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Growth, Optical and Magnetic Properties of Lithium Sulphate Doped l-Threonine Crystal

J. Elberin Mary Theras[1*], D. Kalaivani[1], D. Jayaraman[2], V. Joseph[1]
[1,1]Department of Physics, Loyola College, Chennai, Tamil Nadu, India*
[2]Department of Physics, Presidency College, Chennai, Tamil Nadu, India
[*] elberinraj@gmail.com

Abstract: *Lithium Sulphate doped L-threonine (Li_2SO_4-LT), a semi-organic crystal, has been synthesised and grown by slow evaporation technique at room temperature. The grown crystal was subjected to single crystal X-ray diffraction analysis in order to establish their crystalline nature. Li_2SO_4-LT crystal belongs to the orthorhombic crystal system with space group $P2_12_12_1$. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) study was carried out to quantify the concentration of lithium element in the grown crystal. The grown material has been found to possess wide transparency in the range 240 – 1100 nm with lower cut-off wavelength at 240 nm. The optical band gap was calculated as 4.92 eV using optical absorption spectrum and Tauc's relation. Fourier transform infrared (FTIR) spectroscopic study was performed to identify the functional groups present in the grown crystal. The surface features of the grown crystal were analyzed using Scanning Electron Microscope (SEM) analysis. The magnetic property was studied with the help of Vibrating Sample Magnetometer (VSM). The second harmonic generation (SHG) efficiency was measured by the Kurtz powder technique using Nd:YAG laser and was found to be 1.46 times that of standard potassium dihydrogen phosphate (KDP).*

Keywords: *Slow evaporation technique, X-ray diffraction, FTIR spectroscopy, SEM analysis, Magnetic property*

1. Introduction

Nonlinear optical materials have a predominant role in the technology of photonics, laser technology, optical communication and data storage technology including optical information processing and frequency conversion [1-3].Second order nonlinear optical materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [4,5].In semi-organic materials, the organic ligand is ionically bonded with inorganic host, and hence the new semi-organic crystals are having higher mechanical strength and chemical stability. The semi-organic crystals possess several attractive properties such as high damage threshold, wide transparency and high nonlinear coefficient [6-8]. The importance of amino acid for NLO applications is due to the molecular chirality, absence of strongly conjugated bonds and zwitterionic nature of the molecule. L-threonine molecule can exist in zwitterionic form and hence it is capable of forming compounds with anionic, cationic and neutral chemical compounds. Owing to its basic nature, L-threonine forms a number of salts with different organic and inorganic acids and many of them are found to show evidence of interesting NLO properties [9-11].Li_2SO_4-LT is a semi-organic NLO crystal which is formed by mixing L-threonine and lithium sulphate. Li_2SO_4-LT material crystallizes in the orthorhombic system with space group $P2_12_12_1$**,** exhibiting ferromagnetic behavior. Therefore, in the present work, single crystals of Li_2SO_4-LT were grown and characterized using X-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR), UV-spectral analysis, Scanning Electron Microscope (SEM) analysis, ICP-OES analysis, Vibrating Sample Magnetometer (VSM) and Nonlinear optical studies.

2. Materials and Methods

2.1 Synthesis of Li_2SO_4-LT

The compound Li_2SO_4-LT was synthesised by the reaction of equimolar ratio of L-threonine with lithium sulphate. A saturated solution of lithium sulphate was prepared and L-threonine was added slowly at room temperature. The solution was stirred for 12 hours to get homogeneity. The homogeneous solution was filtered and kept undisturbed for slow evaporation at room temperature. After a period of one month, the crystals were harvested. The grown crystals were purified by recrystallization process. The photograph of the as-grown doped crystal with the dimensions of **30×5×3** mm^3 is shown in Fig.1.

