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Synthesis and Physico-Chemical Characterization of Nonlinear Optical Single Crystals of S-Carboxymethyl L-Cysteine for Optoelectronic Devices Applications

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Abstract. The S-carboxymethyl L-cysteine (SCLC) single crystals have been grown through slow evaporation technique. The lattice parameters of SCLC crystal have been determined using Single-crystal X-ray diffraction. From the transmission spectrum, the optical properties of the SCLC crystals have been investigated. The various functional groups of the SCLC crystal have been confirmed using the Fourier-transform infrared spectroscopy (FTIR). The mechanical properties have been studied using Vickers hardness tester. The nonlinear property is identified by Kurtz and Perry. Further, the electrical properties are studied.

Keywords: Nonlinear optical material; Optical transmission; Dielectric and Photoconductivity.

INTRODUCTION

Developing important applications for optical telecommunications and optical signal processing increasingly relies on non-linear optical phenomena that underlie these optical functions, such as frequency conversion and modulation, amplification and emission, multiplexing and directional switching, optical logical gates, and others[1,2]. In this context, organic materials are noteworthy candidates, provided that their microscopic and macroscopic properties are optimized according to the type of application required. The quasi-unlimited variety of molecular structures accessible through organic synthesis, the possibility of connecting specific nonlinear properties with other functionalities of crucial importance in the development of commercial devices and their exceptionally large second-order, non-resonant nonlinear response are key factors in the development of these materials. Such performance depends heavily on a better understanding of 'molecular engineering,' rules, correlating molecular structures with their nonlinear optical properties to optimize microscopic second-order polarizabilities (β) and third-order polarizabilities (γ). Carboxyl group presented as a carboxylate ion and amino group as an ammonium ion shows the existence of L-cysteine as a dipolar ion [3]. L-cysteine also exhibits a high melting point due to this dipolar nature. Thus, in L-cysteine analogs, more prominence is provided by the researchers to create the NLO crystals [4-10]. The present study focuses on the growth of S-carboxymethyl L-cysteine and the study of its optical, mechanical, ferroelectric, and dielectric properties.

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MATERIAL SYNTHESIS

SCLC single crystals are produced using the method of slow evaporation of solvents. S-carboxymethyl L-cysteine is used for AR grade commercial use. A quantity of these materials has been dissolved in the deionized water. Using a Whatman filter, the solution is filtered. The filtered solution is then kept in a dustless environment for controlled evaporation, which lays the foundation for a clean and dustless output. Successive recrystallization process further has increased the synthesized salt's purity. A transparent single crystal-like a needle is harvested over a period of 32 days.

RESULTS AND DISCUSSION

Single Crystal X-ray Diffraction

The unit cell parameters are a=5,079Å, b=9,617Å, c=8,649Å, and β=94.4°. It belongs to the monoclinic system with space group $P2_1$. It is well known that $P2_1$ is a non-centrosymmetric group of space that satisfies the basic and essential material needed for the compound's second-order NLO activity. Fig. 1. displays the ORTEP diagram of SCLC.

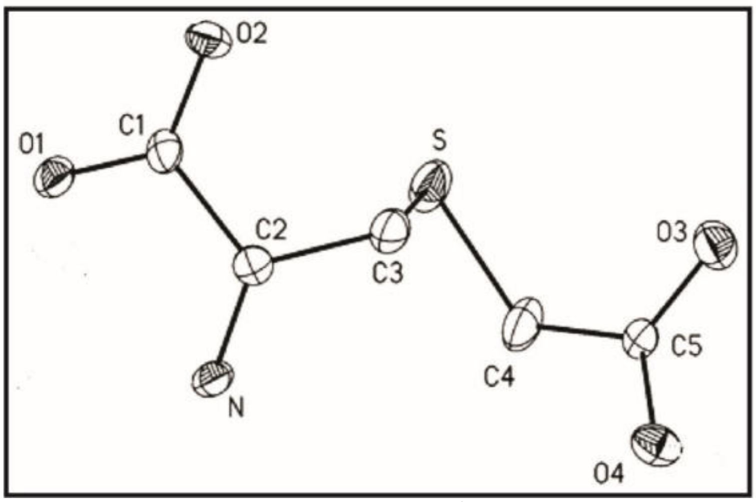

FIGURE 1. ORTEP of SCLC

Powder X-ray diffraction

The powder XRD pattern of the grown crystals is displayed in Fig.2. The significant sharp and strong peak appearance confirms that the prepared crystal has good crystallinity nature. In that view, with the single X-ray diffraction data, the estimated lattice parameters of the grown crystal are well agreed.

