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Studies on the growth, structural, optical, mechanical and dielectric properties of 4-Aminopyridinium oxalate single crystals

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ABSTRACT

4-Aminopyridinium oxalate is an organic crystal has been grown by slow evaporation solution growth technique. The solubility of the 4-Aminopyridinium oxalate crystal increases with increasing temperature. The structure of 4-Aminopyridinium oxalate is confirmed by single crystal X-ray diffraction method. The title compound crystallizes in the monoclinic system and the space group is C_2/c. The presence of various functional groups in the grown crystal is identified from FTIR analysis. The optical property such as transmittance of the grown 4-Aminopyridinium oxalate crystal is obtained from UV-Visible spectroscopic studies. The mechanical stability of the grown crystal has been studied by using Vickers microhardness test and it reveals that the 4-Aminopyridinium oxalate crystal is the soft category material. The dielectric constant and the dielectric loss of the specimen were also studied.

1. 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, good optical transmission characteristics and high optical damage threshold hence, they are preferred in many applications like optical switching, information storage etc., several nonlinear optical complexes formed from aminopyridine and carboxylates groups [1-7]. Pyridine and its derivatives are involved in hydrogen bond interactions and this property plays an important role in heterocyclic chemistry. In many dicarboxylic salts, an oxalic acid intermolecular hydrogen bond is very strong. Oxalic acid forms crystalline oxalate or with various organic molecules through hydrogen bonding and interaction [8, 9]. It is known that oxalic acid acts not only as an acceptor to form various stacking complexes with other aromatic molecules but also as an acidic ligand. 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 of 4-aminopyridine molecules are protonated and oxalic acid is a monoionised state. Hoong-Kun Fun et al has reported the structure of 4-Aminopyridinium oxalate [10]. In the present investigation, we report the growth and structural, optical, mechanical and dielectric properties of 4-Aminopyridinium oxalate single crystals.

2. Materials and methods

4-Aminopyridine (AR grade SRL India) and oxalic acid (AR grade Merck) raw materials were used for the synthesis of 4-aminopyridinium oxalate compound. 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 hours. 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 the

slow evaporation method at room temperature and from the solubility studies the 4APO exhibits positive temperature gradient and high solubility in water.

The chemical reaction may be represented as

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

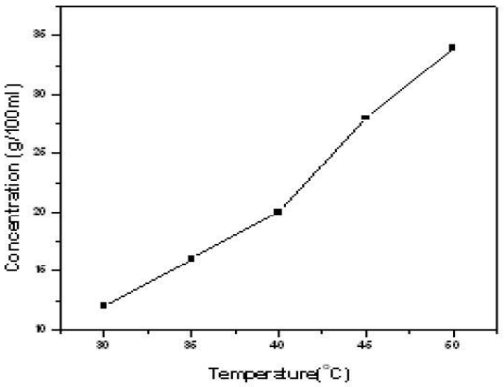


Fig.1. Solubility curve of 4APO

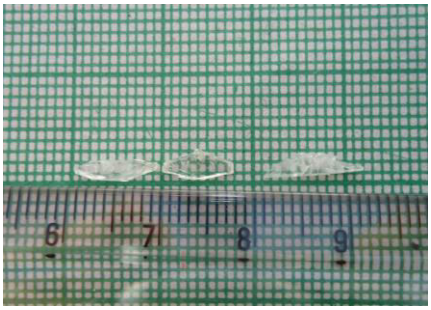


Fig.2. Photograph of 4-APO crystals

3. Results and discussion

3.1. 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 C_2/c. The determined lattice parameters a= 15.5431 Å , b= 5.5824 Å , c= 19.7021 Å 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 10-80° by using Ritz-170 powder X-Ray 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.

