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**Archives of Physics Research, 2014, 5 (3):49-58**
*(http://scholarsresearchlibrary.com/archive.html)*

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**ISSN : 0976-0970**
**CODEN (USA): APRRC7**

# Growth of L-Asparagine Sodium Chloride Acetate (LASCA) crystal and its studies such as structural, optical, mechanical, thermal and dielectric properties

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**ABSTRACT**

*L-asparagine sodium chloride acetate, a new semi organic amino acid single crystal was grown by slow evaporation solution technique (SEST) at room temperature. LASCA crystal of size 6x17x3 mm$^3$ was grown in 18-23 days. The crystallinity was checked and confirmed by Powder XRD studies. Its structure and space group were determined by single XRD study. The optical transmission study showed a lower UV cut off wavelength for LASCA crystal. The mechanical properties of the grown crystal were determined. The dielectric behaviors such as variation of dielectric constant, dielectric loss with frequency for various temperatures were reported. TGA and DTA results showed that LASCA was stable upto 102$^o$C. The SHG efficiency of the crystal was found to be nearly 0.66 times that of standard KDP.*

**Keywords:** Solution growth, slow evaporation technique, XRD studies, Thermal, Mechanical, Spectral and Electrical studies

## INTRODUCTION

Recently, the nonlinear optical single crystals have attracted the researchers and industries due to their wide applications such as second harmonic generation (SHG), Color display electro-optic switches [1], high energy lasers for inertial confinement, fusion research [2] etc. Among biological substances, asparagine is a very important amino acid because it plays a major role in the metabolic control of some cell functions in nerve and brain tissue and is also used by many plants as a nitrogen reserve source [3]. Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their nonlinear optical properties [4-8]. The NLO property of organic or semi organic acids is very interesting [9, 10]. L-asparagine monohydrate (LAM) is an organic compound of the amino acid family and its structure and space group are reported [11]. In addition to the study of important properties like Second Harmonic Generation (SHG) and Laser Damage Threshold (LDT), optical and mechanical, assessment of crystalline perfection are also very important [12, 13]. It is reported in the literature that if NLO crystals are doped with inorganic and organic acids, the properties of the host crystals have been improved [14-17] and this leads us to add sodium chloride and acetic acid to L-asparagine crystal. In this work, growth of L-asparagine sodium chloride acetate (LASCA) crystal and structural, optical, electrical, thermal and mechanical characterization of LASCA single crystals are discussed.

## MATERIALS AND METHODS

### 2.1 Crystal growth and solubility

High purity (99%) L-asparagine and acetic acid were taken in the ratio 2:1. One gram NaCl salt was dissolved in water and that gave NaOH and HCl. These two were used as solvents. The entire solution was stirred for about 3 hours using magnetic stirrer. After getting saturated solution, it was filtered using Whattman filter paper. Now, the solution was subjected to slow evaporation method. After 18-23 days, good transparent quality crystals were obtained and it is displayed in figure 1.

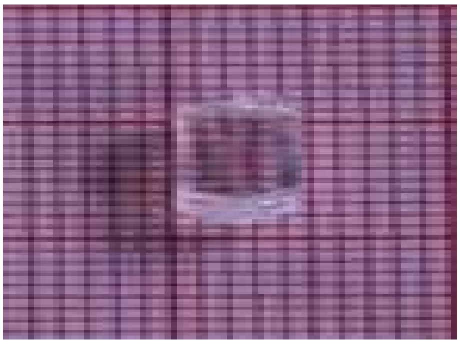

**Fig. 1. Photograph of LASCA crystal**

**2.2 Solubility**

Solubility study was performed using a hot-plate magnetic stirrer and a digital thermometer by gravimetrical method [18]. Fig. 2 shows the solubility curve for LASCA crystal. It is noted from the graph that, the solubility of the grown crystal increases with increase of temperature coefficient, which reveals the fact that slow evaporation technique is the appropriate method to grow single crystal of LASCA.