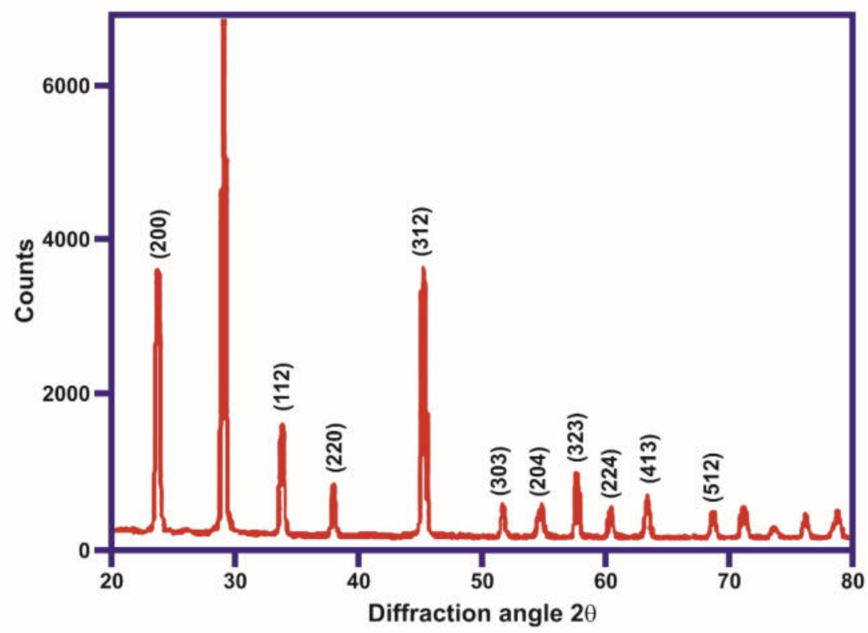

FIGURE 2. Powder XRD pattern of SCLC

FTIR Analysis

Figure 3 shows the FTIR spectrum of SCLC crystal. The characteristic bands of dicarboxylate groups for asymmetric stretching at 1628 and 1592 cm^{-1} and for symmetric stretching at 1428 cm^{-1}. The wideband in this spectrum around 3450 cm^{-1} has confirmed the presence of OH. The NH_3^+ stretching was assigned at 2971 cm^{-1}. The peaks of 1172 and 1048 cm^{-1} reveal the C-N group. The stretching band S-H and C-S appear at 2631cm^{-1}. The group of S-H thiol is attributed at 2924 cm^{-1} [11]. The band of C-S absorption is assigned at 664 cm^{-1}. The N-H bending vibration is assigned at 1569 cm^{-1}. The above discussion also confirms that the sulfur-containing amino acid cysteine is in its Zwitterionic state. The IR spectra also indicate that the carboxylate group is consistent with the crystal structure in different coordination modes.

