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Growth and Characterization of Anthranilic acid Crystals

S.Dinagaran[1], P.Srinivasan[2*], S.Vijayakumar[3], J.Balaji[4]
[1]Department of Physics, University College of Engineering - Thirukkuvalai-610 204, Tamil Nadu, India
sugadinagokul@yahoo.co.in,
[2]Department of Physics, University College of Engineering Panruti-607 106,Tamil Nadu, India.
sril35@gmail.com,
[3]Department of Physics, Government College of Engineering, Dharmapuri-636704, Tamilnadu,India.
srinisir.vijay@gmail.com,
[4]Department of Physics, University College of Engineering Panruti-607 106,Tamil Nadu, India.
ramjbalaj@gmail.com,
*corresponding author and mail respond tosril35@gmail.com

ABSTRACT

Single crystals of Anthranilic acid (AA) have been successfully grown and purity of materials has been increased by repeated recrystallization process. Single crystals have been grown by slow evaporation technique. The grown crystal was characterized by Single crystal X-Ray diffraction, Powder XRD, FTIR, UV-Vis, DTA/TGA, Dielectric studies and SHG respectively. The observed results from various characterization show the suitability of NLO application. The second harmonic generation of the grown crystal was checked using Kurtz and Perry technique. Thermal stability and melting point of the grown crystal were found by thermal analysis. The Physical strength of the grown AA crystal was measured from Vicker's hardness test.

Keywords: Slow evaporation, X-Ray Diffraction, FTIR, Microhardness, Thermal stability

1 INTRODUCTION

In the recent years, nonlinear optics (NLO) crystals have attracted the researchers due to their potential applications in the fields of high energy lasers for internal confinement fusion research [I] colour display and photonics including optical information processing [II-VI]. Organic materials have been known for many applications especially semiconductors, superconductors and NLO productions etc., [VII]. Organic compounds exhibit larger NLO response than inorganic materials due to the presence active π - bands. Organic NLO crystals with high conversion efficiency for second harmonic generation and high optical transparency occurred in UV-Vis region are required for several device applications mainly in optical telecommunications and optical storage device [VIII].

In view of this, it is desirable to search for new NLO crystals which possess shorter cutoff wavelengths, sufficiently large nonlinear coefficient, and transparency in UV region. Hence organic crystals have some factors good with widely used crystals of standard inorganic NLO materials [IX].

In the present investigation, the growth of anthranilic acid (AA) crystal is achieved by slow evaporation technique. The grown crystals were characterized by SXRD,PXRD, FTIR, UV-Vis, and DTA/TGA. The hardness and second harmonic generation efficiency measurements were made. Anthranilic acid (AA) is a potential organic NLO crystal with molecular formula $C_7H_7NO_2$ andits molecular structure is shown in figure.1. There are two nonequivalent molecules per lattice point in the space group $Pna2_1$ and the analysis shows that the two molecules have significantly dissimilar bond lengths. This proof, taken composed with the hydrogen-bonding system, indicates that one molecule is neutral, when the other is a zwitterion. This paper consists of physicochemical properties of AA crystal.

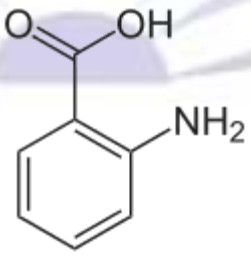

Fig.1. Molecular structure of Anthranilic acid

2 EXPERIMENTAL PROCEDURES

2.1 Crystal Growth

Anthranilic acid crystals were grown from slow evaporation technique by ethanol as solvent. The commercially available anthranilic acid cleaned by several time by ethanol from recrystallization, after that it was taken as raw material for growth. The solvent was taken in a beaker and purified material was added gradually and stirred continuously until to reach supersaturated solution. Then it was filtered by a glass filter paper of 1µm porosity. The filtered solution was strongly

closed with thick filter paper for the rate of evaporation could be minimized. Good quality of single crystals was observed after 2 weeks. The grown crystal is shown in figure.2.

