Chapter – 6

Enhancement in crystalline perfection and optical properties of Benzophenone single crystals: A remarkable effect of liquid crystals

Abstract

The remarkable enhancement in crystalline perfection of Benzophenone crystals, induced by the presence of liquid crystals in melt during the growth, been investigated. The crystal structure was confirmed by powder X-ray diffraction. Nuclear magnetic resonance analyses depicted that liquid crystal molecules did not incorporate in the lattice of grown crystals. The high resolution X-ray diffractometry analysis for (200) diffracting of grown crystals demonstrates, the structural grain boundaries persisting in pure crystals could be eliminated by the aligning effect of liquid crystals. The photoluminescence investigations support the enhancement in crystalline perfection. Along with crystalline perfection improvement the liquid crystals also improved the optical transparency over its entire transparency region and optical polarizing behavior (birefringence) of the Benzophenone crystals.
6.1 INTRODUCTION

Although, organic crystals with higher nonlinear optical (NLO) efficiency have the great importance for their applications in high-energy lasers for inertial confinement fusion research, color display, electro-optic switches, frequency conversion etc. (Feng Pan et al., 1996; Zaitseva & Caman, 2001; Badan et al., 1993), generally it is difficult to grow the bulk crystals of pure organic materials because of their low thermal stabilities and presence of large chromophoric cations and hence, the organic crystals generally grow with structural defects (Jagannathan et al., 2007). Mostly the single crystals of organic NLO materials are being grown by solvent evaporation methods (Halfpenny et al., 1993; Feng Pan et al., 1996; Jagannathan et al., 2007). Due to anisotropic nature, the electro-optic properties of the crystals strongly depend on their crystalline quality; the structural defects like point defects, dislocations, grain boundaries, etc., deteriorate or completely mask the useful physical properties of single crystals. Therefore, to realize the full efficiency of devices based on single crystals, crystals must be free from the above said defects; such defects have been extensively studied by X-ray topography and high resolution X-ray diffractometry (Lipscomb et al., 1981; Bhagavannarayana, Ananthamurthy et al., 2005; Bhagavannarayana, Budakoti et al., 2005). The physical properties of single crystals can be modified for tailor made applications by adding suitable dopants and functional groups (Sweta et al., 2007; Bhagavannarayana et al., 2008). However, such dopants and functional groups hardly control the defects in crystals, rather if their concentration is above a critical limit they may deteriorate the crystalline perfection and henceforth the physical properties (Kushwaha et al., 2010; Bhagavannarayana, Budakoti et al., 2005; Bhagavannarayana & Kushwaha, 2010). However, there are some special class of molecules/dopants which may help in improvement in molecular alignment of the crystals and modify the crystal quality.

The liquid crystals (LCs) possess the high ability of self-organization and induce the alignment of the structures around these at the molecular level via electric field interaction, as reported for the aligning and reorientation of carbon nanotubes (Dierking et al., 2004). Due to such self-aligning behaviour of LCs, these seem to provide a driving force for the better molecular arrangement at the solid liquid
interface during the crystal growth. The magnetic field also has been used to get the aligned growth of crystals (Fujiwara et al., 1999). This chapter represents the investigation, presumably for the first time we have exploited the high alignment capability of LCs to improve the crystalline perfection of Benzophenone (BP) bulk single crystals grown by Czochralski (CZ) method. BP is an organic material with chemical formula \((\text{C}_6\text{H}_5)_2\text{CO}\), it is the parent diarylketone and widely used building block in organic chemistry. It is suitable as a photo initiator (photosensitizer) for the application of ultraviolet-curing. BP is a promising NLO organic material with second harmonic generation (SHG) efficiency almost 3 times better than that of potassium dihydrogen phosphate (KDP). It crystallizes in orthorhombic structure with space group \(P2_12_12_1\) (Hartmut et al., 2000; Lammers et al., 2000). The bulk single crystals of BP are prone to the inherent structural defects like dislocations, grain boundaries etc. (Sankaranarayanan & Ramasamy, 2005; Masaru et al., 1992; Bleay et al., 1978).

