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Structural, optical and mechanical property analysis of magnesium sulphate admixtured L-Threonine: A novel optoelectronic material

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ABSTRACT

L-Threonine is an important amino acid and famous due to their property of frequency conversion and electro optic modulation. Single crystals of magnesium sulphate admixtured L-Threonine was grown by slow evaporation technique. Good quality single crystal with dimension $58 \times 5 \times 10\,mm^3$ was harvested after 60 days. The powder X-ray diffraction pattern of the grown crystal has been indexed. The optical transmission spectrum shows that the magnesium sulphate admixtured L-Threonine possess good optical transparency in the entire visible region with Ultra Violet cut-off wavelength at 250 nm. The presence of fundamental functional groups was identified by Fourier Transform Infra Red spectral analysis. The structure of the grown crystal was established using Fourier Transform-Nuclear Magnetic Resonance spectral analysis. The thermal behaviour of the crystal has been discussed by Thermal Gravimetric Analysis and Differential Thermal Analysis. Magnesium sulphate admixtured L-Threonine was characterized by Energy dispersive analysis of X-ray. The second harmonic generation efficiency of magnesium sulphate admixtured L-Threonine crystal is found to be same as that of potassium dihydrogen phosphate crystal.

1. Introduction

In recent years there has been considerable interest on the synthesis of semiorganic nonlinear optical [NLO] materials with excellent second order optical nonlinearities because of their potential application in telecommunication, optical computing, optical data storage and optical information processing [1]. Semiorganic NLO crystals have good thermal and mechanical properties and large nonlinear coefficients [2,3]. Semiorganic materials include organic–inorganic salts and metal organic co-ordination compounds. Many complexes of amino acids with organic and inorganic salt exhibits non-linear optical properties [4,5]. In particular, optically active amino acid display specific features of interest such as molecular chirality, wide transparency range in the visible and UV (Ultra Violet) spectral region and zwitterionic nature of the molecule, which favours crystal hardness. Among these chiral compounds, L-Threonine is an important amino acid, which shows higher SHG (Second Harmonic Generation) efficiency than that of many other nonlinear amino acids. L-Threonine is an important polar amino acid and its dipole moment is nearly similar to water. In the case of metal-organic combination, the organic ligand is more dominant in the NLO property and metal compounds have high transparency in the UV region [3]. Since many of the inorganic salts possess good mechanical property, it is of interest to add magnesium sulphate with L-Threonine.

In this paper, we report on Magnesium Sulphate Admixtured L-Threonine nonlinear optical crystal, for the first time as far as the authors are concerned. Here after, Magnesium Sulphate Admixtured L-Threonine crystal is named as LTMS.

2. Experimental

2.1. Synthesis and crystal growth

LTMS was synthesized using commercially available L-Threonine (AR grade) and magnesium sulphate (AR grade). L-Threonine and magnesium sulphate heptahydrate were taken in 1:0.5. The calculated amount of salts was dissolved in double distilled water and stirred well using a magnetic stirrer to obtain a homogenous mixture. The solution was allowed to evaporate slowly until the solvent was completely dried. The purity of the synthesized salt was further increased by successive recrystallization process.

The synthesized salt of LTMS was dissolved thoroughly in double distilled water at 32 °C to form a saturated solution. The solution was then filtered twice to remove insoluble impurities. The growth

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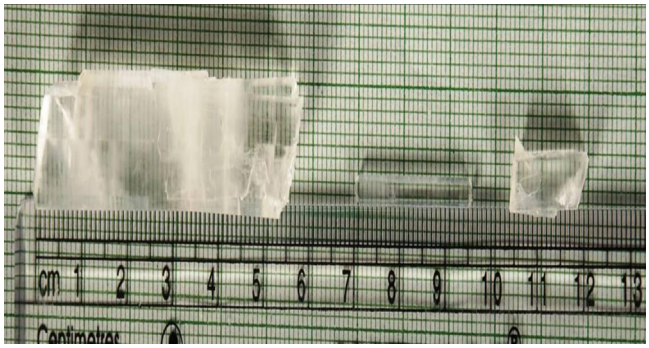

Fig. 1. The photograph of LTMS crystal.

