

Growth and Characterization of Pure and Oxalic Acid Doped L-Arginine Acetate Single Crystals

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ABSTRACT

Single crystals of L-arginine acetate (LAA), a nonlinear optical (NLO) material, have been grown by free evaporation method and characterized chemically, structurally, thermally, optically, mechanically and electrically. Effect of oxalic acid as an impurity (added at different concentrations) on the properties of LAA has also been investigated. X-ray diffraction analysis indicates the crystal system as monoclinic. The functional groups have been identified using Fourier transform infrared spectral analysis. The crystals are found to be thermally stable upto 199.80°C. The UV-Vis spectral analysis shows that these crystals have wide transparency range in the entire visible region. Second harmonic generation (SHG) measurement shows the NLO property. Microhardness measurement indicates that the grown crystals come under soft material category. Dielectric measurements are carried out at various temperatures ranging from 40- 140°C and with various frequencies ranging from 1kHz to 100kHz by the parallel plate capacitor methods. The low dielectric constant values observed for pure LAA indicate that LAA is not only a promising NLO material but also a low dielectric constant value dielectric material.

Key words: L-Arginine Acetate, slow evaporation technique, doping effects.

I. Introduction

L-Arginine is an amino acid that forms a series of complexes upon reaction with different acids [1]. Following this, series of amino acid crystals such as L-arginine acetate (LAA), L-arginine hydrobromide (LAHBr), L-arginine hydrochloride (LAHCl), L-argininediphosphate, L-arginine hydrofluoride (LAHF), L-arginine dinitrate (LHDN) were grown and their studies have been reported. These crystals were reported to have promising NLO properties comparable to that of the well-known inorganic crystals of KDP. L-arginine acetate (LAA) is a nonlinear optical material, which has its powder SHG efficiency nearly three times that of KDP [2]. A considerable interest has been shown recently in studying the effect of impurities (both organic and inorganic) on the growth and properties of some hydrogen bonded crystals. The presence of impurity molecules, even at lower concentrations in the parent solute, may have considerable effect on growth kinetics and other properties on LAA crystals are already reported by several research workers and results obtained are reported [2,3,4,5,6].

In the present work, we have made attempts to grow hybrid materials of LAA crystals by doping oxalic acid taken at different concentrations and investigated the effect of it on the various properties of the crystals. Results obtained are reported herein.

II. 2. Experimental

2.1 Crystal growth

Analytical Reagent grade L-Arginine and acetic acid are taken in the equimolar ratio (1:1) and

dissolved in doubly deionised water to synthesize LAA according to the reaction $(\text{NH}_2)\text{NH}\text{CNH}(\text{CH}_2)_3\text{CH}(\text{NH}_2)\text{COOH} + \text{CH}_3\text{COOH} \rightarrow (\text{NH}_2)^+\text{CNH}(\text{CH}_2)_3\text{CH}(\text{NH}_3)^+\text{COO}^-\text{CH}_3\text{COO}^-$

The solution was stirred well at constant rate to get homogeneity. The solution was transferred to a beaker and it was allowed to evaporate at room temperature for a few days to get the undoped LAA.

To obtain oxalic acid doped LAA, 0.06mol.% 0.08mol.% , 0.1mol% & 0.2mol% of oxalic acid were added to the above solution of LAA and similar procedure was followed. The pure and doped crystals are yielded within a period of 15-20 days. Good quality crystals are obtained for pH 5 and 6 and are represented as pure LAA for LAA, LAAO1, LAAO2, LAAO3, and LAAO4 respectively.

2.2 Characterizations

The densities of the crystals are measured by the floatation method in a mixture of carbon tetra chloride (density-1.592gm/cc) and hexane (0.652gm/cc) taken as high and low density liquids respectively.

CHNS analysis is done using Elementar Vario EL III, Germany, to estimate carbon, hydrogen and nitrogen contents, present in the grown crystals.

