GROWTH, OPTICAL, THERMAL AND MECHANICAL STUDIES OF O-PHENELYENEDIAMINIUM BENZOATE SINGLE CRYSTAL

A.Syed Mohammed Mujaheer[1], G. Foize Ahmad[2], M.Nizam Mohideen[3], I.Md.Zahid[4], M.Gulam Mohamed[5]

[5]PG & Research Department of Physics, The New College, Chennai, India

Abstract

o-Phenylenediamine Benzoate (PDB) was synthesized from o-Phenylenediamine as donor and Benzoic acid as acceptor. PDB crystals were grown by solution growth technique. The cell parameters and crystalline perfection of the grown crystal were studied by single crystal and high resolution X-ray diffraction analyses. The title compound was classified into orthorhombic crystal system with non-centrosymmetric $P2_12_12_1$ space group. The optical transmission properties of the crystal were studied by UV–Vis spectral analysis. PL spectral study revealed the transition mechanism of ions, where a sharp peak observed at 399 nm respectively. The second harmonic generation efficiency of the grown crystal was studied by Kurtz-Perry test. Thermal and Mechanical stability of the material was identified using TG-DTA and Vicker's Microhardness test..

Index Terms: Crystal growth, Optical, Thermal, Mechanical.

I. INTRODUCTION

Predominantly, organic crystals built from acid–base complexes have captivated the attention of many research groups due to their promising applications in integrated photonics, THz wave generation and detection. Efficient second-order nonlinear optical materials require optimization of acentric orientation of the molecules in the crystalline lattice or in a polymer matrix. One of the added advantages of organic materials is that the chemical structure with large physical structural diversities desired for required NLO properties can be modified. In addition to this crystal structures which belong to non-centrosymmetric class for the application of quadratic nonlinear optical effects and crystals having active SHG efficiency is given high priority [1][2]. The complexation of o-phenylenediamine and its derivatives has shown interesting properties with compounds and has found wide range of applications in material science, such as magnetic, fluorescent and dielectric behaviors [3]. The asymmetrical unit of the title compound consists of one benzene-1,2-diamine cation and one benzoic acid anion and as expected during synthesis the carboxyl acid group has protonated one of the amine N atom. In the present investigation, o-Phenelyenediaminium Benzoate single crystal was grown using slow evaporation technique and the grown material was subjected to optical, thermal and mechanical characterization.

II. EXPERIMENTAL

A. Materials, Methods and Growth

o-Phenelyenediaminium Benzoate (PDB) was synthesized from o-Phenylenediamine ($C_6H_8N_2$.,10.81 g) as donor and Benzoic acid ($C_7H_6O_2$.,12.21 g) as acceptor by dissolving in 100 ml of ethanol. The synthesis scheme is shown in Fig. 1.

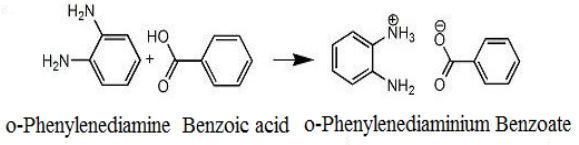

Figure 1. Synthesis scheme of PDB

The solution was allowed to stir for 8 hrs. to obtain homogeneity and then filtered using gravity filtration method. The filtered saturated solution was covered by using polythene sheet with single perforation at the center of the beaker and it was kept in constant temperature bath at 35°C in clean environment for evaporation. After a period one week, colorless shaped crystal of the title compound PDB was harvested from the beaker. Photograph of as grown crystal is shown in Figure 2.

