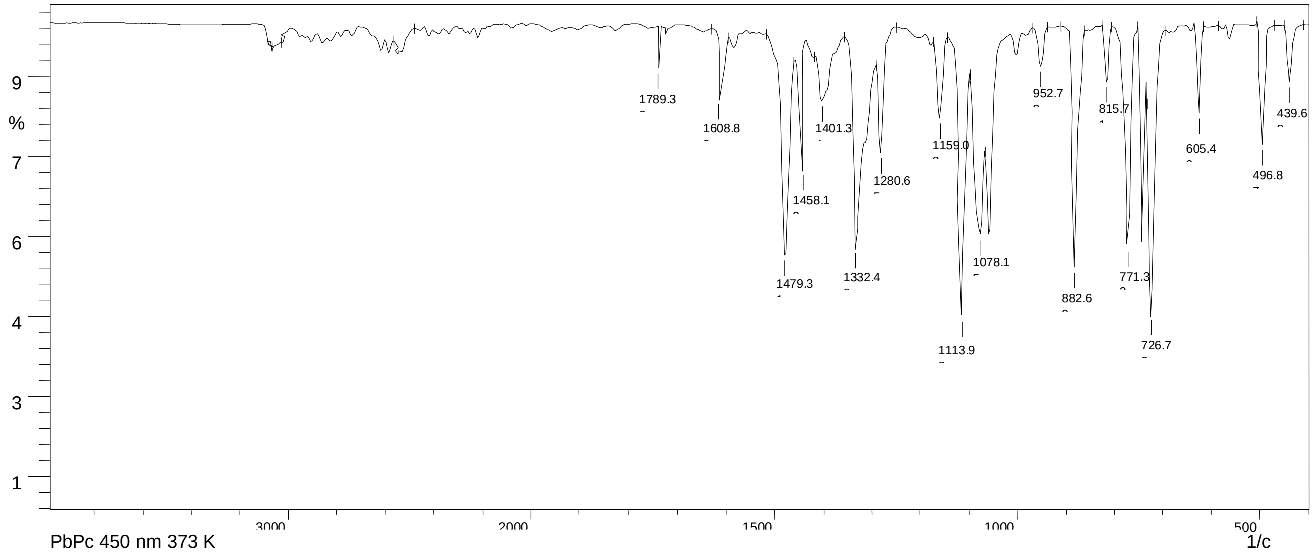
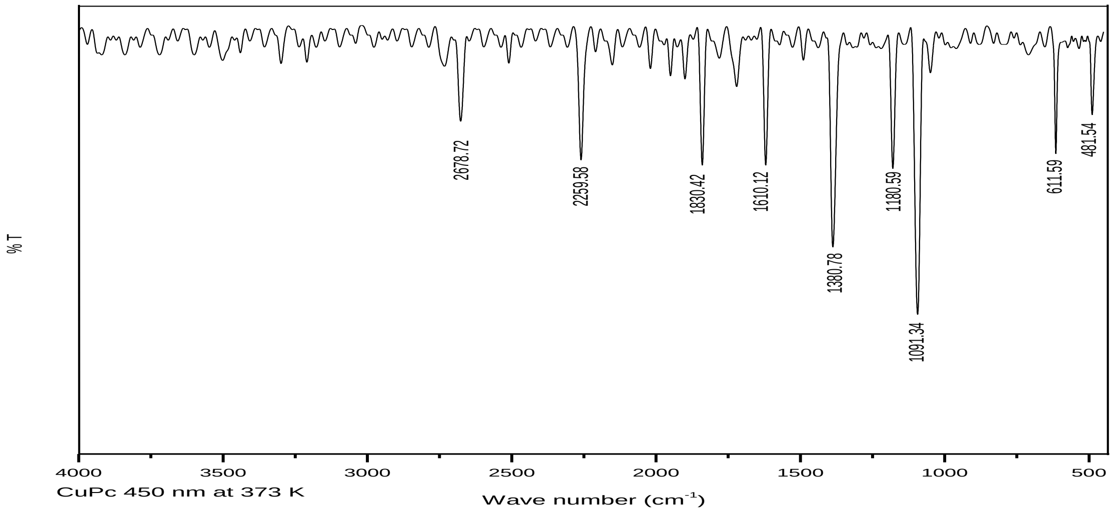


