INVESTIGATION ON GROWTH AND PHYSICOCHEMICAL PROPERTIES OF L-HISTIDINE STANNOUS CHLORIDE (LSC) NONLIEAR OPTICAL CRYSTAL

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ABSTRACT

Semiorganic nonlinear optical L-histidine stannous chloride (LSC) crystal has been synthesized for the first time. The LSC single crystals were grown from aqueous solution by slow evaporation technique at room temperature. The grown crystal was subjected to various characterizations. The grown LSC crystal was analyzed using Single crystal X-ray diffraction to identify the crystal system. From the calculated parameters, the LSNC crystal was found to be orthorhombic in structure. The grown crystal of LSC has good crystalline nature which was observed from Powder X-ray diffraction analysis. The vibration frequencies of the functional groups are identified by FTIR spectroscopic study. The highest emission peak from the PL spectrum was observed to be at 484 nm. Non linear optical property of the crystal was confirmed by SHG test using Kurtz Perry powder technique. Studies of dielectric properties like dielectric constant and dielectric loss as function of frequencies for varying temperatures has been carried out and the results suggested that LSC crystal is good candidates for electro optic modulators and frequency convertors. The work hardening coefficient value 1.27 which indicates moderately hard nature of material.

Keywords: Nonlinear; XRD; PL and Hardness.

1. INTRODUCTION

The field of molecular non-linear optics has benefited from both upstream rejuvenation and downstream application oriented breakthroughs, aiding to bring the field closer to industrial development [1]. Engineering of new nonlinear optical (NLO) materials, structures ,and devices with enhanced figures of merit has developed over thelast two decades as a major force to help drive nonlinear optics from the laboratory to real applications. The NLO process requires materials that manipulate the amplitude, phase, polarization and frequency of optical beam. Among the various amino acids, L-serine is the simplest molecule having goodphysiochemical properties. The importance is due to the fact that amino acids contain chiral carbon atom and crystalline in the non-Centro symmetric space groups; therefore they are potential candidates for optical second harmonic generation. In semi organic crystals,high optical non linearity of a purely organic ion is combined with the favorable mechanical and thermal properties of an inorganic counter ion [2].

Amino acids are interesting materials for nonlinear optical applications, they containa proton donating carboxyl group (COO-) and a proton accepting amino (NH3+) in them except for glycine [3]. Complexes of amino acids with in organic salts are promising materials for optical SHG, as they have a tendency to combine the advantage of the organic amino acid with that of the inorganic salt. Hence L-arginine, L-threonium, L-alanine and L-valine have been subjected for the formation of salts with different inorganic acids. As a result very good semi organic materials such as L-arginine phosphate mono hydrate (LAP)[6], L-histidine hydrochloride[4], L-analine cadmium chloride[5], L-valine hydro chloride[6] are some of the examples which proved very suitable material for NLO applications. Most of the amino acids individually exhibit the NLO

property due to donor amino group NH_3^+ and acceptor carboxyl group COO^- and intermolecular charge transfer [7].

Therefore, amino acid enhances the material properties such as nonlinear and ferroelectric properties [8]. Amino acid family with metal chlorides such as zinc chloride [9], calcium chloride [10], potassium chloride [11], sodium chloride [12], and lithium chloride [13] have been reported in the recent years. Interest has been centered on semiorganic crystal which has the combined properties of both inorganic and organic crystals which make them suitable for device fabrication [14-18].

In this present investigation we concentrated on synthesis, growth and characterization of a new semiorganic nonlinear optical crystal L-histidine stannous chloride (LSC). The grown crystal LSC were characterized using single crystal XRD, powder X-ray diffraction, Fourier transform infrared (FT-IR) analysis, UV-vis spectroscopy and also dielectric constant, dielectric loss have been determined for the first time.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of LSC