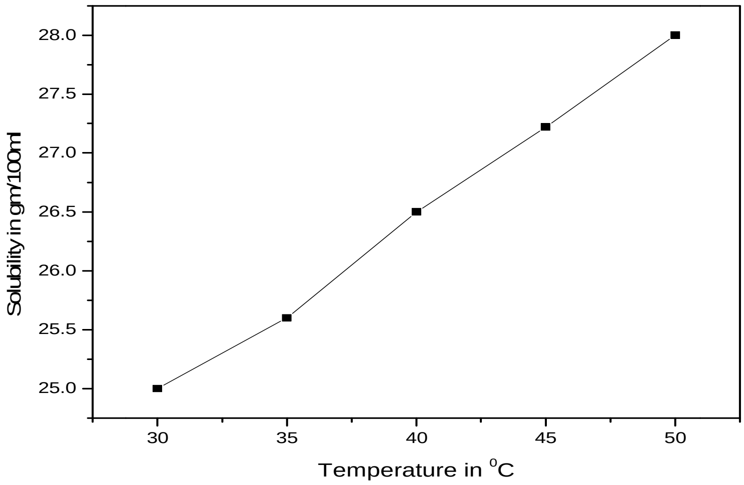


**Fig.2. Solubility of LASCA crystal**

**2.3 Characterization**

Single crystal X-ray diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances, including unit cell dimensions, bond angles and details of site ordering. In this work, the structure of crystal was obtained using an ENRAF NONIUS CAD4 single crystal X-ray diffractometer with MoKα radiation ( λ= 0.71073Å ). X-ray powder diffraction (XRD) is an instrumental technique that is used to identify minerals as well as other crystalline materials. It is particularly useful for identifying fine-grained minerals and mixtures, which may not lend themselves to analysis by other techniques. In this work, the powder x-ray diffractometer PANalytical Model, Nickel filtered $CuK_\alpha$ radiation (1.54056 Å) and their powder X-ray diffraction patterns were obtained.

Fourier Transform Infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission and photoconductivity. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. FTIR absorption spectra of the grown LASCA crystal in the region 4500-400cm$^{-1}$ was recorded on a spectrophotometer such a SHIMADZU-FTIR-8400S using a KBr pellet technique. Energy dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample. An elemental analysis is carried out for LASCA crystal by employing EDAX in order to confirm the composition of elements Na, Cl, C, N and O. Atomic absorption spectroscopy is the most powerful technique for the quantitative determination of trace metals in liquids. Using this method, we can find the total metal content of the sample in the liquid and it can be used to analyze the concentration of different metals in a solution and these studies were carried out using an atomic absorption spectrometer (Model:AA 6300) to confirm the presence of elements in the crystals.

Non Linear Optical (NLO) effects are analyzed by considering the response of the dielectric material at the atomic level to the electric fields of an intense light beam. SHG [19] is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. The powder technique of Kurtz and Perry [20] which used a pulsed Nd: YAG laser was used to test the SHG for the grown LASCA crystal.

Thermal analysis is a branch of material science where the properties of materials are studied as they change with temperature. In this work, the grown LASCA crystal's thermal analysis was carried out using Perkin Elmer thermal analyzer. UV-Visible spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analysis. The UV-VIS-NIR Spectrophotometer was used for spectral transmission studies. The optical transmittance range and the transparency cut off are important parameters for single crystals which are mainly used in optical applications.

The term micro hardness has been widely employed in the literature to describe the hardness testing of materials with low applied loads. The Vickers number ($H_V$) is calculated using the following formula

$H_V = 1.854\ (L/d^2)\ Kg/mm^2$

Where L is load in kilograms and d is the diagonal length of indentation in mm [21]. The relationship between load (P) and diagonal length (d) of indentation is given by $P = ad^n$. This is called Meyer's Law [22]. Here a and n are constants. Using a Leitz micro hardness tester fitted with a diamond pyramidal indentor, the mechanical property of the grown crystals is studied.

The dielectric constant and loss of any given material varies with temperature and also varies as a function of frequency. AC activation energy of a substance is the minimum energy required for the atoms or molecules in the compound to activate while an AC voltage is applied. The relation between AC conductivity on temperature is usually obeying the well known relation [23] and it can be written as

$$\ln \sigma_{ac} = \ln\sigma - E_{ac}/KT$$

## RESULTS AND DISCUSSION

### 2.4.1 Single Crystal XRD

The single crystal XRD data of LASCA indicates that it crystallizes in orthorhombic system with space group $P2_12_12_1$ and the number of molecules per unit cell is Z=4. The unit cell dimensions obtained from single crystal X-ray diffraction analysis are tabulated in table 1.Its lattice parameters are different from pure L-asparagine reported in [11].

