

CHAPTER 5

GROWTH AND CHARACTERIZATION OF SEMI ORGANIC NONLINEAR OPTICAL L-VALINE FERRIC CHLORIDE SINGLE CRYSTAL BY SOLUTION GROWTH TECHNIQUE

5.1 INTRODUCTION

In recent years, many significant achievements have been occurred in the field of nonlinear optics because of the development of new nonlinear optical (NLO) crystals of both organic and inorganic types. Single crystals made from the organic and inorganic compounds play an important role in nonlinear optical device fabrication due to their versatile property such as high second harmonic generation efficiency, fast response and high mechanical strength over the organic counterparts. Organic NLO materials exhibiting large optical nonlinearity have wide application in telecommunication, optical information processing and high optical disk data storage (Aravindan et al. 2007, Chandrasekaran et al. 2012). The materials possessing large second order nonlinear susceptibility with favorable in thermal and mechanical stability are intensively used in many device applications (Kurtz et al. 1968). Hence, there is a great demand to synthesize and grow new organic NLO materials and their single crystals. The advantages of organic materials over inorganic compounds comprise high second order nonlinear optical susceptibility through high molecular Polarizability, fast response time, lower dielectric constant and refractive



index. In the last decades, many researchers have tried to find varieties of new NLO materials for laser applications (Franken et al. 1961). The main drawback in organic nonlinear optical materials is low mechanical strength and poor physico-chemical stability. To overcome these drawbacks an attempt has been made to grow semi-organic nonlinear optical crystals (combination of organic acids and inorganic salts and metal-organic coordination compounds) which makes the material to be nonlinear and good mechanical strength (Sabari Girisun et al. 2011, Prasad & Williams 1991). Amino acid of L-Valine has been exploited for the formation of salts with inorganic acids. As a result, good NLO material such as L-Valine hydrobromide, L-Valinium succinate and L-Valine hydrochloride (Long 1995) were already reported.

In the present work the title compound was successfully synthesized by combining L-Valine and Ferric chloride in equimolar ratio. The single crystals have been grown by solution growth slow evaporation technique using water as the solvent. To have a full understanding about the structure and its NLO properties for the grown crystals single crystal XRD structure analyses, Powder XRD, FTIR, UV-Vis absorption, Thermal analyses (TG/DTA), and SHG measurements were also been carried out. Dielectric and Photo luminescence studies are also taken for the grown crystal. The following studies have been analyzed the crystal structure and the physical properties of the as grown crystal.

5.2 CRYSTAL GROWTH

L-Valine, a proteinogenic amino acid, was mixed with inorganic salt Ferric chloride in aqueous solution in the ratio of (1:1) stirred continuously for 5 h to get a uniform solution. The homogeneous solution was filtered into a clean beaker covered with a clean filter paper to avoid the mechanical disturbance. The filtered solution was allowed to grow at room temperature.



The grown crystals are bright and brown (in the web version) in colour. Good transparent crystals were obtained in a period of about 2 weeks as shown in Figure 5.1.

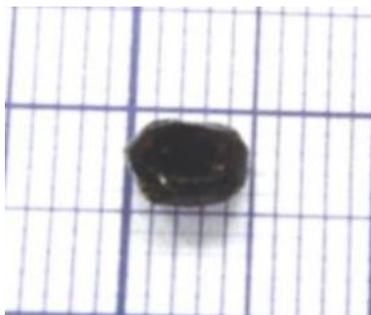


Figure 5.1 Grown LVFC Crystal

5.3 RESULTS AND DISCUSSION

5.3.1 Single Crystal X-Ray Diffraction Analysis

LVFC was subjected to Single crystal X-ray diffraction and powder X-ray diffraction studies. Single crystal X-ray diffraction analysis was carried out to determine the lattice parameters of L-Valine Ferric Chloride crystal using Enraf Nonius CAD/MACH3 single crystal diffractometer instrument. The axial length of unit cells are $a = 24.38 \text{ \AA}$, $b = 24.38 \text{ \AA}$, $c = 24.38 \text{ \AA}$, the inter axial angles are $\alpha = \beta = \gamma = 90^\circ$ and volume of the grown crystal is $V = 14485 \text{ \AA}^3$ LVFC crystallize in Cubic crystal system.

