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Growth and characterization of new semi-organic L-proline strontium chloride monohydrate single crystals

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ABSTRACT

The present communication deals with the synthesis, single crystal growth and characterization of a new nonlinear optical material L-proline strontium chloride monohydrate (L-PSCM). Single crystals have been grown using the slow solvent evaporation technique. Single crystal XRD analysis confirmed that the crystal belongs to the orthorhombic structure with lattice parameter $a=6.6966(3)$ Å, $b=12.4530(5)$ Å, $c=15.2432(5)$ Å and space group $P2_12_12_1$. Presence of various functional groups in L-PSCM and protonation of the ions were confirmed by Fourier transform infrared spectroscopy (FT-IR) analysis. The melting point of the single crystal was found to be 126 °C using DSC. Ultraviolet–visible spectral analyses showed that the crystal has low UV cut-off at 226 nm combined with very good transparency of 90% in a wide range. The optical band gap was estimated to be 5.82 eV. Capacitance and dielectric-loss measurements were carried out at different temperatures in the frequency range 1 kHz–2 MHz. The dielectric constant and loss factor were found to be 21 and 0.03 at 1 kHz at room temperature, respectively. Microhardness mechanical studies show that hardness number (H_v) increases with load for L-PSCM single crystals the by Vickers microhardness method. Second harmonic generation (SHG) efficiency was found to be 0.078 times the value of KDP.

1. Introduction

In the recent past, there have been extensive efforts for the growth of new semi-organic single crystal by researchers because of its potential applications in the nonlinear optical field and in opto-electronic devices. Research on the synthesis of organic and inorganic complexes increased significantly in the last few years [1,2]. The key factor for material selection depends on the physical properties of the crystals and the prospects of their various applications. Specifically, amino acids and strong inorganic acids are good raw materials to produce semi-organic crystals because amino acid crystals have good optical properties such as optical modulation, optical switching, optical logic, frequency shifting, and optical data storage for developing technologies in telecommunications and signal processing [3–5]. L-proline is an abundant amino acid in collagen and is exceptional among the amino acids because it is the only one in which the amino group is a part of the pyrrolidine ring, making it rigid and directional in other biological system [6]. Semi-organic crystals play an essential role in NLO applications such as L-arginine phosphate monohydrate (LAP), D-LAP, L-arginine hydrochloride (LAHC), L-histidine bromide (LHB), L-histidine tetraflouroborate (LHFB), L-phenylalanine L-phenyl-alaninium perchlorate L-arginine dihydrofluoride [7–13], etc., which are some of the interesting nonlinear optical (NLO) materials for which single crystals have already been grown and characterized. However, only a few papers are reported on L-proline complexes such as L-proline cadmium chloride (L-PCC), dichlorobis (L-proline) zinc(II) and l-proline Llithium chloride monohydrate (L-PLCM), which exhibit NLO properties as well as good physical and chemical properties [14–16]. In this class of materials, L-proline strontium chloride monohydrate is found to be a promising crystal for various applications. We have also characterized the samples for their structural, optical, SHG, hardness, and dielectric properties.

2. Experimental details

L-PSCM crystals were grown from an aqueous solution using the slow evaporation technique. L-proline molecule has two groups (a guanadyl and amino), which can be protonated. The starting material was synthesized by taking L-proline and strontium chloride at 1:1 stoichiometric ratio in distilled water used as a solvent. The following reaction is expected to take place, giving the required compound:

$$C_5H_9NO_2 + SrCl_2 \cdot H_2O \rightarrow C_5H_{11}SrNO_3^+, 2Cl^-$$

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A calculated amount of strontium chloride and L-proline was added to water according to their solubility and finally the whole solution was stirred for 2 h using a magnetic stirrer to obtain a homogeneous mixture. The completely dissolved solution was filtered using filter paper to remove the suspended impurities and allowed to crystallize by slow evaporation of the solvent at 30 °C for about 60 days. Well-defined single crystals of good transparency were collected. Single XRD was taken at room temperature using an Oxford single X-ray diffractometer with MoKα radiation (λ=0.71073). FT-IR spectra were recorded using the Perkin Elmer Spectrum BX in the range 400–4000 cm^{-1} at 4 cm^{-1} resolutions using KBr pellets. The UV–vis transmittance spectrum was recorded with a SHIMADZU UV-2501 PC in the range 200–800 nm. Thermal behavior of the sample was studied by differential scanning calorimetry using a Diamond Perkin Elmer system in the temperature range RT—300 °C at a heating rate of 10 °C/min. An open alumina container in nitrogen atmosphere was used. Dielectric constant and loss of L-PSCM were measured using an Agilent E 4980A LCR meter for a frequency range 1 kHz–2 MHz in the temperature range (RT—65 °C). The NLO behavior of grown L-PSCM crystals was tested by the Kurtz powder method [17].

