CHAPTER 4

NUCLEATION KINETICS, GROWTH, CRYSTAL PERFECTION
AND OPTICAL PROPERTIES OF SODIUM ACID PHTHALATE
HEMIHYDRATE SINGLE CRYSTAL

4.1 INTRODUCTION

Sodium acid phthalate hemihydrate is a semi-organic material that can be grown as single crystal easily. The structure of sodium acid phthalate hemihydrate crystal has been reported by Smith in 1975. It crystallizes in an orthorhombic system with the space group of B2ab (Smith 1975). Sodium acid phthalate hemihydrate is a promising crystal exhibiting excellent physical properties such as piezoelectric, pyroelectric, dielectric and NLO properties. It has well-developed platelet morphology with perfect cleavages on the (0 0 1) face. The perfect cleavage (0 0 1) face of sodium acid phthalate hemihydrate is more desirable for any surface morphological analyzes (Goel and Kumar 2012; Goel et al. 2013; Sajan et al. 2011; Smith 1975). In this point of view, several groups have been reported the pure and transition metals doped (Cu, Fe, Ni, Cd, Zn) sodium acid phthalate hemihydrate single crystals (Devi et al. 2016; Ganesh et al. 2005; Goel et al. 2013; Goel et al. 2012; Sajan et al. 2011; Senthil et al. 2011). The choice of impurities is playing significant role in increasing the properties of the crystals (Enculescu and Trautmann 2010). Incorporation of impurities in the materials can be formulated by pinning effect (Maeda et al. 2004). Many reports show that the mechanical, optical, dielectric, laser damage threshold, ferroelectric and photoluminescence properties are influenced by
adding a small amount of impurities as dopants in sodium acid phthalate hemihydrate and potassium hydrogen phthalate single crystals (Devi et al. 2016; Geetha et al. 2006; Goel and Kumar 2012; Goel et al. 2013; Kumar et al. 2011). Addition of transition metal ions influences the optical properties of the sodium acid phthalate hemihydrate and potassium hydrogen phthalate crystals with small changes in its cell values as a result of lattice strain because of dopant substitution and the interaction of transition metal ions with ligands having long π-delocalized system (Devi et al. 2016; Goel and Kumar 2012; Goel et al. 2013; Kumar et al. 2011). In this view, transition metal (Co$^{2+}$) was chosen as a dopant in sodium acid phthalate hemihydrate crystals to improve its optical properties. The present chapter reports the induction period, interfacial tension and critical nucleus and crystal perfection of sodium acid phthalate hemihydrate crystal. And also it reports the optical, thermal stability, dielectric constant, NLO and laser damage threshold analyses of pure and 1% Co$^{2+}$ sodium acid phthalate hemihydrate crystal.

4.2 EXPERIMENTAL PROCEDURE

4.2.1 Material Synthesis

Sodium hydroxide (Merck 99 %) and phthalic acid (Merck 99 %) were used to synthesis the sodium acid phthalate hemihydrate. The same procedure was adopted to synthesis the sodium acid phthalate hemihydrate as discussed in chapter (2) and section (2.2.1) of this thesis. Reaction scheme of sodium acid phthalate hemihydrate:

$$2C_8H_6O_4 + 2NaOH \rightarrow 2(C_8H_5O_4.Na\cdot0.5H_2O) + H_2O$$

4.2.2 Solubility and Metastable Zone Width

The solubility of grown crystals was tested using deionized water in the temperature range between 25 °C and 50 °C with intervals of 5 °C. Initially,
the cryostat was kept at 25 °C, and stirring was continued with immersible magnetic stirrer. The re-crystallized material was added step by step to 100 mL of deionized water in an airtight container until equilibrium concentration of the solution was achieved. The similar procedure was followed to find out the solubility for other temperatures from 30 °C to 50 °C. It is well known that the solubility of materials varies with doping of metals or amino acids. Figure 4.1 shows the solubility of the pure and 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystals. With the addition of dopant (Co\(^{2+}\)) the solubility of the sodium acid phthalate hemihydrate decreased. However, solubility is increasing with temperature for both pure and 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystal which is a normal behavior of any material (Positive temperature coefficient of solubility). The similar behavior was observed for Co\(^{2+}\) doped ADP and Ni\(^{2+}\) doped ADP crystals (Ganesh et al. 2016; Ganesh et al. 2016)