5.3.2 Powder X-Ray Diffraction

Powder X-ray diffraction study was used for the identification of crystallinity of the grown crystal. The $K\alpha$ radiations ($\lambda = 1.5418 \text{ \AA}$) from a copper target were used. The sample was scanned in the range between 10 and 100 2θ . Figure 5.2 represents the indexed powder diffractogram for the

grown crystal of L-Valine Ferric Chloride. The sharp intensity peaks found in spectra shows good crystalline nature and purity of the grown crystal.

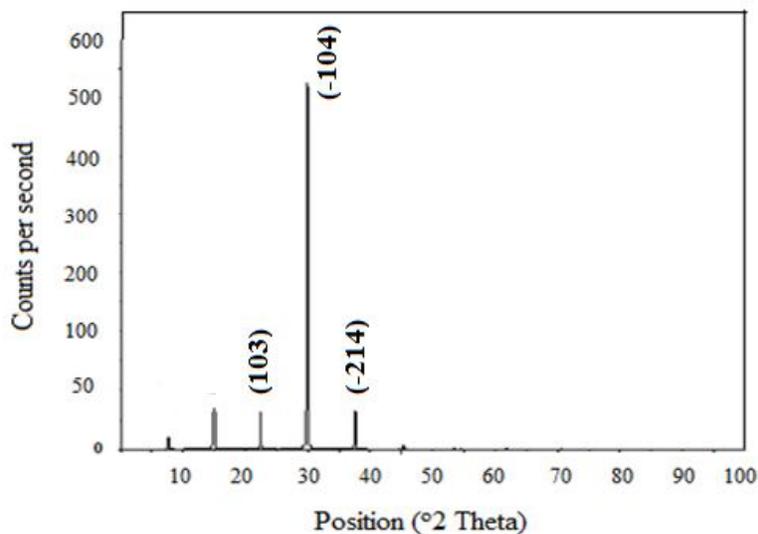


Figure5.2 Powder XRD pattern of LVFC

5.3.3 FTIR Analysis

The infrared spectral analysis was carried out to understand the chemical bonding and it provides useful information about the molecular structure of the compound. Each and every one chemical compounds have their own typical IR spectrum. The FTIR spectrum of L-Valine Ferric Chloride was recorded in the wavelength range of 450-4000 cm^{-1} using Perkin Elmer spectrometer by KBr pellet technique. The assignments are discussed in three different regions namely high wave number region (3500-2000 cm^{-1}) medium wave number region (2000 - 1000 cm^{-1}) and a low wave number region (below 1000 cm^{-1}). The resulting spectrum is shown in Figure 5.3. The peak at 3377.36 cm^{-1} is due to the presence of O-H stretch shown by a broad intense band with the strong absorption corresponding to carboxylic acids (Pal et al. 2002). The C H symmetric stretching vibration appears at 2301.08

cm^{-1} and 1442.75 cm^{-1} are assigned to asymmetric CH_2 bending vibrations. In COOH group, OH bending vibrations were observed at 1350.17 cm^{-1} . The absorption peak at 1190.08 cm^{-1} is characteristics of CH_3 rocking mode vibration in ethyl group (Petrosyan et al. 2005). Another CH_3 rocking vibration mode in ethyl group is found at 1053.13 cm^{-1} $\text{C}=\text{O}$ stretching band observed at 1735.93 cm^{-1} indicates the presence of esters, saturated aliphatic. The absorption peaks observed at 511.14 and 603.72 cm^{-1} are assigned to carboxylate groups. The presence of other functional groups is verified from their respective absorption bands and they are in good agreement with those found in some complex amino acids (Hierle et al. 1984). The mode assignments are tabulated in Table 5.1.

