

SPECTRAL DIFFRACTION AND OPTICAL STUDIES OF SUCCINIC- ACETIC ACID SINGLE CRYSTALS

B.Ravi¹, A.Jegathesan², B. Neelakanda Prasad³, C. Sadeshkumar⁴
and G.Rajarajan^{5*}

¹ Department of Physics, King College of Technology, Namakkal-637 020, T. N., India

² Department of Physics, Paavai Group of Institutions, Pachal-637 018, T.N., India

³ Department of Physics, K.S.R College of Engineering, Tiruchengode-637 215, India

⁴ Department of Physics, Gnanamani College of Technology, Namakkal-637 018, T.N., India

⁵ Selvam Centre for Materials Research, Selvam Educational Institutions,
Namakkal-637 003, T.N., India

*E-mail: grajarajan@gmail.com

ABSTRACT

Single crystals of succinic-Acetic acid (SA) were grown by slow evaporation method. The grown crystals were characterized for the structural parameters by Powder X-ray diffraction (XRD), and functional group analysis by Fourier Transform Infra-red (FTIR), UV-Vis absorption, transmission studies reveals that the grown crystal was optically transparent through the visible range. Thermal analysis was carried out by Thermogravimetry and Differential thermogravimetry analysis methods and the SA crystal was thermally stable upto 189°C. In the dielectric studies, the dielectric constant and dielectric loss of the crystal were studied as a function of frequency and the results were discussed. The optical absorption studies indicate that for the sample, optical transparency window is quite wide, making it suitable for NLO applications.

Keywords : Crystal growth, slow evaporation process, structural studies, optical studies, dielectric studies.

©2013 RASAYAN. All rights reserved

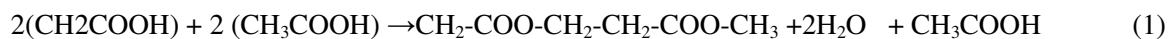
INTRODUCTION

The ferroelectric crystals have a wide range of applications in biological and industries like in optoelectronics field such as capacitors, nonvolatile memory devices, actuators, high-performance gate insulators, etc. Ferro electric crystals possess domains of different orientations of electrical polarization that can be reoriented and brought into alignment by an electric field¹⁻³. Among the most numerous ferroelectrics are perovskites of which a classic example is barium titanate which is widely used in capacitors. Recently, literature reveals that extending crystals of succinic acid for high electron mobility transistor fabrication (HEMT)²⁻¹⁰. Due to their biological and industrial applications, our attention has been focused to investigate the succinic acid crystals, doped with succinic acid crystals and its applications. Here we report the growth of a promising new organic crystal of succinic-acetic acids (SA) grown by slow evaporation, solution growth technique. The grown crystal was confirmed by powder XRD studies. The functional groups of SA were identified by FT-IR and the transmission of the grown crystal was measured using UV-Vis-NIR spectrum. Thermal stability has been studied and the ferroelectric patterns have also been observed on the grown crystals by dielectric measurements.

EXPERIMENTAL

Succinic-acetic single crystals have been grown from aqueous solution by low-temperature solution growth technique by slow evaporation in a constant temperature bath controlled to an accuracy of $\pm 0.01^\circ\text{C}$. The starting material was synthesized from commercially available Succinic acid (AR grade) and Acetic acid (AR grade), taken in the equimolar ratio 1:1. Calculated amount of the reactants were thoroughly dissolved in deionized water and stirred well for about 5 hours using a magnetic stirrer to

obtain a homogenous mixture. Then the solution was allowed to evaporate slowly until the solvent was completely dried. Crystals begin to grow inside the solution and were removed from the solution after 10 days, washed and dried in air. The purity of the synthesized salt was further increased by successive re-crystallization process. The grown crystals are shown in Figure-1. The reaction mechanism is given below-



