

NON-LINEAR OPTICAL STUDIES OF A NEW AMINO COMPOUND L-HYDROXYPROLINE PICRATE

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ABSTRACT

This work targets to analyse nonlinear behaviour of a new amino compound, L-hydroxyproline picrate (LHPP). Nonlinear optics (NLO) is a very interesting area for researchers as it can crown the world with its application in optoelectronics. Tele-communication, optical data processing likewise extends the list of remarkable pertinence of NLO. The higher the second harmonic generation (SHG) efficiency of the crystal, the higher will be its demand for NLO applications. Studies are going on to improvise the SHG efficiency of the materials, which can be done by analysing their structure, mechanical as well as chemical stability, refractive index, thermal dependence, etc; and regenerating them with suitable changes. In the present work, single crystals of L-hydroxyproline picrate (LHPP) are grown through slow evaporation solution growth technique (SEST) and certain characterisations like powder Xrd, UV-vis spectral analysis, TG analysis, Microhardness, Refractive index and SEM are done over the crystals. SHG efficiency of LHPP is obtained using Kurtz and Perry technique. It is found to be 2.75 times that of KDP which means LHPP possesses a good SHG coefficient. In addition to this, transparency of the crystal in the visible region, smoother morphology, perfect crystalline nature, moderate hardness, temperature dependence and all shows that, LHPP is a potential candidate for NLO applications.

KEYWORDS: Nonlinear Optics, Second Harmonic Generation

The study of NLO materials has become an interesting area of research for the young scientists because of its commercially relevant applications in the technology of photonics. Nowadays optics has dominated over electronics in its application areas. Crystallization and characterization of new materials with better second order nonlinearity is important as they find application in tele-communication, high speed data processing, optical data storage and so on; which depends up on different properties like refractive index, chemical and mechanical stability, dielectric constant and transparency (Sheelarani and Shanthi, 2013). Nonlinear behavior of pure organic materials dominates over their inorganic counter parts due to their high conversion efficiency for SHG, good transparency in visible region and extended π delocalisation (larger hyperpolarisability β) (Radoslaw et. al., 2016). In general nonlinearity of molecules with donor acceptor intermolecular charge transfer is remarkable (Sudharsana et. al., 2010). Amino acids which contain carboxyl acid group (COO^-) which is a proton donor and the proton acceptor NH_2^+ , are best candidates for NLO studies (Rajesh and Praveen Kumar, 2014).

MATERIALS AND METHODS

Instruments Used For Characterization

In the present work, powder X-ray diffraction is done using Bruker AXS D8 advance diffractometer. For UV-visible spectral analysis, Varian, carry 5000 spectrometer is used. The Perkin Elmer, Diamond

TG/DTA performed the thermal analysis. JOEL model JSM-6390LV is the instrument that recorded the scanning electron microscopic images. Vicker's microhardness tester detected the mechanical hardness of the crystal. The digital refractometer is made use for the direct measurement of refractive index. The nonlinearity of the crystal is confirmed by the Kurtz and Perry powder technique for the Second harmonic generation (SHG) measurement.

Synthesis and Growth

To prepare L-hydroxyproline picrate (LHPP), 0.001 mole of powder picric acid (Merck) was dissolved in distilled water at 50°C and stirred well for 1 hour. The aqueous solutions of L-hydroxyproline and picric acid were mixed in stoichiometric ratio, to get supersaturated solution, at 50°C. The solution was then stirred well for 6 hours to ensure its homogeneity. Single crystals of LHPP were grown by slow evaporation solution growth technique. The prepared solution was transferred to a 250ml beaker. Nucleation started within two weeks. After 20 days, bigger LHPP crystals of size 12mm x 4mm x 2mm were obtained. The photograph of the LHPP crystal obtained through SEST is shown in Fig.1.

RERULTS

Powder XRD

The crystalline nature of the sample was justified by the sharp peaks at certain 2θ values in the powder XRD spectrum (Fig.2).

