



## Growth and characterization of pure, benzophenone and paratoluidine doped 2A-5CB crystals

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### Abstract

Organic nonlinear optical crystal pure and doped (benzophenone and paratoluidine) 2-amino-5chloro benzophenone (2A-5CB) have been grown by slow evaporation method at room temperature. The lattice parameters of the grown crystals are determined by single crystal XRD. The grown crystals are characterized by FT-IR and FT-Raman, thermal and mechanical studies. The UV-Vis-NIR spectrum of pure and doped 2-amino-5chloro benzophenone (2A-5CB) shows less optical absorption in the entire visible region. Nonlinear optical study reveals that the SHG efficiency of pure and doped 2-amino-5chloro benzophenone (2A-5CB) are nearly 3 times greater than that of KDP. The dielectric constant and dielectric loss of the crystal are studied as function of frequency and the results are discussed. Photoconductivity studies are revealed that pure and doped 2A-5CB crystals have negative photoconducting nature.

**Keywords:** Organic compound, Nonlinear optical material, Dielectric response, Optical transmission

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### INTRODUCTION

Organic crystals find applications in frequency doubling, frequency mixing, electro optic modulation, optical storage and optical communications. The organic compounds with electron rich (donor) and deficient (acceptor) substituents, provide the asymmetric charge distribution in the  $\pi$  electron system and show large nonlinear optical responses. NLO crystals should meet several requirements, such as large phase – matchable nonlinear optical co-efficient, a wide optical and chemical stability and a high damage threshold [1]. A majority of organic crystals have their absorption in the blue light region and some of them have a cut-off wavelength lower than 450 nm. This indicates the possibility of reduced conversion efficiency of SHG due to self-absorption of materials when using a semiconductor laser with 800 nm band [2-3]. Hence, recently there has been a search for newer organic NLO materials with blue light transmittance [4]. 2-amino-5chloro benzophenone (2A-5CB) is an excellent organic NLO crystal. In the present work, we report the growth of a promising nonlinear organic crystal of both pure and

doped (benzophenone and paratoluidine) 2-amino-5-chlorobenzophenone (2A-5CB) ( $C_{13}H_{10}ClNO$ ) crystals which are grown by slow evaporation solution growth technique. The grown crystals were characterized by single crystal X-ray diffraction, UV-Vis-NIR, FT-IR and FT-Raman studies. The grown crystals are also subjected to dielectric, photoconductivity, mechanical and thermal studies.

## MATERIALS AND METHODS

### 2. Experimental procedure for growth of 2A-5CB crystal

#### 2.1 Determination of Solubility

The solubility of pure and doped 2A-5CB salts were carried out in a solvent of ethanol at five different temperatures (30, 35, 40, 45 and 50 °C). The solubility data was determined by dissolving 2A-5CB salt in 100 ml of ethanol at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The same procedure was repeated for different temperatures. The solubility curve for different temperatures are drawn and shown in Fig. 1.

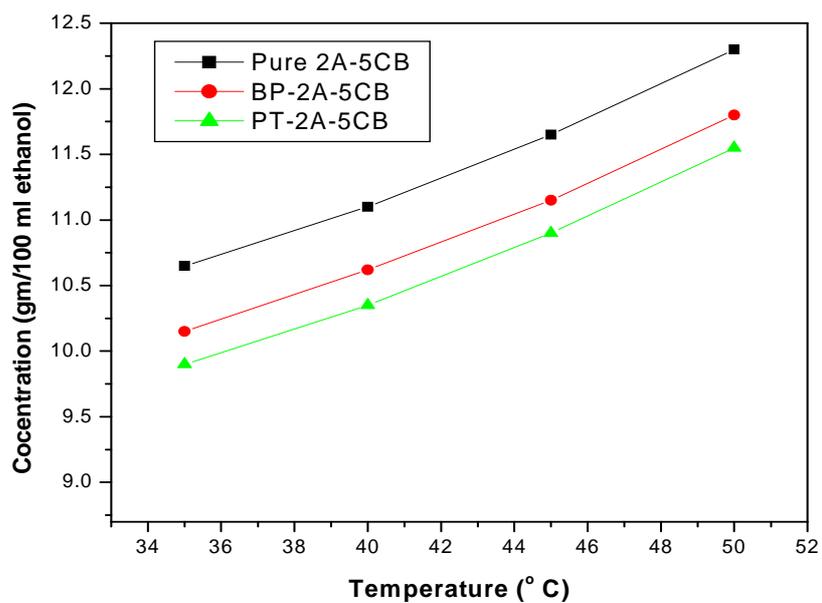
#### 2.2 Growth of pure and doped 2A-5CB crystal

In the present work, commercially available 2A-5CB ( $C_{13}H_{10}ClNO$ ) (molecular weight 231.68) was purified by repeated recrystallization process using ethanol. Since the solubility of 2A-5CB is high (10.65 gm / 100 ml of ethanol at 35 °C) in ethanol, it is very easy to grow good quality single crystal of suitable size. The seed crystals were obtained after three days, among them the defect free and perfectly shaped ones with high transparency were used as the seed crystals for further growth experiment. The seed crystals were first seasoned in the mother solution taken in the Mason Jar crystallizer using nylon thread and then allowed to grow into bigger size. The jar was covered with perforated lid to facilitate the slow evaporation of the solvent at a constant temperature of 305 K. Single crystals of size 14 x 6 x 5 mm<sup>3</sup> are grown in a period of 50-60 days. The crystals tend to grow as needles and appear dark gold in colour with good transparency. Fig. 2(a) shows the photograph of pure 2A-5CB single crystal.

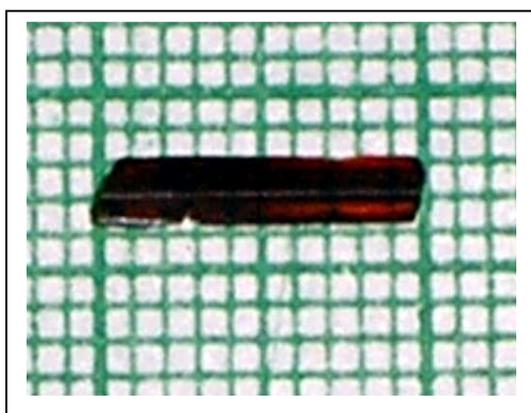
In the case of doped 2A-5CB, the salts were dissolved in ethanol and saturated solutions of benzophenone (5 mole %), benzoic acid (5 mole %) and paratoluidine (5 mole %) doped 2A-5CB were prepared separately at room temperature. The growth experiments were carried out using the same procedure as in the case of pure 2A-5CB. The crystal tends to grow as needles and appear pale yellowish in colour. Figs. 2(b) and 2(c) show the photographs of as grown single crystals of benzophenone and paratoluidine doped 2A-5CB. The optimized growth conditions of pure and doped 2A-5CB single crystals are presented in Table 1.

