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Structural, electrical, ferroelectric and mechanical properties with Hirshfeld surface analysis of novel NLO semiorganic sodium p-nitrophenolate dehydrate piezoelectric single crystal

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Abstract

Novel non-linear sodium para-nitrophenolate dihydrate (SPNPD) single crystals were grown by controlled evaporation method. Various functional groups and chemical bonding were identified by FTIR and Raman analysis. Hirshfeld surface and fingerprint plot were drawn and analyzed for the intermolecular interactions present in crystal structure. UV-visible studies indicate the high transmittance of crystals in visible region with a wide band gap 6.12 eV. In photoluminescence spectrum, a sharp broad emission peak centered at 525 nm indicates green emission. In dielectric study a broad peak with low dielectric constant value was observed at 34 °C which may be due to ferroelectric to paraelectric transition. Piezoelectricity was confirmed by determining the piezoelectric charge coefficient ($d_{33} = 2.24$ pC/N). The hysteresis loop with values of remnant polarization and coercive field as 2.67 μ C/cm² and 7.43 kV/cm, respectively. Piezo-/ferroelectricity were reported for the first time in p-nitrophenolate based compounds. SHG efficiency of this material was found to be 4.15 times of that of KDP. Mechanical strength was confirmed from Vicker's microhardness study and voids volume. Thus promising piezoelectric, ferroelectric behavior of material along with high SHG efficiency and low dielectric constant, established SPNPD as a potential material for transducer, optoelectronics and nonvolatile memory devices applications.

Keywords: Hirshfeld Surface analysis, dielectrics, piezoelectricity, ferroelectricity.

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Introduction

In recent years there has been considerable interest on nonlinear optical materials because of their applications in optical communications, optical computing, high speed information processing, electro-optic shutters and optical data storage.¹⁻² Pure organic crystals have very large nonlinear susceptibilities compared to inorganic crystals but their use in device fabrication is restricted by low optical transparency, poor mechanical properties and the difficulties in the growth of large crystals.³⁻⁴ On the other hand, inorganic materials have excellent mechanical and thermal properties but possess relatively modest optical non-linearities because of the lack of delocalization in π -electrons.⁵ Semiorganic materials combine the high optical non-linearities of organics with good thermal stability and transmittance of inorganics.⁶⁻⁷

Para-nitrophenol is such an organic material which gives variety of derivatives with alkali metal hydroxides.⁸⁻¹¹ In recent years, semi-organic complex products of p-nitrophenol have been attracted for NLO properties because of the presence of the delocalized π - electrons in organic ligand p-nitrophenol resulting in high nonlinear optical coefficients in this kind of materials. Sodium p-nitrophenolate dihydrate $(SPNPD \cdot 2H_2O)$ is such a semiorganic non linear material in which sodium ion (Na^+) is bonded to an organic ligand (nitrophenoxy ion). In this crystal, the π -electron cloud movement from donor to acceptor results in intermolecular charge transfer interaction and hence makes it non-centrosymmetric. Crystals having non-centrosymmetric structure exhibit both SHG and piezoelectric effects.¹²Although, SPNPD is a well established non-linear optical material for long¹³, its piezoelectricity has not been reported yet and therefore its possible applications in piezoelectric devices have not been exploited so far. This piezoelectricity has not been reported in other p-nitrophenolate based compounds as well.⁸⁻¹¹ Furthermore, crystals exhibiting both luminescence and non linear optical properties are used in solid state laser sources. ¹⁴⁻¹⁵ In addition to the NLO property, dielectric behaviour of material plays an important role in device applications. Regarding the NLO device fabrication, materials should also have stringent property imposed by operating frequency like low dielectric constant and required power levels under the electric field.¹⁶ Low

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dielectric constant means material supports an electrostatic field with minimal heat energy dissipation. Thus low-dielectric materials can lower the power consumption and decrease RC delay in microelectronics.¹⁷ Therefore in grown crystal, we have carried out the study of dielectric properties i.e. dielectric constant and dielectric loss over a range of frequencies and temperatures to analyze their electrical properties. Ferroelectric materials have many optoelectronic applications such as capacitors, nonvolatile memory devices, high-performance gate insulators etc. Molecular surface of the grown crystal was computed on the basis of Hirshfeld surface analysis to understand the intermolecular interactions and hardness of the crystal was compared based on void volume estimation.¹⁸⁻¹⁹ Therefore, in the present work we have reported structural characterization, Hirshfeld surface analysis, optical properties, photoluminescence, dielectric behavior, piezoelectric charge coefficient (d₃₃ pC/N), ferroelectricity, non-linear optical and mechanical properties with calculated void volume in details for the first time. Due to the excellent non linear optical property, strong PL emission, low dielectric constant value and good piezo-/ferroelectric behaviour, the grown SPNPD crystals can have technological applications in opto-electronic and microelectronics devices.

