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SYNTHESIS, GROWTH AND CHARACTERIZATION OF L- VALINE DOPED LITHIUM HYDROGEN PHTHALATE CRYSTAL: A POTENTIAL MATERIAL FOR NLO APPLICATIONS

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ABSTRACT

Semiorganic L-Valine doped Lithium Hydrogen Phthalate (LHP) crystals were grown by conventional Slow Evaporation Solution Growth Technique (SEST). Single Crystal XRD provides information regarding the cell parameters. The spectral properties and the presence of functional groups were analyzed FTIR spectral analysis. UV-Vis-NIR spectral analysis suggests that the title material is transparent in the visible region without any strong absorptions. The TG/DTA thermogram provides information regarding the thermal stability of the material. Vicker's microhardness test suggests that the title material is mechanically stable up to 100g.

KEYWORDS

Optical Materials, FTIR, NLO and XRD.

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INTRODUCTION

The semi-organic alkali hydrogen phthalate crystals are widely known for their application in the long-wave X-ray spectrometers[1]. Their optical, piezoelectric, NLO and elastic properties are investigated in detail[2-7]. Acid phthalate crystals were used as substrates for deposition of thin films of organic nonlinear materials[8] and standards in volumetric analysis[9]. Acid phthalate crystals are 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[10,11]. Lithium hydrogen phthalate dehydrate (LHP dihydrate) structure contains a very short hydrogen bond. The hydrogen bonds are a robust motif which can serve as an important constituent part in the solid state[12], including both property[13-15] and growth[16,17] aspects. Potassium acid phthalate (KAP), rubidium acid phthalate (RbAP), cesium acid phthalate (CsAP), ammonium acid phthalate (NH_4AP) crystals have found application as crystal-analyzer in the light-gathering power spectrometer of long-wave radiation used for investigation of spectra and polarization of X-ray radiation. These crystals are used in quality and quantity analysis of light elements (Fe, Al, Mg, F and Si) in objects under investigations. Rubidium acid phthalate and thallium acid phthalate (TIAP) have been used in wide-band high-resolution soft X-ray spectrometers[18]. In this series, LHP dihydrate was grown by slow evaporation solution technique. LHP dehydrate was first described by Smith, Sturm and Ely[9] and the structure analysis was described by Gonschorek *et.al.*[19]. Optical, dielectric, thermal and hardness properties of the semiorganic LHP dehydrate are investigated by A. Senthil *et al.*,[20]. Taking into considerations of the above said reports an attempt was made in the present work to dope L-Valine into the crystal lattice of LHP crystal. Structural, Optical, Thermal, Mechanical and NLO properties of title material are investigated.

Synthesis and Crystal Growth

Lithium hydroxide (Merck, AR grade, 98%) and Phthalic acid (Merck, AR grade, 99.5%) were used as precursors in the synthesis process. Double distilled water was used as a solvent. The purity of the materials was further improved by successive recrystallization. Saturated LHP solution was prepared by following the sequential steps as described elsewhere[20]. To the saturated solution 0.3 mol% L-Valine (AR, Loba, 98%) was doped and stirred well using a magnetic stirrer. Temperature was maintained at 35 °C during the synthesis process. L-Valine doped crystals were obtained after a time span of 30 days. The photograph of L-Valine doped LHP crystal is shown in Figure No.1.

Characterization Analysis

Single Crystal X-Ray Diffraction

The cell parameters of L-Valine doped LHP crystals were obtained using single crystal x-ray diffraction analysis. L-Valine doped LHP crystal belongs to noncentrosymmetric p_{nma} space group crystallizing in orthorhombic symmetry. The unit cell parameters are a= 6.99Å; b= 8.38 Å; c=16. 76 Å and the volume of the unit cell is V= 981.737 $Å^3$. The obtained cell parameters coincide well with the reported literature[20].