**Table 1: Unit cell parameters of LASCA crystal**

| Crystal | Cell parameters | Volume(Å)$^3$ |
|---|---|---|
| L-asparagine sodium chloride acetate | a=3.977Å<br>b=5.628 Å<br>c=24.822 Å<br>$\alpha=\beta=\gamma=90^0$ | 554.25 |

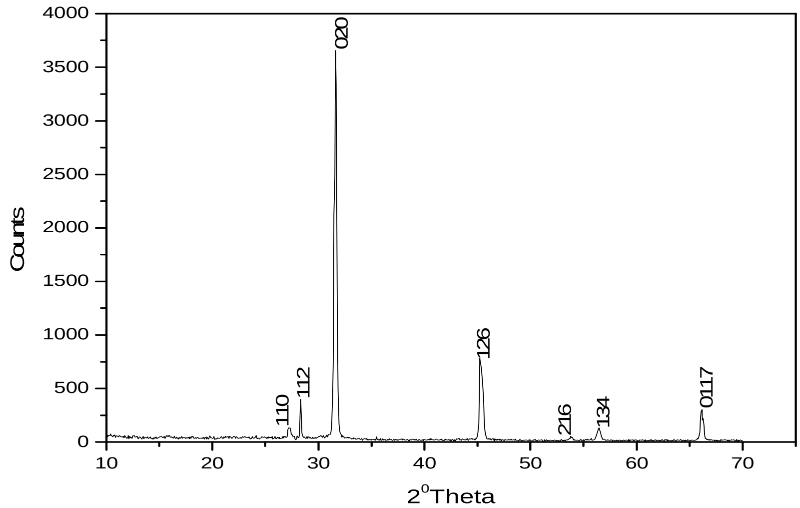


**Fig.3. Powder XRD patterns of L-asparagine sodium chloride acetate**

### 2.4.2 Powder XRD studies

The sample was scanned over the range of 2θ (10-70$^{o}$) degrees. From the X-ray diffraction spectra, the two theta (2θ) values were read directly and relative intensities of the diffraction peaks were estimated. The obtained powder XRD patterns of LASCA sample is presented in figure 3. The reflections of the patterns were indexed by Lipson and Steeple [24] using TREOR and INDEXing software packages. The well defined peaks at specific 2-theta values show high crystallinity of the grown crystal.

### 2.4.3 FTIR studies

FTIR absorption spectra of the grown LASCA crystal in the infrared region 4500-400cm$^{-1}$ were recorded and its spectrum is shown in figure 4 and their assignments were given in table 2 in accordance to the data reported in the literature [25-29]. The fundamental groups such as $NH^{3+}$, $NH^{2}$, $COO^{-}$, CCN, C-N, $CH_3$ and $CH_2$ assignments were made. The assignments $NH^{3+}$were observed at 3450 and 3213 cm$^{-1}$.The wave number at 2720cm$^{-1}$ corresponds to $NH^{2}$ symmetric stretching mode. The wave number at 1454 and 1371 cm$^{-1}$ corresponds to $CH^{3}$ bending and symmetric modes. 1298 and 1184 cm$^{-1}$ corresponds to C-C-N asymmetric and symmetric stretching mode.$COO^{-}$ groups are observed at 711, 645 and 532 cm$^{-1}$ corresponding to bending and rocking modes.