**Table 1: Optimized growth conditions of pure and doped 2A-5CB crystals**

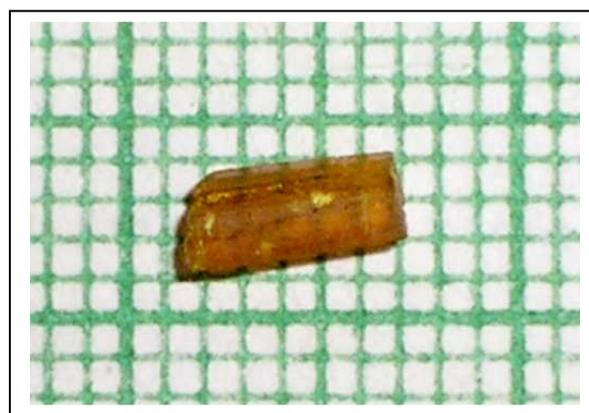
Crystal	Growth Temperature	Period of Growth	Dimensions
Pure 2A-5CB	305 K	10 to 15 days	14x6x4 mm <sup>3</sup>
Benzophenone doped 2A-5CB	305 K	7 to 10 days	12x5x5 mm <sup>3</sup>
Paratoluidine doped 2A-5CB	305 K	7 to 10 days	12x7x4 mm <sup>3</sup>



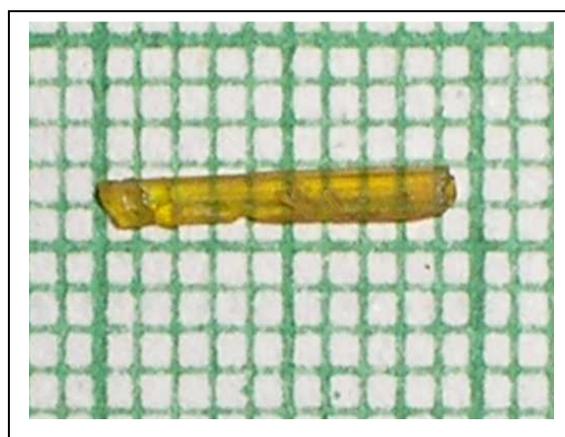
**Fig. 1.** Solubility curve of pure and doped 2A-5CB in ethanol



**(a)** Pure 2A-5CB



**(b)** Benzophenone doped 2A-5CB



**(c)** paratoluidine doped 2A-5CB

**Fig. 2 .** Photographs of as grown single crystals of pure and doped 2A-5CB

### 3. Characterization

#### 3.1 Single crystal X-ray diffraction studies

The single crystal X-ray diffraction of pure and doped 2A-5CB was carried out using ENRAF NONIUS CAD4-F single crystal X-ray diffractometer with MoK $\alpha$  ( $\lambda = 0.7107 \text{ \AA}$ ) radiation. The calculated lattice parameter values of the pure, benzophenone and paratoluidine doped 2A-5CB single crystals are presented in Table 2. It is observed that the crystals have C-face centered monoclinic system with a space group of C $_c$ . The experimentally observed lattice parameters of pure 2A-5CB are  $a = 9.7403 \text{ \AA}$ ,  $b = 19.0005 \text{ \AA}$ ,  $c = 24.7892 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 95.7290^\circ$ ,  $\gamma = 90^\circ$  and  $V = 4564.8232 \text{ \AA}^3$ . Ramesh Babu *et al* have reported the crystallographic data of the crystal as  $a = 9.751 \text{ \AA}$ ,  $b = 10.671 \text{ \AA}$ ,  $c = 24.813 \text{ \AA}$ ,  $\alpha = 87.47^\circ$ ,  $\beta = 83.80^\circ$ ,  $\gamma = 63.154^\circ$  and  $V = 2290.46 \text{ \AA}^3$  [4]. This discrepancy can be removed by transforming the above triclinic data into the C-face centered monoclinic system [matrix 100 -120 00-1] as reported in the present work. The lattice parameters of benzophenone doped 2A-5CB and paratoluidine doped 2A-5CB are found to be slightly different from pure 2A-5CB. These variations may be attributed to the incorporation of benzophenone and paratoluidine in 2A-5CB crystal lattice.

**Table 2: Single crystal XRD data of pure and doped 2A-5CB crystals**

Lattice parameter	Pure 2A-5CB	Benzophenone doped 2A-5CB	Paratoluidine doped 2A-5CB
a ( $\text{\AA}$ )	9.7403	9.7282	9.7392
b ( $\text{\AA}$ )	19.0005	18.993	19.0016
c ( $\text{\AA}$ )	24.7892	24.852	24.7979
$\alpha^\circ$	90	90	90
$\beta^\circ$	95.7290	95.7308	95.7146
$\gamma^\circ$	90	90	90
Crystal System	C-face centered monoclinic	C-face centered monoclinic	C-face centered monoclinic
Space Group	C $_c$	C $_c$	C $_c$
Volume ( $\text{\AA}^3$ )	4564.8232	4568.1807	4566.2891

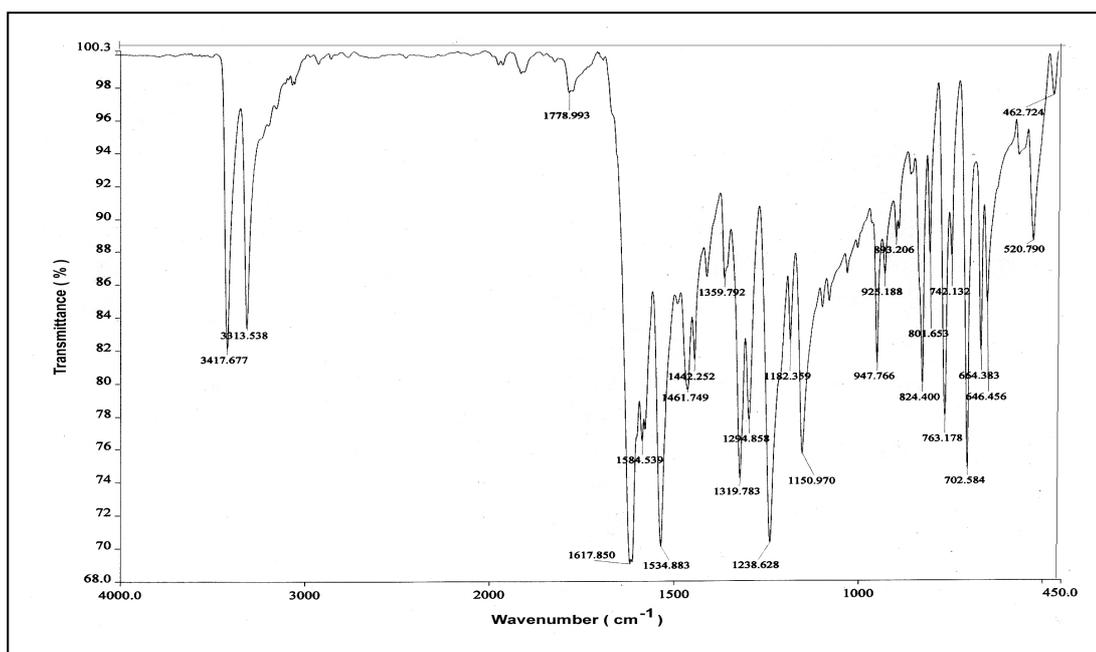
#### 3.2 FT-IR Studies

The FT-IR spectra of pure 2A-5CB, benzophenone and paratoluidine doped 2A-5CB crystals were recorded on BRUKER IFS 66V FT-IR SPECTROMETER using KBr pellet in the range  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  and are shown in the Figs. 3 - 5.

