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A STUDY ON THE GROWTH AND CHARACTERIZATION OF PURE AND PYRENE DOPED BENZIMIDAZOLE SINGLE CRYSTAL

M. J. Jarald Brigit Gilda[1], M. Ambrose Rajkumar[2] and D. Prem Anand[2*]

[1] Physics Research Centre, Department of Physics,
St. Xavier's College (Autonomous), Palayamkottai- 627002,
Tamilnadu, India.

*E-mail: devarajanpremanand@gmail.com

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Abstract. An attempt was made to grow nonlinear optical single crystals of pure benzimidazole (BIZ) and pyrene doped benzimidazole (PDBIZ) by slow evaporation solution growth technique using dimethyl formamide as a solvent. Single crystal X-ray diffraction analysis showed that both the grown crystals belong to orthorhombic crystal system with the space group pna21. The various functional groups in the pure and doped crystals were identified using Fourier transform infrared (FTIR) spectral analysis. The structure has been confirmed by nuclear magnetic resonance (NMR) spectral analysis. The Ultra violet-visible-near infrared (UV-vis-NIR) absorption spectrum shows good optical transparency in the visible region. The thermal stability and melting point of the grown crystals were found by thermogravimetric and differential thermal analyses. The mechanical strength of the grown crystals was evaluated by Vickers microhardness studies. The second harmonic generation (SHG) efficiency of BIZ and PDBIZ were found to be 1.05 and 1.075 times greater than the value of potassium dihydrogen phosphate (KDP).

Keywords: Crystal growth, X-Ray diffraction, FTIR spectroscopy, Nuclear magnetic resonance, UV-vis-NIR spectroscopy, SHG efficiency.

1. INTRODUCTION

After the invention of laser, nonlinear optical phenomena have made a big revolution in the field of optics. Nonlinear optics is the forefront of current research because of its important role in second harmonic generation, frequency conversion, optical modulation and optical parametric oscillation in the areas such as telecommunications, signal processing and optical

interconnections [4,5,15]. Crystallization of several families of organic compounds is of great interest for nonlinear optical applications in the visible and ultra violet regions of the spectrum. Organic crystals with large second order nonlinear susceptibilities are of great interest because of their potential to use as optical parametric amplifier and optical parametric oscillator in the infrared region. Many organic nonlinear optical single crystals with different properties have been reported. But new nonlinear optical single crystals with superior properties are required in order to satisfy the latest technological development [1-3]. In the present investigation, we report the influence of pyrene on the growth and characterization of benzimidazole single crystal; as dopants play a vital role in modifying the properties of organic single crystals [14]. Benzimidazole is a heterocyclic aromatic organic compound formed by the fusion of benzene and imidazole [13]. It is found to have a fused two ring conjugated system with six carbon atoms in aromatic ring and five atoms in the other, having the molecular formula of $C_7H_6N_2$ and molecular weight of 118.3. The smaller ring has nitrogen atoms in the 1 and 3 positions. It crystallizes in non-centrosymmetric nature with orthorhombic crystal structure and space group pna21 [10]. The nonlinear optical single crystal of benzimidazole grown by Vijayan et.al [10] confirms the structure, functional groups, thermal and optical properties. The green emission of benzimidazole using Nd-YAG laser as a source was confirmed [19, 23]. The crystal perfection has been increased to a large extent after thermal treatment of the crystal grown by vertical Bridgmann technique. The carbon present in the grown crystals was identified [21, 22]. The SHG efficiency is found to be 4.5 times that of KDP single crystal [6]. The 50 MeV Si^{7+} ion irradiation induced modifications on structural, dielectric, optical and mechanical properties of Vertical Bridgman grown benzimidazole (BMZ) crystals were studied by Kanagasekaran et al [12]. UV-vis studies reveal the decrease in bandgap values and defects on irradiation. Two different types of second harmonic generation have been observed in a benzimidazole single crystal by Bree and Zwarich [8]. Pyrene is a polycyclic aromatic hydrocarbon consisting of four fused benzene rings, resulting in a flat aromatic system. The chemical formula is C_{16} H_{10}. It has low water solubility, high adsorption coefficient and high stability of the complex aromatic ring structure [9]. An attempt was made to grow pure benzimidazole single crystal and pyrene doped benzimidazole single crystal using dimethyl formamide (DMF) as solvent. The grown crystals were subjected to various studies like X-ray diffraction, Fourier Transform Infrared (FTIR) spectral analysis, Nuclear Magnetic Resonance (NMR) spectral analysis, UV-vis-NIR spectral analysis, Thermal analysis, Microhardness and second harmonic generation.

