

# Alkali P-Nitrophenolates for Short Wavelength Laser Generation

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**Abstract:** Single crystals of alkali p-Nitrophenolates namely sodium p-nitrophenolate dihydrate (SPNP), potassium p-nitrophenolate monohydrate (PPNP) and lithium p-nitrophenolate trihydrate (LPNP) using Group I elements (Na, K, Li) and p-nitrophenols were grown by solvent evaporation method. Single crystal XRD analysis shows that SPNP and LPNP crystallize in noncentrosymmetric space group while PPNP is centrosymmetric. Using Autox software, all the peaks in the recorded powder XRD spectrum of the samples were identified and indexed. The FT – IR spectra of the sample reveals the characteristic vibrations of the functional groups present in alkali-nitrophenolates. A weak absorption band around the region 1589–1641  $\text{cm}^{-1}$  confirms the presence of the phenolic ring. A broad intermolecular hydrogen bonded OH stretching at 3325  $\text{cm}^{-1}$  of p-nitrophenol is shifted which shows the increase in the polarizable nature of p-nitrophenol and thus easily forms a metal (sodium/ potassium/ lithium) coordination compound. UV-Vis spectrum shows that all the crystals are transparent above 400 nm and has a wide optical window in the visible region. Intense absorption peak in the UV region may be due to the colored nature of the compound. Addition of metal ion (sodium/potassium) modifies the optical transparency of the original molecule (p-nitro phenol) and consequently introduces a bath chromic shift of 90/40 nm in the crystal transparency of the samples. Kurtz powder technique result shows that the relative SHG efficiency of SPNP and LPNP was nearly 5 and 9.25 times of KDP.

**Key Words:** p-Nitrophenol, SHG Efficiency, Alkali Metals.

## 1. INTRODUCTION

The p-nitrophenolate derivatives are the other forms of metal-organic coordination complexes. The prototype organic NLO material contains one or more delocalized bonds, typically a ring structure like benzene. When substituted with donor and acceptor at the para position, the bonds get aligned and thus have a large induced dipole moment under the influence of electromagnetic fields. p-nitrophenol is a typical example for the above strategy [1]. It has often been found that such structures, when packed as crystals tend to be centrosymmetric, thus leading to macroscopically vanishing dipole moment. However, when it reacts with the bases, the resulting compound is acidic with a non-vanishing dipole moment for the donor-acceptor  $\pi$ -conjugate systems [2, 3]. The life time of an optical device (electro- optic modulators, parametric oscillator, etc.) is strongly dependent on mechanical and thermal properties of the nonlinear material. Organic materials are more fragile than inorganics owing to van der Waals bonds which maintain the cohesion of molecular packing. Based on these favorable properties, three nitrophenolates namely (i) sodium p-nitrophenolate dihydrate (SPNP), (ii) potassium p-nitrophenolate monohydrate (PPNP) and (iii) lithium p-nitrophenolate trihydrate (LPNP) have been synthesized and their optical properties were thoroughly investigated and reported.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Synthesis and Crystal Growth

The basic chemical reaction considered for synthesis is that a caustic alkali base (alkali hydroxide) will lose a proton in a

weak acidic (p-nitrophenol) leading to the formation of the salt. Thus in the present investigation, the salt is obtained by dissolving p-nitrophenol in alkali hydroxide (NaOH, KOH, LiOH) solution at 32°C in the molar ratio 1:1:30 for p-nitrophenol, alkali hydroxide and double distilled water respectively. By cooling the solution to room temperature a yellow crystalline powder is obtained.

From solubility studies, methanol was found to be the best solvent to grow SPNP and PPNP, while water was chosen for LPNP. Then the prepared solutions were allowed to slow evaporation, after a period of seven days yellow coloured single crystals of SPNP, PPNP and LPNP were obtained.

## 3. RESULTS AND DISCUSSION

### 3.1. Structural Analysis

The grown crystals were subjected to single crystal X-ray diffraction using a Enraf Nonius CAD-4 single crystal X-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.54060 \text{ \AA}$ ) to determine the unit cell dimensions. XRD analysis shows that SPNP crystal belongs to the orthorhombic system with a

noncentrosymmetric space group  $Ima2$ . The PPNP belongs to monoclinic system with a centrosymmetric space group  $P2_1/c$ , which does not exhibit second order NLO activity. Also LPNP crystallizes in monoclinic system with a noncentrosymmetric space group  $Pa$ . Their cell dimensions are given in the Table 1. All the unit cells have ( $Z = 4$ ) tetra molecules and have a suppressed growth along c axis.

