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Study of Urea L-Threonine A Mixed Novel Non Linear Optical Single Crystal for Laser Applications

KEYWORDS: slow evaporation, non linear optical, single crystal XRD, characterization

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ABSTRACT *A novel UreaL-threonine a mixed non linear optical crystal was grown by slow evaporation technique at room temperature. The grown crystal was subjected to characterization studies to testify the material for optoelectronic laser applications. Single crystal XRD analysis, UV-Vis-NIR spectrum, FTIR analysis, second harmonic generation efficiency, Vicker's microhardness test, HRSEM analysis and photoconductivity study was carried out to show the grown crystal is an excellent candidate for non linear optical applications.*

Introduction

The advancement in science and technology have paved the way for search of novel good quality NLO materials that can generate large second order optical nonlinearities, significant for potential applications including telecommunication, optical computing, optical data storage and processing[1]. These applications are based on various properties of materials such as transparency, dielectric constant, refractive index, mechanical capability, thermal, photochemical and chemical stabilities [2]. In many of the organic NLO materials there is a solid framework of conjugated π electrons along with weak Van der Waals and hydrogen bonds which are responsible for most of their NLO properties. Organic NLO materials are superior to their inorganic counterparts due to high conversion efficiency for second harmonic generation and good transparency in the visible region, high resistance to optical damage and so on. Among numerous organic NLO materials, amino acids become the interesting alternative as they contain a proton acceptor carboxyl (−COO) and the proton donor ($-NH_2$). Besides, compounds composed of α-amino acids present some particular features such as molecular chirality, wide transparency range within the visible and UV regions and zwitterionic nature of the molecule favours crystal hardness [3]. L-threonine single crystal has a proven optical non linearity [4], Urea being a potential non linear candidate is combined with L-threonine in equimolar ratio which yielded a Urea L-threonine (ULT) mixed crystal with monoclinic crystal structure. Second harmonic generation efficiency of the grown crystal is of commendable value, optical, mechanical and photoconducting properties of the grown crystal is reported.

Experimental
Synthesis and Crystal Growth

A saturated solution of AR grade L-threonine and Urea is taken in equimolar ratio with water as solvent. The saturated solution was magnetically stirred for three hours to obtain a homogenous solution, this was microfiltered into a beaker. The beaker was tightly sealed with few perforations on it for the solution to evaporate slowly at room temperature. Good optical quality crystals were harvested after 30 days and the photograph of as grown crystal is shown in Fig.1. The crystals were recrystallised several times to enhance purity. The Molecular formula of the grown crystal is given as:

$HO_2CCH(NH_2)CH(OH)CH_3 + \underline{CO(NH_2)_2} \rightarrow O_2CCH(NH_3)CH(OH)CH_3.\underline{CO(NH_2)_2}$

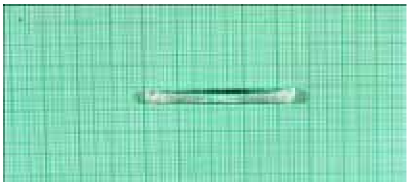

Fig.1 Photograph of as grown urea L-threonine mixed crystal

Results and Discussion of Characterisation Studies
Single crystal XRD Analysis

Single crystal XRD data was collected by ENRAF NONIUS CAD4 single crystal X-ray diffractometer with MoKα (λ=0.71073 Å) radiation. The X-ray diffraction intensity data for a perfect crystal were collected in the 2θ range from 3.35 to 27.4° on a Bruker APEX2 CCD diffractometer with a Mo Kα radiation (λ = 0.71073 Å) at 93K. This study reveals that the grown crystal belongs to monoclinic system of urea with the space group P_{21} and possess the lattice constants of L-threonine[4].