Experimental

Crystal growth and Characterization

Sodium p-nitrophenolate Dihydrate (SPNPD) single crystals were grown by slow evaporation solution technique by taking sodium hydroxide and p-nitrophenol in the molar ratio of 1:1. These calculated salts were dissolved in double distilled water. The resultant solution was stirred well at 45 °C for 4 hrs to ensure the homogeneous temperature and concentration over the entire volume of the solution. The reaction which takes place for the synthesis of sodium p-nitrophenolate dihydrate is as follows:

 $NO_2-C_6H_4-OH + NaOH + H_2O \rightarrow NO_2-C_6H_4-ONa.2H_2O$

The resulting solution was filtered twice and finally it was kept in a constant temperature oil bath at 40 °C with an accuracy of 0.01 °C. The purity of the synthesized salt was improved by performing

recrystallization many times. Yellow colored transparent single crystals of size 9 x 7 x 2 mm³ were harvested from the mother solution in 2-3 weeks as shown in Fig.1 (a). Grown SPNPD single crystals have been characterized from single crystal X-ray diffraction data analysis using an Oxford Diffractometer with graphite monochromatic MoK_a radiation ($\lambda = 0.7107$ Å). Structure of grown crystal was solved by fullmatrix least-square technique on F² using SHELX-97 program.²⁰ Its morphology has been deduced from BFDH and Modified BDFH theory.²¹ For confirming functional groups, the FTIR spectrum of grown crystal was recorded in the middle infrared region of 400 and 4000 cm⁻¹ with Perkin-Elmer spectrum BX spectrophotometer using the KBr pellets while Raman spectra were recorded with FT-Raman spectrophotometer in the range 400–3000 cm⁻¹ using excitation radiation at 514 nm with Ar-ion laser at room temperature. The Hirshfeld surfaces and unit cell voids were generated using Crystal Explorer 3.1 programme.²² Fingerprint plots showing intermolecular interactions were derived from the Hirshfeld surfaces. To know the suitability of crystal for optical applications, the transmission spectra were recorded using an evolution 300 spectrophotometer in the region 200-1100 nm. During this optical analysis, powdered sample was dissolved in distilled water therefore baseline corrections were performed for getting required material data only. Photoluminescence (PL) measurements were taken on Varian Cary Eclipse fluorescence spectrophotometer at room temperature by exciting the crystal at 450 nm. Dielectric measurements were carried out by the impedance analyzer (Agilent E4980A) with sample holder (Agilent Model 16048A) for a frequency range 100 Hz -2 MHz in the temperature range from RT to 58 °C. Crystals were poled using a DC poling unit (electric field range $0-5 \text{ kV mm}^{-1}$) by immersing them in silicon oil. The piezometer charge coefficient (d₃₃) measurement was done by PM-300 piezometer system. For finding NLO property, the grown crystal was subjected to second harmonic generation (SHG) test performed by the Kurtz powder technique. In the experiment, crystals were ground into powder form with uniform particle size of 63 µm, then packed in a microcapillary tube and finally a Q-switched Nd:YAG laser beam of wavelength 1064 nm was passed through it to get SHG efficiency. The second harmonic radiations generated in the sample were focused by a lens and detected by a photomultiplier tube. This SHG output was converted into

electrical signal and displayed on an oscilloscope which indicated the SHG efficiency of the sample. The emission of green light confirmed the SHG property of material. The hysteresis loop was traced using an automatic P-E loop tracer. The mechanical characterization of the SPNPD crystals was done by Vickers microhardness test performed at room temperature. The indentations on crystals were made gently by loads varying from 5 to 100 g for a dwell time of 10 s.



Fig.1. (a) Photographs of yellow colored transparent SPNPD single crystals grown at 40°C. This good transparency indicates high crystal quality. (b) Morphology of the grown crystal obtained using WinXMorph software.

Morphological Studies

The morphology importance (MI_{hkl}) of the planes present in crystal can be solved by BFDH law which states that the rates of growth of the given hkl face are equal to the reciprocal of the interplanar distance d_{hkl} . Morphology of grown crystals with crystal planes and directions is shown in Fig.1 (b) which has been obtained using WinXMorph software.²³ The BFDH law is applicable in many cases in predicting

$$\frac{\mathrm{d}l_{hkl}}{\mathrm{d}t} = \frac{R_{h_1 k_1 l_2} \sin \gamma + R_{h_2 k_2 l_2} \sin \alpha - R_{hkl} \sin(\alpha + \gamma)}{\sin \alpha \sin \gamma}$$

where $R_{\hbar k \epsilon l}$, $R_{\hbar_{2} \kappa_{2} t_{1}}$, $R_{\hbar_{2} \kappa_{2} t_{2}}$ are the normal growth rates of the hkl, h₁k₁l₁ and h₂k₂l₂ faces and their values are equal to reciprocal of their interplanar distances accordingly, $1/d_{hkl}$ according to BFDH law, α and γ are the interfacial angles for given hkl plane. The growth rates and their corresponding Morphological importances (MI) of the (010), (111) and (123) face were computed form BFDH law and modified BFDH laws which are summarized in Table1 and these directly reflects the corresponding area of the crystal faces according to their weightages. It has been found that the experimentally observed morphology of the grown crystal is closely matching with the predictions of both simple BFDH and modified BFDH law which means that the growth rates of the adjacent planes significantly contribute in the growth rate of the SPNPD crystal plane.

 Table 1 Morphological importance of SPNPD crystal faces computed from BFDH and modified BFDH laws.

Faces (hkl)	d _{hkl} (Å)	Calculated relative growth rates from BFDH law	Morphological importance by BFDH law	d _{hkl} /dt	Morphological importance by modified BFDH law
010	19.6850	1.000	1.000	0.7165	1.000
111	4.5787	4.299	0.233	0.5489	1.305
123	2.0075	9.8057	0.102	0.2692	2.661

Results and discussion

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Single crystal XRD analysis and structural description

