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NLO, XRD, FTIR, Studies of Paranitroaniline Mixed KDP

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Abstract: ***Fabrication of nonlinear optical materials which have high-end applications is great promising sector. Synthesis of paranitroaniline (PAN) mixed with potassium dihydrogen phosphate (KDP) is achieved by low cost chemical method.. We studied the characterization of synthesis sample such as NLO, XRD, FTIR. The nonlinear optical properties were studied; found that NLO properties of KDP are changed with mixing with PNA. XRD confirmed the size of nanocrystals to be 12nm with tetragonal lattice system. . FTIR provides comparison of pure KDP and PAN mixing KDP to judge vibrational assignments.***

Keywords: XRD, NLO, KDP, Paranitroaniline,

1. Introduction

In recent years, a large number of research have been performed to investigate different types of nonlinear optical (NLO) materials [1-7] in order to design excellent NLO materials which show potential application in modern communication technology, data storage and optical signal processing [8-11]. In particular, organic nonlinear optical materials have shown great promise in the area of photonics due to their useful physical and optical properties. The microscopic structure-property relationship for such molecules may lead to discovery of improved NLO characteristics material, thus, facilitating the design of new molecules for potential NLO applications. This could be done through study of response electric properties, namely, polarizability, hyperpolarizability of the molecules using computational methods. Theoretical study has been played a crucial role in designing and development of novel materials for nonlinear optics. By modeling a novel compound's electronic, optical and NLO properties it is possible to eliminate the high cost associated with the synthetic exploration which are time consuming and expensive. During the past few decades, after the development of quantum procedures the science of designing nonlinear optical material has taken a different route especially due to the birth of quantum chemistry packages. It is well known that if the molecule has many delocalization π electrons, bigger change of dipole moment from ground state to excited state, large transition moment and noncentrosymmetry structure, the molecule will have strong second order NLO response [12-18]. Para-nitro aniline (PNA) is such a material which known for its nonlinear optical properties. In PNA, the presence of a desirable resonance structure, in addition to the intermolecular charge transfer, leads to high value of polarizability (α) and hyperpolarizability (β). However, the crystalline form of PNA has a centrosymmetric structure that does not show any macroscopic second-order NLO response. We have, therefore considered the some of the derivatives of PNA, which eliminates center of symmetry in the molecule thus leading to noncentrosymmetric crystal structure. On the other hand, a theoretical and experimental investigation [19-22] shows that the NLO response of materials can be improved by optimizing the donor/acceptor strength and/or by extending the conjugated bridge [23-26]. During the past decade, a number of organic and inorganic materials with high nonlinear susceptibilities have been synthesized. However, their device applications have been impeded by the inadequate optical transmittance, poor optical quality and lack of robustness, low laser damage threshold and inability to grown into large size crystals. The molecules in pure organic crystals are often bonded by weak Vander Waals forces of hydrogen bonds, which result in poor mechanical robustness. To overcome these difficulties, the nonlinearities of p-conjugated organics and the favorable crystal growth properties of ionic salts can be combined into a single NLO called semi organics. In the present investigation the synthesis aspects of p-nitroaniline mixed KDP in the ratio 1:0.5. Our work observed particle size by XRD, SEM, NLO properties, FTIR etc.

2. Synthesis

Commercially available Pure Nitro aniline (AR Grade) and KDP (AR Grade) were used for repeated recrystallizations. Highly purified Para Nitroaniline and KDP in stiochiometric ration 1:0.5 and KDP mixed with para nitoaniline in stiochiometric ratio 1:0.5 is used in double distilled water to prepare the solution . After obtaining the saturation the solution was filtered using paper and the solution was optically closed using a perforated polythenane sheet. Seed crystals of size 0.8x0.4x0.2 cm^3were obtained. These crystals were grown in constant temperature bath of controlled accuracy ±0.01° at 40° C where saturation was achieved. When Para-Nitroaniline mixed KDP crystal have surprisingly shown a cotton silk filament fiber nature.

3. Characterization

The grown samples were investigated using different characterization such as NLO, XRD, and FTIR etc.

3.1 NLO Test

The Second harmonic generation behavior was tested by Kurtz powder technique using ND: YAG laser as a source. The grown crystals have been subjected to the nonlinear optical study to measure the SHG efficiency with respect to the Pure KDP. The increase in the SHG efficiencies are due to the weakening of the bond between O–H and C=O due to hydrogen bonding [30, 31, 32].The SHG efficiency of Para nitroaniline mixed with KDP were 1.85 with reference material KDP.

3.2 XRD Pattern

In order to confirm the crystallinity, X-ray diffraction of sample was carried out using XPERT-Pro X-Ray diffractrometer with CuKα radiation facility.

