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Structural and Dielectric studies on unidirectional growth of organic nonlinear optical single crystals of Trans-4-Hydroxy-L-Proline by Sankaranarayananan–Ramasamy method

S. Rajyalakshmi[1], B. Brahmaji[2], Samatha[1], K. Ramachandra Rao[3] and M.C. Rao[4]*

[1]Departmen t of Physics, Andhra University, Visakhapatnam-530003, A.P., India
[2]Anil Neerukonda Institute of Tech. and Science Engineering College, Visakhapatnam-530003, A.P., India
[3]Crystal Growth and Nano Science Research Centre, Department of Physics, Government College (A) Rajahmundry-533105, A.P., India
[4]Department of Physics, Andhra Loyola College, Vijayawad-520008, A.P., India

Abstract: An organic nonlinear optical amino acid Trans-4-Hydroxy–L-proline (HYP) a transparent uniaxial single crystal having dimension of 30 mm diameter and 50 mm length was successfully grown by Sankaranarayanan-Ramasamy (SR) method with a growth rate of 1 mm per day under ambient conditions. The grown single crystal system of HYP and lattice parameters a = 8.31 Å, b = 4.99 Å and c = 14.28 Å were determined from the single crystal X-ray diffraction analysis. HYP is crystallized in monoclinic phase. The crystalline perfection was evaluated using high-resolution X-ray diffractometry. Fourier Transform infrared studies confirm the various functional groups present in the grown crystal. The optical transmission of HYP crystal has transmission with its lower cut off wavelength is 210 nm. SHG measurement confirms that the HYP have nonlinear optical property and was found to be approximately equal to KDP crystal. Dielectric constant and loss factor of HYP were determined at different frequencies and temperatures.

Key words: HYP, Dielectric, HRXRD and Optical transmittance.

Introduction:

The current era by which research and development of progress leads to the enormous scientific and technological advances and experiencing the technological revolution. Nonlinear optical (NLO) materials play an eminent role on information technology and industrial applications. Especially, NLO crystal materials exhibit finest applications such as laser frequency conversion, optical computing, optical information processing [1] optical storage, optical communication, photonics, electro-optic modulation, optical image processing etc. [2]. The organic NLO materials possess hyper NLO coefficients compared with inorganic materials [3]. Amino acids belong to a family of organic materials have wider NLO applications. The organic amino acid compounds like L-cysteine hydrochloride monohydrate [4], L-tartaric acid [5], L-arginine [6], L-Histidine [7] and glycine [8] exhibits NLO applications. Trans-4-hydroxy-L-proline (HYP) ($C_5H_9O_3N$) is a common non-proteinogenic amino acid has a pyrrolidine ring containing a hydroxyl group [9] many studies have been reported on the stability constants [10] and the circular dichroism spectra [11] of HYP metal complexes in aqueous solution. The SHG efficiency of HPTA crystal was found to be 0.8 times [12] and Cd doped HYP was 0.5 times [13] that of KDP crystal was already reported. The HYP differs from Proline by presence of a hydroxyl (OH) group attached to the Gamma carbon atom. Crystals grown by conventional solution technique have different orientations but for devices and applications the crystal with specific orientation and bulk size can be grown from solution by Sankaranarayanan–Ramasamy method [14]. In the present study the HYP single crystal is grown by SR method. The SR method HYP grown crystals were characterized by the Single crystal XRD, HRXRD, FTIR, UV-Vis, SHG, Dielectric and Photoconductivity analysis.

Experimental:

In this study, Analar reagent (AR) grade of HYP was taken according to the solubility data (53g/150 ml). The homogeneous saturation solution of HYP was prepared in Millipore water and stirred well at room temperature. The solution was filtered and transferred to crystal growth vessel and crystallization was allowed to take place by slow evaporation solution growth technique at room temperature. Within 1 day transparent single crystals were obtained by spontaneous nucleation from the solution. The dimensions of about 10 x 8 x 4 mm^3 were observed in the conventional method HYP grown single crystals as shown in Fig.1.

