Chapter 6

Results and Discussion:
Pure & Ni^{2+} Doped Sodium Hydrogen Phthalate Single Crystals
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Abstract

The effect of nickel (Ni) doping on the growth, morphology and physio–chemical properties of sodium phthalate hemihydrate (SP) single crystals grown by slow evaporation solution growth technique has been investigated. Doping of nickel in SP lattice improves the morphology and transparency of the SP crystals as evidenced by UV-Vis studies. X-ray diffraction (XRD) studies reveal that both crystals exhibit orthorhombic phase with slight changes in the lattice parameters of doped crystals. Amount of nickel (3.5ppm) present in doped crystals was found by AAS analysis. The assignment of the observed vibrational modes has been performed by Fourier transform infrared (FTIR) and Raman spectrum. UV-Vis-NIR studies reveals that both pure and doped crystals possess minimum absorption from 320 to 1100 nm with higher transparency in Ni-doped crystals ascertaining the inclusion of metal ion (Ni\(^{2+}\)) in the host lattice. A Photoluminescence (PL) study reveals no change in the peak position and intensity of peaks present in pure SP crystals. Thermo gravimetric study indicates better thermal stability and melting point of Ni-doped crystals as compared to SP crystals. Dielectric tensor decreases in NSP crystals compared to pure SP crystals. The efficiency of second harmonic generation was obtained by the Kurtz-Perry method and doped sample was found to be more efficient for NLO applications.

6.1. Introduction

Nonlinear optical (NLO) properties are of interest wherever the interaction of light and matter is important, e.g., optical computing or laser and fiber optical materials [1]. NLO materials have been utilized in information processing, optical switching, optical frequency conversion, and telecommunications [2]. NLO properties have been studied experimentally and computationally with more focus on organic than inorganic compounds. A few of the organic materials have good non-linearity, mechanical hardness, high resistance to laser damage threshold, and ultra fast non-linear response
time [3-4]. However, due to their thermal instability, many of these organic crystals are of limited use in various applications. Therefore, researchers have started focusing their attention in finding viable alternatives to these materials. Recently, there has been increased interest in organometallic (or semi organic) and coordination complexes which possess most of the characteristics of organic materials with enhanced thermal properties [5-7]. A systematic investigation of the NLO properties for families of related complexes is crucial for improved understanding of structure-property relationships and thus the design of novel NLO materials.

Semi organic hydrogen phthalate crystals are one of the best NLO crystals which are well known for their common use as analyzer for x-ray spectrometers and electro optic processes [8]. These crystals are also used as substrate for deposition of thin film of polymers and conjugated molecules [9-10]. A large number of phthalate crystals (potassium hydrogen phthalate, Rubidium hydrogen phthalate, Cesium acid phthalate, Ammonium acid phthalate etc.) have been investigated in pure and doped form [11-14]. In the phthalate family similar to these crystals is sodium hydrogen phthalate hemihydrate (SP) which is also a promising NLO candidate. However, there is limited information available on doped form of SP crystals; therefore this material has been investigated in detail in pure and doped form in the present study.

The optimization of crystal shape and size is important in industrial crystallization as crystal morphology and size have an impact on a number of important technological areas, including downstream production processes such as filterability, storage and compaction [15]. Habit-modifying additives are often used to optimize crystal morphology through their ability to preferentially bind to specific crystal faces and hence change their relative growth rates. In recent years, great attention has been paid to the study of the influence of doping on several crystals, because doping can modify the physical properties of materials for technological applications [16-19]. Incorporation of dopants in crystals leads to the redistribution of electronic charge, which modify the electric-dipole-photon effect in the energy matter interaction and makes the crystal more efficient for SHG applications [20-21]. Certain transition metal ions often modify the growth habit of a crystal when incorporated into the lattice. Transition metal ions doped crystals are important due to their interesting spectroscopic properties making them suitable for laser and optical fiber applications [22]. Effect of iron (Fe$^{3+}$) doping on sodium phthalate crystals has been investigated [23]. Remarkable
enhancement in optical and thermal properties was observed in Fe-doped SP crystals compared to pure crystals.

In the present chapter, one of the transition metal nickel (Ni) was used as a dopant in sodium phthalate crystals. Pure and Ni doped SP crystals were grown by slow evaporation technique. To see the effect of Ni additive on sodium phthalate crystal properties, they were characterized by powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR), Raman, UV-Vis spectroscopy, photoluminescence (PL) Second harmonic generation (SHG), Laser damage threshold (LDT), Dielectric spectroscopy and thermal (TG-DTA) studies.

