

Growth, Structure and Spectroscopic Studies of an Organic Optical Material: Benzimidazole Benzimidazolium Picrate Crystal

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Abstract

Crystal engineers have focused to control the solid structures through electrostatic, charge transfer, hydrogen bonding interactions. In particular, organic crystals have very good device oriented characteristics like optical response and large optical polarizability for nonlinear optical applications. In this point of view, we have concentrated on the growth of Benzimidazole benzimidazolium picrate crystal by cost effective solution growth method. The specimen has been subjected to different characterization studies. The single crystal XRD confirms the triclinic crystal structure (P-1) and both linear and nonlinearity of the materials have been analysed through UV-visible and SHG studies. Molecular vibrations, polarisational vibrations and presence of various functional groups present in the material have been identified through FTIR and FT-Raman spectral studies. The high intense light radiation test was performed on the crystal and it was estimated to be 1.39 GW/cm². Copyright © VBRI Press.

Keywords: Single crystal, solution growth, FTIR; FT-Raman, LDT.

Introduction

Crystal growth of organic material participate an efficient frequency doubling, electro-optic modulator devices, frequency mixing process etc. [1, 2]. Growth of single crystal depends on solubility, availability of materials, physicochemical properties and shape [3]. Crystal complex is a neutral material as a result of proton exchange within the molecule on behalf of acid and base components [4]. The properties of solid state materials can be tuned through π - π interactions and hydrogen bonding in the organic materials. In particular, methyl group substituted benzimidazole nitrogen provides the suitable proton transfer to the acid material and thus finally forming a complex [5]. In recent past many researchers are working in the field of crystal growth using picric acid for the new organic network with efficient optical properties. Thus it is noted that the picric acid and benzimidazole nitrogen are involved in salt formation and many of the materials are crystallized in the non-centrosymmetric space group exhibits remarkable nonlinear optical phenomena [6-9]. In the present research work, we have been synthesized the new picric acid complex through mechano-chemical synthesis and crystals were grown by low temperature solution growth method.

Experiment

Synthesis and crystal growth

The precursors of high purity materials, Benzimidazole (Sigma Aldrich, 98 %) and picric acid (Sigma Aldrich, 98 %) are taken in the 2:1 molar ratio to obtain the product, Benzimidazole benzimidazolium picrate single crystal. The resultant salt was further recrystallized with acetone as a solvent and the saturated solution was filtered with a whatmann filter paper. The resultant solution was kept in a water bath which was maintained at 35 °C with a temperature accuracy of ± 0.01 °C using a temperature controller system. The growth solution was allowed for evaporation for nearly 20 days and the crystal was harvested consequent to 5 days. The reaction scheme is given in Fig. 1 and the cut-polished crystal of BZP with dimensions 15 × 7 × 2 mm³ is provided in Fig. 2.

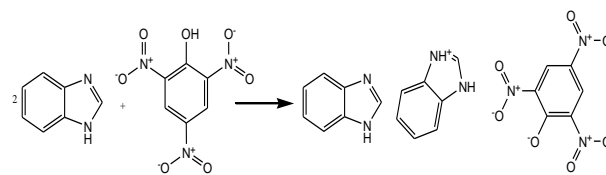


Fig. 1. Reaction scheme of BZP.



Fig. 2. Cut and polished BZP crystals.

Spectral and optical characterizations

An instrument Bruker Kappa APEX II with MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation was utilized to estimate the unit cell and other crystallographic parameters of BZP single crystal. JASCO FTIR 460 Plus was used for the vibrational analysis of the sample in the wavenumber region 4000-400 cm^{-1} at 400 K by KBr pellet technique and the sample powder was also studied for their polarization modes in the region 4000-400 cm^{-1} through FT-Raman, Bruker RFS instrument. The laser light withstanding power of the grown crystal was tested by a Nd: YAG laser source (Quanta ray model lab-170-10) with the pulse width of 6ns operating in the TEM00 mode.

Results and discussion

Single crystal X-ray diffraction study

The prepared single crystal specimen of suitable size (1mm) was subjected to a single crystal X-ray diffractometer for their structural analysis. The obtained results showed that the crystal belong to triclinic crystal system with the space group of P-1. The crystallographic parameters were found to be $a = 12.8293(4) \text{ \AA}$, $b = 11.2817(4) \text{ \AA}$, $c = 14.5416(5) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and unit cell volume is $2104.70(12) \text{ \AA}^3$. The determined results are quite matched with the reported literature [10].

FTIR spectral study

The vibrational FTIR spectrum of the sample BZP is shown in Fig. 3 and the corresponding band assignment are provided in Table 1. The N-H stretching vibrations are noted at 3312 cm^{-1} and 3126 cm^{-1} respectively which are the stretching modes of hydrogen against positively charged nitrogen [11]. Another N-H stretching mode is observed at 3226 cm^{-1} [12]. The modes of vibration at 3102 and 2825 cm^{-1} could be due to aromatic C-H asymmetric and symmetric stretching of Benzimidazole moiety. Like other aromatic nitro compounds, BZP crystal also exhibits two sharp absorption bands which revealed the asymmetric (1566 cm^{-1}) and symmetric (1363 cm^{-1}) stretching vibrations of NO_2 group. The charge transfer mechanism involved in the materials can be understood from the shifting of NO_2 peak from 1607 cm^{-1} (in pure

picric acid) to 1566 cm^{-1} (in BZP crystal). Thus the shifting of NO_2 peak to the lower wavenumber region shows that the increase of electron density on the picric moiety. The aromatic C=C stretching vibrations of Benzimidazole molecule are attributes their modes at 1566, 1415, 1363, and 1316 cm^{-1} respectively [13]. The vibration at 1165 cm^{-1} could be due to the presence of C-H in-plane bending benzimidazolium ring [14] and also the C-N stretching vibrations are observed at 1081 and 956 cm^{-1} respectively. The aromatic hydrogen atoms in the benzene ring show its band at 724 cm^{-1} and are called C-H out of plane bending vibrations [14]. Based on the above band assignments, it is found that the complex has been formed and the various modes of vibrations are completely acknowledged.

