Growth, Optical, ICP and Thermal Studies of Nonlinear Optical Single Crystal: Sodium Acid Phthalate (NaAP)

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Abstract: Good quality single crystals of sodium acid phthalate (NaAP) were grown by slow evaporation technique. Single crystal X-ray diffraction study of the grown crystal reveals that the crystal belongs to orthorhombic system with space group $B2_{ab}$. Fourier transform infrared spectrum confirms the presence of the functional groups of the grown material. Inductively coupled plasma emission spectroscopy analysis is used to confirm the presence of Na element in the sample. Thermal analysis of the NaAP crystal shows that the crystal is stable up to 140°C. Optical transmittance of the grown crystal was recorded in the wavelength range from 200 and 800 nm using UV-Vis-NIR spectrophotometer. The second harmonic generation of NaAP was analysed using Kurtz powder technique.

INTRODUCTION

The optoelectronic technology requires nonlinear optical (NLO) materials for frequency conversion, optical modulation and optical switching applications [1]. In this regard, various inorganic and organic materials has been synthesised and their nonlinear optical properties were investigated [2-4]. Moreover, the physicochemical properties of the organic and inorganic NLO materials were studied in relation to their molecular structure and reported [5, 6]. When compare the organic and inorganic NLO materials, there has been considerable attention in the synthesis of semi-organic materials due to their large nonlinearity, low angular sensitivity, good mechanical hardness and high resistance to laser-induced damage [7,8]. Sodium acid phthalate is one of the promising semi-organic materials for NLO application and many researchers were reported its structural, morphological and optical properties [9–14]. In the present work, single crystal of sodium acid phthalate (NaAP), a semi-organic NLO single crystal have been grown by slow evaporation technique. The grown crystals were subjected to single-crystal X-ray diffraction, Fourier transform infrared (FTIR) analysis, Optical studies, ICP analysis and Thermal analysis. Although the growth of NaAP was already reported, in the present work, the crystallization has been optimized and transparency of the crystal has been improved.

EXPERIMENT

The starting materials with high purity (AR grade) of Phthalic acid and sodium hydroxide (99% purity) were dissolved with a stoichiometric ratio (1:1) in triple distilled water. The prepared solution was kept for solvent evaporation in the dust free atmosphere. Due to slow evaporation of the solvent, spontaneous nucleation occurs and these are grown into crystals of reasonable size. Crystals with clear faces, transparency and less number of visible defects are selected as seed for growing single crystals. The grown crystals are optically transparent and non-hygroscopic and are shown in Fig. 1.

FIGURE 1. Photograph of as grown crystals of NaAP

RESULTS AND DISCUSSION

The single-crystal X-ray diffraction analysis of the grown crystal was carried out using ENRAF NONIUS CAD4 automatic X-ray diffractometer. The calculated lattice parameter values are a = 6.159 Å, b = 9.607Å, c = 13.247Å, $\alpha = \beta = \gamma = 90°$ and the cell volume V = 822.159$Å^3$ and the crystal belongs to orthorhombic structure with the space group $B2_{ab}$ and the lattice parameter values are in good agreement with the reported values [8]. The morphology of the NaAP crystal is made up of various planes viz., (0 0 1) (0 -1 0) (1 -1 0) (1 0 0) (1 1 0) (01 0) (-1 1 0) and (-1-1 0) of which (0 0 1) is a prominent one and it is shown in Fig. 2. Further, it also shows that the prominent and the wider plane (0 0 1) is optically transparent and is quite suitable for optical device applications.