A product LSC was synthesized by equimolar ratio (1:1) of L-histidine (AR grade,Merck) and stannous chloride (AR grade, Merck). The LSC was synthesized by using deionized water as a solvent at room temperature by slow evaporation solution growth technique.The chemical reaction of synthesized compound as follows:

$$C_6H_9N_3O_2 + SnCl_2 \rightarrow Sn\,(C_6H_9N_3O_2)\,Cl_2$$

L-histidine + stannous chloride → LSC

2.2. Crystal Growth of LSC

The LSC crystals have been grown from saturated solution by slow evaporation technique. The saturated solution was prepared by taking 100ml of double distilled water in a beaker. For promoting the solubility the solution was stirred well with the magnetic starrier and the process was continued until the last pinch of the substance was dissolved. After 6 hours, the saturated solution was filtered using what man filter paper. The top of the beaker was covered with polythene paper and make few small holes for evaporation process. The beaker was kept at room temperature without any disturbance. A good optical quality crystal of dimensions 6 x 4 x 2 mm^3, were harvested in the period of 30-35 days. The photography of the as grown LSC crystal was shown in Figure 1.

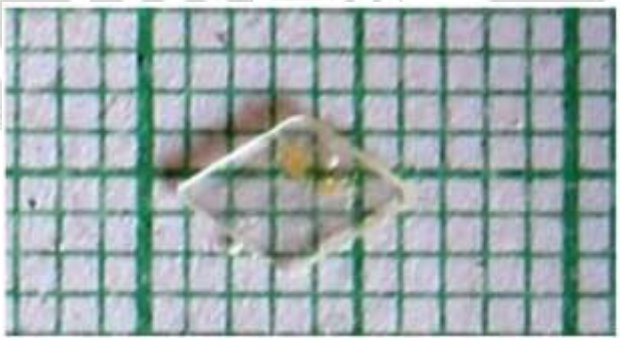

Figure 1. As grown crystal of LSC

3. CHARACTERIZATION TECHNIQUES

3.1. Single crystal X-ray Diffraction Analysis:

The grown LSC crystals have been subjected to single crystal X- ray diffraction studies using an

ENRAF NONIUS CAD4 diffractometer with MoKα radiation (λ=0.71073 A˚) to determine the unit cell dimensions and morphology. The calculated lattice parameter are a = 5.15 A°, b = 7.76 A°, c = 13.67 A° and volume = 547 A°3. It is observed from the single crystal XRD studies that LSC belongs to orthorhombic crystal system.

3.2. Powder X-ray Diffraction Analysis:

The powder samples have been analyzed by using BRUCKER, Germany (model D8 Advance) X-ray diffractometer with cukalpha (wavelength=1.5405A0) radiation. The Powder X-ray diffraction patterns of L-histidine stannous chloride (LSC) crystal is obtained. The well-defined Bragg peaks are obtained at specific 2θ angles. The powder sample was scanned over the range 10– 80o at a scan rate of 1o / min. The well defined peaks are reveals that the grown crystal has good quality and high crystalline nature. The powder XRD pattern of grown crystal LSC as shown in figure 2.

