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RESEARCH ARTICLE

GROWTH AND CHARACTERIZATION OF A NONLINEAR OPTICAL CRYSTAL: L-HISTIDINE SODIUM SULPHATE ANHYDROUS.

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Abstract

A new semi organic nonlinear optic material L-Histidine Sodium Sulphate anhydrous (LHSS) was synthesized. The grown crystals were characterized by single crystal X-ray diffraction analysis to determine the cell parameters and by FTIR technique to study the presence of the functional groups. Thermogravimetric and differential thermal analysis reveals the thermal stability of the crystal. UV-VIS-NIR spectrum shows excellent transmission in the region 200-1100 nm. Mechanical properties of the grown crystal were studied using Vicker's micro hardness test. Second harmonic generation efficiency of the powdered LHSS was tested using Nd:YAG laser and it is found to be 0.3 times of KDP crystal.

Introduction:-

There is a great deal of interest in materials with high nonlinear optical (NLO) responses both from the scientific and technological point of view [1]. Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their NLO properties [2, 3]. Nonlinear optical crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent invisible and ultraviolet ranges are required for numerous device applications, such as laser displays, high density optical storage, photolithography, etc. In recent years, more promising NLO materials with better properties have been identified and studied. A number of such crystals, especially from the amino acid family, have recently been reported [4–8]. The functional amino acid histidine serves as a proton donor, proton acceptor and as a nucleophilic reagent. Histidine frequently occurs at the active sites of enzymes and also coordinates ions in larger protein structures [9]. In the present investigation, the growth aspects of LHSS have been studied and crystals were grown by slow evaporation technique. Characterization studies such as single crystal XRD, FTIR, UV-VIS-NIR, TG/DTA, micro hardness and SHG studies have been carried out for the above crystal.

Experimental details:-

Material Synthesis and Crystal Growth:-

The title compound was synthesized by taking L-histidine and sodium sulphate anhydrous in the equimolar ratio 1:1. The expected chemical reaction for this compound is,

$C_6H_9N_3O_2 + Na_2SO_4 \rightarrow Na\,(C_6H_9N_3O_2)_2.\,SO_4$

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The calculated amounts of the reactants were thoroughly dissolved in double distilled water. Then, it was mixed with continuous stirring for about 2h using magnetic stirrer with hot plate. In order to avoid co-precipitation of multiple phases the mixture of the reactants had to be stirred well. The solution was filtered well to remove suspended impurities and allowed to crystallize by slow evaporation technique at room temperature. The purity of the synthesized salt was further improved by successive recrystallization process. After 4-5 weeks well defined single crystals of LHSS were collected.

Characterization:-

Single crystal and powder X-ray Diffraction Studies

The single crystal X-ray diffraction analysis of LHSS was carried out using Bruker Kappa APEXII single crystal X-ray diffractometer equipped with M_OK_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 = 5.1520 Å , b = 7.3250 Å, c = 18.7560 Å and V = 707.82 $Å^{3.}$ 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_α 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.

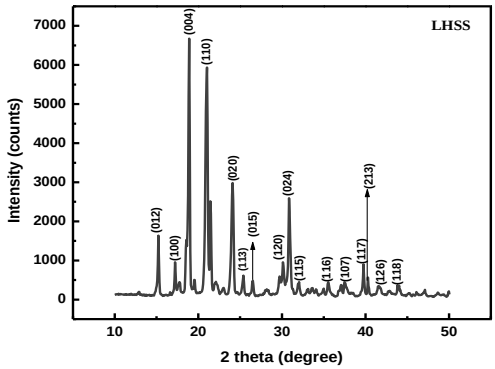

Fig. 1:- Powder XRD patterns of LHSS crystal

FTIR studies:-

The FTIR spectra was carried out using Perkin Elmer FTIR spectrometer by KBr pellet method in the range 4000-400 cm^{-1} as shown in Fig .2. The peaks at 3418 cm^{-1} and 3007 cm^{-1} are assigned to asymmetric and symmetric stretching modes of NH. The wave numbers 2873 cm^{-1} shows the presence of peak due to CH_2 asymmetric stretching vibration. The peak around 1634 cm^{-1} is NH_3^+ asymmetric deformation. The peak at 1446 cm^{-1} is due to COO^- symmetric stretching vibration. CH deformation in the peak is obtained at 1246 cm^{-1}. S-O stretching peak is obtained at 1134 cm^{-1} and S-O bending peak obtained at 621 cm^{-1}. The figure confirms the presence of various functional groups present in the material.

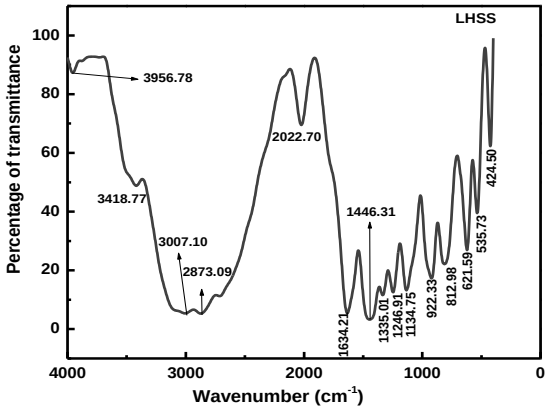

Fig 2:- FTIR spectrum of LHSS crystal

UV-VIS-NIR spectral analysis:-

The UV-VIS-NIR transmission spectrum of LHSS crystal was recorded in the range 190-1100 nm covering the entire near ultraviolet, visible and NIR regions and is shown in Fig .3. This is the advantage of using amino acids

where the absence of strongly conjugated bonds leads to higher optical transparency in the visible and uv spectral regions. From the UV-vis-NIR spectrum, it is seen that the UV transparency lower cut off occurs at 225 nm and the sharp peak at 230 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.

