7.1. Introduction

Phthalic anhydride $[O_6H_4(OO)_2O]$ is a member of the carboxylic acid anhydrides. The material was studied by Groth [282] in the crystalline form and was classified as orthorhombic. The lattice parameters were determined by X-ray diffraction by Williams et al [283], to be $a = 7.90\AA$, $b = 14.16\AA$ and $c = 5.94\AA$. By single crystal rotation techniques, Pandey [284] modified these values as $a = 7.86\AA$, $b = 14.18\AA$ and $c = 5.904\AA$. The crystal was shown to belong either to $C_{2v}^9$ or $D_{2h}^{16}$ space group. Banerji [285] removed this ambiguity in the space group and assigned the non-centrosymmetric space group $C_{2v}^9$, for the crystal.

Though it has been reported [283] that the crystals of this material can be grown from alcohol, acetone or chloroform, the crystals obtained were of small sizes suitable, perhaps, only for X-ray work. Bradley [286] has grown long whisker crystals from vapour and has measured the Youngs and Shear moduli. Buckley [287] has also mentioned the growth of whiskers
of this material by the chemical decomposition of phthalic acid.

Potassium acid phthalate \([\text{COOK}_6\text{H}_4\text{COOH}]\) is an ortho-substituted benzoic acid derivative. Potassium acid phthalate, has been shown to belong to the orthorhombic system by Groth [288]. Okaya et al extended the study of the crystal structure of ammonium acid phthalate to the potassium salt and assigned a space group of \(P2_12_12\) [289]. Later Okaya [290], by more refined experimental techniques, corrected the space group as \(P2_1\text{ab}(\text{C}_{5v}^5)\). The lattice parameters were determined to be \(a = 6.46\,\text{Å}, b = 9.60\,\text{Å}\) and \(c = 13.85\,\text{Å}\).

Bohm et al [291] have reported the growth of large single crystals of this material. The crystals were grown by the slow cooling of aqueous solutions from 50°C to 30°C. Though the crystal finds applications in the fields of soft X-ray spectroscopy [28] and piezoelectricity [26], no attempt hitherto has been made either to study the morphology or the perfection of these crystals.

7.2. Growth of Crystals

a) Phthalic anhydride

Phthalic anhydride was extensively purified, as described earlier, by recrystallisation, column
chromatography and sublimation. The purified material was used for the crystal growth from solution, vapour and melt.

(i) Solution growth

Phthalic anhydride is only sparingly soluble in many solvents. Table (1) gives the solubility data in water, carbon di-sulphide, formic acid and pyridine. Of these solvents only water and pyridine have solubilities suitable for crystal growth. But the possible reaction between water and phthalic anhydride and the high viscosity of pyridine prohibit the use of both these solvents. The organic solvents, such as, acetone, benzene and chloroform, suggested by Williams [283] were more suitable. But, the high volatality of these solvents prevented the growth of large single crystals. These solvents produced rapid evaporation and 'creeping' on the sides of the container. The acetone solutions were found to be relatively more suitable compared to others. The solution grown crystals were small and exhibited prism {110}, brachydome {011} and pyramid {111}. Orthographic projection of a typical crystal of phthalic anhydride is shown in figure (16).

(ii) Whiskers and hollow crystals - Vapour growth

Phthalic anhydride, due to its high vapour pressure, can be conveniently grown from vapour. Table (2)
Table (1)

Solubility of Phthalic Anhydride in Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Temperature in °C</th>
<th>Solubility gm/gm of solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>25</td>
<td>0.62</td>
</tr>
<tr>
<td>Water</td>
<td>155</td>
<td>95.00</td>
</tr>
<tr>
<td>Carbon di-sulphide</td>
<td>20</td>
<td>0.70</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>20</td>
<td>4.70</td>
</tr>
<tr>
<td>Pyridine</td>
<td>20</td>
<td>80.00</td>
</tr>
</tbody>
</table>
Fig.(16) Orthographic projection of a typical crystal of phthalic anhydride.
Table (2)

Vapour pressure of Phthalic Anhydride at various temperatures

<table>
<thead>
<tr>
<th>Temperature in °C</th>
<th>Vapour pressure in mm of Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.5</td>
<td>1.0</td>
</tr>
<tr>
<td>132.0</td>
<td>6.0</td>
</tr>
<tr>
<td>135.0</td>
<td>7.0</td>
</tr>
<tr>
<td>140.0</td>
<td>8.7</td>
</tr>
<tr>
<td>160.0</td>
<td>20.5</td>
</tr>
<tr>
<td>180.0</td>
<td>41.0</td>
</tr>
<tr>
<td>197.0</td>
<td>75.0</td>
</tr>
<tr>
<td>200.0</td>
<td>80.5</td>
</tr>
<tr>
<td>284.5</td>
<td>760.0</td>
</tr>
</tbody>
</table>
gives the vapour pressure of phthalic anhydride at various temperatures.

Crystals were grown by the methods already described [figure (7a) and figure (7b)]. A typical whisker crystal grown by the set up [figure (7a)] is shown in figure (17). Such whiskers were formed on the glass substrate. The whiskers were uniform throughout their length and had parallelogram cross-sections. The parallelogram had angles $58^\circ$ and $122^\circ$. As observed by Bradley [286] these whiskers were bound by \{110\} faces which are the cleavage planes of the crystal. The temperature difference between the source material and substrate ($\Delta T^\circ C$) was found to have a strong effect on the morphology of the crystals. At low values of $\Delta T$ the growth was slow and resulted in whiskers. At large values of $\Delta T$ the whisker crystals were found to develop with a slightly modified morphology at the tip. The crystals grown by the experimental set up, shown in figure (7b), also exhibited similar tendency. Whiskers were formed on the side walls of the furnace tube as well as on the glass disc. The crystals on the glass disc were oriented perpendicular or nearly perpendicular to it.
Fig. (17) A typical whisker crystal of phthalic anhydride (x 36).
while crystals formed on the furnace tube were randomly oriented. At low temperature differences of charge and substrate, uniform transparent hollow crystals with cross sections ranging from wedge to parallelograms were observed. Openings were left in the prismatic walls as shown in figure (18). At high temperature differences of charge and substrate hollow crystals with a bead at top were observed. (figure 19). Beaded crystals were also observed at low temperature differences after long intervals of time. In general the growth process seemed to be the same except for the slow growth rates at low $\Delta T^\circ C$.