2. Experimental procedure

2.1. **Crystal growth.** Commercially available AR grade benzimidazole was dissolved with dimethyl formamide solvent with 1M concentration. The solution was stirred for eight hours to get a homogeneous mixture. It was then filtered using Whatmann filter paper in order to remove the suspended impurities. The filtered solution was hermetically sealed to ensure slow evaporation and kept without disturbance at a temperature of 33°C. After four months, seed crystals are formed which were left for two more weeks to grow into large size, and harvested. With 1M concentration of benzimidazole solution, 0.3 wt% of Pyrene was added and the same

procedure was carried out as before. Good quality single crystal of PDBIZ of considerable size was harvested after five months. The photograph of as-grown pure BIZ and PDBIZ single crystals are shown in Fig.1 and Fig.2

FIGURE 1. As-grown single crystals of BIZ single crystals

FIGURE 2. As-grown single crystals of PDBIZ single crystals

3. RESULTS AND DISCUSSION

Parameter	BIZ	PDBIZ
Crystal structure	Orthorhombic	Orthorhombic
Space group	Pn21	Pna21
Cell parameters	a= 6.806 Å b= 6.939 Å c= 13.49 Å α= 90 ° β= 90 ° γ=90 °	a=6.841 Å b=6.967 Å c= 13.54Å α= 90 ° β= 90 ° γ=90 °
Volume	637 Å^3	645 Å^3

TABLE 1. Cell parameter of BIZ and PDBIZ single crystal

3.1. **Single crystal X- ray diffraction.** The as-grown crystals of pure benzimidazole (BIZ) and pyrene doped benzimidazole (PDBIZ) were subjected to X-ray diffraction analysis using Enraf Nonius CAD4 X-ray diffractometer in order to determine the crystal structure and cell parameters. The unit cell parameters of BIZ obtained are in good agreement with the reported

value [17]. The calculated lattice parameter values of pure BIZ and PDBIZ are presented in Table 1. The study reveals that both the crystals belong to orthorhombic crystal system with a noncentrosymmetric space group pna21. An increase in the values of the cell parameters as well as volume of PDBIZ single crystal suggests that pyrene has entered into benzimidazole crystal lattice.

3.2. **UV-vis-NIR spectral analysis.** The optical absorption spectrum of as grown single crystals of BIZ and PDBIZ has been recorded using UV-vis spectrophotometer Systronics,2202 in the range 200 1100 nm, to find the suitability of crystal for optical applications. The spectra obtained for BIZ single crystal and PDBIZ single crystal are shown in Fig.3. The cut-off wavelength of BIZ single crystal was found to be 300 nm which is in good agreement with the reported value (Ramesh Babu et.al). The cut- off wavelength of PDBIZ single crystal was found to be 372 nm. The large absorption of PDBIZ single crystal due to electronic transitions above 300nm is the key requirement for frequency doubling using diode and solid state lasers [23]. Also both the grown crystals show good transparency in the visible region which enables it to be a good material for optoelectronic applications [16].