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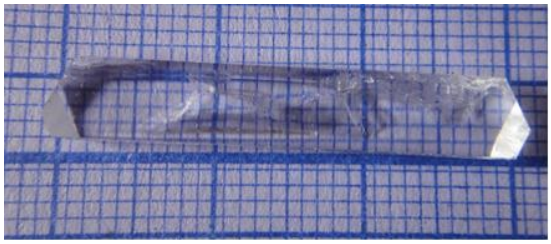

Fig.1 Photograph of as - grown Li_2SO_4-LT single crystal

3 Results and discussion

3.1 Single crystal X-ray diffraction

The grown crystal was subjected to single crystal X-ray diffraction studies using Bruker X8 Kappa APEXII single crystal X-ray diffraction. From the diffraction analysis, it has been found that the title compound crystallizes in orthorhombic system, with non-centrosymmetric space group, $P2_12_12_1$. The lattice parameters were estimated as a=7.76Å, b=5.17Å, c=13.64Å, with the unit cell volume of 547Å3. The space group suggests that the grown crystal is non-centrosymmetric which fulfills the fundamental criterion for the NLO property of crystal.

3.2 ICP-OES elemental analysis

The crystal was subjected to Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis to check the incorporation of lithium sulphate in the host material. It is based on the principle that sample solution is introduced into the core of ICP and all the elements in the solution become thermally excited and emit light at their characteristic wavelength. The emitted wavelength is amplified to yield an intensity measurement that can be converted into an elemental concentration by comparison with calibration standards. To determine the exact weight percentage of lithium present in Li_2SO_4-LT crystal, 20 mg of fine powder of the crystal was dissolved in 15 ml of deionized water. This prepared solution was placed in ICP optical emission spectrometer and thermally excited. The amount of lithium present in the sample was determined as 1.050 mg/L and the amount of sulphur present in the sample was determined as 2.609 mg/L from the emissions of their characteristic wavelengths 670.784 nm and 181.975 nm respectively. From the above analysis, the presence of dopant lithium sulphate is confirmed in the grown crystal.

3.3 UV-vis-NIR spectral analysis

The optical absorption spectrum of Li_2SO_4-LT crystal was recorded in the range of 190 - 1100 nm using Perkin Elmer Lambda 35 UV-vis-NIR spectrometer. The spectrum shown in **Fig.2** indicates very low absorption in the UV, visible and NIR regions for the crystal. The UV cut-off wavelength is observed at 240 nm. A good optical transmittance is essential for the material to be used in UV tunable laser and second harmonic generation (SHG) device applications [12]. The optical absorption coefficient (α) was calculated using the relation [13], $\alpha = 2.3026(1/T)/t$. where T is the transmittance and t is the thickness of the crystal.

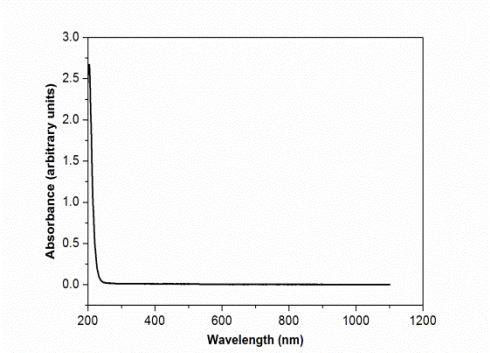

Fig.2 UV-vis-NIR absorption spectrum of Li_2SO_4-LT crystal

The optical bandgap (E_g) was evaluated using the following Tauc's relation, $\alpha h\nu = A (E_g - h\nu)^2$ where A is a constant, E_g is the optical band gap, h is Plank's constant and ν is the frequencyof incident photons. The value of optical band gap was estimated from the plot of $(\alpha h\nu)^2$ against hν (Fig.3) by extrapolating the linear portion of the curve to zero absorption and E_g

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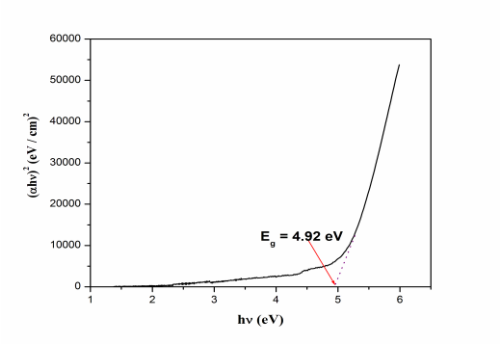


Fig.3 Plot of $(\alpha h\nu)^2$against photon energy (hν)

was found to be 4.92eV.The higher value of optical band gap will enhance the dielectric property of the material to ascertain the enhanced NLO activity. The optical study thus confirms the wide transmission range and dielectric nature of the grown crystal.

