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Role of Sodium Nitrate Addition on Crystal Growth, Structural, Optical, Thermal, Dielectric and Antimicrobial Properties of L-alanine Single Crystals

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ABSTRACT

We have successfully grown L-alaninesodium nitrate (LASN) single crystals by spontaneous nucleation solution growth method. The structural parameters of the grown LASN crystals have been determined using single crystal X-ray diffraction (SXR) and powder X-ray diffraction (PXRD) techniques. The presence of functional groups of LASN crystals have been identified by means of Fourier transform infrared (FT-IR) analysis. Elemental analysis CHN was performed to confirm the inclusion of Sodium nitrate into the crystal lattice of L-alanine. The UV-Vis-NIR study has been carried out within 200-2500 nm to determine the optical transparency and dielectric nature of the grown crystal. Second harmonic generation (SHG) efficiency of grown LASN crystals were studied by Kurtz-Perry technique using Nd: YAG laser and is about 2.2 times higher than that of reference material Potassium dihydrogen phosphate (KDP) crystal. Thermal studies of the grown crystals confirmed its stability up to 216°C. The dielectric constant and dielectric loss of LASN crystal was carried out as a function of frequency and the obtained results were discussed. The *in vitro* antimicrobial behavior of sodium nitrate added L-alanine crystals were studied for the first time using agar diffusion method.

KEYWORDS: Crystal Structure; X-ray diffraction; Nonlinear Optical Material; Dielectric Material.

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INTRODUCTION

L-alanine is a non-essential, hydrophobic, non-polar organic crystal that belongs to amino acid group composed of optically active molecule. L-alanine is one of the simplest among twenty amino acids and it can be considered as the fundamental building block of more complex amino acids which exhibits high nonlinear optical behaviour and anomalous phonon coupling and is a system exhibiting vibrational solitons^{1,2,3}. Organometallic complexes are the key elements for photonic and optoelectronic device applications such as photonic devices, solid-state lasers, optical storage devices, displays, laser, photo-luminescence, electro-luminescence fields and telecommunications (components for optical-fiber amplifiers, fiber lasers)^{4, 5, 6}. New crystals which have high non-linear optical (NLO) efficiency and transparency in the entire visible and NIR regions are required for various devices in the field of optoelectronics and photonics^{7, 8, 9}. Last few decades, many attempts have been made to the research and design of highly efficient non-linear optical (NLO) materials due to widespread applications such as high speed information processing, frequency shifting, optical modulation, optical switching, optical logic, optoelectronics, optical communication and optical data storage^{10, 11}. In addition, recent years great efforts have been made to design and development of new drugs against harmful bacteria and fungi, infectious diseases caused by them are still a major threat to public health. Also, the food industries are required to reduce the use of chemicals due to the increasing pressure of consumers. Bacteria and fungi are very versatile organisms that live in and on animals as part of their natural flora and they can be the cause of numerous infections. Due to these problems, the appearance of undesirable side effects of some antibiotics also leads to the search for new antimicrobial drug agents. Hence, we have grown optically transparent, sodium nitrate added L-alanine single crystal for Non Linear Optical (NLO) and pharmaceutical applications.

EXPERIMENTAL

2.1. CRYSTAL GROWTH

The LASN salt was synthesized using L-alanine (99% Purity, Merck, India) and Sodium nitrate (99%, Purity Merck, India) an equimolar ratio 1:1. The calculated amount of salt was mixed in a 250 ml glass beaker containing 100 ml deionised water at a pH of 6. The mixtures were stirred well continuously upto 6 h to get a transparent solution. The obtained homogeneous solution was filtered with a Whatman No1 filter paper. The filtered solution was collected in a 500 ml crystallization dish. Then, the dish was closed with a Para film contains few pin holes and kept in vibration free clean crystal growth chamber and allowed for slow evaporation of solvent at an

ambient temperature. The solution gets saturated with in few days and attains super saturation in 12 days, after which small crystals were developed from nucleus and then they are allowed for further growth to reach good dimensional quality up to a size of $(8 \times 5 \times 1) \text{ mm}^3$ and harvested in a growth period of 36 days. The grown crystals are shown in Fig. 1 (a) and (b)

