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Nonlinear Optical Properties of Pure L-Alanine Calcium Chloride ($LACaCl_2$) Single Crystal

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Abstract **– A nonlinear optical crystal, L-Alanine Calcium Chloride ($LACaCl_2$) was grown from aqueous solution by slow solvent evaporation method at room temperature. The grown crystals were characterized for spectral, optical and second order nonlinear optical properties. $LACaCl_2$ crystallizes in orthorhombic system. The mode of vibrations of different molecular groups present in the crystal was identified by FTIR study. The grown crystals were found to be transparent in the entire visible region. The NLO property of crystal was found using Nd:YAG laser light of wavelength 1064 nm and measured SHG efficiency was 0.42 times that of pure KDP. Vicker's hardness proves the mechanical stability of the crystal.**

Keywords **– L-Alanine Calcium Chloride, Powder X-Ray Diffraction, UV-Visible Spectroscopy, FTIR, Vicker's Hardness.**

I. INTRODUCTION

Most of the amino acids and their complexes belong to the family of organic and semi-organic nonlinear optical (NLO) materials that exhibit wide applications in second harmonic generation(SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplification, optical image processing. [1–6]. Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their nonlinear optical properties [7–10]. Among the amino acids, L-Alanine is the simplest acentric crystal with a SHG efficiency of about one-third of that of the well known KDP and it is a naturally occurring chiral amino acid with a non-reactive hydrophobic methyl group (CH_3) as a side chain [11–13]. The L-Alanine molecule exists as a zwitterion, where the carboxyl group dissociates and the amino group protonates. Some complexes of L-Alanine have been recently crystallized and various studies have been investigated by many researchers [14–18].

II. EXPERIMENTAL TECHNIQUE

The starting material was synthesized by taking L-Alanine and calcium chloride in a 1:1 stoichiometric ratio. The calculated amount of calcium chloride was first dissolved in deionized water. L-Alanine was then added to the solution. The solution was agitated with a magnetic stirring device for two hours continuously and filtered after complete dissolution of the starting materials. The solution thus prepared was allowed to evaporate at room temperature and allowed to crystallize by slow evaporation of solvent at 32°C. Well-defined single crystals of good transparency were collected in about five weeks. Transparent single crystals of size upto $2\times2\times1mm^3$ were harvested and are shown in Fig.1

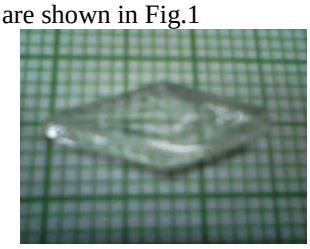

Fig.1. As grown crystal of $LACaCl_2$

III. CHARACTERIZATION

3.1. UV-Visible spectral analysis:

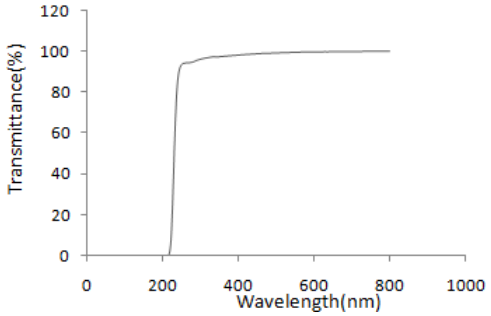

Fig.2. UV–Vis spectrum of $LACaCl_2$ single crystal

The UV-vis-NIR transmittance spectrum is shown in fig 2. It was recorded with SHIMADZU UV-Vis spectrometer in the range 200-800 nm. The crystal shows a good transmittance in the visible region. It is observed that there is no significant absorption in the range 200-800nm. As there is no absorption, the crystal is found to be transparent in the visible and near IR region, an essential parameter required for frequency doubling process. Thus the use of amino acids leads to wider transparency range in the entire visible and UV spectral regions due to the absence of strong conjugated bonds. The lower cutoff at 210nm combined with the very good transparency window makes the material suitable for optoelectronics applications, and for the generation of second harmonics.