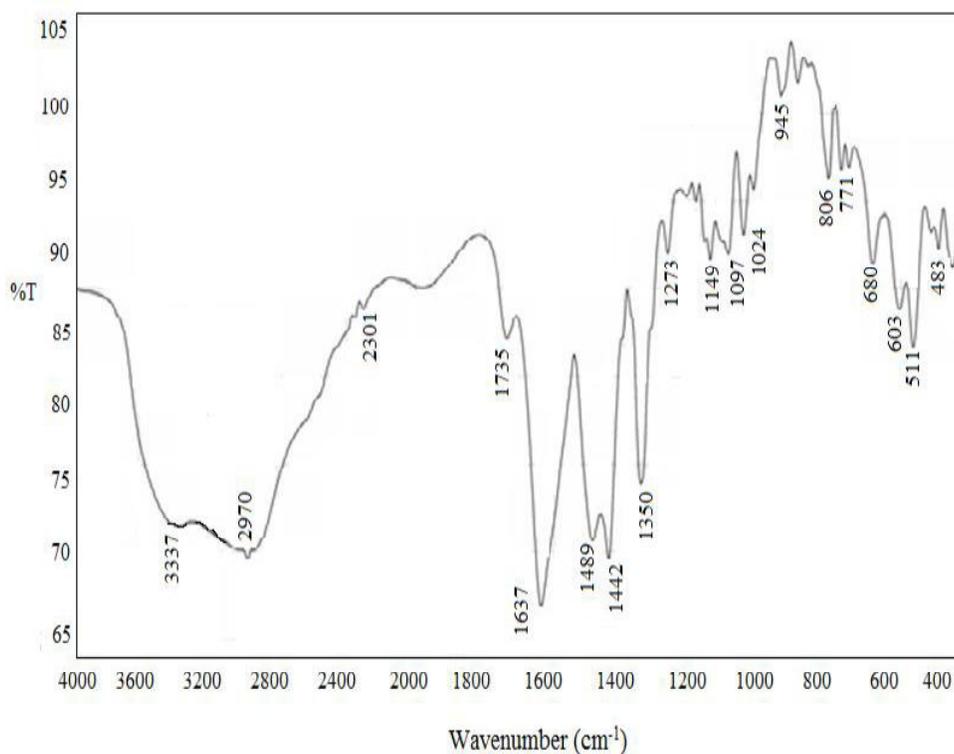


Figure 5.3 FTIR Analysis of LVFC



Table 5.1 FTIR Analysis of LVFC

FTIR cm^{-1}	Mode Assignments
3376.36	O – H Stretch
2301.08	C H Symmetric
1489.05	CH ₂ bending
1442.75	CH ₂ bending
1350.17	COOH, OH bending
1190.08	CH ₃ rocking mode in ethyl group
1735.93	Esters, saturated aliphatic
511.14	Carboxylate group

5.3.4 Thermal Studies

The thermo gravimetric analysis of L-Valine Ferric chloride crystals was carried out for the sample between 50 and 800°C at a heating rate of 20 °C min⁻¹ in nitrogen atmosphere using NETZSCH STA 409C/CD thermal analyzer and the resultant spectrum is shown in the Figure5.4. The TGA illustrates that there is no loss below 180° C illustrating the absence (Williams 1983) of water in the crystal lattice and the sharp weight loss at 270°C, without any intermediate stages, is assigned as melting point of the crystal (Kurtz et al. 1968).

DTA studies also reveal that above 270° C, the material begins to attain an endothermic transition and starts to decompose at 270°C. The DTA thermo gram confirms that the endothermic peaks coincides with that of TGA, thus confirms the thermal stability of the crystal. The sharpness of this peak shows the good degree of crystallinity and purity of the sample (Esthaku peter &Ramaswamy 2010). Thus from the thermal studies, the crystal can retain its



texture up to 270° C. The sharpness of this peak shows the good degree of crystallinity and purity of the sample (Chithambaram et al. 2012). Thus from the thermal studies, the crystal can retain its texture up to 270°C.