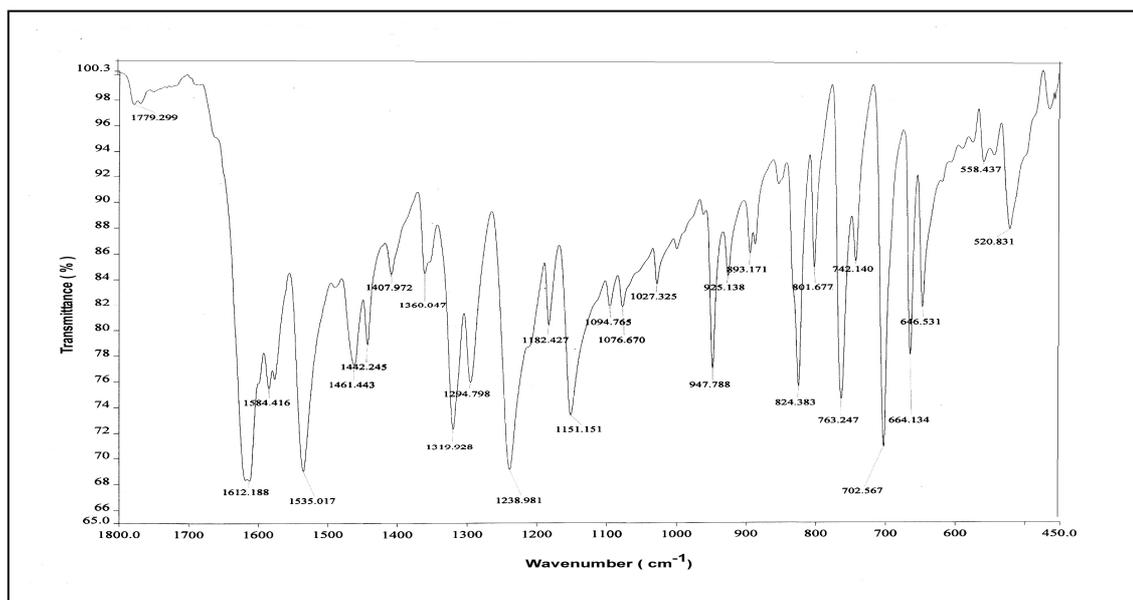
In the FT-IR spectra of pure 2A-5CB crystals (Fig. 3), the asymmetric and symmetric stretching vibrations of NH $_2$  grouping are observed at  $3417.677 \text{ cm}^{-1}$  and  $3313.538 \text{ cm}^{-1}$ , respectively. The aromatic CH stretching vibrations appear weak just above  $3000 \text{ cm}^{-1}$ . A highly intense and well defined peak observed at  $1617.85 \text{ cm}^{-1}$  is due to the C=O stretching vibration of carbonyl group. The NH deformation is assigned to the peaks at  $1584.5 \text{ cm}^{-1}$ . The presence of aromatic amines stretching is clearly identified as a sharp peak at  $1238.628 \text{ cm}^{-1}$ . The C=C vibrations of aromatic ring are confirmed at  $1461.749 \text{ cm}^{-1}$  and  $1534.883 \text{ cm}^{-1}$ . The peaks at  $1319.7 \text{ cm}^{-1}$  and  $1238.6 \text{ cm}^{-1}$  are due to C-N vibrations. The group of peaks between  $1000 \text{ cm}^{-1}$  and  $750 \text{ cm}^{-1}$  are due to aromatic CH bends. A sharp peak with moderate intensity observed at  $702.5 \text{ cm}^{-1}$  is due to the stretching vibrations of C-Cl. The middle infrared spectra of benzophenone and paratoluidine doped 2-amino-5-chlorobenzophenone are shown in Figs. 4 to 5. These spectra are

very well superimposed with the characteristic peaks of pure 2A-5CB as seen in Fig. 3. This fact clearly indicates that the dopant content might be below the detectability limit of IR region.

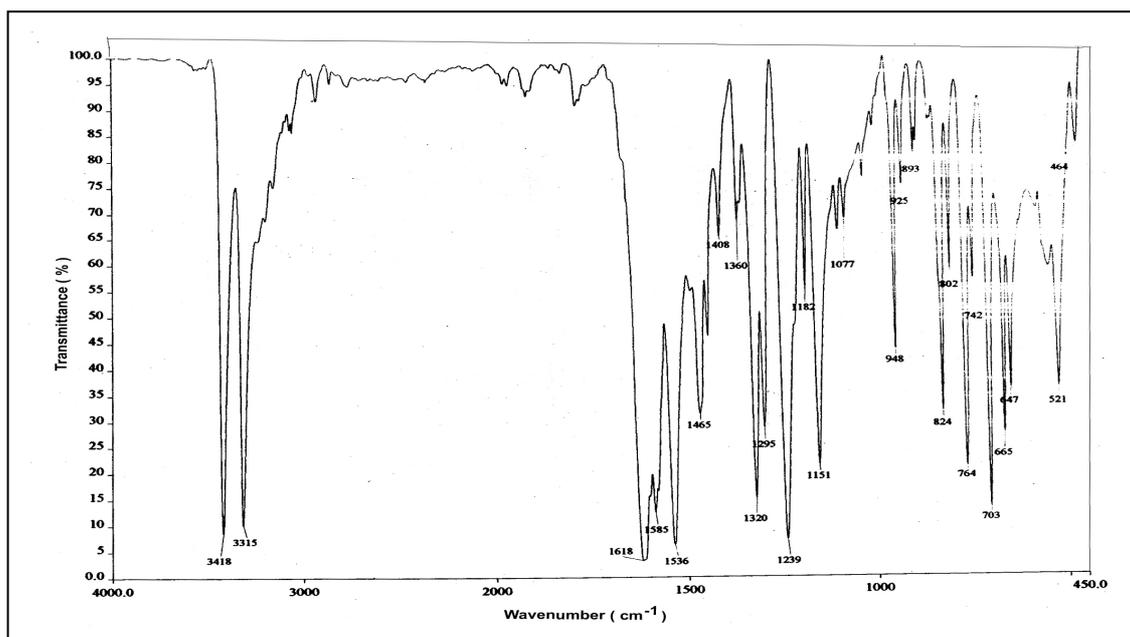
But the intensities of different peaks are slightly deviated as well as the peaks are marginally shifted from that of the parent compound. Particularly in the case of benzophenone substituted 2A-5CB, the peaks appear very much resolved and sharp. Hence, there might be benzophenone in the lattice, which is also confirmed in the TGA analysis discussed. In addition, during the growth of the crystal, the effect of the benzoic acid clearly felt by rapid growth of the crystal and it changes the morphology.



