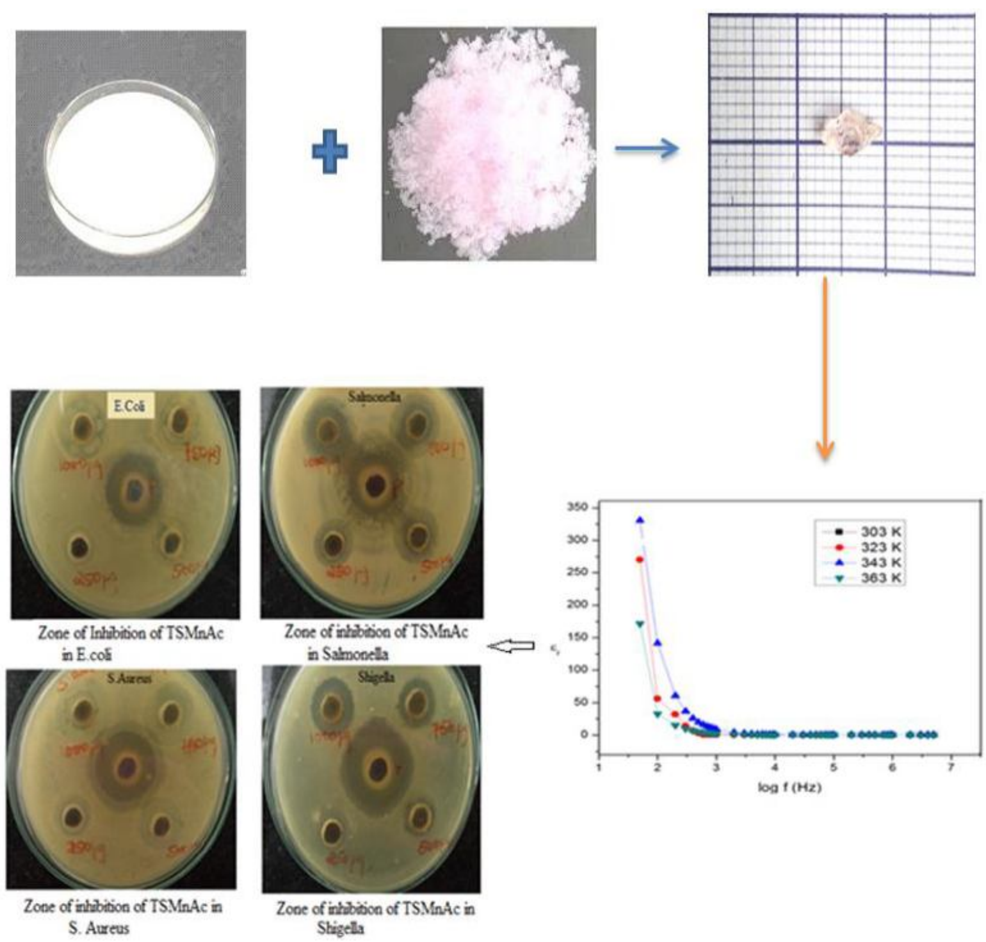
CHAPTER 6

GROWTH AND CHARACTERIZATION OF SINGLE CRYSTAL - THIOSEMICARBAZIDE MANGANOUS ACETATE (TSMNAC)

6.1 GRAPHICAL ABSTRACT OF TSMnAc



6.2 INTRODUCTION

Progress in the field of NLO crystals depends on the development of new crystals For the past few decades high efficient NLO materials has obtained more attention due to their potential applications, such as high-speed information processing, optical communications and optical data storage (Abu El-Fadlet al. 2007, Mukerji et al. 1999, Sangwal et al. 2005). Among the class of NLO materials, the inorganic material possesses high melting point, high mechanical strength and high degree of chemical inertness. But their optical nonlinearity is poor. Whereas, organic compounds are having high nonlinearity due to the weak Vander Waals and hydrogen bonds and possess high degree of delocalization. Organic crystals fall short of vital technological properties including mechanical strength, chemical stability and performance at low and high temperature (Cahoon et al. 1971, Wooster 1953). However, the difficulty is to grow the large and optically good quality single crystals for device applications.