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The structural analysis of grown crystal was carried out by single crystal X-ray diffraction analysis. For this characterization a good single crystal with dimensions 0.5 mm x 0.5 mm x 0.5 mm was chosen. The structure was deposited to CCDC (No. 1403345). It was observed that grown crystal belongs to the orthorhombic system with non-centrosymmetric space group Ima2. The observed cell parameters agree well with the reported values.²⁴⁻²⁷ The details of the crystal data and refinement parameters of the studied crystal are listed in Table 2.1. The molecular structure of grown crystal with the atom numbering scheme has been depicted in Fig.2. Fig.3. shows the packing of the molecules arranged in net pattern. In the structure, sodium cation is bonded with the oxygen atom (O2) of nitro group (NO_2) and also attached with the four oxygen atoms of water molecules (Fig.2). Thus sodium ion exists in a six fold coordinated geometry based on an octahedron. Another significant fact is that phenolic oxygen (O1) atom has strong interaction with hydrogen atoms of water molecules which are attached with sodium atom. Thus, intermolecular hydrogen bonding interactions {O...H (W)} takes place between the non-coordinated oxygen (O1) atom and the hydrogen atoms of water molecules (Fig.3) which minimizes energy and hence helps in stabilization of crystal structure. Further, the atomic coordinates of the non-hydrogen atoms with their equivalent displacement parameters for SPNPD compound are listed in Table. 2.2. Bond lengths and bond angles of atoms present in the material are presented in Tables 2.3-2.4. Also, the hydrogen bonds present in the crystal structure are listed in Table.2.5.

 Table 2.1 Single crystal data and structure refinement of SPNPD crystal.

Empirical Formula	C ₆ H ₈ O ₅ NNa
Formula weight	197.12
Temperature	293K
Wavelength	0.71073 Å (Mo Kα radiation)
Crystal system, space group	Orthorhombic, Ima2
Cell length, a	6.8849(6) Å
Cell length, b	19.6618(1) Å
Cell length, c	6.4413(5) Å
Volume	871.95(12) Å ³
Crystal size	$0.5 \ge 0.5 \ge 0.5 \ \text{mm}^3$
Theta range for data collection	3.3-29.3°
Limiting indices	$-9 \le h \le 8, -26 \le k \le 26, -8 \le l \le 8$
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	1087/1/85
Goodness-of-fit on F ²	0.797
$R[F^2 > 2\sigma(F^2)], wR(F^2)$	0.0295,0.0854

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Table 2.2 Atomic coordinates ($x \ 10^4$) of the non-hydrogen atoms and their equivalent isotropic displacement parameters (Å² x 10³) for SPNPD.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Atoms	X	Y	Ζ	U(eq)	
Na(1)	-2500	-7284(1)	-7079(1)	27(1)	
C(5)	-2500	-5256(1)	-3716(3)	33(1)	
O(1)	-2500	-3217(1)	-2456(2)	26(1)	
O(2)	-2500	-6147(1)	-5989(4)	64(1)	
N(1)	-2500	-5972(1)	-4151(4)	42(1)	
C(3)	-2500	-4355(1)	-1264(3)	40(1)	
C(2)	-2500	-3870(1)	-2853(3)	23(1)	
O(3)	-2500	-6381(1)	-2730(4)	56(1)	
C(1)	-2500	-4109(1	-4911(3)	40(1)	
C(6)	-2500	-4798(1)	-5326(3)	46(1)	
C(4)	-2500	-5045(1)	-1674(3)	39(1)	
O(4)	-69	7364(1)	-9627(1)	30(1)	

Table.2.3 Bond lengths for SPNPD

Atoms	Length
Na(1)-O(2)	2.3437(19)
Na(1)-O(4)#1	2.3491(10)
Na(1)-O(4)	2.3491(10)
Na(1)-O(4)#2	2.4032(10)
Na(1)-O(4)#3	2.4032(10)
Na(1)-O(3)#4	⁹ 2.6567(15)
Na(1)-Na(1)#4	3.3305(4)

Na(1)-Na(1)#3	3.3305(4)	
C(5)-C(6)	1.373(3)	
C(5)-C(4)	1.379(3)	
C(5)-N(1)	1.435(2)	
O(1)-C(2)	1.3071(18)	
O(2)-N(1)	1.233(3)	
N(1)-O(3)	1.219(3)	
C(3)-C(4)	1.381(3)	
C(3)-C(2)	1.400(3)	
C(2)-C(1)	1.407(2)	
O(3)-Na(1)#3	2.6567(15)	
C(1)-C(6)	1.381(3)	
O(4)-Na(1)#4	2.4032(10)	

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Table.2.4 Bond angles for SPNPD

Atoms	angle
O(2)-Na(1)-O(4)#1	105.82(5)
O(2)-Na(1)-O(4)	105.82(5)
O(4)#1-Na(1)-O(4)	90.86(5)
O(2)-Na(1)-O(4)#2	94.48(5)
O(4)#1-Na(1)-O(4)#2	159.42(3)
O(4)-Na(1)-O(4)#2	86.79(3)
O(4)-Na(1)-O(4)#3	159.42(3)
O(4)#2-Na(1)-O(4)#3	88.28(5)
O(2)-Na(1)-O(3)#4	171.64(9)
O(4)#1-Na(1)-O(3)#4	79.88(5)
O(4)-Na(1)-O(3)#4	79.88(5)
O(4)#2-Na(1)-O(3)#4	79.58(5)
O(4)#3-Na(1)-O(3)#4	79.58(5)
O(2)-Na(1)-Na(1)#4	122.19(7)
O(4)#1-Na(1)-Na(1)#4	46.17(2)
O(4)-Na(1)-Na(1)#4	46.17(2)
O(4)#2-Na(1)-Na(1)#4	124.21(3)
O(4)#3-Na(1)-Na(1)#4	124.21(3)
O(3)#4-Na(1)-Na(1)#4	66.17(6)
O(2)-Na(1)-Na(1)#3	87.32(7)
O(4)#1-Na(1)-Na(1)#3	131.20(3)
O(4)-Na(1)-Na(1)#3	131.20(3)
O(4)#2-Na(1)-Na(1)#3	44.85(2)
O(4)#3-Na(1)-Na(1)#3	44.85(2)
O(3)#4-Na(1)-Na(1)#3	84.32(6)
Na(1)#4-Na(1)-Na(1)#3	150.49(4)
C(6)-C(5)-C(4)	121.52(15)
C(6)-C(5)-N(1)	119.70(18)
C(4)-C(5)-N(1)	118.78(18)
N(1)-O(2)-Na(1)	123.66(17)
O(3)-N(1)-O(2)	122.42(19)
O(3)-N(1)-C(5)	120.1(2)
O(2)-N(1)-C(5)	117.5(2)
C(4)-C(3)-C(2)	121.99(19)
O(1)-C(2)-C(3)	121.76(16)
O(1)-C(2)-C(1)	120.81(15)
C(3)-C(2)-C(1)	117.43(16)
N(1)-O(3)-Na(1)#3	140.42(16)
C(6)-C(1)-C(2)	120.71(18)
C(5)-C(6)-C(1)	119.79(18)
C(5)-C(4)-C(3)	118.56(18)
Na(1)-O(4)-Na(1)#4	88.98(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x-1/2,y,z; #2 x+0,-y-3/2,z+1/2

