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Studies on the Growth and Characterization of Benzoyl Alanine NLO Single Crystal

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Abstract : Benzoyl Alanine (BA) an intriguing organic nonlinear optical (NLO) polymorphic material for frequency conversion has been grow by slow evaporation solution growth technique at 300 K. The solubility of BA was determined in acetone at different temperatures. Superior optical quality and defect free crystal of dimension of 1.5x1x1.5 mm^3 was grown and characterized by single crystal XRD, FTIR, ^1H, & ^{13}C NMR, dielectric and photoconductivity studies. The title crystal has found to crystallize into noncentrosymmetric monoclinic $P2_1$ space group. The UV-Vis-NIR spectrum reveals the high percentage of transmission of the sample in the entire visible region. Thermogravimetry and differential thermal analyses were estimated to determine the thermal stability and decomposition temperature of the material. The Kurtz powder second harmonic generation test shows that the compound is a prospective crystalline material for second order non linear optical application. The dielectric measurements are carried out and the nature of variation of dielectric constant and dielectric loss in frequency range of 50 Hz to 5 MHz are studied and recorded. Photoconductivity measurements of BA suggest that it exhibits positive photoconductivity.

Keywords : Benzoyl Alanine (BA), XRD, FTIR, UV, ^1H & ^{13}C NMR, TG/DTA, Dielectric, Photoconductivity.

1. Introduction

In the recent past, efforts have been taken by many researchers to develop ultra-violet lasers for industrial and medical applications. The frequency conversion technique of solid state lasers in non linear optical (NLO) crystal is an effective method of obtaining UV radiation with high beam quality and stability (Abraham Rajasekar et al., 2004). In addition to that crystalline amino acids have been subjected to extensive investigation, in order to study their non linear optical properties (Kitazawa et al., 1994, Misoguti et al., 1996, Wang et al., 1999). Recently efforts have been made to crystallize amino acids mixed with organic and inorganic compounds to develop the capability of generating tunable coherent beams (William Silfvasat, 1998). Much of this research has been directed towards photonics and in solid state electronics. Therefore these organic materials are rated high as compared to inorganic in view of their large electro optic coefficient, low frequency dispersion, low cost, fast and non linear response, broad frequency range and intrinsic tailorability (Haja Hameed et al., 2000, Zaccaro et al., 1999). BA ($C_{10}H_{11}NO_3$) is an amino acid derivative with a free carboxylic acid group. The XRD analysis of BA compound reported by Fu and Wang, 2005 were monoclinic with space group of P21/c and *N*-acetyl phenylglycine polymorph of BA ($C_{10}H_{11}NO_3$) belongs to monoclinic crystal system with space group of P21/n (Fu and Wang, 2005). Using Schotten-Baumann method of benzoylation, we have synthesized BA single crystal using acetone as the solvent. This material exhibits considerable SHG effect when measured by powder method. In this paper we present the growth of BA single crystal by slow evaporation technique along with characterization by FTIR, ^{1}H & ^{13}C, UV-Vis-NIR, NLO, TGA/DTA techniques. The dielectric response and photoconductivity of the sample are also investigated and reported.

2. Experimental results and discussion

2.1 Synthesis and purification

The starting materials benzoyl chloride (E-Merck) and L-alanine (E-Merck) were commercially available. The required amount of L-alanine was dissolved in 10% sodium hydroxide solution maintained at a temperature of 30° C. The appropriate amount of benzoyl chloride was added in successive stages to the solution. BA was formed in the form of precipitate. The precipitate was recrystallized thrice using acetone. The purity of the synthesized compound was ascertained by the characterization of its melting point. The structural confirmation of the product was done with the aid of FTIR and NMR spectral methods.

