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International Journal of Current Research
Vol. 3, Issue, 11, pp.386-389, October, 2011

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

GROWTH, STRUCTURAL AND OPTICAL STUDIES OF L-PROLINE HYDRATE CRYSTALS

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ARTICLE INFO

Article History:
Received 24th July, 2011
Received in revised form
20th August, 2011
Accepted 28th September, 2011
Published online 30th October, 2011

Key words:
Crystal Growth,
Dielectric studies,
UV-Vis studies,
Hardness studies, SEM.

ABSTRACT

L-proline hydrate an intriguing organic material for frequency conversion has been grown by slow evaporation solution growth technique at room temperature. Their structural, optical and physicochemical properties were characterized by X-ray powder diffraction, Dielectric studies, UV-Vis spectra and SEM. The crystal belongs to orthorhombic system with space group $P_{21\ 21\ 21}$. The material has a wide transparency in the entire visible region. It is found that the cutoff wavelength lies in the UV region. The mechanical response of the crystal has been studied using Vickers micro hardness technique.

INTRODUCTION

The search and design of highly efficient nonlinear optical (NLO) crystals for visible and ultraviolet (UV) regions are extremely important for laser processing. In view of this, it is desired to find new NLO crystals which have a shorter cutoff wavelength. High-quality organic NLO crystals must possess sufficiently large NLO coefficient, transparent in UV region, high laser damage threshold power, and easy growth with large dimensions [1–4]. There have been significant advances in order to search and synthesize the newer acentric crystalline materials that could produce green/blue laser light. Synthesis of such materials is of great importance from both scientific and technological points of view because of their applications in opto-electronics such as frequency conversion, high-density optical data storage, optical measurements, etc. Proline (abbreviated as Pro or P) is an α-amino acid, one of the twenty DNA-encoded amino acids. L-Prolines codons are CCU, CCC, CCA, and CCG. L-Proline is not an essential amino acid, which means that the human body can synthesize it. L-Proline is unique among the 20 protein-forming amino acids in that the α-amino group is secondary. The more common L form has S stereochemistry. L-Proline Uses Proline and its derivatives are often used as asymmetric catalysts in organic reactions. The CBS reduction and proline catalysed aldol condensation are prominent examples. L-Proline is an osmoprotectant and therefore is used in many pharmaceutical, biotechnological applications. In brewing, proteins rich in proline combine with polyphenols to produce haze (turbidity). L-proline is widely employed as a laser frequency doubler and exclusive material of choice for electro-optic modulators. Although the crystal growing technology for these materials is highly developed and their nonlinear optical susceptibilities are sufficient for most of the current photonic applications, they have features that are less than desirable. Hence, new nonlinear optical materials are needed to extend the range of photonic applications [5]. For any device fabrication in the electronic industry pure and defectless single crystals are needed. In this point of view, the L-proline hydrate single crystal was grown by slow evaporation solution growth method. The grown crystals were subjected to various characterizations.

Solubility and Crystal growth

The low-temperature solution growth technique[6-9] is widely used for the growth of organic and inorganic single crystals to get more transparent single crystals. The commercially available L-proline ($C_5H_9NO_2$) is purified by repeated recrystallization process. Since L-proline is soluble in deionised water, we have chosen deionised water as solvent for growth. The solubility of L-proline was evaluated as a function of temperature in the temperature range 30°C. A thermostatically controlled vessel was filled with the solution of the title compound and with some undissolved L-proline and stirred for a day. The next day a small amount of the supernatant solution was pipetted out and the concentration of the solute was determined gravimetrically. Fig.1 shows the

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solubility curve of the title compound. We infer that the title compound exhibits good solubility and a positive solubility temperature gradient in water. Single crystals of the title compound have been grown from saturated solution at a pH of 3.7 by slow evaporation solution growth technique at 35°C using constant temperature bath having controlled accuracy of 0.01°C. The crystals with perfect shape and transparency were formed by spontaneous nucleation in the supersaturated solution. The growth of the title compound needed a week; single crystals with good optical quality have been obtained. The photograph of the grown crystals is depicted in Fig. 2.