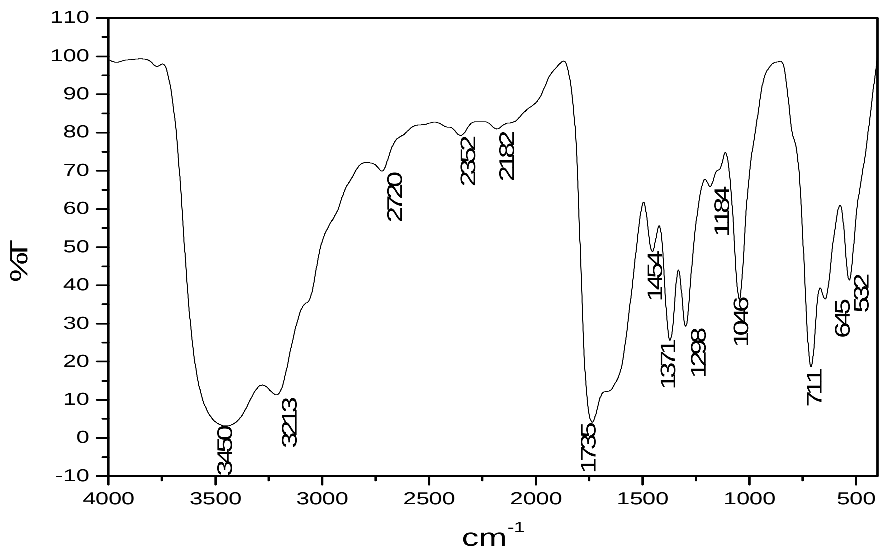


**Fig. 4. FTIR spectrum of LASCA crystal**

**Table 2: FTIR assignments of LASCA crystal**

| Bands/peaks(cm$^{-1}$) | Band Assignments |
|---|---|
| 3450 vw/b | $NH_3^{+}$ asymmetric stretching |
| 3213 vw/b | $NH_3^{+}$ asymmetric stretching |
| 2720 vw | $NH_2$ symmetric stretching |
| 2352 w | Overtones and combination |
| 1735 w | C=O stretching of COOH;Amide |
| 1454 m | $CH_3$ bending degenerate |
| 1371 m | $CH_3$ symmetric bending |
| 1298 m | C-C-N asymmetric stretching |
| 1184 vw | C-C-N asymmetric stretching |
| 1046 m | $CH_3$rcocking |
| 711 m | $COO^{-}$ bending |
| 645 w | $COO^{-}$ bending |
| 532 m | $COO^{-}$ rocking |

### 2.4.4 Identification of various elements by EDAX analysis

Figure 5 shows the EDAX spectra of LASCA crystal and from it the percentage of different elements can be estimated. Table 3 gives the composition of all the elements and the percentage of elements present in the compound and from that it is clear that Na and Cl elements are present in the respective crystal. From the atomic absorption studies the concentration of $Na^{+}$ in the LASCA crystal is found as 169 ppm.

**Table 3 Quantitative results of LASCA crystal**

| Element | Net Counts | Weight % | Atom % |
|---|---|---|---|
| ***C*** | 23560 | 24.84 | 29.74 |
| ***N*** | 16548 | 31.11 | 31.58 |
| ***O*** | 39872 | 41.58 | 37.55 |
| ***Na*** | 10609 | 2.11 | 1.07 |
| ***Cl*** | 4933 | 0.36 | 0.16 |
| ***Total*** | | 100.00 | 100.00 |
| | | | |

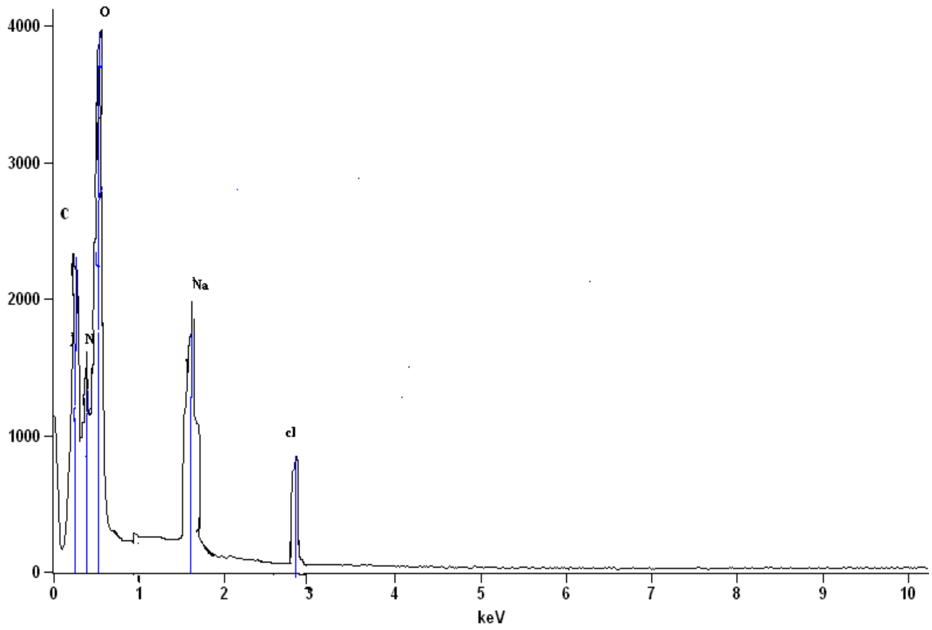


**Fig. 5 The EDAX plot of LASCA crystal**

### 2.4.5 Second Harmonic Generation (SHG):

The grown crystal LASCA was ground to powder to grain size 400-800 µm and the SHG was confirmed by emission of green radiation (532 nm) which was detected by a photomultiplier tube. SHG of LASCA crystal was 0.66 times that of KDP and it is observed that the value of SHG was greater than that of pure L-asparagine.

