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Investigations on the Structural, Optical and Dielectric Behavior of L-Histidinium per chlorate: A Nonlinear Optical Single Crystal

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Abstract:- L-Histidinium perchlorate (LHPCL) a nonlinear optical single crystal was synthesized at ambient temperature. The solubility of LHPCL in water at varying temperatures was determined. Bulk single crystals were grown by the slow evaporation method at constant temperature. Powder X-ray diffraction patterns of the grown crystals were recorded and indexed. The UV cut-off of frequency was identified from the UV–Vis-NIR absorption spectrum. Nonlinear optical study reveals that the Second Harmonic Generation (SHG) efficiency of LHPCL is nearly 3.4 times that of KDP.

Keywords:- NLO, LHPCL, Dielectric studies

I. INTRODUCTION

In recent decades, more attention has been paid towards organic nonlinear optical materials because of their wide transparency in UV and visible region, high nonlinear susceptibility, high laser damage threshold and fast response than the commercially available inorganic materials. By molecular engineering, one can develop many organic crystals displaying better nonlinear optical properties than the inorganic materials, in particular for Second Harmonic Generation [1, 2]. Complexes of amino acids with inorganic acids / salts are promising materials for optical second harmonic generation as they tend to combine the advantages of the organic amino acid with that of the inorganic acid. Histidine is the only standard amino acid having an imidazole side chain with pKa near neutrality. In many enzyme catalyzed reactions, histidine residue facilitates the reaction by serving as a proton donor or acceptor. The function and role of histidine and its residues in living matter is characterized by the imidazole group. In the present paper, we report the optimization conditions for the growth of good quality single crystal of LHPCL by slow evaporation method. The grown single crystal of LHPCL was subjected to various characterization techniques like X-ray powder diffraction, UV-Vis-NIR spectroscopy, dielectric and SHG studies.

II. EXPERIMENTAL PROCEDURE

2.1 Synthesis of LHPCL

LHPCL was synthesized by dissolving stoichiometric amount of a basic amino acid L-histidine (Merck-99%) and high purity perchloric acid in deionized water. To ensure high purity, the material was purified by successive crystallization twice or thrice, using deionized water.

2.2 Solubility determination

In solution growth technique, the size of a crystal depends on the amount of the material available in the solution, which in turn is decided by the solubility of the material in the solvent. Recrystallized salt was used for the studies. Solubility of LHPCL was determined by dissolving the solute in deionized water in an airtight container maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was estimated gravimetrically. The same process was repeated for different temperatures (30, 35, 40, 45 and 50°C). The variation of solubility with temperature is shown in Figure 1.

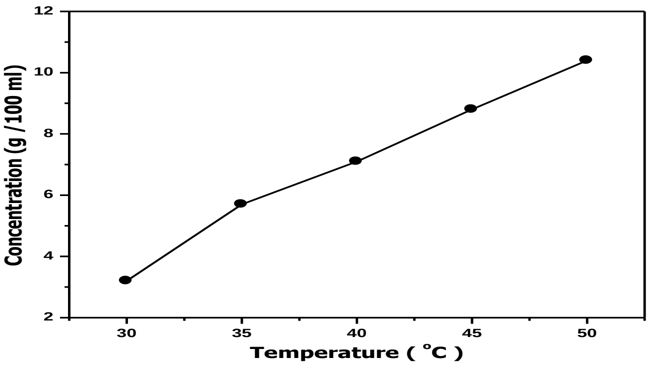

Figure 1 Solubility curve of LHPCL

2.3 Growth of LHPCL crystals

Single crystals with perfect external shape were obtained by spontaneous nucleation. Good quality crystals, free from macro defects were chosen as seeds to carry out the further growth experiments. From the mother solution, a relatively large size crystal was successfully grown in a period of 25 days. Figure 2 shows the photograph of the as grown single crystal of LHPCL.

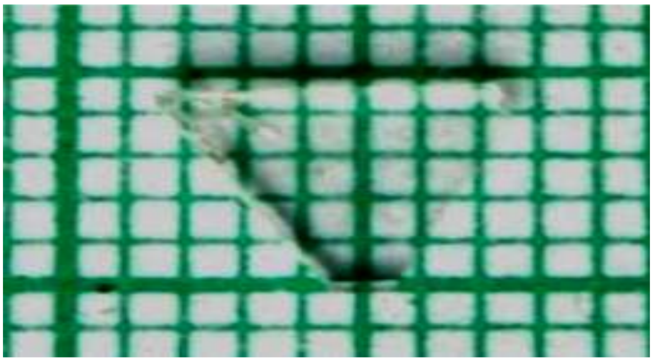

Figure 2 Photograph of as grown single crystal of LHPCL

III. RESULTS AND DISCUSSION

3.1 Powder X-ray diffraction analysis

Powder X-ray diffraction analysis (PXRD) was carried out using an X-ray diffractometer, MODEL RICH SEIFERT, XRD 3000P with monochromatic nickel filtered CuK_{α} (λ = 0.15406 nm) radiation. The sample was scanned over the range 10 - 40° at the rate of one degree/minute. The recorded powder X-ray diffraction pattern of LHPCL is shown in Figure 3. The XRD data of LHPCL indicates that it crystallizes in the monoclinic system with $P2_1$ space group. The XRD data of LHPCL single crystal is given in Table 1. The data of the present work is in good agreement with the reported values [3].

