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Synthesis, growth, spectral and thermal studies on organic nonlinear optical material-L-valine valinium perchlorate single crystal

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ABSTRACT

Organic material of L-Valine valinium perchlorate (LVVPC) was synthesized. LVVPC crystallizes in the monoclinic space group $P2_1$. FTIR, ¹H and ¹³C NMR spectral analyses were carried out in order to confirm the presence of functional groups and the synthesized compound respectively. From the UV-vis-NIR absorption spectrum the cut-off wavelength was found to be 390nm. Powder X-ray diffraction (XRD) pattern of the grown crystal was studied. The second harmonic generation (SHG) analysis was carried and found to be ~3.5 times higher than that of the standard potassium dihydrogen orthophosphate (KDP).

Keywords: Crystal growth; Organic; FTIR; NMR; X-ray techniques

INTRODUCTION

Recently, nonlinear optics (NLO) is at the foremost of prevalent research due to its applications in frequency shifting, optical switching, optical memory and optical modulation for the technological areas such as telecommunications, optical interconnection and signal processing [1]. The field of molecular nonlinear optics has benefited from both upstream rejuvenation and downstream application oriented breakthroughs, aiding to bring the field closer to industrial developments [2]. Engineering of new nonlinear materials, structures and devices with enhanced figures of merit has comported over the past two decades as a major force to drive nonlinear optics from the laboratory to real applications. Due to their potential applications in photonic devices, the nonlinear optical properties of molecules and their hyperpolarizabilities have become an important area of extensive research, and a lot of experimental and theoretical efforts are focused on bulk NLO properties as well as their dependence on the first order hyperpolarizabilities of molecules [3]. Progress in the area of non-linear optics (NLO) depends upon the development of new materials. When compared with the inorganic materials, organic and semiorganic materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response time and good optical properties [4-7]. Amino acids and their salts belong to a family of organic materials and have wider nonlinear optical applications in this respect [8]. Amino acid of L-valine has been used for the formation of salts with inorganic acids [9]. As a result good NLO material such as L-valine hydrobromide, L-valinium succinate and L-valine hydrochloride was the outcome as already reported [10,11]. Hence, in the present investigation we report for the first time the synthesis, growth, spectral and thermal studies on L-Valine valinium perchlorate single crystal.

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Scheme 1 The reaction menchanism involved in the synthesis of L-valine valinium perchlorate

MATERIALS AND METHODS

2.1 Material Synthesis

The title compound was synthesized from analytical reagent grade L-valine (LV) and perchloric acid (PA) 2:1 molar ratio. The calculated amount of L-valine and perchloric acid were dissolved in distilled water and the

solution was stirred well. After refluxing it for 2 h at 100 °C, the solution was naturally allowed to cool to room temperature which yielded colourless crystalline powder of the compound. The purity of the synthesized material was improved by recrystallization process. The reaction mechanism involved in the synthesis of L-valine valinium perchlorate (LVVPC) is given in scheme 1. The purified crystalline powder of LVVPC was dissolved thoroughly in distilled water at 35 °C to form the solution and then it was taken in a beaker which was then properly sealed. The solvent was allowed to evaporate slowly at room temperature and single crystal of size 25 x 16 x 3 mm³ was harvested in a growth period of 27 days.

RESULTS AND DISCUSSION

3.1 Powder and Single crystal XRD analysis

The powder X-ray diffraction (XRD) was recorded using powder X-ray diffractometer with CuK α radiation ($\lambda = 1.5406$ Å). Finely crushed powder of LVVPC crystal w as scanned in the 20 values ranging from 10° to 80°. The peaks were indexed using Check Cell software and are shown in Fig. 1 along with the inset of the grown crystal. Three-dimensional X-ray crystal structure of LVVPC shows that it crystallizes in the monoclinic system with space group P21. The observed unit cell parameters are a =11.250(2) Å, b = 5.8320 (15) Å, c =13.0950 (19) Å, $\beta =91.280(14)^\circ$ and they are in good agreement with the reported values of Pandiarajan et al [12].

