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Synthesis, structural, optical, thermal and dielectric studies of 4-aminopyridinium oxalate single crystal

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ABSTRACT
4-aminopyridinium oxalate (4APO), an organic nonlinear optical single crystal has been grown by slow evaporation solution growth technique. Single crystal X-ray diffraction studies were carried out to determine the unit cell parameters.4APO crystallizes in monoclinic system. The grown crystal has been characterized by Fourier transform infrared and UV-Visible spectral studies. Thermogravimetric analyses (TGA) and differential thermal analysis (DTA) have been carried out to study the thermal behavior of the grown crystal. The mechanical stability of the grown crystal has been studied by using Vickers microhardness test. The Kurtz and Perry powder SHG technique confirms the NLO property of the grown crystal.

Introduction

In the recent years, the research on new organic nonlinear optical materials is attractive for their advantages over the inorganic nonlinear optical materials. The organic nonlinear optical molecules generally have the larger second order nonlinear optical coefficient and hence they are preferred in many applications like optical switching, information storage, second harmonic generation, optical communication etc., [1-6]. Several nonlinear optical complexes formed from aminopyridine and carboxylates have been crystallized and their structural, optical and thermal properties have been investigated because of their significant impact on laser technology, optical communication and data storage [1,7]. Generally conjugated system linking donor and acceptor show a large NLO response and hence they are intensively investigated. Many of the dicarboxylic salts are reported to be active in second harmonic generation and it may be useful to study complexes with carboxylic acids and their properties [8]. Oxalic acid with relatively large conjugation has attracted our attention. The intra molecular hydrogen bond of oxalic acid is very strong. Oxalic acid forms crystalline oxalates with various organic molecules through hydrogen bonding interaction. It is known that oxalic acid acts not only as a acceptor to form various stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions. Acentric molecules consisting of highly delocalized electron donor and acceptor groups exhibit high value second order polarizability [9].

4-aminopyridine is one such donor acceptor molecular compound in which oxalic acid gives one of its proton (H) to the 4-aminopyridine thereby the asymmetric system consists of 4-aminopyridine molecules in protonated form and oxalic acid is monoionised state. Hoong-Kun Fun [10] has reported the structure of 4-aminopyridinium oxalate (4APO). In the present investigation, we report the growth, optical, thermal, dielectric and NLO studies of 4APO single crystals.

Experiment

Material synthesis

4-Aminopyridine ($NH_2C(CH_4)N$) (AR grade SRL India) and oxalic acid ($C_2H_2O_4$) (AR grade Merck) were used as raw materials for the synthesis of 4-aminopyridinium oxalate (4APO). The 4APO salt was obtained by dissolving 4-aminopyridine and oxalic acid in the aqueous solution in the stoichiometric ratio 1:1 and precipitate of crystalline substance was obtained at 30°C with continuous stirring for 4 h.

The chemical reaction may be represented as

$$NH_2C(CH)_4N + C_2H_2O_4.H_2O$$
$$\downarrow$$
$$NH_2C(CH)_4NH^+.C_2HO_4^- .H_2O$$

Solubility studies and crystal growth

The solubility of 4APO was measured by adding excess amount of 4APO in solvent at constant temperature and it was continuously stirred using magnetic stirrer to achieve homogeneous concentration over the entire volume of the solution. On reaching the saturation, the content of the solution was analyzed gravimetrically. The studies were carried out in a constant temperature bath with accuracy 0.01°C. The solubility was determined with different solvents such as water, acetone, ethanol, methanol and mixed solvents for different temperatures (30-50°C) with the interval of 5°C and it has been observed that the 4APO exhibits positive temperature gradient and high solubility in water. The solubility diagram is shown in Fig.1.