**Fig. 3. FT-IR spectrum of pure 2A-5CB single crystal**



**Fig. 4. FT-IR spectrum of Benzophenone doped 2A-5CB single crystal**



**Fig. 5.** FT-IR spectrum of paratoluidine doped 2A-5CB single crystal

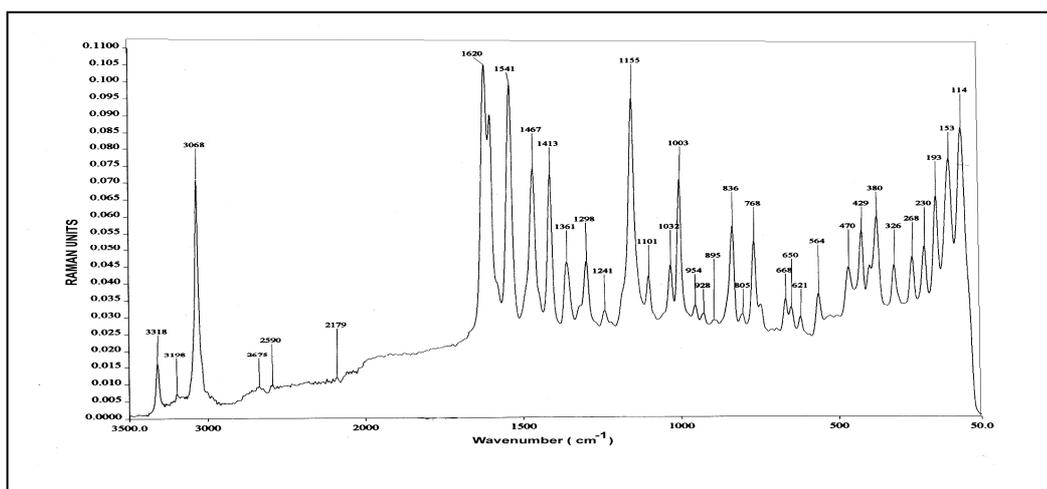
### 3.3 FT- Raman Studies

FT-Raman spectrum has been recorded in the frequency ranging from  $3500\text{ cm}^{-1}$  to  $50\text{ cm}^{-1}$  by using BRUKER FRA 106 FT-Raman spectrometer. The Raman spectra of pure and doped 2A-5CB crystals are shown in Figs. (6-8). From Fig. 6, it is evident that the NH vibration at  $3318\text{ cm}^{-1}$  is very weak. The aromatic CH vibration at  $3068\text{ cm}^{-1}$  is very intense and sharp. Similarly, the C=O stretching appears as a very intense peak at  $1620\text{ cm}^{-1}$  in the lower wave number side is due to  $\text{NH}_2$  deformation. The aromatic ring skeletal vibrations are seen at  $1541$ ,  $1467$  and  $1413\text{ cm}^{-1}$  respectively. The peaks at  $1155$  and  $1003\text{ cm}^{-1}$  are due to CN vibrations. The clusters of peaks below  $1000\text{ cm}^{-1}$  are due to aromatic CH bends. A well-defined peak observed at  $836\text{ cm}^{-1}$  and other sharp peaks identified in the low wave number regions are due to the bending vibration mode of aromatic C-H. The Raman spectra of benzophenone and paratoluidine doped 2A-5CB are shown in Figs. (7 - 8).

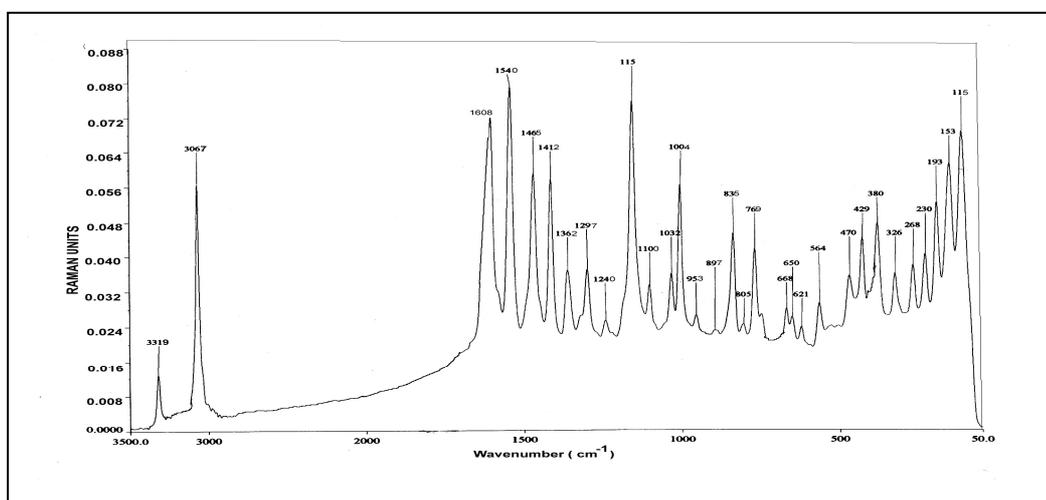
### 3.4 UV-Vis-NIR Studies

The optical transmission spectrum of 2A-5CB single crystal was recorded in the wavelength region of  $200\text{-}2000\text{ nm}$  using VARIAN CARY 5E spectrophotometer meter. The spectrum of pure 2A-5CB crystal is shown in Fig. 9. It is evident that the pure 2A-5CB crystal possesses a wide optical transparency window from  $390\text{-}1400\text{ nm}$ . However, there is an IR absorption observed at  $1200\text{ nm}$ . It is also clearly indicates that the UV cut-off wavelength lies at  $390\text{ nm}$ . The presence of low cut-off wavelength and the wide optical transmission window are the suitable parameters for frequency doubling of laser radiation.

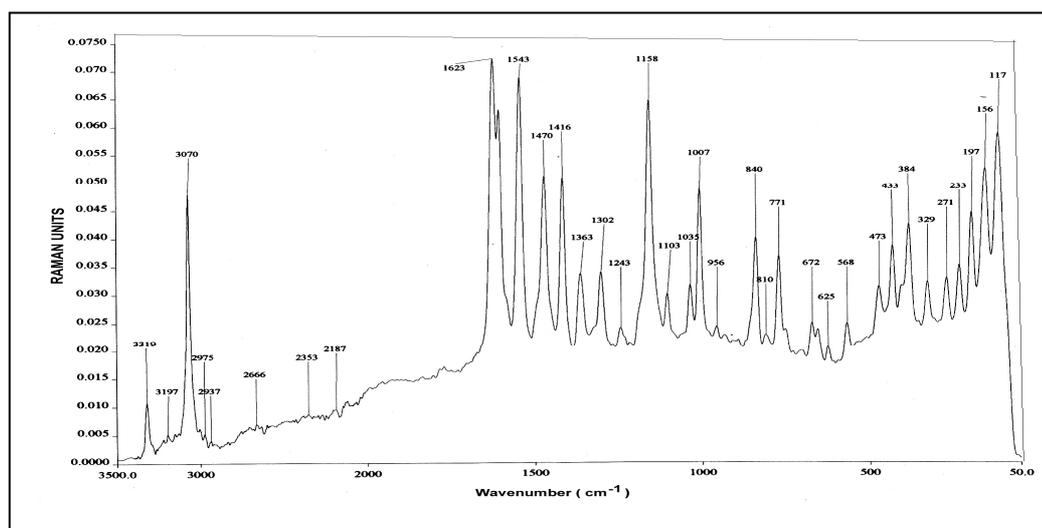
The UV-Vis-NIR spectra of benzophenone and paratoluidine doped 2A-5CB are also shown in Fig. 9. From the spectra it is seen that the doped 2A-5CB crystals are more transparent than the parent crystal in entire transmission range of  $300\text{-}1500\text{ nm}$  without any absorption peak. The above studies reveal that the doped crystals possess improved optical properties.