3.2. Powder X-ray diffraction studies:

The fine powder of the title compound has been subjected to powder X-ray diffraction analysis and the recorded pattern is shown in fig3. The powder sample was scanned in steps of 0.1° for a time interval of 10 seconds over a 2Θ range of 10° to 70°. The sharp and well defined Bragg's peaks at specified 2Θ angles show the crystalline nature and purity of the crystal. New peaks in the XRD

pattern of the grown crystal confirm the incorporation of calcium chloride in the grown crystals.

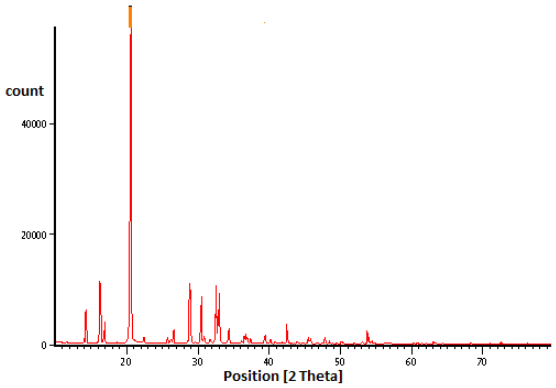

Fig.3. PXRD of $LACaCl_2$ single crystal

3.3. Single crystal XRD

The grown crystal $LACaCl_2$ has been investigated by single crystal XRD and lattice parameters obtained are a= 5.768A˚, b= 6.006A˚, and c= 12.301A˚, & α=β=γ=90° and the cell volume =426.1A˚. The grown crystal crystallized in orthorhombic system with the space group $P2_12_12_1$.

3.4. Fourier Transform Infrared (FTIR) analysis:

The infrared spectrum of the grown crystal has been recorded in the range of 400-4000cm^{-1}. The Fourier transform infrared (FTIR) spectrum of $LACaCl_2$ is shown in fig4.The presence of the functional groups in $LACaCl_2$ crystal are identified.

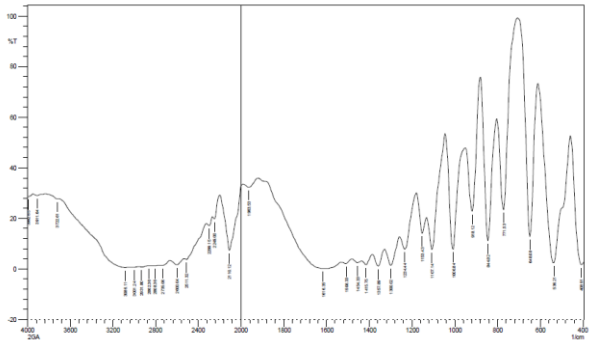

Fig.4. FTIR spectrum of $LACaCl_2$ single crystal

Table 1: FTIR bands/peaks and their assignments $LACaCl_2$crystal.

Wavenumber (cm^{-1})	**Assignment**
2511.32	NH_3^+ asymmetric stretching
2110.12	Combination of asymmetric NH_3^+ bending vibration
1963.53	C=C stretch of COO^- vibration
1616.35	NH_3^+ bending degenerate mode
1454.33	CH_3asymmetric bending
1415.75	COO^- symmetric stretching
1300.02	C-H and N-H bending
1234.44,1153.43	NH_3^+ rocking
918.12	overtone of torsional oscillation of NH_3^+
844.82	C-H bending
771.53	CH_2 rocking
648.08	O-C= O in plane deformation
536.21	torsional oscillation of NH_3^+

3.5. Second Harmonic Generation:

The second harmonic generation (SHG) efficiency was determined by the modified version of the powder technique developed by Kurtz and Perry [19] using Nd: YAG, 10 ns laser with a pulse repetition rate of 10Hz working at 1064 nm. The sample was ground into fine powder and tightly packed in a micro-capillary tube. It was mounted in the path of the laser beam of 3.6mJ pulse energy obtained by splitting the original laser beam.