Table.2.5 Hydrogen bond geometry (Å)

D-H···. А	D-H	Н…А	D····A	D-H··· A
С6-Н6…О21	0.93	2.394	2.687	98.04
C4-H6····O3 ⁱ	0.93	2.434	2.715	97.40
O4-H4A····O1 ⁱⁱ	0.786	2.033	2.785	159.98
04-H4A…01 ¹¹¹	0.786	2.033	2.785	159.98
04-H4B…01 ^{IV}	0.824	2.004	2.811	166.40
$O4-H4B\cdots O1^{v}$	0.824	2.004	2.811	166.40
O4-H4B··O1 ^{vi}	0.824	2.957	3.265	104.75

Symmetry codes: (i) x,y,z; (ii) -x,-y-1,+z-1; (iii) x+1/2,-y-1,+z-1;

(iv) x+1/2,+y-1/2,+z-1/2; (v) -x,+y-1/2,+z-1/2; (vi) x,-y-1/2-1,+z+1/2



Fig. 2 An ORTEP view of the SPNPD crystal structure with the atom numbering scheme. Carbon and oxygen atoms are denoted by black and red color ellipsoid balls while white color balls are for hydrogen atom. Sodium cation strongly interacts with the oxygen atoms of the nitro (NO₂) group and water molecules.



Fig. 3 Crystal packing diagram in which carbon, oxygen and nitrogen atoms are represented by black, red, blue colors, respectively, while bigger grey color atom represents Sodium atom. The hydrogen bonding interactions are shown by dotted green color lines which take place between phenolic oxygen atom and hydrogen atoms of water molecules.

Vibrational Spectroscopy

Vibrational spectroscopy is an important tool in indentifying the functional groups present in the material. Observed FTIR and Raman spectra are depicted in Fig. 4(a) and (b), respectively. In FTIR spectra the broad asymmetric band centered at 3301cm⁻¹ can be assigned to the O-H stretching modes of the two hydrogen bonds which shows that compound contain water molecules. The infrared bands observed at 493, 704 cm⁻¹ correspond to the torsion vibrations of the ring. IR and Raman bands observed at 646, 1115, 1587 and 646, 1110, 1270 cm⁻¹ is due to the ring bending or stretching and stretching vibrations of C-NO₂ and C-O

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respectively. Out of plane symmetric deformation in NO₂ and out of plane bending in C-H vibrations are observed at 758 and 829, 853 cm⁻¹, respectively, in IR spectra. In IR and Raman spectra bands observed at 990, 1172 and 1170 cm⁻¹ respectively are due to the in-plane bending vibrations of C-H bond. In IR and Raman spectra, rocking vibrations of NO₂ are observed at 545 and 548 cm⁻¹ respectively while out of plane bending vibrations of C-H are present at 835 and 860 cm⁻¹ in Raman spectra. Symmetric and antisymmetric bands of NO₂ are observed at 1347 and 1487 cm⁻¹ in Raman and IR spectra respectively. IR and Raman bands at 1301, 1462 and 1409,1524,1579 cm⁻¹ respectively are attributed to the stretching or bending vibrations of the ring. Antisymmetric vibrations of NO₂ are observed at 1469 cm⁻¹ in Raman spectra. Thus vibrational frequencies observed in FTIR and Raman spectra are found to be in good agreement with the reported values.²⁸



crystal. These spectra identify O-H, NO₂ and benzene ring vibrations present in material.

Hirshfeld Surface analysis

Hirshfeld surfaces visualize intermolecular interactions by color-coding having short or long contacts which explore the properties of all intercontacts within crystal structure.¹⁸ These surfaces of a molecule in

the crystal are constructed based on the electron distribution which is calculated as the average sum of the spherical atoms electron densities.²⁹ We use the geometric function d_{norm} plotted onto the Hirshfeld surface. This normalized contact distance d_{norm} based on d_e (distance from a point on the surface to the nearest nucleus external to the surface) and d_i (distance from a point on the surface to the nearest nucleus internal to the surface) and the van der Wall radii of atoms internal or external to the surface (r_i^{vdw}/r_e^{vdw}) identifies the regions of particular importance to the intermolecular interactions which is given by following equation:

$$\mathbf{d}_{\text{norm}} = \mathbf{d}_{i} - \mathbf{r}_{i} \frac{\text{vdw}}{r_{i}} + \mathbf{d}_{e} - \mathbf{r}_{e} \frac{\text{vdw}}{r_{e}} \mathbf{r}_{e}$$
(1)

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where r_i^{vdw} and r_e^{vdw} are Van der Walls radii of two atoms internal and external to the molecular surface. The value of d_{norm} is positive or negative depending upon the intermolecular contacts shorter or longer than r^{vdw} , respectively.

