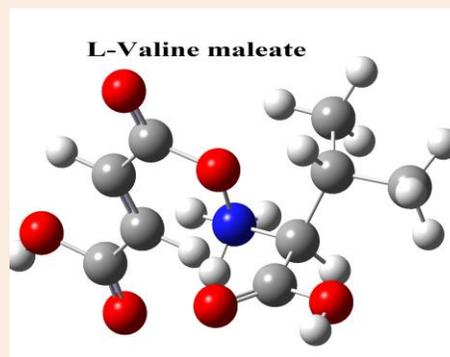


Research Article

Growth, Structural and Spectral Studies on Nonlinear Optical Single Crystal: L-Valine Maleate

C.Usha¹, R. Santhakumari^{2*}, S.Valarselvan³, R. Jayasree⁴ and M.Bhuvaneshwari⁵¹Department of Physics, J.J.College of Arts and Science (Autonomous), Sivapuram, Pudukkottai-622 422, Tamil Nadu, India²Department of Physics, Government Arts College for Women (Autonomous), Pudukkottai-622 001, Tamil Nadu, India³Department of Chemistry, H.H.The Rajah's College (Autonomous), Pudukkottai-622 001, Tamil Nadu, India⁴Department of Physics, Srimad Andavan Arts and Science College (Autonomous), Thiruchirappalli- 620 005, Tamil Nadu, India⁵Department of Physics, Dhanalakshmi Srinivasan Engineering College, Perambalur – 621 212 , Tamil Nadu, India**Abstract**

One of the organic nonlinear optical materials, L-Valine maleate (LVMA) was synthesized. The grown crystal was analyzed by X-ray diffraction pattern; it is proved that LVMA belongs to monoclinic crystal system. The formation of the expected compound, presence of functional groups and modes of vibrations were confirmed by FTIR spectroscopy. ¹H and ¹³C NMR spectral analyses were carried out in order to confirm the chemical structure of the title compound. UV-vis-NIR spectrum recorded from 2 mm thick crystals shows ~50% of transmittance in the wavelength region of 390-1100 nm. Second Harmonic Generation (SHG) efficiency of the powdered L-Valine maleate was estimated using Nd: YAG laser and is ~9.0 times that of potassium dihydrogen orthophosphate (KDP).



Keywords: Growth from solution; Characterization; Organic compound; Nonlinear optical material; X-ray diffraction

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Introduction

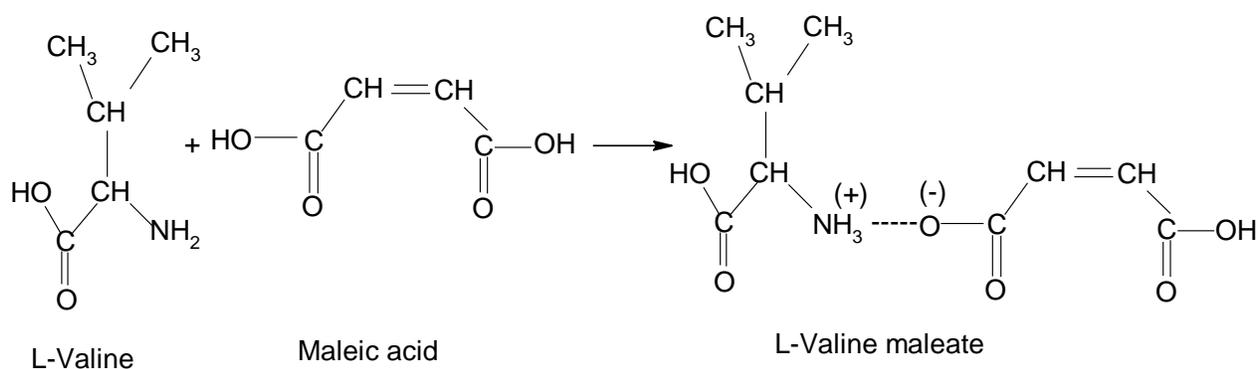
Nonlinear optical (NLO) materials have been extensively studied in the recent years, due to their potential applications in various fields like optical data storage, optical switching, image processing and manipulation [1-3]. Materials with large second-order optical nonlinearities, good optical transparency, short lower cut-off wavelengths, and stable physicochemical performances are required in order to realize many of these applications [4]. Organic crystals are of great interest for the nonlinear optical (NLO) technologies in line with the tendency to replace the classical electronics with organic materials. Searching of new organic NLO materials is an alternative to semi-organic species because of their large nonlinear susceptibility, inherent synthetic flexibility and high optical damage threshold [5]. Amino acids belong to a family of organic materials and are interesting materials for NLO applications as they contain a proton donor carboxyl acid (COOH) group and the proton acceptor amine (NH₂) group. The importance of amino acids in NLO applications is due to the fact that all the amino acids have chiral symmetry and crystallize in noncentro-symmetric space groups [6-8]. L-Arginine phosphate, L-Threonine acetate, L-Hisidine hydrochloride are some of the examples of amino acid complexes which proved their applications in the field of NLO [9-11]. L-Valine is a branched chain amino acid that exists as zwitterions, which create hydrogen bonds, in the form of N—H⁺—O—C, which are very strong bonds. Hydrogen bonds have also been used in the possible generation of non-centrosymmetric structures. It is a prerequisite for an effective second harmonic generation (SHG) crystal [12]. Maleic acid, basically a dicarboxylic acid with large π -conjugation has attracted a great deal of attention [13]. Hence in the present investigation, it is reported for the first time on the growth of L-Valine maleate (LVMA) crystals by slow evaporation solution growth at room temperature and the grown crystals have been subjected to single crystal X-ray diffraction (XRD), Fourier transform