Fig.2. As grown crystal of AA

3 RESULTS AND DISCUSSIONS

3.1 Single Crystal X-ray Diffraction

The single crystal XRD data of the grown AA crystals were obtained by using ENARF NONIUS CAD4 diffractometer and crystallographic data are given in table.1 and the diffraction pattern of AA crystals from single XRD is shown in figure 3. From the single crystal analysis it is confirmed that the grown crystal is belongs to orthorhombic crystal system and the space group of $Pna2_{1.}$

Table 1. Comparison of crystallographic data

Lattice parameter	Brown C.J et al	Present value
a	12.864 Å	12.868 Å
b	10.790 Å	10.808 Å
c	9.314Å	9.338 Å
α	90˚	90˚
β	90˚	90˚
ɣ	90˚	90˚
V	1292.81 $Å^3$	1299 $Å^3$

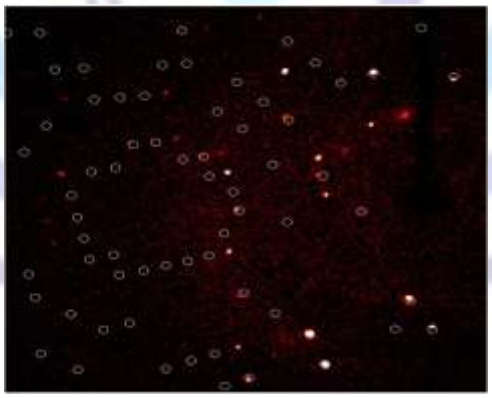

Fig 3: Single crystal XRD pattern of AA crystal

3.2 Powder X-ray Diffraction

The grown anthranilic acid crystals were analyzed by powder X-ray diffraction using Rigaku mini Flex II X-ray diffractometer with Cuk_α (1.54059 A^0) radiation at ambient temperature. When X-ray falls over a crystalline powder, it diffracts in a pattern characteristic to form its structure. Hence the diffraction pattern is obtained from powder of the material, quite than an individual crystal. A diffraction pattern plots scattered intensity against the angle of the detector 2θ. The sharp and very intense XRD peaks were confirmed that the material has the crystalline nature [X]. The lattice parameters values of AA crystal well connected to the literature [XI]. The powder diffraction spectrum of AA crystal is shown in figure.4.

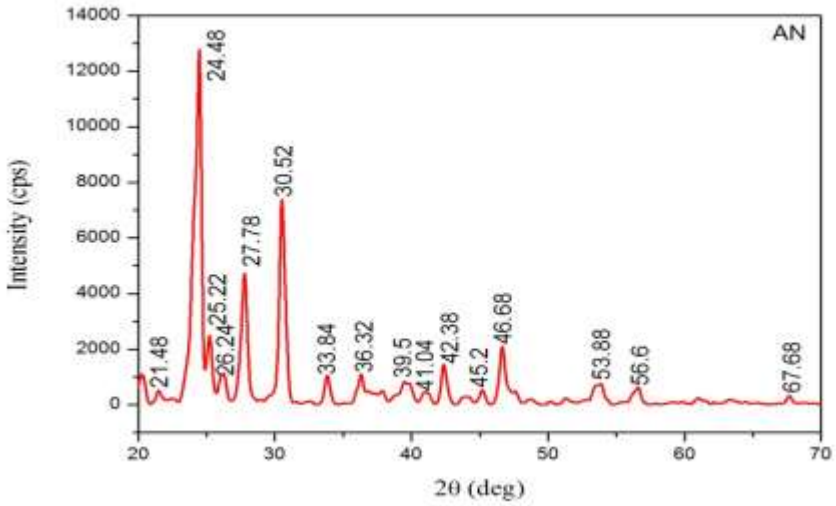

Fig 4: Powder XRD spectrum of AA crystal

3.3 FTIR Spectral Studies

The functional groups presented in the AA compound have been identified by Perkin–Elmer Spectrum RX1 Spectrometer using KBr pellet technique in the region 400-4000 cm–^{1}[XII]. The FTIR spectrum of title compound is shown in figure5. The vibrational assignment of AA crystal is noted in table.2.

