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# Optical, theoretical and mechanical studies on sodium acid phthalate crystal

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ABSTRACT

The semiorganic crystal of sodium acid phthalate (NaAP) single crystals was grown in the solvent of water by slow evaporation method at room temperature. The single crystal X-ray diffraction studies showed the crystal belongs to orthorhombic system. The optical absorption spectrum reveals that the crystal has good transparency in entire visible region. The hardness number of the material is measured by microhardness tester. The fluorescence green colour emission exhibits is semiorganic. The SHG efficiency of NaAP crystal confirms NLO behaviour of green colour emission to provide frequency doubling process for photo electronic applications.



## 1. Introduction

Nonlinear optical materials have attracted many researchers because of its key functions in frequency doubling, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in the areas such as telecommunications, signal processing and optical interconnections [1]. Organic NLO materials have large nonlinear optical susceptibilities but possess poor mechanical and thermal properties. These difficulties were overcome by semiorganic NLO materials [2]. The title materials of sodium acid phthalate single crystals are semiorganic in nature which is grown by slow evaporation technique at normal room temperature. Although the NaAP was already reported, the crystallization has been improved in the present work. Also, the optical, theoretical and mechanical properties were reported for the first time.

## 2. Experimental

### 2.1. Synthesis and crystal growth

The sodium acid phthalate salt was synthesized by analar grade of sodium bicarbonate and phthalic acid at 1:1 ratio dissolved in an aqueous solution using magnetic stirrer which is then filtered by Wattmann filter paper and covered by a plastic sheet with some holes at the top to limit the evaporation and kept in dust free atmosphere, at room temperature. After slow evaporation, the NaAP crystals grown in beaker though they were further purified by repeated recrystallization carried out to minimize the impurities of the raw material. After 10 days of growth, the well transparent with the dimensions $10 \times 8 \times 2\,mm^3$ of NaAP crystals was prepared and is shown in Fig. 1.

## 3. Characterization studies

### 3.1. Single crystal X-ray diffraction analysis

The grown NaAP single crystal was subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer. The determined cell parameters $a = 6.60$ Å, $b = 9.08$ Å, $c = 25.84$ Å; $\alpha = \beta = \gamma = 90^\circ$ and the cell volume $V = 1548$ Å$^3$ are in close agreement with reported values [3,4]. The grown title crystal belongs to orthorhombic system. The valence electron plasma energy, $\hbar\omega_p$ is given by

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \quad (1)$$

where $Z = ((8 \times ZC) + (6 \times ZH) + (1 \times ZNa) + (4 \times Zo)) = 63$ is the total number of valence electrons, $\rho$ is the density and $M$ is the molecular weight of the grown crystal. Explicitly $\hbar\omega_p$ dependent Penn gap and the Fermi energy, is given by

$$E_p = \frac{\hbar\omega_p}{(\varepsilon_\infty - 1)^{\frac{1}{2}}} \quad (2)$$

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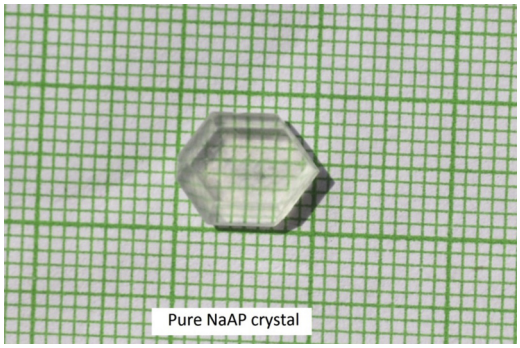


**Fig. 1.** Photograph of as grown crystal.

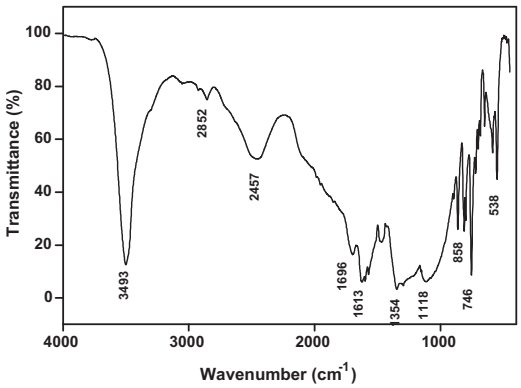


**Fig. 2.** FTIR spectrum of the grown crystal.

and

$$E_F = 0.2948(\hbar\omega_p)^{\frac{4}{3}} \tag{3}$$

Polarizability $\alpha$ obtained using the relation

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3{E_p}^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \quad \text{cm}^3 \tag{4}$$

where $S_0$ is a constant for a particular material which is given by

$$S_0 = 1 - \left[\frac{E_p}{4E_F}\right] + \frac{1}{3}\left[\frac{E_p}{4E_F}\right]^2 \tag{5}$$