infrared (FTIR) spectroscopy, optical transmission, ^1H NMR, ^{13}C NMR spectroscopy and second harmonic generation (SHG) studies.

Experimental

Crystal growth

LVMA was synthesized by reacting analytical grade L-Valine and maleic acid in a 1:1 stoichiometric ratio. The calculated amount of maleic acid was first dissolved in distilled water. L-Valine was then added to the solution slowly by stirring. The LVMA crystal was obtained from L-Valine and maleic acid according to the chemical reaction depicted in scheme 1.



Scheme 1 Chemical reaction of LVMA crystal

Saturated solution of LVMA was taken in a beaker and the mouth was closed with the perforated lid in order to control the rate of evaporation and kept in room temperature for crystallization. One of the transparent LVMA crystals ($0.3 \times 0.3 \times 0.1 \text{ mm}^3$) was obtained from the aqueous solution of LVMA by slow evaporation at room temperature and the same was used as the seed crystal. Slow evaporation at room temperature yielded a good quality single crystal of dimensions $4 \times 2 \times 3 \text{ mm}^3$ from aqueous solution in a growth period of 26 days and is shown in Figure 1.

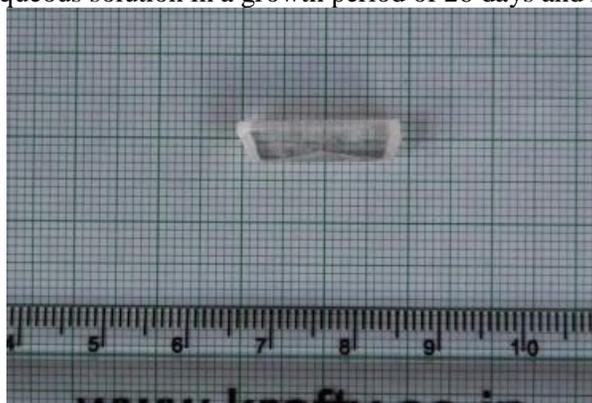


Figure 1 As grown LVMA crystal

Results and Discussion

Single crystal X-ray diffraction

The X-ray diffraction (XRD) data were collected using a computer-controlled Enraf Nonius-CAD4 single crystal X-ray diffractometer. Single crystal of suitable size was selected for the X-ray diffraction analysis and the unit cell parameters were determined using 113 reflections. XRD results show that LVMA crystal belongs to the monoclinic system and the unit cell parameters were compared with the reported value of L-Valine (LV) Torri et al.[12] as given in Table 1.

Table 1 Comparison of crystal data of LVMA crystal

Parameters	Present work	Torii et al. (LV) [12]
a (Å)	7.11	9.71
b (Å)	10.06	5.27
c (Å)	7.44	12.06
β (°)	116.97	110
System	Monoclinic	Monoclinic
V (Å ³)	474	608

FT-IR spectral analysis

Fourier transform infrared (FTIR) spectrum of L-Valine maleate was recorded using Perkin Paragon-500 by KBr pellet technique between 400 cm⁻¹ and 4000 cm⁻¹ and is shown in Fig.2. The functional groups that were present, were identified and compared with similar crystals L-Valine (LV), L-Valine succinate (LVS) [14] as stacked in Table. 2.