6.2. Synthesis and Crystal Growth

All the starting materials were of analytical reagent, and the synthesis and growth process were carried out in aqueous solution. The SP has been synthesized by taking sodium hydroxide and phthalic acid in a 1:1 stoichiometric ratio. The purity of the synthesized salt was improved by successive recrystallization process. Sodium phthalate single crystals were grown by slow evaporation of a supersaturated aqueous solution containing sodium phthalate powder at room temperature. Ni-doped SP single crystals were prepared in the same manner with the addition of 1M% of nickel acetate hexahydrate. Figure 6.1 shows pure and Ni (II) - doped SP single crystals.

Fig. 6.1: Pure and Ni-doped sodium phthalate hemihydrate crystals grown by slow evaporation

6.3. XRD Analysis

X-ray diffraction pattern of pure and Ni doped SP crystals are given in Figure 6.2. XRD patterns of both the samples were refined using checkcell software. The results are in a
good agreement with the reported data [24] and clearly indicate that both pure and doped samples exhibit a single phase. Because the peak positions of the doped SP are similar to the pure sample, it is clear that the Ni$^{2+}$ doping do not change crystalline structure of the host material. Because of smaller ionic radii of nickel compared to sodium, Ni$^{2+}$ (83 pm) cations ($d^8$) are expected most probably to be substituting for the Na$^+$ (116 pm) cations in the SP host lattice and as a result creating cation vacancies in the host lattice without causing much distortion. It was found that crystal system of both the crystals belongs to orthorhombic system with space group B2ab. Obtained refined lattice parameters and volume of both pure and doped crystals are tabulated in table 6.1. Quantitative data shows slight changes in the lattice parameter values and hence the unit cell volume. Only slight changes in peak intensities were observed due to Ni doping in SP lattice.

![Fig. 6.2: X-ray diffraction patterns of pure and Ni doped sodium phthalate hemihydrate crystals](image)

**Table 6.1: The cell parameters of pure and Ni$^{2+}$ doped sodium phthalate single crystals**

<table>
<thead>
<tr>
<th>Property</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (degree)</th>
<th>β (degree)</th>
<th>γ (degree)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure SP</td>
<td>6.6674(8)</td>
<td>9.2376(2)</td>
<td>26.4167(8)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>1627.022</td>
</tr>
<tr>
<td>Ni doped SP</td>
<td>6.7422(4)</td>
<td>9.3283(4)</td>
<td>26.5069(5)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>1667.100</td>
</tr>
</tbody>
</table>
6.4. Vibrational Analysis

Infrared spectroscopy is effectively used to identify the functional groups and determine the molecular structure of the synthesized compounds. The characteristic FTIR spectra for pure and Ni doped SP crystals recorded in the range 4000-400 cm\(^{-1}\) are given in Figure 6.3. The vibrational analysis of SP was performed on the basis of the characteristic vibrations of carboxylic acid, carboxylate and phenyl ring modes. Strong band at 1599 cm\(^{-1}\) corresponds to C-C stretching vibrations of phenyl ring. FTIR bands present at 1450 cm\(^{-1}\) and 1295 cm\(^{-1}\) appears as a weak and strong band respectively in the spectra due to C-C stretching vibrations of phenyl ring. The weak band at 1157 and 1038 cm\(^{-1}\) are due to C-H in plane bending vibrations of phenyl ring. The strong bands at 800 and 812 correspond to C-H out plane bending vibrations of phenyl ring. Vibrational analysis of carboxylic acid present in sodium phthalate crystals is made on the basis of its carbonyl and hydroxyl groups. The IR band present at 702 cm\(^{-1}\) corresponds to the O-H out of plane bending vibration. Strong IR band present at 1573 cm\(^{-1}\) can be assigned to the asymmetric stretching vibration of carboxylate ion. All the vibrational bands assigned in FTIR spectra confirm the formation of SP crystals and agree well with reported values [12]. Very slight changes in vibrational bands were seen in Ni-doped crystals which may be due to lattice distortion as discussed in PXRD.

