Chapter 4

Results and Discussion:
Pure & Fe$^{3+}$ Doped Sodium Hydrogen Phthalate Single Crystals
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Abstract

Single crystals of pure and iron doped sodium hydrogen phthalate hemihydrate have been grown by slow evaporation solution growth technique. The structure and morphology of pure and doped crystals were analyzed by powder X-ray diffraction analysis. From PXRD studies, it was found that both crystals belong to the orthorhombic phase with high crystallinity. Morphology of crystals found to change from rhombic bipyramidal to rectangular shape as a result of Fe-doping in sodium phthalate crystals. The degree of dopant inclusion in doped crystals was ascertained quantitatively by Atomic Absorption Spectroscopy. Vibrational bands of the pure and doped crystals were elucidated by Fourier transform infrared and Raman spectra. From UV-Vis-NIR studies it was found that Fe inclusion in SP crystals resulted in an absorption band at 370 nm in UV region and an increase in transmittance in entire visible region with no appreciable change in optical band gap. Photoluminescence studies revealed that intensity of photoluminescent peaks at 412 nm and 522 nm was enhanced due to Fe-doping with inhomogeneous broadening. From dielectric studies, it was found that dielectric tensor component ($\varepsilon_{33}$) decreases and dielectric loss increases as a result of the inclusion of Fe-ions in the host lattice. Thermal analysis revealed that melting point and thermal stability were enhanced due to the introduction of small ionic radius Fe$^{3+}$ ion in the pure SP crystal. SHG efficiency of Fe-doped crystals was found to be twice of pure SP crystal and comparable to that of potassium dihydrogen phosphate (KDP) crystals. From laser damage threshold studies, LDT values were found to be 0.32 GW cm$^{-2}$ and 0.28 GW cm$^{-2}$, for pure and iron doped crystals respectively.

4.1. Introduction

Extensive investigations have been made on organic nonlinear optical (NLO) materials due to their high nonlinearity, better laser damage resistance and variety of synthesis
methods. The microscopic origin of nonlinearity in these molecular NLO materials is due to the presence of delocalized π-electron systems, connecting donor and acceptor groups, which enhance their asymmetric polarizability [1-2]. In the actual applications, these crystals have certain inherent limitations such as, increased optical absorption and narrow transparency window, apart from poor mechanical and thermal stability. To overcome these difficulties, a new strategy of synthesizing organic–inorganic hybrid compounds have been proposed, thus leading to synthesis of the semi organics systems [3-4]. In this class of materials, the organic ligand is ionically bonded to a suitable metal ion or an inorganic host, thereby imparting improved mechanical and thermal properties. Many efforts are being taken to develop and to study new nonlinear optical materials with specific properties such as large second harmonic generation, effective nonlinear coefficient, short UV cutoff [5-7].