Hirshfeld surfaces mapped with different properties i.e. d_{norm} , curvedness and shape index is very useful tool for visualizing intermolecular interactions and their contribution towards the crystal packing behavior of molecules.²⁹The Hirshfeld surfaces of all the molecules mapped with above mentioned properties are shown in Fig. 5-7.

The red regions in the Hirshfeld surface mapped over a d_{norm} range of -0.75 to 1.10 (Fig. (5.a)) represent the dominant interactions taking place in the crystal. The contributions of different intermolecular interactions present in the crystal structure are provided by two dimensional pictures of fingerprint plots derived from the Hirshfeld surfaces. The Hirshfeld surfaces and the associated fingerprint plots have been generated using Crystal explorer. The 2-D fingerprint plot of de vs di as shown in Fig. 5 (b) summarizes all intermolecular contacts experienced by molecules in SPPNPD crystal. Particular atom pair close contacts have been highlighted by decomposing fingerprint plots.³⁰ In Fig.5(c,d) the O…H (di > de) and H…O (de > di) intermolecular contacts are highlighted in red region on the d_{norm} surface. These interactions (O…H/H…O) appear as large spikes pointing towards lower left in the 2-D plot comprising 8.2% and 6.3%, respectively to the total area of Hirshfeld surface of molecules which reveals that these interactions are around the r^{vdW}

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separation. The C···H contacts corresponding to the π -donor and π -acceptor contribute very less (0.9%) to the total Hirshfeld surface area.



Fig. 5 (a) Hirshfeld surface mapped with d_{ntorm} for structure. (b) Two-dimensional fingerprint plot for SPNPD molecule. (c,d) Front and back views of O···H and H···O intermolecular interactions in SPNPD molecule. (e,f) Fingerprint plots of O···H and C···H interactions showing percentages of contacts contributed to the total Hirshfeld surface area of the molecules.

The shape index (S) represents the local morphology of any given surface in terms of color coded information i.e. hollow (red) and bumps (blue)³¹ and can be expressed as:

Where k_2 and k_1 are two principal curvatures of the surface, $k_1 \le k_2$.

Curvedness (C) is defined as the root mean square curvature of the surface and is given by the following equation³²:

$$C = 2/\pi \ln(k_2^2 + k_1^2/2)$$

Fig.6 (a) and (b) illustrates how shape index and curvedness surfaces are used to identify planar stacking $(\pi \cdots \pi)$ interaction arrangements. On the same region of shape index surface, the presence of red and blue triangles shown by purple color ellipse in Fig.6 (a) indicates that the $\pi \cdots \pi$ interaction is almost identically present in the crystal structure. Blue triangles represent convex region which is formed due to the carbon atoms present in benzene ring of the molecule inside the surface while red triangle having concave regions is due to the carbon atoms of π stacked molecule above it. This pattern of red and blue triangles on the region of both sides of molecule determines the way in which molecules overlap and make contact with each other and also shows how adjacent molecules are related by translation. The mapping of curvedness on Hirshfeld surface (Fig.6 (b)) shows flat green region separated by blue edges. This clearly visible flat SC Advances regions as shown by purple color lines on curvedness surface is another characteristic of $\pi \cdots \pi$ stacking interaction.

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Fig. 6 (a) Hirshfeld surface of SPNPD molecule mapped with shape index. The presence of red and blue triangles has been shown by purple color ellipse in which red and blue color represent the bumps and hollow regions on the shape index surfaces. (b) Hirshfeld surface mapped with curvedness for identifying the planar (green) and curved (blue edge) regions in SPNPD molecule for planar stacking interactions.

The contribution of $\pi \cdots \pi$ stacking interactions (C···C) was further investigated by Hirshfeld surfaces as shown in Fig.7. These decomposed fingerprints have enabled separate contributions of different intermolecular interactions present in crystal structure. The C···C contacts contribute 2.9% to the total Hirshfeld surface area which is very less. H····H interactions are reflected in the distribution of scattered points in the 2-D fingerprint plot which have a relatively significant contribution 19.9% to the total Hirshfeld surface area of the molecules This indicates that stronger H...H bonds exist between the SPNPD

molecules.



Fig.7. Two dimensional Fingerprint plots and Hirshfeld surfaces of H····H and C···C interactions with 19.9% and 2.9%, respectively. These C···C interactions contribute to the total intermolecular interactions area for π ··· π stacking of the SPNPD molecules.

Optical transmission study

For any crystal, the optical absorption or transmittance window and cut off wavelength are very important parameters in providing information about its opto-electronic transitions. UV-visible studies give important structural information because absorption of UV and visible light results in the promotion of electrons in π and σ orbital from the ground state to excited energy states.³³ Fig. 8(a) shows the recorded UV–visible transmittance spectra of the grown crystals which revealed that the 'lower cut-off' in the case of SPNPD samples is around 450 nm and there is very high transmittance (~99 %) in the region 480-110 nm which

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shows that crystal is free of defects such as precipitates and inclusions. In general, absorption peak of benzene is observed around 200 nm. In case of 4-nitrophenol, absorption peaks are strongly shifted because of the presence of hydroxyl and p-substituted nitro groups in benzene ring.³⁴ Although this crystal has a lower cut-off at 450 nm, it is still better compared to those of potassium p-nitrophenolate, guanidinium p-nitrophenolate crystal having lower cut-offs at 510 nm and 505 nm, respectively.⁸⁻⁹ The very low absorption in the entire region of 480-110 nm enables it to be a good candidate for opto-electronic and NLO applications. Below 280 nm the absorbance raises which may be due to the electronic transition π - π * taking place in benzene ring of SPNPD material. The appearance of such absorption peak in lower wavelength region in p-nitrophenolate based compound has been reported by other researcher as well.⁸

The optical constants of the material play an important role in fabricating optical devices. The dependence of the optical absorption coefficient on the photon energy helps in determining the nature of optical transitions of electrons which take place in material.

