Chapter 5

STRUCTURAL STUDIES IN COPPER PHTHALOCYANINE COBALT PHTHALOCYANINE AND LEAD PHTHALOCYANINE THIN FILMS

5.1. Introduction

The technique of X-ray diffraction (XRD) allows accurate determination of lattice d-spacings, lattice parameters, crystallite size and phase identification. Various metal substituted phthalocyanines are of interest as potential materials for thin film gas sensors in view of their thermal stability, high conductivity and sensitivity to a variety of gases.[1-4] The electrical properties of these materials are dependent on the crystal structure and the requirement for gas sensing is that the structure should be well defined and phase should be stable over wide temperature range. The electrical properties of these organic semiconductors depend on the crystal structure relating to various dimorphic forms and there is much interest in how these affect material preparation and thermal treatment. In this chapter the structural studies in CuPc, CoPc and PbPc thin films are dealt with.

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5.2. Theory

Every atom in a crystal scatters an X–ray beam incident upon it in all directions. Because, even the smallest crystal contains a very large number of atoms, the chance that these scattered waves would *constructively interfere is zero except* for the fact that the atoms in crystals are arranged in a regular and repetitive manner. The possible directions in which a crystal can diffract a beam of monochromatic X–rays is determined by the Bragg condition,

$$2d \sin\theta = n\lambda \qquad 5.2.1$$

where d is the distance between atomic planes parallel to the axis of the incident beam, θ, the angle of incidence relative to the planes in question, n, the order of reflection and λ, the wavelength of the incident X–rays. The factor d is related to the (hkl) indices of the plane by the relation.

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad 5.2.2$$

and

$$\sin^2\theta = \frac{\lambda^2}{4}\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right) \qquad 5.2.3$$

It is therefore apparent that the diffraction direction are solely determined by the structure and size of the unit cell. Intensities of the

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diffracted beams are determined by the positions of the atoms within the unit cell. The consequence of this is that although there are theoretically hundreds of possible diffraction directions, there are particular atomic arrangements which reduce the intensity of so many diffracted beams to zero.

The grain size of the film is calculated from the Full Width at Half Maximum (FWHM) of the X–ray peaks using the Scherrer formula[5]

$$L = \frac{k\lambda}{\eta_{1/2} \cos\theta} \qquad 5.2.4$$

here k is the Scherrer constant (k = 0.9), λ = 1.54059 Å, $\eta_{1/2}$ the FWHM in radians and θ, the diffraction angle of the most intense peak.

5.3. Experiment

Commercially available copper phthalocyanine (CuPc), cobalt phthalocyanine (CoPc) and lead phthalocyanine (PbPc) (98% pure) powder from Aldrich company INC. WI. are used as the source materials for thermal evaporation. As the measured and calculated percentage composition of the elements are nearly same, they are not further purified by entrainer sublimation. The source material is evaporated onto glass substrates at a base pressure of 10^{-5} Torr from a molybdenum boat by resistive heating method as discussed in section 2.14 of Chapter 2. The rate of evaporation is fixed at 10–15 nm/minute.

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This will yield crack free and uniform films of about 300 nm thickness. Thickness is measured by Tolansky's multiple beam interference method[6] as described in section 2.17 of Chapter 2. Post deposition annealing was carried out at 50, 100, 150 and 200°C for CuPc, CoPc and PbPc thin films.

Shimadzu XD 610 automated powder diffractometer using Cu K α radiation of wavelength 1.54059 Å was used for X-ray diffraction measurements. X-ray diffractograms were recorded for the CuPc, CoPc and PbPc films at room temperature and different annealing temperatures. The diffractograms obtained are analysed to determine the structure of the films and the grain size.