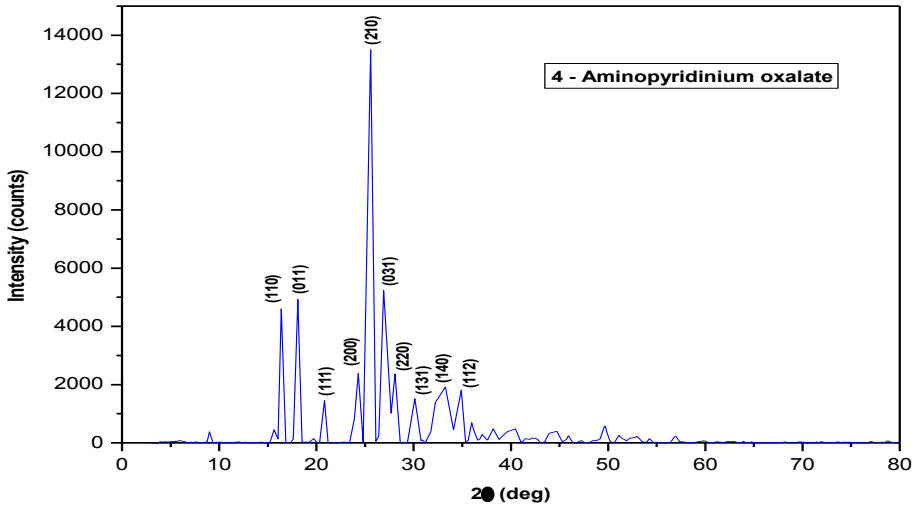


Fig.3. Powder XRD pattern of 4Aminopyridinium oxalate crystal

3.2. FTIR studies

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.

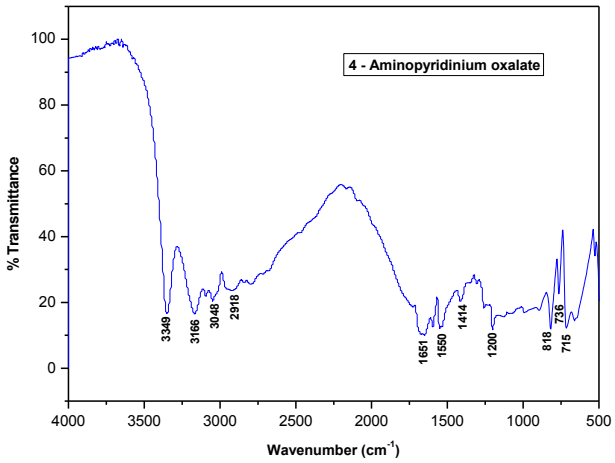


Fig.4. FTIR spectrum of 4APO crystal

3.3 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 cutoff wavelength of 4APO crystal is 302nm. From the recorded spectrum, it is observed that crystal 4APO has high transmittance of above 78% up to 1100nm.

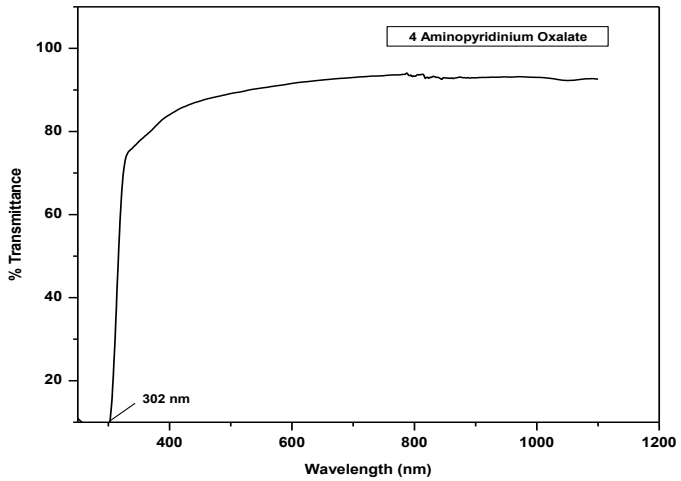


Fig.5. UV-Visible transmission spectrum of 4APO crystal

3.4. 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.6 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 moderately softer category material.

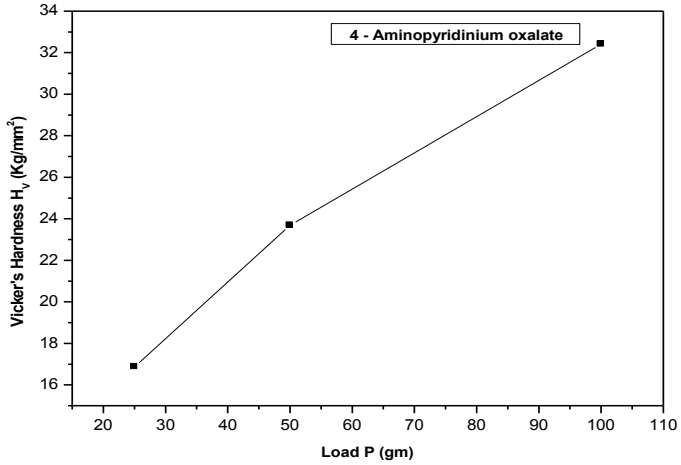
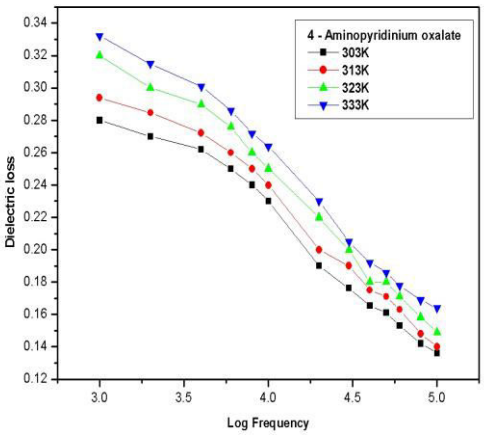