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

 $\alpha = (2.303/t) \times \log(1/T)$

where, 't' is the sample thickness and 'T' is the transmittance.

With the occurrence of a direct band gap, the crystal under study has an optical absorption coefficient (α) which obeys the following relation for high photon energies,

$$(\alpha hv)^2 = A (hv - E_g)$$

Where ' E_g ' is the optical band gap and 'A' is a constant which is nearly independent of photon energy. The graph plotted between $(\alpha hv)^2$ and photon energy (hv) has been shown in Fig.8 (b) and the optical band gap was found to be 2.80 eV which has been evaluated by extrapolating the linear portion of $(\alpha hv)^2$ in the photon energy axis. This band gap value indicates the large transparency range of material which makes it more suitable for optical applications.





Fig.8. (a) Optical transmission spectrum of SPNPD single crystal. (b) Plots of $(\alpha hv)^2$ function of hv with evaluation of band gap of the material.

Photoluminescence

In solids, photoluminescence (PL) is the phenomenon in which electronic states of a solid are excited by light of particular energy and the excitation energy is released as photons with different energy which is related to the electronic structure of the material. Photoluminescence is a useful technique to identify the impurities and find applications in lighting technologies. Generally photoluminescence phenomenon is expected in aromatic molecules which contain multiple conjugated bonds leading to a high degree of resonance stability. SPNPD crystal consists of phenoxy ion (benzene derivative) having delocalized π -electrons in C=C bonds due to which all C=C bonds can have different energy spacing between ground and excited states. It means that there exist a large number of energy states between ground and excited states

which are responsible for radiative recombination resulting in luminescence spectrum in grown crystal. Photoluminescence (PL) spectrum of grown SPNPD crystal was recorded at room temperature by exciting it at 450 nm as shown in Fig.9. A sharp broad emission peak centered at 525 nm was observed in the spectrum which indicates green emission.³⁵ This broad green emission peak is also related to deep level defect transitions i.e. there is a contribution from deep holes in the energy levels.³⁶ This broadening in emission peak is attributed to the presence of strong intermolecular hydrogen bonding interactions present in crystal structure as evidenced in Hirshfield surface analysis. This hydrogen bonding is taking place between oxygen of OH group (phenolic oxygen) attached to benzene ring and hydrogens of water molecules having attached with sodium cation in crystal structure (as discussed earlier in Fig.3.) which causes the dominance of radiationless pathways in decay process. Thus intermolecular interaction will have an important role in SC Advances Accepted crystal packing. Further, the asymmetric nature of the emission spectrum shows that the fluorescing moiety present in crystal interacts differently with the neighbors. Thus grown crystals can be used to fabricate green lasers. Such materials having broad emission peak can be used in new tunable laser system.³⁷

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Dielectric Properties

Dielectric constant measurement is one of the basic electrical properties of solids which give information about the nature of atoms, ions and their polarization mechanism present in a crystal. Basically, dielectric materials enhance the capacitance between the plates of a condenser which can have useful applications in capacitor technology. Dielectric studies of sodium p-nitrophenolate dihydrate crystal were carried out at various frequencies and temperatures. For doing this, we selected good transparent crystal and both surfaces of it were coated with high grade silver paste to make parallel electrodes. The dielectric constant of the material is directly proportional to the polarization (charge displacement) which further depends on the applied electric field and the responses of the different constituents (atoms, ions) of the solids. Fig. 10(a) shows the variation of dielectric constant which decreases from 111 to 30 with increasing frequency at room

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temperature. The higher dielectric constant at lower frequencies is due to the contribution of all polarizations i.e. electronic, ionic, dipolar and space charge polarizations. Further with increase in frequency, the contribution of space charge polarization decreases resulting in decrease in dielectric constant value. At lower frequencies, the dipoles follow the rapidly changing electric field which results in higher dielectric constant value, while dipoles are unable to follow it at higher frequencies and hence leads to reduction in dielectric constant value.

Now, the sample was heated from RT to 58 °C in the frequency range of 20 Hz to 2 MHz at a heating rate of $1 \, ^{\circ}C/min$. Fig. 10(b) shows the variation of dielectric constant with temperature at various frequencies. It is observed from the figure that dielectric constant increases with increase of temperature and it attains a maximum value at 34 °C and then it gradually decreases with further increase in temperature. Thus a transition was observed at 34 °C which may be due to ferroelectric to paraelectric phase transition. It is inferred that grown crystal is a ferroelectric material. The maximum value of dielectric constant obtained at 34 °C was found to be decreased with increasing frequency while the temperature of dielectric maxima (34 °C) with different frequencies remains same showing the absence of any relaxation behavior. The value of dielectric constant was found to be low which enhances SHG coefficient in material in accordance with Miller's rule.³⁸ Also, the low dielectric constant makes the material a potential candidate for microelectronics industries applications. The variation of dielectric loss with temperature at different frequencies is shown in Fig.10 (c). The dielectric loss decreases with increasing frequency which indicates that crystal has minimum defects and it can be used for photonic and electro-optic devices applications. Overall, very low value of dielectric loss clearly reveals the usefulness of dielectric property of material.³⁹ After 5 KHz onwards, dielectric loss goes to very much small value which reveals that material can be used for storing large number of charges without much energy loss.

