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Research Article

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Growth of semi organic sodium p-nitrophenalate para nitro phenol dihydrate single crystal from aqueous solution and their characterization

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ABSTRACT

Sodium p-nitrophenalate para nitro phenol dihydrate (SPPD) is a semi organic non linear optical crystal which has been synthesized. Single crystals (size 3x2.5x1.7mm^3) have been grown by slow evaporation of the saturated aqueous solution. The Grown crystals have been identified from single crystal XRD analysis and FTIR spectroscopic techniques. SAAP was thermally stable up to 52°C as determined by TG/DTA curves. The crystal possesses prominent positive photoconduction in the presence of photoactive centers formed with trap energy levels. The non linear optical activity is confirmed by Kurtz powder test.

Keywords: Crystal Growth; Semi organic; Non Linear Optical Material

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INTRODUCTION

Non linear optical frequency conversion materials have significant impact on laser technology, optical communication and optical data storage. In the past few years a no. of studies was realized on sodium p-nitro phenolate p-nitro phenol dehydrate as a semi-organic non-linear optical material in which the nitrophenoy ions are ionically bonded to the metal ion [1-8]. It has an efficient NLO co-efficient(d_{eff}) 1.2 times larger than that of $KTiOPO_4$ (KTP) [1]. Many device applications of NLO require single crystals in the bulk form. This is achieved only with the semi organic crystals, which exhibits wide transparency large and bulk crystal morphologies. Sodium p-nitrophenolate p-nitrophenol dihydrate is a semi organic NLO material possessing large values of hyper polarizability due to the presence of an organic p-nitrophenol [9].

Minemoto and sonoda [3] have reported the crystal structures of sodium p-nitrophenolate dehydrate. The growth and characterization of a lithium p-nitrophenolate trihydrate was reported by Milton et.al [10]. Motivated by these considerations the growths, characterization, thermal, linear and nonlinear optical properties of SPPD were studied and the results are presented in this paper.

EXPERIMENTAL SECTION

2.1 Material Synthesis

Single crystal of SPPD were grown room the aqueous solution by solvent evaporation method p-nitro phenol and NaOH were taken in the stoichiometric ratio 2:1 and dissolved in excess of deionized water to prepare SPPD solution. The saturated solution obtained according to evaporate continuously at constant temperature. Good quality seed obtained from spontaneous nucleation is suspended in saturated solution. By isothermal solvent evaporation SPPD crystals of size 3x2.5x1.7mm^3 are grown within a period of 30 days[19]. The grown crystals in these case exhibit clear morphologies. The photograph of as grown single crystal is shown in the fig (1). Single crystal X-ray analysis is carried out to find cell parameters. UV visible spectral analysis is recorded for optical transparency of the crystal. Micro hardness studies have been performed to know the mechanical stabilities. The SHG efficiency of the crystal is measured using Nd: YAG laser.

Fig:1 Grown Single Crystal of SPPD

RESULTS AND DISCUSSION

3.1 Xrd Analysis

A carefully selected single crystal of SPPD was subjected to single crystal XRD analysis using ENRAF NONIUS CAD4 diffractometer. The X-Ray diffraction reveals that the crystal belongs to the non-centrosymmetric monoclinic crystal system and the lattice parameters are a=21.10Å b=3.65 Å c=10.32 Å and α=γ=90^o β=117.23^o which are in good agreement with that of reported values in the literature. The powder X-ray diffractogram of SPPD presented has been recorded up to 2θ =70° and at a scan rate 10.13 min.X-ray powder pattern of the crystal was recorded on a XPERT-PRO diffract meter using CuKα (1.5406A˚) radiation. The particle size, dislocation density and strain values were also calculated in table(1).It shows that the FWHM increases towards increase in dislocation density and strain value and decrease in particle size.

Table:1 Structural Parameters

S.no	FWHM(β)	Particle size(D)	Dislocation Density(δ)	Strain Value(ε)
1	0.0400	37.1924	$0.7234*10^{-3}$	0.009725
2	0.0800	19.7549	$2.5810*10^{-3}$	0.01836
3	0.1200	12.852	$6.0889*10^{-3}$	0.02822
4	0.1600	9.54875	$8.9307*10^{-3}$	0.03797
5	0.2400	6.2125	$25.909*10^{-3}$	0.0582

3.4 Photoconductivity study

In order to enhance the crystal application for NLO and photonic devices, photoconductivity measurement is carried out using Keithley- 480 picoammeter in the presence of dc electric field. Polished sample of SPPD is attached into the microscopic slide. Electrical contacts are made on the Sample by silver painted copper wire as electrode with an electrode distance of 0.52 cm. The sample is then connected in series to λ dc power supply and λ picoammmeter. After shielding the sample from all radiations, the applied field is increased from 130 to 3900 v/cm and the corresponding dark current (I_d) in the picoammeter is notified. The samples are then illuminated with radiation from a halogen lamp (100W) and the photocurrent (I_{ph}) due to the generation of carrier by photo excitation is recorded for same applied field. The field dependent photoconductivity of the crystal is shown in fig (6). It is observed that dark current and photocurrent show linear response with respect to applied field. However photocurrent is greater than the dark current. Hence the crystal exhibits positive photoconduction.

