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Growth and Characerization of Sodium 4-Nitrophenolate: 4-Nitrophenol Dihydrate by Gel Growth Technique

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Abstract: Sodium 4-nitrophenolate:4-nitrophenol dihydrate (SPPD) was grown by gel growth technique using sodium meta silicate as the growth medium. The crystal was subjected to single crystal XRD analysis and the material was confirmed. The functional groups present in the SPPD crystal was identified by FTIR and FT Raman analysis. The thermal stability of SPPD was assessed by TG-DSC analysis. From the UV-visible analysis the cut off wavelength was found to be 400 nm. The relative SHG efficiency of SPPD was 1.38 times that of KDP.
Keywords: Growth and Characerization, Sodium 4-Nitrophenolate, 4-Nitrophenol Dihydrate, Gel Growth Technique.

1.0 Introduction

In search of highly efficient NLO materials 4-nitrophenol has been used effectively by various research groups. 4-Nitrophenol derivatives are interesting candidates, as they are typical one-dimensional (1D) donor-acceptor π systems and the presence of phenolic OH favours the formation of salts with various organic and inorganic bases. Dimethylaminopyridinium-4-nitrophenolate:4-nitrophenol [1], 2-Aminopyridinium-4-nitro phenolate:4-nitrophenol and 4-aminopyridinium-4-nitrophenolate [2-3], L-histidine-4-nitrophenolate:4-nitro phenol [4], sodium-*p*-nitrophenolate dehydrate [5], sodium-4-nitrophenolate: 4-nitrophenol dihydrate [6] and L-phenylalanine:4-nitrophenol [7-8] were reported.

Semi-organic single crystals possess unique opto-electronic properties, because organic molecules have delocalized electrons promoting to exhibit various photo responses such as photoconductive, photovoltaic, photo catalytic behaviour, andsoon.Their electron-rich (donor) and electron-deficient (acceptor) substituents provide the asymmetric charge distribution in the π electron system, with enhanced nonlinear optical responses [9].

SPPD crystal was grown and characterized by solution growth technique [6, 10]. In this chapter the growth of SPPD by gel growth technique using silica gel as the growth medium is presented. It was characterized by single crystal X-ray diffraction. It crystallizes in the monoclinic system with space group C_2. From the collected reflections the external morphology of the crystal was drawn and the crystallographic faces were identified using the recorded set of h, k, l reflections. The functional groups of SPPD were identified by

FT-IR and Laser-Raman techniques. The absorbance of the crystal was measured using UV–Visible-NIR spectrum.

2.0 Crystal Growth

The SPPD crystal was grown by gel growth technique using silica gel as the growth medium by single diffusion method. Sodium metasilicate solution was prepared by dissolving commercially available sodium metasilicate in double distilled water (10 g in 20 ml) and stirred well. The solution was filtered and stored as a stock solution in a well cleaned container.

(i) Formation of gel using L-threonine

1.19 g of L-threonine was dissolved in 20 ml of sodium metasilicate stock solution of density 1.04 g/cc. It was taken in a test tube of height 20 cm and internal diameter 2.5 cm. The pH of the solution was 9.4. The solution was aged for 24 hours to obtain a gel.

(ii) Formation of gel using L-histidine

1.30 g of L-histidine was dissolved in 20 ml of sodium metasilicate stock solution of density 1.04 g/cc. It was taken in a test tube of height 20 cm and internal diameter 2.5 cm. The pH of the solution was 9.3. The solution was aged for 24 hours to obtain a gel.

In both experiments 4-nitrophenol is the outer reactant. 1.39 g of 4-nitrophenol was dissolved in 25 ml of acetone, and added over the gel without disturbing the gel surface. The test tube was tightly closed to prevent evaporation of acetone.

Figures 1 (a) and 1 (b) show the crystals in the gel and as-grown crystals in a period of 40 days.

