Growth and Characterization of NLO Single Crystals: L-Serine doped Sodium Nitrate

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ABSTRACT: The growth and characterization of NLO single crystals of L-Serine doped Sodium Nitrate has been continued in view of (i) growing good quality single crystals by conventional method (ii) to enhance the efficiency of second harmonic generation (SHG) using dopant (iii) and other studies like powder XRD, FTIR, UV-Vis, Dielectric measurement and thermal stability. From these important results we summarize that the addition of doping is considerable for enhancement of SHG efficiency which was observed and illustrate its suitability for NLO applications.

I.INTRODUCTION

In recent years, nonlinear optical materials (NLO) have attracted many researchers due to its wide applications in the field of telecommunication, optoelectronic and optical information storage devices. Organic NLO materials exhibits much larger NLO efficiencies compared to their inorganic counterpart, thus promises to meet future requirements for ultrahigh bandwidth photonic devices [1-2] Organic materials have been known for their potential applications in semiconductors, superconductors and nonlinear optical devices [3]. Hence, Organic NLO crystals with high second harmonic generation efficiency and transparency in UV-Vis region are required for numerous device applications. In the field of nonlinear optical crystal growth, amino acids play a vital role. Amino acids exhibit natural chiral properties and crystallize in the non-centrosymmetric space groups, which is an essential criterion for NLO applications.

II.MATERIALS AND METHOD

A. MATERIALS-L-SERINE DOPED SODIUM NITRATE

Amino acids are biochemical building blocks. They form short polymer chains called polypeptides or peptides which in turn confer proteins The building blocks of proteins are α-amino acids substances in which the amino group is located on the α carbon atom immediately adjacent to the carboxylic acid group. Approximately twenty α -amino acids are common constituents of proteins [4]. L-Serine is an organic compound under an amino acid category. It is one of the naturally occurring protenogenic amino acids.

L-Serine exists in a zwitterionic form; the molecule can combine with anionic, cationic and overall neutral constituents. The etherification of the carboxyl group of amino acids plays an important role in the synthesis of peptides, especially due to increased solubility in organic solvents.

B. METHOD- CONVENTIONAL METHOD

In the present work, L- Serine doped sodium carbonate (LSSC) single crystals have been grown by slow evaporation conventional method. According to stoichiometry ratio the title compound was primed by dissolving (AR grade) L-Serine and sodium carbonate using double distilled water as solvent. After stirring continuously for about 8-12 hours at room temperature the supersaturated solution was filtered with Whatman filter paper and kept it in a dust free atmosphere. Further the prepared solution was allowed to evaporate at room temperature and the crystals were obtained conventionally within a couple of weeks. To improve the purity of the crystal, recrystallization process was done twice successively in turn yielded crystals having good optically transparent and defect free with dimensions of $13 \times 5 \times 3$ mm^3 after 20 days as shown in the Figure.1

Figure.1 As grown single crystal of LSSC

III. CHARACTERIZATION

The grown crystals were subjected to various characterizations such as single crystal XRD, powder XRD, FTIR, UV, Photoluminescence, Dielectric measurement, thermal analysis and SHG efficiency results were discussed in detail.

A. SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

The grown L-Serine sodium carbonate crystal was subjected to single crystal X-ray diffraction analysis using KAPPA APEXII to identify the structure and refined the matrix least square technique from the SHELXL program. Further, the analysis revealed that the title crystal belongs to orthorhombic system with non-centrosymmetric space group P_{212121}, Z=4 and the lattice parameters are a= 5.61 (A°), b=8.62 (A°), c=9.39(A°), α=β=γ=90° and Volume= 454(A^3) and the results are in good agreement with the reported value [5,6].

