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Effect of added impurities on the electrical properties of L-arginine acetate single crystals

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ABSTRACT

L-arginine acetate (LAA) single crystal is an interesting nonlinear optical and dielectric material. In order to understand the effect of some impurities (both inorganic and organic) on the electrical properties of LAA, we have grown from aqueous solutions pure and impurity (NaC/KCl/glycine/urea) added single crystals and electrically characterized. DC and AC (with five different frequencies, viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz) electrical measurements were carried out at various temperatures ranging from 40-150^oC along both a- and c- directions. Results indicate an increase of the electrical parameters, viz. σ_{ac}, ε_r, tanδ and σ_{dc} with the increase of temperature. The results also indicate that the organic impurities decrease the ε_r value < 4.0 for a wide temperature range, 40-150^oC.

Keywords : Crystallization, doping effects, electrical measurements

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INTRODUCTION

Crystalline salts of L-arginine have attracted considerable interest among researchers. L-arginine acetate (LAA) is one among them which is considered to be a potential nonlinear optical (NLO) material and several reports are available on it [1-7]. Recently, we have found [7] that LAA is also a promising low ε_r value dielectric material. LAA crystallizes in the monoclinic system with space group $P2_1$ and the lattice parameters are a = 9.226 Å, b = 5.243 Å, c = 13.049 Å, β = 108.92 and V = 597.14 Å^3 [4]. It has a transmission range extending from 240 nm and could be used as an ultraviolet NLO material. It is thermodynamically stable atleast upto 200^{o}C. The measured density is 1.346 g/ml [4].

A considerable interest has been shown recently in studying the effect of impurities (both inorganic and organic) on the nucleation, growth and physical properties of some hydrogen bonded crystals like potassium dihydrogen orthophosphate (KDP), ammonium dihydrogen orthophosphate (ADP), magnesium sulphate heptahydrate (MSH) and zinc tris (thiourea) sulphate (ZTS). The presence of impurity molecules, even at lower concentrations in the parent solute, may have considerable effect on growth kinetics and other properties. Several interesting

results have already been reported on several properties of impurity added KDP [8-19], ADD [8, 19-27], MSH [28-31] and ZTS [26, 32-34] crystals. However, there is no report available on impurity added LAA single crystals.

Ananda Kumari and Chandramani [14] have found that the KDP crystals containing alkali halides (KCl/NaCl/KBr/NaBr/KI/NaI) have appreciable increase in second harmonic generation (SHG) efficiency compared to pure KDP crystals. Deepa et al [13] have observed that the alkali halide (NaCl/NaBr) addition reduces the DC conductivity of KDP single crystals. Anne Assencia and Mahadevan [25] have observed that the DC conductivity of ADP single crystal increases with the increase in impurity (urea/thiourea) concentration. Mahadevan [30] has found that the DC conductivity does not vary systematically with impurity concentration in the case of KCl and KNO_3 added MSH single crystals. However, the conductivity values are larger for impurity added ones than that observed for the pure MSH crystals. Meena and Mahadevan [19] have observed that L-arginine addition leads to reduction of electrical parameters of KDP and ADP single crystals. Considering the above, it can be understood that impurity (various types) addition to LAA is expected to make it a more interesting material. Hence, understanding the effect of different kinds of impurities on the physical properties of this material needs several more investigations.

In the present work, we have grown LAA single crystals by the slow cooling method [7] and investigated the effect of NaCl, KCl, glycine and urea (added separately) as impurities on the electrical properties of it. Results obtained are reported herein.

MATERIALS AND METHODS

Experimental

Analytical reagent (AR) grade samples of L-arginine, acetic acid, NaCl, KCl, glycine and urea along with double distilled water were used for the growth of pure and impurity added LAA single crystals. The LAA salt was prepared by dissolving in water equimolar ratio of acetic acid and L-arginine and kept for the reaction to take place. The product was then purified by repeated crystallization until optically clear tiny crystals were obtained. The LAA was added separately with NaCl, KCl, glycine and urea in $5x10^{-3}$ mole fraction.

Small (seed) crystals were grown from saturated aqueous solution by the free evaporation technique at constant temperature (30^oC). Good quality seed crystals were selected for the growth of large single crystals. Large size single crystals were grown by the slow cooling method using an optically heated constant temperature bath of control accuracy $\pm$ 0.01^oC set at 45^oC. A cooling rate of 0.5^oC per day was employed throughout the growth period (about 30 days). All the five crystals considered (pure and impurity added LAA) grew along the c - direction.

As it was difficult to determine the impurity concentration in the crystal for the organic impurities considered (glycine and urea) since they have no metal atom, no experiment was carried out to determine this. Flame photometric measurements were carried out to determine the metal atom contents in the case of alkali halide impurities. The impurity concentration in the crystal was estimated for all the four impurity added single crystals grown by using the solubility data following the method adopted by Mahadevan and his co-workers [13, 19, 35].

If X- and Y are the initial concentrations (g/100 cc) of A and B the final stoichiometry will be $(X-A_x) : (Y-A_y)$ where A_x and A_y are the solubilities of components A and B respectively. In

order to avoid getting negative value for ($Y-A_y$) in the case of LAA crystal, the above ratio was modified (as done by the previous authors for KDP and ADP crystals) as (10000 X – A_x): (10000 Y – A_y).

The pure LAA crystal grown was subjected to powder X-ray diffraction (PXRD) and Fourier transform infrared (FTIR) spectral measurements to confirm the material of the crystal grown. The PXRD data were collected from powdered samples using an automated X-ray powder diffractometer (PANalytical) with scintillation counter and mono chromated CuK_α (λ= 1.54056Å) radiation. The reflections were indexed following the procedures of Lipson and Steeple [36]. Analysis of the X-ray diffraction peaks was done by the available methods and lattice parameters were determined [37]. The FTIR spectrum was recorded using FTIR Impact 410 spectrometer by the KBr pellet technique. The PXRD measurements were extended to the impurity added LAA crystals also and lattice parameters were determined in all the cases.

The capacitance (C_{crys}) and dielectric loss factor (tanδ) measurements were carried out on all the five grown crystals to an accuracy of $\pm$ 2% using an LCR meter (Agilent 4284A) with five different frequencies, viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz at various temperatures ranging from 40-150^{o}C along a-and c- directions in a way similar to that followed by Mahadevan and his co-workers [7, 17, 19]. The samples were annealed upto 150^{o}C to remove water molecules, if present. The observations were made while cooling the sample. Temperature was controlled to an accuracy of $\pm$ 1^{o}C. Air capacitance (C_{air}) was also measured. Measurement along b- direction was not considered due to the small crystal thickness for all the crystals studied.

