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Growth and Characterization of a Metal-Organic Crystal: L-Histidine Sodium Chloride

Physics

KEYWORDS: Crystal growth, X-ray diffraction, Optical material, Thermal studies, Nonlinear optical materials

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ABSTRACT Semiorganic materials possess several attractive properties such as high NLO coefficient, high laser damage threshold and wide transparency range, high mechanical strength and thermal stability, which make the materials suitable for second harmonic generation (SHG) and other NLO applications. A new semi organic nonlinear optical material L-histidine sodium chloride crystal was synthesized by slow evaporation technique. The grown crystals have been subjected to powder X-ray diffraction studies to identify the crystalline nature. A Fourier Transform Infrared (FTIR) study confirms the presence of functional groups in the grown crystal. The absorption of these grown crystals was analyzed using UV-vis-NIR studies, and it was found that these crystals possess minimum absorption from 190 to 1100 nm. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) have been carried out to study its thermal properties. The Kurtz and Perry powder SHG technique confirms the NLO property of the grown crystal and the SHG efficiency of LHSC was found to be 0.45 times greater than that of KDP crystal.

Introduction

In recent years, great efforts have been made to develop new organic, inorganic and semi-organic nonlinear optical (NLO) crystals due to their widespread applications such as frequency conversion, high-speed information processing, optical communications, and optical data storage (1-3). In the field of nonlinear optical crystal growth, amino acids play a vital role. Amino acids exhibit natural chiral properties and crystallize in the non-centrosymmetric space groups, which is an essential criterion for NLO applications. In addition, amino acids possess particular features, such as weak Vander Waals and hydrogen bonds, wide transparency range in the visible region and zwitterionic nature of the molecules. Complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of organic aminoacid and inorganic salt. Optically active amino acids show high efficient optical second harmonic generation (SHG) and are promising candidates for laser and optical communication technology. Since isomerically pure and optically active substances always meet the symmetry requirements for optical second harmonic generation, there is considerable variation in efficiency for the generation of SHG, ranging from almost zero to greater than that of potassium dihydrogen phosphate crystals. Many optically active organic amino acids are mixed with the inorganic salts in order to enhance their physical and chemical properties. The salt of amino acids like L-arginine [4], L-histidine [5], L-threonine [6], LAP [7], DLAP [8], LAHCl [9], LHB [10] are reported to have high second harmonic conversion efficiency compared to KDP. In the present work, L-histidine sodium chloride crystal was synthesized and the crystals were grown by slow evaporation technique. The grown crystals were characterized by powder X-ray diffraction, FTIR studies, UV-vis spectral analysis, TGA/DTA analysis and SHG test.

Experimental Procedure

Material Synthesis

The title compound was synthesized by taking L-histidine and sodium chloride in the equimolar ratio 1:1. An adduct was formed according to the reaction

$$C_6H_9O_2N_3 + NaCl \rightarrow Na\,(C_6H_9O_2N_3)\,Cl$$

Growth of single crystals

Single crystals of L-histidine sodium chloride was grown from aqueous solution by slow solvent evaporation method. In order to avoid co-precipitation of multiple phases the mixture of the reactants had to be stirred well. Good transparent crystals were harvested after a growth period of 20-25 days. The purity of the solution was improved by successive recrystallization process.

Result and Discussions

Single crystal and powder X-ray Diffraction Studies

The single crystal X-ray diffraction analysis of LHSC was carried out using Bruker Kappa APEXII single crystal X-ray diffractometer equipped with M_0K_α (λ=0.71073 Å) radiation. The compound crystallizes in orthorhombic form with space group $P2_12_12_1$ .The determined lattice parameters are a = 5.1794 Å, b = 7.2043 Å, c = 18.7679 Å and V = 700 $Å^3$. Powder X-ray diffraction pattern of the grown LHSS was recorded over the range 10-50 by employing Bruker AXS Advance powder x-ray Diffractometer. The K radiations from a copper target were used for the diffraction studies and the diffraction pattern is shown in Fig.1. The sharp well defined Bragg's peaks at specific 2θ angles testimonies the crystallinity of the material.

