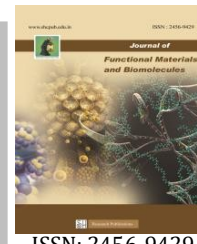




SACRED HEART RESEARCH PUBLICATIONS

Journal of Functional Materials and Biomolecules

Journal homepage: www.shcpub.edu.in



ISSN: 2456-9429

SYNTHESIS, GROWTH AND CHARACTERIZATION OF A NOVEL ORGANIC CRYSTAL: L-VALINE p-NITROPHENOL (LVPNP)

K. R. NaveenKumar^a and L. Anandaraja^{a,*}

Received on 27 October 2022, accepted on 18 November 2022,

Published online on December 2022

Abstract

In the present work an organic optical crystal L-valine p-Nitrophenol (LVPNP) is synthesized by employing slow evaporation solution growth technique (SEST) with double distilled water as solvent. Single crystal X-ray diffraction revealed that material crystallized in monoclinic crystal system with space group P21/n. The crystalline nature and purity of LVPNP crystal was confirmed by powder XRD pattern. The presence of various functional groups and chemical bonds has been identified by using FTIR spectral analysis between 4000 and 400 cm^{-1} . The UV-Visible spectroscopic study showed that the lower cut-off wavelength was found to be 225 nm with wide transparency range and very low absorbance. Energy gap spectrum shows the band gap of the crystal is about 6.11 eV. The fluorescence emission spectrum of the grown crystal has a red fluorescence emission observed at 636 nm.

Keywords: Organic crystal, XRD, FTIR, UV-visible, Fluorescence.

1 Introduction

Organic crystals are latest materials that have good nonlinear response, low cutoff wavelength high NLO efficiency and high laser damage threshold [1-3]. They are mostly studied for their transparent nature which is more than organic and semi-organic crystal. Organic crystals are the key function for the frequency shifting, optical modulation, optical switching, optical logics and optical memories [4]. They are used in field like telecommunication and signal processing which is most important in the modern lifestyle. They can be tuned using various techniques like laser etching, electron beam etching, micro rubbing, dip-pen lithography, rig flex lithography and delicate lithography. Organic materials are synthesized because they are of low cost, less dense, chemically stable and short response to optical excitation property irrespective to their poor mechanical and thermal stability and they are easy to fabricate into devices [5]. The electro optical property of the organic crystal lies on crystal quality, which is required for various

practical applications like optoelectronic devices. The salient feature of organic crystals is they have properties of molecular structure optimization and tuning of optical properties. It used in molecular engineering and chemical synthesis [6]. In the present work Amino acid is used because they play a prominent role in photonic industry. Amino acids naturally exhibit nonlinear property because they have proton accepting carboxylic group and donating amino acid group and also intermolecular charge transfer is possible. Since they have chiral carbon atom they crystallize in asymmetric space group. They give mechanical strength and chemical stability and gives good transparency to the crystal. The 4-Nitro phenol is unidirectional material [7]. The presences of phenolic OH group forms salt with various organic and inorganic bases [8]. 4-Nitrophenol (4-NP) contains chain of hydrogen bonded molecules. The benzene ring is planar but the nitrogen and oxygen atoms are displaced from the benzene ring. Good optical property of 4-Nitrophenol is due to dipole alignment [9, 10]. LVPNP is a donor acceptor molecular compound where L-valine is the donor and p-nitrophenol is the acceptor of electron. In the present work grown crystals of LVPNP was subjected to Single crystal XRD, Powder XRD, FTIR, UV-Visible spectroscopic studies, Fluorescence.

2. Experimental procedure

The organic L-Valine Para-Nitro phenol crystals were grown by using AR grade L-Valine and p-nitrophenol compounds with double distilled water as a suitable solvent. Slow evaporation technique is used to grow the crystal. Title compound L-Valine and p-Nitro phenol was taken in the ratio of 1:1 ratio. Both the compounds were dissolved in double distilled water separately and stirred in magnetic stirrer for 3 h.