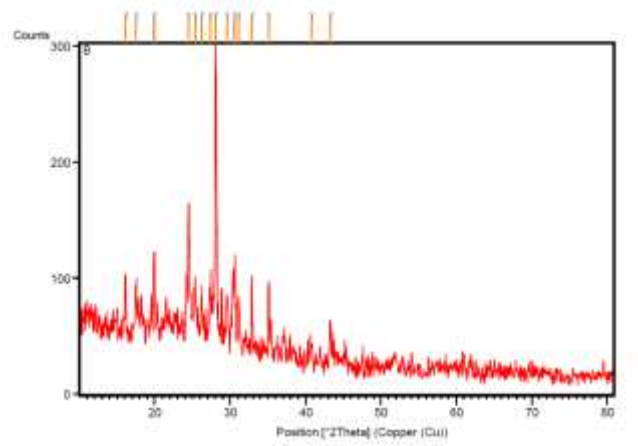

Figure 2. Powder XRD pattern of grown LSC crystal

3.3. Fourier Transform Infrared (FTIR) spectroscopy study:

The FTIR spectral analysis of l-histidine stannous chloride (LSC) crystal was carried out between 4000 and 500 cm^{-1}. The observed spectrum is shown in the figure 3. In the high energy region, there is a broad band between 2100 and 3500 cm^{-1}. The intense sharp peak was observed at 3166 cm^{-1} due to O-H (-H_2O) vibration. The involvement of $NH3^+$ ion in hydrogen bonding is evident by the fine structure of band in the lower energy region. The bands appear in the region 1641 and 1616 cm^{-1} is assigned for C=S. The peak at 1641 is due to asymmetrical $NH3^+$ bending mode. The resolved sharp peak at 1485 cm^{-1} is due to symmetrical $NH3^+$ bending. The C=S absorption band of in the region 1314cm^{-1}. The narrow bands at 797,642,456 cm^{-1} and wide split band at 1485,1314,1281 cm^{-1}correspond to the vibration of Cl groups.

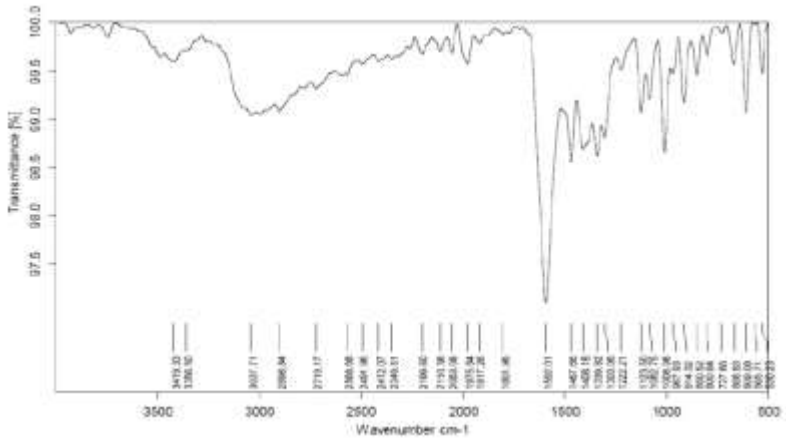

Figure 3. FTIR spectrum of grown crystal LSC

Table 2. Wave assignments of grown LSC crystal.

Wavenumber cm^{-1}	Assignments
3419	O-H bending
3037	NH_3^+ asymmetric stretching
2898	C-H asymmetric stretch
2719, 2566	C-H stretching
2110	Combination of NH_3^+ deformation and NH_3^+ torsion
1592	NH_3^+ asymmetric deformation
1467	NH_3^+ stretching
1408	COO^- symmetric stretching
1339	C-H bending
1303	CH_2 wagging
1222	C-N stretching
1082	C-C-N asymmetric stretching
967	C-C stretching
914	CH_2 rocking
727	C-O-H stretching
540	C-Cl stretching

3.4. Photoluminescence study of LSC crystal

The excitation and emission spectra of LSC was recorded using Cary Eclipse spectrophotometer. The PL study finds wide applications in the field of medical, biochemical and chemical research fields for analyzing compounds. 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 as light. The photon energies reflect the variety of energy states that are present in the material. Figure 4 shows PL emission spectrum recorded in the range of 280–500 nm with an excitation wavelength of 260 nm. The highest emission peak from the spectrum was observed to be at 484.85 nm. Other peaks observed are due to anionic and cationic nature of the sample. From this wavelength it is concluded that LSC emits blue fluorescence.

