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OPTICAL, DIELECTRIC, PHOTOLUMINESCENCE, MECHANICAL AND NONLINEAR OPTICAL STUDIES OF SEMIORGANIC CRYSTAL: LAAC

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ABSTRACT

L-Alanine Ammonium Chloride (LAAC) crystal was grown from aqueous solution by slow evaporation method. The structure confirmation of LAAC crystal has been examined by single crystal XRD analysis which reveals that the crystal belongs to orthorhombic system. The optical transmission study reveals that the grown crystals have good transparency over the entire visible region from 300 nm and used to calculate the various optical parameters. The mechanical stability of the grown crystal was checked by Vicker’s Hardness test. The second harmonic generation test for the grown crystals was performed by the powder technique of Kurtz and Perry experimental setup. Dielectric constant measurements were carried out at different temperatures and frequencies.

KEYWORDS

Optical materials, Dielectric properties and Photoluminescence.

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INTRODUCTION

Amino acid crystals are potential candidates for optical second harmonic generation because all amino acids except glycine contain chiral carbon atom and crystallize in non-centrosymmetric space groups. Complexes of amino acid with inorganic salts are promising materials for SHG and they have a tendency to combine the advantage of the organic amino acid with that of the inorganic salt. Among the amino acids L-alanine is the simplest molecule having SHG efficiency, one-third of that of the well-known KDP. In general, amino acid single crystals have special features like wide transparency in UV as well as in visible region[1,2] and have considerable second harmonic nonlinear optical (NLO) efficiency. L-alanine molecule exists as a zwitterion, where the carboxyl group is dissociated and amino group is protonated and if it is mixed with different organic and inorganic acids to form novel materials, it is expected to get improved NLO properties. Some complexes of L-Alanine have been reported as very good semiorganic nonlinear optical materials which proved very suitable materials for NLO applications[3-5]. In the present work, L-Alanine ammonium chloride is a semiorganic nonlinear optical material and was subjected to various characterization techniques such as single crystal x-ray diffraction, power x-ray diffraction, optical, photoluminescence, dielectric, mechanical and NLO. The experimental results are discussed to explore its effective optical device applicability.

Experimental procedure

Synthesis and Crystal growth

The title compound was synthesized from L-Alanine and ammonium chloride taken in 1:1 equimolar ratio. The required quantity of L-Alanine and ammonium chloride was thoroughly dissolved by adding double distilled water according to their solubility and stirred well for about 5 hours using a magnetic stirrer to obtain a homogenous mixture. The solution was filtered to remove insoluble impurities using Whatman filter paper of pore size ten micrometers. The solution was kept in undisturbed condition and allowed to crystallize by slow evaporation technique at room temperature. Care was taken to minimize the temperature fluctuations and mechanical disturbance. After 34 days, colorless and transparent crystal of LAAC was harvested. The purity of the synthesized salt was improved by successive recrystallization process. The photograph of as-grown crystal is shown in Figure No.1.

Characterization Techniques

The unit cell parameters of the grown crystals were confirmed using ENRAF NONIOUS CAD4 X-Ray diffractometer equipped with $M_o k_\alpha$ radiation (λ= 0.71073 Å). UV-Vis transmittance spectra were recorded using PERKIN ELMER LAMBDA 35 UV-Vis spectrophotometer within the wavelength range of 190 nm to 1100 nm. The grown crystals were subjected to second harmonic generation test using Kurtz and Perry experimental setup using Nd: YAG laser (λ= 1064 nm).

RESULTS AND DISCUSSION

X-ray diffraction analysis

The grown LAAC crystal has been subjected to single crystal X-ray diffraction study to obtain the crystallographic data which reveals that LAAC crystal crystallizes in orthorhombic structure with the lattice parameters and it is recognized as a non-centrosymmetric and thus satisfying one of the basic and essential material requirements for the SHG activity of the crystal.

Here, it is to be mentioned that L-alanine crystal also crystallizes in orthorhombic structure with the lattice parameters a = 6.032 A˚, b = 12.343 A˚, c = 5.784 A˚, $\alpha = \beta = \gamma = 90°$[6]. When we compare the lattice parameters of L-alanine crystal and L-alanine ammonium chloride crystal, it is evident that the addition of ammonium chloride to L-alanine has influenced the cell volume significantly.

The powder X-Ray pattern was collected using JEOL JDX powder X-Ray diffractometer. In the powder XRD pattern (Figure No.2) well-defined sharp Bragg's peaks at specific 2θ values show high crystallinity of the grown crystal without the formation of secondary phases.

Using the method of least squares, the lattice parameters were calculated from the powder XRD data.