Hollow crystals with an opening left in their prismatic faces have been observed in several materials. Iwanaga et al [154] have observed similar morphology in ZnO and ZnSe crystals. They have observed a large number of striations parallel to the whisker axis and have suggested a mechanism which essentially consisted of space filling between the spaces of an array of whiskers growing parallel to each other. But the formation of a hollow crystal with well defined planes requires a regular formation of whisker array even in the nucleation stage. Later the same authors extended their study of these hollow crystals by
Fig. (18) A uniform hollow crystal with an opening in the prismatic wall (x 40).

Fig. (19) A beaded crystal with the side channel (x 100).
electron microscopic observations and have shown that dendritic growth preceded the formation of hopper crystals. In phthalic anhydride striations parallel to the whisker axis were not observed. The growth of phthalic anhydride hollow crystals was seen to begin with the development of one or two of the \{110\} planes that bound the crystal. Figure (20) shows the wedge-shaped crystal tip with \(\text{110}\) and \(\text{-110}\) faces. Observations on the \{110\} faces of the initially grown whisker showed profusely growing short side whiskers. These side whiskers apparently grow in the \(<110>\) directions and the faces of hollow whiskers were produced by the filling of space between these side whiskers. Figure (21) shows the side whiskers growing on an \{110\} face of a whisker. The \(\text{110}\) and \(\text{-110}\) faces after growing approximately to the same extent were found to wind round to form the \{110\} and \(\text{-110}\) faces. The tip of a hollow crystal which has the four faces is shown in figure (22). In the figure the fourth face has not completed growth. As the last face surrounding the cavity has started to grow, this face exhibited a tendency to grow in the \(<001>\) direction rather than in the \(<110>\) direction. Thus the crystal grew in the \(<001>\) direction leaving an opening in their prismatic face. The formation of the narrow
Fig. (20) A wedge shaped crystal tip (x 480).

Fig. (21) Side whiskers growing from an \{110\} face of a whisker crystal (x 400).
Fig. (22) Growing tip of a hollow crystal with an opening in the prismatic wall (x 120).

Fig. (23) Longitudinal view of a hollow crystal showing steps along the groove (x 150).
opening was also facilitated by the increasingly difficult nucleation inside the gap as the faces closed up. The whiskers or hollow crystals were found to cease growth after a certain length along the $<001>$ direction, probably due to the change in temperature as the crystals grow towards the source. Further growth occurred at the tip only. The vapours now condensed at the tip to close the opening and started to fill the cavity at the tip. This occasionally resulted in the formation of steps inside the channel at the tip as shown in figure (23). Further growth took place at the tip forming the $\{010\}$ planes and thus converting the parallelogram cross section, to hexagonal cross section. A partially filled and completely filled hexagonal tips of hollow crystals are shown in figure (24) and (25). After the formation of hexagonal tips the growth proceeded in the $<110>$ directions in which the wedge was first formed. These faces slowly wind round at the tip as shown in figure (26).

The growth process is shown schematically in figure (27).

To study the basal plane growth of these whiskers, the closed crystal-vapour system already described in 6.3(b), was used. The entire length of
Fig. (24) Partially filled hexagonal tip of a whisker crystal (x 200).

Fig. (25) Completely filled tip of a hollow crystal (x 200).
Fig.(26) A hollow crystal with hexagonal tip with a wedge (x 80).
Fig. (27) Schematic diagram showing different stages of growth: (a) to (c) formation of parallelogram tip from wedge shaped tip; (d) transition from parallelogram to hexagon; (e) longitudinal view of the crystal with an opening in the prismatic wall.
the cell could be divided into three regions. The first region, that is the hot zone, contained the material and the heater. The second zone was close to the hot zone and was about 1 to 1.5 cm long. This zone was free of any crystals. In the third zone beyond the second, clusters of crystals were observed. The temperature profile along the cell, at a particular temperature of the hot zone is shown in figure (28).

According to Sears [292], the whisker crystals probably nucleate at the imperfections of the glass substrate. In the present cell, the growth along the whisker axis was suppressed by the upper slide and the growth in the basal plane alone was allowed. The third zone contained crystals in the various stages of growth. The sequential development of the crystals nucleated are shown in figure (29a,b,c). The nuclei, after attaining a critical size was observed to develop side branches in <110> directions as shown in figure (29a). These branches were observed to wind round in the other <110> directions [figure (29b)]. The process was seen to be followed by space-filling, to result in the perfect parallelogram platelet crystals as shown in figure (29c). This growth sequence supported the mechanism suggested for the hollow crystals.
Fig. (28) Temperature profile along the cell.
Fig. (29a, b & c) Sequential development of platelet crystals growing in the (001) plane (x 400)
(iii) Dendritic growth

Due to the active role played by the dendritic branching in the hollow crystal formation and basal plane growth, it was thought useful to study the dendritic growth of this material in detail. Phthalic anhydride dendrites were obtained from solution and melt. Solutions were prepared with different concentrations, in benzene (Analar BDH) and were decanted on microscope slides by a graduated syringe. The slides were kept in an enclosure and were allowed to evaporate. The solutions, on evaporation produced crystals of various morphology. Table (3) gives the relative abundance of each type of habit at various concentrations of the solution. It was seen that dendrites predominated at a concentration of 1/500 gm/cm³.

To grow dendrites from melt, the material was sandwiched between two glass slides and melted by placing it over a wire would strip-heater controlled by a thermostat. The melt after attaining the desired temperatures was transferred quickly to a metal block, kept at different constant temperatures below the melting point of the material. The melt exhibited a tendency to remain supercooled. The habit of crystals showed a strong dependence on the temperature difference.
Table (3)

The habit variation of Phthalic Anhydride with concentration

<table>
<thead>
<tr>
<th>Concentration in gm/cm³</th>
<th>Habit of Crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dendrites</td>
</tr>
<tr>
<td>1/1200</td>
<td>Nil</td>
</tr>
<tr>
<td>1/800</td>
<td>Nil</td>
</tr>
<tr>
<td>1/700</td>
<td>+</td>
</tr>
<tr>
<td>1/600</td>
<td>+</td>
</tr>
<tr>
<td>1/500</td>
<td>+ + +</td>
</tr>
<tr>
<td>1/400</td>
<td>+ +</td>
</tr>
<tr>
<td>1/300</td>
<td>+</td>
</tr>
</tbody>
</table>

The number of + sign indicates the relative abundance of each habit.
between the metal block and the melt ( ΔT°C). At low values of ΔT the habit was that of needles whose thickness decreased with increase of ΔT and at about
ΔT = 30°C to 40°C, dendritic growth was found to set in.

