Growth, Microhardness, Electrical and Dielectric Studies on L-Alanine Hydrogen Chloride NLO Single Crystal

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Manuscript submitted November 25, 2014; accepted May 2, 2015.
doi: 10.17706/ijmse.2015.3.2.159-166

Abstract: L-Alanine Hydrogen Chloride (LAHCL) single crystals were grown using slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to orthorhombic in structure with the space group $P2_12_12_1$. The refractive index of the crystal was determined using Brewster's angle method. Vicker's microhardness measurements for different loads were carried out for grown single crystal. The dielectric studies show that the dielectric constant and dielectric loss decrease exponentially with frequency at different temperatures (30˚C, 60˚C, 90˚C and120˚C). The photoconductivity studies reveal that the crystal exhibits negative photoconductivity. The Kurtz powder test confirms that the SHG efficiency of L-alanine hydrogen chloride is equal to that of KDP. The growth pattern was analysed by etching studies.

Key words: Single crystal, growth from solution, X-ray diffraction, dielectric constant and photoconductivity studies.

1. Introduction

In the modern world, the development of science & technology in many areas has been achieved through the growth of single crystals. Large sized single crystals are essential for device fabrications and efforts are taken to grow large single crystals in short duration with less cost. The search for efficient and new materials in which to carry out investigations on non linear optical processes has been very active since the discovery of second harmonic generation (SHG) in quartz crystal by Franken and his coworkers in 1961. Nonlinear optical (NLO) materials are expected to play a major role in photonics including optical information processing, sensor protector applications, data storage etc. Some organic compounds exhibit large NLO response, in many cases, orders of magnitude larger than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. In this stimulating context, organic nonlinear materials have been recognized as forefront candidates for fundamental and applied investigations involving, in a joint effort, chemists, material scientists and optical engineering.

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. Nonlinear optical (NLO) materials have attracted much attention because of their potential applications in the field of optical communications, high-speed information processing, optical data storage and in emerging optoelectronics technology [1], [2]. Research in organic, semi organic and inorganic functionalized nonlinear optical materials plays a crucial role because of their molecular interactions, bond strength, high molecular polarizability, easy incorporation of ions in the lattice, etc. [3], [4]. Amino acids are interesting materials for NLO application as they contain a proton donor carboxyl acid (-COO) group and the proton acceptor amino ($-NH_2$) group.

LAHC salt was synthesized and solubility was determined at various temperatures. Bulk single crystals of LAHC salt was grown by solution method. The optical absorption study reveals high transparency of the crystal with a UV cut off wavelength of 240 nm. The NLO efficiency of the crystal is found to be 0.76 times that of KDP [5]. The development of NLO materials led to compounds potentially suitable for application in frequency conversion, optical telecommunication, image processing, optical computing, and data storage devices [6-9]. Amino acid family-type crystals have over the years been subjected to extensive investigation by the researchers for their non-linear optical properties [10], [11]. Among amino acids L-alanine (CH_3CHNH_2COOH) is the simplest molecule with second harmonic generation efficiency of about one-third of that of the well known KDP [12, 13]. The growth and studies of L-alanine have also been reported [14]. Similarly, the characterizations of L-Alanine Maleate [15,16], Lalanine Tetra Fluro Borate [17], LalanineAcetate [18], L-Alanine sodium chloride [19], Alanine Barium Chlorie [20], Alaninium Oxalate[21] have also been investigated.

Efforts have been made for the crystallization of amino acid mixed complex materials in order to make them suitable for device applications. In recent years, amino acids have been mainly used as a basis for synthesizing organic and semi-organic compounds. Amino acid family crystals exhibit excellent nonlinear and electro-optical properties. In the present study, bulk single crystals of L-alanine hydrogen chloride were grown and hence attempts are made to characterize the grown crystal by single crystal XRD, refractive index (n), microhardness, dielectric, photoconductivity and etching studies.

2. Experimental Procedure

The L-alanine hydrogen chloride was synthesized by taking L-alanine and hydrochloric acid taken in equimolar ratio in aqueous solution by slow evaporation method. The solution was stirred continuously using a magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation. Among them, defect free seed crystal was selected and suspended in the mother solution, which was allowed to evaporate at room temperature. Large size single crystals were obtained due to collection of monomers at the seed crystal sites from the mother solution after the nucleation and growth processes were completed. Good transparent seed crystals were obtained after a period of 25 days. The crystals were obtained by the solution method. Fig.1 shows as-grown crystals of L-alanine hydrogen chloride.