The equation is

$$C_6H_5COCl + HO_2CCH(NH_2)CH_3 \xrightarrow{10\%\ NaOH} C_{10}H_{11}NO_3 + HCl$$

2.2 FTIR-spectral analysis

The FT-IR spectrum of BA was recorded using FTIR spectrometer (Model: BRUKER IFS 66V FT-IR) in the region 4000 - 400 cm^{-1} and the spectrum is shown in Figure 1. The following vibrations were observed in the spectrum. The NH stretching vibrations and absorption bands appear in the frequency range 3500 – 3400 cm^{-1}. The bands designated in the range between 3100 - 3000 cm^{-1} are assigned to aromatic CH stretching vibrations. The bands appearing between 3000 and 2850 cm^{-1} are assignable to aliphatic CH group stretching. The bands at 2965 - 2880 cm^{-1} are due to CH_3 stretching vibrations. The bands observed between 1830 and 1650 cm^{-1} are due to C=O group stretching vibrations. The bands between 1000 - 700 cm^{-1} are due to the aromatic rings out of plane bending vibrations.

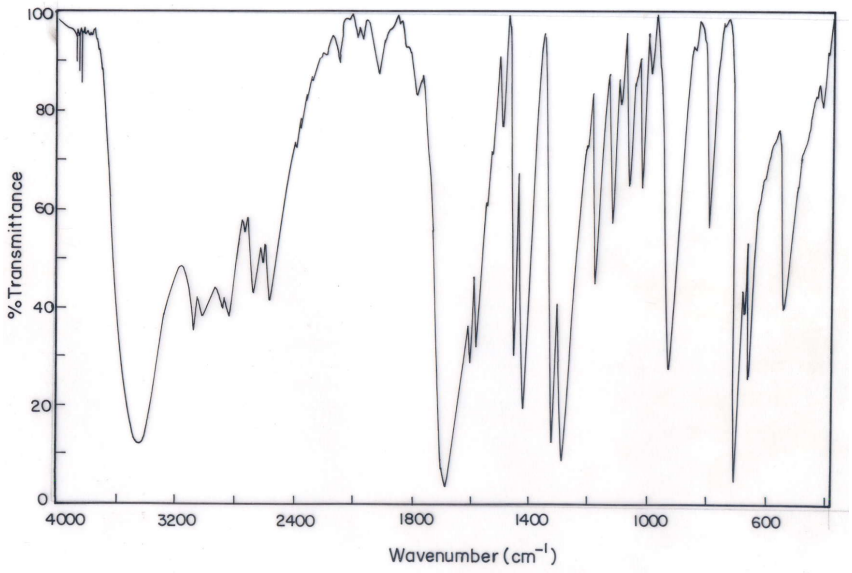

Figure. 1 FTIR spectrum of BA crystal

2.3 ^1H & ^{13}C NMR spectral analyses

The molecular structure of the product was studied using ^1H and ^{13}C NMR spectral methods. ^1H NMR and ^{13}C NMR spectrum of BA was recorded using JEOL: GSX 500 instrument in deutrated chloroform with tetramethylsilane (TMS) as an internal standard. Figure.2 and Figure.3 represent ^1H and ^{13}C NMR spectra. In the ^1H NMR spectrum signals at 7.4 to 7.9 ppm are

assignable to protons from the aromatic ring. The resonance at 4.8 ppm is due to the N-H protons. Signal at 4.4 ppm is due to the protons of C-H attached to COOH group. Signal at 1.36 ppm is due to CH_3 protons. In the ^{13}C NMR spectrum, the signal at 175 ppm is due to C=O carbon of COOH. The signal at 167 ppm is due to C=O carbon of CONH. The signals ranging 129 to 133 ppm are due to aromatic carbons from the phenyl group. The signals 48.7 ppm and 17.3 ppm are due to C-H carbon and CH_3 carbon from alanine respectively.