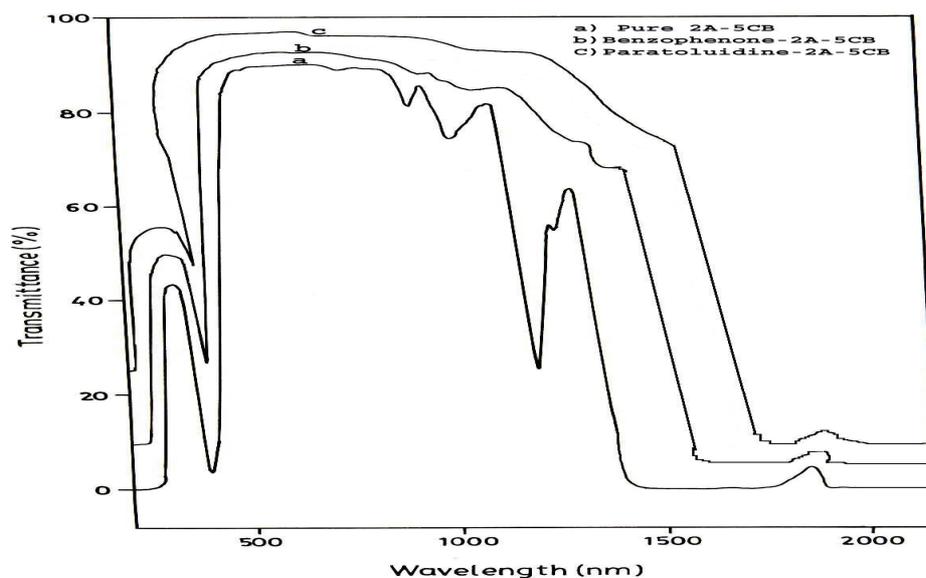
**Fig. 6.** FT-RAMAN spectrum of pure 2A-5CB single crystal



**Fig. 7.** FT-RAMAN spectrum of Benzophenone doped 2A-5CB single crystal



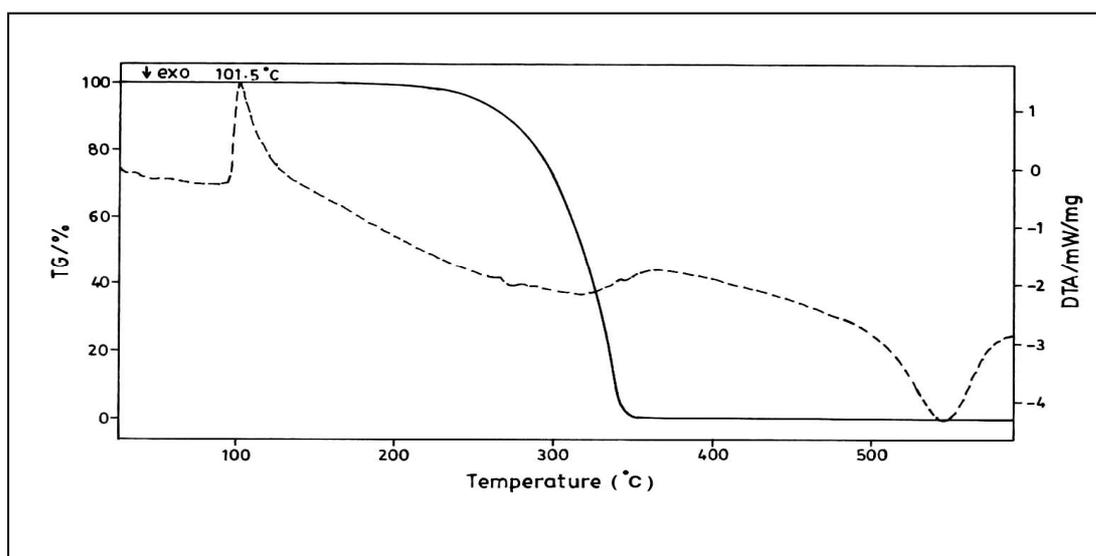
**Fig. 8.** FT-RAMAN spectrum of paratoluidine doped 2A-5CB single crystal



**Fig. 9.** UV-Vis-NIR Spectra of pure and doped 2A-5CB single crystal

### 3.5 NLO Studies

For testing the suitability of pure and doped 2A-5CB crystals for NLO applications, Kurtz and Perry powder technique was performed by illuminating the powder sample with fundamental mode (1064 nm) of a Q-switched, mode locked Nd:YAG laser with input pulse of 9.5 mJ. The second harmonic signal of 1280 mW (pure 2A-5CB), 1305 mW (doped benzophenone) and 1303 mW (doped paratoluidine) respectively were obtained for pure and doped 2A-5CB with reference to KDP (403 mW). Thus the SHG efficiencies of pure and doped 2A-5CB crystals are nearly 3 times more than that of KDP.



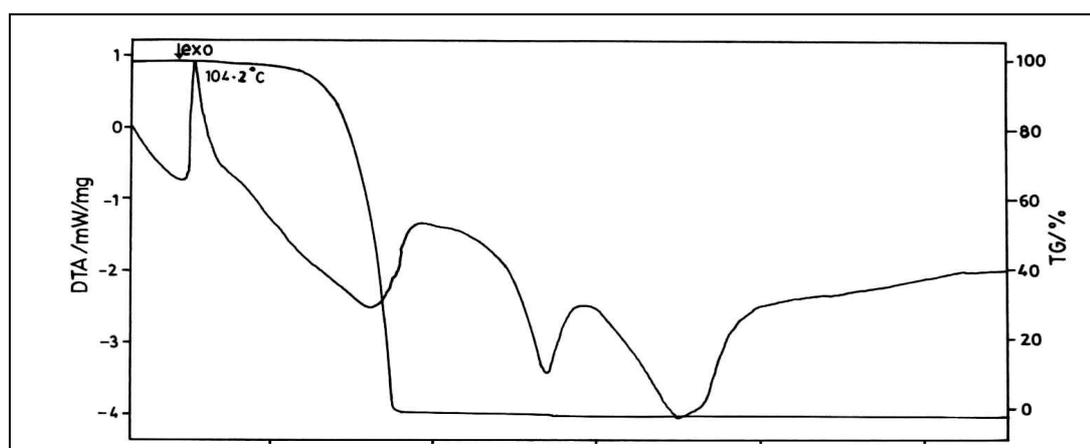
**Fig. 10.** TGA-DTA curves of pure 2A-5CB single crystal

### 3.6 Thermal Studies

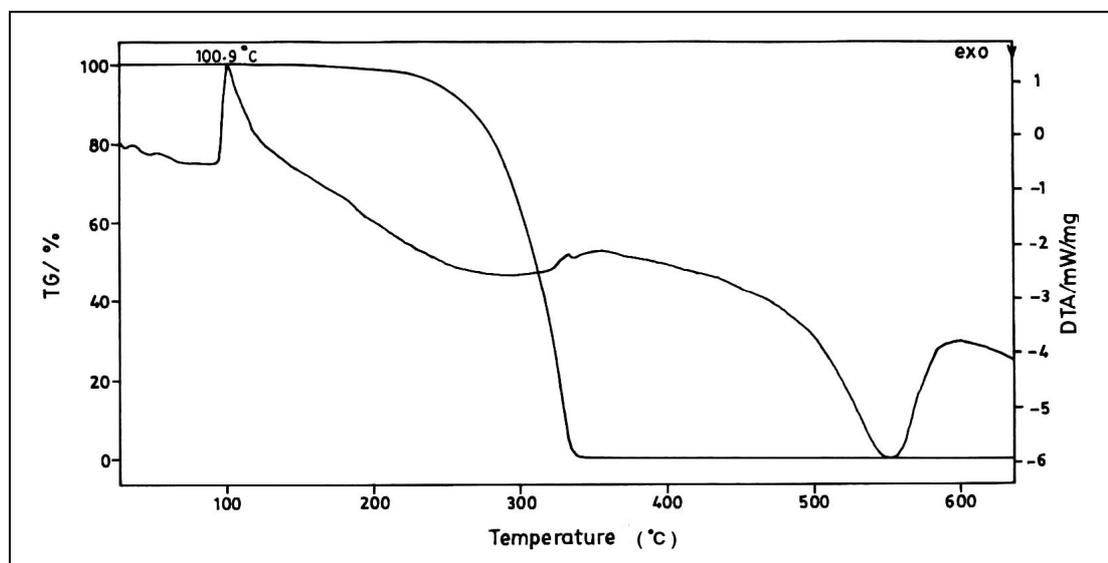
The TGA and DTA thermal studies of both pure and benzophenone and paratoluidine doped 2A-5CB crystals were carried out from room temperature to 600 °C using the instrument NETSZCH