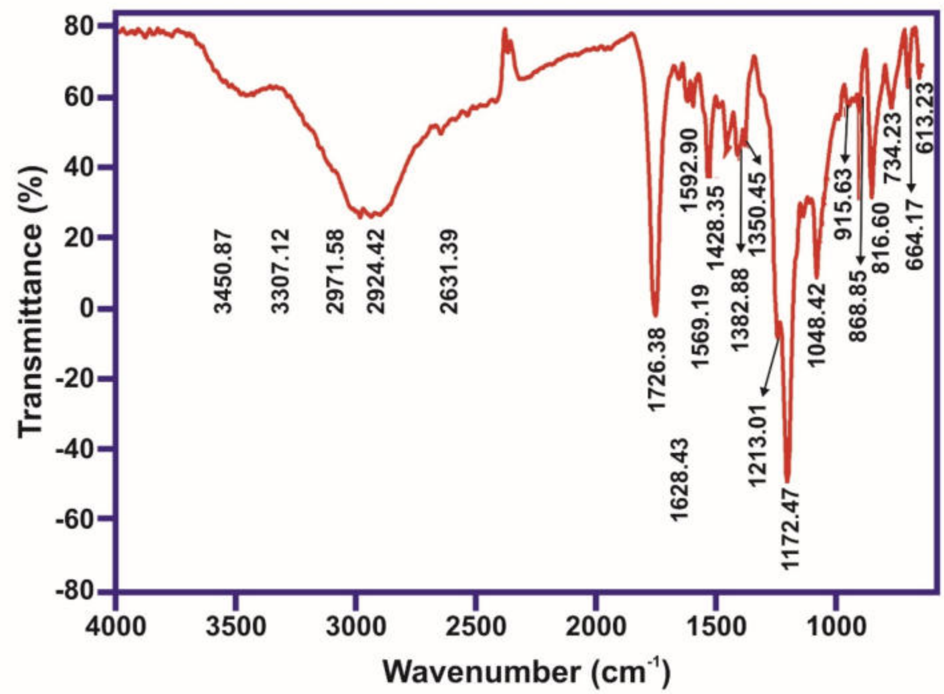

FIGURE 3. FTIR spectrum of SCLC

UV-Vis-NIR Studies

Figure 4 demonstrates the transmission spectrum of the SCLC crystal. The edge of transmission is observed at 273 nm in the lower wavelength region. It is noted that the UV spectrum shows a wide transparency window between 320 -1200 nm at λ_{max} = 273 nm. From the $E_g = 1.243 \times 10^3 / \lambda_{max}$ relationship, the bandgap is calculated to be 4.55 eV, which is the typical value of dielectric material [12,13]. Thus, the analysis of the optical transmission spectrum shows that the SCLC is transparent throughout the visible region without any absorption peak, thus SCLC crystal is useful for electro-optics microelectronic industries and electro-modulators.

