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SYNTHESIS GROWTH AND CHARACTERIZATION OF A NEW NLO MATERIAL: L - THREONINE MANGANESE CHLORIDE

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Abstract

In this present research work, good quality single new NLO material L-Threonine manganese chloride was grown from aqueous solution by a slow evaporation technique at room temperature. Crystals were characterized by X-ray diffraction analysis whose results they crystallize on orthorhombic system. The optical properties of the grown crystal were calculated from UV-Visible spectroscopic study. The functional group was found by FTIR analysis. The nonlinear optical property was confirmed by Kurtz Perry powder technique and discussed the efficiency of the crystal.

Key words: L-Threonine manganese chloride, XRD, UV-Visible Spectroscopy, FTIR and NLO.

1. Introduction

Materials with second order of non-linear optics have greatly attracted due to their possible applications in new technologies of optoelectronics (Madurambal *et al*., 2013; Kumar *et al*., 2006; Angelimary *et al*., 2001). Organic materials have been of particular interest, since non-linear optical responses on these materials are of microscopic origin, thus offering an opportunity to utilize theoretical models along with synthesis flexibility to design and produce new materials (Sagadevan Suersh *et al*., 2012; Mojumdar *et al*., 2011). Most of the organic crystals have inadequate transparency, poor optical quality and low laser damage threshold (Jiang *et al*., 2011). Moreover, growth of large sized single crystals has excellent mechanical and thermal properties but they possess relatively modest nonlinearity. Due to the above reasons, a lot of research has been carried out on semi-organic materials which have combined properties of both organic and inorganic materials (Ravindran *et al*., 2011). Amino acids have interest applications on Non-Linear Optics (NLO) because they are materials of second order (Franken *et al*., 1961). One of their properties was that they are non-volatile crystalline solids, melting at relatively high temperatures; they are insoluble in non-polar solvents and they are soluble in water, so their aqueous solutions behave like solutions with elevated bi-polar momentum. The L-threonine crystallizes with four zwitterionic molecules per unit cell linked by a three dimensional network of NH…O and O-H…) bonds. L-threonine is one of the essential amino acid bearing an alcohol group. Also, optically active amino acids contain many highly efficient optical second - harmonic generators and are promising candidates for a great number of applications. By the physical point of view, the L- threonine manganese

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chloride investigation was relevant both owing to the possibility to observe the behaviour of a system where the hydrogen bond plays a fundamental role (Madurambal *et al*., 2011; Madurambal *et al*., 2013) and the technological importance of a material which shows second-harmonic conversion efficiency greater than one relative to potassium di-hydrogen phosphate.

2. Materials and Methods

Synthesis

Single crystals of L-Threonine manganese chloride was grown by preparing L-Threonine and manganese chloride taken in 1:1 equimolar ratio in deionised water at room temperature and stirred well to yield a homogeneous mixture of solution. The solution was filtered to remove insoluble impurities using Whatman filter paper of pore size 10 micrometers. Then, the solution of L-Threonine manganese chloride was taken in a beaker with a perforated lid in order to control the evaporation rate and kept at room temperature for crystallization. Finally, a well defined single crystal was obtained after 15 days by slow evaporation method. The photograph of the grown crystal of L-Threonine manganese chloride was shown in Fig.1.

Characterization Methods

The optical absorption spectra of the grown crystals were recorded using Perkin Elmer Lambda 35 model UV-Visible spectrometer in the wavelength `region 190-1100nm. The FTIR spectrum of L-Threonine manganese chloride was recorded by PERKIN ELMER RX9 spectrometer using KBr pellet technique in the wavelength range 4000-400cm^{-1}. Powder X-ray diffraction study of the grown crystal was carried out by using Bruker's Xray Diffractometer.

3. Results and Discussion

Powder X-ray diffraction

The lattice parameters of the grown crystal are determined by the single crystal XRD technique and the diffracting planes were identified by recording the powder XRD analysis as shown in Fig - 2. The XRD analysis has confirmed that the crystal belongs to Orthorhombic with space group $P2_12_12_1$. The space group suggests that the grown material is non-centro symmetric which fulfils the fundamental criterion for the material to exhibit NLO behaviour. The powder XRD pattern of L-threonine doped crystals and observed a systematic variation in the intensity of diffraction peaks with varying L - Threonine concentration (Kurtz *et al*., 1968; Dixit *et al*., 2003; Sangeetha *et al*., 2013). The observed values are in good agreement with standard values (Puhal Raj *et al*., 2013).

UV-Vis NIR transmittance studies

The UV-Visible transmission spectrum is very significant for optical material for the reason that of its wide transmittance window. The high precision was definite from the recorded spectrum and it was observed that there was no major absorption in the range 337 -1100 nm. There was an improvement in the use of amino acids, where the absence of strongly conjugated bands leads to a wide transparency range in the visible and UV spectral regions. The lower cut-off wavelength was found to be around 337 nm which was combined to good transparency attests to the usefulness of L-Threonine manganese chloride material for optoelectronic application (Bright *et al*., 2010). A lot of research and well defined peak confirms the good crystalline nature of the L – Threonine manganese chloride crystal due to excellent mechanical and thermal properties but they possess relatively modest nonlinearity.