3.4 FTIR spectroscopy

FTIR spectroscopy was used to identify the functional groups present in the grown crystal. **Fig.4**shows the characteristic absorption peaks recorded for the grown crystal in the spectral range of 400-4000 cm^{-1}. Table 1 provides the various functional modes assigned corresponding to the peaks of FTIR spectroscopy. The band that appears at 2982 cm^{-1} with weak intensity shows CH_3 asymmetric stretching. The peaks corresponding to the wave numbers 2713 $cm^{-1}$and 1457 cm^{-1} represent CH_2 symmetric stretching and C-H in plane bending.

Table 1 FT-IR Assignments of **Li_2SO_4-LT** crystal

Wave number cm^{-1}	Mode	Assignments
2982	CH_3	asymmetric stretching
2713	CH_2	symmetric stretching
2049	NH_3^+	asymmetric deformation
1631	C = O	asymmetric stretching
1457	C - H	in plane bending
1246	O – H	bend of COOH group
1112	C - C - N	symmetric stretching vibration
1038	SO_4	vibration
930	C - C	stretching
700	CO_2	wagging vibration
559	SO_4	presence of sulphate ions
488	NH_3	torsional mode

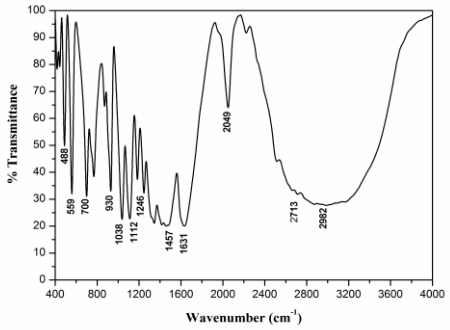
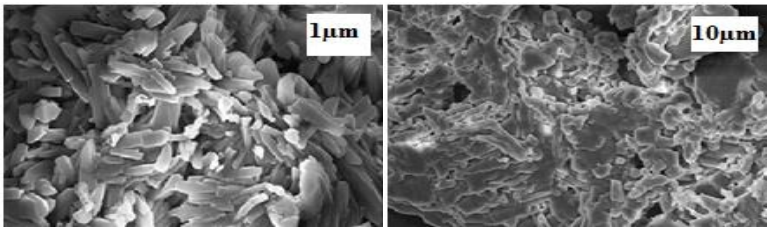


Fig. 4 FTIR spectrum of Li_2SO_4-LT crystal

The peak at 2049 cm^{-1} with strong intensity represents NH_3^+ asymmetric deformation. C=O asymmetric stretching is due to the medium intensity peak at 1631 cm^{-1}. The peaks against 1038 cm^{-1} and 559 cm^{-1} show the presence of sulphate ions in the grown crystal Li_2SO_4-LT. The O-H bend of COOH group is indicated due to the peak at 1246 cm^{-1}. The C-C-N symmetric stretching vibration is observed at 1112cm^{-1}**[14].** The peak against 930 cm^{-1} shows C-C stretching vibration. The peak observed at 700 cm^{-1} represents wagging vibration of CO_2 structure **[15].** NH_3 torsional mode is represented by the peak against 488 cm^{-1}.The presence of COOH and NH groups are thus confirmed from FTIR analysis. The zwitterionic nature of the compound clearly indicates that an imbalance of charges is provided to make the material non-centrosymmetric.