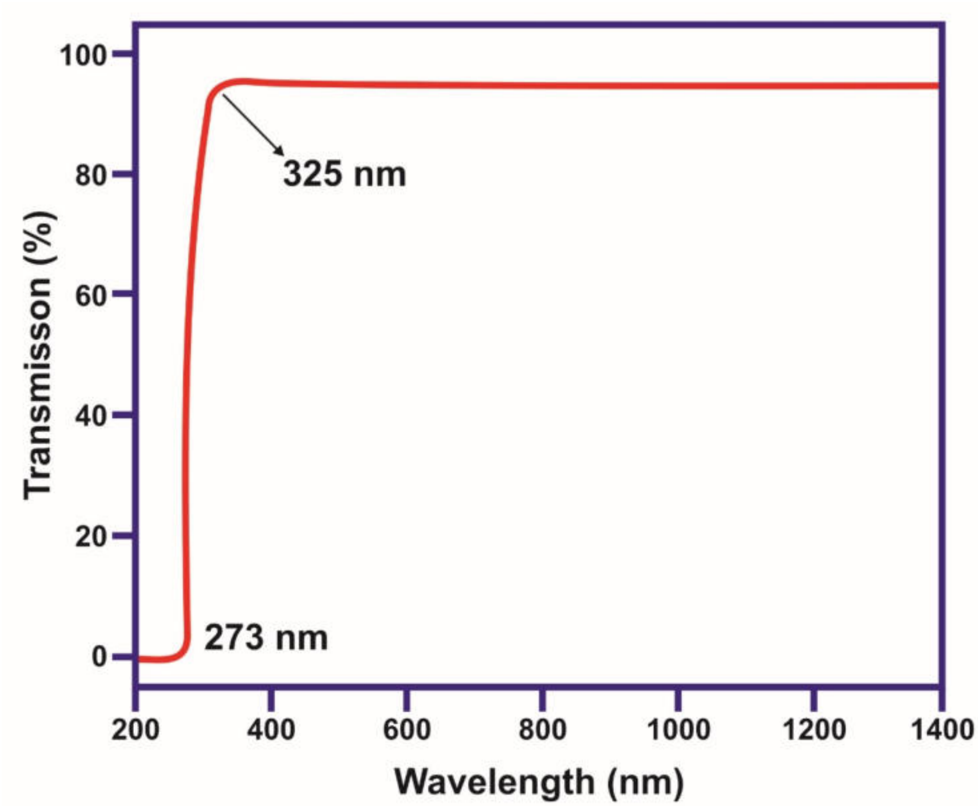

FIGURE 4. The transmission spectrum of SCLC

Second Harmonic Generation Test

The SHG efficiency for the SCLC is measured using the standard Kurtz and Perry powder method [14]. The basic beam of a Q-switched Nd: YAG laser with 1064 nm wavelength, 3.2 mJ input power, 8 ns pulse duration, 10 Hz repeat rate and 1 mm diameter spot size is used. This method is considered as a valuable tool for evaluating the properties of sample homogeneity. Greenlight emission was observed, confirming the non-centrosymmetric nature of the SCLC, which is confirmed by a single crystal XRD analysis.

Vicker's Microhardness Study

Figure 5 shows the change in hardness with the applied load. As the load increases, the hardness increases gradually. Due to the indenter's mechanical stress application, dislocations are generated locally in the region of indentation. Increased crystal hardness value shows that more stress is needed to create dislocations that confirm high crystalline perfection [15]. Meyer index can be calculated by performing least square fit in the graph of log P versus log d as presented in Fig.6. In the present investigation, the calculated value of n is about greater than 2 and demonstrates ISE. According to Onitsch, if $n > 2$ this material belongs to soft category [16]. Hence it is proved that SCLC crystal is soft material.

