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Research Article

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Spectroscopic and thermal characterization of bisthiourea manganese(II) acetate single crystals

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Abstract

In the present article, we prepared a single crystal of bisthiourea manganese(II) acetate by slow evaporation solution growth method. The synthesized crystal was characterized through elemental analysis, Power X-ray diffraction UV-vis-NIR optical transmittance, Emission spectrum, TG, DSC NLO and antimicrobial techniques. The elemental analysis and the thermal studies confirm the stoichiometric of the crystal. The crystalline nature of the crystal was confirmed powder X-ray diffraction pattern. The absorption peaks at 240 and 280 nm are due to electronic transition. The emission spectrum of the crystal exhibits green fluorescence emission. The decomposition pattern and thermal stability of the title crystal were identified by TG-DTA analyses. The thermal anomalies observed in differential scanning calorimetric curve at 180.29°C and 228.34°C in the cooling cycle indicate a second order transition. The infrared spectrum of the crystal characterizes the various chemical bonding molecules in the crystal. The NLO property of the crystal was studied by SHG efficiency analysis. The crystal exhibits good antibacterial and antifungal activities.

Keywords: Crystal growth, Crystallization, XRD, Thermal stability, Spectral analysis, SHG efficiency.

1. Introduction

In nonlinear optics, organic crystals of amino acid complexes find wide applications in the field of optical communication employing electro-optic modulation, signal amplification, high density memories and data storage technology [1]. Nonlinear optical crystals for visible and ultraviolet (UV) region are of great significance in laser processing and in laser spectroscopy [2-7]. Thiourea is a white crystalline solid both occurring naturally and synthetic, which is easily soluble in solvents like water, ammonium triocyanate and ethanol. Thiourea is an interesting inorganic matrix modifier because of its large dipole moment and its typical polar molecule [8]. Among the semi-organic NLO materials, metal complexes of thiourea, have a low UV cut-off wavelength which is applicable for frequency con-version and second harmonic generation [9,10].Thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form extensive network of hydrogen bonds. Thiourea, which is centrosymmetric, yields excellent noncentrosymmetric materials when it is incorporated into the respective inorganic salt. A large number of thiourea compounds reported by various authors, which can form a semiorganic metallic complex when thiourea reacts with inorganic complexes. Examples of these salt complexes are bisthiourea cadmium chloride [11], bisthiourea zinc acetate [12], bisthiourea cadmium formate [13] cadmium thiourea acetate [14], bisthiourea zinc chloride [15] and bisthiourea lithium chloride [16].

Hence in the present work glycine manganese acetate crystal were grown from aqueous solution and were characterized by CHNS analysis, power X-ray diffraction, UV-vis-NIR optical transmittance, Emission spectrum, TGA, DSC, FTIR, NLO and antimicrobial studies.

2. Growth of single crystals of BTMA

Single crystals of bisthiourea manganese(II) acetate were grown by slow evaporation solution growth method at room temperature. Two moles of Thiourea and one mole of Manganese (II) acetate react to form BTMA crystal. Aqueous solutions containing analytical grades of Thiourea and Manganese (II) acetate react in 2:1 molar ratio respectively were prepared by using doubly distilled water. The two solutions were mixed together and stirred well for about 2 hours using mechanical stirrer. The resulting solution was filtered through a filter paper into a clean dry beaker. The beaker was covered by an ordinary filter paper. The filtered solution was kept aside for crystallization process in dust free environment. The crystal, BTMA is formed according to the following equation.

$$2(NH_2\text{-}CS\text{-}NH_2) + Mn\,(CH_3COO) \downarrow Mn(NH_2\text{-}CS\text{-}NH_2)\,(CH_3COO)]_2$$

Under the experimental condition, bright, transparent and light brown coloured BTMA crystals were obtained. Crystallization took place within three weeks. The grown crystals were collected from the mother liquid by using well cleaned forceps. The harvested crystals were recrystallized repeatedly to get crystals of good quality. The photograph of the grown crystals of BTMA is shown in Figure 1.

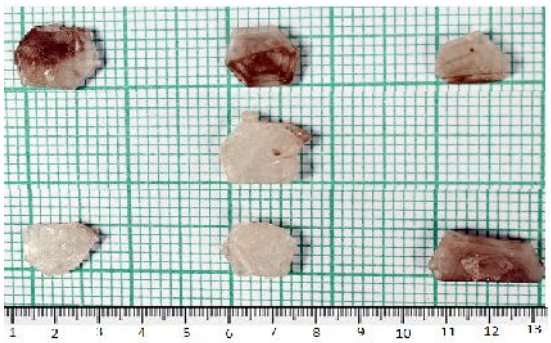

Figure 1. The photograph of the grown crystals of BTMA crystal.