The grown crystals are subjected to single crystal X-Ray diffraction (SXRD) studies using ENRAF – NONIUS CAD4 single crystal X-Ray diffractometer. Pure and doped LAA crystals are subjected to powder X-Ray diffraction analysis (PXRD) using XPERT-PRO diffractometer with monochromated CuK_α radiation. The reflections are indexed, following the procedure of Lipson and Steeple.

The FTIR spectra are recorded using MAGNA 550 model spectrometer. In order to find the transparent nature of the crystals, UV-Vis spectra are recorded in the wavelength range 200-800nm using Vario Cary 500 scan spectrophotometer.

SHG measurements are made on the grown crystals using 1064nm, Quantam ray series). Molelectron powermeter, USA.

Thermal studies are carried out using SDT Q600 V8.3 Build 101 analyser for a temperature range 40° to 800°C in the air atmosphere to understand the thermal stability of the grown crystals.

Strength of the grown crystals are studied by measuring its microhardness with the help of Leitz microhardness tester.

The capacitance (C_{crys}) and dielectric loss factor (tanδ) measurements are carried out to an accuracy of ±1% for all the crystals grown by having the large area faces touching the electrodes by the conventional parallel plate capacitor method using LCR meter (Agilent 4284A) at various temperature ranging from 40-140°C with three different frequencies, viz. 1kHz, 10kHz, and 100kHz. The temperature is controlled to an accuracy of ±1°C. The observations are made while cooling the sample. The dimensions of the crystal are measured using a traveling microscope. Air capacitance (C_{air}) is also measured. Since the variation of air capacitance with frequency is found to be negligible, air capacitance is measured only at the lower frequency is considered. The crystals are shaped and polished and the opposite faces are coated with graphite to form a good conductive surface layer (ohmic contact). The sample was mounted between the silver electrodes and annealed at 140°C for about 30 min to homogenize the sample before taking the readings.

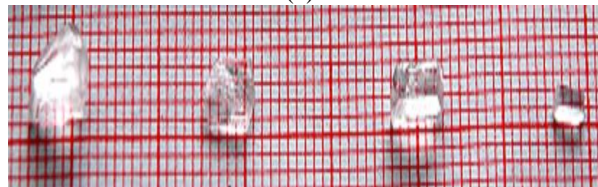
III. 3. Results and discussion

3.1 Densities, Lattice parameters and chemical composition

The crystals grown in the present study, both pure and doped LAA are found to be colourless and transparent. The photographs of the sample crystals grown are shown in Fig.(1). It is found that, as dopant concentration increases the transparency of the crystal increases.



(a)



(b)

Fig (1) photographs of the sample crystals grown (a) LAA- pure LAA (b) from left LAAO1 – LAA+ 0.06mol% oxalic acid, LAAO2 – LAA + 0.08mol.% oxalic acid, LAAO3 – LAA + 0.1mol.% oxalic acid, LAAO4 – LAA + 0.2mol.% oxalic acid

The densities of the crystals are measured by the floatation method in a mixture of carbon tetra chloride (density-1.592gm/cc) and hexane (0.652gm/cc) taken as high and low density liquids and are given in table.2.

The weight percentage of carbon, hydrogen and nitrogen present in both pure and doped LAA are shown in table.1. Oxalic acid also contains C,H atoms. Variation in C,N&H concentration from that C,N,&H of the pure LAA crystal shows the incorporation of the dopants into the crystal lattice.

Table:1 Chemical analysis of pure and doped LAA

Crystal	Composition %		
	C	H	N
LAA	40.98	12.82	24.52
LAAO1	40.89	11.40	24.29
LAAO2	40.92	13.16	24.46
LAAO3	40.88	11.66	24.29
LAAO4	40.82	10.03	24.17

pure and doped LAA crystals. The FTIR analysis of pure and doped LAA is shown in the table 3. The IR spectra of oxalic acid doped crystals of LAA are almost similar to that of the spectrum of pure LAA crystals.

The spectra for doped crystals reveal a remarkable change in absorption level due to stretching modes, in between the band ranging from 1600 to 1200 cm^{-1} when the molar concentration of the doping agent is increased. From these variations, we can expect the dopant inclusion into the crystal lattice.