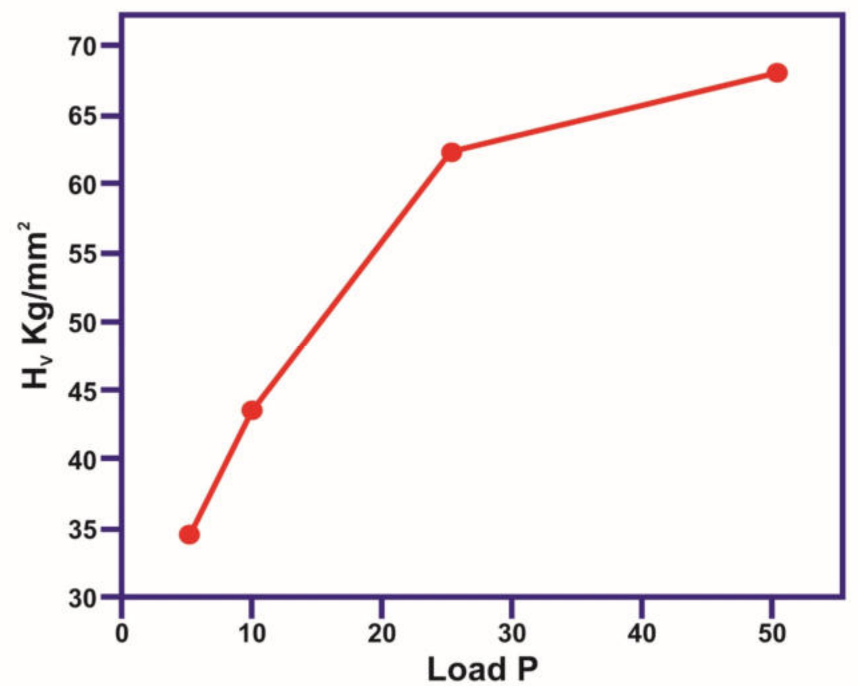

FIGURE 5. Load Vs hardness of SCLC

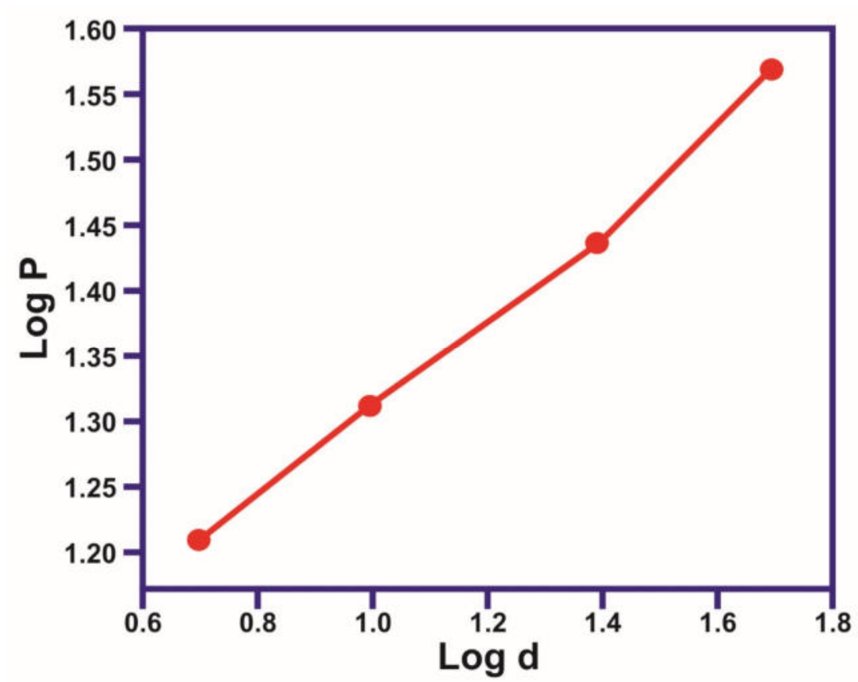

FIGURE 6. log P Vs log d of SCLC

Dielectric analysis

Figure 7(a) and (b) display the dielectric and dielectric loss values obtained for different temperatures values. In both cases, as temperature increases and decreases as frequency increases, the values are found to increase. This is a normal dielectric behavior [17,18]. The electronic exchange of the number of ions in the crystal allows local electrons to be displaced to the applied field [19]. Higher temperature increases are primarily attributable to heat-generated load carriers and impurity dipoles [20]. Figure 7(b) indicates that the dielectric loss at higher frequencies is very low, indicating that there are minimal defects in the grown crystal [21]. The high dielectric constant value at low frequency and high temperature are due to the polarization of the space charge depending on the purity and perfection of the crystal. However, dipolar polarization is more predominantly dependent on temperature than atomic or electronic polarization [22]. However, due to electrode charges, space charging polarization also makes a significant contribution to the low-frequency region. Thermal energy activates more surface load to separate the surface polarization to bound polarization of the load. As a result, the thermal energy net polarization increases. Just as the frequency increases, the polarization of the bound charge becomes more prevalent in comparison to the effects of the surface charge due to the influence of the lattice phonon [23].

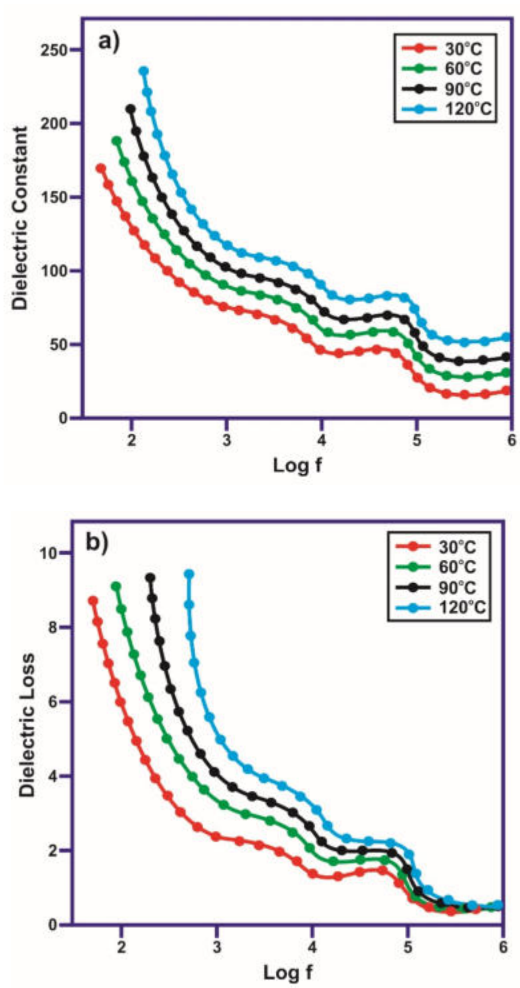

FIGURE 7. a) and b) The plot of log frequency vs. dielectric loss and dielectric constant of SCLC.

