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***Research Paper***

# Optical, Thermal and Mechanical Properties of Novel Urea L-Alanine Hydrogenchloride (U-LAH) Crystals for Laser Applications

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Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their non-linear optical (NLO) properties. To improve the optical properties of L-Alanine Hydrogenchloride (LAH), a semi-organic amino acid crystal, dopant urea has been added and its influence on the growth and properties are studied in the present work. Single crystals of urea doped L-Alanine Hydrogen chloride (U-LAH) were grown by slow evaporation technique at room temperature. The Structural analysis reveals that the grown crystals belong to orthorhombic crystallographic system. FT-IR spectral study reveals the presence of various functional groups and confirms the slight distortion of the structure of the crystal due to doping. The HR-SEM studies showed the existence of striations and visible inclusions due to the presence of dopant urea. UV spectrum shows no significant absorption in the region 255-800nm. TG/DTA shows that the grown crystals have good thermal stability. SHG efficiency of the crystals is confirmed using Q-switched Nd: YAG laser. EDAX spectrum shows the presence of the various elements present in the grown crystal. Microhardness studies reveal that the grown crystal is suitable for device fabrication. From these studies it is inferred that U-LAH crystals exhibit better mechanical and thermal stabilities with improved optical properties.

**Key Words: NLO; XRD; FT-IR; EDAX; HR-SEM; DTA; Mechanical Properties; Hydrogenchloride; Laser Applications**

## 1. Introduction

Among the nonlinear optical (NLO) materials, second harmonic generators are important because of their applications in extending the limited frequencies available from lasers. The outputs of high-peak-power laser systems are regularly shifted towards the ultraviolet (UV) by frequency conversion processes using nonlinear optical materials [1-2]. Since the first demonstration in 1961, non linear frequency conversion has been a materials limited field with practical advances largely controlled by progress in making available improved NLO materials. Optoelectronics is still in its early stages, and as applications become more widespread, non linear optical materials will grow in importance to increase the range of latest technologies. Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their non linear optical properties [3-6]. L-Alanine Hydrogenchloride (LAH) NLO crystals serve as an illustration of the success of this method. It uses harmonic conversions to produce UV suitable for many applications of lasers in the fields of remote laser induced emission spectroscopy, medicine, materials processing and nonlinear optics. To improve the optical properties of LAH, dopant urea has been added and its influence on the growth and properties are studied in the present work.

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## 2. Experimental Procedure

The urea doped L-Alanine Hydrogenchloride single crystals were synthesized, grown by slow evaporation method and characterized by optical and thermal analysis.

### *Synthesis*

A saturated solution of 0.1M urea doped LAH (U-LAH) was prepared in Millipore water and stirred well continuously for few hours using a magnetic stirrer. The solution was then filtered into a beaker and allowed to evaporate at room temperature. The crystals were harvested after a few days. The harvested crystals are found to be transparent with a little hygroscopic nature. There were no observable morphological changes in urea doped crystals are shown in Fig. 1.

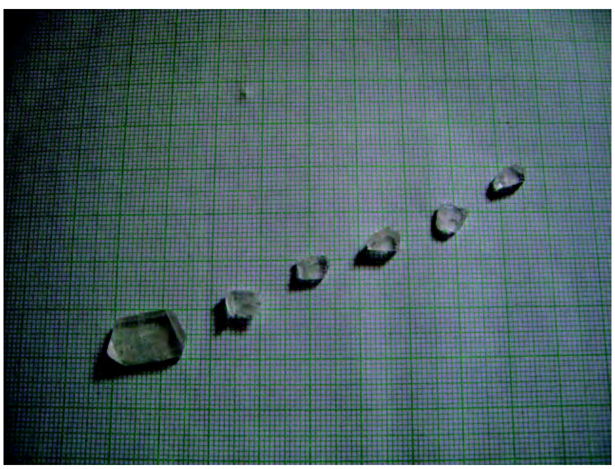

**Fig. 1: Crystals of as grown U doped LAH**

## 3. Results and Discussion

### *X-Ray Diffraction Studies*

Single crystal X-ray diffraction (XRD) analysis of urea doped LAH was carried out using ENRAF NONIUS CAD-4 diffractometer with MoKá radiation ($\lambda$ = 0.7070Å). The lattice parameters of the grown crystals are a = 6.199Å, b = 9.950 Å, c = 11.66 Å, Volume = 732.12 Å and space group $P2_1$. The slight change in lattice parameter from that of pure L-Alanine Hydrogenchloride may be attributed to the incorporation of urea in its lattice. However these values are found to match with the reported values [7].

