CHAPTER 3

GROWTH OF ANTHRACENE, NAPHTHALENE AND DOPED NAPHTHALENE CRYSTALS AND THEIR XRD, UV-VISIBLE, RAMAN STUDIES

3.1 INTRODUCTION

Anthracene and naphthalene crystals are classified as the organic scintillators. The scintillation counting techniques have found a wide variety of important applications in biology, chemistry, geology, medicine, atmospheric science, and industry. Most organic scintillators are either monocrystalline compounds or liquid or plastic solutions. Among the most efficient monocrystalline compounds are naphthalene, anthracene, fluoranthene, p-terphenyl, p-quaterphenyl, and trans-stilbene. In scintillation detector, a larger light output by suitable doping materials is a welcome feature. There is the interesting possibility of producing improved organic crystal scintillators with a reduced decay time and the same or enhanced scintillation efficiency, by introducing lattice defects which do not quench the fluorescence but instead facilitate the exciton-photon transformation and reduce the exciton lifetime. Naphthalene or similar non-absorbing molecules may function in this manner, in anthracene, for example (Birks 1964).

Literature survey shows that naphthalene has been doped by number of molecular crystals like anthracene, pyrene (Chabor and Zschokke-Granacher 1976, Richard Powell 1971, Bowen et al 1949) tetracene (Reed and Lipsett 1957) pentacene (Duppen et al 1983),
1,3-phenylenediamine, 1,4-toluidine, 1,3-toluidine, 1,2-toluidine, aniline, durene, 1,2-nitroaniline, hydroquinone, 1,3-nitroaniline, resorcin, toluene, 1,2-dibromobenzene, 1,2-dichlorobenzene, benzene, p-phenylstilbene, 1,2-di(beta-naphthyl)-ethylene, 1-(beta-naphthyl) 2-(p-bynaphthyl)-ethylene (Lagonaya et al 1966), dibenzoterrylene (Jelezko et al 1996). The molecular structures are given in Figure 3.1.

This chapter mainly focuses on growth of anthracene, naphthalene (pure and doped) crystals. Naphthalene crystals were doped by anthracene and 2,5-diphenyloxazole (PPO). Scott and Laridjani (1974) described the acceptability of organic dopant in organic crystals. Naphthalene is the first organic scintillator (Broser and Kallmann 1947) then anthracene was introduced as an efficient scintillation material which is five times better than the naphthalene (Bell 1948). Single crystals of anthracene have the highest practical scintillation efficiency of any organic scintillator so far reported. For this reason they are commonly used as comparison standards and many observations of the practical efficiencies of other materials are expressed relative to anthracene. The growth of very large crystals is desirable for the absorption and detection of high energy gamma-rays. However, technically it is difficult to grow large anthracene crystals for such applications due to decomposition of the anthracene melt when exposed to atmosphere due to oxygen. In addition, due to the difference in thermal expansion co-efficient of anthracene & container the grown crystals are highly defective. Naphthalene can be grown in larger crystals, several inches in diameter, by controlled slow freezing from the melt. The fluorescence emission is on the edge of phototube spectral response (Birks 1950). Because of very low solubility nature (Madhurambal and Anbu Srinivasan 2006) it is very difficult to grow bigger crystals from solution growth. The anthracene fluorescence emission is well matched with the spectral response of PMTs. The crystal structure of

Figure 3.1 Molecular structure of some organic materials which are doped into naphthalene crystals
naphthalene and anthracene are virtually identical except for the length of the unit cell in the c direction. Both crystals are monoclinic and the two molecules in the unit cell are related by a glide plane perpendicular to the b axis (Schlosser and Philpott 1980).

PPO is a well known scintillating molecule (Kimberly et al 1995). Growth of pure PPO is very tough and it grows as milky crystals. It is a major component of most commercially available scintillation cocktails (Hariharan et al 1997).

Growth of organic crystals from the vapour phase usually results in slow growth of very thin crystal (Karl, 1980 Buckley 1951, Lawson and Neilsen 1958). Thus, when large single crystals are required, these must be grown from the melt, or from saturated solution. In the case of anthracene and naphthalene, the latter method is of doubtful applicability, because the limiting factor in growth from solution is solubility. Solubilities of 20-50 % by weight are required for tolerable growth rates and size. Anthracene and naphthalene solubilities are much lower. There is also the disadvantage of possible solvent occlusion.