Irrespective of the method of growth, the dendrites exhibited the same morphology. It was possible to classify the dendrites into the following categories:

1) Six-armed dendrites
2) Inclined dendrites
3) Perpendicular dendrites

A six-armed dendrite is shown in figure (30). The different primary branches were inclined to each other by ~ 60°. The secondary branches were likewise oriented to the primary branches. This type of dendrites may be formed by twinning about <110> directions. Arbitrarily selecting <110> and <110> as the directions in which the primary branches developed the other primary branches inclined at 60° to them grow on either side in <110> and <110> directions. Because of the symmetry of these directions any direction can be taken as the twin axis.
Fig. (30) A six armed dendrite (x 1000).
The inclined dendrites shown in figure (31) had two \( <110> \) primary branches inclined at \( \sim 60^\circ \) to each other. The secondary and tertiary branches developed in the space enclosed by these primary branches. The formation of inclined dendrites may be considered as a special case of six armed dendrites where only two neighbouring \( <110> \) branches are active.

A typical dendrite with perpendicular branches is shown in figure (32). It was seen that the tips of these perpendicular branches contained crystals of parallelogram shape. Figure (33) and (34) shows the dendritic tips with the parallelogram crystals. The crystals were exactly same as those obtained from the closed crystal–vapour system. From the crystal morphology, the dendritic branches of the perpendicular dendrites were seen to develop in \( <010> \) and \( <100> \) directions. The branch growing in \( <010> \) directions usually had the secondary branches in \( <100> \) directions. In some cases secondary branchings in the \( <110> \) directions were also observed, on either side of a primary branch developed in \( <010> \) or \( <100> \) directions. These branches were seen to wind round in the other \( <110> \) directions to form parallelogram crystals. This process was often found to result in the formation of linear crystal
Fig. (31) A portion of the inclined dendrites showing secondary and tertiary branching (x 400).

Fig. (32) A dendrite with perpendicular branches (x 500).
Fig. (33) The tip of a dendritic branch growing in $<$010$>$ direction ($\times$ 900).

Fig. (34) The tip of a dendritic branch growing in $<$100$>$ direction ($\times$ 500).
chains. The mechanism of growth of these crystals were found to be very similar to the mechanism suggested for hollow crystal formation.

In the case of \( <010> \) primary branches the \( <110> \) secondary branches were found to make an angle of \( \sim 60^\circ \) to each other and in the case of a \( <100> \) primary branches they made an angle \( \sim 120^\circ \) to each other. As growth proceeded the \( <110> \) branch tips were found to change their direction in the other equivalent \( <110> \) directions. Before completing the parallelogram these branches diverged again in the \( <110> \) directions. This process followed by space-filling resulted in linear chain crystals. The linear crystal chains growing in \( <010> \) and \( <100> \) directions are shown in figure (35) and (36). The process is schematically shown in figure (37). It was seen that the ratio of the maximum width \( [AB \text{ in figure (37)}] \) to the width at which the next platelet started to grow \( [CD \text{ in figure (37)}] \) remained as \( 4 : 1 \) for \( <010> \) chain axis and \( 2 : 1 \) for the \( <100> \) chain axis. The dendritic growth, followed by spacefilling, to result in hexagonal platelets is shown in figure (38).

The observations on the phthalic anhydride dendrites showed that the active growth directions in
Fig. (37) Schematic diagram showing the formation of crystal chains.

Fig. (38) An hexagonal crystal growing from solution by the filling-in process (x 600).
whiskers, hollow crystals and dendrites were essentially limited to $<001>$, $<110>$, $<010>$ and $<100>$ directions.

(iv) Spherulitic growth

During the study of dendritic growth from melt, it was seen that the melt exhibited a tendency to supercool in the absence of any external interference. As mentioned in section 7.2(a)iii, the crystallisation started with the development of needles whose width decreased with $\Delta T$. As such, it was thought interesting to examine in detail the crystallisation behaviour in the region of supercooling, by artificial nucleation. The molten material was prepared by heating the material between a glass slide and microscope coverslips. The molten charge was transferred to a metal block maintained at different constant temperatures below the melting point of the material and allowed to cool. Nucleation was artificially induced in these supercooled melts, by cooling the center momentarily. The cooling was effected either by placing a sharp metallic needle tip, or by blowing a jet of air through a fine nozzle at the center of the melt. The nuclei so generated were seen to develop as fibrils growing in all directions. The resultant morphology was similar to spherulites, observed
during the crystallisation of polymers [293,294] and inorganic materials [295]. A spherulite of phthalic anhydride grown from melt viewed under crossed polaroids is shown in figure (39). The simple maltese cross observed, was typical of spherulitic systems. The substructure of these spherulites were fibers whose thickness showed a strong dependence on the supercooling $\Delta T^\circ C$. Figures (40) and (41) show the spherulites grown at $\Delta T = 30^\circ C$ and $\Delta T = 10^\circ C$ respectively. The characteristic periodic splitting [296] was found to become less prominent as the supercooling was reduced and finally disappeared at very small $\Delta T$.

According to Keith and Padden [296] the spherulitic growth is initiated by the impurities inherently present in organic materials. In phthalic anhydride the impurities even if present, does not produce point cooling initiating spherulitic growth. External cooling was found necessary without which no spherulitic growth started. The natural habit of phthalic anhydride crystals are needles or whiskers, as it should be expected according to the unit cell dimensions [297]. This habit was maintained in the artificially initiated spherulitic growth also. The
Fig. (39) A spherulite viewed under crossed polaroids (x 5).
Fig. (40) A spherulite grown at $\Delta T = 30^\circ C (x 36)$. 