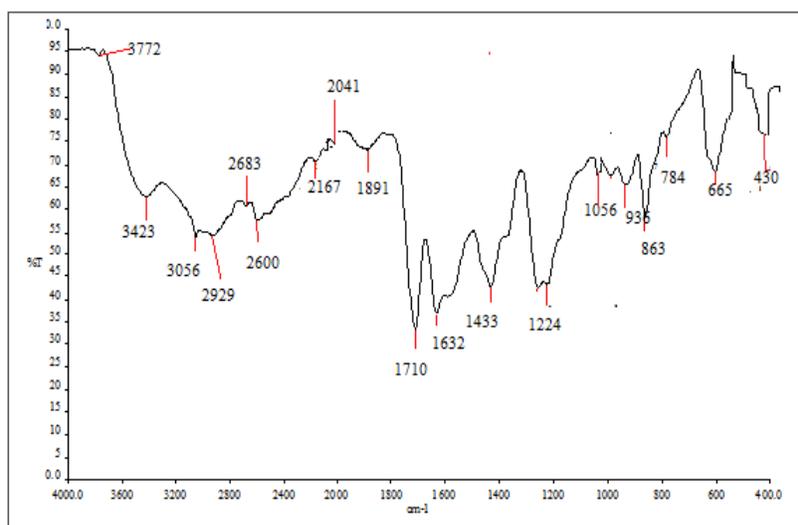


Figure 2 FT-IR spectrum of LVMA crystal

Table 2 Comparison of vibrational frequencies of LVMA crystal

L-Valine [14] (cm ⁻¹)	L-Valine succinate [14] (cm ⁻¹)	LVMA Present Work (cm ⁻¹)	Assignments
3432	3429	3423	NH ₂ ⁺ symmetric stretching
3154	3156	3056	NH ₃ ⁺ asymmetric stretching
2947	2946	2929	CH ₂ asymmetric stretching
2625	2626	2683	NH ₃ ⁺ symmetric stretching
2109	2108	2167	C–O–C stretching
1586	1587	1632	NH ₃ ⁺ symmetric bending
1393	1393	1433	CH ₂ symmetric bending
1063	1063	1056	C–C–N stretching
1030	1029	990	C–C stretching
944	945	936	CH ₂ rocking
894	893	863	C–C–N stretching
770	773	784	NH wagging
662	662	665	COO ⁻ bending
431	430	430	COO ⁻ rocking

The presence of NH_3^+ group in LVMA was shifted to 3056 cm^{-1} . It is due to the protonation of NH_2 group by the COOH group of maleic acid [15, 16]. The strong absorption at 1433 cm^{-1} in LVMA crystal indicates the symmetric bending of CH_2 . The stretching vibrations of C-O-C and C-C-N were positioned at 2167 cm^{-1} and 1056 cm^{-1} respectively. The peak at 936 cm^{-1} in LVMA crystal is due to CH_2 rocking. The bending and rocking vibrations of carboxylic group COO^- were observed at 665 cm^{-1} and 430 cm^{-1} respectively.

UV-vis-NIR spectrum

The grown crystals were subjected to spectral analysis for studying the linear optical properties. The optical transmission spectrum of LVMA crystal of 2 mm thickness was recorded in the range of 200-1100 nm using Varian Cary 5E UV-vis-NIR spectrophotometer (Fig. 3). The recorded UV-vis-NIR transmission spectrum of LVMA shows the lower cutoff wavelength at 390 nm and a wide transparency in the entire region which makes the material suitable for second harmonic generation [17]. The transmittance of the crystal is about 50% in the visible and near infrared region.

