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Growth and investigations of oxalic acid lithium sulphate single crystal for optical sensors applications

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Abstract

An oxalic acid lithium sulphate single crystal has been grown by solution growth method. Crystalline nature of the grown crystal was confirmed by single crystal x-ray diffraction technique. The peak values and the grain size were determined by powder x-ray diffraction method. The functional groups existing in the crystal was identified by FTIR and FT-Raman spectroscopy. The optical transmittance spectrum of the grown crystal was studied using UV-Vis-NIR spectroscopy. The thermal stability of the material was investigated by TGA analysis. The Vickers micro hardness test was carried out to know the mechanical property of the grown crystal. The surface morphology of the material was analysed using scanning electron microscope. The second order nonlinear optical parameters were measured using Kurtz Perry method.

Keywords: *Single crystal, nonlinear optical material, structural properties, optical properties.*

1. Introduction

Crystalline compounds entitled a new class of multifunctional materials with catching attention in the field of data storage, optoelectronic and photorefractive properties for a wide range of applications. Molecular materials are considered now as a very important alternative for electronic components and electrically active devices manufacturing [1]. For future applications in photonics and optoelectronics it will be necessary to utilize compounds. Non-linear optical (NLO) materials play a major role in optical modulation, fibre optic communication, in the area of medicine, photonic and electronic devices as they are capable of producing multiple values of original frequency [2-7]. For NLO materials, we requisite greater physical strength and higher degree of polarization which prompted the development of hybrid organic inorganic materials called semi organics. Researchers are focussing on growing transparent and high quality Semi organic crystals because of their huge need in the industry [7-10]. In this present work we are focussing on the growth, characterization and properties of single crystal oxalic acid lithium sulphate. The title crystal has been grown from the mixture of oxalic acid and lithium sulphate in the splashing solution by the solution growth method. The grown crystal was subjected to characterize using single crystal and powder x-ray diffraction, FT-IR spectroscopy, FT-Raman spectroscopy, scanning electron microscope (SEM), TGA, UV-Vis-NIR optical studies and second harmonic generation.

2. Materials and methods

2.1. Synthesis of oxalic acid lithium sulphate crystal

Oxalic acid, Lithium sulphate and double distilled water were used in the experiment. The oxalic acid lithium sulphate single crystal was grown by slow evaporation solution growth method. The grown compound was synthesised by mixing the compound in an equimolar ratio and dissolved in double distilled water. The whole growth process was carried out in aqueous solution. After obtaining the homogeneous solution, the saturated solution

was filtered and it is kept in an undisturbed condition under normal temperature [11]. Optically transparent and defect free crystal were obtained in the period of 15 days and the grown crystal is shown in Fig. 1.

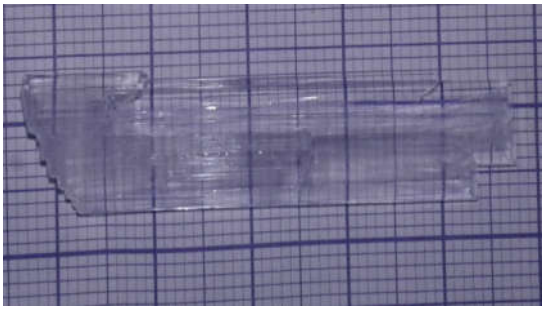

Fig. 1. *Grown crystal of Oxalic acid Lithium Sulphate*

2.2. Solubility of the material

The solubility study was carried out in a constant temperature bath with temperature controller of accuracy ±0.01^{0}C. Solubility of oxalic acid lithium sulphate was determined at different temperatures. The solution was stirred continuously for several hours to achieve homogenization condition [12]. After attaining saturation condition, the equilibrium concentration of the solute was estimated gravimetrically. The solubility curve of oxalic acid lithium sulphate is shown in Fig. 2.