UV-Vis Spectrum

As the absorption of UV and visible light indicates the transfer of the s and p orbital electrons to the higher state from the ground state, we can have an idea regarding the structure of the molecule, from UV-vis spectrum (Martin Britto Dhas et. al., 2008.). UV-vis analysis of LHPP in the range 200nm to 1000nm shows that, it has got a wide range transparency, from 400nm to 900nm (Fig.3) which implies that it is really useful for the SHG applications.

Thermal Analysis

The thermo gravimetric analysis (Fig.4) over a temperature range of 30-700°C says that the weight loss of the sample transpires as three stages. A 10% weight loss occurs at 270°C and a weight loss of 15% is observed at 290°C. A perceptible dip in the TGA with major weight loss (about 45%) at 350°C puts finger on the decomposition of the sample. DTA curve shows a peak at 292.14°C which denotes the melting point of the sample. So the LHPP single crystals melt just before the decomposition.

Microhardness

To get an idea about the mechanical stability of the grown crystal, Vicker's microhardness test was done for the loads of 3, 5, 10, 25 and 50g. A load of 50g caused microcracks on the crystal (Naseema et. al., 2010). The following relation is used to calculate Vicker's microhardness number (H_V)

$$H_V = \frac{1.855P}{d^2} (\text{kg/mm}^2) \quad (1)$$

Here P is the applied load in grams and d is the mean diagonal length in microns. The obtained H_V value for LHPP is 13.01 kg/mm² for a load of 25g. A plot of H_V against P is shown in Fig.5.

Scanning Electron Microscopy

Scanning electron microscopic images of LHPP manifest the smoother morphology of the crystal (Fig.6) (Muthuselvi et. al., 2016). Small tube like structures are visible in the SEM images.

Refractive Index

Refractive index of the crystal was measured using a refractometer. The crystal was dissolved in solvent (water) and a drop of the solution was placed on the sample platform after cleaning the platform using the solvent. Hence refractive index of the sample was found to

be 1.35 at 20°C and its Brix percentage measured was, 11.84%. The dielectric constant value calculated is 1.822.

SHG Measurement

The very familiar Kurtz-Perry powder technique was employed to measure the second harmonic generation efficiency. A source of Q-switched Nd:YAG laser with 1064nm wavelength was used for the study (Jayanthi et. al., 2017). It was found that SHG efficiency of LHPP is 2.75 times that of KDP (potassium dihydrogen phosphate).