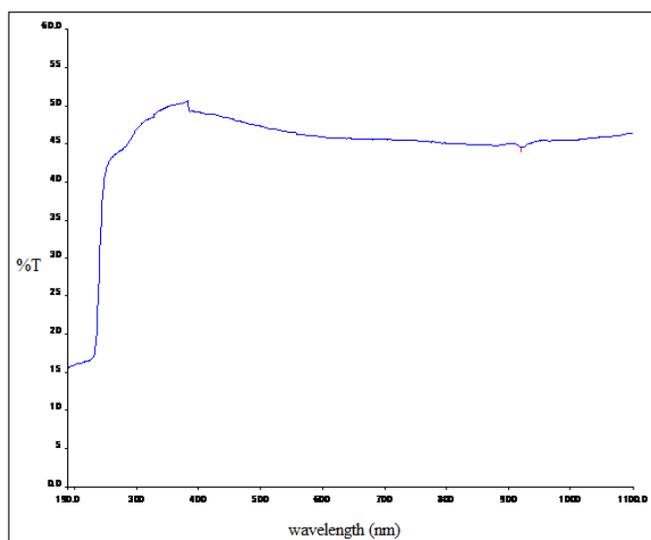


Figure 3 UV-vis-NIR transmission spectra of LVMA crystal

^1H and ^{13}C NMR studies

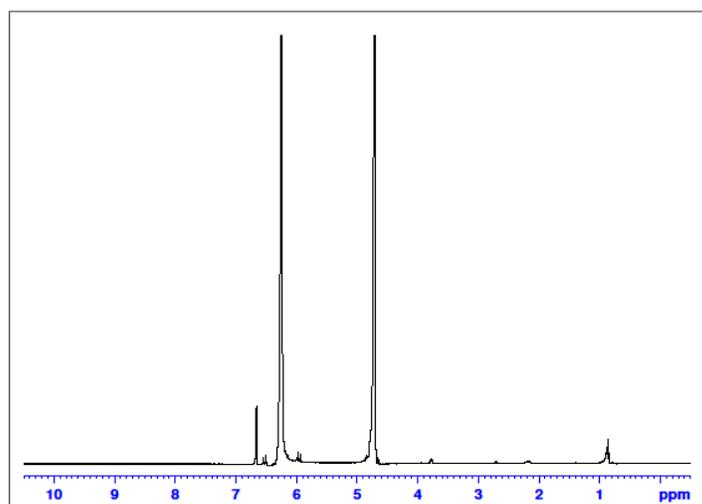


Figure 4 ^1H NMR spectrum of LVMA crystal

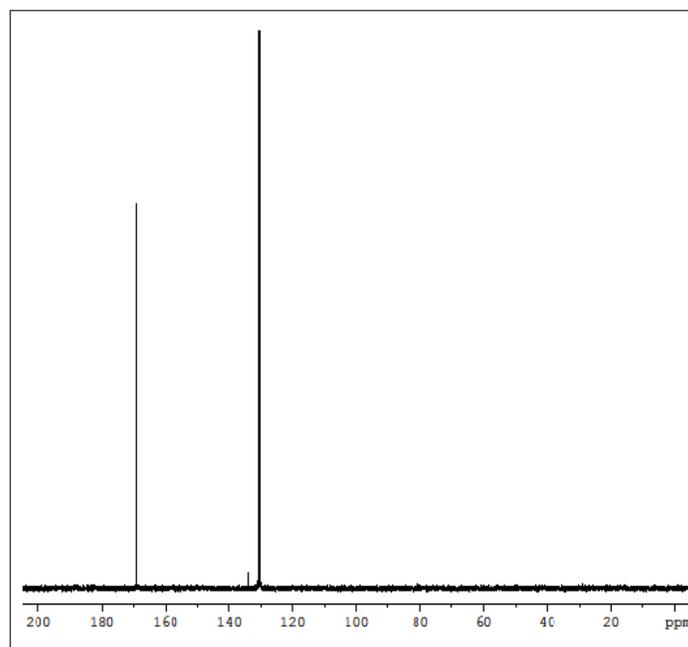


Figure 5 ^{13}C NMR spectrum of LVMA crystal

The ^1H and ^{13}C NMR spectrum were recorded for the crystals dissolved in deionized water (D_2O) using Bruker 300 MHz (Ultrashield)TM instrument at 23°C (300.13 MHz for ^1H NMR and 75.47 MHz for ^{13}C NMR) for the confirmation of molecular structure. The ^1H NMR, ^{13}C NMR spectrum of LVMA is shown in Figs. 4 and 5 respectively.

From the ^1H NMR spectra of LVMA crystal, it is observed that the $-\text{CH}$ group signal is split into a multiplet due to the hyperfine splitting of neighbouring six methyl and one methyne proton, which was confirmed by the signals from δ 0.838 to δ 0.885 ppm. The signal observed at δ 3.77 and at δ 3.78 ppm for LVMA crystal has been attributed to the presence of two methyl groups in an equivalent environment and the splitting is caused by the neighbouring methyne protons as doublet. The two methyl proton signal is split into two doublets due to the coupling of neighbouring $-\text{CH}$ proton which was confirmed by the signals from δ 4.71 to δ 4.74 ppm. The signal at δ 4.78 ppm was due to the solvent D_2O . The signal at δ 5.98 ppm is due to the $-\text{CH}$ group of maleic acid [18]. The signals from δ 6.24 to δ 6.67 ppm are due to the NH_3 protons observed as doublets of doublet.

The ^{13}C NMR spectrum of LVMA (Figure 5) exhibits five signals with respect to five carbon atoms of different chemical environment. The signal at δ 169.28 ppm in LVMA is due to COOH group. The signals at δ 133.86 and at δ 130.48 ppm are due to the carbons at either end of the C–C double bond of the LVMA crystal. The chemical shift values correspond to ^1H NMR of LVMA with assignments is compared with L-Valine (LV), L-Valine succinate (LVS) [14] as given in Table. 3.