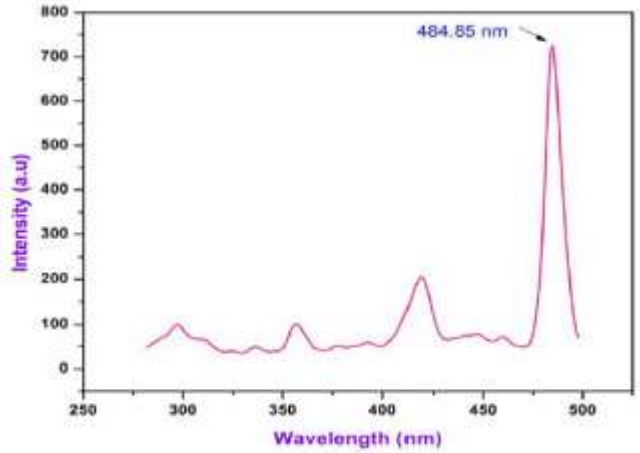

Figure 4. PL emission spectrum of LSC crystal

3.5. SHG EFFICIENCY STUDIES

In the present study, a single shot mode of 8 ns laser pulses with a spot radius of 1mm was used. This experimental setup used a mirror and a 50/50 beam splitter (BS) to generate a beam with pulse energies about 6.2mJ. The input laser beam was passed through an IR reflector and then directed on the micro crystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The light emitted by the sample was detected by photodiode detector and oscilloscope assembly. For the SHG efficiency measurements, microcrystalline material of potassium dihydrogen phosphate (KDP) was used for comparison. When a laser input of 6.2 mJ was passed through LSC, the second harmonic output was generated from the irradiated powder sample of LSC of grain size about 100 μm by a pulsed laser beam. SHG signal of 4.84mJ and 8.8 mJ were obtained from BTLM and KDP respectively. Hence, it is found that the SHG efficiency of LSC is nearly 0.55 times that of KDP. The secondharmonic generation efficiency indicates that the LSC crystal can be used as suitable materialfor non-linear optical devices.

3.6. Dielectric Studies

The dielectric constant and the dielectric loss of the LSC sample were measured using HIOKI 3532-50 LCR HITESTER. Dielectric constant and dielectric loss of the sample have been measured for different frequencies at different temperatures (308 to 368 K). Figure 5 and Figure 6 show the variations of dielectric constant and dielectric loss respectively as a function of frequency at different temperatures. The high value of dielectric constant at low frequencies indicates that there is contribution from all four known sources of polarizations [Moitra et al (2008)], but in the high frequency region, dielectric constant almost become constant. Dielectric constant decreases for high frequencies because of contributions of electric polarization [Meena et al (2008)]. It is evident from Figure 6 that the crystals have avery low dielectric loss in the high frequency region, which indicates the lesser number of defects/impurities in the crystal.