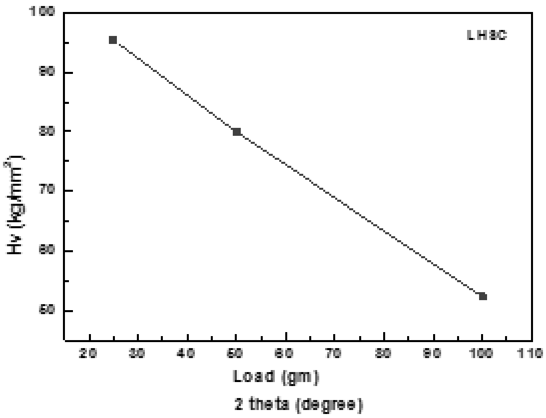

Fig. 1 Powder XRD patterns of LHSC crystal

FTIR studies

The Fourier Transform Infrared (FTIR) spectrum was recorded using Perkin Elmer FTIR spectrometer by KBr pellet technique in the range 4000-400 cm^{-1} to identify the functional groups present in LHSC. The FTIR spectrum of LHSC is shown in figure 2. The presence of imidazole ring in the L-histidine molecule is indicated by the peak at 2927 cm^{-1} by the vibration of C-H stretch in the ring. The peak at 3428 cm^{-1} indicates its NH_2stretch of the amino group of the L-histidine molecule. The strong peak at 2375 cm^{-1} and 2274 cm^{-1} are assigned for the carboxylic acid with conjugated C-C and O-H stretching vibrations. The stretching vibrations of C=O and C-O strong peaks are assigned at 1610 $cm^{-1}$and 1390 cm^{-1}. The peaks ascribed at 1115 cm^{-1} and 1246 cm^{-1} are due to C-N and C-O stretching vibrations in the chemical compound. The band at 779 cm^{-1} and 615 cm^{-1} represent the organic halogen namely sodium chloride attached to the C-Cl stretch of the molecule. The assignments confirm the presence of various functional groups present in the synthesized material.

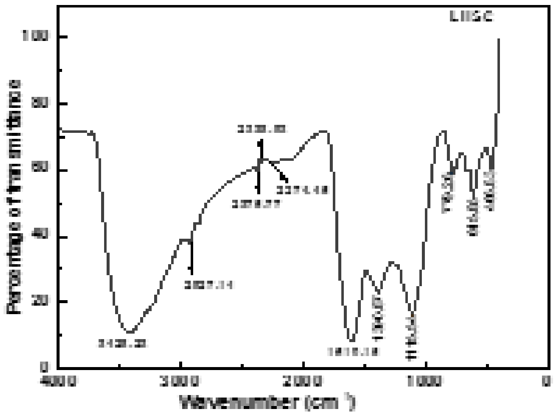

Fig.2 FTIR spectrum of LHSC crystal

UV-VIS-NIR spectral analysis

For optical application, especially for SHG, the material considered must be transparent in the wavelength region of interest. The UV-VIS-NIR transmission spectrum of LHSC crystal was recorded in the range 190-1100 nm covering the entire near ultraviolet, visible and NIR regions and is shown in Fig.3. From the UV-vis-NIR spectrum, it is seen that the UV transparency cut off occurs at 280 nm due to the $\pi - \pi^*$ electron transition. There is no remarkable absorption in the entire region of the spectra. This is good enough for the production of shorter wavelength violet-green radiation from the infrared laser sources. This transparent nature in the visible region is a desirous property for this material for NLO applications.