5.4. Results and Discussion

The phthalocyanine molecule is a square planar molecule consisting of a divalent metal ion surrounded by four benzopyrrole units as shown in Figure 1.3.1. The phthalocyanine compounds exist in different phases, the most common are α, β and γ-phases, the β form being thermodynamically more stable.[7] The first two are most commonly studied forms, having two distinct crystalline structures.[8] Figure 5.4.1 shows the X-ray diffractogram of CuPc film of 300 nm thickness at room temperature. The X-ray used is monochromatic Cu K_α radiation from a 25 mA beam of 30 keV electrons. A continuous

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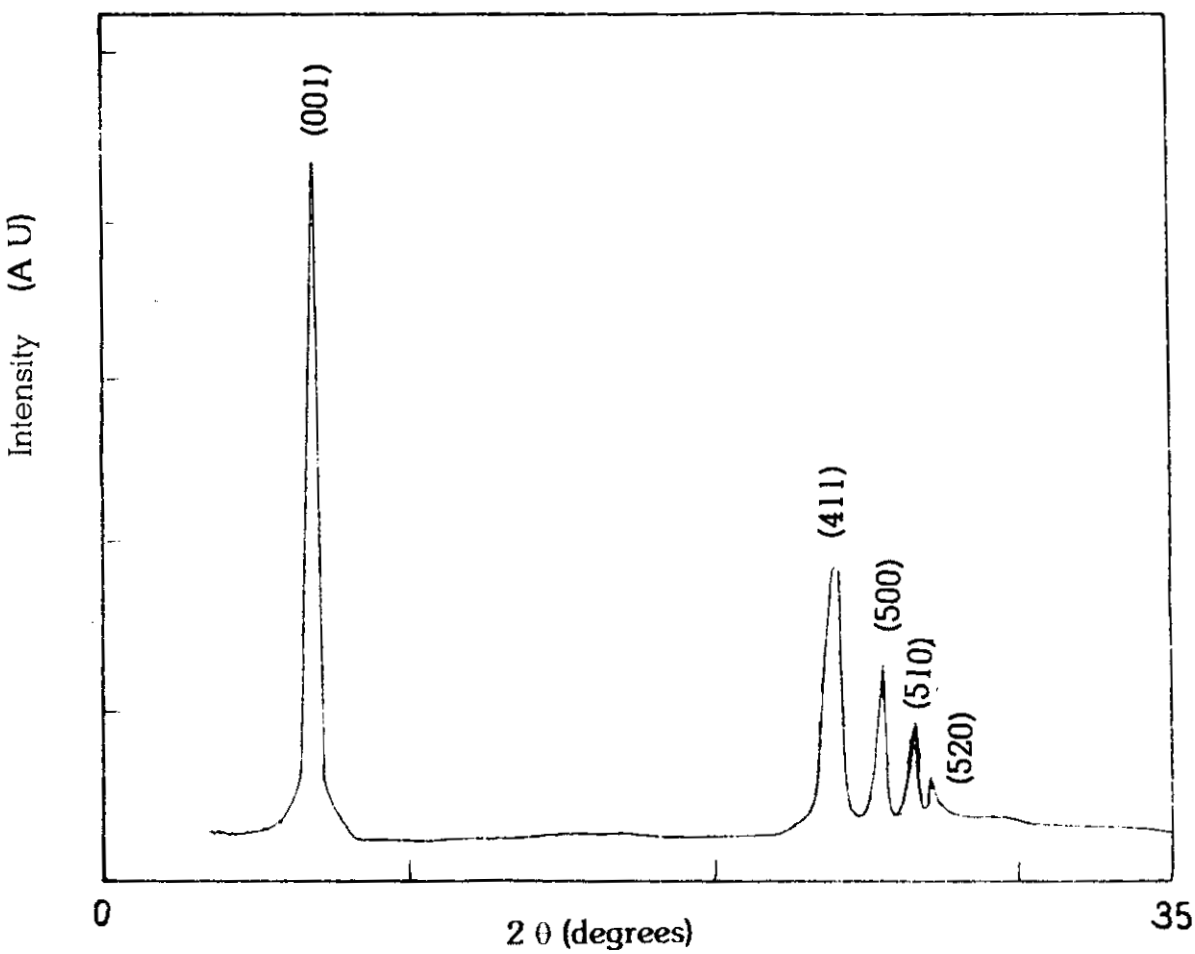