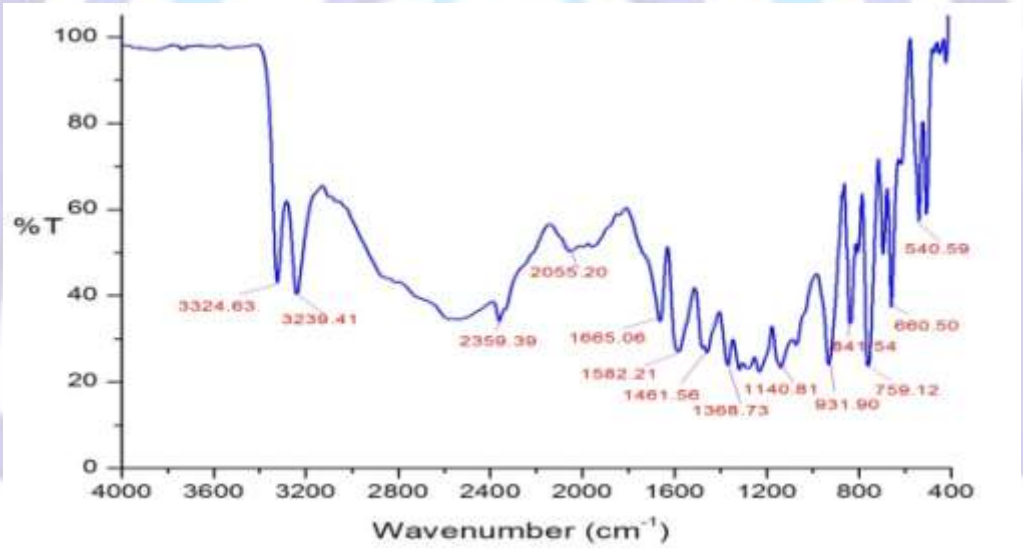

Fig 5: FTIR spectrum of AA crystal

Table 2. Vibrational assignment of AA crystal

Wavenumber (cm^{-1})	Vibration Assignments
660.50	Aromatic ring bend
759.12	C-H out of plane bending due to ortho substitution in benzene ring
841.54	NH_2 out of plane bending
931.90	O-H stretching (carboxylic acid)
1140.81	C-N stretching
1582.21	C-C in aromatic ring (benzene)

1665.06	C=O stretching (carboxylic acid)
3239.41	NH_2 bend overtone
3324.63	Symmetric N-H_2 stretching

3.4. Second Harmonic Generation (SHG) studies

The SHG of the crystal was checked using the powder SHG technique developed by Kurtz and Perry [XIII]. An Nd:YAG laser beam of wavelength 1064 nm, with beam energy of 1.1 mJ/pulse and pulse width of 8ns with a repetition rate 10 Hz were used. The grown single crystal was grained into fine powder and then packed in a micro size capillary of uniform bore and exposed to laser radiations. The 532 nm radiation was collected from sample holder. Hence the second harmonic generation is confirmed by the emission of green light of wavelength 532nm. KDP and Urea crystals were powdered to the identical particle size and were used as reference materials in the SHG measurement. The comparison of SHG signal output for the AA with that of standard KDP and Urea as mentioned in table3. The efficiency of AA is 1.11 times higher than KDP and 0.67 times higher than Urea. Due to its high SHG efficiency, it is used as electro-optic modulators [XIV].