Semi organic crystals of phthalic acid derivatives are potential candidates for NLO and electro-optic processes. The hydrogen phthalate crystals are widely known for their application in long-wave X-ray spectrometers. Their optical, piezoelectric, NLO and elastic properties have been investigated in detail [8–9]. Acid phthalate crystals are also used as substrates for deposition of thin films of organic non linear materials [10]. Potassium acid phthalate (KAP), rubidium acid phthalate (RbAP), cesium acid phthalate (CsAP), thallium acid phthalate (TIAP) and ammonium acid phthalate (NH$_4$AP) are few of the important reported semi-organic phthalic acid crystals. In this series, Sodium hydrogen/acid phthalate hemihydrate (SP) single crystal is an excellent candidate for SHG applications in the phthalic acid family [11]. It can be synthesized by reacting sodium hydroxide (ionic and inorganic) and phthalic acid (organic) in equimolar ratio. It shares the properties of both organic and inorganic constituents. It crystallizes in orthorhombic system with lattice parameters: a=6.75 Å, b= 9.31 Å and c= 26.60 Å and space group B2ab [11]. SP is a non-linear optical material of alkali phthalate family which are widely used in the field of x-ray spectroscopy as monochromator and analyzer [12]. The platelet morphology of phthalate crystals has excellent physical properties due to which they have been used in various devices [13-14]. They are also promising material for quantitative and qualitative analysis of light elements. The non linearity in phthalate crystals originates from the contribution of polarizable aromatic rings of phthalate ions [15].
It is well known that doping in the semi organic crystals influence the various properties like morphology, transmittance, optical and thermal properties without affecting the crystalline structure. Effect of various impurities (Fe, Ce, Mn, Cr, Zn, Na etc.) on potassium hydrogen phthalate crystals have been investigated in detail [16-17]. These impurities affect the growth kinetics, morphology, quality and various other properties of phthalate crystals [18, 19-21]. The interaction of transition metal ions with ligands having long π-delocalized system provides one of the most fascinating areas of coordination chemistry and non-linear optics [18]. Therefore in the present investigation, transition metal (Fe$^{3+}$) was chosen as a dopant in SP crystals to improve its optical properties. Na$^+$ ion in SP lattice is situated in an irregular octahedral environment surrounded by six O atoms, four from the ionized carboxyl groups, one from an un-ionized carboxyl group, and one from the water molecule. Since Fe$^{3+}$ prefers hexa-coordination, this Na$^+$ site is favorable for the trivalent ions [22]. As ionic radii of Fe$^{3+}$ is very small as compared to that of Na$^+$, therefore they will replace Na$^+$ conveniently and with each replacement two cation vacancies are created [23]. Distribution of vacancies and interaction of vacancies with surrounding cations is expected to result in a change in dipole moment of the FSP crystals, due to which it’s optical and electrical properties can be controlled.

*In the present chapter, it is aimed to grow large single crystals of pure and Fe doped sodium phthalate hemihydrate and to see the influence of Fe doping on the morphology, optical and thermal properties of pure SP crystals.*

### 4.2. Synthesis and Crystal Growth

All of the starting materials were taken of analytical-grade reagents. Sodium hydrogen phthalate salt was prepared by dissolving sodium hydroxide (NaOH) and phthalic acid (C$_8$H$_6$O$_4$) in a molar ratio of 1:1 in distilled water. The solution was stirred and subsequently kept at a constant temperature of 40 °C for several days for controlled evaporation. The synthesized salt was purified by successive recrystallization and utilized for growth of pure and Fe-doped sodium phthalate crystals. Then SP salt was dissolved in distilled water and stirred continuously for 2 days at a constant temperature. The resulting solution was filtered and kept undisturbed in a water bath at constant temperature (30 °C) to initiate nucleation. Well defined and transparent
crystals of dimension up to 20mm×15mm×5mm were formed in around 20 days due to spontaneous nucleation. The crystals were optically transparent with rhombic bipyramidal morphology and non-hygroscopic in nature.

To grow Fe doped crystals, various concentrations of \( \text{Fe(NO}_3\text{)}_3 \) were added to the saturated aqueous solution of sodium phthalate and then stirred again for 2 hrs. For a doping concentration higher than 0.5 M\%, it was found that Fe was not able to dissolve in the solution and it gets collected at the bottom of the beaker. Therefore it was not possible to grow crystals for such doping concentration. For lower concentrations of Fe, the obtained solutions were filtered and left undisturbed at constant temperature (30\(^\circ\)C) in a water bath (accuracy 0.1\(^\circ\)C) with covered perforated lid with small holes in it. It was found that good quality crystals were grown only for lower concentrations of Fe; the best being for 0.2 M\%. Apparently, at high concentrations of the dopant, the adsorption film blocks the growth surface and inhibits the growth process [24-25]. Hence further growth were tried with this percentage of Fe-doping in which in around 30 days, transparent crystals of dimension upto 50 mm x 10mm x 5mm were seen with light yellow color. Bulk crystals were grown using optimized growth parameters like stirring time duration, concentration, temperature etc. Photographs of the as grown doped and undoped crystals are shown in Figure 4.1 in which pure crystals were found to exhibit rhombic bipyramidal morphology whereas doped one exhibits rectangular morphology.

