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SYTHESIS AND CHARACTERIZATION OF NON-LINEAR OPTICAL SPNPD CRYSTAL

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ABSTRACT

The non-linear sodium para-nitrophenolate dihydrate (SPNPD) single crystals were grown by slow evaporation method. The powder X-ray diffraction analysis was conducted on the fine crystalline powder sample to confirm the crystalline nature of the grown crystal. Various functional groups and chemical bonding were identified by FTIR. In the photoluminescence spectrum, a sharp broad emission peak centered at 544 nm indicates green emission. The SHG efficiency of this material was found to be 4.15 times that of KDP which confirms that the grown crystal is an incredibly good to achieve high SHG efficiency.

1.INTRODUCTION

In modern optical communication, non-linear optics score more attention, especially in ultrafast signal processing. Non-linear optics describes the properties of light in a non- linear media, where the polarization density responds nonlinearly with electric field of the light. This unique property of non-linearity can be attained through high intensity lights like Laser. Materials that possess non-linear response to the electric field associated with the light of the laser beam, are called Non-linear optical materials [NLO]. The Non-linear interaction of light with matter relates to various optical phenomena such as the generation of new light frequencies, the alteration of materials optical properties to exhibit self-focusing and Raman amplification [1]. Although it explains the Non-linear response of phase or path of the incident light. The NLO materials are classified based on the order 'n' of the nonlinear susceptibility (χ^{n}), which describes the material's polarization response to the electric field of light radiation.

The search for new materials with high optical nonlinearities is a major area due to their practical applications such as optical communication, computing, optical information processing, disk data storage, laser fusion reactions, laser remote sensing, color display, medical diagnostics, etc. Most of the organic NLO crystals usually have poor mechanical and thermal properties and are susceptible for damage during processing even though they have large NLO efficiency. Also, it is difficult to grow larger size optical quality crystal of these materials for device applications [2]. More research works have been conducted on organic crystals, which emphasizes that their use progressed by their low optical transparencies, poor mechanical properties, low laser damage thresholds and inability to produce and process large crystals.

Pure inorganic NLO materials have excellent mechanical and thermal properties but possess modest optical nonlinearity because of the lack of extended π – electron delocalization [2-3]. In semi organic materials, the organic ligand is ionically bonded with inorganic host. As a result, they have higher mechanical strength and chemical stability [3]. Hence, it may be useful to prepare semi-organic crystals which combine the positive aspects of organic and inorganic materials resulting in useful nonlinear optical properties. Many investigations have been made on the nitrophenol family, which ensures that nitrophenol is a better proton acceptor for metallic hydrogen complexes. The sodium para-nitrophenolate dihydrate single crystal structure was reported by Minemoto and his co-workers [4,5].

In this work, the sodium para-nitrophenolate dihydrate (SPNPD) single crystals were grown by the slow evaporation method. The crystal morphology formation is based on whether it grows in water or methanol [6,7]. In recent times, researchers give more importance to para nitrophenol crystals due to their wide applications in optoelectronics especially in Second Harmonic Generation (SHG). The para nitrophenol (4- nitrophenol) is a phenolic group opposite to that of the hydroxyl group on the benzene ring. The 4-nirophenol can be used as a pH- indicator. The p-nitrophenol crystallizes in orthorhombic system with Non centrosymmetric space group which will be essential for having NLO properties. In sodium para-nitrophenolate dihydrate (SPNPD) single crystals, nitro -phenoxy ions are ionically bonded to sodium through hydrogen bonding, which make it superior to others. Some novel reports shown that nonlinear optical crystals like 3-nitroaniline and 3-nitrophenol [8], Triglycine zinc chloride [9] shows various photo-induced properties because of the significant difference between the intra-molecular and inter-molecular chemical bonds present in the material.

