

## Studies on Nucleation, Growth and Characterization of Nonlinear optical crystal-L-valine formamide

S. Radhakrishnan<sup>1\*</sup>, D. Jayaraman<sup>1</sup>, Kalaivani<sup>2</sup>

<sup>1</sup>Department of Physics, Dr. M.G.R Educational and Research Institute University, Chennai-95.

<sup>2</sup>Department of Physics, Loyola College, Chennai.

**Abstract:** Single crystals of organic material L-valine formamide were grown by solution growth technique. The Nucleation kinetics was discussed to optimize the growth condition for obtaining better quality crystals. The grown crystal was then subjected to XRD study, UV-vis-NIR and FT-IR spectroscopy and NLO study. The Thermal properties were also analyzed using Thermo Gravimetric Analysis. XRD study confirms that the crystal belongs to monoclinic system with noncentro-symmetric space group  $P2_1$ . Finally, the SHG efficiency was evaluated to confirm the NLO behavior of the behavior.

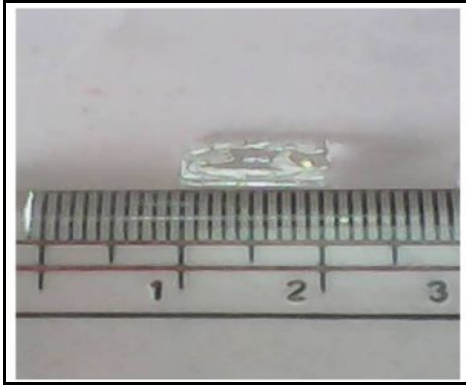
**Keywords:** Solution growth, Nucleation Kinetics, XRD study, FT-IR spectral study, Thermo Gravimetric Analysis, NLO material.

### 1. Introduction

The field of nonlinear optics has developed considerable amount of interest among the researchers to synthesis new nonlinear optical materials due to their potential applications in the areas of optical switching, optical data storage for the developing technology in telecommunication and signal processing [1-3]. L-valine belongs to amino acid group. When it is combined with other organic or inorganic compounds, the new compound formed will possess high optical nonlinearity and chemical flexibility. In the present investigation, L-valine formamide crystal (LVF) was first grown using solution growth technique. The growth condition was optimized using classical nucleation theory. The grown crystal was then characterized using XRD, UV-vis-NIR and FTIR spectroscopy and NLO study to ascertain the structure, transmission range, functional groups present in the compound and nonlinear optical property of the material. The Thermal Gravimetric Analysis was also carried out to analyse thermal stability and phase transition. Finally, NLO property was tested and SHG efficiency of the material was measured using Kurtz and Perry powder technique.

### 2. Experimental

Single crystals of LVF were grown using the starting materials L-valine and Formamide dissolved in double distilled water with stoichiometric ratio 1:1. The solution was continuously stirred with magnetic stirrer to ensure homogeneity of the solution. The solution was filtered and covered with a perforated lid. The solution was allowed to evaporate gradually and isothermally. This led to super-saturation resulting in the formation of tiny crystals of LVF with dimensions of 11 X 6 X 5 mm<sup>3</sup>. The photograph of the as-grown crystal is shown in Fig.1.



**Fig.1 Photograph of as- grown LVF crystal**

### 3. Nucleation Kinetics

A crystal nucleus of LVF is formed in the mother solution due to supersaturation achieved during slow evaporation. The change in Gibbs free energy ( $\Delta G$ ) due to phase change is written as [4],

$$\Delta G = 4\pi r^2 \sigma_0 + \frac{4}{3} \pi r^3 \Delta G_v$$

where  $\sigma_0$  is the interfacial or surface energy per unit area and  $\Delta G_v$  is the volume free energy change per unit volume which is a negative quantity. At the critical stage, the condition  $d(\Delta G)/dr = 0$  is applied to obtain the radius of the critical nucleus ( $r^*$ ), critical Gibbs free energy change ( $\Delta G^*$ ) and nucleation rate  $J$ . The expressions for nucleation parameters are thus obtained as

$$r^* = \frac{-2\sigma_0}{\Delta G_v}$$

$$\Delta G^* = \frac{16\pi\sigma_0^3}{3\Delta G_v^2} \quad \text{and}$$

$$j = A \exp\left(\frac{-\Delta G^*}{kT}\right)$$

where  $A$  is the pre-exponential factor and it is found to be  $10^{30}$ .

