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Growth and Characterization of L-Proline – An Organic NLO Crystal

KEYWORDS
Characterization; microhardness; SHG; amino acid; solution growth

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ABSTRACT *Nonlinear optical amino acid single crystals of L-proline were successfully grown by slow evaporation solution growth method. The grown crystal was subjected to different characterization in order to test its suitability for device fabrication. Single crystal X-ray diffraction studies were carried out to find the lattice parameters. The optical transmittance and lower cut-off wavelength of the crystal was estimated by UV-Vis-NIR studies. The Vickers microhardness test was also carried out to test the mechanical stability and the hardness parameters are determined. The SHG activity of the grown crystal was confirmed using Kurtz powder method.*

1. Introduction

Photonics has become an active field of research due to modern society's demand for improved telecommunications and data processing. The design of devices that utilize photons instead of electrons in the transmission of information has created a need for new materials with unique optical properties [1]. In view of this, it is desired to find new NLO crystals which have a shorter cut-off wavelength. Synthesis of such materials is of great importance from both scientific and technological point of view. L-proline is a α-imino acid, since it contains an imino group (-NH) instead of an amino group (NH_2) and it is widely used as a laser frequency doubler and electro optic modulator. Some of the L-proline based crystals such as prolinium picrate [2], L-proline cadmium chloride monohydrate [3], prolinium tartarate [4], dichlorobis L-proline (zinc II) [5], L-proline lithium chloride monohydrate [6], etc. have been reported. In the present investigation we report the synthesis and growth of L-proline using deionized water as a solvent and its characterization.

2. Experimental details

The commercially available material of L-proline (LP) was purified by repeated recrystallization process and the purified salts were taken as the charge material for synthesis. The recrystallized LP salt was subjected to continuous stirring using motorized magnetic stirrer with hot plate maintained at a temperature of $50^{o}C$. On reaching saturation, equilibrium concentration of the solute was determined gravimetrically [7]. The dried salt was collected and the supersaturated solution was prepared using deionized water as solvent at $40^{0}C$, in accordance with the solubility data. The solution was filtered using 4 micro Whatmann filter paper and the filtered solution was taken in a beaker closed with perforated paper for slow evaporation. After 21 days good quality crystals of L-proline has been harvested from the mother solution.

The lattice parameters were determined by single crystal XRD analysis using ENRAF NONIUS CAD4 diffractometer. The transmission spectra were recorded using a Varian Carry 5000 spectrophotometer in the range of 200-2500 nm. The nonlinear optical conversion efficiencies were tested using a modified setup of Kurtz and Perry. The microhardness of the grown crystals was measured using a Leitz Weitzier microhardness tester with a diamond indenter.

3. Results and discussion

The as grown LP crystal is shown in Fig. 1. The single crystal XRD measurements indicate that the grown crystal belongs to orthorhombic system with space group $P2_12_12_1$. Since this space group is recognized as noncentrosymmetric, there is possibility of second harmonic generation from the crystal. The lattice parameters obtained are a = 11.642(3) Å, b = 9.037(5) Å, c = 5.261(3) Å, and $\alpha = 90^0$, $\beta = 90^0$, $\gamma = 90^0$ and the volume is 553.50 $Å^3$.

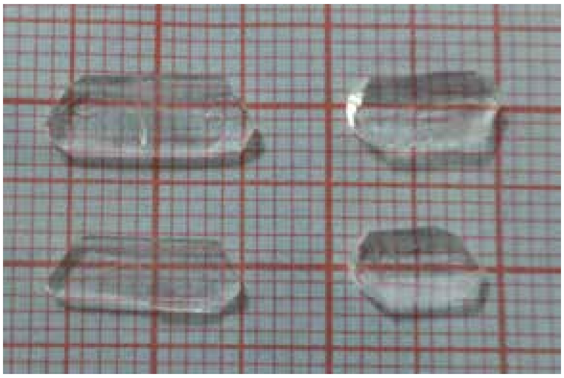

Fig. 1 Photograph of LP crystal

The optical transmittance spectrum of LP is shown in Fig. 2(a). Optically transparent single crystal of thickness about 2 mm was used for this study. There is no appreciable absorption of light in the entire visible range as in the case of all amino acids [8]. This shows the absence of any overtones and absorbance due to electronic transitions. The sharp wavelength cutoff occurs at 209 nm. The optical transmittance study shows that LP is a potential candidate for SHG. Transparent nature in the visible region is an important property for any NLO material from device point of view. A sharp fall in the transmittance is observed at 209 nm corresponds to the fundamental absorption in the UV region. Absorption in the near ultraviolet region arises from in connection with the theory of electronic structure, which predicts that the band structure is mostly affected near the band extreme. A major objective of this study is to determine the magnitude of the optical energy band gap. Single crystals are mainly used in optical applications and hence optical transmittance window and the transparency lower cut off is very important for the realization of SHG output in this range using lasers. The less absorption in the region between 209 and 1100 nm shows that these crystals are useful for the SHG generation of Nd:

YAG laser of λ = 1064 nm. The value of band gap energy was estimated from the graph between hν and $(\alpha h\nu)^{1/2}$ by extrapolating the linear portion of the curve to zero absorption as shown in Figure 2(b). The band gap energy is thus calculated as about 3.4 eV for the LP crystal.