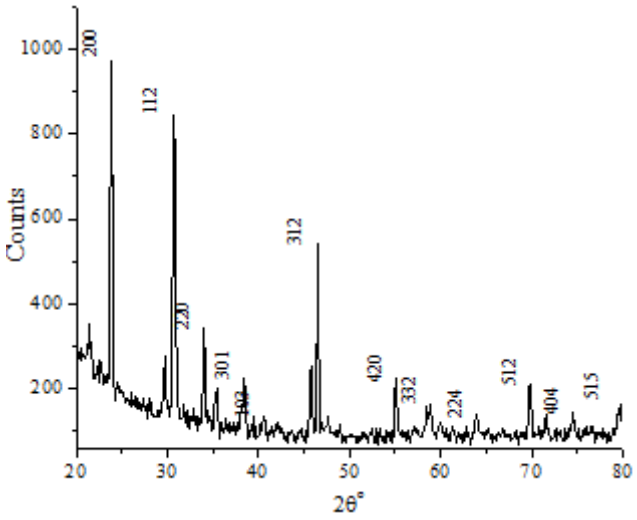

Figure 1: XRD pattern of Paranitroaniline mixed KDP

The diffraction peaks for paranirtoaniline mixed KDP (1:0.5) at 2θ =23.861, 34.007, 38.41, 55.99 degrees, were chosen to calculate the size of the nanoparticles. Size of sample PNAK2 nanoparticles calculated form XRD data 12nm. The nanocrystals are Tetragonal lattice system Lattice Parameter: a = 7.455 Å, b = 7.455Å, c = 6.97 Å, Lattice Parameter: Alpha = 90˚ Beta= 90˚ Gama = 90˚, Volume (Å) = 386.50659.

3.3 FTIR Pattern

FT-IR spectra of the pure paranitroaniline mixed KDP (1:0.5) sample PNAK1 and KDP mixed paranitroaniline (1:0.5) sample PNAK2 synthesis materials are shown in Figure 2. The FTIR spectrum of synthesis samples are recorded by using Perkin Elmer spectrometer in the frequency region of 4000 cm^{-1} to 600cm^{-1}. The frequencies with their relative intensities obtained in FTIR of pure Para nitroaniline PNAK1, PNAK2 their probable assignments are presented in Table 1.

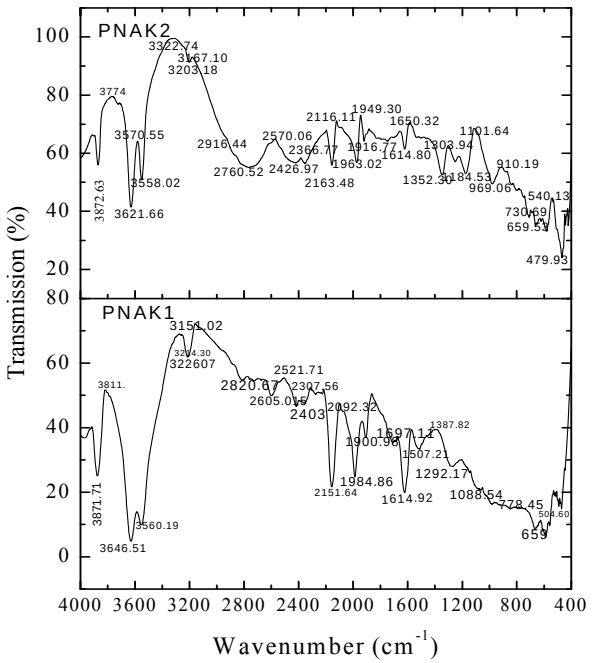

Figure 2: FTIR spectrum of para-nitroaniline mixed KDP

Table 1: Observed FT- IR frequencies (cm^{-1}) of pure p-nitroaniline and mixed crystals of KDP with p-nitroaniline.

Pure p-nitroaniline	PNAK1	PNAK2	Vibration assignment
	3871	3872	Free O-H stretching
3482s 3361vs	3646 3560	3621 3558	NH_2-asymmetric stretching NH_2-symmetric stretching
3108w	3151	3167	C-H stretching (Benzene ring)
1650-2000w	2092-2605	1963-2426	Overtone region (Benzene ring)
1590s-1633s	1614-1697	1614-1677	Scissoring NH_2 and stretching C-C
1477s			NO_2 stretching
1295s 1169m 1113m	1292 1088 -----	1352 1184 1101	C-H in-plane bending ----,,---------- ----,,----------
1000w	-----	-------	Rocking NH_2
	3214	3203	O-H stretching (H-bonding)
	2820	2760	P-O-H asymmetric stretching
	2403	2426	P-O-H bending
	1614	1614	OH-P=O stretching
	1292	1352	P=O stretching
	1088	1164	P=O stretching
956w 829w	------- -------	969 --------	C-H out of plane bending -----,,----------
	----------	-------	P-O-H stretching
747ms	778	730	Wagging -NO_2
690m	659	659	Twisting -NO_2
524m	504	479	Rocking –NO_2
487m			C-NH_2- in plane bending

4. Result and Discussion

The sample material paranitroaniline mixed KDP was prepared by simple chemical method. The grown sample has been subjected to the nonlinear optical studies to measure the SHG efficiency with respect to pure KDP.. The SHG efficiency of para nitroaniline mixed with KDP was 1.85

with reference material KDP. The X-ray diffraction show the nano crystal sized 12 nm (PNAK2) is tetragonal lattice system, with unique lattice parameters.

FTIR spectra observed related to vibrations, stretching and bending of H- atoms belonging to different groups such as O-H, C-C,P=O stretching, NH_2, P-O-H asymmetry stretching, C-H bending, NO_2 twisting, wagging. The study put light on characters enhancement of sample useful in modern communication, technology, data storage, optical signal process. The study has future scope in applications in above said areas.

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