2.1. Characterization techniques

The elemental analysis of the crystal is recorded at using Vario EL III CHNS instrument at Sophisticated Test and Instrumentation Centre, Cochin University of Science and Technology, Cochin. The powder X-ray diffraction pattern of

the crystal is obtained at using XPER-PRO instrument at Alagappa University, Karaikudi. The UV-visible spectrum is recorded at using JASCO V-670 Spectrophotometer Series instrument at VIT University, Vellore. The emission spectrum of the crystal was recorded using JASCO FP 6600 spectrophotometer in the wavelength range between 400 and 800 nm at University of Hyderabad. The thermal analysis (TGA) is recorded at VIT, Vellore using SDT Q600 V20.9 Build 20. The crystal was heated from room temperature to 800^{O}C at nitrogen atmosphere. The low temperature DSC of the complexes was obtained using a METTLER TOLEDO instrument model under nitrogen atmosphere at a heating rate of 10K/min. The samples were cooled from 30°C to -150°C and heated back from 0°C to 500°C in the heating run. The FTIR spectrum of the crystals is recorded using Perkin Elemer RXI spectrometer using KBr pellet techniques in the frequency region 4000 to 400 cm^{-1} at Archbishop Casmir Instrumentation Centre, St.Joseph's College, Trichy. The second harmonic generation efficiencies of the complexes were carried out by modified Kurtz-Perry powder technique using Nd: YAG laser. The antimicrobial studies of the crystal were studied by agar disc diffusion method.

3. Results and discussion

3.1 Elemental analysis

The experimental and calculated percentage of Carbon, Nitrogen, Hydrogen and Sulphur are very close and within the experimental error. The elemental analysis data of crystals confirms the stoichiometric ratio of the crystal. The C H N S data of the BTMA crystal is given in Table 1.

Table.1. Elemental analysis data of BTMA crystal.

	C %	H %	N %	S %
Experimental	20.21	6.44	23.45	25.76
calculated	19.51	5.73	22.75	26.04

3.2. Powder X-ray diffraction pattern analysis

The sharp and well defined Bragg peaks at 2Θ angle indicates the crystalline nature of the compounds. The powder X-ray diffraction of the crystal is shown in Figure 2. The unit cell parameters are a =19.6453, b=8.5439, c =4.1946, α= β = ϒ = 90^{o} and volume = 704.06 ^{3}. This data indicates that the grown crystal belongs to orthorhombic system.

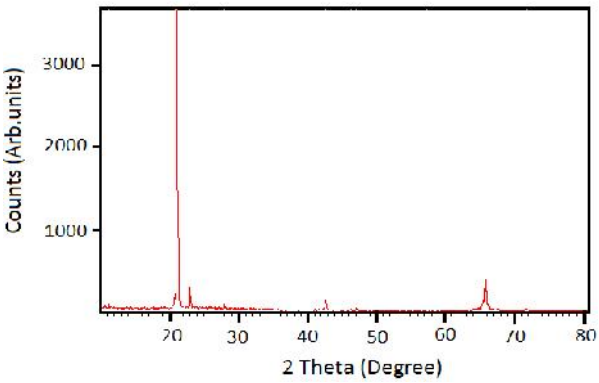

Figure 2. Powder X-ray diffraction pattern of BTMA crystal.

3.3. UV-Visible transmittance spectral study

The UV-visible Transmission spectrum of BTMA crystal is shown in Figure 3. The absorption peaks observed at 240 nm and 280 nm are due to electronic transitions. There is no absorption between 300 nm and 1200 nm. Hence it is a potential contender for nonlinear optical applications.

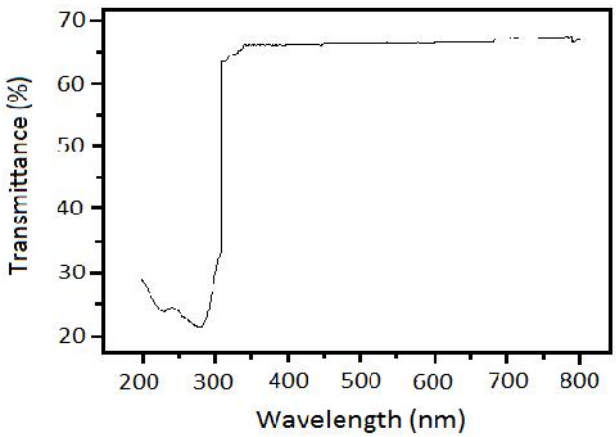

Figure 3. UV-Visible spectrum of BTMA crystal.