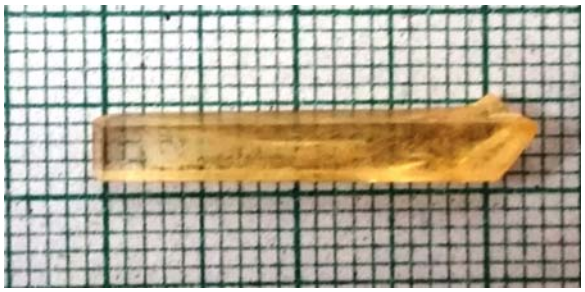

Figure 2. Photograph of as grown PDB crystal

B. Solubility Studies

Solubility is an important parameter, which converses the growth procedure. If the solubility is too high, it is difficult to grow bulk single crystals with optical quality and if too low ,it restricts the size and growth rate of the crystals. Initially, the solubility of the PDB was studied by using different solvents in pure or mixed forms to understand the growth parameters of PDB. The various combinations of solvents were taken on a trial and error basis, which were water, ethanol, methanol, acetonitrile, methanol-water, acetonitrile-water and methanol-acetonitrile. But, PDB crystal formation was observed in the ethanol solvent system, and for other systems, the crystallization rarely appeared. In order to evaluate and optimize the growth parameters, the solubility of PDB in ethanol was determined using gravimetric analysis for different temperatures namely 30 ºC - 50ºC. The solubility of PDB exhibits good and positive temperature gradient solubility in ethanol as a function of temperature as shown in Figure 3.

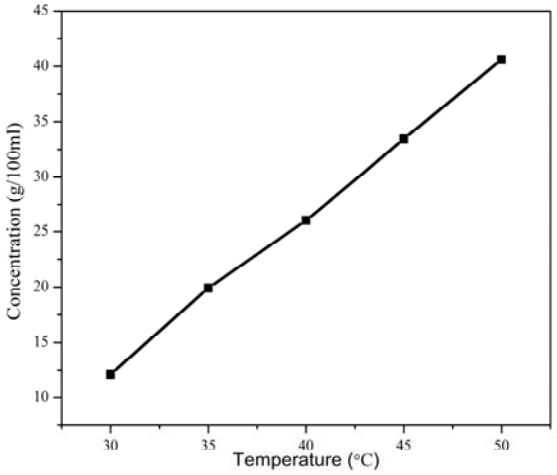

Figure 3. Solubility of PDB

III. RESULTS AND DISCUSSION

A. X-Ray Diffraction Studies

Single crystal X-ray diffraction data of PDB was elucidated using ENRAFNONIUS CAD-4 single crystal X-ray diffractometer. X-ray diffraction analysis was carried using the good quality single crystal of PDB in order to reveal the unit cell parameters, space group and crystal system. It is revealed from the analysis that the PDB crystal belongs to orthorhombic crystal system with P 2_1 2_1 2_1 non-centrosymmetric space group. The estimated cell dimension are a=6.0324(7) Å, b = 12.172 (1) Å , c =16.332 (4) Å , V = 1221.0 (5) $Å^3$ and it agree very well with the reported data [4]

B. High Resolution X-Ray Diffraction

DC curve recorded for diffraction plane using $MoK_{\alpha 1}$ radiation for a typical PDB single crystal specimen is shown in Figure 4. On close observation, it is realized that the curve is not a single peak. On deconvolution of the diffraction curve, it is clear that the curve contains one additional peaks. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles, which is 53 arc s. away from the main peak (highest intensity peak) on the right side of the spectrum. This additional peak correspond to internal structural low angle boundaries (tilt angle > 1 arc min. but < 1 deg.) [5]. The full width at half maximum (FWHM) of the main peak 37 arc s and very low angle boundary is 49 arc s respectively. The relatively low values of FWHM of the grains in

comparison with that of the real crystals, depicts that the crystalline perfection is good. It may be mentioned here that such low angle boundaries could be detected in the diffraction curve only because of the high-resolution of the diffractometer used in the present investigation or entrapment of solvent molecules, thermal fluctuations and/or mechanical disturbances during the growth process. The influence of such defects may not influence much on the NLO properties. However, a quantitative analysis of such unavoidable defects is of great importance particularly in case of phase matching applications [6].

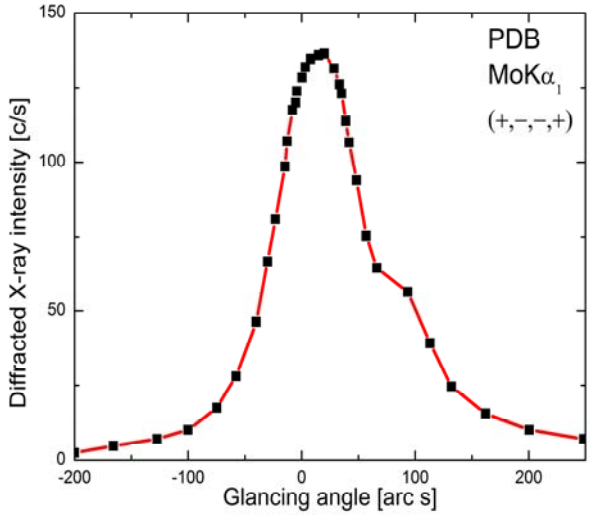

Figure 4. HRXRD spectrum of PDB

C. UV-Vis Transmission

Ultraviolet-visible transmittance studies was performed on the 1mm thick PDB crystal sample and the spectrum recorded is in the wavelength range 190-900 nm as shown in Figure 5. The lower cut-off wave length was found to be 290 nm and the material was transparent up to 67%.