$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2}\right) + \left(\frac{k^2}{b^2}\right) + \left(\frac{l^2}{c^2}\right)$$

Where,

D is the lattice spacing

Hkl are the miller indices

A, b, c are the lattice parameters

λ is the wavelength of the x-ray used (CuKα = 1.5406 Å)

V is the volume of the unit cell

2θ is the diffraction angle

The estimated cell parameters are a = 6.040 A˚, b = 12.256 A˚, c = 5.742 A˚,$\alpha = \beta = \gamma = 90°$. And from the cell parameters it is evident that the material retains its orthorhombic structure.

Optical transmission analysis

The optical transmittance and lower UV cutoff wavelength plays an important role in identifying the potential of an NLO materials. In these materials the UV-vis range from 200 to 400 nm is very important for the realization of SHG output in this range using diode and solid-state lasers[7]. The percentage of transmittance of LAAC crystal is 45%which is shown in Figure No.3. The spectrum of LAAC shows that the crystal has good optical transmission in the entire visible region. The transmission property of the crystal in the entire visible region ensures its suitability for second harmonic generation (SHG) applications. The UV absorption edge was observed to be around 300 nm. The dependence of the optical absorption coefficient on the photon energy helps us to study the band structure and the types of transitions of electrons.

The optical absorption coefficient (α) was calculated from the transmittance using the following relation:

$$\alpha = \frac{2.3026 \log(\frac{1}{T})}{d}$$

Where T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal under study as an absorption coefficient (α) obeying the following relation for high photon energies hν

$h\nu\alpha= A(h\nu-E_g)^{1/2}$

Where E_g is optical band gap of the crystal and A is a constant.

The variations of $(\alpha h\nu)^2$ versus hν in the fundamental adsorption region are plotted in FigureNo.4. In the high photon energy region, the energy dependence of the absorption coefficient reveals the occurrence of a direct band gap and E_g can be evaluated by extrapolation of the linear part. The band gap is found to be 4.5eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region and indicates its suitability for optoelectronic devices like LED and laser diodes[8].

Mechanical properties of LACC crystal

The mechanical stability of l-alanine ammonium chloride crystals were assessed by Leitz- Wetzler's Vickers' microhardness tester fitted with a diamond indenter. The indentations were made using Vicker's pyramidal diamond indenter for loads ranging from loads ranging from 25g to 100g with a constant indentation time of 10s. Vicker's microhardness number (H_v) is given by the following relation:

$$H_v= (1.8544 \text{ x } p) /d^2 \text{ kg/mm}^2$$

Where P is the applied load in g, d is the diagonal length in mm. The variation of the Vicker's hardness number with the applied load is shown in Figure No.5. From the figure it is evident that the Vicker's hardness number increases with the increase in load thus satisfying the normal indentation effect[9].

The plot of log d vs log p (Figure No.5) yields a straight line graph and its slope gives the work hardening coefficient, n and it was found to be 3.82 according to Meyer's relation,

$P= K_1d^n$

Since the work hardening coefficient is 3.82, according to Onstich[10], LAAC crystal belongs to the soft material category.

Photoluminescence Emission Analysis

The PL emission spectrum of LAAC crystal was recorded using Cary Eclipse Spectroflurometer. The sample was excited at 384 nm and the emission spectrum was recorded which is shown in FigureNo.6. The emission peak was observed at 593 nm which corresponds to green emission. The strong green emission peaking at 593 nm arises due to the oxygen vacancies.

The band gap energy was calculated using the formula,

$Eg= hc/\lambda e$

Where h, c and e are the constants and λ is the wavelength of the fluorescence. The band gap energy was found to be 3.3 eV.

Dielectric Studies

The dielectric study for LAAC crystal was carried out using Agilent 4284-A LCR meter. The observations are made in the frequency range 100 Hz-1 MHz at various temperatures. The plot of temperature vs dielectric constant is depicted in Figure No.7. The dielectric constant decreases with increase in temperature. This effect can be attributed to the effect of charge distribution by mean carrier hopping on defects. At low temperature, the charge on the defects can be rapidly redistributed so that defects closer to the positive side of the applied field become positively charged. This leads to a screening of the field and overall reduction in the electric field. Because the capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased capacitance observed as the temperature is lowered. The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies. At low frequencies, all these polarizations are active. The space charge polarization is generally active at lower frequencies and high temperatures. The low dielectric loss shows the crystals are of enhanced optical quality[10].This is in good agreement with the result of optical studies and this parameter is of vital importance for various NLO devices.

