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XRD,Optical,SHG and Hardness Studies of L- Alanine Crystals Grown in Aqueous Solution of Hydrofluoric Acid

KEYWORDS L-alanine; admixtured crystal; solution growth; XRD; band gap; SHG; density; hardness

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ABSTRACT *A Nonlinear Optical (NLO) material has a nonlinear response to the electric field associated with the light of a laser beam, leading to a variety of optical phenomena such as generation of new light frequencies. L-alanine is an NLO material and it has a Second Harmonic Generation (SHG) efficiency of about 0.3 times that of KDP. To alter the various properties of L-alanine, single crystals of L-alanine have been grown in the aqueous solution of hydrofluoric acid and in this work, L-alanine was admixtured with hydrofluoric acid (LAHF) in the molar ratio of 1:1. The grown crystals were colorless and transparent and they were subjected to various studies for characterization.*

1. Introduction

In recent years, many significant achievements have been made in the field of nonlinear optics because of the development of new nonlinear optical (NLO) crystals of both organic and inorganic type [1-3] The need for nonlinear optical materials is much more than other materials because of their significant impact on laser technology, optical communication, optical data storage technology etc [4]. Amino acids are a group of organic compounds containing two functional groups such as amino group and carboxylic group. Most of the amino acids and their complexes belong to the family of organic and semiorganic nonlinear optical (NLO) materials that have potential applications in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplification, optical image processing. Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their nonlinear optical properties. Among the amino acids, L-alanine is the simplest acentric crystal and it is a naturally occurring chiral amino acid with a non-reactive hydrophobic methyl group (CH_3) as a side chain. L-alanine molecule exists as a zwitterion, where the carboxyl group dissociates and the amino group protonates. Efforts have been made on the amino acid mixed organic-inorganic complex crystals, in order to improve the chemical stability, laser damage threshold and nonlinear optical properties. If L-alanine is mixed with different organic and inorganic acids to form novel materials, it is expected to get improved NLO properties [5]. Some complexes of L-alanine have been recently crystallized and various studies have been investigated by many researchers [6-9]. Keeping this in mind, L-alanine is mixed with hydrofluoric acid to form L-alanine hydrogen fluoride crystal by slow evaporation method. But the results showed that the expected crystal is in fact L-alanine crystal with the altered properties in comparison that of L-alanine grown in water. We report here the investigations on the characterization of L-alanine crystals grown in aqueous solution of hydrofluoric acid.

2. Solubility and Growth

The salt of L-alanine admixtured with hydrofluoric acid (LAHF) was synthesized by taking L-alanine (99% purity) and analar grade hydrofluoric acid in the molar ratio of 1:1 in double distilled water. The dissolved solution was heated at 50 oC for the synthesis of LAHF salt. The purity of the synthesized salt was further increased by repeated re-crystallization. The solubility of the synthesized salt was measured by gravimetrical method [10]. Fig.1 shows the solubility curve for LAHF sample and it is observed that the solubility of LAHF sample in water increases with temperature, exhibiting a positive temperature coefficient of solubility.

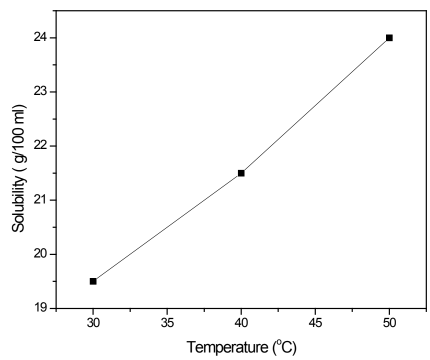

Figure 1: Solubility curve of LAHF sample

The saturated solution of the re-crystallized salt of LAHF was prepared in accordance with the solubility data and the calculated amounts of the reactants were thoroughly dissolved in double distilled water and stirred well for about 2 h using a magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution. The solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation method. The harvested crystal of LAHF is shown in the figure 2.