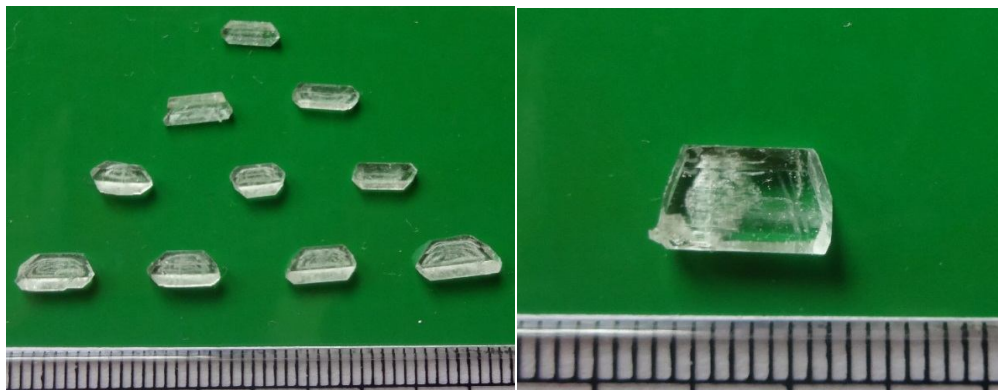


Figure: 1 (a) and 1 (b) Photograph of the grown LASN single crystals

RESULTS AND DISCUSSION

3.1. Single crystal X-ray Diffraction analysis

Single crystal X-ray diffraction parameters of the grown LASN crystal is analysed using Enraf Nonius CAD4 X-ray Diffract meter with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) to obtain the lattice parameters and space group. The single crystal X-ray diffraction data revealed that the grown LASN crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. The space group indicates that the crystal is non centrosymmetric which is an elementary condition for SHG applications. From the SXRD data, the calculated lattice parameter values are found to be $a = 5.7749 \text{ \AA}$, $b = 6.027 \text{ \AA}$, $c = 12.356 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$ and the unit cell volume, $V = 430.1 \text{ \AA}^3$.

3.2. Powder X-ray Diffraction analysis

PXRD studies carried out using Bruker AXS D8 Advance x-ray diffract meter with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation using a tube voltage and current of 40 kV and 30 mA respectively. The powdered sample was scanned over a range $10^\circ - 50^\circ$ at the scan rate of 1° per min. The powder X-ray diffraction pattern of grown LASN crystal is shown in Fig. 2 Powder X-ray Diffraction study reveals that LASN crystal crystallizes into the orthorhombic structure with space group $P2_12_12_1$. The peaks obtained from PXRD pattern affirm high crystalline nature of the grown LASN crystal and the obtained peaks position are well matches with the data available in JCPDS Card No: 22-1532^{12, 13}. Slight variations in the lattice parameter values show the role of dopant in the lattice of grown crystal, which is also confirmed by the slight shift observed in peaks.

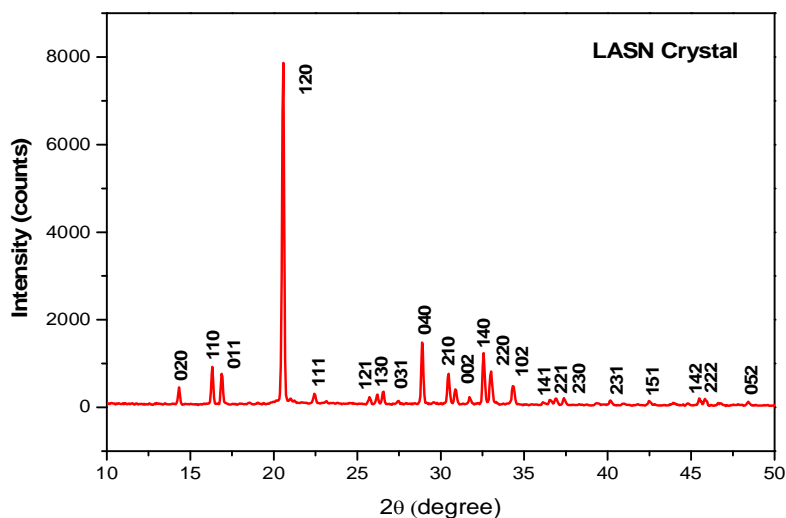


Figure: 2 PXRD pattern of the grown LASNcrystal

3.3. Elemental analysis

To determine the inclusion of Sodium nitrate in to the grown LASN crystal, CHN analysis was carried out on the sample. Carbon, Hydrogen, Nitrogen analysis of the grown LASN crystals was carried out using Elementar Vario EL III analyser. The results of the elemental analysis shows that the grown LASN single crystal contain Carbon = 39.79% Hydrogen = 8.99% and N = 15.98%. The obtained results confirmed that the CHN analysis of the LASN powdered sample shows good agreement with the reported work ¹⁴.

