SYNTHESIS, GROWTH AND CHARACTERIZATION OF SEMIORGANIC NONLINEAR OPTICAL CRYSTAL: L-ARGININE MONOHYDROCHLORIDE BARIUM NITRATE (LAMBN)

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ABSTRACT

Appropriate amounts of l-arginine monohydrochloride and barium nitrate were dissolved in double distilled water at room temperature. Transparent and defect less bulk crystal of LAMBN with dimension 6 x 5 x 3 mm^3 have been grown by solution growth method. Single crystal X-ray diffraction study reveals that LAMBN crystal belongs to orthorhombic crystal system and the measured lattice parameters values are a=8.28 Å, b=9.37 Å, c=14.938 Å, α=β=γ=90º and volume V=1158.94 Å. In Powder XRD, the powdered sample was scanned over in the range of 10 to 80º at a scan rate of 1° per minute. Thus, the powder XRD pattern observed well defined Bragg's peaks reveal that the LAMBN crystal is in good crystalline nature. FT-IR analysis was carried out to identity the various functional groups present in LAMBN. In the recorded optical transmission spectrum, the UV cut-off wavelength at 262 nm and high transmission percentage of LAMBN crystal from 262 nm to 1000 nm are observed.

Keywords: *Solution growth; XRD; FTIR and UV.*

1. INTRODUCTION

Non - linear optics plays an important role in the emerging photonic and optoelectronic technologies. Nonlinear optical materials find wide applications in the area of laser technology, optical communication and the data storage technology [1]. Non-linear optical (NLO) crystals with high conversion efficiency for second harmonic generation (SHG) and transparent in the visible and ultra violet ranges are required for various devices in field of optoelectronics and photonics [2-4]. Some complexes of the amino acids with simple organic and inorganic salts appear to be promising for optical second harmonic generation (SHG). This research is extended to semi-organic NLO material crystal so as to obtain superior NLO crystal by combining the advantages of organic and inorganic materials [5].

Hence Semi-organic single crystals are attracting great attention in the field of non linear optics because of their high optical nonlinearity, chemical flexibility of ions, high mechanical strength, thermal stability and excellent transmittance in the UV-Vis region [6-9]. Among the various process of semi organic non-linear optical materials, metal complexes have received potentials interest, because they can be effectively used as the better alternatives for KDP crystals in the frequency doubling process and laser fusion experiments [10, 11]. Materials of amino acids possess particular feature, such as week vander waals and hydrogen bonds, wide transparency range in the visible region and zwritterionic nature of the molecules [12, 13].

The potentials NLO properties of L- arginine phosphate mono hydrate crystals[14], and its deuterated compound[15], have stimulated a wide interest in the complexes of L-arginine and other amino acids[16,17]. One of the three basic amino carboxylic acid [18], L-lysine reacted with other carboxylic acids has also been studied for its intrinsic polarities. Several crystals composed of L-lysine with NLO properties have been grown and characterized [19, 20]. In this present investigation we report on synthesis, growth and

physicochemical properties of l-arginine monohydrochloride barium nitrate (LAMBN) nonlinear optical crystal using slow evaporation method. The grown crystals were characterized using single crystal XRD, Powder X-ray diffraction, Fourier transform infrared (FT-IR) analysis, UV-vis spectroscopy have been determined.

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.

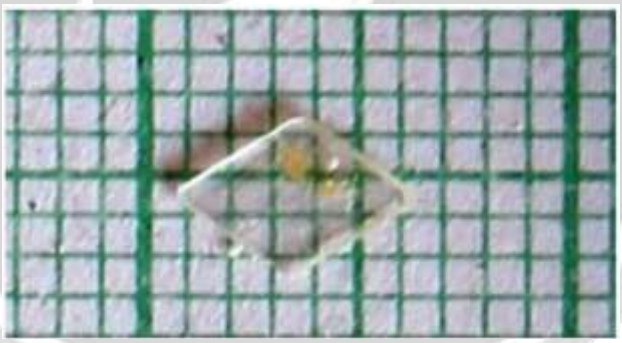

Figure 1. As grown crystal of LSC

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.