Characterization studies

Powder X-Ray diffraction studies were carried out using Rich Seifert diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54060 \text{ \AA}$) radiation. Fourier transform infrared (FTIR) spectrum of SA crystal was recorded at a resolution 2 cm^{-1} in the range of $400\text{--}4000 \text{ cm}^{-1}$ employing Perkin-Elmer FT-IR spectrometer model SPECTRUMRX1 using KBr pellets technique. The optical absorption spectra of SA crystals were recorded in the range $190\text{--}1100 \text{ nm}$ using Lambda 35 double-beam spectrophotometer. Thermal stability and physiochemical changes of the sample were analyzed by recording the TGA and DTA spectrum using the instrument NETSZCH SDT Q 600 V8.3 Build 101, in the temperature range $0\text{--}300^\circ\text{C}$ in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. The dielectric constant and dielectric loss of SA crystal were measured using HIOKI 3532 LCR HITESTER in the frequency range $50 \text{ Hz--}5.5 \text{ MHz}$. In order to ensure good electrical contact between the crystal and the electrodes, a sample of $5.6 \text{ mm} \times 2.8 \text{ mm} \times 2.2 \text{ mm}$ was coated with silver paint.



Fig.- 1: Grown Succinic-acetic acid crystals

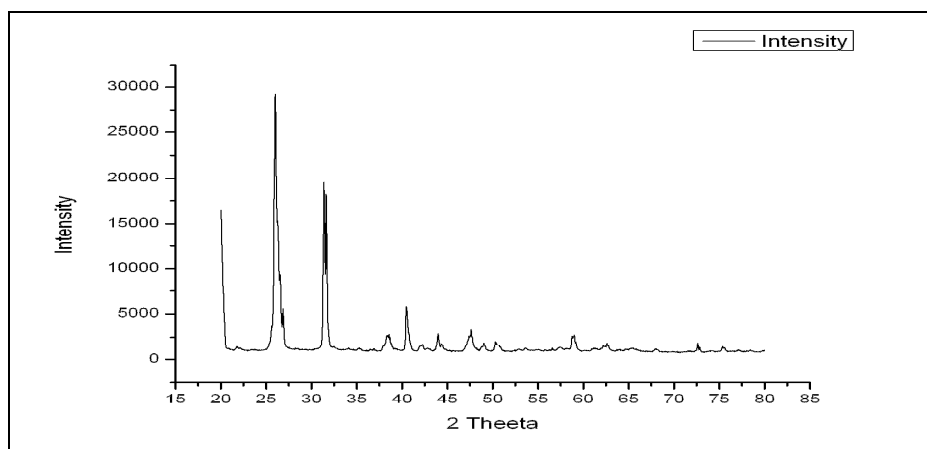


Fig.-2: Powder xrd pattern for SA crystal

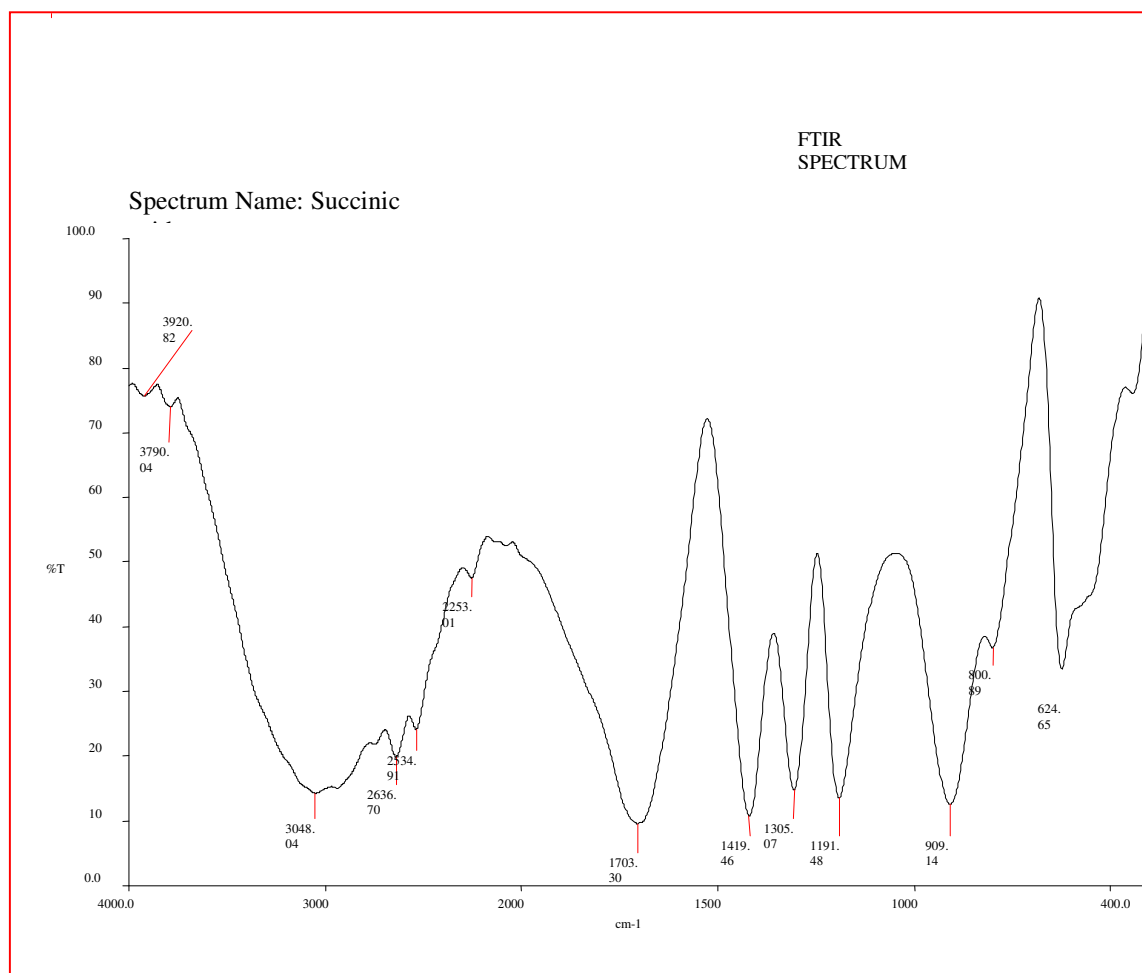


Fig.- 3: FT-IR spectrum of SA crystal.

RESULTS AND DISCUSSION

Powder XRD analysis

The structural parameters of the single crystals were studied by X-Ray powder diffraction method. X-Ray diffraction studies were carried out using Rich Seifert diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54060 \text{ \AA}$) radiation. Powder diffraction patterns were scanned for the range of 2θ values from 20 degree to 80 degrees at the rate of 5 degrees. The well-defined