![FTIR spectra of pure and Ni-doped sodium phthalate hemihydrate crystals](image)

Fig. 6.3: FTIR spectra of pure and Ni-doped sodium phthalate hemihydrate crystals
Raman spectra of pure and doped crystals recorded in the range 50-3200 cm\(^{-1}\) are given in Figure 6.4. Strong Raman band at 3071 cm\(^{-1}\) and 1600 cm\(^{-1}\) corresponds to C-H and C-C stretching vibrations of the phenyl ring respectively. Strong bands at 1155 and 1039 cm\(^{-1}\) in Raman spectra are due to C-H in plane bending vibrations of phenyl ring. Strong band at 815 cm\(^{-1}\) in Raman spectra corresponds to C-H out of plane bending vibrations of phenyl ring. Vibrational analysis of carboxylic acid present in sodium phthalate crystals is made on the basis of its carbonyl and hydroxyl groups. Raman band present at 1355 cm\(^{-1}\) corresponds to C-O stretching vibrations of carboxylic group. All the Vibrational bands assigned in Raman spectra confirm the formation of SP compound. Slight changes in bands present at lower frequencies were observed in doped samples.

![Raman spectra of pure and Ni-doped sodium phthalate hemihydrate crystals](image)

**Fig. 6.4: Raman spectra of pure and Ni-doped sodium phthalate hemihydrate crystals**

### 6.5. Atomic Absorption Spectroscopy

The presence of nickel in the crystal lattice was determined by AAS. Experimental results reveal that 3.5 ppm of nickel is present in the nickel doped SP crystals. This shows that amount of Ni present in the NSP crystals is less than that of amount of Ni initially added to the aqueous solution while crystallization.
6.6. Optical Characterization

6.6.1. UV-Vis Analysis

The UV-Vis-NIR spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves the promotion of electron in σ and π-orbital’s from the ground state to higher energy states. Figure 6.5a presents the transmittance zone of both pure and Ni doped SP crystals above 150 nm (ultra-violet wavelength). [25-27] Noticeable characteristic in the transmittance spectrum is a wide transparency window within the range of 330–1150 nm which is highly desirable for NLO crystals because the absorptions in an NLO material near the fundamental or second harmonic signals will lead to the loss of the conversion of second harmonic generation efficiency [28]. Due to this property, SP and NSP crystals have potential uses for second harmonic generation (SHG) using an Nd: YAG laser (1064 nm) to emit a second harmonic signal within the green region (532 nm) of the electromagnetic spectra. [29]. It was found that cut-off wavelength (~325 nm) is almost same for both crystals; but there is a remarkable enhancement in the transmittance of sodium phthalate crystals due to Ni doping. Transition metal ion Ni$^{2+}$ contains d$^8$ configuration having 2 unpaired electrons and phthalate ion contains lone pair electrons of oxygen. When Ni ion is added in the SP host lattice, substitution of Na$^+$ by Ni$^{2+}$ creates a lot of cation vacancies in the host lattice and then there occurs some interaction of d electrons of Ni with lone pair of phthalate ions (ligand). This ligand interaction and interaction of vacancies with surrounding cations leads to higher transmittance in Ni doped crystals.

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons [30]. The optical absorption coefficient (α) was calculated from the transmittance using the following relation,

$$\alpha = \frac{2.303}{t} \times \log \left( \frac{1}{T} \right)$$
where $T$ is the transmittance and $t$ is the thickness of the crystal. To study the nature of energy band gap ($E_g$) variation, the following equation was used:

$$\alpha h\nu = A(h\nu - E_g)^n$$

where $n$ is an index determined by the nature of the electron transition during the absorption process, ($n = 2$ for allowed direct transition, and $n = 1/2$ for allowed indirect transition) and $A$ is a constant nearly independent of photon energy, known as the disorder parameter [31]. For the present case, $n=1/2$ was found to be best fitted for both pure and Ni$^{2+}$ doped SP showing indirect transition nature of the material. Plot of $(\alpha h\nu)^2$ vs. photon energy for pure and Ni$^{2+}$ doped SP is given in Figure 6.5b and optical band gap found to be 4.04eV and 4.08eV for pure and doped crystals respectively.