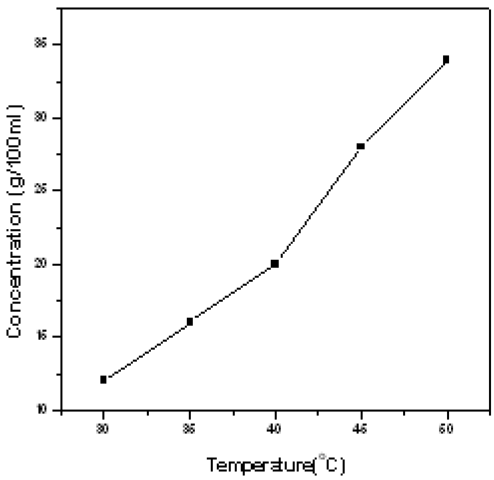

Fig.1. Solubility curve of 4APO

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The saturated solution of 4APO was prepared at room temperature (30°C) in a beaker with a perforated lid in order to control the evaporation rate and kept for crystallization. Single crystals of 4APO were obtained after 15 days by slow evaporation method at room temperature. Optically transparent crystal of 4APO with dimensions 23mm × 14mm × 8mm is shown in Fig.2.

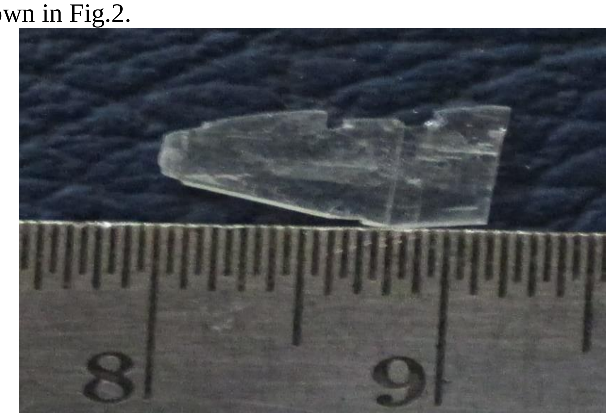

Fig.2. Photograph of 4APO crystal

Results and discussion

Single crystal and powder X-ray diffraction studies

Unit cell parameters of the grown 4APO crystal were obtained using NONIUS CAD-4/MACH 3 Diffractometer with MoKα radiation of wavelength 0.17073Å. It is observed that the 4APO crystal belongs to the monoclinic system with space group C2/c. The determined lattice parameters a=15.5431 Å, b= 5.5824 Å, c= 19.7021Å and volume =1649.6016 $Å^3$ are in close agreement with the reported values [10]. Powder X-ray diffraction pattern of grown 4APO was recorded over the range 10-70^o by using Ritz-170 powder X-ay diffractometer with Nickel filtered CuKα radiations (λ=1.5406 Å) and the diffraction pattern is shown in Fig.3. The well defined Bragg's peaks at specific 2θ angles confirmed the crystallinity of 4APO single crystal.