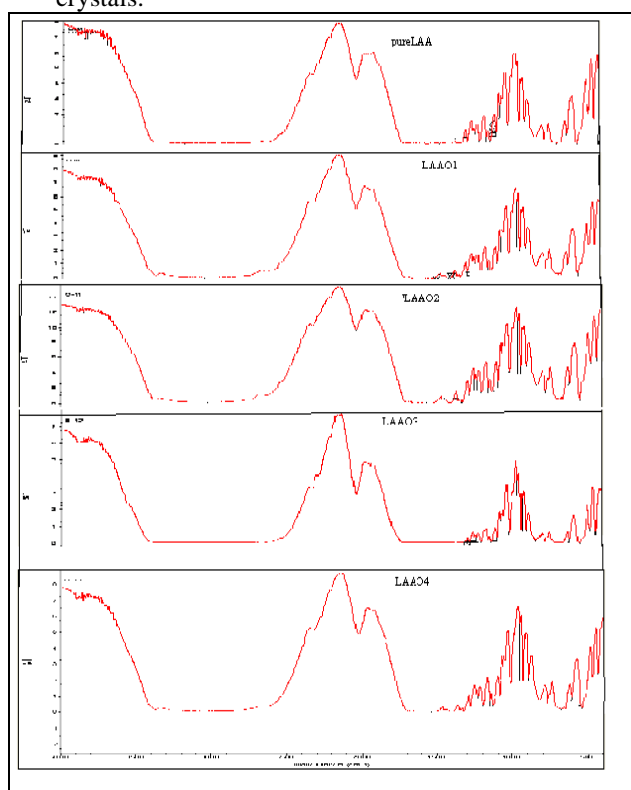


Fig:3 FTIR spectra for the samples from the top pure LAA, LAAO1, LAAO2, LAAO3 andLAAO4

Table 3: FTIR Analysis

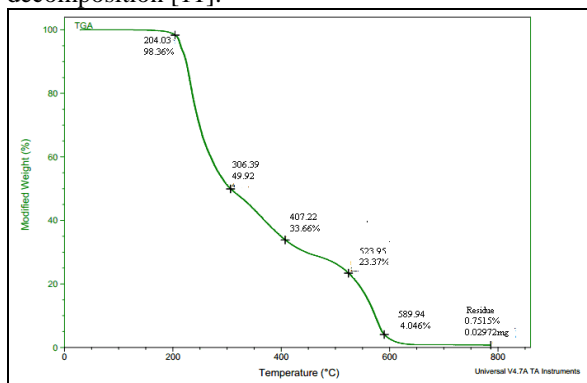
LAA Reported cm^{-1}	LAA (present work) cm^{-1}	LAAO1 cm^{-1}	LAAO2 cm^{-1}	LAAO3 cm^{-1}	LAAO4 cm^{-1}	Assignment
3750-2300	3900-2300	3900-2300	3900-2300	3900-2300	3900-2300	3750-2300 NH and CH stretching vibrations
2025	2025.78	2025.78	2025.77	2025.90	2025.79	Asym.NH3+ bending
1532	1557.11	1647.63	1539.56	1580.43	1536.97	Asymmetric stretching modes of COO-
			1400.37			CH3 symmetric deformation
		1322.66	1323.00		1322.71	Stretching vibration of CO
	1278.09	1277.93	1278.08		1278.01	CH ₂ twisting
1228	1229.10	1228.82	1228.99	1229.98	1228.94	C-C-COO vibrations
1197	1197.02	1196.87	1196.22	1197.05	1197.13	-COO vibrations
1093	1089.74	1089.51	1089.63	1089.63	1089.57	C-CN stretching vibrations
928	928.93	928.92	929.00.88	928.94	928.94	C-CH bending
				914.83		Overtone of torsional oscillation of NH3+
670	675.87	653.24	653.09	6752.19	671.47	NH out of plane bending