peaks at specific 2θ values show high crystallinity of the grown crystals of Succinic-acetic acids. The lattice parameter values of SA crystals have been calculated by Full Prof Suite software package. The resultant peaks in the diffractogram (Figure- 2) shows an intense peak at $26.1082(3)^\circ$ (intense peak). It is observed that SA belongs to triclinic system and its volume is 341.62°A and cell parameters values are tabulated in Table-1.

Table-1: The cell parameters of SA crystal.

A(°A)	B(°A)	C(°A)	α	β	γ	Space group	Volume(°A)
7.0511	9.7836	4.6868	93.26	91.05	96.35	P21(Triclinic)	341.62

Table- 2: FTIR absorption frequencies of Succinic-acetic acid single crystal

S.No	Wave Number (cm ⁻¹)	Assignment
1	3790	O-H Stretching
2	3045	CH ₂ Stretching
3	2635	O-H Stretching
4	2253	C-H Stretching
5	1703	COO ⁻ Stretching
6	1419	COO ⁻ Symmetry Stretch
7	1309	CH ₂ - wagging
8	1191	CH ₃ symmetry Stretching
9	909	O-H out of plane
10	800	COO ⁻ -bending
11	624	C-OH Stretching

Interpretation Of FTIR Spectrum

The infrared spectrum of SA crystals have been carried out to analyse the chemical bonding and molecular structure of the compound. The FT-IR spectrum of the crystal has recorded in the frequency region from 400 cm⁻¹ to 4000 cm⁻¹ with Perkin–Elmer FTIR spectrometer model SPECTRUMRX1 using KBr pellets containing SA powder obtained from the grown single crystals. The observed FT-IR spectrum of SA is as shown in Figure- 3. The strong absorption at 1419 cm⁻¹ indicates the symmetric stretching vibration frequency of carbonyl group. The bending and rocking vibrations of COO⁻ are observed at 800.89 cm⁻¹ and 624.65 cm⁻¹, respectively. CH₂ wagging (1305cm⁻¹) and C-CH₃ stretching (1191cm⁻¹) vibrations are also observed. The frequency of absorption of O-H Stretching at 3048.04 cm⁻¹ confirms the presence of succinic acid.