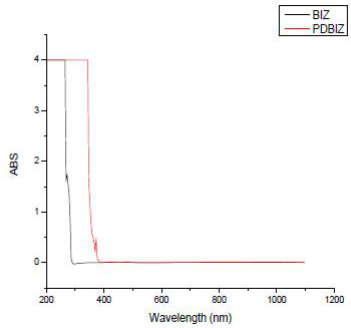

FIGURE 3. UV-vis-NIR spectra of BIZ and PDBIZ single crystals

3.3. **FTIR Spectral Analysis.** The FTIR spectral analysis has been carried out to analyze the chemical bonding and molecular structure of the compound. The FTIR spectra recorded in the range 550 4000 cm^{-1} using Jasco-FTIR 4100/Japan spectrometer of BIZ single crystal and PDBIZ single crystal are shown in Fig.4 and Fig.5, respectively. From the known values of the positions of the peaks, the functional group of both the crystals was assigned [17, 7].In the spectrum of BIZ single crystal, the broad banded absorption ascribed to the N-H stretching vibrations indicates the presence of polymeric association. The bands near 2600-3200 cm^{-1} in the spectra are ascribed to a strong hydrogen bond of the type N-HN showing proton transfer. The C-H stretching peaks are evident between 3000 -3100 cm^{-1}. The imines show peak at 1655.59 cm^{-1} due to C=N- stretching. The aromatic ring skeletons of benzimidazole are indicated by the peaks at 1479.13, 1455.99, 1405.85 and 1361.498 cm^{-1}. The C-N stretching vibration is observed at 1244.83 cm^{-1} and the C-H bending vibrations are observed below 1200 cm^{-1}. A

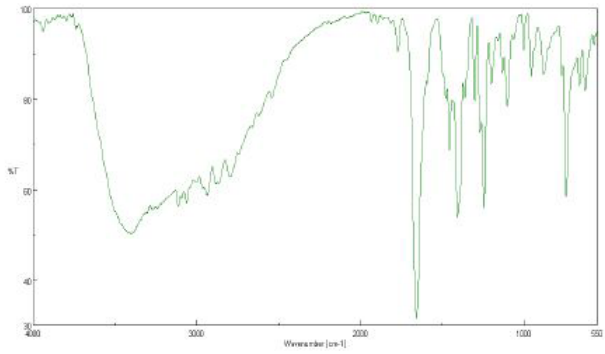

FIGURE 4. Fourier transform infrared (FTIR) spectra of BIZ and PDBIZ single crystal

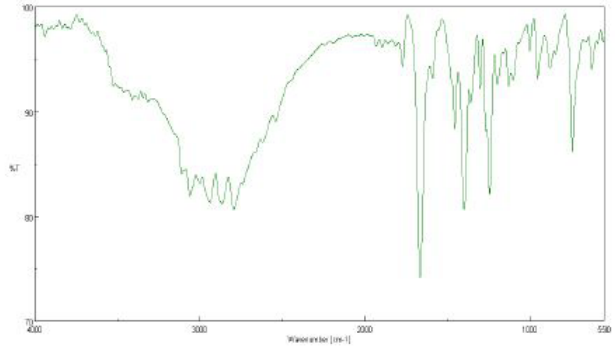

FIGURE 5. Fourier transform infrared (FTIR) spectra of BIZ and PDBIZ single crystal

single intense peak at 743.424 cm^{-1} indicates the ortho substitution of benzene ring possessing four hydrogen atoms. In the spectrum of PDBIZ single crystal, the broad envelope between 2600 and 3100 cm^{-1} is due to the overlapping of N-H and C-H stretching modes. The number of peaks in this region suggests that doping of pyrene has changed the benzimidazole lattice. Also there is a shift in the frequency band in the lower frequency region. The C=N- stretching peak is observed at 1665.23 cm^{-1} and the C-N stretching vibration is observed at 1243.86 cm^{-1}. The FTIR spectrum suggests that pyrene has entered in to benzimidazole crystal lattice.

