


RESEARCH ARTICLE

**STRUCTURAL COMPARISON OF MANGANESE-IMINODIACETATE SYNTHESISED BY
HYDROTHERMAL AND SOLVENT FREE SYNTHESIS**
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Abstract

A new solvent free mechano chemical synthesis of microporous metal organic framework manganese iminodiacetate is obtained by grinding manganese acetate and iminodiacetic acid together for 10 minutes using a pestle and mortar without any heat being applied. The compound was characterized by using XRPD, FTIR, TGA and SEM analysis.

Keywords: Metal-organic framework; iminodiacetic acid; FTIR, TGA, SEM.

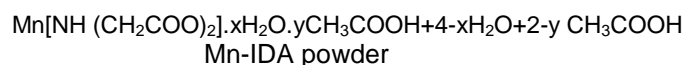
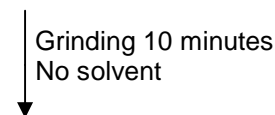
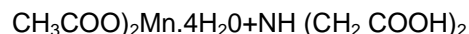
Introduction

Solvent free synthesis in particular a reaction between metal salts and organic ligands, to give co-ordination polymers or metal-organic framework is of great interest due to the sorption characteristics of solvent molecules in their microporous structures. It has been reported already by Stuart L. James that mechanochemical synthesis of copper-isonicotinate, a metal-organic framework with permanent porosity can be prepared which is used for absorption of small molecules as guest in their cavities. Solvent free synthesis of metal-organic framework will therefore be a great advancement. Here we report on a mechano chemical synthesis of metal-organic framework namely manganese iminodiacetate which has three dimensional connectivity. The reaction is initiated by grinding manganese acetate and Iminodiacetic acid together by using pestle and mortar for 10 minutes to give micro porous metal-organic framework.

Experimental

1 mmol of manganese acetate tetrahydrate and 1 mmol of iminodiacetic acid are taken in a mortar

and ground for 10 minutes. The formation of the compound was indicated by the characteristic odour of acetic acid which is formed as a by-product. The reaction is given below.


Results and Discussion

The XRPD pattern of material-1, the two reactants manganese diacetate and iminodiacetic acid are quite different which reveals that Mn-IDA powder is highly crystalline since the peaks are quite different to starting materials were found and the reaction is quantitative. It is shown in figure 1.

Fig.1 Comparison of XRPD patterns of starting materials iminodiacetic acid, Mn(OAc)₂·4H₂O, and the Mn-IDA powder.

