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Synthesis, Growth, Optical, Structural and Mechanical Characterization of SPNP and KPNP Single Crystal using Ethanol as a Solvent

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Abstract: ***Single crystals of sodium para nitro phenol (SPNP) and potassium para nitro phenol (KPNP) was synthesized at room temperature by slow evaporation solution growth technique using ethanol as a solvent upto the size of 12 × 3 × 2 mm³ and 15 × 2 × 2 mm³ respectively. The grown crystals were characterized by UV- Visible, photoluminescence, Kurtz- Perry test, single crystal X-ray diffraction analysis and Vicker's microhardness studies. Structural identification of grown crystals was done by single crystal X-ray diffraction and it shows both the crystals are belongs to triclinic crystal system. The SPNP and KPNP crystal emits green light radiation as evident from the PL measurement. The UV -Visible study revealed that the grown crystal has high transmission window with cut off wavelength of 207 nm and 208 nm respectively. And also the direct optical band gap was estimated to be 3.23 eV and 3.20 eV using Tauc's plot. The SHG output of grown crystals was recorded by Kurtz Perry technique and it is found to be nearly five times greater than the reference KDP. The Vickers hardness test confirms the mechanical stability of the material.***

Keywords **:** ***Hardness, NLO,*** **Optical,** ***SHG.***

I. INTRODUCTION

Researcher recently focus the solid state material with displays supreme second order non linear optical properties to examine their several kinds of potential application in modern electronics such as optical storage devices, opto electronics, computing and telecommunication devices, high speed information processing [1,2]. Inorganic material comprehensively utilized in these fields due to their excellent mechanical strength and chemical stability even so the poor nonlinearity. At the same time, the organic materials are

posses superior nonlinear optical property, however it is too complicate to grow the material in bulk size [3, 4]. Therefore the material researchers search for a new semi-organic NLO material because of their high chemical flexibility, thermal and mechanical stability and outstanding optical nonlinearity [5 – 7]. From the literature survey, the presence of hydroxyl group, nitrogroup and phenyl group in paranitrophenol forms a conjugated molecular configuration with noteworthy electron transfer actions like electron donor and acceptor [8 – 10]. Based on the literature, the authors have the curiosity to grow the novel material for the family of paranitrophenol. In this article, we report the synthesis, crystal growth of sodium para nitro phenol (SPNP) and potassium para nitro phenol (KPNP) single crystal using ethanol as a solvent by slow evaporation solution growth technique and the grown materials were characterized by optical, structural and mechanical studies and their results are discussed in detail.

II. CRYSTAL GROWTH

A. Growth of SPNP crystal

SPNP crystal was synthesized using AR grade of para nitro phenol ($C_6H_5NO_3$) and sodium hydroxide (NaOH) in the molar ratio 2:1. The required quantity of para nitro phenol and NaOH was estimated according to the following reaction (Fig. 1). The calculated amount of para nitro phenol was first dissolved in the ethanol. Then NaOH was added to the solution slowly with stirring. The saturated solution filtered into a clean beaker and closed with covers and kept in a dust free in atmosphere. The purity of the synthesized salt was improved by recrystallization process (at least three times). Good quality and red coloured single crystal of size 12 × 3 × 2 mm³ was obtained during the period of 15 days. The photograph of as grown crystal as shown in fig. 3(a).

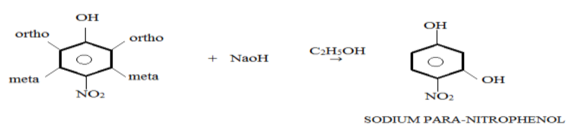

Fig. 1: Reaction scheme of SPNP

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B. Growth of KPNP crystal

The crystal growth procedure includes the following steps. The analytical grade Para-nitrophenol ($C_6H_5NO_3$) and potassium hydroxide (KOH) were taken in stoichiometric ratio of 2:1 and dissolved in 50 ml ethanol. The title compound was prepared according to the following chemical reaction in the fig. 2. The same procedure was adopted to grow the KPNP crystal. The yellow coloured crystal of dimension 15 × 2 × 2 mm^3 were obtained after a period of 18 days and the photograph of the grown crystal is depicted in the fig.3(b).