### 2.4.6 Thermal analysis:

The thermal stability and various transitions (endothermic and exothermic) are shown in figure 6.

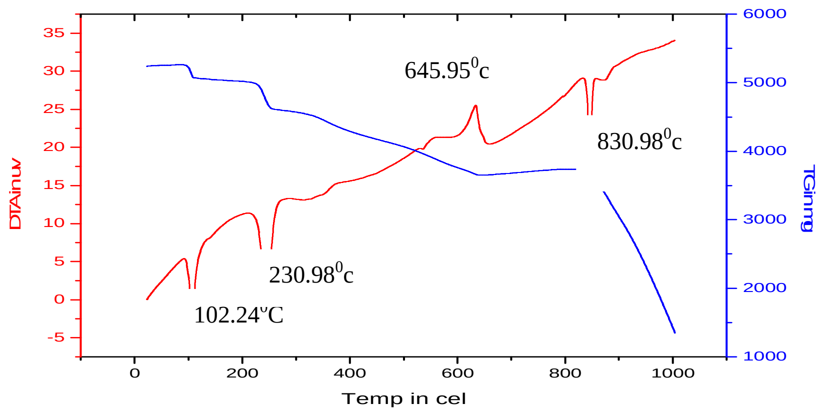


**Fig 6: TGA/DTA curves of LASCA crystal**

From the DTA curve, the peaks observed at 102.24$^o$C and 230.98$^o$C are endothermic and it represents the release of water molecule from the sample [30]. A strong peak is observed at 830.98$^o$C. An exothermic peak is observed at 645.95$^o$C. A heavy weight loss in noticed from 830$^o$C to 1000$^o$C. The value of decomposition point of the grown LASCA crystals is at 230.98$^o$C.

**2.4.7 UV-Vis transmittance spectra**

The recorded transmittance spectra of LASCA sample in the wavelength range 200-1200nm is shown in figure 7.

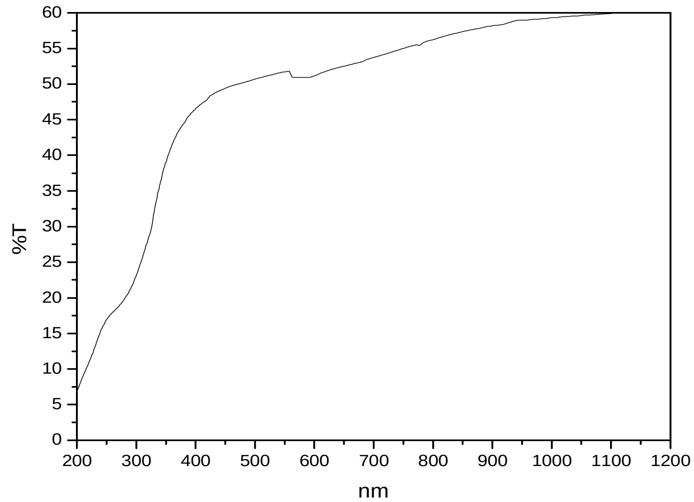


**Fig 7: UV-Visible transmittance spectra of LASCA crystal**

From the above figure it was noticed that there was no significant absorption in the entire UV-Visible and NIR ranges for the grown LASCA crystal and the lower cut off wavelength was 220nm. Thus forbidden energy gap of grown crystal is calculated using

$E_g = hc/\lambda$ and it is 5.64 eV.

**2.4.8 Mechanical studies:**

The Vickers microhardness number ($H_V$) as a function of the applied test load is shown in figure 8. The work hardening coefficient can be estimated from the plots of log d versus log P and the same is presented in figure 9.

