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# Investigation on Growth and Characterization of Non – linear Optical Crystal L – Valine Magnesium Chloride

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**Abstract :** New nonlinear optical (NLO) single crystal of L –Valine magnesium chloride (LVMgCl) was grown by slow evaporation method. The grown crystal was characterized by X-ray diffractometry (XRD), UV–vis–NIR, Fourier Transform infrared (FTIR), TG - DTA and Microhardness studies. Single crystal X-ray diffraction analysis reveals that LVMgcl belongs to monoclinic crystal system. The optical absorption studies show that the crystal is transparent in the entire visible region with lower cut-off wavelength at 24enm. FTIR studies have been carried out to identify the functional groups present in the crystal. The thermal stability of LVMgCl single crystal has been analyzed by TGA/DTA studies. The grown crystals were subjected to microhardness studies, to analyse the mechanical behavior of the grown crystal. Finally, NLO test was performed by Kurtz and Perry powder technique to confirm the Second Harmonic Generation by the grown crystal.
**Keywords :** Solution growth, X – ray diffraction (XRD), Vicker's hardness test, NLO.

## Introduction

Nonlinear optical materials can find useful and interesting applications in the field of optoelectronics, photonics, laser remote sensing, colour display, holography, etc [1, 2]. L-Valine, a branched chain amino acid, has been exploited for the formation of salts with inorganic acids which exhibit enhanced physiochemical properties. Amino acids are organic materials and hence they can have very large nonlinear susceptibilities. In recent years, efforts have been made to synthesize amino acid mixed organic and inorganic complex crystal in order to improve the chemical stability, laser damage threshold, thermal, mechanical, linear and nonlinear optical properties [3].

In this present investigation, single crystals of L - Valine magnesium chloride were grown by slow evaporation method. The grown crystal was characterized by single crystal XRD, FT IR, UV–Visible, thermal and microhardness and NLO studies to analyse the structure, optical, thermal, mechanical and non – linear optical properties of the crystal.

### Synthesis and Growth of LVMgCl

The crystal L-valine magnesium chloride was synthesized by taking L –Valine and Magnesium hydroxide as starting materials with molar ratio 1:1. The calculated amount of L – Valine was dissolved in deionized water and then Magnesium hydroxide in combined solvent of deionized water and HCl. Both the solutions were mixed and stirred well for 24 hrs continuously and then filtered. The filtered solution was allowed to evaporate slowly. After a period of 45 days, the single crystals of LV MgCl with dimensions of 5 ×

20 × 2 mm3 were harvested successfully. The photograph of as-grown LVMgCl single crystal is shown in Fig. 1.

**Fig. 1 Photograph of the as grown LVMgCl single crystal**

## Result and Discussion

### Single Crystal XRD Analysis

Single crystal X – ray diffraction analysis has been carried out on the grown crystal using a computer controlled ENRAF NONIUS CAD4 X –ray diffractometer. Single crystal XRD analysis reveals that LVMgCl crystal belongs to monoclinic system. The calculated unit cell parameters are found to be a = 5.434 Å, b = 7.053 Å, c = 10.381 Å and β = 91.63° and volume V = 397.6 $Å^3$. The crystal data have been presented in Table 1.

**Table 1 Single crystal XRD data of LVMGCL**

| Lattice parameters | Single crystal XRD data |
|---|---|
| Crystal system | Monoclinic |
| a (Å) | 5.434 Å |
| b (Å) | 7.053 Å |
| c (Å) | 10.381 Å |
| α (deg) | 90° |
| β (deg) | 91.63° |
| γ (deg) | 90° |
| Volume ($Å^3$) | 397.6$Å^3$ |

### UV – vis - NIR Spectral Analysis

The optical absorption spectrum of single crystal was recorded in the wavelength range of 200 – 1100 nm. The absorption spectrum of LVMgCl crystal is shown in the Fig. 2. The spectrum indicates very low absorption in the entire visible and NIR regions. The UV cut of wavelength occurs at 248 nm. It reveals that the grown crystal is transparent in the UV visible region. Further, the transparent region indicates that the grown crystal can clearly transmit the wavelength of 1040 nm for generating SHG.