B. POWDER X-RAY DIFFRACTION ANALYSIS

Powder X-ray diffraction study was carried out by employing a SIEFERT 3003 TT diffractometer with a characteristic CuKα (λ=1.540598Å) radiation from 10° to 80° at a scan rate of 2°/min. The powder XRD pattern for the grown crystal is shown in Figure.2.The appearance of sharp and strong peaks confirms good crystallinity of the grown sample. The lattice parameters calculated and are found to be a= 5.674 (A°), b=8.597 (A°), c=9.270(A°), α=β=γ=90° and Volume= 452(A3). The results of powder XRD and single crystal XRD studies are found to be in good agreement with the data available in the JCPDS card no: 27-1989. A slight shift in the sharp peak position (22.78°) towards the lower angle side may be due to the addition of sodium carbonate in L-Serine crystal and it is also confirmed by a slight variation observed in the lattice parameters of the grown crystal.
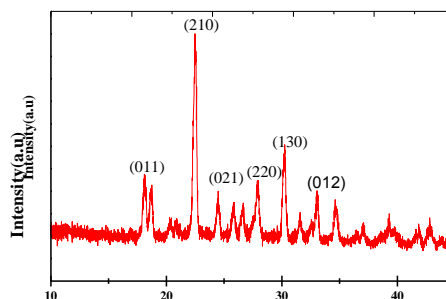

Figure.2 Powder X-ray diffraction pattern of LSSC

C. FOURIER TRANSFORMS INFRARED (FT-IR) SPECTRAL ANALYSIS

FT-IR spectrum of L-serine sodium carbonate single crystals are recorded in the range 400-4000 cm-1 using on Perkin Elmer RXI FTIR spectrometer. The frequency assignments of the expected functional groups are given below. The resulting FTIR spectrum is shown in Figure.3. In this spectrum, the broad band at 3447 cm-1is due to the presence of OH. Frequencies observed at 3092 and 2730 cm^{-1} are attributed as NH3+stretching and CH stretching, respectively. COO- anti symmetric stretching vibration is observed at 1599 cm^{-1}.The CH_2 bending vibrations are at 1469 and 1383cm^{-1}.The bending and rocking vibrations due to CH group have been observed at 1342 and 1304 cm^{-1} respectively. The CN Stretching vibrations produce peaks around 968cm^{-1}. The C-N groups are revealed by the peaks observed at 1126 and 1013 cm^{-1}. The peaks observed at 918, 610 and 525 cm^{-1}indicates the presence of CH_2 group.
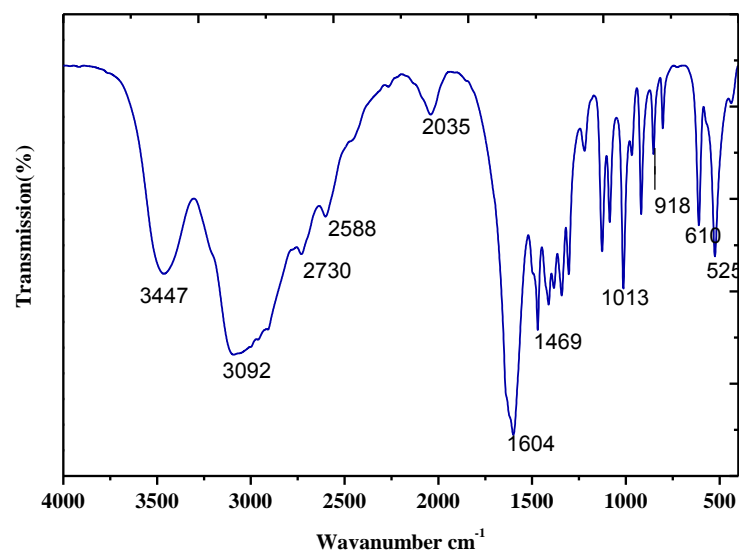