![Solubility curve of (a) pure and (b) 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate](image_url)

**Figure 4.1** Solubility curve of (a) pure and (b) 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate
The saturated solution (for 25 °C) of the title compound was prepared in accordance with the presently measured solubility data and it was overheated to 10 °C (4 °C/hour) above its saturated temperature to get homogeneity of the solution. After getting the homogeneity, the solution temperature was gradually cooled at a rate of 4 °C/hour with continuous stirring. The first visible speck was noted when the temperature of the water bath attained 18.5 °C which represented the nucleation temperature. The similar experimental procedure was followed for 30 °C, 35 °C, 40 °C, 45 °C and 50 °C. Since the time taken for the formation of first visible nucleus after the attainment of the critical nucleus is very small, the observation of the first nucleus may be taken as the critical nucleus. Solubility and nucleation curves for different temperatures are shown in Figure 4.2.

### 4.2.3 Induction Period Measurement

Induction period for different supersaturation ratios (S=c/c*= 1.07, 1.08, 1.09, 1.10, 1.11 and 1.12) at a specific temperature of 40 °C. A supersaturated solution of sodium acid phthalate hemihydrate was prepared in
the crystallizer according to predetermined solubility data. The solution was continuously stirred using an immersible magnetic stirrer to completely dissolve all the solids and the stirring rate was set at 420 rpm. The saturated solution was preheated to 50 °C (4 °C/ hour) and it was maintained for 30 minutes.

**Figure 4.3 Induction period of sodium acid phthalate hemihydrate as a function of supersaturation**

After that, the solution temperature was decreased at 3 °C/ hour for attaining the desired temperature to reach expected supersaturation level. The crystallizer was kept isothermally at 40 °C until the time taken for the formation of first critical nucleus was detected. The induction period is assessed and induction period versus supersaturation is plotted in Figure 4.3.

### 4.2.4 Crystal Growth

Two 500 ml of saturated solution was prepared (35 ºC) according to solubility data. One is pure sodium acid phthalate hemihydrate and another is 1% Co²⁺ doped sodium acid phthalate hemihydrate. For 1% Co²⁺ doping in sodium acid phthalate hemihydrate, 1 mol % of Co (II) in the form of cobalt
(II) sulfate heptahydrate (CoSO₄·7H₂O) was introduced in the prepared solution. Both pure and 1% Co²⁺ doped sodium acid phthalate hemihydrate solutions were continuously stirred for 10 hours to get homogeneous solutions. The solutions were kept in two separate beakers and allowed for slow evaporation. After two weeks good quality crystals were harvested which are shown in Figure 4.4.

![Figure 4.4](image)

**Figure 4.4 (a) Pure sodium acid phthalate hemihydrate (b) 1% Co²⁺ doped sodium acid phthalate hemihydrate crystals**

4.3 RESULT AND DISCUSSION

4.3.1 Nucleation Kinetics of Sodium Acid Phthalate Hemihydrate

The solubility and metastable zone width of sodium acid phthalate hemihydrate crystal at different temperatures is shown in Figure 4.2. The solubility linearly increases with increasing temperature. The metastable zone width of grown crystal very slightly decreases with the increasing of temperature, which is the essential aspect for bulk size crystal growth. It has a narrow metastable zone width (ranging 5.5 °C-6.5 °C). The variation in induction period with supersaturation ratio is shown in Figure 4.3. The induction period decreases with increase of supersaturation ratio, which confirms that nucleation rate enhances with increasing supersaturation ratio.
Figure 4.5  $\ln (\tau) \text{ vs } (\ln S)^{-2}$ of sodium acid phthalate hemihydrate

Table 4.1  Nucleation kinetics parameter of sodium acid phthalate hemihydrate crystal at 313 K