It is interesting to note that elements in the complexes that are more electronegative induce more delocalization of electrons, favoring the noncentrosymmetric structure [4].

This is the reason why, PPNP is centrosymmetric while LPNP and SPNP are noncentrosymmetric as the electro negativity of alkali metals Li (0.98), Na (0.93) and K (0.82) falls down as one move down the Group.

**Table 1. Cell Parameters of Nitrophenolates**

Sample	a (Å)	b (Å)	c (Å)	$\beta$ (deg)	V (Å <sup>3</sup> )
SPNP	6.896 (7)	19.709 (6)	6.443 (3)	90	875.68 (9)
PPNP	10.561 (3)	7.379 (2)	11.299 (4)	117.80	778.72 (3)
LPNP	10.838 (8)	7.519 (4)	11.31 (4)	90.54	925.7(9)

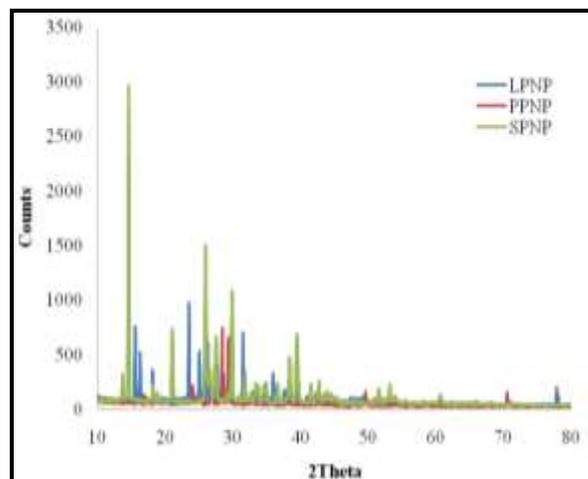
$$\alpha = \gamma = 90^\circ$$

The powder samples were subjected to powder XRD (Figure 1) analysis using a X'Pert diffractometer with CuK $\alpha$  radiation ( $\lambda=1.5418$  Å). The computer program AUTOX was used to index all the observed reflection in the XRD pattern and to calculate the corresponding lattice parameters. The lattice parameter evaluated from PXRD agrees very well with single crystal XRD data.

The figure 1C explains the comparison of particle size, lattice constant variation with the calcination temperature. In is observed from the figure that, particle size increases with increasing calcination temperatures and lattice constant decreases with temperatures.

### 3.2 Molecular Characterization

The FT – IR spectra of SPNP, PPNP and LPNP reveals that the characteristic vibrations of the functional groups present in nitrophenolates.



**Figure 1 Powder XRD Pattern of Nitrophenolates.**

The absorptions in the lower frequency region (400 – 500 cm<sup>-1</sup>) are due to the overtones of the fundamental vibrations of p-nitrophenolates. The vibrational frequencies of the functional groups present in alkali p-nitrophenolates are compared with the p-nitrophenol (PNP) in Table 2

**Table 2. FT-IR bands of alkali p-nitrophenolates.**

Wavenumber (cm <sup>-1</sup> )				Assignment
PNP	LPNP	SPNP	PPNP	
3325	3408	3189	3211	$\nu_s$ (OH)
3060	3059	–	3045 *	$\nu_s$ (C-H)
1613	1666	1682	1665	$\delta$ (O-H)
1590	1573	1576	1601	$\nu_s$ (NO <sub>2</sub> )
1494	1495	1484	1467	$\nu_s$ (C=C)
1326	1320	1302	1343	$\nu_{as}$ (NO <sub>2</sub> )
865	855	853	846	$\nu_{as}$ (C=C)
817	822	814	757	$\delta$ (C-H)
710	705	703	699	$\delta$ (C=C)
642	647	644	629*	$\delta$ (O-H)
–	497	494	483	(Li/ Na/ K)

$\nu_s$  – symmetric stretching

$\nu_{as}$  – asymmetric stretching

$\delta$  - bending

A weak absorption band around the region 1589 – 1641 cm<sup>-1</sup> confirms the presence of the phenolic ring. The shift in broad intermolecular hydrogen bonded OH stretching at 3325 cm<sup>-1</sup> increase the polarizable nature of p-nitrophenol to a higher order and it easily forms a metal coordination compound and hence confirms the molecular structure of the synthesized compounds.

