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Structural, Vibrational and Thermal Properties of Semi Organic Nonlinear Optical Glutamic Added Lithium Sulphate Monohydrate Crystal

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ARTICLE DETAILS

Article history:

Received 24 February 2018

Accepted 22 March 2018

Available online 02 April 2018

Keywords:

Optical Studies

Mechanical Studies

NLO Study

ABSTRACT

Glutamic acid lithium sulphate monohydrate crystal is a new semiorganic nonlinear optical material. It was grown from a mixture of aqueous solution of glutamic acid and lithium sulphate monohydrate by slow evaporation technique at room temperature. The powder XRD analysis was carried out to identify the structural parameters of the grown crystals. The presence of functional groups of both reactants was qualitatively analyzed by means of Fourier transform infrared (FT-IR) spectrometer study. In UV-vis study, the existence of wide transparency window and band gap was investigated for optoelectronic device applications. In Kurtz-Perry powder technique, the second harmonic generation (SHG) efficiency of GLSMH crystal is found to be 1.933 times greater than that of KDP crystal.

1. Introduction

The non-linear optical (NLO) materials are at the fore front of the researches due to their wider applications in photonics and optical communication devices. Owing to the increasing need of new materials with high NLO efficiency and improved physical properties, new approach has been developed to hybrid organic-inorganic materials with their advantages for technological applications [1]. The materials that have a potential to tailor high optical nonlinearity of an organic ion with favorable mechanical and thermal properties of an inorganic counter ion, turned out to be superior quality semi organic materials [2, 3]. Extensive research has revealed that Amino acids serve as attractive organic candidates, as they contain the chiral nature, wide hydrogen bonding network, a proton donor carboxyl (-COOH) group and a proton acceptor amine (-NH₂) group with a side chain (R) group specific to each amino acid. Complexes of amino acids with inorganic salts are suitable for optical device applications. Hence amino acids offer a wide range of choice to synthesize the new semi organic materials with large enhancement in properties of NLO crystals [4]. L-proline lithium bromide monohydrate [5], L-proline lithium chloride monohydrate [6], L-valine cadmium chloride monohydrate [7], L-valine ferric chloride [8], L-arginine hydrochloride bromide [9], L-arginine hydrobromide monohydrate [10] and L-threonine copper (II) monohydrate [11] are some of the amino acid based semi organic materials reported with enriched NLO efficiency and optical quality. Glutamic acid is a monoamino dicarboxylic α -amino acid and a significant constituent of proteins such as myosin, insulin and edestin. It was shown to be phase matchable for optical second harmonic generation of 1.06 μm and has nonlinear optical co-efficient [12-13]. From the literature, it is inferred that L-glutamic acid has been proved to have improved NLO efficiency upon the reaction with inorganic hydrochloric acid [14] and hydrobromic acid. The combination of simplest amino acid glycine with lithium sulphate monohydrate exhibits high nonlinear optical property. However there is no report available so far on the compound of L-Glutamic acid with lithium sulphate monohydrate. The present work reports for the first time the synthesis, crystal growth and characterization of a new semi organic material, where the glutamic acid has been chosen to be the organic ion and Lithium sulphate monohydrate that has potential applications in technological devices, such as pyroelectric, nonlinear optical, and ferroelectric devices to be the inorganic counterpart in the present study [15-17]. The improved nonlinearity and physical properties

are typical of the strategy targeted in engineering semi organic material for nonlinear optical device applications. Having gone through many articles regarding single crystal grown by slow evaporation method which has NLO properties, and especially the last four articles mentioned in the literature survey has given vigour to do a project in lithium sulphate monohydrate and glutamic acid. Besides, the synthesis of lithium sulphate monohydrate oxalate gives a clear idea about the semi-organic materials for NLO applications. Also it is obvious that lithium sulphate monohydrate (LSMH) is an inorganic material and has a NLO property and glutamic acid is an organic material and when both are combined together it forms a semi-organic material for an enhanced NLO properties. Hence, the work focuses on the preparation of pure lithium sulphate monohydrate (LSMH) and glutamic added lithium sulphate monohydrate (GLSMH) and comparison of the same for NLO applications.