### *FTIR Spectral Studies*

The FTIR analysis was recorded in the region 400-4000 $cm^{-1}$ using Bruker IFS 66V spectrometer to confirm the presence of functional groups in the grown crystal. The middle IR spectrum of U-LAH is shown in Fig. 2. N-H stretching frequencies of amino group are found between 3100 $cm^{-1}$ and 2600 cm for U-LAH crystal. The U-LAH compound shows absorption at 1594 $cm^{-1}$ indicating the presence of primary amino group. The characteristic absorption for the -NH group in the aromatic ring is observed at 1307 $cm^{-1}$. The broad absorption around 3081 $cm^{-1}$ indicates the co-presence of C=O stretching and O-H stretching. The broad envelope between 2112 $cm^{-1}$ and 3081 $cm^{-1}$ includes overlapping of stretching modes due to N-H and C-H. The peak at 1455 $cm^{-1}$ is due to the asymmetric stretching modes of $NH^{3+}$ and $COO^-$ respectively. The FTIR spectra and the corresponding band assignment clearly indicate that the functional groups of U-LAH are slightly altered from the pure LAH.

### *HR-SEM Analysis*

HR-SEM analysis was carried out in order to study the nature and surface features of the grown crystal using FET Quanta FEG 200 High resolution Scanning Electron Microscope. The maximum magnification possible in the equipment is 3, 00,000 times with a resolution of 3mm. The surface of the U-LAH crystal was coated with a thin film of carbon to make the sample conducting. From the Fig. 3 it is clear that the size of the grown crystal is 5 microns thick. It also shows the existence of striations and visible inclusions due to the presence of dopant urea in the crystal and temperature variations during the growth process.

### *UV-Vis-NIR Studies*

Non linear optical effects can be used for the generation of new optical frequencies, not available with existing lasers, in particular compact blue coherent light sources. Therefore an absorption spectrum is very important for any NLO material because a non linear material will be of practical use only if it has a