In order to overcome all these difficulties a new semi organic crystal was grown. Semi-organic materials have the potential for combining high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganic (Miller 1952). Ligands like thiourea, allylthiourea, thiocyanate and thiosemicarbazide with S and N donors are capable to combine with metal to form stable complexes through coordinated bonds. These complexes show ligand to meal charge transfer by an electron movement from ligand to metal and metal to ligand in addition to $\pi - \pi^*$ conjugation. Here, Amino acid groups combine with inorganic salts to form new semi organic crystal. Thiosemicarbazone helps the free thiosemicarbazone ligands and their metal complexes to improve second harmonic generation (SHG) efficiency (Charles Kittle 1993). In this respect, acetophenone thiosemicarbazone (APTSC), thiosemicarbazide cadmium chloride monohydrate (TSCCCM) and thiosemicarbazide lithium chlorides [TSLC] have been identified as good semi organic nonlinear optical materials (Venkataramanan et al. 1997, Prabhakaran et al. 2004). In this present work, Manganous Acetate is combined with thiosemicarbazide to form a new semiorganic nonlinear optical material. This paper reports the synthesis, crystal growth and characterization studies of TSMnAc single crystal grown by solution method. The title compound subjected to X-ray diffraction, NLO studies, thermal analysis, Micro hardness, Dielectric studies, SEM Analysis and Antimicrobial activity are presented and discussed.

6.3 EXPERIMENTAL PROCEDURE

6.3.1 Material Synthesis

The new semi organic material thiosemicarbazide Manganous Acetate [TSMnAc] was synthesized by mixing an aqueous solution of thiosemicarbazide with Manganous Acetate in the stoichiometric ratio of 1:1.The chemical reaction is given below.

$$Mn(CH_3Co)_2 + NH_2\text{-}NH\text{-}CS\text{-}NH_2 \rightarrow Mn(NH_2\text{-}NH\text{-}CS\text{-}NH_2)(CH_3Coo)_2 \quad (6.1)$$

As thiosemicarbazide has a coordinating capacity to form a variety of metal-thiosemicarbazide complexes the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. The calculated amount of Manganous Acetate was first dissolved in deionized water. Then Thiosemicarbazide was added to the solution slowly. The solution was agitated with a magnetic stirrer and filtered after complete dissolution of the starting materials. The prepared solution was left stand by for several days at room temperature thereby good quality transparent crystal were obtained in 4 weeks shown in Figure6.1.

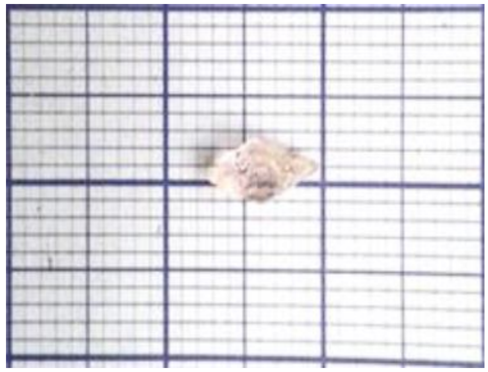


Figure6.1 Grown Crystal of TSMnAc

6.3.2 Solubility

The solubility study was carried out in a constant temperature bath with temperature controller of accuracy ±0.01^0 C. Solubility of thiosemicarbazide Manganous Acetate was determined at four different temperatures 30, 35, 40 and 45ºC. The solution was stirred continuously or several hours to achieve homogenization using a magnetic stirrer. After attaining saturation, the equilibrium concentration of the solute was estimated gravimetrically. The solubility curve of TSMnAc is shown in Figure6.2.