Different dopants in BP have been studied (Arivanandhan et al., 2006; Sixl et al., 1986) for the modification of various physical properties. However, no study is available for dopants which are having aligning capability. Hence, we have use liquid crystals as dopants during the growth of single crystals of BP via Czochralski method. The single crystals of pure and LC doped BP were grown under the identical growth conditions. The nuclear magnetic resonance (NMR) spectroscopy was performed to investigate the \(^1\text{H}\) and \(^{13}\text{C}\) structure of BP and incorporation of LCs into the crystal lattice of BP. The powder X-ray diffraction used to confirm the structure of both the crystals. The high resolution X-ray diffractometry (HRXRD) analysis was carried out to assess the influence of LC on the crystalline perfection. The photoluminescence emission (PL) spectroscopy was employed to assess the defects in grown crystals. The optical transmission spectra were recorded in the entire UV-Vis-NIR range of wavelengths. The birefringence nature was examined by an optical polarizing microscope. The observed remarkable enhancement in the crystalline perfection and optical properties in BP crystals by LC doping has been discussed in detail.
6.2 CRYSTAL GROWTH

In this section the growth of bulk crystals has been described. Single crystals of the title material were grown by Czochralski technique. For this, a CZ crystal puller designed, developed and fabricated at the National Physical Laboratory (NPL) (Bhagavannarayana et al., 2011) was used. The details about the growth are provided in chapter-2 [§2.1.3]. The pulling and rotational rates were set at 3 mmh⁻¹ and 30 rpm respectively. The temperature of the furnace was controlled using a Eurotherm temperature controller with an accuracy of ±0.1 K. For the bulk crystal growth, the seed crystals were prepared from the pure crystal, which have been primarily grown by using micro-capillary method (Hiscocks, 1969). The growth conditions for both the kinds of crystals were kept identical and the harvested pure and LC doped crystals are shown in Fig. 6.1(a) and (b) respectively. In comparison to the pure crystal, the LC induced/doped crystal possesses apparently more transparency. The yellow colour arrows on the top of each crystal indicate the growth direction, i.e. [100]. The specimens from bulk crystals were cut normal to [100]. The cut and polished specimen were subjected to the crystalline perfection and other optical characterizations.

6.3 CHARACTERIZATION STUDIES

To investigate the incorporation of LC molecules in the grown BP single crystals, ¹H and ¹³C-NMR spectra have been recorded by using Bruker make NMR spectrometer. The dimethyl sulphoxide was used as a solvent and spectrometer was operated at 400 MHz frequency. The diffraction spectra for the powdered specimens of pure and doped crystals have been recorded in the 2-theta range of 20 – 50° at ambient conditions. All the experimental conditions were kept constant throughout the complete experiment. The crystalline perfection of pure and doped crystals was evaluated by employing the HRXRD (Lal & Bhagavannarayana, 1989) [§3.3]. The specimen wafers from the bulk crystals were cut with great care using diamond cutter. The physical surfaces of crystals corresponding to the (200) diffraction planes were properly lapped and polished, and the diffraction curves of these planes were recorded in symmetric Bragg geometry via ω-scan configuration.
Fig. 6.1: (a) and (b) the photographs of Cz grown pure and LC induced BP single crystals respectively. The yellow arrows indicate the growth direction of crystals which is [100]

(Bhagavannarayana & Kushwaha, 2010). In the present study, the X-ray power, beam size and configuration of the diffractometer were kept same throughout the experiments for both the specimens. The obtained HRXRD results are discussed in detail in §6.4.3.

The PL excitation and emission spectra for the pure and doped specimens were recorded at room temperature. A filter of 395 nm was placed between specimen and detector to stop the harmonics of the excitation wavelength in reaching into the detector. The [100] cut ~2 mm thick crystals were subjected to record the transmission spectra in the entire UV-Vis-NIR range of wavelengths (200–1100 nm) [§3.12].