*Corresponding author: e-mail: anandaraj@shcpt.edu

^a PG and Research Department of Physics, Sacred Heart College (Autonomous), Tirupattur-635601, India

Both the solution were mixed together and stirred for 5 h. The final solution was filtered using whatman filter sheet and covered by aluminum foil with perforated holes to reduce contamination. The solution was carefully kept for slow evaporation without any disturbance in

room temperature and was regularly checked for crystal growth. After 10 days of synthesis nucleation started. Good quality of transparent crystals of size $10 \times 3 \times 2 \text{ mm}^3$ were harvested in a period of about 20 days after synthesis. Fig.1 shows the photograph of grown single crystal of LVPNP.

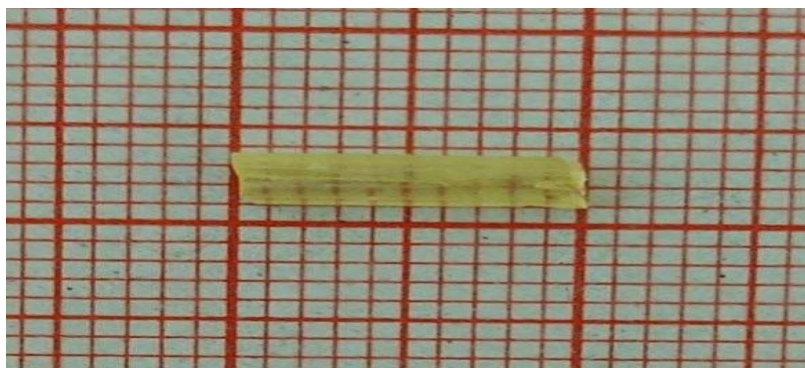


Fig. 1 Grown single crystal of LVPNP

3. Characterization studies

Single crystal XRD

Single crystal XRD analysis was carried out to study the lattice parameters and to know its space group and structure. A good transparent defect free part of the crystal was selected for taking single crystal X-ray diffraction. It was taken using Bruker Apex-II CCD single crystal X-ray diffractometer with the radiation of Moka ($\lambda = 0.710734 \text{ \AA}$). It shows that the crystal belongs to the monoclinic system with space group $P2_1/n$. The cell parameters of the crystal are given below in Table 1.

Table 1

Cell parameters of the grown crystal LVPNP

Cell parameters	LVPNP Crystal
a	3.77 \AA
b	11.08 \AA
c	14.69 \AA
α	90°
β	92.86°
γ	90°

Powder XRD analysis

The grown L-Valine p-nitro phenol crystals were finely powdered and subjected to powder X-ray diffraction. Powder XRD was recorded using powder X-ray diffractometer with CuK α radiation ($\lambda = 1.54060 \text{ \AA}$) is shown in Fig.2. The hkl value of the peaks matches with JCPDS file card numbered 38-1964 and 22-1930. The XRD pattern has 4 major peaks and the maximum intensity peak was found around 21.197° with hkl value (111). The sharp intense peaks represent the good crystalline nature and purity of the crystal [11, 12]. The peak at 21.197° reveals that the crystal has very good transparency nature and it will be suitable for better optical models.