<table>
<thead>
<tr>
<th>$S$</th>
<th>$\tau$(sec)</th>
<th>$\Delta G_r \times 10^6 \text{ J/m}^3$</th>
<th>$\Delta G^* \times 10^{-21} \text{ J}$</th>
<th>$r^*(\text{nm})$</th>
<th>$i^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.07</td>
<td>7566</td>
<td>-0.1715</td>
<td>0.1107</td>
<td>10.2943</td>
<td>2745</td>
</tr>
<tr>
<td>1.08</td>
<td>6420</td>
<td>-0.1978</td>
<td>0.0729</td>
<td>8.8562</td>
<td>1752</td>
</tr>
<tr>
<td>1.09</td>
<td>5340</td>
<td>-0.2241</td>
<td>0.0617</td>
<td>7.8090</td>
<td>1201</td>
</tr>
<tr>
<td>1.10</td>
<td>4620</td>
<td>-0.2473</td>
<td>0.0507</td>
<td>7.0764</td>
<td>894</td>
</tr>
<tr>
<td>1.11</td>
<td>4380</td>
<td>-0.2707</td>
<td>0.0433</td>
<td>6.4647</td>
<td>681</td>
</tr>
<tr>
<td>1.12</td>
<td>3720</td>
<td>-0.2941</td>
<td>0.0358</td>
<td>5.9501</td>
<td>531</td>
</tr>
</tbody>
</table>
A plot is drawn between (lnτ) and (lnS)\(^{-2}\) using experimental values in order to estimate the interfacial tension. For that ‘m’ value is directly calculated from the slope of the plot (Figure 4.5). The interfacial tension for sodium acid phthalate hemihydrate has been estimated as 7.23 mJm\(^{-2}\) at temperature 313 K. The value of radius of critical nucleus (r\(^*\)), Gibbs free energy per unit volume (ΔG\(_{v}\)), critical free energy barrier (ΔG\(^*\)) and the number of molecules present in the critical nucleus (i\(^*\)) using the classical nucleation theory are given in Table 4.1. With the increase in the supersaturation ratio, the critical radius of the nucleus, the critical free energy barrier and the number of molecules present in the critical nucleus were decreased. The critical radius of nucleus as a function of supersaturation is shown in Figure 4.6.

![Figure 4.6 Radius of critical nucleus as a function of supersaturation](image)

The critical free energy barrier (ΔG\(^*\)) and critical radius of sodium acid phthalate hemihydrate (r\(^*\)) were found to be 0.1107×10\(^{-21}\) J to 0.0358×10\(^{-21}\) J and 10.2943 nm to 5.9501 nm, at various supersaturation ranges (1.07 - 1.12). At low supersaturation the formation of critical nucleus requires more free energy change. Hence, radius of critical nucleus is large. In addition the
number of molecules (i*) present in the critical nucleus is also more. While increasing the supersaturation ratio the formation of critical nucleus requires low free energy change. Thus, radius of critical nucleus is small and the number of molecules present in the critical nucleus is less. i* value decreases with increasing supersaturation. The observed results in this work are found to be in agreement with the reported results (Lenka and Sarkar 2014; Sun et al. 2016).

4.3.2 XRD and Morphology Studies

The cell parameters of the pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals are given in Table 4.2. Single crystals of both pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystallize in orthorhombic crystal system. The slight variation in the doped crystal may be due to incorporation of metal ion in pure crystal matrix and it induces strain in crystal lattice. Figure 4.7 exhibits the XRD pattern of pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate.

![Figure 4.7 PXRD pattern of (a) pure and (b) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate](image-url)

Figure 4.7 PXRD pattern of (a) pure and (b) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate
The observed peaks for pure and 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystals are (0 1 2), (0 0 4), (1 1 1), (0 2 0), (0 1 6), (1 1 5), (2 1 2) and (0 3 8) and there is no change in the peak position. However, it is observed from Figure 4.7 that the doping of Co\(^{2+}\) in sodium hydrogen phthalate crystal shows slight variation in peak intensities. These peaks are in good agreement with the previous values (Goel and Kumar 2012; Goel et al. 2013; JCPDS No: 32-1895).