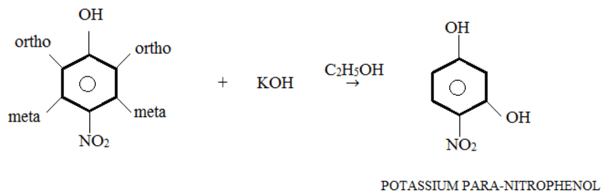

Fig. 2: Reaction scheme of KPNP

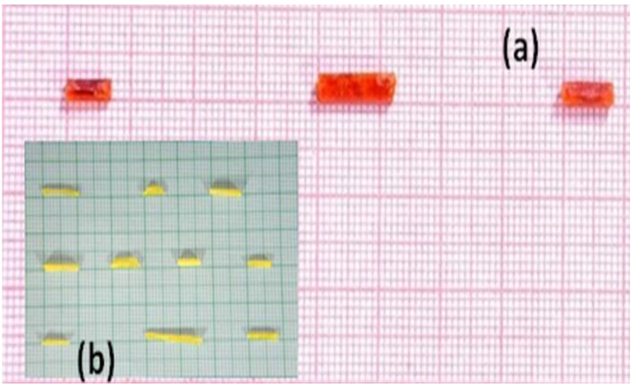

Fig. 3: (a) As grown SPNP crystal (b) KPNP crystal

III. RESULT AND DISCUSSION

A. *Single Crystal X-ray Diffraction*

The structure of grown crystal was examined by single crystal XRD analysis and the lattice parameters values were determined using Enraf Nonius CAD-4 diffractometer with a Mo-Ka (λ =0.71073 Å) radiation. It was found that the both the grown SPNP and KPNP crystal belongs to triclinic crystal system. The measured crystallographic data are given in table.1.

Table 1. SXRD data of grown crystals

Parameter	SPNP	KPNP
a	3.71 Å	6.44 Å
b	10.45 Å	9.34 Å
c	10.85 Å	12.25 Å
α	116.82^0	89.86^0
β	99.80^0	76.57^{0},
γ	90.14^0	90.60^0
Volume	421 $Å^3$	737 $Å^3$
Crystal System	Triclinic	Triclinic

B. *UV-Visible Analysis*

A UV-Visible spectral analysis of grown SPNP and KPNP crystal were recorded in the range of 190-1100 nm using Lambda 35 UV- Visible spectrometer. The optical absorption spectrum of grown single crystal is shown in fig. 4. The optical cut off wavelength of the SPNP and KPNP were found to be at 207 nm and 208 nm respectively which represent the grown sample as potential material for device fabrica``tion.

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

$$\alpha = \frac{2.3036 \log \left(\frac{1}{T}\right)}{t} \qquad (1)$$

Where T is the transmittance and t is the thickness of the crystal. As a direct band gap, for high photon energies (hυ) the absorption coefficient (α) obey the following relation

$$\alpha = \frac{A(h\upsilon - Eg)^{1/2}}{h\upsilon} \qquad (2)$$

Where E_g is the optical band gap of the crystal and A is a constant. Optical band gap was determined by plotting a graph between $(\alpha h\nu)^2$ versus energy of photon (hν) as shown in fig.3a and 3b. The band gap energy of SPNP and KPNP material is estimated at 3.23 eV and 3.20 eV using Tauc's plot (Fig.5 a & b) and its reveals that the grown crystal as in the category of insulating material.

