SYNTHESIS, GROWTH AND OPTICAL PROPERTIES OF ORGANIC MATERIAL: 2-AMINOANILINIUM PHOSPHITE

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Abstract: 2-Aminoanilinium Phosphite (2-AP) was synthesized and single crystals were grown by slow evaporation technique. X-Ray diffraction analysis was carried out to estimate the cell parameters and to interoperate the crystalline perfection of the grown crystal. UV–Vis spectral analysis showed the existence of wide transmission window. Photoluminescence spectrum was obtained for grown material. The laser induced surface damage threshold and relative second harmonic generation properties for the grown crystal were studied using Q-switched Nd:YAG laser.

IndexTerms - Crystal growth; Optical property; Laser damage threshold; SHG.

I. INTRODUCTION

In the nonlinear optical domain organic molecular crystals have posed a few challenges and have captivated the interests of many researchers in the recent times due to their striking optical device applications such as optical switches, optical modulators, optical communications, optical data storage etc. Developing and designing the organic molecular NLO crystals have been precisely overlooked nowadays because its acentric molecular ordering have absorbed deal of attention. While organic nonlinear optical crystals exhibit a degree of high nonlinearity better than their inorganic counterparts and a more beneficial option for optical device diligence[1-3]. Dihydrogenphosphite (HPO$_3$H$_2$) has been observed in the solid state both in its monoanionic and dianionic forms and materials comprising of organophosphonate anions and organic cations are much concerned in the arena of supramolecular chemistry and crystal engineering. Numerous applications in the fields of biomolecular sciences, catalysis, liquid crystal development, ferroelectrics, non-linear optics have been explored as a result of the reaction between inorganic oxy acids (H$_3$PO$_4$), (H$_3$PO$_5$) and organic amines [4-7]. The structure of 2-Aminoanilinium Phosphite was reported by Abdallah K Idrissi et al [8]. In the present investigation, organic single crystal of 2-Aminoanilinium Phosphite was grown and herein the grown crystal was subjected for various characterizations.

II. EXPERIMENTAL

2.1 Synthesis and Crystal growth

The starting reagents of commercially available 1,2-diaminobenzene (C$_6$H$_4$N$_2$) (Aldrich, 99%) and phosphorous acid (H$_3$PO$_4$) (LobaChemie, 99%) were taken in equimolar ratio 1:1. The calculated amount of Phosphorous acid was dissolved in distilled water, and then the appropriate amount of 1,2-diaminobenzene was added slowly to the solution. The resultant solution was continuously stirred for about six hours to achieve homogeneous solution. The filtered solution was allowed for slow evaporation which yielded the spontaneous nucleated crystals. The synthesized compound was purified further by successive recrystallization process in D$_2$O and it was utilized for the crystal growth. The chemical synthesis scheme of the 2-AP compound is shown in Fig.1. The 2-Aminoanilinium Phosphite(2-AP) crystal was grown by employing solvent evaporation solution growth technique. The highly purified 2-AP salt was dissolved in D$_2$O and solution was saturated at 35°C in a constant temperature bath with an accuracy of ±0.01°C. The optically good transparent 2-AP crystal with dimension of 10 x 4 x 2 mm$^3$ was harvested in a growth period of 25 days and is shown in Fig.2.

Figure 1. Synthesis scheme of 2-Aminoanilinium Phosphite
RESULTS AND DISCUSSION

3.1 Single Crystal XRD

Single crystal X-ray diffraction analysis was carried using the good quality single crystal of 2-AP in order to reveal the unit cell parameters, space group and crystal system. It is revealed from the analysis that the 2-AP crystal belongs to Monoclinic crystal system with P2_1/c centrosymmetric space group. The unit cell parameters are found to be a = 11.195(4), b = 6.021(3), c = 13.255(5), α = 90.00°, β = 109.680(6), γ = 90.00° and is found to be in good agreement with the reported data. Then, the grown 2-AP crystal was crushed to a uniform fine powder and subjected to powder X-ray diffraction study. From the obtained powder X-ray diffraction spectrum, the presence of well-consistent Bragg peaks at specific 2θ angles corroborated the crystallinity of the grown crystal. The recorded powder XRD pattern is shown in Fig.3.

