Structural, Optical and Thermal Behaviour of Potential NLO Material Towards Device Fabrication

M.PARTHASARATHY *

Department of Physics, Vels Institute of Science, Technology & Advanced Studies (VISTAS), Pallavaram, Chennai 600 117, Tamilnadu, India.

ABSTRACT: Good quality bulk single crystals of L-serine methyl ester hydrochloride were successfully grown using solution growth technique. The grown crystal was confirmed by single crystal and powder X-ray diffraction analyses. The theoretical factor group analysis of the title compound predicts that there are 114 vibrational optical modes and are seen to decompose into $\Gamma_{114} = 56A+55B$ with three acoustic modes (A+2B). The melting point of the material obtained using melting point apparatus is 168°C and thermal stability of was investigated using differential scanning calorimetry analysis. The second harmonic generation was tested by Kurtz-Perry powder method using Nd:YAG laser.

INDEX TERMS : X-ray diffraction; Recrystallization; Characterization; Growth from solutions; Single crystal growth; Nonlinear optic materials.

I. INTRODUCTION

Nonlinear optical (NLO) materials capable of generating the second harmonic frequency, plays an important role in the field of optoelectronics and photonics [1, 2]. Due to the technological importance of these nonlinear crystals, the need for high quality organic crystals has grown dramatically in the last decade. Many natural amino acids individually exhibit the nonlinear optical properties [3] because they have a donor NH_2 and acceptor COOH and also intermolecular charge transfer is possible. L-serine 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 molecular structure of the LSMEHCl crystal is shown in Fig.1. The Esterification of the carboxyl group of amino acids plays an important role in the synthesis of peptides, especially due to the increased solubility in organic solvents [4].
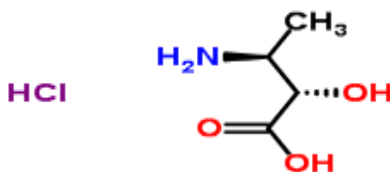

Fig.1. Molecular structure of L-serine methylester hydrochloride

II. MATERIALS AND METHODS

The single crystals of L-serine methyl ester hydrochloride were successfully grown from slow evaporation solution growth technique at room temperature using mixed solvent of methanol and water. Transparent single crystals were obtained from mother solution after   45 days. The as grown crystals are shown in Fig.2.

Fig.2. As grown single crystals of LSMEHCl

The single crystal X-ray diffraction analysis of LSMEHCl crystal was carried out using ENRAF NONIUS CAD4 X-ray diffractometer and its lattice parameters were determined.   A powder X-ray diffraction study was carried out by employing a BRUKER D2 PHASER diffractometer. The theoretical factor group analysis of the title compound was carried out.   UV-Visible spectrum was recorded in the region of 200 – 1100 nm using VARIAN CARY 5E spectrometer. The thermal behaviour was studied by thermogravimetric analysis using a NETZSCH STA 409C/CD thermal analyzer in the nitrogen atmosphere. The melting point of the material was measured by melting point apparatus (VEEGO MODEL: VMP-PM). The second harmonic generation (SHG) of the crystal was tested by Kurtz –Perry powder method.

III.   RESULTS AND DISCUSSION

The single crystal XRD study enumerates that the LSMEHCl belongs to the monoclinic crystal system with a space group $P2_1$ and the lattice parameters are a = 5.217(6) Å,   b = 6.437(7) Å, c = 11.740(14) Å, $\alpha = \gamma = 90°$, $\beta = 90.496(17)°$ and V = 394Å^3. The obtained   single crystal XRD data are in good agreement with the reported literature values [5].

