International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.8, pp 227-233, 2015

A Potentially Useful Semiorganic Nonlinear Optical Material L-Asparagine Potassium Penta Borate Octa Hydrate (Lasppb) for Opto-Electronic Device Fabrication

K.Kamatchi[1*] and T.Radhakrishnan[2]

[1*] Department of Physics, SRC, SASTRA University, Kumbakonam, Tamilnadu, India-612 001.
[2]Department of Physics, SRC, SASTRA University, Kumbakonam, Tamilnadu, India-612 001.

Abstract: L-Asparagine potassium penta borate octa hydrate(LASPPB) single crystals were synthesized from its aqueous solution at ambient temperature. Single crystal XRD confirmed the orthorhombic nature of the crystals. The UV-Vis spectroscopy highlighted the transparent nature of the LASPPB crystal. The lower cut-off wavelength was equivalent to 204 nm. The optical band gap was 6.06eV. The various functionalities incorporated in the synthesized compound were analysed by FTIR technique. The Second harmonic efficient of the LASPPB was 0.77 times that of KDP. The TG/DTA analyses showed the thermal stability and the melting point of LASPPB. The micro hardness test revealed the soft category of the material.
Key words: Single crystal, UV-Vis study, FTIR-study, Thermal stability, microhardness.

1. Introduction:

Non linear materials have the spectrum of advantages in the areas of optical data storage, optical communication, electro-optic applications etc.,[1-4]. Also, the nonlinear single crystals find wide applications in various industries like microelectronics, semiconductors, photonics, sensors etc.,[5-6]. Hence, the search for the new single crystals is an evergrowing task. In this series,the semiorganic materials retain the merits of organic and inorganic materials[7-8]. L-Asparagine one of the organic amino acid is important for protein structure and metabolism of cells and nerves. Potassium penta borate octa hydrate is a mid-alkaline salt. It has been widely used and assumed great asset for NLO devices in UV laser generation[9]. This potassium penta borate was combined with aminoacids like L-Alanine, Glycine and reported[10-11]. Also, L-Asparagine was discussed by many researchers[12-19]. In this present study, L-Asparagine is combined with Potassium penta borate octa hydrate in 1:1 ratio and its growth and characterization are discussed.

2. Experimental:

2.1 Synthesis:

The title compound LASPPB was synthesized by taking analar AR grade L-Asparagine and Potassium penta borate octa hydrate in 1:1 ratio and triply ionized water was used for the synthesis of the crystal. A magnetic stirrer was used for the dissolution of the contents for 4 to 6 hours. The solution was filtered and

allowed for slow evaporation. After 7 days, we got single crystals of LASPPB successfully and one well defined seed crystal was taken and suspended in the mother solution to get the bulk crystal.

2.2 Characterization:

Using Enraf Nonius X-ray Diffractometer, the lattice parameters were calculated. A λ-35 double beam spectrometer was used to identify the transmission property in the range of 190-1100nm. The amino acid and borate groups in the LASPPB were confirmed by using the Perkin Elmer FTIR spectrometer (Model SPECTRUM RXI). The wavelength range used in the spectrometer was 400-4000 cm^{-1} method adopted was KBr pellet method. A Q-switched mode locked Nd:Yag laser of wavelength 1064nm was used with a pulse width of 10ns and a repetition rate of 10 Hz was made to pass through the sample. The green signal generated in the LASPPB of wavelength 532nm confirmed the second harmonic generation. Using the model SII EXSTAR thermal analyzer, the thermo gravimetric analysis(TG) and differential thermal analysis(DTA) were done on the title compound in the nitrogen atmosphere. The rate of heating used was 20˚c per minute. Shimadzu HMV-2000 microhardness tester was employed to calculate the hardness number of the LASPPB for various loads.

3. Results and Discussion:

3.1 Single Crystal XRD studies:

The unit cell parameters of the LASPPB crystal are calculated as a = 5.614Å, b = 9.907Å, c = 11.847Å, α=β=γ=90˚ and the volume of the cell is V = 656$Å^3$. The number of molecules per unit volume is 4 and the space group is $P2_12_12_1$. Also, the LASPPB crystal belongs to the orthorhombic system. The photograph of the LASPPB crystal is shown in Fig.1 Table.1 shows the details of the unit cell of the LASPPB.

