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INFLUENCE OF PICRIC ACID ON ORGANOMETALLIC BISTHIOUREA MANGANESE CHLORIDE CRYSTALS

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Abstract— **The objective of the present work is to analyze the effect of picric acid on Optical quality single crystals of Bisthiourea Manganese Chloride (PBTMC) have been grown by slow evaporation growth technique using water as solvent. The influence of picric acid has a tendency to improve the crystalline perfection into a significant level. The coordination of thiourea with divalent transition metal ions takes place through Sulphur atom and picric acid. A detailed Comparision of vibrational data of PBTMC with similar metal complex revealed that the inclusion of picric acid in the formation of solid complexes was confirmed by means of FTIR Spectroscopy. The opticalstudies of the crystals was determined by UV- Visible studies. Areduction in the lower cutoff frequency is observed in the optical absorption spectrum of PBTMC which recommends the crystal for optoelectronic application. Dielectric behaviour of these crystals show very low value of dielectric constant at higher frequencies and increases their possibilities towards NLO devices. The significance of this work results a good pathway to make it potentially useful for NLO applications.**

Index terms- **Slow Evaporation, Organometallic material, FTIR, Dielectric Studies, UV-Vis Spectral analysis.**

I. INTRODUCTION

Crystal growth involves a variety of research fields ranging from surface physics, crystallography and material science. Though it has been studied more than 100 years, crystal growth still plays an important role in both theoretical and experiment research fields, as well as in applications like optoelectronics, thermography, light emitting diodes and laser technology[1]. For scientific and technological progress crystal growth and characterization have becomean interested research area in the past decades. All basic solid materials comprise of single crystal and they are backbone of the modern technology. The influence of single crystal is noticed in the optics and acoustics, semiconductors, in jewelers industries and in various medicalapplications[2].In crystallization process the morphology and the physical properties of crystal are greatly affected by the presence of additives and impurities[3].The derivatives of picric acid plays a vital role in anti-microbial activity especially in biological applications[4]. To improve the crystalline perfection of the material, the inclusion of picric acid plays a vital role in the growth process of PBTMC.

Single crystals of thiourea are being used extensively and have vast demand in the electronic industry as electronic modulator, polarization filter, optical voltmeter, electronic light shutter and as elements of electro-optic and electro-acoustic devices [5].Thiourea (NH2CSH2) is an interesting matrix modifier as a results of its large dipole moment.It forms a good network of hydrogen bondseffectively and it belongs to the family of orthorhombic crystal system [6].These crystals also exhibit piezoelectric effect, which is utilized in scanning electron microscopy (SEM), infrared (IR), ultraviolet (UV), detection and imaging[7].Organic molecules have Poor physical strength and higher degree of Polarization whilegreaterphysical strength and lesser degree of polarization are the characteristics of inorganic materials.But they possess poor thermal stability. Hence there is a necessity to grow materials which are thermally stable.Hence, an attempt is made to grow such a material by combining organic compound with inorganic counterparts. Compared to organic molecules, metal complexes offer a larger variety of structures of similar environmental stability and a much greater diversity of tunable electronic properties [8].

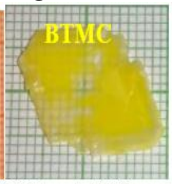
In the present work, the structural, vibrational, optical and dielectric properties of PBTMC crystals are investigated. An added advantage is that large single crystalscan be grown from slow evaporation solution growth[9]. The grown crystals were characterized by FT-IR, UV-vis Spectrum and dielectric study.