Fig. 1 HYP crystal grown by Conventional method

The growth behavior of single crystals were controlled by the crystallographic structure according to the chemical bonding theory of single crystal growth [15] which helps to study the growth history of single crystals. In the present study the saturation solution of HYP was prepared and transferred into a seed crystal mounted glass ampoule and kept into water bath at constant temperature. To avoid multi-nucleation and to increase the evaporation rate a ring heater with 38 ^{0}C was positioned at the top of the growth ampoule was connected to the temperature controller for solvent evaporation and covered with dust free cover at the top of the glass ampoule to avoid contamination of the HYP solution. At the bottom of the glass ampoule around the growth region another ring heater with 34 ^{0}C with ±0.01 ^{0}C accuracy is kept for the growing crystals. After 7 days the seed crystal mounted at the bottom starts to grow. The SR method grown HYP crystal was harvested with in a period of 40 days of 30 mm diameter and 50 mm length as shown in Fig.2 and the growth rate is 1.5 mm/day depends on the temperature of ring heaters. The day wise analysis (a) to (f) of SR method grown HYP single crystal is shown in Fig. 3.

Fig. 2 HYP crystal grown by SR method

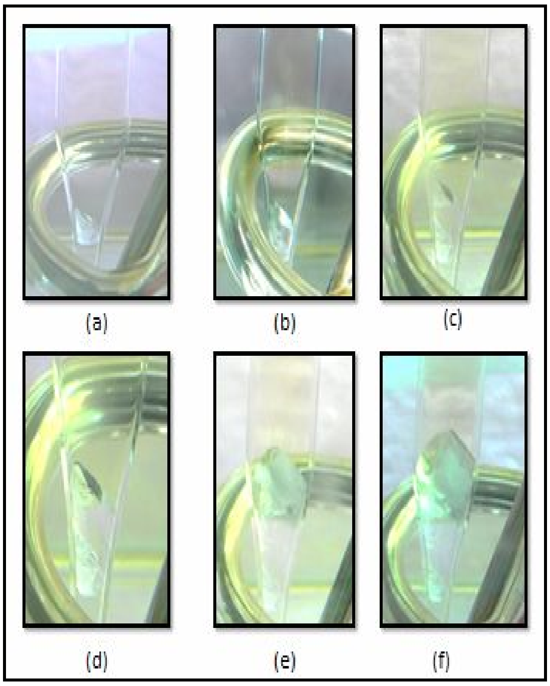

Fig. 3 Day wise crystal growth analysis of HYP single crystal grown by SR method

The single crystal XRD analysis of SR method grown HYP single crystal was carried out using Enrafnonius CAD4X-ray diffractometer. A PAN AlyticalX'Pert PRO MRD high-resolution X-ray diffraction (HRXRD) system with $CuK\alpha_1$ radiation was employed to assess the crystalline perfection. FTIR spectrum of HYP single crystal was recorded using a KBr pellet on Perkin Elmer RXI FTIR spectrometer. The optical transmittance spectrum was recorded with Labindia analytical UV3092 spectrophotometer. The second harmonic generation (SHG) efficiency HYP single crystal was determined by using Kurtz powder SHG method. The dielectric parameters like dielectric constant and dielectric loss were performed on HYP single crystals using Impedance Analyser.

Results and Discussion:

In the present investigation the HYP single crystal is grown by SR method. The HYP grown crystals were characterized by the single crystal XRD, HRXRD, FTIR, UV-Vis, SHG, Dielectric and Photoconductivity analysis.

Single crystal X-ray diffraction analysis:

The single crystal XRD analysis of SR method grown HYP single crystal was carried out using Enrafnonius CAD4X-ray diffractometer to determine the unit cell parameters. The measured cell parameters are $a = 8.31$ Å, $b = 4.99$ Å and $c = 14.28$ Å, $\alpha = \gamma = 90^0$, $\beta = 90.25^0$, HKL index 5.55, -13.86, -0.18, $V = 591$ Å^{3}and $2\theta = 64.23^0$. HYP is crystallized in monoclinic phase. HYP molecule exists as a zwitter ion leads to the cationic amino group and anionic carboxylate ion by the proton transfer of uncommon ionization state [16].