Fig.1 The photograph of LASPPB

Table.1 Details of the unit cell of LASPPB

Parameter	LASPPB
a	5.614Å
b	9.907 Å
c	11.847 Å
α=β=γ	90˚
Volume	656 $Å^3$
System	Orthorhombic
Space group	P212121
No. of molecules per unit volume	4

3.2 UV-Visible studies:

The migration of the electrons in the σ and π orbital from the ground to higher energy states by absorbing UV visible light can be studied by recording the UV-Visible spectrum. The recorded transmittance for LASPPB is 98% starting from the UV- lower cut-off wavelength of 204nm to 1100nm. It is shown in Fig.2 This transparent nature is the mandatory condition for the Opto-electronic applications like infrared diode, IR sensor modules, photovoltaic cell and laser applications[20-21]. The optical band gap of the LASPPB was 6.06eV

and it was calculated using the formula Eg = $1.243x10^3/\lambda max$. This larger band gap shows the lower incorporation of the defects in the crystal.

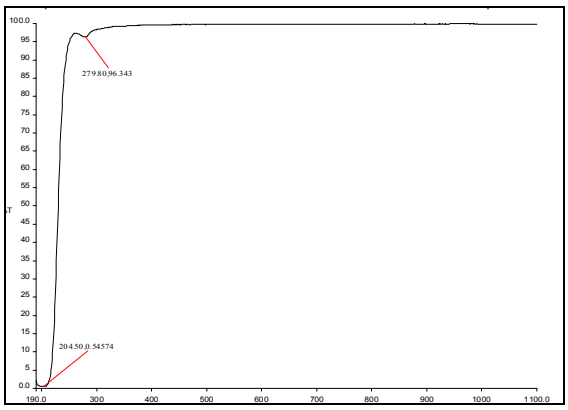

Fig.2 UV-VIS Study

Table.1 Details of the unit cell of LASPPB

Parameter	**LASPPB**
a	5.614Å
b	9.907 Å
c	11.847 Å
α=β=γ	90˚
Volume	656 $Å^3$
System	Orthorhombic
Space group	P212121
No. of molecules per unit volume	4

Table. 2 Spectral Band Assignments of the LASPPB:

Wave number cm^{-1}	Band Assignments
3347	O-H stretching vibration
3384	O-H stretching vibration
3116	NH_2 stretching vibration
2945	NH_3 stretching vibration
2527	C-H symmetric stretching vibration
2005	N-H stretching
1644	NH_3 deformation vibration
1431	B-O terminal symmetric stretching vibration,symmetric vibrations of COO-
1358	C-Hbending,B-O asymmetric stretching
1308	CH_2 wagging
1233	C-H_2rocking,B-O asymmetric stretching
1147	B-O asymmetric stretching
1074	C-N stretching
892	CH_2 rocking
807	C-C stretching

3.3 FTIR Analysis:

To analyze the different functionalities in the LASPPB, the FTIR spectrum,(Fig-3) has been recorded for the wavelength range of 400-4000 cm^{-1} using Perkin Elmer Fourier Transform Infrared Spectrometer (model spectrum RXI) by KBr pellet method. They are shown in Table.2 The O-H stretching vibrations are confirmed

by the peaks at 3447cm^{-1} and 3384cm^{-1} [15] . The peak at 3116cm^{-1} measures the NH_2 stretching vibration. The NH_3 stretching vibration gives the strong absorption peak at 2945cm^{-1}. The symmetric stretching of C-H produced a peak at 2527cm^{-1}. The N-H stretching vibration gave its characteristic peak at 2005cm^{-1}. The NH_3 deformation vibration produced a peak at 1644cm^{-1}. Symmetric vibration of COO^- and B-O terminal stretching vibrations are positioned at 1431cm^{-1}. Meanwhile, C-H bending vibration is identified at the wavelength of 1358cm^{-1}. The asymmetric stretching vibrations of B-O are assigned at 1233cm^{-1} and 1147cm^{-1} [22]. Also, the peak at 1308cm^{-1} is because of the CH_2 wagging. Moreover, the peaks at 1074cm^{-1} and 807cm^{-1} are due to C-C stretching and C-N stretching. The rocking of CH_2 is observed at 892cm^{-1}.