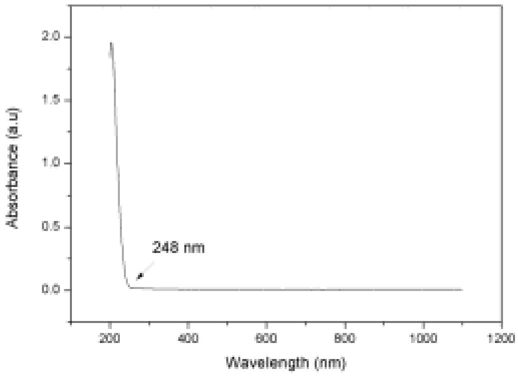


**Fig. 2 UV –vis - NIR spectrum of LVMGCL single crystal**

### FTIR Spectral Analysis

FTIR spectrum of LVMgCl crystal was recorded in the wavenumber range 500 – 4000 $cm^{-1}$ using Perkin Elmer spectrometer and KBR pellet technique. Fig. 3 shows the FTIR spectrum of the grown crystal. The peak seen around 2594 $cm^{-1}$corresponds to symmetric C-H absorption band. The peak at 1743 $cm^{-1}$is due to N-H symmetric stretching. The absorption at 629 $cm^{-1}$ corresponds to C-H in plane bending. The frequency assigned at1483 $cm^{-1}$ indicates carboxylic group O – H stretch. 1340 $cm^{-1}$ is assigned to C-C-H in plane deformation. The peak at1604 $cm^{-1}$is due to N-H-symmetric bending. 1028 $cm^{-1}$ corresponds to C-N stretching.531 $cm^{-1}$corresponds to the torsional oscillations of the $NH_3$ group.

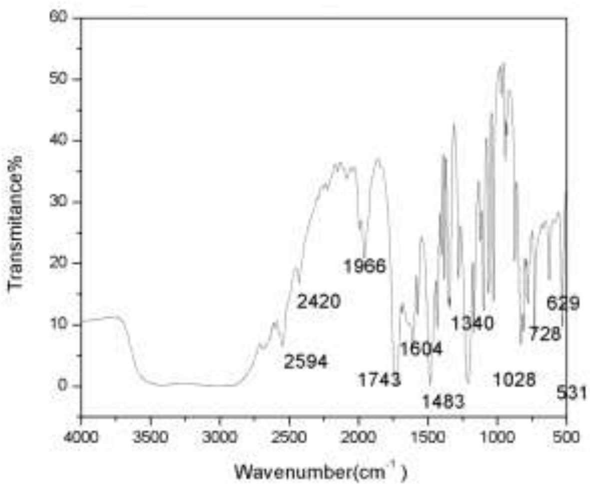


**Fig. 3 FTIR spectrum of LVMGCL**

### Thermal Analysis

To analyze the thermal stability, melting point and phase transition of L-valinemagnesium chloride (LVMgCl), the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carriedout using Perkin Elmer STA 6000. From TGA curve, it is observed that the weight loss starts at 213 °C and is maximum at 300 °C. The complete process of weight loss is also indicated due to the sharp peaks of DTA curve at 238 °C and 273 °C in the range of 213 – 300 °C. The weight loss is due to the liberation of vapours like $Cl_2$, $N_2$, $NH_3$, etc. Hence, it is predicted that the grown crystal is thermally stable up to 213 °C.