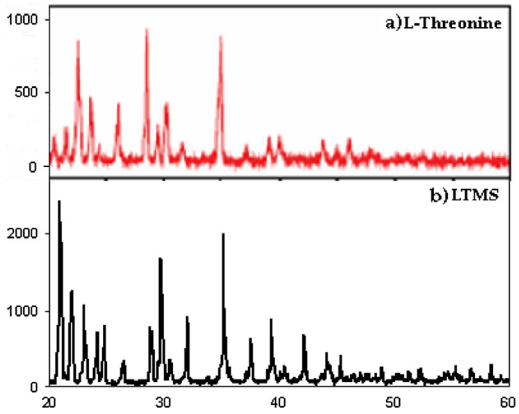

Fig. 2. Powder XRD patterns of a) L-Threonine and b)LTMS.

of LTMS crystals were carried out by low temperature solution growth technique by slow evaporation, in a constant temperature bath controlled to an accuracy of ± 0.01 °C. The solution was maintained at 35 °C. Transparent crystals of size 58 × 5 × 10 mm^3 were obtained after 60 days. Fig. 1 shows the grown crystals of LTMS.

2.2. Characterization

In order to estimate the structure the powder X-ray analysis of the grown crystal was carried out using an X-ray diffractometer (Model JDX 8030) with Cu Kα (λ = 1.5418 Å) radiation. FTIR (Fourier Transform Infra Red) spectrum was recorded by the KBr pellet technique using a SPECTROMRX1 FTIR spectrometer to confirm the functional groups. The ^{1}H and ^{13}C NMR spectra were recorded for the crystals by dissolving in water (D_2O) using Bruker 300 MHz (ultrasheild)^{TM} instrument at 23 °C (300 MHz for ^{1}H NMR (Nuclear Magnetic Resonance) and 75 MHz for ^{13}C NMR) for the confirmation of molecular structure. The transparency range was investigated by λ35 model PerkinElmer double beam UV–VIS–NIR (Ultra Violet–Visible–Near Infra Red) Spectrometer in the range from 190 nm to 1100 nm. In order to confirm the presence of $MgSO_4$, LTMS crystals were subjected to EDAX (Energy Dispersive Analysis X-Ray) analyzing using FESEM instrument attached with EDAX. TGA (Thermal Gravimetric Analysis)/ DTA (Differential Thermal Analysis) were carried out using the instrument NETSZCH SDT Q600 V8.3 Build 101 at a heating rate of 20 °C/min in nitrogen atmosphere in temperature range 0 °C–1200 °C. The qualitative measurement of the SHG efficiency was determined using powder technique developed by Kurtz and Perry. The SHG measurement was carried out using Q-switched mode locked Nd:YAG laser with first harmonic output at 1064 nm, with an input energy of 2.9 mJ /pulse and a pulse width of10 ns at a repetition rate of 10 Hz. The Vickers hardness measurement was made on the crystals using Shimadzu (Japan) HMV-2 hardness tester.

3. Results and discussion

3.1. Powder XRD analysis

The crystalline structure of the grown crystals was checked by taking the X-ray diffraction (XRD) pattern of the powder samples of LTMS. The presence of sharp peaks indicates the high crystallinity of the grown crystals. The Powder XRD pattern of LTMS is shown in Fig. 2. Additional reflections were seen and it indicates the presence of Magnesium Sulphate crystallites within the mixed crystals, which is identified by comparing with powder diffraction pattern of pure L-Threonine. The *h k l* values are found using powder V 1.00 software and are shown in Table 1.

3.2. UV–VIS–NIR spectral analysis

The UV visible spectrum in Fig. 3 shows the excellent transparency of the crystal in the entire UV–Vis–NIR region. According to reference [6] lower cut off wavelength in pure L-Threonine occurs at 220 nm and the optical transparency region lies between 250 nm and 900 nm. Lower cut-off is shifted to shorter wavelength in magnesium sulphate admixtured L-Threonine crystals. It is inferred from the results that LTMS crystal has high transmission in the entire UV–vis–NIR region and makes it a suitable material for optoelectronic applications.

Table 1
Powder XRD data of LTMS crystal.

2θ	d_{hkl} (Å)	*h k l*
13.320	6.6417	011
17.460	5.0750	100
17.620	5.0293	012
18.560	4.7767	101
20.880	4.2509	110
21.960	4.0442	111
23.020	3.8603	020
24.120	3.6867	112
24.780	3.5900	004
26.460	3.3657	022
28.760	3.1016	113
28.920	3.0848	120
29.440	3.0315	121
30.520	2.9266	023
31.980	2.7962	005
35.120	2.5531	123
35.640	2.5170	201
37.620	2.3890	211
39.020	2.3064	130
39.360	2.2873	124
40.140	2.2446	033
40.460	2.2276	025
42.180	2.1407	220
42.320	2.1339	221
44.120	2.0509	204
44.280	2.0439	125
44.460	2.0360	222
45.420	1.9952	214
47.080	1.9286	041
48.380	1.8798	035
48.920	1.8603	042
52.240	1.7496	142
54.760	1.6749	310
55.420	1.6565	127
56.760	1.6206	312
58.520	1.5759	045
61.500	1.5065	242
79.540	1.2041	404
79.780	1.2011	344