The nucleation parameters have been calculated for the LVF crystal at different super-saturations at room temperature and are presented in Table 1. The super-saturation for which nucleation rate  $J=1$  is called critical supersaturation ( $S_c$ ). The predicted critical supersaturation was found to be 3.037 at room temperature from the plot of  $\ln J$  versus super-saturation  $S$  (Fig.2). The theoretical prediction was tested at the time of harvesting the crystal at room temperature and the super-saturation was measured as 3.00. Hence the crystal should be grown just within critical super-saturation 3.037 to obtain good quality crystal. In the present investigation the supersaturation measured (3.00) is found to be below the theoretically predicted value (3.037).

**Table 1. Nucleation Parameters of LVF**

S	$-\Delta G_v \times 10^7 \text{ J/m}^3$	$r^* \text{ nm}$	$(-\Delta G^*)/KT$	J (nuclei/cm <sup>3</sup> /sec)
2.96	20.456	1.15	72.387	0.0365
2.98	20.674	1.904	71.497	0.0895
3.0	20.801	1.892	70.629	0.211
3.02	20.930	1.880	69.956	0.507
3.04	21.055	1.869	68.929	1.159
3.06	21.179	1.858	68.123	2.596
3.08	21.303	1.847	67.337	5.7
3.10	21.421	1.837	66.594	11.98
3.12	21.543	1.827	65.843	25.57
3.14	21.664	1.817	65.11	52.85

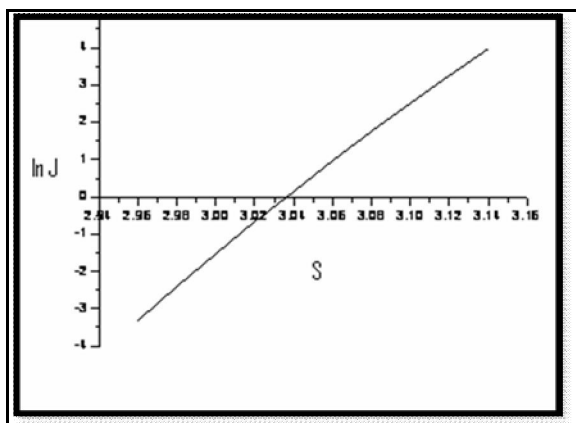


Fig. 2 A plot of  $\ln J$  vs.  $S$

## 4. Results and Discussion

### 4.1 Single Crystal XRD analysis

Single crystal XRD was studied for the grown crystal using EnrafNonius CAD 4 single crystal diffractometer coupled with computer program. The calculated unit cell parameters are found to be  $a=9.75\text{\AA}$ ,  $b=5.32\text{\AA}$  and  $c=12.09\text{\AA}$ ;  $\alpha=\gamma=90^\circ$ ,  $\beta=90.62^\circ$  and volume  $V=627 (\text{\AA})^3$ . From the lattice parameters value, it is concluded that the grown crystal is monoclinic with space group  $P2_1$ .

### 4.2 UV-vis-NIR optical absorption study

Fig.3 shows UV-vis-NIR optical absorption spectrum of LVF recorded in the wavelength range of 200–1100 nm. The material shows transparent nature from 260 nm onwards. It is observed that the material can readily transmit the laser beam of wavelength 1064 nm in the infrared region for analyzing the NLO activity of the crystal.