The value of $\alpha$ so obtained agrees with that obtained using Clausius–Mossotti equation which is given by,

$$\alpha = \frac{3M}{4\pi N_a \rho}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right) \tag{6}$$

All these calculated data for the grown crystal are shown in Table 1.

### 3.2. FTIR studies

The presence of functional groups and vibrational frequencies of NaAP crystal are identified by FTIR spectroscopy. The recorded spectrum of the grown crystal was carried out between the range 400–4000 $cm^{-1}$ using PerkinElmer spectrum one and is shown in Fig. 2. An absorption band in the range 538–858 $cm^{-1}$ appears due to the C—H out-of-plane deformations of the aromatic ring. The spectral band attributed at 1118 $cm^{-1}$ is due to the C—H in-plane deformation of the aromatic ring. The C—O stretching vibrations was obtained as a peak at 1354 $cm^{-1}$. The peak at 1613 $cm^{-1}$ was assigned due to the C—C skeletal aromatic ring vibrations. The carboxyl group C=O vibrations appear near 1696 $cm^{-1}$. All these assignments are in very good agreement with that of the reported values [5].

### 3.3. Optical absorption studies

An optical absorption spectrum of NaAP crystal was recorded in the range of 200–1100 nm using Varian Cary 5E UV–vis-NIR spectrophotometer. A transparent crystal of 2 mm thickness was used for this measurement. From the spectrum (Fig. 3), it is evident that the compound has low cut-off wavelength at 312 nm which is sufficient for SHG laser radiation of 1064 nm for frequency doubling process [5].

**Table 1**
Some theoretical parameters on NaAP crystals.

| Parameters | Values |
|---|---|
| Plasma energy (eV) | 20.37 |
| Penn gap (eV) | 2.35 |
| Fermi energy (eV) | 16.40 |
| Polarizability ($cm^3$) | |
| Penn analysis | $4.78 \times 10^{-23}$ |
| Claussius–Mosotti equation | $4.80 \times 10^{-23}$ |

The optical absorption coefficient ($\alpha$) was calculated from the transmittance using the following relation,

$$\alpha = \frac{1}{t}\log\left(\frac{1}{T}\right) \tag{7}$$

where $T$ is transmittance, and $t$ is thickness of the crystal.

Owing to the direct band gap, the crystal under study has an absorption coefficient ($\alpha$) obeying the following relation for high photon energies ($h\nu$);

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{8}$$

where $E_g$ is optical band gap of the crystal, and $A$ is a constant. The plot of variation of $(\alpha h\nu)^2$ vs. $h\nu$ is shown in Fig. 4. $E_g$ is evaluated by the extrapolation of the linear part, and the band gap is found to be 4.01 eV.

#### 3.3.1. Determination of optical constants

The optical behaviour of materials is important to determine its usage in optoelectronic devices. Knowledge of optical constants of a material such as optical band gap and extinction coefficient is quite essential to examine the material's potential optoelectronic applications. Further, the optical properties may also be closely related to the material's atomic structure, electronic band structure and electrical properties. The extinction coefficient ($K$) for the grown crystals can be determined using formula.

$$K = \frac{\alpha\lambda}{4\pi} \tag{9}$$

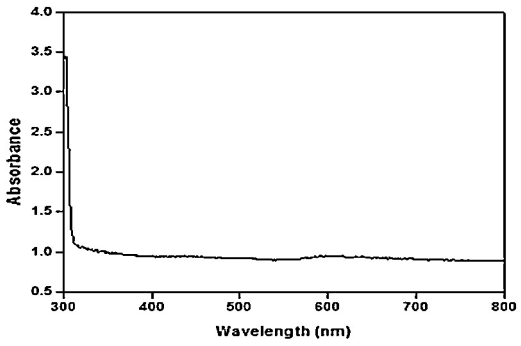


**Fig. 3.** Optical absorption spectrum of the NaAP crystal.