Second harmonic generation

Kurtz and Perry [19] test was performed to estimate the SHG efficiency of the powdered LVMA 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 having been monochromated (monochromator-model Triax-550). The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 3052B). The input laser energy incident on the powdered sample was 3.4 mJ. Powder SHG efficiency obtained for LVMA is about ~ 9.0 times that of potassium dihydrogen orthophosphate (KDP).

Table 3 The chemical shifts in ^1H NMR spectrum of LVMA

Chemical shifts (ppm)			Group identification	Assignments
L-Valine (LV)[14]	L-Valine succinate (LVS) [14]	Present work		
0.83	0.84	0.84 0.85 0.86 0.87 0.89	—CH ₃	Multiplet
3.45	3.48	3.74 3.78	—CH—	Doublet
		4.71 4.74	—CH—	Doublet
4.69	4.69	4.78	D ₂ O	Singlet
		5.94 5.98	—CH ₂ —	Doublet
		6.24 6.25	—NH ₃ —	Doublets of Doublets
		6.26 6.27		

Conclusion

Transparent crystals of L-Valine maleate were grown using slow evaporation method from saturated solution. A grown crystal was characterized by X-ray diffraction and was confirmed that the LVMA crystal belongs to monoclinic system. The UV-vis-NIR spectral studies confirm that the grown crystals have wider transparency range in the visible and UV spectral regions and the LVMA crystals have lower cut-off at 390 nm. The good transparency shows that LVMA crystal can be used for nonlinear optical applications. The modes of vibration of the molecules and the presence of functional groups were identified using FT-IR technique. The chemical structure of the grown crystals was established by ¹H and ¹³C NMR techniques. Powder SHG efficiency of LVMA estimated is about ~9.0 times that of potassium dihydrogen orthophosphate.

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References

- [1] Moitra S, Seth S.K, and Kar T, J. of Cryst.Growth 2010, 312, 1977.
- [2] Gonsago C.A, Albert H.M, Malliga P, Pragaam A.J.A, J. of Thermal Analysis and Calorimetry 2012,107, 1231.
- [3] Babu G.A, Ramasamy P, Current Applied Physics 2010, 10, 214.
- [4] Vimalan M, Kumar T.R, Tamilselvan S, Sagayaraj P, Mahadevan C. K, Physica B 2010, 405, 3907.
- [5] Dhanuskodi S., Manikandan S., Cryst. Res.Technol. 2004, 39, 586.
- [6] Razzetti C, Ardoino M, Zanotti L, Zha M, Parorici C, Cryst. Res. Technol.2002, 37, 456.
- [7] Kandasamy A., Mohan R., Lydia Caroline M., Vasudevan S., Cryst. Res. Technol., 2008, 43,186.

- [8] Misoguti L, Varela A.T, Nunes F.D, Bagnato V.S, Melo F.E.A, Mendes Filho J, Zilio S.C, Opt. Mater. 1996, 6, 147.
- [9] Ramesh Kumar G, Gokul Raj S, Mohan R, Jayavel R, Cryst. Growth and Des. 2006, 6, 1308.
- [10] Ramesh Kumar G, Gokul Raj S, Mohan R, Jayavel R, J. Cryst. Growth 2005, 283, 193.
- [11] Petrosyan H.A, Karapetyan H.A, Antipin M.Yu, Petrosyan A.M, J. Cryst. Growth 2005, 275, e1919.
- [12] Torii K, Iitaka Y, Acta Cryst. 1976, 26, 1317.
- [13] Natarajan S, Britto S.A.M, Ramachandran E, Cryst. Growth and Des. 2006, 6, 137.
- [14] Raja C.R, Joseph A.A, Spectrochim. Acta part A 2009, 74, 825.
- [15] Nagamoto K, "IR Spectra of Inorganic and Coordination compounds" (second edition, Wiley & Sons, New York, 1978
- [16] Sajjan D, Binoy J, Pradeep B, Krishna K.V, Kartha V.B, Joe I.H, Jayakumar V.S, Spectrochim. Acta part 2004, A 60, 173.
- [17] Rao C.N.R, "Ultraviolet and visible Spectroscopy of organic compound", Prentice Hall Pvt. Ltd., New Delhi 1984, 60-64.
- [18] Brice P.Y., "Organic Chemistry," Pearson *Edition* (Singapore), *New Delhi*, 2002.
- [19] Kurtz S. K, Perry T.T, J. Appl. Phys. 39 (1968) 3798.

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