Figure 1 (a) SPPD crystals in gel

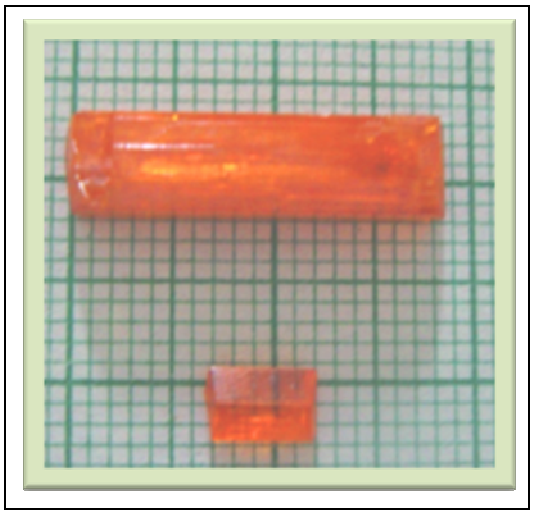

Figure 1 (b) Grown SPPD single crystals

3 Results and Discussion

3.1 Single crystal XRD analysis

The unit cell dimensions were determined from accurately measured 2θ values (the angular deviation from the direct undeviated beam) of about 25 reflections on an Enraf-Nonius CAD-4 diffractometer with MoKα radiation at room temperature employed with ω/2θ scan mode. Accurate unit cell parameters and orientation matrix for the crystal were obtained by a least-squares fit of several reflections in the range $15<\theta<25^{o}$. From the collected reflections the morphology of the crystal (Figure 1 (c)) was drawn and the crystal

faces were identified using the recorded set of h, k, l reflections. From the single crystal X-ray diffraction analysis it is confirmed that the title compound crystallizes in the monoclinic system with a space group of C_2. The lattice parameters were a = 21.197(16) Å, b = 3.675(4) Å, c = 10.332(4) Å, β = 117.23(7)° and cell volume 715(1) Å^3. The crystallographic data are presented in Table 1 and the data are in good agreement with the reported literature [6].

Table 1 Crystallographic data of SPPD crystal

Lattice parameters	Present work	Reported value (Meiyappan Muthuraman et al 1999)
a	21.197(16) Å	21.173(5)Å
b	3.675(4) Å	3.669(1)Å
c	10.332(4) Å	10.352(1) Å
β	117.23(7)˚	117.21(2)
Z	2	2
Volume V	715(1) Å^3	715.2(3)Å^3

3.2 FTIR analysis

The FT IR spectrum of the SPPD was recorded on a BRUKER IFS 66V FTIR spectrometer (KBr pellet technique) in the range of 400-4000 cm^{-1}. The recorded spectrum is shown in Figure 2. The peak at 3471 cm^{-1} is due to O-H stretching vibration of water. Presence of water in the crystal is also confirmed by its peak due to bending vibration at 1684 cm^{-1}. The aromatic C-H stretching vibration yielded a weakly resolved peak at 3102 cm^{-1}. The fine structures between 3000 and 2200 cm^{-1} are due to hydrogen bonding of water.

The vibrations of the aromatic ring yielded their peaks at 1575, 1455 cm^{-1}. The asymmetric and symmetric vibrations of the NO_2 group occurred at1563 and 1346 cm^{-1}, respectively. The aromatic C-O vibration occurred at 1274 cm^{-1}. The C-H bending vibration of aromatic ring occurred at 844 cm^{-1}. Generally C-N vibration occurs close to 850 cm^{-1}, but here it was shifted to 964 cm^{-1}. It is a clear evidence for strong resonance interaction between aromatic ring and the nitro group. From the spectrum it is concluded that sodium 4-nitrophenolate:4-nitrophenol dihydrate carries water in its crystal lattice which is also evident from its single crystal XRD analysis.