**Table 4.2 Unit cell parameters of pure sodium acid phthalate hemihydrate and 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate single crystals**

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Pure sodium acid phthalate hemihydrate</th>
<th>1% Co(^{2+}) doped sodium acid phthalate hemihydrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>6.76</td>
<td>6.79</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.32</td>
<td>9.36</td>
</tr>
<tr>
<td>c (Å)</td>
<td>26.32</td>
<td>26.51</td>
</tr>
<tr>
<td>α = γ = β (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

Crystal morphology is an important consideration in many applications like optimum packing, separation, pharmaceutical materials and so on (Docherty et al. 1991). The analyses of crystal growth morphology are significant for its device application, in which only some peculiar facets are usable and for nonlinear optical (NLO) applications and it is also crucial in
understanding of physico-chemical properties. Crystals expose a large form of shapes which are depending on the chemical composition, many weak noncovalent intermolecular forces and the growth conditions (Coombes et al. 2002; Evans et al. 2002; Ter Horst et al. 2002). The morphology of sodium acid phthalate hemihydrate is shown in Figure 4.8. The crystals have a well-defined morphology with a prismatic habit and it has a cleavage normal to the c-axis.

Figure 4.8 Morphology of sodium acid phthalate hemihydrate

4.3.3 FTIR Analysis

Figure 4.9 shows FTIR spectra of pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals. The doping of 1% Co$^{2+}$ in sodium acid phthalate hemihydrate crystal commonly gives rise to a moderate shift in some of the vibrational frequencies and variation in peak intensities. The peak position in pure sodium acid phthalate hemihydrate crystal at 3499 cm$^{-1}$ is shifted to 3496 cm$^{-1}$ for doped crystal, it may be due to the O-H stretching vibration.
The C=O band at 1693 cm\(^{-1}\) is shifted to 1690 cm\(^{-1}\). The band noted at 1567 cm\(^{-1}\) is shifted to 1564 cm\(^{-1}\) which is attributed to the asymmetric stretching vibrations of the carboxylate ion (COOH). The peaks present at 1463 cm\(^{-1}\), 1298 cm\(^{-1}\) are shifted to 1469 cm\(^{-1}\), 1295 cm\(^{-1}\). These bands are due to C-C stretching vibrations of the phenyl ring. The C-O peak at 1347 cm\(^{-1}\) is shifted to 1346 cm\(^{-1}\) for doped crystal. The bands at 808 cm\(^{-1}\), 755 cm\(^{-1}\) and 651 cm\(^{-1}\) shifted to 806 cm\(^{-1}\), 753 cm\(^{-1}\) and 649 cm\(^{-1}\) are assigned to the C-C-H out of plane bending vibrations. Nevertheless, there is no other appreciable difference which supports that addition of small concentration of metal ion does not affect the functional groups of the sodium acid phthalate hemihydrate crystal. The noted frequencies are in good agreement with the reported values (Sajan et al. 2011).

4.3.4 Energy Dispersive X-ray Spectrometer (EDX)

The grown crystal was subjected to EDX analysis to confirm the presence of the dopant (metal) in the 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate single crystal.
Figure 4.10 EDX spectrum of 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate

The presence of C (51.09 %), O (41.32 %), Na (7.41%) and Co (0.17%) are observed in the EDX spectrum (Figure 4.10). It confirms the Co$^{2+}$ ion incorporated in the sodium acid phthalate hemihydrate crystal lattice.

4.3.5 High-Resolution X-ray Diffraction (HRXRD)

Figure 4.11 High-resolution X-ray diffraction curve of sodium acid phthalate hemihydrate
Figure 4.11 shows HRXRD curves for the sodium acid phthalate hemihydrate crystal recorded for the (0 0 1) plane. It is seen that, diffraction curve (DC) contains a single peak. The full width at half maximum (FWHM) value of the curve is 12.5 arc sec, which is expected for a nearly perfect single crystal from the plane wave theory of dynamical X-ray diffraction (Bhagavannarayana et al. 2007). It is worth to notice that, the angular deviation of glancing angle based on the peak position (at zero glancing angle), the scattered intensity in the negative direction is higher than that of the positive direction. It may be due to the tensile strain around the defect core (Batterman and Cole 1964; Sun et al. 2016).

4.3.6 UV-Vis-NIR Analysis

The transmission range has been studied for pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals. The transmission spectra of pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate single crystals are depicted in Figure 4.12.