Fig. (41) A spherulite grown at $\Delta T = 10^\circ C (x 36)$. 
substructure of these spherulites were found to be fibres growing in C-direction. The melt in between the initial fibres, crystallised slowly to thicken them. The fibre tips were faceted [Figure (42)]. Jackson and Hunt [298] on the basis of studies on organic materials and metals have shown that the freezing pattern depended on the value of a defined as equal to $\Delta S_f / R$, where $\Delta S_f$ is the entropy of fusion and $R$, the gas constant. They have shown that materials having high $\alpha$ values exhibit faceted growth while those with low $\alpha$ values freeze like metals. For phthalic anhydride $\alpha \sim 7$, and the observed faceted growth was thus in accordance with the theory. During spherulitic growth the initial fibre tip developed perturbations and grew out as branches. The branches were developed in non-crystallographic directions. The angle made by these branches with the initial fibre decreased with decrease of $\Delta T$ and at very low values of $\Delta T$ the non-crystallographic periodic splitting was completely absent. At these supercooling the spherulitic substructure was well defined ribbons. These spherulites were examined by chemical etching. An etchant, composed by $\text{NH}_4\text{OH}$ and $\text{H}_2\text{O}$ in the ratio 1:3 by volume, found suitable for delineating
Fig. (42) Faceted tips of spherulitic fibers (x 200).
dislocations on \{110\} and \{001\} faces of phthalic anhydride single crystals [299], produced etch pits on the ribbon surfaces. The pits were characteristic of \{110\} surfaces. The ribbons exhibited large number of grain boundaries running approximately along the radial direction. Examination of a large number of spherulites showed that the spherulitic film had always their \{110\} faces alligned parallel to glass surfaces. This type of auto alignment under non-epitaxial, non-seeded conditions have been observed on several compounds [300]. The formation of large number of grain boundaries suggested a slight lattice mismatch during the crystallisation of the fibres. As stated earlier the angle made by the branches with the initial whisker decreased with decrease of $\Delta T$. The circular volume requires a uniform fibril flux, which is met by the periodic splitting at large values of $\Delta T$. At low values of $\Delta T$ the space filling between diverging fibres result in small angle grain boundaries. The formation of grain boundaries in these spherulitic ribbons were found to be very similar to the formation of such boundaries in dendrites with displaced secondary branches [301]. Figure (43) shows schematically the fibre coarsening and subsequent development of grain boundaries.
Fig.(43) Fibre coarsening and development of grain boundaries. Dotted lines are grain boundaries.
The spherulitic ribbons, when cooled quickly from the growth temperature exhibited parallel striations. These striations were always parallel to the fibre axis. Figure (44) shows such striations parallel to the \(<001>\) directions. On phthalic anhydride single crystals, such striations on \(\{110\}\) faces have been observed [299]. By comparison, the parallel striations were identified as slip lines produced by the thermal strain. The upper and lower faces in contact with the glass slides were \(\{110\}\) faces as evidenced by chemical etching. The slip planes active in this crystal had been identified as \(\{110\}\) planes [299]. The slip lines on any \(\{110\}\) plane should appear as parallel lines. The schematic diagram figure (45) shows the slip process.

Phthalic anhydride spherulites were also grown from solution. Concentrated solutions prepared at \(30^\circ C\) were cooled to \(~19^\circ C\). A seed was introduced to the solution and the solution was left for evaporation. After a few days spontaneous nucleation was found to occur on the seed crystal and three-dimensional spherulites developed within one or two weeks. The spherulite was seen to have needle substructure. The
Fig. (44) Parallel striations on spherulitic ribbons (x 250).

Fig. (45) Schematic diagram of the slip process in ribbons.
needles had hexagonal cross sections and were bounded by \{110\}, \{010\} or \{100\} faces. The needle axis was always the \langle 001 \rangle direction. A typical spherulite is shown in figure (46). The characteristic periodic splitting is clearly shown in figure (47). The needles had fairly uniform cross sections, except at the splitting portion and exhibited essentially the same interfacial angles as observed on vapour grown hexagonal whiskers.

(v) Single crystals—Melt growth

The melting point of phthalic anhydride is at 131.1 ± 0.01°C and is much lower than the boiling point (284.5°C). The material exhibit a 23% volume reduction on solidification [302]. As such, the Bridgman method was thought fit for the production of large single crystals. Since the melt exhibited supercooling tendencies it was essential to observe the growth, continuously. The furnace described in 6.3(c) were fabricated for this purpose. The upper zone alone was found sufficient for growing single crystals. The temperature of this zone was maintained at 200°C. The ampoule containing the material, prepared as described earlier in 6.3(c)ii, was kept in the hot
Fig. (46) A typical solution grown spherulite (x 2).

Fig. (47) Cross sectional view of the solution grown spherulite (x 4).
some so as to melt completely. The ampoule was then lowered slowly by means of a geared motor.

The purity of the material was found to affect the growth seriously. If the commercially available material was used, the impurities segregated at the bottom and were circulated throughout the melt by convection currents. The melt containing impurities had a yellow colour. During crystallisation the impurities were partially rejected into the melt and a dark yellow band was formed at the top of the solidified charge. The impurities were partially incorporated in the crystal giving it an yellow colour. The purified material was colourless in the molten state. To obtain single crystals various tip shapes of growth tubes were used [303]. Of the various tip shapes used, single crystals were obtained with tubes having narrow capillary tips [figure (10)]. Another parameter of importance in obtaining single crystals, was the slope of the tube walls, immediately after the tip. By varying the slope it was found that, an angle of 15° made by the wall with the tube axis, consistently gave good quality single crystals. Higher angles usually resulted in the production of bi-, or tri-crystals. The speed of
descend was varied to different values and a speed of 2-3 mmh$^{-1}$ was found most suitable for single crystal growth. Under these conditions, the crystals always grew with the $<001>$ direction parallel to the tube axis. According to Bradley [286] the crystals have excellent cleavages along $\{110\}$ faces. The crystals cleaved well parallel to the tube axis. The crystals were cut perpendicular to the tube axis by the solvent-string cutter described earlier in 6.3(d), using benzene as the solvent. A cut crystal and a cleaved slab are shown in figure (48).

b) Potassium acid phthalate

Potassium acid phthalate possesses a large solubility and large positive temperature coefficient of solubility in water. The solubility curve of potassium acid phthalate is shown in figure (49). The first detailed report on the growth of large single crystals, of this material was made by Bohm et al [292]. They showed that crystals as large as 6.5cm x 4cm x 1.5cm could be easily grown by the slow cooling of aqueous solutions. In the present study the crystals were grown both by the method of slow cooling and slow evaporation. The seed crystals for the crystal growth was prepared by the evaporation
Fig. (48) A cut crystal and a cleaved slab (mm grid).