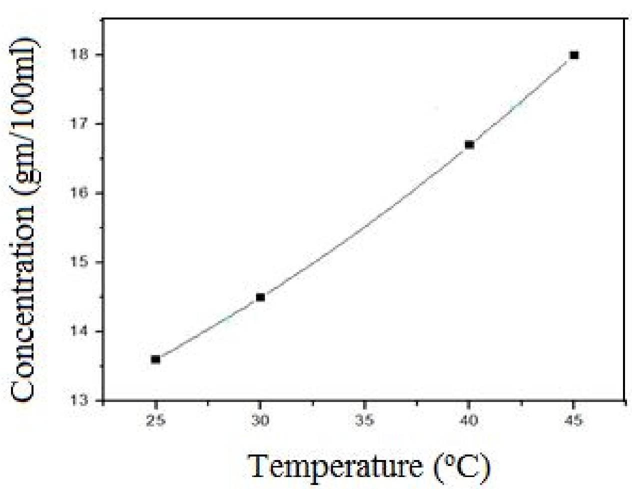


Figure6.2 Solubility curve of TSMnAc

6.3.3 Characterization Techniques

Single crystal XRD was recorded by Enraf Nonius CAD/MACH3 single crystal X-ray diffractometer to find the molecular structure, atomic coordinates, bond lengths, bond angles and molecular orientation. The powder XRD pattern of crystal was obtained using a BRUKER AXS D8 Advance X-ray diffractometer with CuKα radiation (λ = 1.54056°A) at room temperature. The electronic absorption and transmittance spectra of the compound were recorded using Lambda 35 UV–Visible spectrophotometer in the wavelength range from 190 to 700 nm. Mechanical properties of the grown TSMnAc crystal were studied using M H – 5 hardness testers. The dielectric studies of the compound were recorded at room temperature using a TH 2816 A DIGITAL LCRZ METER in the frequency region 50Hz–2MHz. The Antimicrobial activity (antibacterial and antifungal activity) of the grown crystal was calculated by agar well diffusion method. To know the surface morphology of the crystal Scanning Electron Microscopy (SEM) was carried out.

6.4 RESULTS AND DISCUSSION

6.4.1 Single Crystal X-Ray Diffraction Analysis

TSMnAc was subjected to Single crystal X-ray diffraction and powder X-ray diffraction studies. The X-ray data were collected using an Enraf Nonius CAD/MACH3 single crystal diffractometer instrument for grown Thiosemicarbazide Manganous Acetate crystal. The calculated lattice parameter values are a = 4.99Å, b =6.07Å andc = 7.41Å and α = 77.50 β = 77.01, γ = 83.86 and the volume of the grown crystal is 213 $Å^3$. The XRD data prove that the crystal is Triclinic in structure. The XRD results are in good agreement with the reported values and thus confirm the growth of grown TSMnAc crystal.

6.4.2 Powder X-Ray Diffraction Analysis

Powder X-Ray diffraction study was used for the identification of crystallinity of the grown crystal. The Kα radiations from a copper target were used. The sample was scanned in the range between 10 and 100°C. Figure6.3 represents the indexed powder diffractogram for the grown crystal of TSMnAc. The sharp intensity peaks found in spectra shows good crystalline nature and purity of the grown crystal.