Table3. Comparison of SHG signal output

Input power mJ / pulse	KDP mV	Urea mV	AA mV
1.1	120	200	134

3.5.UV-visible spectroscopic studies

Good optical transmittance and lower cut-off wavelengths are very important properties for NLO crystals. Optical behaviour of AA crystal was measured by Lambda 35 UV-VIS spectrophotometer in the wavelength range of 190 - 1100 nm. The UV-Vis transmittance spectrum is shown in figure 6. The strong absorption occurred at 321nm. The crystals are broadly transparent possessing a transmission of greater than 99% for light with incident wavelengths from 392 - 1100 nm. There is no absorption band between 392 and 1100 nm. This nature in the visible region is required for nonlinear optical applications [XV-XVI].

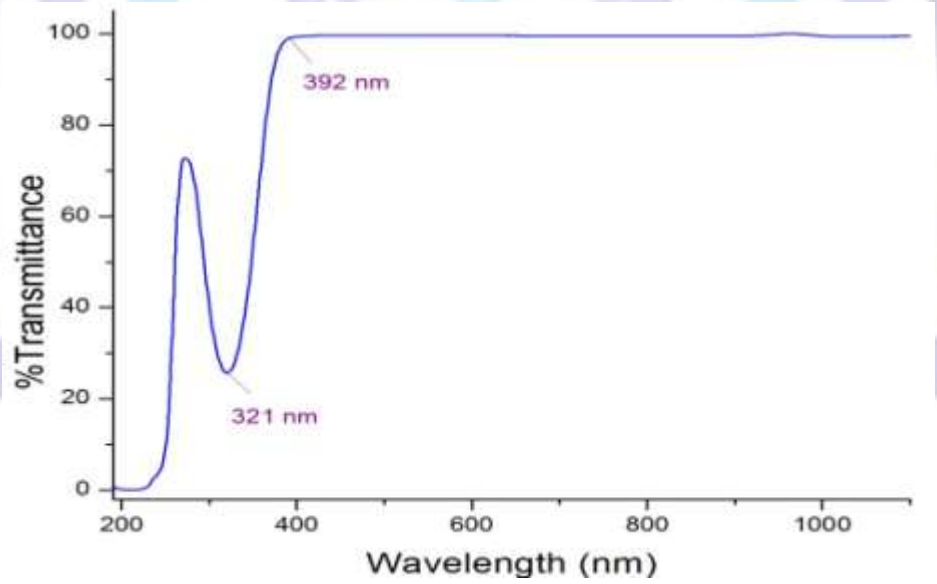

Fig 6:UV-Visible transmittance spectrum of AA crystal

3.6.TGA/DTA analysis

TG and DTA analysis of AA crystals were carried out by simultaneously in N_2 atmosphereat a heating rate of 20^{o}C/minute for a temperature range of 30^{o}C - 400^{o}C using NETZSCH – STA 449F3- simultaneous thermal analyzer system. The resulting of TGA- DTA analysis curves for AA is shown in figure.7. It is clearly observed from the TGA spectrum, the material has thermal stability up to 147^{o}C. The major weight loss of sample (90%) occurred from the temperature range from 200^{o}C to 255^{o}C. From the DTA curves, two endothermic peaks were noted at 147^{o}C and 255^{o}C. The first endothermic peak at 147^{o}C represents the melting point of the AA and the second endothermic peak at 255^{o}C represents around its boiling point. The Differential scanning calorimetric analysis was carried for sample AA crystal by using NETZSCH – STA 449F3- simultaneous thermal analyzer system. The resulting of TGA-DSC analysis curves for AA is shown figure.8. DSC traces the smooth curve up to 118^{o}C which indicates the removal weakly entrapped water from the

crystal lattice and another very sharp intense endothermic peak observed at 160^{o}C, it indicates the decomposition of crystalline material. The last endothermic peak at 255^{o}C mentioned the onset temperature, which is bulk decomposition of compound.

