Synthesis, growth and characterization of Oxine and Resorcinol doped m-Dinitrobenzene NLO active crystals

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ABSTRACT: Nonlinear optical active single crystals of Oxine and Resorcinol doped m-Dinitrobenzene crystals have been grown from saturated solution with methanol solvent by slow evaporation solution growth technique at room temperature. The grown Oxine and Resorcinol doped DNB crystals were characterized by powder XRD analysis, UV-Vis spectroscopy, FTIR spectroscopy and Second Harmonic Generation (SHG) studies. The crystalline nature of the materials has been confirmed by powder X-Ray diffraction method. To know the optical transparency and lower cutoff wavelength of the doped DNB crystals, the UV-Vis absorption and transmission spectra were recorded. Functional groups were identified by FTIR spectroscopy. The SHG efficiency of crystals estimated by Kurtz-Perry powder technique was found to be four times larger than that of urea and almost five times equal to that of urea respectively.

Keywords: m-Dinitrobenzene, SHG and NLO material

1 Introduction

The revolutionary change in optics is greatly enhanced due to the introduction of nonlinearity in the crystalline materials. Organic materials possessing high second harmonic conversion efficiency are having great demand in telecommunications, optical computing, and optical data-storage applications [1, 2]. Such materials have large nonlinear optical coefficients, suitable transparency and excellent comprehensive properties [3–6]. The advantage in working with organic material is that one can tune the chemical structure appropriately to the desired nonlinear optical properties. The performance of the organic NLO materials in the optical region placed a great demand on these materials due to these reasons. Several attempts have been made by the scientists to identify the good quality nonlinear organic crystals. In this work an attempt has been made to investigate optical and NLO characterization of m-dinitrobenzene with doping oxine and resorcinol. An attempt was made already to investigate the influence of dopants (oxine and resorcinol) with m-dinitrobenzene by using Bridgman-Stockbarger method on optical properties of bulk and film samples obtained using crystalline fragments from the melt growth ingots [7].

In this paper, the single crystal of dinitrobenzene (DNB) doping with 1% mole of oxine and 10% mole of resorcinol is grown by slow evaporation solution growth technique at room temperature. Basic characterization such as powder X-ray diffraction analyses, UV–Vis spectroscopy, Fourier transform infrared (FT-IR) analysis and SHG response of the grown crystals have been carried out.

2. Experimental

2.1 Synthesis of material
AnalaR grade readily available organic materials of Oxine, Resorcinol and Dinitrobenzene were employed for the synthesis of the title compound. Saturated solutions of the Oxine doped Dinitrobenzene and Resorcinol doped Dinitrobenzene with the molar ratio of 1% mole and 10% mole of dopant respectively were prepared separately in methanol. The mixtures were stirred well for about one hour and clear solutions obtained were heated up to 50°C in water bath when a yellow crystalline precipitate and light brown crystalline precipitate of doped DNB obtained. The precipitated adduct were filtered off separately. By slow evaporation method, the synthesized doped DNB were recrystallized separately to improve the purity of the material since high quality crystals are warranted for evaluating the nonlinear optical properties of molecular materials[8].

2.2. Solubility

As a first step towards to the crystallization of doped DNB, their solubility studies in methanol and acetone were carried out in the temperature range 30 – 45°C. The solubility curves of Oxine doped DNB and Resorcinol doped DNB are shown in figures 1 and 2.

Figure 1 Solubility curve of Oxine doped DNB.

Figure 2 Solubility curve of Resorcinol doped DNB

2.2. Growth of single crystal

Single crystals of Oxine and Resorcinol doped DNB were grown separate saturated solutions by slow evaporation method at room temperature. The solutions were stirred well for about 30 minutes. The solutions were then filtered through a quantitative Whatmann 41 grade filter paper into clean dry beakers. The each beaker was covered with punctured butter sheet. Proper care was taken to minimize mechanical disturbance and temperature fluctuations. Yellow coloured Oxine doped DNB and Resorcinol doped DNB crystals were obtained in about 5 - 7 days’ time.

3. Results and Discussion

3.1 Powder x-ray diffraction method

X-ray powder diffraction pattern of the Oxine and Resorcinol doped DNB crystals are shown in figures 3 and 4. The sharp and well defined Bragg’s peaks at specific 2θ angles confirm the crystalline nature of the complex compound. X-ray diffraction pattern shows the variation of diffracted intensity with various glancing angles. The
peaks in the diffraction pattern are characteristics of the spectrum. From XRD spectral data, the microscopic structural parameters grain size (t), dislocation density (ρ) and strain (η) values are calculated from '2θ' values of different peaks and they are tabulated in table 1, for major prominent peak (2θ) of Oxine and Resorcinol doped DNB.