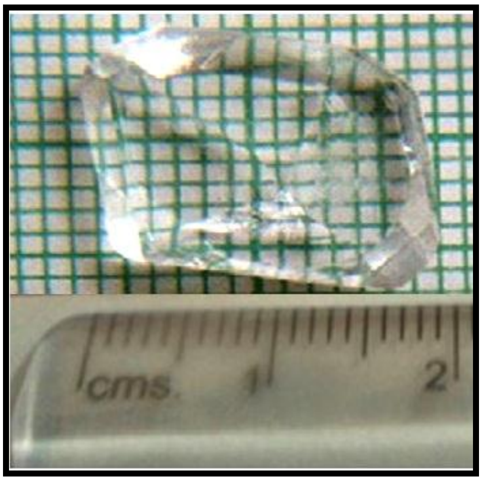

Fig. 1. The grown single crystal of L-alanine hydrogen chloride

2.1. Characterization Techniques

The grown crystal was characterized by the following techniques:

2.1.1. Single-Crystal X-Ray Diffraction

Single crystal X-ray diffraction is an analytical technique in which X-rays are employed to determine the actual arrangement of atoms within a crystalline specimen. Single crystal X-ray diffraction (XRD) is a non-destructive tool to analyze crystal structure of compounds, which can be grown as single crystals. XRD is employed for finding unit cell parameters, space groups; three-dimensional co-ordinates of atoms in the unit cell and mean thermal motion amplitudes of atoms in the unit cell. Single crystal X-ray diffractometer collects intensity data required for structure determination. Accurate measurements of intensities of reflections of all Miller indices within a specified reciprocal radius (usually 25^0 for MoKα and $68^0$for CuKα) is needed to find the structure, while unit cell parameters depend only on direction of reflections. For single-crystal work, the specimen should be smaller than cross section diameter of the beam. Larger crystals can be cut down to proper smaller crystals that contain strong diffracting elements. In the present study, the single crystal X-ray diffraction analysis was performed using an Enraf Nonius CAD4-F single crystal X-ray diffractometer, with graphite monochromated MoKα radiation. X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials.. The crystal was scanned for 2θ values from 20° to 60° at a rate of 2°/min. Figure 2 shows the Powder XRD pattern of the LAHCL crystal. The diffraction pattern of the LAHCL crystal has been indexed.

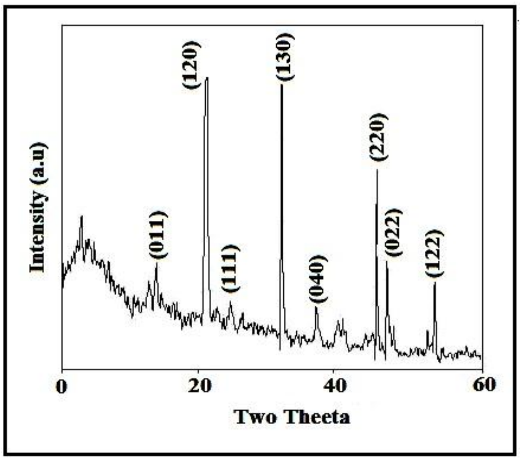

Fig. 2 Powder XRD pattern of LAHCL

2.1.2. Refractive index measurement

The refractive index of the L-alanine hydrogen chloride crystal was determined by Brewster's angle method. A polished single crystal of L-alanine hydrogen chloride with 1 mm thickness was mounted on a rotating mount at an angle varying from 0 to 90 degrees. The angular reading on the rotary stage was observed, when the crystal was perfectly perpendicular to the intra-cavity beam.