3.4 Emission spectral study

Emission spectrum of the crystal is shown in Figure 4. The emission spectrum of the crystal was recorded in the wavelength range between 400 and 800 nm. The peak observed at 580 nm indicates that the grown crystal shows green fluorescence emission.

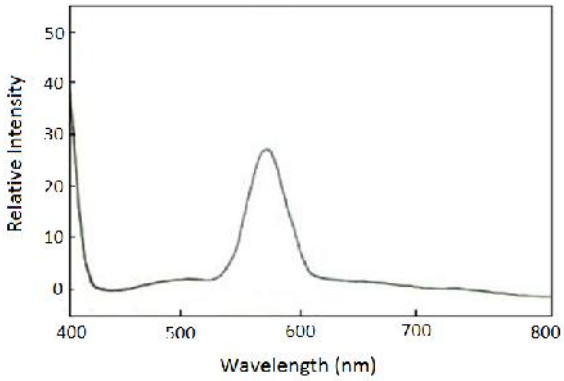

Figure 4. Emission spectrum of BTMA crystal.

3.5. Thermo gravimetric analysis

The TGA thermogram of the crystal is shown in Figure 4. When the crystal heated from 0°C to 500°C, it decomposes into two stages. In first stage decomposition occurs between from 68°C and 120°C, which may be due to loss our molecules of hydrogen. The experimental weight loss is 2.67% and calculated weight loss is 2.33%. Afterwards the crystal stable up to 185°C, the second stage decomposition occurs between 150°C and 300°C. The weight loss is due to loss of molecules of methyl group, sulphur, nitrogen, and CO_2 and also metal, Manganese (Mn). The experimental weight loss is 97.20%. The calculated weight loss is 97%. These differences in weight loss may be presence of occluded and absorbed water molecules in the crystal. It is thus evident from the TG study that compound is formed in the stoichiometric ratio.

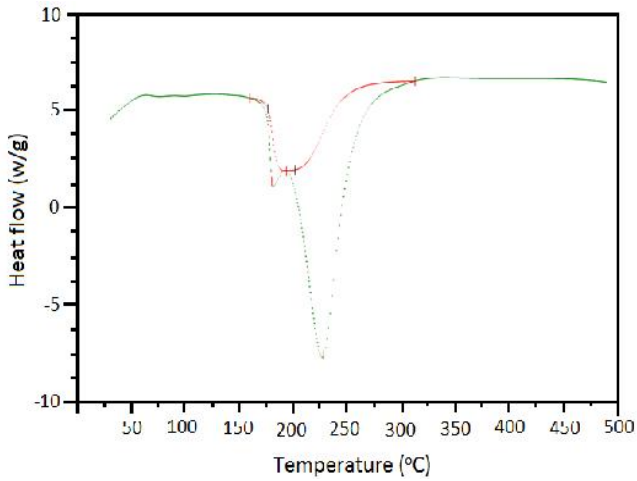

Figure 6. Low temperature DSC curve of BTMA crystal.

3.6. Low temperature DSC analysis

The low temperature DSC curve for BTMA crystal is given in Figure 5. The crystal shows thermal anomalies in the cooling cycle occurring at 180.29°C and 228.34°C. No thermal anomaly is observed in the cooling cycle (not indicated in the curve). This thermal hysteresis indicates a second order phase transition. This second order phase transition is due the gradual ordering of Mn^{2+} and NH^{+} ions.

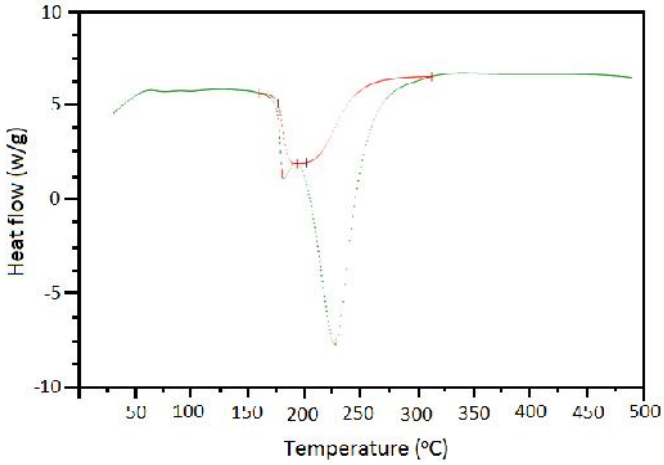

Figure 6. Low temperature DSC curve of BTMA crystal.