![Fig. 6.5: (a) UV-vis – NIR spectrum of pure and Ni- doped SP crystals with increased transparency due to Ni-doping. (b) Variation of $(\alpha h\nu)^2$ vs. $h\nu$ of the pure and Ni-doped SP crystals](image)

### 6.6.2. Photoluminescence Analysis

Photoluminescence spectra of pure and nickel doped sodium phthalate single crystals recorded at room temperature in the range 350-700 nm are given in Figure 6.6. Appearance and explanation of PL peaks at 412 and 522 nm in pure SP crystals has already been discussed in earlier chapters. Inclusion of nickel ions in host SP lattice did not have much effect on the peak position and intensity of peaks. Slight quenching of peak at 412 nm was observed with no change in other peak at 522 nm. This shows that nickel dopant did not affect the luminescence properties of SP crystals.
Fig. 6.6: PL spectrum of pure and Ni-doped SP crystals with photoluminescent peaks at 412 nm and 522 nm

6.7. Non-linear Optical Characterization

6.7.1. SHG Efficiency

SHG efficiency of pure and doped crystals was measured by Kurtz powder technique [32]. The input laser beam was passed through IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 1.65 mm. The second harmonic output was generated by irradiating the powder samples of grain size 63 µm by a pulsed laser beam. The output from the sample was monochromated to collect the intensity of the 532 nm component and to eliminate the fundamental. For the SHG efficiency measurements, microcrystalline material of KDP was used for comparison with same particle size (63 µm). The second harmonic signal generated in the crystals was confirmed from the emission of green radiation by the sample and the optical signal was collected by a photomultiplier tube (PMT). The optical signal incident on the PMT was converted into output voltage at the CRO. The attainment of second order effects requires favorable alignment of the molecule within the crystal structure [33]. From the analysis, it was found that the SHG output relative efficiency is 2.3 mV for pure SP crystals and 4.9 mV for Ni-doped SP crystals. Comparing these results with the SHG output of pure KDP (4.8 mV); it was found that SHG efficiency of pure and Ni-doped SP crystal is 0.5 and 1.1 times that of KDP respectively. SHG efficiency of
sodium phthalate is twice that of potassium phthalate crystals [14]. Ni doping in sodium phthalate crystals enhances SHG efficiency twice and four times that of sodium phthalate and potassium phthalate crystals, respectively. This shows that inclusion of Ni ions in the SP lattice resulted in the significant improvement in non-linearity of SP crystals. As discussed above, because of ligand interaction of d electrons with lone pair electrons of oxygen atoms, transmittance increases in Ni doped SP crystals. Therefore increase of SHG value in NSP crystals is expected in the visible region.

6.7.2. Laser Damage Threshold

Laser damage threshold values of pure and Ni-doped SP crystals were examined on (001) plane of the crystals. AQ-switched Nd: YAG laser operating at 1064nm radiation was used. The laser was operated at the repetition rate of 10 Hz with pulse width of 10 ns. For the LDT measurements, 1mm diameter beam was focused on the samples. During laser radiation, the power meter records the energy density of the input laser beam for which the crystal gets damaged. The surface damage threshold of the crystals was calculated using the expression:

\[
P_d = \frac{E}{\tau \pi r^2}
\]

where \(E\) is the energy (mJ), \(\tau\) is the pulse width (ns) and \(r\) the radius of the spot (mm).

Laser damage threshold value was found to be 0.32 GW cm\(^{-2}\) for both pure and doped crystals.

6.8. Dielectric Analysis

The variation of dielectric tensor and loss with frequency (10 mHz-10 MHz) at different temperatures (20-100 °C) for pure and Ni doped SP crystals are shown in Figure 6.7a,b and Figure 6.7c,d, respectively. It was observed from figure 6.7a,b that dielectric constant increases very slightly with temperature up to 60 °C and then it increases very rapidly in the temperature range (60-100 °C). There is a sudden rise in dielectric constant and loss near decomposition temperature (90-100 °C) which may be due to large ionic polarization of the crystals due to disordering effect of dipoles around this temperature originating from phthalate ion groups and sodium ions [34].
At 100°C, in pure SP dielectric constant was found to be ~400 while in doped crystal dielectric constant was observed to be ~72 only. Same behavior was observed for dielectric loss in both samples. In both cases dielectric loss at very low frequency was found to be ~3 at 100°C. Both pure and doped crystals followed a normal dielectric behavior: decreasing dielectric constant with increasing frequency. This is because of polarization mechanism occurring in the crystal with changing frequency and temperature. The electronic exchange of the number of ions in the crystals gives local displacement of electrons in the direction of applied field that gives rise to polarization. As the frequency increases, a point will be reached where the space charge cannot sustain and comply with the external changing field and hence the polarization decreases, giving rise to diminishing values of dielectric constant. Evidently, dielectric dispersion is noticeable at lower frequency and higher temperature [35]. Increase of dielectric constant with temperature can be due to space charge polarization near grain boundary interfaces which depends on the purity of the sample [36]. Due to Ni doping...
in sodium phthalate crystal lattice, polarization decreases by large amount due to which a drastic decrease in dielectric constant value was seen. Decrease of dielectric constant with Fe-doping in SP has been reported in our earlier reports [23]. It is observed that value of dielectric constant in Ni-doped crystals is small compared Fe-doped crystals. This may be due to large ionic radii of nickel compared to iron. The low value of dielectric loss in pure and doped crystals at higher frequencies suggests that the crystal possesses enhanced optical quality with lesser defects and this is of vital importance for NLO applications [37].