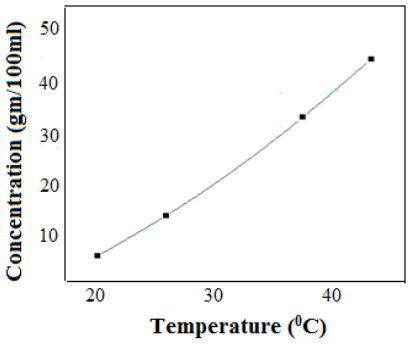

Fig. 2. *Solubility of oxalic acid lithium sulphate*

2.3. Characterization

Single crystal XRD was recorded by Enraf Nonius CAD/MACH3 single crystal X-ray diffractometer. The powder XRD pattern of crystal was obtained using a BRUKER AXS D8 advance X-ray diffractometer with CuKα radiation (λ = 1.54). Fourier Transform Infrared Spectrometer (FTIR) analysis was carried out using PerkinElmer spectrometer with the scan range of MIR 450-4000 cm^{-1}. The optical absorption and transmittance spectra were recorded using Lambda 35 UV–Visible spectrophotometer in the wavelength range of 190-700 nm. The thermal analysis was carried out to find the weight loss of the title crystal using NETZSCH STA 449 F3. Scanning electron microscopy (SEM) image was recorded using Inspect F50 from FEI. The second harmonic generation (SHG) efficiency of the material was studied using Kurtz-Perry powder technique using Nd: YAG laser beam.

3. Results and discussions

3.1. Single crystal x-ray diffraction analysis

Single crystal X-ray diffraction analysis was carried out to find the unit cell parameters of as grown crystal. The single crystal XRD study reveals that the title material belongs to triclinic crystal system with a space group P_1 which is recognized as noncentrosymmetric, thus satisfying one of the basic and essential requirements for NLO material. The unit cell parameters of the grown crystal are, *a* = 3.62 Å, b = 6.13 Å, c = 11.91 Å and volume of the material is found to be 257 Å^3.

3.2. Powder x-ray diffraction analysis

Powder X-ray diffraction studies were used to confirm the crystallinity of the oxalic acid lithium sulphate single crystal. The powder x-ray diffraction pattern of the grown crystal is shown in Fig. 3. The presence of sharp and strong peaks confirms the good crystallinity of the grown crystal.

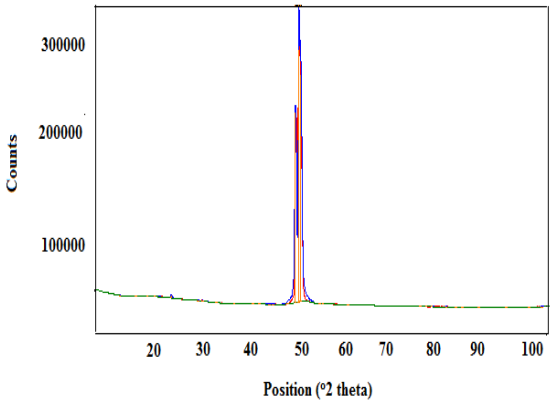

Fig. 3. *Powder XRD pattern of oxalic acid lithium sulphate*

From the XRD pattern, it is observed that, each peak has got a finite width. The grain size is determined by measuring the width of the line with highest intensity peak. The grain size can be calculated by using the formula

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (1)$$

Where, β is full with of half maxima (radian) and D is grain size of the crystal. The calculated average grain

size is 0.89 nm. The analysis of different diffraction peaks indicates the formation of system. The diffraction peaks at 2θ value were measured very carefully and converted into d value using the Bragg's equation putting n=1. The size of the crystal is very small compared to the other single crystals [13]. This variation in size explains the influence of addition of Lithium sulphate on the size of the crystal.

