International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.5, No.4, pp 1679-1683, April-June 2013

Growth And Characterisation Of Nonlinear Optical Single Crystals Of L-Valine Oxalate

Deepa Jananakumar[1]*, P Mani[2]

[1] Department of Physics, Velalar College of Engineering and Technology, Erode 638012, India
[2]Department of Physics, Hindustan University Padur, Chennai, 603103, India

***Corres.author : deepaavanthikaa@yahoo.co.in**
Telephone number: +91 9488652656

Abstract: An organic nonlinear optical material, L-Valinium oxalate (abbreviated as LVO) has been successfully synthesized and good quality single crystals have been grown by Slow Evaporation Technique at ambient temperature. The purified form of LVO is achieved by repeated crystallization. The cell parameters of LVO have been determined using single crystal X-ray diffraction technique and the crystal system is found as monoclinic. From the UV–Vis–NIR absorption spectrum, the good transparency is revealed from 290 nm to 1100 nm. The mode of vibration of different molecular groups present in LVO was identified by FT-IR spectral analysis. The thermogravimetric (TGA) and differential thermal analysis (DTA) studies show the thermal behaviour and crystal was thermally stable up to 256°C. Second harmonic generation (SHG) conversion test was made to explore the nonlinear optical behaviour of this material using Kurtz and Perry method.

Key words: Nonlinear Optical Single Crystals,L-Valine Oxalate, Characterisation, Growth .

1. Introduction

Growth of nonlinear optical (NLO) single crystals with good quality initiates the development of many novel devices in the field of optoelectronics and optical communication such as optical modulator, optical data storage and optical switches [1,2]. Organic crystals can exhibit higher nonlinear optical efficiencies than those of inorganic materials due to large optical susceptibilities, high optical threshold for laser power and low frequency dispersion [3, 4]. Amino acid family crystals are of interest due to their attractive nonlinear optical properties [5]. When mixing of organic acid with amino acid, NLO property is increased due to the zwitterionic nature and high transparency range [6, 7]. In this point of view, a number of novel amino acids mixed with non linear organic crystals have been investigated and reported such as L-alaninium oxalate [8], L-prolinium tartarate [9], and L-alaninium succinate

[10] due to their potential use in SHG. Hence it will be very useful to synthesize organic NLO materials and study their structural, physical, thermal and optical properties. In this article, we report the growth and characterization of new organic NLO crystal L-valinium oxalate.

2. Crystal growth

Single crystals of LVO were obtained by slow evaporation of an aqueous solution containing L-valine (GR grade) and oxalic Acid (GR grade) in the 1:1 stoichiometric ratio. The weighed reactants were thoroughly dissolved in deionised water and stirred well using a magnetic stirrer to get saturation. The saturated solution was filtered and transferred to crystal growth

vessels and tightly covered by polythene paper. To achieve slow evaporation, some holes were made on the polythene paper. The crystallization was allowed to take place by slow evaporation at a temperature of 35 °C in a constant temperature bath of accuracy ± 0.01 °C. Purification of the salts was done by repeated crystallization process until optically clear crystals were obtained. Optically transparent seed crystals were harvested. The LVF crystals of size 8×6×3mm3 were obtained by isothermal slow evaporation technique at room temperature [11] in a period of three weeks as shown in the Fig. 1.