II. EXPERIMENTAL

A. SYNTHESIS AND GROWTH

The commercially available ofbisthiourea manganese chloride (BTMC) crystals were grown by slow evaporation solution growth technique using water as solvent. The material (BTMC) was synthesized by taking Thiourea and manganese chloride with molar ratio of 2:1.Calculated amounts of the chemicals were dissolved in deionized water and stirred well using a magnetic stirrer for about 4 hours.**Fig.1** shows the grown crystal of BTMC. The dopant picric acid 2% was mixed with the solution. The influence of the picric acid helps to improve the crystallization process further. The saturated solution of the salt of PBTMC was prepared by dissolving the salt in de-ionized water by continuous stirring of the solution using a magnetic stirrer and the saturated solution was filtered using Whatmannfilter paper. Then the filtered solution was taken in a petri dish.Purity of the crystal was improved by successivere-crystallization process.The supersaturation of the solution was found by observing the first crystal formed at the bottom of the petri dish due to the slow evaporation of the solvent. The yellow crystals were harvested within a week.The photograph of the as grown single crystal is shown in **Fig.2**andgrowth conditions are given in **table 1**

Fig.1 Photograph of the grown BTMC crystal [11]



PBTMC

Fig.2 Photograph of the grown PBTMC crystal (Present Work)

Table 1:

Solute	Thiourea, Manganese chloride, picric acid
Solvent	De-ionized water.
Method	Slow evaporation
Growth period	Within a week
Purification	Re-crystallization
Size of the crystal	14mm×1mm×9mm

III. CHARACTERIZATION TECHNIQUES

A. A.FT-IR ANALYSIS

In order to analyze the synthesized compound qualitatively for the presence of functional groups in the molecule, the Fourier transform infrared (FT-IR) spectrum was recorded using a Perkin-Elmer spectrometer by KBr pellet technique in the range 4000–400 cm^{-1}. In the FTIR spectrum of BTMC, the NH stretching vibrational bands of NH_2 group were observed at 3804cm^{-1}while in PBTMC shifted into 3919cm^{-1}. These bands were found shifted to higher wave number region when compared to that of the free ligand. This shift may be due to the increase in the polar character of thiourea molecule because of the formation of S → M bonds in $Mn[TU]_2$ Cl_2 complex. The bands observed at 1086 cm^{-1} in the investigated BTMC crystal and 1083cm^{-1} in the picric acid corresponds to the N–C–N stretching vibration shifted to 1063cm^{-1} in the PBTMC crystal.The NO_2 vibration was observed at 663cm^{-1} in picric acid crystal while it shifted into 629 cm^{-1} in PBTMC crystal. The peaks 1201cm^{-1} and 629cm^{-1} confirms the presence of picric acid.[10-12]**Fig.3** shows the FTIR spectrum of BTMC crystal. **Fig.4** shows the FTIR spectrum of PBTMC which reveals the presence of thiourea, manganese chloride and picric acid

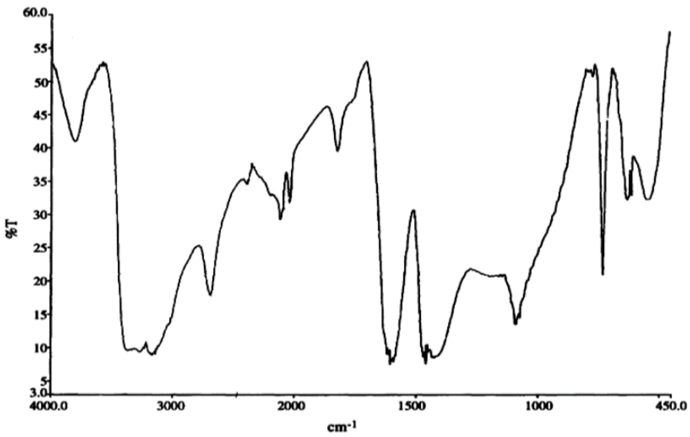


Fig.3 FT-IR Spectrum of BTMC[11]

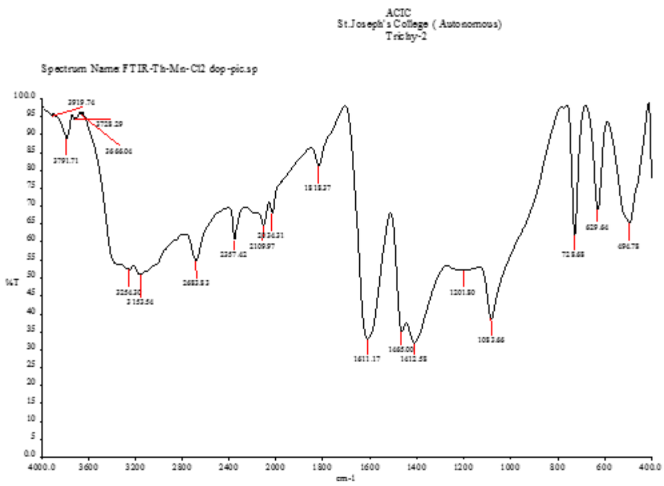


Fig.4 FT-IR Spectrum of PBTMC (Present Work)