![Fig. 4.1: Pure and Fe-doped sodium phthalate hemihydrate crystals grown by slow evaporation](image_url)
The morphology of growing crystal is broadly governed by two factors, the internal structure of the crystal and external parameters such as supersaturation, temperature level, the presence of solvent and impurities. The important parameters controlling the growth rate are the energy required to create a step at the crystal surface and free-energy barrier for an adsorbed impurity ions to be incorporated into the crystal [26]. If the surface relaxations are large enough then small nuclei will grow into platelets, although large nuclei still grow into large three dimensional crystals [27]. Rectangular morphology of Fe-doped SP crystals may be due to the surface relaxation effect caused by the inclusion of Fe$^{3+}$ into SP lattice. The presence of Fe$^{3+}$ in the solution controls the growth rate in all directions and leads to produce rectangle shape good size crystals for Fe-doped SP. The main reason for the change in crystal morphology is the modification of the growth rates in crystallographic axes due to surface relaxation by the iron dopant [28]. In FSP crystals, the growth rate is anisotropic; it is high along a-axis relative to the growth along b and c axes.

4.3. PXRD Analysis

To confirm the crystal structure, pure and Fe-doped SP crystals were finely grinded and subjected to powder X-ray diffraction (PXRD) analysis using Bruker, D8 Discover with graphite-monochromated CuKα radiation ($\lambda=1.5408$ Å). The PXRD pattern was obtained in the range 5 to 80° with step size and step time as 0.01° and 1 sec, respectively. The well defined Bragg’s peaks at specific 2θ angles showed high crystallinity of both pure and doped crystals. It was observed that both crystals belong to the orthorhombic structure having space group B2ab. The evaluation of lattice parameters from powder XRD pattern and peak indexing were carried out using the software checkcell. The cell parameters obtained for both the spectra’s were found to agree well with the reported values [11]. A comparison is shown in Table 4.1. It was found that doping did not have any significant effect on the orthorhombic structure of pure sodium phthalate hemihydrate crystals; only slight changes in the lattice parameters (Table I) were observed with change in the morphology of the crystals. No new peak was seen due to Fe doping; only changes in intensities of some peaks were observed. It was found that peak intensity at (020) plane increased along with slight
change in intensities of some other peaks. X-ray diffraction pattern for the grown samples is shown in Figure 4.2.

![X-ray diffraction patterns of pure and Fe doped sodium phthalate hemihydrate crystals](image)

**Fig. 4.2:** X-ray diffraction patterns of pure and Fe doped sodium phthalate hemihydrate 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>Fe doped SP</td>
<td>6.6977(4)</td>
<td>9.3132(6)</td>
<td>26.5263(1)</td>
<td>90.00</td>
<td>90.00</td>
<td>90.00</td>
<td>1654.620</td>
</tr>
</tbody>
</table>

**4.4. Atomic Absorption Spectroscopy**

The amount of iron metal incorporated in doped sodium phthalate crystal was detected by analytic Jena’s Zeenit 700P atomic absorption spectrometer (AAS) which is one of the most widely used quantitative analytical methods. It is used for quantitative determination of metals and metalloids down to absolute amounts as low as $10^{-14}$ g. AAS determines the presence and concentration of metals in liquid samples. To evaluate amount of Fe incorporated in doped samples liquid solutions were prepared in
aqua-regia. The data revealed that the dopant concentration present in the FSP crystal is 6.5 ppm although we have used 0.2M% of Fe during the growth. This shows that quantity of iron metal ion entering into the crystalline matrix is much less in comparison with the quantity introduced into the aqueous growth medium. It could be due to the limitations of the accommodating capability of the material.