### 3.2 UV-Visible absorption spectrum

UV-visible spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves the promotion of the electron from the ground state to higher energy states. The UV-visible absorption spectrum of Oxine and Resorcinol doped DNB recorded in the range 200 – 600 nm. The figure 5 depicts the electronic absorption spectra of the Oxine and Resorcinol doped DNB. The spectra reveal strong absorption bands attributed to the charge transfer transition in addition to the usual π- π* bands of dinitrobenzene in the complex and appears around 345nm and 355nm. The formation of charge transfer molecular complex is confirmed through the longer wavelength absorption band arising due to the promotion of an electron from the highest occupied molecular orbital (HOMO) of donor to the lowest unoccupied molecular orbital of acceptor (dinitrobenzene). There is no significant absorption in the range 360- 600 nm, which provides the wide transparency window for the grown crystals.

### 3.3 UV-Visible transmission spectrum

The UV-visible transmission spectra of grown Oxine and Resorcinol doped DNB crystals recorded using SYSTRONICS DOUBLE BEAM UV-Vis spectrophotometer in the range 300 – 600 nm. The potential of a NLO material is generally identified by the transmission spectrum. A given NLO material can be of utility only if it has a wide transparency window without any absorption at the fundamental and second harmonic wavelengths. The figure 8 shows the transmittance spectra. The grown Oxine and Resorcinol doped DNB crystals have no absorption beyond the wavelength 370 nm (visible region). Hence they illustrate to know the suitability of the grown crystals for second harmonic generation and various optical applications [9, 10]. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and type of transition of electrons [11]. The optical absorption coefficient (α) was calculated from the transmittance using the following relation,

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Oxine-DNB</th>
<th>Resorcinol-DNB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major prominent peak (2θ)</td>
<td>21.5857</td>
<td>21.1001</td>
</tr>
<tr>
<td>Grain size (t) nm</td>
<td>61.8767</td>
<td>123.6527</td>
</tr>
<tr>
<td>Dislocation density (ρ) x 10^{13} lines / m²</td>
<td>26.1183</td>
<td>6.54</td>
</tr>
<tr>
<td>Strain (η) x 10^{-4}</td>
<td>7.82</td>
<td>2.87</td>
</tr>
</tbody>
</table>
\[ \alpha = -\frac{1}{t} \ln \left( \frac{1}{T} \right) \]  

(1)

Where \( T \) is the transmittance and \( t \) is the thickness of the sample.

Owing to the indirect band gap, the crystal under study has an absorption coefficient \( (\alpha) \) obeying the following relation for high photon energies \( (h\nu) \):

\[ \alpha = \frac{A(h\nu - E_g)^2}{h\nu} \]  

(2)

where \( E_g \) is optical band gap of the crystal and \( A \) is a constant. The plot of variation of \((\alpha h\nu)^{1/2}\) vs. \( h\nu \) for Oxine and Resorcinol doped DNB are shown in figures 8 and 9.

3.4 FTIR Analysis

The FT-IR spectra of Oxine and Resorcinol doped DNB single crystals were recorded employing PerkinElmer FT-IR spectrometer using the KBr pellet technique. The spectra depicted in the figures 9 and 10. They show the presence of characteristic absorption bands due to the varied force constants in the donor and the acceptor species on account of the prevalent charge transfer mechanism. This makes the crystals more ionic than other organic crystals. Normally in an acid base reaction, a proton transfer from the acceptor (acid) to the donor (base) is expected to occur. The assignment of various

Figure 5 UV-Visible absorption spectrum of O/R-DNB.

Figure 6 UV-Vis transmittance spectrum of O/R-DNB.

Figure 7 plot of variation of \((\alpha h\nu)^{1/2}\) vs. \( h\nu \) for O-DNB.

Figure 8 Plot of variation of \((\alpha h\nu)^{1/2}\) vs. \( h\nu \) for R-DNB.

Eg is evaluated by the extrapolation of the linear part [12]. The optical band gap energy are found to be 2.84 eV and 2.98 eV for Oxine and Resorcinol doped DNB, respectively.
absorption frequencies of the grown Oxine and Resorcinol doped DNB single crystals are given in Table 2.

