Physio-Chemical Properties of Piperazinediium *bis*(4-Nitrophenolate)dihydrate: A Non-linear Optical Crystal

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Good quality single crystals of piperazinediium *bis*(4-nitrophenolate)dihydrate (PBPNDP) have been grown from aqueous solution by slow evaporation solution growth technique. Unit cell parameters of the grown crystal were confirmed by single crystal X-ray diffraction analysis and the synthesized compound is crystallized in triclinic system. Various functional groups and their vibrational frequencies were recognized from the FT-IR spectrum. The grown crystal has wider transparency nature in the visible region and the lower cut-off wavelength is found at 329 nm. Thermal stability of the crystal was examined by recording the TGA/DTA curve. The dielectric studies were performed. The mechanical properties of the crystal were estimated by Vickers hardness test. The relative second harmonic efficiency (non-linear optical) of the compound is found to be 2.4 times greater than that of potassium dihydrogen phosphate (KDP). The laser damage threshold (LDT) for the grown crystal were measured as 9.43 GW/cm² with Nd:YAG laser assembly.

Keywords: Crystal growth, Piperazinediium *bis*(4-Nitrophenolate)dihydrate, FTIR, Thermal, Dielectric, Micro Hardness, Non-linear optical.

INTRODUCTION

Currently much interest in organic nonlinear optical (NLO) crystals due to their potentially high non-linearity and rapid response in electro-optic effect compared to inorganic non-linear optical materials. The organic non-linear optical crystals may play an important role in third-harmonic generation (THG), frequency mixing, electro-optic modulation and optical parametric oscillation, *etc.*, *p*-nitrophenol derivatives are interesting candidates, as they are a typical one-dimensional donor-acceptor π system and the presence of phenolic O-H favours the formation of salts with various organic and inorganic bases [1]. *p*-Nitrophenol is an organic material having both the electron donor -phenolic group and electron acceptor -nitro group and it forms donor acceptor bridge. This donor- π -acceptor structure is added advantage to convert the frequency of the light. Among the organic molecular non-linear optical crystals, ionic crystals of nitrophenol has large band gap for photonic transition [2]. Mixed analogs of non-linear optical crystal are found to show extended optical and physical properties and hence they can be extensively used for molecular engineering application [3]. Piperazine plays an important role as a unit present in the more complex molecules studied in several fields [4-6]. Piperazine in crystals has a chair conformation with N-H bonds in the equatorial positions and resides

at the crystallographic inversion center [7]. Detailed investigations of linear and nonlinear optical coefficients enable to fabricate materials, appropriately designed at the molecular level for specific applications such as optoelectronic devices [8,9]. Piperazine yielding symmetrically substituted salts has been investigated for a long time [10-13]. These studies are investigated by the antimicrobial activities of quaternary piperazinium salts. Some of these salts show spasmolytic, anthelmintic or germicidal activities. The piperazine ring is frequently used as a building block for pharmaceuticals [14,15]. Recently it has been found that some polycationic ligands, including piperidine and piperazine rings, exhibit a substantial degree of selective RNA binding [16]. The base piperazine is an electron donor and *p*-nitrophenol is an electron acceptor compound. There is maximum possibility of reaction between these two compounds and this reaction may yield a product as piperazinediium *bis*(4-nitrophenolate)dihydrate. Hence we planned to synthesis and grow the crystal of piperazinediium *bis*(4-nitrophenolate)dihydrate. The crystal structure of piperazinediium *bis*(4-nitrophenolate)dihydrate (PBPNDP) was reported by Xiong *et al.* [17] and the reported structure confirm the presence of intermolecular hydrogen bonds between the piperazine cation and *p*-nitro-phenolate anion. In this manuscript we report the growth and characterization of piperazinediium *bis*(4-nitrophenolate)dihydrate (PDBPNPD) single crystal.