Lattice parameters	Present work	Reported (Arie Schouten and Martin Lutz., 2009)
a	5.217 (6) Å	5.226 (9) Å
b	6.437 (7) Å	6.393 (14) Å
c	11.740 (14) Å	11.642 (4) Å
crystal system with space group	Monoclinic, $P2_1$	Monoclinic, $P2_1$
α	90º	90º
β	90.496 (17)º	90.090 (1)º
γ	90º	90º

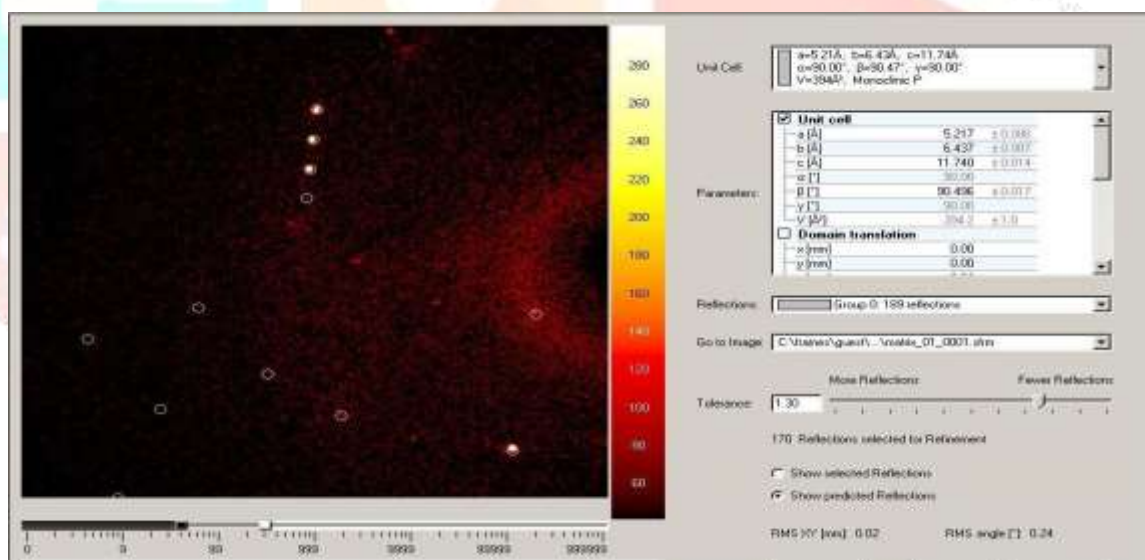**Table 1. Crystallographic data of L-serine methyl ester hydrochloride**

Fig.3. Photographic unit cell parameters view of LSMEHCl

Powder X-ray diffraction analysis has been carried out to confirm the crystallinity and also to identify the lattice parameters and the pattern was recorded for the powdered material in the range 10 - 80° at a scan rate of 1°/min. The obtained X-ray diffraction pattern of LSMEHCl is shown in Fig.4. The intense peaks were indexed using POWDER X software package.
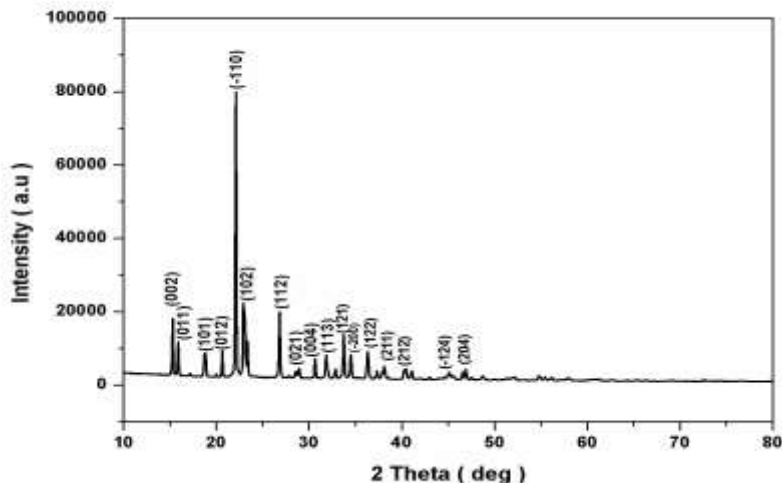
Fig.4. Powder X-ray diffraction pattern of LSMEHCl

The factor group analysis of LSMEHCl was performed by following the procedures outlined by Rousseau et al [6]. LSMEHCl crystallizes in the Monoclinic crystal system with noncentrosymmetric space group $P2_1(C_2^2)$. The primitive unit cell contains two molecules which occupies general sites of C_1 (2) symmetry. A single molecule of LSMEHCl possesses 19 atoms which gives rise to (2×19) 38 atoms in a unit cell. Group theoretical analysis of the fundamental modes of LSMEHCl predicts that there are 114 vibrational optical modes and are seen to decompose into Γ_{114} = 56A+55B along with three acoustic modes (A+2B).

