Introduction

The field of non-linear optics has been in the hands of the materials scientists for the past five decades. In general, most of the organic molecules designed for non-linear optical (NLO) applications are the derivatives of an aromatic system substituted with donor and acceptor substitutions [1-9]. For NLO materials with large second-order nonlinearities, noncentrosymmetric at both the molecular and the macroscopic level is a prerequisite for nonvanishing molecular hyperpolarizabilities $\beta$ and macroscopic susceptibilities $\chi^{(2)}$[10].

The organic non-linear materials have an order of magnitude of higher second harmonic generation efficiencies and also exhibit significantly greater laser damage thresholds. Therefore considerable effort has been extended in search of organic crystals as optical parametric amplifiers, oscillators, Q-switched intracavity second harmonic generation devices and high optical damage threshold in last few decades [11-16]. P-hydroxy acetophenone ($C_8H_8O_2$) is one of the organic NLO materials belonging to the non-centrosymmetric crystal classes with space group $P2_12_12_1$ [17-19]. P-hydroxy acetophenone and Cd$^+$ doped PHAP were obtained from aqueous solution by slow evaporation technique by using the same process as in the case of pure p-hydroxy acetophenone, 10% of cadmium chloride substituted in p-hydroxy acetophenone. The photographs (Fig.1, 2) of good quality grown crystals of dimension $12 \times 7 \times 3$ mm$^3$ and $17 \times 14 \times 3$ mm$^3$ are grown within a period of 20 days.

Growth of PHAP and Cd$^+$ PHAP Single Crystals

The slow evaporation technique was adopted to grow the above crystals using methanol and water as solvent. The p-hydroxy acetophenone (99.99%) has been purified by repeated recrystallization process to improve the optical quality as well as the size of the crystal. The saturated solution of p-hydroxy acetophenone was obtained by dissolving the re-crystallized salt in methanol and water with continuous stirring using magnetic stirrer and was allowed to evaporate the excess amount of solvent at 305 K to obtain seed crystals due to spontaneous nucleation within 4 days. These crystals were separated from the solution and re-crystallization was performed to obtain bulk crystals. The single crystals of doped p-hydroxy acetophenone...
Results and discussion

Single crystal X-ray diffraction studies

Single crystal X-ray diffraction analysis for the grown p-hydroxy acetophenone crystals has been carried out to confirm the crystallinity and also to identify the unit cell parameters using ENRAF NONIOUS CAD-4 automatic X-ray diffractometer. From the analysis, both pure and doped crystals are found to belong to orthorhombic system with space group $P_{21}2_12_1$. The lattice parameters of PHAP and Cd$^+$ doped PHAP are listed in table 1. The small variations in the lattice parameters may be due to the inclusion of cadmium (Cd$^+$) ions in p-hydroxy acetophenone crystal lattice.

Table 1. Lattice parameters of the grown crystals

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>PHAP</th>
<th>Cd$^+$PHAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>9.540</td>
<td>9.364</td>
</tr>
<tr>
<td>b</td>
<td>24.343</td>
<td>24.362</td>
</tr>
<tr>
<td>c</td>
<td>6.132</td>
<td>6.723</td>
</tr>
<tr>
<td>V($\text{Å}^3$)</td>
<td>1424</td>
<td>1546</td>
</tr>
</tbody>
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UV-Vis Spectral Analysis

The UV-Vis spectra are recorded using VARIAN CARY 5E UV-Vis spectrometer in the range of 200-800 nm. The absorption spectrum obtained is displayed in figure 3 and 4. UV spectra reveal the conjugated system and the extent of substitution on the conjugated systems present in an organic compound. When the absorbance is examined from longer to shorter wavelength, the maximum absorbance occurs in the wavelength range 200-340 nm. The UV cut-off wavelength for pure crystal is 270 nm and Cd$^+$ doped crystal is 260 nm. From the spectrum less absorption in entire visible region is observed the wavelength ranging 800-350 nm shows the crystals are well suited for second harmonic generation devices [20].

FT-IR spectral analysis

FT-IR spectra (Fig. 5&6) are recorded using BRUKER IFS-66V, FT-IR spectrometer to confirm its functional groups and qualitative assignment. The spectra are recorded by KBr pellet technique in the region 4000 cm$^{-1}$ to 450 cm$^{-1}$. The bands observed in the region arise due to OH stretching, C-H stretching and C-O stretching. The broad inter molecular hydrogen bonded O-H stretching is observed 3134 cm$^{-1}$. The C-H stretching is observed at 2812 cm$^{-1}$ and 2611 cm$^{-1}$. The peak observed at 1644 cm$^{-1}$ is due to C=O stretching. The absorbance of peak at 1437 cm$^{-1}$ is arising from O-H bonding. Frequency 1364 cm$^{-1}$ belongs to CH$_2$ bending modes. The C-O stretching vibrations are appeared at 1283 and 813 cm$^{-1}$. The peak observed at 1585 cm$^{-1}$ is assigned to C-O bonding and the observed peak at 1233 cm$^{-1}$ is due to C-O stretching are appeared only in parent crystal. The broad peak observed at 713 cm$^{-1}$ is appeared only in the doped crystal which is confirm the incorporation of Cd$^+$ ions in PHAP material.

Thermal Analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) for PHAP and Cd$^+$PHAP were taken using NETSZCH STA 409/C/Cd system about 24.85 mg of the sample was heated in a crucible between 30˚C to 820˚C at heating rate of 20K/10 min in nitrogen atmosphere. The resulting TG and DTA spectra are shown in the figure 7, 8. The weight change in the sample with temperature was studied by TG and the energy change in the sample with temperature was studied by DTA. The TG curve for PHAP indicates the sharp single stage of weight loss in the range 320˚C - 180˚C. The weight losses of sample up to 200˚C and above this temperature the weight losses due to its evaporation after its melting. The DTA curve shows that PHAP melts at temperature 163˚C and it undergoes an irreversible
endothermic transition at 230°C followed by another endothermic peak at 842°C. From TG curve for Cd\textsuperscript{2+}PHAP, the weight loss of 41.3% is observed in the temperature range 140°C to 341°C due to the evolution of water from the sample. From DTA curve for Cd\textsuperscript{2+}PHAP, it is found that the material is stable up to 163°C. Cd\textsuperscript{2+}PHAP undergo an irreversible endothermic transition at 163°C where decomposition starts the material is fully decomposed at 530°C which corresponds to the melting point of the material.

Figure 7 TG/DTA spectrum of PHAP crystal

Figure 8 TG/DTA spectrum of Cd\textsuperscript{2+}PHAP crystal

Conclusions

Good quality single crystals of pure and cadmium doped p-hydroxy acetophenone were grown by slow evaporation technique. The lattice parameters of these crystals were determined using X-ray diffraction method. From single crystal XRD studies, it was found that the compounds crystallize in the orthorhombic system with a space group P\textsubscript{2}1\textsubscript{1}2\textsubscript{1}2\textsubscript{1}. Optical absorption studies on these samples reveal the absorption region. FTIR spectral studies were carried out on the materials which confirm presence of the functional groups. Thermal analysis has been carried out on the compound and reported that the melting point of the crystal is 163°C. The above characterizations and the physicochemical properties which confirm that the grown crystal is suitable for the fabrication of various optical devices.

References