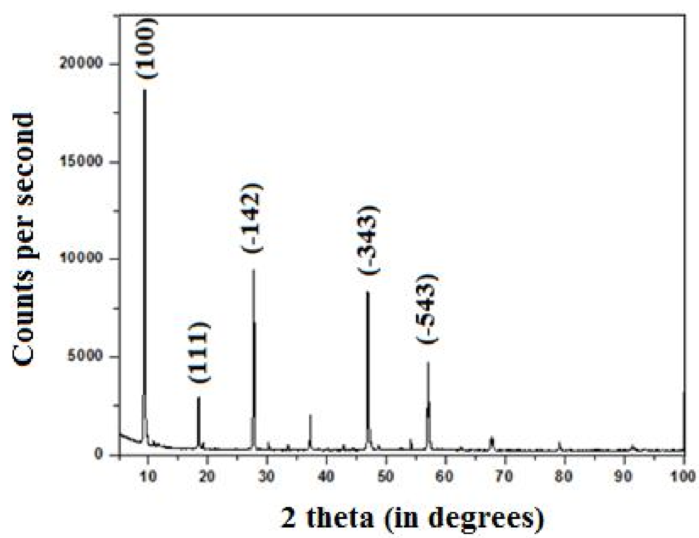


Figure6.3 Powder XRD pattern of TSMnAc

6.4.3 Optical Absorption Analysis

Optical absorption and transmission property is an important characteristic of a nonlinear optical material. Figure6.4 shows the UV spectrum of the compound scanned between 190 and 900 nm. There is no absorption band in the region between 230 and 900nm. This shows the absence of absorbance due to electronic transitions above 230nm. Hence the crystal of TSMnAc is expected to be transparent to all the UV-visible radiation between these two wavelengths (Malibari1991). Using the relation

$$E_g = 1240/\lambda \tag{6.2}$$

The band gap energy was found to be 5.39 eV.

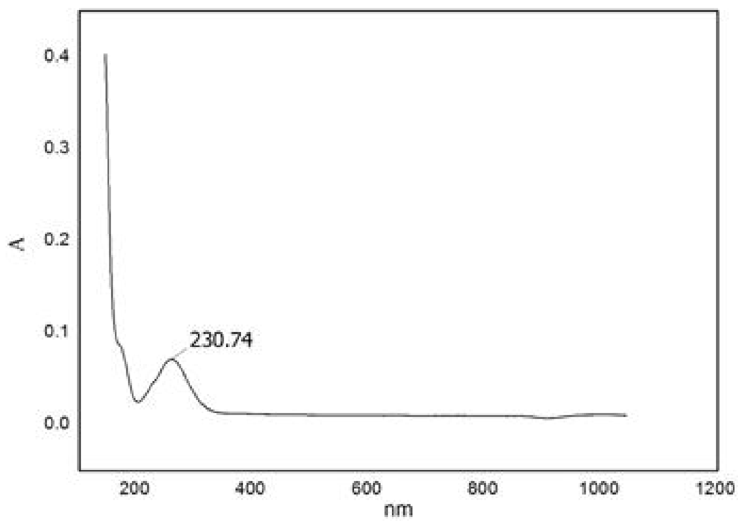


Figure 6.4 Absorption Spectra of TSMnAc

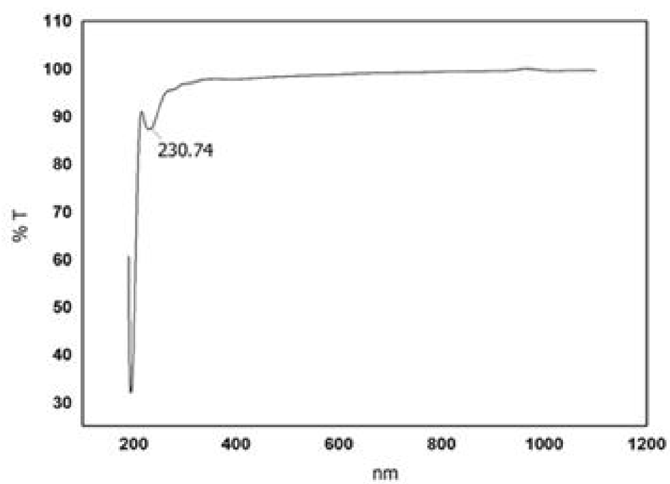


Figure 6.5 Transmission spectra of TSMnAc

Transmission spectra are very important for any NLO material. The transmission spectra obtained is shown in the graph Figure 6.5. The transmittance window in the visible region and IR region enables good optical transmission of the second harmonic frequencies of ND:YAG lasers.

6.4.4 Mechanical Studies

One of the methods to determine the mechanical behaviour of the grown crystal is micro hardness test. It is correlated with other mechanical properties like elastic constants, yield strength, brittleness index and temperature of cracking (Zhou et al. 2006). The indentation marks were made on the surface of TSMnAc single crystal at room temperature by applying load of 25, 50 and 100 g. The Hv is found to increase with increase in the load from 25 to 100 g and crack occurs at higher loads. Mechanical properties of the grown TSMnAc crystal were studied using MH–5 hardness testers. The diagonal lengths of the indented impression were measured using calibrated micrometre attached to the eyepiece of the microscope.