Figure 2. Photograph of as-grown 2-Aminoanilinium Phosphite crystal

Figure 3. Powder XRD pattern of 2-Aminoanilinium Phosphite
3.2 High Resolution XRD studies

High resolution X-ray diffraction curve was recorded using MoKα radiation for a typical 2-AP single crystal specimen as shown in Fig.4. On close observation, one can realize that the curve is single peak. The FWHM (full width at half maximum) of the main peak is 66 arc s. The relatively low values of FWHM of the grains in comparison with that of the real life crystals depicts that the crystalline perfection is fairly good [9]. It may be mentioned that such low angle boundaries could be detected in the diffraction curve only because of the high-resolution of the diffractometer used in the present investigation.

![Image of HRXRD Spectrum of 2-AP](image1)

Figure 4. HRXRD Spectrum of 2-AP

3.3 UV Vis Transmittance

UV-Visible spectral studies are helpful in the investigation of NLO materials to find NLO response and spectroscopic absorbance in the appropriate wavelength range. Ultraviolet-visible transmittance studies was performed on the 2mm thick 2-AP crystal sample and the spectrum recorded is in the wavelength range 190-900 nm as shown in Figure 5. The lower cut-off wave length was found to be 340 nm and the material was transparent up to 45%.

![Image of UV-Visible transmission spectrum of 2-AP crystal](image2)

Figure 5. Uv-Visible transmission spectrum of 2-AP crystal

3.4 Laser Damage Threshold

Nonlinear optical materials should tolerate high laser intensity which possesses its suitability in laser application. Laser damage threshold measurement was carried out for 2-AP crystal by using Nd:YAG laser system, which delivered laser pulses at
1064 nm with pulse width 6 ns and repetition rate 10 Hz. The surface LID threshold of 2-AP crystal was calculated using the relation,

\[ P(d) = \frac{E}{\tau A} \quad \text{Eq. 1} \]

where \( E \) is the intensity of the irradiant laser beam (mJ), \( \tau \) is the pulse width (6 ns) and \( A \) is the area of the circular spot size (cm\(^2\)). For 2-AP crystal, the multiple shot laser damage threshold energy density obtained from the Q-switched Nd:YAG laser was found to be 3.39 GW/cm\(^2\) compared to KDP reference crystal (0.20 GW/cm\(^2\)).

### 3.5 Photoluminescence studies

Photoluminescence (PL) technique, the spectrum emitted by the radioactive recombination of Photo generated minority carriers, is a direct way to measure the band gap energy. The excitation and emission spectra of 2-AP were recorded in (RF-5301) spectrofluorometer. The excitation spectrum was measured in the range between 320-700 nm. The sample was excited at 310 nm, a peak at 387.9 is observed in the emission spectrum as shown in Fig. 6.

![Photoluminescence spectrum of 2-AP](image)

**Figure 6.** Photoluminescence spectrum of 2-AP

### 3.6 Nonlinear optical study

The second harmonic generation efficiency was studied by employing the Kurtz and Perry powder technique [10] which remains a valuable tool for the initial screening materials for SHG property. Q-switched Nd:YAG laser with the fundamental beam of 1064 nm, repetition rate of 10 Hz and pulse width 10 ns was used to measure the SHG efficiency of 2-AP. The standard reference material potassium dihydrogen phosphate (KDP) was used to compare the SHG efficiency. The grown single crystal of 2-AP was crushed into powder with a uniform particle size and then packed in a micro-capillary tube of uniform pore size (125 – 150 \( \mu \)m) and exposed to laser radiation. The SHG output was converted into electrical signal and was displayed on a digital storage oscilloscope. The optical signal incident on photo multiplier tube was converted in to voltage output. The SHG output signal intensity of 40 mV was measured for 2-AP crystalline powder while that for standard KDP crystalline sample was 30 mV for an input energy of 30 mJ/pulse. Thus it is clear that the SHG efficiency of 2-AP was found to be 1.41 times than that of standard reference material KDP.

### 4. Conclusion

Single crystal of 2-AP was successfully grown by the slow evaporation solution growth method. The grown crystal has been confirmed by using single crystal X-ray diffraction studies and found that it belongs to the monoclinic system with space group P2\(_1\)/C. The crystalline perfection was examined from HRXRD and Powder XRD spectrum. The cut-off wavelength of 2-AP from the transmittance spectral analysis was found to be 340 nm. Laser induced damage threshold value (3.39 GW/cm\(^2\)) of the 2-AP crystal was estimated. PL spectral study revealed the electron excitation wavelength (387.9 nm) in the grown crystal. The relative second harmonic generation efficiency of the grown 2-AP crystal was found to be 1.41 times that of KDP crystal.
REFERENCES