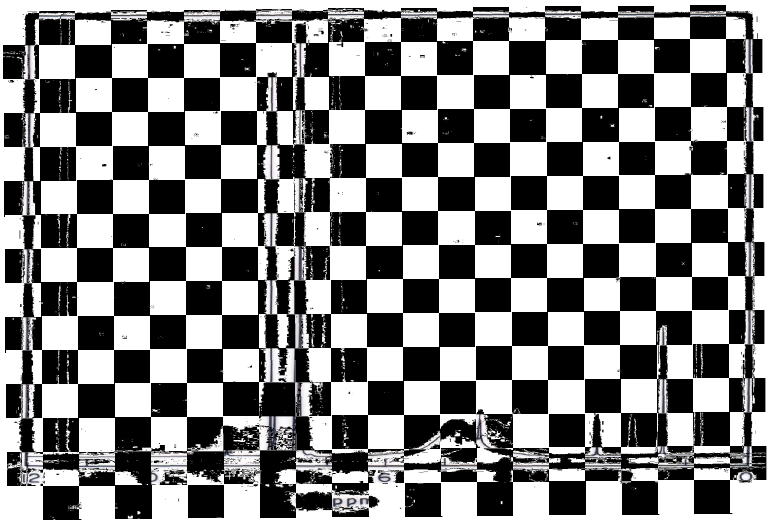

Figure. 2 ^1H NMR spectrum of BA crystal

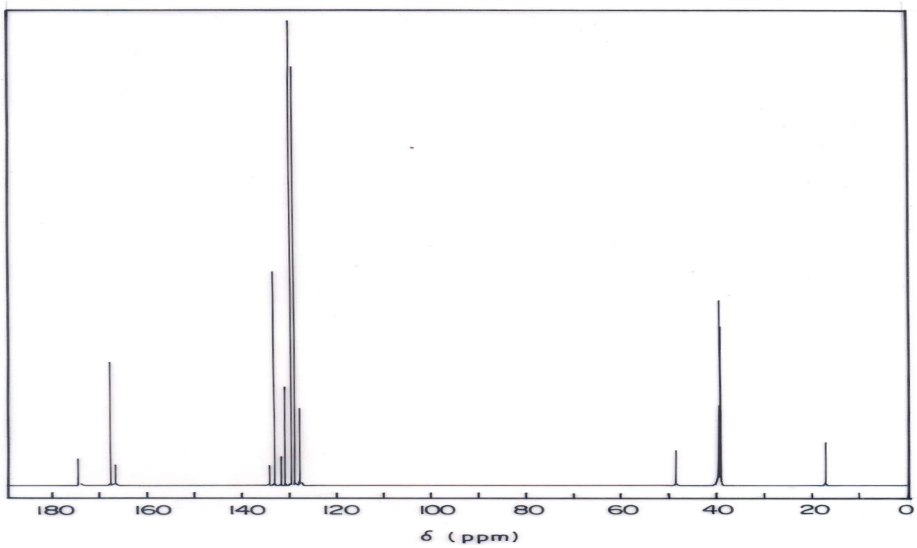

Figure. 3 ^{13}C NMR spectrum of BA crystal

2.4 Solubility studies

The synthesized salt was used to measure the solubility of BA in acetone. A 250 ml glass beaker filled with 100 ml of acetone was placed inside a constant temperature bath whose temperature was set at 25° C. An acrylic sheet with circular hole at the middle through which a spindle from an electric motor placed on the top of the sheet was introduced into the solution. A Teflon paddle was attached at the end of the rod for stirring the solution. BA salt was added in small amount. The addition of salt and stirring were continued till the formation of precipitate, which confirmed the supersaturation of the solution. Then, 20 ml of the saturated solution was pippeted out and poured into the Petri dish of known weight. The solvent was completely evaporated by keeping the solution in open air for three days. The amount of salt present in 20 ml of the solution was measured by subtracting the weight of empty Petri dish. From this, the amount of salt present in 100 ml of the solution was found out. In the same manner, the amount of the salt dissolved in 100 ml at 25, 30, 35, 40, 45 and 50° C were found out. Figure.4 shows the solubility curve of BA in acetone at different temperatures. It is seen from the solubility curve that the solubility of BA in acetone increases with increase in temperature. The solubility coefficient is an important parameter for studying the solubility diagram. Using the formula $(ds/dT)/S_0$, where S is the solubility (g/100 ml) and T is the temperature. S_0 is the solubility in g/100 ml corresponding to T_0, the temperature for which the solubility coefficient is determined. Solubility coefficients per degree Celsius of T_0 values 25, 30, 35, 40 and 45° C were calculated. The solubility coefficient is 0.03 per °C at 25, 30 and 35°C and 0.04 per °C for temperatures studied. The regular behaviour in the solubility diagram makes BA suitable for the growth by temperature lowering and slow evaporation techniques using acetone as the solvent.