2.1.3. Microhardness test

Hardness is an important factor in the choice of ceramics for abrasives, bearings, tool bits, wear resistance coatings etc. Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage Measurement of hardness is a non-destructive testing method to determine the mechanical behaviour of the materials. The hardness depends not only on the properties of the materials under test but also largely on the conditions of measurement. Microhardness tests have been applied to fine components of clock and instrument mechanisms, thin metal strip, foils, wires, metallic fibers, thin galvanic coatings, artificial oxide films, etc., as well as the thin surface layers of metals which change their properties as a result of mechanical treatment (Machining), rolling, friction and other effects. The microhardness method is widely used for studying the individual structural constituent elements of metallic alloys, minerals, glasses, enamels and artificial abrasives. Hardness of the material is defined as the resistance it offers to the motion of dislocations, deformations or damage under an applied stress. The Vickers hardness (H_v) numbers [22] at different loads were calculated using the following relation,

$$H_V = 1.8544 p / d^2 (kg / mm^2) \quad (1)$$

where P is the applied load in kg and d the average diagonal length in mm.

2.1.4. Dielectric studies

A study of the dielectric properties of solids gives an electric field distribution within solid. The frequency dependence of these properties gives great insight into the material applications. Suitably cut and polished samples (with known dimensions) are subjected to dielectric studies using HIOKI 3532-50 HITESTER LCR meter with a conventional four terminal sample holder. The samples are prepared and mounted between the copper electrodes. In order to ensure good ohmic contact the sides of the crystal was coated with silver. The experiment was carried out for frequencies varying from 50 Hz to 5 MHz and for four different temperatures, 30°C, 60°C, 90°C and 120°C, respectively. The dielectric constant and dielectric loss of the crystals have been calculated using the relations,

$$\varepsilon = Cd / \varepsilon_0 A \quad (2)$$

$$\varepsilon^{'} = \varepsilon \tan \delta \quad (3)$$

where d is the thickness and A is the area of the sample [23] .

2.1.5. Photoconductivity studies

The crystal sample is well-polished and surfaces are cleaned with acetone. This is attached to a microscope slide and two electrodes of thin copper wire (0.14 cm diameter) are fixed onto the specimen at some distance apart using silver paint. After this it is annealed at a temperature of 100 ^{0}C to perfect dryness. A DC power supply, a Keithley 485 picoammeter and the prepared sample are connected in series. The sample was covered with a black cloth and the dark current (Id) of the crystal was recorded with respect to the different applied voltage. Then sample was illuminated by the radiation from 100 W halogen lamp containing iodine vapour and tungsten filament and the corresponding photocurrent (Ip) is recorded for the same values of the applied voltage.

2.1.6. NLO Test – Kurtz powder SHG method

The SHG conversion efficiency of LAHCL was determined by the modified version of the powder technique developed by Kurtz and Perry [24] . The crystal was mock into powder and it was densely packed in a micro capillary tube of uniform bore. A Q-switched Nd: YAG laser beam of wavelength 1064 nm with an input power of 6.2 mJ/pulse and a pulse width of 8 ns with a repetition rate of 10 Hz was made to fall normally on the sample. The output from the sample was monochromated to collect the intensity of 532 nm component and to eliminate the fundamental wavelength. The second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected and a photo multiplier tube.

2.1.7 Etching studies

The nonlinear optical properties such as SHG efficiency, damage threshold etc, depend on the crystalline perfection. Chemical etching is a very simple and elegant technique to reveal the crystal defects and the crystal growth mechanism, which is able to develop some features such as growth striations, etch spirals; rectangular etches pits, etc., on the crystal surface.

3. Results and Discussion

3.1. Single-Crystal X-Ray Diffraction

The lattice parameter values are found to be a = 6.17 Å, b = 9.92 Å and c = 11.76 Å, α= β =γ = 90, and volume of the unit cell is 723.06 Å^3. The XRD data prove that the crystal is orthorhombic in structure with the space group $P2_12_12_1$. These values are found to agree with the reported values [25].

3.2. Refractive Index Measurement

The refractive index of the L-alanine hydrogen chloride crystal was determined by rotating the crystal. The crystal was rotated until the reflection of laser light vanishes and this angle has been noted. Brewster's angle (θp) for L-alanine hydrogen chloride was measured to be 57·5º. The refractive index was calculated using the relation $n = \tan \theta p$, and found to be 1·57 are positive [26].

3.3. Microhardness Test

The variation of Hv with applied load P is shown in Fig.3. According to the normal indentation size effect (ISE), microhardness of crystals decreases with increasing load and in reverse indentation size effect (RISE) hardness increases with applied load [27,28].