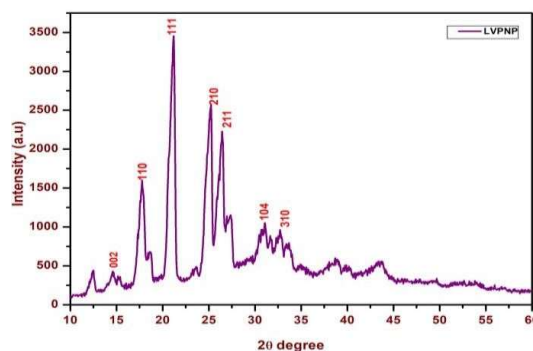


Fig. 2 Powder XRD pattern of LVPNP crystal

Functional group analysis

FTIR spectroscopy study gives information regarding functional group and the nature of hydrogen bonding present [13-16]. Finely powdered LVPNP Sample was used for the Fourier transform infrared analysis. It was recorded between 400 - 4000 cm^{-1} wavenumber range by using KBR pellet technique. It is an important analysis to find the chemical bonding and functional group. The broad peak between 3500-2000 cm^{-1} shows the N-H and C-H combination bands [17,18]. The existence NH_3^+ symmetric stretching is confirmed by bands at 1495 cm^{-1} and 1165 cm^{-1} and they are strong [19]. The COO- stretching band is found at 1450 cm^{-1} and 1190.62 cm^{-1} . The bending of OH from water molecule at 1612 cm^{-1} . The nitro group is present and is it seen strongly at 1326.53 cm^{-1} peak. C-H bending is observed in the peaks at 754 cm^{-1} and 694 cm^{-1} . The NH_2 wagging was found at 634 cm^{-1} . The CH stretching from amino acid is weak and confirmed from peak at 2823.54 cm^{-1} . The CCO bond is observed at 850 cm^{-1} . Hence from the above details and from the Fig.3 the mixed nature of L-valine and p-Nitrophenol is seen in the grown crystal.

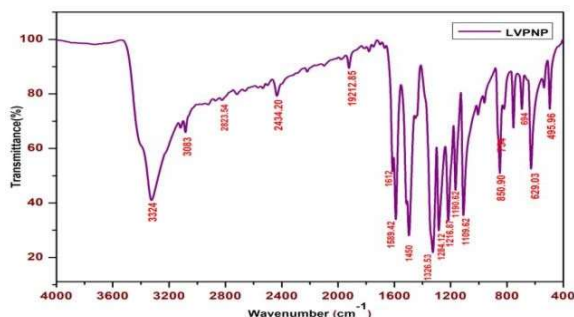


Fig.3 FTIR spectrum of LVPNP crystal

UV-Visible spectral analysis

UV visible optical studies were carried out in the region of 200-1100 nm. It was recorded using varian Cary 5e-uv spectrometer. Amino acid is a bipolar molecular structure that has both amino group and carboxylic acid group which increases transparency in the UV Visible region. Finely Powdered sample is dispersed in water and subjected to optical absorbance studies. Transmittance was found to be 97.7% in UV-Visible region. High transparency with less absorption is characteristic of amino acid. The high optical transmittance may be due to low defects and less dislocation density [8-10]. The high transmittance shows reduced crystals point and line defects. The lower cut off wavelength of LVPNP was found to be 225nm. Fig.4a and Fig.4b shows the UV-vis transmittance and absorbance spectrum. The lower cut off wavelength of L-Valine is 240nm [20-22]. After 315 nm the sample shows good transmittance and less absorption.

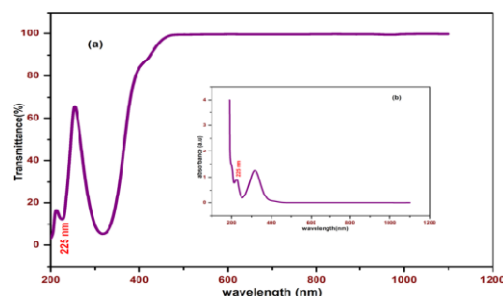


Fig.4 (a). UV-Vis transmission and (b) Absorption Spectrum of LVPNP grown crystal

Using the transmittance value the tau's plot was drawn. The absorption co-efficient value was found using
$$a = \frac{2.302 \log \frac{I_0}{I}}{t}$$
 Where, a is absorption co-efficient, T is transmittance, t is thickness of the crystal. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons. The drawn band gap energy spectrum plot with $(ah\nu)^2$ on y-axis and energy band $h\nu$ on x-axis is shown below (Fig.5). A line is drawn interconnecting the linear part of the curve and the energy band. Energy gap E_g is determined from the line intersection of the extrapolated line with the photon energy axis. It gives the band gap of the material. For LVPNP crystal band gap was found to be 6.11 eV. The wide range of band gap shows the crystal has good transparency [23,24]. The width of energy gap depends on concentration of defects, less defect concentration increases the width of the energy gap. The larger optical band gap of L-valine p-nitrophenol crystal indicates lesser the defect concentration of the crystal. Since the grown crystal has larger band gap it can be used for opto electronics and non linear application and frequency conversion purpose.