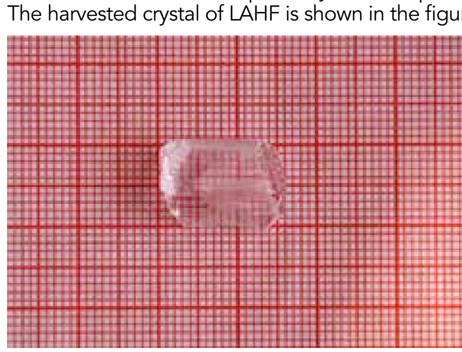

Figure 2: Grown crystal of LAHF

3. Characterization

3.1 Determination of crystal structure and density

The structure of the grown LAHF crystal was analyzed by employing a Bruker-Nonious MACH3/CAD4 single crystal X-ray diffractometer. From the single crystal X-ray diffraction data, it is observed that the LAHF crystal belongs to orthorhombic structure with the lattice parameters a = 5.759(2) Å, b = 6.042(4) Å, c=12.358(3) Å, $\alpha = \beta = \gamma = 90°$ and V =430.01(1) Å3. The obtained structural data for the grown crystal of this work are almost coincided with those of L-alanine crystal and therefore the crystal structure of LAHF crystal is not changed [11]. The floatation method was employed for the precise determination of density of crystals. The liquids like xylene and carbon tetrachloride were used for the measurement of density. After mixing xylene and carbon tetrachloride in a suitable proportion in a specific gravity bottle, a small piece of crystal was immersed in a mixture of the liquids. When the sample was attained in a state of mechanical equilibrium, the density of the crystal would be equal to the density of mixture of liquids. The density was calculated using the relation $\rho = (w3-w1)/(w2-w1)$, where w1 is the weight of empty specific gravity bottle, w2 is the weight of the specific gravity bottle with full of water and w3 is the weight of the specific gravity bottle full of the mixture of xylene and carbon tetrachloride. The obtained value for density of LAHF crystal by floatation method is 1.394 g/cc. The density was also calculated from the crystallographic XRD data using the relation $\rho=(MZ)/(NV)$ where M is the molecular weight of the LAHC crystal, Z is the number of molecules per unit cell, N is Avogadro's number and V is volume of the unit cell and it was found to be 1.377 g/cc.

3.2 Linear optical studies

To obtain the linear optical properties, transmittance spectrum of the grown LAHF crystal in the wavelength range of 190-1100 nm was recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer and it is shown in Fig. 3. At about 241 nm, a sharp fall to zero in the transmittance is observed for LAHF sample and the crystal has sufficient transmittance in the entire visible and near IR region. The sharp fall at 241 nm for the sample corresponds to the fundamental absorption edge and the band gap energy is found to be 5.14 eV [8].

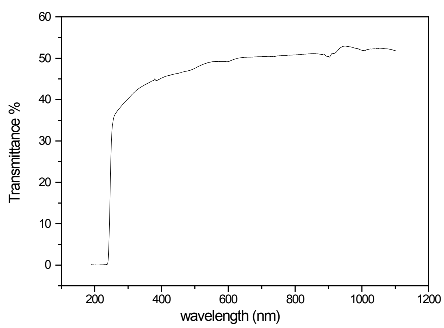

Figure 3: UV-visible transmittance spectrum for LAHF crystal

3.3 Vickers microhardness test

Hardness is one of the important mechanical properties of solid material and it can be used as a suitable measure of the plastic properties and strength of the material. Microhardness testing is one of the best methods to understand the mechanical properties of materials such as fracture behavior, yield strength, brittleness index and temperature of cracking. Transparent crystals free from cracks were selected for microhardness measurement. Before indentations, the crystals were carefully lapped and washed to avoid surface effects. Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter. The well polished LAHF crystal was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The indentation time was kept as 10 s for all the loads. The hardness number was calculated using the relation given in the literature [10]. The obtained values of hardness number (Hv) for different loads (P) for LAHF crystal is shown in table 1 and it noticed that the hardness number increases with the increase of load obeying the reverse indentation size effect.

Table 1: Values of hardness number for LAHF crystal

Load (g)	Hardness number (kg/mm2)
25	38.05
50	55.25
100	77.6

3.4 Nonlinear Optical (NLO) studies

The NLO activity in reference to SHG of a sample can be checked using the Kurtz and Perry method [12]. A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 6 ns was passed through the powdered sample. The SHG behavior was confirmed from the output of the laser beam having the green emission.(λ = 532 nm). The second harmonic generation signal of 9.3 mJ for LAHF sample was obtained for an input energy of 0.68 J. But the standard KDP crystal gave an SHG signal of 8.8 mJ for the same input energy. Thus, it is noticed that the SHG efficiency of the grown LAHF sample is 1.05 times that of the standard KDP crystal. It is to be mentioned here that the particle size has been maintained at about 150 microns for both LAHF and KDP samples.

4. Conclusions

Single crystals of LAHF have been grown by slow evaporation solution growth technique and the grown crystals were transparent with a well defined external appearance. The solubility of LAHF crystal is observed to be increasing with increase in temperature. The unit cell parameters for LAHF crystal have been evaluated by single crystal XRD and the structure is confirmed to be orthorhombic. The optical absorption study reveals high transparency of the crystal with a UV cut-off of 241 nm. The NLO efficiency of LAHF sample is found to be 1.05 times that of KDP. The microhardness study reveals the mechanical strength of the material.

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