The optical polarizing nature of grown crystals was analyzed by an optically polarized microscope. The specimens were mounted on rotational table and the beam transmitted through the crystal was converted into an electrical signal, which was measured by an oscilloscope with the rotation of crystal through 360° around the axis along incident beam. A digital camera was used to record the photograph at maxima and minima conditions of polarizer.
6.4 RESULTS AND DISCUSSION

6.4.1 Powder X-ray diffraction analysis

The recorded PXRD spectra of the grown crystals are shown in Fig. 6.2. Both the spectra have identical features except changes in the peak intensities. The spectra confirm the orthorhombic crystal structure and $P2_12_12_1$ space group (Hartmut et al., 2000). In the LC assisted BP crystal the intensity of peak at $\sim 23.94^\circ$ which was maximum in pure crystal spectrum, got significantly reduced and the peak at $\sim 22.2^\circ$ attained the maximum intensity in the studied 2-theta range. This feature of spectrum may be due to the improvement in the crystalline quality of the crystal lead by LC molecules. The spectrum of the doped crystals attained the similar features to that of reported in literature (Hartmut et al., 2000). The detailed study about the behaviour of structural defects with the influence of LC during growth process is described in the following section of HRXRD.

6.4.2 Nuclear magnetic resonance analysis

NMR spectroscopy is a powerful tool to reveal the number and nature of hydrogen and carbon atoms presented in organic compounds (Dani et al., 1995)
Fig. 6.3: The $^1$H NMR spectra (a) and (b) are respectively for pure and LC doped BP specimens, the $^{13}$C NMR spectra (c) and (d) are respectively for pure and LC doped BP specimens and helps to assess the overall molecular structure of the compound and also useful to investigate the variations in the electronic structure of crystals (Sharma 2000). The recorded $^1$H and $^{13}$C NMR spectra for pure and LC doped specimens are shown in Fig. 6.3. Both kinds of spectra have the identical features for pure as well as doped specimens. The pure BP molecules consists of two symmetrical benzene rings.
connected through the carbonyl group (C=O), as shown in the inset of the figures. In the recorded $^1$H NMR spectra, three signals are observed which are corresponding to the $^1$H present in BP: 2H(triplet; $t$) at $\delta = 7.50$ ppm, 1H($t$) at $\delta = 7.62$ ppm, and one 2H(doublet) at $\delta = 7.69$ ppm. In the $^{13}$C-NMR, the signal at $\delta = 196.0$ ppm corresponds to the carbonyl group (C=O) attached to the two symmetrical benzene rings. However, the four signals in the range of $\delta$ between 128 to 138 ppm are corresponding to the four distinguished C atoms in the benzene rings (one attached to the carbonyl group, and the other three are corresponding to ortho, meta and para positions). The $^1$H and $^{13}$C NMR spectra for the LC doped BP specimen do not show any chemical shifting or any extra peak in comparison with the pure BP specimen. Therefore, the NMR results reveal that the BP crystals grown with an addition of LCs do not contain the molecules of LCs.

6.4.3 High-resolution X-ray diffraction analysis

The single crystal X-ray diffraction analysis was carried out to investigate the crystal structure and unit cell parameters. However, no variations in the crystal system or lattice parameters of pure and doped BP crystals were observed. The results confirmed that the LC molecules were not incorporated into the BP crystal lattice during the growth of single crystals, in tune with NMR analysis. The unit cell parameters of BP ($a$, $b$, and $c$ respectively 10.28, 12.12 and 7.99 Å; Hartmut et al., 2000) are much smaller as compared with the size of LC molecules (~20–30 Å in length; http://liq-xtal.cwru.edu/lcdemo.htm) and therefore eliminate the possibility of entering LC molecules in to the BP lattice matrix. However, the LC molecules present in molten state of BP during the growth process may lead to the modifications in crystalline quality as revealed by HRXRD.