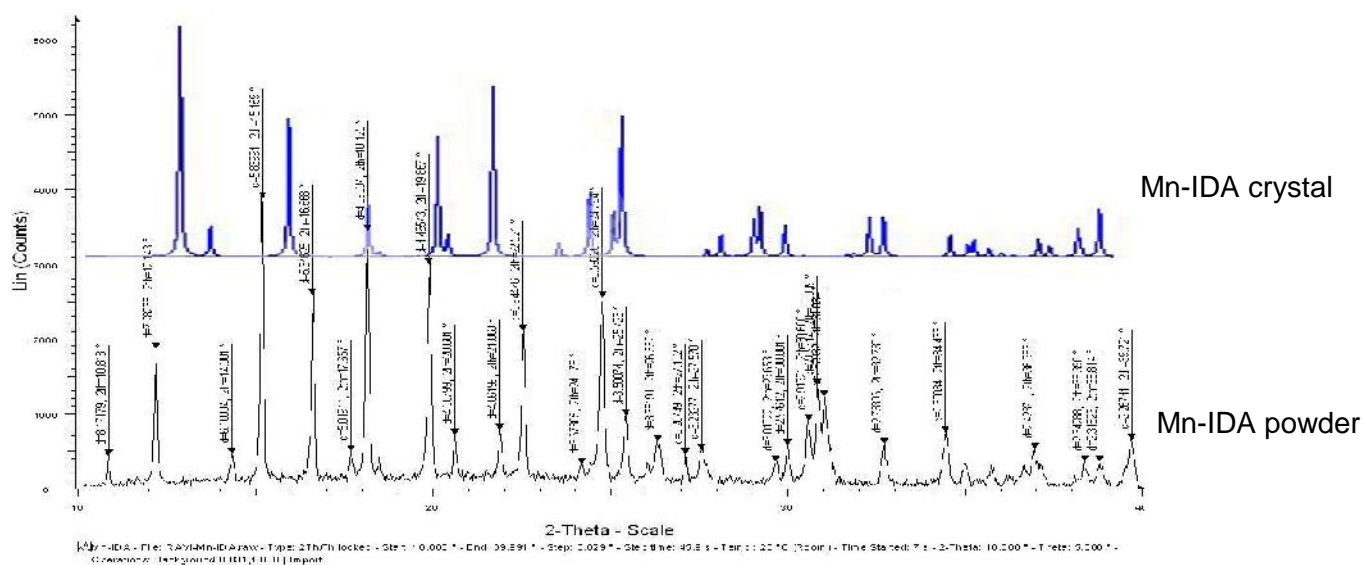


The same compound manganese iminodiacetate was crystallised using hydrothermal reaction between manganese diacetatetetrahydrate and iminodiacetic acid in a Teflon coated auto clave to 150°C for 24 hours. The x ray structure of the crystal was solved to have tetragonal geometry which consists of Mn(II) centres doubly bridged by carboxylate group to form infinite chains with water molecules co-ordinated to the Mn(II) ion occupying

axial positions. XRPD pattern of the single crystal was simulated using mercury 2.3 software.

The Powder x – ray diffraction pattern of Mn-IDA powder was similar to the pattern simulated from the single crystal diffraction data using mercury 2.3 software which reveals that they have similar structures. It is shown in figure 2.

Fig.2 Comparison of XRPD patterns of Mn-IDA powder and the pattern for the single crystal simulated using mercury 2.3 software



The FTIR spectrum for both Mn-IDA crystal and powder are quite similar.

The peak at 3752cm^{-1} corresponds to O-H stretching of alcohols present in the crystal. Both the spectrum showed symmetric and asymmetric

stretching of COO⁻ group which reveals that the metal is co-ordinated to the oxygen atom of carboxyl group. The FTIR spectrum of crystal and powder is shown in figure 3 and Table 1.

Fig. 3 FTIR spectrum of Mn-IDA crystal and Mn-IDA powder

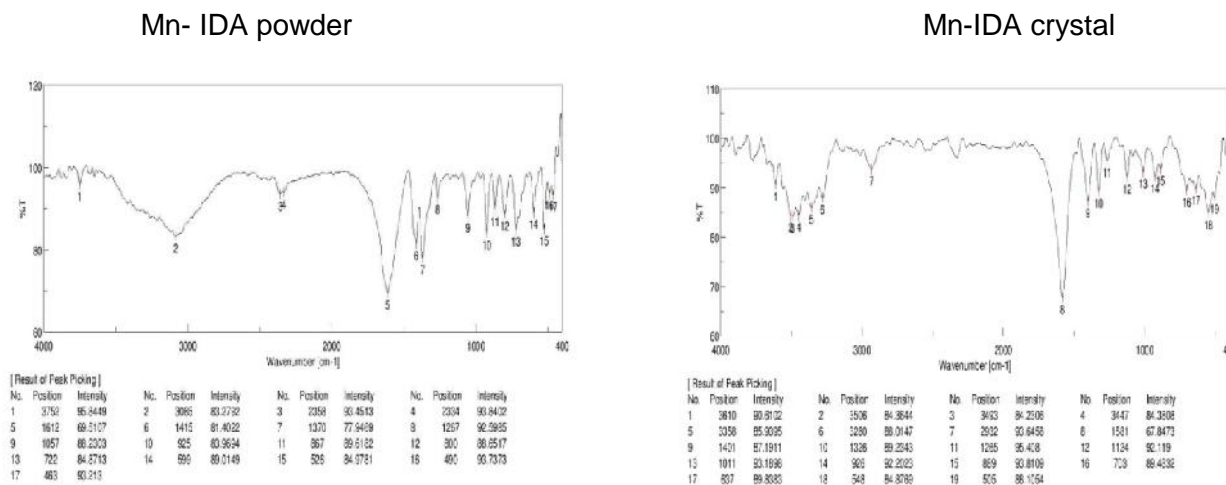


Table 1: IR Absorption Frequencies.