High-resolution X-ray diffractometry:

A PAN AlyticalX'Pert PRO MRD high-resolution X-ray diffraction (HRXRD) system with $CuK\alpha_1$ radiation was employed to assess the crystalline perfection of SR method grown HYP single crystal. Fig. 4 shows the diffraction or rocking curve (RC) recorded for a typical HYP single crystal specimen in symmetrical Bragg geometry.

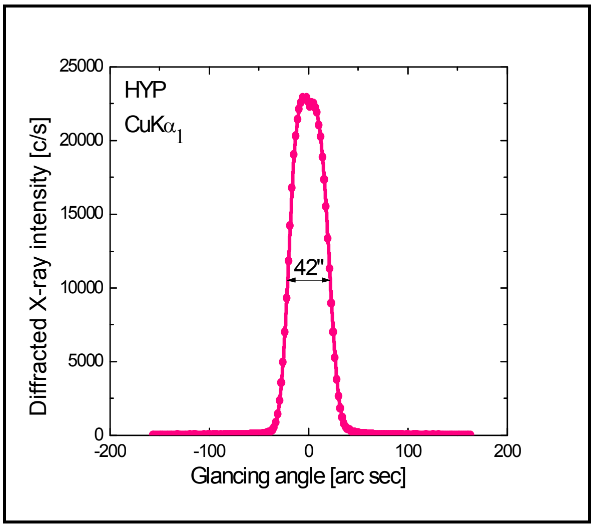

Fig. 4 Diffraction curve recorded for a typical HYP single crystal using (100) diffracting planes with CuKα$_1$ radiation

As seen in the figure, the RC contains a single peak and indicates that the specimen is free from structural grain boundaries. The FWHM (full width at half maximum) of the curve is 42 arc sec which is somewhat higher than that expected from the plane wave theory of dynamical X-ray diffraction [17] for an ideally perfect crystal, which could be in the range of a fraction of an arc sec to a few arc sec. This much broadening of rocking curve without the presence of any splitting and without any asymmetric asymmetry with respect to the peak position can be attributed to defects like normally observed, dislocations, Frankel defects (due to simultaneous existence of vacancies as well as interstitial defects) etc. [18]. However, these defects with lesser density as in the present case hardly give any affect on the performance of the devices based on such crystals. If the concentration is high, the FWHM would be much higher and often lead to structural grain boundaries. Point defects up to some extent are unavoidable due to thermo dynamical considerations and growth conditions [19].

FTIR analysis:

Fourier Transform Infrared Spectroscopy (FTIR) is used to identify the functional groups present in organic materials. The ligand HYP consists of three potential chelating groups. The -OH and -NH groups of HYP are neutral whereas -COOH group is deprotonated [20]. FTIR spectrum of SR method grown HYP single crystal was recorded in the range of 4000-500 cm^{-1} using a KBr pellet on Perkin Elmer RXI FTIR spectrometer and the recorded spectra were shown in the Fig. 5.