3.2 Thermal, Optical and mechanical properties

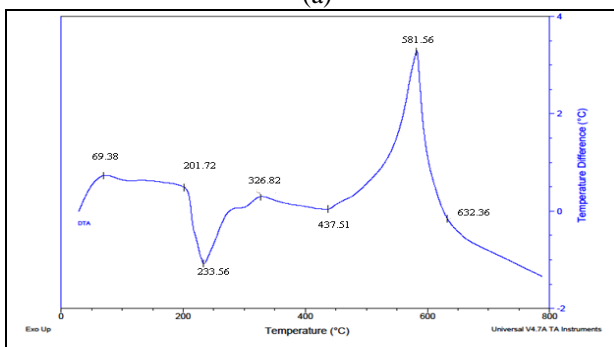
The TG/DTA analyses of LAA are shown in fig.5.(a), (b).and (c). From the curves it is observed

that the decomposition of LAA starts at 204.03°C. This is supported by the DTA analysis where the endothermic reaction is observed at 201.72°C. It can be seen from the thermal analysis that LAA is subjected to continuous heating does not remain stable for a long temperature change. However it is decomposed at a temperature 581.56°C and forms a residue. Above 632.36°C the product is stable without any prominent weight loss. For LAAO4 the TG/DTA curves are shown in fig.2(d). It starts decomposing at 199.80°C. Other decomposition temperature points are 282.64°C, 400.41°C, 516.55°C and 580.71°C. Above 741.09°C there is no prominent weight loss.

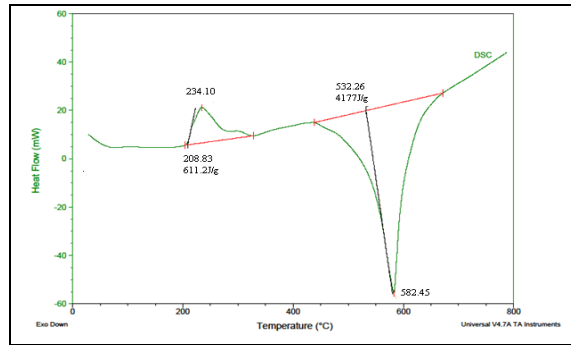
The DSC analysis for LAA and LAAO4 are carried out between 20°C and 750°C in air atmosphere. The curves are shown in fig 5(c) and (e) respectively. Since there is no endo or exothermic transitions below 200°C, the materials are proved to be stable in this region. The resistivity of the materials against thermal crack is evident as the DSC trace is smooth upto nearly 200°C. It is the property observed for compounds where the lattice force is more predominating than the covalent bonding forces in molecules. It is also observed that the electrostatic force that originated as a result of perfect proton transfer between acetic acid and L-arginine becomes dominating to provide resistance to melting before decomposition [11].



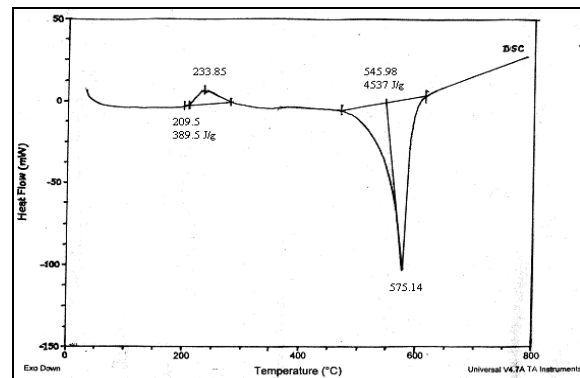
(a)



(b)



(d)



(e)

Fig.5 TG/DTA and DSC curves of pure LAA and LAAO4 crystals

The range and percentage of optical transmission of pure and doped LAA crystals are studied by using the UV – Vis spectra of the grown crystals recorded in the range 200 – 800nm. The spectra of pure and oxalic acid doped LAA are shown in the fig.4.