Crystals with high transparency and surface defect-free (i.e. without any pit or crack or scratch on the surface, tested with a traveling microscope) were selected and used. The extended portions of the crystals were removed completely and the opposite faces were polished and coated with good quality graphite to obtain a good conductive surface layer. The dimensions of the crystals were measured using a traveling microscope (Least count = 0.001 cm).

The dielectric constant of the crystal was calculated using the relation (as the crystal area was smaller than the plate area of the cell) [7]

$$\varepsilon_r = \left(\frac{A_{air}}{A_{crys}}\right)\left(\frac{C_{crys} - C_{air}\left(1 - A_{crys}/A_{air}\right)}{C_{air}}\right),$$

where A_{crys} is the area of the crystal touching the electrode and A_{air} is the area of the electrode.

The AC conductivity (σ_{ac}) was calculated using the relation [7]

$$\sigma_{ac} = \varepsilon_o \varepsilon_r \omega \tan\delta,$$

where ε_o is the permittivity of free space (8.85 x 10^{-12} C^2 N^{-1} m^{-2}) and ω is the angular frequency.

The DC electrical conductivity measurements were carried out on all the five grown crystals to an accuracy of $\pm$3 % using the conventional two-probe (parallel plate capacitor) technique at various temperatures ranging from 40 to 150^{o}C along a- and c- directions in the way similar to that followed by Mahadevan and his co-workers [11, 19]. The resistance of the crystal was measured using a million megohmmeter. The observations were made while cooling the sample as in the case of dielectric measurements. Temperature was controlled to an accuracy of $\pm$1^{o}C. The samples were prepared and annealed in a way similar to that followed for dielectric measurements. The DC conductivity σ_{dc} of the crystal was calculated using the relation [19],

$$\sigma_{dc} = d/(RA)$$

where R is the measured resistance, d is the thickness of the sample and A is the area of the face in contact with the electrode.

RESULTS AND DISCUSSION

The crystals grown in the present study (pure LAA to a size of 15 x 5 x 24 mm^3, LAA + NaCl to a size of 12x4x20 mm^3, LAA+KCl to a size of 13x4.5x15 mm^3, LAA + glycine to a size of 10x6x12 mm^3 and LAA+ urea to a size of 14x5x16 mm^3) are found to be stable, colourless and transparent. Figure 1 shows the photograph of sample crystals grown.

The FTIR spectrum (Figure 2) obtained in the present study for the pure LAA is essentially identical with the already published [4] one with the understandable slight difference arising from instrumental and presentational errors. This shows that the grown crystal can be characterized as LAA crystal. The PXRD pattern for pure LAA (see Figure 3 (a)) obtained in the present study is also essentially identical with the already published one which again confirms the material of the grown crystal. The PXRD patterns obtained for the impurity added LAA crystals are nearly identical (but with some intensity differences) with that for the pure LAA (see Figure 3). This indicates that the impurity molecules considered in the present study do not disturb the LAA lattice significantly.

The lattice parameters obtained in the present study are provided in Table 1. The lattice parameters obtained in the present study for the pure LAA compare well with those obtained by Muralidharan et al [4]. However, the lattice volumes obtained for the impurity added LAA crystals indicate that the impurity molecules have entered into the crystal matrix of LAA.

Table 2 gives the estimated impurity concentrations in the crystal. The measured metal atom contents in the case of NaCl and KCl added LAA compare well with that estimated by using the solubility data. This confirms the presence of impurity molecules in the crystal matrix of LAA in the case of all the four impurity added LAA crystals.

Figure 1: Photograph of the sample crystals grown From left are: Pure LAA, NaCl added LAA, KCl added LAA, glycine added LAA, and urea added LAA