2.SYNTHESIS OF THE MATERIAL

The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of single crystals. It is the most widely used method for the growth of single crystals when the starting materials are unstable at hot temperatures, and which undergo phase transformations below melting point. In the low temperature solution growth, crystals can be grown from solution if the solution is supersaturated [2,8]. In the present work, the slow evaporation of the solvent method is preferred. Slow cooling is the easiest method to grow bulk single crystals from solution, which performed under atmospheric conditions. The Sodium p-nitrophenolate dihydrate (SPNPD) single crystals were grown by slow evaporation by taking sodium hydroxide and p-nitrophenol in the molar ratio of 1: 1 and further dissolving it in double distilled deionized water. The reaction place for the synthesis of sodium p-nitrophenolate dihydrate is as follows:

$$\mathbf{C_6H_5NO_3 + NaOH + H_2O \rightarrow NO_2\text{-}C_6H_4\text{-}ONa\ 2H_2O}$$

The purity of the synthesized salt, further increased by successive recrystallization process using double distilled water. The prepared solution completely stirred for getting homogenous solution. After continuous stirring (for at least two hours), the solutions became homogeneous. To remove the impurities formed during the stirring, a filtration process is performed. The excess solvent (water) evaporates slowly to reach the saturation level of the solutions. A well-controlled evaporation was maintained to avoid further nucleation. After two weeks, yellow-colored transparent single crystals started to grow at room temperature. The crystals were carefully collected from the mother solution after 19 days are shown in Figure 1. The prepared crystals were used to perform various characterization studies. The prepared crystals were yellow color due to the maximum absorbance at 405 nm.

Fig 1: The grown sodium para-nitrophenolate dihydrate crystals

3.RESULTS AND DISCUSSION

3.1 XRD ANALYSIS

The structural analysis of a grown crystal was performed by single crystal X-ray diffraction analysis with D8 Advance X- ray diffractometer with Cu Kα radiation (λ=1.5406Å) operated at 40KV and 100 mA. The X-ray diffraction pattern of the sodium para-nitrophenolate dihydrate crystals are shown in Figure 2, where Miller indices of the peak are marked. The well - defined peaks indicate that the grown crystals were of excellent quality.

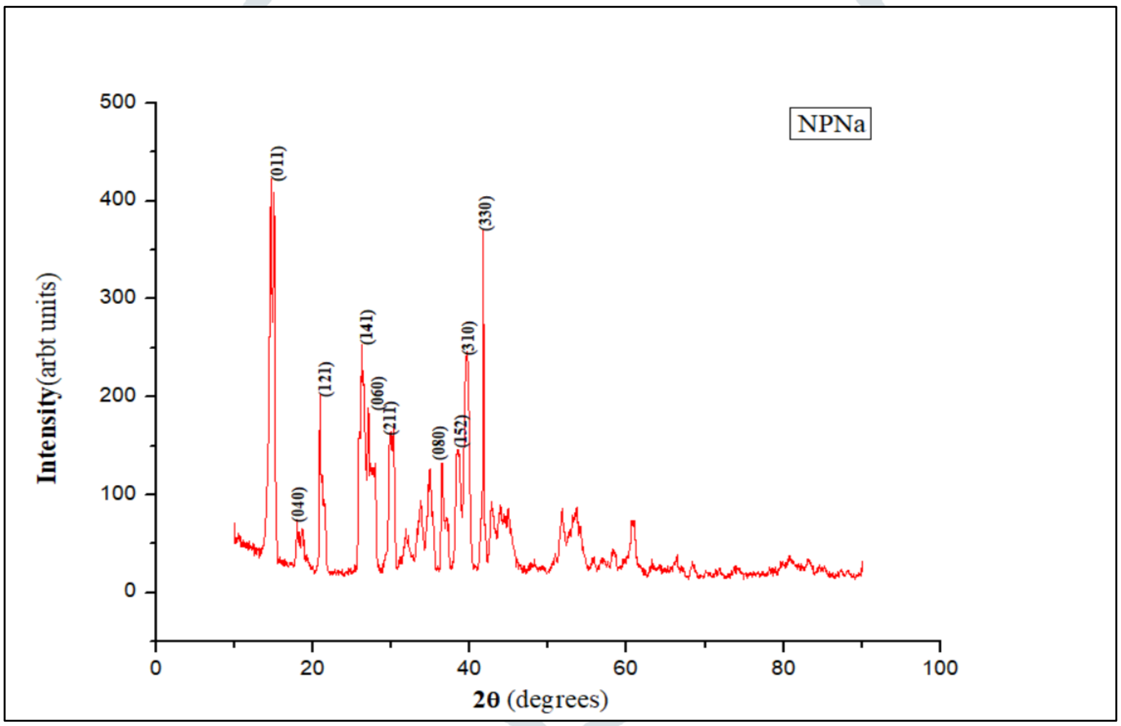

Fig 2: XRD pattern of SPNPD crystal

The desired sharp peaks observed in the XRD pattern ensure the quality and the crystalline nature of the sample. The diffraction peaks plotted at different 2θ values and the corresponding (hkl) values and interplanar distances are shown in Table 1, which confirmed the orthorhombic structure by comparing and matching with the standard card of CCDC (no.1403345) and lattice parameters calculated as shown in Table 2

