

Synthesis and Structural Analyses of Lithium Hydrogen Phthalate Dihydrate (LHP) Single Crystals

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Abstract—Single crystals of Lithium Hydrogen phthalate dihydrate (LHP), was grown from aqueous solution by slow evaporation technique. The grown crystals were subjected to Single crystal XRD, fourier transform infrared spectroscopy, UV-Vis-NIR spectral analysis and thermal analysis have been carried out to confirm the formation of the compound. The grown crystals were tested for its nonlinear optical (NLO) nature by using laser techniques. The results have been discussed in detail.

Keywords—Crystal growth, single crystal XRD, FTIR, UV-Vis-NIR and nonlinear optical materials

I. INTRODUCTION

The semi-organic alkali hydrogen phthalate crystals are widely known for their application in optical, long wave x-ray spectrometer and for nonlinear optical applications. [1–6]. Acid phthalate crystals crystallized as noncentrosymmetric or centrosymmetric rhombic structures depending on the cation, since in 3D crystallographic frame the bonding orientation of growth units is dramatically determined by these cations, on the basis of the chemical bonding theory of single crystal growth [7-10]. One such compound Lithium Hydrogen Phthalate dehydrate (LHP) also known as lithium acid phthalate possesses good thermal stability and non-linear optical properties [11-20]. The hydrogen bonds are a robust motif which can serve as an important constituent part in the solid state, including both property and growth aspects.

In the present work, single crystal of Lithium hydrogen phthalate (LHP), a semi-organic NLO, has been grown by slow evaporation technique. The grown crystals were subjected to single-crystal X-ray diffraction, Fourier transform infrared (FTIR) and thermal analysis. Nonlinear optical properties were investigated in detail.

II. EXPERIMENTAL PROCEDURE

Stoichiometric quantities of Lithium hydroxide (95% Lobo chemicals) and phthalic acid were mixed in 1:1 ratio in aqueous solution for 3 hours. The mother solution was then filtered and it was allowed to evaporate to form Lithium Hydrogen Phthalate dehydrate (LHP) single crystals. Good quality crystals were obtained by successive recrystallization.

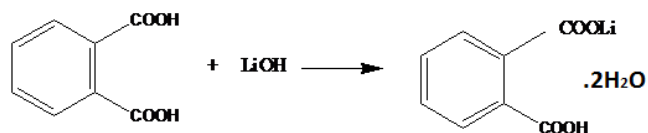


Fig. 1 Reaction mechanism between Phthalic acid and Lithium hydroxide to form Lithium Hydrogen Phthalate dihydrate

The grown crystals of LHP were shown in Fig.2. The grown crystalline samples were subjected to different characterization studies like X-ray diffraction and spectroscopic analysis for the formation of compounds.

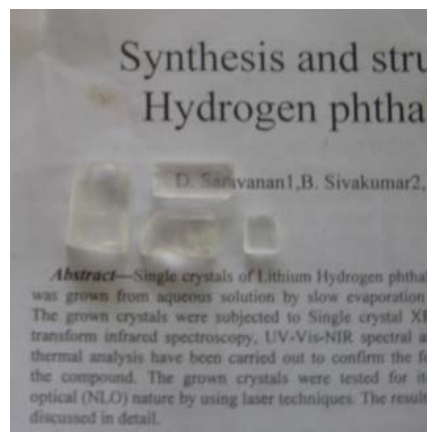


Fig. 2 As grown crystals of LHP from aqueous solution

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III. RESULTS AND DISCUSSION

A. Single crystal X-ray diffraction analysis

Good quality single crystals were used for single crystal X-ray diffraction analysis using Enraf-Nonius CAD-4 diffractometer equipped with MoK α radiation $\lambda=0.71073\text{\AA}$. $\omega/2\theta$ scan mode was employed for data collection. LHP crystallizes in Orthorhombic system with Pnma space group. The unit-cell parameters were found to be $a = 16.8356(10)\text{\AA}$; $b = 6.8187(5)\text{\AA}$; $c = 8.1967(6)\text{\AA}$; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ at 293 K which is in close agreement with that of reported values [12].

B. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were recorded by KBr pellet technique using a Bruker model IFS 66V spectrophotometer in the wavelength range 400 – 4000 cm^{-1} for LHP is shown in Fig.3. The frequency observed at 2890 and 3009 cm^{-1} of Lithium Hydrogen Phthalate crystal attributed to OH stretching vibrations. A Peak at 2525 cm^{-1} in the IR spectrum is assigned to the C-H Stretching. The absorptions 1687 cm^{-1} corresponds to the C=O absorption band. The Peak at 1585 cm^{-1} are assigned to Asymmetric stretching of O=C=O (ring structure). In Lithium Hydrogen Phthalate, the vibration at 1453 cm^{-1} corresponds to C-O-H in plane bending. Then, The peak appeared at 1403 cm^{-1} assigned to Symmetry Stretching of O=C=O. The Peak at 1281 corresponds to C-O Stretching vibrations (strong). The O-CH₂ set to vibrations at the peak 1153 cm^{-1} . The sharp absorption at 1071 cm^{-1} is assigned to O-H-O bond asymmetric ring stretching. The Peak at 907 cm^{-1} is assigned to O-H...O out of plane. The Peaks at 740 and 693 cm^{-1} are assigned to LiO stretching. The broad peak above 3000 cm^{-1} may be attributed to the OH stretching of the water molecule present in the compound [19,20].