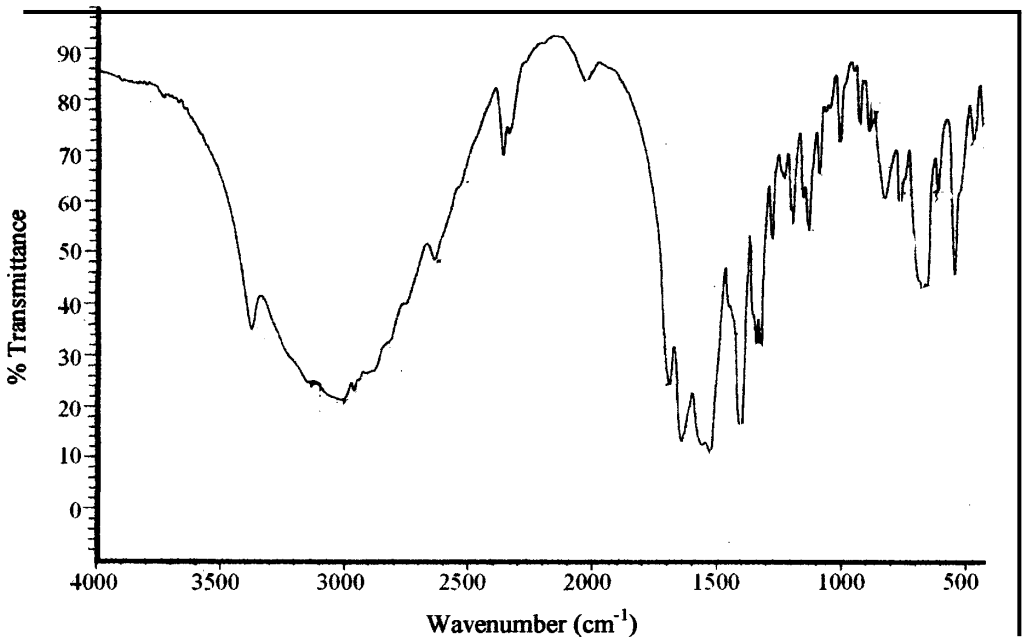
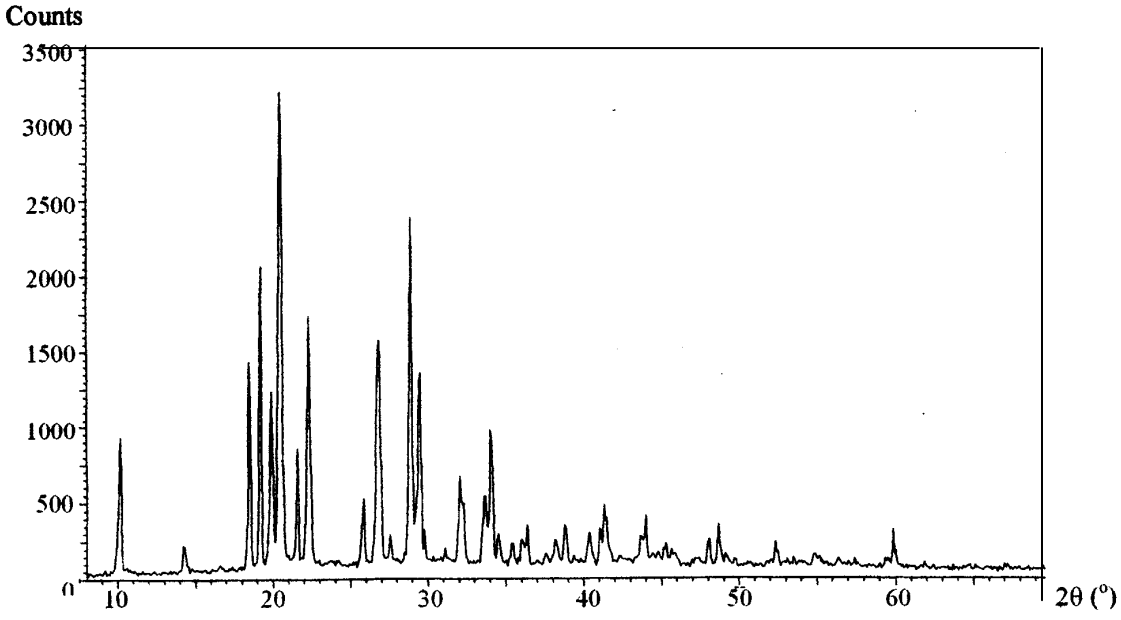
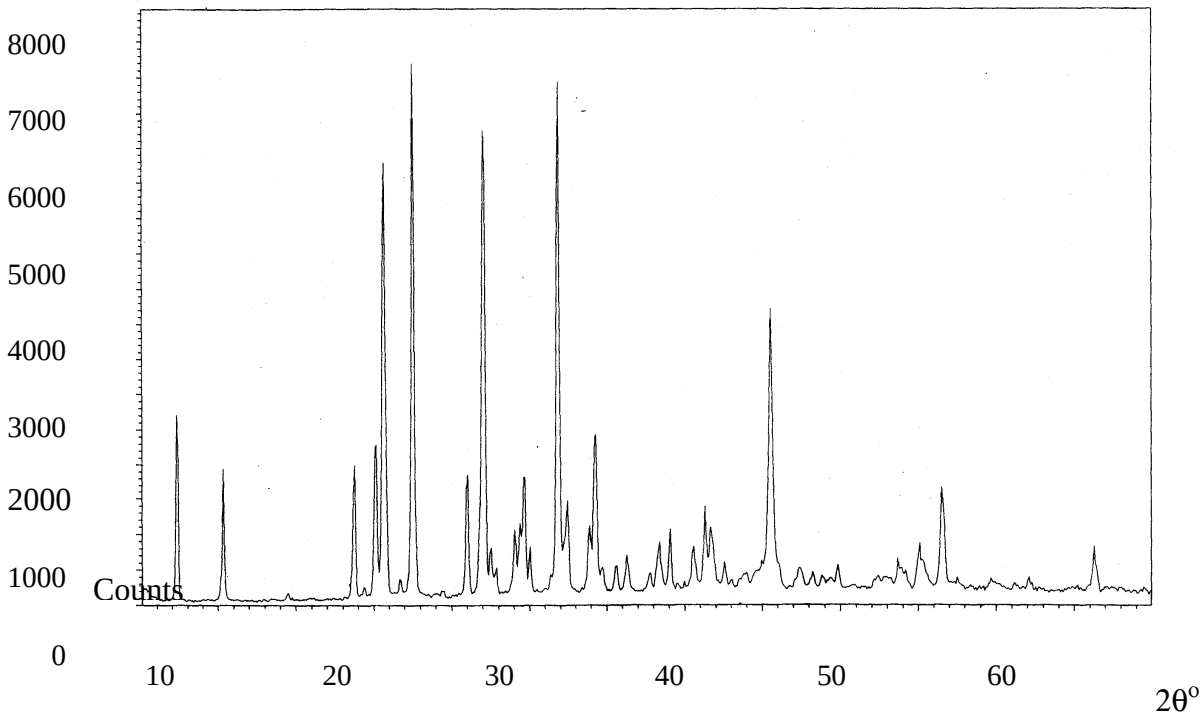


