

## Thermally Induced phase Transition in Crystalline Lead Phthalocyanine thin Films

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### Abstract

The structural properties of thin film of Lead Phthalocyanine (PbPc) on a glass substrate is prepared by vacuum deposition method. The thickness of the films were 150nm, 300nm and 450nm. The effect of film thickness, structural and annealing of the Lead Phthalocyanine thin films are investigated by X-ray diffraction and Scanning Electron Microscopy (SEM). The results obtained from X-ray diffraction measurement indicate the monoclinic structure with a (001), (320), (111) and (420) orientation and triclinic structure with (400) orientation. Thickness of 450 nm is annealed at 323 K and 373 K. The film consist of triclinic (200), (300) and (400) phases for 323 K annealed sample and (100) reflection of triclinic phase for 373 K annealed sample. SEM is one of the best tools to investigate the surface smoothness and to find the grain size of the particles. From the image it is evident that the surface of the films is smooth and grain size is less than a micrometer.

**Key words:** Lead Phthalocyanine, diffraction, Scanning electron microscopy, monoclinic and triclinic.

### Introduction

In the research on Phthalocyanines, some attention has been given to Lead Phthalocyanine (PbPc) because of its characteristic structural and electrical properties. Lead Phthalocyanine is an attractive material for device applications in various field such as Opto electronics, gas sensors, OLEDs, FETs, etc. [1-3].

PbPc was chosen as a model compound since it has a somewhat higher specific conductivity compared to conventional divalent Pc materials [4,5]. The lead in Phthalocyanine is important factor for the opto electronic properties. Lead Phthalocyanine with a shuttle-cock shaped molecule structure [6] has unique

properties among Phthalocyanine families i.e., one dimensional conduction nature of Pb ions [7,8]. The one dimensional conduction nature of Pb is caused by the orbitals of the lead atom distributed perpendicular to the molecular plane of the Pc ring. Kera et al reported that one of the non bonding orbitals of oxygen atom in OTiPc is distributed perpendicular to the molecule plane. OTiPc thin film also has a shuttlecock shaped molecular structure similar to PbPc [9]. In fabricating organic devices with PbPc, it is necessary to control the orientation of the molecular plane in Pc films [10-13]. The electrical properties of Pc, Copper Pc and PbPc films were investigated by in situ field effect measurement [14]. Metal-Pc films which consists of amorphous and/or polycrystal states have been used generally as carrier transport layers in organic devices. Important to investigate the opto electronic properties of Pc films which depend on the orientation of the molecular plane [15-18].

The basic electrical conduction process observed in these materials depend on many factors including the Pc species, the phase of the micro-crystalline comprising the film, thickness and the electrodes materials. Phthalocyanine exhibit semi conducting behaviour and their electrical conductivity is affected by the presence of various gases. Wright has reviewed the particular gas sensing properties of Phthalocyanines to various gases [19]. Yasunaga et al have described some of the effects of oxygen on the conductivity of Lead Phthalocyanine [14]. The present systematic investigation was to prepare homogeneous thin films of PbPc and to study their structural properties using XRD and SEM.

In this paper, we will report on the structural properties of PbPc thin films prepared by evaporation and deposition technique. Aim of the work was to clarify the crystal structure of the PbPc thin films and its surface composition of PbPc thin films.