Fig. (49) Solubility curve of potassium acid phthalate in water.
of aqueous solutions placed in a partially covered petri dish. Platelet crystals having \{001\} faces were found to be the most suitable for growth. The seeds were either fixed by epoxy resin or placed at the bottom of the beaker. A typical crystal grown is shown in figure (50). The grown crystals had the same morphology as the seeds. The crystals exhibited a tendency to grow laterally to develop the \{001\} faces rather than in a direction normal to it. For the various studies, crystals with larger dimensions in the \langle 001 \rangle direction were necessary. The solutions were doped with various chemicals such as KOH, KNO₃ and thiourea. It was seen that only thiourea was effective in modifying the habit. The addition of thiourea was found to promote growth in the \langle 001 \rangle directions while slowing the growth on other faces. The crystalline morphology was essentially the same as that of crystals grown from pure solutions.

7.3. Dislocation Etch Studies

a) Phthalic anhydride

Various chemicals were tried to find out a suitable etchant for delineating the dislocations in phthalic anhydride. HNO₃, H₂SO₄ and other acids
Fig. (50) A typical crystal of potassium acid phthalate (mm grid).
produced excessive reaction and the reaction products were difficult to remove. The various organic acids caused only general dissolution.

Ammonium hydroxide (NH₄OH) have been reported to react with phthalic anhydride to produce phthalamic acid [304]. The reaction is highly efficient with 94% - 97% product yield.[305,306]. The suitability of NH₄OH as an etchant was examined by varying the composition of NH₄OH : H₂O solution. The effect of varying the composition and etching time is shown in table (4). It was seen that well defined etch pits developed for a composition of NH₄OH : H₂O in the ratio 1 : 3 by volume. The optimum etching time was found to be between 15 to 20 seconds. The etchant was capable of producing etch pits both on the {100} and {110} faces. A grain boundary revealed on a {100} face is shown in figure (51). Successive etching of the same face neither produced new pits nor changed the orientation of earlier pits. The delineation of grain boundaries and the nature of the etch pits on successive etching strongly indicated that the pits were formed at the emergence points of dislocations on these surfaces. The dislocation density was found to be ~ 10⁴ cm⁻² on {001} faces, which was reduced, on annealing at 80°C for 12 hours, to ~ 10² cm⁻².
The effect of composition variation of the etchant on the etch pit morphology, on \{001\} and \{110\} faces

<table>
<thead>
<tr>
<th>Volume of NH$_4$OH in c.c.</th>
<th>Volume of H$_2$O in c.c.</th>
<th>Etching time in secs.</th>
<th>Remarks {001}</th>
<th>Remarks {110}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>30</td>
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<td>No pit</td>
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<td>No pit</td>
<td>No pit</td>
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<td>No pit</td>
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<td>10</td>
<td>30</td>
<td>5</td>
<td>General dissolution</td>
<td>No pit</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>Well defined etch pits</td>
<td>Etch pits observed</td>
</tr>
<tr>
<td></td>
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<td>20</td>
<td>Well oriented etch pits</td>
<td>Well oriented etch pits</td>
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<td>15</td>
<td>30</td>
<td>5</td>
<td>Pit edges gets slightly curved</td>
<td>Pits get slightly modified</td>
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<td>15</td>
<td>Rapid etching</td>
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<td>Excessive dissolution</td>
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Fig. (51) A grain boundary on \{001\} face (x 800).
On the \{110\} faces the etch pits exhibited a two-fold symmetry. One to one correspondence was observed on matched cleavages and on both sides of thin slabs. A typical 1:1 correspondence on matched cleavage surfaces is shown in figure (52).

It was possible to classify the etch pits seen on \{110\} faces into three categories.

1) Etch pits exhibiting well-defined planes
   [marked A in figure (53)]

2) Etch pits having a flat bottom
   [marked B in figure (53)]

3) Etch pits having a tail
   [marked C in figure (53)].

Pits of type A, on successive etching, persisted and got enlarged. They may be formed at the sites of emergence of dislocations perpendicular to the \{110\} faces. Pits of type B disappeared on subsequent etching. These pits may be formed at sites where impurities had segregated, or where the dislocations had moved away, by abrupt bending [307]. Flat bottomed pits have been observed also at points where the dislocations have moved away due to the applied stress [308]. In the C-type pits, the tail developed continuously upon etching. This behaviour indicated that these pits were produced
Fig. (52) 1:1 correspondence of etch pits on matched cleavage faces of phthalic anhydride (x 180).

Fig. (53) The etch pits on \{110\} faces (x 500).
at sites where the dislocations were almost parallel to the \{110\} faces. Dislocations parallel to or almost parallel to the surfaces have been known to exhibit this behaviour [309,310]. The dislocation density on \{110\} faces of unannealed samples were found to be $\sim 10^2 \text{cm}^{-2}$. On annealing at 80° for 12 hours, most of the dislocations were found to disappear. On annealed and unannealed samples large areas completely free of dislocations were seen on both \{110\} and \{001\} faces.

Thermal etching was also tried on phthalic anhydride crystals. The \{110\} faces responded to a stream of hot air and produced etch pits on these faces. But continued etching failed to sustain the original pattern and produced random appearance of new pits. Chemical etching failed to show an 1:1 correspondence between the thermally produced etch pits and the chemically produced etch pits.

b) Potassium acid phthalate

Potassium acid phthalate crystals were cleaved along \{001\} planes and various chemical etchants were tried to delineate the dislocations. The various chemical etchants, described in literature and found suitable for delineating dislocations in
other crystals [311], were not successful in potassium acid phthalate crystals. Other etchants prepared by considering the various chemical reactions of the material also proved to be unsuitable.