6.9. Thermal Analysis

TG-DTA curves for pure and Ni-doped SP single crystals are shown in Figure 6.8a and b respectively. These thermo-grams give the effect of Ni-dopant on thermal stability and melting point of the pure SP crystals. In pure SP crystal, initially weight loss was observed to be 4.75% in the temperature range 92-127 °C which matches closely with the theoretical weight loss (4.56%) of half water molecule of the compound. This is followed by further weight loss of 42.80 % in the temperature range 134-221 °C which can be due to decomposition or release of some other products like CO\textsubscript{2} from the anhydrous compound. However, in Ni-doped crystals initial weight loss was observed to be 4.62% in the temperature range 94-137 °C and further weight loss observed to be 43.21 % in the temperature range 204-323 °C. This shows that Ni-doping in SP lattice increases the temperature of stability of compound. It is also observed that there are more flat plateaus of thermal stability in NSP crystal compared to pure SP crystals. In DTA curves sharp endothermic peaks was observed corresponding to these losses showing good crystallinity of the grown crystals. In pure SP, an endothermic peak at 117 °C and 211 °C corresponds to loss of lattice water and melting of the compound, respectively. On the other hand in Ni-doped crystals these were observed at 122 °C and 301 °C. These results clearly indicate the enhancement of thermal stability and melting point of sodium phthalate crystal due to incorporation Ni in the SP lattice. Beyond melting point, it was observed that residue left in pure SP is 35% whereas it is 50% for NSP crystals. This shows that Ni-doped crystals are more thermally stable than pure crystals and can be used in NLO devices conveniently without melting upto higher
temperatures. It was also observed that nickel inclusion has more impact on melting point of sodium phthalate crystals compared to iron [23].

![Fig. 6.8: TG-DTA curve of (a) pure and (b) Ni-doped SP crystals with melting point at 211°C and 301°C respectively](image)

6.10. Summary

- Single crystals of novel NLO material: sodium phthalate were successfully grown by slow evaporation solution growth technique in pure and doped form.
- The presence of nickel in NSP crystal lattice was qualitatively confirmed by FT-IR and Raman analysis.
- From AAS analysis 3.5 ppm of nickel was found in NSP crystals.
- Lattice parameters of pure and Ni doped SP crystal was determined through powder X-ray analysis. Slight changes in lattice parameters and peak intensities were observed in NSP crystals.
- Optical absorption studies shows that sodium phthalate crystals are transparent in entire UV-Vis region and this transparency increases in Ni doped crystals due to ligand interaction.
- PL studies revealed that Ni did not have any effect on luminescence properties of SP crystals.
- NLO studies shows that Ni doping in SP crystals improves the SHG efficiency to almost double that of pure SP crystal.
- LDT studies revealed that Laser damage threshold of SP crystals did not get affected by inclusion of Ni-dopant.
- Results of dielectric measurements show that in both pure and doped crystals dielectric constant increases with temperature because of variation of polarization. Due to Ni-doping in SP lattice dielectric constant decreases by a large amount.

- From thermal measurements, it was found that melting point and thermal stability of sodium phthalate crystals increases due to Ni doping ascertaining inclusion of nickel in sodium phthalate lattice.

- Higher SHG efficiency and melting point of NSP crystals makes them more promising material for NLO applications compared to pure SP crystals.
6.11. References