2. Experimental Methods

2.1 Materials

The materials used are lithium sulphate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) (Merck) (99% AR grade), glutamic acid (Merck) (99% AR grade), de-ionized water and NaOH to adjust pH.

2.2 Synthesis of Crystal Growth

Lithium sulphate monohydrate crystal was synthesized from glutamic acid and lithium sulphate monohydrate by taking in equimolar ratio (1:1). A calculated amount of the reactants was dissolved in deionized water and stirred well using magnetic stirrer and a homogeneous mixture was obtained. The solution was filtered and allowed for slow evaporation at room temperature. After a span of 15 days, a single nucleation started and the grown crystals were harvested over a period of 30 days. A calculated amount of the reactants was dissolved in deionized water and stirred well using magnetic stirrer and a homogeneous mixture was obtained. After that the PH of the saturated solution was adjusted to 10.4, which is one unit greater than that of the Pka value using NaOH to stimulate the dissociation of the compound. The solution was filtered and allowed for slow evaporation at room temperature. After a span of 15 days, a single nucleation started and the grown crystals of the size $3 \times 2.5 \times 1 \text{ mm}^3$ were harvested over a period of 30 days. The photograph of grown crystals is shown in Fig. 1.

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2.3 Characterization of Pure and Glutamic Added LSMH

Structural analysis were confirmed by X-Ray powder diffraction (XRD), the presence the vibrational modes were identified using Fourier transform infrared spectrometry (FT-IR), UV-visible spectrum confirm the absorption of grown crystal. The stability of the material was found by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) technique. The powder SHG technique confirms the presence second harmonic generation of the material.

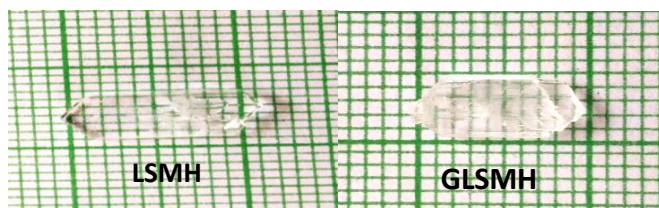


Fig. 1 The photograph of LSMH and GLSMH

3. Results and Discussion

3.1 Structural Analysis

The unit cell parameters and crystalline phase of the grown crystals have been determined by analyzing the powder XRD pattern of L-glutamic lithium sulphate monohydrate that was recorded by employing XPERT-PRO diffractometer system with $\text{CuK}\alpha$ radiation of wavelength $\lambda = 1.54060 \text{ \AA}$. The XRD pattern of L-GLSMH in Fig. 2 shows the sharp and major reflecting planes confirming crystalline purity. The analysis of powder XRD pattern was done using the powder X software. The indexed peaks in the pattern depict standard assigned peaks of lithium sulphate monohydrate along with few additional peaks. There is observed change in the intensity of faces 1 0 1 and 1 1 0, compared with the standard XRD pattern of LSMH crystals. The powder XRD data revealed that the L-GLSMH was crystallized in monoclinic structure having space group P_{21} with unit cell parameters: $a = 17.8892 \text{ \AA}$, $b = 5.8714 \text{ \AA}$, $c = 9.6801 \text{ \AA}$. The slight changes in the lattice parameters in reference to the pure LSMH and minute alteration in the 1 0 1 and 1 1 0 face intensities indicate the strain imposed by glutamic acid on the lattice site of the lithium sulphate monohydrate.