**Table 2 FT-IR spectral data of Oxine and Resorcinol doped DNB**

<table>
<thead>
<tr>
<th>Assignments</th>
<th>Wave number (in cm(^{-1}))</th>
<th>Oxine doped DNB</th>
<th>Resorcinol doped DNB</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H (aromatic) stretching vibration</td>
<td>3108.84, 3094.49</td>
<td></td>
<td>3108.86, 3094.38</td>
</tr>
<tr>
<td>C-H (aromatic) Asymmetric stretching vibration</td>
<td>2873.47</td>
<td></td>
<td>2873.17</td>
</tr>
<tr>
<td>C-N stretching vibration</td>
<td>2360.69, 2340.38</td>
<td></td>
<td>2360.75, 2340.46</td>
</tr>
<tr>
<td>Asymmetric NO(_2) stretching vibration</td>
<td>1615.03, 1601.94</td>
<td></td>
<td>1615.27, 1601.96</td>
</tr>
<tr>
<td>Symmetric NO(_2) stretching vibration</td>
<td>1526.14</td>
<td></td>
<td>1541.51, 1526.29</td>
</tr>
<tr>
<td>O-H stretching vibration</td>
<td>1347.67</td>
<td></td>
<td>1347.67</td>
</tr>
<tr>
<td>C-O stretching vibration</td>
<td>1274.01</td>
<td></td>
<td>1274.00</td>
</tr>
<tr>
<td>Aromatic C-H in-plane bending</td>
<td>1094.06, 1068.37</td>
<td></td>
<td>1068.39</td>
</tr>
<tr>
<td>NO(_2) Scissoring</td>
<td>913.70, 906.08</td>
<td></td>
<td>913.69, 906.13</td>
</tr>
<tr>
<td>Aromatic C-H out of plane bending</td>
<td>837.00, 817.38</td>
<td></td>
<td>836.99, 817.22</td>
</tr>
<tr>
<td>NO(_2) wagging vibration</td>
<td>726.05, 712.05</td>
<td></td>
<td>726.14, 712.22</td>
</tr>
<tr>
<td>O-H out-plane bending</td>
<td>652.02</td>
<td></td>
<td>652.06</td>
</tr>
</tbody>
</table>

**Figure 9** FTIR spectrum of O-DNB.

**Figure 10** FTIR spectrum of R-DNB.

### 3.5 Second Harmonic Generation

The modified Kurtz and Perry powder technique was used to examine the SHG property of Oxine and Resorcinol doped DNB single crystals [13]. The crystals were grained into powder of particle size in the range 100-150 μm and tightly packed in a micro-capillary tube. They were mounted in the path of the laser beam (wavelength λ = 1064 nm) of 3.1 mJ/p energy obtained by splitting the original laser beam. The output light was passed through a monochromator transmitting only the second-harmonic (green) light of wavelength 532 nm. The green light intensity was registered by a photomultiplier tube and converted into an electrical signal. The signal was then displayed on the oscilloscope screen. Potassium dihydrogen phosphate (KDP) and urea grained into a powder of uniform particle size were used as the reference in the SHG measurement. The SHG conversion efficiency of Oxine and Resorcinol doped DNB single crystals were computed by the ratio of signal amplitude of the grown
crystal sample to that of KDP and urea signal amplitudes recorded for the same input power. The SHG efficiency of the grown Oxine and Resorcinol doped DNB crystals are 474 mV and 540 mV respectively. The SHG efficiency of the grown Oxine doped DNB crystal was found to be four times larger than that of urea (112 mV) and twenty three times larger than that of KDP (20 mV). The SHG efficiency of the grown Resorcinol doped DNB crystal was found to be almost five times equal to that of urea (112 mV) and twenty seven times larger than that of KDP (20 mV). Comparison of Relative SHG efficiency is tabulated in table 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SHG output (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KDP</td>
<td>20</td>
</tr>
<tr>
<td>Urea</td>
<td>112</td>
</tr>
<tr>
<td>Oxine doped DNB</td>
<td>474</td>
</tr>
<tr>
<td>Resorcinol doped DNB</td>
<td>540</td>
</tr>
</tbody>
</table>

Table 3 Comparison of Relative SHG efficiency

4 Conclusions

The Non Linear optical single crystals of Oxine and Resorcinol doped DNB single crystals were synthesized and grown by adopting slow evaporation technique at room temperature. X-Ray diffraction pattern reveals that the crystalline nature of the grown single crystals. The well defined Bragg peaks at specific 2θ values confirm the crystallinity of the grown crystals. The microscopic structural parameters are calculated for prominent peak values. UV-vis absorption analysis reveals π-π* transition around wavelength 345 and 355 nm for O-DNB and R-DNB respectively, which confirms the formation of charge transfer between donor (dopant) and acceptor (m-Dinitrobenzene) in grown crystal. UV-vis absorption analysis illustrates the suitability of the grown transparent crystals for second harmonic generation and various optical applications. The FTIR spectra illustrated that the presence of characteristic absorption bands are due to the presence of various functional groups in the Oxine and Resorcinol doped DNB NLO crystals. The Second Harmonic Generation (SHG) property of the grown Oxine and Resorcinol doped DNB single crystals were examined through modified Kurtz and Perry powder technique. The SHG studies reveal that the SHG efficiency of Oxine and Resorcinol doped DNB crystals are 474 mV and 540 mV respectively, which is found to be four times larger than that of urea (112 mV) and almost five times equal to that of urea (112 mV). Hence the grown charge transfer adduct ODNB may be the best candidate for nonlinear optical (NLO) applications and optoelectronic devices.
References


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Competing Interests:

The authors declare that they have no competing interests.

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