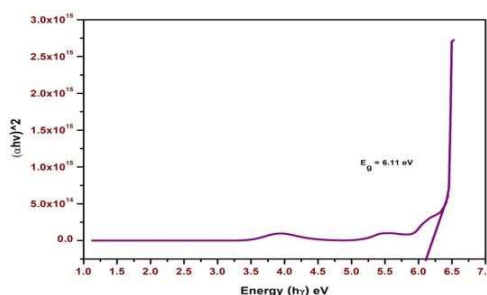


Fig.5 Band gap energy spectrum.

3.5 Fluorescence

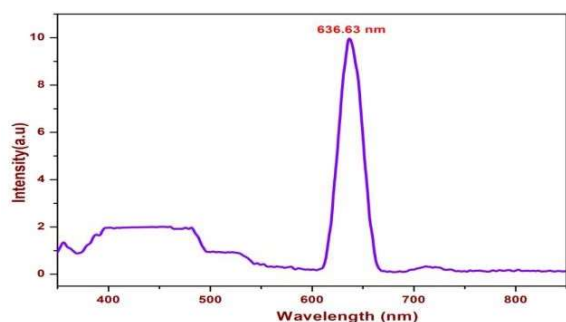


Fig.6 Fluorescence spectrum of LVPNP

Fluorescence is a process where a photon is absorbed by grown material and re radiated. The powdered sample of LVPNP crystals was subjected for fluorescence analysis with excitation wavelength of 325nm. Fluorescence technique is noninvasive and nondestructive. It was taken using Varian cary eclipse fluorescence spectrometer. The spectrum was recorded in the range between 300 to 900 nm where the transmission is maximum (Fig.6). The maximum emission intensity peak at 636 nm shows the crystal has been near red fluorescence emission. The presence of emission peak at 450 nm is due to the nitro group present in the compound [25].

4. Conclusion

A new organic L-Valine p-Nitro phenol crystal was synthesized using slow evaporation method using double distilled water as solvent and the characterization studies were carried out. Single crystal XRD shows the lattice parameters and structure of crystal by well-defined arrangements of atoms. Powder XRD confirms the good crystalline nature and purity of the crystal. FTIR analysis confirms the bonds strength and functional group present in the crystal. UV-Visible spectral analysis confirms the good transparency and less absorbance with lower cut off wavelength of 225 nm and the smaller width band gap confirms the defect free crystal with large band gap of 6.11eV. The good transmittance and less absorbance is seen which is most required for a organic optical material. Fluorescence studies confirm the emission of red light with maximum intensity in the UV-Visible region around 636nm indicates its application in production of red LED. Due the high transmission range and the LVPNP crystal can be used in telecommunication, optical computing and dynamic image processing.

Conflicts of Interest

The authors declare that they have no known conflicts of interests.

Acknowledgements

The authors thank Abdul Kalam Research Centre (AKRC) - Sacred Heart College (Autonomous) Tirupattur, SAIF-IIT Madras, Archbishop Casimir Instrumentation Centre (ACIC)-St. Joseph's college (Autonomous), Tiruchirappalli for providing their facilities for characterization .