Fig. 6.4(a) shows the rocking curve recorded for a typical CZ-grown undoped BP single crystal specimen using (200) diffracting planes in symmetrical Bragg geometry. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On de-convolution of the diffraction curve, it is clear that the curve contains three additional peaks, two of them are 45, 88 arcsec away from the main peak at higher angle side and the third one is 66 arcsec away from the main peak at lower angle side.
These three additional peaks correspond to three internal structural low (tilt angle > 1 arcmin but less than a degree) and very low angle (tilt angle ≤ 1 arcmin) boundaries (Bhagavannarayana, Ananthamurthy et al., 2005). The tilt angles (tilt angle may be defined as the misorientation angle between the two crystalline regions on both sides of the structural grain boundary) of these grain boundaries are 45, 43 and 66 arcsec from their adjoining regions. The FWHM (full width at half maximum) of the different boundaries are 32, 52, 31 and 100 arcsec mentioned in Fig. 6.4(a). Though the specimen contains grain boundaries, the low FWHM values and the low angular spread of around 400 arcsec (less than one tenth of a degree) of the diffraction curve indicate that the crystalline perfection is reasonably good.
It may be mentioned that revealing of such very low angle boundaries is possible because of the high-resolution of the multicrystal X-ray diffractometer used in the present investigation. The low angle boundaries in the pure BP crystals may be developed due to the thermal fluctuations at the liquid solid interface as the fractional change $\Delta T/T$ in temperature is supposed to be high at its low melting point ($\sim$49 °C). It is a well-known fact that LCs have great tendency of the alignment below their solid liquid phase transition temperature due to their large electric dipole moment (Dierking et al., 2004). This unique aligning nature of LCs is presumed to assist the improvement of crystalline perfection of BP single crystals grown in the presence of LCs. The RC for LC doped BP single crystal shown in Fig. 6.4(b) is recorded under identical conditions as that of RC in Fig. 6.4(a) for pure BP. The single and sharp peaked rocking curve illustrates that the crystal does not contain any structural grain boundaries. The FWHM of the diffraction curve is 25 arcsec which is close to that expected from the plane wave dynamical theory of X-ray diffraction for a perfect single crystal (Batterman & Cole, 1964). The details about the theoretical aspects of the diffraction curve and how it can be obtained from the dynamical theory are described in our recent articles (Bhagavannarayana & Kushwaha, 2011; Senthilkumar et al., 2011). For a better comparison of crystals with considerable difference in quality as in the present case of undoped and doped BP crystals, one should discuss about the integrated intensity ($\rho$) i.e. the total area under the diffraction curve, which has a tremendous difference in the diffraction curves of doped and undoped specimens. To understand this aspect, the following theoretical background is essential.

There are two main theories which enable one to calculate intensity of X-ray diffraction from single crystals, namely the kinematical theory and the dynamical theory. In a crystal, atoms are arranged in a periodic fashion. The smallest building block is the unit cell. Under the kinematical conditions each unit cell acts as an independent unit for the purpose of X-ray diffraction and intensity of diffracted beam is obtained by adding up the contribution of all such cells. The interaction of diffracted waves from different unit cells is ignored. The amplitude and phase of the resultant wave is defined by a factor known as structure factor $F_{hkl}$ for the $hkl$ reflection (it may
also denoted as $F_{hkl}$ and the intensity of the scattered X-ray ($I$) is proportional to $|F_{hkl}|^2$ or:

$$ I \propto |F_{hkl}|^2 ; F_{hkl} = \sum_j f_j \exp(-2\pi(hu_j + kv_j + lw_j)) \quad (6.1) $$