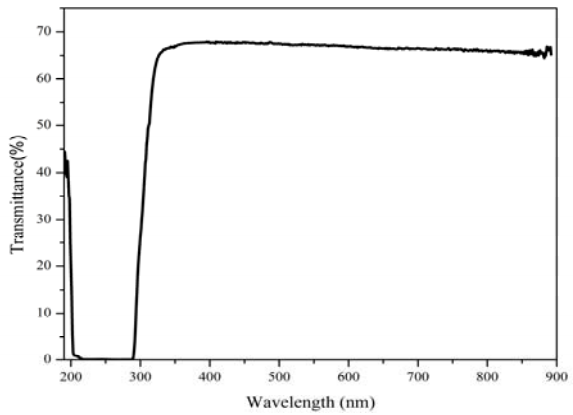

Figure 5. UV-Vis transmission spectrum

D. Optical bandgap energy (E_g) calculation

The optical absorption coefficient (α) was calculated using the relation,

$$\alpha = (1/d) \log (1/T) \quad (1)$$

where d is the thickness of the crystal and T is the transmittance. Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\upsilon$),

$$h\upsilon\alpha = A\,(h\upsilon - E_g)^{1/2} \quad (2)$$

where A is a constant, E_g is the optical band gap, h is the Planck's constant, and υ is the frequency of the incident photons [7]. The band gap of grown PDB crystal was estimated by plotting $(\alpha h\upsilon)^2$ versus $h\upsilon$ and it is shown in Fig.6. The band gap energy of grown PDB crystal was found to be 4.25 eV. Therefore, from the band gap energy, it is observed that the grown material has added advantages for optical and optoelectronic device applications.

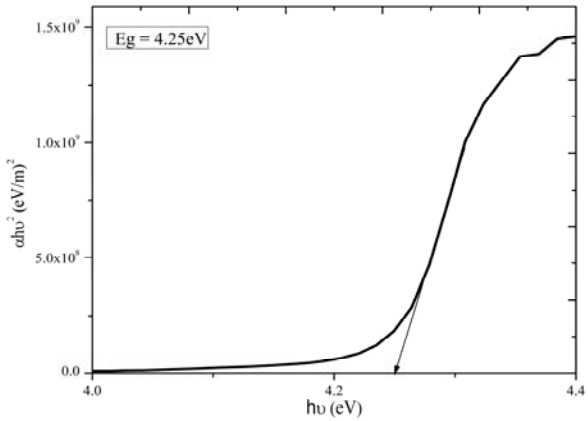

Figure 6. Tauc's plot of PDB

E. Photoluminescence

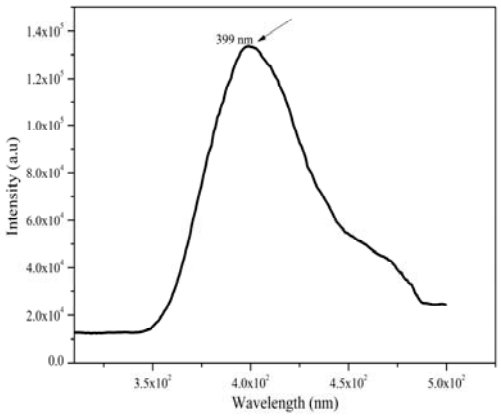

Figure 7. PL spectrum of PDB

An intense emission band has appeared in the range 290–500 nm, owing to the emission of ultraviolet radiation. PL spectrum of the grown PDB crystal sample (Fig.6) showed a sharp emission peak at 399 nm (3.10 eV). On the short-wavelength end of the visible spectrum is the near ultraviolet (near-UV) band ranging from 320 to 400 nm which corresponds to the near band-edge exciton of crystal sample [8]. Potentiality of the grown material in UV filters and optoelectronic device application was confirmed from the PL analysis.