The selective self seeding vertical Bridgman technique (SSVBT) technique was chosen for the present study. The investigation is concerned with several important criteria to be observed before crystals can be grown successfully, namely, the purity of materials, the temperature gradient, the rate of crystal growth, and the shape of the growth vessel. These are of paramount importance for growing crystals (Marciniak and Waclawek 1981).

The lower melting point of the organic crystals often offers the advantage that transparent glass-made growth apparatuses can be used, in which the growth process can be easily followed by direct observation. There
are many uses for transparent furnaces in materials processing and fluid and solid mechanics at elevated temperatures. Transparent furnaces can be used for research in crystal growth, sintering, metal joining, and annealing, high temperature materials properties, and the behavior of flowing systems that use high temperature liquids. In the area of crystal growth, some of the capabilities introduced by a transparent furnace are: 1) Nucleation can be observed; if multiple nucleation sites occur solidification can be restarted, 2) The melt/solid interface can be viewed as a result of differences in density and emissivity between the liquid and solid, 3) Surface tension effects can be studied as a result of these liquid-solid differences, 4) Convection can be studied through index of refraction changes with temperature, 5) Internal temperatures can be monitored by tomographic means, and 6) A variety of crystal defects are visible, depending on the optical properties of the crystal (Stephen et al 1997).

3.2 CONSTRUCTION OF FURNACE

A glass tube was used for Bridgman furnace; the furnace separated into two zones, each 30 cm long. Each zone was wound with thin A1 Kanthal of thickness 0.5 mm having total resistance of 50 ohms. For winding, ceramic thread has been used for grip in the glass material. The space between the winding was kept as 2 mm. The setup was enclosed by a concentric borosilicate glass tube, which ensured the thermal insulation. The schematic diagram of the vertical growth furnace with translation setup is shown in Figure 3.2.
The setup has been enclosed by a black envelope to provide light shielding for the material during growth because of photo plastic nature (Kojima 1981) and dimerisation of the grown crystals is possible due to UV-Visible light exposure at high temperatures. The growth furnace was placed on the wooden stool whose bases are supported by vinyl sheets to avoid vibration and the stool was leveled using spirit level so that the furnace had no asymmetric tilt. With this arrangement and by virtue of the heavy weight of the furnace itself mechanical vibration was practically eliminated. The temperature of the furnace was controlled by programmable Eurotherm PID controllers. The photograph of the two zone glass furnace is shown in Figure 3.3.
3.3 TRANSLATION SETUP

Because there is no forced convection in the melt during Bridgman growth, a slower growth rate should be used to grow the crystals with higher quality. The rate of crystal growth sets an upper limit to the rate at which the crystal-growing vessel can be lowered in the oven. A rate of 1-2 mm/h has been recommended as an upper limit for organic crystals, in contrast to 20 mm/min for metals and 1-4 mm/h for ionic crystals (Sherwood 1960). The larger diameter crystals should be grown by even slower growth rate. However the reports proposed a constant growth rate for full growth of
crystals. But the organic crystals are of low thermal conductivity. So, if the diameter of the ampoule increases the translation rate must be reduced.

A translation assembly has been developed using a DC motor with multistage gear setup. A conical screw type mechanism (Figure 3.2) was used to translate the ampoule. The screw was fixed to the end of the gear setup. One end of a Teflon thread was rolled in the conical type screw and the other end was fixed on the ampoule via metal wire and two pulleys. The thread was rolled towards the bigger diameter form the end of the screw. A 2 cm long cylindrical rod has been fixed at the end of the conical screw. When the DC motor rotates with a constant speed, the translation smoothly decreases as the diameter of the screw decreases then the translation was at a constant rate.

3.4 TEMPERATURE PROFILE STUDY

The temperature profile studies were carried out using a programmable temperature-time data logging system as described in previous Chapter. The Figure 3.4 shows the on-line temperature profile for the transparent two zone furnace with the setting points of 220°C (I-zone) and 200°C (II-zone).