Sl. No	h	k	l	2θ	d_{hkl}
1	0	1	1	14.6490	6.04210
2	0	4	0	17.9755	4.93076
3	1	2	1	20.9005	4.24684
4	1	4	1	26.2175	3.39638
5	0	6	0	27.126	3.28465
6	2	1	1	29.843	2.99150
7	0	8	0	36.4745	2.46139
8	1	5	2	38.4115	2.34161
9	3	1	0	39.602	2.27391
10	3	3	0	41.7005	2.16420

Table1: hkl values with interplanar distances of as grown crystal

The obtained lattice parameters are shown in Table 1 and confines that the grown crystals belong to orthorhombic structure with Volume (V) = 870.70340 $Å^3$ and consistent with the results reported using the single crystal X-ray diffraction. This agrees with the earlier results reported by S. Brahadeeswaran, V. Venkata-ramanan, et.al 1998[10].

Lattice parameters				Cell volume, V ($Å^3$)	Molecular mass, M (g/mol)	Density, ρ $\rho = \frac{MZ}{VN}$ (g/cm^3)
	a	**b**	**c**			
Reported	6.8920	19.6920	6.4390	873.8835	197.12	1.873
Calculated	6.87721	19.69116	6.42964	870.70340	197.12	1.88

Table2. Lattice parameters, cell volume and density values of sodium para-nitrophenolate dihydrate crystal.

3.2 PHOTOLUMINESCENCE

The photoluminescence (PL) spectrum of the grown SPNPD crystal was recorded at room temperature by exciting it at 450 nm as shown in Figure 3.