References

- [1]. P.Karuppasamy, T.Kamalesh, Muthu Senthil Pandian, P.Ramasamy, Sunil Verma, A.K.Karnal, , AIP Conf. Proc 2265, (2020), pp 030399(1-4).
- [2]. R.Gandhimathi, R.Dhanasekaran, Cryst. Res. Technol. 47 (2012) pp. 385-390 .
- [3]. R.Omegala Priakumari, S. Grace Sahaya Sheba, M. Gunasekaran, Optik 125 (2014), pp 4633-4636
- [4]. V.Sivasubramani, MohdAnis, S.S. Hussaini, G.G. Muley, M. SenthilPandian, P. Ramasamy, , Matter. Res. Innov 21 (2016) pp 426-433
- [5]. J. Vidhya, K.Vija.yakumar, C.Pari , J OVONIC RES 15, (2019) pp. 325 - 334
- [6]. C.Rathika Thaya Kumari, P.Jayaprakash, M.Nageshwari, M.Peer Mohamed, P.Sangeetha and M.LydiaCarolyn, Mol.Cryst.Liq.Cryst 658, (2017), pp.186-197.
- [7]. P. Karuppasamy, T. Kamalesh, K. Anitha, S. Abdul Kalam, MuthuSenthilPandian P. Ramasamy, Sunil Verma, S.VenugopalRao, Opt.Mater, 84 (2018) pp.475-489.
- [8]. T. Kamalesh, P. Karuppasamy, MuthuSenthilPandian ,P. Ramasamy , Sunil Verma, AIP Conf Proc, 2115, (2019) pp. 303-397
- [9]. S. Muralidharan, T. Srinivasan, Y. Vidyalakshmi, D. Velmurugan, R.Gopalakrishnan, ChemTech Res. 2014, 6(5), pp 2946-2951.
- [10]. M.KrishnaMohan, S.Ponnusamy, C.Muthamizhchelvan, Mater.Chem.Phys 195 (2017) pp. 224-228
- [11]. A.Thirugnanam, P. Praveen Kumar, AIP Conf. Proc 2259, (2020), pp. 020009(1-6)
- [12]. M. JoiceMalini, R. Kunjitham, M.K. Sangeetha, S. Ramalingam, Chem.Phys.Lett 768 (2020), pp. 138268(1-34)
- [13]. J.Chandrasekaran, P.Ilayabarathi, P. Maadeswaran, , Opt.Commun, 285 (2012) pp.3872-3876.
- [14]. G.Rajeswari, M.K.Sangeetha, G.Thanapathy, Int.j.sci;basicappl 9 (2019) pp.51-63.
- [15]. Michel Fleck, Aram M. Petrosyan, J. Cryst. Growth, 312 (2010) 2284–229.
- [16]. G.G. Muley, M.N. Rode and B.H. Pawar, , ActaPhys.Pol. Vol. 116 (2009) pp.1033-1038.
- [17]. M. Mahadevan , M. Magesh , K. Ramachandran , P. Anandan, M.Arivanandha, Y.Hayakawa, Spectrochim. Acta A, 130 (2014), pp 416-422
- [18]. B.Dhanalakshmi, S.Ponnusamy, C.Muthamizhchelvan, J.Cryst.Growth, 313 (2010), pp.30-36 .
- [19]. M.Prakash, M.LydiaCaroline, D. Geetha, Spectrochim. Acta A, 108 (2013), pp. 32–37.

-
- [20]. K. Kamatchi, P. Umarani, T. Radhakrishnan, C. Ramachandra Raja , Optik 172(2018),pp.674-679.
- [21]. P.Geetha, S.Krishnan, R.K. Natarajan, V. Chithambaram , Curr Appl Phys ,15(2015),pp.201-207.
- [22]. C.Ramachandra Raja, A. Antony Joseph, Spectrochim. Acta A, 74(2009),pp.825-828
- [23]. C. Usha , R. Santhakumari, Lynnette Joseph, D. Sajan, R.Meenakshi, A.Sinthiya, Heliyon 5(2019),pp. e01574(1-21).
- [24]. S. Ramalakshmi, K.A. Vijayalakshmi,,J.chem.,13(3), (2020),pp. 1394-1400
- [25]. Huayun Han, Yinglin Song, HongweiHou, Yaoting Fan , Yu Zhu , Dalton Trans (2006), pp.1972–1980