![UV-Vis-NIR spectra](image)

**Figure 4.12 UV-Vis-NIR spectra of (a) pure sodium acid phthalate hemihydrate (b) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate**
The 1% Co\textsuperscript{2+} doped sodium acid phthalate hemihydrate crystal has higher transmittance than the pure sodium acid phthalate hemihydrate crystal. The UV-Vis-NIR spectra of pure and 1% Co\textsuperscript{2+} doped sodium acid phthalate hemihydrate reveals that the cut-off wavelength of both the samples is 300 nm. The d-orbital electrons of Co\textsuperscript{2+} ion interact with lone pair of oxygen atoms of sodium acid phthalate hemihydrate, which leads to the ligand interaction. Due to this ligand interaction, transmittance of 1% Co\textsuperscript{2+} doped sodium acid phthalate hemihydrate crystal increased (Ballhausen 1962).

4.3.7 Chemical Etching Analysis

In the present investigation the etch patterns were analyzed on the (0 0 1) face of the grown crystal.

Figure 4.13 Etching pattern for (a) pure sodium acid phthalate hemihydrate (b) 1% Co\textsuperscript{2+} doped sodium acid phthalate hemihydrate for 10 sec
Water was used as an etchant and the experiment was carried out at 35 ºC for an etching time of 10 sec. The etched surface was dried with tissue papers and etch pattern was captured using an optical microscope with 10X magnification. Figure 4.13 depicts the surface pattern of pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate. Oval shaped etch pits are developed on the (0 0 1) face. The density of etch pits has been determined using following formula:

$$\text{Etch pit density} = \frac{\text{(number of etch pits)}}{\text{(area)}}$$  \hspace{1cm} (4.1)

The average dislocation etch pit density was estimated to be 9.34×10$^3$ cm$^{-2}$ for the title compound and found to be comparable with reported values (Mori et al. 2002; Shkir et al. 2014). The etch pits density is larger for pure crystal as compared to the 1% Co$^{2+}$ doped crystal. The etch pits density of pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals are estimated to be 9.34×10$^3$ cm$^{-2}$ and 3.03×10$^3$ cm$^{-2}$, respectively. The low etch pits density is related with more systematic packing of the atoms during growth. It exhibits that the grown crystal possesses good quality (Shkir et al. 2014).

4.3.8 Thermal Analysis

The TG/DTA curve for pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate are shown in Figure 4.14. There is no considerable weight loss noted in the temperature range between 35 ºC and 118 ºC, after that TG shows that weight loss happened at various steps upto 560 ºC after that constant weight was observed. The initial weight loss starts at 120 ºC and about 4 % of the total mass and corresponding endothermic peaks were noted at 124 ºC and 132 ºC for pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystal. This may be due to the elimination of water (half-water) molecule in the title material. Second stage weight loss of 44 % is observed between 219 ºC and 300 ºC. The decomposition point observed at 269 ºC, 287 ºC and 276
°C, 296 °C for pure and doped crystals may be due to decomposition of the phenyl group in the sodium acid phthalate hemihydrate crystals.

![TGA/DTA spectra](image)

Figure 4.14 TG/DTA spectra of (a) pure sodium acid phthalate hemihydrate (b) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate

Third weight loss (13 %) from 497 °C to 559 °C is due to the liberation of carbon monoxide. At the end, only 39 % of the sample is left. This shows that substitution of Co$^{2+}$ in sodium phthalate lattice increases the bond energy of Co$^{2+}$ doped crystal as the ionic radius of Co$^{2+}$ (0.745 Å) is very small.
as compared to Na ion (1.02 Å), hence interaction between Co$^{2+}$ ion and phthalic acid increases. Due to this fact thermal stability and decomposing point increase in 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystal. The similar behavior was observed for Fe added sodium acid phthalate hemihydrate (Goel and Kumar 2012).