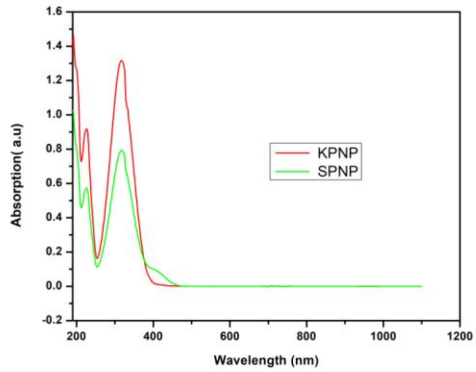

Fig.4 UV – Visible absorption spectrum grown crystal

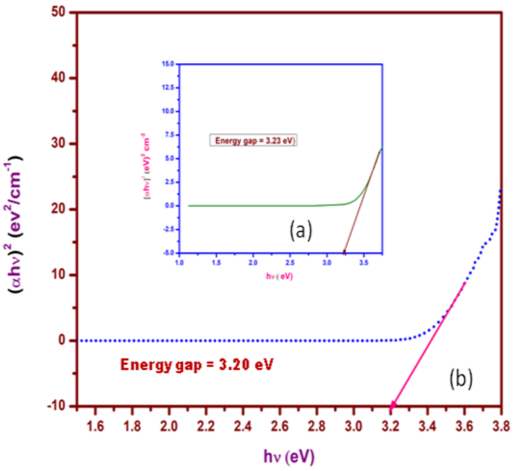

Fig.5 (a) Tauc's plot of SPNP crystal (b) KPNP crystal

C. *Photoluminescence*

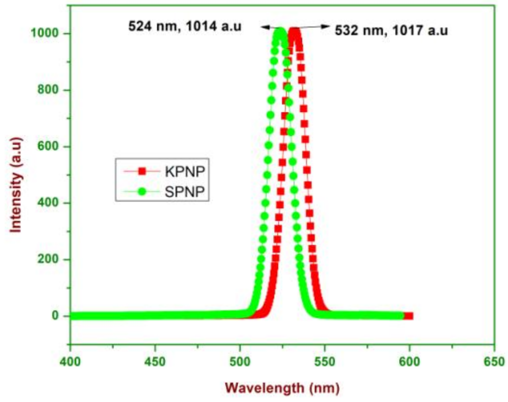

Fig. 6 PL spectrum of SPNP and KPNP crystal

The photoluminescence of the grown crystals of SPNP and KPNP were carried out at room temperature using a Perkin Elmer–LS 45 Luminescence spectrometer at room temperature between the ranges from 400 nm to 600 nm and is shown fig.6.The strong emission peak was observed from both SPNP and KPNP samples at 524 nm and 532 nm respectively. It confirms that the grown crystals emit green radiation. The emission of ion lies in green region that corresponds to $\sigma - \sigma^*$transition.

D. NLO Test

The SHG property of grown crystals was investigated through the modified Kurtz and Perry Powder technique [18, 19]. The grown single crystal of SPNP & KPNP was powdered and packed in a micro capillary of uniform bore. A Q-Switched Nd:YAG laser beam of wave length 1064 nm with an input energy of 0.7015 Joules and pulse width of 6 ns with a repetition rate of 10 Hz was made to fall on the sample.

The power of the incident beam was measured using a power meter. The output from the sample was passed over a monochrometer, which separates 532 nm (SHG) signal from 1064 nm and was absorbed by $CuSO_4$ solution that removes the 1064 nm radiation. A BG-38 filter kept in the path also removes the residual1064 nm radiation. The SHG output is finally detected by a photomultiplier tube (Hama-matsu R 2059, a visible PMT) and displayed on oscilloscope.

The SHG is confirmed by the emission of green radiation from the sample. The output power was measured to be 40.6 mJ for SPNP and 41.8 mJ for KPNP material respectively. For the same input, potassium dihydrogen orthophosphate (KDP) emitted the green light with the output energy of 8.91 mJ. The SHG efficiency of SPNP & KPNP crystal was found to be 4.55 and 4.69 times that of KDP crystal.

The SHG efficiency of some para-nitro phenol based samples are provided in table 2.

E. *Vickers Microhardness Test*

The grown KPNP crystal of micro hardness test was carried out using Vickers Micro hardness Econömet VH-1MD instrument at room temperature and constant indentation time of 10 s. The indentation marks were well developed on polished surfaces of the sample by varying the load from 10 g to 100 g (fig. 7). The hardness of crystal provides detail about the strength, molecular bindings and the resistance that the lattice offers to the local deformation.