The Vickers micro hardness values were calculated from the standard formula

$$Hv = 1.8544 \, (P/d^2) \text{ kg/mm}^2 \qquad (6.3)$$

Where P is the applied load and d is the mean diagonal length of the indentation. The corresponding trace is shown in the Figure 6.6, from which it is observed that the hardness increases with the increase of load up to 100g and crack occurs at that load. The micro hardness value was taken as the average of the several impressions made.

According to the normal Indentation size effect (ISE), micro hardness of crystal decreases with increasing load and in Reverse indentation size effect (RISE) hardness increases with applied load. In our case, Hv increases with applied load (Murray et al. 1995).

The elastic stiffness constant (C_{11}) for different loads calculated using Wooster's(Vijayan et al. 2006, Long) empirical formula C_{11}= Hv $^{(7/4)}$ is given in Table 1 which gives an idea about tightness of bonding between neighboring atoms (Arivuselvi & Ruban Kumar 2015) .

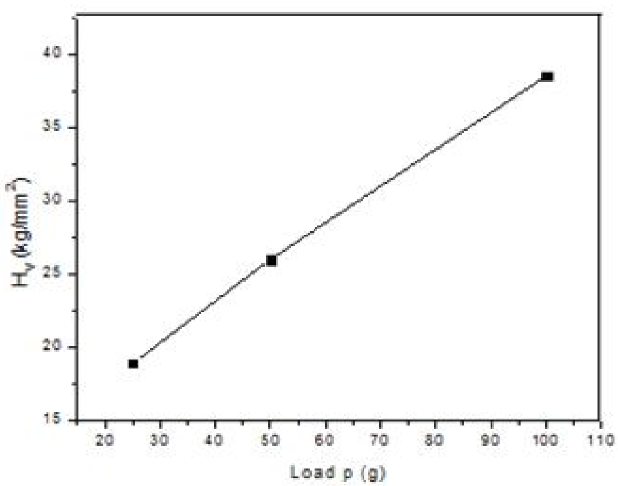


Figure 6.6 Variation of hardness with load P

6.4.5 Dielectric Studies

Good quality single crystal of TSMnAc was selected for the dielectric measurements using TH 2816 A Digital LCRZ Meter in the frequency from 50 Hz to2 MHz. Typical sample thickness was in the range of 0.82 mm. The sample was polished by soft tissue paper. Silver paste was applied on both opposite faces to make a capacitor with the crystal as a dielectric medium. The sample was placed between two copper electrodes, which act as a parallel plate capacitor. Dielectric studies give useful information about charge transport mechanism inside the crystal. The variation of dielectric constant with log frequency is shown in Figure 6.7.

The value of dielectric constant decreases with increase in frequency. At higher frequencies the value of dielectric constant is low and at low frequencies the value of dielectric constant is high. The high value of dielectric constant may be due to the four polarizations namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these four polarizations gradually. The very low value of dielectric constant at higher frequencies are important for these materials in the construction of photonic and NLO devices.