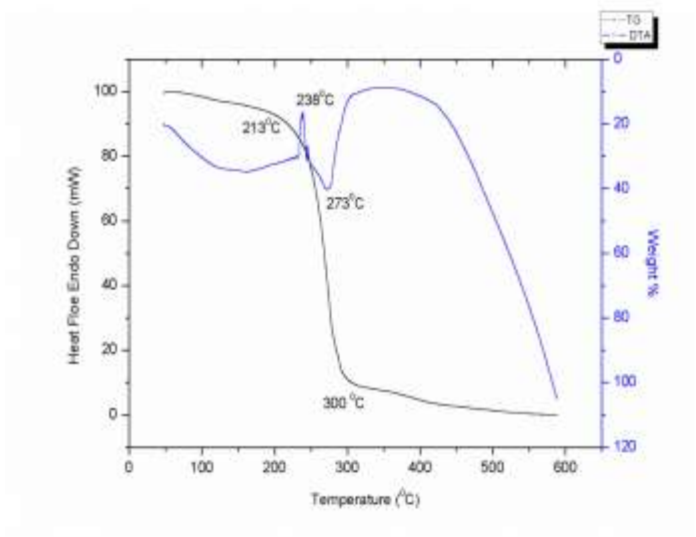


**Fig. 4 TG DTAcurve of LVMGCL**

## Microhardness Studies

Hardness is an important mechanical property. The mechanical characterization of the LVMgCl single crystal was carried out by Vickers hardness test at room temperature. Crystals free from cracks with flat and smooth surfaces were chosen for the static indentation tests. The LVMgCl crystal was placed on the platform of the microhardness tester. The applied loads are in the range of 1 - 50 g and the Vickers hardness number was calculated using the relation,

$H_v$= 1.8544 P / $d^2$ kg $mm^2$

where P is the applied load and d is the diagonal length of the impression in mm. The maximum applied load was restricted to 100 g as micro - cracks were observed at higher loads.

The relation between hardness number ($H_v$) and load (P) for LVMgCl is shown in Fig. 5. It is concluded from the graph that the Vickers hardness increases with increasing load. The work hardening coefficient (n) was calculated using the graph of log P vs log d (Fig. 6). According to onstich concept if n > 1.6, the material comes under soft material and if n < 1.6, the material comes under hard material. In the present case n = 4.112 and henceLVMgCl comes under soft material category.

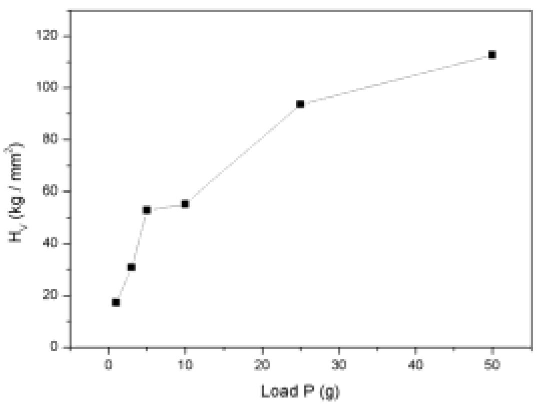


**Fig. 5 Variation of hardness number with load P**

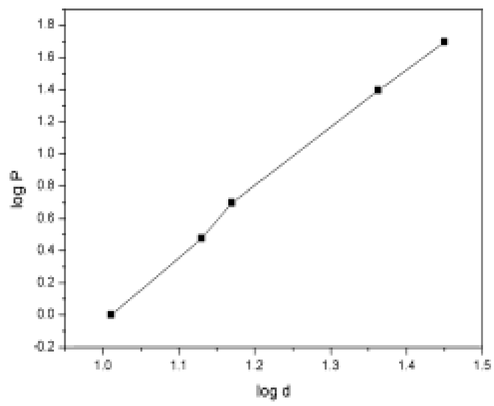


**Fig. 6 Variation of log P with log d**

**NLO Test**

The grown crystal was tested by Kurtz and Perry technique to confirm the non – linear optical (NLO) property of the grown crystal. The material was powdered and filled in a micro capillary tube of about 1.5 mm diameter. A Q- switched Nd: YAG laser source was used to illuminate the sample with a wavelength of 1064 nm and pulse width 8 ns. The emission of green radiation of wavelength 534nm confirms the second order generation by the crystal. The output was measured as 8.2 mV. The sample was replaced by KDP powder material and the output was measured as 6.5 mV for the same incident wavelength. The SHG efficiency of L – Valine Magnesium chloride is found to be 1.2 times that of KDP. It is therefore predicted that LVMgCl is one of the promising NLO materials due to better non – linear property of the grown crystal.