On etching with water, the surface showed general dissolution rather than etch pits, due to the large solubility of potassium acid phthalate in water. To control the dissolution, acetone was selected as a dilutant due to the miscibility of water and acetone. On the basis of trial and error method, a composition of H₂O in acetone in the ratio 1 : 5 volume was found to produce excellent etch figures on these surfaces, when etched for 5-10 seconds. An interferogram of an etch figure is shown in figure (54). The interferogram clearly showed that the etch figures were pits.

On etching the matched cleavages 1 : 1 correspondence of etch patterns were seen, as shown in figure (55). Very thin cleaved slabs of which both sides were etched showed similar etch patterns. On successive etching no spurious development of pits were observed. The above observations strongly suggested that the etch pits were produced at the emergence points of dislocations on {001} faces.

Figure (56) shows an interferogram of an etched {001} face. The fringe pattern clearly showed
Fig.(54) PECO fringes at an etch figure.

Fig.(55) 1:1 correspondence observed on the matched cleavage faces of potassium acid phthalate crystal (x 400).
Fig. (56) Fiseau fringes on an etched {001} face of potassium acid phthalate crystal.
the asymmetry of the pit. The pits were observed to be hexagonal with two faces having a curvature. By Weiss zone law, if \([uvw]\) are indices of a zone axis parallel to the face \((hkl)\) which is being etched, then

\[ hu + kv + lw = 0 \]  \hspace{1cm} (121)

In complex structures the various zone axis which satisfy this condition may have atoms in common. The common atoms may trigger the dissolution from one axis to another. According to Wooster [312] this triggering of dissolution from one direction to another result in etch frames bounded by curved lines. In potassium acid phthalate the curvature of the two adjacent faces of the etch figure was so gradual as to appear as pyramidal in microphotographs.

It was seen that pits like that marked A in figure (55) had no correspondence on the matched face. This type of mismatching have been observed in several crystals [309,313,314] and have been attributed to the bending away of dislocations.

The etch pits on \{001\} cleavages of these crystals exhibited various morphologies. The pits were classified as follows, according to the shape:
1) Pyramidal pits with a sharp bottom
   (type A and marked A in figure 55)

2) Flat bottomed pits
   (type B and marked B in figure 55)

3) Flat bottomed pits having a small
   A-type pit at the center
   (type C; figure 57)

4) Flat bottomed pits having a row of
   smaller pits along a diagonal
   (type D; figure 58).

The A-type pits could be further classified as those having flat sides and stepped sides. The A-type pits, in general, were formed at points where the dislocations intersected the surface normally. The flat sided pits were deeper compared to the terraced pits. Similar observations on other crystals have shown that the deeper pits were formed at edge dislocation sites while the terraced shallow pits were formed at screw dislocation sites [315, 316, 317, 318].

The formation of terraced pits have been attributed to the dissolution anisotropy of crystal faces, by Gatos [319]. According to him if the etch rates $R_d > R_v > R_1$, terraced pits will result where
Fig. (57) A flat bottomed pit with a small A-type pit at the center (x 2800).

Fig. (58) A flat bottomed pit having a row of pits along the diagonal (x 2800).
$R_d$, $R_v$ and $R_1$ are the rates of dissolution along the dislocation line, perpendicular to the surface and parallel to the surface respectively.

The appearance of terraced and flat sided pits on the same surface indicated that the terraced pits were formed at screw dislocation sites. A typical terraced pit is shown in figure (59).

The flat bottomed pit of the type shown in figure (55), were observed on several crystals [307, 308,320,321]. From the abundance of flat bottomed pits, it may be inferred that they are formed neither at points of impurity segregation nor at inclusions [320]. The most reasonable explanation for the occurrence of these pits is the bending away of dislocations at the cleavage plane [314].

Successive etching of the same crystal surface showed interesting features. Two A-type pits existing close together, on etching merged together to form a C-type pit, which on subsequent etching remained as such or split again into two A-type pits. Large number of such pits were observed. In some cases the C-type pits persisted for a long time before splitting into two or more pits. Such behaviour suggested the occurrence of branching and coalescence of
Fig. (59) A terraced pit (x 4000).
dislocations proposed by Read [322]. On sodium chloride Amelinckx [323] has observed that the nodal points of dislocation networks are preferentially decorated, for no apparent reason. Joshi et al [324, 325] have reported the appearance of flat bottomed pits with smaller pits at their centre at the nodal points of dislocations. With the etch/etch procedure for multiple etching it was possible to observe the C-type pits very near the node. It can be reasonably suggested that the mixed character of the dislocations very near the node gives rise to the outer flat bottomed pit while the pit at the centre corresponds to the coalesced part of the dislocation. A schematic diagram of the dislocation branching is shown in figure (60).

In the D-type pits, a row of smaller pits, arranged along the diagonal of a flat bottomed pit were seen. Such a pit is shown in figure (58). The small pits had exactly the same shape as that of the outer pit. On successive etching the number of pits increased or decreased systematically. When etched towards the seed the pits in general decreased in number. Careful observations on these type of pits showed that the small pits were A-type and they changed into C-type pits on successive etching.
Fig. (60) Schematic diagram of dislocation branching.

Fig. (61) Schematic diagram of dislocation branching resulting in D-type pits.
Prolonged etching often resulted in a single C-type pit. The systematic reduction in the number of small pits to a single pit, suggested that these pits were produced at the emergence points of dislocation branches, from a single dislocation. Figure (61) shows schematically the branching behaviour which resulted in D-type pits.

The dislocation density was found to be \( \sim 10^4 \text{cm}^{-2} \). The dislocation configuration in these crystals were studied by alternately cleaving and etching. The crystals were etched from the as grown surface towards the seed by cleaving off thin layers. The dislocation density was found to decrease towards the seeds. Figure (62a,b,c) shows the successive stages. The etch pits were observed only at the central portion of the crystals. The majority of the dislocations were traced back to the seed. In several solution grown crystals such dislocation propagation from the seed have been observed [326,327].