Figure 14 FTIR Spectrum of CuPc film of thickness 450 nm annealed at 373



The material characterization of these films by FT-IR spectroscopy clearly provides a convenient diagnostic technique in the development of PbPc and CuPc based thin film sensors [29].

IV. CONCLUSION

EDAX analysis is used to find the elemental composition. The percentage of lead, copper and carbon were increases with thickness. The presence of Silicon, Sodium and Oxygen peaks are due to the glass substrates. The percentage of carbon is increased when annealed at high temperature (373 K). The composition of the films deposited at higher thickness and annealed temperatures are found to be in more percentage.

FT-IR analysis identifies the presence of functional groups which absorb at definite frequencies. The spectral pattern in this region depends strongly on the molecular structure of the complexes and its chemical structure for the central metal. The FTIR spectroscopy analysis indicates presence of both α and β-phases of phthalocyanines in both the samples. We have utilized grazing angle FTIR spectroscopy to analyze molecular orientations in phthalocyanine films deposited over glass substrate. The CuPc samples showed preferential orientation along parallel direction of the substrate surface in vacuum coated thin films. Our results suggest that metal ions play an important role in defining molecular orientation in thin films.

REFERENCES

1. C. D. Dimitrakopoulos and P. R. L. Malenfant, Adv. Mater. (Weinheim, Ger.) 14, 99(2002).
2. G. Horowitz, Adv. Mater. (Weinheim, Ger.) 10, 365 (1998).
3. R. D. Yang, J. Park, C. N. Colesniuc, I. K. Schuller, W. C. Trogler, and A.C. Kummel, “Ultralow drift in organic thin-film transistor chemical sensors by pulsed gating” J. Appl. Phys. 102, 034515, (2007).
4. F. Liao, C. Chen, and V. Subramanian, "Organic TFTs as gas sensors for electronic nose applications", Sensors and Actuators B-Chemical. Vol. 107, pp. 849-855, (2005).
5. J. B. Chang, V. Liu, V. Subramanian, K. Sivula, C. Luscombe, A. Murphy, J. Liu, and J. M. J. Frechet. “Printable polythiophene gas sensor array for low-cost electronic noses” Journal of Applied Physics, 100(1):014506, (2006).
6. R. Ben Chaabane, A. Ltaief, L. Kaabi, H. Ben Ouada, N. Jaffrezic-Renault and J. Davenas,”Influence of ambient atmosphere on the electrical properties of organic thin film transistors” Mater. Sci. Eng., C 26, 514, (2006).
7. G. Guillaud, J. Simon, and J. P. Germain, Metallophthalocyanines: “Gas sensors, resistors and field effect transistors” Coord. Chem. Rev. 178–180, 1433 -1484, (1998).
8. S. Cipolloni, L. Mariucci, A. Valletta, D. Simeone, F. De Angelis and G. Fortunato "Aging effects in high performance Pentacene Thin Film Transistors." Thin Solid Films, vol. 515 , pp. 7546-7550 (2007).
9. D. Knipp, T. Muck, A. Benor, and V. Wagner, “Environmental stability and electronic transport of pentacene thin film transistors” J. Non-Cryst. Solids 352, 1774 (2006).
10. Y. Qiu, Y. Hu, G. Dong, L. Wang, J. Xie, and Y. Ma, “H_2O effect on the stability of organic thin-film field-effect transistors” Appl. Phys. Lett. 83,1644 (2003).
11. Z.-T. Zhu, J. T. Mason, R. Dieckmann, and G. G. Malliaras, “Humidity sensors based on pentacene thin-film transistors” Appl. Phys. Lett. 81, 4643 (2002).
12. C. R. Kagan, A. Afzali, and T. O. Graham, “Operational and environmental stability of pentacene thin-film transistors” Appl. Phys. Lett. 86, 193505 (2005).
13. Y. Natsume, “Characterization of solution-processed pentacene thin film transistors” Phys. Status Solidi A 205, 2958-2965 (2008).
14. Mrwa A., Friedrich M., Hofmann A. and Zahn D.R.T. (1995) ‘Response of PbPc to high NO_2 concentration’, Sensors and Actuators B, Vol. 24-25, pp. 596-599, (1995).
15. M. Pope, C.E. Swenberg, Electronic Process in Organic Crystals, Clarendon Press, Oxford, (1992).