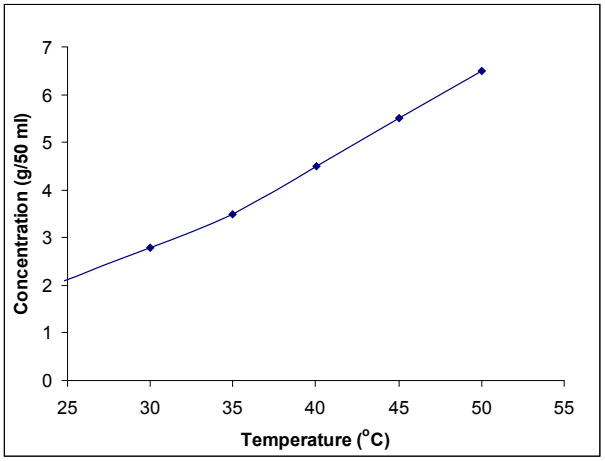

Figure. 4 Solubility curve of BA crystal in acetone

2.5 Crystal growth

The solvent of the supersaturated solution was allowed to evaporate through the perforated lid of the container. Tiny crystals were formed at the bottom of the container due to spontaneous nucleation. Among them defect free ones were chosen as seeds for growing bulk crystals. By seeding the supersaturated solution and evaporating the solvent, defect free crystal of superior optical quality and dimensions upto a size of 1.5x1x1.5 cm^3 were harvested after a period of 10-15 days. The photograph of as grown crystal of BA is shown in Figure. 5.

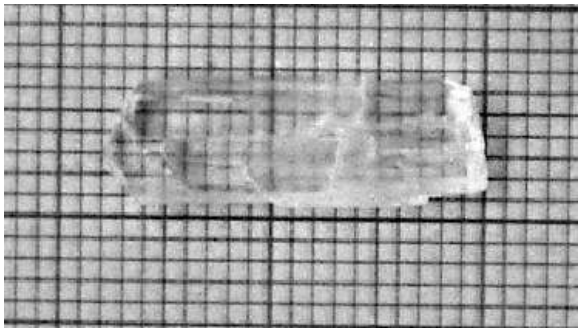

Figure. 5 Photograph of as grown BA crystal

2.6 Single crystal XRD

The growth crystal was subjected to single crystal X-ray diffraction studies using an automatic diffractometer ENRAFNONIUS (The Netherlands) with M_oK_α (λ=0.7170 Å) radiation and its unit cell dimensions are determined. From the crystallographic symmetrical point of view it is found that the crystal belongs to monoclinic crystal system with P_{21} space group. The lattice parameters a = 8.878 Å, b = 10.967 Å, c = 9.882 Å, α = 111.860°, β = 90.237°, γ=90.183° and Volume $(Å)^3$ = 962.161 A^3.

2.7 Transmittance studies

Transparency of BA crystal was measuring a Varian carry 5E model spectrophotometer in the range 200-800 nm. The lower cut off wavelength lays around 200 nm. From the results of UV-visible spectral data, it can be expended as a potential material for SHG in the visible region drawn to blue and violet light, which makes it suitable for optoelectronic application. As there is no change in transmittance in the entire visible range upto 200 nm, BA can find application as window in spectral instruments in these region. Optical transmission spectrum of BA is shown in Figure. 6.