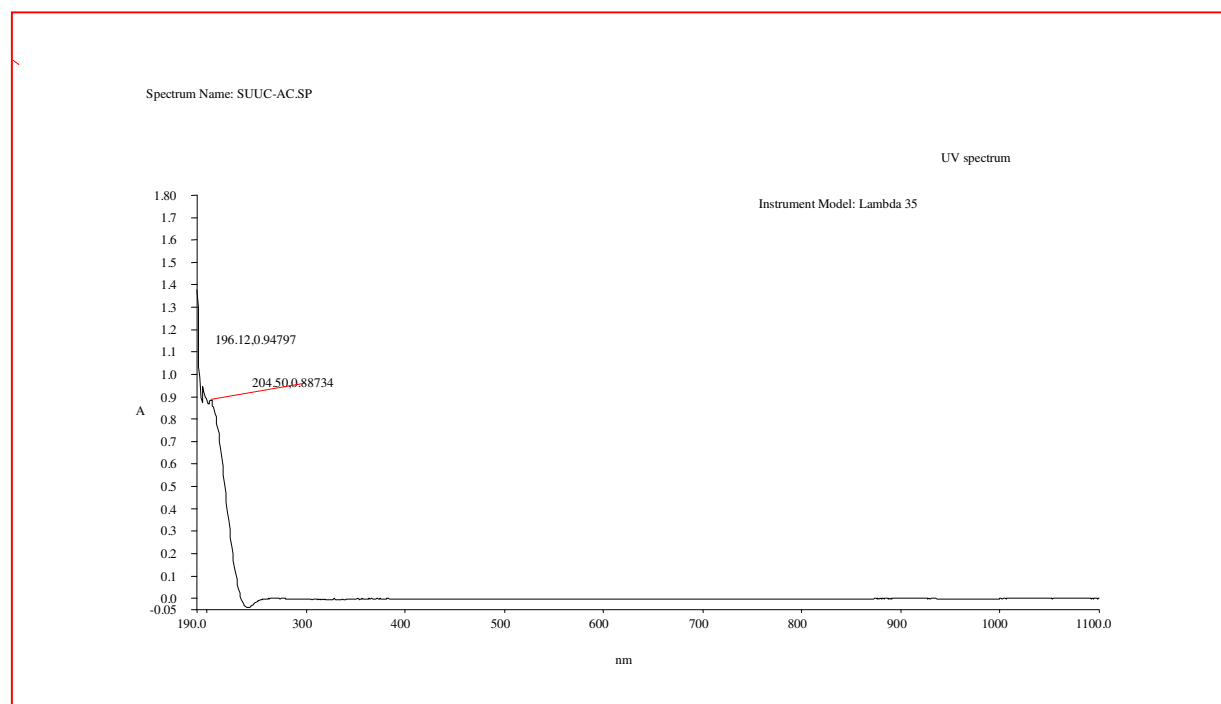


Fig.- 4: Absorption spectrum of LAS crystal.

UV-Vis Transmittance -Absorption studies

The optical transmittance and absorption spectrum of grown SA crystal has been recorded with a Lambda 35 double-beam spectrophotometer in the range 190–1100 nm to find the suitability of crystal for optical applications. The crystal shows a good transmittance (Figure- 5) in the visible region which enables it to be a good material for optoelectronic applications¹². From the spectrum (Figure-4), there is no significant absorption in the entire range tested. A good optical transmittance from ultraviolet to infrared region is very useful for optical applications¹³. From the UV–Vis–NIR spectrum, it is clear that the transparency of the grown crystals extends up to UV region. The lower cut-off wavelength is as low as 384 nm. The lower cut-off near 384 nm in transmittance spectrum combined with the very good transparency, makes the usefulness of this material for optoelectronic and nonlinear optical applications.