Table4: cutoff wavelength and forbidden bandgap energy .

samples	Cutoff wavelength (nm)	Forbidden bandgap E_g (eV)
LAA	236.36	5.256
LAAO1	238.09	5.217
LAAO2	241.66	5.141
LAAO3	239.83	5.180
LAAO4	231.17	5.374

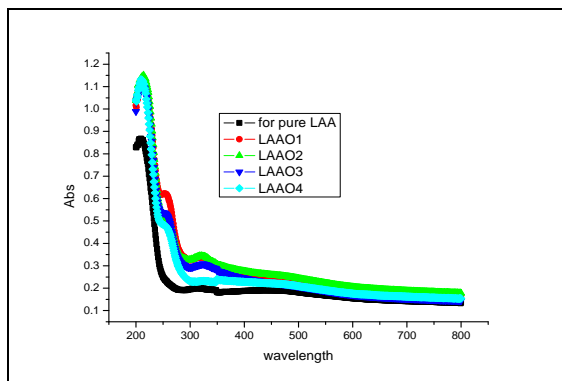


Fig.4 UV-Visible Spectra for the samples

The cutoff wavelength and forbidden energy gap (E_g) of both pure and doped LAA crystals are given in table 4.

It is observed that the lower cut off wavelength is around 240nm, and the transparency conveniently extends to 800nm. From the high energy edge of transmission the forbidden energy gap E_g for both pure and oxalic acid doped LAA crystals are around 5.3 eV.

The SHG of the grown samples were confirmed by Kurtz & Perry method. Nd:YAG laser of 1064nm wavelength was used to irradiate the samples. Second harmonic signal was captured by the oscilloscope through the photomultiplier tube. Urea crystal was used as a reference material in the SHG measurement. The samples are tested using i/p pulse 0.68J. The second harmonic signal obtained for both pure and doped LAA crystals, with reference to urea and the SHG efficiencies are found to be comparable to urea.

Table:5 SHG efficiencies of pure and doped LAA crystals

i/p power = 0.69J

Crystal samples	Output power(mJ)	Efficiency
LAA	7.2	.81 times urea
LAAO1	6.1	.69 times urea
LAAO2	5.2	.59 times urea
LAAO3	7.8	.89 times urea
LAAO4	7.6	.85 times urea

Hardness is defined as the resistance offered by a material to external mechanical action endeavoring to scratch, indent, or any other way affects its structure. Microhardness measurements of the grown crystals were done using Vicker's Hardness Indenter using Leitz Weitzler Hardness Tester. The indentation time was fixed. Vicker's Hardness Number (H_V) is calculated using the relation

$$H_V = 1.8554P/d^2 \text{ Kgmm}^{-2}$$

Where P is the load applied and d is the diagonal length of the indented impressions. A plot between the load P and hardness number H_V is shown in fig.6 which indicates that the hardness number increases with increasing load. Hardness number is found to be varying with the variation in the concentration of the dopant in the lattice of the crystals.

Table3 :Microhardness data for pure and doped LAA crystals

Crystal	Microhardness number (H_V) for a load of (kg/mm^2)			Work hardening coefficient(n)
	25g	50g	100g	
Pure LAA	60.45	91.30	109	3.36135
LAAO1	16.10	31.8	39.9	4.40778
LAAO2	30.25	47.30	77.85	6.26963
LAAO3	37.75	44.05	57.05	2.83932
LAAO4	38.1	54.95	72.70	2.24796

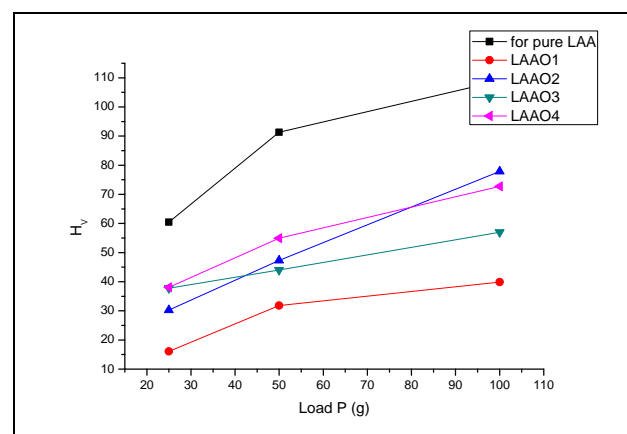


Fig.6 Variation of Vicker's hardness number with load P for pure and doped LAA crystals.