	OH	NH	CH ₂	$\begin{matrix} \text{C}=\text{O} \\ \\ \text{C}-\text{O}^- \end{matrix}$	C-O	C-N
Mn-IDA powder	-	3500-3200 cm^{-1}	2932 cm^{-1} 1401 cm^{-1} 926 cm^{-1}	1581 cm^{-1} 1326 cm^{-1}	1265 cm^{-1}	1124 cm^{-1}
Mn-IDA crystal	3752 cm^{-1}	-	3085 cm^{-1} 1415 cm^{-1} 925 cm^{-1}	1612 cm^{-1} 1370 cm^{-1}	1267 cm^{-1}	1057 cm^{-1}

The CHN analysis gave similar percentage composition of manganeseiminodiacetate crystal as well as powder which shows that they have

similar crystal arrangements. It is given in table 2 which is shown below.

Table 2: CHN Analysis Report

Sl.no	Sample code	Wt. in Mg	%carbon	%hydrogen	%nitrogen
01.	Mn-IDA crystal	1.861	27.39	3.76	7.78
02.	Mn-IDA powder	1.441	22.10	3.12	6.37

The comparison of TGA curves revealed that extra 5.7% (15.94%) is lost in the interval 0^oc–200^oc for the Mn-IDA powder compared to Mn-IDA Crystal(10.28%) which revealed that some extra

amount of water and acetic acid is present in the powder. Around 32.45% is lost which corresponds to the decomposition of the crystal structure at 600^oc. It is shown in figure 4a and 4b.

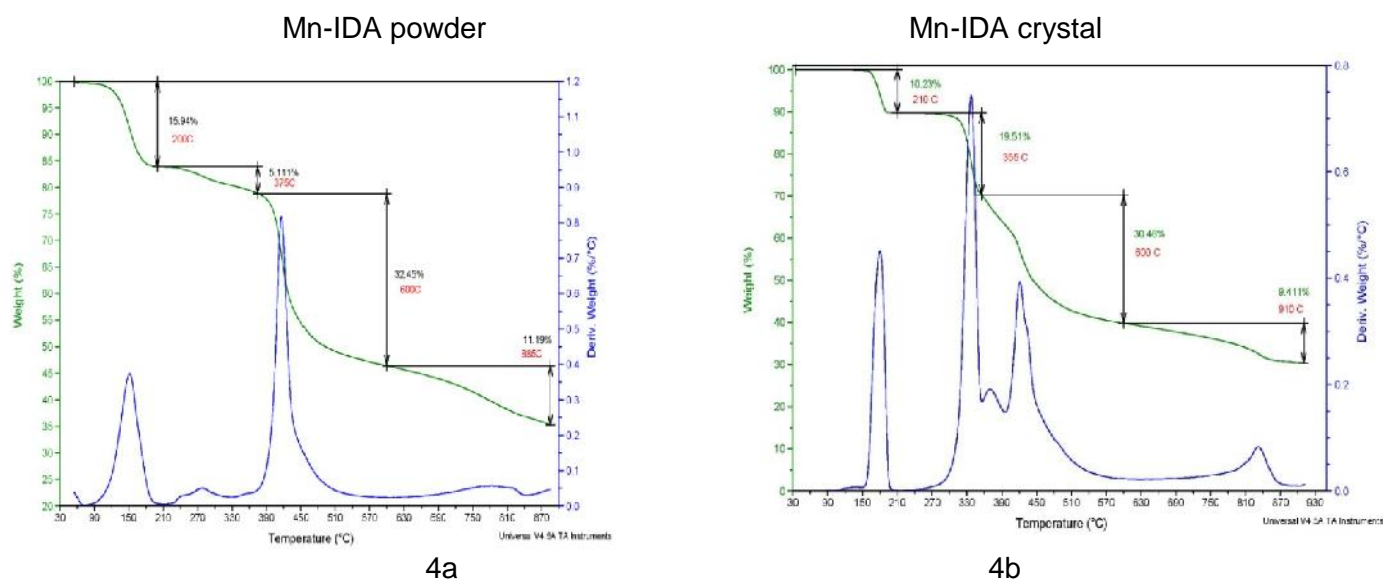
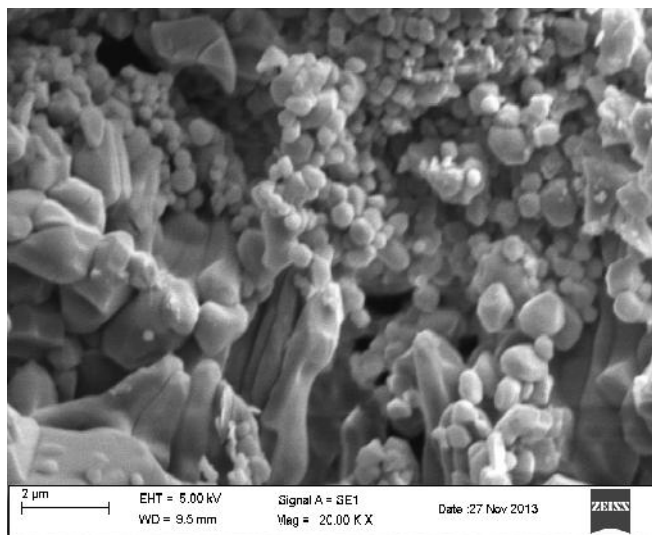