Fig.6. Load (P) vs hardness number (H_v) of 4APO crystal

3.5. Dielectric studies

The dielectric studies on 4Aminopyridinium oxalate single crystal were carried out using a HIOCKI 3532-50 LCR HITESTER instrument. A sample of thickness 5cm × 4cm × 5cm 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 the free space. C is the capacitance, t is the thickness of the sample and A is the area of the cross section. Fig.4 (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.7 (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 with different temperature as shown in fig.7 (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].



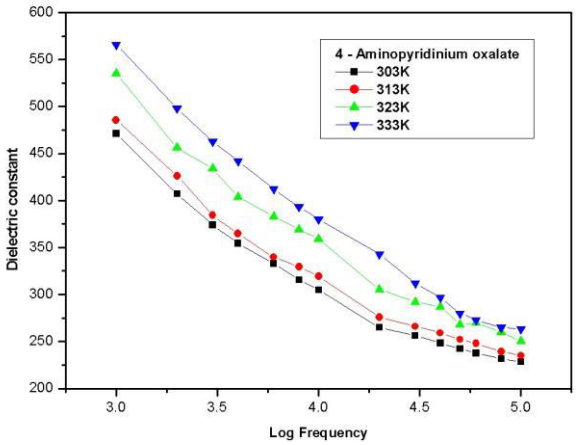


Fig.7(a) Dielectric constant versus frequency **Fig.7(b) Dielectric loss versus frequency**

Conclusion

Optical quality single crystals of 4Aminopyridinium oxalate were grown by slow evaporation technique. From Single crystal X-ray and powder diffraction studies confirm the unit cell parameters and 4APO crystal belongs to the 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 dielectric constant and dielectric loss studies of 4APO established the normal dielectric behavior.

References

[1] Periyasamy.B.K, Jebas.R.S, Thailampillai.B, Mater. Lett. 61 (2007) 1489-1491.
[2] Munn.R.W, Ironside.C.N, Principles and Applications of Nonlinear Optical Materials,

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Chapman and Hall, London, 1993.
[3]Dalton.L.R, Sullivan.P.A, Olbricht.B.C, Bale.D.H, Takayesu.J, Hammond.S, Rommel.H, Robinson.B.H, Tutorials in complex Photonics Media, SPIE, Belling-ham,WA,2007.
[4]Kaino.T, Cai.B, Takayama.K, Adv. Funct. Mater.12 (2002) 599-603.
[5]Barden.J, Hierle.R, Perigaud.A, Zyss.J, Williams.D.J, Nonlinear optical properties of Organic molecules and polymeric materials ACS Series, vol.223, American Chemical Society, Washington, DC, 1993.
[6]Prasad.P.N, Williams.D.J, Introduction to Nonlinear Optical effects in Molecules and Polymers, Wiley, Newyork, 1991.
[7]Caroline.M.I, Vasudevan.S, Mater.Lett.62 (2008) 2245-2248.
[8]Anandha Babu.G, Ramasamy.P, J. Cryst.Growth 311 (2009) 1185-1189.
[9]Oudar.J, Hierle.R, J.Appl.Phys.48 (1977) 2699-2704.
[10]Hoong-Kun Fun, Jain John, Samuel Robinson Jebas, Balasubramanian.T, Acta Cryst.E65 (2009), 0748-0749.
[11]Sangwal.K, Mater. Chem.Phys.63 (2000) 145-152.
[12]Onitsch.E.M, Mikroskopia 2 (1947) 131.
[13]Hanneman.M, Metall, Manchu 23 (1941) 135.
[14]Boomadevi.S, Dhanasekarean.R, J.Cryst.Growth 261 (2004) 70-76.
[15]Rao.K.V, Smakula.A, J.Appl.Phys. 36 (1965) 2031-2038.
[16]Arjuna.S, Mohan Kumar.R, Mohan.R, Jayavel.R, Mater.Res. Bull.43 (2008)2018-2015.