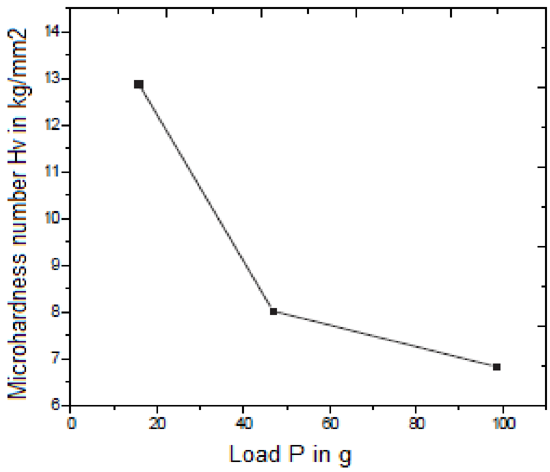

Fig. 3. Variation of hardness with load

3.4. Dielectric Studies

The response of dielectric constant and dielectric loss as a function of frequency is shown in Figs.4 and 5, respectively. From the plots it is observed that the dielectric constant and dielectric loss decrease with increasing frequency and attain saturation at higher frequencies. Dielectric constant is found to decrease with increasing frequency, at room temperature. The high value of dielectric constant at lower frequencies may be due to the presence of all the four polarization namely, space charge, orientational, ionic and electronic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually [29]. From the Fig. 5 shows the variation of dielectric loss with applied frequency and it was observed that the dielectric loss was reduced at higher frequencies. The low values of dielectric constant and loss at higher frequencies reveal the good optical quality of the grown crystals with less defects, which is the desirable property of the materials to be used for various optical and communication devices [30].

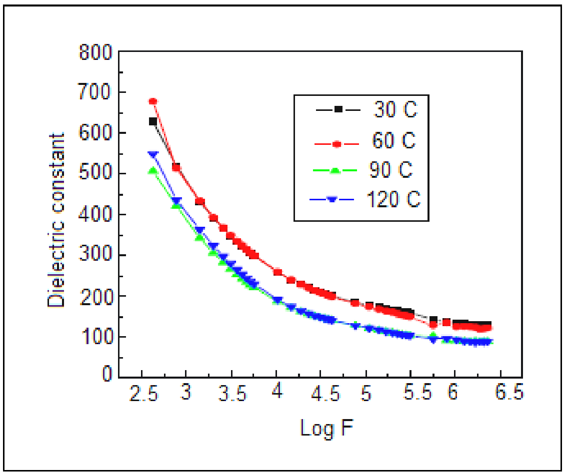

Fig. 4. Variation of dielectric constant with log frequency

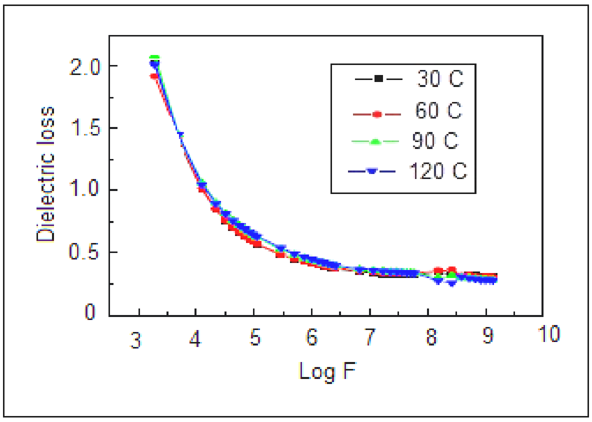

Fig 5 .Variation of dielectric loss with log frequency

3.5. Photoconductivity Studies

The field dependent photoconductivity of the crystal was shown in Fig.6. From the figure, photocurrent is found to be less than that of the dark current for all ranges of applied field enunciates negative photoconductivity. The negative photoconductivity in this case may be due to the reduction in the number of charge carriers or their lifetime in the presence of radiation. Decrease in lifetime with illumination, could be due to the trapping process and increase in carrier velocity [31]. In Stockmann's model, a two level scheme is proposed to explain negative photoconductivity [32]. The upper energy level is situated between the Fermi level and the conduction band, whereas the other one is located in the neighborhood of the valence band. The lower level has high capture cross-section for electrons from the conduction band and holes from the valence band. As a result, sooner the sample is kept under exposed light, the recombination of electrons and holes take place, resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity [33]. It is seen from the plots that both Id and Ip of the sample increase linearly with applied field. It is observed from the plot that the dark current is always higher than the photocurrent, thus confirming the negative photoconductivity nature of the grown single crystal.