3.4. FTIR analysis

The FTIR spectrum of the grown LASN crystal have been recorded within the frequency range from 400-4000 cm^{-1} by using Perkin Elmer spectrometer using KBr pellet technique and is shown in Fig.3

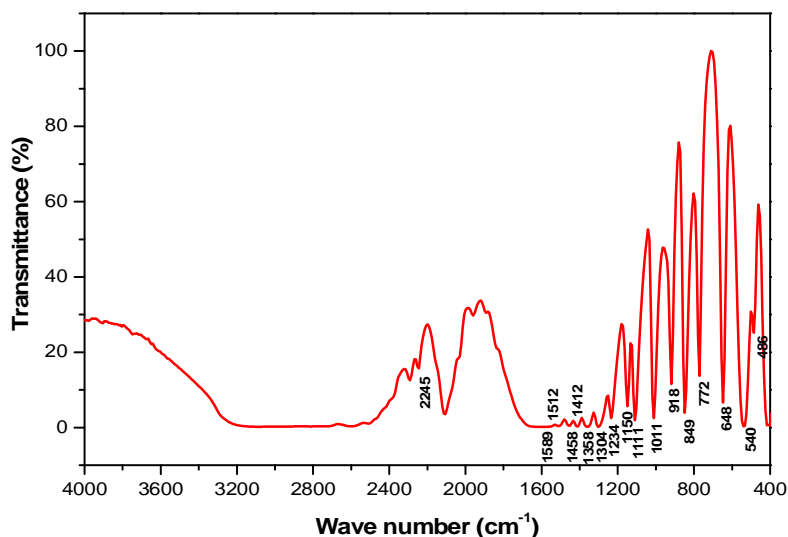


Figure: 3 FTIR spectrum of grown LASN crystals

The vibration peak at 2245 cm^{-1} is due to CH_3 stretching while the transmission peaks observed at $1589, 1512\text{ cm}^{-1}$ corresponds to the ammonium group (NH_3^+ bending). The peaks observed at 1458 cm^{-1} is corresponds to the asymmetric CH_3^+ bending. The peak observed at 1412 cm^{-1} is attributed to symmetric stretching of C-COO^- . The sharp peaks observed at $1358, 1111, 849$ and 772 cm^{-1} are due to NO_3 stretching. C-H and N-H bending is observed at 1304 cm^{-1} . The band observed at 1234 and 1150 cm^{-1} are due to NH_3^+ rocking. The vibration peaks observed at 1011 and 918 cm^{-1} is attributed to overtone of torsional oscillation of NH_3^+ . The COO^- in plane deformation is attributed to the peak at 648 cm^{-1} . The vibration peak at 540 cm^{-1} is due to torsional oscillation of NH_3^+ . The peak observed at 486 cm^{-1} is corresponds to the NH_3^+ in plane rocking. The presence of nitro groups in the obtained spectrum confirms the grown LASN crystal. The presence of functional groups are in good agreement with the reported work ^{15, 16}. The observed wave numbers and the proposed band assignments of the FTIR spectrum of LASN crystal are given in Table No.1.

Table No. 1: Band assignments of LASN crystal

Wave number [cm ⁻¹]	Band assignments
2245	CH ₃ stretching
1589	NH ₃ ⁺ bending
1512	NH ₃ ⁺ bending
1458	asymmetric CH ₃ ⁺ bending
1412	symmetric stretching of C-COO ⁻
1358	NO ₃ stretching
1304	C-H and N-H bending
1234	NH ₃ ⁺ rocking
1150	NH ₃ ⁺ rocking
1111	NO ₃ stretching
1011	overtone of torsional oscillation of NH ₃ ⁺
918	overtone of torsional oscillation of NH ₃ ⁺
849	NO ₃ stretching
772	NO ₃ stretching
648	COO ⁻ in plane deformation
540	torsional oscillation of NH ₃ ⁺
486	NH ₃ ⁺ in plane rocking

