CHAPTER 2

MODIFIED VERTICAL BRIDGMAN SETUP DESIGN, GROWTH AND CHARACTERIZATION OF NAPHTHALENE AND BENZIL SINGLE CRYSTALS

2.1 MODIFIED VERTICAL BRIDGMAN TECHNIQUE

Melt growth techniques are more convenient and faster for growing single crystals. The materials which melt congruently do not decompose before melting and those do not undergo phase transformation between the melting point and room temperature can be grown as single crystal by Bridgman technique. Bridgman technique is the simplest method for the growth of crystals from melts. Currently, double zone furnaces are used to grow crystals by Bridgman technique. The disadvantage of using the double zone furnace is that one needs complicated electronic circuits to control the temperature. To overcome this problem the single zone furnace is used. The advantage of using the single zone furnace is that the large size good quality transparent organic single crystals can be grown and simple system. Due to the technological requirements, the single zone furnace is much used to grow organic single crystals.

2.1.1 Furnace Construction

Single zone transparent vertical Bridgman furnace is used to grow large size good quality transparent single crystals. In the Bridgman setup, two cylindrical open ended glass tubes made up of borosil glass are used. The
furnace inner tube has 100 cm length with 4 cm diameter and the wall thickness is 2 mm. The furnace was wound with thin A1 kanthal wire of thickness 0.5 mm. Initially the space between the winding was kept as 2 mm and then it was gradually increased to 1.5 cm towards the end of the tube. It is shown in Figure 2.1.

![Furnace winding by kanthal wire](image)

**Figure 2.1 Furnace winding by kanthal wire**

It was covered with the ceramic glass wool. Then it was covered with an outer glass tube of length 100 cm with its diameter 8 cm and the wall thickness is 3.5 mm, which ensured the thermal insulation. The setup was 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 advantage of using transparent furnace is that the nucleation can be directly observed, if multiple nucleation sites occur solidification can be restarted. The single zone furnace temperature was controlled and maintained using a Sensor Micro Electronics temperature controller with an accuracy of ± 0.1°C. Sensor Micro Electronics temperature controller accompanied by thyristor having ampere-rating 10 amp, which is operational at 230 volt, has been employed with Chromel Alumel Thermocouple as sensor, for temperature control. The maximum current output from the thyristor was fixed as 2 amp. This helps to prevent the
melting of the glasswares due to overshoot in temperature and it also prevents thermal fluctuation for long run. The schematic diagram of modified vertical Bridgman setup is shown in Figure 2.2. The designed modified vertical Bridgman setup is shown in Figure 2.3.

Figure 2.2 Schematic diagram of modified vertical Bridgman setup
2.1.2 Translation Assembly

In the vertical Bridgman technique the translation rate is one of the most important parameter for the crystal growth. The crystal quality and the optical transmittance are mainly dependent on the translation rates. The rate of crystal growth sets an upper limit to the rate at which the crystal growing ampoule can be lowered in the furnace. Due to low thermal conductivity of organic substances, good single crystals can only be obtained when growth rates are relatively low. Growth rates of organic substances do not usually exceed 1 mm/h, while growth rates for metals and inorganic substances may reach 20 mm/h (Jones 1974). Large crystals could be grown in 8 to 10 days at 0.5 to 1 mm/h (Sherwood et al 1960). The slower growth rate should be used to grow the larger diameter crystals of good quality. The high transparent good quality crystals can be grown using the constant growth rate for full growth of crystals. The organic crystals are having low thermal conductivity, so if the diameter of the ampoule increases the translation rate must be reduced.
The design of translation setup is commonly based on ac/dc motors and stepper motors. While using a conventional dc or ac motor, it is difficult to accurately determine the exact position of the load, motor speed, or how much total motion has been produced, unless external positioning sensors, encoders, servo loops, and controlling devices (brakes, clutches, etc.,) are employed. Many motors run at a speed in rpm that is too high and this involves a gear train to reduce the speed and increase the torque to usable levels. While this may not always be a problem, conventional motors can be difficult to use for certain applications. When precise control is desired and high speed is not a factor a stepper motor may be advantageous.

The position resolution and smoothness of conventional stepper motor can be increased by microstepping mode. And other advantage of microstepping is that there are less mechanical parts involved, hence requiring less initial construction and reduced maintenance in the long run. This advantage was the reason a microstepping mode of operation was chosen for achieving smooth, vibration-free, and slow translation. The reliability of low current electronic equipment far exceeds that of mechanical devices. Linear translation is accomplished by directly coupling the rotating shaft of the stepper motor to the growth ampoule through a string and pulley; a resolution of 40 nm linear translation is observed for one step. This assembly has precision of 0.001 mm/h to 99.999 mm/h translation rates. This translation assembly is mainly used to grow the organic single crystals.