Photoconductivity

Figure 8 displays the variation of the dark current as well as the photocurrent with the applied field at different illumination levels. At different fields applied, the current reading was noted. According to the resulted plots, it was seen that both the samples dark current and photocurrent rise linearly with the field applied. At negative photoconductivity (same applied field), the dark current was seen to be higher than the photocurrent. The negative photoconductivity shown by the sample may be due to the reduction in the number of mobile charging carriers in the presence of radiation. The Stockmann model can explain the decline in negative photoconductivity in mobile charging carriers [24]. Meanwhile, in the presence of radiation, the negative photoconductivity in a solid was attributed to the decrease in the number or lifetime of charging carriers [25].

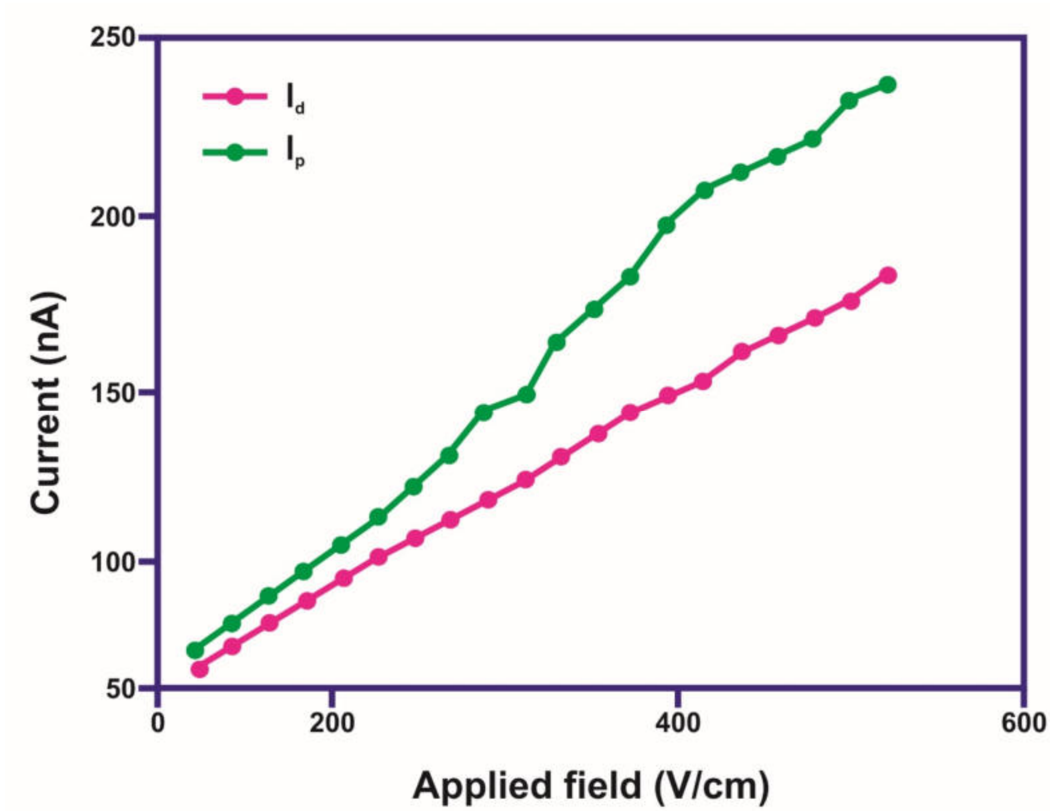

FIGURE 8. Field dependence conductivity of SCLC

CONCLUSION

The slow evaporation method in ambient environments successfully synthesized transparent single crystals of S-carboxymethyl L-cysteine. Single-crystal XRD analysis estimated the lattice parameters. FTIR has confirmed the presence of different functional groups of SCLC. The UV - VIS - NIR transmission spectrum showed that the SCLC was transparent with a lower edge at 273 nm throughout the visible region. The SHG efficiency of SCLC has been tested. The dielectric measurements revealed that for electro-optic modulation, SCLC crystal has a normal dielectric behavior. The analyzed properties demonstrate that SCLC material can be a promising candidate for NLO device applications.

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