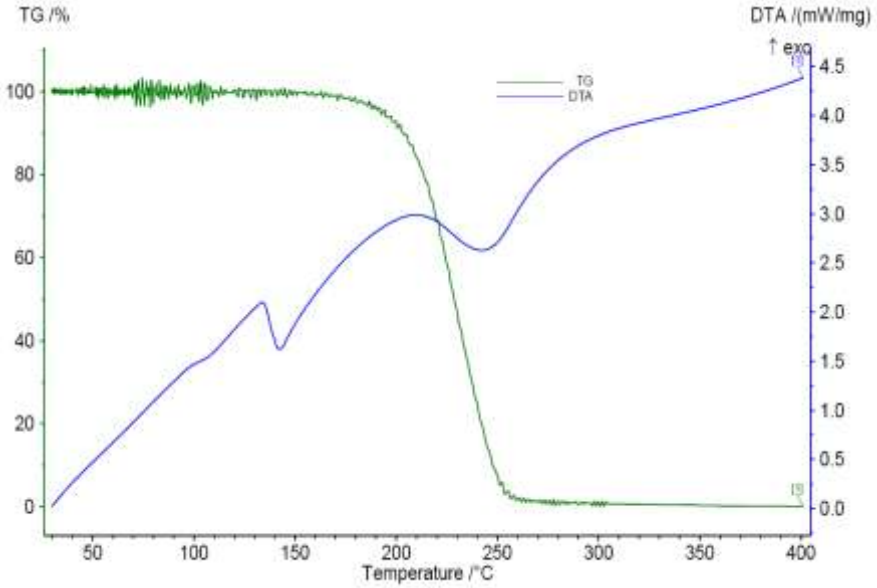

Fig 7: TGA-DTA curve of AA crystal

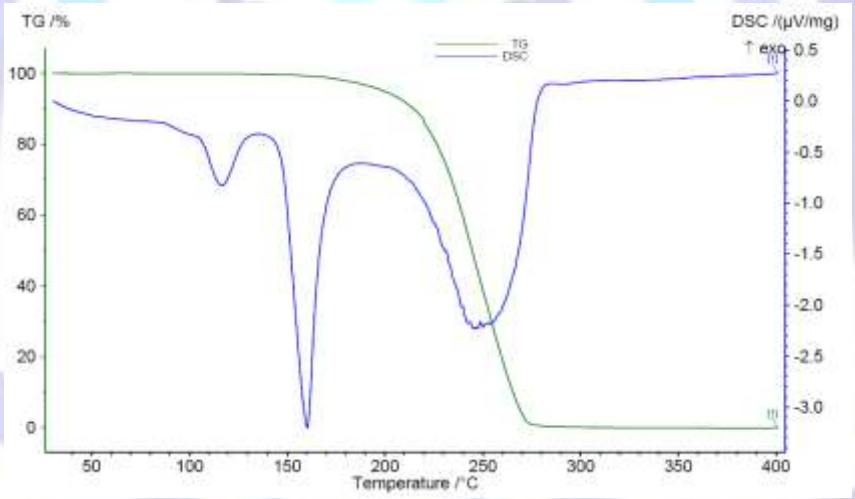

Fig8: DSC curve of AA crystal

3.7 Mechanical Stability

The resistance presented by a material to the motion of dislocation, deformation or damage under the given stress is measured by the hardness of the crystal [XVII-XVIII]. During the making of NLO crystals mechanical stress is applied on the crystal when cutting and polishing. So it is essential to know how stress on the crystals could not cause any crack. The ratio of the applied load to the anticipated area indentation gives the hardness. To find the surface hardness of the grown AA microhardness was measured for a load of 25-100 gm using Shimadzu- make- model-HMV-2T

The Vickers hardness number (Hv) was calculated using the below formula,

$$Hv = (1.8544\ P) / d^2\ \ Kg/mm^2$$

Where, P is the applied load and d is the mean diagonal length of the indentation. The increase of the hardness with load up to 100g is represented in figure 9 which proves the use of grown crystals in which can withstand thermal local stresses. The relation connecting the applied load and diagonal length'd' of the indenter is derived from Meyer's law.

$$P = ad^n$$

Where, n is the Meyer's index or work hardening coefficient. In order to find work hardening index (n), a graph is plotted (figure10) with log P against log d which gives a straight line. From the slope of the line, the Mayer's index number was found. According to Onitisch, 'n' lies between 1 and 1.6 for moderately hard materials and it is more than 1.6 for soft materials [XIX]. The observed value of Meyer's index for AA is 3.09 and hence AA belongs to the soft materials category.