EXPERIMENTAL

Crystal synthesis and growth: The as-purchased 4-nitro phenol (99 % Pure) and piperazine (Merck Product) were used as starting materials to prepare the solution for the synthesis of PDBPNPD. Piperazine and 4-nitro phenol were taken in the molar ratio 1:2 and dissolved one by one in excess of water by continuous stirring. After the solution became homogeneous, it was filtered and transferred to another beaker, then allowed to evaporate the excess water at below 40 °C. Yellow colour crystalline salt was obtained at the bottom of the beaker. It was dried and purified by recrystallization process. The seed crystals were obtained by SEST method from a super saturated solution prepared from the synthesized salt (Fig.1).

Fig. 1. Photograph of grown PBPNDP single crystal

Single crystal XRD studies were carried out using ENRAF NONIUS CAD-4 single X-ray diffractometer to determine the lattice parameters and the space group. The optical properties of the grown crystals were studied using the Perkin-Elmer Lambda 35 UV-visible spectrometer in the wavelength region from 190 to 800 nm. The FTIR spectrum of the grown PBPNDP crystals were recorded using Perkin Elmer spectrophotometer by KBr pellet method, in the region 4000-400 cm^{-1} . The dielectric study were carried out using the instrument, HIOKI 3532-50 LCR HITESTER meter. Thermogravimetric (TG) and differential thermal analysis (DTA) for the crystal samples were carried out in nitrogen atmosphere by EXSTAR TG/DTA 6200 thermal analyzer to study the thermal properties of the as-grown crystal. Non-linear optical properties were tested by Kurtz Perry powder technique. Laser damage threshold study was also carried out for the PBPNDP crystal using Nd:YAG laser.

RESULTS AND DISCUSSION

Solubility: The solubility of piperazinedium bis(4-nitrophenolate)dihydrate (PBPNDP) was ascertained for six different temperatures namely 35, 40, 45, 50, 55 and 60 °C. A constant volume of 100 mL of saturated solution was used in this experiment. The measurement was performed dissolving the PBPNDP salt in deionized water in an airtight container maintained at a constant temperature with continuous stirring. The solution was constantly stirred for 2 h using a magnetic stirrer for homogenization. It is noted from Fig. 2 that PBPNDP has a positive gradient of solubility.

Single crystal X-ray diffraction analysis: The grown crystal of PDBPNPD was confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 X-ray diffracto-

Fig. 2. Solubility curve of PBPNDP single crystal

meter and its lattice parameters were determined. Single crystal X-ray diffraction study reveals that PBPNDP crystal belongs to the triclinic system with non-centrosymmetric space group P1. The obtained lattice parameter values are in good agreement with the reported literature [17] values is shown in Table-1.

TABLE-1
SINGLE CRYSTAL XRD LATTICE
PARAMETERS DATA OF PBPNDP

Present work	Reported [Ref. 10]
$a = 6.39 \text{ \AA}$	$a = 6.401 \text{ \AA}$
$b = 6.68 \text{ \AA}$	$b = 6.715 \text{ \AA}$
$c = 11.21 \text{ \AA}$	$c = 11.219 \text{ \AA}$
$\alpha = 100.30^\circ$	$\alpha = 100.37^\circ$
$\beta = 92.72^\circ$	$\beta = 92.89^\circ$
$\gamma = 100.03^\circ$	$\gamma = 99.99^\circ$
$V = 462 \text{ \AA}^3$	$V = 465.492 \text{ \AA}^3$

UV-vis-IR analysis: The UV-vis-NIR spectrum (Fig. 3) were recorded in the wavelength range 190 to 900 nm using a Perkin-Elmer Lambda 35 UV-visible spectrometer. The absorption spectrum depicted that crystal is transparent upto

Fig. 3. UV spectrum of PBPNDP single crystal

900 nm. The lower cut-off wavelength of the crystal were found to be 329 nm and is short enough for the SHG of Nd:YAG laser radiation at 1064 nm or other applications in the blue region. A small peak occurred at around 450 nm in the spectrum may be due to the $n-\pi^*$ transitions [18]. The protonation of imidazole ring in the acid medium changes conjugated bond lengths, which indicates an alternation in the intra molecular charge transfer. The presence of this protonation is believed to account for the inclination of the molecular transition dipole moment with respect to the direction in the non-protonated molecule. As a result, it can be used as a potential material for SHG in the visible region down to blue and violet light, which makes it suitable for laser frequency doubling and related optoelectronic application.