3.5 GROWTH CONTAINER (AMPOULE)

The production of good seed crystal is difficult for organic materials. Different containers have been discussed in respect to organic crystal by Lipsett (1957), Sherwood and Thomson (1960) and Arulchakkaravarthi et al (2002a). Though the double walled ampoule growth was used earlier, the effect of the distance between the inner seeding capillary
Figure 3.4 Online temperature profile

and the outer tube, which is vital for all time occurrence of the single crystals, has been done by Arulchakkaravarthi et al. (2002a). In the SSVBT method reported, the double wall ampoule-grown crystals were single crystals for all the growth runs and the quality of the crystals was better compared to the conventional growth. The lower end of the inner tube has a capillary of 0.5–1 mm. If the angle of the capillary to the vessel axis is less than 45° the ab cleavage plane anthracene crystals will grow parallel to the vessel axis, but if this angle is greater than 45° the ab-cleavage plane will grow perpendicular to the vessel axis (Sherwood 1960). The substance after melting fills the annular space between the inner and outer tubes and acts as an insulator to prevent thermal shocks entering the inner tube during growth. The space above the melt level also acts as a thermal insulator due to vacuum. The inner wall cone angle of 20°–24° was helpful to avoid multi twinning and strain induced by the contraction of the walls of the ampoule. A model ampoule for our growth is shown in Figure 3.5 which is similar to the SSVBT ampoule used by Arulchakkaravarthi et al 2002a. The hole was helpful to evacuate the air between the inner and the outer wall.
3.6 PURIFICATION PROCESSES

The commercially purchased material contains impurities. Before crystal growth the purification is important. In this work the following purification procedures were involved.

3.6.1 Recrystallisation from Solvent

This process involves identifying a suitable solvent in which the material to be recrystallised or purified has high solubility at elevated temperature (typically near the boiling point of the solvent) and low solubility at low temperature. The solid (or mixture) is dissolved in a minimal volume of hot solvent, filtered to remove any insoluble components in the mixture and the solution is slowly cooled to allow the product to crystallise. The formation and growth of crystals is a complex process that involves the removal of molecules from solution (molecule by molecule) and stacking them into a regular condensed state where the molecules are packed in a

Figure 3.5 Ampoule design for crystal growth
crystal lattice. Like molecules tend to pack more efficiently, so the growth of crystals tends to bring together molecules of the same type. The effect of dissolving a solid in a solvent and then permitting it to crystallise is that the crystals that form contain less impurities than the material that was originally dissolved. Successive recrystallisations can produce extremely pure crystalline samples.

3.6.2 Sublimation Purification

A single-zone furnace for sublimation purification was constructed. The zone is controlled with a temperature controller and K-type thermocouple. The purification ampoule utilized is 30 cm long and 2 cm in diameter. The ampoule is sealed with materials under the low pressure (~10⁻³-10⁻⁶ torr). The device operates by subliming stock material and transporting molecules to the cooler region, where they are deposited. Impurities are left in the high temperature region, and volatiles are transported to the cold trap. The purified material is collected from the middle region. Generally it takes at least three sublimation runs to complete this stage in the material purification process.

The zone refinement process has been used successfully to remove impurities that are generally not removable by other purification methods. A furnace designated for zone refinement processing has been designed and built. The furnace consists of three asbestos cement sheets A, B and C (Figure 3.6) of thickness 0.5 cm and radius 15 cm. The asbestos cement sheets A and C have holes at the centre, slightly greater than the diameter of the tube in which the zone refining is to be carried out. The diameter of the hole in the central asbestos sheet B is about 2 mm more than that of A and C. The heating coil is wound on B (Figure 3.6D). An ordinary Kanthal heating
element is used as a heating coil. The closed electric connections were taken out through a twin bore ceramic tube. The three asbestos cement sheets along with the heating coil and thermocouple were fixed by screws and nuts, and were kept in a stand. This furnace provided temperature of up to 350°C with a heating zone of about 1.5 cm. A sample to be purified is sealed in an ampoule. A small, evacuated, and sealed ampoule (filled with material to be purified) is then pulled upward along the length of the furnace by a motor at a pre-determined speed. This was repeated many times. The purified materials were collected and filled in another ampoule. Then the ampoule traversed downward direction and it repeated many times. Impurities migrate away from the melted region, which slowly pushes the impurities to the ends of the entire material sample.