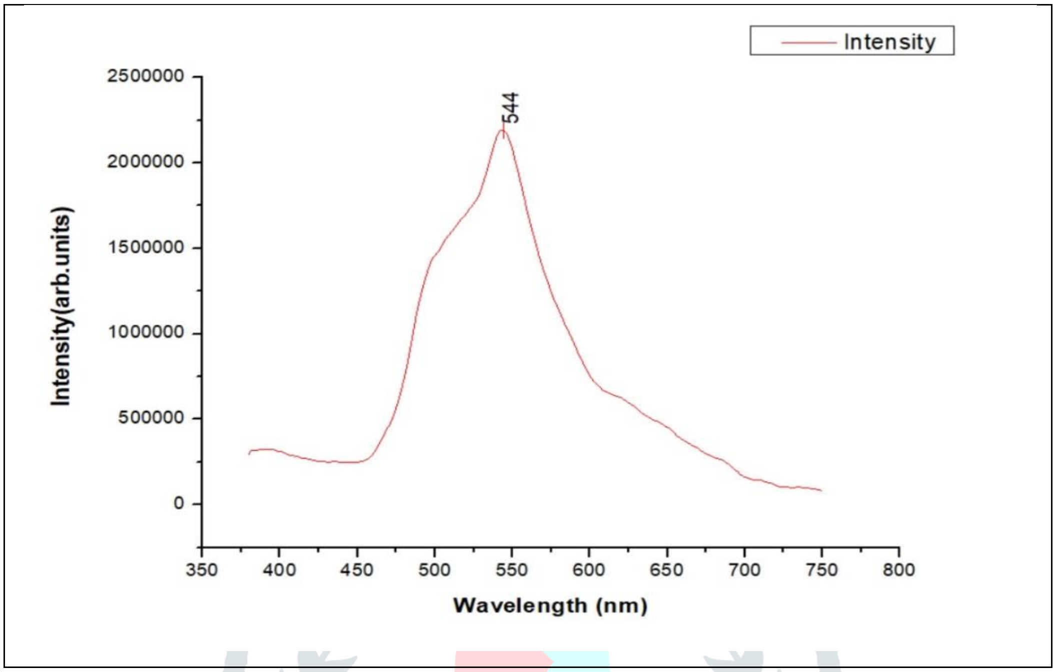

Fig 3: Photo Luminescence Spectra of SPNPD crystal

A sharp broad emission peak centered at 544 nm was observed in the spectrum, which indicates green emission. This broad green emission peak indicates the deep level defect transitions i.e., there is a contribution from deep holes in the energy levels. The hydrogen bonding interactions in the crystal structure. The hydrogen bonding takes place between the oxygen of the OH group (phenolic oxygen) attached to the benzene ring and the hydrogens of water molecules attached to the sodium cation in the crystal structure which causes the dominance of radiation less pathways in the decay process. Thus, the intermolecular interaction will have a key role in crystal packing [11]. Thus, the grown crystals can be used to fabricate green Lasers. Such materials having a broad emission peak can be used in advanced tunable laser systems.

3.3 FOURIER INFRA-RED SPECTROSCOPY (FTIR)

The FTIR spectrum of grown sodium para-nitrophenolate dihydrate crystal were recorded between 500- 4000 cm $^{-1}$ with KBr pellet technique by a Bruker, vertex 70 FTIR spectrometer. The FTIR spectrum was shown in Fig 4.