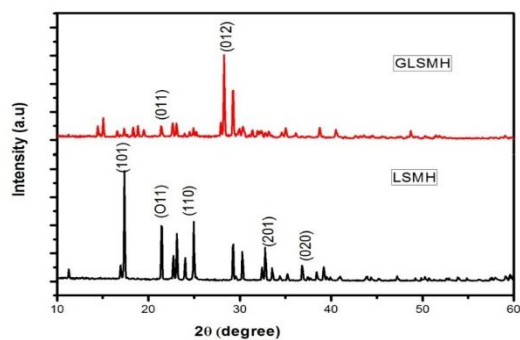


Fig. 2 Powder XRD pattern of LSMH & GLSMH

3.2 Functional Group Analysis

The functional groups of the compound have been identified by using FTIR spectrum that was recorded for the fine powder of Lithium sulphate monohydrate in the wavelength region between $400\text{--}4000 \text{ cm}^{-1}$ using Perkin Elmer Spectrum RX I spectrometer. The spectrum of LSMH is shown in Fig. 3. The assignments are discussed in three different regions: a high wave number region ($4000\text{--}3000 \text{ cm}^{-1}$), a functional group region ($3000\text{--}1500 \text{ cm}^{-1}$), and a fingerprint region ($1500\text{--}400 \text{ cm}^{-1}$) [18]. The broad peak observed at 3499 cm^{-1} is attributed to O-H stretch vibration of lithium sulphate monohydrate. The characteristic stretching vibrations of SO_4^{2-} group appear at 1111 and 638 cm^{-1} , which are in good agreement with compounds containing lithium sulphate monohydrate [19].

The functional groups of the compound have been identified by using FTIR spectrum that was recorded for the fine powder of L-glutamic lithium sulphate monohydrate in the wavelength region between $400\text{--}4000 \text{ cm}^{-1}$ using Perkin Elmer Spectrum RX I spectrometer. The spectrum of L-GLSMH is shown in Fig. 3. The assignments are discussed in three different regions: a high wave number region ($4000\text{--}3000 \text{ cm}^{-1}$), a functional group region ($3000\text{--}1500 \text{ cm}^{-1}$), and a fingerprint region ($1500\text{--}400 \text{ cm}^{-1}$). The broad peak observed at 3497 cm^{-1} is attributed to O-H stretch vibration of

lithium sulphate monohydrate. The strong peaks at 1723 and 1761 cm^{-1} are assigned to C=O stretch. This is slightly shifted due the compound formation. The NH_3^+ symmetric deformation is observed at 1514 cm^{-1} . The characteristic stretching vibrations of SO_4^{2-} group appear at 1115 and 638 cm^{-1} [18, 19], which are in good agreement with compounds containing lithium sulphate monohydrate.

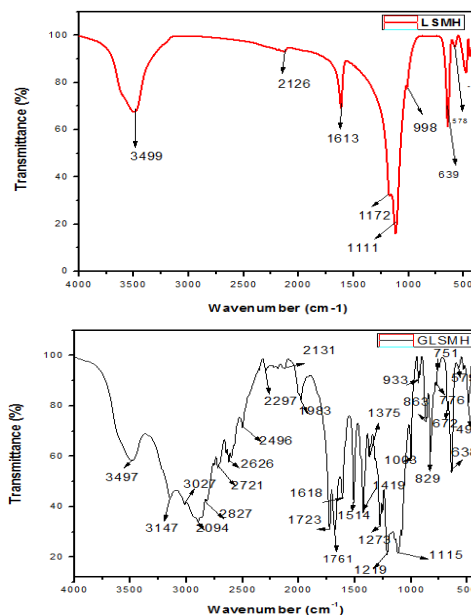


Fig. 3 FTIR spectrum of LSMH and GLSMH

3.3 Linear Optical Analysis

The optical transmission range, transparency cut-off and absorbance band are important optical parameters for laser frequency conversion applications [20]. Hence, the estimation of optical transmission range of the grown crystal for NLO applications becomes significant. The optical transmission spectra of lithium sulphate monohydrate crystal were recorded using Perkin Elmer Lambda 35, a high resolution UV Visible spectrophotometer in the wavelength region 190 nm to 1100 nm and the resulting spectrum is given in Fig. 4. The grown crystal has lower cut off wavelength 226 nm along with sufficient transmission in the entire visible region. This makes it a potential material for blue light emission. The optical band gap (E_g) evaluated is 5.49 eV . The existence of wide transparency in LSMH crystal offers reduced scattering and absorption of light in the visible region owing to the intrinsic property of the counter ion (amino acid), and minimized defects (structural and crystalline). This enforces substantial enrichment of optical quality of the grown GLSMH crystals. The good optical transparency observed in GLSMH crystal pronounces it as a suitable material for the transmission of SHG radiation of Nd:YAG laser, in designing NLO devices and UV tunable lasers.

