

# Study on structural, spectral, and optical properties of Copper Sulphate doped L-Methionine Crystal

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## ABSTRACT

Crystals of L-Methionine admixture with Copper Sulphate Pentahydrate were grown by a solution growth technique from aqueous solution at a constant temperature. The grown crystals were blue coloured, hygroscopic, and transparent. The lattice parameters of the grown crystals were determined by X-ray diffraction technique. UV-visible transmittance spectrum of the sample was recorded to study the optical transparency of the grown crystal. The presence of the dopant in the doped crystals was confirmed qualitatively by the FT-IR spectroscopy. The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique.

**Keywords:** Crystal growth, L-Methionine, copper sulphate pentahydrate, transparency.

## 1 Introduction

Semi-organic NLO materials are found advantageous over organic and inorganic crystals [1]. L-Methionine is sulfur-containing proteinogenic, hydrophobic amino acid [2], whereas copper sulphate pentahydrate is hygroscopic. L-methionine copper sulphate pentahydrate (LMCS) is a biaxial NLO crystal belonging to the orthorhombic crystal structure and  $P_{21}$  lattice type. The effect of sulphate and metal complex like copper doping on optical properties has been studied [3-4]. The effect of copper sulphate leads to a change in the lattice parameters of the crystal. Care has been taken to increase in the stability of solution during crystal growth, by controlled temperature and concentration of the solution.

## 2 Experimental

### 2.1. Material synthesis and crystal growth

Analytical grade of L-Methionine and copper sulphate pentahydrates (Loba Chemie) were taken as per their solubilities measured in distilled water to grow crystals. The solution was stirred continuously for several hours and the solution was vacuum filtered by Whatman's filter paper. The solution was kept undisturbed at 40 °C in PID controlled constant temperature bath. **Fig. 1** shows, the good quality crystals of LM+CS were grown within 21 days by allowing slow evaporation of supersaturated solution at constant temperature.



Fig. 1 Photograph of grown LM+CS.

### 2.2. Characterizations

The grown crystals were subjected to FTIR Spectroscopy, and their optical properties (Linear and Non-Linear) were studied. Optical transmission of grown crystals was measured by UV-Visible spectrometer (JASCO UV/VIS/NIR Spectrophotometer MODEL-670) in the spectral range 2000-190 nm. The grown crystal exhibits very limited transmission range. The FTIR spectroscopy was done on using instrument FTIR spectrophotometer (Model-ALPHA-II, Bruker, Japan) within the wave number range of 400-4000  $\text{cm}^{-1}$ . Powder XRD data was recorded on an X-ray diffractometer (Rigaku UltraX18, 18kW, Germany) in the range  $2\theta = 20^\circ - 80^\circ$  using  $\text{CuK}\alpha$  radiation of wavelength 1.5404 Å. The SHG efficiency was measured by using Kurtz and Perry powder method.

## 3 Results and Discussion

### 3.1 Crystal Structure:

Powder XRD data was recorded on an X-ray diffractometer (Rigaku UltraX18, 18kW, Germany) in the range  $2\theta = 20^\circ - 80^\circ$  using  $\text{CuK}\alpha$  radiation of wavelength 1.5404 Å. PowderX software was used to analyse the recorded powder XRD data of the LM+CS. The indexed powder XRD pattern is shown in **Fig. 2**.

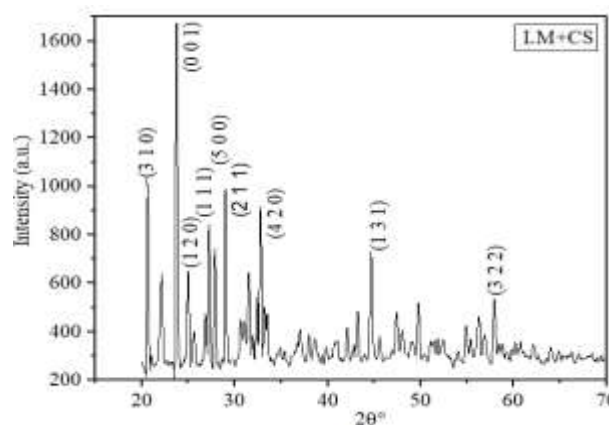


Fig. 2 Powder XRD pattern of LM+CS crystal.

High intensity peaks which are characteristics of the materials are present in the spectrum. It implies to good their crystalline nature and confirmed by well developed (001) zone. It has Strong Bragg reflections related to FCC orthorhombic system. XRD analysis reveals that the grown crystal is belongs to orthorhombic structure with non-centrosymmetric space group  $P_{21}$ . A prominent peak (001) is at  $2\theta = 23.69^\circ$ , The Interplaner distance “d” is calculated using Bragg’s equation The ‘d’ value corresponding to prominent peak is 3.75 Å, Crystallinity of the crystal material is found to be 42.32%.