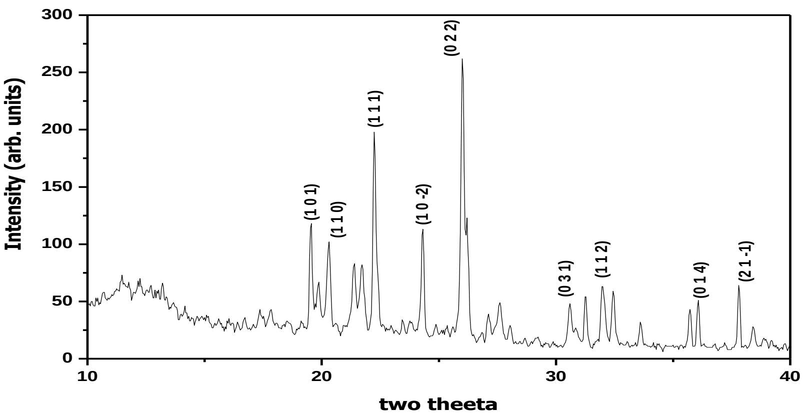

Figure 3Powder X-ray diffraction pattern of LHPCL

Table 1 Crystal XRD data of LHPCL

Empirical Formula	**$C_6H_{10}N_3O_6Cl$**
Crystal system	**Monoclinic**
Space group	**$P2_1$**
a (Å)	**5.022**
b (Å)	**9.161**
c (Å)	**10.351**
β°	**92.269°**

3.2 UV-Vis-NIR study

The UV-Vis-NIR absorption spectrum of LHPCL is shown in Figure 4. It is observed from the spectrum that LHPCL has a wide optical transmission window. The lower cut-off wavelength of the crystal is found to be 280 nm, and thus ascertain the fact that the crystal can be used for laser applications. Using Tauc relation a graph was plotted to estimate the band gap values. Figure 5 shows the plot of $(\alpha h\nu)^2$ versus hν, where α is the optical absorption coefficient and hν is the energy of the incident photon. The energy gap (E_g) is determined by extrapolating the straight line portion of the curve to $(\alpha h\nu)^2 = 0$. From this graph, the band gap (E_g) is found to be 4.9eV.