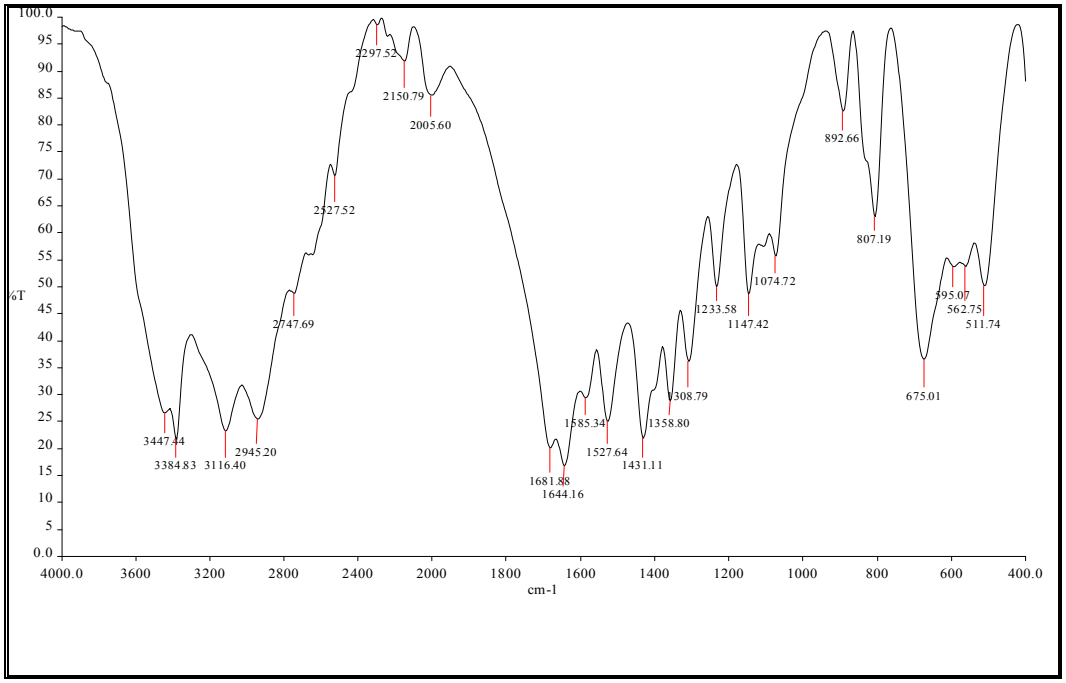

Fig.3 FTIR-Study

3.4 Second Harmonic Generation Analysis:

The non linear optical property of LASPPB was tested by the the Kurtz powder method[23]. For this, a powder sample was densely packed between two mirrors and 1064nm wavelength of laser beam with an input pulse of 6ns and repetition rate of 10Hz was incident on it. The emission of green colour light of wavelength 532nm was detected by the photomultiplier tube and hence LASPPB can be used as a second harmonic generator. The compared SHG efficiency of the LASPPB was equivalent to 77% with that of standard KDP.

3.5 TG/DTA Studies:

The simultaneous TG and DTA test was performed on the LASPPB sample weighing 5.688mg using a SII EXSTAR 6000 model thermal analyzer in atmosphere of nitrogen. The range of temperature of 30˚c to 800˚c with a heating rate of 20˚c per minute was used for the analysis. The TG/DTA curves of the LASPPB were shown in Fig-4. From this, it was observed that a weight loss of 12.3% at 114.8˚c occurs because of the release of water molecules present in the crystal lattice.Then at 253.1˚c, there is a weight loss of 24.7% occurs. This may be due to the release of potassium, borate and the remaining amino acid group present in the crystal lattice. The DTA analysis shows one endothermic transition between 114˚c and 253˚c which agrees well with the TGA curve. The another sharp endothermic peak at 253˚c is assumed as the melting point of the LASPPB crystal. Hence it is observed that LASPPB is suitable for device fabrications.