Table 1. Cell parameters of Urea L-threonine mixed crystal

Cell parameters Å	Urea L-threonine mixed crystal	L- Threonine
a	7.75	7.738
b	5.15	5.14
c	13.65	13.61
Crystal Structure	Monoclinic	Orthorhombic
Space Group	P_{21}	P_{212121}

UV-VIS-NIR Spectrum

The optical absorption spectral analysis of the grown crystal was carried out between 200 nm to 2000 nm using Varian Cary 5E spectrophotometer. The recorded spectrum is as shown in Fig.2. The crystal is transparent in the entire visible region with the lower cut-off wavelength at around 220 nm. The optical properties of NLO materials can provide some useful information of the nature of their components and the transparency in the entire visible range makes the reported crystal applicable for NLO devices.

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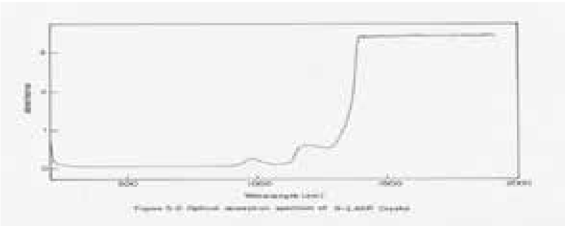

Fig. 2 Optical Absorption Spectrum of Urea L-threonine mixed crystal

Second Harmonic Generation measurements

The second harmonic generation efficiency of the grown crystal was carried out using the Kurtz powder technique [5]. The sample is irradiated at 1064 nm Nd:YAG pulsed laser. The generation of the second harmonic was confirmed by the emission of green light from the powdered sample. The SHG conversion efficiency of the reported crystal is calculated to be 0.52 times of KDP which is more efficient than pure l-threonine crystal.

Fourier transform infrared spectral analysis

The FTIR spectrum, Fig.3 was recorded using BRUKER IFS 66V FTIR spectrometer with KBr pellet technique for the range 4000–400 cm^{-1} to determine the functional groups in the ULT mixed crystal. The IR band positions and their assignments are given in Table 2. During the formation of the salt, NH_2 group in the free acid is converted into NH_3^+ ions. C-H stretching can be observed at 2905 cm^{-1} which is shifted to the higher frequency region and the degenerative deformation of NH_3^+ and torsional vibration of NH_3^+ can observed at 2050 cm^{-1}. The peak at 1615 cm^{-1} shows the asymmetric stretching mode of CO_2^- and the peak at 932 cm^{-1} exhibits the C-C stretching mode of L-threonine in the crystal formed, NH_2 wagging can be noticed at 870 cm^{-1}, 702 cm^{-1} can be assigned to the in plane deformation of CO_2^-, C-C=O in plane vibration appears at 542 cm^{-1} and the peak at 489 cm^{-1} shows the asymmetric stretching of N-C-N of urea. The FTIR vibrational spectrum establishes the presence of NH_3^+ group in the crystal confirming the protonation of amino acid group[6] facilitating the formation of urea L-threonine mixed crystal.

Table 2 FTIR Spect ra of ULT- mixed Crystal

Wave Number cm^{-1}	Functional Group Assignment
2905	C-H stretching mode
2050	Degenerative deformation of NH_3^+ and torsional vibration of NH_3^+
1615	Asymmetric stretching of CO_2^-
932	C-C stretching
870	NH_2 wagging
702	In plane deformation of CO_2^-
542	C-C=O in plane vibration
489	Asymmetric stretching of N-C-N