4.5. Vibrational Analysis

Infrared and Raman spectroscopy is effectively used to identify the functional groups in the grown crystals. FTIR spectra were recorded in the range 400–4000cm\(^{-1}\) with Perkin Elmer spectrum BX spectrophotometer using the KBr pellet technique. FT-Raman spectra was recorded using FT-Raman spectrophotometer in the wave number range 50-3200cm\(^{-1}\) using excitation radiation at 514 nm with Ar-ion Laser working at 30mW at room temperature. FTIR and Raman spectra of pure and doped SP crystals are presented in Figure 4.3 and Figure 4.4 respectively.

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

Fig. 4.3: FTIR spectra of pure and Fe-doped sodium phthalate hemihydrate crystals

Strong IR band at 1599 cm\(^{-1}\) corresponds to C-C stretching vibrations of phenyl ring. 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 cm\(^{-1}\) 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. 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.

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

Fig. 4.4: Raman spectra of pure and Fe-doped sodium phthalate hemihydrate crystals

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 FTIR and Raman spectra confirm the formation of SP crystals and agree well with reported values [29]. Very negligible changes in vibrational bands were seen in the spectra’s of doped crystals.
4.6. Optical Characterization

4.6.1. UV-Vis Analysis

Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has a wide transparency window in the visible region. For optical analysis, the transmittance spectrum for pure and Fe-doped SP crystal was recorded using a Perkin lambda 35 scanning double beam spectrophotometer equipped with a 50 mm integrating sphere in the region 200-1100 nm (Figure 4.5a).

It was found that cut-off wavelength did not change due to Fe-dopant but transmittance increases in doped crystals. Broad absorption band in the ultraviolet region centered at around 370 nm was found in FSP crystals with higher transmittance in visible region (inset Figure 4.5a). In the case of FSP crystals, Fe$^{3+}$ is surrounded by six oxygen atoms. The d-orbital electrons of Fe interact with lone pair of oxygen atoms of SP, which leads to the ligand interaction [30]. Due to this, absorption band appeared and transmittance of light in FSP crystals increases in visible region. So, the grown crystals are useful for optoelectronic applications and the second harmonic generation (frequency conversion). This shows that the substitutional doping of Fe in the SP lattice improved their optical quality in the entire visible region. In addition, occurrence of absorption band (at 370 nm) makes FSP crystals suitable candidate for short wavelength holographic recording [31].
The absorption coefficient ($\alpha$) was determined from the transmittance $T$ using the relation:

$$\alpha = \frac{2.303}{t} \log \left( \frac{1}{T} \right)$$

where $t$ is the sample thickness and $T$ is the transmittance.

To study the band gap ($E_g$) nature and to estimate the value of the energy gap $E_g$, the following equation was used:

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

in which $n$ 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 [32]. For the present case, $n=1/2$ was found to be best fitted for both pure and Fe$^{3+}$ doped SP showing indirect transition nature of the material. Plot of $(\alpha h\nu)^2$ vs. photon energy for pure and Fe$^{3+}$ doped SP is given in Figure 4.5b and optical band gap found to be 4.04eV and 4.08eV for pure and doped crystals, respectively.

### 4.6.2. Photoluminescence Studies

Photoluminescence spectroscopy is a selective and extremely sensitive probe of discrete electronic state [33]. PL occurs when a system is excited to a higher energy level by absorbing a photon, and then spontaneously decays to a lower energy level, emitting a photon in the process. The photoluminescence (PL) analysis of pure and doped SP crystals was carried out using Horiba Jobin Yvon Spectrophotometer at an optical excitation wavelength of 325 nm and spectra are given in Figure 4.6.