Table 2. SHG efficiency of some para-nitro phenol based samples

Parameter	SHG Efficiency (Reference with KDP)	Reference
P- nitro phenol urea	3.5 times	S. Selvakumar, A. Leo Rajesh [11]
Sodium P-nitrophenalate Para-nitrophenol dehydrate (SPPD)	5 times	S. Selvakumar et al [12]
L-Lysine 4-nitrophenolate monohydrate (LLPNP)	4.45 times	M. Mahadevan et al [13]
SPNP	4.55 times	Present Work
KPNP	4. 69 times	Present Work

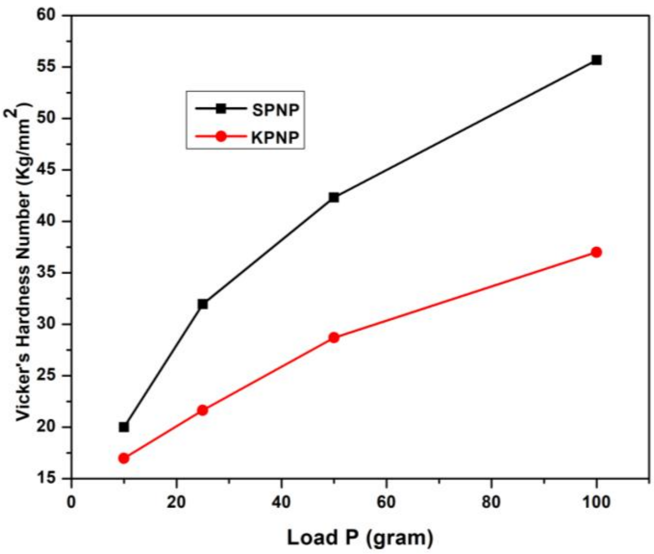

Fig. 7 Vickers microharness spectrum of SPNP and KPNP crystal

The micro hardness value correlates with other mechanical properties such as elastic constant and yield strength. The diagonal length of the indentation (d) in micro meter for different applied load P (g) between 10 g to 100 g measured for a constant indentation period of 10 sec for all trails .The diagonal length of the indentation marks and the crack length were measured, using a micrometer eyepiece. The Vickers hardness number (H_v) was calculated using the relation,

$$H_v = 1.8544\ P/d^2\ \text{kg mm}^{-2} \quad (18)$$

Where, P –Applied load in kg and d – diagonal length of the indentation marks in mm [23, 24]. The variation of H_v with applied load for grown crystal is shown in fig.4.4. According to normal indentation size effect (ISE), the hardness of the crystal decreases with increasing load P and in reverse indentation effect (RISE), hardness increases with the increasing load P[23, 24]. If we increase the load beyond the 100 g the crystal will be breaked.

According to Mayer's law

$$P = A\ d^n \quad (19)$$

Where, A is a constant and exponent n is the Mayer's number. The Mayer's law gives the relation between load P and indentation d.

The plot log P versus log d shown in fig.4.5 yields a straight line and slope of the straight line gives the work hardening co-efficient (n). According to Onstrich [25] the lattice is soft if 'n' greater than 1.6 (n >1.6) and lattice is hard if 'n' less than 1.6 (n <1.6). From the fig.4.5 the work hardening co-efficient of SPNP and KPNP crystal were found to be 3.87 and 3.67 respectively. The result is confirmed that the grown crystal belongs to soft category of the material.

IV. CONCLUSION

Single crystals of sodium para nitro phenol (SPNP) and potassium para nitro phenol (KPNP) was successfully grown by slow evaporation technique using ethanol as a solvent and harvested large size of $12 \times 3 \times 2$ mm^3 and $15 \times 2 \times 2$ mm^3 respectively. The structure of grown crystal was SPNP and KPNP crystal belongs to triclinic crystal system and the optical cut off wavelength of the SPNP and KPNP were found to be at 207 nm and 208 nm respectively which represent the grown sample as potential material for device fabrication. The band gap energy of SPNP and KPNP material is estimated at 3.23 eV and 3.20 eV and its reveals that the grown crystal as in the category of insulating material. The strong emission peak was observed from both SPNP and KPNP samples at 524 nm and 532 nm respectively and PL plot confirms that the grown crystals emit green radiation. The SHG efficiency of SPNP & KPNP crystal was found to be 4.55 and 4.69 times greater than KDP crystals. The work hardening co-efficient of SPNP and KPNP crystal were found to be 3.87 and 3.67 respectively and the result is confirmed that the grown crystal belongs to soft category of the material.

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