2.1.3 Temperature Profile

The solid-liquid interface, where the crystallization takes place, is another important factor for growing high quality single crystals. Among different variations of the Bridgman technique temperature, conditions for single crystal growth sometimes differ greatly in respect to both the
geometrical distribution of temperature and the magnitude of the temperature gradient in the furnaces. For organic materials, temperature control is particularly important during crystal growth; many organic materials are sensitive to overheating due to chemical instability. Low thermal gradients are also required for preventing the grown crystal from plastic deformation or cracking (Lan and Song 1997).

In the furnace, the temperature controller thermocouple was used to lower temperature along the axis of the furnace at a desired rate (10 mm/h) using a nano stepper motor drive. From the lowering rate and the time interval between the consecutive data, the temperature distance plot is obtained. The temperature profile can be changed by changing the setting temperature. Temperature profile of the furnace is shown in Figure 2.4. The temperature gradient of the furnace is 0.5-1°C/cm.

![Temperature profile of furnace](image)
2.2 GROWTH OF NAPHTHALENE SINGLE CRYSTALS

In the recent years, scintillation counting techniques have found a wide variety of important applications in biology, chemistry, geology, medicine, atmospheric science and industry. Many organic and inorganic scintillators are available (Birks 1964). The large transparent blocks of naphthalene is the first material to produce the large volume organic scintillator to produce the photons from β-rays and γ-rays (Perlmutter 2000). Naphthalene is a transparent organic compound with melting point at 80°C which normally freezes with a non-faceted interface (Wilcox 1970). The molecular structure of naphthalene is shown in Figure 2.5.

![Molecular structure of naphthalene](image)

**Figure 2.5 Molecular structure of naphthalene**

Naphthalene crystals have monoclinic structure with centrosymmetric space group P2_1/a with two molecules per unit cell and cleaves readily on the (0 0 1) plane (Cruickshank 1957, Mcghie et al 1976). Melt growth techniques are more convenient and fast method for growing crystals. Melt techniques such as Bridgman technique and Czochralski technique are best suitable to grow large size bulk single crystals. In the case of some organic materials solution growth methods are not suitable due to undesired solvent or compound associations occurring during the growth. The solvent inclusions in to the crystals reduces it’s the optical quality. The growth of naphthalene single crystal, the solution growth is not possible to grow large size crystals because of its low solubility. The naphthalene crystals
can be grown using vertical Bridgman technique because of its congruent melting at 80°C (Karl 1980).

In the Bridgman growth the, solid–liquid interface shape is a key factor to determine the quality of the growth. Hence, different growth ampoule designs for the growth of crystals have been developed (Sherwood et al 1960). The measurement of dielectric constant and dielectric loss as a function of frequency and temperature is of interest both from theoretical point of view and application aspects. Practically, the presence of a dielectric between the plates of a condenser enhances the capacitance.

In the present study naphthalene single crystals are grown by the vertical Bridgman technique with three different sized conical ampoules are used. The good quality crystal is used for the characterization studies. The grown crystals were characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FTIR), Ultraviolet visible (UV–vis), photoluminescence (PL), differential thermal analysis (DTA), dielectric and microhardness studies.

2.2.1 Crystal Growth

The naphthalene single crystals were grown by modified vertical Bridgman technique. By changing the ampoule size and the translation rate the parameters, the quality of the grown crystals is affected. The temperature control was achieved by sensor micro-electronics temperature controller with an accuracy of ± 0.1°C. A translation assembly with precision of 0.001 mm/h has been developed by nano-stepper motor drive connected with motor driven by a pulse frequency modulation type electronic circuit controller was employed for the translation of growth ampoule. The growth ampoules were made of borosil glass. The three types of single wall ampoules used, whose heel part are of constant 20 mm diameter with the tip part gradually decreased
up to 1 mm. The different cone length for ampoule-1 is 5 cm cone length, ampoule-2 is 9 cm cone length and the ampoule-3 is 15 cm cone length. Figure 2.6 shows the designed single wall ampoules with different cone lengths.

![Designed single wall ampoules with different cone lengths](image)

**Figure 2.6** Designed single wall ampoules with different cone lengths

The ampoules filled with naphthalene (Sigma–Aldrich) was evacuated to $10^{-4}$ torr and then sealed off. The temperature in the upper part of the furnace was maintained close to the melting point of naphthalene. The material melted in the hotter region and the melt was homogenized for 24 h to avoid bubble formation during crystal growth. In the present study the translation rates 0.5 mm/h, 0.3 mm/h and 0.1 mm/h were employed and optimized rate 0.1 mm/h is used as the ideal for growing good quality crystals. Figure 2.7 shows the naphthalene single crystals grown by the present study using various ampoule sizes. It is understood from the grown crystals that increasing the cone length improves the crystal quality. It is optimized that the cone length of 15 cm gives good quality crystals. High
quality crystals with 20 mm diameter were grown by the optimal conditions. Crystals with high transparency and large surface defect-free crystals were grown using ampoule-3 with long cone size. These crystals were used for the characterization studies.