Both pure and doped crystals were excited at 325nm and spectra were recorded in the range 350-700 nm. PL spectra showed a broad greenish emission of high intensity centered at 522 nm in addition to a less intense peak at 412 nm. Photoluminiscent peak of low intensity at 412 nm can be attributed to the intrinsic defects in the forbidden band region of pure SP crystals [34]. The emission band at 522 nm can be assigned to the transitions between filled $\pi$ to $\pi^*$ orbital of the metal and the...
ligand and radiative recombination between deep donors and shallow acceptors [35]. Fe-doping in these crystals gives rise to change in FWHM and area under both peaks. Fe-doping also caused inhomogeneous broadening of peaks which could be due to some energy levels created in the excited state and also due to high concentration of defects as a result of Fe-doping. Cation vacancies due to Fe doping in SP crystals are responsible for the enhanced PL emission property in visible region of the spectra. Increase in PL intensity of doped crystals may also be due to transfer of energy through the dopant energy level.

![PL spectrum of pure and Fe-doped SP crystals with photoluminescent peaks at 412 nm and 522 nm](image)

**Fig. 4.6: PL spectrum of pure and Fe-doped SP crystals with photoluminescent peaks at 412 nm and 522 nm**

### 4.7. Non-linear Optical Characterization

#### 4.7.1. SHG Efficiency

The most widely used technique for confirming the SHG from prospective second-order NLO material is the Kurtz powder technique [36]. It is used to identify and confirm the non-centrosymmetric crystal structure in the crystals. Although many materials have been identified that have higher molecular non-linearities, the attainment of second order effects requires favorable alignment of molecule within the crystal structure. The efficient SHG demands specific molecular alignment of crystals to be achieved facilitating non-linearity in the presence of dopant. To check the SHG efficiency,
crystals were ground into powder to uniform particle size of 63µm. For comparison, KDP crystal was also ground into powder form in the same particle size. An Nd: YAG laser beam of wavelength 1064 nm was made to fall normally on the sample capillary. The emission of green light confirmed the SHG property in SP and FSP crystals. The SHG intensity was found to be 2.3 mV and 4.2 mV for SP and FSP crystals respectively, while that for KDP it is 4.8 mV. Thus, the NLO efficiencies of SP and FSP crystals are 0.5 and 0.9 times that of KDP respectively. The SHG efficiency is doubled due to Fe incorporation. As discussed above ligand interaction increases transmittance in entire visible region, due to which SHG is also expected to increase and the present results supports this expectation. Due to the presence of transition metal dopants, there is an increase in polarizability of molecule which also tends to increase the SHG efficiency and hence improves optical properties [16,17]. Hence Fe doped SP crystals are more suitable for NLO applications.

### 4.7.2. Laser Damage Threshold

Laser-induced damage is one of the most important considerations in the choice of a material for NLO application. It gives information about the maximum permissible laser power which a crystal can withstand without getting damaged [37]. The maximum output power can be obtained by increasing the power density of the fundamental beam which is proportional to the harmonic conversion efficiency. However, a high power intensity beam can often cause damage of the crystal. Hence, the damage studies become important for newly discovered materials.

For LDT measurements, 1mm diameter beam of Q-switched Nd:YAG laser ($\lambda=1064$ nm) was focused along [001] direction of the crystals with repetition rate of 10 Hz and pulse width of 10ns. The surface damage threshold of the crystals was calculated using the expression:

$$\text{Power density (P_d)} = \frac{E}{\tau \pi r^2}$$

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

Laser damage threshold values are found to be 0.32 GW cm$^{-2}$ and 0.28 GW cm$^{-2}$ respectively, for SP and FSP single crystals.
4.8. Dielectric Analysis

Dielectric studies were performed on both pure and doped crystal to study the variation of dielectric constant and dielectric loss as a function of oscillating electric field and varying temperature. The study of dielectric constant of a material gives an outline about the nature of atoms, ions, bonding and conduction mechanism in the material. From the analysis of dielectric constant as a function of frequency and temperature, the different polarization mechanism in solids can be understood. Dielectric measurements were carried out by using a Novo control α-S high-resolution dielectric analyzer in a frequency range from 10 mHz to 10 MHz, and temperature ranging from room temperature to 373 K. The dielectric permittivity of a crystalline material is a second rank tensor. For an orthorhombic system there are three independent components of dielectric tensor: $\varepsilon_{11}$, $\varepsilon_{22}$ and $\varepsilon_{33}$ corresponding to a, b and c-directions respectively. Dielectric measurements were carried out along the c-direction for both pure and doped crystals. The variation of dielectric tensor ($\varepsilon_{33}$) and dielectric loss with frequency (10 mHz-10 MHz) at different temperatures for pure and Fe doped SP crystals along c-direction are given in Figure 4.7a, 4.7b and Figure 4.7c, 4.7d respectively.