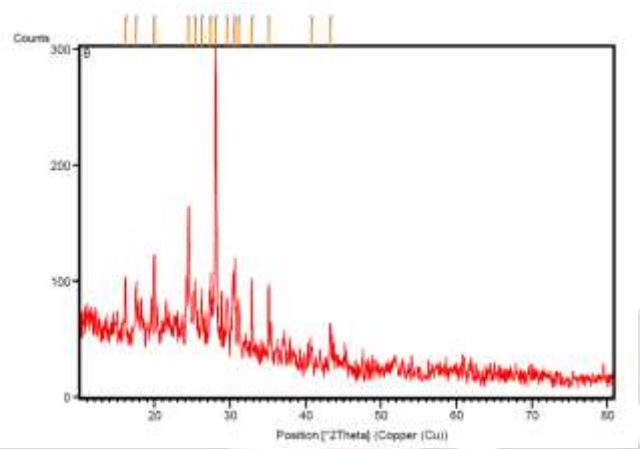

Figure 2. Powder XRD pattern of grown LSC crystal

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.

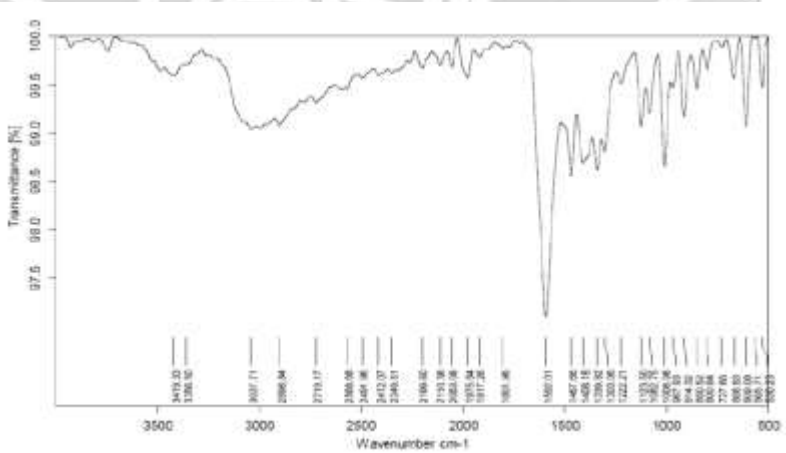

Figure 3. FTIR spectrum of grown crystal LSC

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.

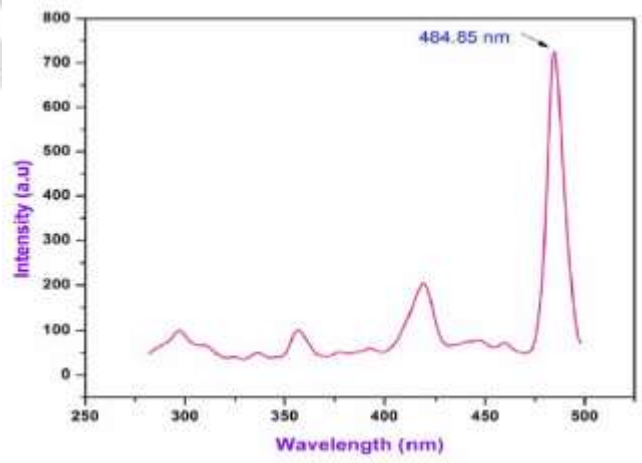

Figure 4. PL emission spectrum of LSC crystal

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.