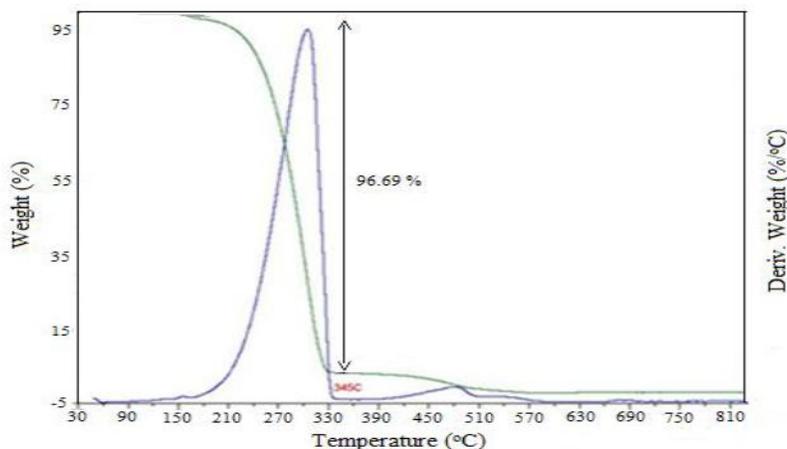


Figure 5.4 TG/DTA curve of LVFC

5.3.5 Linear Optical Property

The crystal LVFC sample is dissolved in water to measure the absorption and transmission spectrum shown in Figure 5.5 using LAMBDA-35 UV-Vis spectrometer 190-1100 nm. In the UV Vis spectrometer the lower cut off wavelength as recorded from the absorption spectrum is 295 nm. From the graph it is evident that LVFC crystal has UV cut-off below 300 nm, which is sufficiently low for SHG application. The crystal has very low absorption in the entire visible and NIR region. From 400 to 600 nm the absorption is absent it shows the material exhibiting NLO property (Sangwal&Klos 2005). Using the relation

$$E_g = 1240/\lambda$$

The band gap energy was found to be 4.20 eV.



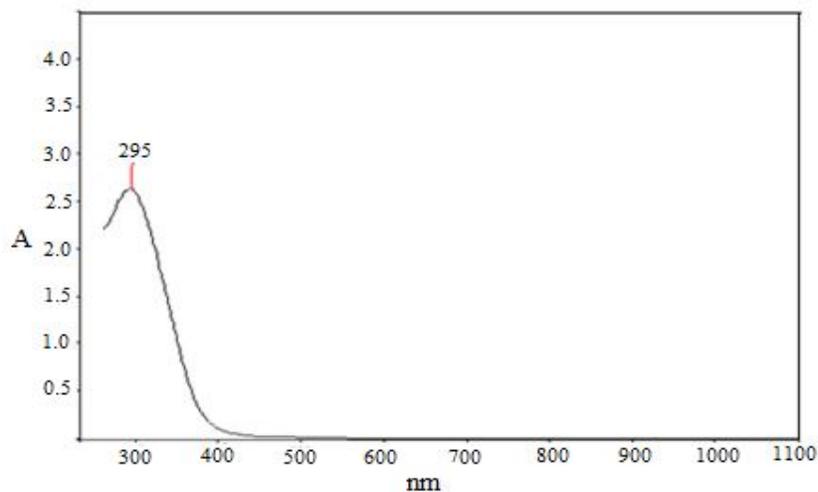


Figure 5.5 Absorption spectrum of LVFC

Transmission spectra are very important for any NLO material. The transmittance window in the visible region and IR region enables good optical transmission of the second harmonic frequencies of ND: YAG lasers.

5.3.6 Micro Hardness Analysis

To determine the mechanical behavior of the grown NLO crystal is micro hardness test. The Hardness of the crystal gives information about molecular binding, yield strength and elastic constants of the material. Mechanical strength of the grown crystal was studied using LEITZ WETZLER Vickers micro hardness tester. The grown LVFC was carried out for the load 25gms - 100 gms for 10 s and the average value of the hardness were found out using MH - 5 hardness testers. The hardness of the crystal is calculated using the following relation:

$$Hv = 1.8544 P/d^2 \text{ kg/mm}^{-2}$$

Where, Hv is the Vickers hardness number (VHN),

P is the indentation load in kg and

d is the diagonal length of the impression in mm.

1.8544 is a constant of a geometrical fraction for the diamond pyramid.

The Micro hardness value was taken as the average of the several impressions made. According to the normal Indentation Size Effect (ISE), micro hardness of crystal decreases with increasing load and in Reverse Indentation Size Effect (RISE) hardness increases with applied load. In our case, Hv increases with applied load. A graph was plotted between hardness number (Hv) and applied load P as shown in Figure 5.6. From the graph, it is found that the hardness value increases with the increase of load (Narayana Moolya et al. 2005). Higher the hardness value, greater the stress required to form dislocation, thus confirming greater crystalline perfection of the crystal. The hardness number was found to increase with the load up to 100 g and after a load of 100 g, Hv suddenly decreases as cracks developed in the material. This may be due to the release of internal stresses generated locally by indentation.

