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Spectral, optical and mechanical studies on L-histidine hydrochloride monohydrate (LHC) single crystals grown by unidirectional growth technique

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ABSTRACT

Single crystals of nonlinear optical L-histidine hydrochloride monohydrate (LHC) were grown in an aqueous solution by the unidirectional crystal growth method within a period of 45 days along (1 0 1) plane. The grown crystals were subjected to single crystal X-ray diffraction analysis to confirm their orthorhombic structure having space group $P2_12_12_1$. Values of several physical parameters were determined for the grown crystal. Optical transmission studies revealed very low absorption and band gap energy was calculated for the LHC crystals. Further, some optical constant were also determined for the grown crystals. Anisotropy in Vicker's microhardness led to the assessment of fracture toughness, brittleness index and yield strength for the synthesized crystals. Nonlinear optical studies were carried out for the grown crystal and second harmonic generation (SHG) efficiency was found to be three times that of KDP crystals.

1. Introduction

In the recent years, there has been considerable interest among scientists in the development of novel nonlinear optical (NLO) materials, which combine high optical nonlinearity and chemical flexibility of organics with high mechanical strength of inorganics [1–3]. The key factors for material selection depend not only on laser conditions but also on physical properties of the crystal, such as transparency, damage threshold, phase matching, conversion efficiency and temperature stability [4,5]. In view of this, considerable interest has been evidenced in the synthesis of semi-organic materials due to their high nonlinearity, high resistance to laser induced damage, low angular sensitivity and good thermal and mechanical properties [6–8]. Besides second harmonic generation (SHG), such kinds of crystals may be interesting for field-induced optical and nonlinear optical effects [9,10]. L-Histidine hydrochloride monohydrate ($C_6H_9N_3O_2$ $HCl.H_2O$) (LHC) belongs to one such class of semi-organic nonlinear optical crystal, which crystallizes in the orthorhombic structure with the space group $P2_12_12_1$ [11,12]. In the present work, using a modified Sankaranarayanan–Ramasamy (mSR) method [13,14], single crystals of LHC were grown and the grown crystals were subjected to theoretical, optical and mechanical studies.

2. Experiment

2.1. Synthesis and growth of seed crystals

L-Histidine hydrochloride monohydrate crystals were synthesized by mixing L-Histidine (Merck) and hydrochloric acid (AR grade) in an aqueous solution in the ratio of 1:1. By repeated re-crystallization, purity of the synthesized salt was further increased and the supersaturated solution of LHC was kept undisturbed at room temperature. Optically transparent defect free seed crystal was obtained within a period of 20 days, which was chosen for unidirectional growth along (1 0 1) plane.

2.2. Experimental setup and crystal growth

An optically good quality seed crystal was mounted on the bottom of an ampoule, filled with supersaturated solution of LHC and placed along the axis of the growth assembly. Here, an assembly of alternating 40 W filament lamps provides a temperature gradient for the growth. Temperature at the top of the ampoule was maintained at 45 °C using a temperature controller setup for evaporation of the saturated solution.

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Fig. 1. Photograph of grown LHC single crystals.

To maintain steady temperature around the ampoule, it was rotated 90° per second using a stepper motor along the axis of the growth setup. The temperature gradient makes the concentration gradient maximum at the bottom and minimum at the top of the ampoule for avoiding spurious nucleation along the axis of the ampoule. Growth rate of the crystal was found to be around 1.45 mm per day. Crystals of 65 mm length and 12 mm diameter have been grown successfully within a period of 45 days. Morphology of the grown crystal is like that of the growth vessel. A photograph of the grown crystal is shown in Fig. 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction analysis for the grown crystal was carried out using an ENRAF NONIUS CAD-4 X-ray diffractometer. This analysis reveals that the LHC crystal had the orthorhombic structure with the space group $P2_12_12_1$ and lattice parameters in Å are found to be $a=6.729$, $b=15.116$ and $c=8.513$, which agree well with reported values [15]. Valence electron plasma energy, $\eta\omega_p$, is given by

$$\eta\omega_p = 28.8(Z\rho/M)^{1/2} \quad (1)$$

where $Z=(6Z_C)+(12Z_H)+(3Z_N)+(3Z_O)+(1Z_{Cl})=50$ is the total number of valence electrons, ρ the density and M the molecular weight of the LHC crystal. Explicitly dependent on $\eta\omega_p$ are Penn gap and Fermi energy [16], as given by

$$E_p = \frac{\eta\omega_p}{(\varepsilon_\infty - 1)^{1/2}} \quad (2)$$

and

$$E_F = 0.2948(\eta\omega_p)^{4/3} \quad (3)$$

Polarizability α is obtained using the relation [17]

$$\alpha = \left[\frac{(\eta\omega_p)^2 S_0}{(\eta\omega_p)^2 S_0 + 3E_p{}^2}\right]\frac{M}{\rho} \times 0.396 \times 10^{-24}\,\mathrm{cm}^3 \quad (4)$$

where S_0 is a constant for the material, which is given by

$$S_0 = 1 - \left[\frac{E_p}{4E_F}\right] + \frac{1}{3}\left[\frac{E_p}{4E_F}\right]^2 \quad (5)$$

The value of α so obtained agrees well with that of Clausius–Mossotti equation, which is given by

$$\alpha = \frac{3M}{4\pi N_a \rho}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right) \quad (6)$$

All these calculated data for the grown crystal are shown in Table 1.

3.2. Optical transmission studies

The optical transmission spectrum of L-histidine hydrochloride monohydrate (LHC) single crystal was recorded in the wavelength region 200–1100 nm and is shown in Fig. 2. For optical fabrications, the crystal should be highly transparent in the considered region of wavelength [18,19]. Favorable transmittance of the crystal in the entire visible region suggests its suitability for second harmonic generation [20,21]. The UV absorption edge for the grown crystal was observed to be around 240 nm. The dependence of optical absorption coefficient on photon energy helps to study the band structure and type of transition of electrons [22].

Optical absorption coefficient (α) was calculated from transmittance using the following relation:

$$\alpha = \frac{1}{t}\log\left(\frac{1}{T}\right) \quad (7)$$

where T is the transmittance and t the thickness of the crystal.

As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$):

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (8)$$

where E_g is the optical band gap of the crystal and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig. 3. E_g is evaluated using extrapolation of the linear part [23]. The energy

Table 1
Theoretical data on LHC single crystals.

Parameters	Values
Plasma energy (eV)	12.34
Penn gap (eV)	2.83
Fermi energy (eV)	28.51
Polarizability (cm^3)	
Penn analysis	0.9279×10^{-22}
Clausious–Mossotti	0.9324×10^{-22}

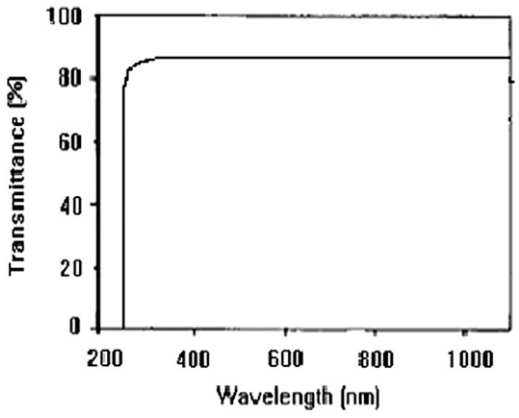

Fig. 2. Optical transmission spectrum of LHC crystals.