Annealing, at different elevated temperatures and for different durations of time, had no effect on the dislocation density. This indicated that the dislocations were immobile, probably due to the branchings and other interactions, of dislocations observed in these crystals.
Fig. (62a), (62b), (62c) Dislocation distributions on crystal surfaces revealed by the etch/cleave/etch procedure (x 90).
7.4. Investigations on Slip

a) Phthalic anhydride

Phthalic anhydride crystals grown by the Bridgman's method were cleaved along \{110\} planes and cut perpendicular to the <001> direction. The \{001\} and \{110\} surfaces were indented with the Hanemann's indentor described earlier (6.5). On \{001\} faces the pyramidal indentation produced two sets of parallel lines inclined at 58° or 122° to each other, as shown in figure (63). On \{110\} faces, only one set of slip traces parallel to the \textbf{C}-direction was produced, as shown in figure (64). According to the crystal structure, the projection of \textbf{110} planes should appear as lines making 58° or 122° to each other on the \{001\} plane and as parallel lines on \{110\} planes. This strongly indicated that the slip planes involved were \{110\}.

Figure (65) shows the slip process.

Ball indentations produced cracks on the \{001\} face. Typical cracks are shown in figure (66). The cracks clearly followed the different <110> directions. The observed slip and crack were typical of the 'cleavage brittle fracture' exhibited by brittle materials \[328\].
Fig. (63) Slip traces on a \{001\} face (x 600).

Fig. (64) Slip traces on a \{110\} face (x 320).
Fig.(65) Schematic representation of the slip process.

Fig.(66) A typical crack produced on \{001\} face (x 100).
b) Potassium acid phthalate

The typical indentation mark on \{001\} faces of potassium acid phthalate is shown in figure (67). The cracks were initiated at very low loads. The circular markings were produced by "chipping" [329] in the \{001\} cleavage planes, common in brittle materials having a pronounced cleavage. On \{100\} and \{010\} faces, the indentations produced only one set of parallel traces along the \langle010\rangle and \langle100\rangle directions respectively as shown in figure (68) and figure (69). The \{001\} slip plane alone is compatible with the traces observed on \{001\}, \{100\} and \{010\} faces. Figure (70) shows the slip process.

7.5. Topography of Crystal Surfaces

a) Phthalic anhydride

The cleavage faces exhibited the usual river pattern. Detailed examination of the cleavage surfaces, by multiple-beam-interferometry was found impossible due to the low adhesion of reflective metallic coatings on the crystal.

b) Potassium acid phthalate

The cleavage surfaces of potassium acid phthalate crystals exhibited river patterns typical
Fig. (67) Cracks initiated by indentation on {001} face of potassium acid phthalate crystal (x 200).

Fig. (68) Slip traces on the {010} face (x 250).
Fig. (69) Slip traces on the \{100\} face (x 250).

Fig. (70) Schematic diagram of the slip in potassium acid phthalate crystals.
of ionic materials [330,331]. These crystals exhibited good vacuum stability and metals could easily be evaporated on to the crystal surfaces by vacuum evaporation.

The cleavage surfaces were examined by multiple-beam-interferometry [279]. A typical interferogram of a cleavage surface, taken with mercury green light is shown in figure (71). The interferogram clearly showed large areas, free of cleavage steps and other irregularities. The cleavage was found perfect, comparable to or better than mica. Figure (72) shows a typical F3CO fringe pattern at a step. The cleavage often exhibited 'V' type terminations, level discontinuities and micro-cleavage patterns. Figure (73) shows the microcleavages observed on a cleavage step.

7.6. D.C. Conductivity of Phthalic Anhydride and Potassium Acid Phthalate Crystals

a) Phthalic anhydride

The conductivity of phthalic anhydride crystals were found to be highly anisotropic, the room temperature conductivities being two orders of magnitude higher in the <001> direction, than in a direction perpendicular to it. The variation of conductivity with temperature is shown in figure (74a,b,c). It was seen that the plot of log σ against 1/T was linear.
Fig. (71) Piseau fringes on a cleavage surface.

Fig. (72) FEOO fringes on a cleavage step.
Fig. (75) FECD fringes on a cleavage surface, showing fine structures.
Fig. (74a, b, c) The variation of conductivity with temperature: (a) along c-axis; (b) perpendicular to c-axis; (c) conductivity of the melt.
The anisotropy of conduction could be explained considering the structure of molecules and the crystal. Phthalic anhydride is an aromatic compound with the following chemical structure \([\text{C}_6\text{H}_4(\text{CO})_2\text{O}]\).

\[
\begin{align*}
\text{The molecule is almost flat and in the crystal these flat molecules are stacked face-to-face along the 001 direction [286]. The chemical bonding gives rise to 10 \(\pi\)-electrons. The intermolecular bonding can thus be conveniently described by means of \(\pi\)-bonding. In aromatic compounds, like anthracene, the molecular orbital overlap of \(\pi\)-electrons have been found responsible for the observed conduction anisotropy and the maximum overlap of orbitals in a direction perpendicular to the molecular plane have been found to cause an increase in conductivity 5 to 10 times than in a direction parallel to the molecular plane [332]. The molecular overlap have been found to influence the mobility of charge carriers in several materials [333,334,335].}
\end{align*}
\]

The conductivity variation with temperature yielded a thermal activation energy \(\sim 2.7 \text{ V}\), from the relation,

\[
\sigma = \sigma_0 \exp(-E/2kT) \quad (122)
\]
assuming an intrinsic semiconduction. Though the conductivity exhibits an anisotropy, the activation energy parallel and perpendicular to the $<001>$ direction remained practically the same.

The conductivity of the molten phthalic anhydride was several orders of magnitude higher than that observed in the solid state, at the same temperature. The variation of the conductivity of the melt with temperature is shown in figure (74c). Similar behaviour has been observed by Reihl [336] in napthalene. Forster et al [337] have also observed a sharp rise in conductivity in bensene upon melting, the activation energy remaining virtually constant. But in some cases the activation energy has been found to decrease in fusion [338]. A decrease in the activation energy for conduction in the molten state has been found to be due to a fundamentally different transport mechanism operating in the molten state [339]. The observed activation energy of $\sim 2.07eV$ in the molten state of phthahlic anhydride, compared to the value of $\sim 2.7eV$ in the solid state indicated that the transport mechanism in the molten state was entirely different from that in the solid state.