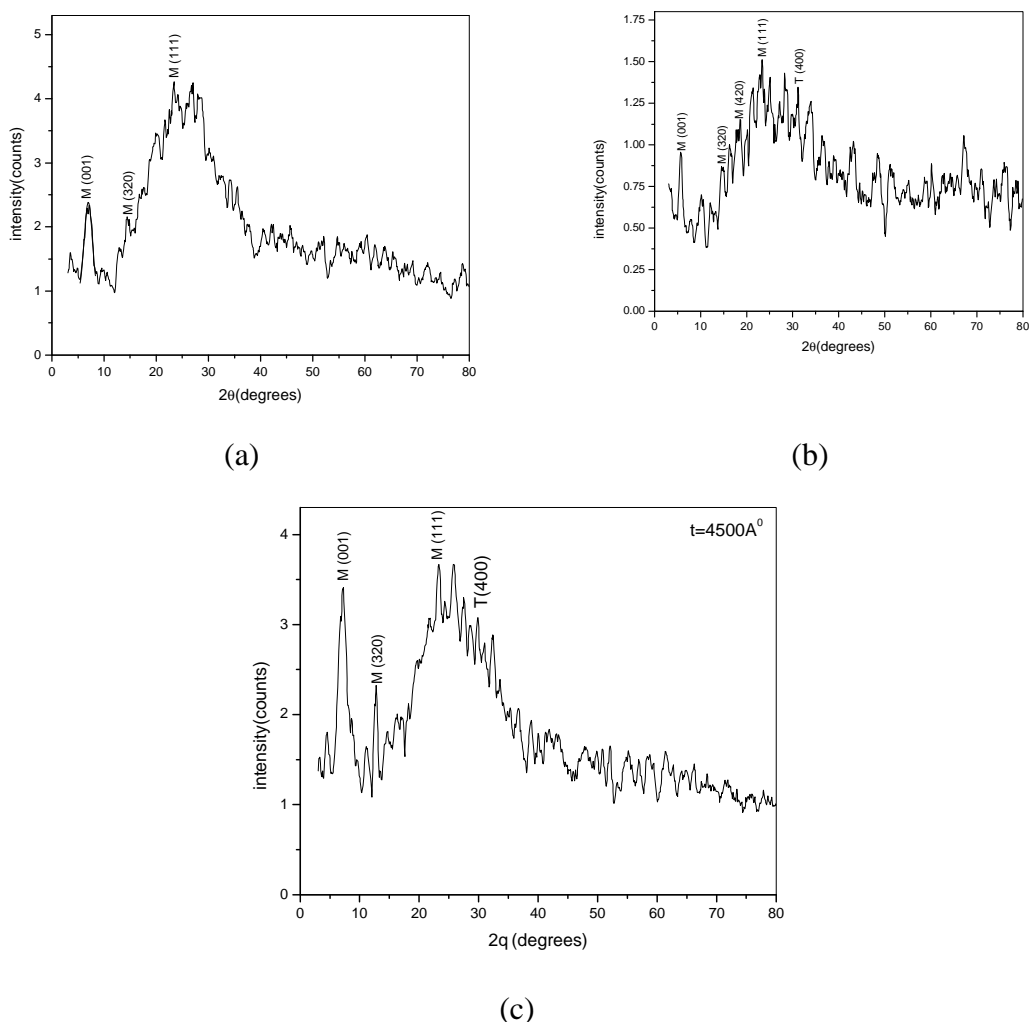
## **Experiment**

The powder of lead phthalocyanine (80% dye, sigma Aldrich company, Bangalore, India) was kept in a molybdenum boat of 100 amps and heated with high current controlled by a transformer. The transformer is capable of supplying 150amps at 20volts is used to provide the accessory current for heating the molybdenum source which was used for the evaporation process. Prior to each evaporation, the evaporant material was carefully degassed at lower temperature for about 45 minutes with the shutter closed. Deposition of PbPc on pre-cleaned glass substrates under the pressure of  $10^{-6}$  Torr was achieved by slowly varying the current. The rate of evaporation was properly controlled and maintained constant during all the evaporations. Rotary drive was employed to maintain uniformity in film thickness. The thickness of the films was measured by Quartz crystal monitor. The adhesion of the films to the substrate seems to be extremely good. The samples prepared in a similar environment were used for studying their various properties. The structures of the films were examined by  $\theta$ -2 $\theta$  X-ray diffraction using a Cu  $K\alpha$  source. The morphology was examined with scanning electron microscopy.

## Results and Discussion

### XRD analysis of PbPc Thin Films - Effect of thickness

The X-ray diffraction patterns of thermally evaporated PbPc thin films of thickness 150 nm, 300 nm and 450 nm prepared at room temperature are shown in Fig. 1. The patterns at lower thickness (150 nm) shows peaks at  $2\theta$  values  $6.85^\circ$ ,  $14.16^\circ$  and  $24.55^\circ$  that were assigned to monoclinic (001), (320) and (111) lines respectively. The patterns at thickness (300 nm) shows an extra peak at  $2\theta$  value  $17.49^\circ$  and is assigned to the monoclinic (420) line. A peak at  $2\theta$  value  $30.26^\circ$  coinciding with the triclinic (400) line is seen for higher thickness (450 nm). The peak values are in good agreement with the previous literature works [11,16].



