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Synthesis, structural and optical properties, ferromagnetic behaviour, cytotoxicity and NLO activity of lithium sulphate doped L-threonine

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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 (a=7.66 Å, b=5.11 Å, c=13.60 Å) with space group $P_1^2 2_1 2_1$. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) study was carried out to quantify the concentration of lithium element in the grown crystal. The results show that 0.07 mol of lithium sulphate has been incorporated into the parent system. 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 coercivity and retentivity of the material were measured from the hysteresis curve as 550.06 G and 79.50×10^{-6} emu respectively. 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay method was performed to understand the cytotoxicity or anticancer activity of the sample. The cell viability and cytotoxicity of the sample against MCF-7 cells were estimated as 49.41% and 50.59% respectively at a concentration of 250 μg. 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).

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. Owing to the basic nature, L-threonine (LT) 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]. Even though the crystallographic data of Li_2SO_4-LT slightly deviate from those of pure LT, the physical properties of Li_2SO_4-LT are entirely different from those of pure LT. The optical band gap, transmission range, SHG efficiency, surface features and magnetic property of Li_2SO_4 doped LT are different due to the incorporation of Li_2SO_4 into lattices of pure LT. Lithium sulphate has pyroelectric and ion conducting properties. When it is incorporated into the crystal lattices of L-threonine, the electrical conductivity increases. When lithium sulphate is dissolved in water along with L-threonine, lithium sulphate has endothermic disassociation. As a result, the physical properties of the Li_2SO_4-LT have been changed. When a U-tube containing pure L-threonine solution placed perpendicular to a magnetic field, the level of the solution decreased. This confirms the diamagnetic behaviour of L-threonine. When Li_2SO_4 is doped with L-threonine, the diamagnetic behaviour is changed into ferromagnetic behaviour. The change of other properties due to the

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dopant into the crystal lattices of L-threonine is discussed under the corresponding subtitles.

Lithium sulphate doped L-threonine (Li_2SO_4-LT) is a semi-organic NLO crystal which is formed by mixing L-threonine and lithium sulphate. The NLO activity of the grown crystal was enhanced due to zwitterionic nature of the material. The charge transfer from $COOH^-$ to NH_2^+ is responsible for the enhanced NLO activity.Li_2SO_4-LT is also a ferromagnetic material which belongs to the category of soft magnetic material with small hysteresis loss. The doped material shows improved optical property as evident from optical study. When amino acids form coordination complexes, the chemical species formed can perform biological functions too as exemplified by the interaction of enzymes [12,13]. There are various studies performed on pure LT, L-threonine Zinc Acetate, Magnesium Sulphate admixtured L-threonine, L-threonine Cadmium Chloride and Potassium Iodide doped L-threonine [14–18].

Therefore, in the present work, single crystals of Li_2SO_4 doped LT crystals were grown and characterized using X-ray diffraction (XRD) study, ICP-OES analysis, UV–vis–NIR optical absorption, Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscope (SEM) analysis, Vibrating Sample Magnetometer (VSM) measurement, Cytotoxicity and Nonlinear optical studies. The various characterization studies were performed with a view to analyze the crystal system, composition of the materials, transmission range, functional groups, surface features, magnetic property and cytotoxic activity of the grown material.

2. Material preparation

Lithium sulphate and L-threonine were taken with 1:1 M ratio and dissolved in water at room temperature. The solution was stirred for 12 h 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. Recrystallization is a technique used to purify chemicals. It works only when the proper solvent is used. By dissolving both the starting materials in an appropriate solvent, the impurities can be coaxed out of the solution, leaving the other behind. The repeated recrystallizations were thus used to purify the crystals. The following chemical reaction for the synthesis of the material was expected to take place

$$C_4H_9NO_3 + Li_2SO_4 \rightarrow C_4H_9NO_3 \cdot Li_2SO_4$$

1mole + 1mole 2mole

At this stage, it is not possible to confirm the formation of a semi-organic material L-threonine lithium sulphate. It requires some more studies (ICP-OES analysis and XRD study) to confirm whether the grown material has been formed due to chemical reaction or doping. The photograph of the as-grown crystal with the dimensions of **30 × 5 × 3** mm^3 is shown in Fig.1.

3. Results of characterization studies

3.1. ICP-OES elemental analysis – Incorporation of dopant

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) study was carried out to analyze the elemental composition of the grown material. To determine the exact weight percentage of lithium present in Li_2SO_4-LT crystal, 76.18 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 0.015 mg/15 ml and the amount of sulphur present in the sample was determined as 0.039 mg/15 ml from the emissions of their characteristic wavelengths 670.784 nm and 181.975 nm respectively. Actually we expected to form a complex semi organic material, L-threonine lithium sulphate due to 1:1 M ratio of the starting materials. But the results of the ICP-OES study reveal that only 0.07 mol of lithium sulphate has been incorporated into crystal lattices of pure L-threonine to influence the surrounding and distort lattice locally which leads to the slight changes in the lattice parameters of the parent system. The remaining 0.93 mol of lithium sulphate goes into the solution. Since lithium sulphate (Li_2SO_4) is a salt of strong acid and strong base, it is not possible for the salt to react with L-threonine. Hence the grown material is not a complex semi-organic material L-threonine lithium sulphate. Since 0.07 mol of lithium sulphate is present in the grown material, it is concluded that the grown material is Lithium sulphate doped L-threonine crystal (Li_2SO_4-LT).

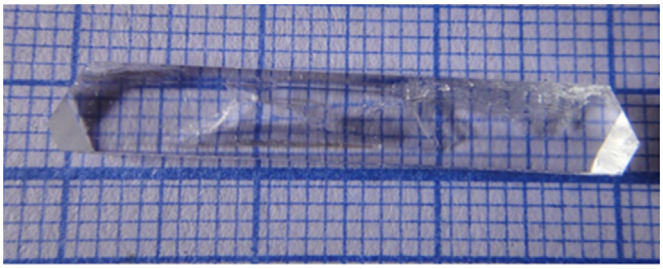

Fig. 1. Photograph of as - grown Li_2SO_4-LTcrystal.

3.2. XRD study - Structure of Li_2SO_4-LT

The structure of the grown crystal was studied using Bruker X8 Kappa APEXII single crystal X-ray diffractometer. From the diffraction analysis, it has been found that the title doped material crystallizes in orthorhombic system, with non-centrosymmetric space group, $P2_12_12_1$. The lattice parameters were estimated as a=7.66 Å, b=5.11 Å, c=13.60 Å, with the unit cell volume of 532 $Å^3$. The slight deviation of cell parameters of the doped crystal Li_2SO_4-LT from those of pure LT [14] confirms the incorporation of Li_2SO_4 in the host lattices of LT. The incorporation of the dopant Li_2SO_4 in the parent system is understood from ICP- OES elemental analysis.

Table 1 presents the crystallographic data of both Li_2SO_4-LT and pure LT. The space group suggests that the grown crystal is non-centrosymmetric in nature.

3.3. Optical property – UV–vis–NIR optical absorption spectrum

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

Table 1
Crystallographic data of **Li_2SO_4-LT** and **LT** crystals.

Name of the grown crystal	Li_2SO_4-LT (doped crystal)	LT (pure)
Crystal system	Orthorhombic	orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a	7.66 Å	5.15 Å
b	5.11 Å	7.75 Å
c	13.60 Å	13.66 Å
V	532 $Å^3$	546 $Å^3$
Crystal size	30 × 5 × 3 mm^3	30 × 5 × 5 mm^3