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Growth, Spectroscopic and Optical Studies of meta-Nitro Aniline NLO Organic Crystal

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Abstract*: *In this paper a single crystal of Meta nitro aniline (mNA) an organic nonlinear optical (NLO) was grown by slow solvent evaporation technique at 30-40°c temperature, acetone was used as a solvent. A good yellow –reddish colour crystal of mNA was obtained in duration of 2 weeks. The grown crystal was subjected to different characterization such as single crystal X-ray diffraction, Fourier transform infrared spectroscopy, UV-visible spectroscopy and NLO-Optical studies. The grown crystal was characterized by XRD analysis, which shows that crystal was perfectly crystalline in nature and belongs to orthorhombic structure. The lattice parameters are a=6.47Å, b=19.33Å, c=5.08Å, V=635.33Å^3. FTIR spectrum was recorded using spectrophotometer by KBr pellet technique in the region 4000-500 cm-1. This study was recorded to confirm the functional groups of respected compound. UV-visible spectrum was recorded by UV spectrophotometer in the rang 200-900 nm. UV visible transmittance studies show that the grown crystal s have wide optical transparency in the entire visible region, the cut-off wavelength is occur at 239 nm. The optical energy band gap is found to be 4.1 eV. The second harmonic generation (SHG) efficiency of the material was estimated using Nd: YAG laser as a source.

Keywords: Nonlinear optical crystal, NLO-Studies, Solution growth technique, FTIR Spectroscopy, UV-Spectroscopy X-ray diffraction

1. Introduction

The research in the field of organic NLO materials has gained momentum in the recent past on their interesting nonlinear optical effects extended to frequency conversion, optical switching, telecommunication, colour display, and second harmonic generation etc[1-5]. An organic molecule should have high second order hyperpolarizability to exhibit large NLO properties because of increasing intermolecular charge transfer by extending л-conjugated system[6]. Using organic molecules for the nonlinear media has several advantages, such as low cost, low dielectric constant, ease to fabrication[7]. Also, one of the advantages in working with organic materials is that they allow to the fine chemical structure and have large structural diversity [8].

Meta nitro aniline is favourable material for NLO application. The molecular formula of mNA (Meta nitro aniline) has $C_6H_6N_2O_2$ and its melting point is 112°c. mNA crystals have a very large nonlinear susceptibility, which are in many cases several orders of magnitude higher than that of inorganic crystals. In present paper, we report the conditions for the growth of good quality single crystal of mNA by slow evaporation method using acetone as a solvent. The grown single crystal was subjected to characterization techniques like X-ray, FTIR Spectroscopy, and UV-Spectroscopy.

2. Experimental

2.1 Single crystal growth

The organic material mNA was growing by constant bath temperature method. Appropriate selection of solvent for the growth of the material is very important in the crystal growth process. Acetone was found to be the suitable solvents for preparing the growth solutions. Homogeneous solution was prepared by dissolving 10 gm of mNA in 30 gm acetone as a solvent. A saturated solution was prepared at a temperature 40°c. The solution was filtered using filter paper. The filtered solution was taken in a beaker which was sealed to avoid the evaporation of the solvent. A good yellow-reddish colour crystal of mNA was obtained in duration of time 2 weeks. As show in fig (1)

Figure 1: Grown single crystal of mNA

2.2 Analyses

The X-ray diffraction of the sample was studied by RR-CAT Indore with CuK_α radiation (λ = 1.5406 nm). The FTIR spectrum was recorded using the KBr pellet technique. Optical study was recorded by using UV-spectrophotometer. NLO property of the crystal was confirmed by Kurtz powder technique using Nd: YAG laser as source.

3. Results and Discussions

3.1 X-ray Diffraction Analysis

To obtain the unit cell parameter and to confirm the crystalline of grown crystals, X-ray diffraction study was carried out. The single crystal X-ray diffraction has been carried out from at RR-CAT Indore; copper K_α radiation of wavelength 1.54Å was used in all the diffraction studies. The sample was scanned over the range 0 to 60° at a scan rate of 1°/ min. The peaks were indexed by comparing the XRD data with the standard data given in the literature. It was found that crystal was perfectly crystalline in nature. It is observed that the mNA single crystal belongs to orthorhombic system with (110) orientation and unit cell dimensions were observed to be

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a=6.47Å, b=19.33Å, c=5.08Å and V= 635.33Å^3 [9]. As show in fig (2).

Table 1: Lattice parameter of mNA crystal

Theoretical Values (Å)	a=6.48	b=19.23	c=5.06
Experimental values (Å)	a=6.45	b=19.33	c=5.08

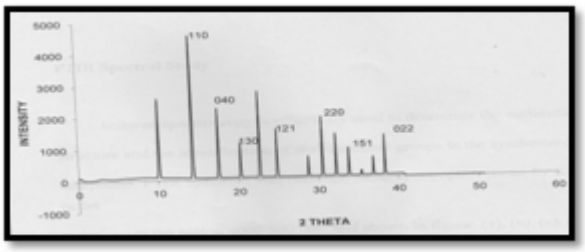

Figure 2: XRD spectrum of mNA

3.2 FTIR Spectroscopy

To analysis qualitatively the presence of the functional group in the grown crystal. FTIR spectrum was recorded using spectrophotometer by KBr pellet technique in the region 4000-500 cm^{-1}. For the organic molecule, the FTIR region has been divided into fractional group and fingerprint region. The fingerprint region is those lying between 1340 to 900 cm^{-1}, whereas fractional group region extends from 4000 to 1300 cm^{-1}. From the spectrum shows the asymmetric and symmetric stretching modes of free NH_2 group, which are observed at 3434 & 3211 cm^{-1}. The peaks at 2297 to 2662 cm^{-1} indicates asymmetric and symmetric stretching in C-H bond, peak at 2283 cm^{-1} Indicated C=N stretching. The peak 1624 cm^{-1} show the C=O carbonyl groinup in the compound. The peak that appears at 1522 cm^{-1} due to vibration of NO_2 stretching modes was not much broad. The vibration at the peak 984 cm^{-1} indicated the presence of the benzene ring in the MNA molecule[10-11]. The peaks 868 cm-1 show the meta position of the substituted molecules in the benzene ring of mNA as show in fig (3).