Figure 3.6 Zone refining setup
3.7 CRYSTAL GROWTH

3.7.1 Growth of Anthracene Crystals

Robertson (1958) determined the crystal structure of anthracene and Cruickshank (1956) and later Mason (1964) refined it with \( a = 8.561 \, \text{Å}, \) \( b = 6.035 \, \text{Å}, \) \( c = 11.163 \, \text{Å}, \) \( \beta = 124^\circ \), \( Z = 2, \) monoclinic, \( P2_1/a, \) \( M = 178.2 \, \text{g mol}^{-1} \) and \( D = 1.26 \, \text{Mg m}^{-3} \). It has a perfect cleavage plane parallel to \(<001>\) direction. Single crystals of anthracene can be grown from the vapour phase, from the melt, and from its saturated solutions. Selection of the suitable method depends upon the melting point, crystal structure, and chemical properties of the material, as well as on the required shape and size of the crystals (Karl 1980). The quality of the crystals grown from recrystallized material was very much better than that of crystals grown from material purified by chromatography (Sherwood 1960).

Anthracene (>99%) was commercially purchased from Sigma Aldrich. Since anthracene is derived from coal tar the presence of impurities like carbazole, phenanthrene, pyrene, fluorine and methyl derivatives of anthracene are more possible. So the materials have been subjected for purification by using various techniques. Anthracene was purified from recrystallisation by various authors from various solvents. A detailed study on purification of anthracene has been done by McDowell (1908). He used kerosene, xylol, chloroform and alcohol as solvent for recrystallization. The purification was done by means of recrystallisation using acetic acid, toluene and ether by Sherwood and Thomson (1960). But Robinson and Scott (1967) used ethylene chloride and pentane for purifying the anthracene. Marciniak and Waclawek (1981) had purified from dimethyl sulphoxide and hexane. Dimethyl sulphoxide, dimethyl formamide and hexane were used by Arulchakkaravarthi et al (2002b). Dimethyl sulphoxide and ethonal were used in the present study. Commercially purchased anthracene was purified by
fourfold recrystallization using dimethylsulphoxide (DMSO) as the solvent, which removed carbazole, effectively. Then the recrystallized anthracene was washed in ethyl alcohol. The recrystallized anthracene was then purified by sublimation and zone refining.

Finally the zone heating of the substance was done in high vacuum of about $10^{-6}$ Torr, which was obtained by using Hind High Vacuum diffusion pump. The main aim of the vacuum is the removal of oxygen, otherwise anthracene will oxidize. The zone refining glass tube was 30 cm long with diameter of 2 cm. The substance was zone purified for about 30 times in the upward direction by using above described vertical zone purification assembly at the rate of 2-1 cm/h. The purified material was taken in another ampoule and it was passed through the zone about 30 times in the downward direction. The impurity-segregated parts were removed and the pure substance was taken for growth. The substance melted at 217 °C in a specially designed double walled ampoule under vacuum (about $10^{-6}$ Torr). Vacuum in the crystal growth tube ensures higher quality crystal since inert gases have been found to adversely affect crystal quality (Karl 1980). The upper zone temperature was maintained at 3°C above the melting point using PID controller with accuracy ± 0.1°C. The lower zone was maintained at 150°C. The temperature sensors were fixed in the middle of each zone. The temperature profile obtained for this temperature setting is shown in Figure 3.4.

The translation of the melted substance from upper zone to the lower zone allows directional freezing of the substance from the bottom to the top of the growth vessel. Initially the translation speed was set to 1 mm/h. Due to the above described translation mechanism the translation rate was varied from 1 mm – 0.3 mm/h as the diameter of the ampoule increases and the translation rate was maintained at 0.3 mm/h in the cylindrical region. After many attempts the successful growth was achieved by translating the
ampoule as stated above. After the completion of full growth the temperature was decreased step by step from 1-10 °C/h. However, a rate greater than 1.5 mm/hr resulted in the formation of polycrystals. The crystal grown in the vessel had (001) cleavage plane vertical. The grown crystal with ampoule is shown in Figure 3.7. The grown crystal fluoresces in violet color when kept in sunlight (Figure 3.8).