F. Thermal Analysis

Thermogravimetric analysis measures the change in mass of a sample on heating and to study the crystallization. TG-DSC trace of PDB is shown in Fig.7. From the obtained curve it is observed that decomposition takes place in two stages. The first stage occurred within the range 190–280° C corresponds to 38.33 % weight loss of P_2H_4, NH_3 and NO_2. The second composition stage is due to the decomposition of CO occurred within the range 281-320°C with weight loss 13.99%. The final stage corresponds to the decomposition of residual species. From the DSC curve, the sharp peak of endothermic observed at 183.38 °C represents the melting point of PDB compound.

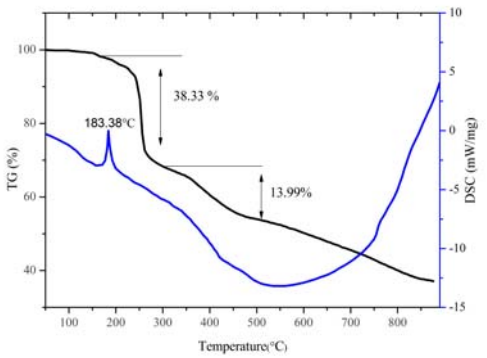

Figure 8. Thermal spectrum of PDB

G. Mechanical Stability

The measurement of hardness of a material is very important property especially for post growth processes and also for device fabrications. Indentations were made on flat polished plane of the PDB crystal at room temperature for different loads 10, 25, 50 and 100 g using Vicker′s hardness tester fitted with a diamond intender and a light microscope. The Vicker′s microhardness number (H_v) was calculated using the relation,

$$H_v = 1.8544\ P/d^2\ (kg/mm^2) \quad (3)$$

where P is the applied load in g, d is the diagonal length of indentation impression in mm and H_v is the hardness number in kg/mm^2. Figure 9 illustrates that the Vicker′s hardness number varies with the applied load and it clearly indicates that PDB crystal possesses good mechanical strength. The size of indentation and load are related through Meyer's law

$$P = k_1 d^n \quad (4)$$

(or)

$$\log P = \log k_1 + n \log d \quad (5)$$

where k_1 is the standard hardness constant and n is the Meyer index (or work-hardening coefficient). The plot of log P Vs. log d, drawn with fitting data before cracking (after least square fitting) gives a straight line in Figure 9., which is in good agreement with Meyer's law. The value of 'n' found from the slope of the graph is 1.88. According to Onitsch and Hanneman [9][10], the grown PDB crystal belongs to the category of soft materials.

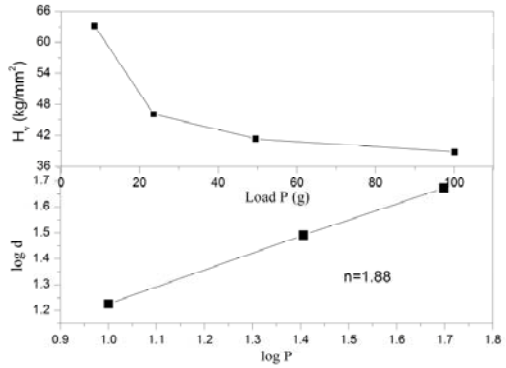

Figure 9. Hardness plots of PDB

Hays and Kendall's theory of resistance pressure, explains the relationship between indentation test load (P) and indentation size (d).

$$P - W = k_2 d^2 \quad (6)$$

where W is the sample resistance pressure (or Newtonian resultant pressure) and it represents the minimum load that causes an indentation and k_2 is an another constant.

$$W = k_1 d^n - k_2 d^2 \quad (7)$$

The elastic stiffness constant was calculated using the Wooster's empirical relation,

$$C_{11} = (H_v)^{7/4} \quad (8)$$

which gives an idea about the tightness of bonding between the neighboring atoms. The values of C_{11} are also given in Table 4.4. From the hardness value, the yield strength 'σ_v' of a material was calculated using the relation,

$$\sigma_v = H_v / 3 \quad (9)$$

Load (g)	H_v (kg.mm^{-2})	Meyers index (n)	C_{11} (GPa)	σ_v (GPa)
10	64.35	1.8	8.99×10^{11}	21.45
25	45.61	1.8	8.79×10^{10}	15.20
50	41.18	1.8	5.91×10^{10}	13.72
100	38.95	1.8	3.79×10^{10}	12.98

F. Second Harmonic Generation

The second harmonic generation efficiency was studied by employing the Kurtz and Perry powder technique [11] which remains a valuable tool for the initial screening materials for SHG property. Q-switched Nd:YAG laser with the fundamental beam of 1064nm, repetition rate of 10 Hz and pulse width 10 ns was used to measure the SHG efficiency of PDB. The standard reference material potassium dihydrogen phosphate (KDP) was used to compare the SHG efficiency. The optical signal incident on a photomultiplier tube was converted into voltage output.