Figure. 3 FT-IR spectrum of LSSC

D. UV-VISIBLE SPECTRAL ANALYSIS

Optical window width is an important characteristic of an NLO material. Hence, it is necessary that the transmission of electromagnetic waves of the UV-Vis-NIR range is measured. From the transmission spectrum as shown in Figure.4 it is observed that the LSSC crystal have good transmission in the entire visible region and the lower cutoff is found to be 206 nm. The absence of absorption in the region between 200-1100 nm shows that this crystals is suitable for optical window applications
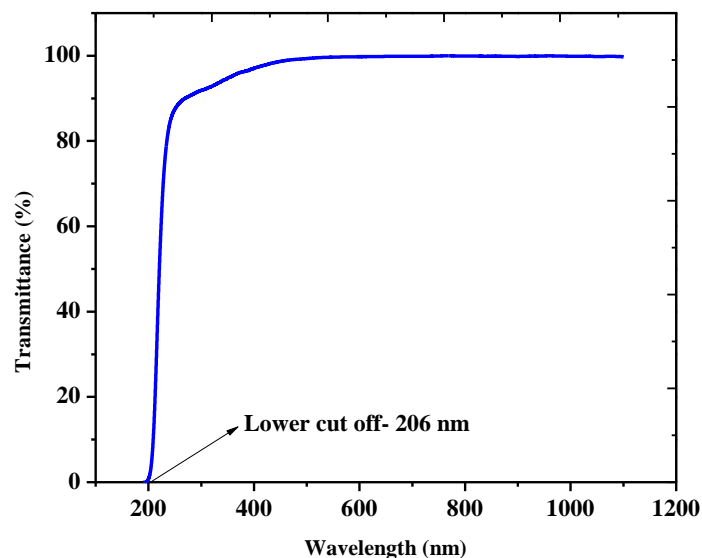

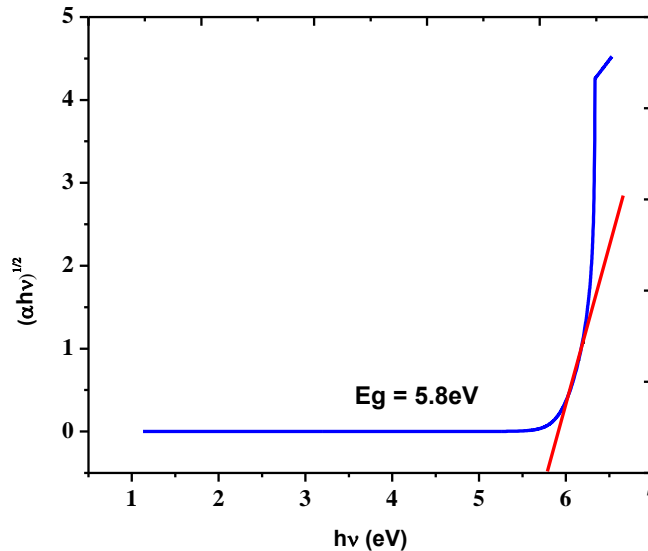Figure.4 Optical transmittance spectrum of LSSC

Figure.5 PL spectrum of LSSC

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and type of transition of electrons. The optical absorption coefficient (Į) was calculated from the transmittance data using the following relation,

$$\alpha = (1/d) \log (1/T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where T is the transmittance and d is the thickness of the crystal. The absorption coefficient (α) is related to band gap energy (Eg) obeying the following relation for high photon energies (hν) as [7],

$$\alpha = A (h\nu – Eg)1/2 / h\nu \quad (2)\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where Eg is the optical band gap of the crystal and A is a constant. Talc's plot of (αhν)2 against photon energy (hν) at room temperature is shown in Figure.5. The linear behavior of the plot is the evidence of indirect transition between valence band and conduction band. Hence, optical band gap (Eg) was estimated by the extrapolation of the linear part of the plot and the band gap energy of the material was found to be 5.8eV. The larger optical band gap shows that the defect concentration in the grown crystal is very low. The internal efficiency of the device also depends upon the absorption coefficient. Hence by tailoring the absorption coefficient and tuning the band gap of the material, one can achieve the desired material which is suitable for fabricating various layers of the optoelectronic devices as our required.