### 3.3 Linear Optical Characterization

Optical transmittance of the crystalline samples was recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the UV – Vis region. In SPNP single crystals, 60% optical transmittance occurs at 520 nm and it has a good optical transmittance window in the region 520-1500 nm. In PPNP, the intramolecular charge transfer between the donor and acceptor groups give an intense absorption band ( EtOH as solvent ) in the UV region with  $\lambda_{\text{max}}$  at 388 nm and 310nm. This may be due to the colored compound absorbing in the visible region. In LPNP, 80 % transparency occurs at 450 nm and is almost transparent till 1500 nm (Figure 2). Addition of metal ion (sodium/potassium/lithium) modifies the optical transparency of the original molecule (p-nitro phenol) and consequently introduces a bath chromic shift of 90/40 nm in the crystal transparency.

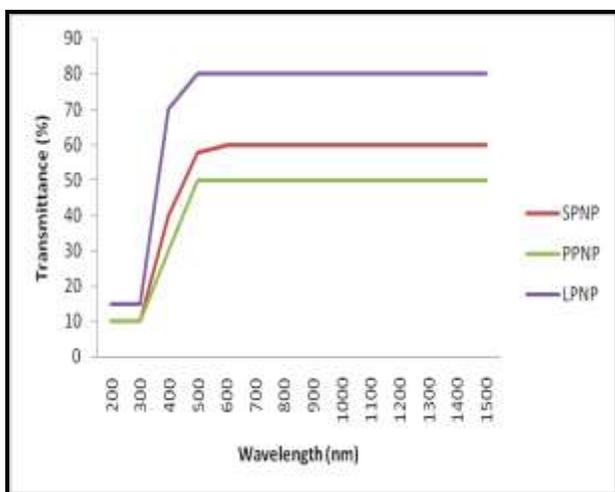


Figure. 2 Optical Transmittance of Nitrophenolates

### 3.4 Non-linear Optical Characterization

The synthesized salts of p-nitrophenolates were imposed for SHG test by Kurtz powder technique using a Q-switched Nd:YAG laser (1064 nm, 10 ns, 10 Hz). The test reveals that SPNP, LPNP exhibits SHG and no SHG signal was observed for PPNP. In SPNP and LPNP, metal atom is ionically bonded with p-nitrophenol introducing the noncentrosymmetry, which is an essential criterion for SHG. The results are compared with the pulverized KDP and the relative powder SHG efficiency was found to be 5 and 9.25 times greater than KDP for SPNP and LPNP respectively.

It is worthwhile to note that a material with smaller ionic radii has larger polarizability and hence larger nonlinear polarization[4]. Thus LPNP with lowest ionic radii alkali (Li = 0.76 Å) metal has higher SHG efficiency than other alkali

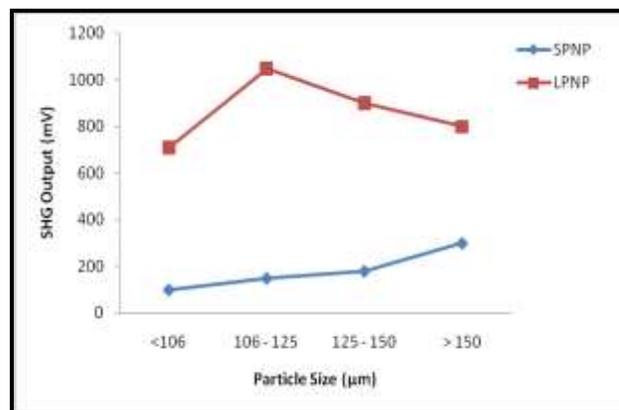


Figure. 3 Particle size vs. SHG output.

nitrophenolates. The intensity of the SHG output as a function of particle size was measured. The SHG output of SPNP increases with respect to the range of particle sizes, indicating the phase matchable character of the SPNP. While for LPNP, SHG output decreases with increase in particle size, showing the non-phase matchable nature of LPNP (Figure 3).

## 4. CONCLUSION

In the present investigation, attempts were made to synthesize certain semiorganic NLO materials based on nitrophenolates by acid-base reaction using alkali metals. Single crystals of considerable sizes were grown following the low temperature solution growth technique. X-ray diffraction studies reveal that SPNP and LPNP crystallize in the noncentrosymmetric space group with prominent crystallographic planes suitable for further studies. All the crystals exhibit a wide optical transmittance window (450 – 1500 nm) in the UV-Vis region irrespective of the substitutions. From the powder SHG efficiency studies the phase matchable SPNP and non phase matchable LPNP with high SHG efficiency (nearly 5 and 9.25 times of KDP) are found to be the potential candidates for the generation of short wavelength lasers by frequency doubling phenomena.

## 5. REFERENCES

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