Fig. 4a TGA curve of Mn-IDA powder and **4b** TGA curve of Mn-IDA crystal

SEM Analysis showed that different morphologies shown by samples prepared by grinding for 1 minute compared to that grinding for 5 minutes. The 1 minute sample showed well defined forms and edges compared to the 5 minutes sample. It

reveals that the essential role of grinding is to finely divide and intimately mix the reactants and not to make it to completion although it is accelerated by continued grinding. It is shown in figure 5.

Fig. 5 SEM image of samples prepared by grinding for 1 minute and for 5 minutes

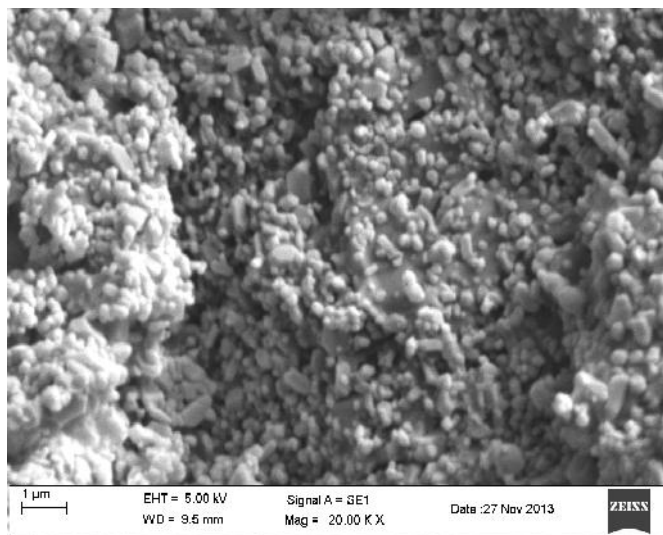


1min

EDAX analysis for both Mn-IDA powder and crystal gave similar percentage composition for the elements which reveal that both represent the same compound. It is shown in figure 6a and 6b.