Various models have been suggested for the electrical conduction in organic crystals. Eley and
Parfit [340] proposed a tunnel model in which the molecules were excited thermally or optically from the normally occupied \( \frac{N}{2} \textsuperscript{th} \) \( \pi \)-orbital to \( [(\frac{N}{2})+1] \textsuperscript{th} \) \( \pi \)-level. \( N \) denotes the number of conjugated \( \pi \) electrons in the molecules. The conduction was limited by the probability of electron/hole tunneling to the corresponding orbital in the adjacent molecule. According to this picture phthalic anhydride with its 10-\( \pi \) electrons should have an activation energy \( \sim 2.5 \text{eV} \).

Wilk [341] studied the effect of the number of linearly joined ring systems on the activation energies and found a relation

\[
E = (17-n)^2/100
\]

(123)

where \( n \) denoted the number of rings. For phthalic anhydride \( n = 1 \) and hence according to this equation, the activation energy should be \( \sim 2.56 \text{eV} \).

The possible relation between the conduction band and the triplet excited levels was examined by Northrop et al [342] and Rosenberg [343]. The triplet hypothesis [244] envisages the participation of charge carriers in conduction via a triplet excitation. In a singlet state there is no net electronic spin angular momentum, whereas in a triplet state there is a net
positive electronic spin angular momentum. The excited triplet state lies lower in energy than the corresponding singlet excited state. Optical transitions between triplet states and a singlet ground state are forbidden and hence weak. The transitions from the upper singlet state to ground state results in fluorescence and is characterised by short life times of the order of $10^{-8}$ seconds. The triplet-ground state transitions gives rise to phosphorescence which are weak and have comparatively long life times of the order of $10^{-2}$ seconds. The carriers can be either thermally or optically excited to the lowest triplet states which by subsequent motion produce the conductivity. The phosphorescence spectra of phthalic anhydride have been studied by Iwata et al [344]. The 0-0 band has been found to occur at 25800 cm$^{-1}$ and the phosphorescence maxima at 23600 cm$^{-1}$. Hardy et al [345] have also studied the photoluminescence spectrum of phthalic anhydride. The fluorescence have been observed at 29411 cm$^{-1}$. The phosphorescence have been found to occur at 21276 cm$^{-1}$. According to those values the energy levels of phthalic anhydride should be like that shown in figure (75). The activation energy for triplet excitation can thus be inferred to be between 2.6eV and 2.9eV.
Fig.(75) Energy level diagram of phthalic anhydride crystal.
The observed value of 2.7eV for the thermal activation energy in phthalic anhydride is comparable to 2.64eV of the triplet state. Thus the triplet exciton participation in electrical conduction may be reasonably suspected.

A necessary, but not sufficient, test of the intrinsic nature of the conductivity is a comparison of the observed value of $E$ with the quantity $I_c - A_c$ [346], where $I_c$ and $A_c$ are the ionisation and electron affinity of the molecule in the crystal. For phthalic anhydride, $A_c \sim 2.72eV$ [347,348], $I_c$ may be calculated from the relation

$$I_c + A_c = I_g + A_g$$

(124)

where $I_g$ and $A_g$ are the ionisation potential and electron affinity of the molecule in the gaseous state. $I_g + A_g$ had been observed to be a constant for most of the aromatic molecules and is taken as $\sim 8eV$[349]. Hence, $I_c \sim 5.78eV$. The value of $I_c - A_c \sim 2.56eV$ is in reasonable agreement with the observed value of 2.7eV for the activation energy. This strongly suggested that the conduction in phthalic anhydride was intrinsic.

b) Potassium acid phthalate

The conductivity variation with temperature is plotted in figure (76a,b,c). The conductivity
Fig. (76a, b, c) The variation of conductivity with temperature in potassium acid phthalate: (a) along $<010>$ direction; (b) along $<001>$ direction; (c) along $<100>$ direction.
exhibited a strong anisotropy with the crystal direction. The conductivity along the \(<100>\) direction was the largest. Conductivity was less along \(<010>\) and \(<001>\) direction, being lowest along the \(<001>\) direction. The plot of \(\log \sigma\) against \(1/T\) exhibited a knee typical of ionic crystals. In alkali halides such behaviour have been observed and have been attributed to the difference of mechanism involved in the conduction process at lower and higher temperatures and the observed change in the slope of the \(\log \sigma - 1/T\) plot has been attributed to the presence of divalent impurities [350,351].

The activation energy of ionic materials change as the temperature is increased. The commonly encountered shapes of the \(\log \sigma Vs. 1/T\) plots are shown in figure (77). In certain cases the activation energy increases [case (a) of figure (77)] and in others it decreases [case (b) of figure (77)] with increase of temperature. In case (a) the change in activation energy is brought out by a change from extrinsic [portion (i) of curve (a)] to intrinsic [portion (ii) of curve (a)] conductivity [352]. In the case (b) the activation energy is decreased with
Fig. (77a) The commonly encountered shapes of \( \log \sigma \) vs. \( 1/T \) plots.
the increase of temperature and both the portions (iii) and (iv) corresponds to the extrinsic mode. The change in slope have been found to be caused by a change in the number of excited carriers, \( n \), relative to the number of impurity levels \( N \), less the total number of carriers \( N_e \). In (iii) \( n \ll N-N_e \) and in (iv) \( n \gg N-N_e \).

In potassium acid phthalate crystals both these cases have been seen to arise, as can be seen from figure (76a,b,c).

The observed anisotropy of electrical conduction could reasonably be explained on the basis of the crystal structure. The crystal structure is ionic with potassium ions and acid phthalate ions. The phthalate ions have two carboxyl groups one of which is ionised \([290,353]\). The phthalate ions are stacked along the \( <100> \) axis by an a glide perpendicular to b axis. The phthalate ion chains extending in the \( <100> \) directions are bonded by O-H...O hydrogen bonds. The chains are interconnected by potassium ions each of which is surrounded by six oxygen atoms. The observed conductivity in \( <100> \) axis may be due to the enhanced molecular overlap and hydrogen bonding in the \( <100> \) direction.
Though the presence of the knee can be explained as due to the ionic nature of conductivity, the exact mechanism of conduction could not be established.