4.3.9 Dielectric Studies

Pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals were cut along the (0 0 1) direction with the thickness of 2 mm for the measurements.
Figure 4.15 Dielectric constant for (a) pure sodium acid phthalate hemihydrate (b) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate. Dielectric loss for (c) pure sodium acid phthalate hemihydrate (d) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate

The dielectric behavior of crystal is highly influenced by applied field and temperature. Hence, in the present analysis the dielectric constant and dielectric loss were measured at various temperatures at interval of 10 ºC. The dielectric constant and dielectric loss of pure and 1% Co$^{2+}$ doped sodium acid
Phthalate hemihydrate crystals are shown in Figure 4.15 (a-d). Both dielectric constant and dielectric loss increase with increasing temperature and decrease with increasing frequency for pure and doped crystals. The dielectric constant is governed by the ionic, electronic, dipolar and space charge polarization activity (Anis et al. 2016). At higher frequency, the decrease of both dielectric constant and dielectric loss is assigned to the occurrence of periodic reversal of the applied electric field at the interface which reduces the contribution of charge carriers (Mishra & Rao 1998; Ramesh & Arof 2001; Ramesh and Chai 2007; Tareev 1979), whereas dielectric constant and dielectric loss values were higher at lower frequencies for all temperatures. This may be due to all types of polarization actively present which depends on applied electric field. In the present analysis, high value at a lower frequency may be owing to the bearing of space charge polarization in pure and doped sodium acid phthalate hemihydrate crystals. The dielectric constant is high for pure crystal as compared with doped crystal. According to Miller’s rule the crystals with lower dielectric constant lead to high second harmonic generation (SHG) coefficient (Miller 1964). The low dielectric constant of 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate is a suitable material for NLO activity and also desirable for electro-optic modulators, optoelectronics and photonic devices (Anis and Muley 2017). The low dielectric loss shows the improved quality of pure and 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystals. The similar behavior was observed for Zn doped sodium hydrogen phthalate and Fe added sodium acid phthalate hemihydrate (Goel and Kumar 2012; Goel et al. 2013).

4.3.10 Vickers Microhardess Study

The static indentations were carried out at room temperature with the constant indentation period of 10 sec on (0 0 1) face. The plot of hardness versus load for the pure and 1% Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystals is shown in Figure 4.16. The hardness value increases upto 30 g, when load is increased above 30 g the hardness value is decreased for pure and 1%
Co$^{2+}$ doped sodium acid phthalate hemihydrate crystal. The hardness of 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystal is significantly higher than that of pure sodium acid phthalate hemihydrate crystal. Photographs of indentation at different loads have been depicted in Figure 4.17.

![Graph showing Vickers Microhardness of pure and 1% Co$^{2+}$ doped crystals](image)

**Figure 4.16 Vickers Microhardness of (a) pure and (b) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals**

At low loads indentation pierced only top layer resulting in increase in hardness with load. Increasing load increases dislocations in the indented area making closed networks of interacting dislocations resulting in decrease in hardness (After 30 g for pure and doped crystal). On increasing load further dislocations and their mutual interactions increase leading in load independent hardness (Goel et al. 2013). The addition of 1% Co$^{2+}$ increases the hardness of the crystal. Hence, larger hardness value for 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystal shows greater stress needed to form dislocation of the crystal (Anis and Muley 2017).
Figure 4.17  Photograph of Vickers indentation of (a-e) pure and (f-j) 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystal at various loads
4.3.11 Laser Damage Threshold

