Scientific Journal of Impact Factor (SJIF): 4.72
e-ISSN : 2348-4470
p-ISSN : 2348-6406
International Journal of Advance Engineering and Research Development
National Conference On Nanomaterials, (NCN-2017)
Volume 4, Special Issue 6, Dec.-2017 (UGC Approved)

Synthesis, growth, structural, optical, spectroscopic, thermal and nonlinear optical studies of L-proline doped potassium dihydrogen phosphate single crystals

C. Babu[1], G. Srinivasan*[1]

[1](PG & Research Department of Physics, Govt. Arts College for Men (Autonomous), Nandanam, Chennai, Tamilnadu, India.)

Abstract:- *Single crystals of L-Proline doped Potassium dihydrogen phosphate a nonlinear optical material has been obtained by slow evaporation technique at room temperature. The crystal structure, cell parameter and cell volume of the grown crystal was carried out using single crystal X-ray diffraction studies. The grown crystal belongs to monoclinic system. A Fourier Transform Infrared Spectroscopic study reveals the presence of functional groups and the modes of vibration of the grown crystal. The optical absorbance range of the grown crystal was obtained by UV- Visible - NIR spectroscopy. Thermal behavior of the grown crystal has been characterized by TGA/DTA studies. The nonlinear optical properties of the grown crystals were measured using Kurtz-Perry powder technique. The Laser damage threshold (LDT) energy density has been found to be 1.94 GW/cm^2.*

1. Introduction

In recent years, nonlinear optical crystal finds a wide range of applications due to their high quality and performance in the field of industries such as (laser, high speed computer, electro-optic and acoustic devices, and optical information storage device). A non linear optical material also serves as a major function in optical logic, frequency shifting, frequency doubling etc [1-3].

Organic amino acids are fascinating compounds formed by weak vanderVaal's interaction, hydrogen bonds they contain a proton donor carboxyl acid (- COO) group and proton acceptor amino group in them. Therefore due to these substantial properties they act as a supreme candidate for NLO applications [4-5]. Usually most of the organic nonlinear optical single crystals have poor mechanical and thermal properties and are easily susceptible for damage during processing even though they have large NLO efficiency [6].

In the present work, single crystals of L-Proline has been grown from a mixture of L-Proline and KDP aqueous solution by adopting slow evaporation method at room temperature. The grown crystal has been subjected to various characterization studies such as Single crystal X-ray diffraction, UV-Visible studies, FTIR analysis, LDT studies and NLO test.

2. Experimental procedure

The title compound was synthesized by taking L-Proline and AR grade (Loba Chemie) and KDP in 1:2 molar ratio. They were dissolved in double distilled water and stirred well using magnetic stirrer for about 3 hours to form a transparent solution. The solution was then poured in a 150 ml beaker and covered with aluminum foil with small holes before leaving it for slow evaporation at room temperature. The good quality single crystals (fig.1.) were obtained after 18 days.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The grown crystal were subjected to single crystal X-ray diffraction analysis which was carried out using an ENRAF NONIUS CAD4 X-ray diffractometer with MOKα (λ = 0.71073 Å) radiation to identify the cell parameters. The single crystal X-ray diffraction analysis confirm that the crystal fall under monoclinic system. The estimated unit cell parameter values of the grown crystal are, a = 10.539 Å, b = 6.940 Å, c =7.445 Å, with V = 385.5Å^3.

3.2. UV – Visible spectral analysis

The optical absorption spectrum was carried out using by Varian Carry 5E UV-Vis Spectrophotometer between the range 200 nm - 800 nm. The recorded absorption spectrum is shown in fig.2. The lower cutoff wavelength of the grown crystal is 324 nm. The optical absorption spectrum of grown crystal shows a good absorbance in the entire visible region and confirms the absence of absorbance from 387 nm to 800 nm. Therefore the crystals are suitable for UV tunable laser (Optoelectronic device) [7]. The spectrum shows that the absorption peak at 324 nm is due to $n \rightarrow \pi^*$ transition. The direct optical band gap energy of the grown crystal is 3.79 eV. The experimental value is found to be 3.91 eV (fig.3) which almost matches with the theoretical result.

3.3. Laser damage threshold studies

Laser Damage Threshold (LDT) is a major factor which affects the applications of nonlinear optical materials. The laser damage threshold values for the grown crystal were measured using a Q-Switched Nd: YAG laser (1064 nm, 6 ns pulse width). The energy of the laser beam was measured using a coherent energy/power meter (model EPM 200).