![Ampoules 1, 2, and 3](image)

**Figure 2.7 Photograph of naphthalene Single crystals**

### 2.2.2 X-ray Diffraction Studies

The grown naphthalene crystal was confirmed by powder XRD analysis. Powder X–ray diffraction analysis was carried out using a XPERT–PRO diffractometer with CuKα (λ = 1.54056 Å) radiation using a tube voltage and current of 40 kV and 30 mA respectively. The sample was scanned over the range 10–70° at the rate of 1° min⁻¹. The powder XRD pattern is shown in Figure 2.8. The obtained (hkl) values are in good agreement with the JCPDS file (card no: 13-0824). The prominent well defined Bragg’s peak at specific 2θ angle reveals the high crystallinity of the grown single crystal.
2.2.3 FTIR Studies

The FTIR spectrum of naphthalene was recorded by Perkin–Elmer FTIR Spectrum RXI Spectrometer using KBr pellet technique in the frequency range 400–4000 cm\(^{-1}\). The FTIR spectrum obtained is shown in Figure 2.9. There is a sharp and less intense peak at 3050.18 cm\(^{-1}\) is assigned to the C–H stretching of naphthalene. The ring skeletal vibration of naphthalene is assigned from the well resolved peaks between 800 cm\(^{-1}\) and 1600 cm\(^{-1}\). The high intense sharp peak at 779.33 cm\(^{-1}\) is assigned to CH bending. The FTIR spectrum is good agreement with the reported literature (Selvakumar et al 2005).
2.2.4 Optical Properties

The UV–vis and photoluminescence (PL) absorption spectral measurements were carried out to optically characterize the grown naphthalene crystal. The UV–vis absorption spectrum of the grown crystal was recorded using a Perkin-Elmer Lambda 35 UV–vis spectrophotometer. The spectrum is shown in Figure 2.10. The absorption maximum occurs at 219.32 nm. The crystal is fully transparent through the entire visible region and up to 290 nm in the UV region. So, the naphthalene crystal grown in the present study can be used as a window material for the entire range of electromagnetic radiation from 290 nm to the near infrared region.

Photoluminescence spectrum of the grown naphthalene crystal has been recorded using the spectrofluorometer with 450W high pressure Xenon lamp as excitation source at room temperature. The spectrum is shown in
Figure 2.11. The high intensity peak is observed at 410 nm. The results indicate that the naphthalene single crystal has a violet emission; it suggests that it can be used as a violet-light emitting material.

Figure 2.10 UV–vis absorption spectrum of naphthalene crystal

Figure 2.11 PL spectrum of naphthalene
2.2.5 Thermal Properties

The thermal property of the grown naphthalene crystal was analyzed by differential thermal analysis (DTA) using a Perkin-Elmer diamond TG/DTA instrument. The temperature range considered was 35–150°C. Figure 2.12 shows the DTA pattern. The DTA pattern indicates that the sharp endothermic peak observed at 82°C, it indicates the melting point of the grown naphthalene crystal. Sharpness of the endothermic peak observed in DTA indicates good degree of crystallinity of the sample.

![Figure 2.12 DTA pattern of naphthalene](image)

2.2.6 Electrical Properties

Dielectric constant is one of the basic electrical properties of solids. Dielectric properties are correlated with electro-optic property of the crystals (Boomadevi et al 2004). Crystal portion with high transparency and defect-
free (i.e., without any pit or crack or scratch on the surface, tested with a traveling microscope) large size $7 \times 7 \times 2 \text{ mm}^3$ was used for the dielectric measurements. The crystal portion was cut into a proper rectangular parallelepiped shaped and polished. The opposite faces were polished and coated with good graphite to obtain a good conductive surface layer. The capacitance ($C_{\text{crys}}$), Air capacitance ($C_{\text{air}}$) and dielectric loss factor ($\tan \delta$) were measured using the conventional parallel plate capacitor method (Perumal et al 2005 and Priya et al 2008) with five different frequencies, viz., 100Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz using an LCR meter (Agilent 4284A) at various temperatures ranging from 308 K to 348 K. The temperature was controlled to an accuracy of $\pm 1$ K. The observations were made while cooling the sample. The dimensions of the crystal portion were measured using a traveling microscope (least count = 0.001 cm). Air capacitance was also measured. Since the variation of air capacitance with temperature was formed to be negligible, air capacitance was measured only at the minimum temperature (308 K).

The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = \frac{C_{\text{crys}}}{C_{\text{air}}}$$

where $C_{\text{crys}}$ is the capacitance of the crystal and $C_{\text{air}}$ is the capacitance of the air of same dimension as that of the crystal sample.

As the crystal area was smaller than the plate area of the cell, parallel capacitance of the portion of the cell not filled with the crystal sample was taken into account and, consequently, the above relation becomes
\[
\varepsilon_r = \frac{C_{\text{crys}} - C_{\text{air}} \left(1 - \frac{A_{\text{crys}}}{A_{\text{air}}}\right)}{C_{\text{air}}} \cdot \frac{A_{\text{air}}}{A_{\text{crys}}}
\]

where \( A_{\text{crys}} \) is the area of crystal touching the electrode and \( A_{\text{air}} \) is the area of electrode.