**Figure 1:** XRD Patterns of PbPc Films for thicknesses.

a) 150 nm    b) 300 nm    c) 450 nm

From the XRD patterns of PbPc films of different thicknesses, it is clear that as thickness increases, triclinic grains (T) are seen along with monoclinic (M) forms of PbPc. Thus evaporated PbPc films at room temperature are monoclinic at lower thickness or a mixture of monoclinic and triclinic forms at higher thickness [16, 20]. These evaporated films are polycrystalline in nature.

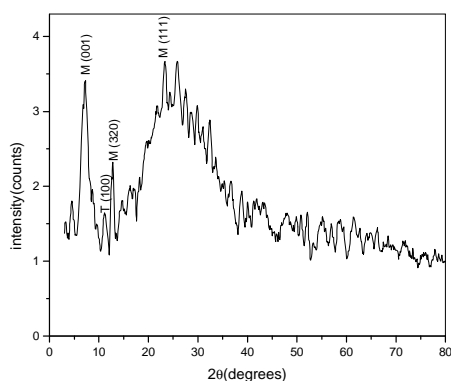
A weak intensity of (320) reflection and absence of (h00) reflections in all thicknesses implies a low degree of crystallinity of the monoclinic film compared with the triclinic film. The XRD patterns shows weak diffraction peaks for (320) and (420) monoclinic lines of PbPc. PbPc molecules in the monoclinic modification are composed of well-defined structure which clusters themselves, consist of orderly arranged molecular stacks. Within the stacks there exist two substructures which have opposite orientations of the shuttlecock Pc structure. Such a structure explains the weak diffraction peaks of monoclinic crystals [11, 16, 21, 22]. In this phase, the molecules stack linearly to form a molecular column parallel to the c axis [16, 20].

### Effect of temperature

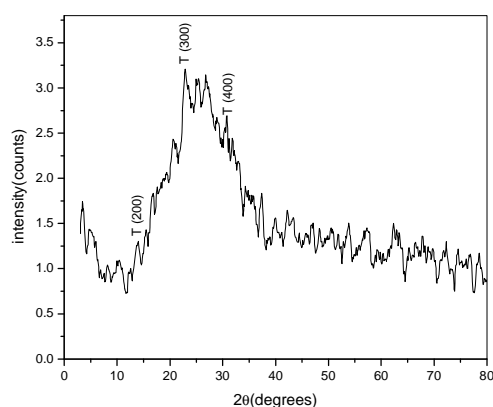
The XRD patterns of PbPc films for thickness 450 nm at different temperatures are shown in Fig. 2. The peaks obtained at room temperature were assigned to the monoclinic phase with some triclinic grains.

The XRD graphs at 323 K shows peaks at  $2\theta$  values  $14.9^\circ$ ,  $22.4^\circ$  and  $30.3^\circ$  assigned to the triclinic (200), (300) and (400) lines respectively. Here all peaks are of small range. When temperature is again increased to 373 K one more peak at  $2\theta$  value  $7.43^\circ$  arise which gets assigned to the (100) reflection of triclinic phase. The results are consistent with the previous literature works [11, 16].

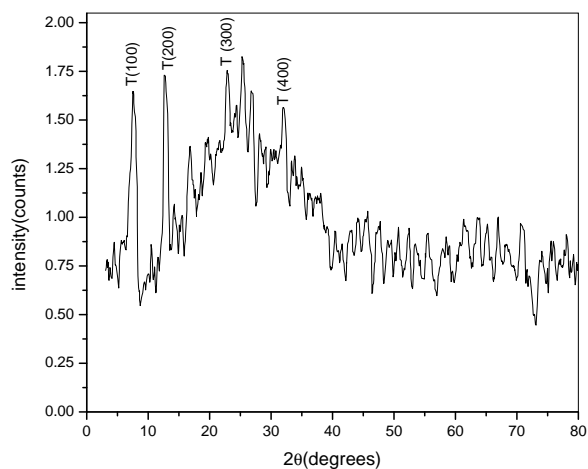
From the XRD patterns at different temperature it is concluded that as temperature increases the number of peaks for triclinic phase increases. In the triclinic structure, the molecular stack along the a-axis orienting their convex and concave sides alternatively. Annealing at 373 K changes the structure to triclinic with (100) as the direction of preferential orientation. So when annealing is carried out in air at 373 K, triclinic phase becomes predominant [20]. The annealed films are also polycrystalline in nature.