Electrical conduction in crystal takes place when an electron jumps from lower energy state to higher energy state. The variation of the ac conductivity (σ_{ac}) with temperature at different frequencies is plotted in Fig.10 (d). The ac conductivity (σ_{ac}) of grown crystal was calculated using the relation:

where ε_0 is the permittivity of free space and 'f' is the frequency of the applied field. It is observed from the figure that ac conductivity increases with increase in frequency which is attributed to the reduction in the space charge polarization at higher frequencies. ⁴⁰ With increase in temperature, more and more defects are produced and the movements of these defects result in increased conductivity. Further, the sharp change in conductivity at 34 °C supports the phase transition as observed in dielectric constant study (Fig. 10(b)). The variation of conductivity with temperature shows that the conduction process is thermally activated.

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Poling and d₃₃ measurements

Crystal symmetry plays an important role in piezoelectric effect which is defined as the ability of materials to produce an electrical charge on applying mechanical stress. Piezoelectric studies were carried out on

grown crystals. Firstly, the sample was poled by applying a moderate dc electric field of 1.5kV/mm for 25 min at room temperature because the poling process improves the net alignment of the dipoles of the material in the direction of applied field. In general, Piezoelectric coefficient (d_{ii}) can be defined as:

 $d_{ij} = (\partial D_i / \partial T_j)_E$

where D, T and E are the electric displacement, stress and electric field respectively. The variation of the electric displacement ΔD with external stress T under a constant applied electric field E is directly proportional to the dipole movement. Larger is the polarizability, greater will be the piezoelectric coefficient of the material. The piezoelectric coefficients can be reported in terms of d₃₃, d₁₅ and d₃₁ etc. In the present study, piezoelectric properties were confirmed by determining the piezoelectric charge coefficient, d₃₃ pC/N which can be defined as the generation of polarization in c- direction when stress is applied in the same direction. This d₃₃ measurement was done along the poling direction of crystal axis across the basal surfaces using PM-300 Piezometer system by applying a tapping force of 0.25 N and tapping frequency of 110 Hz. The piezoelectric coefficient of the crystal was found to be 2.24 pC/N which is in comparison with that of Quartz (2.3 pC/N) and Triglycine sulphate crystal (TGS= 10.22 pC/N)⁴¹⁻⁴² and hence SPNPD material finds its applications in transducer devices, sensing microstructures on electronic micro- chips and electric voltage sources. ⁴³⁻⁴⁴ In semiorganic crystals, the hydrogen bond and π - π stacking interactions have an important role in analyzing piezoelectric properties of crystal.⁴⁵ These π - π interactions present in crystal can screen the H-bond from the applied electric field.⁴⁵ It means that the contribution of H-bond is higher than π -system along the poling direction of crystal axis as described in Hirshfield surface analysis (Fig. 5-7) resulting in a significant d₃₃ value. Thus piezoelectricity reported in grown crystal makes it a better candidate for device applications among all reported p-nitrophenolate based compounds.⁸⁻¹¹

Hysteresis Loop

Ferroelectricity property in materials can be defined as the presence of spontaneous electric polarization which can be reversed by an applied electric field. The ferroelectric behaviour of grown crystal

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was confirmed by tracing P–E hysteresis loop at room temperature which is being reported for the first time. Hysteresis loop of grown SPNPD crystal is shown in Fig.11. It is found that grown crystals can sustain a switching ac electric field upto 10 kV/cm beyond which cracks are developed in them. So, we cannot apply a field more than this value to achieve saturation polarization. Therefore, grown crystal does not show saturation in polarization curve. The Ferroelectric loop has an oval shape which may be due to its T_c lying just near the room temperature. From the hysteresis loop, the values of the remnant polarization (P_r) and coercive field (E_c) are found to be 2.67 μ C/cm² and 7.43 kV/cm, respectively. We define coercive field (E_c) as the minimum applied electric field strength which is required for switching full remnanat polarization. Till now ferroelectric behavior has not been reported in many other alkali p-nitrophenolate hydrate compounds. ⁸⁻¹¹ Due to ferroelectric behavior reported in grown crystal, this material can have many optoelectronic applications such as capacitors, nonvolatile memory devices, high-performance gate insulators etc.



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Nonlinear optical studies

The efficiency of a nonlinear optical material in transferring energy from fundamental beam to second harmonic beam is determined by second harmonic generation efficiency (SHG) parameter. The SHG efficiency of grown crystals was determined using Kurtz and Powder technique⁴⁶ which also identifies the materials having non-centrosymmetric structures. In semiorganic crystals, due to the presence of strong intermolecular interaction, wave functions overlap to a great extent which results in the delocalization of π electrons.⁴⁷ Grown crystal crystallizes in Ima2 space group, which fulfils the required symmetry condition of second harmonic generation. SPNPD crystal basically consist of a metal ion (Na⁺) surrounded by an organic ligand (phenoxy ion) which is a benzene derivative and contains delocalized π -electron. Therefore, these crystals are expected to exhibit high NLO properties. To check the SHG efficiency of SPNPD, KDP crystal was taken as a reference material and was powdered to same particle size of 63µm. A Q- switched Nd-YAG laser of wavelength 1064 nm was passed through the powdered sample. The SHG property in SPNPD crystals was confirmed from the output of the laser beam having green emission of wavelength 532 nm. The SHG efficiencies of SPNPD and KDP crystals were found to be 14.1 mV and 3.4 mV respectively. Thus SHG value of grown crystal was found to be 4.15 times of that of KDP which is a very higher value than some reported p-nitrophenolate based semiorganic compounds.⁸⁻¹¹This higher SHG value in grown crystal compared to other similar p-nitrophenolate materials is due to the much ease of electron delocalization arising from less electronegativity of sodium atom which makes it a potential material for NLO device applications.