Figure 5.4.1 : XRD pattern of CuPc film of thickness 300nm

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scanning is employed to observe the preferred orientation of the deposited CuPc crystallites. The scanning speed is fixed at 0.2 degrees/ minute. Indexing is carried out by comparing the diffractogram with the American Society for Testing Materials (ASTM) data and the lattice constants are calculated. Miller indices are calculated and given in Table 5.4.1. The film deposited at room temperature is identified to be of α–form. The differences in the d values are attributed to higher X–ray absorption, sample purity, particle size, preferred orientation and crystal texture.[9] The structure of CuPc thin films at room temperature is adjudged to be tetragonal with six molecules per unit cell which is in agreement with Robinson and Klein.[10] Well defined diffraction peak in the (001) direction gives the direction of the preferential orientation. The lattice parameters are obtained as $a = b = 1.755$ nm, $c = 1.267$ nm and $\beta = 90°$. The crystal structure assumes a similar configuration reported by Debe and Kam[11] and Komiyama et. al.[12] Robinson and Klein[10] have reported a = b = 1.737 nm and c = 1.279 nm.

Table 5.4.1: Calculated and Observed Values of Interplanar Distance (d) & (hkl) Values [10] for α CuPc Film of Thickness 300 nm.

Peak	Calculated			Observed	
	2θ (°)	d (nm)	(hkl)	2θ (°)	d(nm)
A	6.99	1.264	(001)	6.975	1.267
B	23.97	0.3711	(411)	23.9	0.372
C	25.10	0.3550	(500)	25.32	0.352
D	26.80	0.333	(510)	26.95	0.331
E	27.50	0.324	(520)	27.13	0.329

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Figure 5.4.2(a) shows the X-ray diffractogram of CoPc thin film of thickness 100 nm. Indexing is carried out and peaks are identified using the standard ASTM data. The most intense peak is in the (001) direction. Figure 5.4.2(b) shows the diffractogram of CoPc film of thickness 300 nm. Four additional peaks in the range $24° < 2\theta < 28°$ are obtained. These peaks are due to the diffraction from planes separated by approximately the interstacking distances along the b-axis. As the film thickness increases, no change in intensity is observed in the direction of preferential orientation.[13] Table 5.4.2. gives

Table 5.4.2: Calculated and Observed Values of Interplanar Distance (d) and (hkl) Values for α-CoPc Film.

Peak	Calculated			Observed	
	2θ (°)	d (nm)	(hkl)	2θ (°)	d (nm)
A	6.998	1.279	(001)	6.99	1.281
B	14.02	0.639	(002)	—	—
C	18.26	0.482	(320)	18.3	0.485
D	24.22	0.400	(411)	24.4	0.365
E	25.46	0.347	(500)	25.18	0.354
F	26.93	0.341	(510)	26.9	0.331
G	27.96	0.323	(520)	28.0	0.319

the calculated and observed interplanar distances of CoPc thin film of thickness 300nm. The lattice parameters obtained for CoPc films are $a = b = 1.748$ nm and $c = 1.281$ nm and the structure is identified as tetragonal which is the α-form. Robinson and Klein[10] reported tetragonal structure for CoPc films. Ashida et al.[14] and Assour[8] have reported that the structure is orthorhombic. But Shihub and Gould[15]