Table 1: Lattice parameters of LM+CS.

| Parameters  | LM + CS      |
|---|--------------|
| Period of growth  | 21 days      |
| Dimension mm <sup>3</sup>                                   | 40 × 15 × 5  |
| a (Å)   | 15.99        |
| b (Å)   | 7.31         |
| c (Å)   | 3.75         |
| $\alpha$ (°)  | 90°          |
| $\beta$ (°)   | 90°          |
| $\gamma$ (°)  | 90°          |
| Volume (Å <sup>3</sup> )                                    | 438.32       |
| Space group   | $P_{21}$     |
| Prominent peak at $2\theta$ (degree)                        | 23.69        |
| Crystal structure   | FCC          |
| Crystal system  | Orthorhombic |
| Interplaner distance d (Å)                                  | 3.75         |
| Crystallinity (%)   | 42.32        |
| Average Crystallite size nm                                 | 60.47        |
| Lattice strain ( $\epsilon$ ) × 10 <sup>-3</sup>            | 2.4          |
|   | 4            |
| No. of molecule per unit cell (Z)                           |              |
| Average dislocation density( $\delta$ ) (nm <sup>-2</sup> ) | 3.04E-04     |
| X-ray density ( $\rho_x$ ) mg/m <sup>3</sup>                | 6.20E+00     |
| Atomic radii (Å)  | 5.65         |

The values were compared with the crystallographic data of L- methionine and copper sulfate [5-7], it is found that there is change in structure of the L- methionine and the values of cell parameters of LM+CS have varied which confirms the incorporation copper Sulfate into the L- methionine. There are many reasons for changes in the lattice parameter such as stress, strain, defects, and changes in imperfections in the crystal lattice. Also, the increase in lattice parameter shows that the compressive stresses get produced in the

crystal during the growth process. **Table: 1**, gives different lattice parameters of LM+CS.

The crystallite size is calculated from the Scherrer formula. The average crystallite size comes out to be 60.47 nm. The dislocation density is depending upon the crystallite size and lattice parameter of crystal [8]. The average dislocation density comes out to be 0.003 nm<sup>-2</sup>. The shears force leads to move dislocations from one grain boundary to another grain boundary. This induced dislocation density in the crystal lattice is a result of transition of  $\pi$ - $\pi^*$  conjugated electrons. Various parameters calculated from the XRD data [9]. The X-ray density was calculated from lattice parameter values. X-ray density ( $\rho_x$ ) depends on the unit cell volume and molecular weight of the sample. This X-ray density comes out to be 6.2 mg/m<sup>3</sup> for LM+CS. The atomic radius was calculated using lattice parameter values . The calculated value of atomic radius is 5.65 Å for crystal.

### 3.2 UV-visible-NIR spectroscopy

The absorption of UV and visible light involves promotion of the electrons in the  $\sigma$  and  $\pi$  orbital to higher states, the UV-VIS-NIR spectrum gives information about the structure of the molecules in the crystals. The optical Transmission spectrum of LM+CS crystal shown in **Fig. 3** was recorded between 190-2000 nm. The lower cutoff wavelength is 340 nm. Maximum absorption was observed in UV region (190-380 nm) and very low transmission in the limited range of visible region where transmission peak is obtained at 500 nm, which shows  $\pi$  to  $\pi^*$  transitions of carboxyl group. A small hump was observed in the near infrared (IR) region. This depicts limited access to the laser wavelength of 1064 nm from Nd:YAG source for second harmonic generation (SHG).

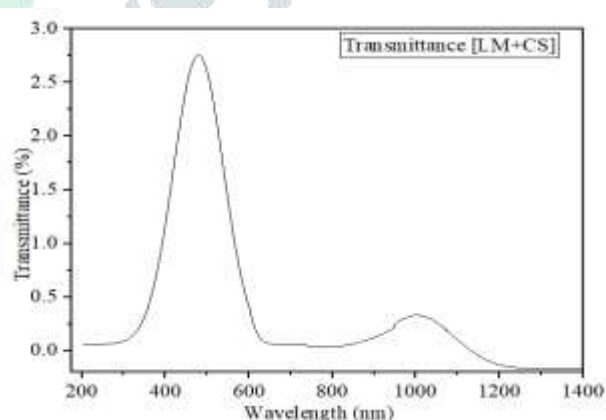


Fig. 3 UV-VIS-NIR absorption spectrum LM+CS crystal.