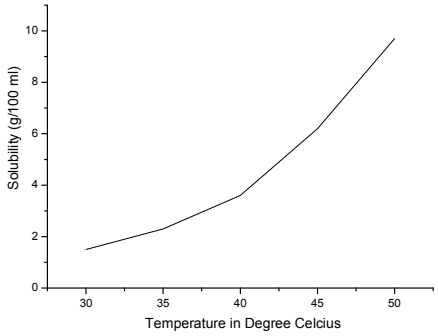

Fig. 1. Solubility curve of L-proline hydrate

Fig. 2. Photograph of the grown L-proline hydrate crystal

Powder X-ray diffraction studies

From the results of powdered X-ray data, the diffraction data showed that the crystal belongs to Orthorhombic system with $P_{21\,21\,21}$ space group. The lattice parameter values of the crystal have been calculated using least-squares fit method and they are found to be a = 11.550 Å, b = 9.020 Å, c = 5.200Å making an angle α=β=γ of 90°. It reveals the excellent crystallinity of the grown material. The crystallographic data obtained in the present study were found to be in good agreement with the data reported in literature. Chemical structure of L-proline hydrate was shown in Fig. 2.

Hardness Studies

In order to study the mechanical properties, micro hardness [10-11] measurements were carried out on L-proline hydrate single crystals. Indentations were made using a Vickers indenter for various loads from 25 to 500 g. It is observed that the Vickers hardness value increases with applied load. According to Onitsch [12] if n > 2, the micro hardness number Hv increases with increasing load. The hardness is generally measured as the ratio of applied load to the surface area of the indentation. The grown crystal with smooth and dominant face was selected for micro hardness studies. Indentations were carried out using Vickers indenter for varying loads (25-500 g), for each load, several indentations were made and the average value of diagonal length was used to calculate the micro hardness. In ideal circumstances, measured hardness values should be independent of the applied load. But in practice, load dependence is observed. Vickers micro hardness number was determined using $H_v = 1.8544\ P/d^2\ Kg/mm^2$. It is observed that the Vickers hardness value increases with applied load. The plot drawn between the corresponding loads and hardness values of the L-Proline hydrate is shown in Fig. 3.

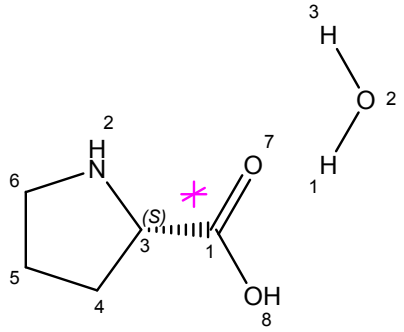

Fig. 2. Chemical structure of L-proline hydrate

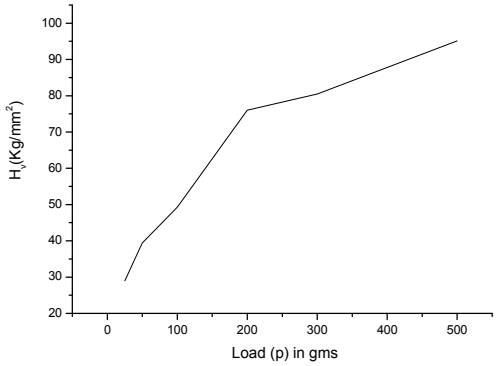

Fig. 3. Mechanical behaviour of L-Proline hydrate

Dielectric Studies

The frequency dependent measurements of capacitance C and tan d, were obtained using a computer controlled LCR HiTester (HIOKI, 3532-50) for different frequencies. The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 1 MHz at room temperature. Fig. 4 shows the plot of dielectric constant (ε_r) versus applied frequency of the L-Proline hydrate crystal. The applied frequency is represented by logarithmic values in the plot. The dielectric constant [13-15] of a material is generally composed of four types of contributions, viz. ionic, electronic, orientational and space charge polarizations. All of these may be active at low frequencies. The variation in dielectric constant with frequency is shown in Fig. 4. It is observed that the dielectric constant decreases ceaselessly with increase in frequency .The large values of dielectric constant at low frequency enumerates that there is a contribution from all four known sources of polarization namely, electronic, ionic,

dipolar and space charge polarization. Space charge polarization is generally active at lower frequencies and high temperatures and betokens the perfection of the crystals. Further, the space charge polarization will reckon on the purity and perfection of the material.