Figure 2: The FTIR spectrum obtained in the present study for pure LAA crystal



(a)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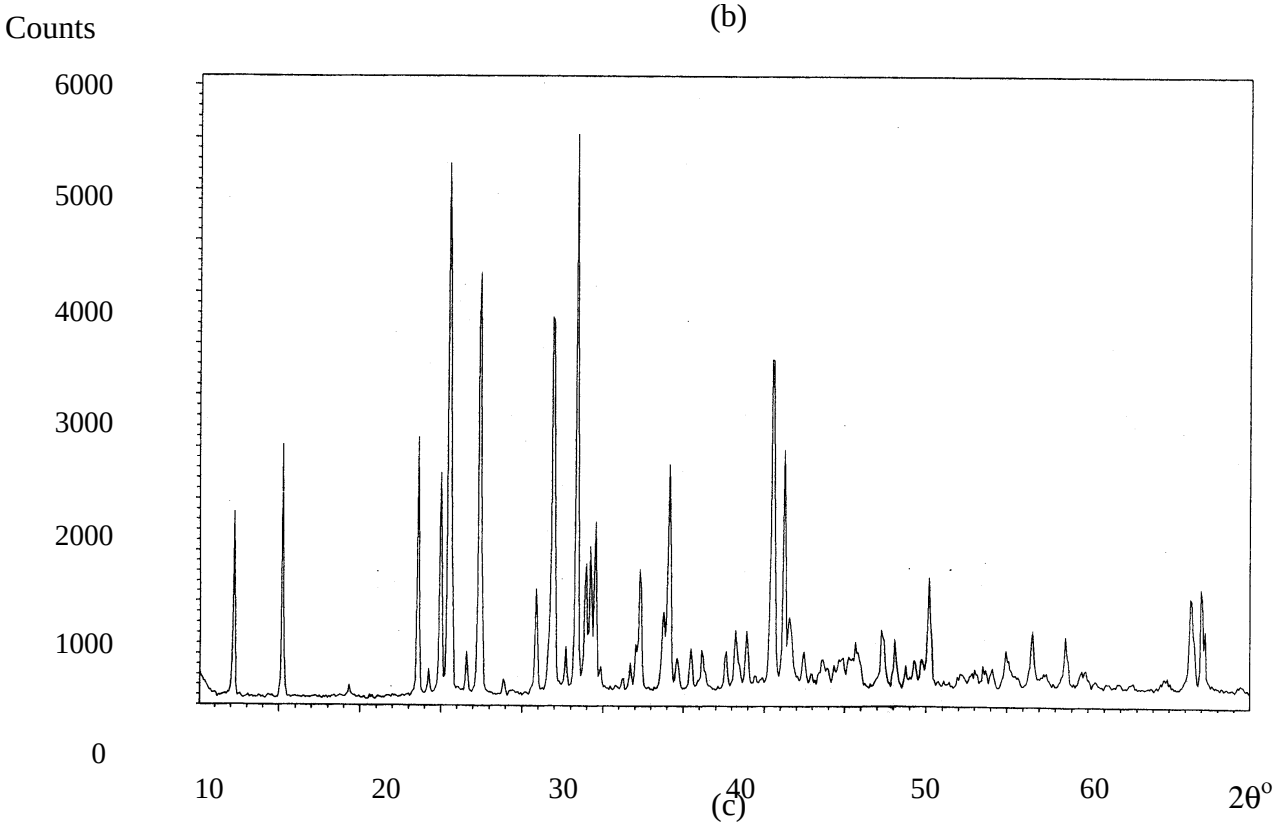
(b)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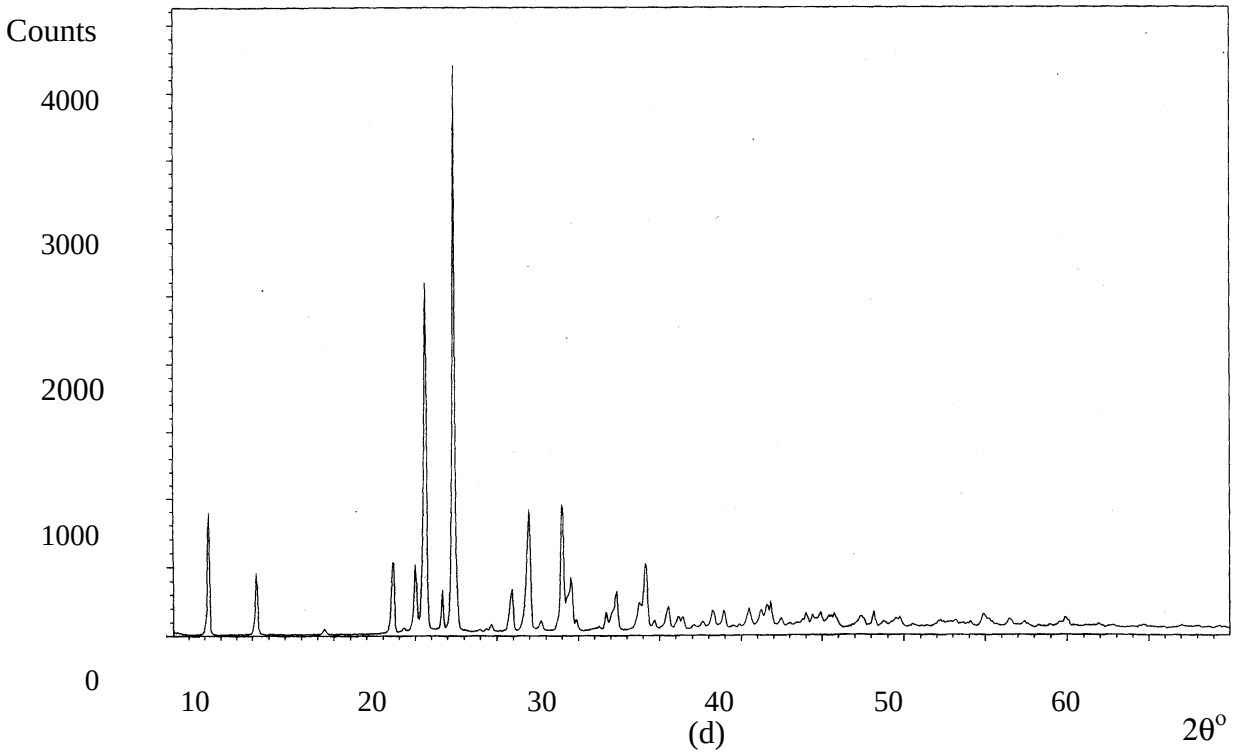

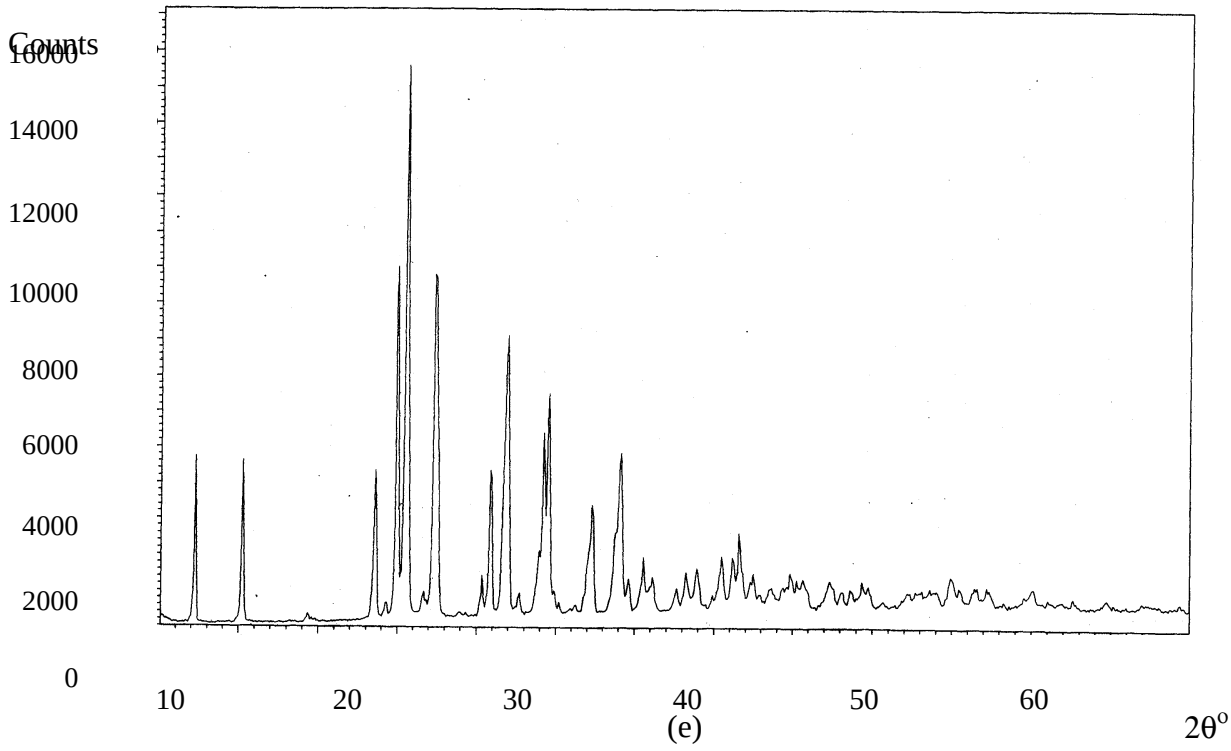

Figure 3: The PXRD patterns obtained in the present study for pure and impurity added LA
(a) For pure LAA (b) For LAA + NaCl (c) For LAA + KCl
(d) For LAA + glycine (e) For LAA + urea