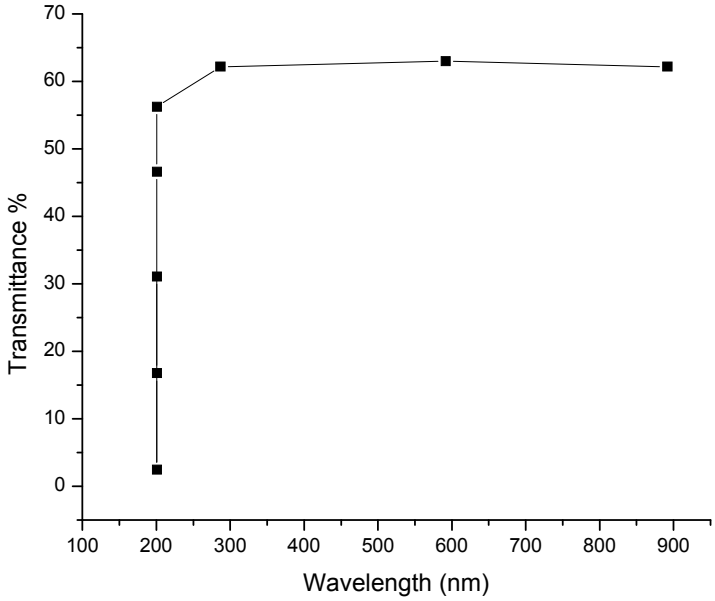

Figure. 6 Transmission spectrum of BA crystal

2.8 Second Harmonic generation

A quantitative measurement of the conversion efficiency of BA was estimated by Kurtz powder technique using a Q-switched Ne:YAG laser. A fundamental laser beam of 1064 nm wavelength, 8 ns pulse in depth with 10 Hz pulse rate was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter and it is 5.7 mJ/pulse. The crystal was grained into powder and it was packed densely between two transparent glass slides. The relative efficiency of BA crystal (20 mV) is 2 times greater than that of potassium di-hydrogen phosphate (9mV).

2.9 TG/DTA ANALYSIS

Thermal behaviour of the sample was assessed by TG/DTA analysis using thermal analysis instrument NETZSCHSTA 409C. The TGA was carried out in nitrogen atmosphere at a heating rate of 20° C/min in the temperature range of 50 to 800° C. The TGA/DTA curve of BA crystalline sample is shown in Figure.7. From the TG curve it can be suggested that BA is stable upto 220° C and decomposition is not expected below this temperature. From the DTA curve, it is observed that BA is stable above its melting point and it can be suggested that it has favorable crystal growth properties that allows the growth directly from the melt.

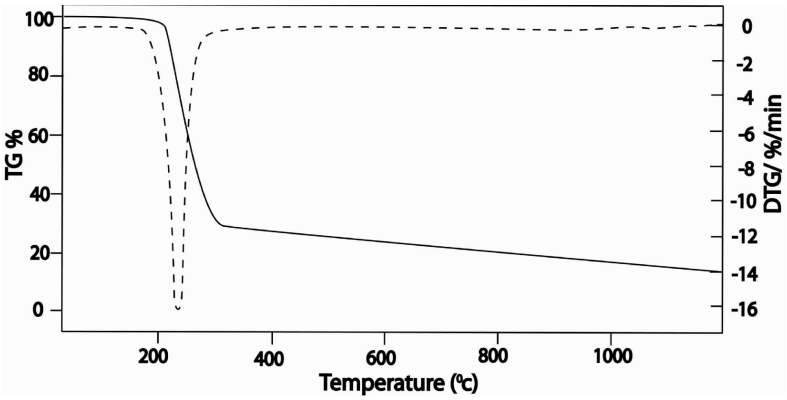

Figure. 7 TG/DT curves of BA crystal

3.1 Dielectric studies

Dielectric measurements were carried out using HIOKI3532-50 LCR Hitester in the frequency range 50 Hz - 5 MHz. The experiment was performed with defect free samples which were cut and polished using fine grade alumina powder to obtain good surface finish. Electrodes were applied so that it behaves as a parallel plate capacitor using air drying silver paste. Dielectric permittivity measurements were carried out with crystalline sample kept inside a dielectric cell (Westphal) at room temperature. Figure. 8 shows the variation of dielectric constant (ε) as a function of log frequency. The study reveals that the dielectric constant decreases as the frequency increase. At high frequency, the dipolar orientation effect is dominant whereas at low frequencies below 10 kHz ionic and electronic polarizations are effective. The large value of dielectric constant at low frequency may be attributed to presence of space charge polarization. Figure. 9 shows the variation of dielectric loss of BA crystal as a function of log frequency.

