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# Manganese Mercury Thiocyanate Doped Zirconium Silicate Crystal Structure for Photo-Electronic, Electro-Optic and Sensor Applications

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***Abstract***

*Manganese mercury thiocyanate is a well-known organometallic crystal prized for its nonlinear optical properties. The high second harmonic efficiency of nearly 18 times that of urea and the wide optical transmittance window (373–2250 nm) of MMTC indicate that this material is an excellent candidate for photonics device fabrication. The metal thiocyanates and their Lewis-base adducts are one of the interesting themes of structural chemistry. For MMTC is a very flexible structure, scientists often mix it with other chemicals to alter the crystal grid for specific laser technologies. Here single crystals of manganese mercury thiocyanate (MMTC) and MMTC doped zirconium silicate were grown by slow evaporation solution growth technique using triply distilled water as solvent at ambient temperature. The single crystal X-ray diffraction studies reveal that the system of MMTC doped zirconium silicate crystal is monoclinic with different cell parameter values than MMTC as a=5.07A˚, b=14.32A˚, c=9.63A˚ and v=698A$^3$˚ with change in system or space group as Monoclinic with angles α=γ=90˚, β=93.21˚ concluding that so synthesised crystal is newly formed so far not synthesised by any researchers. Also the crystals structure is refined and crystal data is collected.*

**Keywords**: Single crystal, monoclinic, MMTC, zirconium silicate, ambient temperature, organometallic compound

## INTRODUCTION

Single crystals have promising applications in the area of photonics due to its unique properties. Recently researchers have focused on organometallic compounds because of its unique charge transfer capability associated with charge transfer transitions either from metal to ligand or ligand to metal. Keeping in mind "combining the inorganic distorted polyhedran with asymmetric conjugate organic molecules" a great deal of attention on organometallic materials in nonlinear optical field is made [1–4]. It is found that transition metal; inorganic compounds and coordinated complex emerged promising building block for opto–electronic materials. In general it is said that metal complexes offer variety of structures of similar environmental stabilities of even higher stability with greater diversity of tunable electronic properties. The transfer of electron density from the metal atom and the conjugated ligand system in metal ligand bonding in organometallics results in molecular hyperpolarizabilities [5–10]. Recently thiocyanate (SCN) ligand have good optical properties due to CN group and moreover with S and N donors they are capable of combining with metal to form stable complexes by co-ordinated bonds. By the crystal growth general formula $AB(SCN)_4$, taking into account different materials percentage of constituent materials and different percentage of

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different dopants which are not tried, various A group and B group of materials are selected .The parent material which increases the CN and CS stretching vibrations and reducing the SCN bending vibration to get better optical properties are selected in order to increase the electron transformation.

Many reported studies involving II B metal complexes of Zn, Cd, Hg & Mn which crystallize in noncentrosymmetric space group $I_4$ and crystals such as ZCTC, ZMTC, ZTS, MMTC, CMTC etc. are identified as promising materials exhibiting excellent physical and chemical properties. Newly discovered Lewis base adducts of CMTC and MMTC like cadmiummercurythiocyanate dimethylsulphoxide [$CdHg(SCN)_4(H_6C_2DS)_2$, CMTD] and manganesemercury thiocyanateglycolmonomethylether [$MnHg(SCN)_4(C_3H_8O_2)$, MMTG] crystals are studied [11–14]. Latest reported studies are the influence of cadmium and magnesium on the physical properties of the MMTC, comparative study of pure and alkaline (Ba, Ca) metal doped on CMTC, physical properties of metal substituted NMTC crystals, crystal growth and characterization of $La^{3+}$ doped organo metallic non-linear optical single crystals of MMTC, crystal growth of $Mg^{2+}$ doped CMTC single crystals by gel technique, impedance analysis growth and electrical properties of bimetallic thiocyanate ligand based single crystals of $MnHg(SCN)_4$ and $CdHg(SCN)_4$, synthesis, growth and characterization of zinc manganese thiocyanate crystal by replacing Hg by Mn, Cd by Zn are studied. RMTC having high applications as NLO material in semiconductor diode as SONLO, its crystal growth, structure with monoclinic system was studied by researchers. Since MMTC doped Zirconium silicate is not reported so far I have chosen for my research its synthesis and structure refinement and data collection is discussed in this research paper [15–18].