The ε_r, tanδ, σ_{ac} and σ_{dc} values obtained in the present study with a frequency of 1kHz are shown in Figures 4-11. The ε_r, tanδ, σ_{ac} and σ_{dc} values obtained at 40°C with all the five frequencies

are provided in Table 3. The remaining data are not provided in order to limit the space. It has been found that the ε_r, tanδ and σ_{ac} values increase with the increase in temperature along both a- and c- directions and with all the five frequencies considered in the present study. The ε_r and tanδ values are found to decrease whereas the σ_{ac} value is found to increase with the increase in frequency along both a- and c- directions and at all temperatures. This is a normal dielectric behaviour. This can be understood on the basis that the mechanism of polarization is similar to the conduction process.

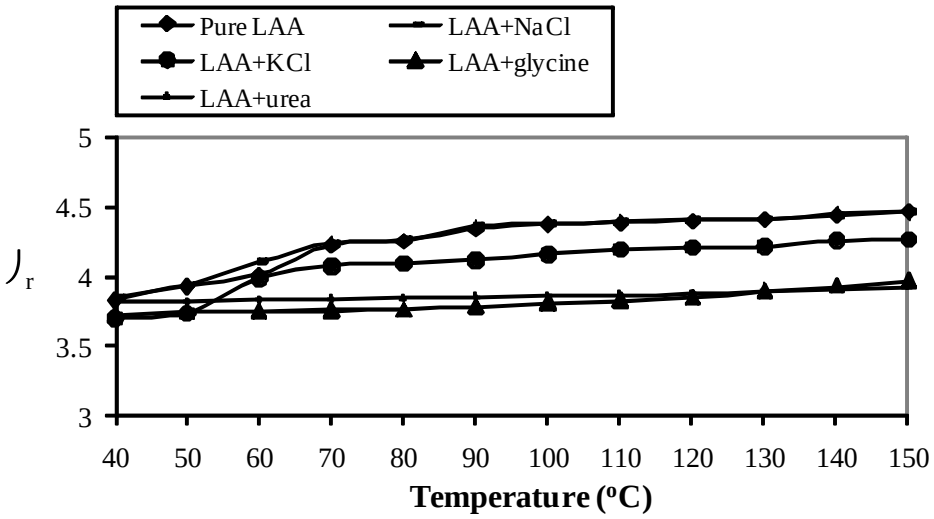

Figure 4: The dielectric constants for pure and impurity added LAA crystals along a- direction

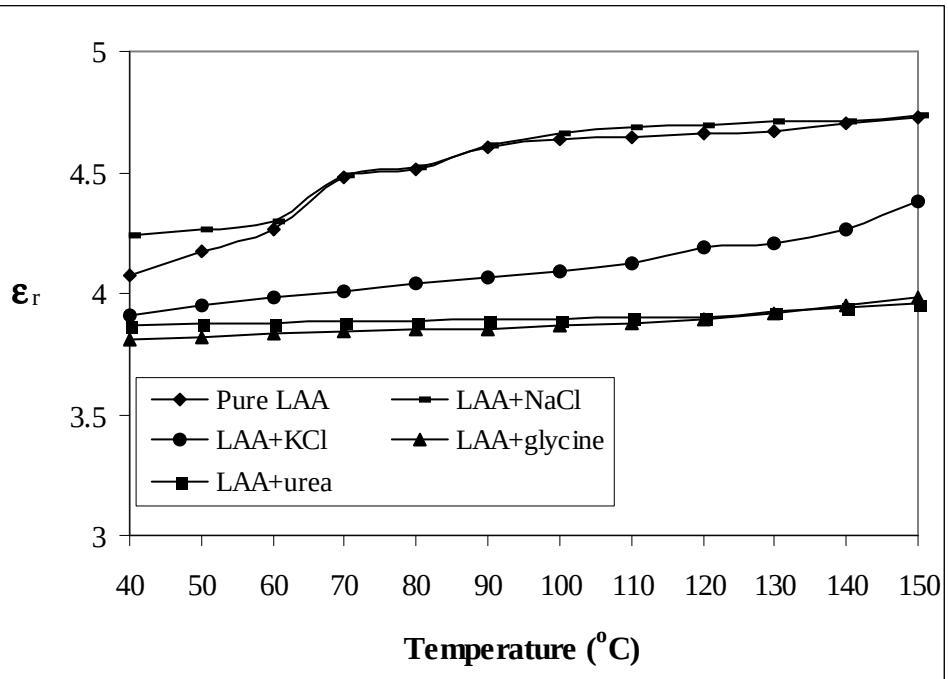

Figure 5: The dielectric constants for pure and impurity added LAA crystals along c- direction

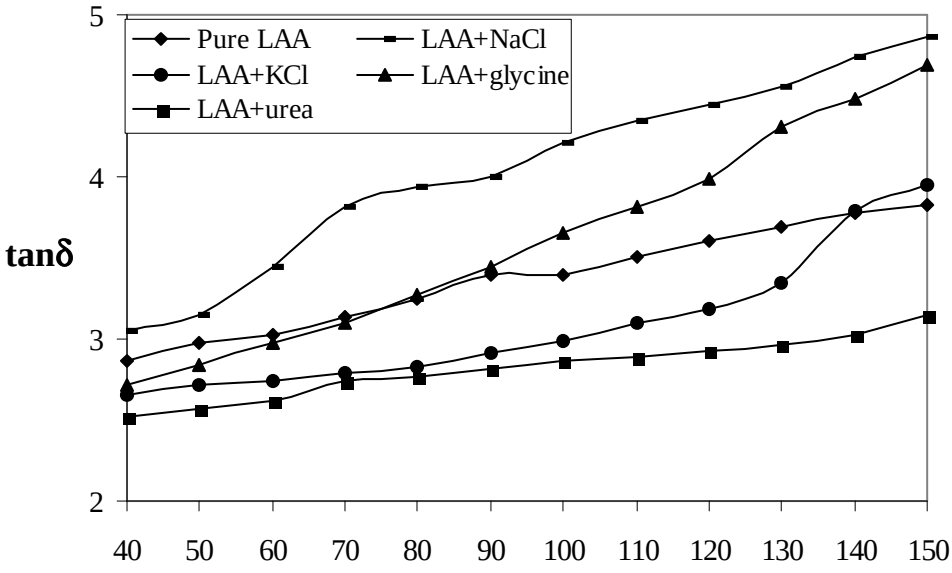

Figure 6: The dielectric loss factors ($x10^{-2}$) for pure and impurity added LAA crystals along a- direction