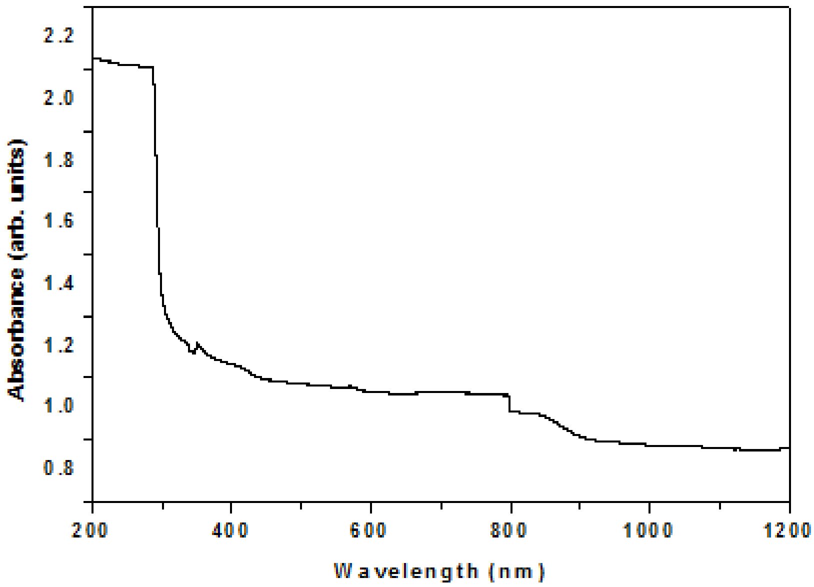

Figure 4 UV-Vis-NIR spectrums

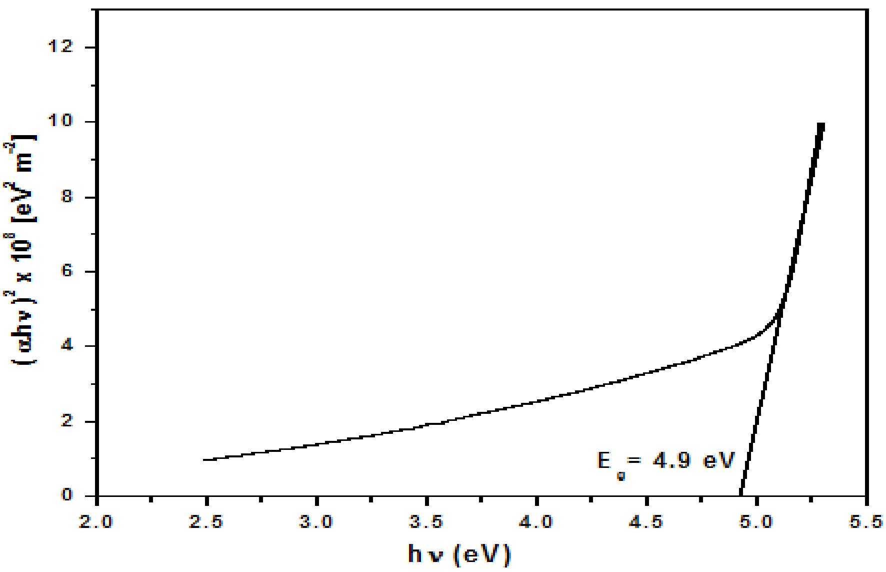

Figure 5 Plot of $(\alpha h\nu)^2$ versus photon energy (hν)

3.3 Nonlinear optical (NLO) test

To confirm the nonlinear optical property, Kurtz and Perry powder technique was carried out for LHPCL crystal [4]. The SHG efficiency of the grown crystal was checked by passing a Q-switched, mode locked Nd:YAG laser of 1064 nm and pulse width of 8 ns (spot radius of 1 mm) on the powder sample of LHPCL. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample. Photodiode detector and oscilloscope assembly detected the light emitted by the sample. The SHG efficiency of the LHPCL crystal was evaluated by taking the microcrystalline powder of KDP as the reference material. For a laser input pulse of 6.9 mJ, the SHG signal (532 nm) of 90 mV and 302 mV were obtained for KDP and LHPCL samples respectively. Hence, it is observed that the SHG efficiency of LHPCL is 3.4 times higher than KDP.

3.4 Dielectric studies

Figure 6 shows the plot of dielectric constant (ε_r) versus applied frequency. The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely; space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The variation of dielectric loss with frequency is shown in Figure 7. The characteristic of low dielectric loss with high frequency for a given sample suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application [5].

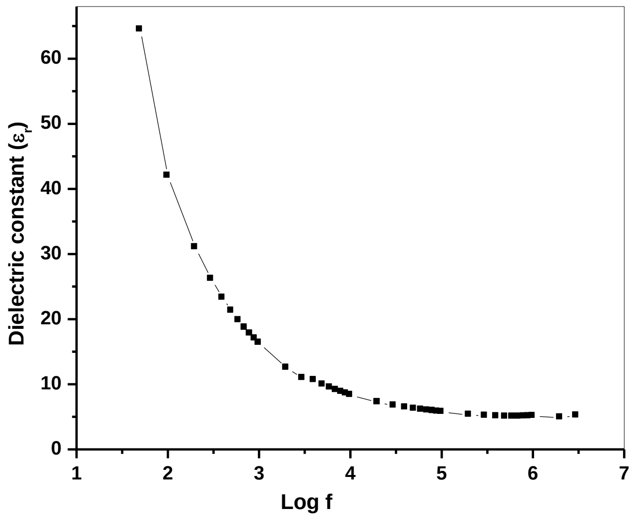

Figure 6 Variation of dielectric constant with frequency

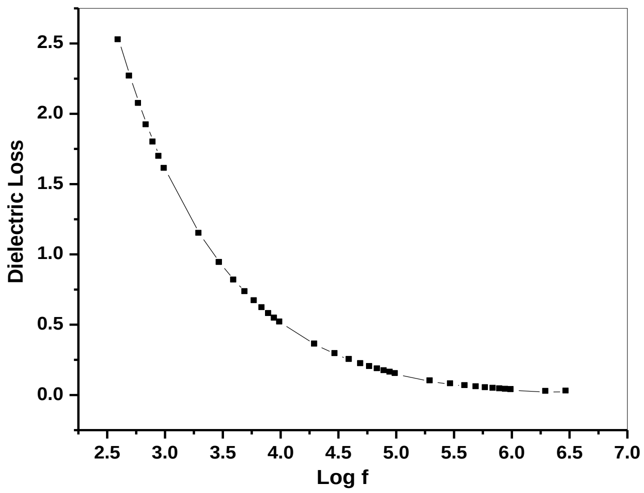

Figure 7 Variation of dielectric loss with frequency

IV. CONCLUSION

Good quality LHPCL single crystals are grown by slow evaporation technique in a period of 25 days. X-ray diffraction studies confirmed that LHPCL crystal is Monoclinic in structure and belongs to $P2_1$ space group. Interestingly, optical absorption studies indicate the minimum absorption in the entire visible region for LHPCL. SHG efficiency is found to be better than KDP. It is found that both dielectric constant and loss decrease with increase in frequency. Thus preliminary studies suggest that LHPCL is a promising nonlinear material, which can be possibly used for photonics device fabrication.

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