16. Tang C.W. and Van Slyke S.A. 'Organic electroluminescent diodes', Appl. Phys. Lett., Vol. 51, p. 913 (1987).
17. Collin R.A. and Belgachi A. 'Electrical and optical studies on thin films of indium phthalocyanine chloride', Mater. Lett., Vol. 9, pp. 340-349, (1989).
18. Machida Y., Saito Y., Taomoto A., Nichogi K., Waragi K. and Asakawa S. 'Electrical Switching in Evaporated PbPc Films', Jpn. J. Appl. Phys. Vol. 28, pp 297-298, (1989).
19. B.A. Gregg, 'Excitonic Solar Cells' J. Phys. Chem. B 107, 4688 (2003).
20. Peumans P. and Forrest S.R. 'Very-high-efficiency double-heterostructure copper phthalocyanine/C_{60} photovoltaic cells', Appl. Phys. Lett., Vol. 79, p. 126(2001).
21. Prabahar S. and Dhanam M. 'CdS thin films from two different chemical baths-structural and optical analysis', J. Crys. Growth, Vol. 285, pp. 41- 48. (2005).
22. A. Ahmad and R. A. Collins, "FTIR characterization of triclinic lead phthalocyanine" J. Phys. D: Appl. Phys. 24 1894-1897 (1991).
23. A.N. Sidorov, "Fourier-transform infrared and UV–vis spectroscopes of nickel phthalocyanine thin films", Opt. Spectrosc. 40,280,(1976).
24. A.J. Dann, H. Hoshi and Y. Maruyama, "Spectral dependence of the anisotropy of $\chi(3)$ of epitaxially grown vanadyl phthalocyanine film", J. Appl. Phys. 67, 1371,(1990).
25. G.N. Meshkova, A.T. Vartanyan and A.N. Sidorv, "Fourier-transform infrared and UV–vis spectroscopes of nickel phthalocyanine thin films", Opt. Spectrosc. 43, 151(1977).
26. D. Campbell and R.A. Collins, "A study of the interaction between nitrogen dioxide and lead phthalocyanine using electrical conduction and optical absorption" Thin Solid Films 295, 277-282(1997).
27. W.J. Kroenke and M.E. Kenny, "Low Hue Photobleaches",Inorg.Chem. 3277–282,(1964).
28. T.Kobayashi, F. Kurokawa, N. Uyeda and E. Suito, "Structural Properties and UV to NIR Absorption Spectra of Metal-free Phthalocyanine (H2PC) Thin Films", Spectrochim. Acta. A 26, 1305,(1970).
29. R. Seoudi, G.S. El-Bahy and Z.A. El-Sayed, "FTIR, TGA and DC electrical conductivity studies of phthalocyanine and its complexes" J. Mole. Stru. 753, 119-126,(2005).
30. F.H. Moser and A.L. Thomas, "Phthalocyanine compounds", Reinhold publishing New York (1963).
31. Janczak and R. Kubiak, "Catalytic trimerization of 2- and 4-cyanopyridine isomers to the triazine derivatives in presence of magnesium phthalocyanine", Polyhedron 21, 265,(2002)