The laser beam was passed along the (0 0 1) surface of the sodium acid phthalate hemihydrate crystal. Initially 5 mJ was enforced on the surface of the pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals and no damage is seen up to 20 sec and the energy was increased to 15 mJ and similar behavior is noted. Again, in 20 mJ, a small dot like damage is seen in the volume of the pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals in 4 sec. At the same energy, when the time was increased to 16 sec for pure and 20 sec for 1% Co$^{2+}$ doped crystal damage was noted. The laser damage threshold of the crystal was determined using the formula 2.11 (Boomadevi et al. 2004; Wood 2003). The power density is 11.36 GW cm$^{-2}$. The damaged spots of the crystals are shown in Figure 4.18. Interferences are observed due to cleavage nature of sodium acid phthalate hemihydrate crystal on the (0 0 1) face. It is seen that the 1% Co$^{2+}$ doped crystal is able to withstand laser irradiation for a time longer than the pure crystal. The surface damage of the crystal image was taken using an optical microscope. Figure 4.18 depicts the damage patterns for a (0 0 1) surface. Since (0 0 1) is the cleavage plane, we can see colors due to interference effects caused by reflections of light at microscopic layers cleaved as a result of damage. Cleavage occurs on (0 0 1) and (0 0 ̅1) planes in sodium acid phthalate hemihydrate crystal. Subsequently, (0 0 1) is the cleavage surface, it exhibits the colors due to interference effects induced by reflections of light. The material surface is damaged after laser irradiation, which may be due to the cleaved stripe surrounding the damaged core of the crystal. Similar, damage morphology behavior is observed in other crystals such as Glucuronic acid $\gamma$-lactone (Saripalli et al. 2017), lithium D-isoascorbate monohydrate (Rao et al. 2012), imidazolium L-tartrate (Ji et al. 2013) and cyclotrimethylenetrtinitramine (Yan et al. 2016).
Figure 4.18 (a) Without laser radiation, Interference effects at the layers cleaved due to laser damage for [(b,c,d) pure sodium acid phthalate hemihydrate and (e,f) 1% Co^{2+} doped sodium acid phthalate hemihydrate]
Damage site of the title compound is shown in Figure 4.18(d). The tiny circular blobs surrounding the core of the damage are leading to catastrophic damage. The cause of the damage is mainly due to thermal effects resulting in melting or decomposition of the material. The TG/DTA curve confirms that title compound decomposes at 124 °C. In the present case surface damage happens due to decomposition of the material (Ji et al. 2013; Rao et al. 2013).

4.3.12 Second Harmonic Generation (SHG) Measurements

The powdered crystals were exposed to laser radiation. The emission of green light confirms the SHG behavior and collected by photo multiplier tube. The SHG intensities were determined to be 55 mV and 60 mV for pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals, for potassium dihydrogen phosphate (KDP) it is 50 mV. The NLO efficiencies of pure and 1% Co$^{2+}$ doped sodium acid phthalate hemihydrate crystals are 1.1 and 1.27 times that of KDP. The addition of dopant enhances the non-linear optical property of sodium acid phthalate hemihydrate crystals. Sodium acid phthalate hemihydrate comprises Na$^+$ ion surrounded by O atoms and the ionized carboxyl groups (Smith 1975). The organic molecules having more NLO effect is due to its π-electron system. The second harmonic generation of a material can be greatly enhanced by changing molecular alignment through inclusion complexation, hence transition metal ion used as a dopant to increase the NLO efficiency. Owing to the presence of Co$^{2+}$ metal ion dopant, there is an enhancement in second-order polarizability of molecules which increases the SHG efficiency (Wang and Eaton 1985).
4.4 CONCLUSIONS

Nucleation kinetics of sodium acid phthalate hemihydrate was analyzed. The induction period was assessed at various supersaturation ratios in the range of 1.01 to 1.12 at a temperature of 40\(^\circ\) C. With the increased supersaturation, critical radius and critical free energy barrier decreased. The critical radius values vary from 10.29 nm to 5.95 nm. Good quality single crystals of pure and 1\% Co\(^{2+}\) doped sodium acid phthalate hemihydrate were grown. The band noted at 1567 cm\(^{-1}\) is attributed to the asymmetric stretching vibrations of the carboxylate ion. HRXRD study confirms the grown crystal has good crystalline perfection. The optical transmittance of 1\% Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystal is greater than that of pure sodium acid phthalate hemihydrate crystal. The etch pits density of the pure and 1\% Co\(^{2+}\) doped crystals are calculated to be 9.34\times 10^3 \text{ cm}^{-2} and 3.03\times 10^3 \text{ cm}^{-2}, respectively. The thermal stability and decomposing point increase in 1\% Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystal. The dielectric studies show that the doped crystal has lower dielectric constant compared to pure crystal in the temperature range of 40 \degree C-80 \degree C. The hardness of Co\(^{2+}\) doped sodium acid phthalate hemihydrate crystal is significantly higher than that of pure sodium acid phthalate hemihydrate. The power density is 11.36 GW cm\(^{-2}\). The SHG efficiency of 1\% Co\(^{2+}\) doped sodium acid phthalate hemihydrate is found to be 1.27 times that of KDP crystal. All these results show that the presence of metallic dopant (Co\(^{2+}\)) plays an important role in improving the optical and thermal properties of the sodium acid phthalate hemihydrate crystals.