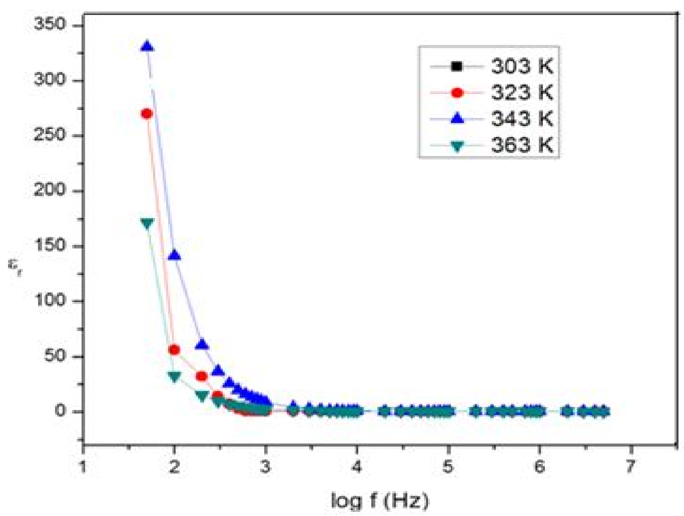
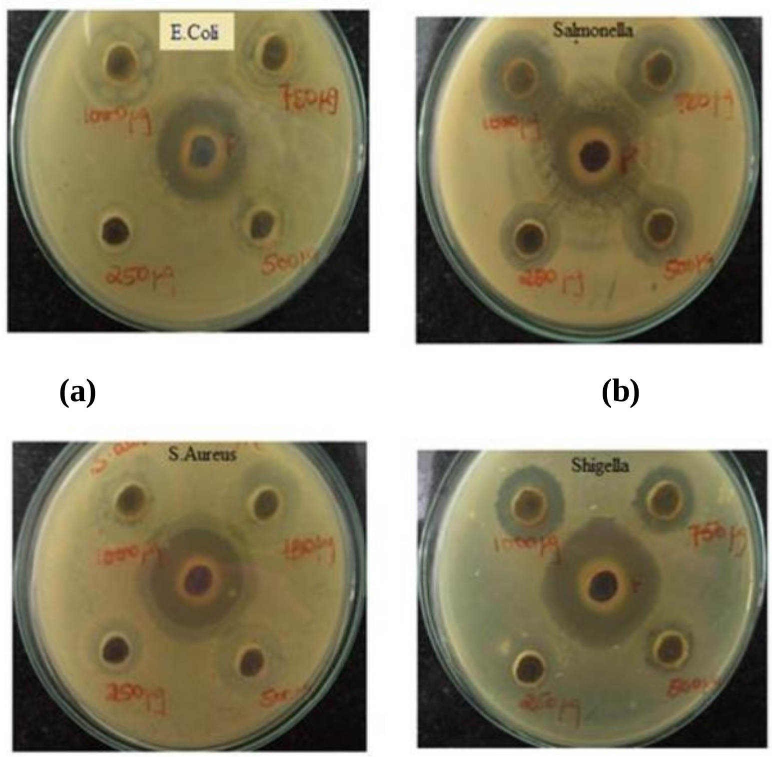


Figure 6.7 Variation of Dielectric constant with applied frequency

6.4.6 Antibacterial Studies

The variation in the effectiveness of the different compounds against different organisms depends on their impermeability of the microbial cells or on the difference in the ribosome of the microbial cells (Aggarwal et al. 2004, Kamatchi & Radhakrishnan 2015). Antibacterial activities were investigated by using agar well diffusion method, against the Staphylococcus aureus (RCMB 010010) {as Gram-positive bacteria} and Salmonella typhi (RCMB 010043) and Escherichia coli (RCMB 0100052) and Shigella flexneri {as Gram-negative bacteria}. Different concentrations of samples (250, 500, 70, 1000µg/well) were used in this study. Nutrient Agar (NA) plates were inoculated with test organisms. The plates were evenly spread out. Then wells were prepared in the plates with a cork borer. Each well was loaded with 0.1ml of corresponding concentration of sample and 10 µg of Tetracycline dissolved in 1 mL of DMSO (Dimethyl sulfoxide) was used as a positive control for antibacterial activity. The plates were incubated for 24h at 37°C. Tetracycline was used as a standard drug for the comparison bacterial results. The diameter of zone of inhibition in millimeters for the grown crystal is shown in table 6.1.