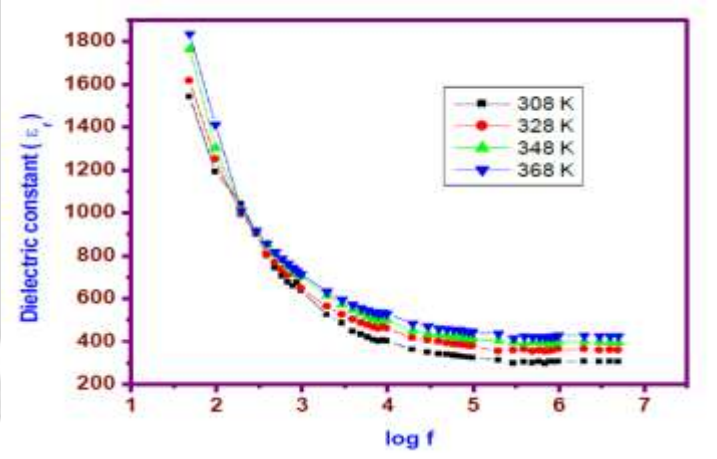

Figure 7. Variation of dielectric constant with log frequency for LSC crystal

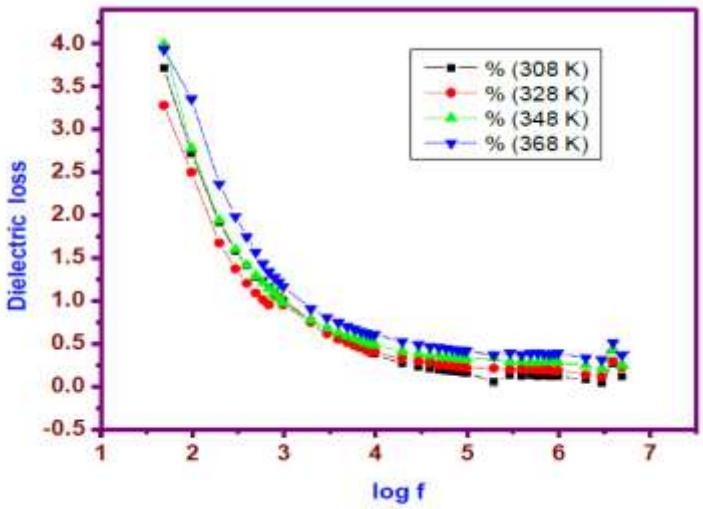

Figure 8. Variation of dielectric loss with log frequency for LSC crystal

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)].

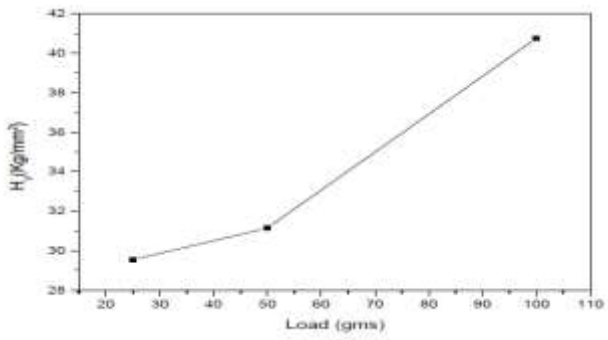

Figure 9. Plot of load (p) Vshardness (Hv) for LSC crystal.

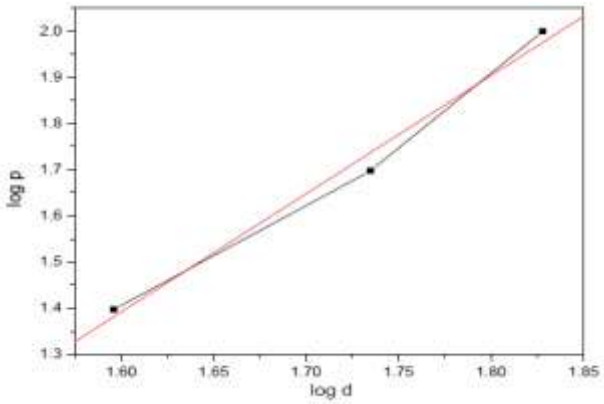

Figure 10. Plot of log d Vs log p for LSC crystal.

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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