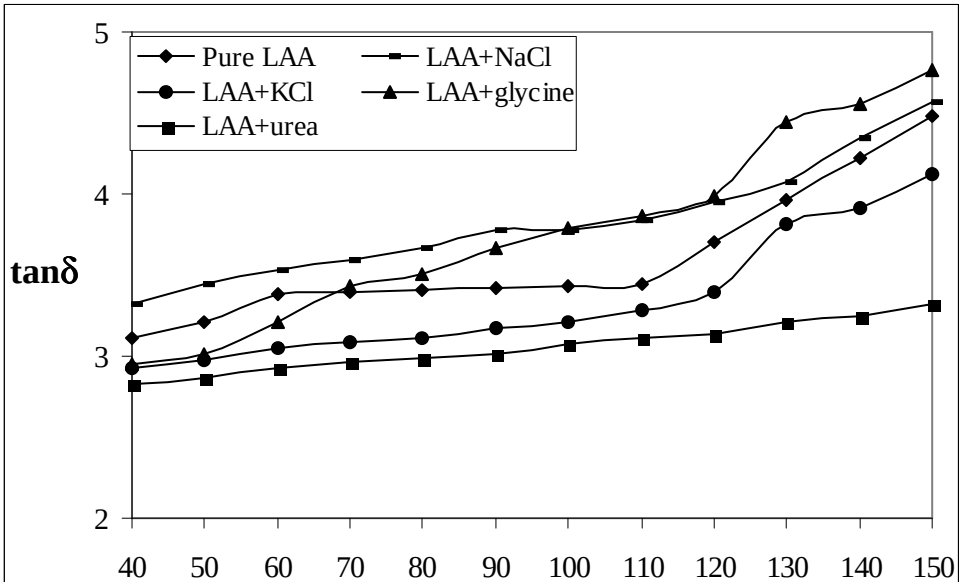

Figure 7: The dielectric loss factors ($x10^{-2}$) for pure and impurity added LAA crystals along c- direction

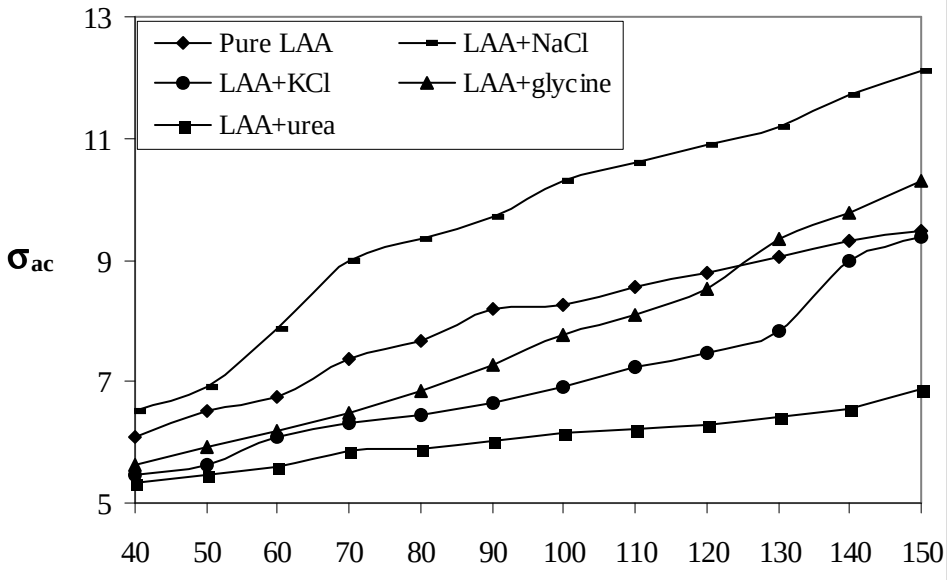

Figure 8: The AC elecrical conductivities (x10^{-9} mho/m) for pure and impurity added LAA crystals along a- direction

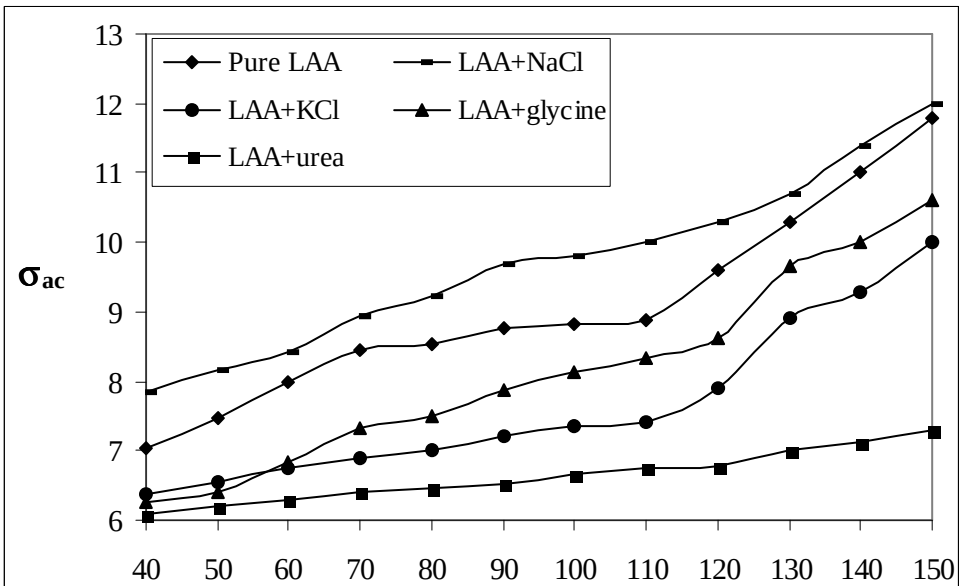

Figure 9: The AC elecrical conductivities (x10^{-9} mho/m) for pure and impurity added LAA crystals along c- direction

