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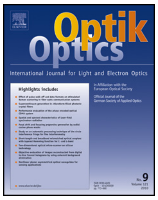

Growth and characterization of L-Histidinium chloroacetate (LHCA): A new nonlinear optical material

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ABSTRACT

A new second order NLO semiorganic crystalline material L-Histidinium trichloroacetate LHCA with the chemical formula $\{[(C_3N_2H_4)CH_2CH(NH_3)(CO_2)]^+CH_2ClCOO^-\}$ was synthesized and single crystals were grown in first time by slow solvent evaporation technique in an aqueous solution medium at ambient temperature. The grown crystal of dimension $10 \times 11 \times 12\,mm^3$ was harvested in a period of 30 days. Single crystal X-ray diffraction data reveals that the crystal belongs to the triclinic system with non-centrosymmetric space group P_1. The peaks in powder X-ray diffractogram were indexed corresponding to the (*hkl*) plane orientations showing the crystalline purity and perfection. The characteristic vibrational frequencies corresponding to functional groups in LHCA molecule were confirmed by FTIR spectral analysis. The locations of hydrogens attached with different chemical moieties were identified by their resonance in $_1H^1$ NMR spectrum. UV – vis – NIR spectrum shows LHCA has lower cut-off wavelength at 220 nm in UV region and the direct optical band gap energy of 3.52 eV. Dielectric behavior of the LHCA crystal was studied for various frequencies at different temperatures. SHG efficiency was found to be 1.8 times greater than KDP. TG/DSC curve reveals that LHCA possess good thermal stability compared with most of the organic compounds. Mechanical strength of the crystal was studied by Vicker's hardness Test.

1. Introduction

Today's technology is seeing a rapid change and its reflection on materials is splendid. The technological development to a larger extent is dependent on the development of crystal growth. Hence the growth of single crystals has become inevitable for any further development in materials science research. Large size single crystals are essential for device fabrication: polarizers, transducers, infrared detectors, ultrasonic amplifiers, ferides, solid state lasers, acousto-optic materials and in computer industries [1–4]. Moreover, nonlinear optical materials find immense applications in telecommunication, optical computing, optical data storage and optical information processing [5–7]. Organic NLO materials including high optical nonlinearities, fast response time, facile modification of molecular properties through precise synthetic methods and high optical damage thresholds. However, the transfer of these materials into actual devices is not straight forward, as stringer requirements such as noncentrosymmetric packing of NLO chromophores, low optical losses from either absorption or scattering and environmental and photochemical stabilities have to be considered. Even if noncentrosymmetric was to be achieved, the NLO chromophores need to be packed with an ideal orientation in the crystals in order to attain a maximum efficiency with phase matching conditions [8,9]. NLO crystals are expected to posses the advantage of both inorganic and organic materials. 'Semiorganic' is salt in which typically high optical nonlinearity of a purely organic ion is combined with the favorable mechanical and thermal properties of an inorganic counter ion. In semiorganic, polarizable organic molecules are stoichiometrically bond within inorganic host molecules [10,11]. Other critical material properties including favorable crystal growth properties, high optical damage threshold, large thermal conductivity, adequate birefringence for phase matching and good mechanical characteristics. A major advantage of most salts is that, their ionic bonding network provides a high degree of mechanical integrity and increases the like hood of favorable growth and mechanical properties for the resulting crystals. Further many of these crystals

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are rapidly grown from solution, thus providing a means for economically obtaining large aperture, optically homogeneous, high damage threshold crystals. Perhaps of greatest significance, however, is the high degree of chemical flexibility of an ionic salt approach. Ionic salt materials offer an important and extremely flexible approach for the development of new material applicable over a very broad range of frequencies [12]. In this report, amino acids are interesting materials for NLO applications. Most of the natural amino acids show nonlinear optical effect. The tetrahedral array of four different groups about α-carbon atom consist optical actively amino acid. In solid state, amino acid contains a deprotonated carboxyl acid group (COO^-) and protonated amino group (NH_3^+). This zwitterionic nature favors crystals hardness, thus making them ideal candidates for NLO devices. But amino acids are organic materials, so they can have very large nonlinear susceptibilities relative to inorganic crystals but exhibit low damage thresholds and poor processibility. In recent years, efforts have been made to synthesize amino acid mixed organic – inorganic complex crystals in order to improve the chemical stability, laser damage threshold linear and nonlinear optical properties [13–18]. A number of authors have reported L-Histidine family crystals and its analogues [19]. Dhanuskodi et al. have crystallized L-Histidine tetrafluoroborate. Its SHG efficiency was found to be 5 times greater than KDP [20]. The growth of L-Histidinium perchlorate, a semiorganic NLO crystal having high thermal stability upto 272 °C was reported [21]. L-Histidine tetrafluoroborate crystal shows high transmittance in UV region and its lower cut-off wavelength was found to be 232 nm [22]. L-Histidine hydrochloride monohydrate, a novel semiorganic NLO crystal crystallizes in noncentrosymmetric orthorhombic space group [23]. L-Histidinium 2-nitro benzoate crystallizes in monoclinc $P2_1$ space group and its SHG efficiency was observed that 2.2 times greater than that of KDP [24]. L-Histidinium dinitrate has wide transparency region 260 – 1100 nm is suitable for optical applications [25]. L-Histidinium trichloroacetate crystallizes in monoclinic $P2_1$ of monoclinic system [26]. In a similar way L-Histidinium chloroacetate, a new NLO material is chosen for the study. The title compound LHCA is a potential candidate for such useful properties, since it contains molecular units with delocalized π-electrons and additional electron donor and electron acceptor group. The aim of the present work is to study the structural properties of LHCA by XRD analyses and to study its vibrational frequencies by FTIR, proton NMR, spectral analyses. Hence, attempt has been made to investigate its optical behavior through UV – vis – NIR study. The electro-optic properties have been studied by Dielectric measurement. The Kurtz – Perry powder test has been carried out to test the SHG efficiency.