FTIR spectral analysis

The spectral properties of L-Valine doped LHP crystals were analyzed by Fourier Transform Infrared spectral analysis in the region 4000–400cm^{-1} by KBr pellet technique. The spectrum is shown in Figure No.2. The functional groups present in L-Valine doped LHP crystals were identified with the help of available data[6-22]. A set of absorption bands within the region 500–900 cm^{-1} are due to C–H out-of-plane deformations of aromatic ring. The band at 1969 cm^{-1} is due to C–C stretching vibrations. Symmetrical and asymmetrical stretching of O–H–O is at 1147 and1064 cm^{-1}, respectively. Symmetric and asymmetric stretching of O–C=O is at 1400and 1584 cm^{-1}, respectively. The C=O absorption band is at 1685 cm^{-1}. The band at 2522 cm^{-1} is due to C–H stretching vibrations. The band at 2998 cm^{-1} is due to O–H stretching hydrogen bond.

UV-Visible spectral analysis

The optical property of L-Valine doped LHP crystal was examined by UV-Visible spectral analysis. From the UV spectrum Figure No.3 it is evident that the crystal is transparent in the entire visible region without any strong absorption. The lower cut off wavelength is at 310 nm and the percentage of transmission of L- Valine doped LHP crystal is 26%. Transparencies in the entire visible region with a wide transmission window are the key properties of a material to possess NLO property. The results of the UV spectrum suggest the suitability of the title material in nonlinear optical device fabrications.

Thermal Analysis

The thermal stability of L-Valine doped LHP crystal was assessed by TG/DTA analysis. The TG/DTA thermogram is shown in Figure No.4. From the TGA thermogram it is evident that the sample is thermally stable upto 100 °C denoting the presence of water in the crystal lattice of the crystal. The weight loss occurs in three different stages. A major weight loss occurs in the second stage at 199 °C which is due to the loss of loosely bonded atoms in the dopant. The third stage weight loss occurs at 225 °C due to the release of feeble bonding in the parent material. After the decomposition occurring at 600 °C, a part of the title material is left as char. The result was compared with the reported literature[20] and it was observed that L-Valine doped LHP crystal is a better material than undoped LHP crystal. From the DTA thermogram, a sharp endotherm coinciding with the TGA curves around 199 °C which signifies the melting point of the sample. The sharpness of the endothermic peak suggests the crystallinity of the sample. The thermal analysis of the material suggests the possible application of the material in lasers.

Mechanical Stability Analysis

The mechanical stability of L-Valine doped LHP crystals were assessed by Leitz-Wetzler's Vickers' micro hardness tester fitted with a diamond indenter. The indentations were made using Vicker's pyramidal diamond indenter for loads ranging from 25g to 100g with a constant indentation time of 10s. Vicker's microhardness number (H_v) is given by the following relation:

$$H_v = \frac{1.8544P}{d^2} \text{ kg/mm}^2$$

Where P is the applied load in g, d is the diagonal length in mm. The variation of the Vicker's hardness number with the applied load is shown in Figure No.5. From the figure it is evident that the Vicker's hardness number increases with the increase in load thus satisfying the normal indentation effect[23]. The work hardening coefficient was calculated and it was found to be 4 and hence the material comes under soft material category.

Nonlinear Optical analysis

Powder SHG measurements were carried out using were carried out using Kurtz and Perry[24] experimental setup. A Q switched Nd: YAG laser (Quanta Ray spectra Physics model Prolab 170) was used in the experiment.

The laser operates at 1064 nm and 8 ns pulse with the repetition rate of 10 Hz and energy 0.68 mJ/pulse. Emission of green radiation of wavelength 532 nm from the crystalline sample confirms the SHG activity of L-Valine doped LHP crystal. The converted SHG output was displayed on a digital storage oscilloscope. From the obtained data the SHG efficiency of L-Valine doped LHP sample is 1.9 times that of KDP. This property of enhancing the frequency makes L-Valine doped LHP crystal an eligible candidate in frequency doubling applications.