The surface laser damage threshold values of the grown crystal was calculated using the formula Power density (Pd) = $E/\tau\pi r^2$ where E is the energy (mJ), τ is the pulse width; r is radius of the spot in mm. The obtained value of LDT is 1.94 GW/cm^2. The laser damage in the samples leads to stress induced fracture and thermo-chemical degradation. Due to high values obtained in LDT the material can be used for fabricating NLO devices [8].

3.4. FT-IR spectral analysis

The FT-IR Spectrum was analyzed for powder crystals using BRUKER-Fourier Transform Infrared Spectrometer by KBr pellet technique in the range 400 cm^{-1} to 4500 cm^{-1}. The observed spectrum of grown crystal is shown in fig.4.

In FT-IR the peaks at 3418 cm^{-1} and 3264 cm^{-1} are assigned to OH asymmetric and symmetric vibration of water molecule respectively. The peaks at 3188 cm^{-1} and 3048 cm^{-1} are due to (N-H) asymmetric and symmetric vibration. The bands at 2785 cm^{-1} is due assigned a C-H stretching vibration. A peak at 2149 cm^{-1} is assigned due to combinational and asymmetrical bending vibration of NH_3^+ and 1689 cm^{-1} which is assigned due to the stretching of the CO-OH group [9]. The twisting and rocking, vibrations of CH_2^+ are observed at 1270 cm^{-1} and 1073 cm^{-1}. A strong peak at 524 cm^{-1} is assigned to HO-P-OH bending vibration [10].

3.5. Thermal studies

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are used analyze the thermal stability, phase transition, different decomposition stages, and melting point of the crystal. The TGA/DTA analysis of LP doped KDP crystal was carried out in nitrogen atmosphere at a heating rate of 20◦C between the temperatures 0◦C to 800 0◦C using CNST thermal analyzer. TGA/DTA curve of the grown crystal are shown in fig.5. From the TGA curve, it is clear that the grown crystal is stable upto 189.29 ◦C and decomposition starts only after 189.29 ◦C.

From the DTA curve it is observed that a very strong endothermic peak at 208◦C corresponds to the melting point of the crystal. The sharpness of the endothermic peak shows a good degree of crystallinity and the purity of the sample. It is seen that at different stages, various gaseous fraction like CO, CO_2, NH_3 are liberated leading to the bulk decomposition of the compound before 732 ◦C [11].

3.6. Nonlinear optical (NLO) studies

The second order nonlinear optical conversion efficiency of the grown single crystal has been measured by Kurtz and Perry test [12] . A Q-switched Nd: YAG laser (λ = 1064 nm) with a pulsed duration of 8 ns and frequency repetition rate of 10 Hz has been used. The grown crystal was ground into powder samples with uniform particle size and filled into the micro capillary tube. The second harmonic generation gives positive results due to the emission of bright green radiation (λ = 532 nm) as the output for the KDP sample which has been taken as the reference material. The output signal was found to be 6.98mV. For the same input, KDP emitted the green light with the output signal of 12.21 mV. Second harmonic generation efficiency was found to be 0.571 times that of the value of standard KDP crystal.

4. Conclusion

Single crystals of L-Proline KDP have been grown by slow evaporation technique using aqueous solution at room temperature. The single crystal XRD studies confirm that grown crystal belongs to monoclinic system. FT-IR spectroscopic analysis confirmed the various functional groups and modes of vibration of the grown crystal. The lower cutoff wavelength (324 nm) and the absorbance range (200 nm - 800 nm) observed from the UV-Vis NIR spectrum confirms its suitability for SHG applications. The thermal studies indicate that the grown crystal is stable upto 189.29◦C. The SHG efficiency of the grown crystal is 0.571 times than that of the standard KDP crystal.