3.5 Scanning Electron Microscopy (SEM)

SEM micrographs were recorded using Quanta FEG 200 scanning electron microscope.



Figs. 2 (a) and (b) SEM images of Li_2SO_4-LTcrystal

Figs. 5(a) and (b) show the SEM images of the grown crystal with resolutions 1µm and 10µm respectively. From the image of **5(a),** it is understood that plate like morphology is more dominant than the rod shaped morphologies. This may be due to the incorporation of Li_2SO_4 in the host lattices as predicted from ICP – OES analysis. The micrograph shown in **Fig.5(b)** indicates different layers with aggregation of micro crystals of different sizes. This confirms the presence of various elements present in the grown crystal.

3.6 Magnetic property - Ferromagnetic behavior

The magnetic property of the grown material was studied using a vibrating sample magnetometer (Lakeshore model 7407) at room temperature.

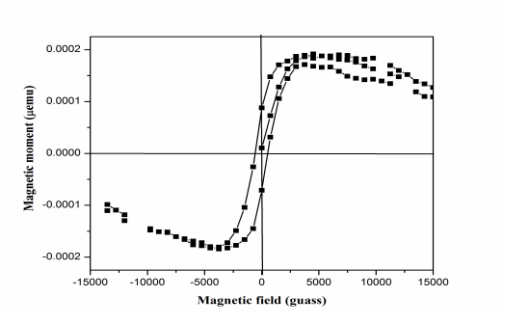


Fig.6 Plot of magnetic moment versus magnetic field for Li_2SO_4-LT crystal

Fig.6 shows the plot of the magnetic moment of the Li_2SO_4-LT crystal as a function of the applied magnetic field at room temperature. The S shaped curve observed in the central part of the plot suggests that the material shows magnetic ordering during magnetization. The plot clearly shows the ferromagnetic behavior of the crystal. Since the shape of the loop is very steep, the material is said to be a soft magnetic material. The smaller area of the loop suggests that the hysteresis loss is small. The coercivity and retentivity of the sample are found to be550.06G and 79.50×10^{-6}emu respectively.

3.7 NLO activity - SHG efficiency

The nonlinear optical property was tested using Kurtz and Perry powder technique **[16].** The crystal was ground into a homogeneous powder and densely packed between two transparent glass slides of a cell. A Q-switched Nd: YAG laser (DCRII) was used as light source. A laser beam of fundamental wave length 1064 nm, 8ns pulse width, and 10 Hz pulse rate was allowed to strike the sample cell normally. The power of the incident beam was measured using a power meter. The Second Harmonic Generation (SHG) output of wavelength 532 nm was finally detected using a photomultiplier tube.

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KDP crystal was powdered to the identical size and was used as a reference material to measure SHG efficiency. The SHG efficiency of doped Li_2SO_4-LT crystal was found to be 1.46 times that of KDP. Therefore, it is concluded that the doped crystal is a potential nonlinear optical material with more efficiency.

Conclusion

Semi-organic crystals of Li_2SO_4-LT were grown by slow evaporation technique within a period of 1 month. The doped crystal was subjected to single crystal X-ray diffraction analysis and it was confirmed that the crystal belongs to the orthorhombic system with space group $P2_12_12_1$. The presence of dopant in the grown crystal was confirmed by ICP-OES analysis. The optical absorption study confirmed that the doped crystal has low absorption in the UV, entire visible and NIR region with UV cut-off wavelength at 240 nm. The presence of various functional groups was confirmed by FTIR analysis. The surface features of the grown crystal were discussed using SEM analysis. The ferromagnetic property of the material was analyzed by VSM study. The coercivity and retentivity of the sample are found to be 550.06G and 79.50×10^{-6}emu respectively. The second harmonic generation (SHG) efficiency was measured by the Kurtz powder technique using Nd: YAG laser and was found to be 1.46 times that of standard potassium dihydrogen phosphate (KDP). Hence, the grown material can also be considered as a potential NLO candidate for the fabrication of nonlinear optical devices involving frequency–doubling process.

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