# Study on growth, spectral, optical and thermal characterization of an NLO crystal: Ammonium Citrate Dibase (ACD)

**A.R.S. Janci Rani Juliet, Research Scholar in Physics(Reg.No.7438), Holy Cross College, Nagercoil, Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli, Tamilnadu, India.**
**julie79sudha@gmail.com**
**S. Mary Delphine, Head and Associate Professor in Physics, Holy Cross College, Nagercoil, Tamilnadu, India.**
**delphine_mry@yahoo.co.in**
**S. Janarthanan, Assistant Professor in Physics, Adhi College of Engineering and Technology, Kancheepuram, Tamilnadu, India. srijana76@gmailcom**
**R. Sugaraj Samuel, Assistant Professor in Physics, The New College, Chennai, Tamilnadu, India.**
**sugarajsamuel@yahoo.com**

**Abstract. Ammonium citrate dibase (ACD) single crystals were synthesized and grown by slow evaporation method. The structure of the grown crystal was confirmed by single crystal X-ray diffraction (SXRD) and powder X-ray diffraction (PXRD) techniques. The Fourier transform infrared spectroscopy (FTIR) and proton Nuclear Magnetic Resonance ($^1$HNMR) studies were used to identify the various functional groups and the position of protons of the grown ACD. The thermal behaviour of the Ammonium citrate dibase was analyzed by the thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The grown crystals were subjected to UV–Vis–NIR studies which revealed the transmission properties of the grown crystal. The nonlinear optical (NLO) property of the crystal was confirmed by powder second harmonic generation (SHG) test.**

***Keywords — Ammonium Citrate Dibase, Nonlinear optical crystal, Optical transmission, Second harmonic generation***

## I. INTRODUCTION

Materials with high nonlinear optical retort play a vital role because of their potential applications in many fields such as advanced optical communication and data storage systems. The frequency conversion materials have a significant impact on laser technology [1],[2],[3]. Of late, the material scientists are swiftly encouraged with the novel and hopeful materials which offer larger and closer optical nonlinearities compared to their inorganic counterparts [4],[5]. Several crystal growth techniques used by crystal growers for growing organic single crystals mainly the solution and melt growth techniques depend mainly on the properties of the materials. The solution growth can be considered as a superior method because good optical transparency of crystals and uniform mixing of dopant in the lattice are achieved in this method. Crystal growth in the region of high super-saturation is not an easy task because extraneous materials are inclined to be formed from the growth solution. This condition typically leads to the deterioration of the main crystal and the execution of growth run. This gives the problem of solution stability which is one of the most important challenges for rapid growth [6]. Recently, citrate crystals are widely studied that includes Trisodium citrate pentahydrate [7], sodium potassium citrate [8], bismuth citrate crystals and its reaction with potassium hydroxide [9], lithium dihydrogen citrate, sodium dihydrogen citrate, zinc citrate, manganese citrate etc., [10-14]. In the present investigation, the single crystal Ammonium Citrate Dibase (ACD) was characterized for NLO applications. The crystalline characteristics were studied by X-ray diffraction. The fundamental functional groups were confirmed by FTIR and $^1$HNMR spectroscopy. Thermal stability was analyzed by TGA-DTA analysis and the second harmonic generation (SHG) study was also performed for crystalline powder of ACD crystals.

## II. EXPERIMENTAL

### *A. Crystal Growth*

Single crystals of Ammonium citrate dibase (ACD) were grown from saturated aqueous solution of commercially available citric acid and ammonium carbonate in the molar ratio of 1:2 which were purchased from Sigma-Aldrich (AR grade). The solution was stirred well for 12 hours to get homogeneous saturated solution. The prepared solution was filtered using whattmann filter paper, covered with a perforated cover and finally was kept in constant temperature

 DOI : 10.18231/2454-9150.2018.0960 

bath for evaporation process. The purity of the synthesized compound was increased by the recrystallization process. Slow evaporation of solvent gave rise to crystallization of transparent and colourless ACD crystals which were harvested in 30 to 35 days. As grown ACD crystals are shown in Figure 1.

## III. RESULTS AND DISCUSSION

### A. *X-ray diffraction study*

Single crystal X-ray diffraction analysis was carried out using an ENRAF CAD-4 diffractometer with $MoK_\alpha$ ($\lambda$ = 0.7107 Å) radiation to identify the crystal system and to estimate the lattice parameters. From the single crystal XRD analysis, it has been observed that the grown crystal possess orthorhombic structure with lattice parameters, a = 10.692 Å, b = 6.312 Å, c = 14.536 Å and V = 981.004 $(Å)^3$. The single crystal data are found to be in good agreement with reported values [15]. The powdered ACD sample was scanned over the range of 10°-70° at the rate of 1° per min. using Rich–Seifert diffractometer with CuKα (1.5406 Å) radiation. From the powder X-ray data, the various planes of reflections were indexed using XRDA 3.1 program. The indexed powder X-ray diffraction pattern for ACD crystal is shown in Figure 2.