FTIR analysis

In the FTIR spectral analysis was carried out in the middle infrared region extending from 450 to 4000 cm^{-1} using Perkin Elmer spectrometer. The FTIR spectrum of L-alanine ammonium chloride is shown in Figure No.8. In the higher energy region, there is a broad intense band due to the N-H stretch of NH_3^+ symmetric stretching mode of vibration is appeared at 3403.91cm^{-1}. The C-H stretching and C-N stretching mode of vibrations is observed at 2600.36 cm^{-1} and 917.84 cm-1 respectively. The assignments of the fundamental vibrational modes due to COO^-, NH_3^+, CH_2, CH groups were made. The carboxylic group is found to exist as the COO^-, in the crystal and it is well known that an ionized carboxylic group has identified in the regions 1303.79 cm^{-1}, 1233.14 cm^{-1} and 1360.69 cm^{-1} respectively. The O-C-O bending mode at 771.97 cm^{-1} has been identified. The COO^- rocking mode of vibrations is observed at 538.61cm^{-1}.

In amino acids containing NH_3^+ group, the stretching and bending vibrational wavenumbers are expected[11,12] in the regions 1660–1610 cm^{-1} and 1550–1480 cm^{-1}. These observations bands at observed at 1596.56 cm^{-1} and 1456.17 cm^{-1} respectively. The asymmetric stretching mode of NH_3^+ group is observed at 1596.56 cm^{-1}. The C-C-N stretching mode of vibration is observed at 917.84 cm^{-1} and 848.08 cm^{-1} respectively. The characteristic vibrations of the grown crystal has been compared with those of L-alanine and the shifts are observed maybe attributed to the formation of NH_3^+ and COO^-[13,14].

NLO studies

Powder SHG measurements were carried out using were carried out using Kurtz and Perry[15] experimental setup. A Q switched Nd: YAG laser (Quanta Ray spectra Physics model Prolab 170) was used in the experiment. The laser operates at 1064 nm and 8 ns pulse with the repetition rate of 10 Hz and energy 0.68 mJ/pulse. Emission of green radiation of wavelength 532 nm from the crystalline sample confirms the SHG activity of LAAC crystal. The converted SHG output was displayed on a digital storage oscilloscope. From the obtained data the SHG efficiency of L-Alanine Ammonium chloride sample is 1.2 times that of KDP. This property of enhancing the frequency makes L-Alanine Ammonium chloride crystal an eligible candidate in nonlinear optical applications.