2. Experimental

2.1. Material synthesis and preparation

L-Histidine chloroacetic acid was synthesized by aqueous solution containing stoichiometric amounts of L-Histidine and chloroacetic acid. First a homogeneous solution of L-Histidine was prepared by dissolving required amount of L-Histidine acid in doubly deionized water with constant stirring at 45 °C for 2 h. To this solution of L-Histidine, required quantity of chloroacetic acid solution was added with constant stirring and heating at 50 °C for another 4 – 5 h. The resultant solution was filtered and pH of the solution measured to be 6.37. The crystalline salt of L-Histidinium chloroacetate (LHCA) has been taken as raw material. The reaction scheme for preparing L-Histidinium chloroacetate (LHCA) is shown in Fig. 1. Saturated LHCA solution was prepared at room temperature with water as solvent. LHCA is found to have positive gradient of solubility. Fig. 2 shows the solubility curve for LHCA crystal. The prepared solution was filtered with a micro filter. The solution was taken in vessels closed with perforated cover and kept in a dust-free atmosphere. The crystals were harvested when they attained an optimal size and shape in a week. The grown crystals are transparent, defect free, optical good quality crystals of dimensions 10 × 11 × 12 mm^3 were harvested in a period of a month time. The photograph of as grown LHCA NLO single crystal is shown in Fig. 3.

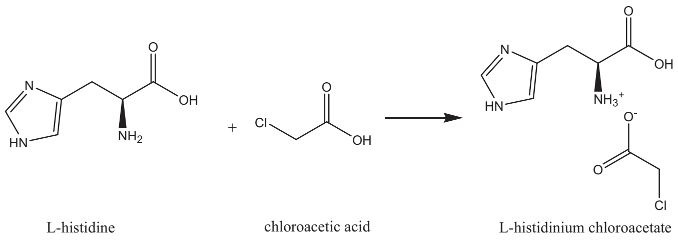

Fig. 1. Reaction scheme for L-Histidinium chloroacetate.

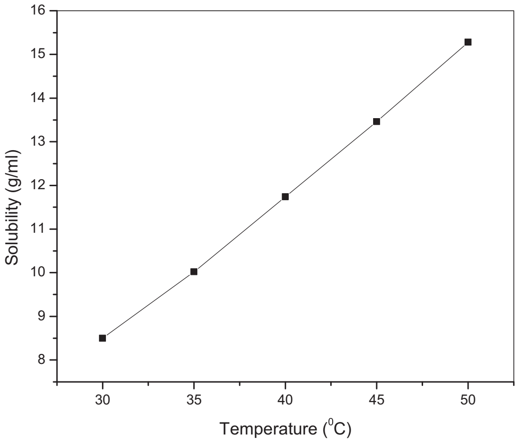

Fig. 2. Solubility curve for L-Histidinium chloroacetate.

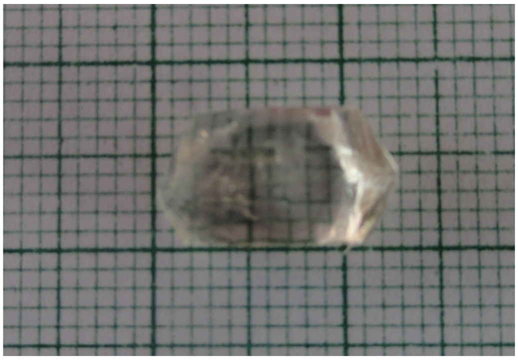

Fig. 3. Photograph of as grown LHCA NLO single crystal by slow evaporation method.

3. Characterization

3.1. Single crystal X-ray diffraction

A good transparent LHCA crystal is subjected to single crystal X-ray diffraction (MESSRS ENRAF NOXIIUS, The Netherlands). $M_0K\alpha$ radiation source with graphite monochromator was used. The structure was solved and refined by SHELXL- 97. The cell parameters determined for LHCA are $a = 6.883\ (7)$ Å, $b = 8.981\ (8)$ Å, $c = 15.386$ Å, $\alpha = 90.014\ (13)$, $\beta = 89.989\ (17)$, $\gamma = 89.99\ (3)$ and $V = 951.10\ mm^3$. It is concluded from X-ray data that LHCA crystal is triclinic with P_1 space group.