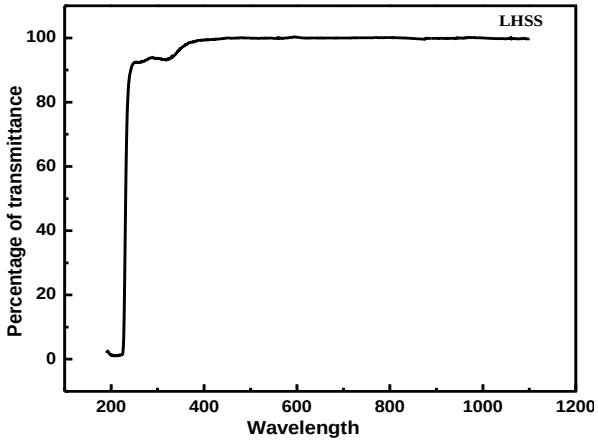

Fig 3:- UV – VIS spectrum of LHSS crystal

Thermal analysis:-

Thermogravimetric and differential thermal analysis (TG/DTA) gives idea about phase transition temperature, the melting point of the chemical decomposition of the grown crystals. The TG/DTA thermograms of LHSS crystals are presented in Fig.4. From the results, it is found that the sample is stable upto 280^{o}C.From the curve, it is noticed that there is a gradual weight loss between 280^{o}C-300^{o}C and 300^{o}C-398^{o}C. It is seen that at different stages various gaseous fractions like CO, CO_2, NH_3 etc., are liberated and beyond 398^{o}C bulk decomposition occurs. There is an endothermic peak at 280^{o}C observed in the DTA curve and it corresponds to the melting point of the sample. Based on this result it is said that the compound can be used for NLO applications upto this temperature (280^{o}C). The sharpness of its endothermic peak shows degree of crystallinity of the sample [10].

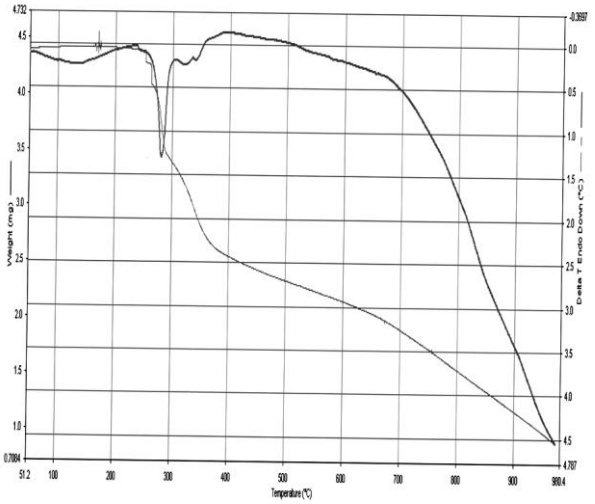

Fig 4:- TG/DTA spectrum of LHSS crystal

Microhardness Studies:-

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 [11]. 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 $Hv=1.8544P/d^2$ kg/mm^2, 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. It was observed that hardness increases with increase in load upto 100g.

Beyond the load of 100g multiple cracking were developed in the crystal surface due to the release of internal stress generated locally by indentation.

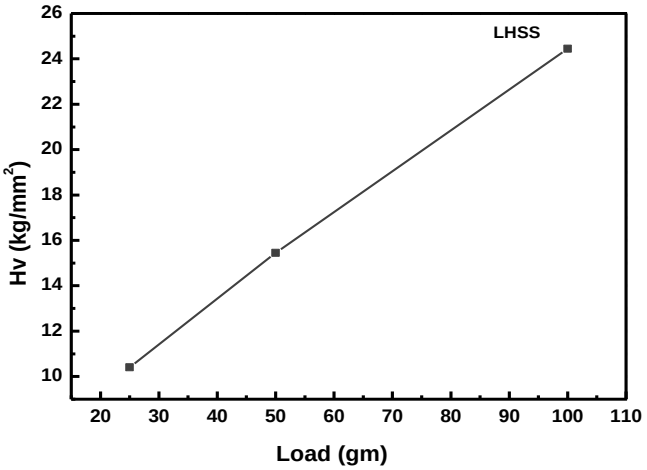

Fig 5:- Graph of load (vs) Hv for LHSS crystal

SHG efficiency studies

The space group $P2_12_12_1$ allows contribution of a molecular non-linearity. The study of nonlinear optical conversion efficiency has been carried out using the modified experimental setup of Kurtz and Perry[12].A Q-switched Nd:YAG laser beam of wavelength 1064 nm, pulse width of 8 ns and with a repetition rate of 10Hz was used. The grown single crystal of LHSS was powdered with a uniform particle size and then packed in a microcapillary uniform bore and exposed to laser radiations. The generation of second harmonics was confirmed by the emission of green light. The SHG conversion efficiency of LHSS is found to be about 0.3 times that of KDP.

Conclusion:-

The semi organic crystal of LHSS was grown by slow evaporation solution growth technique at room temperature. The sharp well defined Bragg's peaks confirm the crystalline nature of the synthesized material. The grown LHSS crystal was confirmed by single-crystal XRD analysis and the lattice parameters were obtained. It is found that the crystal belongs to the orthorhombic crystal system with space group $P2_12_12_1$.FTIR spectroscopic analysis confirms the presence of functional groups in the compound. Thermal stability of the grown crystal was identified and the way of decomposition was studied in thermal analysis. The degree of crystallinity and purity from a sharp endothermic peak was also confirmed. From the optical studies the energy band gap was found out as 8.8eV also the hardness studies expose the nature of the grown material. The NLO efficiency has been confirmed by Kurtz-Perry powder second harmonic generation (SHG) experiments.

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