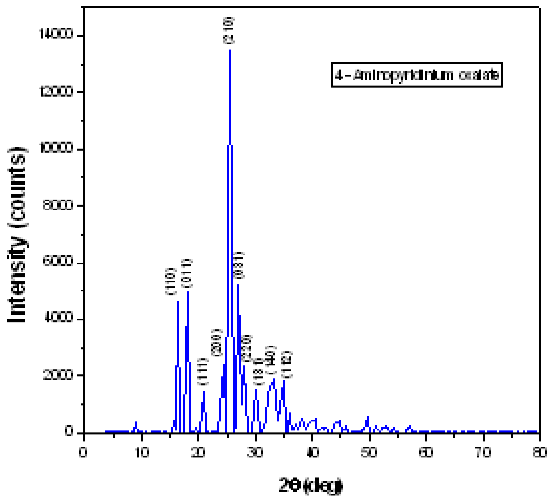

Fig.3. Powder XRD pattern of 4APO crystal

FTIR studies

The FTIR spectrum recorded for 4APO to confirm the presence of functional groups in the grown crystal is shown in Fig. 4. A strong peak observed at 3349 cm^{-1} is assigned for NH stretch of primary amine group in 4-aminopyridine. Meanwhile the generation of ammonium ion due to acceptance of proton from oxalic acid is confirmed by the peak attributed at 3166 cm^{-1}. The peak at 3048 is assigned for C-H stretching and aromatic compound is present. The stretching vibration of C-H is assigned at 2918 cm^{-1}. The band at 1651 cm^{-1} indicates that N-H bending. The peak at 1550 cm^{-1} is assigned for N-O asymmetric stretching. The stretching vibrations of C-C Peaks are assigned at 1414 cm^{-1}. The absorption at 1200 cm^{-1} indicates that the amines are present in the compound. The absorption at 736 cm^{-1} indicates the aromatic ring in the compound. The peak at 818 cm^{-1} is assigned for C-CH bending and the peak at 715 cm^{-1} is assigned for C-H rocking respectively. Hence, the coordination of amine and carboxylic compounds are confirmed by the presence of prominent functional groups in the FTIR spectrum.

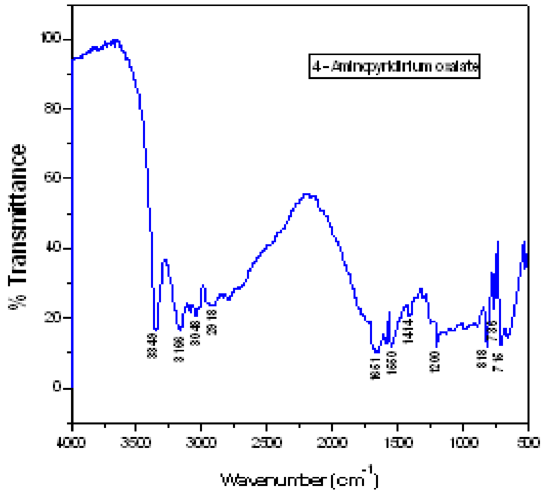

Fig.4. FTIR spectrum of 4APO crystal

UV-Vis transmittance studies

The UV-Vis transmission spectrum of 4APO crystal was recorded with PerkinElmer Lamda 35 Spectrophotometer in the range 190-1100nm and the recorded spectrum is shown in Fig.5. The studies were carried out without any antireflection coatings. A sample of 1mm thickness is used. The cutoff wavelength of 4APO crystal is 302nm. From the recorded spectrum, it is observed that crystal 4APO has a transmittance of above 85 % up to 1100nm.

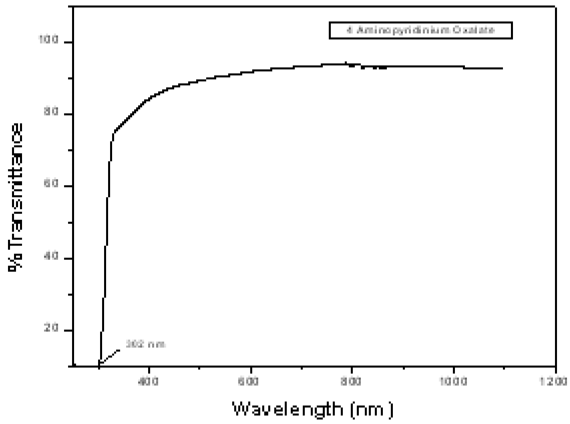

Fig.5. UV-Visible transmission spectrum of 4APO

Thermal studies

The results of TGA and DTA using SDT- Q600 TA instruments for 4-aminopyridinium oxalate are illustrated in Fig.6. It is observed that there was no weight loss up to 194.20°C in the TGA trace. Hence the crystal was confirmed to have absence of water of crystallization. A minute weight loss occurred at 194.20°C followed by major weight loss starting at 233.47°C. It was due to decomposition of 4APO. In the DTA trace, there was a minute endotherm at 194.20°C and major endotherm starting at 223.47°C, Both these endotherms matched with the decomposition in the TGA trace. Therefore, it was established that this material could be applied to NLO applications up to 194.20°C.