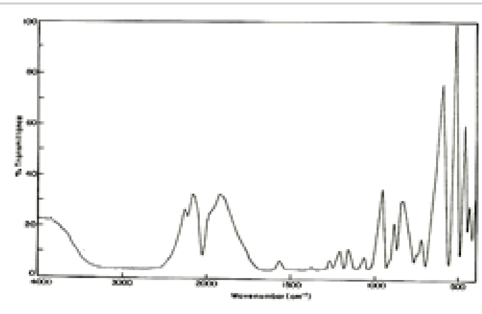

Fig. 3 FTIR specrum of ULT crystal

Vicker's Microhardness Study

Micro hardness studies play a key role in device fabrication. Good optical quality crystals are in need with sufficient mechanical strength. Vicker's hardness measurements are taken on the (001) plane of the grown crystal using Reichert MD 400E Ultra Microhardness tester fitted with diamond indenter. Indentations were made using Vicker's pyramidal indenter for various loads from 10gm to 55gm. Hardness number of the crystal is calculated using the relation, $Hv = 1.8544\ P/d^2\ Kg/mm^2$ where P is the applied load in Kg and d is the average diagonal length of the indented impression in millimeter. Typical Normal Indentation Size Effect (ISE) says that microhardness of crystals decreases with increasing load [7] as shown in Fig.4. Vicker's Hardness value was measured to be 42 for a typical load of 10gm and the time of indentation is 10s. Development of crack could be observed at load of 50gm it propagates further at 55gm this is due to the release of internal stress locally.

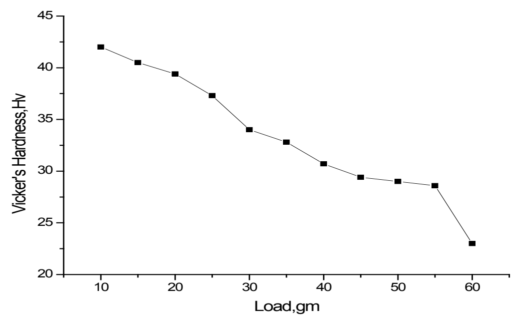

Fig.4 Plot of Vicker's Microhardness

HRSEM Analysis

Nonconducting organic crystals are coated with carbon before exposure to electron beam. HRSEM analysis of the primary surface investigation by Metallax-II metallurgical microscope in reflection mode depicts the crystal having closely packed layered growth, Fig.5.

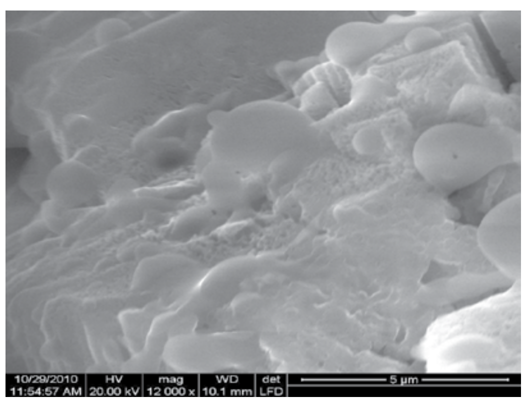

Fig.5 HRSEM photograph of ULT mixed crystal

Photoconductivity study

Photoconductivity of the crystal was studied using Keithley 485 Picoammeter and the sample was irradiated with halogen lamp. Photocurrent and dark current increases with applied voltage as shown in Fig.6. The dark current is higher than photocurrent for the same field applied,this is termed as negative photoconductivity. This can be attributed to the decrease in mobile charge carriers in the presence of radiation [8].

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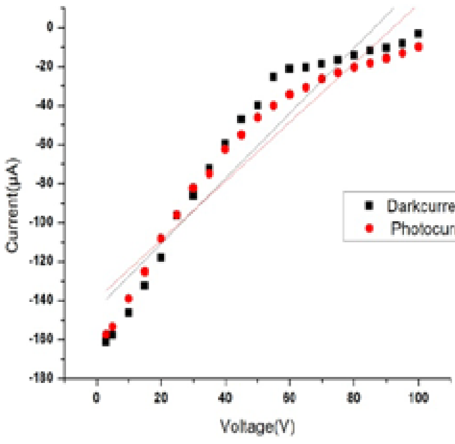

Fig.6 Field dependent conductivity of reported crystal

Conclusion

A novel urea l-threonine mixed crystal grown by slow evaporation technique at room temperature is reported. It has wide transparency range making it a valuable material for optical applications, FTIR spectrum proves the presence of L-threonine and urea in the grown crystal, second harmonic conversion efficiency of ULT mixed crystal is found to be 0.52 times of KDP. The ULT mixed crystal also exhibit good mechanical strength and photoconductivity. Thus these characterisation studies make ULT mixed crystal a promising non linear optical material suitable for optoelectronic device fabrication.

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