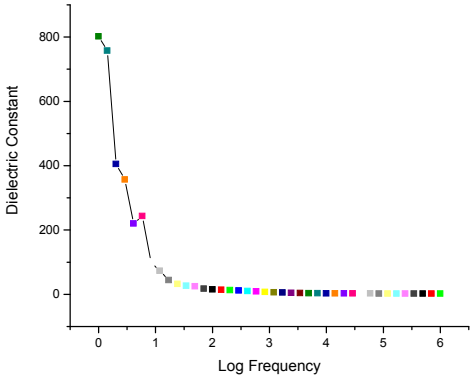

Fig. 4 Dielectric behaviour of L-Proline hydrate

Optical Studies

L-Proline hydrate crystals transmission was studied in the spectral range 290–800 nm Perkin Elmer Lambda 35 UV visible spectrophotometer. The spectrum is shown in Fig. 5. It shows good transparency. The lower cut off of the crystal is found to be 300 nm. The absorption seen in the range 300-500 nm may be due to C=O grouping, and thereafter the transmission becomes almost constant and there is no change in transmittance in the entire visible range upto 800nm, these materials can find application as window in spectral instruments in that region.

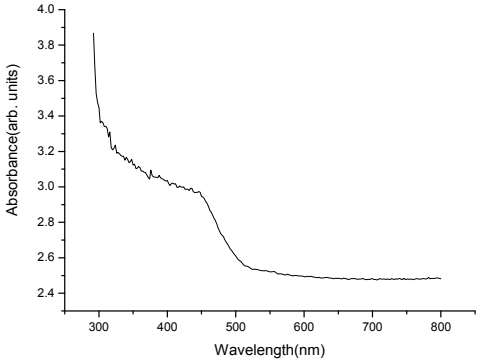

Fig. 5. Optical spectra of L-Proline hydrate

Scanning Electron Microscopy Studies (SEM)

Chemical analysis and morphological studies were carried out using scanning electron microscopy (SEM model JSM 840A). Fig. 6 depict the SEM image of the crystal. It shows some darker and brighter uneven areas. This might be due to solvent inclusions, which is most commonly observed in solution growth. Interesting features of surface morphologies are observed in SEM, actually exhibits stepped structure. Variations in step directions and the appearance of wider steps could be attributed to the general roughness / grain boundary.

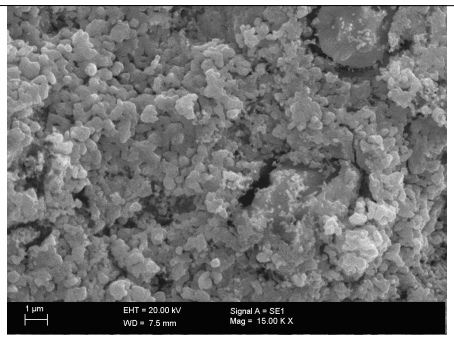

Fig. 6. The SEM image of the crystal

Conclusion

Good optical quality L-Proline hydrate single crystals were grown by the slow evaporation method from aqueous solutions. The material of the grown crystals was confirmed by XRD studies. The present study indicates that the dielectric parameters, ε_r increase at low frequencies. In addition, the results obtained in the present study indicate that the crystal is not only potential NLO material but also promising low ε_r value dielectric materials, expected to be useful in the microelectronics industry. The mechanical and optical properties were examined. As there is no change in transmittance in the entire visible range upto 800nm, these materials can find application as window in spectral instruments in that region.

Acknowledgement

The authors are thankful to Shri.Ch.Seshendra Reddy and Shri.C.R. Kesavulu, Department of Physics, Sri Venkateswara University, Tirupati 517 502, India for measurements.

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