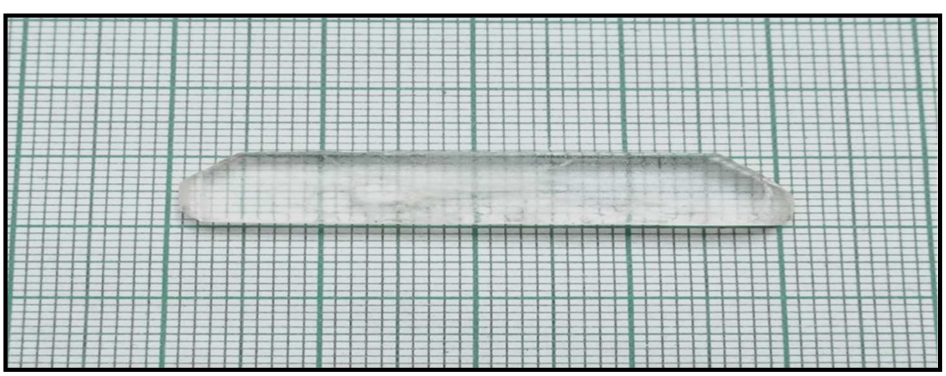


Figure No.1: As grown LAAC crystal

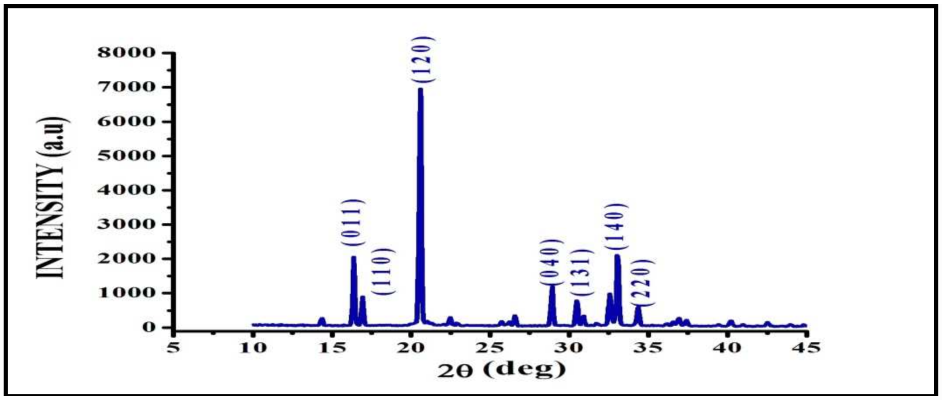


Figure No.2: Powder XRD pattern of LAAC crystal

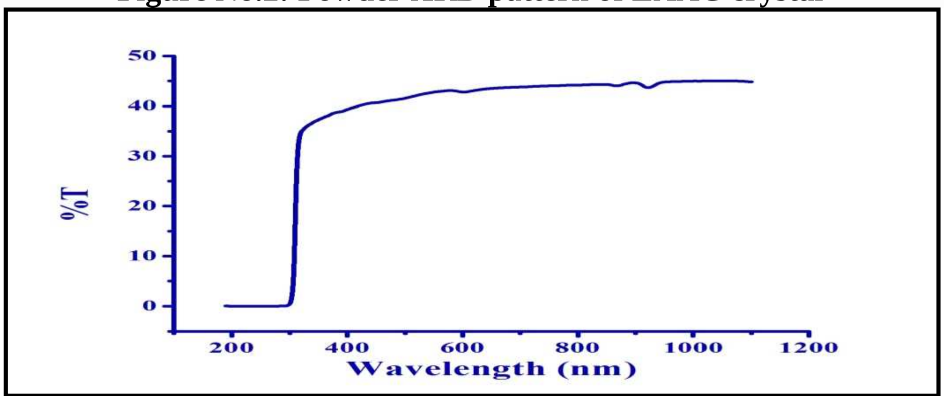


Figure No.3: UV Transmission spectrum of LAAC crystals

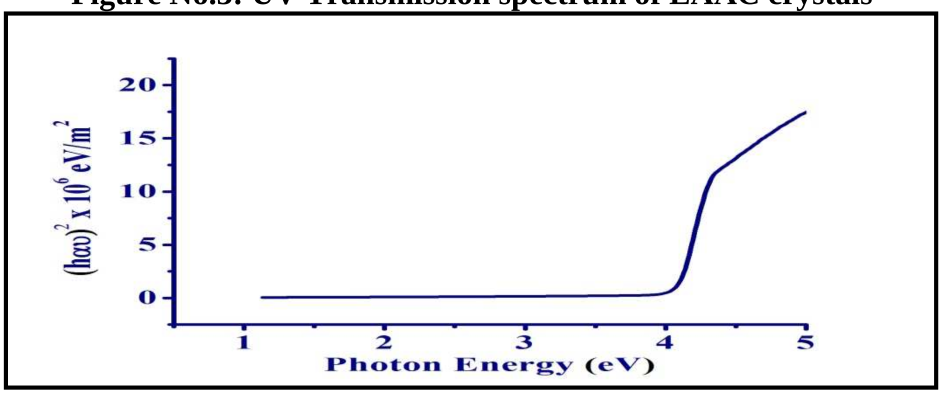


Figure No.4: Variations of $(\alpha h\nu)^2$ versus hν

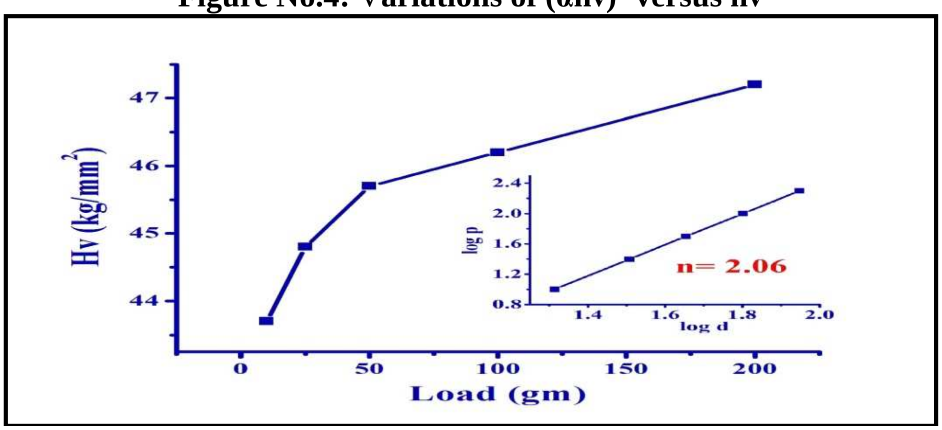


Figure No.5: Vicker's microhardness test

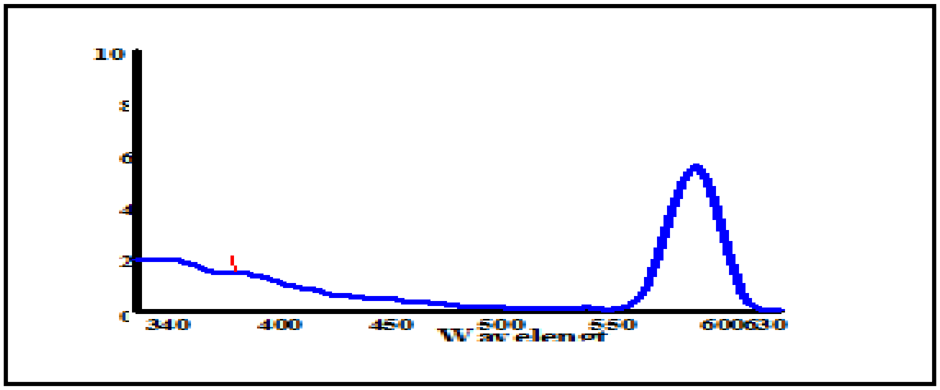


Figure No.6: Photoluminescence Emission spectrum of LACC crystal

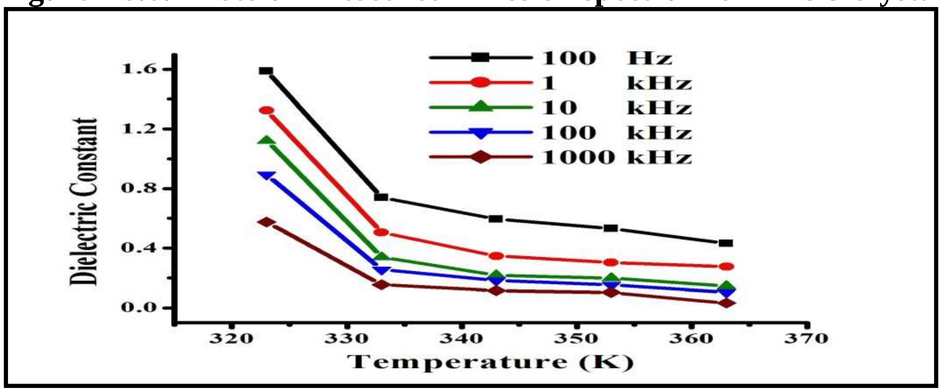
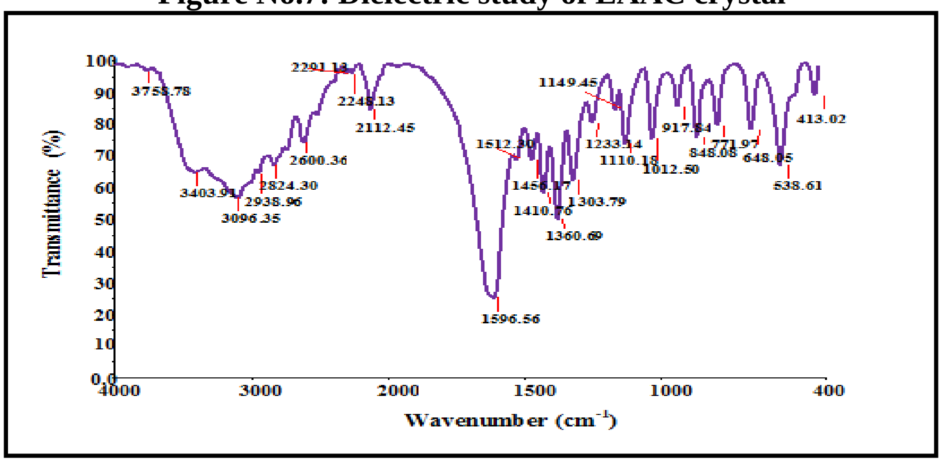


Figure No.7: Dielectric study of LAAC crystal



FigureNo.8: FTIR spectrum of LAAC crystal

CONCLUSION

L-Alanine Ammonium Chloride (LAAC) crystal was grown from aqueous solution by slow evaporation method. The structural confirmation and crystallinity analysis of LAAC crystal has been examined by single crystal XRD and powder XRD analysis. The presence of functional groups was identified by FTIR analysis. The optical transmission study reveals that the grown crystals have good transparency over the entire visible region from 300 nm. The mechanical stability of the grown crystal was checked by Vicker's Hardness test. The second harmonic generation test for the grown crystals was performed by the powder technique of Kurtz and Perry experimental setup. Dielectric constant measurements were carried out at different temperatures and frequencies. The results suggest that the title material is an eligible candidate in nonlinear applications.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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