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Studies on the growth and characterization of Sodium 4-Nitrophenolate dihydrate (S4NP) NLO single Crystals

A. Sathish Kumar[a], S. Anbarasu[a], K. Kaviyarasu[a], T. Kishore Kumar[b] & Prem Anand Devarajan[a*]

[a] Centre for Nanoscience and Nanotechnology, Department of Physics, St. Xavier's College (Autonomous), Palayamkottai - 627002, Tamilnadu, India.

[b] Department of Physics, Presidency College, Chennai – 600 005, Tamilnadu, India.

*Corresponding author: dpremanand@yahoo.co.in

Abstract : Single crystals of Sodium 4-nitrophenolate dihydrate were conveniently grown from ethanol solution by employing slow evaporation technique. The as grown S4NP crystals were subjected to XRPD, FTIR and UV - vis - NIR spectral analysis. The results are discussed in detail.

Key words : Sodium 4-nitrophenolate, slow evaporation, XRPD, FTIR, UV-vis-NIR

1. Introduction

Second order non- linear optical crystals with aromatic ring have been the foci of infinite scientific interest attracting mucvh attention because of their high non-linearity, new response and tailor made flexibility [1-4]. Materials with large second order optical non-linearities find variety of applications in the area of laser technology, laser communication and data storage technology [5-6]. Moreover organic compounds are formed by weak Vander Waals and

hydrogen bonds and single degree of delocalization. Hence they are optically more non-linear than inorganic material. A major drawback of crystalline organic NLO material is the difficulty in growing large, optical quality single crystals; and also the often fragile nature of these crystals makes them difficulty to process. In order to overcome the above said drawbacks, a new class of materials has to come to be known as semi organics. In the class of semi organics the high efficient optical quality NLO materials form a polarizable organic molecule is stoichiometrically bonded to an inorganic host. Sodium 4-nitrophenolate is a class of semi organic NLO material having high values of hyper polarizablity. The Nitrophenoxy ion is ionically bonded to sodium ion coupled with infra molecular hydrogen bonding. Minemoto et al. and Brahadeeswaran et al have studied the crystal growth, topography and chemical etching properties of S4NP [7-8]. The growth and characterization of Lithium p-nitrophenolate was reported by Milton et al [9]. Recently Dhanuskodi et al have synthesized, grown and characterized S4NP NLO single crystal [10] using ethanol solvent. In our present work we herein report the growth and characterization of S4NP NLO single crystal by slow solvent evaporation technique using methanol as the solvent. The as grown crystals were grown and characterized by XRPD, FTIR and UV-vis-NIR spectral analyses.

2. Experimental Techniques

2.1 Materials

All the chemicals used in this work were purchased from E-merck, Analytical grade. Sodium hydroxide (99.9% pure) and 4-Nitrophenal (99.9% pure) were used without further purification.

2.2. Synthesis & Growth

Sodium hydroxide and 4-Nitrophenol were taken in an appropriate amount of stoichiometric ratio and they were dissolved in distilled water. The reaction is as follows.

$$(NO_2)\text{-}C_6H_4\text{-}OH + NaOH + H_2O \rightarrow (NO_2)\text{-}C_6H_4\text{-}ONa \,.\, 2H_2O$$

The saturated solution of S4NP was dissolved in Ethanol solvent at room temperature. The solution was filtered thrice using whatmann filter paper. Within 25 days single crystals of S4NP of dimensions 12x14x10 mm^3 were harvested. Defect free and transparent seed crystals were chosen for characterization studies. The photograph of as grown sulphamic acid is shown in Fig.1.

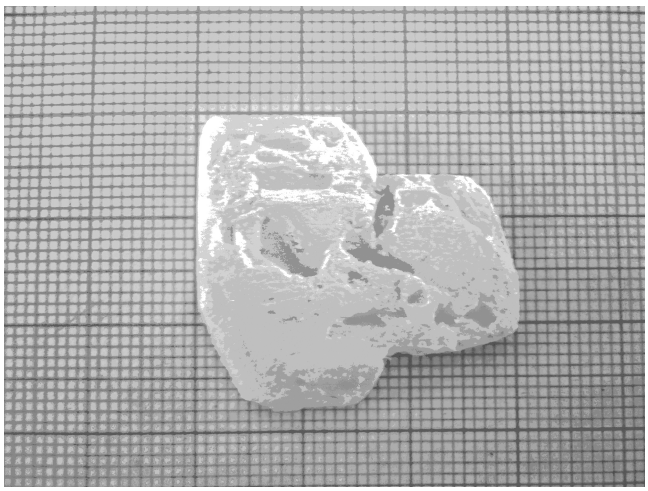

Fig.1. Photograph of as grown S4NP NLO single crystal

3. Characterization Techniques

3.1. XRPD Analysis

The XRPD pattern of S4NP single crystal was collected using XPERT Powder diffractometer with CuK_{α} (λ=1.541 Å) radiation in the range of 2θ from 10-50^0 at a scanning rate of 2^0/min. X-ray powder diffraction was used to identify the purity of S4NP single crystal. The relative intensity of peaks and x-ray diffractogram are shown in Fig.2. The positions of the powder XRD peaks were found to be in good agreement with single crystal XRD data [10].