(a) (b)

(c) (d)

Figure 6.8 (a) Zone of Inhibition of TSMnAc in E.coli(b) Zone of Inhibition of TSMnAc in E.coli(c) Zone of Inhibition of TSMnAc in S.Aureus (d) Zone of Inhibition of TSMnAc in Shigella

The photograph of antibacterial activity of the bacteria's are shown in Figures 6.8 (a),(b),(c),(d) respectively. From the data it is observed that the TSMnAc crystal has good inhibitory action against gram positive and gram negative bacteria's (Ilango et al.2015, Vijayalakshmi et al. 2015). Moreover the antibacterial action of the TSMnAc crystal towards E. coli, Staphylococcus aureus, Salmonella typhi is stronger than that towards Shigella flexneri.

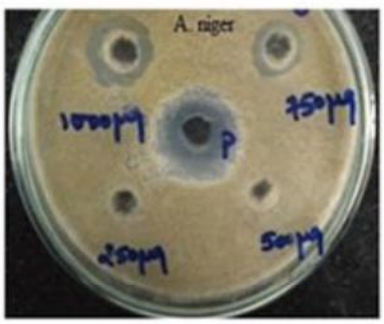
Hence this result provides a strong platform for further researchers to probe and develop organism specific antibiotic.

Table 6.1 Antibacterial activity of TSMnAc at different concentrations (25, 50, 75, 100 μg/ml)

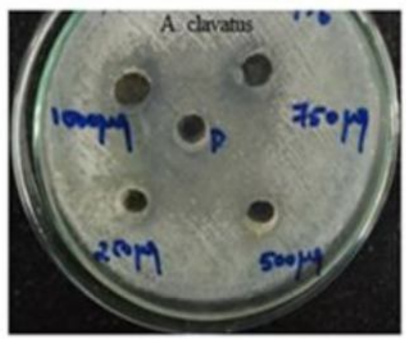
Antibacterial ActivityDiameter of Zone of Inhibition (mm) for different concentration (μg/ml)				
Bacterial Strains	25	50	75	100
E.coli	13	17	19	21
Staphylococcus aureus	18	20	23	25
Salmonella typhi	18	21	24	29
Shigella flexneri	9	15	18	21

6.4.7 Antifungal Studies

The synthesized compounds TSMnAc were tested for antifungal activity by using Ketoconazole as standard drug against three fungal strains including Aspergillus Niger, candida albicans and Aspergillus clavatus using agar well diffusion method. Antifungal activity was carried out using well diffusion method. Petri plates were prepared with 20 ml of sterile DA (Hi-media, Mumbai). The test culture was swabbed on the top of the solidified media and allowed to dry for 10 min. Wells were made on the media using a well borer. Different concentrations of the sample (250, 500, 750 & 1000 μg/per well) were loaded on the wells. Ketoconazole (10μg/1ml) was used as a positive control. These plates were incubated for 48 hrs at 28°C. Zone of inhibition was recorded in millimeters (mm). The filamentous fungi were grown on Sabouraud dextrose agar (SDA) slants at 28ºC for 10 days. The spores were collected using sterile double distilled water and stored in refrigerator. The grown crystals were found to be moderate active compared to the standard (Goebbert et al. 2009). The activity of the TSMnAc crystal was found to increase with the concentrations of the samples. The diameter of zone of inhibition in millimeters for the grown crystal is shown in table 62 the photograph of antifungal activity of the Aspergillus niger, candida albicans and Aspergillus clavatus are shown in Figures6.9 (a),(b),(c) respectively.



(a)



(b)

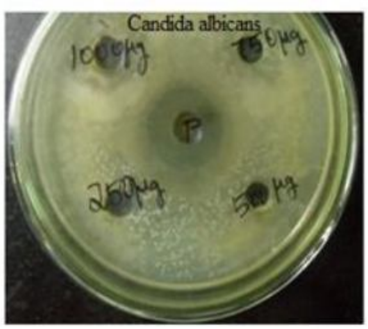


Figure 6.9 (a) Zone of Inhibition of TSMnAc in A.niger (b) Zone of Inhibition of TSMnAc in A. clavatus (c) Zone of Inhibition of TSMnAc in Candida albicans

Table 6.2 Antifungal activity of TSMnAc at different concentrations (25, 50, 75, 100 µg/ml)