3.5. Optical transmission studies

The UV-Vis-NIR transmission spectrum of the grown LASN crystal was recorded on a Varian (Model-Cary 5000) UV-Vis-NIR spectrophotometer between the wavelength range 200 and 2500 nm. The UV-Vis-NIR transmission spectrum of the grown LASN crystal is shown in Fig. 4. From UV-Vis-NIR transmittance spectrum, it is observed that the grown crystal is transparent in the entire visible, NIR regions without any absorption peak and has a lower cut-off wavelength of 278 nm. The bandgap energy of the grown crystal was found to be 4.463 eV using Planck's energy equation ($E_g = \frac{hc}{\lambda_{\min}}$ nm) with the data of lower cut-off wavelength. The value of bandgap energy confirms the dielectric nature of the material. These are the essential properties for photonic and electro-optic materials¹⁷.

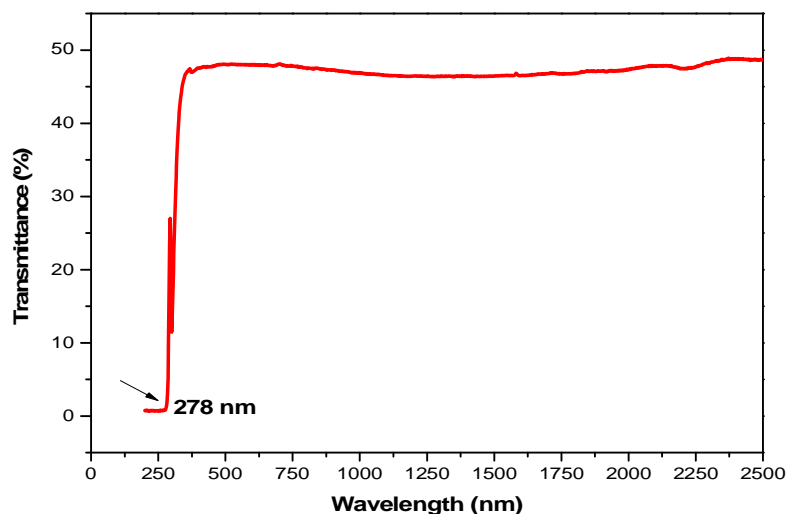


Figure:4 UV-Vis-NIR spectrum of the grown LASNcrystals

3.6. Second Harmonic Generation Studies

The SHG efficiency of the grown LASN crystal was studied using the Kurtz-Perry powder technique¹⁸. The grown LASN crystals were powdered into a uniform particle size of about 150 μm and then orderly filled in a micro-capillary tube of constant bore. A Q-switched Nd: YAG laser beam with 1064 nm of wavelength, pulse energy of 1.2 mJ pulse⁻¹, pulse width of 10 ns and repetition rate of 10 Hz was made to fall on the sample cell. The SHG behaviour was confirmed by the emission of green light (532 nm). The SHG efficiency of the grown LASN crystal (75 mV) is found to be 2.2 times higher than that of reference material KDP (34 mV) crystal.

3.7. Thermal studies

The designing of NLO devices requires the materials with high thermal performance for which the thermo gravimetric (TG) and differential thermal analysis (DTA) curves were investigated for the grown LASN crystal using the TQA-500 thermal analyser. The TGA and DTA curves displayed in fig. 5 (a) and 5 (b) were simultaneously recorded in the range of 45 to 345 $^{\circ}\text{C}$ in a homogeneous nitrogen atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The analysis of TGA curve revealed that the thermal stability of LASN crystal is stable up to 216 $^{\circ}\text{C}$, which gives the clear evidence of purity of LASN and absence of water molecules, while the slight decomposition at 171 $^{\circ}\text{C}$ occurs due to low temperature resistivity of amino acids. The weight loss from 216 to 284 $^{\circ}\text{C}$ may be due to decomposition of sodium nitrate and L-alanine. In DTA analysis the occurrence of sharp endothermic peak observed at 284 $^{\circ}\text{C}$, which resembles to the melting point of LASN crystal. The