The AC electrical conductivity, \( \sigma_{ac} \) was calculated using the relation

\[
\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta,
\]

where \( \varepsilon_0 \) is the permittivity of free space (8.85x10\(^{-12}\) C\(^2\) N\(^{-1}\) m\(^{-2}\)), \( \omega \) is the angular frequency. (\( \omega = 2\pi f \), where \( f \) is the AC frequency considered) and \( \tan \delta \) is the dielectric loss factor.

![Graph showing dielectric constants observed for naphthalene crystal](image-url)
Figure 2.13 (b) Dielectric loss factors observed for naphthalene crystal

Figure 2.13 (c) The AC electrical conductivities ($\times 10^{-8}$ mho/m) observed for the naphthalene crystal

Figures 2.13 (a-c) shows the dielectric constants observed for the naphthalene crystal, the dielectric loss factors observed for the naphthalene crystal and the AC electrical conductivities ($\times 10^{-8}$ mho/m) observed for the
naphthalene crystal, respectively. It can be seen that the dielectric parameters, viz., $\varepsilon_r$, $\tan \delta$ and $\sigma_{ac}$ increase with the increase in temperature. The $\varepsilon_r$ and $\tan \delta$ values decrease with the increase in frequency while the $\sigma_{ac}$ value increases with the increase in frequency. The electrical conduction is mainly a defect controlled process in the low temperature region. The presence of impurities and vacancies mainly determine this region. The energy needed to form the defect is much larger than the energy needed for its drift. The conductions of the crystal in the higher temperature region are determined by the intrinsic defects caused by the thermal fluctuations in the crystal (Bunget et al 1984).

For many substances, as the temperature increases more and more defects are produced which, in turn, increases the conductivity. The defect concentration will increase exponentially with temperature and consequently the electrical conduction also increases (Shanmugham et al 1985). The intrinsic defects caused by the thermal fluctuation in a crystal determine the conductivity of the crystal at higher temperatures (Somasekhara Udupa et al 1997). If the sample crystal is placed in a stationary electric field (as in the present study) the carriers may be considered to be contained in an enclosure bounded by the capacitor plates. As the carriers may not leave the enclosure, they accumulate in the regions close to the plates which cause a concentration gradient to be formed and this gradient needs diffusion current. At equilibrium the diffusion current density equals that of the drift current. Charge accumulation is related to in homogenities of the material, the implementation of impurity ions by diffusion in the vicinity of electrodes or chemical changes in layers close to electrodes (Bunget et al 1984 and Freeda et al 2000).
Naphthalene is a planer compound not having any hydrogen bond in the crystal. So, conductivity in naphthalene crystal may be associated with the incorporation into the crystal lattice of impurities and the formation of corresponding defects. Also, the planar structure is expected to have charge transfer between the molecules. So, the conductivity is more of electronic in nature. The dielectric constant of a material is generally composed of four types of contributions, viz., ionic, electronic, orientational and space charge polarizations. All these may be active at low frequencies; the nature of variations of dielectric constant with frequency and temperature indicates the type of contributions that are present in them. Variation of $\varepsilon_r$ with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defect. The variation at low temperatures is mainly due to the expansion and electronic and ionic polarizations. The increase at higher temperatures is mainly attributed to the thermally generated charge carriers and in purity dipoles. In the case of naphthalene, the increase in dielectric constant with temperature is essentially due to the temperature variation of electronic polarizability.

### 2.2.7 Mechanical Properties

The mechanical property of the grown naphthalene crystal was analyzed by Vicker’s microhardness studies. Leitz Wetzler hardness tester fitted with a Vicker’s diamond pyramidal indenter and attached with Leitz incident light microscope was used. Three different loads 25 g, 50 g and 100 g were applied and the time of indentation was kept constant as 10 s for all the trials. The Vicker’s microhardness was calculated using the expression, $H_V = 1.8544 \left( \frac{p}{d^2} \right)$ where $p$ is the applied load in kg and $d$ is the average diagonal length in mm.
Figure 2.14 Plot of Vicker’s hardness number ($H_v$) versus load (g) for naphthalene crystal

Figure 2.14 shows the plot of load (p) versus Vicker’s hardness number ($H_v$) for the naphthalene crystal grown in the present study. It is observed that the Vicker’s hardness number increases with the increase in load. The Meyer’s number ($n$) should be between 1 and 1.6 for hard materials and above 1.6 for softer ones. As per Meyer’s analysis, the $n$ value of the grown naphthalene is 3.969. The naphthalene crystal grown in the preset study is of soft category.