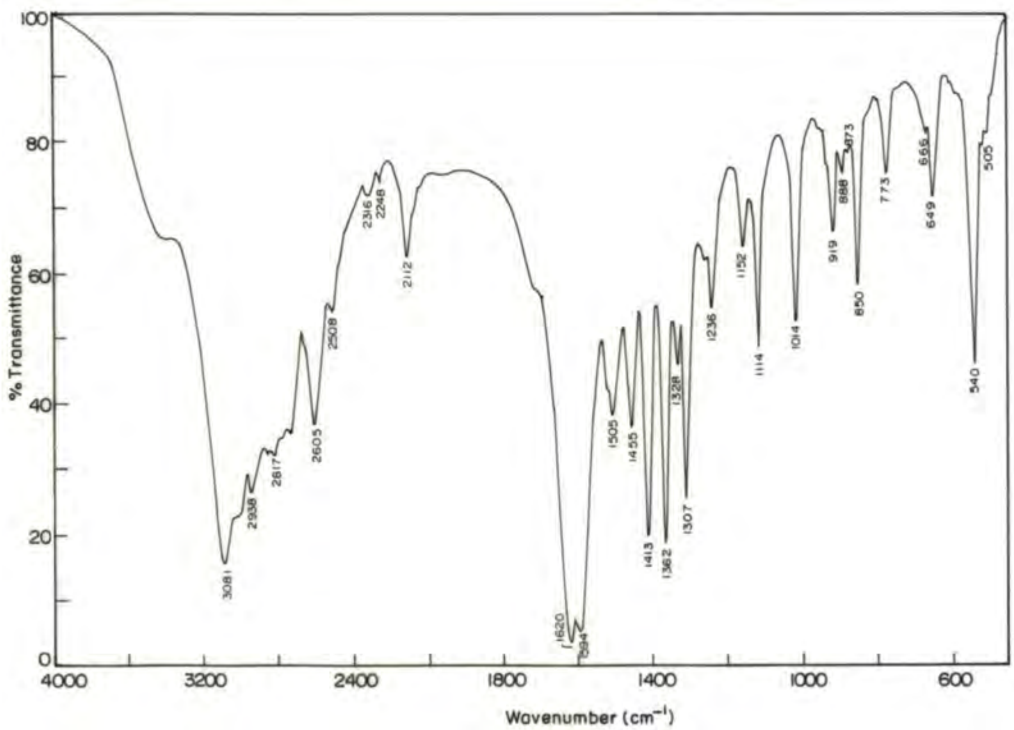


**Fig. 2: FT-IR spectral analysis of U doped LAH**

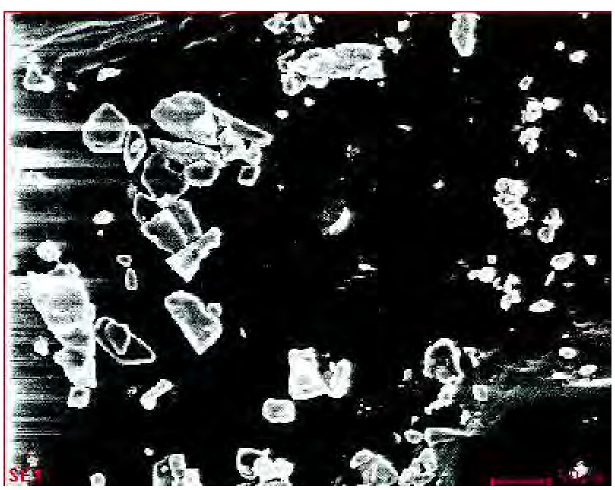

**Fig. 3: HR-SEM analysis of U doped LAH**

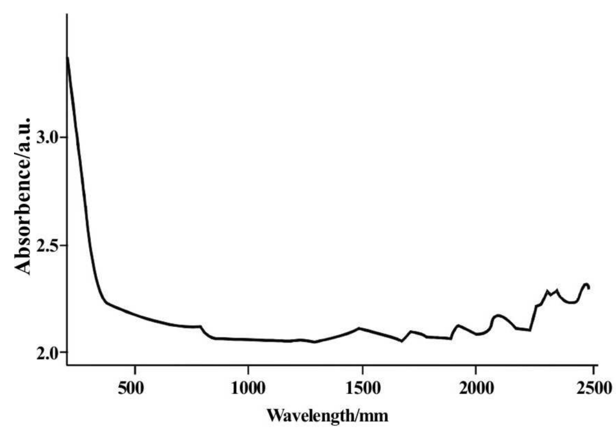


**Fig. 4: UV-Vis-NIR spectrum of U doped LAH**

wide transparency window, both in the visible and the blue regions. Optical absorption studies for the grown U-LAH crystal is carried out using Varian Carry 5E model dual beam splitter between 250nm-2000nm. Fig. 4 shows the UV-Vis-Nir spectrum of U-LAH crystal. The spectrum indicates that U-LAH is having minimum absorption in the entire visible region. It has better cut-off wavelength starting at 255nm which is an important requirement for NLO materials having nonlinear optical applications [8].

### *Thermal Study*

The thermo gravimetric analysis of U-LAH single crystals was carried out in the temperature range 30-1400°C at a heating rate of 20k/min in the nitrogen