(a)



(b)



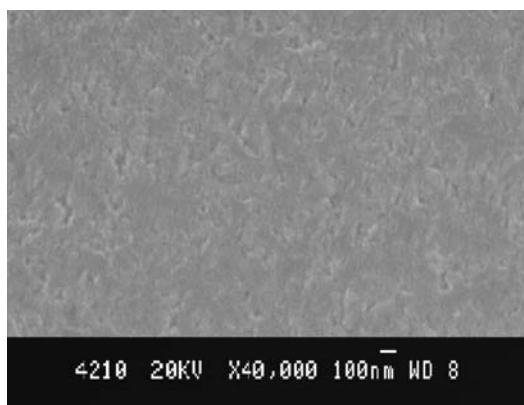
(c)

**Figure 2:** XRD Patterns of PbPc Films for thickness 450 nm at temperatures  
a) 303 K      b) 323 K      c) 373 K

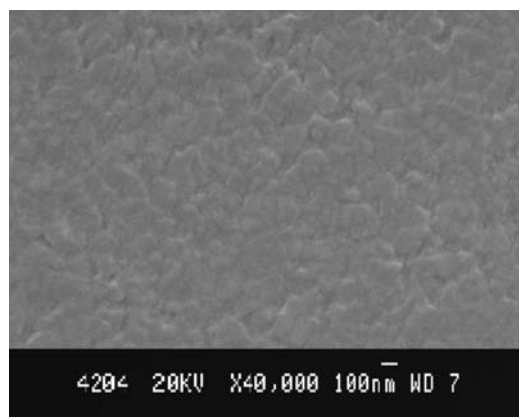
### SEM Analysis of the film - Effect of thickness

Fig.3. shows the SEM photographs of PbPc films with thicknesses 150 nm, 300 nm and 450 nm. The SEM image of lower thicknesses shows very fine particles and disordered phases [20, 21]. Along with these fine particles rod like structures are seen in the case of film with higher thickness 450 nm.

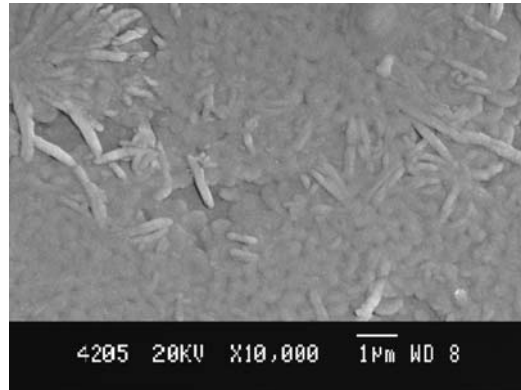
From the SEM image of the films, it is clear that the grain size of the films increase with increase in the thickness. The surfaces of the films are rough. The area fraction of the powder agglomeration on the film increases as the PbPc content increases.



(a)



(b)



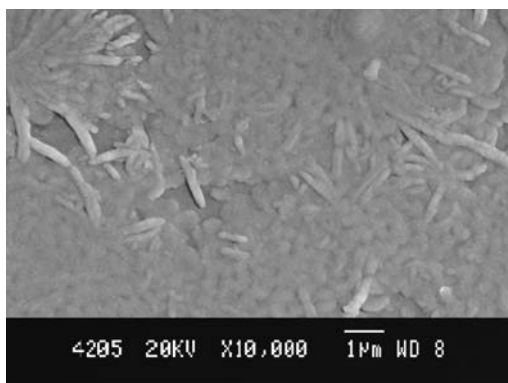
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**Figure 3:** SEM images of PbPc films for thicknesses  
 a) 150 nm    b) 300 nm    c) 450 nm

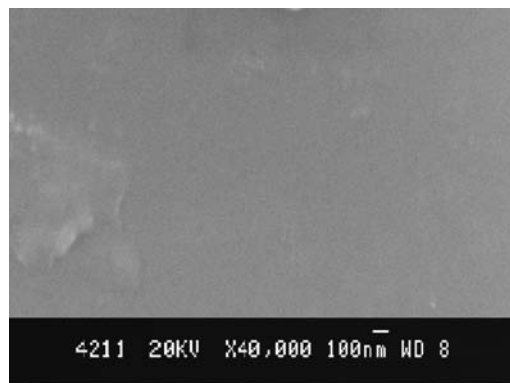
The agglomerations of PbPc powder make the film structure porous. The higher the PbPc content, the more numerous are the agglomerations and the higher is the porosity. The porosity and the amount of PbPc on the film are responsible for the increase in film thickness with increasing PbPc content