3.3. FTIR studies

The recorded FT-IR spectrum bears the signatures of all the functional groups in the present work, as shown in Fig. 4. The changes in 3020-2700 cm ^{1} clearly evidenced that the band of this region mainly represents the CH_3 and CH_2 groups of lipids, since absorption in 2997 cm ^{1} region is derived from asymmetric stretch of CH_3 group, in 3042-2771 cm ^{1} from asymmetric stretch of CH_2 in 3019-2771 cm ^{1} from symmetric stretch of CH_3 [13]. Within this region, four prominent bands were revealed in control which located at 3042, 3019, 2997 and 2771 cm ^{1}. The dominant bands around 2997 and 2771 cm ^{1} were observed to CH_3 stretching vibration, while bands around 3019 and 3042 cm ^{1} were assigned to CH_2 stretching vibration. The amide band of proteins is located in the region from 1700 to 1600 cm ^{1}, which is primarily due to the C=O stretching vibration of the amide groups in weakly coupling with the in plane N–H bending and C-N stretching. The weak band at 1226.5 cm^{-1} is due to the symmetric stretch of C-C bond while the band at 963.26 cm^{-1} is attributed to the rocking mode of methylene group. A moderate sharp band appeared at 516.8 cm ^{1} which might be due to CO_2 wagging. These peaks clearly represent the presence of various functional groups in the title compound.

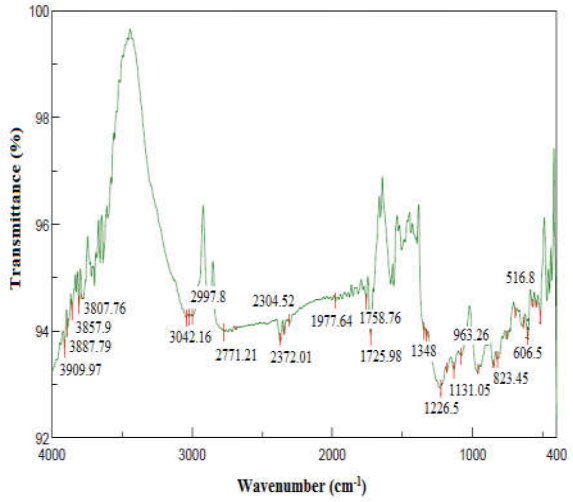

Fig. 4. *FTIR spectrum of oxalic acid lithium sulphate*

The laser Raman spectrum Fig. 5 was recorded using Raman System, in the range of 400 - 4000 cm-1. The C═N and C═C stretching vibrations are observed at 1626 cm^{-1} and 1469 cm^{-1} respectively. Comparison of vibrational frequencies from FTIR and Laser Raman spectrum of grown crystal is tabulated in Table 1.

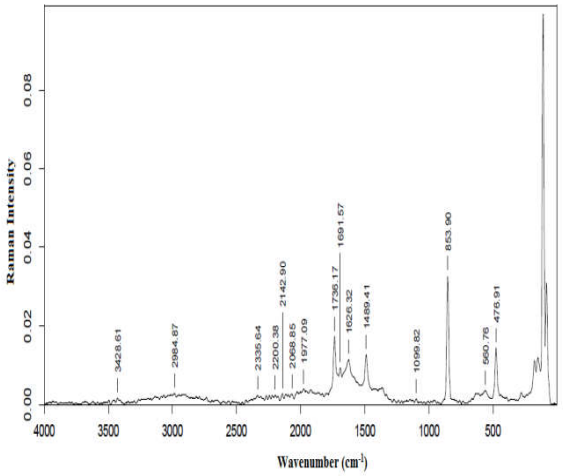

Fig. 5. *FT Raman Spectrum*

Table 1. *Vibrational frequencies of FT-IR and FT-Raman Spectroscopy*

FT-IR	FT-Raman	Functional Group
2997	2964	-C–H stretch Alkenes
2343	2335	-C≡N stretch Nitriles
1977	1977	-C≡C-stretch alkynes
1725	1736	-C=O stretch α, β–unsaturated esters
1079	1099	-C–N stretch aliphatic amines
850	853	-C–Cl stretch alkyl halides
569	560	-C–Br stretch alkyl halides

3.4. UV-Vis-NIR optical studies

Fig. 6 shows the optical transmittance spectrum for the grown crystal. From the transmission spectrum, it is found that the sample has a lower cut off wavelength at 230 nm.

The optical absorption coefficient was calculated using the relation [14].

$$\alpha = \frac{2.303 \log\left(\frac{1}{T}\right)}{d} \qquad (2)$$

Where T is the transmittance and d is the thickness of the crystal. The energy dependence of the absorption coefficient suggests the occurrence of the direct band gap. As shown in Fig. 7, the band gap energy is found to be 3.2 eV. The transmittance

window in the visible region and IR region enables good optical transmission of the second harmonic frequencies of ND: YAG lasers.