2.3 GROWTH OF BENZIL SINGLE CRYSTALS

The increasing demand on organic materials for technological applications has prompted researchers to look for newer promising materials (Tao et al 1992, Gunter 2000 and Thompson et al 2001). Nonlinear optical (NLO) materials have been attracting a great deal of interests due to their applications such as high speed information processing, optical communications, optical electronics and optical data storage (Wong et al 1996 and Natarajan et al 2006). Moreover microelectronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant ($\varepsilon_r$) materials (Hatton et al 2006).
Benzil ($C_{14}H_{10}O_2$) is a non-hygroscopic organic material with good NLO properties (Rai et al 2001). The molecular structure of benzil is shown in Figure 2.15.

![Molecular structure of benzil](image)

**Figure 2.15 Molecular structure of benzil**

Growth and studies of benzil single crystals using different crystal growth techniques are available in literature. Solution grown benzil single crystal has very slow growth rate compare to melt method and its structural perfection and crystal quality are low (Scheffen-Lauenroth et al 1981). Lan and Song have grown benzil crystal by vertical dynamic gradient freeze technique and studied its optical properties (Lan and Song 1997). In Czochralski technique, it is very difficult to stabilize the growth of benzil (Bleay et al 1978, Aggarwal et al 1992 and Aggarwal et al 1993). In Bridgman technique, benzil crystals were grown by using single wall ampoules (Rai et al 2001, Aggarwal et al 1993 and Shankar et al 1996). As better quality single crystals are needed for device application, it is necessary to improve the method of growth. An effective control of growth environments is very much necessary. In order to achieve this, we have made an attempt to grow benzil single crystals using double wall ampoule with nano translation by the modified vertical Bridgman technique. For comparison purpose, benzil single crystals were also grown using the conventional single wall ampoule. The grown crystals were characterized by carrying out single crystal X-ray diffraction (XRD), powder XRD, Fourier transform infrared (FTIR), High resolution X-ray diffraction (HRXRD), UV-vis-NIR, photoluminescence (PL), thermal, dielectric and SHG studies.
2.3.1 Crystal Growth

Benzil single crystals were grown by modified vertical Bridgman technique using the single zone furnace. Benzil crystals were grown by using two types of ampoules. First one is the single wall ampoule (Figure 2.16 (a)) and second one is double wall ampoule with the cone angle 23° (Figure 2.16 (b)). In Bridgman technique, the conical shape of the ampoule is an important parameter, since conical tip in the ampoule is the point of initiation of the solidification and controls further growth (Udayashankar et al 2001). Researchers reported that the ampoules with cone angles in the range 15–24° are found to be the most optimum to obtain inclusion-free good quality transparent crystals (Mohan et al 2000, Arulchakkaravarthi et al 2001 and Balamurugan et al 2008). Here selected the cone angle of 23° for double wall ampoule for the growth of benzil single crystals.

![Schematic diagram of (a) single wall ampoule, (b) double wall ampoule](image)

Figure 2.16 Schematic diagram of (a) single wall ampoule, (b) double wall ampoule

For crystal growth, both single and double wall ampoules were filled with benzil (Sigma Aldrich) and evacuated to $10^{-4}$ torr and then sealed off. The temperature in the upper part of the furnace was maintained close to
the melting point of the benzil. The material melts in the hotter region and the melt was homogenized for 24 h to avoid bubble formation during crystal growth. Here the growth was initiated by moving the ampoule from the hot zone to cold zone very slowly with translation rate 0.03 mm/h to initiate lesser number of nuclei in the outer tube of the ampoule. The substance after melting fills the annular space between the inner and outer tubes acts as an insulator to prevent thermal shocks entering the tube during the growth. The space above the melt level also acts as a thermal insulator due to vacuum. As the tip of the ampoule passed the interface, the crystallization of the molten benzil was initiated by self–nucleation and the crystal growth was started and continued through the length of the melt. After growth the heating profile was reduced slowly at a rate of 1 °C/h in order to avoid cracks due to the difference in the thermal expansion coefficient between the glass and crystal. The as grown benzil single crystals using single and double wall ampoules are shown in Figure 2.17 (a) and 2.17 (b) respectively. The crystals were removed from the ampoules carefully. Figure 2.3.3 (c) shows the cut and polished portion of the crystal grown by double wall ampoule.

Figure 2.17 Photograph of (a) single wall ampoule grown crystal, (b) double wall ampoule grown crystal, (c) cut and polished portion of double wall ampoule grown crystal
2.3.2 X-ray Diffraction Studies

Single crystal X-ray diffraction data of benzil crystal were collected by using Enraf Nonius CAD4 single crystal X-ray diffractometer with MoKα radiation in the wavelength of 0.717073 Å to identify the structure and estimate the lattice parameters values. At the room temperature, the observed lattice parameters are shown in Table 2.1. The grown benzil belongs to hexagonal system with non-centrosymmetric space group P3121. The obtained cell parameters are in good agreement with the JCPDS file (card no: 30–1539).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Literature JCPDS file (card no: 30–1539)</th>
<th>Present study</th>
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<td>a</td>
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<td>8.44 Å</td>
</tr>
<tr>
<td>b</td>
<td>8.410 Å</td>
<td>8.44 Å</td>
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<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>γ</td>
<td>120°</td>
<td>120°</td>
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<tr>
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</table>