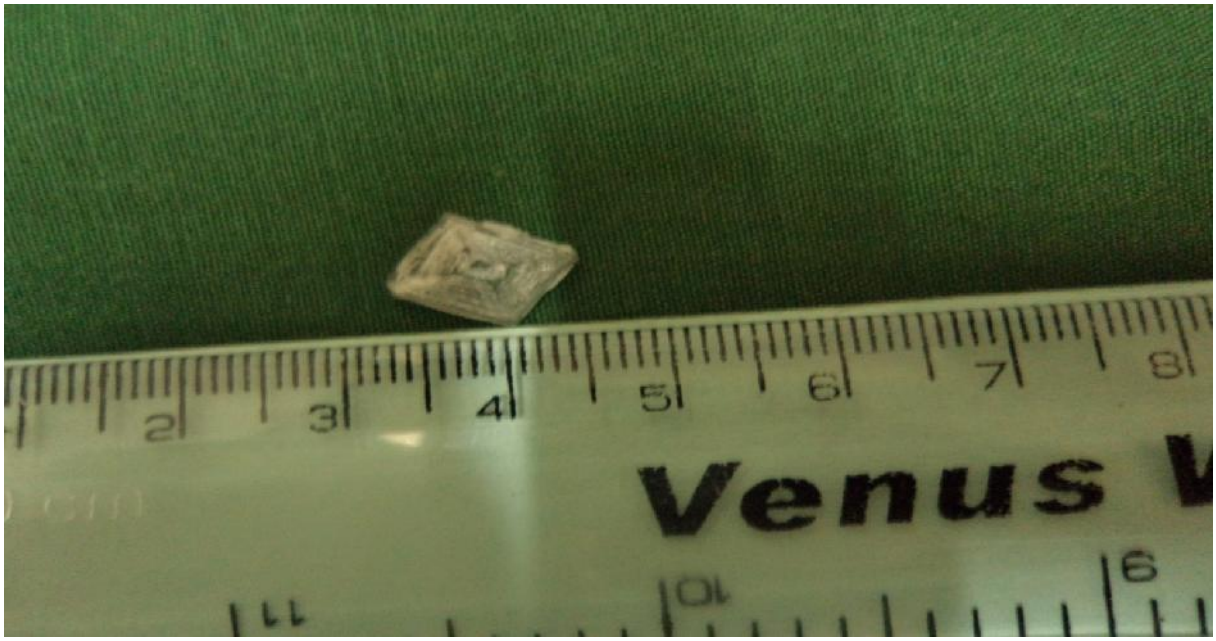

Fig. 1 As grown single crystals of LVO

3. Characterization

Single crystals of LVO have been grown by slow evaporation technique and crystal system was identified by single crystal XRD method using ENRAF NONIUS CAD-4 single X-ray diffractometer with MoK_{α} (λ=0.71073 Å) radiation. The transparency range was investigated by λ 35 model Perkin-Elmer double beam UV–Vis–NIR spectrometer in the range from 190 nm to 1100 nm. The presence of functional groups was confirmed from 400 cm^{-1} to 4000 cm^{-1} with Perkin-Elmer FT-IR spectrometer model SPECTRUMRX1 using KBr pellets technique. Thermal behaviour of grown crystal was determined using the instrument NETSZCH SDT Q 600 V8.3 Build 101. The second harmonic generation of sample is demonstrated by Kurtz and Perry method using Nd: YAG laser as source.

4. Results and discussion

4.1. Single crystal XRD analysis

The obtained XRD data of LVO single crystal were a=21.303 A°, b=7.503 A°, c=5.541 A°; α=γ=90° and β=91.48°, the cell volume=859.7 $A°^3$. The XRD data of LVO crystal indicates that the grown crystal belongs to monoclinic system.

4.2. UV–Vis–NIR spectral analysis

Optical transmission spectrum of LVO was studied in the range from 190 nm to1100 nm by a Varian Cary lambda model double beam spectrophotometer. When the transmittance is monitored from longer to shorter wavelength, LVO has optical transparency from 250 nm to 1100 nm. It is clearly evident that the lower cut off wavelength lies near 290 nm and it is essential parameters for frequency doubling process using diode and solid state laser [11]. There is no absorption in the entire visible region and up to 290 nm. It is very useful for non linear optical applications of grown crystals because if there is any absorption in the fundamental 1064 nm and second harmonic generation of Nd: YAG laser in 532 nm, conversion efficiency of SHG will decrease. The transmittance spectrum is as shown in Fig. 2.

4.3. FT-IR spectral analysis

The co-ordination of L-valine with oxalic acid was confirmed by FT-IR studies. The FT-IR spectra of the grown L-valinium oxalate single crystal were recorded in the frequency region from 400 to 4000 cm^{-1} with Perkin-Elmer FT-IR spectrometer model SPECTRUMRX1 using

KBr pellets containing LVO powder obtained from the grown single crystals. In the higher energy region, the peaks at 3071 cm^{-1} and 2546 cm^{-1} are assigned due to NH_3^+ asymmetric and symmetric stretching respectively [12,13]. The existence of NH_3^+ and COO^- groups was confirmed by absorption at 3071 cm^{-1} and 1441 cm^{-1}. It is evident that grown crystal has zwitterionic nature. It was observed that two bands at 2872 cm^{-1} and 1338 cm^{-1} correspond to stretching and wagging of CH_2 group. The absorption band at 1052 cm^{-1} established the presence of C–CN. The presence of NH_3^+ is clearly illustrated by the peaks at about 1622 cm^{-1}, 1501 cm^{-1} and 1140 cm^{-1} in the title compound. The sharp peak at 927 cm^{-1} is due to C–CH bending. The wagging vibration of C–C=O is positioned at 582 cm^{-1}. The bending and rocking vibrations of COO^- were obtained at 671 cm^{-1} and 473 cm^{-1} respectively.