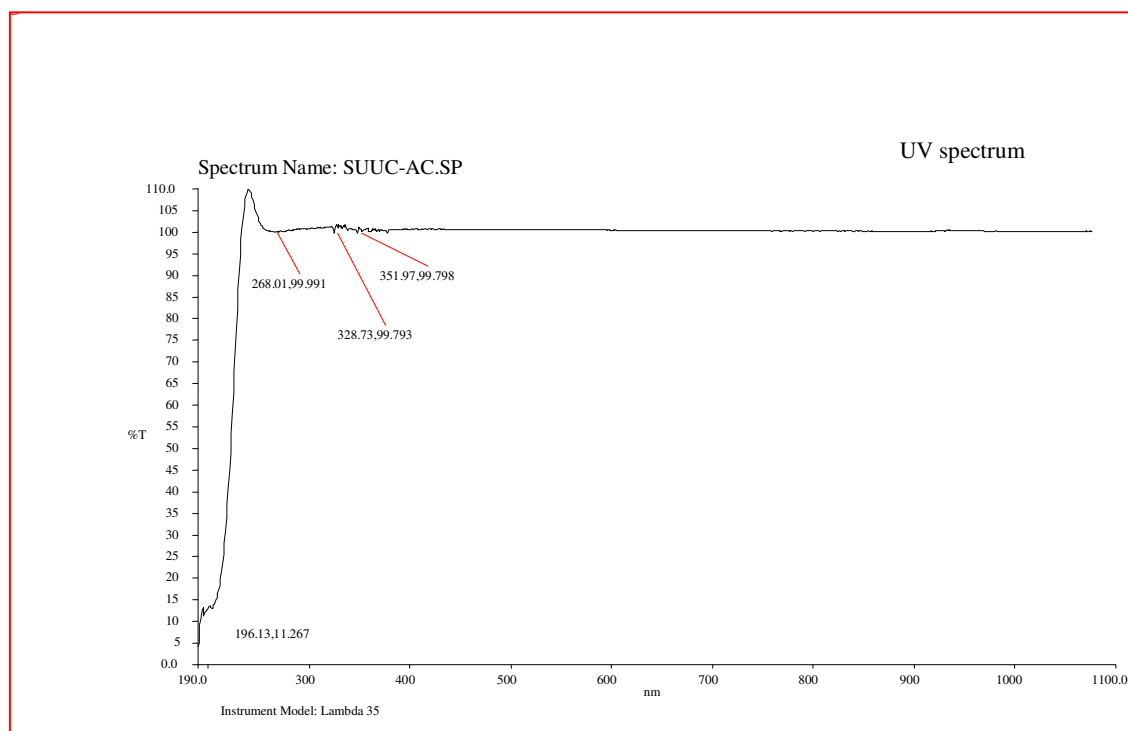


Fig.- 5: Transmission spectrum of SA crystal.

Thermal analysis

The Thermo Gravimetric Analysis (TGA), and Differential Thermal Analysis (DTA) spectra of grown SA crystal have been obtained using the instrument NETSCH SDT Q 600 V8.3 Build 101. The TGA and DTA have been carried out in nitrogen atmosphere at a heating rate of 20°C/min from 0°C to 300°C. The initial mass of the materials taken to analysis was 6.1400 mg and the final mass left out after the experiment was only 1.629 % of initial mass. The TGA trace in the Figure- 6. shows that the material exhibit very small weight loss of about 1.6 % in the temperature up to 160°C due to loss of water. TGA curve shows that there is a larger amount of weight loss (95%) occurs in between 189°C and 220°C which indicates that the decomposition of SA crystals. From the TGA, DTA analyses, it is clearly understood that the SA is thermally stable upto 189°C.

Dielectric Studies

Dielectric properties are correlated with electro-optic property of the crystals¹³. The dielectric constant is the measure of how easily a material is polarized in an external electric field¹⁴. The dielectric studies on succinic-acetic acid single crystals are carried out using the instrument, HIOKI 3532-50 LCR HITESTER. Carefully cut and polished samples of grown crystals of dimension 5.6x2.8x2.2 mm³ having

silver coating on opposite faces is placed between the two copper electrodes and thus a parallel plate capacitor is formed¹⁵. The capacitance is measured in the frequency range of 100Hz to 5.5MHz. The dielectric constant is calculated using the relation-

$$\epsilon_r = Cd/A \epsilon_0$$

(2)

where C-capacitance and d-thickness of the crystal.