3.4. **NMR spectral analysis.** The molecular structure of benzimidzole is shown in Fig.4.The ^{1}H NMR and ^{13}C NMR spectral analyses are the two important analytical techniques used to study the structure of organic compounds. The ^{1}H NMR spectra recorded with Bruker 300 MHz spectrometer using deuterated DMSO as solvent for BIZ and PDBIZ single crystals are given in Fig.6, and Fig.7 respectively. The proton NMR spectrum of BIZ shows four different signals which indicate four different hydrogen atoms. The singlet at 12.48 ppm corresponds to the hydrogen on the N-H group which is not coupling with other H atoms. The peak at 8.25

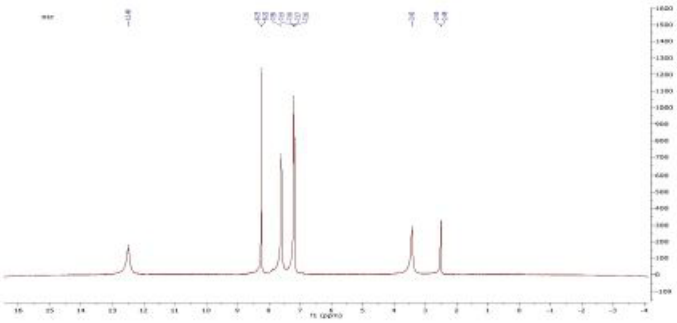

FIGURE 6. ^{1} H NMR spectra of BIZ single crystals

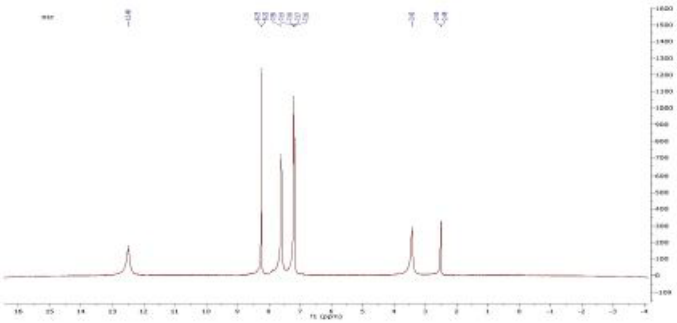

FIGURE 7. ^{1}H NMR spectra of PDBIZ single crystals

ppm is attributed to the C-H in the imidazole ring. The peak at 7.59 ppm corresponds to H at the para position of the benzene ring and the other peak between 7.16 and 7.19 ppm corresponds to the two equivalent hydrogen atoms in the ortho and meta position of the ring. The peaks at 2.50 and 3.43 ppm correspond to the solvent. In the proton NMR spectrum of PDBIZ, the peaks appear to be small as the intensity range on the Y-axis is taken to be large. All the peaks corresponding to BIZ single crystal are likely to appear in the spectrum. In addition, there are many peaks between 8.55 and 8.03 ppm which indicates the proton of pyrene has been accepted by benzimidazole. The ^{13}C NMR spectra of BIZ and PDBIZ are presented in Fig.8 and Fig.9, respectively. In the carbon NMR spectrum of BIZ single crystal, the peak at 142.80 ppm corresponds to the two bridging carbon in the benzene ring and the peak at 115.21 is assigned to the single carbon lying between the two imidazole nitrogen. The remaining four carbons in the benzene ring produce signal at 122.59 ppm and the peaks between 39.49 and 41.16 ppm are due to the deuterated solvent. In the carbon NMR spectrum of PDBIZ single crystal, the carbons in the aromatic ring of benzimidazole and pyrene appears between 131.48

and 124.68 ppm. The two bridging carbon appears at 142.80 ppm. Hence it is evident from both proton and carbon NMR spectra that pyrene compound has incorporated into the BIZ lattice.

