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Synthesis, Growth, SEM and Microhardness studies of an organometallic single crystal: TMTM

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Abstract: In the present work, bulk size (21x15x5 mm^3) single crystal of Tetra thiourea mercury (II) tetra thiocyanatomanganate(II); $Hg(N_2H_4CS)_4Mn(SCN)_4$ (TMTM) has been grown for the first time from an aqueous solution using slow solvent evaporation technique and presented. The color of the crystal is so impressive due to Mn ions incorporated in the resulting compound.The grown crystal is subjected to thermal and microhardness studies and the results are systematically presented.
Keywords: Crystal growth, NLO, Thermal Studies.

1. Introduction and Experimental

Recently, the frequency conversion crystalline materials with best suited physico-chemical properties grabbed the attention of scientists as they are capable of performing the variety of task in photonics and opto-electronics. It is interesting to note that Tetrathioureamercury (II) Tetrathiocyanatomanganate (II); $Hg(N_2H_4CS)_4Mn(SCN)_4$ (TMTM) is a highly efficient second harmonic generation crystalline material whose conversion efficiency is about 12 times superior to KDP. Earlier, the crystal structure of TMTM was reported by Wen-Tao Yu et al [1]. Latter, growth and its properties were systematically studied by Rajarajan et al. [2]. In the present work, the microhardness and thermal properties of TMTM were studied and reported.

1.1 Synthesis and crystal growth

The bulk size (21x15x5 mm^3) single crystal of TMTM has been grown for the first time from an aqueous solution (optimized pH 3.5-4.0) using simple slow solvent evaporation and presented (Fig 1).

$$4(N_2H_4CS) + 4(NH_4SCN) + Hg\,Cl_2 + MnCl_2 \rightarrow Hg\,(N_2H_4CS)_4Mn(SCN)_4 + 4NH_4Cl$$

Well-defined and optically good quality TMTM crystals of suitable size were obtained by the slow evaporation process over a period of 40-45 days.

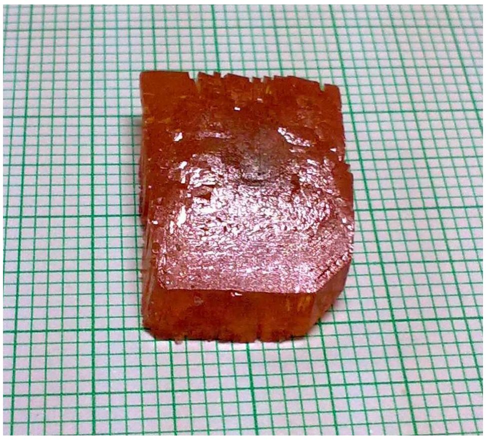

Fig. 1 As grown single crystal of TMTM

1.2 X-ray diffraction studies

TMTM single crystal was solved by direct technique and refined by full the matrix least-square technique using the SHELXL program. The cell parameters obtained by single crystal XRD are given in Table 1.

1.3 Fourier transform infrared (FT-IR)

The functional groups of TMTM are confirmed by recording the FT-IR spectrum in the range of 4000–400cm^{-1}. The IR bands of TMTM in comparison with MMTC are listed in Table.2.

Table.1 Single crystal XRD data of TMTM

Crystal formula	Hg $(N_2H_4CS)_4Mn(SCN)_4$
Crystal System	Tetragonal
Space group	I4
a(A°)	17.441(7)
b(A°)	17.441(7)
c(A°)	4.182(4)
α(°)	90
β(°)	90
γ(°)	90
Volume(A°)	1272.11(12)
Z	2

Table.2 Comparison of FT-IR spectral data of TMTM single crystal with MMTC

Wave number (cm^{-1})		
TMTM	MMTC	Assignment
3579.0		H_2O stretching
3369.0		$\upsilon_{as}(NH_2)$
3283.0		$2\delta (NH_2)$
3189.0, 3118.0		$\upsilon_{s}(NH_2)$
2888.0, 2707.0, 2663.0, 2328.0		Combinations and Overtones
2069.0	2115.8, 2131.2	υ (CN)
1627.0,1610.0		$\delta (NH_2)$
1499.0		υ (NCN)
1420.0, 1380.0		$\upsilon_1 (SCN_2H_4)$
1099.0		$\upsilon_2 (SCN_2H_4)$
813.0	896.9, 939.3	2δ(SCN)
703.0		υ ‘ (CS)
609.0		υ (SCN)
540.0,523.0		δ_{as} (NCN)
463.0	447.5, 468.5	δ (SCN)

1.4 Hardness Studies

The Vicker's microhardness measurements were carried out on the grown crystals of TMTM using Reichert MD400E ultra microhardness tester. Single crystal of TMTM was polished and load was applied on the most prominent face (001) from 10 g to 120 g for a constant indentation period of 10 sec. For various loads, the Vickers's hardness number (VHN) values were found. The Vicker's Hardness Number (VHN) of TMTM crystals were estimated for different applied loads. A plot drawn between the hardness value (H_v)and corresponding load (p) is shown in Figure 2. It is seen from the study that the hardness number sharply increases with the increasing load up to 40 g. Further, the value becomes steady till 75g. Beyond that the hardness number becomes saturated for further increasing loads, which in turn reflect the breakdown of TMTM sample. The VHN value corresponds to the saturation is found to be 62.4 Kg/mm^2. A graph is plotted between the square of the length of diagonal and load (Fig 2). From the graph, it is observed that the plot is almost straight line passing through the origin, which indicates the very minimum error in the studied range of loading. The plots of log d versus log p clearly established that the value of work-hardening coefficient (n) as greaterthan 2.

1.5 Thermal studies

The DSC trace of TMTM indicates that there is a sharp endothermic at 199.06°C which indicate the melting point of the sample. The thermal stability of TMTM (199.06°C) almost comparable to CMTC (198.5°C) and is relatively more stable than TMTM (185°C)[18] and CMTD (154°C).

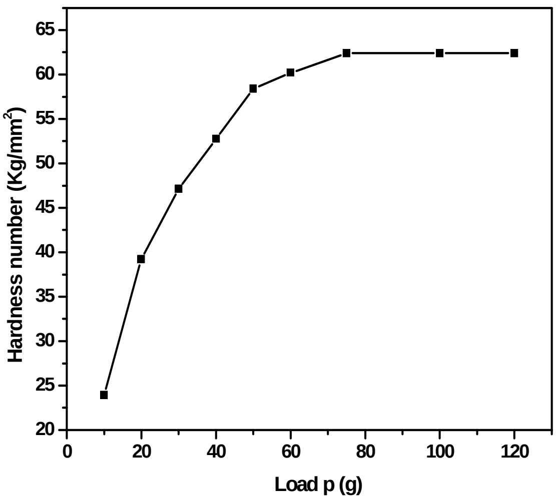

Fig.2 Vickers hardness profile of TMTM as a functionn of load

Conclusion

In the present work, the bulk size (21x15x5 mm^3) TMTM single crystal has been grown from an aqueous solution by slow evaporation technique. The FT – IR Studies of TMTM suggest that in Hg- SCN –Zn bridge, thiourea strongly interacts with Hg through sulphur. The VHN value of TMTM is found to be 62.4 Kg/mm^2. Thermal studies confirm the better thermal stability of TMTM (199.06°C) over the other organometallic counter parts like CMTC (198.5°C) and CMTD (154°C).

References

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