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Growth and Characterization of L-Histidine Doped Thiourea Single Crystals by Slow Evaporation Method

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ABSTRACT

Single crystals of pure and L-Histidine doped Thiourea (LHTU), an organic nonlinear optical (NLO) material; have been grown by slow evaporation technique at room temperature. The crystalline nature of grown crystal was confirmed by powder X-ray diffraction analysis (XRD). The functional group of the grown crystals was found by FTIR analysis. The spectral bands have been compared with similar Thiourea complexes using FTIR spectrum in the range 400-4000 cm⁻¹. The UV-Vis study was performed to know the optical behaviour of the grown crystals. Surface morphology was studied by scanning electron microscopy (SEM) analysis.

Keywords: L-Histidine, Thiourea, LHTU, X-Ray Diffraction, UV-Vis, Scanning Electron Microscopy.

1. INTRODUCTION

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber communications, which depend on optic materials/crystals such semiconductors, as superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezoelectric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material chemical engineering, science, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications [1, 2]. Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals [3]. The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high

performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research.

Nonlinear optical crystals are very important for laser frequency conversion [4]. Potassium dihydrogen phosphate (KDP) is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also KDP has a high laser damage threshold. Potassium titanyl phosphate (KTP) is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of Nd:YAG laser. It has high optical nonlinearity, large temperature and angular allowance and it is nonhygroscopic and mechanically hard. The method of growing crystals varies widely; it is mainly dictated by the characteristics of the material and its size [5]. In recent years there has been considerable progress in the development of coherent UV sources based on non-linear optical processes. The demand for nonlinear optical crystals with superior properties is increasing due to quantum jump in the design of nonlinear optical devices with higher performance. With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace [6-8]. To enable a material to be potentially useful for NLO applications, the material should be available in bulk single crystal form [9]. And so, crystal growth of new nonlinear optical materials and investigation into their properties has become most



Figure 1: Pictogram of L-Histidine grown single crystal.



Figure 2: Pictogram of Thiourea grown single crystal.



Figure 3: Pictogram of L-Histidine doped Thiourea grown single crystal.

indispensable and efficacious disciplines in the field of materials science and engineering. The rapid development of optical communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel semi organic systems of considerable potential and high performance. There are three major stages involved in this research. The first is the production of pure materials and equipment associated improved with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices. In this paper, the method of crystal growth with emphasis on low temperature solution growth technique was described. The solvent to be chosen to grow good quality crystals from solution is also discussed.

2. EXPERIMENTAL 2.1. Material Preparation

An essential prerequisite for success in crystal growth is the availability of material of the highest purity. Solute and solvents of high purity are required, since impurity may be incorporated into the crystal lattice resulting in the formation of flaws and defects. Sometimes impurities may slow down the crystallization process by being adsorbed on the growing face of the crystal, which changes the crystal habit. A careful repetitive use of standard purification methods of recrystallization followed by filtration of the solution would increase the level of purity.

2.2. Seed Preparation

Seed for crystal are prepared by slow evaporation method. In this method, some amount of water (say 100 ml) is taken in a 100 ml beaker. The given substance L-Histidine, Thiourea, L-Histidine doped Thiourea is made to dissolve in water until we get a saturated solution. Then, the highly dissolved salt solution is filtered by whatman (110 mm Ø) filter paper and poured in a petridish. The petridish is covered with a plastic with a few small holes for evaporation of solvents. The apparatus is placed undisturbed till the seeds of sufficient size of the given salt L-Histidine, Thiourea, L-Histidine doped Thiourea are obtained in the petridish. Now the seeds are harvested for crystal growth.

2.3. Preparing the Solution

Making of the solution is the most time consuming step. There appear to be short cut for obtaining a solution precisely equilibrated at a desired temperature, but it may be helpful to mention some common pitfalls. A precisely saturated solution can never be made simply by combining the necessary amount of water and salts as determined by solubility curves, first, because an astonishingly larger amount to complete dissolution introduces gross errors. According, here a highly soluble L-Histidine, Thiourea, L-Histidine doped Thiourea salt solutions were prepared in a 100 ml beaker by continuous stirring by magnetic stirrer for obtaining required amount of corresponding salts in the distilled water. It is then filtered and 50 ml of the saturated solution is taken in a beaker for crystal growth. When the previous data are not available, it is necessary to introduce a test crystal. If the solution is not agitated, it is often possible to observe children streams; rising, if the solution is super saturated (since the solution is being depleted of solute as the crystal grows), or since the test crystal is dissolving locally rousing the density of the solution under saturation is fairly easily detected in the course of a day or less, by the rounding of the corners or the enlargement and change of shape of the seed crystal. Slight super saturation will often produce partial filling or the easier to observe essentially for 18 hours or so; it is safe to introduce seeds to growth run. The pictograms of the grown L-Histidine, Thiourea and L-Histidine doped Thiourea (LHTU) single crystals were depicted in figs. 1 to 3.