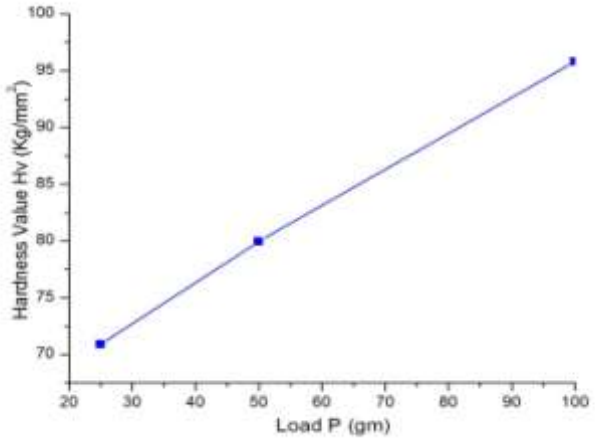

Fig.9: Plot of Vicker's hardness versus load P of AA crystal

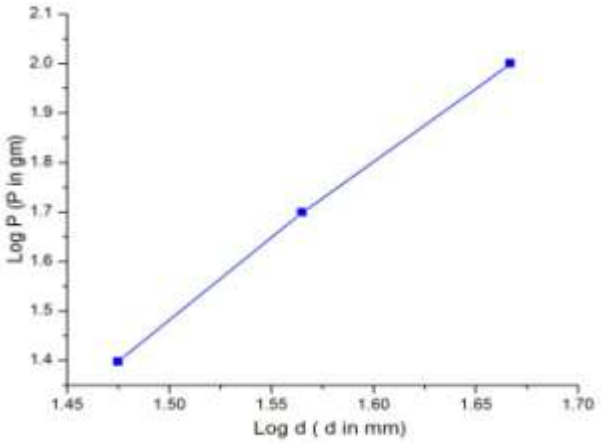

Fig 10: log P versus log d

3.8. Electrical conductivity studies

The dielectric property of the AA crystals was studied using HIOKI 3532 LCR HITESTER in the frequency region 50Hz - 5MHz. The studies were carried out from 313K to 333K.The variation of dielectric constant with frequency is shown by figure 11. The dielectric constant is higher in the region from 50Hz - 5MHz and gradually decreases with increase in frequency and continues up to 5MHz. After that all other higher frequencies, it almost remains constant. The four types of polarizations in the material are the reasons for the high value of dielectric constant at low frequency [XX]. In accordance with Miller rule, at higher frequency dielectric constant has low values which is a suitable parameter for the enhancement of SHG coefficient [XXI].

Figure 12 shows the variation of dielectric loss with frequency. The crystal possesses enhanced optical quality with only few defects plays a vital role for the fabrication of nonlinear optical devices due to low dielectric loss with high frequency for the samples [XXII].Figure 13 shows the frequency dependence of the AC conductivity in the frequency range 10^1Hz - 10^7Hz in the temperature interval 313K to 333K. It is observed that the conductivity increases with increasingfrequency. This frequency dependence of the AC conductivity is given by the power law [XXIII].

The power-law dependence of the frequency is of a universal nature and corresponds to the short ranges that are separated by energy barriers of varied heights. This rule is credited to hopping conduction.