From the plots, it can be noted that the hardness of the crystal increases with increasing load for both pure and doped samples. Log d vs Log P graphs are drawn, the slope of the curves 'n' for the pure and doped LAA are determined using least square fit method and the values of "n" are found to

be greater than 2, hence the materials are said to be soft ones.

According to Onitsch, if $n > 2$ the materials are said to be soft ones. He also found that microhardness increases with increasing load when $n > 2$ and decreases with increasing load when $n < 2$. The increase in H_v for increasing load observed in the present study is a good agreement with the theoretical prediction.

The study of dielectric constant of a material gives an outline about the nature of atoms, ions and their bonding in the material. The capacitances and dielectric loss factors are measured along the major growth direction of all the crystals using the conventional parallel plate capacitor method with frequencies 1KHz, 10KHz, & 100KHz using an LCR meter at various temperatures ranging from 40-140°C. The observations are made while cooling the samples. The dimension of the crystals are measured using travelling microscope ($LC = 0.001\text{cm}$). Air capacitances are also measured. As the variation of air capacitance with frequencies is found to be negligible, air capacitance is measured at the minimum frequency 1KHz.

The dielectric constant of the crystals is calculated by using the relation

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

where d is the thickness of the sample, A is the area of the face in contact with the electrode and ϵ_0 is the permittivity of the free space $= 8.854 \times 10^{-12} \text{ F/m}$.

As the crystal area is smaller than the plate area of the cell, parallel capacitance of the portion of the cell not filled with the crystal is taken into account and consequently, the above relation becomes

$$\epsilon_r = (A_{\text{air}}/A_{\text{cryst}}) ((C_{\text{crys}} - C_{\text{air}}) (1 - A_{\text{cryst}}/A_{\text{air}}))/C_{\text{air}}$$

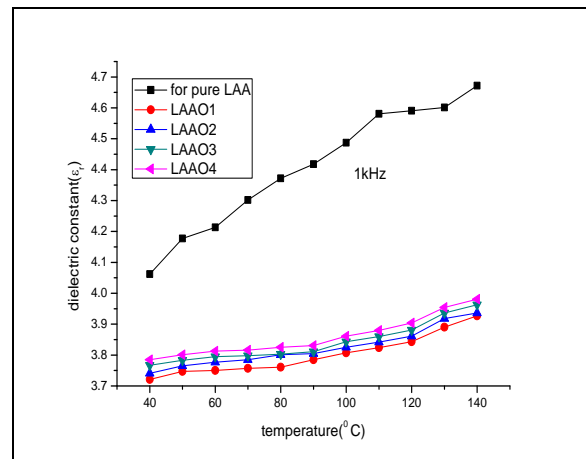
where C_{crys} is the capacitance with crystal (including air), C_{air} is the capacitance of air, A_{crys} is the area of the electrode.

The AC electrical conductivity, σ_{AC} is calculated using the relation .

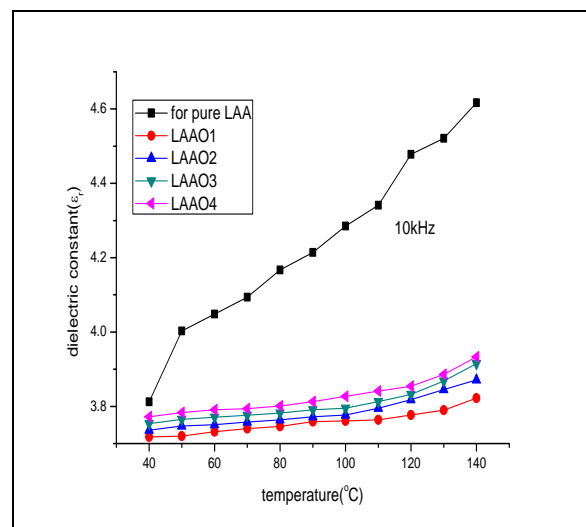
$$\sigma_{AC} = \epsilon_0 \epsilon_r \tan \delta \omega$$

where ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) ω is the angular frequency ($\omega = 2\pi f$; $f = 1\text{KHz}, 10\text{KHz} \& 100\text{KHz}$) in the present study and $\tan \delta$ is the dielectric loss factor.