FTIR Spectra

The Fig. 4 shows the FTIR Spectrum of L-Threonine manganese chloride. Fourier transform infrared studies (FTIR) were used to conform the presence of various functional groups in the crystals (Lucia Rose *et al.*, 2011). The broad absorption of medium intensity peaks at 3167.06 cm^{-1} and 3029.10 cm^{-1} was assigned due to NH_3^+ asymmetric and symmetric stretching vibration.

Figure - 1: Morphology of L-Threonine manganese chloride

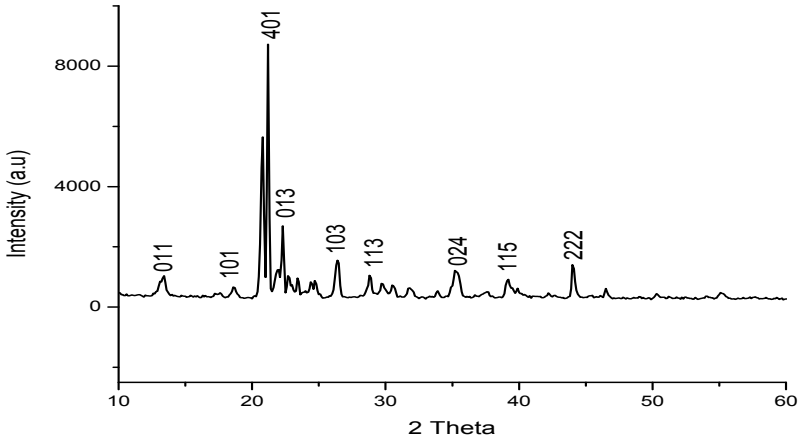

Fig - 2: XRD pattern of L-Threonine manganese Chloride

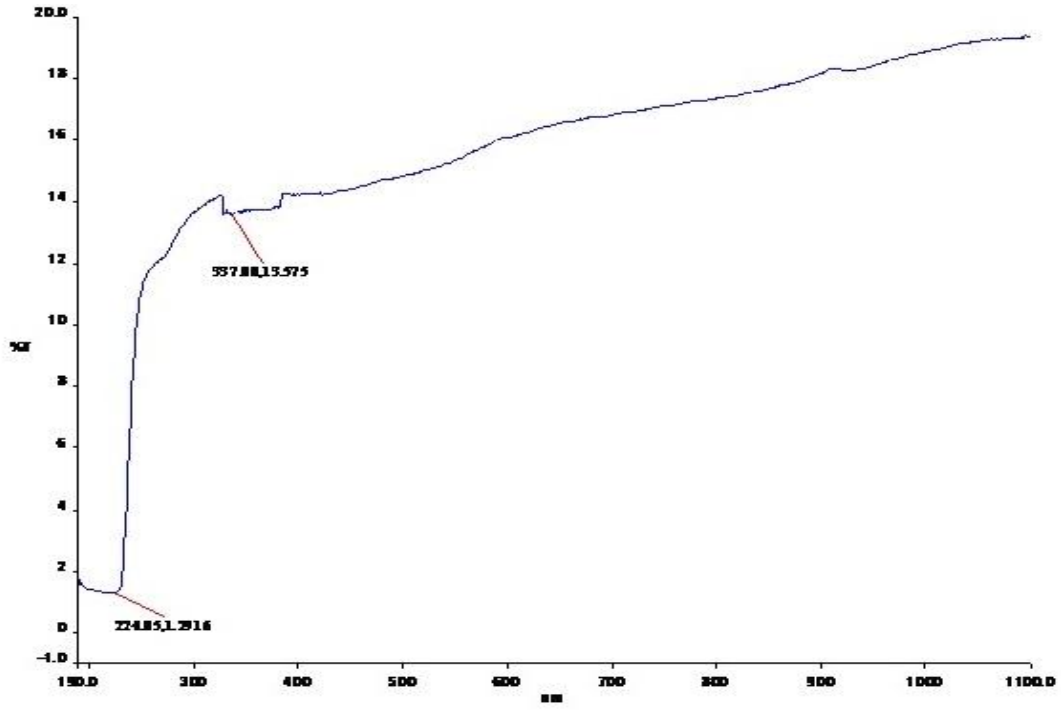

Fig – 3: UV-Visible transmission spectrum

Table - 1: Vibrational assignments of L-Threonine manganese chloride single crystal

Wave number cm^{-1}	Vibrational assignments
3167.06	NH_3^+ asymmetric stretching
3029.10	NH_3^+ symmetric stretching
2874.27	C-H symmetric stretching
1629.26	NH_3^+ asymmetric deformation
1480.18	NH_3^+ symmetric deformation
1417.24	COO^- asymmetric stretching
1247.84, 1112.86	NH_3^+ rocking
559.53	C-C-N deformation