3.6 Micro Hardness Study:

The microhardness of a substance is an important parameter to define the strength of its material. The hardness testing provides useful information about the mechanical properties like elastic constants, yield strength etc. of the substance. Hardness is the resistance offered by the crystal for localized plastic deformation. The microhardness of the LASPPB was tested by using Vicker's test by varying the applied load. The plot of

hardness Vs load is shown in Fig-5. This denotes the increase of hardness number as the applied load increases. This behaviour is known as the reverse indentation size effect (RISE). The graph of log P Vs log d is shown in Fig-6. From this plot, the work hardening coefficient, n can be found and it is equivalent to 3.6. According to Onitsch, materials for n>1.6 are soft and hence, the LASPPB is a soft material[24-25].

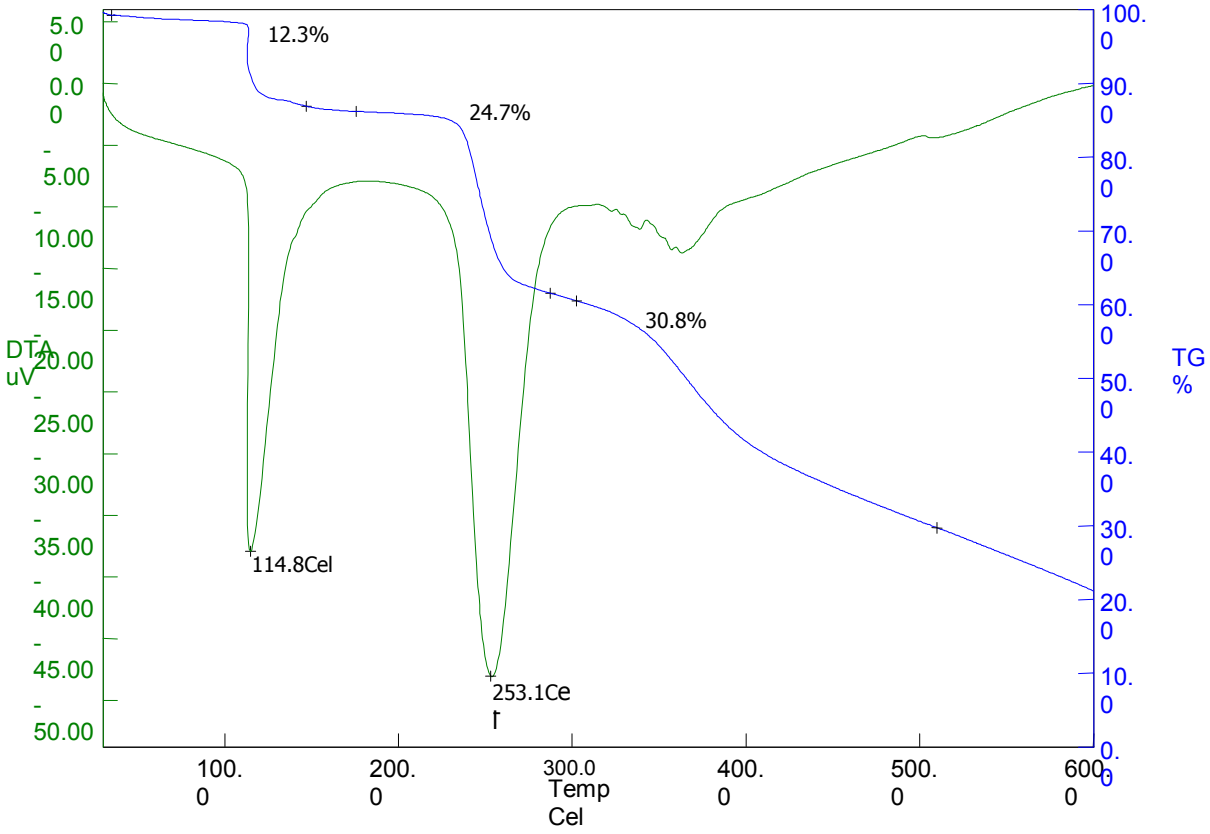

Fig.4 TG/DTA Diagram

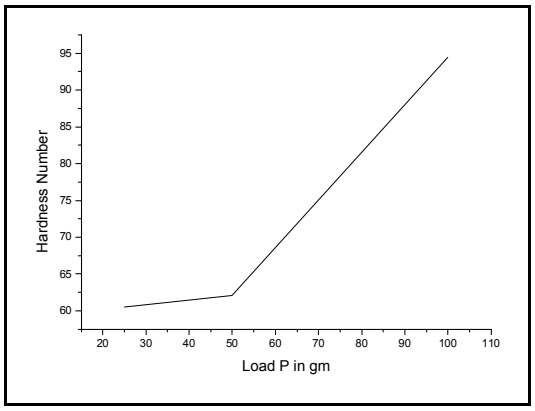

Fig.5 Hardness Number Vs Load Diagram

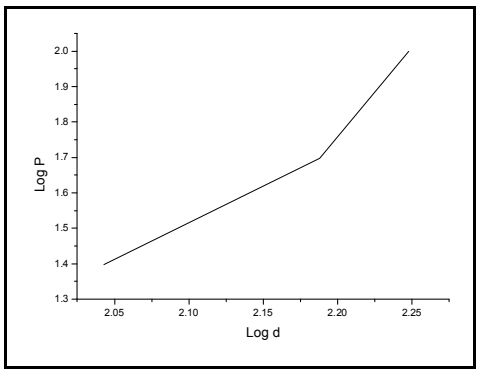

Fig.6 Log P Vs Log d Diagram

4. Conclusion:

Single crystals of L-Asparagine potassium penta borate octa hydrate LASPPB are synthesized successfully. The single crystal study confirms the orthorhombic nature of the crystal. The transparent nature in the UV-visible and Infrared region confirms the non linear property of the crystal and the opto-electronic device fabrication. The FTIR study proves the amino group and the borate groups. The TG/DTA analyses explain the thermal stability and the melting point of LASPPB is equivalent to 253˚c.The microhardness study reveals the soft category of the LASPPB crystal.

Acknowledgement:

The Author thanks to SAIF-IIT Chennai, BSAR University, Chennai, St.Joseph's College, Tiruchy, India.

References:

1. Madhurambal G, Mariappan M, Mojundar S. Thermal, UV and FTIR Spectral Studies of Urea-Thiourea Zinc Chloride Single Crystal. J.Therm Anal Caloim, 2010; 100:853-6