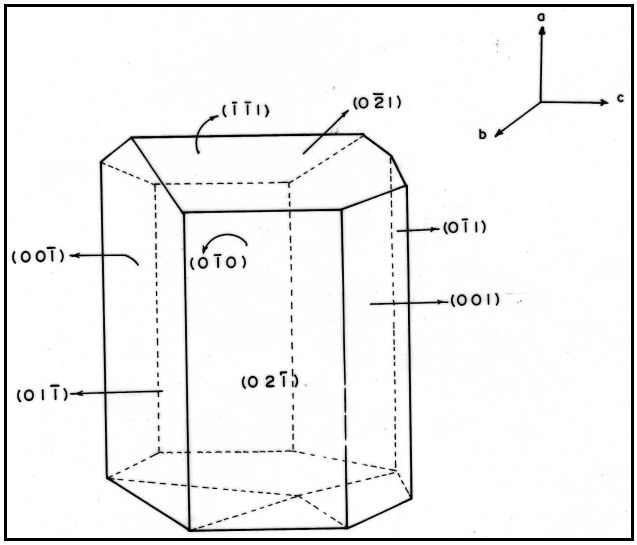

Figure 1 (c)Morphology of SPPD single crystal

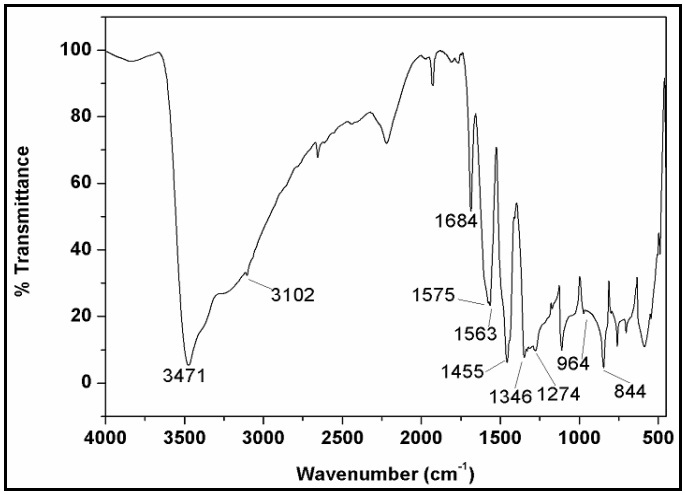

Figure 2 FTIR spectrum of SPPD

3.3 Laser Raman spectral analysis

The Raman spectrum of the compound is shown in Figure 3. The peak at 3473 cm^{-1} is due to O-H stretching vibration of water. It is very weak as the O-H bond is very much polar. The aromatic C-H stretching vibration at 3020 cm^{-1} was weak. The asymmetric NO_2 stretching weak vibration occurred at 1528 cm^{-1}. In contrast the symmetric NO_2 stretching intense vibration occurred at 1312 cm^{-1}. The aromatic C-H bending vibrations were due to the peaks at 1173 and 861 cm^{-1}.

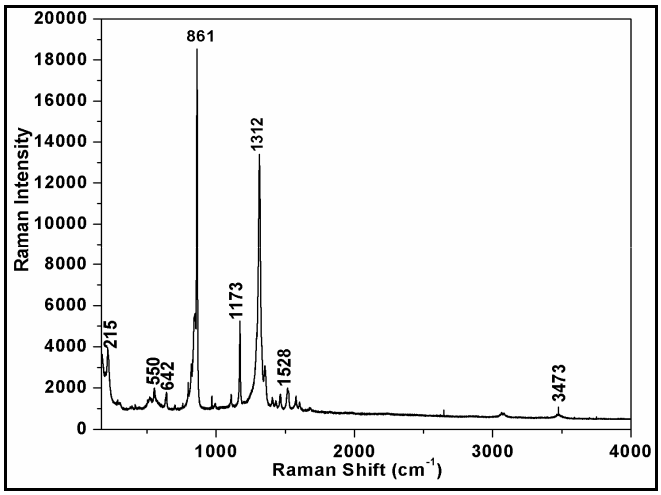

Figure 3 Laser Raman spectrum of SPPD

3.4 TG-DSC analyses

The thermogravimetry (TG) and differential scanning calorimetry (DSC) studies (Figure 4) of SPPD were carried out on NETZSCH STA 449 F3 JUPITER. The thermogram was recorded in the nitrogen atmosphere between 30 and 500°C at a heating rate of 5°C/min. The results of TGA of SPPD are illustrated in Figure 4. The initial weight loss below 150°C is assigned to loss of water of crystallization. The total water loss corresponds to two molecules of water. It is followed by two major weight losses, one between 150°C and 225°C and the other between 300°C and 350°C. They are assigned to loss of 4-nitrophenol and sodium 4-nitrophenolate in sequences. The results of DSC analysis are also illustrated in the same figure. The endotherm which occured at 124.9°C coincides with the loss of water. It is followed by another minor endotherm at 149.7°C, which is assigned to partial melting [6]. There is no corresponding weight loss in the TGA trace at this temperature. The initial major weight loss in TGA occurred as an endothermic process in the DSC trace. The second major weight loss occurred at 330.7°C as an exothermic process.