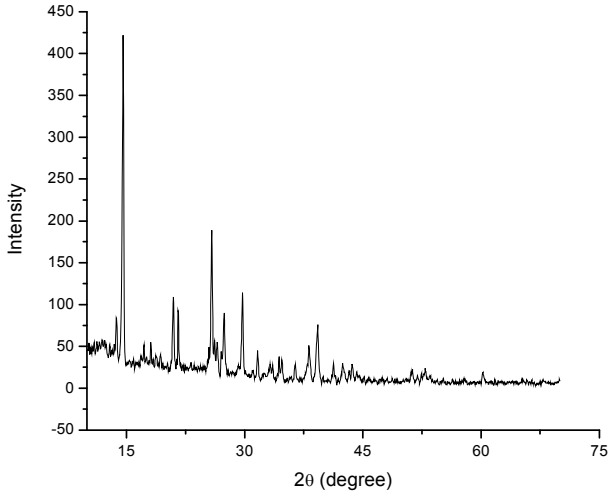

Fig.2. XRPD spectrum of S4NP NLO single crystal

3.2 FTIR Analysis

Fourier transform infra red (FTIR) spectrum was recorded in the spectral range 400-4000 cm^{-1} using Perkin-Elmer Lambda-35 FTIR spectrometer, where the S4NP crystalline sample was in Pellet form in KBr phase. The FTIR spectrum is shown in Fig.3. The vibrational bands assignable to 1588 and 1313 cm^{-1} are to H-OH bending and NO_2 stretching vibration. The wavenmbers in the finger print region is attributed to the fundamental vibrational overtone of 4-nitrophenolate. A band locating at 493 cm^{-1} is due to the hydrates of sodium. Thus the various functional groups in the molecule were identified.

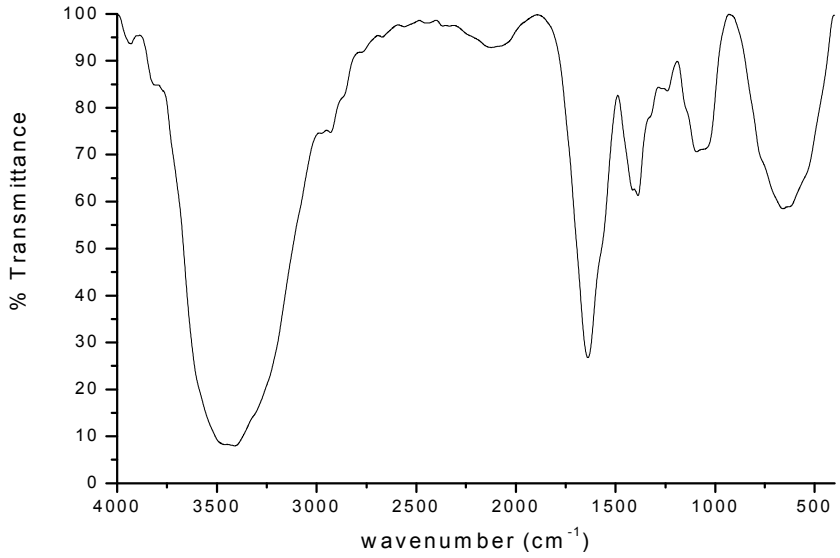

Fig.3. FTIR spectrum of S4NP NLO single crystal

3.3. UV-vis-NIR

The absorption spectra of NLO material play a major role in device fabrication [11]. The plot of absorbtion Vs wavelength (nm) of S4NP single crystal is shown in Fig. 4. The absorbance is not registered in the wavelength range from 470 nm to 1200nm. At 222 nm a sharp size of absorption to maximum was observed indicating a single transition in the near visible region of the crystal. The nearly sharp size in absorption at 222 nm suggests nearly similar distribution of energies among all molecules of the single crystal.

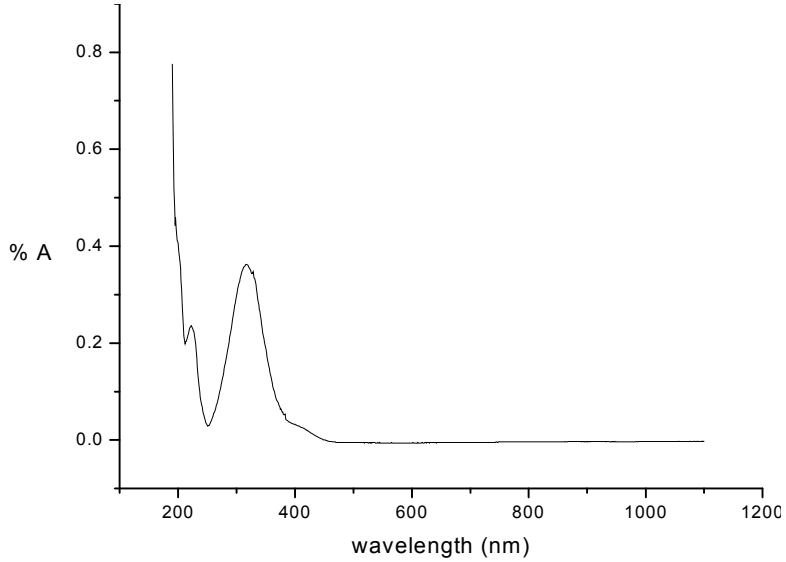

Fig. 4. UV-vis-NIR spectrum of S4NP NLO single crystal

4. Conclusion

Single crystal of S4NP was grown using ethanol as the solvent. XRPD data of S4NP agrees well with single crystal XRD data. The various functional groups in the molecule were identified using FTIR analysis. The cut off wavelength of crystal was estimated using UV-vis-NIR analysis.

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