3.2 FT-IR spectral analysis

Fourier transform infrared (FTIR) spectrum of LVVPC was recorded in the region of 400-4000 cm⁻¹ employing Perkin Elmer Fourier transform infrared spectrometer using KBr pellet technique. The band obtained at 3151 cm⁻¹ is due to the NH₂⁺ symmetric stretching. The peak at 2970 cm⁻¹ is due to CH₂ asymmetric stretching and the peak at about 2751 cm⁻¹ is due to NH₃⁺ symmetric stretching. The band appeared at 2363 cm⁻¹ confirms the OH stretching frequency. Mono substituted benzenes show CH₂ deformation vibration in the region 1351 -1326 cm⁻¹ [13]. The peak observed at 10657 cm⁻¹ is due to the C—C—N stretching vibration. The peak at 774 cm⁻¹ and the peak at 715 cm⁻¹ are due to the NH wagging and COO bending vibrations espectively. The band appears at 542 cm⁻¹ is attributed to the C—C=O wagging vibration. Thus the FTIR spectrum confirms the presence of functional groups.

3. ¹H and ¹³C NMR spectral analyses

The proton(¹H) and Carbon (¹³C) NMR spectral analyses were carried out on the LVVPC crystal in CDCl3 using Bruker AC200-NMR Spectrometer and are shown in Figs. 2 and 3 respectively. In the proton NMR spectrum of LVVPC, the peaks observed as doublet at I =0.98 ppm are corresponding to methyl group (CH₃). The aromatic proton is observed at I = 2.24 ppm as a multiplet and resonated at I = 3.56 ppm as doublet. In the carbon NMR spectrum of LVVPC, a peak observed at I =16.73 ppm as doublet is due to methyl group CH₃ [13]. The aromatic carbon is observed at I = 60.37 ppm as singlet. The carboxylic carbon is observed at I = 174.09 ppm as singlet. Thus the formation of L-Valine valinium perchlorate is confirmed by proton and carbon NMR spectral analyses.



Fig.2 The proton NMR spectrum of LVVPC

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3.4. UV-vis-NIR spectral analysis

Optical absorption spectrum of LVVPC was recorded in the range of 200-1200 nm using Varian Cary 5E UV-vis-NIR spectrophotometer . A transparent crystal of 2 mm thickness was used for this measurement. From the spectrum, it is evident that the compound has a very low UV cut off wavelength at \sim 390 nm which is sufficient for SHG laser radiation of 1064 nm for frequency doubling process [14].

3.5. Electrical conductivity measurements

Determination of the electrical conductivity (EC) is a rapid and convenient means of estimating the concentration of ions in solution. Since each ion has its own specific ability to conduct electric current, EC is only an estimate of the total ion concentration. The Electrical conductivity value of LVVPC in distilled water at the concentration of 10^{-3} mole/dm³ is 30 µS cm⁻¹, which indicates the non-electrolyte nature of the compound [15].

3.6.Thermal analysis

Thermal stability of LVVPC was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) using 2950 TGA HR V5.4A instrument between the temperatures 20 °C and 400 °C at a heating rate of 40 °C/min under nitrogen atmosphere (Fig 4). Initial mass of the material subjected to the analysis was 28.99 mg but the final mass that remained after the experiment was only 2.5% of the initial mass at 400 °C, indicating bulk decomposition of the sample [15]. An endothermic peak observed at 150 °C in DTA corresponds to the mel ting point of LVVPC In TGA, a gradual and significant weight loss was observed as the temperature increases above the melting point.