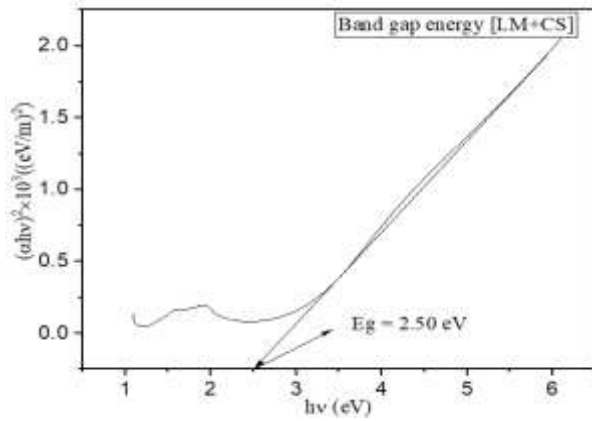


Fig. 4 Band gap of LM+CS crystal.

The Tauc's plot of  $(\alpha h\nu)^2$  against photon energy ( $h\nu$ ) at room temperature in **Fig. 4** shows behavior ( $\alpha$ -absorption coefficient and  $h$ -planks constant) which can be considered as an evidence of the indirect transition, low transmission, and limited optical transmission. Using Tauc's plot, band gap of the LM+CS crystal is 2.50 eV. Various parameters calculated in average from optical data **Table 2**. The optical susceptibility ( $\chi_{op}$ ) and Optical Polarizability ( $P_{op}$ ) describes the degree of polarization of the material. Both the parameters are decreases with doping of copper sulfate into L-methionine. Thus, doping of copper sulfate pentahydrate in L-methionine crystal reduces its nonlinear response.

Table 2: Optical data of LM+CS

| SAMPLE  | LM+CS    |
|---|----------|
| Lower cutoff Wavelength (nm)                                    | 340      |
| Bandgap Energy $E_g$ (eV)                                       | 2.5      |
| Refractive Index ( $n$ )  | 2.6755   |
| Optical Reflectance ( $R$ )                                     | 0.2078   |
| Absorption Coefficient $a$ ( $cm^{-1}$ )                        | 21.526   |
| Extinction Coefficient $K$ ( $L \cdot mol^{-1} \cdot cm^{-1}$ ) | 1.16E-4  |
| Optical Conductance $\sigma_{op}$ ( $10^{10} S^{-1}$ )          | 13.756   |
| Optical Susceptibility $\chi_{op}$ (mV)                         | 0.5699   |
| Optical Polarizability $P_{op}$ ( $Cm^2V^{-1}$ )                | 1.80E-37 |

### 3.3 FTIR studies:

In order to identify the functional groups that are present in LM+CS crystal, FTIR spectrum was recorded in the range between  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  using Bruker  $\alpha$ -2. The resulting spectrum is shown in the **Fig. 5**.

Presence of amino group confirmed due to N-H bond stretch appears as a weak medium which is somewhat of a broad band (however it is not as broad as the O-H band). This weak medium broadband is positioned at the left end of the spectrum, in the range of about  $3250$  to  $3600 \text{ cm}^{-1}$  and peak at  $3471.97 \text{ cm}^{-1}$ .

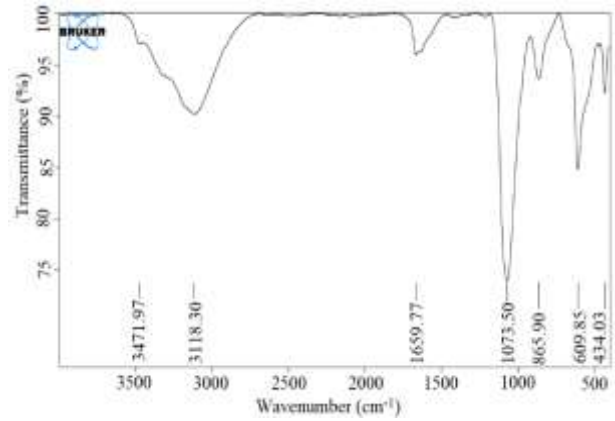


Fig. 5 FTIR spectrum LM+CS crystal.

Zwitterionic form of L-methionine having a anionic carboxy group and a cationic amino group, Presence of carboxylic acid functional group of amino acid (as it has O-H, C=O bonds), The carboxylic acids shows weak but broad band covering a wide range of  $2700 \text{ cm}^{-1}$  to  $3250 \text{ cm}^{-1}$  for the O-H stretch and peak at  $3118.30 \text{ cm}^{-1}$ . At the same time, they also show the weak band towards right side of the spectrum around  $1659.77 \text{ cm}^{-1}$  corresponding to C=O, C=C stretch. The absorption due to carboxylic group of LM+CS is observed at  $434.03 \text{ cm}^{-1}$ , The bending vibration of S-O group were identified at  $609.85 \text{ cm}^{-1}$ . Similarly, the U-shaped absorption peaks due to amine group of methionine is observed at  $1073.50 \text{ cm}^{-1}$ . The vibration mode of metal ion  $Cu^{2+}$  may be observed as Cu-O-H vibration is assigned to  $865.90 \text{ cm}^{-1}$  [10-14].