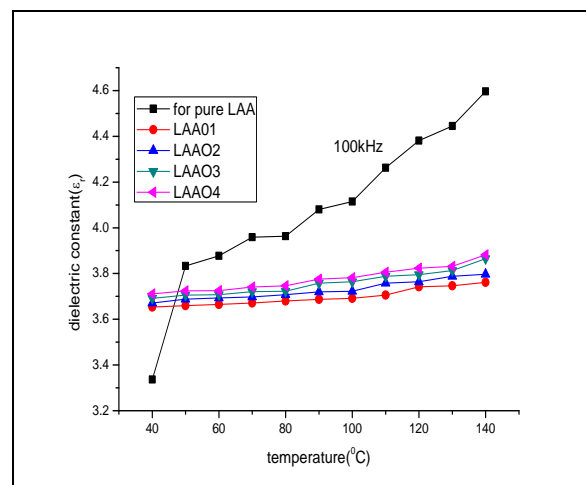
The ϵ_r , $\tan \delta$ and σ_{AC} values in the present study with frequencies 1KHz, 10KHz, 100KHz are shown in fig.7



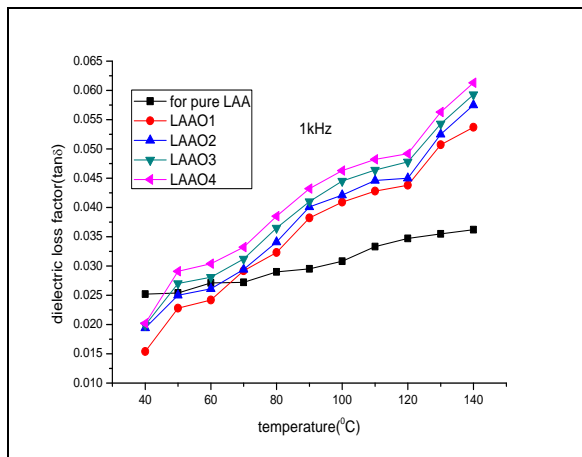
(a)



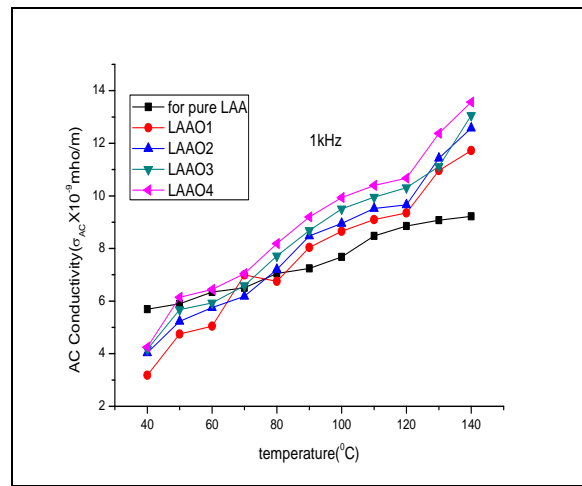
(b)



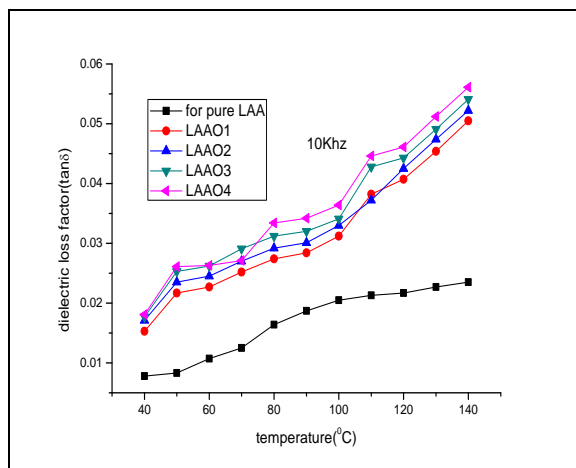
(c)