Powder X-ray diffraction study was carried out by employing XPERT–PRO diffractometer with CuKα (λ = 1.54056 Å) radiation using a tube voltage and current of 40 kV and 30 mA respectively. The powdered sample was scanned over the range of 10 – 70° at the rate of 1°min⁻¹. The powder X-ray diffraction pattern of the grown crystal is shown in Figure 2.18. The obtained (hkl) peaks are indexed. The positions of the peaks are in good agreement with the JCPDS file (card no: 30-1539).
Figure 2.18 Powder X–ray diffraction pattern of benzil

2.3.3 FTIR Studies

FTIR spectrum of benzil was recorded by Perkin–Elmer FTIR Spectrum RXI Spectrometer using KBr pellet technique in the frequency range 400–4000 cm\(^{-1}\) to identify the presence of functional groups in the grown crystal. Figure 2.19 shows the FTIR spectrum of the benzil single crystal. The intense broad peak at 3431 cm\(^{-1}\) is due to O–H stretching. The absorption peaks at 3062 and 2823 cm\(^{-1}\) are assigned to aromatic C–H stretching (Silverstein et al 1991). A highly intense and well defined sharp peaks observed at 1660 and 1590 cm\(^{-1}\) are due to the C=O stretching vibration of ketone group (Silverstein et al 1991). The peaks at 871, 788 and 716 cm\(^{-1}\) are assigned to aromatic C–H bending.
2.3.4 HRXRD Studies

The crystalline perfection of the grown benzil single crystals were characterized by HRXRD by employing a multicrystal X-ray diffractometer developed at National Physical Laboratory (NPL) (Lal and Bhagavannarayana 1989). The well-collimated and monochromated MoKα beam obtained from the three monochromator Si crystals set in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,−,−,+ ) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The DC was recorded by the so-called ω scan wherein the detector was kept at the same angular position 2θB with wide opening for
its slit. This arrangement is very appropriate to record the short range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or due to low angle and very low angle structural grain boundaries (Bhagavannarayana et al 2010).

Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the crystal and the possible layers which may sometimes form on the surfaces on crystals grown by solution methods (Bhagavannarayana et al 2006) and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchent of water and acetone mixture in 1:2 volume ratio.

![Figure 2.20](image)

**Figure 2.20** (a) High-resolution X-ray diffraction curve recorded for a typical single wall ampoule grown benzil single crystal using (110) diffracting planes in symmetrical Bragg geometry with MoKα₁ radiation
Figure 2.20 (a) shows the high-resolution diffraction curve (DC) recorded for a typical single wall ampoule grown benzil single crystal specimen using (110) symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer described with MoKα₁ radiation. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains an additional peak, which is 32 arc s away from the main peak. This additional peak depicts an internal structural very low angle (tilt angle ≤ 1 arc min) boundary (Bhagavannarayana et al 2005) whose tilt angle (misorientation angle between the two crystalline regions on both sides of the structural grain boundary) is 23 arc s from its adjoining region. The FWHM (full width at half maximum) of the main peak and the very low angle boundary are respectively 24 and 34 arc s. Though the specimen contains a very low angle boundary, the relatively low angular spread of around 200 arc s of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good. Thermal fluctuations or mechanical disturbances during the growth process could be responsible for the observed very low angle boundary. It may be mentioned here that such very low angle boundaries (which may hardly deteriorate the properties) could be detected with well resolved peaks in the diffraction curve only because of the high-resolution of the multicrystal X-ray diffractometer used in the present studies.

Figure 2.20 (b) shows the high-resolution diffraction curve (DC) recorded for a typical double wall ampoule grown benzil single crystal specimen using (110) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα₁ radiation. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains two additional peaks, which are 24 and 18 arc s away from the main peak.
Figure 2.20  (b) High-resolution X-ray diffraction curve recorded for a typical double wall ampoule grown benzil single crystal using (110) diffracting planes in symmetrical Bragg geometry with MoK$_\alpha_1$ radiation

These two additional peaks correspond to two internal structural very low angle boundaries whose tilt angles are 24 and 18 arc s from their adjoining regions. The FWHM of the main peak is 20 arc s and that of both the low angle boundaries is 25 arc s. Though the specimen contains very low angle boundaries, the relatively low angular spread of around 100 arc s of the diffraction curve and the low FWHM values show that the crystalline perfection is reasonably good. Thermal fluctuations or mechanical disturbances during the growth process could be responsible for the observed very low angle boundary. Considering the ampoules used in the growth of benzil crystals in the present study, the main peak observed becomes sharper when the single wall ampoule is replaced by the double wall ampoule. This indicates an improvement in the quality of the benzil crystal grown by using the double wall ampoule.
2.3.5 Thermal Properties

Thermogravimetric (TG) and differential thermal analyses (DTA) of benzil single crystal were carried out using SDT Q600 simultaneous thermal analyzer in the temperature range 30–300°C in inert nitrogen atmosphere at a heating rate of 10°C min\(^{-1}\). A platinum crucible was used for heating the sample. The results obtained from TG and DTA thermal studies are shown in Figure 2.21.