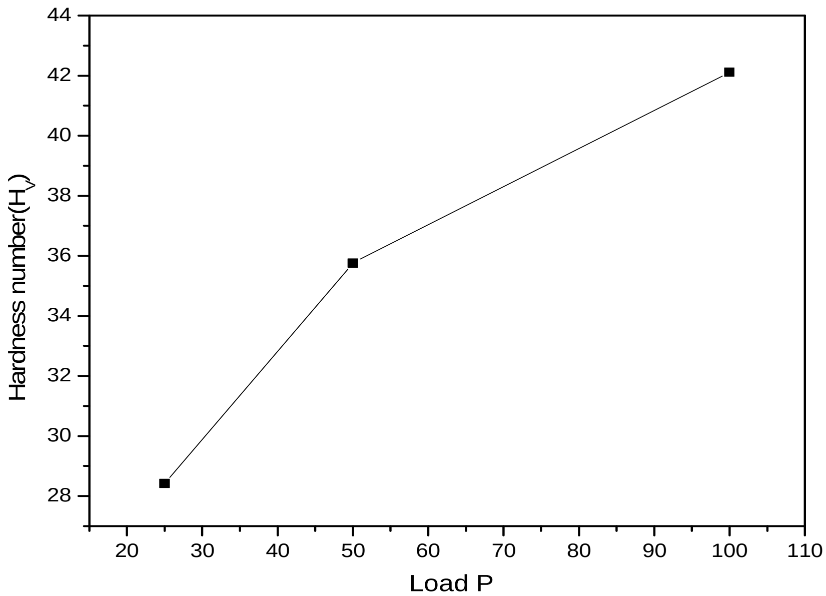


**Fig.8 Plots between hardness number ($H_V$) and applied load for LASCA crystal**

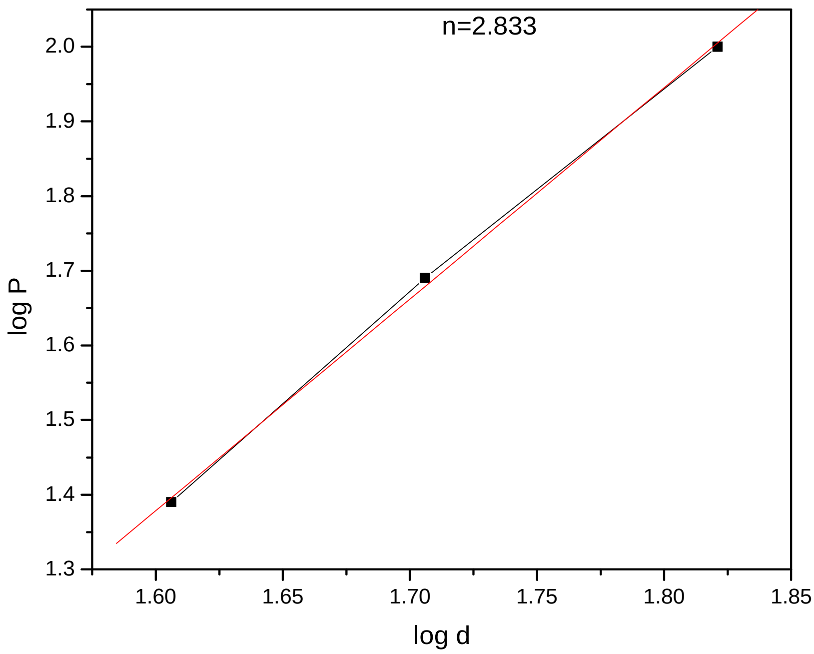


**Fig.9 Plot of log P versus log d for LASCA crystal**

From the graph, it is observed that $H_V$ increases with increasing load and work hardening coefficient (n) is 2.8337 which is greater than 1.6. According to Onitsch [31] and Hanneman [32], if n is greater than 1.6, the material belongs to the category of soft materials and hence it is concluded that the grown crystal LASCA belongs to soft material.