## MATERIALS AND METHODS

### Synthesis and crystal growth

Manganese mercury thiocyanate (MMTC) was synthesized from the commercially available materials ammonium thiocyanate, mercuric chloride and manganese sulphate. First MMTC was synthesized by taking ammonium thiocyanate, mercuric chloride and manganese sulphate in the ratio 4:1:1 and the reaction is as follows;

$$4NH_4SCN + MnSO_4 + HgCl_2 \rightarrow MnHg(SCN)_4 + 4NH_4SO_4$$

Then manganese mercury thiocyanate doped zirconium silicate crystal was synthesized by mixing MMTC and zirconium silicate in 1:1 ratio taking triply distilled water as solvent in a conical flask and the contents were stirred for 3 hours in a magnetic stirrer then the stirred solution was filtered in order to remove impurities and was maintained undisturbed in a beaker covered by polythene paper with few holes on the cover rubberbanded at the neck of beaker and kept for slow evaporation undisturbed at ambient temperature. The crystal growth has taken place in around 30days and it is let undisturbed for another 15days for large single crystals. The branch shaped colourless, transparent crystals of MMTC doped zirconium silicate are shown in Figures 1(a, b).

## RESULTS AND DISCUSSION

### Single Crystal X-ray Diffraction Analysis

The single crystal X-ray diffraction analysis is done by Bruker AXS (Kappa Apex II) X-ray diffractometer. Here the unit cell values of MMTC doped zirconium silicate crystal is determined as in the Table 1.

In the below table, the cell parameter values is a=11.274A˚, b=11.274A˚, c=4.25A˚ and v=542A˚$^3$ with tetragonal system and angles α=β=γ=90˚ for pure MMTC crystal. The cell parameter values are moderately modified due to the change in occupational sites of the dopant zirconium silicate to MMTC matrix, its cell parameter values are a=6.2451A˚, b=12.6841A˚, c=9.3685A˚ and v=710.04A$^{3\circ}$ with change in system or space group as Monoclinic with angles α=γ=90˚, β=106.90˚ differing and forms a new single crystal whose crystal structure is refined and data as follows in Table 2.

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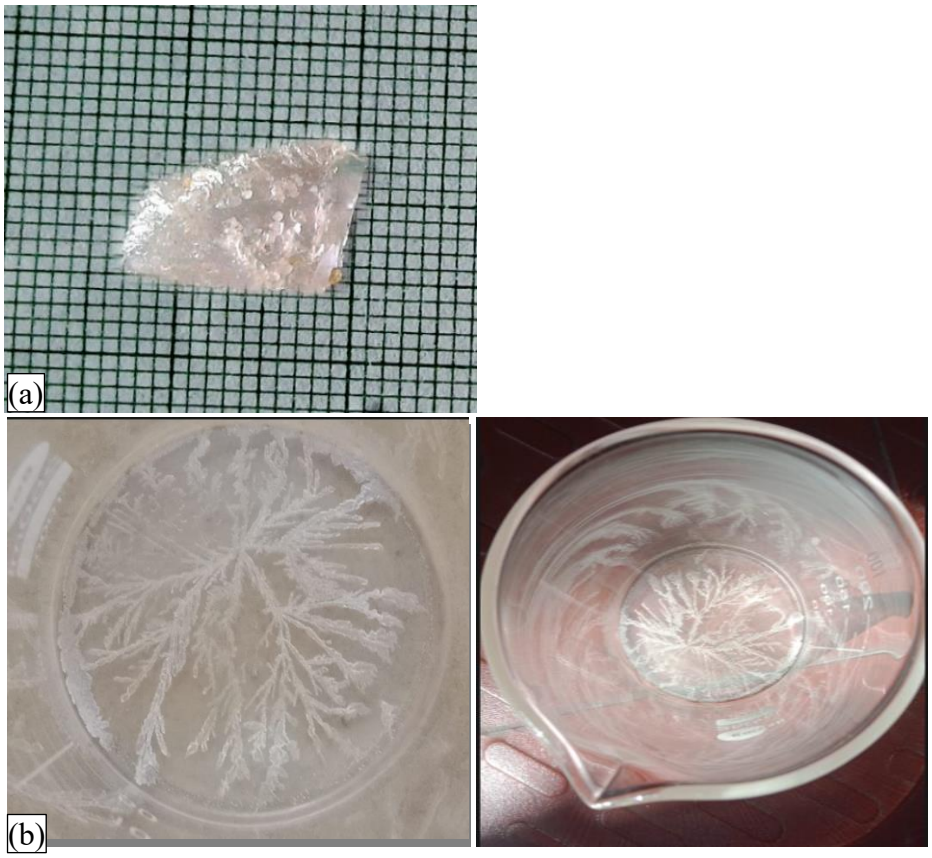