3.7. FTIR spectral analysis

The FTIR observed spectrum is shown in Figure 6. The asymmetric stretching of NH_2 molecule peak observed at 3798 cm^{-1}. The peaks at 394 and at 3298 cm^{-1} are due to the NH stretching vibrational bands in NH_2. The NH_2 group associated with broad band is found at 3149 cm^{-1}. The peak at 2688 cm^{-1} is due to asymmetric stretching vibration NH molecule. The peak at 2342 cm^{-1} is presence of NH stretching vibration. The stretching vibration of CH_2 is observed at 2217 cm^{-1}. The peak at 2035 cm^{-1} is due combination band of NH_2. The band observed at 1567 cm^{-1} is presence of asymmetric stretching of NH^+. The wagging of CH_2 is found at 1343 cm^{-1}. The peak at 1416 cm^{-1} is due to symmetric stretching of COO^-. The rocking of NH^+ occurs at 1084 cm^{-1}. The peak at 1028 cm^{-1} is due to -CN stretching vibration. The peak at 892 cm^{-1} and 933 cm^{-1} indicates the rocking of CH_2. The C=S stretching vibrations peak observed at 771cm^{-1}. The peak at 731cm^{-1} is presence of C=S symmetric stretching vibrations. The rocking of COO^- is found at 667 cm^{-1}. The peak at 617 cm^{-1} indicates that presence of symmetric N-C-N stretching. The peak at 488 cm^{-1} skeletal vibration may be due to $Mn(CH_3COO)$.

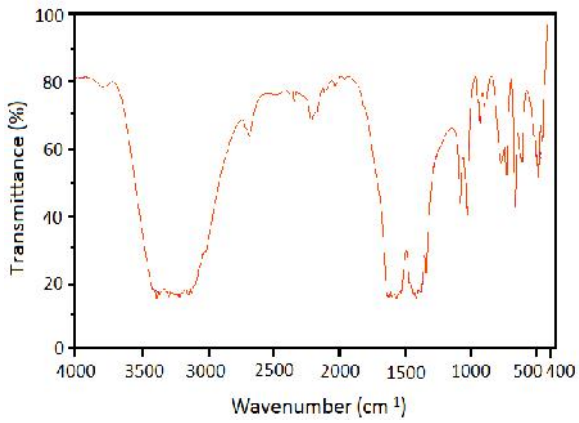

Figure 7. FTIR spectrum of BTMA crystal

3.8. Non linear optical study

Kurtz-Perry test was performed to find the NLO property of the BTMA crystals. Kurtz technique is used as a screening technique to identify the materials with the capacity for phase matching in addition to indentifying the materials with non-Centro symmetric crystal structures. The crystals were ground into powder and densely packed in between two glass slides. An Nd:YAG laser beam of pulse width 10ns at a wavelength of 1064 nm and 10Hz fundamental radiation was made to fall normally on the sample cell. The emission of green light confirms by the crystal, it indicates the grown crystal possesses SHG efficiency.

3.9 Antimicrobial activity studies

A small amount (about µg) of the grown crystal weighed and dissolved in 1 ml of DMSO solvent to obtain stock solutions. The diameter zones were measured which exhibit the growth of tested microorganism. The crystal showed excellent microbial activities against various bacterial and fungal strains.

3.9.1 Antibacterial activity study

Antibacterial in vitro study, the bacterial species Ptoteus sp., Esheria coli, Speudomonas sp., Staphylococcus aureus (Clinical isolate), Enterococcus faccalis, Speudomonas aeruginosa, Staphylococcus aureus (Lab isolate), Staphylococcus epidermidis were prepared at a concentration of 100 µg/mla dn Tetraglycine was used as a standard drug for the comparison of bacterial results and the results obtained are given in Table 3. From the data, it is found that the crystal shows good exhibition activity against Speudomonas sp., Enterococcus faccalis and Staphylococcus aureus (Clinical isolate) bacteria species and the crystal shows marked good exhibition activity against Ptoteus sp. and Esheria coli bacteria species. The synthesized crystal shows no good exhibition activity against Speudomonas aeruginosa, Staphylococcus aureus (Lab isolate) and Staphylococcus epidermidis bacteria species.

3.9.2 Antifungal activity study

The antifungal activity of the crystal was measured using Nystatin as a standard drug for the comparison of antifungal results. The antifungal exhibition activity results of the crystal

are given in Table 4. From the data, it is observed that the crystal shows good antifungal exhibition activity against Aspergillus niger, Penicillium sp and the grown crystal shows remarkable exhibition activity against Aspergillus fumigates and the crystal shows no exhibition activity against Candidia albicans and Aspergillus flavus fungal species. The antifungal data indicates that the synthesized crystal exhibits marked enhancement in the antifungal agent.