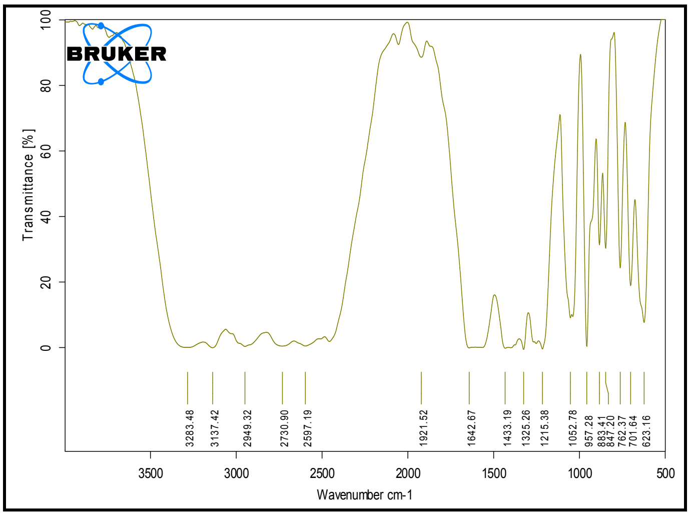

Fig. 5 FTIR spectra of HYP single crystal

HYP spectrum shows a strong and broad peak from 2450-3300 cm^{-1} is due to O-H stretching of –COOH with the carboxyl group. The strong peak from 3400-2450 cm^{-1} is due to O-H stretching of –COOH. Generally carboxyl IR appears at 1720 cm^{-1} but here due to the positive resonance effect of NH, it reduces to 1643 cm^{-1}. The medium peak observed at 1433.19 cm^{-1} is due to C-C stretching (in ring). The strong peak observed at 1325.26 cm^{-1} is due to C-N stretching. The medium peak observed at 1215.38 cm^{-1} is due to C-H wagging. The medium peak observed at 1052.78 cm^{-1} is due to C-OH stretching. The strong peak observed at 883.41 cm^{-1} is due to N-H wagging. The sharp peak observed at 762.37 cm^{-1} is due to ring mode in plane. The medium peak observed at 701.64 cm^{-1} is due to O-H OOP (Out of plane) deformation. Thus the functional groups are confirmed.

UV– Vis NIR studies:

The optical transmittance spectrum of SR method grown HYP single crystal was recorded with Labindia analytical UV3092 spectrophotometer in the wavelength range of 190 -850 nm (Fig. 6).

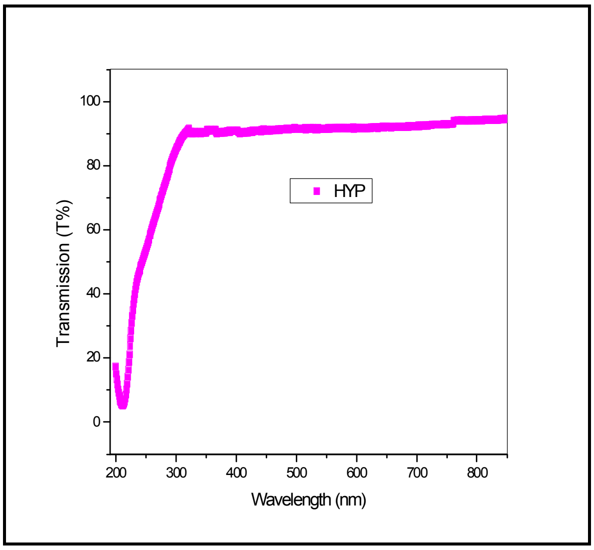

Fig. 6 UV-Vis transmission spectrum of HYP single crystal

The lower UV cutoff wavelength for SR and conventional method grown HYP is 210 nm and have transmittance around 90%. The high transmittance shows the crystal was free from volume defects [21] in SR method grown crystal. The SR method grown crystals of SA, TGS, KAP and KDP transparency has been reported already [22, 23].

Nonlinear optical studies:

SHG efficiency of SR method grown HYP single crystal was determined by using Kurtz powder SHG method [24]. The grown single crystal of HYP was powdered and then packed in a one side closed microcapillary tube and exposed to laser radiations was irradiated using the fundamental beam of 1064 nm from Q-switched Nd: YAG laser with the input beam energy of 2.5 mJ/p. The pulse width is about 10 ns with a repetition rate of 10 Hz. The emission of green light confirms the generation of the second harmonics. The second harmonic signal was about 1.0 mV which was nearly equal to KDP crystal as a reference material. But the standard KDP crystals gave an SHG of 10 mV/pulse from the same input energy. Hence it was confirmed that the grown material have NLO efficiency approximately equal to the KDP crystal.