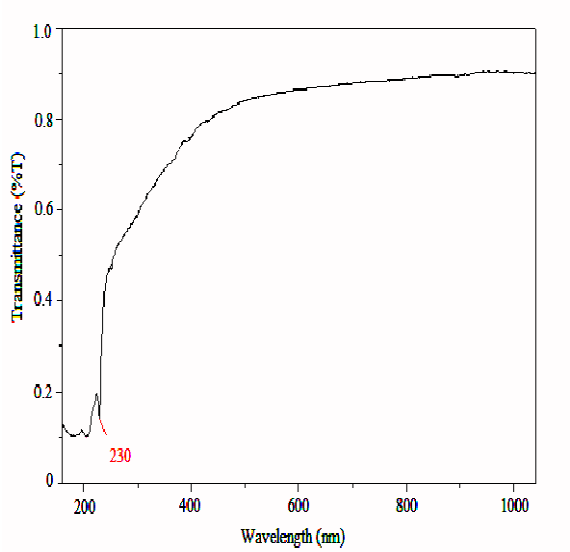

Fig. 6. *UV-Vis-NIR optical transmittance spectrum of oxalic acid lithium sulphate*

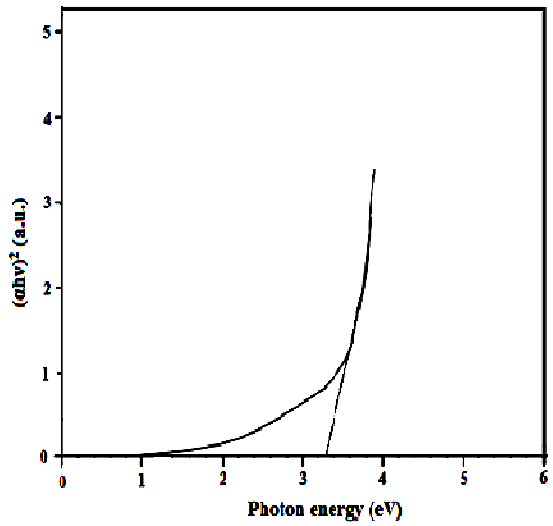

Fig. 7. *Plot of (αhv)² vs hv*

3.5. Thermal Analysis

The thermo gravimetric analysis (TGA) of the grown crystal has been carried out in the temperature range of 0-600°C. Alumina pan was used for heating and the analysis was carried out in nitrogen atmosphere at a heating rate of 20°C/min. The results are shown in Fig. 8.

In gravimetric analysis, it was found that the grown crystal were stable up to 215°C. The melting point of grown crystal is 215°C [15]. The increment in the decomposition temperature is evident for the doped crystals, suggesting that the substitution of lithium enhances the thermal stability.