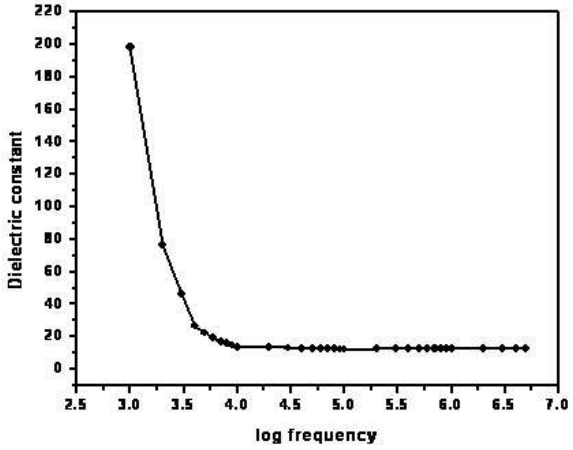

Figure. 8 Variation of dielectric constant of BA crystal as a function of log frequency

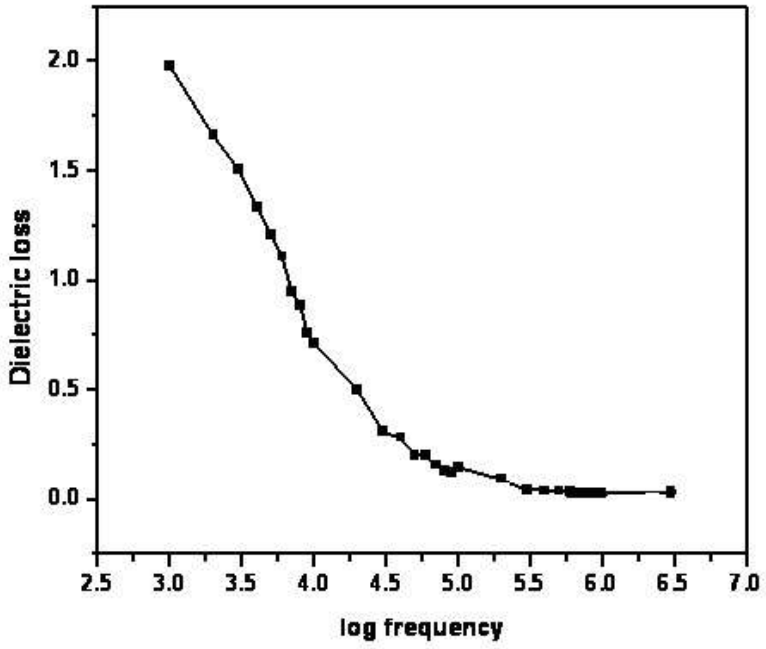

Figure. 9 Variation of dielectric loss of BA crystal as a function of log frequency

3.2 Photoconductivity studies

Photoconductivity of the crystal was studied using Keithley 485 picameter. Dark conductivity of the sample was observed by connecting the BA crystal in series to a dc power supply and a picoameter as described by Xavier and Goldsmith, 1995. Electrical contacts were made at a spacing of about 1 cm on the sample using silver paint. The DC input was increased from 0 to 300 V in steps of 10V and the corresponding dark currents (I_d) were noted from the electrometer. For measuring the photocurrent, the sample is illuminated with a halogen lamp (100 W) by focusing a spot of light, on the sample with the help of the convex lens. The DC input was increased from 0 to 300 V in steps of 10 V and the corresponding photocurrents were measured. The variation of photocurrent (I_p) with applied field is shown in Figure.10. The current gets increased when the sample is illuminated and it decreased suddenly when the illumination was stopped, and thus revealing that the BA crystal exhibits positive photoconductivity.