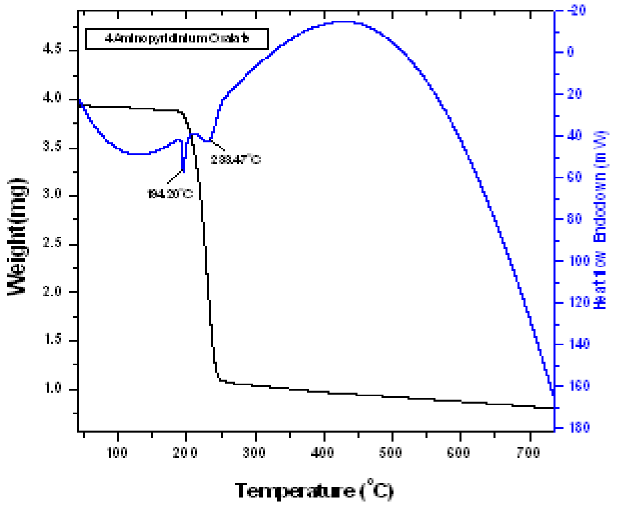

Fig.6. TGA/DTA curve of 4APO crystal

Mechanical studies

Vickers's microhardness measurements were done at room temperature by using hardness tester attached with Micro-Duromat Leitz Metallax II microscope. The vicker's microhardness number H_V was calculated using the relation $H_v = 1.8544(P/d^2)$ kg/mm^2. Where P is applied load (g) and d is the diagonal length (μm) of the indentation. Fig.7 shows the variation of H_v as a function of applied load (P) ranging from 5 to 45 g of 4APO crystal. It is inferred from the figure that H_v increases with increasing load P. The phenomenon of dependence of microhardness of a solid on the applied load is known as the reverse indentation size effect [11]. Meyer's law relates that load and size indentation as $P=k_1d^n$. where k_1 is the material constant and n is the Meyer's index. Hence log P=log d_1+n log d. The slope of the graph of log P against log d gives the values of n and it is determined to be n=3.75. According to Onistch [12] and Hanneman [13]. The value of n is 1-1.6 for hard materials and above 1.6 soft materials. Thus, 4APO crystal belongs to soft material category.

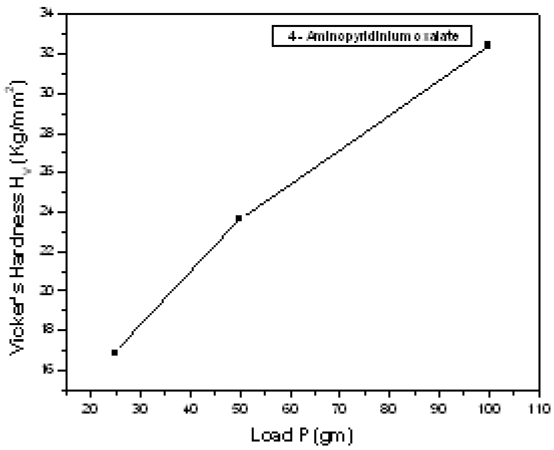

Fig.7. Load (P) vs. hardness number (H_v) of 4APO crystal

Dielectric studies

The dielectric studies on 4APO single crystal were carried out using a HIOCKI 3532-50 LCR HITESTER instrument. A sample of thickness cm × cm × cm having silver coating on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was measured by varying the frequency from 100Hz to 3 MHz. The dielectric constant was calculated by using the relation.

$$\varepsilon_r = Ct / \varepsilon_0 A$$

where ε_0 is the permittivity of free space, C is the capacitance, t is the thickness of the sample and A is the area of the cross section. Fig.9(a) shows the plot of dielectric constant versus applied frequency. The dielectric constant and dielectric loss are inversely proportional to the frequency. The dielectric constant has a higher value in the lower frequency region (3Hz). The increase in dielectric constant at low frequency is attributed to the space charge polarization [14]. Fig.9 (a) implies that the 4APO exhibits normal dielectric behavior. In normal dielectric behavior, the dielectric constant decreases with increasing frequency and reaches a constant value, depending on the fact that beyond a certain frequency of the electric field, the dipole does not follow the alternating field. The dielectric loss is also studied as a function of frequency at room temperature as shown in fig.9 (b). These curves suggest that the dielectric loss strongly depends on the frequency of the applied field, similar to what commonly observed with the dielectric constant in the ionic system [15,16].