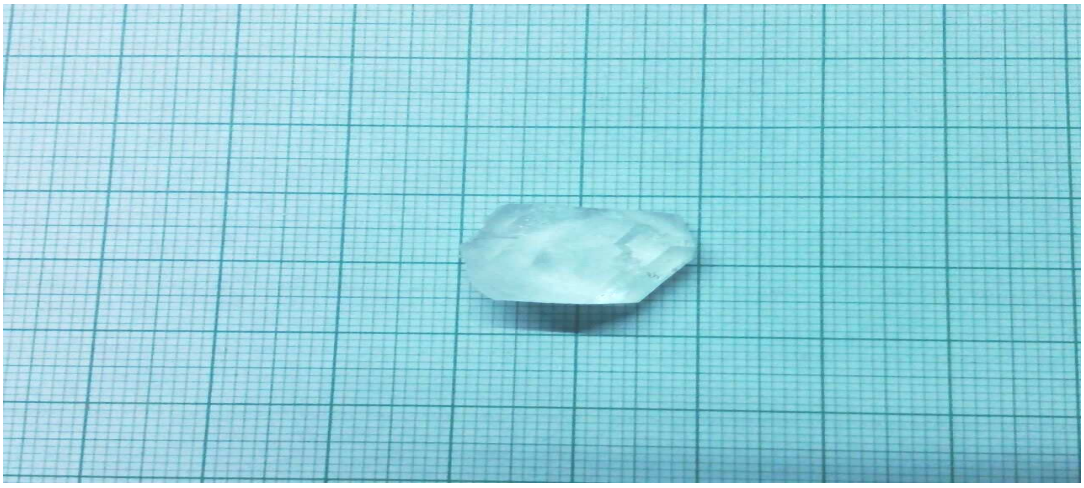

Figure No.1: Photograph of L-Valine doped LHP crystal

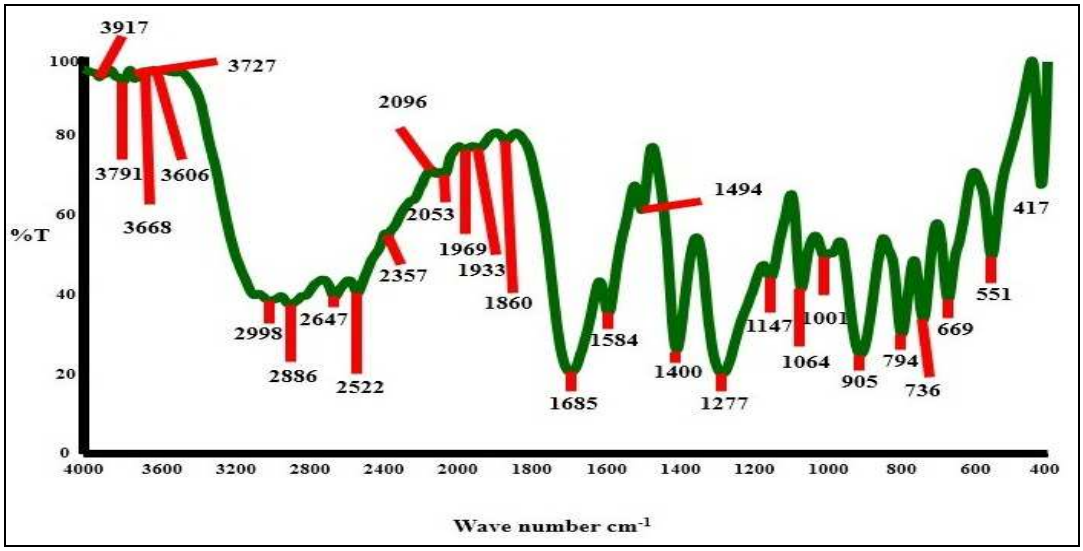

Figure No.2: FTIR spectrum of L- Valine doped LHP crystal

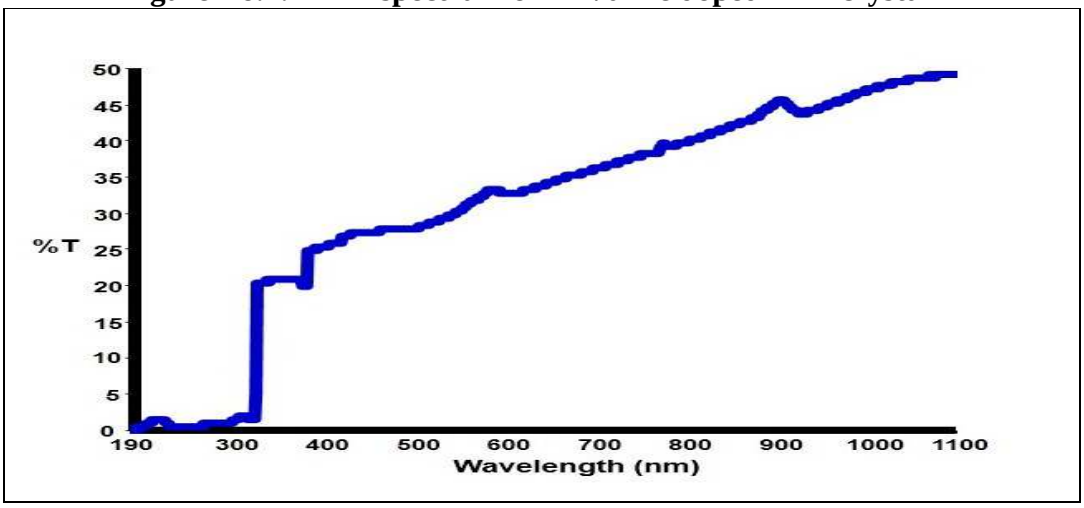

Figure No.3: UV-Vis-NIR spectrum of L- Valine doped LHP crystal

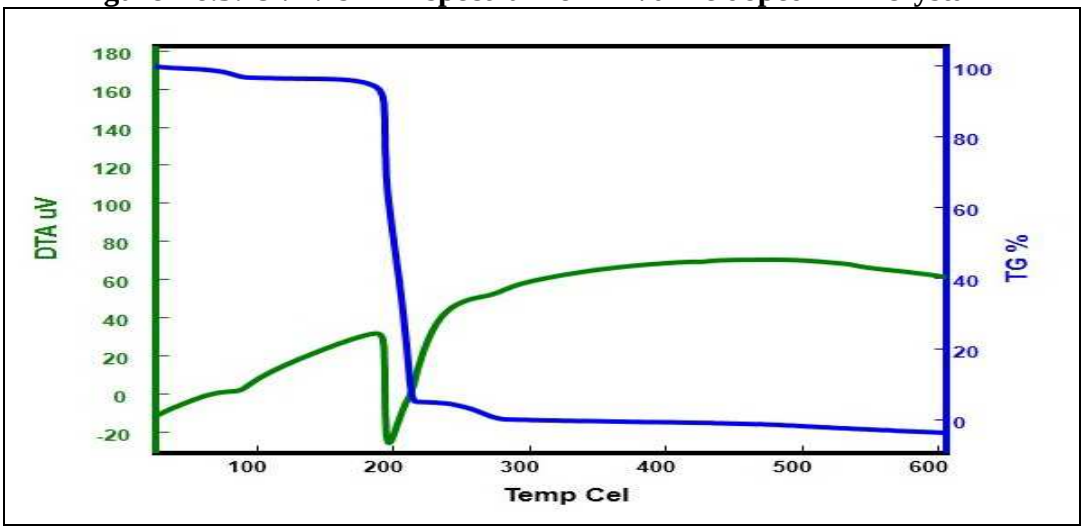

Figure No.4: TG/DTA thermogram of L- Valine doped LHP crystal

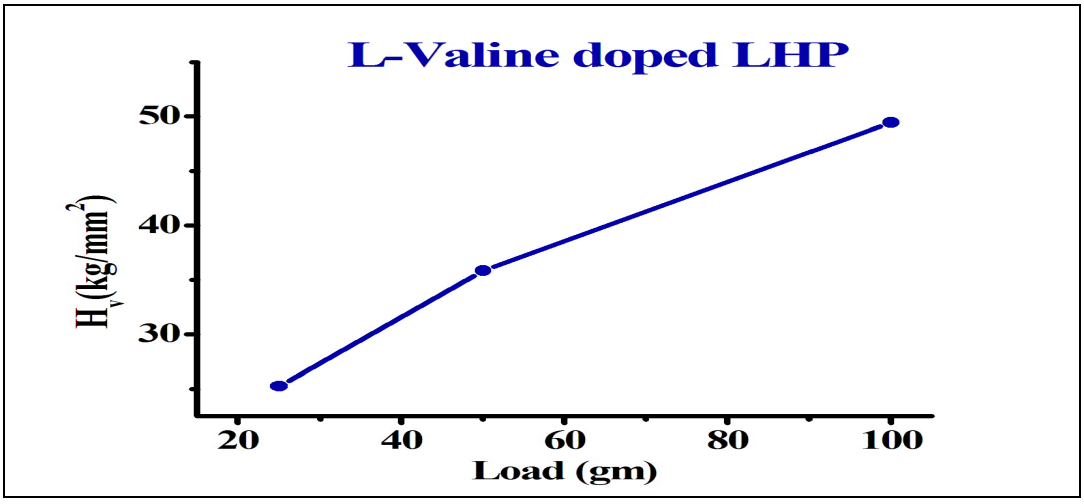