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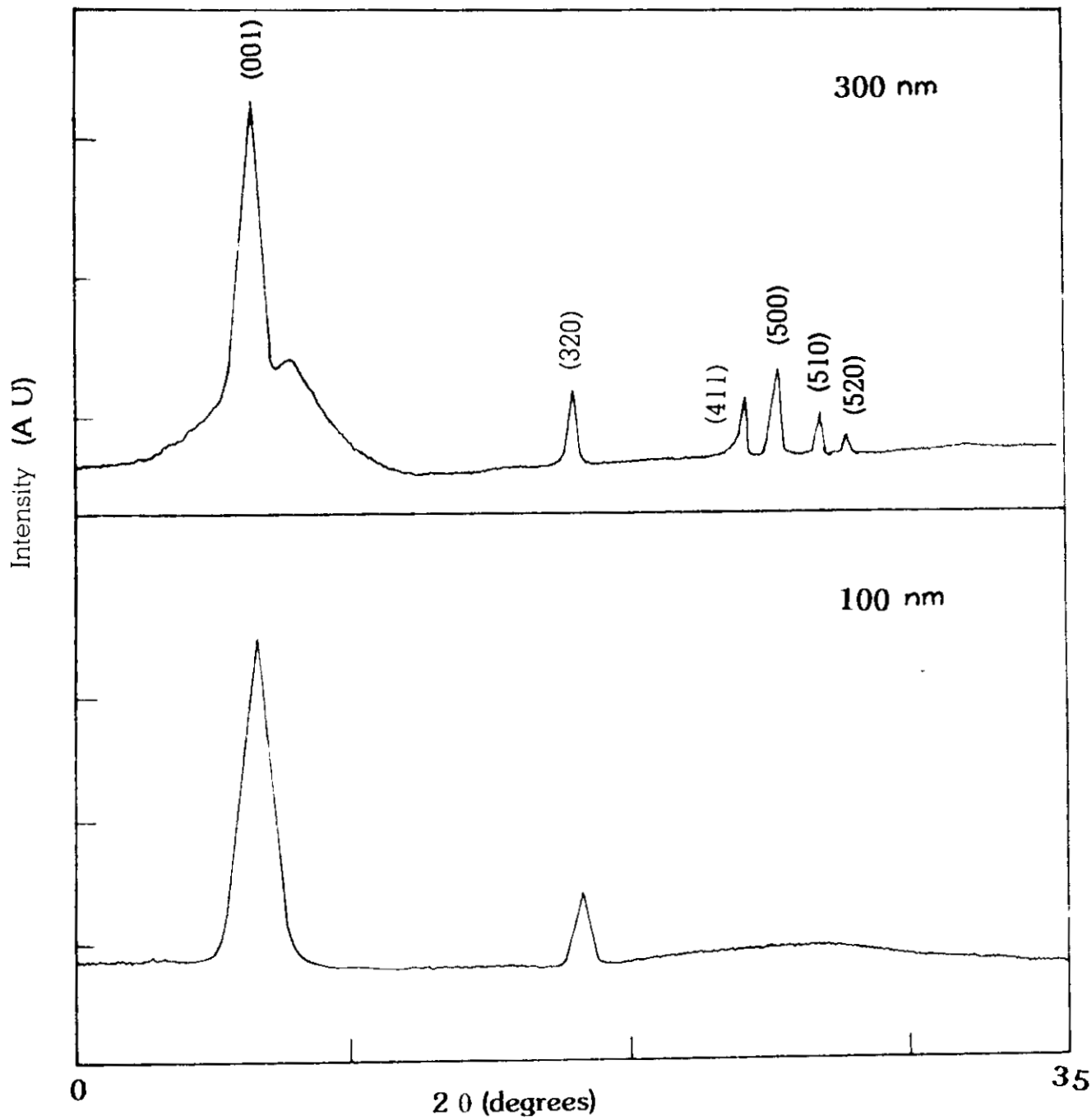

Figure 5.4.2 : XRD pattern of CoPc film of thickness (a)100nm (b) 300nm

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have concluded that it is difficult for them to distinguish the two phases. Nevertheless the present study confirms that the structure is tetragonal for CoPc thin films.

The recorded X-ray diffractogram for lead phthalocyanine is as shown in Figure 5.4.3. By comparing the diffractogram with that of Miyamoto et al.[16] the structure is identified as monoclinic with preferential orientation in (320) direction. PbPc molecules in the monoclinic modification are composed of clusters of well defined structure, which clusters themselves consist of orderly arranged stacks. Within the stack there exists two substructures which is the most likely explanation for weak diffraction intensity of PbPc monoclinic peak. The lead phthalocyanine molecule has a unique shuttle-cock shaped structure with two crystal structures.[17] The position of lead atom in the PbPc skeleton differs from the position of the central metal atom in other phthalocyanines. Most metal substituted phthalocyanines have planar molecules, but in PbPc, the lead atom deviates by 0.27-0.40Å (in free molecules) from the plane and the rest of the molecule distorts away from it.[18]