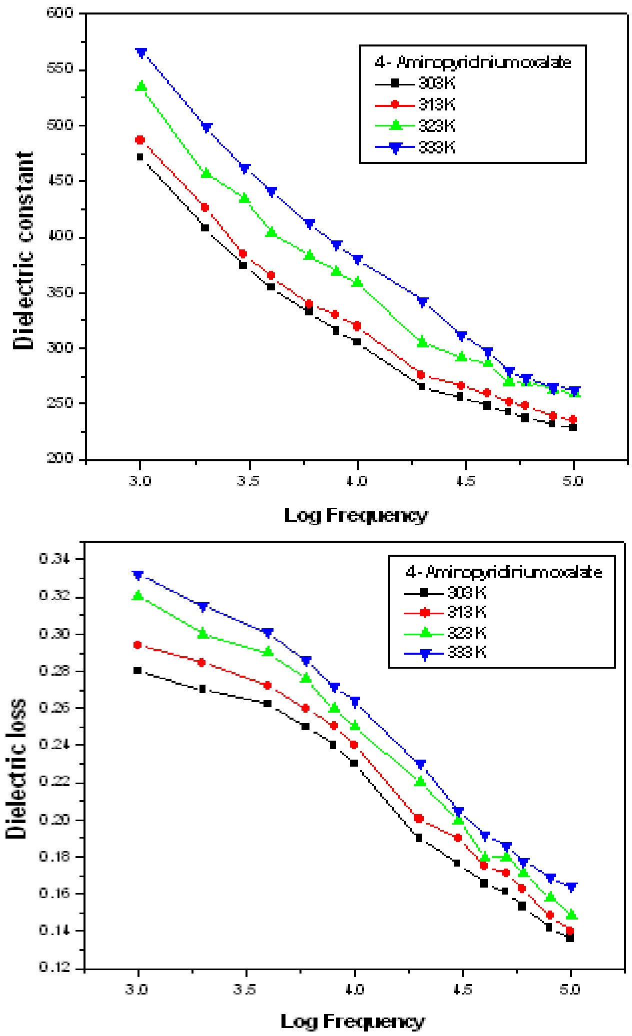

Fig.9. Variation of (a) dielectric constant and (b) dielectric loss with temperature and frequencies for 4APO crystal.

Nonlinear optical studies

NLO efficiency of the grown 4APO crystal was measured by the Kurtz and Perry technique [17]. A Q-switched Nd-YAG laser was used as light source. A laser beam of fundamental wavelength 1064nm 8 ns pulse width, with 10 Hz pulse rate was made to fall normally on the sample cell. KDP crystal was powdered and was used as reference material in the SHG measurement. The input laser energy incident on the powdered sample was chosen to be 5.65mJ/pulse. The second harmonic signal of 288 mV was obtained for 4APO while KDP gave an

SHG signal of 55mV for the same input beam energy. Thus the relative efficiency of 4APO was found to be 5.2 times higher than that of KDP.

Conclusion

Optical quality single crystals of 4APO were grown by slow evaporation solution growth technique. From single crystal X-ray diffraction studies, it is found that 4APO crystal belong to monoclinic crystal structure. The presence of various functional groups was confirmed by FTIR spectrum. Optical transmission studies showed that the crystal is transparent in the visible region with the cut-off at 302 nm and hence it is suitable for frequency conversion applications. The thermal studies and the Vickers's microhardness test revealed that the thermal stability and mechanical strength of the grown crystal respectively. The dielectric constant and dielectric loss studies of 4APO established the normal dielectric behavior. The SHG efficiency of 4APO was found to be 5.2 times greater than that of KDP crystal.

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