The optical transmission spectra of glutamic lithium sulphate monohydrate crystal were recorded using Perkin Elmer Lambda 35, a high resolution UV Visible spectrophotometer in the wavelength region 190 nm to 1100 nm and the resulting spectrum is given in Fig. 4. The grown crystal has lower cut off wavelength 256 nm along with sufficient transmission in the entire visible region. This makes it a potential material for blue light emission [19, 20]. The optical band gap (E_g) evaluated is 4.85 eV . The existence of wide transparency in L-GLSMH crystal offers reduced scattering and absorption of light in the visible region owing to the intrinsic property of the counter ion (amino acid), and minimized defects (structural and crystalline). This enforces substantial enrichment of optical quality of the grown L-GLSMH crystals. The good optical transparency observed in L-GLSMH crystal pronounces it as a suitable material for the transmission of SHG radiation of Nd:YAG laser in designing NLO devices and UV tunable lasers [20].

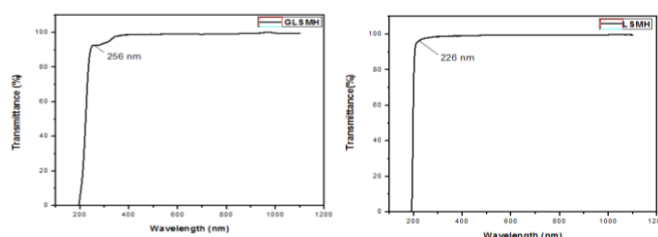


Fig. 4 UV-Visible spectrum of LSMH and GLSMH

3.4 TGA and DTA Analysis

The TGA and DTA curve of LSMH crystals were shown in Fig. 5. The water molecules will be evaporated at the temperature of 103 °C of LSMH. The phase transition takes place from 103 °C upto 127 °C. from the DTA curve, there is one exothermic and one endothermic peaks were observed. The TGA and DTA curve of GLSMH crystals were shown in Fig. 5. The water molecules will be evaporated at the temperature of 206 °C of GLSMH. The phase transition takes place from 103 °C upto 243 °C. from the DTA curve, there is one exothermic and one endothermic peaks were observed.

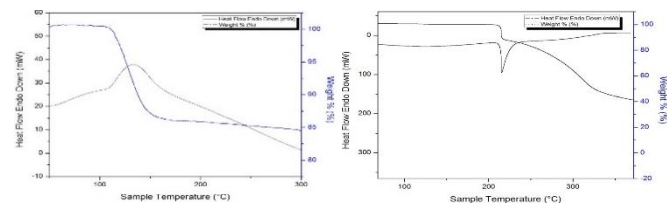


Fig. 5 TGA and DTA curve of LSMH and GLSMH

3.5 Nonlinear Optical Analysis (SHG Measurement)

The second harmonic generation efficiency of the crystal was studied by the powder technique developed by Kurtz and Perry [21]. The powdered sample of the grown crystal was packed into quartz capillary tube. After that, the sample was radiated by the beam of wavelength 1064 nm from Nd: YAG laser source. The output indicates that the SHG efficiency of L-GLSM is 1.933 times greater than that of KDP. This enhanced NLO coefficient is another important expected outcome of semiorganic crystal formation.

4. Conclusion

New semi organic good quality L-glutamic lithium sulphate monohydrate crystals were grown from solution by slow evaporation technique. The structure of the grown crystal was found to be monoclinic with space group $P2_1$ and the reflecting planes were indexed. The cut off wavelength and optical band gap value signify that this material possesses enhanced optical quality. The functional group identification communicate that this grown crystal is a hybrid of organic (L-glutamic acid) ion with inorganic (lithium sulphate monohydrate) ion. The improved work hardening coefficient and nonlinear optical efficiency are the achievements of engineering semiorganic material. Wide optical transparency in the visible region, improved work hardening coefficients and enhanced NLO properties are highly favourable parameters for NLO device fabrication.

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