2. Verma S, Singh MK, Wadhavan VK,Suresh C. Growth morphology of Zinc tris(thio urea) sulphate crystals. J.Phys. 2000; 54: 879-88.
3. Ravikumar SM, Melikechi N, Selvakumar S, Sagayaraj P. Growth and characterization of Non linear optical bimetallic Thio cyanate complex of MCCTC Crystal. J.Crystal Growth 2009; 311: 2454-8.
4. Ramajothi J, Danuskodi S. Crystal growth, Thermal and Optical Studies on a semiorganic nonlinear optical material for blue-green laser generation. Spectrochim Acta A, 2007; 68:1213-9.
5. K.Ambujam, C.Preema Thomas, S.Aruna, D.Prem Anand, P.Sagayaraj,Mat & Manufact. Processes,22, 346(2007).
6. D.Ledoux, A.Lepers, J.Perigaud, J.Badan and J.Zyss, Opt.Commun, 80,1 (1990).
7. K.Nagarajan, S.Kumara Raman, R.Sundaram, Cry.Res.Tech.,44,4 (2009).
8. Z.Kotler,R.Hierle, D.Josse, J.Zyss and R.Masse, J.Opt.Soc.Am.B,9,534 (1992).
9. C.JustinRaj, S.Krishnan, S.Dinakaran, J.Mary Linet, R.Uthra Kumar, R.Robert and S.Jerome Das. Growth, Optical, Mechanical, Dielectrical and Theoretical Studies of Potassium Penta Borate Tetra Hydrate (KB_5O_8. $4H_2O$) by Modified Sankaranarayanan-Ramasamy Method. J.Mater.Sci. Technol. Vol.25, No.6, 2009.
10. K.Kamatchi and T.Radhakrishnan. Synthesis, Optical, Thermal and Microhardness Studies of L-Alanine Potassium Penta Borate Octa Hydrate(LAPPB). Journal of Applied Sciences 2014.1670-1673.DOI:10.3923/jas.2014.1670.1673.
11. K.Kamatchi, S.Gopinath and T.Radhakrishnan. Thermal, Spectral and Mechanical Analysis of Glycine Potassium Penta Borate Octa Hydrate (GPPB) crystal.. International Journal of Chem Tech Research. Vol.7, No.01, pp 408-411.2014-15.ISSN-0974-4290.
12. A. Thomas Joseph Prakash, S.Kumararaman. Growth and characterization of L-Asparagine thiourea monohydrate (LATM): A non linear optical single crystal Materials Letters Vol.62, Issue 24 Sep 2008 pages 4003-4005.