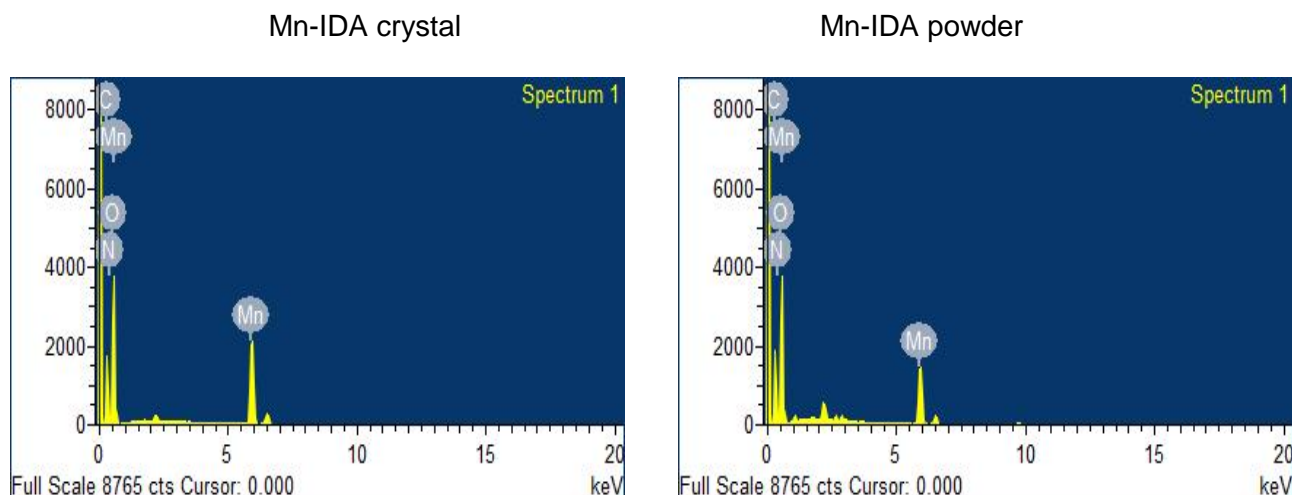
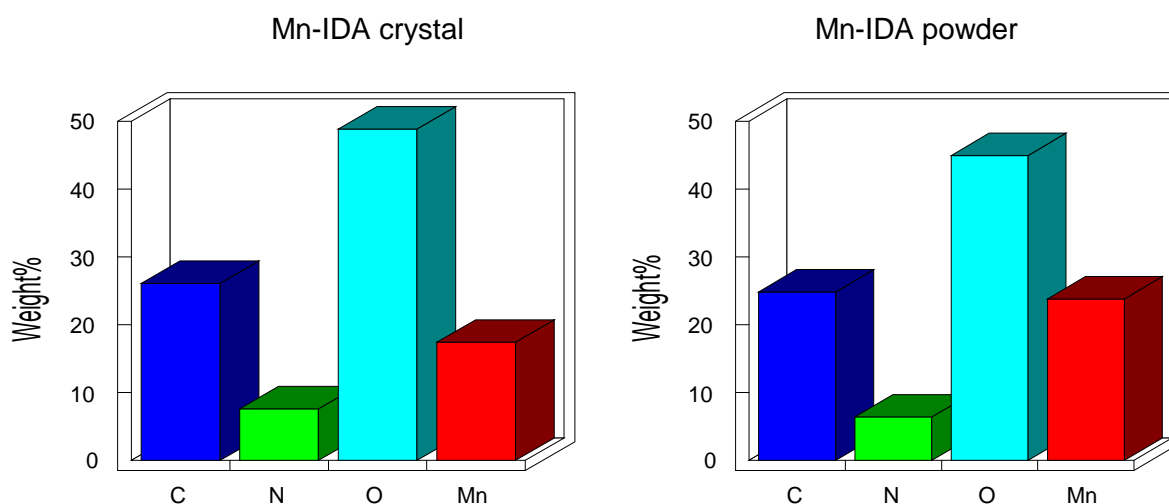
Conclusions

The comparison of CHN analysis, EDAX analysis, XRPD patterns and the IR spectrum of both the



5 min

powder and the crystal reveals that it is possible to prepare the compound without the aid of the solvent. The SEM patterns taken for 1 minute showed well defined forms and edges compared to the 5 minutes sample which suggests that the essential role of grinding is to finely divide and intimately mix the reactants. In summary the method is quantitative quick and highly efficient.

Fig. 6a EDAX spectrum of Mn-IDA crystal and Mn-IDA powder**Fig. 6b** Bar diagram of Mn-IDA crystal and Mn-IDA powder

Acknowledgements

i).The authors are grateful to the single crystal diffraction centre IIT-Madras for their technical support.

ii).The authors are grateful to the department of chemistry IIT-Madras for helping in taking out XRPD, TGA, FTIR, and CHN analysis.

iii).The authors are grateful to the Anna university crystal growth centre for taking SEM images and EDAX analysis.

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