FTIR: The aromatic CH_2 stretching vibration occurs at 3024 cm^{-1} [3]. The presence of methyl in piperazine lattice is evident by its CH_2 stretching at 3024 cm^{-1} . The peak 2623 cm^{-1} are assigned to deformation N-C-H stretching, respectively. The nitrophenol group C- NO_2 stretching and CH in plane bending occurs at 1165 cm^{-1} [19] and 1113 cm^{-1} [20], respectively. The peaks at 821 , 754 and 703 cm^{-1} are assigned to in plane C-N-C, NO_2 scissoring, in plane C-C-C bending. Thus, band due to the asymmetric stretching vibration for nitro groups forced out of plane of the ring by *para* substitution was found at 1573 cm^{-1} with strong intensity (Fig. 4). The ring deformation and torsional mode vibrations of PDBPNPD are well found in the vibrational mode. CH in-plane bending vibrational peaks is observed at 981 cm^{-1} , respectively. Peaks observed at 847 cm^{-1} assigned to CH out-of-plane bending vibration [21]. The very strong bands appeared at 1573 cm^{-1} assigned to C- NO_2 stretching vibrations. The frequency observed at 1466 cm^{-1} is due to aromatic C-C stretching vibration. The deformations such as C-O stretching are assigned to peaks 1275 cm^{-1} , respectively.

Fig. 4. FTIR spectrum of grown PDBPNPD crystal

Thermal analysis: The powder form of grown PDBPNPD was loaded into a capillary tube and was placed in the melting point apparatus (VEEGO MODEL: VMP-PM). The temperature was slowly increased at a heating rate of $2\text{ }^\circ\text{C/min}$ and monitored using lens-attached scale. The material started melting at $115\text{ }^\circ\text{C}$, which indicates the melting temperature of the title

material. The error in the measurement is $\pm 0.1\text{ }^\circ\text{C}$. This experimentally determined value is in accordance with the data obtained from TG/DTA. Thermogravimetric and differential thermal analyses give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal [2,22]. The Thermogravimetric and differential thermal analyses of the PDBPNPD were carried out between 25 and $800\text{ }^\circ\text{C}$ at a heating rate of 10 K/min in the nitrogen atmosphere. The simultaneous TG-DTA measurement was performed on 4.462 mg of PDBPNPD powder sample and the resultant curves are shown in Fig. 5. From TG curve, it is clear that there is no weight loss between room temperature and $95\text{ }^\circ\text{C}$ and hence it shows that the PDBPNPD is stable up to $95\text{ }^\circ\text{C}$. In the DTA curve, two prominent endothermic peaks were observed for the PDBPNPD compound. First endothermic peak was observed at $115\text{ }^\circ\text{C}$ and second endothermic peak was noted at $196\text{ }^\circ\text{C}$. TG curve showed a single stage complete weight loss between 95 and $196\text{ }^\circ\text{C}$ (96.2%) which illustrates the simultaneous melting and decomposition of the piperidinium and phenolate moiety and also the removal of almost all fragments as gaseous products.