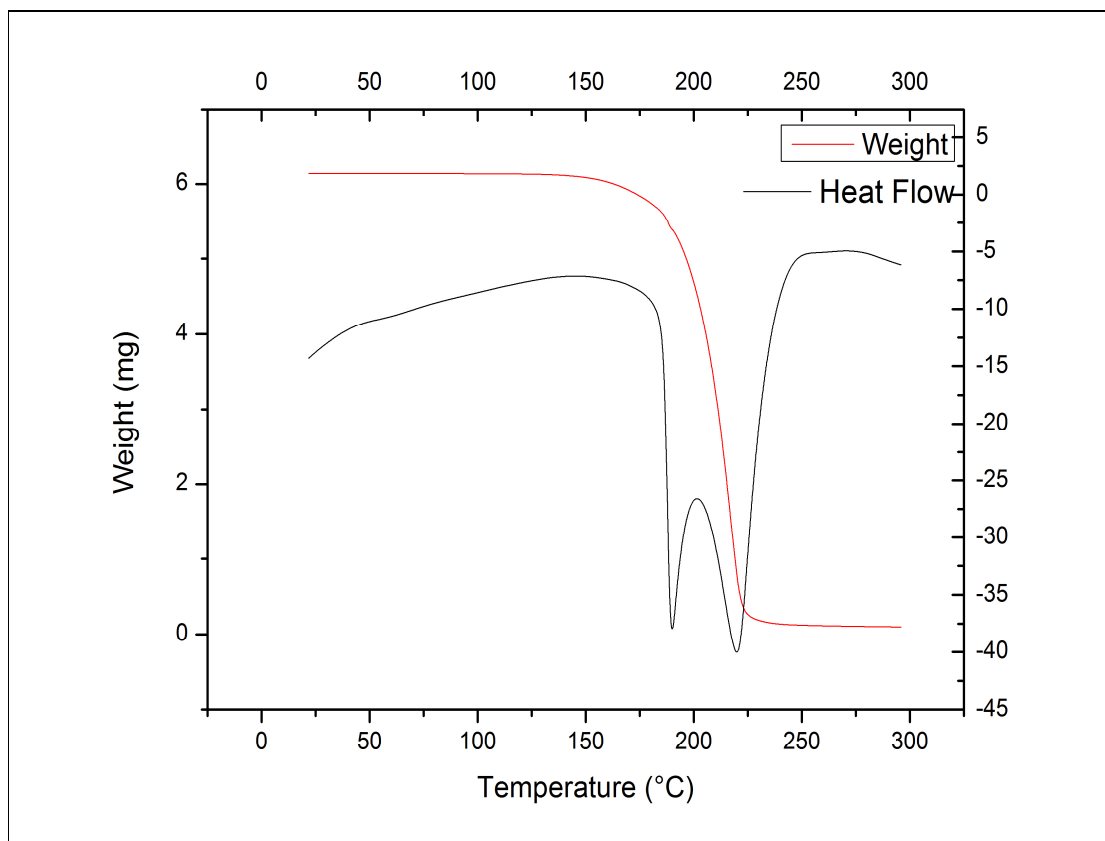


Fig.- 6: TGA/DTA curve of SA crystal.

Figure-3 shows the plot of dielectric constant (ϵ_r) versus applied frequency. It is observed from the plot (Figure-7a and b) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region. The larger values of dielectric constant at lower frequencies are due to the impedance to the motion of charge carriers at the electrodes, space charge and macroscopic distortion results¹⁶. The dielectric constant is low at high frequencies. This is due to the fact that at higher frequencies the ionic and electronic polarizations are only active¹⁷. According to Miller rule, the lower values of dielectric constant are a suitable parameter for the enhancement of the optical properties¹⁸. The dielectric loss is studied as a function of frequency at room temperature is shown in the Figure- 7 (b). These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric constant.

SEM analysis

SEM analysis gives information about the nature and suitability for device fabrication and also it is used to check the presence of imperfections. SEM analysis was carried out using SU 6600 field emission scanning electron microscope. The SEM micrographs of SA are shown in Figure- 8. The photographs

clearly reveal the step like growth pattern on the surface of the grown crystal and also the formation of few isolated islands in SA crystals.