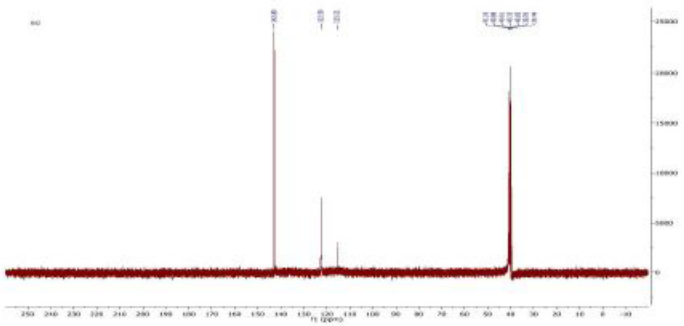

FIGURE 8. ^{13}C NMR spectra of BIZ single crystals

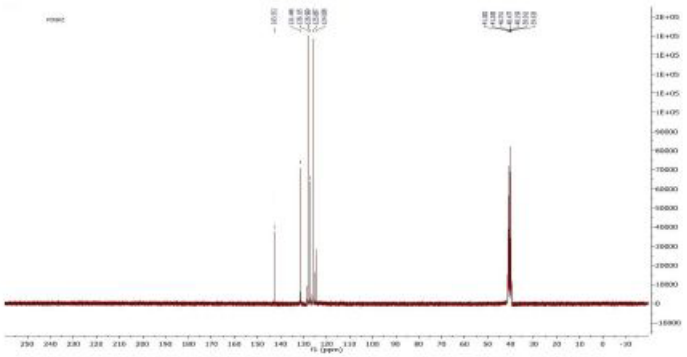

FIGURE 9. ^{13}C NMR spectra of PDBIZ single crystals

3.5. **Thermal Analyses.** The thermal studies were performed on the grown crystals to study the thermal stability and melting point of the material. The analyses were carried out in nitrogen atmosphere in the temperature range of 25°C 800°C with a heating rate of 10°C/min. Fig.10 shows the TG/DTA graph of BIZ single crystal. The thermo gravimetric analysis (TGA) of BIZ single crystal shows no weight loss up to 170°C. A gradual weight loss that occurs between 170°C to 221°C is due to evaporation of the sample and a steep weight loss around 250°C is due to the decomposition of the sample. Beyond 290°C, the sample completely decomposes without any residue. The differential thermal analysis (DTA) shows an endothermic peak at 173°C which indicates the melting point of BIZ single crystal. Another peak at 271°C indicates the complete decomposition of the sample. Fig.11 shows the TG/DTA graph of PDBIZ single crystal. The thermo gravimetric analysis of PDBIZ shows a very small percentage loss in the beginning and then no loss specific loss up to 160°C. Beyond that the sample decomposes

gradually. The endothermic peak at 151°C indicates the melting point of PDBIZ single crystal. The DTA analysis shows no endothermic or exothermic peak below the melting point for both the crystals which suggests the absence of any isomorphic transformation below the melting point. Also, it is found that the thermal stability and melting point of PDBIZ single crystal is less than that of BIZ single crystal and its application for NLO can be considered below the melting point.

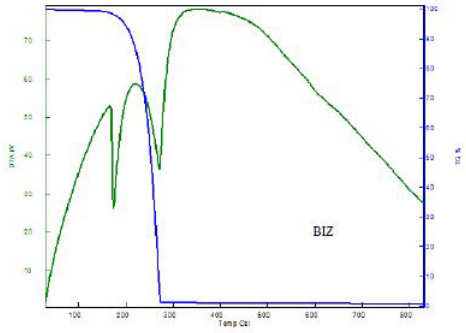

FIGURE 10. TG/DTA curve of BIZ single crystal

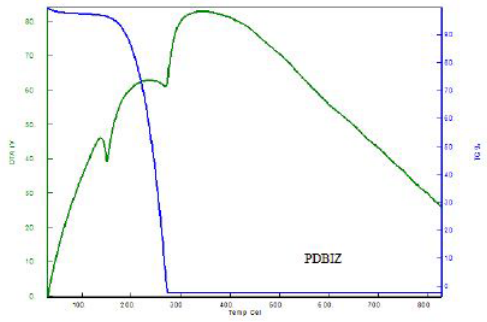

FIGURE 11. TG/DTA curve of PDBIZ single crystal

3.6. **Microhardness studies.** Mechanical strength of BIZ and PDBIZ single crystals was studied using a Leitz Weitzler Vickers microhardness tester fitted with a Vickers diamond pyramidal indenter attached to an incident light microscope. The indentations were made at room temperature with a constant indentation time of 5s. The diagonal length of the indentation impression was measured using a microscope. In order to get accurate results for each applied load, three indentations were made on the sample and the average diagonal length (d) of the indenter impressions was estimated. The hardness Hv of the crystal was calculated using the following relation