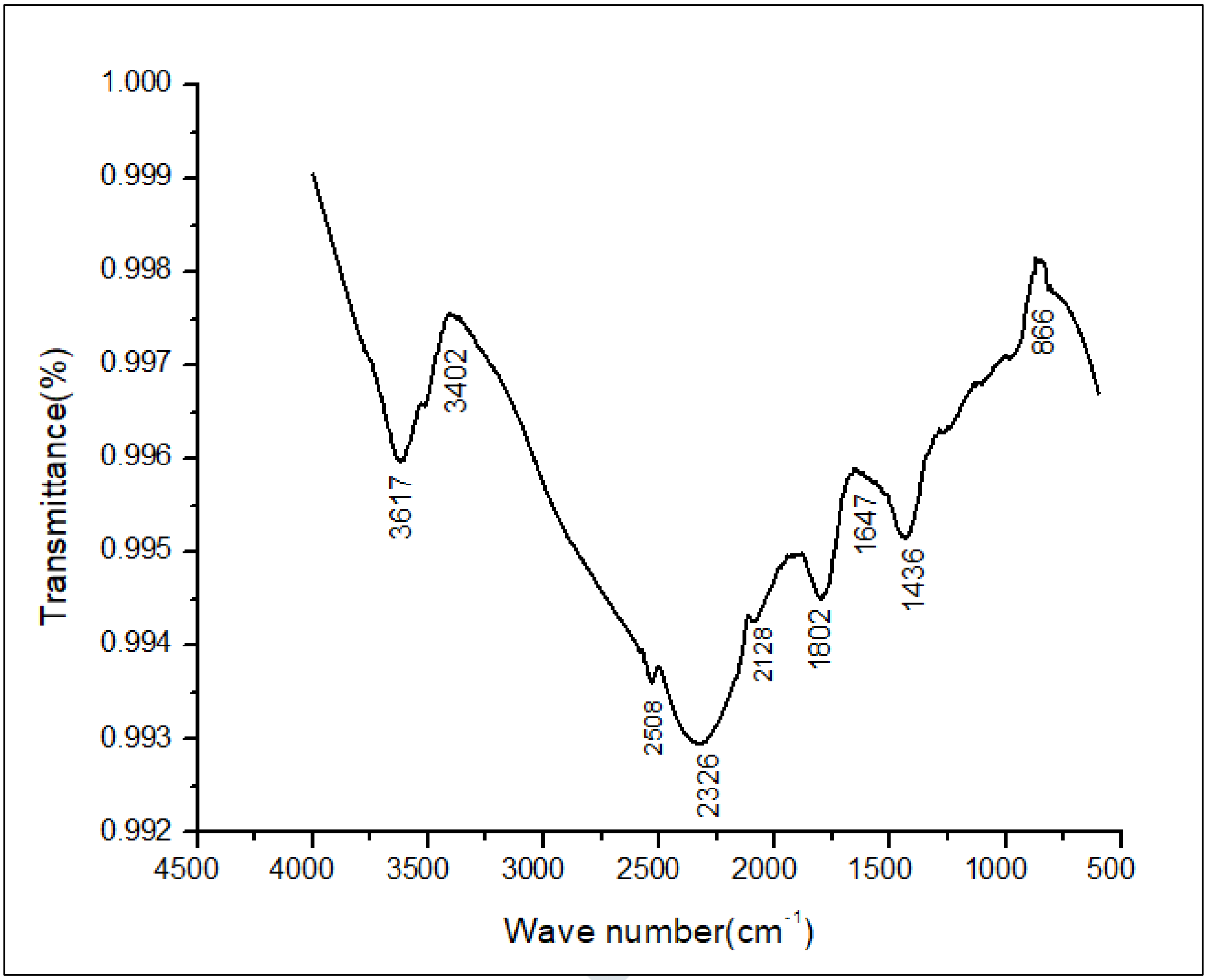

Fig 4: FTIR Spectrum of SPNPD

In observed spectrum, a broad diffusion in the range of 3500-2500 cm^{-1} indicates OH stretching mode of vibration. A sharp intensity peak at 3617 cm^{-1} indicates that the sample contains oxygen related groups such as phenol or alcohol. This strongly characterizes the quality of the prepared sample. The spectrum contains a peak at 3402 cm^{-1}, assigned to the O-H stretching vibration of water molecules. There are no other aromatic structures in this region between 3400 -2510 cm^{1}. No other peak was observed in this region. A shoulder peak at 2326cm^{-1} has been observed in the spectrum, which corresponds to C=N=O asymmetric stretching vibration. A weak absorption peak at 2128 cm^{-1} corresponds to C=C absorption. The peak observed at 1802cm^{-1}, due to C==O stretching [12]. Another peak observed at 1647cm^{-1} due to C = O stretching vibration. The peak 1436cm^{-1} arises due to aromatic ring skeleton vibration [13]. The peak observed at 866cm^{-1}, which indicates C-H in-plane bending. The bands in the region of 580- 670 cm^{-1} indicate the presence of C-CO deformation [14,15].

3.4 SECOND HARMONIC GENERATION STUDY

The efficiency of transferring energy of a nonlinear optical material from a fundamental beam to a second harmonic beam is determined by the second harmonic generation efficiency (SHG) parameter [16,17]. The SHG efficiency of the grown crystals was determined using the Kurtz and Perry Powder technique which also identifies the materials as having non-centrosymmetric structures. The grown crystal was crushed and made into fine powders. A sharp beam of wavelength 1064 nm from the Nd: YaG laser was allowed to pass on the sample and the out coming beam is examined at various points. The study reveals the emission of green light from the crystal, which confirms the second order NLO phenomena of the material by doubling incoming frequency.

The SHG efficiency of SPNPD crystals was calculated as 14.1 mV. In semi organic crystals, due to the presence of a strong intermolecular interaction, wave functions mostly overlap which results in the delocalization of π-electrons. The grown crystal crystallizes in the Ima2 space group, which fulfils the required symmetry condition of second harmonic generation. The SPNPD crystal consists of a metal ion (Na+) surrounded by an organic ligand (phenoxy ion) which is a benzene derivative and contains delocalized π-electrons. Therefore, these crystals are expected to exhibit good NLO properties [18].

4. CONCLUSION

The NLO sodium para-nitrophenolate dihydrate (SPNPD) single crystals were grown by the slow evaporation method. The crystalline nature of the grown crystal was studied using powder X-ray diffraction analysis. Various functional groups and chemical bonding were identified by FTIR. A sharp broad green emission peak appeared at 544 nm and photoluminescence behavior was studied. The SHG efficiency of SPNPD and KDP crystals were found to be 14.1 mV and 3.4 mV, respectively. Thus, the SHG value of the grown crystal was found to be 4.15 times that of KDP which is a much higher value than some reported p-nitrophenolate based semi organic compounds. The grown crystal exhibits superior second harmonic generation (SHG) performance compared to analogous p-nitrophenolate materials. This enhancement in SHG efficiency can be attributed to the increased delocalization of electrons within the crystal structure, facilitated by the low electronegativity of the sodium atom present. Consequently, the grown crystal emerges as a promising candidate material for applications in nonlinear optic (NLO) devices, owing to its exceptional nonlinear optical properties.

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