Here, $u_j$, $v_j$ and $w_j$ are the fractional coordinates of the atom whose scattering factor is $f_j$ and the summation being over all the atoms in the unit cell. The structure factor can be zero for a set of lattice planes. Finite intensity will be expected only from those set of lattice planes, for which $F_{hkl} \neq 0$. The kinematical theory has been very successful in structural crystallography. For quantitative intensity analysis it is necessary to use small specimens. Corrections due to primary and secondary extinctions are necessary. One is mainly concerned with determination of integrated intensity which is basically the area under the diffraction curve as mentioned above. For an ideally imperfect (or mosaic) crystal with linear absorption coefficient, $\mu$ it can be expressed as (James, 1950; International Tables for X-ray Crystallography Vol. III, 1962):

$$ \rho_{mosaic} = \frac{N^2 \lambda^3}{2\mu} |F_{hkl}|^2 \left( \frac{e^2}{mc^2} \right)^2 \frac{1 + |\cos 2\theta|^2}{2\sin 2\theta} \quad (6.2) $$

Here, $N = \text{number of unit cells}$, $\theta$ is the Bragg diffraction angle, $e/mc^2$ is the classical electron radius = $2.818 \times 10^{-13}$ cm ($e$ and $m$ are the charge and mass of the electron respectively and $c$ is the velocity of light), $\mu$ being the linear absorption coefficient. The exploring beam has been assumed to be un-polarized.

In the case of large perfect crystals, the kinematical approach cannot be used to give peak intensity and shapes of diffraction curves. Dynamical theory of X-ray diffraction (James, 1950; Batterman & Cole, 1964; Pinsker, 1978) takes into account interactions between waves scattered from all irradiated atoms or scattering units. Any atom inside the crystal receives scattered waves from all the other atoms in addition to the incident beam (after attenuation due to scattering and absorption). In this approach the integrated intensity for ideally perfect crystal is given by (James, 1950; International Tables for X-ray Crystallography Vol. III, 1962):

$$ \rho_{perfect} = \frac{8}{3\pi} N^2 \lambda^2 |F_{hkl}| \left( \frac{e^2}{mc^2} \right) \frac{1 + |\cos 2\theta|}{2\sin 2\theta} \quad (6.3) $$
One important difference between eqs (2) and (3) is that in case of ideally mosaic crystals, the integrated intensity is proportional to the square of the structure factor whereas in ideally perfect crystals, it is simply proportional to the magnitude of structure factor. Because of this clear contrast, the experimental value of $\rho_{\text{mosaic}}$ is expected to be much more than that of $\rho_{\text{perfect}}$. Therefore, as observed in the present case one can conclude that the quality of LC-added crystal is much superior.

The above discussion and the low value of FWHM of the rocking curve [Fig. 6.4(b)] reveal that the crystal is not only free from the boundaries but also free from mosaic blocks. The present results reveal that LC molecules strongly influence the perfection of BP crystals and avoid the formation of structural grain boundaries. The large molecular size of liquid crystals provides us a suitable way to attain the high molecular alignment in bulk crystals without their incorporation in the lattice of host crystal.

6.4.4 Photoluminescence emission analysis

The defects in the single crystals play an important role in the assessment of their optical properties and PL is very sensitive to the defects present in single crystals (Guozhen et al., 1999; Tournie et al., 1996). The PL excitation and emission spectra for pure as well as LC doped BP single crystals are recorded under the identical conditions and shown in Fig. 6.5. The excitation spectra of both the crystals indicate the strong absorption at 311 nm and the emission spectra were recorded corresponding to this excitation wavelength. The pure crystal exhibits the high optical density for excitation and high intensity for PL emission at 447 nm. The strong blue emission from the pure BP crystal is attributed to the intrinsic defects, which act as the color centers (Pankratov, et al., 2007; Xu, et. al., 1998). This is in tune with HRXRD analysis, and in our earlier studies also we have observed the dependency of PL intensity on the intrinsic crystal defects in LiF crystals (Bhagavannarayana, Kushwaha et al., 2011). For the LC doped crystals the defects are significantly reduced, therefore emission intensity drastically reduced almost to half. However, neither any shift in the peak position nor any additional peak has been observed. As it is clear from NMR analysis that LC molecules are not incorporating into the crystal lattice,
except providing the driving force (catalytic action) for better alignment to the BP molecules, due to their large dipole moment and high aligning nature (Dierking et al., 2004) these do not introduce any change on crystal structure.