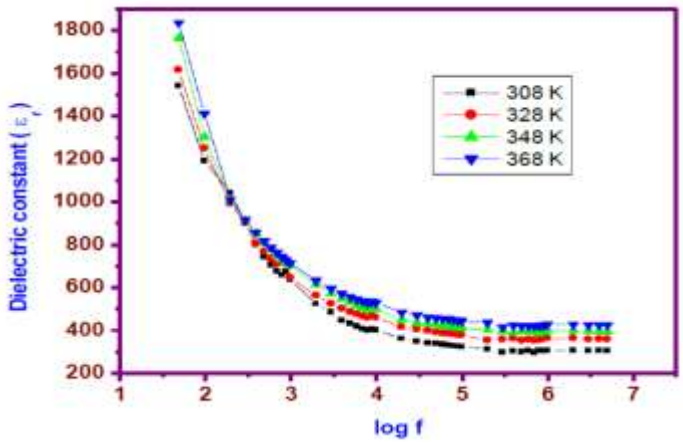

Figure 7. Variation of dielectric constant with log frequency for LSC crystal

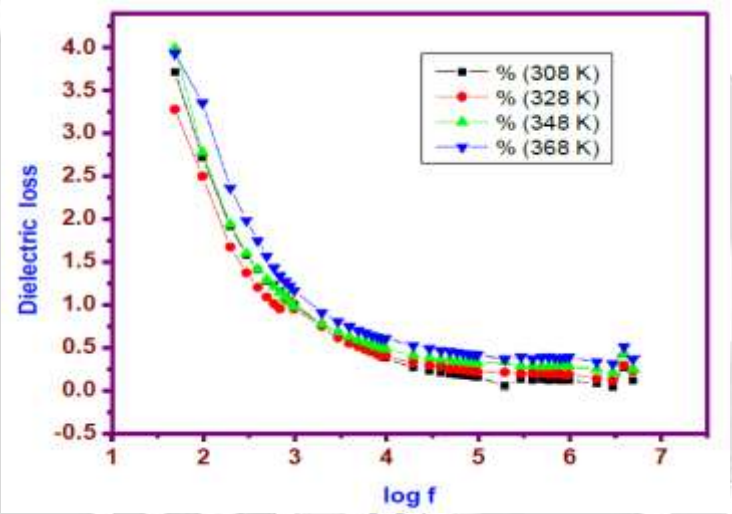

Figure 8. Variation of dielectric loss with log frequency for LSC crystal

3.7. Microhardness studies of LSC Crystal

The mechanical properties of the crystal are evaluated by mechanical testing which reveals certain mechanical characteristics. The fastest and simplest type of mechanical testing is the hardness measurement. Among the different testing methods, the Vicker's hardness test method is more commonly used. In the present study, Vicker's hardness test was carried out on the grown crystal using SHIMADZU HMV microhardness tester fitted with a diamond pyramidal indenter. Microhardness measurements were done on LSC for the applied load (p) varying from 25 to 100g for a constant for indentation time 10s.Several indentations were made for each load and the diagonal length (d) of the indentation was measured. Vicker's hardness number was determine using the formula $HV = 1.8544\ P/d^2$ (Kg/mm^2). A graph was plotted between Hv and load (p) (Figure 9). It is observed that Hv increases with applied load which is known as reverse indentation size effect (RISE). For an indentation load of 100 g, crack was initiated on the crystal surface, around the indenter. This is due to the release of internal stress locally initiated by indentation. The work hardening coefficient (n) has been calculated from the slop of straight line between log p and log d (Figure 10) and it is found to be 1.27 which indicates moderately hard nature of material [Onstrich (1956)].

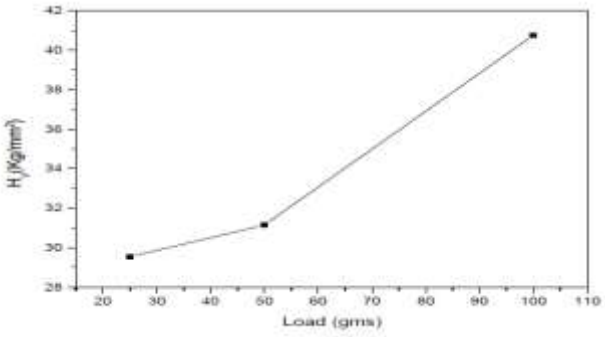

Figure 9. Plot of load (p) Vshardness (Hυ) for LSC crystal.

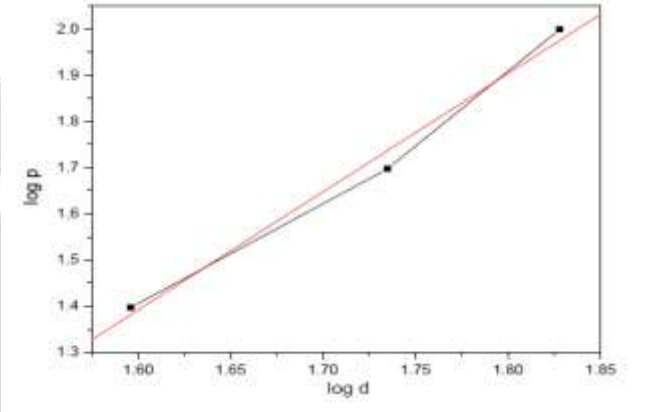

Figure 10. Plot of log d Vs log p for LSC crystal.

4. CONCLUSION

A new NLO semiorganic material L-histidine stannous chloride (LSC), has been synthesized and crystals were grown by slow evaporation method. The lattice parameter values have been evaluated by single crystal XRD analysis. The sharp well defined peaks confirmed the crystalline nature of the material. The functional groups have been confirmed from FT-IR analysis. The highest emission peak from the PL spectrum was observed to be at 484.85 nm. The SHG efficiency of LSC is nearly 0.55 times that of KDP. The second harmonic generation efficiency indicates that the LSC crystal can be used as suitable material for non-linear optical devices. The dielectric constant and the dielectric loss of the LSC sample were measured. The work hardening coefficient value 1.27 which indicates moderately hard nature of material.

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