![Figure 2.21 TG/DTA spectrum of benzil](image)

The TG analysis shows that the material exhibits single sharp weight loss starting at 145°C and below this temperature no significant weight loss is observed. The DTA shows a sharp endothermic peak observed at 96°C which is assigned to melting point of the grown crystal at which no weight loss in TGA has been noticed. And another sharp endothermic peak observed at 226°C which is assigned to decomposition. Before melting no characteristic exothermic or endothermic peaks observed. It is observed that no phase transition or decomposition occurs up to the melting point. Sharpness of the endothermic peaks observed in DTA indicates good degree of crystallinity of the sample. The melting and decomposition point of the grown crystal were also confirmed by using MONATCH melting point apparatus.
2.3.6 Optical Studies

NLO single crystals are mainly used in optical applications, in which optical transmission range and the transparency finds an important place. The optical transmission spectrum of single and double wall ampoules grown benzil crystals were recorded in the range 190–1100 nm using Lambda 35 spectrophotometer. Cut and polished crystals of 2 mm thickness were used for the studies. Lan and Song (1997) have observed the cutoff wavelength at about 440 nm for benzil crystal. UV-vis-NIR spectra recorded for both samples are shown in Figure 2.22.

![UV-vis-NIR spectra of benzil single crystal](image)

**Figure 2.22 UV-vis-NIR spectra of benzil single crystal**

It shows that both crystals have transparency greater than 60 % with cutoff wavelength around 434 nm. It is observed that double wall ampoule grown crystal has high transparency than single wall ampoule grown crystal. In the growth with double wall ampoule the temperature stress in the inner tube is less than that of the outer tube and for this reason the good crystal can be grown, hence the transmittance is increased. However, in the
present study, we have observed an improvement in the optical transmittance when the single wall ampoule is replaced by the double wall ampoule. This can be attributed to the improvement in the control of thermal environments and the consequent improvement in the quality of the crystal grown when double wall ampoule is used.

### 2.3.7 Photoluminescence Studies

Photoluminescence spectra of the grown crystals were carried out by using the spectrofluorometer with 450 W high pressure Xenon lamp as excitation source at room temperature. The grown crystals were excited at 398 nm and the emission spectra of single and double wall ampoules grown crystals are shown in Figures 2.23 (a, b).

![Figure 2.23 (a)](image)

**Figure 2.23 (a) PL spectrum of single wall ampoule grown benzil**
Figure 2.23 (b)  PL spectrum of double wall ampoule grown benzil

Both single and double wall ampoule grown crystals exhibit high intensity sharp peaks observed around 520 nm. The results indicate that the benzil single crystal has a green emission. The green emission of benzil suggests that it may be used as a green light emitting material. Further, the double wall ampoule grown crystal exhibits high PL yield when compared to that observed for the single wall ampoule grown crystal.

2.3.8  Dielectric Studies

Crystals with high transparency of size $7 \times 6 \times 2$ mm$^3$ were used for the dielectric measurements. The opposite faces were polished and coated with high quality graphite to obtain a good conductive surface layer. The capacitance ($C_{\text{crys}}$), Air capacitance ($C_{\text{air}}$) and dielectric loss factor (tan $\delta$) were measured using the conventional parallel plate capacitor method with four different frequencies, viz., 100 Hz, 1 kHz, 10 kHz and 100 kHz using an
Agilent 4284A LCR meter at various temperatures ranging from 313 K to 353 K. The temperature was controlled to an accuracy of ± 1 K. The observations were made while cooling the sample. The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = \frac{C_{\text{cryst}}}{C_{\text{air}}}$$

The AC conductivity ($\sigma_{ac}$) was calculated using the relation:

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$

where $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-12}$ farad / m) and $\omega$ is the angular frequency ($\omega = 2\pi f$).

Figure 2.24 Double wall grown benzil crystal (a) Plot of dielectric constant versus temperature, (b) plot of dielectric loss versus temperature, (c) plot of AC electrical conductivities ($\times 10^{-8}$ mho/m) versus temperature
Figure 2.24 (Continued)
Figure 2.24 (a–c) shows the variation of dielectric constant ($\varepsilon_r$), dielectric loss ($\tan \delta$) and AC conductivity ($\sigma_{ac}$) observed for benzil crystal grown with double wall ampoule. It can be seen that the dielectric parameters, viz., dielectric constant ($\varepsilon_r$), dielectric loss ($\tan \delta$) and AC conductivity ($\sigma_{ac}$) increase with the increase in temperature. The dielectric constant ($\varepsilon_r$) and dielectric loss ($\tan \delta$) values decrease with the increase in frequency while the AC conductivity ($\sigma_{ac}$) value increases with the increase in frequency. This is a normal dielectric behaviour. This can be understood on the basis that the mechanism of polarization is similar to the conduction process. The electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. The high value of dielectric constant at low frequencies may be associated with space charge, dipolar, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. Space charge polarization is generally active at lower frequencies and higher temperatures and indicates the perfection of crystals. The low value of dielectric loss at high frequency implies that the crystal possesses good optical quality with lesser defects and this parameter is of vital importance for NLO materials in their applications (Rao et al 1965).