4. Second Harmonic Generation studies

Kurtz and Perry [16] test was performed to estimate the Second harmonic generation (SHG) efficiency of the powdered LVVPC crystal. The crystal was illuminated by Spectra Physics Quanta Ray DHS2. Nd:YAG laser output wavelength of 1064 nm with pulse width of 8 ns and repetition rate 10 Hz. The second harmonics signal, generated in the crystal was confirmed from the emission of green radiation by the crystal. The SHG radiation of 532 nm green light was collected by a photomultiplier tube (PMT-Philips Photonics-model 8563) after being monochromated (monochromator-model Triax-550). The optical signal incident on the PMT was converted into voltage output at the

R. Santhakumari *et al*

CRO (Tektronix-TDS 3052B). The input laser energy incident on the powdered sample was 3.4 mJ. Powder SHG efficiency obtained for is about 3.5 times that of potassium dihydrogen orthophosphate (KDP). The relatively higher NLO efficiency is due to the crystal structure of LVVPC which consists of strong hydrogen bonding between valine and valinium molecules formed by the perchlorate ion and bifurcated hydrogen bond in the case of the water molecule with perchlorate O (oxygen) atoms [12].



Fig.4 TGA/DTA curve of LVVPC

CONCLUSION

A new organic crystal LVVPC was synthesized. The single crystal XRD shows that LVVPC crystallizes in the monoclinic system. FTIR spectral analysis confirms the presence of functional groups constituting LVVPC. The proton (^{1}H) and Carbon (^{13}C) NMR spectral analyses confirm the synthesized compound. The optical study shows that the lower cut-off wavelength is 390 nm. The electrical conductivity measurement confirms the non electrolyte nature of the grown crystal. TGA/DTA reveals the thermal stability of the crystal. Powder SHG efficiency of LVVPC estimated is about ~3.5 times greater than that of potassium dihydrogen orthophosphate and is due to the presence of strong hydrogen bonds in the crystal structure.

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REFERENCES

[1] Kandasamy A, Siddeswaran R, Murugakoothan P, Suresh Kumar P, Mohan R, Cryst.Growth Des. 2007; 7: 183-186.

[2] Prakash M, Lydia Caroline M, Geetha D, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2013**;108: 32–37.

[3] Srinivasan P, Kanagasekaran T, Gopalakrishnan R, Crystal Growth and Design, 2008 vol.8, No.7, 2340-2345.

[4] Dhanuskodi S, Mary PAA, J. Cryst. Growth 2003; 253: 424-428.

[5] Prasad P N, Williams DJ, "Introduction to Nonli near Optical Effects in Molecules and Polymers", J ohn-Wiley & Sons Inc., New York, **1991** pp. 35-38.

[6] Vijayan N, Ramesh Babu R, Gunasekaran M, Gobalakrishnan R, Kumaresan R, Ramasamy P, Lan CW, J. *Cryst. Growth* **2003**; 249: 309-315.

[7] Vijayan N, Ramesh Babu R, Gunsekaran M, Gobalakrishnan R, Ramasamy P, J. Cryst. Growth 2003; 256: 174-182.

[8] Baraniraj T, Philominathan P, Spectrochim, Acta Part A 2010; 75: 74-76.

[9] Sweta Moitra, Tanusree Kar, J. Cryst. Growth 2008; 310: 4539.

[10] Ramachandra Raja C, Antony Joseph A, Spectochimica Acta Part A 2009; 74: 825.

[11] Kirubavathi K, Selvaraju K, Valluvan R, Vijayan N, Kumararaman S, Spectrochimica Acta Part A 2008; 69: 1283.

[12] Pandiarajan S, Sridhar B, Rajaram RK, Acta Cryst. 2001; E57: o466-o468.

[13] Silverstein RM, Webster FX (Eds.), "Spectrometric Identification of Organic Compounds", sixth ed., Jo hn Wiley and Sons, Inc., in Canada, **1998**.

[14] Rao CNR, "Ultraviolet and Visible Spectroscop y of Organic Compound", Prentice Hall Pvt Ltd., New Delhi, **1984**.

[15] Willard HH, Merritt LL, Dean JA, Settle FA, "I nstrumental Methods of ChemicalAnalysis", C.B.S. Publishers, India, **1986**.

[16] Kurtz SK and Perry TT, J. Apply. Phys. 1968: 39; 3798-3813.