Figure 3.7  Anthracene crystal with ampoule

Figure 3.8  Cut and polished anthracene crystals
3.7.2 Growth of Naphthalene Crystals

Bragg (1921) determined the crystal structure of naphthalene and later Cruickshank (1957) refined it with \( a = 8.235 \, \text{Å}, \, b = 6.003 \, \text{Å}, \, c = 8.658 \, \text{Å}, \, \beta = 123^\circ, \, Z = 2, \) monoclinic, \( P2_1/a, \) \( M = 128.2 \, \text{g} \, \text{mol}^{-1} \) and \( D = 1.162 \, \text{Mg} \, \text{m}^{-3}. \)

Naphthalene is a transparent organic compound melting at 80 °C, which normally freezes with a non-faceted interface (Wilcox 1964) and it also cleaves readily on the (001) plane like anthracene. Naphthalene does not react with air (Lipsett 1957) and it has a low vapour pressure (10 kPa) at its melting point. It can be grown in open ampoule. Due to the sublime nature of naphthalene, it was grown in a closed ampoule system.

The sublimation of naphthalene was done in a glass tube 30 cm long and diameter 2 cm using the two zone furnace. The temperature of the lower part of the tube was maintained at 60 °C and the upper part was around 40 °C. In 40 hrs >95 % of the substance was sublimed in upper part. The middle portion was collected for zone refining process (50 passes).

Double walled selective self seeded ampoule was used to grow naphthalene crystals. The tube was evacuated to \(-10^{-4} \, \text{Torr}\) and then sealed off. The tube was placed in the vertical Bridgman furnace with two temperature zones, where the temperatures of the upper and lower zones were kept at 82 °C and at 50 °C, respectively. The corresponding temperature profile is shown in Figure 3.9.

Many trials were made to optimize the translation rate. The translation rate was started at a rate of 1 mm/h (to initiate less number of nucleations) then increased to 3 mm/h and it was decreased to 1 mm/h.
Towards the end of the cone, the translation rate was maintained at 1 mm/h in the cylindrical region. The grown crystal was free from visible inclusions. The crystals were grown at different rates of 0.5, 1.5, 2, 2.5 mm/h. However, as the growth was conducted at a rate more than 2 mm/h, the crystal quality deteriorates. So the growth rate in the range of 1-2 mm/h is desirable to grow good quality crystals. When the tip of the tube crossed the interface, the crystallization of the molten naphthalene was initiated by self-nucleation and it had (001) cleavage plane vertical. After the crystal growth, the crystals were slowly cooled down to room temperature at the rate of 1-2 °C/h. Since the surface of naphthalene crystals deteriorate by sublimation the surface was preserved by coating them with optical grease. Growth of naphthalene crystals was easier than anthracene crystals and also it grows faster than anthracene.
3.7.3 Growth of Anthracene Doped Naphthalene Crystals

Based on literature survey naphthalene crystals with 0.01 mole anthracene/mole naphthalene have been grown from melt because in this concentration the naphthalene shows maximum fluorescence efficiency. This concentration is interesting for scintillation detector because it shifts the luminescence to higher wavelength, which matches the spectral sensitivity of most of the phototube without much change in luminescence efficiency.

Zone purified naphthalene sample was carefully powdered and mixed with 0.01 mole of anthracene/mole naphthalene using an agate mortar. The mixture was placed in a container and sealed at a pressure of ~10^{-4} torr. The container, filled with the powdered material, was then placed in the melt zone of the furnace. The furnace was heated to 90°C at a rate of 30°C/h. When the material was molten the container was slowly lowered by a controlled
lowering assembly. The translation rate was initially less than 0.5 mm/h to initiate less number of nucleation in the outer tube and then after 3 mm of growth, the rate was increased to 1 mm/h to suppress all the slow growing grains. Subsequently the rate was reduced to 0.5 mm/h gradually and it maintains with same rate towards the end of the growth. The grown crystal of anthracene doped naphthalene with container is shown in figure. The crystals were observed to be clear inside without any macro-defects as the growth rate was controlled in the range 1-0.5 mm/h. Few attempts were also made with the growth rate >1 mm/h. But all the time polycrystals have been obtained.