single sharp endothermic peak confirms the good crystalline nature of LASN crystal. It is also noticeable that the melting point of the grown LASN crystal is significantly higher than L-threonine crystal. Hence, it could be a potential material for fabrication of NLO devices ranging upto 284 °C¹⁹.
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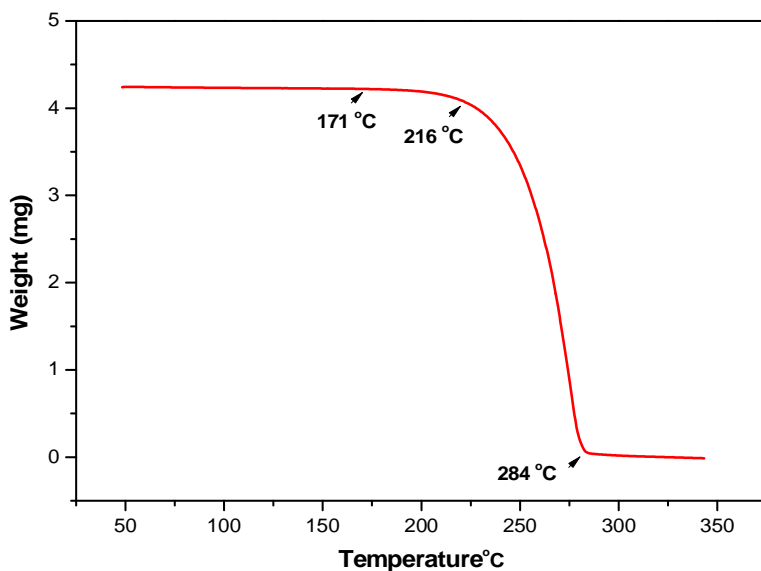


Figure:5 (a) TGA curve of the grown LASN Crystal

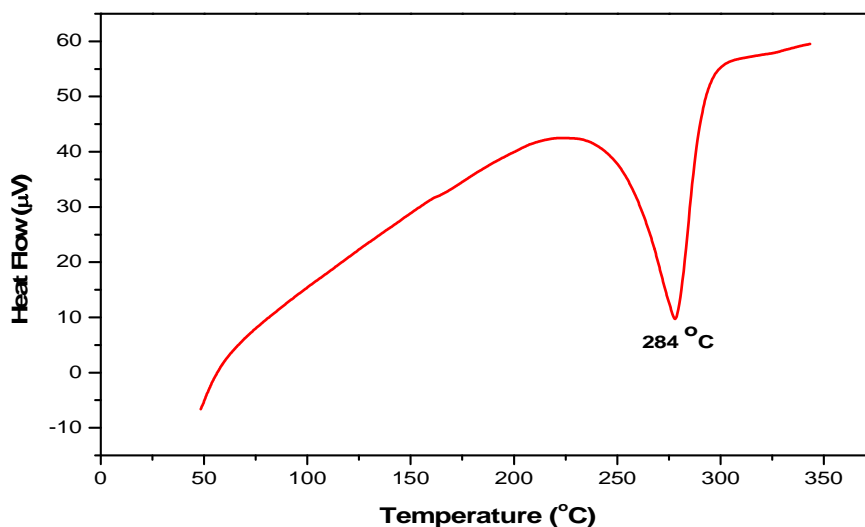


Figure:5 (b) DTA curve of the grown LASN Crystal

3.8. Dielectric studies

For dielectric measurements, a good quality LASN single crystal of thickness (d) 1mm was electrode on either side with a silver coating to make it behave like a parallel plate capacitor. The capacitance (C_{crys}) and dielectric loss ($\tan \delta$) were employed using the conventional parallel plate capacitor method with the frequency range 10 Hz to 5 MHz using a HIOCKI LCR HITESTER (Model 3532-50) instrument. The plots of dielectric constant (ϵ_r) versus log frequency and dielectric loss (ϵ'') versus log frequency of the grown LASN Single crystal are depicted in Fig. 6 (a) & (b).