Potassium dihydrogen orthophosphate (KDP) ground into samples of identical size was used as reference material in the SHG measurements. Conversion efficiency was computed by the ratio of amplitude of the $LACaCl_2$ sample to that of the KDP signal amplitude recorded for the same input power. The SHG efficiency of the grown $LACaCl_2$ crystal was found to be 0.42 times that of KDP.

3.6. Microhardness Studies:

Microhardness studies have been carried out on pure $LACaCl_2$ single crystal using a Leitz Wetzlar Vicker's microhardness tester. The static indentations were made at room temperature with a constant indentation time of 10 s for all the loads. The hardness was calculated using the relation $H_v=1.8544P/d^2$ kg/mm^2,where p is applied load and d is the diagonal length of the indentation depression in diameter. The relation between hardness number (H_V) and load (P) for $LACaCl_2$ is shown in fig 5. The plot of log p vs log d is a straight line and is shown in fig 6, which is in good agreement with Meyer's law. The slope of the graph gives the n value as 2.933.According to Onitsch and Hanneman, for hard materials, value of n should be less than 1.6 and for the soft one, n should be greater than 1.6. Hence the grown crystal is a relatively softer material. The elastic stiffness constant is calculated for different loads using the relation $C_{11}= (H_v)^{7/4}$ [20] and the table 2 lists the computed values of C_{11} for $LACaCl_2$.

Table 2: Elastic stiffness constant for different Loads

S. No.	H_v kg/mm^2	C_{11} x 10^{14} Pa
1.	30.45	3.9
2.	38.35	5.9
3.	45.8	8.06
4.	51	9.7

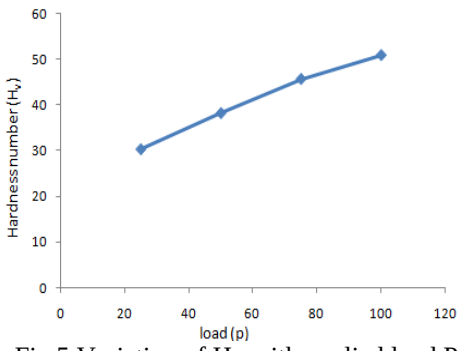

Fig.5.Variation of H_V with applied load P

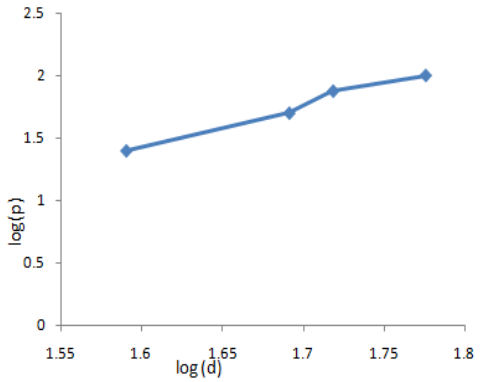

Fig.6. Variation of log (p) with log (d)

IV. CONCLUSION

$LACaCl_2$ crystal has been grown from aqueous solution by slow evaporation technique at room temperature. The sharp and well defined Bragg's peaks of powder XRD pattern at specified 2Ɵ angles shows the crystalline nature and purity of the crystal. The lattice parameters of $LACaCl_2$ are determined by single crystal XRD. It belongs to orthorhombic crystal system with the space group $P2_12_12_1$.The FTIR analyses confirm the presence of various functional groups. The lower cutoff wavelength at 210nm and the wide transparency range (200nm–800nm) observed from the UV–Vis spectrum confirms suitability of the material for optoelectronic applications. SHG studies validate the use of $LACaCl_2$ crystal as a promising material for NLO applications. Vickers Microhardness value was calculated in order to understand the mechanical stability of the grown crystal and the calculated value of n being 2.933 proves that the grown crystal belongs to the category of soft materials.

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