### B. *FTIR Spectral Analysis*

To confirm the presence of various functional groups in the grown ACD crystal, the Fourier Transform Infrared (FTIR) spectrum was recorded using BRUKER IFS 66 V spectrometer in the wavelength range 4000–400 $cm^{-1}$ by KBr pellet technique. The FTIR spectrum of ACD is shown in Figure 3. The OH – strong band appeared at 3399 $cm^{-1}$. The strong peaks at 3196 $cm^{-1}$ and 3076 $cm^{-1}$ are attributed to CH alkyl stretching. The band at 1727 $cm^{-1}$ is due to C=O stretching vibration of carboxylic group. The peaks at 1500 $cm^{-1}$ and 1429 $cm^{-1}$ correspond to OH asymmetric stretching. The bands at 1321 $cm^{-1}$ and 1101 $cm^{-1}$ are due to H-O-C bending respectively as mixed modes. The CN stretching as mixed modes are assigned to 1283 $cm^{-1}$.

### C. *$^1$HNMR spectral analysis*

$^1$HNMR spectrum of the ACD sample was recorded using Jeol: GSX400 instrument. The $^1$HNMR spectrum of ACD is shown in Figure 4. A peak observed at 13.49 ppm is due to the presence of proton in carboxylic acid. A sharp singlet at 7.3 ppm can be attributed to ammonium group. The peak observed at 6.71 ppm is attributed to OH group attached to the carboxylic group. The doublets at 2.91ppm and 2.5 ppm can be attributed to methylene in the citrate group.

### D. *UV-Vis-NIR Spectral Analysis*

UV-vis-NIR spectral study is a useful tool to determine the transparency of the crystal, which is an important requirement for a material to be optically active [16]. The UV–Vis-NIR spectrum occurs due to the electronic transitions in the molecule. This is a characteristic peak of a compound. The optical absorption spectrum of ACD crystal was recorded using CARY 5E UV-Vis-NIR spectrophotometer in the region of 200 – 800 nm. The spectrum is shown in Figure 5. The curve shows a small absorption in the IR region. The lowest cut off wavelength was found to be at 206 nm which may be due to $n \rightarrow \pi^*$ electronic transition of carboxyl group. As ACD is found to be transparent in the entire visible region it is suitable for second harmonic generation [17].

### E. *Thermal Analysis*

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are of immense importance as far as the fabrication technology of material is concerned. They provide the information about the thermal stability of the material for fabrication where a considerable amount of heat is generated during the cutting process and laser irradiation. The TG-DTA for the grown crystals were carried out at nitrogen atmosphere in NETZSCH thermal analyzer to study the thermal property of the as grown crystal. The thermal analysis of ACD crystal was carried out between 25°C and 1200°C at a heating rate of 20°C $min^{-1}$. The TG-DTA graphs of ACD are shown in Figure 6. The powdered sample of about 2.2 mg of ACD crystal was used for the analysis. In the TGA curve it is observed that there is a weight loss at 197.27 °C indicating the sublime nature of the crystal. Hence, the crystal can be used up to 197.27 °C for any application. The DTA curve shows a sharp endothermic peak at 197.27 °C which matches with the observed weight loss in TGA.

### F. *NLO Studies*

The NLO efficiency of the grown crystal was found by Kurtz and Perry powder technique [18]. The fundamental beam of 1064 nm from Q switched Nd: YAG laser of pulse energy 405 mJ $pulse^{-1}$ and width 8 ns was used to test the second harmonic generation (SHG) property of the crystal in powder form. The emission of green radiation from the crystal confirmed the second harmonic generation of the ACD crystal. With the generation of SHG signal in the sample of ACD, the NLO property has been confirmed.

## IV. CONCLUSION

The ACD was successfully synthesized and good quality crystals were grown by slow evaporation technique. From the X-ray diffractions studies the crystal parameters and the space group were identified. The presence of various function groups and the protons were confirmed by FTIR and $^1$H NMR analysis respectively. The transparency of ACD crystal in the entire visible region was confirmed using the UV-Vis-NMR spectral analysis. The TG-DTA studies revealed that the grown crystal is stable up to 197.27°C. As grown crystal, ACD exhibits its strong second harmonic generation capacity so that it could be used for NLO devices.

 DOI : 10.18231/2454-9150.2018.0960 

## ACKNOWLEDGMENT

The authors are grateful to Dr. M. Vanjinathan, Assistant Professor in Chemistry, D.G. Vaishnav College and Chennai, India for his help and support in understanding the spectral analyses and interpretations.