Table 2: FTIR of PBTMC Crystals

Thiourea(cm^{-1})[9]	Picric(cm^{-1}) [12]	BTMC(cm^{-1}) [9]	PBTMC(cm^{-1}) (PresentWork)	Assignment
3380	-	3804	3919	ν(N–H)
3279	-	3262	3254	ν (N–H)
3190	3108	3165	-	ν (N–H)
3177	-	-	3153	ν (N–H)
1620	1630	1618	1611	δ(N–H)
1477	-	1459	1465	ν(N–C–N)
1414	1437	1424	1412	ν (C–N)
-	1275	-	1201	ρNH2
1082	1083	1086	1063	ν(C–N)
730	779	731	728	νNO2
-	663	-	629	δ(N–C–S)
494	-	538	-	

ν - Stretching; ρ - rocking; δ – deformation

B. .UV-VISIBLE SPECTRAL ANALYSIS:

The single crystals ae mainly used for optical applications. Thus the study of optical transmission range of grown crystal is important. The optical transmission spectrum was recorded using Perkin Elmer Lambda 35 spectrophotometer in the wavelength region 190-1000nm. Efficient non-linear optical crystals have an optical transparency lower cut-off wavelengths between 200-400nm **[13]**. In the absorption spectrum, lower cutoff region lies in the range of 212nm. TheUV–Vis-NIR spectrum the lower cut off is found near 247 nm, which is an advantage in organometallic materials over their inorganic counterparts.[11]Very low absorbance in the entire visible region would be attributed to the delocalization of electronic cloud through charge transfer.

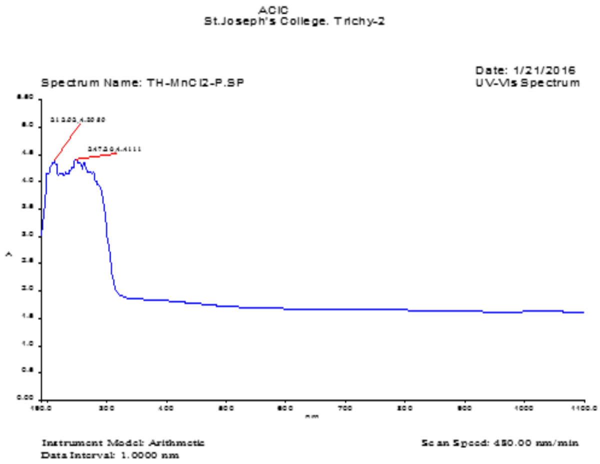


Fig.5 UV-Vis Spectrum analysis of PBTMC

C. DIELECTRIC STUDIES:

The study of dielectric constant of a material gives an outline about the nature of atoms, ions and their bonding in the material. From the analysis of dielectric constant as a function of frequency and temperature, the different polarization mechanism in solids can be understood.[14] The selected samples were cut using a diamond saw and polished using paraffin oil and fine-grade alumina powder to obtain a good surface finish and coated with conducting silver paste in order to increase the ohmic contact. The dielectric constant is calculated using the formula

$\varepsilon' = cd/\varepsilon_0$ ----------------- (1)

where C is the capacitance, d is the thickness, A is the area and ε_0 is the absolute permittivity of the free space having the value $8.854*10^{-12}Fm^{-1}$. The imaginary dielectric constant (ε'') was calculated using the relation

$\varepsilon'' = \varepsilon' \tan\delta$ ----------------- (2)