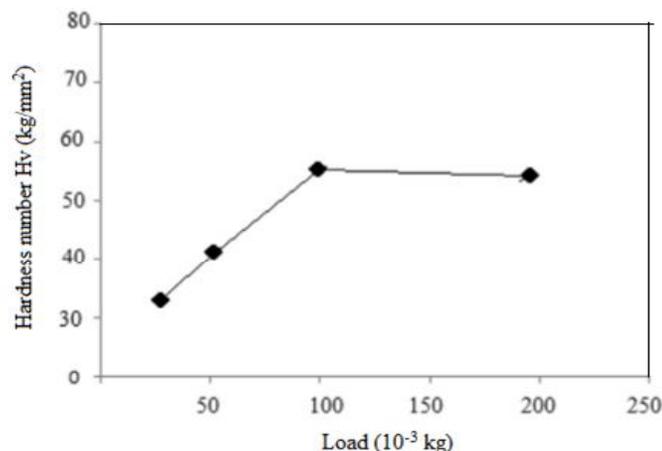


Figure 5.6 LVFC as a function of applied load



5.3.7 Photoluminescence Studies

Photoluminescence in solids is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released in general is equal or longer than that of the exciting light. This difference in wavelength is caused by a transformation of the exciting light, to a greater or lesser extent, to non-radiation vibration energy of atoms or ions (Kalsi 1996). PL emission spectrum was acquired at room temperature for a spectral resolution of 0.2 nm and excitation wavelength of 370 nm in solid phase, which shows only one high intense emission band with peak wavelength at 561 nm. The photoluminescence graph is shown in Figure 5.7. The results indicate that LVFC crystals have been green fluorescence emission. The band gap energy was calculated (Wooster 1953) using the formula

$$E_g = hc/\lambda e$$

here h, c, and e are constant, λ wavelength of fluorescence.

where, $h = 6.62 \times 10^{-34} \text{ m}^2 \text{ kg/s}$ (Planck's constant)

$c = 3 \times 10^8 \text{ ms}^{-1}$ (Velocity of light)

$e = 1.6 \times 10^{-19} \text{ J}$

The band gap energy calculated is about 2.221 eV for LVFC crystal.



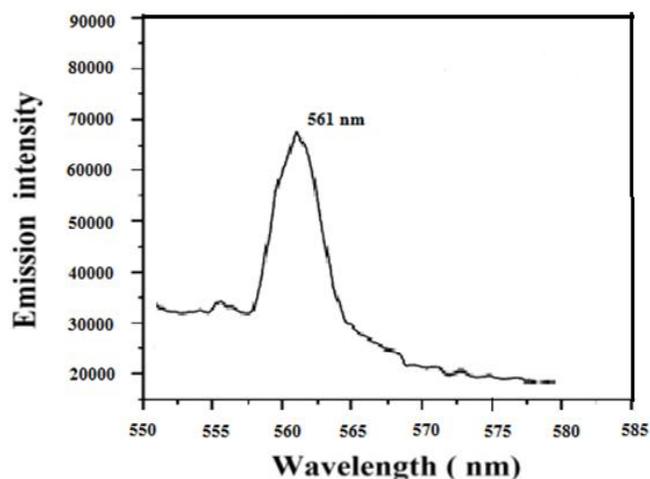


Figure5.7 Photoluminescence spectrum of LVFC

5.3.8 Kurtz Powder SHG Test

The second harmonic generation of LVFC single crystal was studied by Kurtz and Perry using Nd: YAG laser. It is important to evaluate the efficiency of NLO materials (Silverstein et al. 1991, Rao 1984). The beam of 1064 nm from Q switched Nd: YAG laser was used to test the second harmonic generation (SHG) property of LVFC crystal. The input laser beam of energy 4.2 mJ was passed through an IR detector and then directed on the microcrystalline powdered sample packed in a capillary tube. The SHG signal generated in the sample was confirmed by the emission of green radiation (532 nm) from the sample and the optical signal was collected by a Photomultiplier tube. The optical signal incident on PMT was converted into a voltage output at the CRO. The LVFC crystal shows an SHG efficiency of 1.4 times greater than that of standard NLO material like KDP crystals. The comparative efficiency is shown in Table 5.3.

Table 5.2 Comparative Efficiency of LVFC

Crystal	Input Power	Output Power	Efficiency
KDP Crystal	4.2 mJ	30 mW	1.0
LVFC Crystal	4.2 mJ	42 mW	1.4

The input laser beam was passed through an IR detector and then directed on the microcrystalline powdered sample packed in a capillary tube. The wavelength was scanned continuously with an aid of a monochromator in the spectroscopy and an intensity spectrum was recorded. The SHG signal generated in the sample was confirmed from emission of green radiation from the sample. The output beam voltage of LVFC sample was found to be 380 mV. Hence, from the above discussion the result obtained from the nonlinear optical study highlighted the SHG efficiency of the LVFC crystal was 3.65 times higher than KDP crystal.