E. PHOTOLUMINESCENCE STUDY

In Photoluminescence (PL) techniques, the spectrum emitted by the radioactive recombination of photo generated minority carriers is used to measure the band gap energy. However a large amount of impurities induces a large free carrier density in the bands. Consequently, a different carrier interaction causes remarkable modification of the line shape and spectral energy of PL spectrum. The emission spectrum of the grown single crystal of LSCC was recorded in the range of 200-800 nm respectively as shown in the Figure.6. The emission peak is observed at 468 nm for the excited wavelength 250 nm. This result indicates that the grown crystal has blue emission [8].
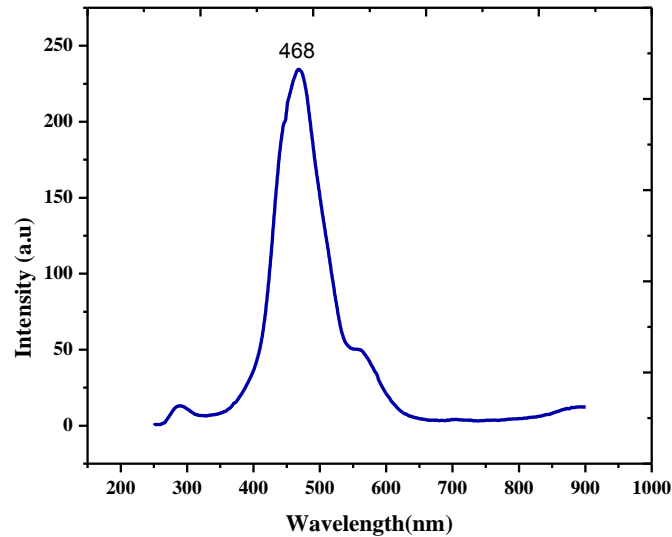
Figure. 6 PL Spectrum of LSSC

F. THERMAL ANALYSIS

Thermo gravimetric and Different thermal analysis give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal. The thermo gravimetric and differential thermal analysis of the crystal was carried out between 0 ^{o}C and 1000 ^{o}C at a heating rate of 10K/min in the nitrogen atmosphere. The resulting spectrum is shown in Figure.7. There is no weight loss up to 150 ^{o}C, hence the material is free of any solvent entrapped in the crystal lattice. A major weight loss was observed just above 150°C.it is assigned to degradation of LSSC. The total degradation occurred in three stages and it is extended up to 930 ^{o}C. There is a sharp endothermic peak with a maximum at 210ºC which corresponds to the major weight loss of about 56.33%. Hence this endothermic peak is assigned to melting point of the compound. The sharp peaks of this endothermic peak show the good degree of crystallinity of the grown crystal. The subsequent endothermic peaks that follow this melting point corresponding to the decomposition of the compound. The TGA and DTA curves for the powder sample of LSSC are shown in Figure.7. From the result of DTA, it is established that no transformation in the structure was observed before melting. Hence the material can be exploited for any suitable application up to its melting (190 ^{o}C).
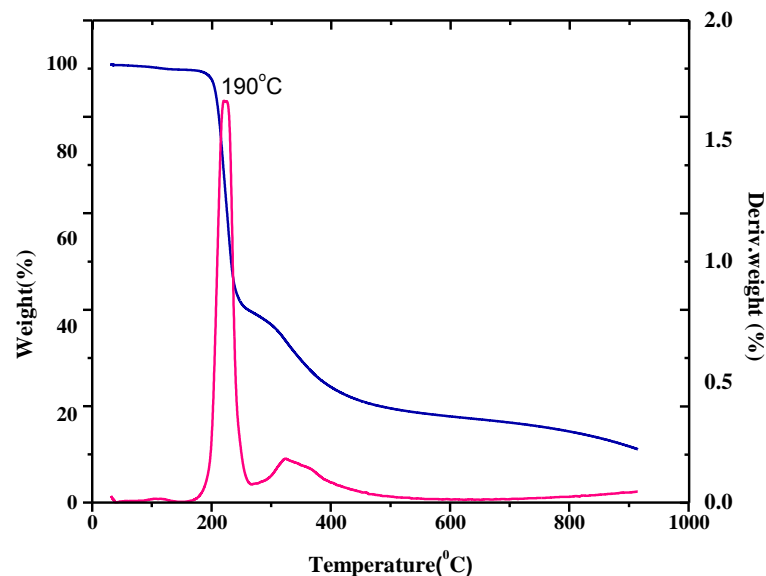