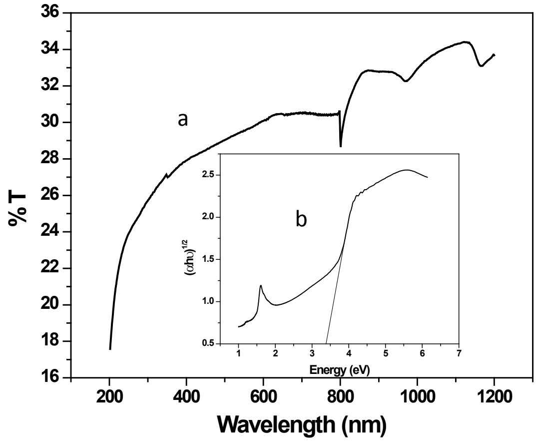

Fig. 2 (a) UV-Vis-NIR spectrum and (b) Tauc's plot of LP

Second harmonic generation (SHG) test is important to check whether a sample is NLO active or not and it was carried out by powder Kurtz and Perry technique [9]. The crystal was ground into a homogenous powder and densely packed between two transparent glass slides. A Q-switched Nd: YAG laser beam of wavelength 1064 nm (pulse width 6 ns) was allowed to strike the sample cell normally. With this source radiation, the generation of second harmonics was confirmed by the emission of green light from the sample. Second harmonic output of 4.2mJ was obtained for an input energy of 0.68J. A sample of powdered potassium dihydrogen phosphate (KDP) was used as the reference material in the SHG measurement and the output was found to be 8.8mJ. The SHG efficiency for LP crystal is found to be 0.47 times that of KDP sample.

Hardness is one of the important mechanical properties of solid material and microhardness test is one of the best methods to understand the mechanical properties of materials. Transparent crystals free from cracks were selected for microhardness measurements. Before indentation the crystals were carefully lapped and washed to avoid surface effects. The crystal was then subjected to Vickers microhardness test and the Vickers hardness number H_v is calculated using the relation

$H_v = 1.8544\ P/d^2$ (kg / mm^2)

Where d is the diagonal length of the indentation and P is the applied load in gram. The variation of H_v for various loads is shown in Fig. 3(a). The Vickers microhardness test revealed that the hardness number of LP is 84.2 Kg/mm^2 and above which cracks develop on the smooth surface of the crystal due to the release of internal stress generated locally by indentation. The hardness of the crystal indicates that it can be used in device fabrication. According to normal indentation size effect (ISE), microhardness of crystals decreases with increasing load and in reverse indentation size effect (RISE), the hardness value increases with increasing load. In LP, H_v increases with increase in load up to 100 gm, hence exhibiting reverse ISE effect. The traditional Meyer's law, which gives the relationship between load P and size d, is

$P = Ad^n$

where the exponent n in the Meyer's number and A is a constant. For normal ISE behavior the exponent $n < 2$. When $n > 2$, there is reverse ISE behavior and when $n = 2$, the hardness is independent of applied load. According to Onitch and Hannemann, [10, 11, 12] if the value of n is between 1 and 1.6, the material is hard and if it is greater than 1.6 the material is soft. Figure 3(b) shows the plot of log P versus log d. The straight line in the graph shows its agreement with Meyer's law. From the plot, the value of n is found to be 3.01. Hence LP belongs to soft material category.

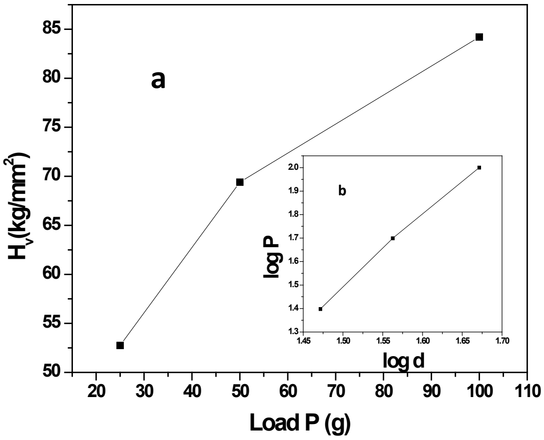

Fig. 3 (a)Plot of load vs H_v (b) Plot of log d vs log P

Elastic stiffness constant is a measure of the ability of the material to resist deformation and it gives an idea about the tightness of bonding with the neighboring atoms. The elastic stiffness constant (C_{11}) for different loads are calculated using Wooster's empirical formula $C_{11} = H_v^{7/4}$. In the case of LP crystal, the stiffness constant is found to increase with the applied load.

Conclusion

L-proline crystals were successfully grown by SEST method and the properties are characterized through various characterization techniques. Single crystal XRD studies shows that L-proline crystallizes in orthorhombic structure. The band gap is determined from UV-Vis-NIR studies as E_g = 3.4eV. Microhardness analysis reveals that LP belongs to soft material category. SHG studies show that LP shows SHG efficiency 0.47 times that of the standard KDP crystal.

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