6.4.5 UV-Vis-NIR optical analysis

The optical transmission spectra in the entire UV-Vis-NIR range for pure as well as doped BP crystals are shown in Fig. 6.6. Both the crystals have good optical transparency for the entire wavelength 400-1100 nm. However, the doped crystal is having better optical transparency in comparison to that of pure crystal over the entire transparency range. The enhancement in the transparency of doped crystal may be attributed to the absence of structural grain boundaries. The grain boundaries present in the specimen lead to the multiple refraction and scattering of the incident beam and hence reduce the optical transparency (Rolf et al., 2003; Schroeder et al., 1981). Because of the different mis-orientations of grain boundaries in the pure crystal the change in the direction of incident beam occur. To visualize this concept a schematic of grain boundaries for the behaviour of incident beam wave at grain boundaries is shown in the inset of Fig. 6.6.
Fig. 6.6: The UV-Vis-NIR transmission spectra of pure and LC doped BP single crystals. The inset indicates multiple refraction and scattering of incident beam at the grain boundaries persisting in pure BP crystals.

6.4.6 Polarized optical microscope birefringence analysis

Benzophenone is a birefringence material and therefore possesses the polarising ability for the electromagnetic optical beam. From Fig. 6.7 one can clearly see the two images of the letters (NPL) and a straight line in the background of single crystal. These two images are due to splitting of incident beam into ordinary ($n_o$) and extraordinary ($n_e$) components. The measured oscilloscope signal versus angular rotation plots of crystals are shown in Fig. 6.8(a). As the crystal was rotated from 0 to 360 degree four maxima and four minima were observed. The maxima and minima of the plots correspond to the bright and dark states. The four maxima correspond to bright stages which occur due to the splitting of beam in ordinary and extraordinary components (Florian et al., 2005; Harris et al., 1964). Both pure and doped crystals show same behaviour with the angular rotation. However, in comparison to the pure crystal, the LC doped crystal exhibits higher signal corresponding to the bright states, whereas no change in the minima of the plots corresponding to the dark states has been observed. The increase in the signal for doped crystals at brighter states may be attributed due to the enhanced optical transparency.
**Fig. 6.7:** Cut and polished Benzophenone single crystal showing its birefringence behavior

**Fig. 6.8:** (a) Graphs indicating optical polarization behaviour of pure and LC doped crystals, (b) and (c) are the photographs of bright and dark stages recorded at maxima and minima conditions of transmission respectively
The photographs recorded for the bright and dark states are shown in Fig. 6.8(b) and (c) respectively. However, the only nominal increase in the optical signal due to polarization is as follows. Optical polarizability is a direction dependent property and hence different grains in the crystal make different angles with the incident light and therefore, in a crystal containing structural grain boundaries, the expected optical polarizability is lesser than that of a perfect crystal of the same material. However, as observed experimentally, the structural grains are mis-oriented to each other by an average angle (tilt angle) of around an arcmin. But the optical polarizability is not very sensitive for such small angles of the order of an arcmin, which could be the reason for only a slight difference between optical polarizability of pure BP and LC-doped BP.

6.5 CONCLUSION

To the best of our knowledge for the first time we have successfully exploited the high ordering/aligning capability of LCs to grow the nearly perfect bulk single crystals of BP by CZ technique. The PXRD analysis confirmed that the liquid crystal present in melt during the single crystal growth process did not influence the basic crystal structure of BP. The structural grain boundaries, commonly persisting in the pure BP single crystal could be successfully eliminated by adding a small quantity of LCs in the molten of BP during the crystal growth process. We also conclude that LC with large electric dipole moment lead to the significant enhancement in crystalline perfection and optical properties. The enhanced crystalline perfection and optical properties envisage the suitability of BP crystals for their high energy laser photonic applications. This present finding may be extended for the use of LCs for other low melting organic NLO crystals to improve their structural and physical properties.