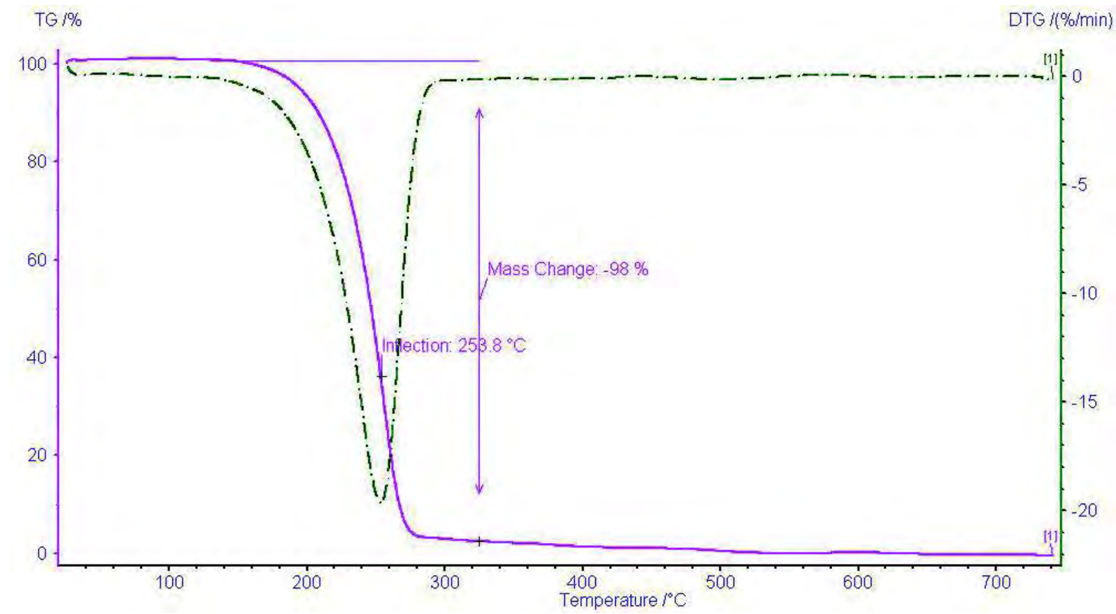


**Fig. 5: TG/DTA curve of U doped LAH**

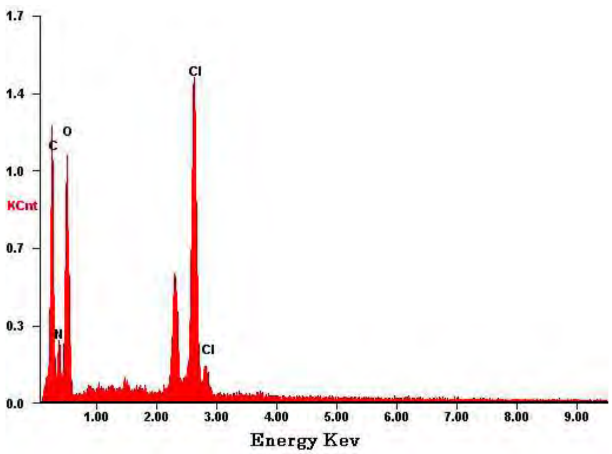


**Fig. 6: EDAX spectrum of U doped LAH**

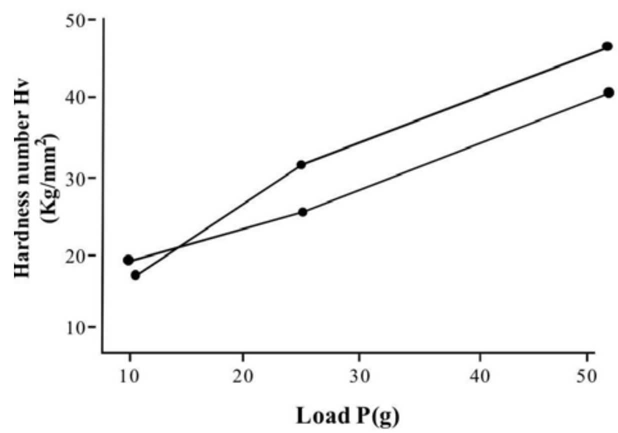


**Fig. 7: Load *vs*. hardness number**

atmosphere. The thermogram and its differential theromogravimetric trace are shown in Fig. 5. It is seen from the thermogram that there is no major weight loss between 100 and 200°C. This indicates that there is no inclusion of water in the crystal lattice, which was used as the solvent for crystallization. The TG spectrum reveals that a single major weight loss occurs at 258.8°C and it continues up to 280°C.The decomposition temperature of U-LAH at 258°C ensures the higher stability range of the crystal [9].

In the DTA spectrum an irreversible endothermic peak observed around 260°C corresponds to the decomposition temperature of the material. The sharpness of the endothermic peak shows a good degree of crystalline nature and purity of the sample. Another notable observation is that there is no phase transition till the material melts and thus enhances the temperature range for the usefulness of crystals for nonlinear applications.

### *Second Harmonic Generation*

The fundamental beam of 1064nm from Q-switched Nd:YAG laser of pulse energy 6mJ/sec with pulse width of 8NS and repetition rate 10Hz was used to test the second harmonic generation (SHG) of U-LAH crystal [10]. The emission of green radiation from the sample confirms the SHG in the crystal. The results obtained from U-LAH shows a powder SHG efficiency better than the other grown NLO amino acid family crystals.