Antifungal Activity	Diameter of Zone of Inhibition (mm) for different concentration (µg/ml)			
Bacterial Strains	25	50	75	100
Aspergillus niger	08	10	15	18
Aspergillus clavatus	09	11	14	17
candida albicans	08	11	12	16

6.4.8 SEM Studies

The Scanning electron microscopy (SEM) image of the grown crystal was recorded using FEI Quanta FEG 200 - High resolution Scanning Electron Microscope to study the surface morphology of TSMnAc crystal. A two dimensional image was generated over a selected area of the sample. Since TSMnAc is a semi organic crystal, which is poor conducing in nature, the sample was subjected to gold/carbon coating. From the Figure 6.10, it is clear that the surface of the grown crystal appears very smooth though it has pots and microcrystal on the surface. The grain boundaries are clearly seen which shows the perfect growth of the crystal.

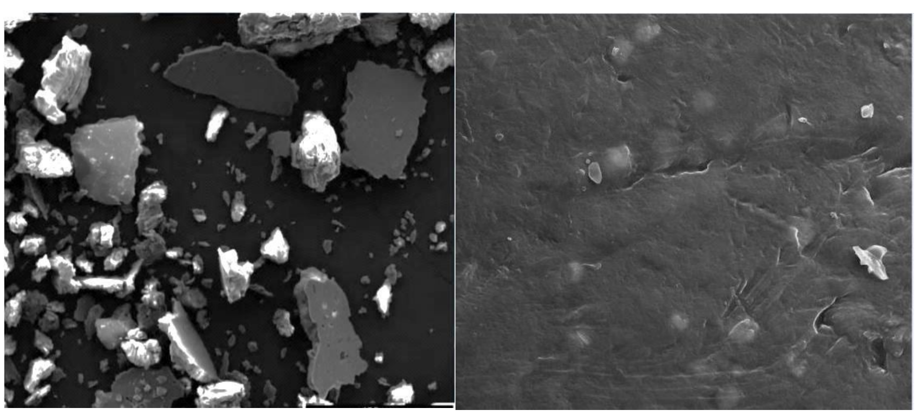


Figure6.10 SEM images of TSMnAc

6.4.9 Nonlinear Optical Studies

Kurtz and Perry powder method is an important tool for researchers searching for organic/semi organic/inorganic NLO material. The crystal was ground into fine powder and packed in the micro capillary tube. A Q-switched Nd: YAG laser (1064 nm) has been used. The input pulse energy of 3.2 mJ/pulse and pulse width 8ns was incident on the crystalline powder. The SHG signal at 532 nm is detected using a photomultiplier tube (PMT). The generation of the second harmonics was confirmed by the emission of green radiation. It is observed that the measured second harmonic generation efficiency of TSMnAc crystal was twice the time greater than that of KDP crystal.

6.5 CONCLUSION

Thiosemicarbazide with Manganous Acetate (TSMnAc) single crystal has been grown by solution growth slow evaporation technique. The Single crystal X-ray diffraction studies confirm the grown crystal belongs to Triclinic (P) system. The powder X-ray diffraction study confirms the crystallinity of the grown crystal. The UV-Vis-NIR Spectrum of the grown crystal shows good transmittance in the entire visible region enabling its use in optical applications. In the UV Vis spectrometer the lower cut off wavelength was recorded from the absorption spectrum is 230.74 nm. The band gap energy was found to be 5.39 eV. Vickers micro hardness reveals that the hardness number Hv increases with increasing load exhibiting Reverse Indentation Size Effect and Meyer's index, n, Yield strength, and elastic stiffness constant have been carried out by indentation method. The dielectric constant and dielectric loss measurements of the crystal at different temperatures and frequencies of the applied field are measured and calculated. The antibacterial results revealed that newly synthesized crystal show higher activity than the ligand but markedly lower than the standard drug. From the

SEM analysis the grown crystal shows stepped growth which may be the consequence of constant rate of evaporation of solvent at room temperature. The SHG measurement has confirmed the NLO property of the grown crystal.