Several innovative developments have been made for the development of new low $\varepsilon_r$ value materials to replace silica ($\varepsilon_r \approx 4.0$). However, there is still a need for new low $\varepsilon_r$ value dielectric materials. As the utility in the electronic circuits with water proof conditions, water soluble materials in the single crystal form would be very much interesting. Recently, Mahadevan and his coworkers (Goma et al 2006 and Meena et al 2008) have reported reduction in $\varepsilon_r$ value in the case of potassium dihydrogen orthophosphate (KDP) added with urea and L-arginine. Also, L-arginine acetate (LAA) and L-arginine oxalate (LAO) (Meena et al 2008 a) have been found to be promising low $\varepsilon_r$ value dielectric materials. Figure 2.24 (a) indicates that the $\varepsilon_r$ values observed for benzil crystal in the present study are low, < 4.0 upto 323 K for all the four frequencies considered.
Figure 2.25 (a) Dielectric constants with 1 kHz frequency compared

Figure 2.25 (b) Dielectric losses with 1 kHz frequency compared
Low $\varepsilon_r$ values have been observed for higher frequencies even at high temperatures. This indicates that the benzil crystal grown in the present study can be considered as a promising low $\varepsilon_r$ value dielectric material. The present study, in effect, indicates that the grown benzil single crystal is not only a potential NLO material but also a promising low $\varepsilon_r$ value dielectric material.

A comparison of $\varepsilon_r$ and $\tan \delta$ values observed with 1 kHz frequency is done in Figure 2.25 (a, b) for benzil crystals grown using single and double wall ampoules. Replacement of single wall ampoule with the double wall ampoule increases the $\varepsilon_r$ value and decreases the $\tan \delta$ value. This also confirms that the quality of the benzil crystals has been improved when grown using double wall ampoule.

2.3.9 SHG Studies

SHG conversion efficiency of the grown benzil crystal sample was measured by the Kurtz and Perry technique. Nd:YAG ($\lambda = 1064$ nm) laser irradiates the powder sample of benzil kept in the triangular cell. The monochromator was set at 532 nm. NLO signal was captured by the oscilloscope through the photomultiplier tube. The Nd:YAG laser source produces nanosecond pulses (8 ns) of 1064 nm light and the energy of the laser pulse was around 30 mJ. The beam emerging through the sample was focused on to a Czerny–Turner monochromator using a pair of lenses. The detection was carried out using a Hamamatsu R928 photomultiplier tube. The signals were captured with an Agilent infinium digital storage oscilloscope interfaced to a computer. The generation of the second harmonic was confirmed by the emission of green light. Potassium dihydrogen phosphate (KDP) sample was used as the reference material in the SHG measurements. The result reveals that the SHG efficiency of benzil is 2 times higher than that of KDP.
2.4 CONCLUSION

The modified vertical Bridgman setup was designed successfully and optimized the temperature profile using the temperature controller and the translation assembly. Naphthalene and benzil single crystals were grown by the modified vertical Bridgman technique using single and double wall ampoules with nano translation. The grown crystals were confirmed by XRD and FTIR analysis. HRXRD analysis reveals that the crystalline perfection of the grown benzil crystals was reasonably good. UV–vis absorption spectrum indicates the grown naphthalene crystal has maximum absorption at 219.32 nm and it is found to be transparent in the entire visible region and up to 290 nm. The grown benzil crystals have good optical transmittance in the visible and near IR regions. Photoluminescence studies show that the grown naphthalene crystal has violet emission at 410 nm and the benzil crystals have green emission around 520 nm. Thermal studies reveal that the grown crystals have good thermal stability. Dielectric measurements show that the grown crystals dielectric constant, dielectric loss and AC conductivity values increase with the increase of temperature which can be understood as due to the temperature variation of electronic polarizability. The Vicker’s hardness number increases with the increase of load and the grown naphthalene crystal is in soft material category. The SHG analysis reveals that the efficiency of benzil is 2 times higher than that of KDP. The results obtained in the present study indicate that the grown benzil single crystal is not only a potential NLO material but also a promising low dielectric constant value dielectric material, expected to be useful in the microelectronics industry. In addition, the present study indicates that the benzil crystal grown with double wall ampoule is superior to that grown with single wall ampoule.