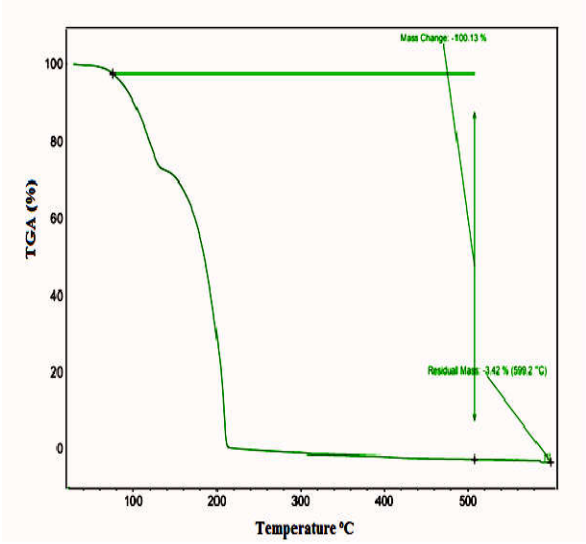

Fig. 8. *TGA curve of oxalic acid lithium sulphate*

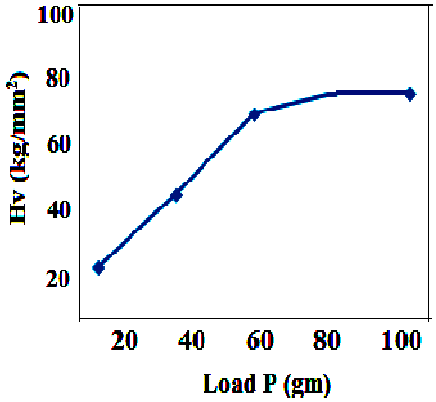

Fig. 9. *Variation of Vickers micro hardness number Hv with load*

3.6. Second-order NLO studies

The oxalic acid lithium sulphate crystal was tested using the powder technique of Kurtz and Perry [16] by a pulsed Nd:YAG laser for studying second-order NLO properties. The grown crystal was powdered in the grain size of 100 μm and the input laser beam was passed through IR reflector and directed on the powdered sample. Potassium dihydrogen phosphate (KDP) was used as the reference sample. The second harmonic generation (SHG) was confirmed by the emission of green light (λ = 532 nm) in the sample. The measured relative SHG efficiency of oxalic acid lithium sulphate crystal is 1.2 times greater than that of the standard KDP sample [17].

3.7. Micro Hardness Studies

The variation of Hv as a function of applied load is shown in Fig. 9. It is found that Hv increases with increase in load. Meyer's index number was calculated from Meyer's law which relates the load and indentation diagonal length. Indentations were made on smooth faces. Vickers micro-hardness tester having accuracy of ± 20 Vickers was used. The Vickers micro hardness number was calculated by $Hv = 1.854\ P/d^2$ Where p is applied load in g or N and d is diagonal length in mm. From the graph it is clearly indicates the presence of crack patterns around the indentation mark; which were found to be dependent on the indenter orientation. They have also observed that the indentation increased with increase in applied load.

3.8. SEM analysis

Fig. 10 shows the SEM image of the grown crystal. A two dimensional image was generated over a selected area of the sample [18]. Since oxalic acid lithium sulphate is a semi organic single crystal, which is poor conducing in nature, the sample was subjected to gold/carbon coating. From the Fig. 10, it is clear that the surface of the grown crystal appears very smooth surface and it has pots and microcrystals on the surface. The grain boundaries are clearly seen which shows the perfect growth of the crystal.

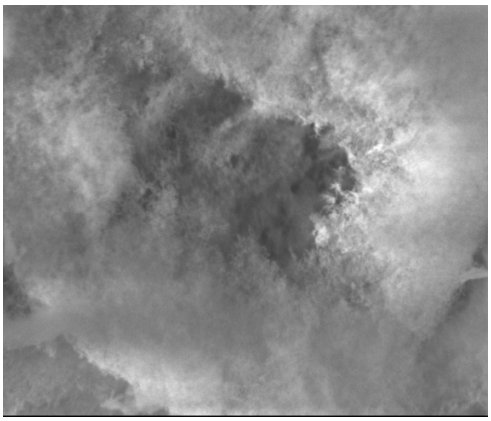

Fig. 10. *SEM image of oxalic acid lithium sulphate*

4. Conclusions

The optical crystal of oxalic acid lithium sulphate has been grown successfully by solution growth method. Structural and crystallinity of the grown crystal were confirmed by single crystal X-ray diffraction technique. The peaks value and the grain size were determined by powder x-ray diffraction method. The functional groups of the grown crystal were identified by FT-IR and FT-Raman spectroscopy. Optical transmittance spectrum exhibited a lower cut-off wavelength at 230 nm and the energy band gap was found to be 3.2 eV. The thermal stability of the material was investigated by TGA analysis and is evident that the substitution of lithium, enhancing the thermal stability of oxalic acid lithium sulphate. The calculated SHG efficiency of oxalic acid lithium sulphate crystal is found to be 1.2 times larger than that of the standard KDP sample. The Vickers micro hardness test exhibited the strong mechanical strength of the sample. The SEM image showed the smooth surface of oxalic acid lithium sulphate crystal.

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