## V. REFERENCES

[1] H.S. Nalwa, S. Miyata, "Nonlinear Optics of Organic Molecules and Polymers," *CRC Press, Boca Raton*, FL, 1997.

[2] D.S. Chemla, J. Zyss, "Nonlinear Optical Properties of Organic Molecules and Crystals," *Academic Press, Orlando*, FL, vol. 1, 1987.

[3] S.Sadhasivam, N.P. Rajesh, "Growth and characterization of organic nonlinear optical single crystal 2,7-dihydroxy naphthalene," *Optics and Laser Technology* , vol. 93, pp. 133–137, 2017.

[4] Arunkumar A, Ramasamy P, "Synthesis, crystal growth and structural characterization of Lithium fumarate semi-organic single crystals," *Mater. Lett.* Vol.123, pp.246–249, 2014.

[5] I.Md. Zahid, C. Amirtha Kumar, A. Malarkodi, K.S. Joseph Wilson, R. Mohan Kumar, " Studies on the Crystal growth and Optical properties of novel organic material: O-Phenylenediaminium bis-hydrogen phosphonate," *Materials letters*, vol. 209, pp. 167-170, 15 December 2017.

[6] Zaitseva, N. P., Carman, L. M., Rozsa, R. B., De Yoreo, J. J., Dehaven, M. R., Spears, H. R., Bell, W. R., James, D. L., Vital R. L., "Rapid Growth of Large-Scale (40-50-cm) KDP Crystals, Lawrence Livermore National Laboratory," UCRL-LR-105821-97-4, pp 223- 229.

[7] N. Suneetha and D. Rajan Babu, "Growth and Characterization of Trisodium Citrate Pentahydrate- a nonlinear optical material," *International Journal of Pure and Applied Mathematics*, vol.118, No.18, pp.4589-4599, 2018.

[8] Jiaqi Ni, Keqing Han, Muhuo Yu, and Chenyu Zhang, "The Influence of Sodium Citrate and Potassium Sodium Tartrate Compound Additives on Copper Electrodeposition,". *Int. J. Electrochem. Sci*., vol.12, pp. 6874 – 6884, 2017.

[9] E. S. Naidenko, YU. M. Yukhin, L. I. Afonina and K. B. Gerasimov, "Obtaining Bismuth-Potassium Citrate," *Chemistry for Sustainable Development*, vol.20, pp. 523-528, 2012.

[10] Zeynep Yarbas¸I, Abdulhalik Karabulut and Bunyamin Karabulut, "EPR Studies of Copper-Doped Potassium Dihydrogen Citrate ($C_6H_7KO_7$) Single Crystal," *Appl Magn Reson* , vol. 41, pp. 51–57, 2011

[11] Prashant Dwivedi, Ram Kripal and Madan Gopal Misra, "EPR and optical absorption studies of Cu2+ ions doped magnesium citrate decahydrate single crystals," *Journal of Alloys and Compounds* , vol. 499, pp. 17–22, 2010.

[12] Tadeja Birsa Celic, Zvonko Jaglicic, Karoly Lazar and Natas Zabukovec Logar, "Structure and magnetic properties of a new iron(II)citrate coordination polymer," *Acta Cryst.* B69, pp. 490– 495, 2013.

[13] N.D. Pandya, J.H. Joshi, H.O. Jethva, and M.J. Joshi, " Structural, Spectroscopic and Thermal Studies of Potassium Di-Hydrogen Citrate Crystal," *Mechanics, Materials Science & Engineering*, ISSN 2412-5954, MMSE Journal, May 2017.

[14] M. Matzapetakis, N. Karligiano, A. Bino, M. Dakanali, C. P. Raptopoulou, V. Tangoulis,A.Terzis, J. Giapintzakis and A. Salifoglou, "Manganese Citrate Chemistry: Syntheses, Spectroscopic Studies, Structural, Characterizations of Novel Mononuclear, Water-Soluble Manganese Citrate Complexes," *Inorg. Chem*., vol.39, pp. 4044-4051, 2000.

[15] Love, W. E., Patterson, A .L., "X-ray crystal analysis of the substrates of a Aconitase.III. Crystalisation, cell constants and space groups of some alkali citrates," *Acta Crystallogr*. vol.13, pp.426-428, 1960.

[16] C.N.R. Rao, Ultraviolet and visible spectroscopy, *chemical applications, Plenum Press*, 1975.

[17] N.P.Zaitseva, L.N.Rashkovich, and S.V.Bogatyreva, "Stability of $KH_2PO_4$ and $K(H,D)_2PO_4$ solutions at fast crystal growth rates," Journal of Crystal Growth, vol. 148, no. 3, pp. 276–282, 1995

[18] S.K.Kurtz and T.T.Perry, "Powder technique for the evaluation of nonlinear optical materials, *J. Appl Phy*. ,Vol.39, pp.3798-3813, 1968.