Table 3: Vibrational group assignment of LM+CS crystal

| Wavenumber ( $cm^{-1}$ ) | Vibrational group       |
|--------------------------|-------------------------|
| 609.85                   | S-O stretching          |
| 865.90                   | Cu-O-H vibration        |
| 1073.50                  | NH <sub>2</sub> wagging |
| 1659.77                  | C=O, C=C stretch        |
| 3118.30                  | C=O stretching          |
| 3471.97                  | N-H stretching          |

### 3.4 SHG Measurements:

SHG intensity of the samples was tested by the modified version of the powder technique developed by Kurtz and Perry in 1968 using Quanta Ray Spectra Physics model: Prolab 170 Nd:YAG laser beam of wavelength  $1064 \text{ nm}$  with an input power of  $1.2 \text{ mJ}$  and pulse width of  $10 \text{ Hz}$  was made to fall on the sample [15]. The second harmonic generation was confirmed by emission of green radiation ( $532 \text{ nm}$ ), which was finally detected by a photomultiplier tube and measured with digital storage oscilloscope. The measured output in mV is found to be very less. Hence it is a potential material for frequency conversion in very limited region of IR.

## 4. Conclusions

A semi organic NLO crystal, LM+CS was successfully grown by slow evaporation solution growth method at constant temperature  $40 \text{ }^\circ\text{C}$ . Powder XRD method reveals the orthorhombic crystalline structure of the grown crystal. FTIR analysis confirms the presence of various functional groups in the crystal. Limited transparency of the crystal is analysed from UV-VIS-NIR spectrum. It is observed that the crystal exhibits very low transparency in the limited range of visible and IR region.



As the band gap is found to be 2.5 eV, only long wavelength (infrared) and the visible spectrum are transmitted. Hence it has very small SHG efficiency in comparison with KDP.

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### References

- 1) S. Nalini Jayanthi, A. R. Prabhakaran, D. Subashini, K. Thamizharasan, **Vol. 11**, No. 5, May 2014, p. 241 – 247, Crystallizations and characterization of NLO active glycine Copper sulphate crystal.
- 2) Kazuo Torii and Yoich Iitaka Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan, Crystal Structures and Molecular Conformations of L-Methionine and L-Norleucine, *Acta Cryst.* (1973). B29, 2799
- 3) Ravi U, Srinivasan K, Anbukumar S, Ramasamy P. Growth, and characterization of sulphate mixed L-arginine phosphate and ammonium dihydrogen phosphate/potassium dihydrogen phosphate mixed crystals. *J Cryst Growth* 1994; 137:598–604.
- 4) M.A. Mamun, Omar Ahmed, P.K. Bakshi, M.Q. Ehsan January 2010 Journal of Saudi Chemical Society 14(1):23-3.
- 5) A note on the crystal structure of anhydrous copper sulphate. B. Rama Rao, *Mineralogisch Kristallographisches, Institute der Universitat, Gottingen. Lotzestr. 16-18, Deutschland, Acta Cryst.* 14, 321, (1961).
- 6) G.E. Bacon, D.H. Titterton, *Z. Kristallogr* 141, 330 (1974).
- 7) The Crystal Structure of Copper Sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  By C. A. Beevers and H. Lipson, George Holt Physics Laboratory, University of Liverpool (Communicated by W. L. Bragg, F.R.S. Received April 4, 1934.
- 8) By John J. Maddafn, Edward L. McGandy, Nadrian C. Seeman, *Acta Cryst.* 28, 2377–2382, (1972).
- 9) R. Ittyachan, P. C. Thomas, D. Prem Anand, M. Palanichamy, and P. Sagayaraj, *Mat. Chem. Phys.* 93, 272, (2005).
- 10) R. Thilagvathi, Dr. P. Selvarajan, V. Vasantha Kumari, international journal of advanced scientific and technical research – issue-2 volume 6, December 2012, ISSN 2249-9954.
- 11) A.S. J. Lucia Rose, P. Selvarajan, S. Perumal, *Spectrochim. Acta A*, 81 (2011) 270.
- 12) Briyan C. Smith, *Infrared spectral Interpretation. A systematic Approach*, CRC press (1999), New York.
- 13) M.A. Mamun, Omar Ahmed, P.K. Bakshi, M.Q. Ehsan, January 2010 Journal of Saudi Chemical Society 14(1):23-31,
- 14) N. Hema, D. Jayalakshmi, R. Usha, D. Shalini and V. Revathi Ambika, *Elixir Materials Science* 98 (2016) 42636-42638.
- 15) Kurtz SK, Perry TT. A powder technique for the evaluation of nonlinear optical materials. *J Appl. Phys* 1968. 39:3798–813.