Table 3. Antibacterial activity of BTMA crystal

Bacteria	Strontium crystal	Tetracycline
Ptoteus sp.		19
Esheria coli	22	24
Speudomonas sp.	28	22
Enterococcus faccalis	25	23
Staphylococcus aureus (Clinical isolate)	29	26
Speudomonas aeruginosa	-	23
Staphylococcus aureus (Lab isolate)	-	20
Staphylococcus epidermidis	-	25

Table 4. Antifungal activity of BTMA crystal

Fungi	Strontium crystal	Tetracycline
Aspergillus niger	26	23
Penicillium sp	31	22
Aspergillus fumigatus	22	21
Candidia albicans	-	22
Aspergillus flavus	-	23

4. Conclusions

Glycine bisthiourea manganese(II) acetate, a non-centrosymmetric semi organic NLO single crystals were grown from aqueous solution by slow evaporation technique at room temperature. The stoichiometric ratio of the crystal was analyzed by C H N S study. Crystalline nature and information on unit cell measurements of the grown single crystal have been identified by using X-ray powder diffraction study. The UV-Vis-NIR spectroscopic study revealed that the grown crystal has good optical transmittance and shows that the grown crystal suitable for the optoelectronic applications. The emission spectrum of the crystal shows green fluorescence emission. The thermal stability of the compound was studied by TG analysis and found that it is stable up to 185^{o}C. The second order phase transition was ascertained by DSC technique. The functional groups present in the sample were identified by FTIR spectral analysis. BMTA single crystal response to NLO has been verified with the Nd:YAG laser. The synthesized crystal shows good antibacterial and antifungal activities.

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References

[1] S.P. Waje, M. Hashim, W.D.W. Yusoff, Z. Abbas, Appl. Surf. Sci. 256 (2010) 3122-3127.
[2] S. Suresh, D. Arivuoli, J. Min, Mater. Character. Eng. 10 (2011) 517-526.
[3] P. Singh, M. Hasmuddin, M. Shakir, N. Vijayan, M.M. Abdullah, V. Ganesh, M.A. Wahab, Mater.Chem. Phys. 142 (2013) 154-164.
[4] N. Vijayan, R. Ramesh Babu, R. Gopalakrishnan, P. Ramasamy, W.T.A. Harrison, J. Cryst. Growth 262 (2004) 490-498
[5] M.D. Aggarwal, J. Choi, W.S. Wang, K. Bhat, R.B. Lal, Angela D. Shields, B.G. Penn, D.O. Frazier, J. Cryst. Growth 204 (1999) 179-182.
[6] G. Zou, L. Huang, N. Ye, C. Lin, W. Cheng, H. Huang, J. Am. Chem. Soc. 135 (2013) 18560-18566.
[7] G. Zou, N. Ye, L. Huang, X. Lin, J. Am. Chem. Soc. 133 (2011) 20001-20007.
[8] N. P. Rajesh, V. Kannan, M. Ashok, K. Sivaji, P. Santharaghavan, P. Ramasamy, J. Cryst. Growth. 262 (2004) 561.
[9] G. Xing, M. Jiang, Z. Sao, D. Xu, Bis (thiourea) cadmium chloride a novel nonlinear optical crystal of organometallic complex, Chin. J. Lasers 14 (1987) 302-308.
[10] H.O. Marcy, L.F. Warren, M.S. Webb, C.A. Ebbers, S.P. Velsko, G.C. Kennedy, C.C. Catella, Second harmonic generation in zinc tris (thiourea) sulfate, Appl. Opt.31 (1992) 5051-5060.
[11] P. Jeyakumari, J. Ramajothi, S. Dhanuskodi, J. Cryst. Growth 269 (2004) 558–564.
[12] V. Kannan, N.P. Rajesh, R. Bairava Ganesh, P. Ramasamy, J. Cryst. Growth 269 (2004) 565–569.
[13] S.M. RaviKumar, N. Melikechi, S. Selvakumar, P. Sagayaraj, Physica B 403 (2008) 4160–4163.
[14] N.P. Rajesh, V. Kannan, M. Ashok, K. Sivaji, P. Santhana Raghavan, P. Ramasamy, J. Cryst.Growth 262 (2004) 561-566.
[15] S. Selvakumar, K. Rajarajan, S.M. Ravikumar, I. Vetha Potheher, D. P. Anand, P. Sagayaraj, Cryst. Res. Technol. 41 (2006) 766-770.
[16] N. Karthick, R. Sankar, R. Jayavel, S. Pandi, J. Cryst. Growth 312 (2009) 114–119.

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