![Figure 3.11 Anthracene doped naphthalene crystal with ampoule](image)

**3.7.4 Growth of PPO Doped Naphthalene Crystals**

PPO was obtained from Loba Chem. Ltd. (India) and the sublimed material was used for dopant. A small quantity of PPO was dissolved in liquid naphthalene, and a single crystal was grown by the vertical Bridgman method. The above said two zone vertical Bridgman furnace was used with
temperature in the upper zone above the melting point of naphthalene and that of the lower zone below 80°C.

The growth was initiated by moving the ampoule from the hot zone to cold zone very slowly (0.3-0.5 mm/h) to initiate lesser number of nuclei in the outer tube of the ampoule. After observing the solidification process, the growth rate was increased (1-3 mm/h). During the process the grains oriented along the fast growing directions (<001>) suppress the slow-growing grains. After nearly 5 mm growth, the fast-growing grains attain larger size and one of the grains enters the capillary of the inner tube and acts as a seed for the growth. After a few mm of further translation, crystal starts to grow into the wider part of the inner tube. At this stage, translation rate was gradually lowered to maintain a flat interface.

The growth runs were performed with 0.01, 0.03, 0.05 and 0.07 M % naphthalene in order to study the effect of variation in PPO concentration on the scintillation properties of naphthalene. The optimum crystal growth rates in the cylindrical region for 2 cm diameter ampoule were: 1 mm/h for 0.1 M % PPO doped naphthalene, 0.7 mm/h for 0.03 M % and 0.5 mm/h for 0.05 and 0.07 M % doped naphthalene.

3.8 CHARACTERIZATION
3.8.1 X-Ray Diffraction Analysis

The phase analysis and lattice parameters measurement of grown crystals were performed by X-ray diffraction (XRD), Si was used as standard sample. Powder X-ray diffraction (XRD) data of our grown crystal samples were collected using Rich Seifert diffractometer with CuKα radiation of wavelength 1.5418 Å at room temperature. Intensities for the diffraction peaks were recorded with a scan speed of 1°/min.
Figure 3.12  PPO doped naphthalene crystals with ampoules
The XRD patterns of anthracene (Figure 3.13), naphthalene (Figure 3.15b) and PPO (Figure 3.14) closely resemble to that of JCPDS card No. 39-1848, 13-0824 and 06-0085 respectively. Figure 3.15 shows the XRD patterns of pure naphthalene, NA and NPPO crystals. No additional peaks were observed in the diffraction spectrum due to the dopant molecules, which confirms that the structure (monoclinic) is same for pure naphthalene or in other words there is no change in phase due to dopant. The differences in the peak amplitude can be attributed to the different sizes and orientation of the powdered grains. The peak broadening can be attributed to the lattice strain due to the dopant molecules. From the XRD analysis it is inferred that the dopant molecules have entered into the lattice.

![Figure 3.13 Powder X-ray diffraction pattern of anthracene](image-url)
Figure 3.14 powder X-ray diffraction pattern of PPO

Figure 3.15  Powder X-ray diffraction pattern of PPO doped naphthalene, pure naphthalene and anthracene doped naphthalene
3.8.2 UV-Visible Analysis

The UV-Vis absorption spectrum was recorded using Shimadzu UV-1061 spectrophotometer in the range 200–1100 nm, which includes entire near ultraviolet, visible and the higher energy part of near infrared region. Optically polished 5x5x1 mm³ single crystals were used for this study. The UV-Visible absorption and transmittance spectra of anthracene, naphthalene and anthracene doped naphthalene crystals are shown in Figure 3.16 and Figure 3.17 which show bathocromic (red) shift with respect to the pure naphthalene crystals and hyposochromic (blue) shift with respect to pure anthracene crystals. This shift indicates a coupling and charge transfer between the naphthalene and the anthracene molecules.