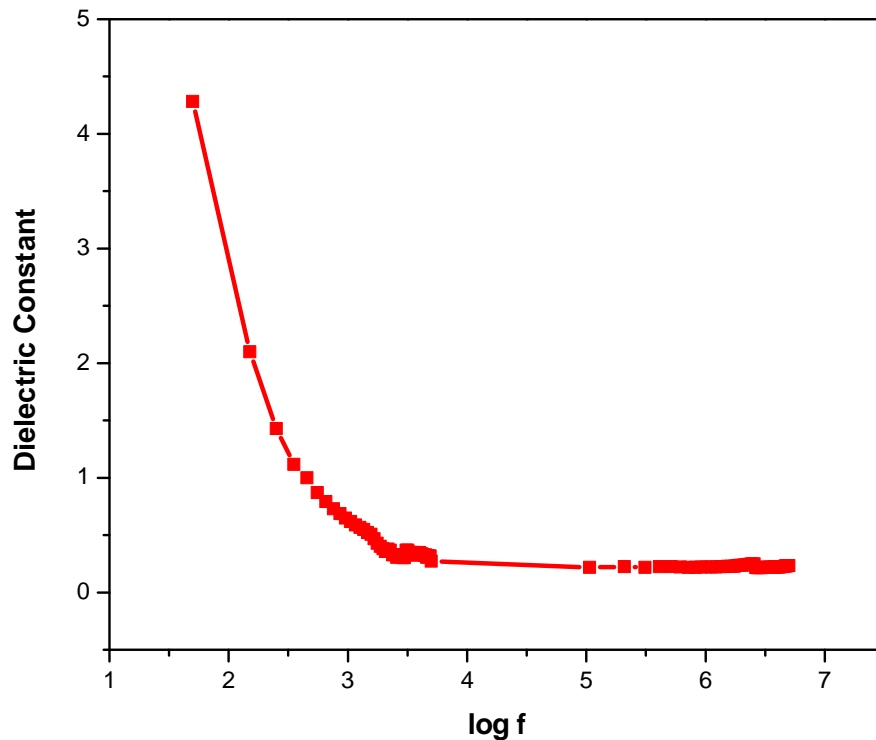


Figure:6 (a) Plot between log f and dielectric constant

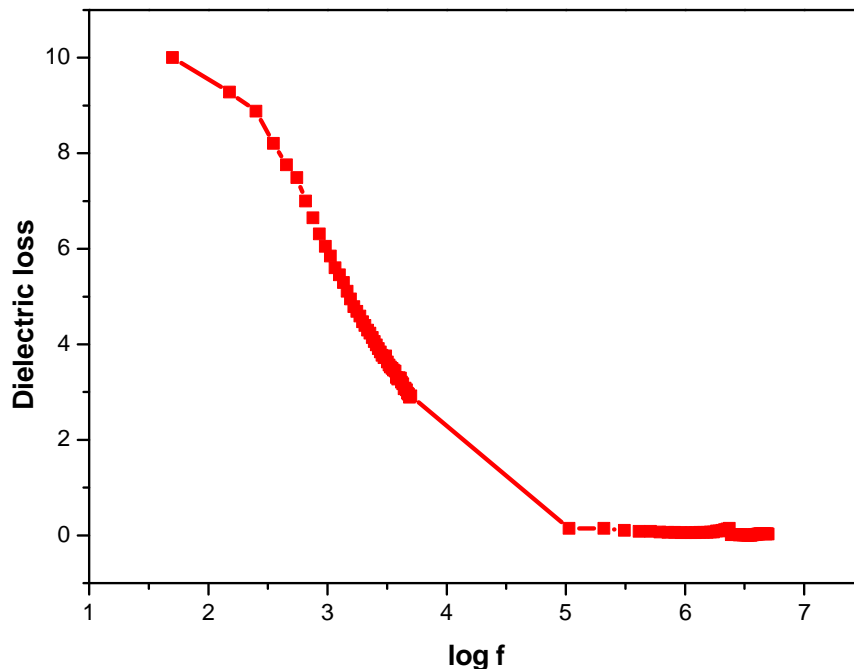


Figure:6(b)Plot between log f and dielectric loss

The graph reveals that the dielectric constant and dielectric loss exhibits similar variation with frequency. It is observed at low frequencies, dielectric constant and dielectric loss values are high. Then frequency increases, dielectric constant and dielectric loss decreases slowly, finally it becomes almost a constant at higher frequencies. The high value of dielectric constant at low frequencies may be due to the presence of four types of polarizations namely; space charge, electronic, dipolar and ionic polarization. The low value of dielectric constant at higher frequencies may be due to the loss of these four polarizations gradually. One of the four Polarizations, space charge is generally active at the lower frequency range and it indicates the perfection of crystal^{21, 22}. At high frequencies low value of dielectric loss indicates that the crystal possess good optical quality with lesser defects and this parameter is of extremely significant for photonic and NLO materials in their applications²³.