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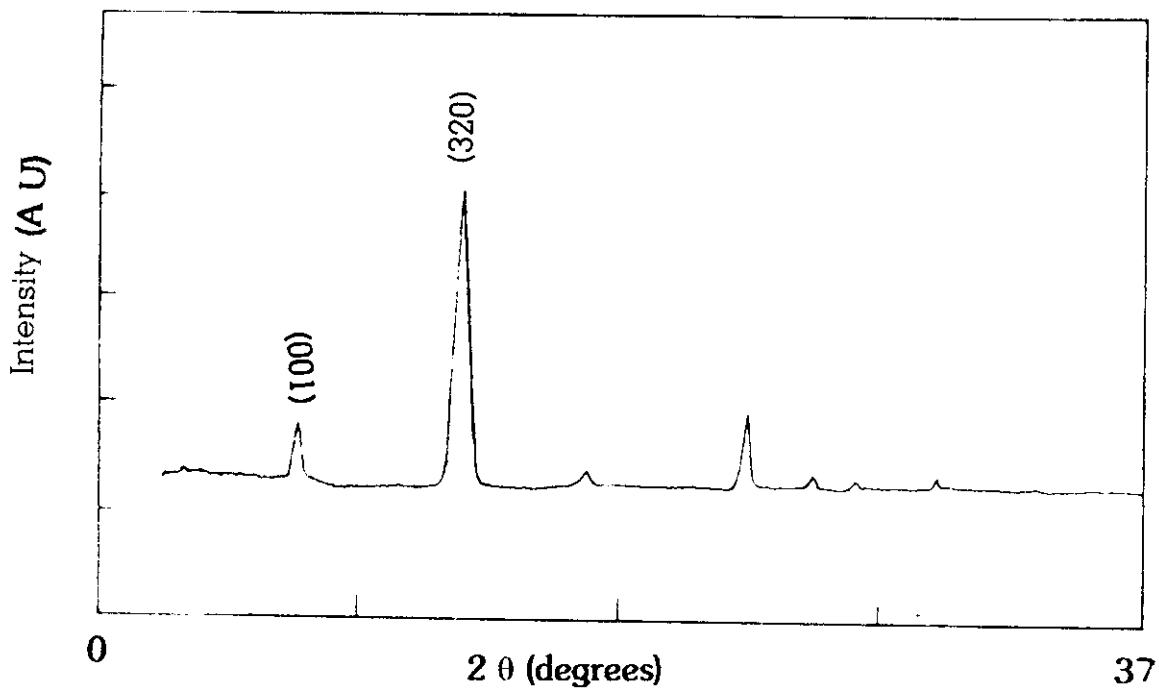

Figure 5.4.3 : XRD pattern of PbPc film of thickness 300nm

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5.4.A Effect of Annealing

Figure 5.4.4. shows the X-ray diffractograms of the annealed CuPc thin films. The annealing is carried out for two hours at 50, 100, 150 and 200°C. The preferential orientation is in the (001) direction at $2\theta = 6.51°$. The grain size is calculated and collected in Table 5.4.3.

Table 5.4.3:Variation of Grain Size with Annealing Temperature for CuPc Film

Annealing temperature (°C)	Microcrystalline grain size (nm)
50	13.6
100	21.9
150	12 0
200	80.0

The grain size increases initially and then decreases at 200°C. The reduction in grain size can either be due to partial resublimation, recrystallisation or phase transformation from α to β. Sharp and Abkowitz[20] have reported that β–CuPc is monoclinic in structure.

Figure 5.4.5. shows the diffractograms of CoPc films of thickness 300 nm at annealing temperatures 100, 200, 250 and 300°C. The grain size is calculated using Scherrer formula 5.2.4. and is collected in Table 5.4.4 The grain size continuously increases and is found to decrease at 300°C.