## Conclusion

Single crystals of L – Valine Magnesium chloride were grown successfully with dimensions of 5 × 20 × 2 $mm^3$ using slow evaporation solution growth technique. From the results of XRD analysis, it is predicted that the crystal belongs to monoclinic system with lattice parameters a = 5.434 Å, b = 7.053 Å and c = 10.381 Å. The grown crystal is found to poses wide transmission range for better SHG conversion efficiency. From the FTIR spectrum the functional groups of the grown material were identified. The thermal stability of the material was analyzed using TGA and DTA studies. The mechanical behavior of the grown crystal was discussed using Vicker's hardness test. The SHG efficiency of the grown material was measured and found to be more than that of KDP. Therefore L – Valine Magnesium chloride is one of the promising NLO materials to find applications in the area of laser technology, laser communication and data storage technology.

## References

1. MarcyH. O., WarrenL. F., WebbM. S., EbbersC. A., VelskoS. P., KennedyG. C. and CatellaG. C., Second-harmonic generation in zinc tris(thiourea) sulfate, Applied Optics,1992,Vol. 31, Issue 24,pp. 5051-5060 .
2. GambinoR. J., Bull. Mater. Res. Soc.1990, 15, 20.
3. AngeliMaryP. A., DhanuskodiS., Growth and Characterization of a New Nonlinear Optical Crystal: BisThiourea Zinc Chloride, Cryst. Res. Technol., 2001, 36, 1231.
4. VenkataramanV.,DhanrajG., WadhawanV.K., SherwoodJ.N., BhatH.L., Crystal growth and defects characterization of zinc tris (thiourea) sulfate: a novel metalorganic nonlinear optical crystal, J. Cryst. Growth, 1995, 154, 92–97.
5. MoitraS.,KarT., Growth and characterization of L-valine – a nonlinear optical crystal, Cryst. Res. Technol., 2010, 45, 70–74.
6. MaadeswaranP.,Chandrasekaran J., Synthesis, growth and characterization of L-valine cadmium chloride monohydrate – a novel semiorganic nonlinear optical crystal, Optik2011, 122, 1128–1131.
7. Moitra S., Seth S. K., Kar T., Synthesis, crystal structure, characterization and DFT studies of L-valine L-valinium hydrochloride, J. Cryst. Growth,2010, 312, 1977–1982.
8. Kirubavathi K., Selvaraju K., Valluvan R., Vijayan N., Kumararaman S., Synthesis, growth, structural, spectroscopic and optical studies of a new semiorganic nonlinear optical crystal: L-valinehydrochloride, Spectrochim.ActaA, 2008, 69, 1283–1286.
9. Ramachandran. E, Natarajan S., Synthesis of L-valine crystals, Cryst. Res Technol., 2009, 44, 641–646.
10. Dhanuskodi S., Vasantha K., X-ray diffraction, spectroscopic and thermal studies on a potential semiorganic NLO material: lithium bis-L-malato borate, Spectochim. Acta, 2005, 61, 1777–1782.
11. Moitra S., Kar .T, Second harmonic generation of a new nonlinear optical material L-valinehydrobromide, J. Cryst. Growth, 2008, 310, 4539–4543.
12. Kurtz S. K., Perry T. T., A powder technique for the evaluation of nonlinear optical materials, J. Appl. Phys., 1968, 39, 3798–3813.

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