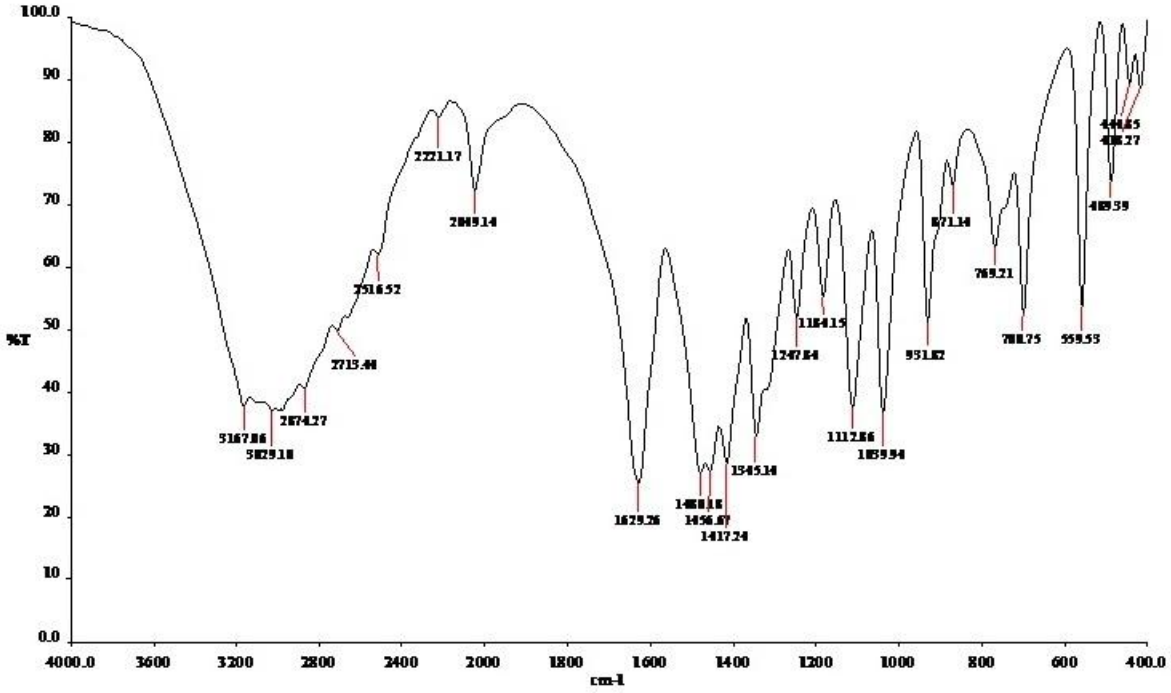

Fig – 4: FTIR spectrum of L-Threonine manganese chloride

Due to the stretching vibration involving carbon and nitrogen of amino group exists a peak at 1039.94 cm^{-1}. The asymmetric NH_3^+ deformation occurs at 1629.26 cm^{-1}. The absorption peak at 1480.44 cm^{-1} was due to symmetric NH_3^+ deformation vibration. The peak at 1417.24 cm^{-1} reveals the COO^- symmetric vibration. The peak at 2874.27 cm^{-1} indicates the C-H stretching vibration. The NH_3^+ rocking vibration was observed at 1247.84 cm^{-1} and 1112.86 cm^{-1}. The C-C-N deformation was present at 559.53 cm^{-1}. Hence, the presence of functional groups was confirmed from the above assignments (Clark *et al*., 1984).

NLO Test

The SHG behaviour of the powdered material was studied using Kurtz Perry method (Gargaro *et al*., 1993; Nagarajan *et al*., 2015). The sample was ground into very fine powder and tightly packed in a micro capillary tube. Then, it was mounted in the path of Nd:YAG laser beam of 9.6 mj pulse energy obtained by splitting the original laser beam. The output light was passed through monochromator which was detected green light at 532 nm. This confirms the NLO behaviour of the material (Ramesh *et al*., 2014). The green light intensity registered by a photomultiplier tube and converted into an electrical signal. The same particle size of KDP was used as a reference material. SHG efficiency of L-Threonine manganese chloride was greater than that of KDP (Chandramohan *et al*., 2014).

4. Conclusion

Single crystals of L-Threonine manganese chloride were grown by slow evaporation technique. Powder XRD confirms the structure of the crystal. FT-IR analysis confirms the presence of functional groups present in the crystal. The optical transmittance of the crystal was found to be around 330 nm. However, the second harmonic generation (SHG) efficiency and the UV – Vis. Spectroscopy studies included that as L – Threonine manganese chloride increased the SHG efficiency and optical transmission percentage increased. The SHG efficiency shows that the crystal has a higher efficiency than KDP.

5. References

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