References

[1] N.Vijiyan, G. Bhagavannarayana,K.Nagarajan and V. Upadhya, Materials Chemistry and Physics. 115, 656 (2009).
[2] S. Natarajan, G.Shanmugam and S.A.Martin Britto Dhas,Crystal Research & Technology.43**,** 561 (2008).
[3] A. Kandasamy, R. Siddeswaran, P. Murugakoothan, P. Suresh Kumar, and R. Mohan,Crystal Growth & Design.7, 183 (2007)
[4] T.Pal, T.Kar, Gabriele Bocelli, Lara Rigi, Crystal Growth & Design.3, 13 (2003).
[5] C.Justin Raj, S.Jerome Das, Crystal Growth & Design. 8**,** 2729 (2008).
[6] S. Natarajan, G. Shanmugam, S.A. Martin Britto Dhas, Crystal Research & Technology. 43,561(2008).
[7] K.Vasntha, S.Dhanuskodi, Journal of Crystal Growth. 269, 333 (2004)

[8] B. Sivasankari, P. Selvarajan, International Journal for Light and Electron Optics**.** 127, 4928 (*2016*)
[9] M.Fleck, A, M.Pettrosyan, Journal of Molecular Structure. 1079, 460 (2015).
[10] S.Balamurugan, P.Ramasamy, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 71, 1978 (2009)

[11] Manoj K.Gupta, Nidhi Sinha, Binay Kumar, Physics B.406 63- 67, (2011).
[12] S.K.Kurtz, T.T. Perry, Journal of Applied Physics. 39, 3813 (1968).

List of figure captions

C. Babu, G. Srinivasan / Synthesis, growth, structural, optical, spectroscopic, thermal and nonlinear optical studies of L-proline doped potassium dihydrogen phosphate single crystals

Fig.1 Photography of grown crystal

C. Babu, G. Srinivasan / Synthesis, growth, structural, optical, spectroscopic, thermal and nonlinear optical studies of L-proline doped potassium dihydrogen phosphate single crystals.

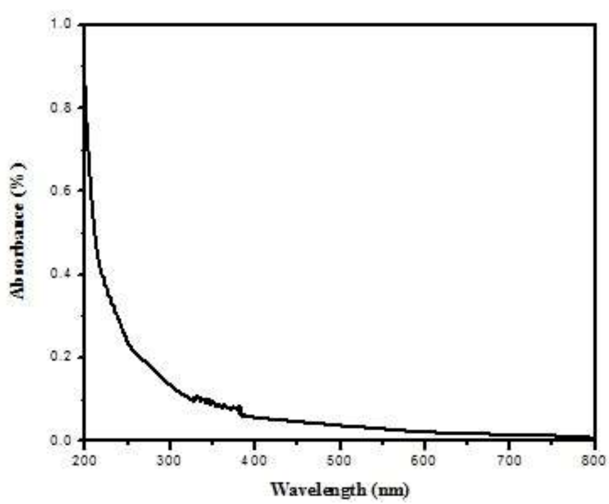

Fig.2 UV-Visible Spectrum of L-Proline doped KDP crystal

C. Babu, G. Srinivasan / Synthesis, growth, structural, optical, spectroscopic, thermal and nonlinear optical studies of L-proline doped potassium dihydrogen phosphate single crystals.