**Figure 1.** (a) Image of MMTC, (b) Image of MMTC doped zirconium silicate crystals.

**Table 1.** Cell parameter values of pure MMTC and MMTC doped zirconium silicate crystals.

| Lattice Parameter Values | $a_A^0$ | $b_A^0$ | $c_A^0$ | $v_A^{03}$ | System/space group/Beta angle |
|---|---|---|---|---|---|
| MMTC | 11.274 | 11.274 | 4.25 | 542 | Tetragonal/$I_4$/ $90^0$ |
| MMTC doped Zirconium silicate | 6.2451 | 12.6841 | 9.3685 | 710.04 | Monoclinic/ $P2_1/c$ /$106.90^0$ |

An ORTEP figure is a 3D visual summary of your refined crystal structure, it shows the exact locations of atoms in the molecule and displays the lines (bonds) connecting them. It also includes an atom- labelling scheme to identify each specific atom in the structure, their exact distance and their vibration. Since the manganese mercury thiocyanate doped zirconium silicate crystal system is monoclinic, we can say that it is highly non-linear optical material. In this crystal structure Mn(II) is bonded octahedrally to oxygen(water) along with the presence of two sulphate anion and two ammonium ion. In this complex manganese is bonded to oxygen of water(aqua) ligand by coordination bond and existing in oxidation states +2 and is named as Diammonium disulphate manganesehexaaqua complex where manganese is three aqua (oxygen of water) one sulphate and one ammonium in ORTEP diagram and in packing diagram it is doubled to form full structure moitey.

**Table 2.** Crystal data for MMTC doped zirconium silicate crystal.

| Empirical formula | $H_{20}MnN_2O_{14}S_2$ |
|---|---|
| Formula weight | 391.24 |
| Temperature [K] | 300(2) |
| Crystal system | monoclinic |
| Space group (number) | $P2_1/c$ (14) |
| *a* [Å] | 6.2451(3) |
| *b* [Å] | 12.6841(6) |

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| **Empirical formula** | **$H_{20}MnN_2O_{14}S_2$** |
|---|---|
| *c* [Å] | 9.3685(5) |
| α [°] | 90 |
| β [°] | 106.9070(10) |
| γ [°] | 90 |
| Volume [Å$^3$] | 710.04(6) |
| *Z* | 2 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.83 |
| $\mu$ [mm$^{-1}$] | 1.293 |
| *F*(000) | 406 |
| Crystal size [mm$^3$] | 0.148×0.309×0.327 |
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo $K_\alpha$ (λ=0.71073 Å) |
| 2θ range [°] | 5.57 to 56.58 (0.75 Å) |
| Index ranges | −8 ≤ h ≤ 8 −16 ≤ k ≤ 16 − 12 ≤ l ≤ 12 |
| Reflections collected | 16172 |
| Independent reflections | 1761 $R_{int}$ = 0.0353 $R_{sigma}$ = 0.0203 |
| Completeness to θ = 25.242° | 100.0 |
| Data/Restraints/Parameters | 1761/0/118 |
| Goodness-of-fit on $F^2$ | 1.091 |
| Final *R* indexes [$I$≥2σ($I$)] | $R_1$ = 0.0248 w$R_2$ = 0.0616 |
| Final *R* indexes [all data] | $R_1$ = 0.0287 w$R_2$ = 0.0649 |
| Largest peak/hole [eÅ$^{-3}$] | 0.32/−0.39 |