Figure.7. TG and DTA curve of LSSC

G. DIELECTRIC STUDIES

The dielectric studies of LSSC single crystal was carried out using the Numeric Phase sensitive multimeter (PSM) instrument at room temperature. Capacitance values are measured for frequencies varying from 50 Hz to 5MHz. Figure.8 (a) and Figure.8 (b) shows the variations of dielectric constant and dielectric loss with log frequency for LSSC crystal at room temperature. It is observed that the dielectric constant and dielectric loss decreases with increasing log frequency and attains a constant value in the high frequency region. The low value of dielectric constant and dielectric loss in the high frequency suggests that the LSSC crystal possesses enhanced optical quality with lesser defects and these parameters is of vital importance for nonlinear optical materials towards particular applications.
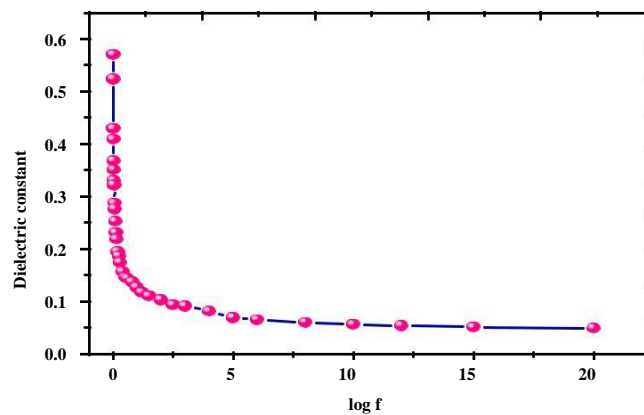

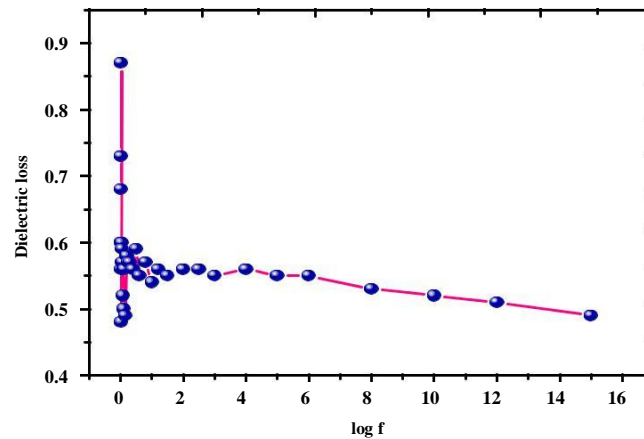Figure.8 (a) Log frequency versus dielectric constant

Figure.8 (b) Log frequency versus dielectric loss

H. SECOND HARMONIC GENERATION (SHG) EFFICIENCY

The relative SHG efficiency of LSSC crystal was determined using Kurtz and Perry powder technique. It enables to measure the SHG efficiency of new materials relative to standard potassium dihydrogen phosphate (KDP). A Q-switched Nd:YAG laser operating at 1064nm and 10ns pulse width with an input repletion rate of 10Hz and energy 1.2mJ/pulse. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532nm from the crystalline powder. The SHG output was converted into electrical signal and was displayed on a digital storage oscilloscope. From the obtained data it is found that SHG efficiency of the grown LSSC sample is 1.96 times greater than that of well-known standard potassium dihydrogen phosphate (KDP).

IV. CONCLUSION

The grown L-serine sodium carbonate (LSSC) single crystal by a slow evaporation method is found to have good NLO property compared to KDP (i.e., Nine times >). Single XRD analysis confirms that the grown crystal belongs toorthorhombic system with space group P_{212121}. The lattice parameters were estimated by single crystal and powder XRD analysis which are in good agreement with the reported values. The presence of various functional groups of thegrown crystal was confirmed by FTIR analysis. The UV-Vis-NIR spectrum shows its wide transparency in the entire visible region having lower cut-off wavelength of 206 nm making it a potential candidate for NLO applications. From the optical absorbance spectrum, the band gap was found to be 5.8 eV. The photoluminescence spectrum is evident for blue emission. Thermal studies indicate that LSSC crystal is thermally stable upto 210°C. Dielectric study indicate that the dielectric constant and dielectric loss decreases with increasing log frequencies at room temperature, which indicates the suitability of LSSC crystal for photonic and nonlinear optical applications.

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