3.9. Antibacterial and Antifungal Applications

Antibacterial and antifungal study was carried out against ACDP declared harmful pathogens. The Past few years, various techniques have been used for the development of antifungal and antibacterial activity²⁴. Until now, the antifungal and antibacterial actions of L-alanine sodium nitrate single crystals are not available in the literature.

The antibacterial test was used to find out the growth inhibition of bacteria. Bacterial cultures were maintained at 37°C using incubator. Agar disk diffusion is most widely used *in vitro* investigation method for microorganisms. The required quantity of culture is prepared and autoclaved at 121°C for 20 minutes. Also, prepared culture was permitted to cool under laminar air flow. Sterilized Petri dishes were used for this experiment. Around 20 ml of culture was aseptically transferred into each sterile petri dish and permitted to solidify. The plates were inoculated by dunking a sterile swab into inoculums. The additional inoculums was evacuated by squeezing and rotating the swab solidly against the side of the tube, over the level of the fluid. The swab was marked everywhere throughout the surface of the medium three times, rotating the plate through an angle of 60 °C after every use. Lastly, the swab was passed round the edge of the agar surface. The immunization was dried for a couple of minutes, at room temperature, with the lid closed. Discard the drag in a plate. add solution in the bore. The Petri plates were placed in an incubator at 37°C within 30 minutes of preparation for bacteria. After 18 hrs incubation for bacteria, the diameter of the zone (including the diameter dish) was measured and noted in mm. The measurements were taken with a ruler, from the bottom of the plate, without opening the lid. The antimicrobial activity was measuring the width of the strong inhibition zone all over the place in the disc using measurement scale [mm].

For the first time, LASN crystals tested against ACDP declared harmful pathogens such as Gram positive (*Bacillus cereus*, *Streptococcus aures*, *S.aures*), Gram negative (*Klebsiella*, *Shigella* and *Pseudomonas*) bacterial strains and *Aspergillus* fungi by agar disk diffusion technique. The inhibition zone widths for grown crystals are listed in Table No. 2.

Table No.2:Zone of inhibition for selected bacterial and fungi strains [mm]

Sample	Zone of inhibition (mm)
<i>B. Cereus</i>	13
<i>S.aureus</i>	14
<i>Strepto.aureus</i>	15
<i>Shigella</i>	16
<i>Pseudomonas</i>	18
<i>Klebsiella</i>	17
<i>Aspergillus (fungi)</i>	17

The results of the samples show excellent antibacterial activity against *Klebsiella*, *Shigella*, *Pseudomonas* and antifungal activity against *Aspergillus*²⁵. Hence, the grown LASN crystals may be considered for drug delivery applications.

CONCLUSIONS

Good optical quality LASN single crystals have been grown from aqueous solution by spontaneous nucleation solution growth method. The unit cell parameters have been determined by single XRD analysis and they agree well with the reported values. The Powder XRD study reveals that the grown crystals crystallizes into the orthorhombic structure with space group $P2_12_12_1$, which makes it ideal for dielectric and NLO applications. FTIR analysis confirms the functional group present in the crystal. The UV–Visible–NIR transmission spectrum of LASN crystals confirm wide transparent window in the entire visible, NIR regions. It is an important requirement for the materials having NLO properties. The powder SHG efficiency of the grown LASN crystals was studied by Kurtz's and Perry powder method employing Nd: YAG laser. It was found to be 2.2 times higher than that of reference KDP Crystalline powder. Thermal studies revealed that the grown LASN crystals are thermally stable up to 216°C while fabricating photonic and electronic devices. The dielectric constant and dielectric loss of grown crystal was carried out as a function of frequency and the results were discussed. Thus the grown LASN single crystals with noticeable optical, thermal and dielectric properties revealed its greatest reliability in designing components for optoelectronics, photonics convertors and distinct NLO devices. The antimicrobial activity results of the grown crystal show excellent antibacterial activity against *Klebsiella*, *Shigella*, *Pseudomonas* and antifungal activity against *Aspergillus*. Hence, the grown LASN crystals may be considered for drug delivery applications.

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