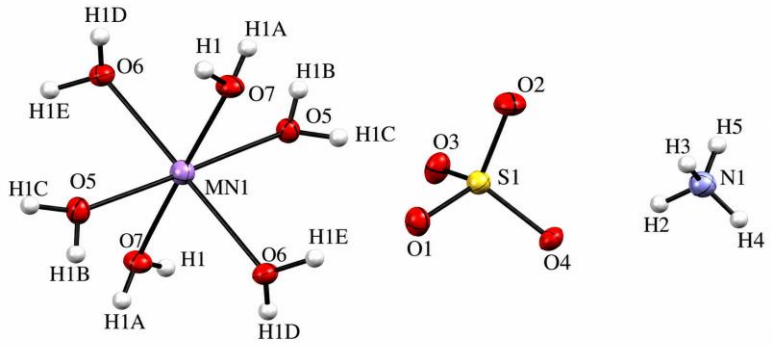



**Figure 2.** ORTEP diagram of MMTC doped zirconium silicate crystal.

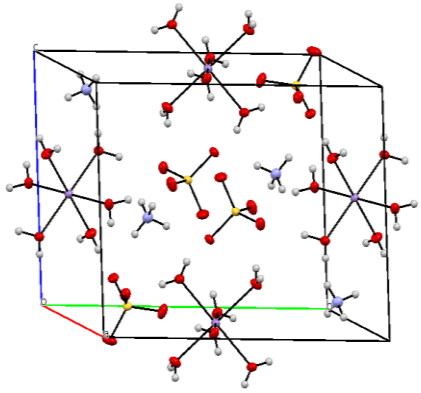


**Figure 3.** Packing diagram of MMTC doped zirconium silicate crystal.

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The bond length of Mn-O varies from 2.1468(12)-2.1902(12)Å, S-O it ranges from 1.4572(14)-1.4768(11)Å, O-H bond length is 0.71(3)-0.87(3)Å and N-H is 0.86(3) Å. The bond angle of H-O-H is 110º(2)º, Mn-O-H angle ranges from 114(2)-123.0º(17), O-Mn-O varies from 87.89(5)-180º(0). The O-S-O bond angle ranges from 107.99(8)-110.64º(8), H-N-H is $105^0$(2)-116º(2).

A packing diagram shows the arrangement of molecules or ions themselves in a 3D space to form a crystal lattice, also displays several key features of the crystal structure like repeated unit cells, symmetry, intermolecular forces, packing density and storage of gases or liquids. In this crystal the manganese atom and sulphate, ammonium ions are packed together in a flexible repeating pattern (Figure 3) crystal structure is monoclinic with repeated unit cells a=6.2451A˚, b=12.6841A˚, c=9.3685A˚ and v=710.04$A^{3°}$, Z=2, and space group $P2_1/m$, noncentrosymmetry, packing density 1.83 g/$cm^3$ with block shape.

## CONCLUSION

The optically transparent, colourless, single crystals of MMTC doped zirconium silicate (branch shaped) and MMTC were grown by slow evaporation solution growth technique at ambient temperature. Single crystal X-ray diffraction studies say that MMTC doped zirconium silicate crystal is with monoclinic system with $P2_1/m$ space group with modifications in cell parameter values as a=6.2451A˚, b=12.6841A˚, c=9.3685A˚ and v=710.04$A^{3°}$, α=γ=90˚ than pure MMTC crystals also with beta angle 106.90˚ which shows the formation of new crystal with molecular formula $H_{20}MnN_2O_{14}S_2$ named Diammonium disulphate manganesehexaaqua complex with molecular weight 391.24g. Since this crystal is monoclinic in nature it is concluded for this crystal to posses high nonlinear optic (NLO) character applying in optoelectronic, photonic, laser technologies, semiconductor diode, microchips and LEDs. In this crystal structure Mn(II) is bonded octahedrally to oxygen(water) along with the presence of two sulphate anion and two ammonium ion. In this complex manganese is bonded to oxygen of water(aqua) ligand by coordination bond and existing in oxidation states +2 and is named as Diammonium disulphate manganesehexaaqua complex where manganese is three aqua (oxygen of water) one sulphate and one ammonium ion.

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