The SHG output signal intensity of 48.7 mV was measured for PDB crystalline powder while that for standard KDP crystalline sample was 17.4 mV for an input energy of 5 mJ/pulse. Thus it is clear that the SHG efficiency of PDB was found to be 2.79 times greater than that of standard reference material KDP.

IV. CONCLUSION

The title compound of o-Phenylenediaminium Benzoate was successfully synthesized and the single crystal was grown by slow evaporation solution growth method. Solubility study was carried out to optimize growth parameters. Single crystal X-ray diffraction study confirms orthorhombic crystal system with space group $P2_12_12_1$. Crystalline perfection of the grown crystal were confirmed by High Resolution X-ray Diffraction study. UV cut-off wavelength (290 nm) and transparency (above 67%) over the entire range of UV–visible region show that PDB is a good candidate for NLO applications. Band gap energy was calculated using Tauc's plot (4.25 eV). PL spectral study revealed the electron excitation wavelength (399 nm) for the grown PDB crystal. Thermal analysis confirmed that the material is thermally stable upto 188.83°C. Microhardness test confirmed the soft nature of synthesised material. Elastic stiffness constant value (C_{11}) and yield strength (σ_v) were calculated for the grown crystal. The second harmonic generation relative efficiency of the grown crystal was found to be 2.79 times greater than that of KDP crystal. Hence, the present investigation reveals that PDB crystal can be useful in the domain of nonlinear optical applications.

REFERENCES

[1]. Nalwa. H. S and Miyata. S, Nonlinear Optics of Organic Molecules and polymers, Boca Raton, FL, CRC Press, 1996.

[2]. Chemla. D.S, Zyss. J, Nonlinear Optical Properties of Organic Molecules and Crystals ,Academic Press. New York, 1987.

[3]. Zahid. Md. I, Amirtha Kumar. C, Mohan Kumar. R, "Crystal Growth, Spectral and Optical Studies of 2-Aminoanilinium Benzoate Single Crystal," MMSE. Journal., vol.9, no.2, pp. 126 – 130, April 2017.

[4]. Zhang.Y, " 2-Aminoanilinium Benzoate," Acta Cryst. E., vol.66, pp. o3296, Nov. 2010.

[5]. Lal. K, Bhagavannarayana. G, "A High resolution diffuse X-ray scattering study of defects in dislocation-free silicon crystals grown by the float zone method and comparison with Czochralski grown crystals, " J. Appl. Crystallogr. vol. 22, pp.209–215, 1989.

[6]. Zahid. Md. I, Amirtha Kumar. C, Mohan Kumar. R "Synthesis, Studies on Crystal

Growth and Optical properties of novel organic material: o-Phenylenediaminium bis hydrogen phosphonate," Materials Letters, vol. 209, pp. 167–170, 2017

[7]. Rai.R.N, Mudunuri.S.R, Reddi.R.S.B, Satuluri.V.S.K, Ganeshmoorthy.S, Gupta.P.K, "Crystal growth and nonlinear optical studies of m-dinitrobenzene doped urea", J. Cryst. Growth, vol. 321, pp.72-77, 2011.

[8]. Reichman J, "Handbook of Optical Filters for Fluorescence Microscopy," Chroma Technology Corp, USA, 1998.

[9]. Onitsch. E.M, "Systematic metallographic and mineralogic Structures," Mikroscopia, vol. 2, pp.131-151, 1947

[10]. Hanneman. M, Metall, Manchu, vol.23, pp.135-139, 1947.

[11]. Kurtz.S.K, Perry.T.T, "A Powder Technique for the Evaluation of Nonlinear Optical Materials," *J. Appl . Phys., vol.* 39, pp. 3798-3813, 1968.