Figure No.5: Load vs Hv plot of L- Valine doped LHP crystal

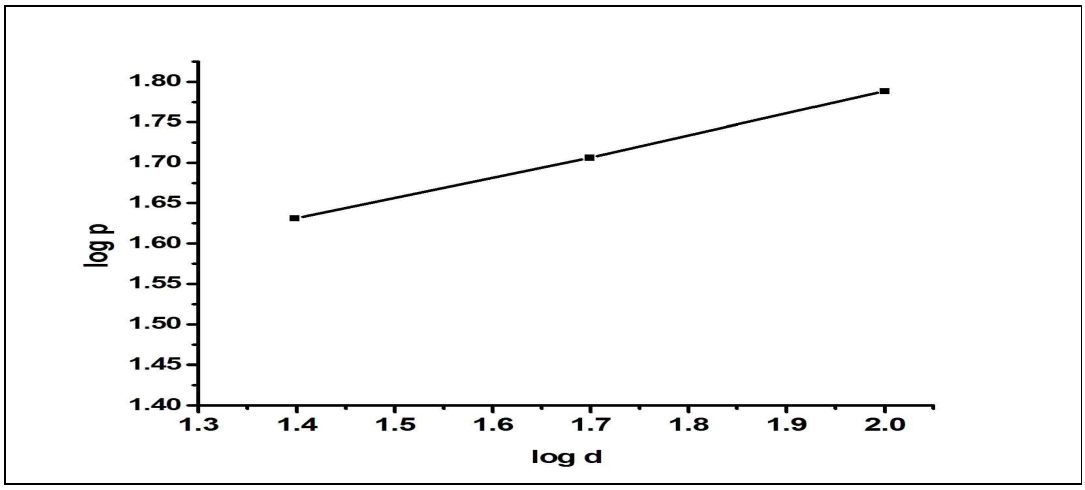

Figure No.6: WHC of L- Valine doped LHP crystal

CONCLUSION

Single crystals of L-Valine doped LHP were grown by conventional slow evaporation solution growth method. The cell parameters were confirmed by single crystal x-ray diffraction. The presence of functional group was analyzed by FTIR spectral analysis. The optical property was examined by UV-Visible NIR spectrum. The thermal and mechanical stability was assessed by TG/DTA analysis and microhardness studies respectively. The nonlinear optical property of the title material was studied by Kurtz and Perry experimental set up for NLO testing. The results suggest that the title material is an effective material in NLO device fabrications.

CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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