Where tanδ is the dielectric loss measured directly from the impedance analyzer. The alternating current (ac) conductivity σ_{ac} is calculated using the relation,

$\sigma_{ac} = 2\Pi f \varepsilon_0 \varepsilon' \tan\delta$ ------------------ (3)

Where f is the frequency of the applied ac field Hz.The dependence of the Dielectric constant ε', imaginary Dielectric constant ε'', and Dielectric loss tanδ frequency of the applied ac field was studied. The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency. The high values of dielectric constant at lower frequencies may be due to the presence of combinations of all four polarizations, namely space charge, orientation, electronic and ionic polarization.[15] The low value of dielectric constant at higher frequencies occurs due to the loss of these polarizations and also it reveals the good optical quality of the grown crystals with less defects, which is the desirable property of the materials to be used for various optical and communication devices.**Fig.6**shows the variation of Dielectric constant (ε') with frequency. The Dielectric constant (ε') was decreases and the log frequency increases.**Fig.7**shows the variation of Dielectric loss with frequency. The Dielectric loss (tanδ) decreases and the log frequency increases.**Fig.8** shows the variation of Ac conductivity with frequency. The log frequency was decreases and the Ac conductivity increases.

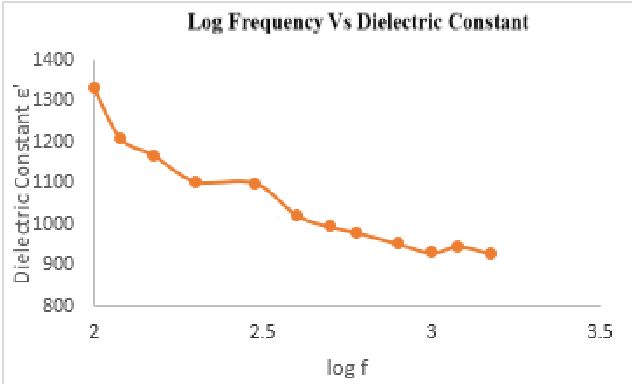


Fig.6 Plot of Dielectric constant Vs Frequency

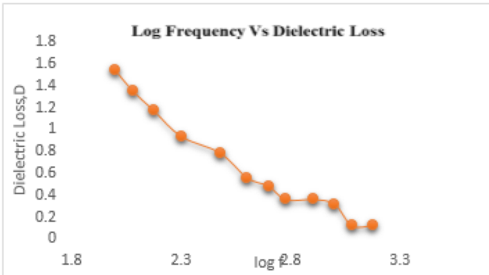


Fig.7 Plot of Dielectric loss Vs Frequency

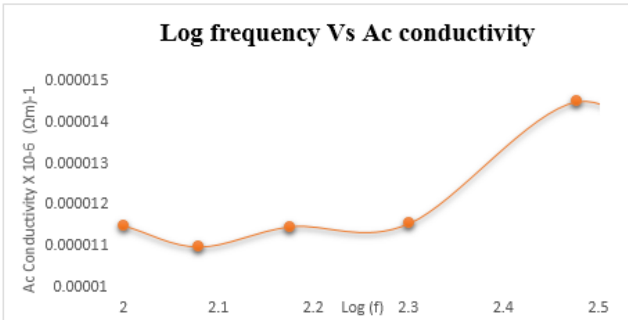


Fig.8 Plot of Ac conductivity Vs Frequency

IV. CONCLUSION

Good quality crystals of Picric doped BTMC were grown by slow evaporation technique and yellow crystals were harvested within a week. The coordination of thiourea with divalent metal ions takes place through Sulphur atom with the influence of Picric acid and vibrational data were compared using FT-IR and exhibits all the salient features reported in literature. New peaks in the FTIR spectra conclude that the mixed compounds of Thiourea, Manganese Chloride and Picric acid are added. A reduction in the lower cutoff frequency observed in the optical absorption spectrum of PBTMC recommends the crystal for optoelectronic applications. The low value of dielectric constant and dielectric loss of PBTMC at higher frequency is important for the fabrication of materials towards photonic, electro optics devices and high frequency response devices.

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