3.5 Thermal studies

To analyze the thermal stability of the material, the Thermo Gravimetric analysis (TGA) and Differential thermal analysis (DTA) were carried out using Schimadzu DT-40 analyzer at a heating rate of 10˚C/min in the nitrogen atmosphere. The DTA curve shows in the fig: 4 that SPPD starts to decompose at a temperature around 395˚C and it undergoes an exothermic transistion at 425˚C followed by another endothermic at a temperature of 603˚C. The TGA Trace indicates a weight loss of about 20% in the temperature range of 52˚C-455˚C due to liberation of water molecules. The second stage has a weight loss of about 49% in the temperature range of 455˚C-690˚C. The third stage shows weight loss of 10% in the temperature range of 690˚C-875˚C. Prolonged heating upto875˚C the TGA shows almost three weight loss stages. The thermal stability of SPPD is more compared to the organic crystal like N-methyllititone trihydrate. [9]

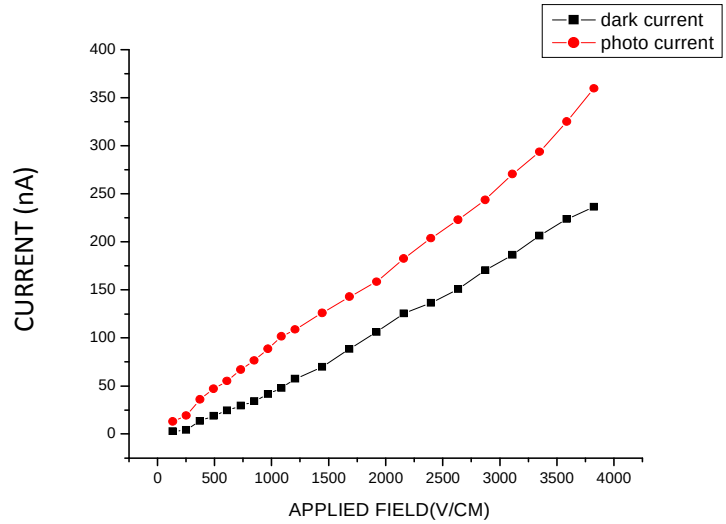

Fig: 5 Field Dependent Conductivity of SPPD Single Crystal

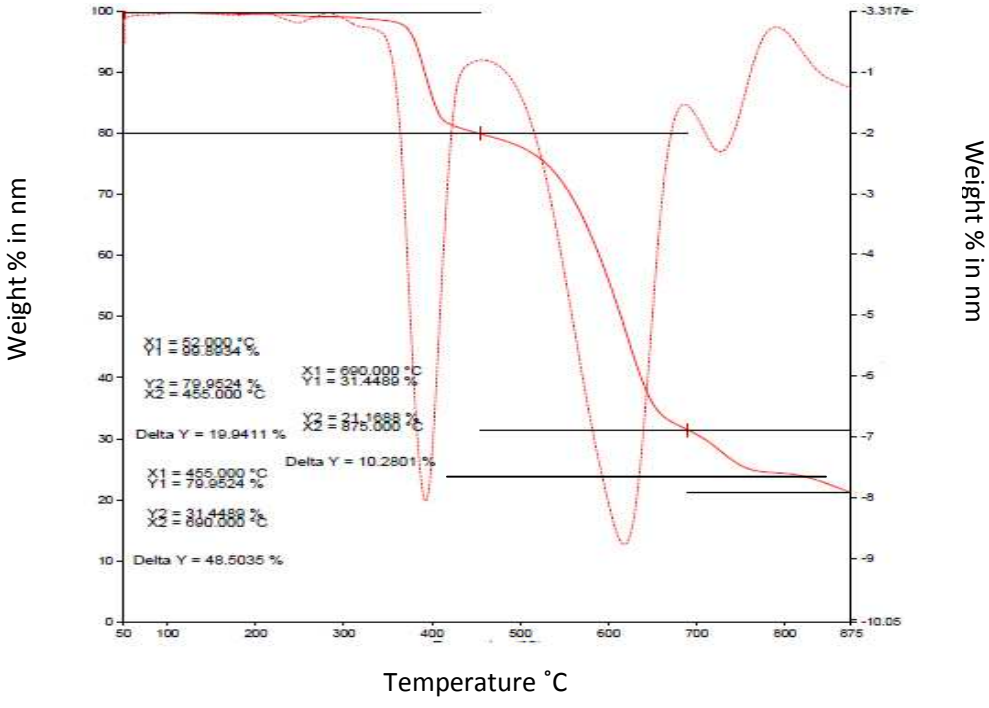

Fig: 4: TG/DTA studies of SAAP

3.6 FT-IR

The Fourier Transform IR (FTIR) spectrum of the title material was recorded using KBr pellet technique between 400-4000cm^{-1} by PEFTIR spectrometer in fig: 5. The absorption in the region (400-500cm^{-1}) is due to the overtones of the fundamental vibration of p-nitrophenolate. The presence of hydrates of sodium is confirmed by the band at 441.01cm^{-1} (9). The symmetric C-H Vibrations of the out -of- plane deformation (Wagging) are identified in the IR spectrum at 773cm^{-1}. The vibrational modes corresponding to the C-H-in plane bending were observed in the IR spectrum