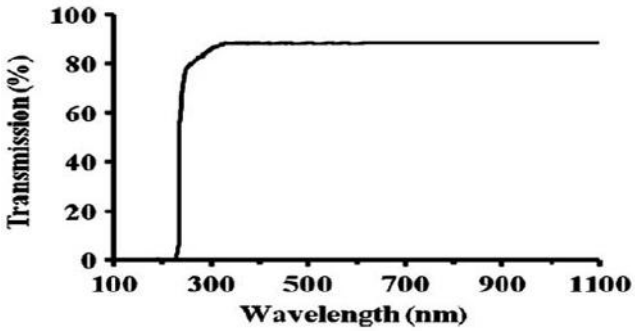

Fig.2 Transmittance spectrum of LVO

Table 1 Functional group assignments of L Valine oxalate

Wavenumber cm^{-1}	Assignments
3071	NH_3^+ asymmetric stretching
2872	CH_2 asymmetric stretching
2630	CH symmetric stretching
2546	NH_3 symmetric stretching
1622	NH_3 asymmetric stretching
1501	NH_3 symmetric stretching
1411	COO^- symmetric stretching
1338	CH_2 wagging
1280	C-CH bending
1140	NH_3 rocking
1115	C-N stretching
1052	C-CN stretching
927	C-CH bending
882	C-C stretching
831	COO^- rocking
786	CH_2 rocking
745	C-C skeletal stretching
671	COO^- bending
582	C-C=O wagging
473	COO^- rocking

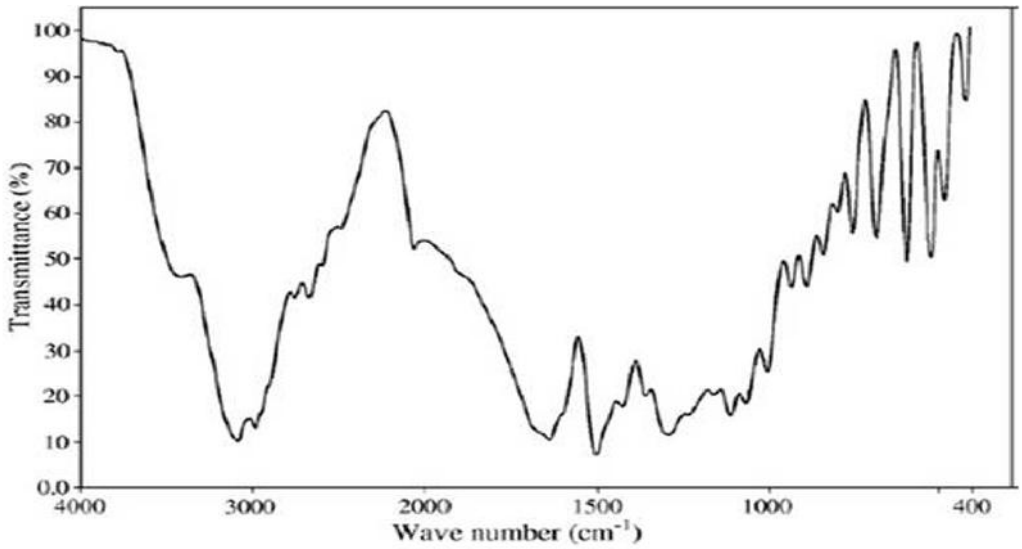

Fig.3 FTIR spectrum of LVO

4.4. Thermal analysis

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) using the instrument NETSZCH SDT Q 600 V8.3 Build 101, determined the thermal characterization. The TGA and DTA were carried out in nitrogen atmosphere at a heating rate of 10°C/min from 0 °C to 1100 °C and it is shown in Fig. 4. The initial mass of the materials to analyses as 2.975 mg and the final mass left out after the experiment was only 6.943% of initial mass. The TGA trace shows that the material exhibit small weight loss of about 2.07% in the temperature range of 78.4 °C to 186.5 °C due to loss of water. As the weight loss is sharp, it may be attributed to loss of lattice water. There is a major weight loss of about 85.53% which occurs between 185.6 °C and 275.58 °C due to decomposition of LVO compound and it shows that decomposition is almost completed. The small exothermic peak at 424 °C may be due to decomposition of carbon in L-valine in the residue [14]. There is one more weight loss between 822.3 °C and 970 °C due to the decomposition of the remaining residue.