STA 409C and are shown in Figs. 10-12. The experiment was carried out in nitrogen atmosphere at the heating rate of 10 K/min. A single major weight loss starting at about 220 °C is observed from the TGA trace of pure 2A-5CB (Fig. 10). The decomposition completes at about 350 °C leaving no residue. But below 220 °C, there is no weight loss, hence the crystal is completely free of any entrapped or physically adsorbed ethanol. However the DTA thermogram clearly indicates the endothermic peak appearing at 101.5 °C, which corresponds to the melting point of the sample and the same has been verified using the capillary melting point apparatus.

The TGA and DTA traces of benzophenone and paratoluidine doped 2A-5CB are shown in Figs. (11-12). The TGA thermograms for the doped samples almost appear similar with a single stage weight loss as in the case of pure ones. In the doped samples also sharp weight loss start just above 220 °C leading to zero percent residue. Hence, there is complete degradation of the compound into volatile fragments, but below this temperature there is no weight loss, hence the crystal is free of any entrapped solvent, similar to that of parent 2A-5CB.



**Fig. 11. TGA-DTA curves of Benzophenone doped 2A-5CB single crystal**



**Fig. 12. TGA-DTA curves of paratoluidine doped 2A-5CB single crystal**

However, in the DTA traces (endothermic peaks) the melting point of the doped samples shows a marginal increase (104.2 °C – benzophenone and 100.9 °C paratoluidine). From the above thermograms of pure and doped 2A-5CB, it is evident that the dopants (benzophenone and paratoluidine) have altered the melting point of 2A-5CB by 3 °C and 1 °C, respectively.

### 3.7 Microhardness studies

The variations of Vickers hardness number with applied load for pure and benzophenone and paratoluidine doped 2A-5CB crystals on (1 1 0) plane is shown in Fig. 13. The plot indicates that the hardness of the pure and doped 2A-5CB crystal decreases with increasing load. The decrease of the microhardness with the increasing load is in agreement with the normal indentation size effect (ISE). By plotting log P versus log d, the value of the work hardening coefficient (n) of pure, benzophenone and paratoluidine doped 2A-5CB was found to be 1.25, 1.15 and 1.07 respectively. According to Onitsch,  $1.0 \leq n \leq 1.6$  for hard materials and  $n > 1.6$  for soft materials [5]. Hence, it is concluded that 2A-5CB is a hard material.

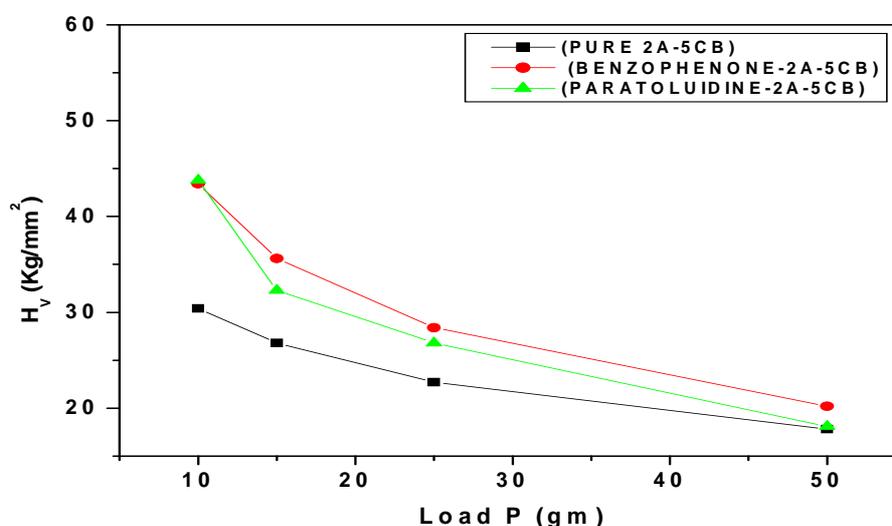


Fig. 13. Variation of Vickers hardness number with load for pure and doped 2A-5CB single crystals along (110) plane

### 3.8 Dielectric Studies

The electric properties of dielectric substances are usually described in terms of the dielectric constant. For most materials, this quantity is independent of the strength of the electric field over a wide range of the latter, but in the case of alternating fields, it depends on the frequency. It also depends on parameters such as the temperature, which define the state of the material.

Figs. 14a – 16a show the plots of dielectric constant against log frequency of the applied a.c. field at various temperatures (308 K, 328 K, 348 K and 368 K) for pure, benzophenone and paratoluidine substituted 2A-5CB crystals. The dielectric constant  $\epsilon_r$  at low frequencies depends on the excitation of bound electrons, lattice vibrations, dipole orientations and space-charge polarization (atomic or electronic). At very low frequencies all four contributions may be active. The manner of variation of dielectric constant with frequency indicates which contributions are present.

It is observed that the dielectric constant  $\epsilon_r$  decreases with increase in frequency in all the samples. In the present work, one can observe the increase in the value of dielectric constant of the doped sample. The large value of dielectric constant at low frequency is due to the presence of space charge polarization. The space charge contribution depends on the purity and perfection of the material. Its influence is mainly noticeable in the low frequency region [6]. With increase

in temperature the dielectric constant decreases as dipole has acquired thermal energy and deviated from better orientation.

Figs. 14b-16b shows the variation of dielectric loss with log frequency of the applied a.c. field at various temperatures for the 2A-5CB (pure and doped 2A-5CB) single crystals. It is observed that the dielectric loss decreases with increase in frequency in the case of all samples. It attains the minimum value from 10 kHz onwards.

The low values of dielectric loss suggest that the grown crystals are of moderately good quality. In the lower frequency region, dielectric loss shows larger values due to the loss associated with ionic mobility [7]. The trend of dielectric constant and dielectric loss as a function of frequency is slightly altered by the dopants when compared to the pure one.