The UV-Vis spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in the σ and π orbital from the ground state to higher energy state. The plot between transmittance and wavelength for LSMEHCl crystal is shown in the Fig.5. The cut off wavelength is observed at 235 nm. The crystal is transparent in the entire visible region between 400 and 1100 nm. The wide range of transmission is an important requirement for a crystal exhibiting NLO behaviour.
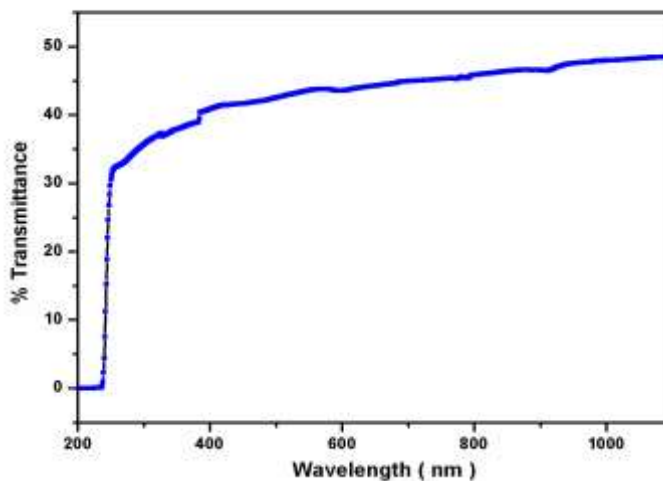

Fig.5. UV-Vis transmission spectrum of LSMEHCl

The powder form of grown LSMEHCl was loaded into a capillary tube and was placed in the melting point apparatus. The material starts melting at 168°C, which indicates the melting temperature of the title material.

This experimentally determined value is in accordance with the data obtained from DSC curve. A sharp endothermic peak was observed at 168°C,that corresponds to melting point of the title compound. The recorded DSC spectrum is shown in Fig.6. Hence the material can be exploited for NLO application up to its melting (168°C).
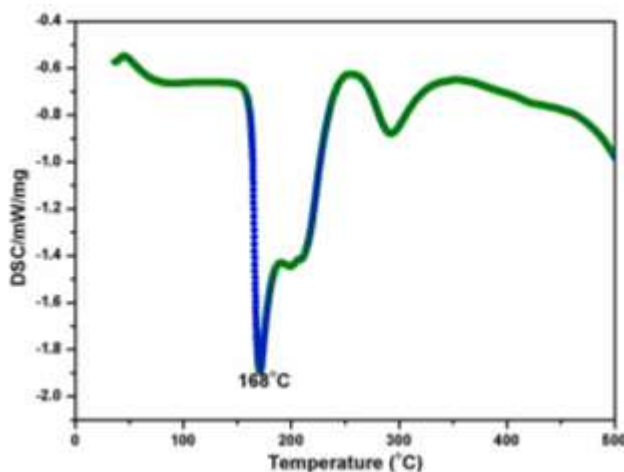

Fig.6. DSC spectrum of LSMEHCl

The SHG efficiency of the title compound was determined using Kurtz and Perry powder technique [7]. A Q-switched Nd:YAG laser operating at 1064 nm and 8 ns pulse width with an input repetition rate of 10 Hz and energy 0.68 mJ/pulse. Potassium dihydrogen phosphate (KDP) was used as the reference material. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm from the crystalline powder. The continuous increase of SHG with increase of particle size confirms the phase matching behaviour of the material [8].

IV. CONCLUSION

Optical quality single crystals of L-serine methyl ester hydrochloride were grown by solution technique. The single crystal XRD study reveals that it belongs to the Monoclinic crystal system. The theoretical factor group analysis of the title compound predicts that there are 114 vibrational optical modes and are seen to decompose into $\Gamma_{114} = 56A+55B$ with three acoustic modes (A+2B). Optical transmission spectra revealed the optical properties of the grown crystal. Thermal studies indicate that the title material suitability for NLO applications up to 168°C. Hence the crystal could be a potential material for the nonlinear optical applications.

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