5.3.9 Dielectric Studies

The dielectric study for the grown LVFC crystal was carried out by using HIOKI HITESTER model 3532-50 LCR meter. The techniques used for the measurement of dielectric constant are either reflection coefficients or resonant frequencies. The material is characterized to load a resonant cavity and the sample permittivity is evaluated from the shift of the resonant frequency value compared to that of the empty cavity. The dielectric constants have been calculated using the equation

$$\epsilon_r = cd/A\epsilon_0$$

where, A is the area of the sample

D is the thickness of the sample



C is the capacitance of the sample

ϵ_0 is the permittivity of free space and

ϵ_r is the dielectric constant of the sample

The low value of dielectric loss at high frequencies suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for NLO applications. The variations of the dielectric constant and dielectric loss as a function of frequency and dielectric constant are shown in Figure 5.8.

The dielectric constant increases with increase in temperature. As the frequency increases, the dielectric constant values are found to decrease exponentially and stabilize at high frequencies. The decrease in dielectric constant at high frequencies may be attributed to the contribution of the electronic, ionic, Orientational and space charge polarizations which depend strongly on frequency.

At low frequencies, all the above four contributions are active (Shankar et al. 2007). The metals are capable of decreasing the capacitance; the metal complex has a lower dielectric constant. The very high value of dielectric constant (ϵ_r) observed at low frequencies, which may be due to the presence of all the four polarizations namely; space-charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually.

The characteristic of low dielectric constant with high frequency for a given sample suggests that the sample possess optical quality with lesser defects and this parameter shows the importance for various NLO materials and their applications.



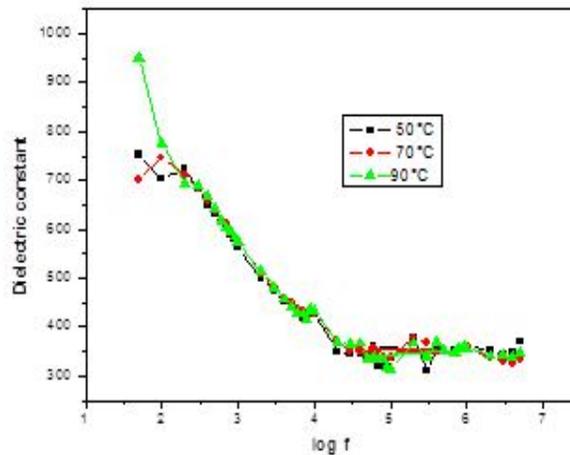


Figure 5.8 Variation of Dielectric constant Vs Frequency

5.3.10 Scanning Electron Microscope Analysis

A well-grown LVFC single crystal was selected for the investigation of surface morphology by using SEM. The minor and major magnifications of SEM were about 250 times. SEM acceleration voltage was 25,000 V and the sample was kept in a high vacuum 18,200 mm working distance and monochromatic colour mode was employed. 2 mm focusing of LVFC crystal SEM is shown in Figure 5.9. In the surface analysis of SEM picture of LVFC crystal, smooth, fine grain boundaries and few valley regions are observed.



Figure 5.9 Scanning electron Microscope picture of LVFC

5.4 CONCLUSION

Optically good quality Single crystal of L-Valine Ferric chloride has been grown successfully by slow evaporation technique using water as solvent. The well-grown crystal is characterized using various spectroscopic techniques. The crystalline natures of the material are confirmed from the sharp well-defined peaks. Transparent crystals of good quality have been harvested with in a period of 14 days. Single crystal XRD shows the cubic structure of the crystal. The presence of functional group was confirmed by FTIR analysis. Melting point of the grown crystal has been estimated by the thermal analysis. The green fluorescence emission of the crystal LVFC confirmed its fluorescence behaviour. The result of the second harmonic generation test conducted on the experimental crystal confirms the non-linear nature of the crystal. Kurtz powder technique shows that the SHG sufficiency of LVFC is nearly 3.65 times of standard KDP. In the surface analysis of SEM picture of LVFC crystal, smooth, fine grain boundaries and few valley regions are observed. Thus, the optical, NLO and thermal properties of the crystal indicate the suitability of this crystal for photonics device fabrications.