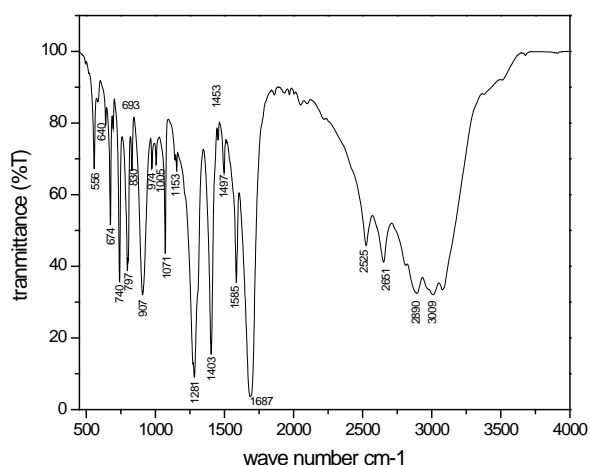


Fig. 3. FTIR spectra of LHP crystals

C. UV-Vis-NIR analysis

UV-Vis-NIR measurement was carried out for Lithium Hydrogen phthalate single crystals in the wavelength range 200-1200nm using a Varian Cary 5E UV spectrometer and is shown in Fig.4.

The maximum UV absorption occurs at 205 nm. After this wavelength, absorption abruptly decreases. The material possesses a very good optical transparency even up to 1200 nm. This property would be much useful in field of an optical material.

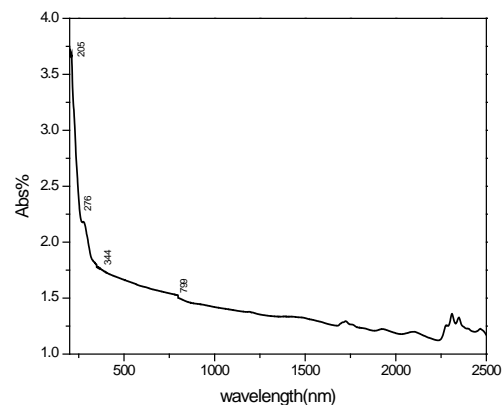


Fig. 4. UV-Vis-NIR spectra of LHP crystals

D. Thermal analysis

Differential scanning calorimetric (DSC) was carried out for LHP single crystals in the temperature range 30-500°C in a nitrogen atmosphere at a heating rate of 10°C/minute using a NETZSCH-GmbH thermal analyzer.

An endothermic thermal event occurs at 185 °C shows Lithium starts to melting then at 214.5°C shows the melting point of the Phthalic acid and then forming Phthalic unhydrate. The thermal events obtained at 229.7°C correspond to the decomposition of the Lithium Hydrogen Phthalate absorb -2884 J/g. Hence, it is inferred that the LHP crystals are thermally stability up to temperature 180 °C [20].

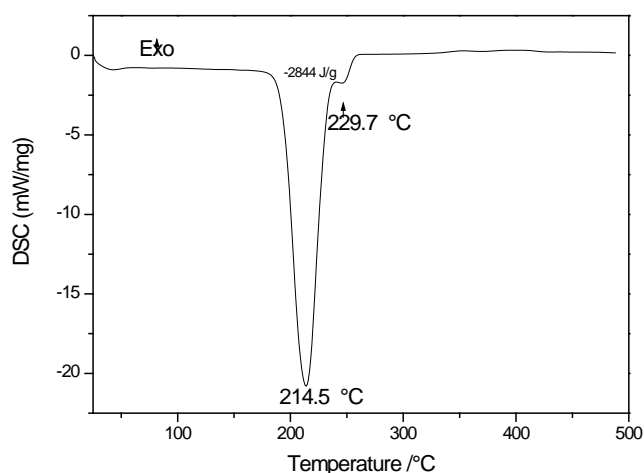


Fig. 4 DSC pattern of LHP crystals

E. Nonlinear optical properties

The nonlinear absorption and refractive index of LHP crystals (thickness $\approx 0.945 \times 10^{-3}\text{m}$) were estimated using the single beam Z-scan method with laser beam intensity of 60mW and the wavelength of source used for the measurement was 632.8 nm.

Nonlinear refractive index (n_2) of the LHP was calculated

as $3.317 \times 10^{-11} \text{ cm}^2/\text{W}$ the value of nonlinear absorption coefficient has been found to be $\beta \sim 5.789 \times 10^{-3} \text{ cm}^2/\text{W}$.

IV. CONCLUSION

Single crystals of Lithium Hydrogen Phthalate dehydrate (LHP) crystals have been synthesized and grown by the slow evaporation technique. Single crystal XRD measurement reveals that the grown crystal belongs to the orthorhombic system with a space group of Pmna. The various functional groups present in the grown crystal have been ascertained through FTIR spectrum. Optical absorption studies confirm the transparent nature of the grown crystals of LHP. Thermal measurement confirms the thermal stability of the grown crystals. Third order nonlinear property was also investigated by the Z-scan technique. The values of n_2 and β thus obtained were $4.631 \times 10^{-11} \text{ cm}^2/\text{W}$ & $2.1897 \times 10^{-6} \text{ cm}^2/\text{W}$ respectively.

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