3. RESULTS AND DISCUSSION *3.1. X-Ray Diffraction analysis*

The X-ray diffraction spectra were recorded for L-Histidine (LH), pure Thiourea (TU) and L-Histidine (1%) doped Thiourea (LHTU) grown crystals are shown in Figs. 4 to 6. All the diffraction peaks can be well indexed to the orthorhombic structure compared with pure L-Histidine, L-Histidine (1%) doping on Thiourea does not alter its orthorhombic structure but there is a reduction observed at FWHM of the XRD patterns. Therefore, L-Histidine (1%) is an important dopant to improve the crystal growth. The Lattice parameter (a) was calculated by selecting the (102) plane using the formula [10-12],

$$\sin^2\theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

From that the calculated value of 'a' is 7.3087Å which is in good agreement with that of JCPDS - Card No: 31-1934 shown in the table 1.

3.2. Fourier transform infrared spectroscopy

The FTIR spectra of L-Hisditine, Thiourea, L-Hisditine doped Thiourea grown crystals are shown in figures 7 to 9 respectively. In the higher wavelength region, the peak at 3779 cm⁻¹ is assigned to O-H stretching vibration. The region3511 cm⁻¹ and 3107 cm⁻¹ with strong intensity represents N-H stretching mode. The broad envelope positioned in between 3503 cm⁻¹ and 2773 cm⁻¹ corresponds to the symmetric and asymmetric stretching modes of NH₂ group. The peak at 3080 cm⁻¹ with medium intensity refers C-H



Figure 4: XRD pattern of grown L-Histidine single crystal.



Figure 5: XRD pattern of grown Thiourea single crystal.



Figure 6: XRD pattern of grown LHTU single crystal.

asymmetric stretching. Combinational overtones extend to the bands from 2359 -2364 cm⁻¹. The peak at 1638 cm⁻¹ indicating the C=O stretching mode of vibration. The NH₂ bending vibrations occur at 1618, 1619 and 729 cm⁻¹.

					Lattice par	ameter (A)
Crystal	System	2θ(degree)	FWHM	hkl	Calculated	Reference
L-Histidine	Orthorhombic	34.95	0.12	200	5.129	5.143
		24.49	0.16	020	7.263	7.294
		38.89	0.16	008	18.509	18.674
Thiourea	Orthorhombic	23.25	0.16	200	7.644	7.644
		20.81	0.16	020	8.527	8.559
		32.57	0.24	002	5.493	5.492

Table 1: X-Ray diffraction data for L-Histidine and Thiourea grown crystals.

Table 2: The infrared absorption frequencies (cm⁻¹) of pure and L-Histidine doped Thiourea single crystals.

	Frequencies (c	_		
Thiourea	L-Histidine	L-Histidine doped Thiourea	Assignments	
3779	-	3779	OH-stretching	
3511	-	-	NH-stretching(primary amide)	
3503	2773	3093	NH ₂ -symmetric and asymmetric stretching	
-	2712	-	CH ₂ asymmetric stretching	
2360	2364	2359	C-H Combinational overtone	
-	1638	-	C= O stretching	
1619	-	1618	NH ₂ bending	
-	1606	-	Asymmetric bending of NH ⁺³ and C=N stretching	
-	1498	-	NH ₂ bending	
1471	-	1470	CH ₂ bending	
1413	1415	1413	C=S stretching	
-	1336	-	C-C stretching	
-	1186	-	C-N stretching	
-	1168	-	C-H in plane bending	
-	1128	-	N-H bending	
1083	1078	1083	C-C -N stretching	
-	1068	-	C-H in plane bending	
-	867	-	C-N deformation	
-	822	-	Ring deformation	
-	805	-	C-N deformation	
729	-	729	C=S stretching	
-	696	-	C= O deformation	
668	-	667	C-H out of plane bending	
633	630	632	C-C deformation	
486	491	486	N-C-N stretching	



Figure 7: FTIR spectrum of grown L-Histidine single crystal.



Figure 8: FTIR spectrum of grown Thiourea single crystal.



Figure 9: FTIR spectrum of grown LHTU single crystal.