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Microhardness analysis

Hardness testing is one of the important tools used for determining mechanical properties of solids which gives information about the strength, molecular bindings, elastic constants and yield strength of the material.⁴⁸⁻⁴⁹ Mechanical strength, including voids, plays an important role in device fabrication. In order to study the mechanical property, the Vickers microhardness measurement was carried out on flat and smooth surfaces of grown SPNPD crystals at room temperature. The loads 5-100 g were applied on the crystals for a dwell time of 10 s which result in micro- indentations on the surfaces. Beyond 100 g of the applied load, multiple cracks were observed on the crystal surface around the indenter which may occur due to the internal stress released. The length of both diagonals of indentations was measured using Quantimet software and the average of the diagonals (d) for different loads was considered.

The Vickers microhardness number (H_v) of crystal was calculated using the following formula:

$$H_{\rm V} = 1.8544 \text{ x P/d}^2$$

Where P is applied load in kilograms and d is the average of two indentation diagonal lengths in µm. Fig.11





(a) shows the variation of H_V with applied loads ranging from 5 g to 100 g for SPNPD crystal. It is observed from the figure that the Vickers hardness parameter (H_v) increases with the increasing applied load, suggesting the reverse indentation size effect (RISE).⁵⁰⁻⁵¹ In RISE the 'relaxation' in the material results in a release of the indentation stress along the surface away from the indentation site which may be due to the crack formation or elastic deformation of the tip of the indenter.

The Meyer's work hardening coefficient (n) was calculated from the Meyer's law⁵² which gives a relationship between load and the size of indentation as:

 $P = k_1 d^n$

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 $\log P = \log k_1 + n \log d$

where k_1 is material constant and 'n' is the Meyer's index.

In order to find the value of 'n', a graph was plotted between log P and log d as shown in Fig.11(b) which gives a straight line after least square fitting. From the slope of the line the value of n was found to be 4.89. According to Onistch and Hanneman⁵³, the value of 'n' should lie between 1 and 1.6 for hard materials and more than 1.6 for soft materials. So SPNPD crystal is categorized as a soft material.

The anisotropic properties of the molecular solids are determined equally by the empty spaces as well as the filled ones. ¹⁹ Voids in the crystal can be defined as the region of empty space between the molecules in the crystal and this empty space is the region which lie outside the normal vanderwalls surface area of molecules in the unit cell and within which no nuclei exists. Voids in the crystalline material have been visualized by constructing (0.002 au)-isosurface of procrystal electron density. This 0.002 au electron density isosurface contain more than 98% of the electronic charge of molecules and identifys the empty space in crystal by detremining the shape and size of molecules. Fig.13 displays the voids surface of grown crystal. The volume of void was computed to be 467.71 Å³ while from Single crystal XRD analysis, volume of unit cell comes out to be 871.95 Å³. Thus volume occupied by voids is around 53.64% of unit cell volume which is condiderably higher than the voids volume (30.7%) calculated in the case of L-alanyl-L-

valine¹⁹. This higher value of volume occupied by voids reveals that grown crystal is very soft crystal which has been also supported by Vicker's microhardness study in form of Meyer's index value. Void volume, surface area and void volume as a percentage of total unit cell volume of grown crystal computed at (0.002 au)-isosurface has been summarized in Table 3.

Table3 Different parameters of voids in the SPNPD crystal.

	TTTTTTTTTTTTT		
Grown Crystal	Volume/ A ^s	Surface area/ A ⁻	% of unit cell volume
			U
SPNPD	/67 71	273.80	53.64
SI MI D	407.71	273.09	55.04
			7
			†C
			či la do
Fig. 13 SPNPD unit ce	ell void at (0 002 au)-isosur	face	
	11 , 014 ut (0.002 uu) 1505ut		

Conclusion

Good quality sodium p-nitrophenolate dihydrate single crystals have been grown from aqueous solution by adjusting the growth parameters. Experimentally observed morphology of crystal matches very well with

BDFH and modified BDFH laws. FTIR and Raman studies confirmed the formation of desired material. The nature of the intermolecular interactions present in crystal structure was studied by Hirshfeld surface analysis. The fingerprint plots which have been generated from Hirshfeld surface enabled to decode the quantitative contribution of interactions towards the crystal packing. The mapping of shape index and curvedness on Hirshfeld surface analysis gives characteristic of $\pi \cdots \pi$ stacking interactions. Optical studies show that the grown crystals have very high optical transmittance. In the PL spectra, a broad band observed at 525 nm suggests its applications for fabricating green laser and new tunable laser system. This broadening in PL emission peak is mainly caused by the presence of strong intermolecular hydrogen bonding interactions in crystal structure which plays an important role in crystal packing. Low value of dielectric constant and dielectric loss indicates the suitability of material for NLO applications in accordance with the Miller's rule. The piezoelectric charge coefficient (d_{33} pC/N) was found to be 2.24 pC/N showing the contribution of hydrogen bonding interaction along the poling direction of crystal axis and hence gives possibility for transducer devices applications. Ferroelectricity reported in grown crystal makes it favorable for nonvolatile memory devices, high-performance gate insulators applications. Because of very high observed value of SHG (4.14 times of that of KDP) efficiency, SPNPD crystals are useful for laser and photonics devices. In micro-hardness study the Meyer's index 'n' was found to be 4.89 which revealed that SPNPD crystal belongs to soft material category. Further, the void volume (53.63% of total unit cell volume) also confirms that grown crystal is very soft crystal. Hence, semiorganic crystal SPNPD is not only a potential material for device fabrication in optoelectronics but also a promising low dielectric constant material showing piezoelectric and ferroelectric behavior.

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