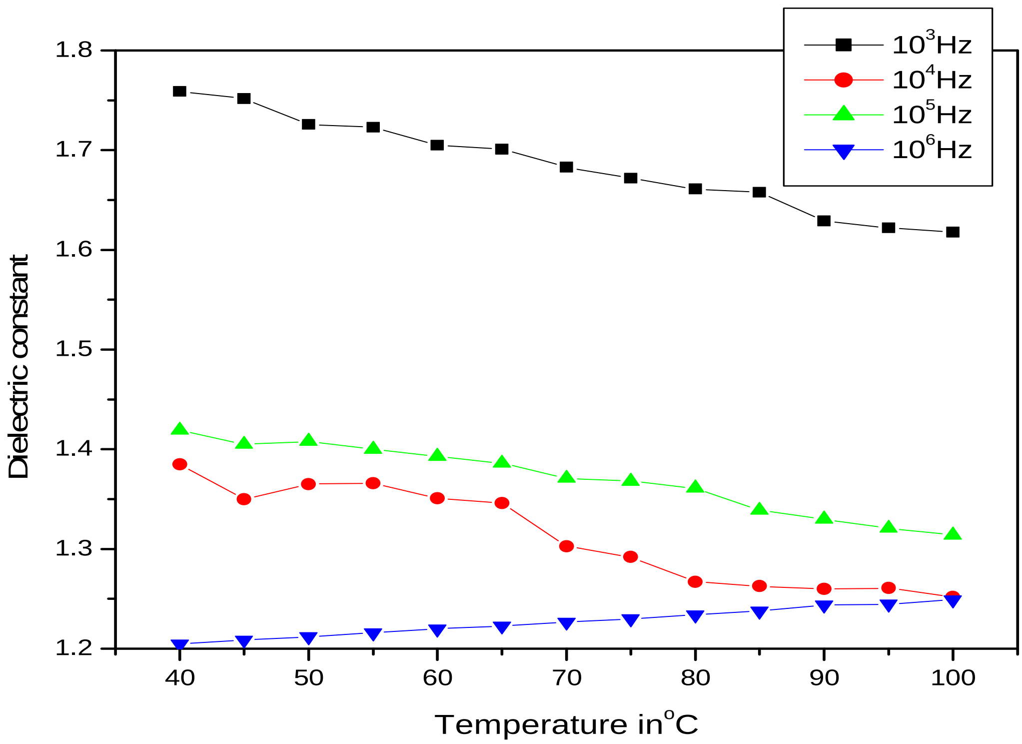


**Fig.10 Plots between dielectric constant and temperature for different frequencies of LASCA crystal**

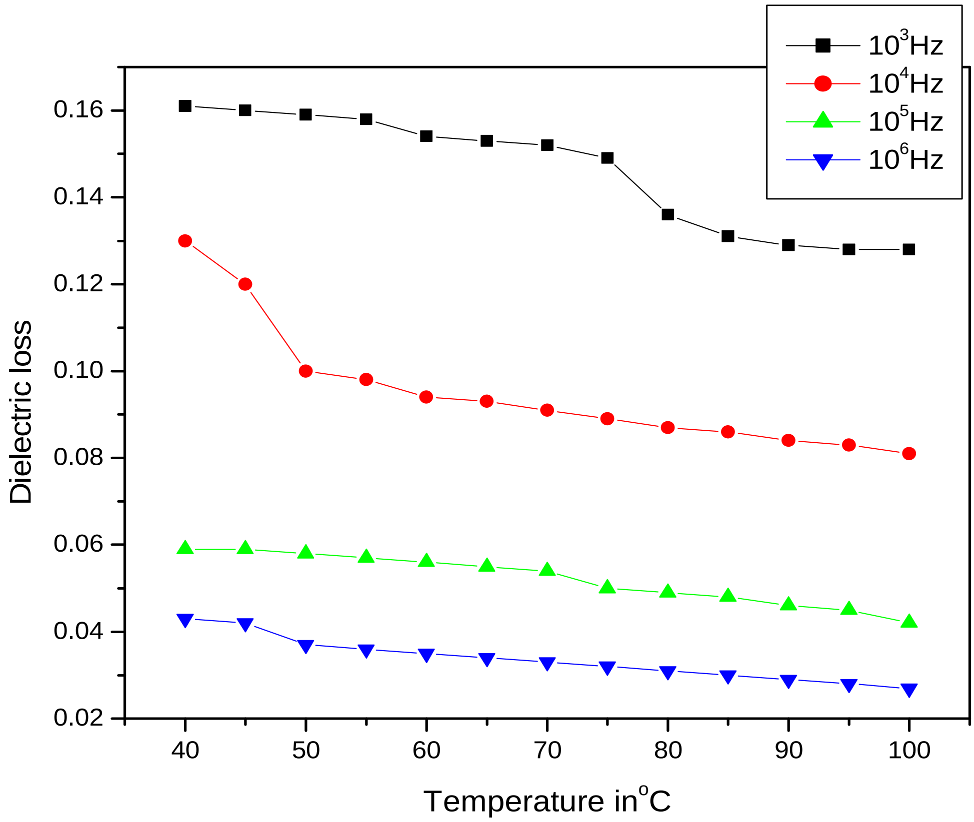


**Fig. 11 Dielectric loss for different frequencies for LASCA crystal**

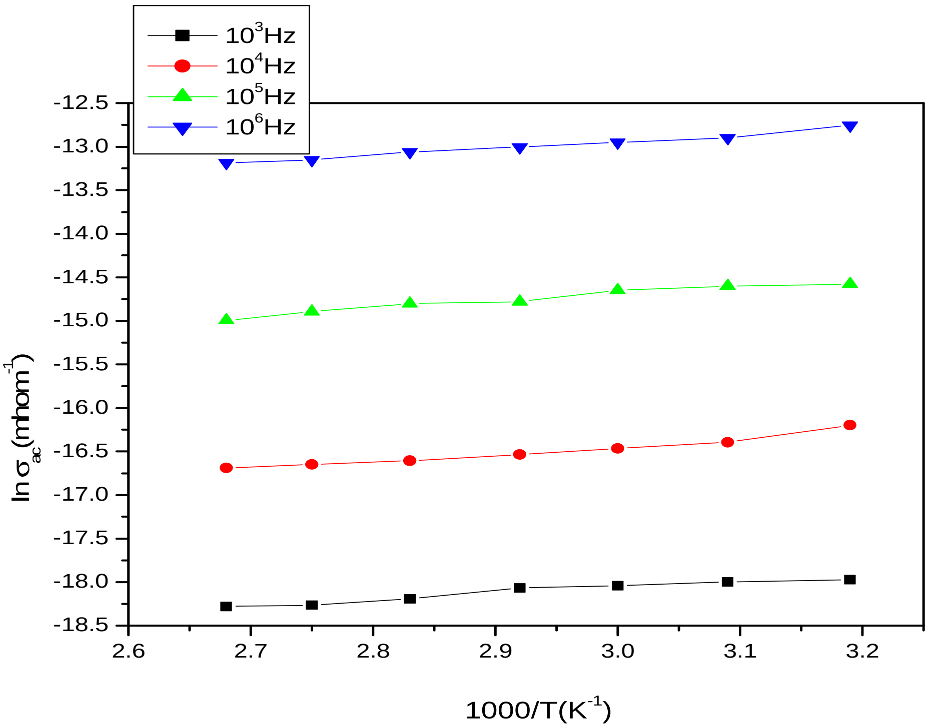


**Fig.12: Plots between ln $\sigma_{ac}$ versus 1000/T for LASCA crystal**

### 2.4.9 Dielectric characterization

The values of dielectric constant and dielectric loss were measured for LASCA crystal for different frequencies under temperature ranges from 40$^{o}$C to 100$^{o}$C and same have been plotted in figure 10 and figure 11.

The values of dielectric constant and dielectric loss increase with respect to temperature and decrease with increase of frequency for the grown LASCA crystal. Using the values of dielectric constant and dielectric loss for a particular frequency its corresponding $\sigma_{ac}$ is calculated. The plots of ln $\sigma_{ac}$ versus 1000/T are depicted in figure 12.

The ac conductivity increases with increase of temperature and frequency and the activation energy for the grown crystal is 0.0323 at f = $10^3$ Hz and 0.0078 at f = $10^6$ Hz. Thus it is clear that if the frequency of applied AC voltage is low, more energy is needed to activate the charged species, but for the same system at higher frequency less energy is enough to activate the charge carriers.

## CONCLUSION

In this investigation, growth aspects of LASCA crystal have been studied. The solubility of LASCA crystal was estimated using water as solvent. The single X-ray diffraction study shows the orthorhombic structure of grown crystal. The crystanallity of the grown sample is confirmed from Powder X-ray study. The various functional groups are confirmed from FTIR analysis. The various elements present in the LASCA crystal such as Na, Cl, N and O are identified from EDAX analysis. From the atomic absorption study the concentration of $Na^+$ in the LASCA crystal is obtained. The value of decomposition point of the grown LASCA crystal is at 230.98$^{o}$C. The SHG efficiency of the grown crystal is 0.66 times that of KDP. The forbidden energy gap and low cut off wavelength of LASCA crystal are also obtained. The grown crystal belongs to the category of soft material. The dielectric constant, dielectric loss and ac conductivity were estimated and the activation energy also has been calculated.

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