Fig. 4.7: Frequency dependence of dielectric tensor component ($\varepsilon_{33}$) and dielectric loss at different temperatures for pure (a,b) and Fe doped (c,d) SP samples
For dielectric measurements single crystals of dimensions 4.53x4.04 mm$^2$ with thickness 3.41 mm (SP) and 8.66x3.34 mm$^2$ with thickness 1.86 mm (FSP) were taken. It was found that $\varepsilon_{33}$ decreases from 270 at 10 mHz to 25 at 10 MHz (at 80 °C) while for the Fe doping resulted in a reduced values as 90 and 25, respectively in the same range of frequency and temperature. Krishnan et al. have reported the dielectric value of 355 at 50 Hz (at 75 °C) for pure SP crystals [38]. A very comprehensive report on dielectric tensor along a, b and c-directions in SP crystal at room temperature is also reported by S. Haussuehl [39]. The decrease in dielectric tensor with frequency at all temperatures is observed in both the crystals which is a normal dielectric behaviour. The electronic exchange of a number of ions in the crystal gives local displacement of electrons in the direction of applied field, which in turn gives rise to polarization. The large value of dielectric constant at low frequency suggests that there is a contribution from all the four known sources of polarization, namely, electronic, ionic, dipolar and space charge polarizations [40]. Space charge polarization is generally active at lower frequencies and high temperatures and indicates the perfection of the crystals. As frequency increases, a point is reached where space charge cannot sustain and comply with the changing external field and hence polarization decreases, giving rise to diminishing values of dielectric constant [41-42].

It was also observed from the plots that the dielectric tensor ($\varepsilon_{33}$) of pure and Fe-doped SP crystals increases slightly with temperature upto 60°C and then it increases rapidly in the temperature range 60-100 °C. Similar behaviour is observed for dielectric loss ($\tan \delta$) of both samples. This kind of behaviour is due to vibrations of molecules about their mean positions which lead to increase of polarization when temperature is increased. In the temperature region (20- 60 °C) vibrations of molecules will be less and hence increase of polarization will be less and there is a slight increase in the values of dielectric tensor. It is reported that low value of dielectric loss is noticed for a crystal containing less number of defects. Since production of defects in the crystal will be less in the temperature range 20-60 °C, the value of dielectric loss increases slightly in this temperature range. The rapid increase of dielectric tensor and loss in the temperature range 60-100 °C for the crystals of this work can be attributed to the large ionic
polarization due to disordering effect of dipoles which is more apparent near decomposition temperature (90-100°C) and large production of defects in this temperature range [43-44]. In fact, the changes in the dielectric parameters like dielectric tensor and dielectric loss are ascribed to changes in the different kinds of polarizations. When temperature is increased, the ionic distance increase and hence there is an increase in space charge polarizations. This leads to the increase of dielectric parameters with temperature [45-46]. It was observed that at all temperatures dielectric tensor ($\varepsilon_{33}$) decreases with Fe doping which may be because of small size of Fe as compared to Na ion. Dielectric loss increases for Fe doped sample which shows that defect concentration is increasing with Fe doping in SP crystals. As already discussed, there is creation of cation vacancies due to the replacement of Na$^+$ with Fe$^{3+}$, which might be the reason for higher loss in doped crystals [47].