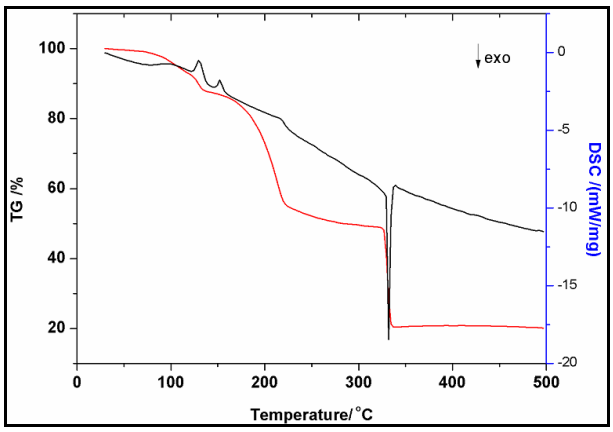

Figure 4 TG and DSC curves of SPPD

3.5 UV-Vis-NIR spectral analysis

The absorption spectrum of SPPD, shown in Figure 5, was recorded on a Varian Cary 5E UV-Vis-NIR spectrophotometer in the region 200-2250 nm. The cut off wavelength was around 400 nm. The low absorbance in the entire visible and near-IR region is an important requirement for NLO applications. The sharp absorbance maximum close to 322 nm is assigned to π-π^* transition in the quinonoid structure of SPPD.

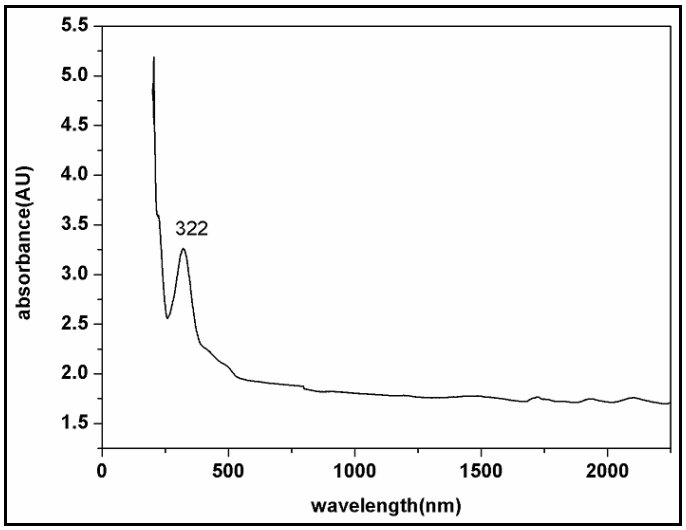

Figure 5 UV-Vis-NIR of SPPD

3.6 Second harmonic generation (SHG) test

The second harmonic generation (SHG) was tested using Kurtz and Perry powder technique. A fundamental laser beam of 1064 nm wavelength (Nd:YAG laser) with the energy of 2 mJ/pulse was used for SHG analysis. KDP was used as reference material in the SHG experiment for comparison. The SHG output of SPPD was equal to 20 mV and for KDP 14.5 mV. The relative SHG efficiency of SPPD was found to be 1.38 times that of the standard KDP [12].

4 Conclusion

LAPP was grown by slow evaporation solution growth technique using a solvent mixture composed of deionised water and ethanol. The lattice parameters were identified from single crystal XRD analysis. The functional groups were identified by FT IR and FT Raman spectra. The thermal analysis showed that the crystal could be used for NLO application up to 60^{o}C. The UV-Visible spectrum for LAPP crystal showed low transmittance in the range of 200-490 nm due to π-π* transition of 4-nitrophenol group. There was no absorption at 532 nm which is an important requirement for SHG at 1064 nm. It showed green emission. Its SHG efficiency was 5.7 times that of the standard KDP.

The SPPD crystal was grown by gel growth technique using silica gel as the growth medium. The grown crystal was confirmed by the single crystal X-ray diffraction and the functional groups were identified from Fourier transform infrared spectrum and Laser Raman spectra. The TG and DSC studies showed thermal stability up to 80°C. The UV-Vis-NIR absorption spectrum showed transparent nature between 400 and 2250 nm. There was a sharp absorbance maximum close to 322 nm due to π-π* transition in the quinonoid structure. The SHG was 1.38 times that of KDP. Hence the crystal is a valid candidate for the NLO applications.

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