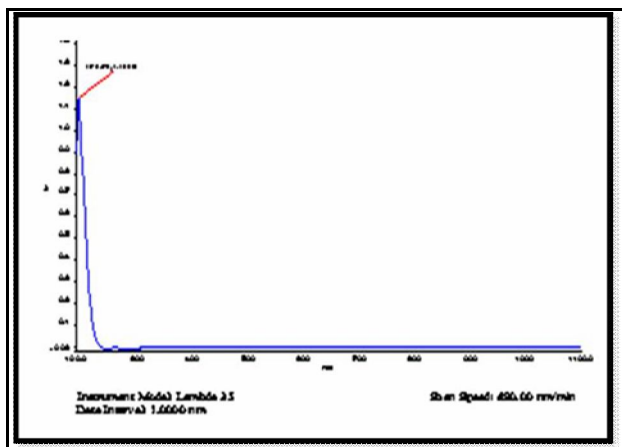
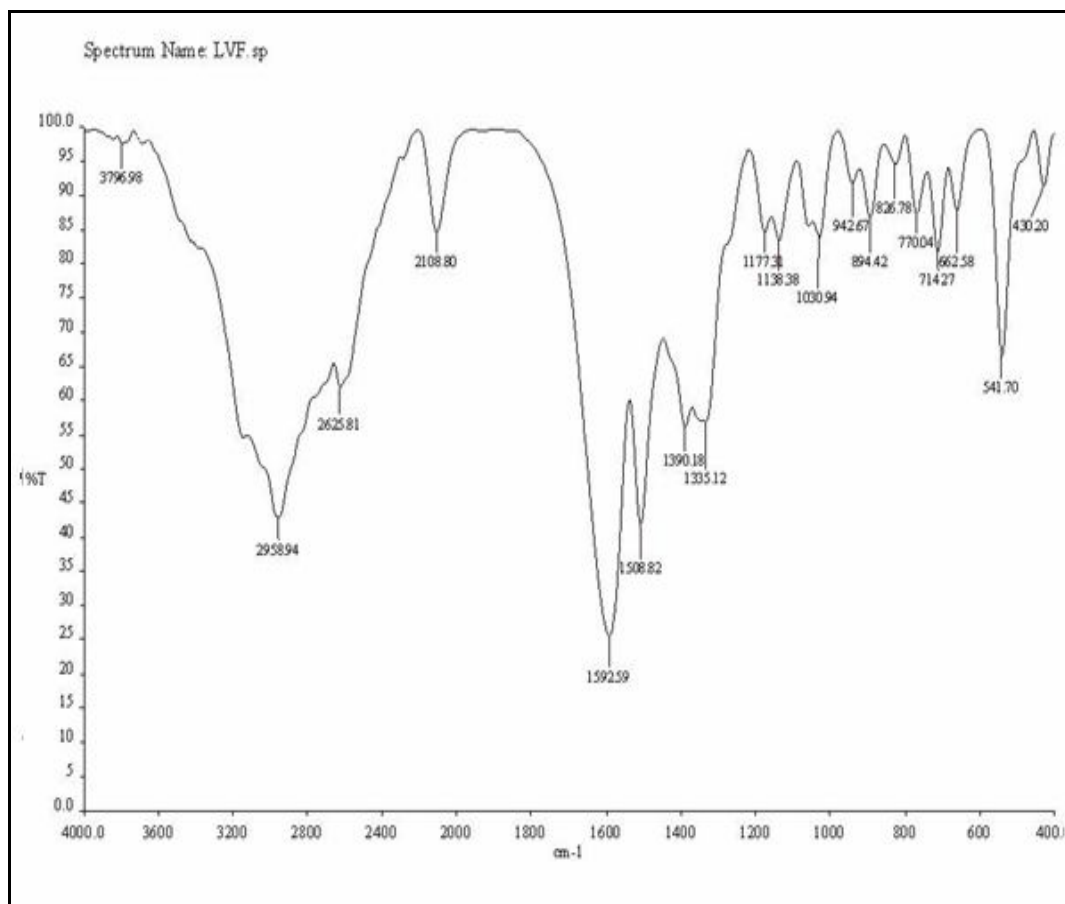