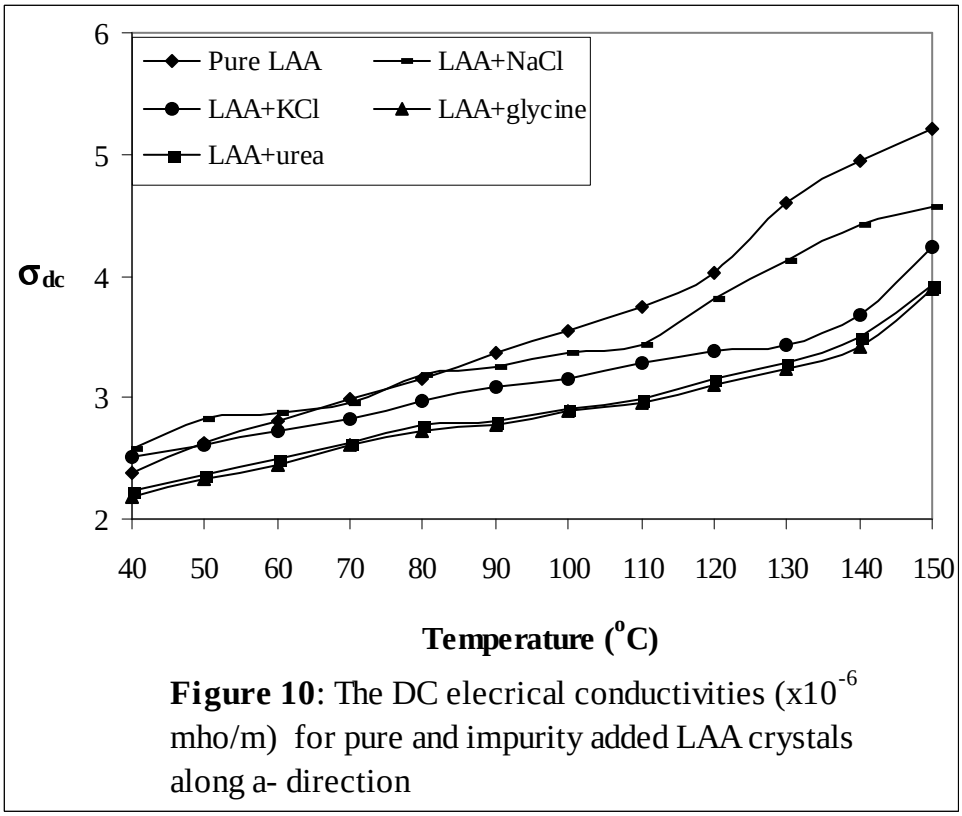

Figure 10: The DC elecrical conductivities (x10^{-6} mho/m) for pure and impurity added LAA crystals along a- direction

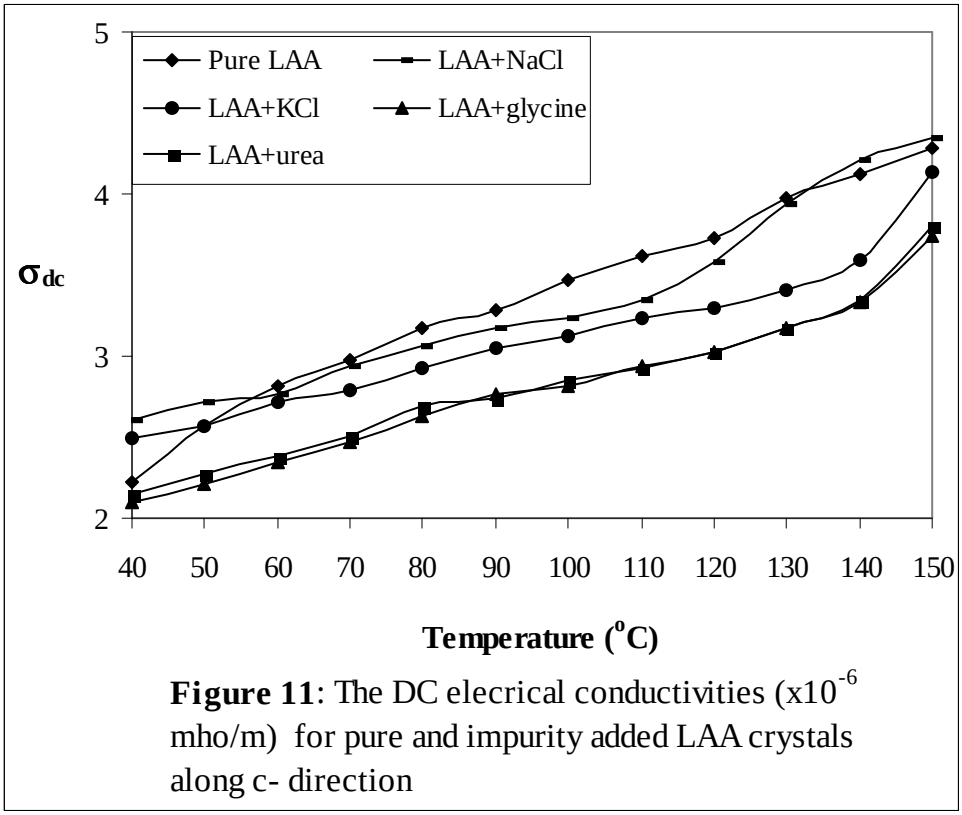

Figure 11: The DC elecrical conductivities (x10^{-6} mho/m) for pure and impurity added LAA crystals along c- direction

The electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization.

The conduction mechanism in LAA has been explained [7] by the rotation of the acetate ions. When the temperature of the crystal is increased there is a possibility of weakening of the hydrogen bonding system due to this rotation of the acetate.

Variation of ε_r with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The variation at low temperatures is mainly due to the expansion and electronic and ionic polarizations. The increase at higher temperatures is mainly attributed to the thermally generated charge carriers and impurity dipoles. The electronic polarizability practically remains constant in the case of ionic crystals [38]. The increase in dielectric constant with temperature is essentially due to the temperature variation of ionic polarizability.

Both the electrical conductivities (σ_{ac} and σ_{dc}) increase, in all the five crystals studied, smoothly through the temperature range considered in the present study; there is no sharp increase that would be characteristic of a superprotonic phase transition [19].

In addition, it should be noted that the σ_{ac} values are more than the σ_{dc} values at all temperatures with low frequencies along both directions. This property has earlier been observed in the case of pure and impurity added KDP and ADP single crystals [19, 27]. The reason for this is not understood at present. However, it may be mentioned that when AC voltage is applied some obstruction is given by the natural impurities in random directions which may cause the reduction in AC conductivity.

It is a known fact that glycine and urea are simple organic substances and are expected to occupy the interstitial positions. Moreover, the impurity concentration considered in the present study is small. The NaCl and KCl are well known (model) ionic substances and are expected to exist as ions in the crystal. If the probability of occupation of an interstice is f, then the probability of finding a vacant neighbour site is (1-f). Even for very high concentrations, of the order of 10^{20} cm^{-3}, f does not exceed 10^{-2} so that in real cases with concentration of interstitials of the order of $10^{15} – 10^{20}$ cm^{-3}, (1-f) = 1 [39]. The impurity concentration considered in the present study is within this maximum possible limit of interstices. So, the impurity molecules can be assumed to be added to the LAA crystal matrix. Glycine and urea are expected to create additional hydrogen bonds. The Cl^- ion in NaCl and KCl are expected to move.