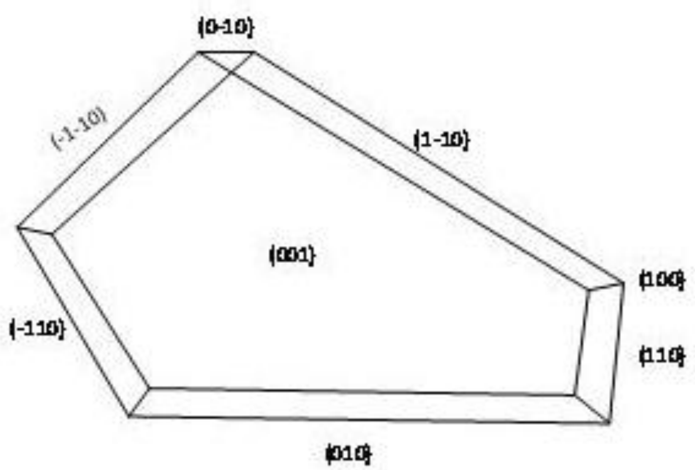

FIGURE 2. Morphology of NaAP crystal.

Fourier transform infrared (FTIR) spectra of NaAP crystal was recorded in the range of 400–4000 cm^{-1}. An absorption bands in the region 500–900 cm^{-1} appears as shown in Fig.3, which are due to the C–H out-of-plane deformations of the aromatic ring. The spectral band between 1210 and 1320 cm^{-1} is owing to the C–O stretching vibration. The carboxyl group C=O vibrations appear near 1703 cm^{-1}. The peaks at 1571 and 1627 cm^{-1} are due to the C–C skeletal aromatic ring vibrations of NaAP crystal. The FTIR qualitatively confirms the synthesized NaAP crystal.

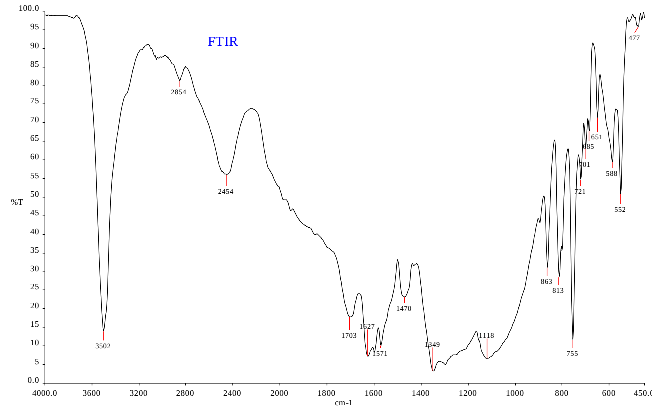

FIGURE 3. FTIR spectrum of NaAP crystal

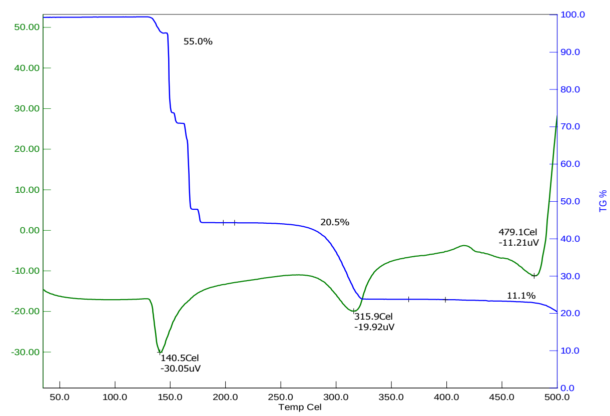

FIGURE 4. TGA/DTA curves of NaAP crystal**.**

The thermal behavior of NaAP was studied by the thermogravimetric (TG) and differential thermal analyses (DTA). The analyses were carried out under nitrogen atmosphere at a heating rate of 10°C/min in the temperature range of 50–500°C. The TG and DTA curves of NaAP are shown in Fig.4. The DTA curve shows an endothermic peak at 140.5°C, where the melting of the sample begins. At the molten stage, the decomposition of the NaAP started as the weight loss was observed at the same temperature. Moreover, the decomposition process occurs in three main stages as it was clearly observed in the TG curve. The first stage of decomposition was observed with weight loss of 55.0 % in the temperature ranges 135-176°C. Second major weight loss (20.5 %) was observed in the temperature range of 265-325 °C due to the removal of residual C_2H_6, NH_2 and CO moiety from the previous intermediate compound. The final residues, which have combination of carbon and nitrogen, were removed during the final stage of the decomposition. From the TG and DTA analysis it was confirmed that the material is stable up to 140°C.