Dielectric Studies:

The dielectric parameters like dielectric constant and dielectric loss were performed on SR method grown HYP single crystals using Impedance Analyser. Dielectric constant measurements were carried out on HYP sample at different temperatures (30 ^{0}C, 60 ^{0}C and 90 ^{0}C) in the frequency ranges 100 Hz to1 MHz. From the Fig. 7, the dielectric constant 0.475 is the maximum value and 0.02 is the minimum value. The dielectric constant increases at lower frequency. The high dielectric constant value of the crystal at low frequency is attributed due to space charge polarization. The space charge contribution has strong influence in the low frequency region and depends on the purity and perfection of the material. A graph is plotted between the dielectric loss and log frequency for different temperatures (30 ^{0}C, 60 ^{0}C and 90 ^{0}C). From the Fig. 8, it is observed that the dielectric loss decreases at higher frequencies.

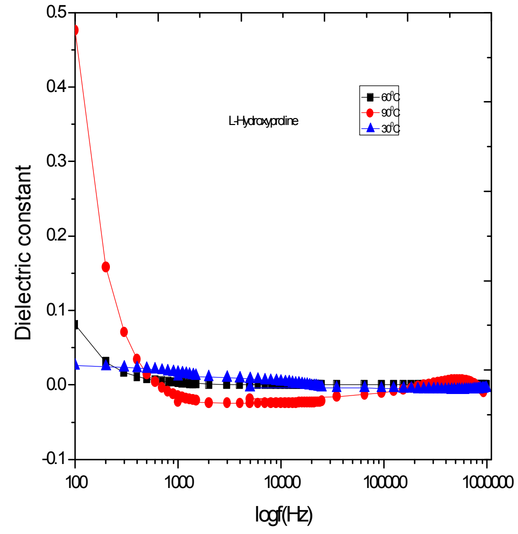

Fig. 7 Dielectric constant of HYP single crystal

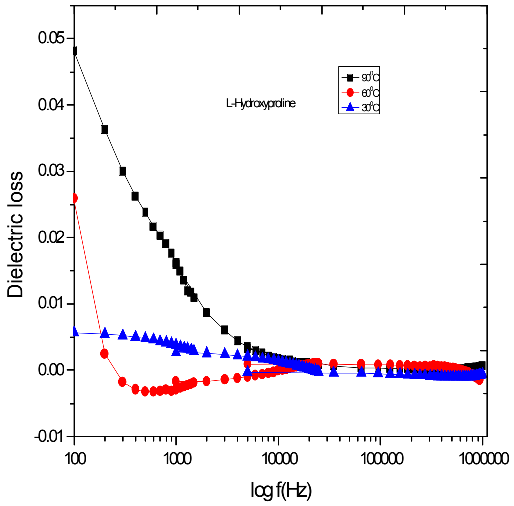

Fig. 8 Dielectric loss of HYP single crystal

At higher frequencies due to the low value of dielectric constant and dielectric loss its optical quality is enhanced with lesser defects which are important parameters and useful for NLO applications [25]. The obtained results suggest that the dielectric constant and loss strongly depend on the frequency of applied field and the temperature of the samples.

Conclusions:

HYP single crystal with 30 mm diameter and 50 mm length was successfully grown by grown by SR method. The grown single crystal system of HYP lattice parameters a = 8.31 Å, b = 4.99 Å and c = 14.28 Å and crystallized in monoclinic. Rocking curve of 42 arc sec was obtained for HYP single crystal contains a single peak and indicates that the specimen is free from structural grain boundaries. FTIR studies confirm the various functional groups present in the grown crystal. The optical transmittance of HYP crystal with its lower cut off wavelength is 210 nm is observed. SR method grown HYP single crystal have nonlinear optical property and was found to be approximately equal to KDP crystal. The dielectric constant increases at lower frequency and the dielectric loss decreases at higher frequencies in SR method HYP grown single crystal.

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