The results obtained in the present study indicate that the organic impurities considered are able to reduce the electrical parameters. In the case of NaCl and KCl, NaCl is able to increase while KCl is able to decrease the electrical parameters eventhough the change is observed to be small.

In accordance with the Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of second harmonic generation (SHG) coefficient [41]. The characteristic of low dielectric loss at high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical material and their applications. In the present study, we have observed small values for the dielectric loss factor ($\tan\delta$) at all temperatures for all the five frequencies considered. Moreover, the SHG coefficient for LAA is reported [4] to be comparable to that for KDP. This shows that the dielectric parameters observed in the present study for the organic impurity added LAA help us in understanding the higher SHG efficiency of LAA added with glycine and urea.

Microelectronics industry needs replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant (ε_r) materials, as an interlayer dielectric (ILD) which surrounds and insulates interconnect wiring [40]. Silica has $\varepsilon_r \approx 4.0$, in part as a result of the Si-O bonds. Several innovative developments have been made for the development of new low - ε_r value dielectric materials. As the utility is in the electronic circuits with water proof condition, water soluble material in the single crystal form would be very much interesting. Recently, Mahadevan and his co-workers [17, 19] have reported the possibility of reducing the ε_r value by adding organic molecules, namely, urea and L-arginine to KDP.

It is already known [7] that LAA is a promising low- ε_r value material. It is interesting to note that the organic impurity addition leads to a reduction of dielectric constant for a wide temperature range significantly and consequently leads to low - ε_r value dielectric material which is gaining more importance nowadays in the microelectronics industry. Both glycine and urea are found to be equally good in reducing the ε_r value. Oxygen content of the impurity may be a considerable factor in choosing the impurity for reducing the ε_r value.

Table 1: Lattice parameters of pure and impurity added LAA crystals

Parameter	Values obtained for				
	Pure LAA	LAA + NaCl	LAA + KCl	LAA+glycine	LAA+urea
a(Å)	9.174	9.214	9.166	9.129	9.181
bÅ)	5.172	5.149	5.177	5.168	5.186
cÅ)	13.478	13.224	13.217	13.306	13.187
β(°)	110°8′	111°24′	111°3′	111°25′	111°36′
V(Å^3)	600.4	584.1	585.3	584.4	583.8

Table 2: Estimated impurity concentrations in the crystal

System	Impurity concentration (x10^{-3} mole fraction)		
	In the solution	In the crystal (estimated by)	
		Using solubility data	Flame photometric measurement
Pure LAA	-	-	-
LAA + NaCl	5.0	4.240	4.180
LAA + KCl	5.0	4.670	4.580
LAA + glycine	5.0	4.158	-
LAA + urea	5.0	4.385	-

Table 3: The ε_r, tanδ and σ_{ac} (x10^{-9} mho/m) values at 40°C for pure and impurity added LAA crystals

System	Parameter	With a frequency of				
		100 Hz	1 kHz	10 kHz	100 kHz	1MHz
Pure LAA	(a) Along a- direction					
	ε_r	4.036	3.831	3.669	3.577	3.417
	Tanδ (x10^{-2})	3.396	2.859	0.976	0.791	0.431
	σ_{ac} (x 10^{-9} mho/m)	0.762	6.09	19.9	157	819
	(b) Along c- direction					
	ε_r	4.286	4.072	3.903	3.807	3.503
	Tanδ (x10^{-2})	4.075	3.107	1.046	0.831	0.500
	σ_{ac} (x 10^{-9} mho/m)	0.971	7.04	22.7	176	975
LAA + NaCl	(a) Along a- direction					
	ε_r	4.107	3.851	3.734	3.612	3.466
	Tanδ (x10^{-2})	3.73	3.05	2.19	1.86	0.88
	σ_{ac} (x 10^{-9} mho/m)	0.852	6.53	45.5	374	1700

	(b) Along c- direction					
	ε_r	4.291	4.243	3.927	3.825	3.623
	Tanδ ($x10^{-2}$)	3.98	3.32	1.15	0.88	0.61
	σ_{ac} ($x\ 10^{-9}$ mho/m)	0.950	7.84	25.1	187	1230
LAA + KCl	(a) Along a- direction					
	ε_r	3.993	3.701	3.407	3.300	3.210
	Tanδ ($x10^{-2}$)	3.12	2.65	0.81	0.75	0.68
	σ_{ac} ($x\ 10^{-9}$ mho/m)	0.693	5.45	15.3	138	1210
	(b) Along c- direction					
	ε_r	4.174	3.910	3.840	3.722	3.451
	Tanδ ($x10^{-2}$)	3.40	2.93	0.81	0.71	0.48
	σ_{ac} ($x\ 10^{-9}$ mho/m)	0.789	6.37	17.3	148	923
LAA + glycine	(a) Along a- direction					
	ε_r	3.862	3.723	3.710	3.655	3.579
	Tanδ ($x10^{-2}$)	3.14	2.71	2.56	2.11	1.86
	σ_{ac} ($x\ 10^{-9}$ mho/m)	0.674	5.61	52.8	429	3700
	(b) Along c- direction					
	ε_r	3.894	3.811	3.755	3.702	3.643
	Tanδ ($x10^{-2}$)	3.25	2.95	2.71	2.55	1.91
	σ_{ac} ($x\ 10^{-9}$ mho/m)	0.704	6.25	56.6	525	3870
LAA + urea	(a) Along a- direction					
	ε_r	3.865	3.815	3.774	3.724	3.693
	Tanδ ($x10^{-2}$)	2.91	2.52	2.22	1.87	0.91
	σ_{ac} ($x\ 10^{-9}$ mho/m)	0.625	5.34	46.4	386	1880
	(b) Along c- direction					
	ε_r	3.914	3.871	3.821	3.783	3.755
	Tanδ ($x10^{-2}$)	3.01	2.83	2.68	2.10	1.41
	σ_{ac} ($x\ 10^{-9}$ mho/m)	0.655	6.09	56.9	442	2940

CONCLUSION

Single crystals of L-arginine acetate (LAA) added separately with NaCl, KCl, glycine and urea were grown by the slow cooling method and characterized by X-ray powder diffraction (PXRD) and electrical (both AC and DC) measurements. The FT-IR spectral and PXRD measurements have confirmed the material of the LAA single crystals grown. Estimation (using the solubility data and AAS measurement) of impurity concentration in the crystal and determination of lattice volume indicate that the impurity molecules have entered into the crystal matrix of LAA. The variation of dielectric constant observed with temperature could be understood as essentially due to the temperature variation of ionic polarizability. Glycine and urea have been observed to play an important role in reducing the ε_r value (< 4.0 for a wide temperature range, 40-150^oC) significantly to make LAA a more interesting material in the microelectronics industry.

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