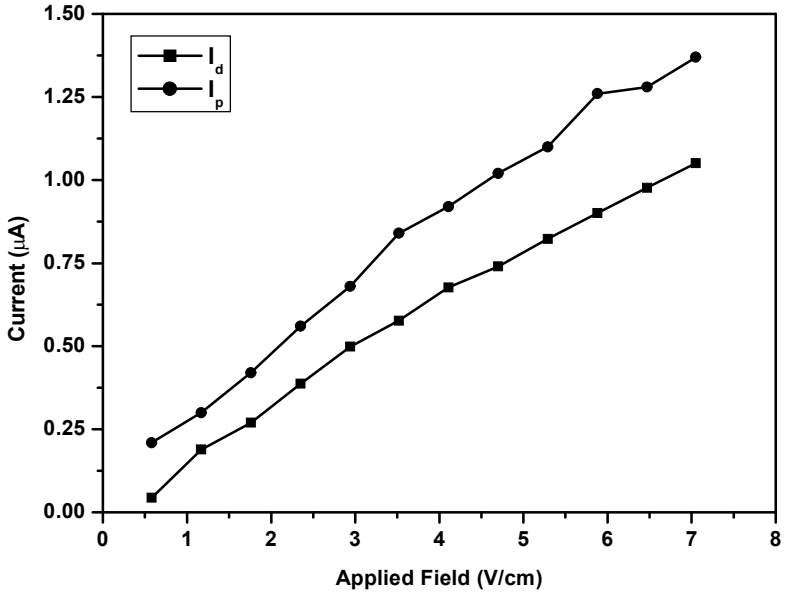

Figure. 10 Field dependent conductivity of BA single crystal

Conclusion

Benzoyl Alanine (BA) has been synthesized from acetone solvent by slow evaporation. The crystal structure of the compound has been solved using single crystal XRD. The presence of functional graphs and vibrational structure as confirmed through FTIR, ^{1}H and ^{13}C NMR spectral analyses. Thermal analysis was carried out and it is observed that the crystal is stable upto 220°C. The powder SHG efficiency indicates that BA crystals show efficiency of about two times that of KDP. The optical transmittance window is good enough for the production green laser by frequency conversion. The dielectric studies ascertain that the crystal has lesser defects. From the photoconductivity studies the positive photoconductivity nature of the sample is confirmed.

Acknowledgements

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References:

[1] Abraham Rajasekar S, Thamizharasan K, Jesudurai Joe G M, Prem Anand D and Sagayaraj P (2004) The role of metallic dopants on the optical and photoconductivity

properties of pure and doped potassium pentaborate (KB5) single crystals. Mater. Chem. Phys. 84 (1), 157-161.

[2] Kitazawa M, Higuchi R, Takahashi M, Wada T and Sasabe H (1994) Ulraviolet generation at 266 nm in a novel organic nonlinear optical crystal: 1-pyrrolidone-2-carboxylic acid. Appl. Phys. Lett. 64 (19), 2477-2479.

[3] Misoguti L, Bagnato V S, Zilio S C, Varela A T, Nunes F D, Melo F E A and Mendes Filho J (1996) Optical properties of L-alanine organic crystals. Opt. Mat. 6 (3), 147-152.

[4] Wang W S, Aggarwal M D, Choi J, Gebre T, Shields Angela D, Penn Benjamin G and Frazier Donald O (1999) Solvent effects and polymorphic transformation oforganic nonlinear optical crystal L-pyroglutamic acid in solution growth processes: I. Solvent effects and growth morphology. J. Cryst. Growth 198-199 (1), 578-582.

[5] William Silfvasat T (1998), 'Laser fundamentals', Cambridge University press edition, Cambridge.

[6] Haja Hameed A S, Ravi G, Dhanasekarn R and Ramasamy P (2000) Studies on organic indole-3-aldehyde single crystals. J. Cryst. Growth 212 (1-2), 227-232.

[7] Zaccaro J, Baruchel J and Ibanex A (1999) Crystalline perfection of 2-amino-5 nitropyridinium dihydrogenphosphate-arsenate hybrid crystals for non-linear optical properties. J. Mater. Chem. 9 (2), 403-407.

[8] Fu A –Y and Wang D –O (2005) N-Benzoylalanine. Acta Cryst. E61 (8), o2336-o2337.

[9] Fu A –Y and Wang D –O (2005) N-Acetyl-N-phenylglycine. Acta Cryst. E61 (8), o2504-o2505.

[10] Xavier Francis P and Goldsmith George J (1995) Photoconductivity of iodine-doped single crystals of phthalocyanine. Bull. Mater. Sci. 18 (13), 283-287.