13. P.Rajesh P.Ramasamy Comparative Study on L-Asparagine monohydrate doped ADP crystals Physica B: Condensed matter Vol.405 Issue 5 Mar 2010 pages 1287-1293.
14. A.S.I.Joy sinthiya P.Selvarajan. Studies of L-Asparagine crystals admixured with Ammonium Chloride(LAAC) grown by solution method. Indian Journal of Applied Research Vol.3 Issue.9 Sep-2013 ISSN-2249-555X
15. A.S.I.Joy Sinthiya, P.Selvarajan Growth, XRD, Spectroscopic, Hardness and SHG studies of L-Asparagine monohydrate single crystals. International of Advanced scientific and technical research Vol.3 Issue:3 May-June 2013 ISSN-2249-9954.
16. F.Yogam, I.Vetha potheher, R.Jeyasekaran, M.Vimalan, M.Antony Arockiaraj P.Sagayaraj Growth, thermal and optical properties of L-asparagine monohydrate NLO single crystal.,. J Therm Calorim DOI:10.1007/s 10973-013-3138-8.
17. F.Yogam, I.Vetha Potheher, A.Cyrac Peter, P.Sagayaraj and M.Vimalan S.Tamilselvan. Growth and characterization of organic nonlinear optical single crystal of L-Asparaginium Picrate(LASP),. Archieves of Applied Research 3(1): 267-276.
18. A.S.I.Joy Sinthiya and P.Selvarajan. Growth and characterization of L-asparagine monohydrate crystals admixured with Cesium chloride.. International Journal of ChemTechResearch May-June 2014. Vol.6 No.3, pp-2013-2016. ISSN-0974-4290.
19. Grace, Sahaya Sheba, P.Omegala Priyakumari M.Gunasekaran Growth and characterization of L-Asparagine(LAS) Crystal Admixture of Paranitrophenol (PNP): A NLO Material.. International Journal Chemical, Nuclear, Metallurgical and Materials Engineeing Vol.8, No.1 2014.
20. S.Selvasekarapandian, K.Vivekanandan, Cry.Res.Tech., 32,2 (1997).
21. Fernaando Loretta, T.Joesphine Rani, World J Sci and Tech, 1,3 (2011).
22. V.Joseph, S.Gunasekaran and V.Santhanam. Photoconductivity and dielectric studies of potassium penta borate crystal (KB5). Bull.Mater.Sci. Vol.26, No.4 June 2003 pp-383-386, Indian Academy of Sciences.
23. S.K.Kurtz, T.T.Perry. A Powder technique for the evaluation of nonlinear optical materials. J.Appl.Phys.39(1986) 3798-3813.
24. E.M.Onitsch, Microskope 95(1950) 12.
25. M.Hanneman, Metall.Manch 23 (1941) 135.

*****