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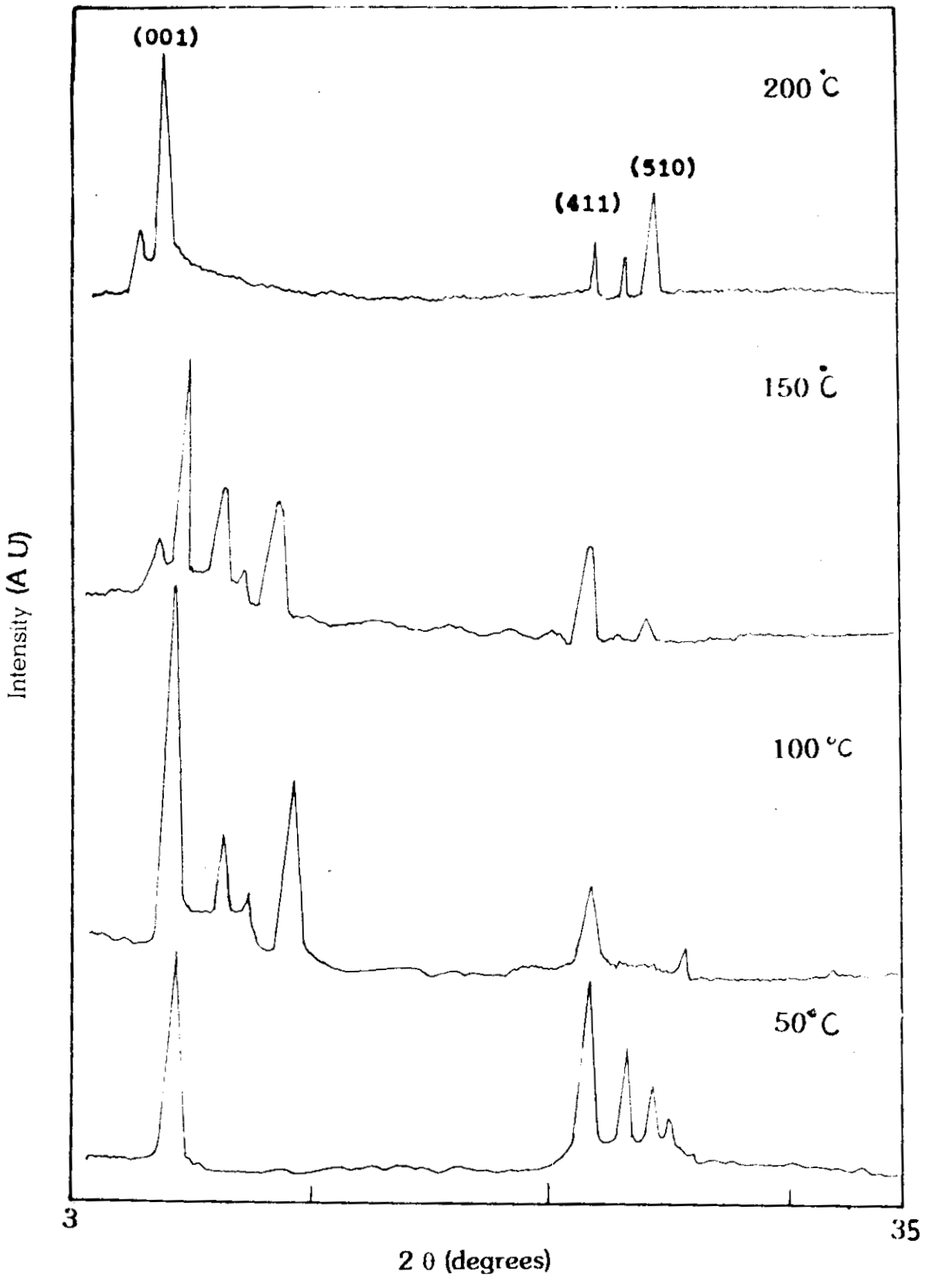

Figure 5.4.4: XRD pattern of CuPc film annealed at Ta = 50, 100, 150 and 200°C.