#### **Effect of temperature**

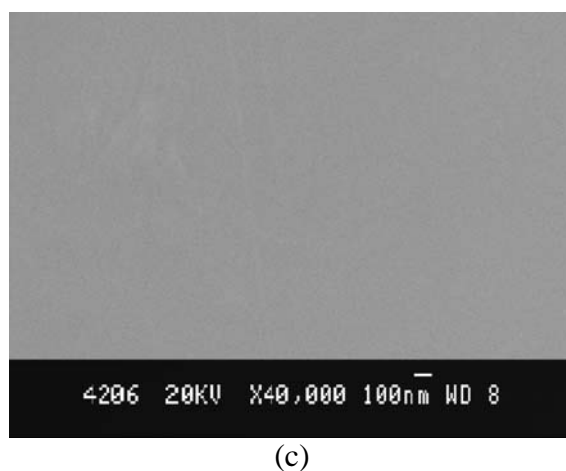
Fig. 4. shows the SEM images of PbPc films at room temperature (303 K) and at two annealed temperature (323 and 373 K). The film at 303 K shows a mixture of fine particles and rod like structures. As the temperature increases the smoothness and uniformity of the film also increases.



(a)



(b)



**Figure 4:** SEM images of PbPc films for thickness 450 nm at temperatures  
a) 303 K      b) 323 K      c) 373 K

In annealed films, the rod like crystal deform and become small particles as a result of the oxidation of phthalocyanine by adsorbed and /or diffuse in the bulk oxygen, therefore no larger rod like crystals were observed and small particle appeared, taking a different form from the fine particles observed for the film annealed at 373K temperature. Therefore the formation of the fine particles may proceed as a result of the interaction between the absorbed oxygen and phthalocyanine. These absorbed tendencies imply that the surface of phthalocyanine particles is oxidized by annealing at 373K and the crystal growth is depressed by the formation of lead oxide on the surface. For the more the rod like crystals deform and becomes small particles as a result of the oxidation of the phthalocyanine by absorbed or diffuse in bulk oxygen.

The surface of the PbPc films is rough. These are powder agglomerations that were confirmed as PbPc. The area fraction of the powder agglomeration on the films increases as the PbPc. The area agglomerations of PbPc Powder make the film structure porous [22] The higher the PbPc content, the more numerous are the agglomeration and the higher is the porosity. The porosity and the amount of PbPc on the films are responsible for the increase in film thickness with increasing PbPc content. The thickness of the film increases after annealed at 373 K. Therefore, the heat is responsible for the increase in film thickness. Since the films expand, it is believed that the porosity is increased.

The topography of the film of thickness 450 nm is shown in figure 4. It is apparent that the deposited films formed on glass consist of fine particles and disordered phases that exist between the interparticles. Even at a higher magnification, well crystallized particles were not detected. It appears, therefore, that the degree of crystallinity of the fine particles was poor in the deposited films.

## Conclusion

Films of Lead Phthalocyanine of thicknesses 150nm, 300nm and 450nm are prepared by vacuum deposition method. From the XRD patterns of PbPc films of different thicknesses, it is clear that as thickness increases, triclinic grains (T) are seen along with monoclinic (M) forms of PbPc. Thus evaporated PbPc films at room temperature are monoclinic at lower thickness or a mixture of monoclinic and triclinic forms at higher thickness. These evaporated films are polycrystalline in nature. PbPc molecules in the monoclinic modification are composed of well-defined structure which clusters themselves, consist of orderly arranged molecular stacks. Within the stacks there exist two substructures which have opposite orientations of the shuttlecock Pc structure. From the XRD patterns at different temperature it is concluded that as temperature increases the number of peaks for triclinic phase increases. The SEM image of lower thickness film of 150 nm shows small cloud like structure, the size of which increases with increasing thickness. Along with these cloudy structure rod like structures are seen in the case of film with higher thickness 450 nm. As the film is annealed the smoothness and uniformity of the film increases.

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