Fig. 5. TG/DTA curve of PDBPNPD crystal

Dielectric studies: The dielectric characteristics of the material are important to know the transport phenomena and the lattice dynamics in the crystal. It also gives the information about the nature of atoms, ions, bonding and their polarization mechanism in the material. PDBPNPD single crystal cut into rectangular dimension was subjected to dielectric study using HIOKI 3532-50 LCR HITESTER meter. The surface of the sample was coated with silver paste for firm electrical contact. The experiment was carried out in the frequency range 50 Hz to 5 MHz at room temperature. The dielectric constant of the crystal has been calculated using the relations:

$$\epsilon = Cd/A\epsilon_0 \quad (2)$$

where d is the thickness and A is the area of the sample. The response of dielectric constant as a function of frequency is shown in Fig. 6. From the plots it is observed that the dielectric constant decreases with increasing frequency and attain saturation at higher frequencies. Dielectric studies furnish a great deal of information regarding the dielectric constant that

Fig. 6. Dielectric constant of PBPMPD crystal

Fig. 7. Dielectric loss of PBPMPD crystal

arises from the contribution of different polarizations, namely electronic, ionic, atomic, space charge, *etc.* developed in the material subjected to the electric field variations. The large dielectric constant at low frequency for the crystals in the present study is due to the presence of space charge polarization arising at the grain boundary interfaces [23]. The low values of dielectric constant at higher frequencies reveal the good optical quality of the grown crystals with less defects, which is the desirable property of the materials to be used for various optical and communication devices [24].

The dielectric constant measured at different temperatures almost remains the same at higher frequencies. It indicates the temperature variation has no influence on the dielectric property of the material. The electronic exchange of a number of ions in the crystals gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. At higher frequencies, the measure of dielectric loss is relatively low since the electric wave frequency is not equal to that of natural frequency of the bounded charge and hence the radiation is very weak. The measure of low dielectric loss (Fig. 7) at various frequencies is also due to dipole rotations. At high frequencies orientation polarization ceases and hence the energy need not be spent to rotate dipoles. The higher value of dielectric constant and dielectric loss at lower frequencies may be attributed to the space charge polarization and charged lattice defects crystals with high dielectric constant lead to more power dissipation and hence at higher frequencies, the power dissipation in the crystal may have lower value [25]. The low dielectric loss and dielectric constant at higher frequencies of PBPMPD show the material to be a potential candidate for nonlinear optical applications.

AC electrical conductivity studies: The AC conductivity has been calculated for the crystal PBPMPD using HIOKI 3532 LCR HITESTER in the frequency range 50 Hz to 5 MHz. Fig. 8 shows the variation of AC conductivity with log of frequencies. It is seen that the value of ac conductivity increases with increase in frequency. The electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. The slope of the plot of ac conduc-

Fig. 8. Variation of AC conductivity with log of frequency

tivity *versus* temperature (Fig. 9) gives the activation energy required for the conduction process of the charge carriers. The value is found to be 1.68 eV and the lower value of activation energy establishes that the crystal contains less number of defects. The material is therefore useful for various micro-electronic and nonlinear optical applications.

Fig. 9. Activation energy of PBPMPD crystal

Micro hardness studies: Hardness of a material is the measure of resistance it offers to local deformation. In the case of crystals, it can be understood in terms of resistance offered to dislocation motion. In general, it comes from the intrinsic resistance of crystals and resistance caused by imperfection in the crystal [26]. The mechanical properties of crystalline materials are closely related with their physical properties and determine the performance of devices prepared from the solids. Hardness measurements were made on PBPMPD sample at room temperature using a Leitz Wetzler microhardness tester with Vickers pyramidal diamond indenter. Loads ranging from 10 to 50 g were used for making indentations.

The hardness value was estimated from the relationship:

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

where, load (P) is in kilogram, diagonal length of indentation (d) is measured in millimeter and 1.8544 is a geometrical factor. A plot between hardness number and load is shown in Fig. 10. As load increases, hardness value increases. It exhibits the reverse indentation size effect. A plot shown in Fig. 11 obtained between log P and log d gives more or less a straight line. The relation connecting applied load and diagonal length d of the indenter is given by Meyer's law:

$$P = ad^n \quad (4)$$

here, n is the Meyer's index or work hardening coefficient, which has been calculated from the slope of the straight line and a is a constant. The work hardening coefficient 'n' is found to be 1.0, which indicates that PBPMPD has a hard material. As per the concept put forward by Onitsch [27], hardness increases with load when the hardness coefficient 'n' is lesser than 2.