The same behavior was observed for PPO doped naphthalene crystals (Figure 3.18). The absorption edge is same for all concentration of PPO. The absorptions are due to the transition of aromatic $\pi-\pi^*$ (E-band) for their individual molecules. It reveals the incorporation of dopant molecules into naphthalene crystals. The final (inhomogeneous) concentration was not measured, but it was probably less than the initial concentration. As the PPO concentration is increased the transmittance is reduced (Figure 3.19).

3.8.3 Raman Spectral Analysis

The Raman spectra of grown crystals were recorded on a JASCO NR-1100 Raman spectrophotometer that has the precision of 2 cm⁻¹. The spectrum was recorded in the region 2000–200 cm⁻¹ using the 488 nm line of an argon ion laser for the excitation operating at 200 mW power. The reported wave numbers are expected to be accurate within ±1 cm⁻¹. Optically polished 5 x 5 x 2 mm³ single crystals were used for this study. The observed Raman
Figure 3.16  Absorption spectra of anthracene, naphthalene and NA crystals

Figure 3.17  Transmittance spectra of anthracene, naphthalene and NA crystals
Figure 3.18 Absorption spectra of naphthalene and NPPO crystals

Figure 3.19 Transmittance spectra of naphthalene and NPPO crystals
spectrum of naphthalene and anthracene is shown in Figures 3.20 and 3.21 respectively. The observed Raman peaks were assigned to the corresponding wavenumber and it is compared with previous reported spectrum. It is in better agreement with the wavenumber and Raman intensity data (calculated as well as experimental) by Hideaki Shinohara et al (1998).

Figure 3.22 shows the observed Raman spectra of NA crystal and Figure 3.23 shows the Raman spectrum of 0.03%PPO doped naphthalene crystal. The unobserved changes in the spectral features from the pure to doped crystals mean that the corresponding phonons are not sensitive to the low impurity content. The same behaviour was found in other molecular crystals, namely in biphenyl and naphthalene (Bellows and Prasad 1979) and p-terphenyl (Amorim da Costa 1997, Amorim da Costa and Amado 1999). These unobserved changes have been interpreted that the mixture lattice is analogous to the crystal lattice of the dominating component. This may be due to the very low concentration of impurities which does not essentially influence either the line parameter of the vibrational spectrum in the external frequency region, or probably the crystal packing. This is the evidence for the absence of inter molecular bonding between the dopant and naphthalene molecules. However 0.07 M % of PPO doped crystals has some spectral distortions in the lower wavenumber side (Figure 3.24). But the peaks are same as pure naphthalene crystals. There were no new scattering peaks, indicating that dopants have entered the lattice of the crystal, replacing other molecules, rather than entering the space of lattice. However, compared with the naphthalene crystal, the intensity of the peaks of doped crystals varied.
Figure 3.20  Raman spectrum of naphthalene crystal

Figure 3.21  Raman spectrum of anthracene crystal
Anthracene doped naphthalene crystal

PPO doped naphthalene crystal

Figure 3.22 Raman spectrum of NA crystal

Figure 3.23 Raman spectrum of 0.03M% PPO doped naphthalene crystal
3.9 CONCLUSIONS

Pure and doped naphthalene crystals were grown using the self seeded Bridgman growth. A two zone furnace was constructed and the temperature profiles were studied using an integrated-circuit temperature sensor IC LM35 with automated data logger. A home-made translation setup was constructed for growth of low thermal conductivity materials in conical type ampoules. The continuous decrease of the ampoule translation rate was helpful in sustaining the flat interface throughout the growth and it helps in the yield of highly transparent crystals. Good seeding was done using the double walled crucible with additional necking facility. Growth rate of crystal is not same as pure materials and optimized growth rate was found out. The
grown crystals were characterized using powder X-ray diffraction studies and the calculated cell parameters were in accordance with the JCPDS data. The diffraction spectrum of doped crystals is same as for pure naphthalene or in other words there is no change in phase due to dopant. The UV-Visible transmission studies confirm that the dopant molecules are present in naphthalene crystal. The doped crystal shows the red shift in the absorbance spectra. The results on Raman spectral features of doped naphthalene in relation to the corresponding features observed for pure crystalline naphthalene show that the crystal doping in such small amounts does not lead to noticeable changes of the intermolecular interaction energy. The characterization analysis reveals that the dopant molecules are entered into the lattice.