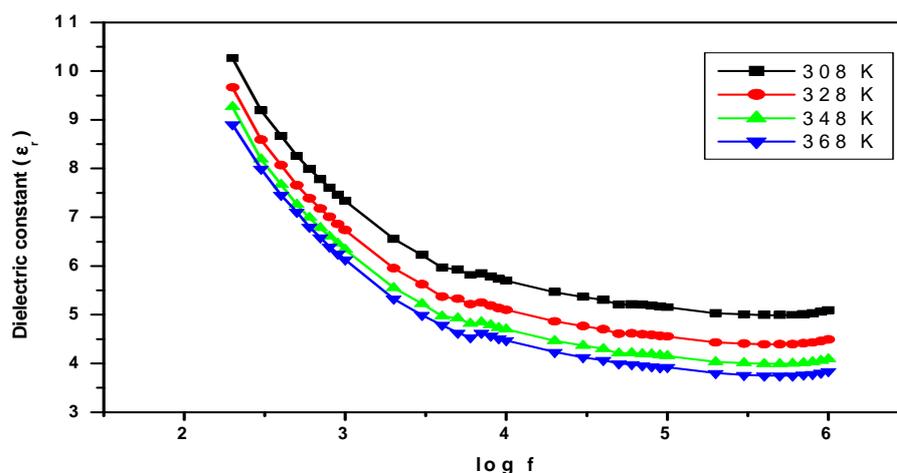


Fig. 14a. Variation of dielectric constant of pure 2A-5CB crystal as a function of frequency at different temperatures

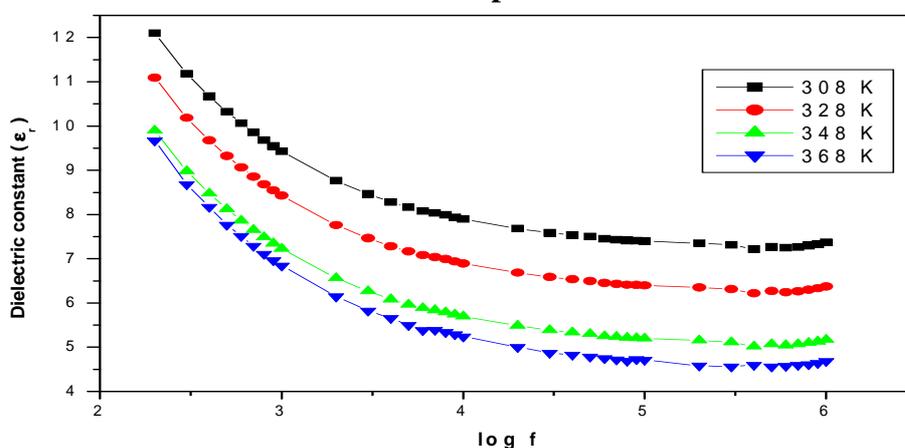


Fig. 15a. Variation of dielectric constant of Benzophenone doped 2A-5CB crystal as a function of frequency at different temperatures

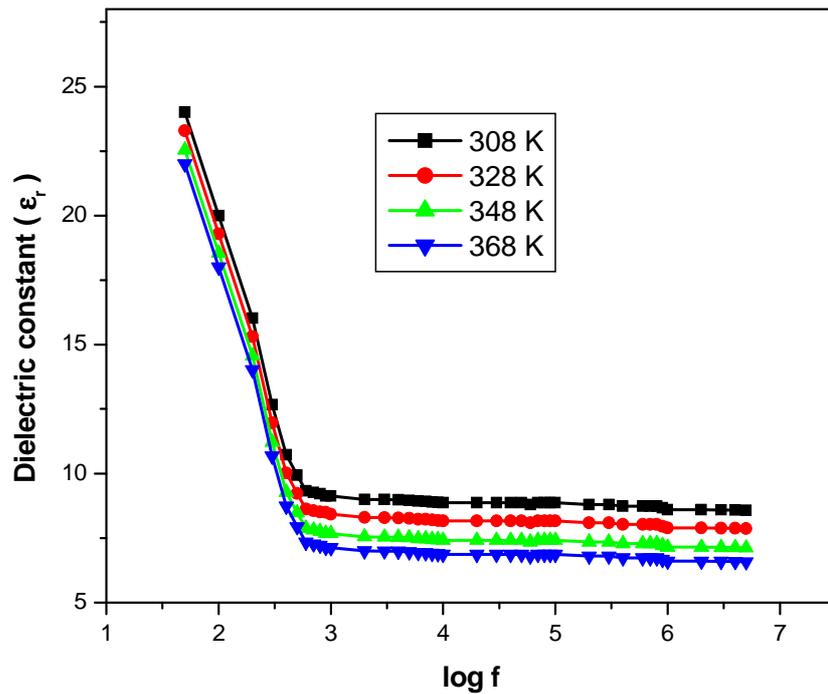


Fig. 16a. Variation of dielectric constant of paratoluidine doped 2A-5CB crystal as a function of frequency at different temperatures

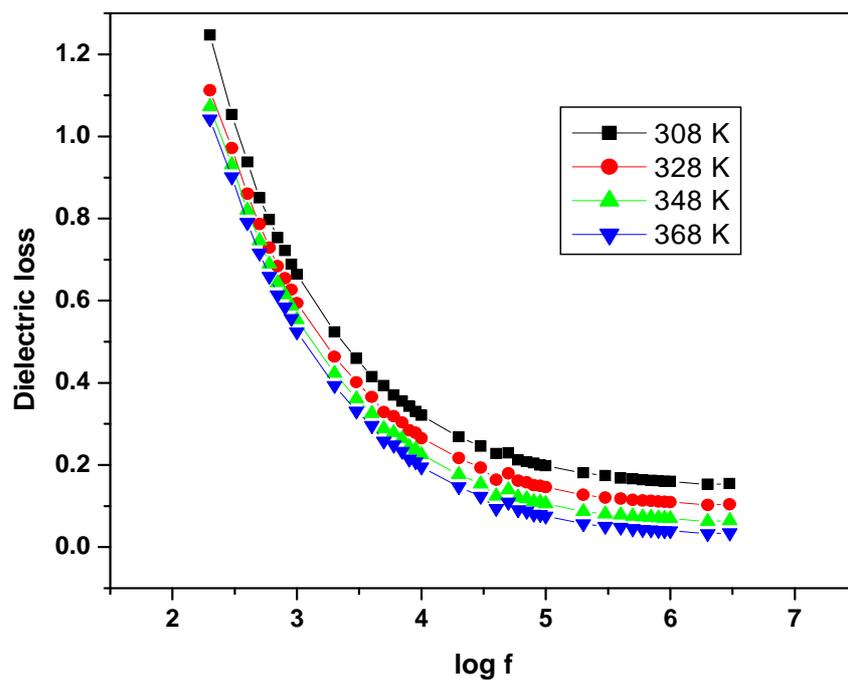
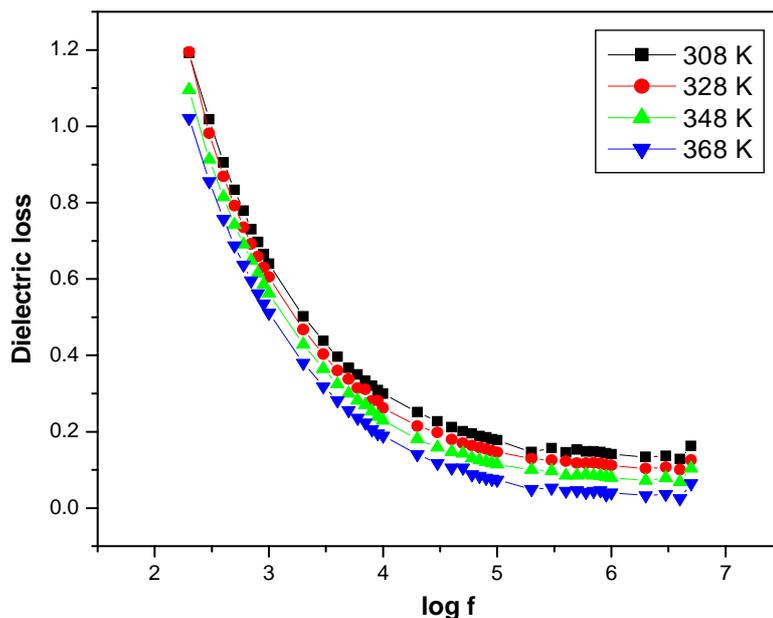
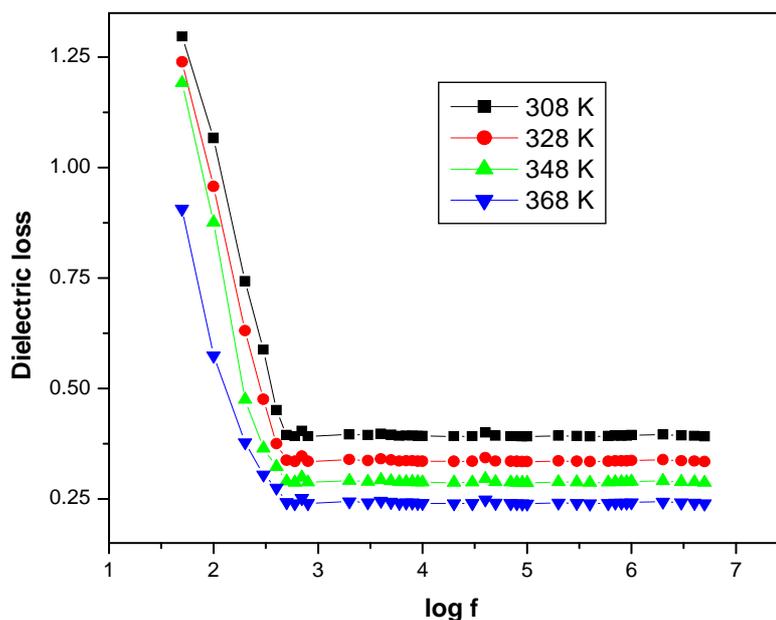