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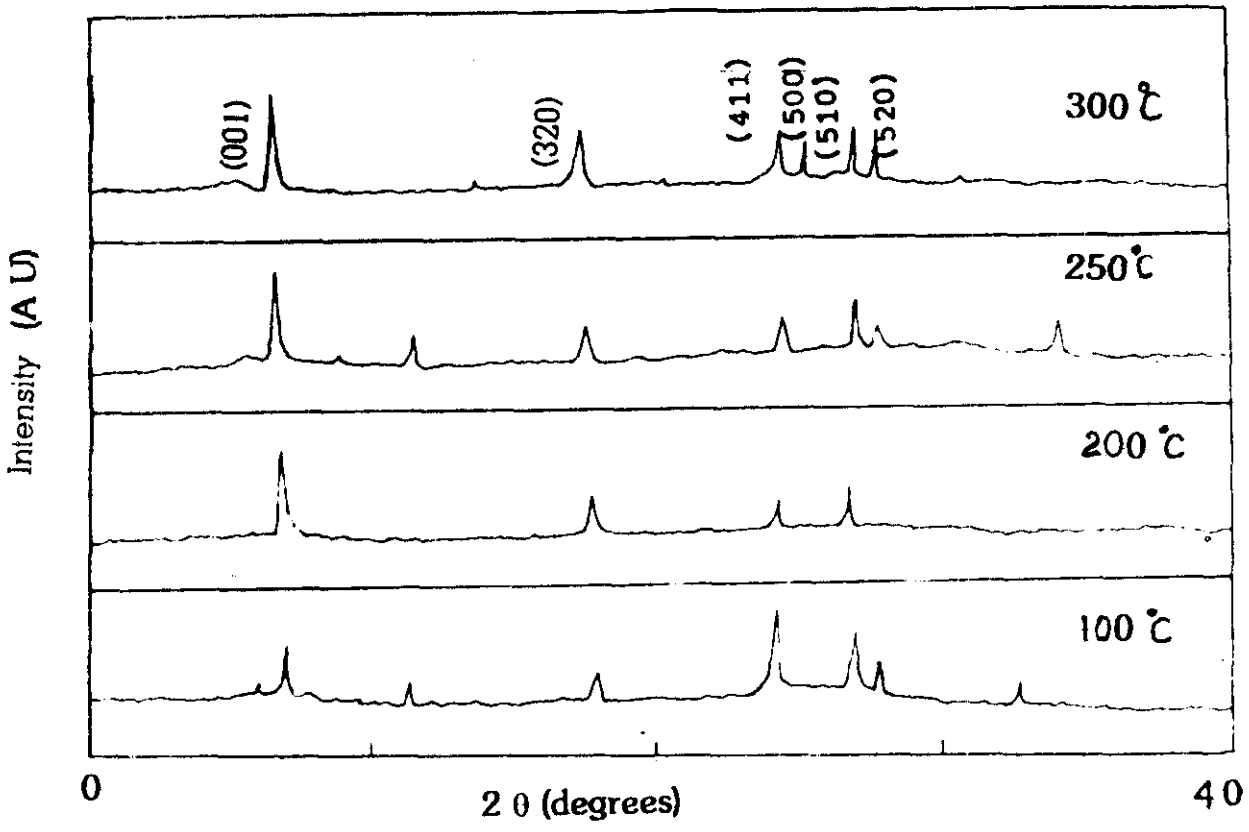

Figure 5.4.5: XRD pattern of CoPc film annealed at Ta =100, 200, 250 and 300°C.

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Table 5.4.4: Variation of Grain Size with Annealing Temperature for CoPc Films

Annealing temperature (°C)	Microcrystalline grain size (nm)
100	28
200	40
250	61
300	50

Even after the phase transformation, the preferential orientation remains in the (001) direction. The β form for CoPc film is orthorhombic as reported by Shihub and Gould.[15]

Figure 5.4.6. shows the XRD pattern of the lead phthalocyanine thin film annealed at 50, 100 and 150°C. The annealing rate is kept as 5°C/ minute. At 50 and 100°C the structure is monoclinic with some triclinic grains. At annealing temperature of 150°C, the triclinic phase becomes predominant and preferential orientation changes to (100) direction. Grain size is calculated for annealed PbPc films using Scherrer formula and is given in Table 5.4.5.

Table 5.4.5:Variation of Grain Size with Annealing Temperature for PbPc Films

Annealing temperature (°C)	Microcrystalline grain size (nm)
50	8.0
100	14.0
150	11.7