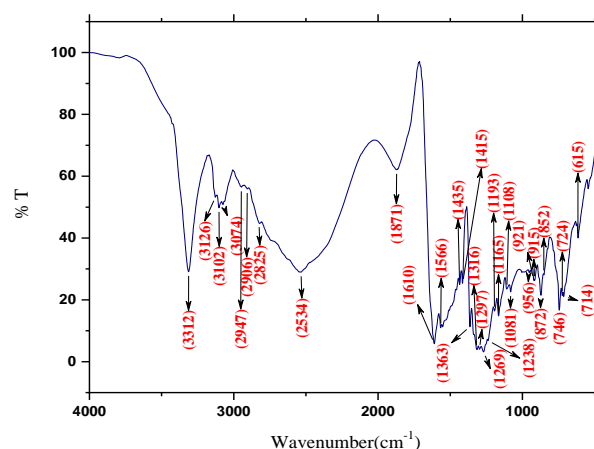


Fig. 3. FTIR Spectrum of BZP crystal.

Table 1. FTIR and FT-Raman band assignments of BZP crystal.

Wavenumber (cm^{-1})		Assignment
FT-IR	FT-Raman	
3312,3126	3124.92	N-H stretching
3102	-	N-H stretching
3089,3074,2947	3076.71	Aromatic C-H stretching
2825,2534	-	C-H symmetric stretching
1871	-	Stretching mode of carboxylate anion
1610	1611.20	C=C stretching
1566, 1363	1570.20,1552.95, 1364.37	NO_2 stretching
1415	1478.25. 1415.75	Phenyl stretching
1316	1337.72,1311.54	C-O stretching
1297,1269, 1193	1279.29	C-O stretching.
1165	1167.13, 1111.82	C-H in plane bending
1081,956,921	1078.31,1006.12, 944.92,917.40	C-N asymmetric stretching
872,746	886.85, 848.90, 821.99, 775.76	C-H out plane bending
724,714,615	724.85, 613.34	C-H out-plane bending

FT-Raman spectral study

The molecular vibrations of BZP material is also analysed through Raman spectral analysis which gives the structural and bonding informations. **Fig. 4** shows the FT-Raman spectrum of BZP molecule and their respective modes of assignments are listed in **Table 1**. A peak appeared at 3124.92 cm^{-1} is due to N-H bond vibrations and NO_2 stretching vibrations present in the molecule are observed at 1570.20 , 1552.95 and 1364.37 cm^{-1} respectively. The C-H in plane bending vibrations of the benzimidazolium ring present in the compound has been identified at 1167.13 cm^{-1} and this is further supported by the FTIR band at 1165 cm^{-1} . The sharp intense Raman peaks at 1078.31 , 1006.12 , 944.92 , 917.40 cm^{-1} could be due to the C-N asymmetric stretching vibration. The Raman band at 724.85 cm^{-1} could be due to C-H out-plane bending vibration of BZP molecule. The various vibrational peaks in the FT-Raman spectrum confirm the presence of all the vibrational bonds in the BZP molecule.

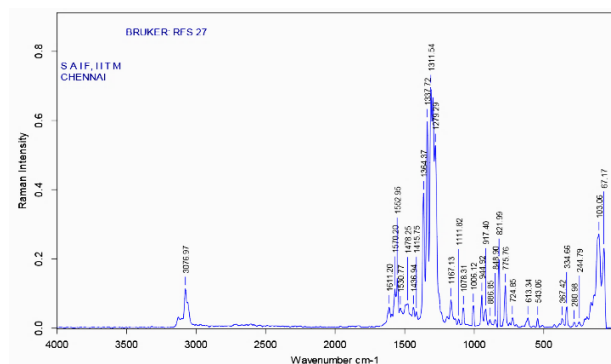


Fig. 4. FT-Raman Spectrum of BZP crystal.

Laser damage threshold study

A crystal surface damage by high intense laser is an important study to know the laser light withstanding capacity of the material and is essential for the laser optical device fabrications. When a laser light of high intense pulse is incident on the surface of a crystal, surface gets damaged at a particular power and it was measured through a power meter which is connected to the laser setup. The pulse energy can also be estimated through a phototube connected with an oscilloscope unit. In the present case, a multiple shot (6 pulses) of a laser is used and the laser damage threshold density was measured to be 1.39 GW/cm^2 .

Conclusions

In the present research work, low temperature solution growth method was employed and a crystal of dimension $15 \times 7 \times 2\text{ mm}^3$ was successfully grown with in the period of 25 days. The grown BZP crystal was subjected to various characterizations like single crystal XRD, FTIR and FT-Raman in order to understand its crystal structure and the presence of chemical bonds and functional groups. Crystal show optimal laser

damage threshold value (1.39 GW/cm^2). Results of the grown material reveals excellent crystal stability, suitable size requirement and laser withstanding capacity and thus the material can be opted for various laser optical applications.

Conflict of interest

There is no conflict of interest.

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