### *EDAX Analysis*

Energy dispersive X-ray analysis (EDAX) is a micro analytical technique that uses the characteristics spectrum of X-rays emitted by the sample after excitation by high-energy electrons. This analysis is used to obtain information about the elemental composition of the grown crystals. In the present study, the urea doped L-Alanine Hydrogenchloride crystal was analyzed by INCA 200 energy dispersive X-ray micro analyzer. The EDAX spectrum of U-LAH single crystal is shown in Fig. 6. From the recorded spectrum the elements present in the grown crystal can be identified.

## 4. Microhardness Test

The good quality of the semi organic crystals is very much needed for device fabrication. In single crystals, the second harmonic generation is always lower from the more perfect sectors. The good quality crystals are needed not only with good optical performance but with good mechanical behavior. The microhardness studies were carried out on the grown crystals using Vicker's microhardness tester attached with an optical microscope. Loads of 10, 25 and 50g were used for microhardness studies. Fig. 7. shows the relation between the hardness and load. The hardness of U-LAH increases with increase of load. The cracks are formed in the crystal at 50g, which is moderately higher when compared to other semi organic crystals.

## 5. Conclusion

Single crystals of U-LAH were grown by slow evaporation technique in a period of few days. X-ray diffraction studies confirm the crystalline of the grown crystal. The presence of various functional groups and the modes of vibrations were identified by FT-IR spectroscopy. HR-SEM supports for the applicability of the crystals of high optical quality with lesser defects for NLO applications. The useful transmission extends from 250 to 1500nm which makes it valuable for those applications requiring blue/green light. Significant wider optical transparency and lower cut-off value down to 250nm makes it a promising material for NLO applications involving frequency doubling processes. From the TG/DTA studies the grown U-LAH crystals is found to be thermally stable up to 258°C. EDAX studies confirm the elemental composition of the grown crystal. The microhardness studies confirm the suitability of the grown crystal for processing and device fabrication. With these promising optical properties U-LAH chosen for our study should be a potential material for frequency conversion applications.

## References

1. Dmitriev VG, Gurzadyan GG and Nicogosyan DN *Handbook of Nonlinear Optical Crystals*, Publisher City: Springer-Verlag, New York (1999)
2. Chemla DS and Zyss J *Nonlinear Optical properties of Organic Molecules and Crystals*, New York: Academic (1987)
3. Ramajothi J and Danuskodi S Crystal growth, thermal and optical studies on a semiorganic nonlinear optical material for blue-green laser generation. *Spectrochem Acta A* (2007) **68** 1213-1219
4. Alosious Gonsago C, Helen Merina Albert, P.Malliga and Joseph Arul Pragasam A Crystallisation, spectral, and thermal characterisationof L-histidine methyl ester dihydrochloride (LHMED), *J Therm Anal Calorim* DOI 10.1007/s10973-011-1719-y, in press
5. Kandasamy A, Siddeswaran R, Murugakoothan P, Suresh Kumar P and Mohan R Synthesis, growth and characterization of L-proline cadmium chloride monohydrate (L-PCCM) crystals- a new nonlinear optical material. *Cryst Growth Des* **7** (2007) 183-186

6. Dhanuskodi S and Vasantha K Structural, thermal and optical characterization of a NLO material:L- alaninium oxalate *J Cryst Res Technol* **39** (2004) 259

7. Yamada K, Sato A, Shimizu T, Yamazaki T and Yokoyama S L-Alaninehydrochloride monohydrate *Acta Cryst* **E64** (2008)

8. Vijayan N, Rajasekaran S, Bhagavannarayana G, Ramesh Babu R, Gopalakrishnan R, Palanichamy M and Ramasamy P Growth and Characterization of Nonlinear Optical Amino Acid Single Crystal: *L Alanine Cryst Growth Des* **6**(11) (2006) 2441-2445

9. Meenakshisundaram SP, Parthiban R, Kalavathy G, Madhurambal G, Bhagavannarayana G and Mojumdar SC Thermal and optical properties of ZTS single crystals in the presence of 1,10-phenanthroline (Phen) *J Therm Anal Calorim* **100** (2010) 831

10. Kurtz K and Perry TT A powdertechnique for the evaluation of non-linear optical materials. *J Appl Phys* **39** (1968) 3798.