Table 2: Wave number assignment of mNA crystal

Wave number cm^{-1}	*Assignment*
3211,3202	Symmetric stretching of NH_2
3434,3429	Asymmetric stretching oh NH_2
2297 to 2262	Sym. And asym. Stretch of C-H
1624,1622	C=O carbonyl group
1768,1740	C=N Stretching
1522,1520	NO_2 Vibration
984 to 928	Presence of benzene ring in MNA

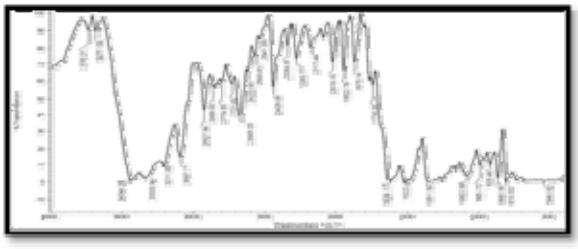

Figure 3: FTIR spectrum of mNA crystal

3.3 UV-Spectroscopy

The UV-visible spectrum of mNA was recorded using shimadzu UV spectrophotometer in the range 200-900 nm. The spectrum gives information about the structure of molecules and optical energy band gap of molecules, because the absorption of UV and visible light involves promotion of the electron from ground state to higher states. The observed nature of absorption in the visible region is a desirable property for NLO applications. The crystal shows good optical transmittance up to 14% in the entire region. It shows lower cut off at 239 nm. This reveals that in the grown crystal the absorption is almost absent in the visible region due to its high transparency. The absorption spectrum of MNA crystal is shown in figure 4(a). The optical absorption coefficient (α) was calculated by using the relation

$$\alpha = 2.3026 \left(\frac{1}{T}\right)/t \quad (1)$$

where 'T' is the transmittance and ' t' is thickness of the crystal.

Optical band gap (E_g) was evaluated from the transmission spectra and optical absorption coefficient (α) near the absorption edge is given by [12-13]

$$(\alpha h\upsilon)^2 = A\,(h\upsilon - E_g) \quad (2)$$

Where 'A' is a constant, 'E_g' is the optical band gap, 'h' is Planck constant, and 'υ' is the frequency of incident photons. The band gap of mNA crystal was estimated by plotting $(\alpha h\upsilon)^2$ versus hυ as shown in figure 4(b) and extrapolating the linear portion near onset of absorption edge to the energy axis. From the figure, the value of band gap was found to be 4.1eV.

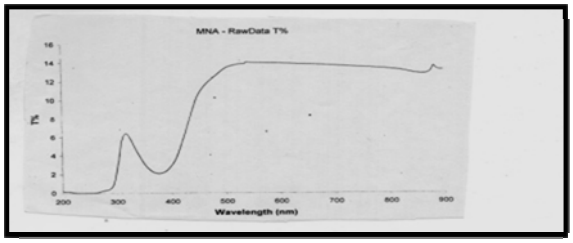

Figure 4 (a): Absorption spectrum of mNA crystal

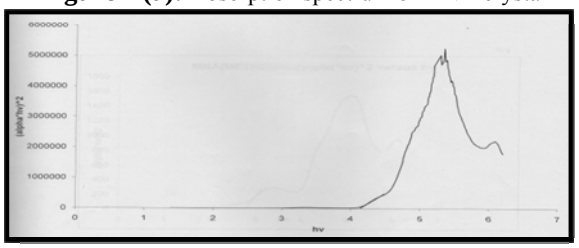

Figure 4 (b): Optical band gap of mNA crystal

3.4 Nonlinear Optical Studies

The grown crystal was characterized one of the optical study by second harmonic generation efficiency. NLO efficiency was carried out by Kurtz and Perry powder technique to determine the materials with non-centrosymmetric crystal structure. Both mNA and KDP crystals were powdered to uniform particle size in order to make relative comparisons with known KDP SHG materials [14]. The crystalline powder sample was filled airtight with micro capillary tubes of the uniform bore of about 1.5 mm in diameter. A high intensity pulsed Nd: YAG laser of wavelength 1064 nm with pulse energy was 6.2 Mj/sec and pulse width about 10 ns

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were used. The second harmonic signal was generated from crystalline powder sample was confirmed by the bright green light emission (λ= 532 nm) of 91.66 mW and 1115.22 mW respectively were obtained for KDP and mNA samples. Microcrystalline materials of KDP are used for comparison with mNA for the SHG experiments. Thus the SHG efficiency of mNA is higher than KDP.

4. Conclusion

In this paper we report synthesis, characterization, nonlinear properties of mNA crystal. Single crystals of mNA, was successfully synthesized and grown from the acetone by slow evaporation technique. It is clear that the crystals are needle like and transparent reddish-yellow. Single crystal X-ray diffraction analysis was used to estimate the unit cell parameters easily crystallize in an orthorhombic system with non-centrosymmetric (110) orientation. The FTIR analysis confirms the functional groups of the grown mNA crystal. UV-Visible spectroscopy confirms the information of the charge transfer complex. The second harmonic generation of the grown crystal was confirmed by Kurtz and Perry technique using Nd: YAG laser thus mNA was found higher than KDP efficiency.

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