Laser damage threshold studies (LDT): In non-linear optical crystals the harmonic conversion efficiency is proportional to the power of the fundamental beam. Hence away to increase the efficiency is to focus the beam into the crystal. However this often leads to the breakdown of the materials, catastrophically damaging the maximum permissible power for a particular crystal defined as damage threshold. The laser damage threshold of an optical crystal is an important factor affecting its applications. The laser damage threshold depends

Fig. 10. Variation of load with hardness number

Fig. 11. Variation of log P with log D

on specific heat, thermal conductivity, optical absorption, etc. If the material has high specific heat, the laser damage threshold will be high. If the material has a low laser damage threshold it severely limits its applications, even though it has many excellent properties, like high optical transmittance and high SHG efficiency [28]. The laser damage threshold of the PBPMPD crystal was calculated by using the following relation:

$$\text{Power density, } P(d) = E/\tau A \quad (5)$$

where 'E' is the input energy (mJ), 'τ' is the pulse width (ns) and 'A' is the area of circumference (cm²). The measured laser damage threshold value for PBPMPD crystal is 9.433 GW/cm². The LDT value of PBPMPD crystal is found to be higher than that of potassium dihydrogen phosphate and some of the important organic non-linear optical materials [29,30]. The high laser damage threshold value of PBPMPD crystal can find useful applications in high power laser devices. The results were compared with the other crystals in Table-2.

TABLE-2
COMPARISON OF LASER DAMAGE
THRESHOLD WITH GROWN CRYSTAL

Crystals	Laser damage threshold (GW/cm²)
Potassium dihydrogen phosphate (KDP)	0.2
Urea	1.5
Benzimidazole	2.9
Methyl p-hydroxybenzoate	2.77
Piperazinediium bis(4-nitrophenolate)dihydrate	9.43

SHG measurement: The second harmonic generation efficiency of the crystal were carried out using the Q-switched Nd:YAG laser beam of wave-length 1064 nm, using Kurtz Powder technique [31]. The input laser beam was passed through an IR reflector and was then directed to the microcrystalline powdered sample packed in a capillary tube. Photodiode detector and oscilloscope assembly detect the light emitted by the sample. The SHG was confirmed by the emission of green radiation of wavelength of 532 nm. Potassium dihydrogen phosphate crystals were powdered to the identical grain size and used as reference materials in the SHG measurement. The powdered SHG efficiency of PBPMPD crystal was found to be 2.4 orders

of magnitude higher than that of potassium dihydrogen phosphate and its comparison of signal output is shown in Table-3.

TABLE-3
COMPARISON OF SHG SIGNAL OUTPUT

Input energy (joule)	Potassium dihydrogen phosphate (mJ) [Ref. 32]	PBPNPD (mJ) Present work
0.701	8.91	21.3 (2.4 times greater than KDP)

Conclusion

Good quality single crystal PBPNPD were grown by slow evaporation method at room temperature. The solubility of the crystal were analyzed gravimetrically and it is found that it possess positive temperature coefficient of solubility which is necessary for growing bulk single crystals. The cell parameter were determined by Single XRD and it is ascertained that the crystal belongs to triclinic system. The presence of functional group is confirmed by FT-IR. UV-vis-NIR spectrum reveals that the material has a good transmittance in the visible region with cutoff wave-length 329 nm. The dielectric studies of PDBPNPD reveal that the dielectric constant decreases ceaselessly with increase in frequency succeeded with a frequency independent behaviour at high frequencies. Thermal analysis recommends that the material can be placed for any application below 115 °C. Vickers micro hardness shows that the material exhibits reverse indentation size effect, which is the important criteria for fabricating optoelectronic devices. The measured laser damage threshold for the grown crystal was 9.43 GW/cm². SHG efficiency is 2.4 times than that of potassium dihydrogen phosphate.

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