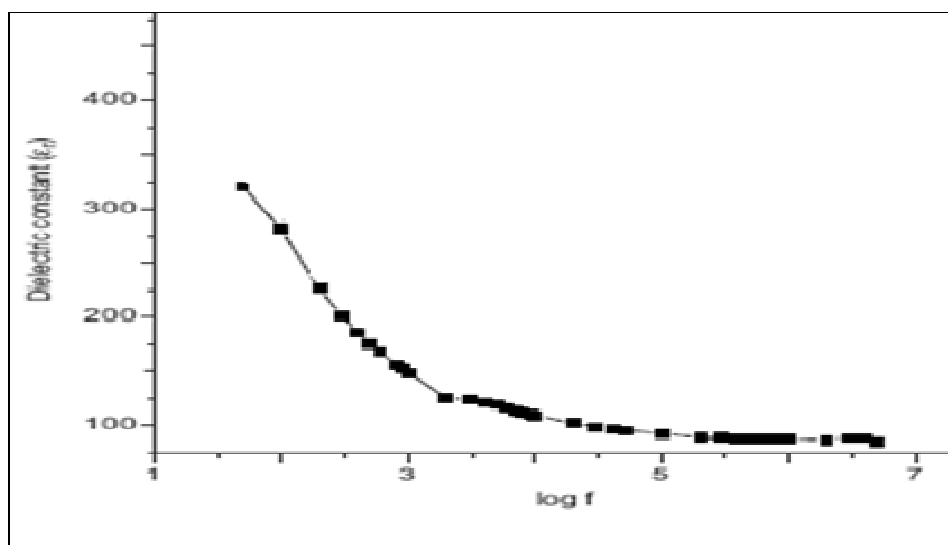


Fig.- 7a: log(f) Vs dielectric constant of SA crystal

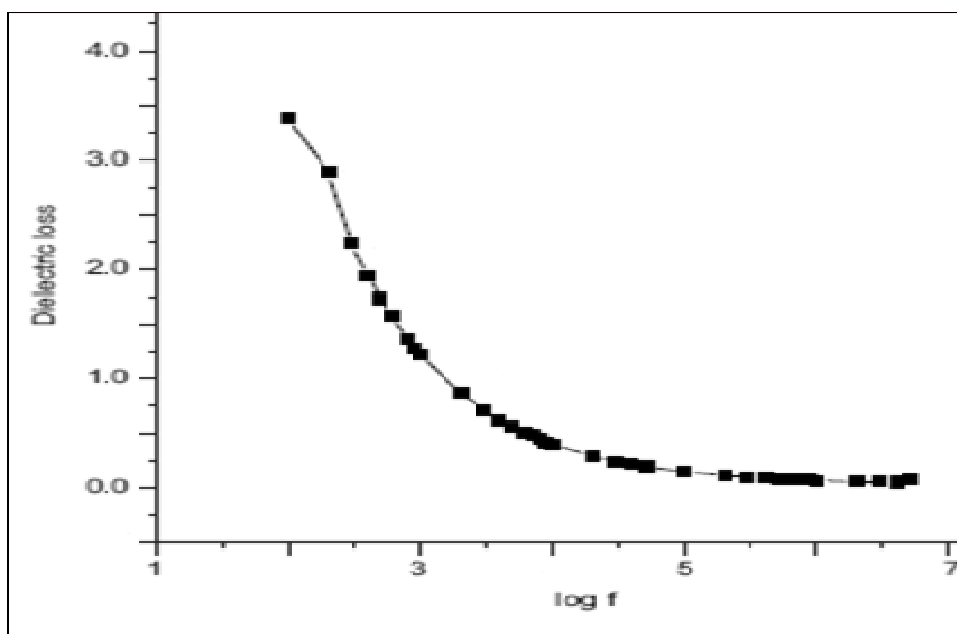


Fig.- 7b: log(f) Vs dielectric loss of SA crystal

CONCLUSION

High quality single crystals of succinic-acetic acid were grown by the slow evaporation method under room temperature. Grown crystals were characterized by powder XRD and confirmed that the crystals were belongs to Triclinic system with space group P21/c. FTIR analysis was performed to study the molecular vibrations and functional groups of the grown crystals and UV-Vis transmittance-absorption spectrums were recorded to confirm the transparency of the crystals. Thermal stability up to 220°C of the

crystal was confirmed using TGA/DTA. Very low dielectric constant values, indicating that the crystal possesses improved pyroelectric properties and low dielectric loss revealing the purity of the crystals.