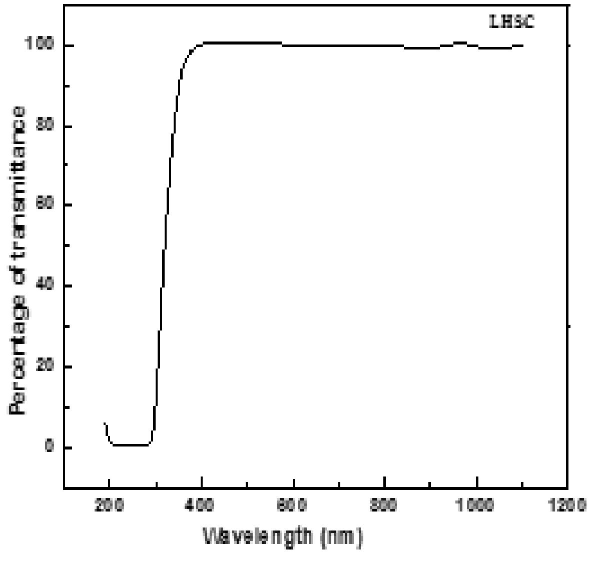

Fig.3 UV – VIS spectrum of LHSC crystal

Thermal analysis

Thermogravimetric and differential thermal analysis (TG/DTA) gives idea about phase transition temperature, the melting point and the chemical decomposition of the grown crystals. The TG/DTA thermograms of LHSC crystals are presented in Fig.4. There is no significant weight loss below 260˚C which indicates that the crystal is moisture free and is thermally stable. From the curve, is it noticed that a gradual weight loss occurs between 260˚C - 330˚C and 330˚C - 365˚C. It is seen that at different stages various gases like CO2, NH3, Cl are liberated. The sharp endothermic peak at 260˚C confirms that the material is thermally stable upto this temperature. Based on this result it is said that the compound can be used for NLO applications upto this temperature (260˚C). The sharpness of its endothermic peak shows the good degree of crystallinity of the sample [11].

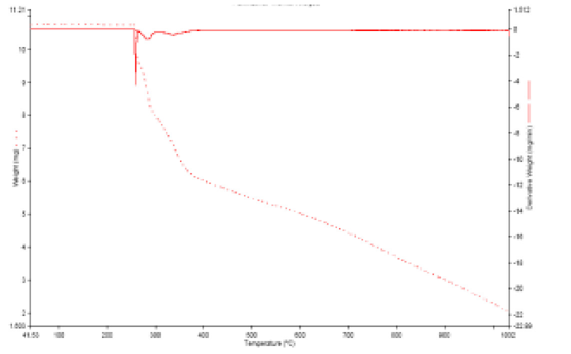

Fig.4 TG/DTA spectrum of LHSC crystal

Microhardness Study

Microhardness testing is one of the best methods of understanding the mechanical properties of materials such as fracture behavior, yield strength, brittleness index and temperature of cracking [12]. The Vicker's micro hardness study was made on the as grown face of LHSS for the static indentation tests in air at room temperature. The Vickers micro hardness values are calculated using the formula Hv=1.8544P/d2 kg/mm2, where P is the applied load and d is the average diagonal length of the indentation. A plot is drawn between the Hardness value and corresponding load are shown in Fig.5. In LHSC a steep rise and fall in hardness number is obtained in the range of 25 to 100 g. The micro hardness values reduced rapidly from 95.4 to 52.3 kg/mm2 on increasing the load from 25 to 100 g. For an indentation load of 100 g, cracks are initiated on the grown crystal's surface, around the indenter.

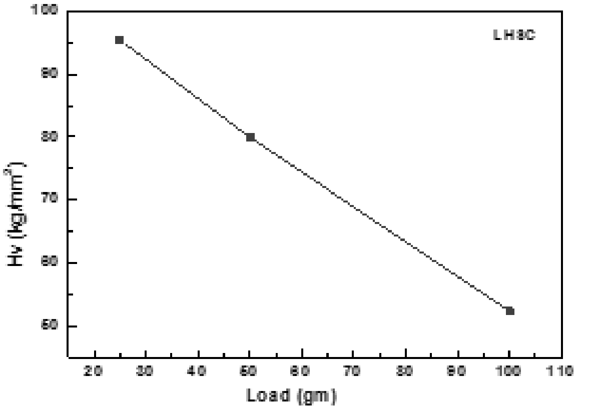

Fig.5 Graph of load (vs) Hv for LHSC crystal

Nonlinear Optical Studies

Kurtz and Perry [13] second harmonic generation (SHG) test was performed to estimate the NLO efficiency of powdered LHSC crystal. The grown single crystal of LHSC was powdered and illuminated using Q-switched Nd:YAG laser beam of wavelength 1064nm with pulse width of 8ns and repetition rate 10 Hz. The second harmonics signal, generated in the crystal was confirmed from the emission of green radiation by the crystal. A sample of potassium dihydrogen ortho phosphate also powdered to the same particle size as the experimental sample used as a reference material in the present measurement. Powder SHG efficiency obtained for LHSC is about 0.45 times that of potassium dihydrogen orthophosphate crystal.

Conclusions

Single crystals of LHSC were grown from solution method. The unit cell parameters were confirmed by single crystal X-ray diffraction analysis. The sharp well defined peaks conforms the crystalline nature of the material. It is found that the crystal belongs to the orthorhombic crystal system and space group P212121. Functional groups were identified using FTIR spectral analysis. Thermal analysis indicated that the crystal has good thermal stability. The optical property has been assessed by UV-vis measurement showed the absence of absorption in the entire visible region. Powder test with Nd:YAG laser radiation shows second harmonic generation. Hence it could be suggested that this material is better befitted for optical applications.

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