$$H_v = 1.8544\ P/\ d^2\ Kg/\ mm^2$$

where P is the applied load and d is the mean diagonal length of the indenter impression. Variation of hardness number with applied load for both BIZ and PDBIZ single crystals are shown in Fig.12. It is seen from figure that the hardness increases as the load is increased. From the results it is observed that the hardness of BIZ single crystal increases when it is doped with pyrene. This increase in the hardness value of doped sample can be attributed to the incorporation of pyrene in the lattice of BIZ crystal. The addition of pyrene has enhanced the strength of bonding with BIZ and hence hardness increases.

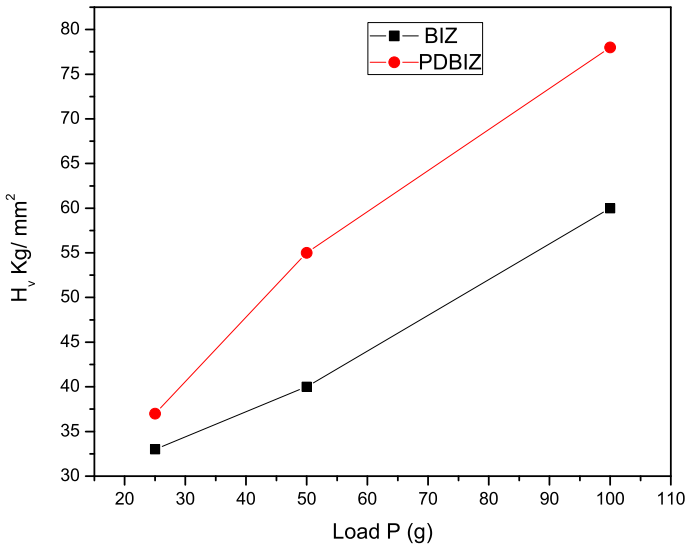

FIGURE 12. Variation of hardness number with applied load for PDBIZ single crystals

3.7. **Nonlinear optical test.** The as-grown crystals of BIZ and PDBIZ single crystals were subjected to nonlinear optical test in order to confirm the NLO property. Both the grown crystals were ground into fine powder and packed in capillaries of uniform bore and exposed to laser radiation of 1.1 mJ/pulse. A powder of KDP was taken as reference material. The output from the sample was allowed through a monochromater and was measured by means of a photomultiplier tube and oscilloscope assembly. The relative measured outputs from both the samples with respect to KDP are tabulated in Table.2. From the observation, it is found that the second harmonic efficiency of BIZ single crystal is 1.05 times and of PDBIZ single crystal is 1.075 times greater than that of KDP crystal. Moreover the efficiency of the doped crystal is greater than that of pure crystal. Hence it is evident both the grown crystals can be used for photonic device fabrication.

Sample	Powder Output
KDP	120
BIZ	126
PDBIZ	129

TABLE 2. Values of SHC power output

4. CONCLUSION

Single crystals of pure BIZ and PDBIZ were successfully grown by slow evaporation technique at room temperature. The lattice parameters determined by single crystal X-ray diffraction technique confirm both the pure and doped crystals belong to orthorhombic crystal system with space group Pna21. The UV-vis absorption spectrum reveals the transparency of both the crystals in the entire visible region and suggests its usefulness for nonlinear optical applications. The cut-off wavelength of PDBIZ is found to be larger than that of BIZ single crystal. The FTIR and NMR spectral analysis confirms the functional groups and the structure of the grown crystals. The thermal stability and melting point of the doped one is found to be less than the pure BIZ single crystal. Moreover the doping of pyrene into benzimidazole has enhanced the mechanical strength and SHG efficiency of benzimidazole single crystal.

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