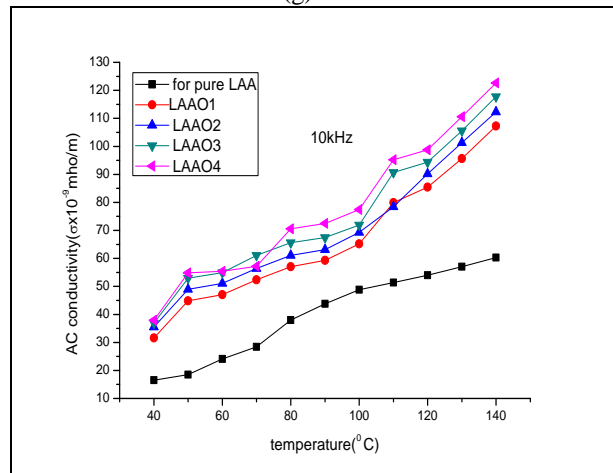
(d)



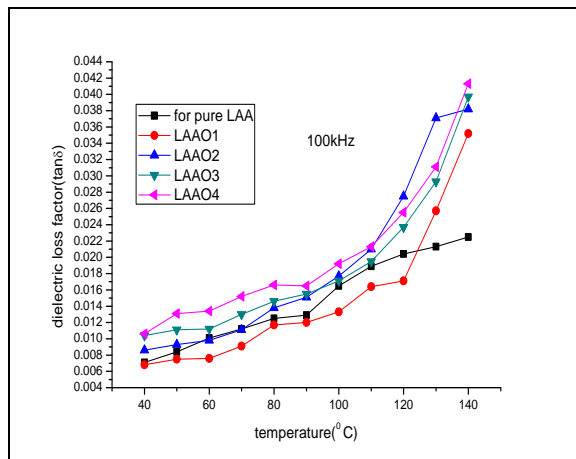
(g)



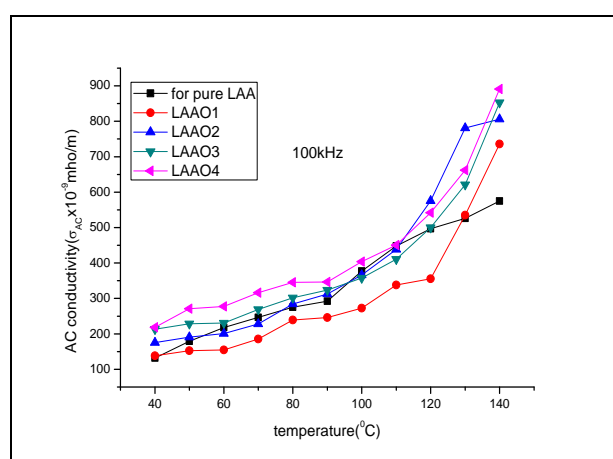
(e)



(h)



(f)



(i)

Fig 7. (a), (b), (c) temperature vs ϵ_r
 (d), (e), (f) temperature vs $\tan\delta$
 (g), (h), (i) temperature vs σ_{AC}

It has been found that, ϵ_r , $\tan\delta$ are found to decrease whereas σ_{AC} values are found to increase with the increase in frequency. This is normal dielectric behaviour.

IV. CONCLUSION

Pure and oxalic acid doped LAA are grown by slow evaporation method. Single crystal X-ray studies confirm that both the pure and doped LAA crystals belong to monoclinic system. The PXRD patterns were indexed. The data obtained by XRD analysis and evaluation of lattice parameters have confirmed that the dopant oxalic acid have entered into the lattices of LAA crystals. The samples were chemically confirmed by obtaining CHNS data. Optical absorption in the visible range and the small variation in the UV range is due to the crystalline perfection of the grown crystals. Nonlinear property was confirmed and the SHG efficiency was found. From Vicker's microhardness test, it is confirmed the grown pure and doped crystals are soft materials making the grown crystals to be the efficient NLO materials. From dielectric studies of the crystals it is known that the organic impurity oxalic acid have reduced the ϵ_r value for a wide temperature range, 40-140° C to make LAA a more interesting material in the microelectronics industry.

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