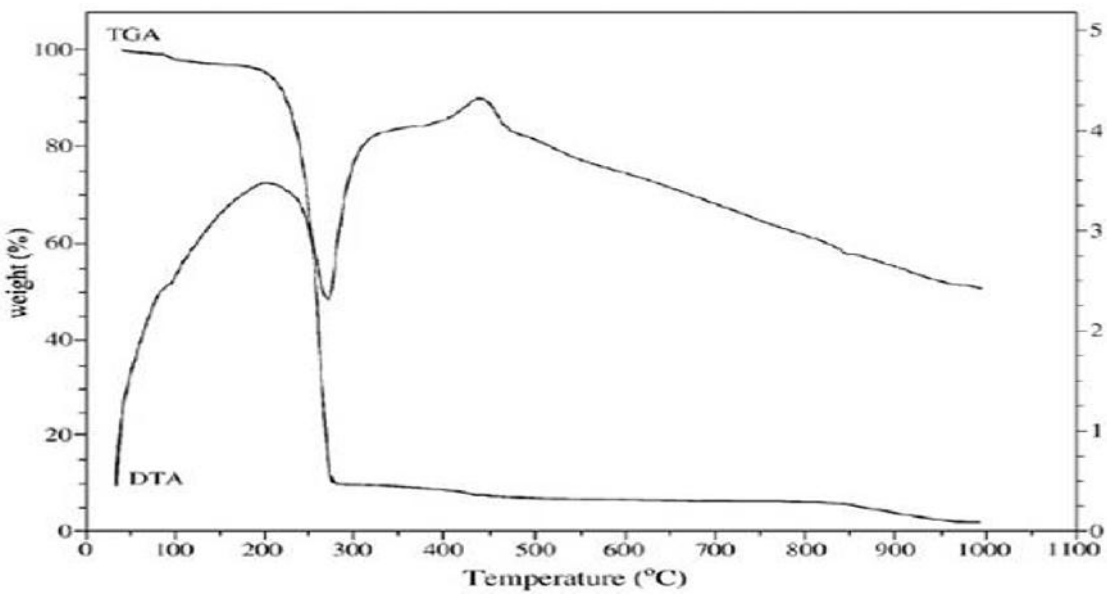

Fig. 4 DTA-TGA thermogram of LVO

4.5. Non linear optical studies

The NLO property of grown LVO crystals was studied by Kurtz and Perry [15] by passing the output of first harmonic generation laser beam of wavelength 1064 nm. A Q-switched Nd: YAG laser beam of wavelength was used with pulse width of 8 ns and the repetition rate being 10 Hz. Photodiode and oscilloscope assembly examined the output light from the sample. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation from the sample. The output power was measured as 14 mV. For the same input, KDP crystals were emitted the green light with the output power of 50 mV.

Conclusion

Good quality organic NLO crystals of LVO have been successfully grown by slow evaporation technique. The cell parameter was measured by single crystal XRD method and confirms the crystal system as monoclinic. The absence of absorption in the entire visible region in UV–Vis–NIR spectrum of LVO makes the crystal in to a suitable material for optoelectronics applications. The presence of functional groups was confirmed by FT-IR analysis. Thermal studies reveal that LVO does not decompose before melting and its suitability for NLO application up to 266 °C. The SHG test shows that the LVF crystals are promising material for the nonlinear optical applications involving frequency doubling process.

Acknowledgments

The authors thank to sophisticated analytical Instrumentation facility (STIC), Cochin. The authors are grateful to Prof. P.K. Das, IISc., Bangalore for extending the facilities to measure SHG efficiency. Authors would like to thank St. Joseph's College, Trichy, India, for spectral facilities.

References

1. Dmitriev VG, Gurzadyan GG, Nicogosyan DN. Handbook of nonlinear optical crystals. New York: Springer Verlag; 1999.
2. Wong MS, Bosshard C, Pan F, Gunter P. Adv Mater 1996; 8:677.
3. Zyss J, Nicoud JF, Coquillay M. J Chem Phys 1984,81,4160.
4. Ledoux I, Badan J, Zyss J, Migus A, Hulin D, Etchepare J, Grillon G, Antonetti. J Opt Soc Am 1987; B. 4:987.
5. Kitazawa M, Higuchi R, Takahsshi M. Appl Phys Lett 1994; 64:2477.
6. Bhat MN, Dharmaprakas SM. J Cryst Growth 2002; 236:379–80.
7. Nicoud JF, Twieg RJ, Chemla DS, Zyas J. Nonlinear optical properties of organic molecules and crystals. London: Academic Press; 1987.
8. Dhanuskodi S, Vasantha K. Cryst Res Technol 2004; 39:259–65.
9. Martin Brito Dhas SA, Natarajan S. Cryst Res Technol 2007;42:471–6.
10. Ramachandra Raja C, Gokila G, Antony Joseph A. Spectrachim Acta A 2009; 72:753–6.
11. Ramaswamy S, Sridhar B, Ramakrishnan V, Rajaram. Acta Cryst 2004;E 60:01691.
12. Martin Britto Dhas SA, Natarajan S. Cryst Res Technol 2008; 43:869–73.
13. [un ZH, Xu D, Wang XQ, Liu XJ, Yu G, Zhang GH, Zhu LY, Fan HL. Cryst Res Technol 2007;42:812–6.
14. Ramachandran E, Natarajan S. Cryst Res Technol 2009;44:641–6.
15. Kurtz SK, Perry TT. J Appl Phys 1968; 39:3798.

*****