Fig.3 UV-vis-NIR optical absorption spectrum

### 4.3 FTIR spectral study

FTIR spectrum of the grown crystal recorded in the range  $4000-400\text{ cm}^{-1}$  is shown in Fig.4. The peak at  $2958\text{ cm}^{-1}$  indicates  $\text{CH}_3$  asymmetric stretching. The peaks corresponding to  $2625\text{ cm}^{-1}$  and  $2108\text{ cm}^{-1}$  are due to N-H---O valence stretching combination and O-H---O stretching respectively [5].  $\text{COO}^-$  symmetric stretching occurs at  $1390\text{ cm}^{-1}$ .  $\text{NH}_3^+$  degenerative deformation,  $\text{NH}_3^+$  symmetric deformation and  $\text{NH}_3^+$  asymmetric deformation are observed corresponding to the peaks  $1592\text{ cm}^{-1}$ ,  $1508\text{ cm}^{-1}$  and  $1335\text{ cm}^{-1}$  respectively. C-C stretching is due to the peaks observed at  $1177\text{ cm}^{-1}$ ,  $1031\text{ cm}^{-1}$  and  $894\text{ cm}^{-1}$ . The peaks due to  $714\text{ cm}^{-1}$  and

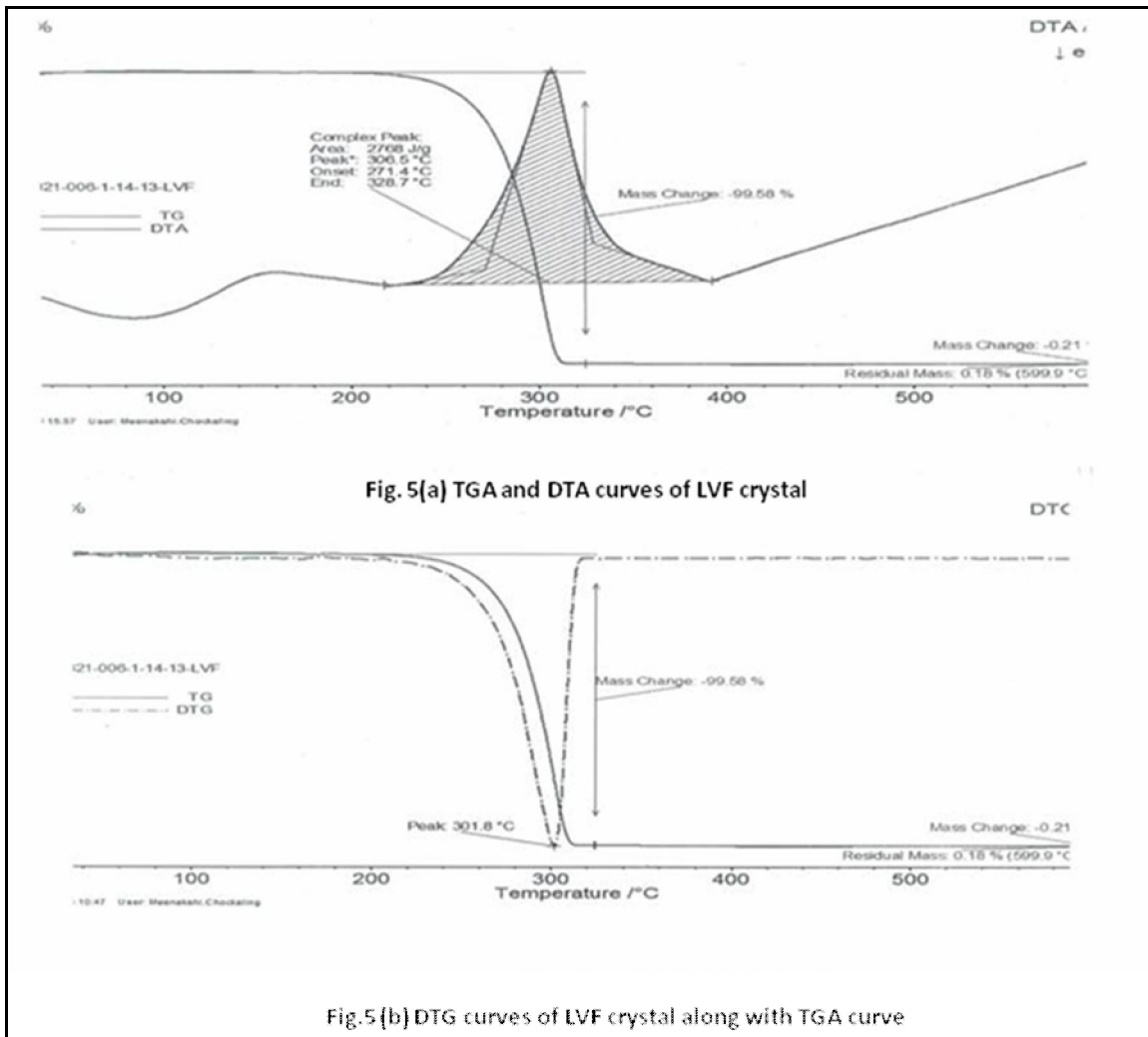
663  $\text{cm}^{-1}$  show C-H out of plane bending. The peak corresponding to 542  $\text{cm}^{-1}$  is due to C-CO deformation [6, 7]. Hence, FTIR spectrum clearly confirms the functional groups present in the grown crystal.