at 914cm^{-1} (11). In addition to this, the stretching vibration of c=o band falls to 1696cm^{-1}. The C-H stretching vibration bands of the aromatic ring appear at 2913cm^{-1} and there is a broad envelope carrying peaks due to OH stretch at 3319cm^{-1}.

Table:2FT-IR Assignments

WaveNumber cm^{-1}	Mode	Assignments
441	-	Hydrates of sodium
773	C-H	Out-of-plane deformation(wagging)
914	C-H	Plane bending
1696	C=O	Stretching vibration
2913	C-H	stretching vibration
3319	OH	stretch

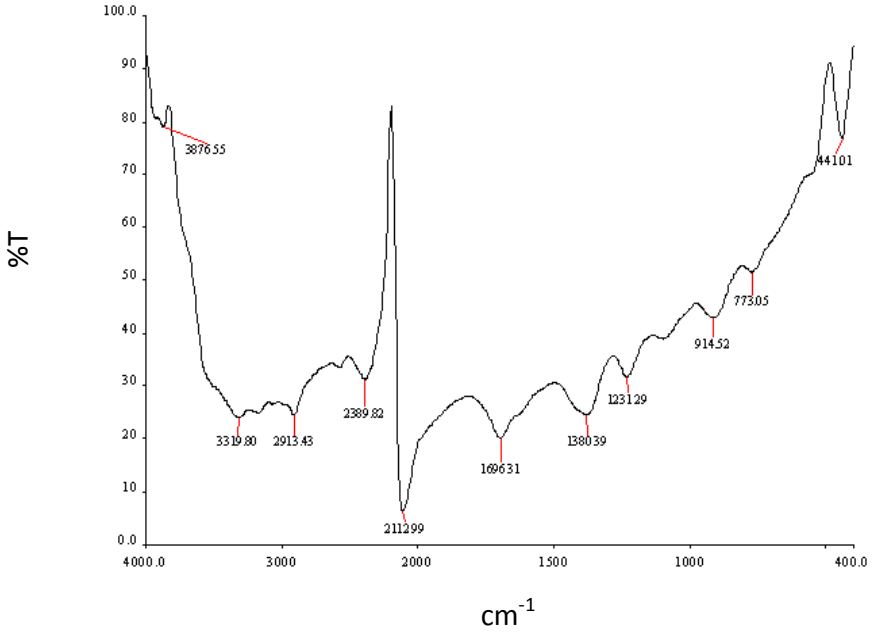

Fig: 5: FTIR spectrum of SAAP

3.8 NLO Studies

Performing the Kurtz powder test, the second harmonic efficiency of the crystal is measured as a function of intensities. The incident fundamental beam of 35 ps pulse width, 10hz repetition rate and 2.35mJ pulse-1 energy at a wavelength of 1.064μm from Q-switched Nd: YAG laser is directed onto the sample. The SHG signal at 532nm is detected at various points on the sample in transmittance mode using a photomultiplier tube (PMT) and boxcar averarager. The SHG in the crystal is confirmed with the emission of green radiation from the crystal.

CONCLUSION

Good optical quality single crystals of SPPD have been grown by adjusting the growth parameters employing the technique of slow evaporation from its aqueous solution. The crystal structure and lattice parameter were confirmed

by X-ray diffraction analyzers which belongs to monoclinic structure. FT-IR studies confirm the functional group present in the compound. The TG/DTA show the good thermal stability of the material. Owing to its SHG efficiency, SPPD is considered as a promising material for NLO application.

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