Asymmetric bending of NH⁺³ and C=N stretching present at the peak 1606 cm⁻¹. The peak at 1498 cm⁻¹ is due to NH₂ bending vibration. CH₂ deformation vibrations are identified by the sharp band at 1470 cm⁻¹. The peaks at 1415-1413 cm⁻¹ corresponds to the C=S stretching. The C-C stretching mode of vibration occurs in 1336 cm⁻¹ peak. The peak at 1186 cm⁻¹ gives rise to C-N stretching mode of vibration. The spectra show absorption bands in the region of 1168 cm⁻¹ and 1068 cm⁻¹ which are due to in-plane C-H bending vibration. The band 1128 cm⁻¹ signifies the N-H symmetric bending. C-C-N stretching vibration obtained at 1083-1078 cm⁻¹. The bands at 867 cm⁻¹ and 805 cm⁻¹ revealed that C-N deformation mode. The ring deformation occurs the peak at 822 cm⁻¹. C=O deformation is identified by the band at 696 cm⁻¹. C-H out-of plane bending peaks obtained at 667 cm^{-1} and 668 cm^{-1} . The bands $630-633 \text{ cm}^{-1}$ represents C-C deformation. The absorption bands in the region of 486-491 cm⁻¹ which are due to N-C-N stretching vibration. The assignments confirm the presence of various functional groups present in the material, tabulated in Table 2. The weak absorption at 1608 cm⁻¹ (Fig.7) indicates the presence of NH^{3+} and C=N stretching vibration. The absorption around 1619 cm⁻¹ is NH₂ bending and this band would be shifted into lower wavelength region 1618 cm⁻¹ (Fig.9) compared with Fig.8. Our investigations were well compared with earlier reports [10-19].

3.3 UV-VIS-DRS

The UV-Vis. spectrum analysis has been carried out using shimadzu UV-Vis. spectrophotometer in the wavelength range of 200-800 nm. Transmission

(1/abs) spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window [19]. The optical transmission spectra for L-Histidine. Thiourea and L-Histidine doped Thiourea are recorded and are shown in figs 10 to 12. From the transmittance spectra, it is observed that LHTU has high transmittance in the entire visible and near IR region. This is very important materials possessing nonlinear optical for properties. The UV cut-off wavelength for the pure and L-H doped Thiourea crystals are found to be 278 to 224 nm respectively, which makes it valuable for those applications requiring blue-green light [20]. The good optical transmittance in the entire visible region and the lower cut off wavelength (λ_{cut}) was observed as this is due to π - π^* transition in the compounds. The band gap energy ($E_g = hc/\lambda$) was found to be 4.45 eV and 5.53 eV for pure and L-H doped thiourea crystals. The large transmission in the entire visible region and short cut off wavelength enables it to be a potential material for second and third harmonic generation [21].

3.4. SEM Studies

Morphologies of as grown L-Histidine (LH), Thiourea (TU) and 1% L-Histidine doped Thiourea (LHTU) crystals were observed by SEM. As shown in figures 13-15, the above mentioned three crystals prepared under the condition posses an anomalous morphology. However, the doped crystals have given a more irregular structure and a greater particle size than that of undoped (pure) crystals (L-Histidine and Thiourea). From Figures 13 to 15, it seems reasonable to believe that the increase in



Figure 10: UV-Vis. spectrum of L-Histidine single crystal.



Figure 11: UV-Vis. spectrum of Thiourea single crystal.



Figure 12: UV-Vis. spectrum of LHTU single crystal.

particle size and rougher surface morphology are responsible for the increasing of surface area for doped crystals; which was also reported in previous work on doping L-Histidine with often elements [17,18,20]. The greater particle size of the doped ones can be explained by the fact that minimum crystal defects have been formed, when the dopant ions occupy regular lattice sites inside and for on the surface of Thiourea.



Figure 13: SEM image of grown L-Histidine single crystal.



Figure 14: SEM image of grown Thiourea single crystal.

4. CONCLUSIONS

From the present investigation it is understood that the L-Histidine (1%) doping is helpful in growing big LHTU crystal from the solution. X-Ray diffraction studies confirmed that the pure and L-Histidine doped Thiourea crystals were crystallized in orthorhombic system. The presence of the L-Histidine in to the Thiourea crystal lattice was confined qualitatively by both powder XRD and FTIR analysis. From UV-Vis optical transmittance studies, the values of band gap energy was determined to be 4.45eV and 5.53eV for pure and L-H doped thiourea crystals respectively. The morphology analysis shown that the smaller particles (from undoped crystals) transformed into elongated grains, the effect of greater grain alignment opens up new possibilities for improved performance.

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