4.9. Thermal Analysis

TG and DTA analyses are of immense importance as far as fabrication technology is concerned, as they provide thermal stability of the material for fabrication, where a considerable amount of heat is generated during the cutting process. Thermal behavior of the samples were studied by thermo gravimetric (TGA) and differential thermal analysis (DTA) using a Diamond Perkin Elmer system in the temperature range RT to 650 °C at a heating rate of 10 °C/min. TG/DTA plots of pure and Fe doped sodium phthalate hemihydrate crystals are given in Figure 4.8a and 4.8b, respectively.

**Fig. 4.8:** TG-DTA curve of (a) pure and (b) Fe doped SP crystals with melting point at 211°C and 286°C respectively
The TGA trace of SP crystal appears nearly straight up to 92 °C (thermal stability) and weight loss of 4.75% occurs between 92-127 °C which is due to loss of structural crystal water. This value of weight loss matches closely with the theoretical percentage of half water molecule in the grown crystal. Further, major weight loss of about 30.23% occurring in two stages between 134 and 221 °C. The weight loss in these stages may be due to the decomposition and volatilization of the material. In the DTA curve there appears one endothermic peak at 117 °C which corresponds to the loss of lattice water as this lies in temperature range 92-117 °C. This is followed by the endothermic peak at 211 °C which can be assigned to the melting point of the SP crystals. However for Fe-doped SP crystals, the thermal stability increases upto 110 °C, weight loss (4.57%) of crystal water (half water molecule) takes place between 110 and 149 °C. Next weight loss (39.06%) occurs in the temperature range 207-310 °C. In the DTA curve, first endothermic peak appears at 129 °C while the other at 286 °C. This shows that substitution of Fe in sodium phthalate lattice increases the bond energy of Fe doped crystal as the ionic radius of Fe is very small as compared to Na ion, therefore interaction between Fe ion and phthalic acid increases [48]. Due to this fact thermal stability and melting point increases in Fe doped SP crystals. It was found that thermal stability of doped SP is higher than that of pure SP crystals because there is no flat plateau in pure SP crystals in TGA curve. In addition, it was also observed that at the end the residue left in doped SP crystal is higher than what left in the case of pure SP crystals. Therefore, FSP crystals are superior in comparison to undoped SP crystals for application in devices requiring higher thermal stability.

4.10. Summary

- Good quality single crystals of pure and Fe doped SP have been successfully grown using slow evaporation solution growth technique.
- Morphology of iron (Fe) doped sodium phthalate crystals was found to change from rhombic bipyramidal to rectangular shape.
- In Powder X-ray diffraction studies, no change in the orthorhombic crystal structure of sodium phthalate crystals was observed due to Fe-doping. However, Intensity of some of peaks increased while other remains unchanged.
6.5 ppm of Fe was found to be present in Fe-doped sodium phthalate crystals in AAS studies.

The functional groups in pure and Fe-doped sodium phthalate crystals were confirmed by FTIR and FT-Raman spectra in which no appreciable change was observed.

In UV-Vis-NIR studies, appearance of absorption band at 370 nm in UV-region with increased transparency in entire visible region have been observed implying application of FSP crystals in holographic data storage applications.

In Photoluminescence study, two photoluminiscnet peaks at 412 nm and 522 nm have been observed in both pure and doped crystals. The enhancement in the intensity and inhomogeneous broadening of PL peaks in doped crystals was observed.

A significant enhancement in the SHG efficiency of FSP crystal has been observed. SHG value of FSP crystal was found to be twice as compared to that observed for pure sodium phthalate crystals.

From laser damage threshold studies, LDT values for pure and doped crystals have been found to be 0.32 and 0.28 GW/cm², respectively.

From dielectric studies, it was found that dielectric tensor component ($\varepsilon_{33}$) decreases while dielectric loss increases in Fe doped SP crystals as compared to pure crystals.

Thermal analysis revealed that the pure sodium phthalate crystals are stable upto 92 °C; whereas doped crystals are thermally stable upto 110 °C. Melting point of FSP crystals (286 °C) is also higher than that of pure sodium phthalate crystals (211 °C). This shows that FSP crystals are better for device application point of view.
4.11. References


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