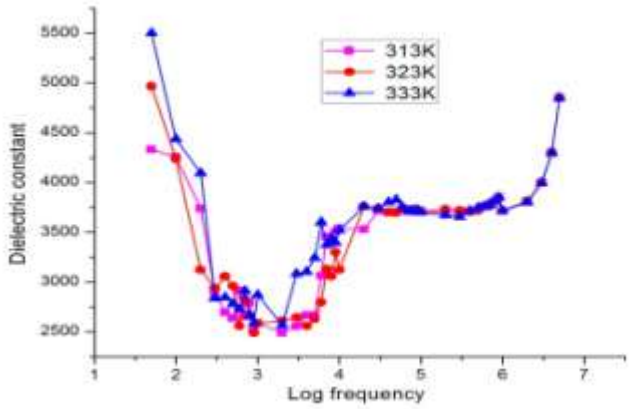

Fig 11: Variation of dielectric constant with logarithmic frequency

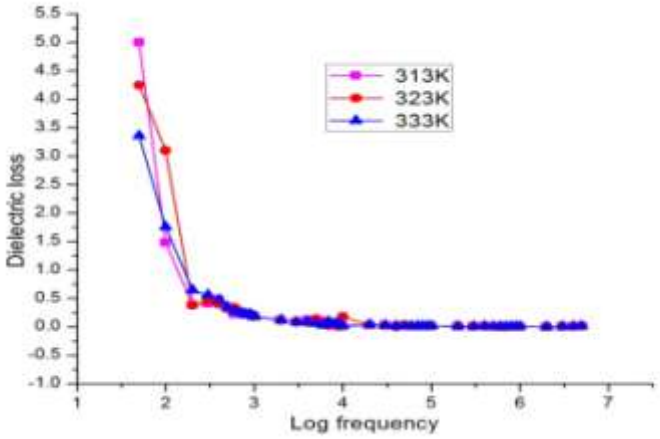

Fig12: Variation of dielectric loss with logarithmic frequency

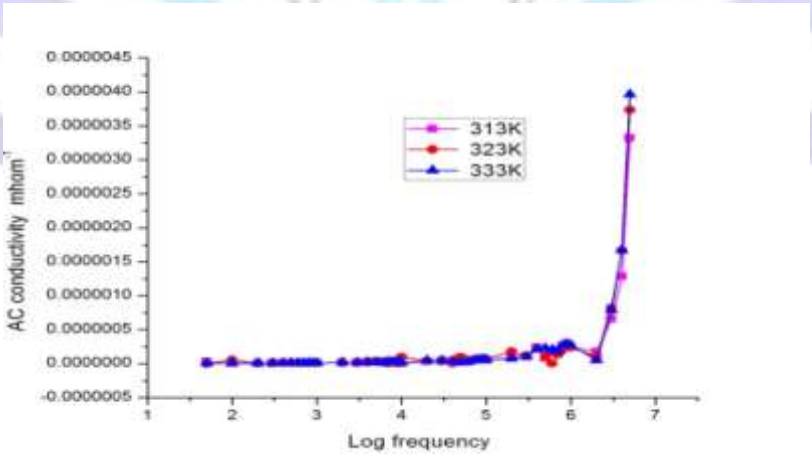

Fig 13: Variation of AC conductivity with logarithmic frequency

4 CONCLUSIONS

Optical quality of Anthranilic acid single crystals were grown by slow evaporation technique at room temperature from ethanol. Single XRD confirms AA crystal belongs to orthorhombic system and space group $Pna2_1$. Sharp peaks of powder XRD of the crystal show good crystalline of the compound. The FTIR spectrum of the grown crystal confirmed the vibrational frequencies of various functional groups of AA. The TGA/DTA analysis revealed melting point and thermal

stability of the AA crystal. UV –Vis studies revealed that AA is transparent between 390 and 1100 nm. Vicker's hardness test confirms the softness of the crystal. Second harmonic generation test conducted for the powdered AA crystal using Nd:YAG laser showed that its relative SHG efficiency is greater than KDP and Urea. Dielectric studies revealed that AA crystal has low dielectric constant at high frequencies.

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