Inductively coupled plasma emission spectroscopy analysis was used to confirm the Na element in NaAP crystal sample. It was found that the composition of Na present in the NaAP crystal was measured as 9.969 mg/L using PERKIN ELMER OPTIMA 5300 DV ICP-OES. The result confirms that Na is present in the NaAP crystal.

The UV-VIS optical transmission spectrum of the grown crystal was recorded in the range of 200 to 800 nm as shown in Fig. 5. The thickness of the sample used for the measurement was 2 mm. The optical transmittance spectrum shows low cutoff wavelength of 222 nm for the NaAP crystal and the calculated energy band gap is 5.56 eV, which is suitable for NLO application. Moreover, the crystal shows more than 80 % transparency, which shows the high optical quality of the grown crystal.

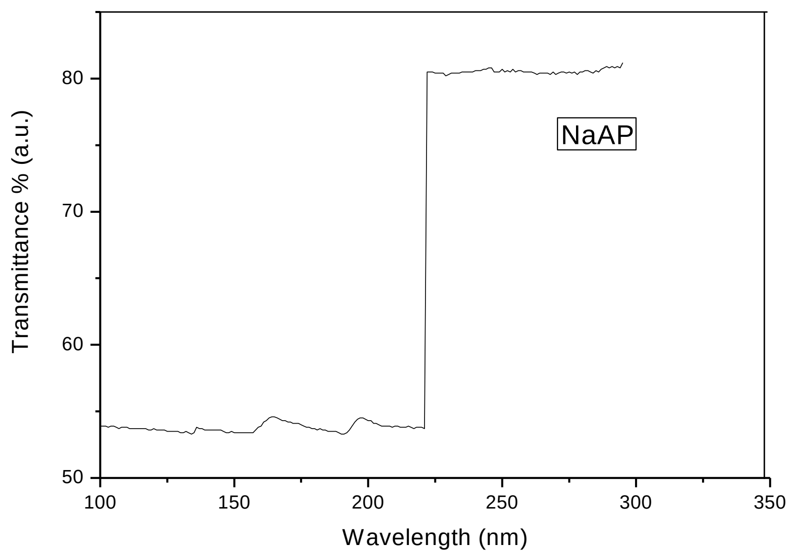

FIGURE 5. Optical transmission spectrum of NaAP crystal.

The SHG of NaAP crystal was analysed by Kurtz and Perry powder technique [15]. The powder samples prepared from the grown crystals have been placed in between the two quartz plates. Q-switched High Energy Nd:YAG Laser (QUANTA RAY Model LAB – 170 - 10) was irradiated into the sample loaded quartz plates. The frequency conversion was confirmed by the emission of green light from the powder sample of the grown crystal. KDP sample has been used as the reference material and output power values from the grown and reference samples were measured and tabulated (Table 1). From the table, it is confirmed that the SHG of the grown crystal is 1.45 times higher than KDP.

Table 1. Measured SHG energy of the NaAP and reference samples

Sl. No.	**Name of the Sample**	**Output Energy (mJ)**	**Input Energy (J)**
1	KAP	5.18	0.705
2	NaAP	10.32	0.705
3	KDP (Reference)	7.11	0.705

CONCLUSION

The NaAP crystals with high optical transparency were grown by slow evaporation method. The structural properties of the grown crystal was analysed by single crystal X-ray diffraction method. The functional groups of the grown crystals were identified by FTIR analysis. The Thermal analysis of the grown crystals confirms that the material is stable up to 140°C. The presence of Na in the NaAP crystal was confirmed by ICP analysis. The optical transmission study confirms that the grown crystals more than 80% transparency in the visible region. The SHG of the grown crystal is higher that KAP and KDP crystals which shows that the material is one of the promising material for NLO applications.

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