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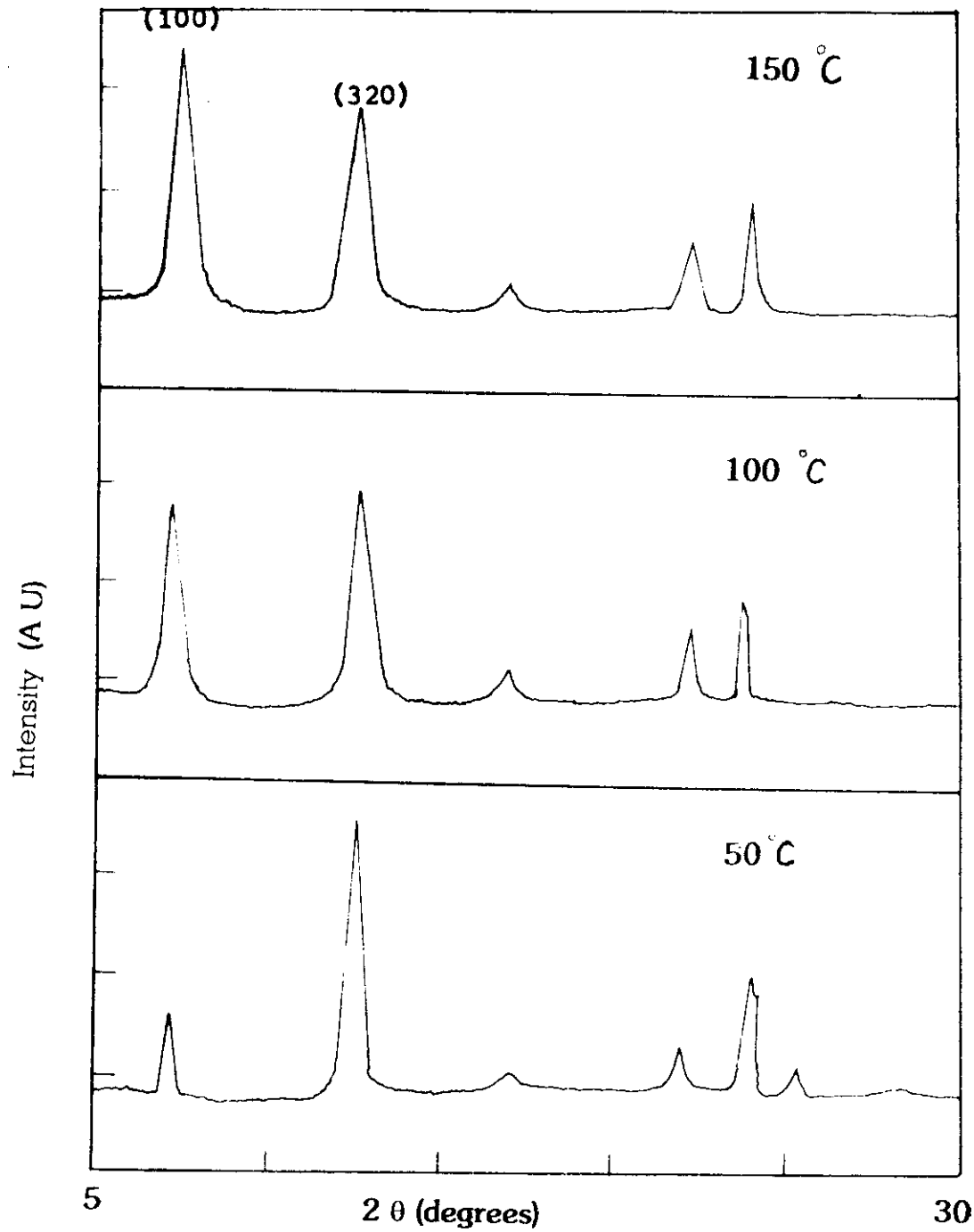

Figure 5.4.6: XRD pattern of PbPc film annealed at Ta = 50, 100 and 150°C.

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The change in grain size at 150°C is an indication of phase change from α to β form. The β form is triclinic for PbPc which is a stable phase.

5.5. Conclusion

Diffraction peaks obtained for the films prepared at different annealing temperatures are sharp which is due to increased crystallinity. The CoPc and CuPc films prepared at room temperature is tetragonal in structure whereas PbPc film is monoclinic. A sharp change in grain size is observed for film annealed at 200°C for CuPc. But CoPc exhibits marked difference in grain size for films annealed at 300°C. It indicates a phase change from α to β phase. However for PbPc films this change in grain size is observed at 150°C.

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