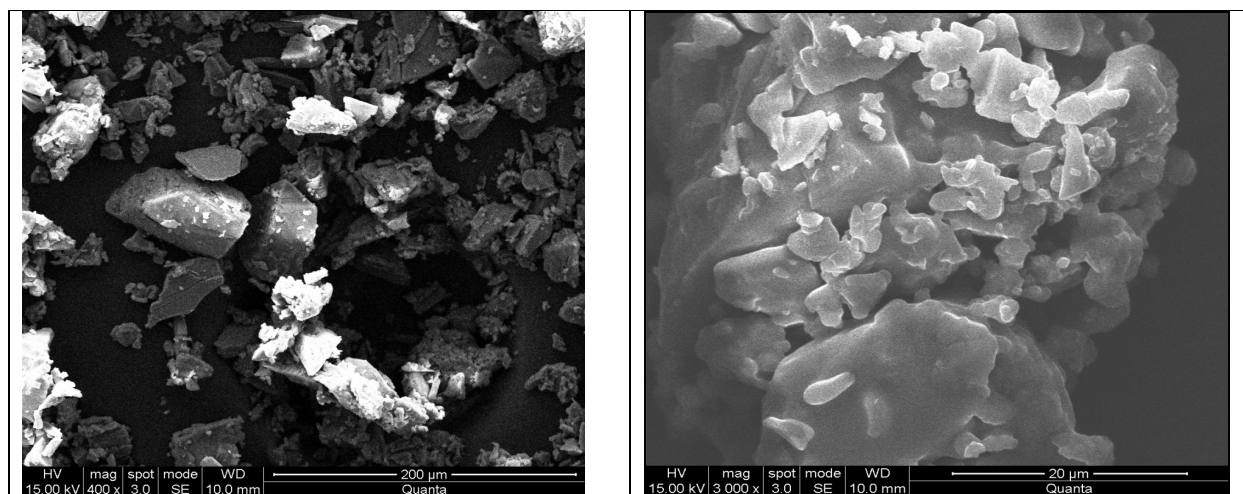


Fig.-8: SEM images of grown SA crystals

ACKNOWLEDGMENTS

The authors are thankful to St. Joseph's College, Trichy, India, and SASTRA University, Thanjavur, India for spectral facilities. The authors also express their gratitude to, SRM University, Chennai, India for XRD facilities.

REFERENCES

1. K. Vinod Wadhawan, Introduction to Ferroic Materials, Gordon and Breach Publishers, London (New York)(2000).
2. Antony R. West, Solid State Chemistry, John Wiley and Sons, Singapore, p115,102(1998).
3. Kittel Charles, Introduction to Solid State Physics, New Delhi, Wiley Eastern Limited (1993).
4. Sachio Horiuchi, Reiji Kumai, Yoshinori Tokura, *J. Am. Chem. Soc.*, **127**,5010(2005).
5. B.B.Ivanova, M.Spiteller, *J. Phys. Chem. A*, **114**(15), 5099 (2010).
6. K.Rajarajan, P.Joseph Ginson, M.Ravi Kumar, I .Vetha Potheher, A. Joseph Arul Pragasam, K. Ambujam, P.Sagayaraj, *Materials and Manufacturing Processes.*, **22**, 370 (2007).
7. Tanusri Pal, Tanusree Kar, Gabriele Bocelli, and Lara Rigi, Synthesis, Growth, and Characterization of l-Arginine Acetate Crystal- A Potential NLO Material, *Cryst. Growth Des.*, **3**(1), 13(2003).
8. O. Auciello, J.F. Scott, and R. Ramesh, *Phys. Today*, **51**, 22 (1998).
9. J. Dolinsek, D. Arcon, Hae Jin Kim, J. Seliger, V. Zagar, P. Vanek, J. Kroupa, Z. Zikmund, J. Petzelt, *Phys. Rev. B* , **57**, R8063(1998).
10. Lesley Smart and Eaine Moore, Solid State Chemistry, Chapman and Hali, 2nd edition, p79(2004).
11. S. Krishnan, C. Justin Raj, S. Jerome Das, *J. Crystal Growth*, **310** ,3313(2008).
12. S. Suresh and K. Anand, *Advances in Applied Science Research*, **3**(2),815(2012).
13. S.Boomadevi, H.P.Mittal, R.Dhanasekaran, *J.Cryst.Growth.*, **261**,55(2004).
14. S.Goma, C.M.Padma, C.K.Mahadevan. *Lett.*, **60**, 3701(2006).
15. J.Madhavan, *J. Cryst.Res.Technol.*, **42**(1), 59 (2007).
16. S.K.Arora, V.Patel, B.Amin, A.Kothari., *Bull.Mater.Sci.*, **27**, 141-147(2004).
17. V.Rajendran, S.Gnanam, *Der Pharma Chemica*, **3** (6), 606 (2011).
18. C.Miller, *Appl.Phys. Lett.*, **5**, 17(1964).

[RJC-1075/2013]