**Fig.4 FTIR spectrum of the grown crystal**

#### 4.4 Thermal Analysis

To analyse thermal stability, melting point and phase transition of LVF, the differential thermal analysis and differential scanning calorimetric studies were carried out in the temperature range 20-600°C at a heating rate 25°C/min. Fig.5 (a) shows the recorded TGA and DTA curve.



**Fig.5 (b) DTG curves of LVF crystal along with TGA curve**

The TGA curve in Fig.5 (a) shows that the material has very good thermal stability up to 271°C since there is no decomposition of the material in the range 20-271°C. The weight loss occurs in the temperature range 271.4 to 328.7°C and mass change is 99.58 %. There is no phase transition till it melts. The complete decomposition process is confirmed due to corresponding endothermic peak of DTA curve at 306.5°C. This is also supported by exothermic peak of DTG curve shown in Fig.5 (b) at 301.8°C. The small peaks of DTA curve before the complete decomposition process may be due to evaporation of water molecules and some vapours.

#### 4.5 NLO study

The grown crystal LVF is found to be non-centrosymmetric space group from XRD study. Since the non-centrosymmetric crystals lack inversion symmetry,  $\chi_2 \neq 0$ , the grown material LVF is capable of emitting second harmonic light. Second harmonic generation of the grown crystal was tested experimentally using Kurtz and Perry powder technique [8]. A high intense laser beam of wavelength 1064 nm was allowed to illuminate the crystal LVF with a pulse width of 8ns and power 4.3 mJ/pulse. The emission of green radiation of wavelength 532 nm from the sample confirms that the material exhibits nonlinear optical property. The output radiation from the crystal was converted in to electrical pulses using a photomultiplier tube. The output power was measured as 15.8 mV and compared with that (7.2mV) of KDP. Hence, the grown crystal LVF possesses SHG efficiency more than double that of KDP.

## 5. Conclusion

Good quality LVF single crystals were grown by slow evaporation technique. Single crystal XRD analysis has confirmed that the grown crystal belongs to monoclinic system with space group  $P2_1$ . The nucleation kinetics of LVF predicts the maximum limit critical supersaturation as 3.037 to obtain good quality crystal. UV-vis-NIR absorption study confirms the lower cut off wavelength at 260nm. FTIR spectral study reveals the functional groups present in the grown crystal. Thermogravimetric analysis shows that the grown crystal is thermally stable up to 271.4°C. The efficiency of the SHG of the grown crystal has been found to be more than double that of standard material KDP. Hence, the grown crystal LVF is one of the promising NLO materials for device fabrication in photonics and optoelectronics.

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