## Figures

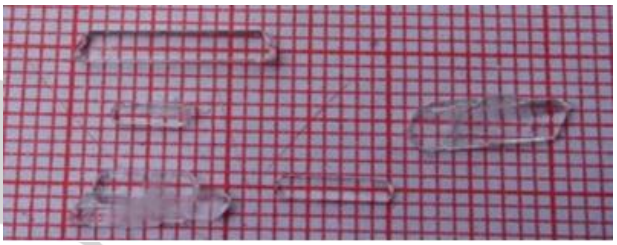

FIGURE 1. AS GROWN CRYSTALS OF ACD

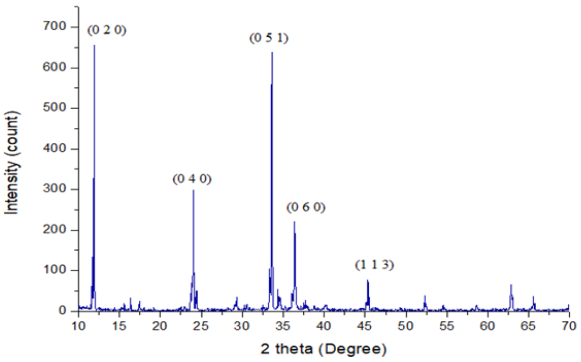


FIGURE 2. PXRD DATA OF ACD

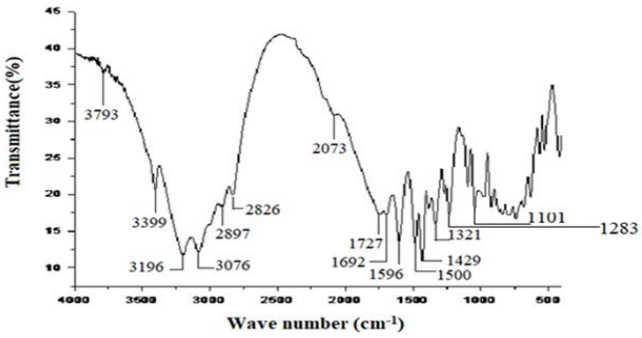


FIGURE 3. FTIR SPECTRUM OF ACD

 DOI : 10.18231/2454-9150.2018.0960 

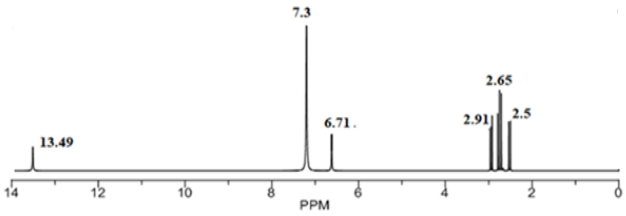


Figure 4. $^{1}$H NMR spectrum of ACD

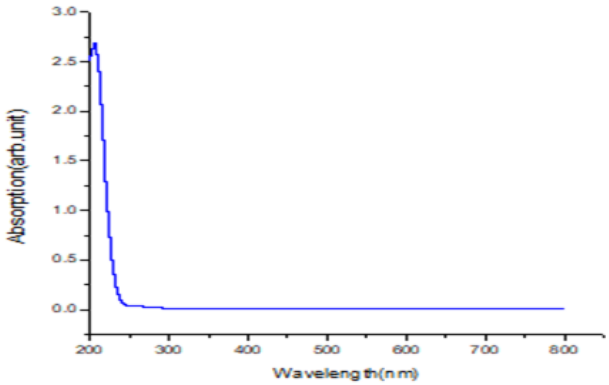


Figure 5. UV-Vis-NIR spectrum of ACD

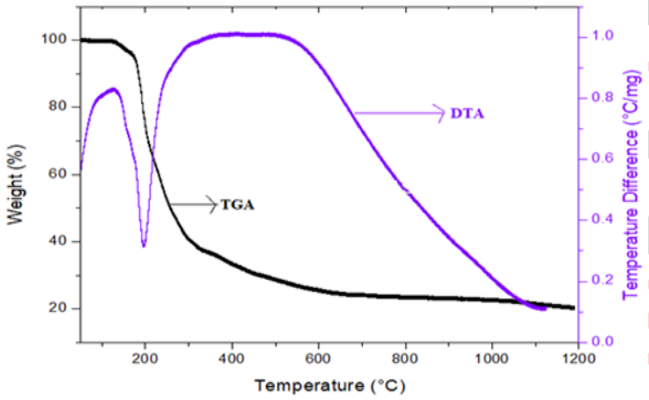


Figure 6. TG/DTA curves for ACD

 DOI : 10.18231/2454-9150.2018.0960 