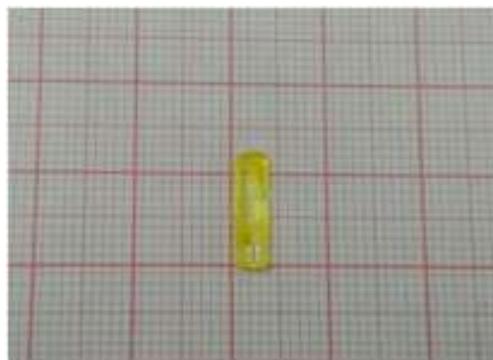


Figure 1: The grown LHPP crystal

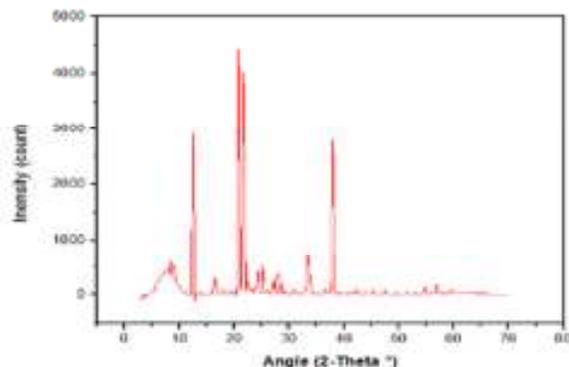


Figure 2: Powder XRD spectrum of LHPP

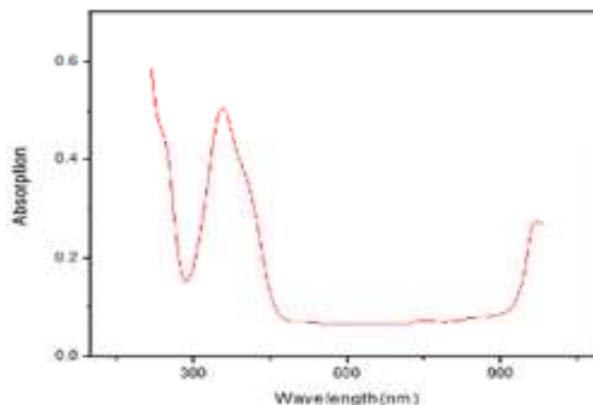


Figure 3: UV-Visible spectrum

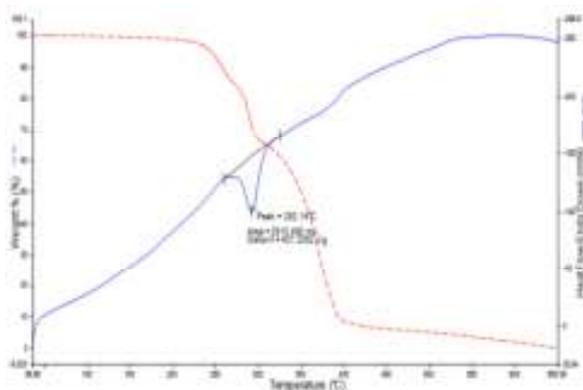


Figure 4: TGA/DTA

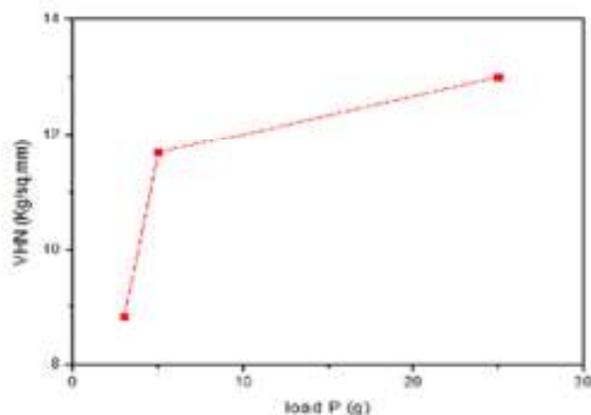


Figure 5: VHN vs load P

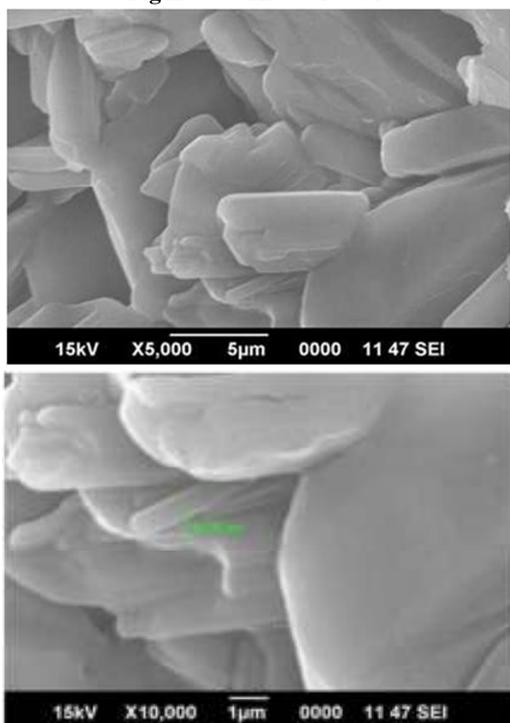


Figure 6: Scanning electron microscopic images.

DISCUSSION

LHPP single crystals grown by SEST have a better crystalline nature. As it is transparent in the visible region LHPP is giving a good response to the second harmonic generation. Its SHG efficiency is found to be 2.75 times that of standard KDP. Surface of the crystal is absolutely clear and smooth under different magnification scales. It has got a moderate hardness with hardness coefficient 13.01kg/sq.mm. Melting of LHPP occurs at 292.14°C and it can withstand a temperature of 350°C above which it decomposes. In all aspect LHPP is a good material for the nonlinear optical applications.

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