3. Results and discussion

3.1. Single crystal XRD

Single crystals of L-proline strontium chloride monohydrate are shown in Fig. 1a. Single crystal XRD studies of the L-PSCM single crystals are carried out using an Oxford-Diffraction XCallibur with a sapphire CCD detector and Enhance diffractometer (MoKα radiation, graphite monochromator; λ=0.71073 Å). The structure was solved by the direct method and refined by the full matrix least-square technique using the SHELXL-97 program [18–20]. The diagram of the structure was obtained through the ORTEP program [21] and the molecular structure of L-PSCM single crystal is shown in Fig. 1b. The lattice parameters from single crystal X-ray data of L-PSCM crystal are shown in Table 1.

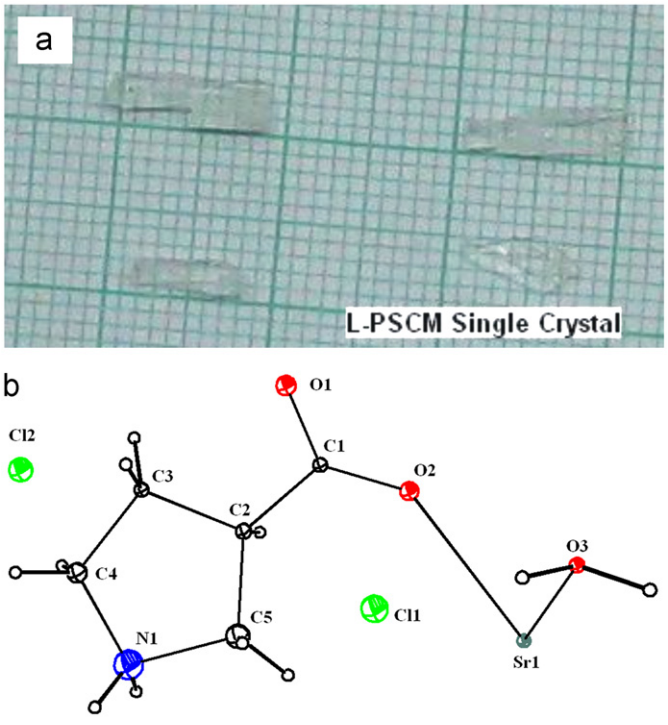

Fig. 1. (a) As grown L-PSCM single crystal. (b) Molecular structure of L-PSCM single crystal.

3.2. FT-IR study

For qualitative analysis of various functional groups in L-PSCM, the FT-IR spectrum was obtained in the range 4000–400 cm^{-1}. The observed spectrum is shown in Fig. 2. The vibrational frequency of various functional groups of L-PSCM and the tentative frequency assignment are presented in Table 2. In the high energy region, there is a broad band between 3700 and 2900 cm^{-1}, with a small intense peak at 3172 cm^{-1} due to O–H (–H_2O) vibration. Absorption in the 2741–2474 cm^{-1} region resulted from superimposed O–H and

Table 1
Crystal data and structure refinement by SHELXL-97 software.

Empirical formula	$C_5H_{11}SrNO_3^+,2Cl^{-1}$
Molecular weight	291.67
Crystal system	Orthorhombic
a	6.6966(3) Å
b	12.4530 (5) Å
c	15.2432 (5) Å
Space group	$P2_12_12_1$
α	90°
β	90°
γ	90°
Volume	1271.99
Z	4
Temperature	293 K
R	0.148

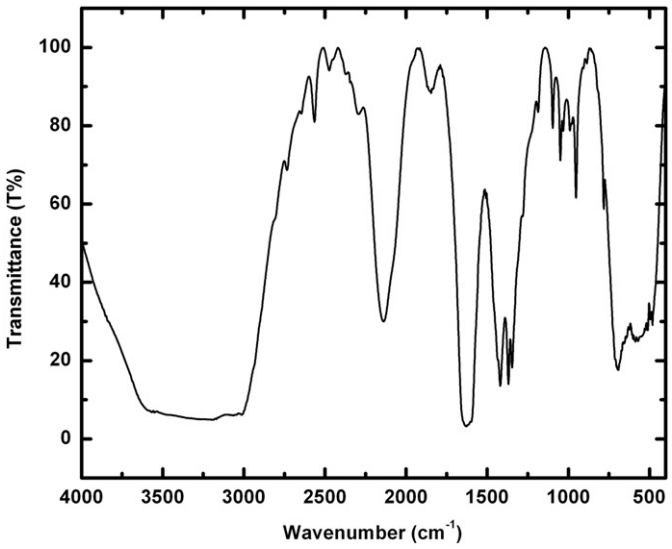

Fig. 2. FT-IR spectral band assignment of L-PSCM single crystal.

Table 2
Vibrational band assignments of L-PSCM.

Wave number (cm^{-1})	Assignments
2741, 2565, 2474	Superimposed O–H and NH_2^+ stretching bands
1628	(NH_2^+) asymmetric stretching
1419	Symmetric mode of COO^- and C–N stretching
1369, 1334	(NH_2^+) symmetric stretching
1100	(CH_2^+) wagging
1045	(C–N) symmetric stretching
954	(CH_2^+) rocking
691	COO^- wagging