Fig. 14b. Variation of dielectric loss of pure 2A-5CB crystal as a function of frequency at different temperatures



**Fig. 15b.** Variation of dielectric loss of Benzophenone doped 2A-5CB crystal as a function of frequency at different temperatures

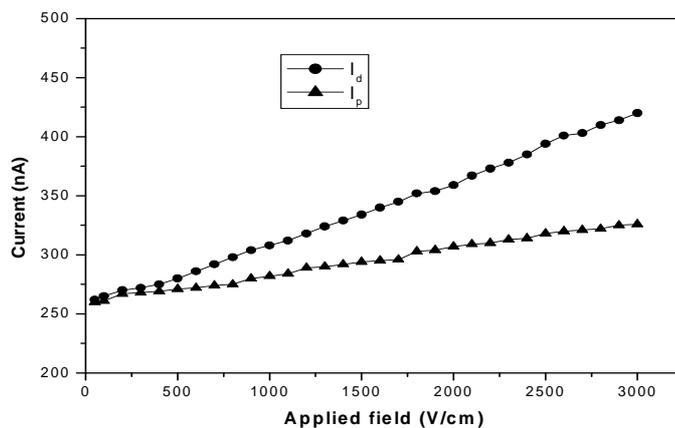


**Fig. 16b.** Variation of dielectric loss of paratoluidine doped 2A-5CB crystal as a function of frequency at different temperatures

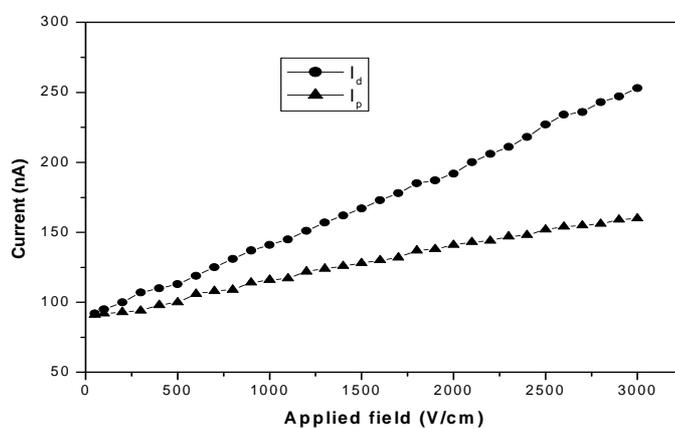
### 3.9 Photoconductivity Studies

Field dependence of dark and photocurrent of pure and doped 2A-5CB crystals are shown in Figs. 17- 19. The photocurrent is found to be less than the dark current at every applied electric field. This phenomenon is known as negative photoconductivity. It is interesting to note that both pure and doped 2A-5CB crystals exhibit negative photoconductivity. It is also observed that the

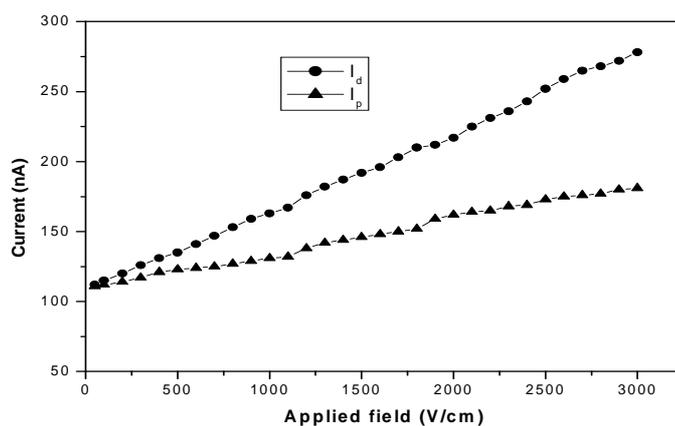
dopants have slightly altered the strength of dark current when compared to 2A-5CB pure sample.



**Fig. 17.** Field dependent conductivity of pure 2A-5CB single crystal



**Fig. 18.** Field dependent conductivity of Benzophenone doped 2A-5CB single crystal



**Fig. 19.** Field dependent conductivity of paratoluidine doped 2A-5CB single crystal

## CONCLUSION

Single crystals of pure and doped 2A-5CB are conveniently grown by employing slow evaporation technique. The grown crystals were confirmed by single crystal XRD. The various functional groups present in the crystals were identified and confirmed. It is further observed from the FT-IR spectra of doped 2A-5CB that the intensities of different peaks are marginally shifted from that of the parent compound. The FT-Raman spectra of both pure and doped 2A-5CB crystals revealed the presence of -NH, -CH vibrations, -NH<sub>2</sub> deformation and aromatic ring skeletal vibrations. In the spectrum of doped crystals, marginal changes in peak positions are observed. The cut-off wavelength of pure sample was found to be 390 nm. However the doped samples are more transparent than the parent crystal in the entire transmission range of 300-1500 nm. The above study reveals that the doped crystals possess improved optical properties. NLO test confirms the enhancement of the NLO property for the doped samples. DTA curve of pure sample indicates that the endothermic peak appears at 101.5 °C (melting point). Microhardness studies reveal that the pure and doped samples are hard materials. Dielectric studies indicate that the presence of dopants has altered the dielectric response. The photoconductivity studies confirm the negative photoconducting nature of the sample.

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