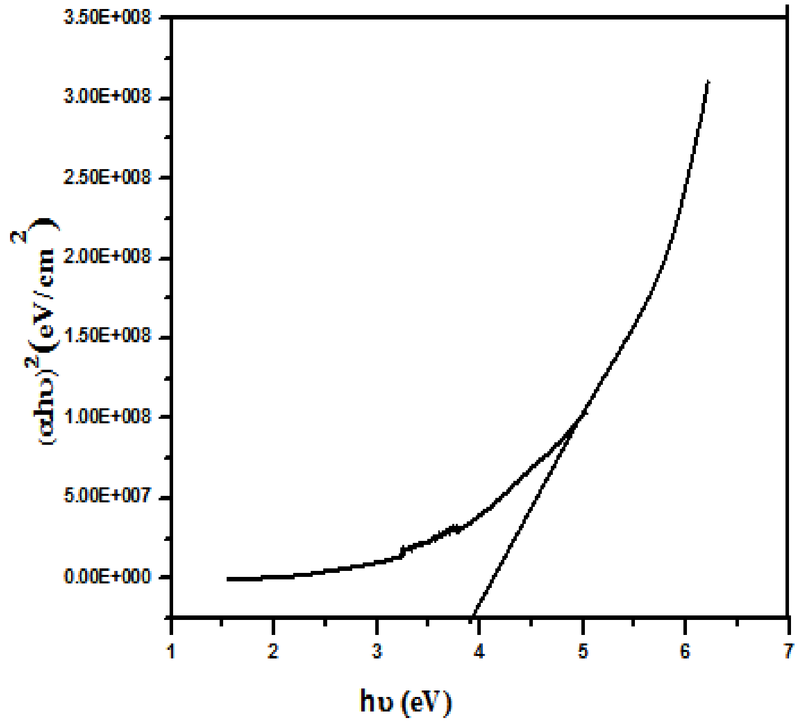

Fig.3 Photon energy Spectrum of L-Proline doped KDP crystal

C. Babu, G. Srinivasan / Synthesis, growth, structural, optical, spectroscopic, thermal and nonlinear optical studies of L-proline doped potassium dihydrogen phosphate single crystals.

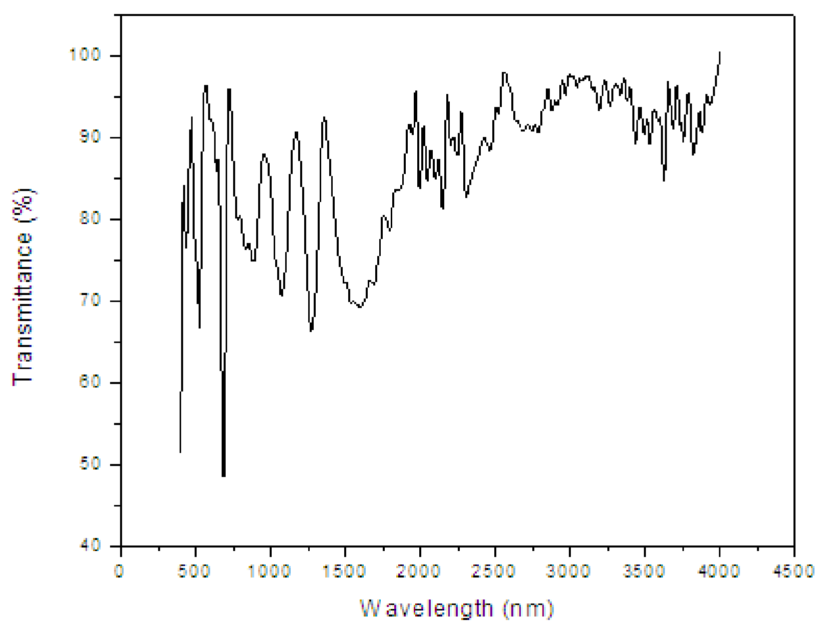

Fig.4 FT-IR spectrum of L-Proline doped KDP crystal

.

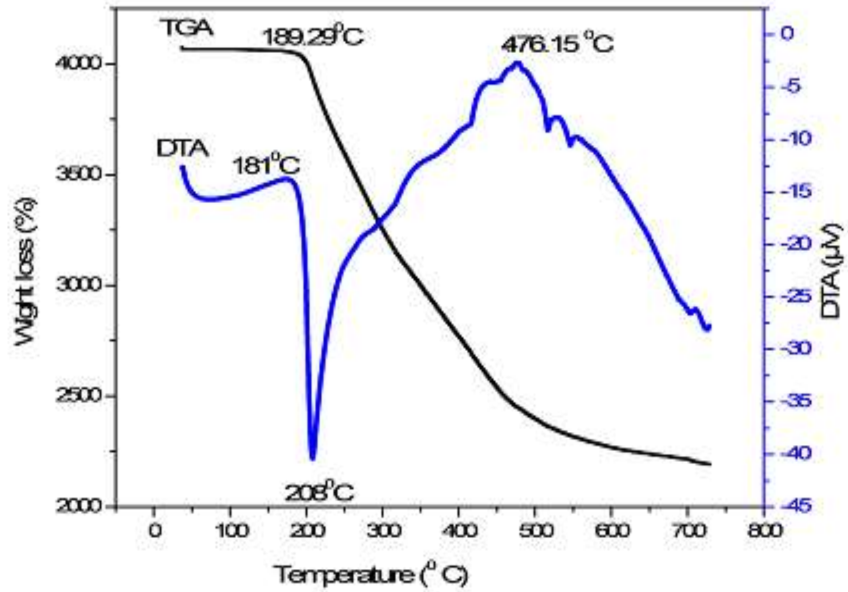

Fig.5.TGA/DTA curve of L-Proline doped KDP crystal