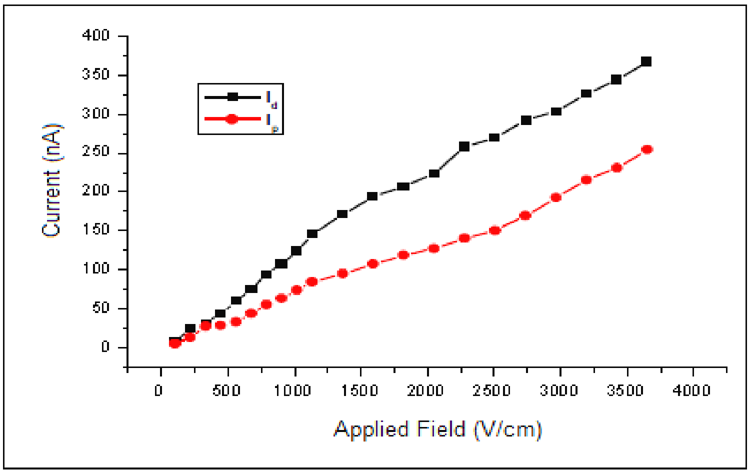

Fig.6. Field dependence of dark and photocurrents

3.6. NLO Test–Kurtz Powder SHG Method

The generation of the second harmonic was confirmed by a strong bright green emission emerging from the powdered sample. A potassium dihydrogen phosphate crystal was used as a reference material in the SHG measurement. The relative conversion efficiency was calculated from the output power of L-alanine hydrogen chloride crystals with reference to KDP crystals. It is observed that the conversion efficiency of L-alanine hydrogen chloride is equal to that of KDP crystals.

3.7 Etching Studies

Etching studies on L-alanine hydrogen chloride crystals were carried out using water as etchant. Etch pits were observed on the (1 0 0) plane when etched with water for 60 sec. The etching photographs of L-alanine hydrogen chloride crystals are shown in Fig. 7. From the Fig. 7 it is evident that when the crystals were etched for 60sec, well defined etch pits were observed.

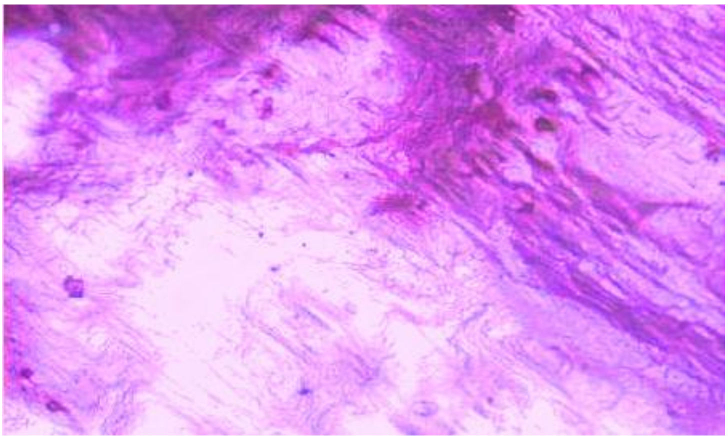

Fig. 7. Etch pattern for L-alanine hydrogen chloride crystal

4. Conclusion

Single crystals of L-alanine hydrogen chloride were grown from aqueous solution by slow evaporation technique. The grown crystals were characterized by single crystal XRD and it is confirmed that the crystal belongs to the orthorhombic system with space group $P2_12_12_1$. Refractive index of the grown crystal was measured to be 1.57. The mechanical behavior is studied by Vickers hardness method. Dielectric measurements were carried to analyse the dielectric constant and dielectric loss at different frequencies and temperatures. The photocurrent was less than the dark current, signifying negative photoconducting nature. NLO study reveals that the grown crystal has SHG efficiency equal to that of KDP crystal. From the etching studies well defined etch pits were observed on the surface of the specimen. It may due to vacancy of atoms on the surface of the specimen.

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