SUPPORTING INFORMATION

Two-step magnetic transition in hybrid organic-inorganic materials of the (*m*-xylylenediamine)$MeSO_4$ (Me – Mn, Fe, Co, Ni) type

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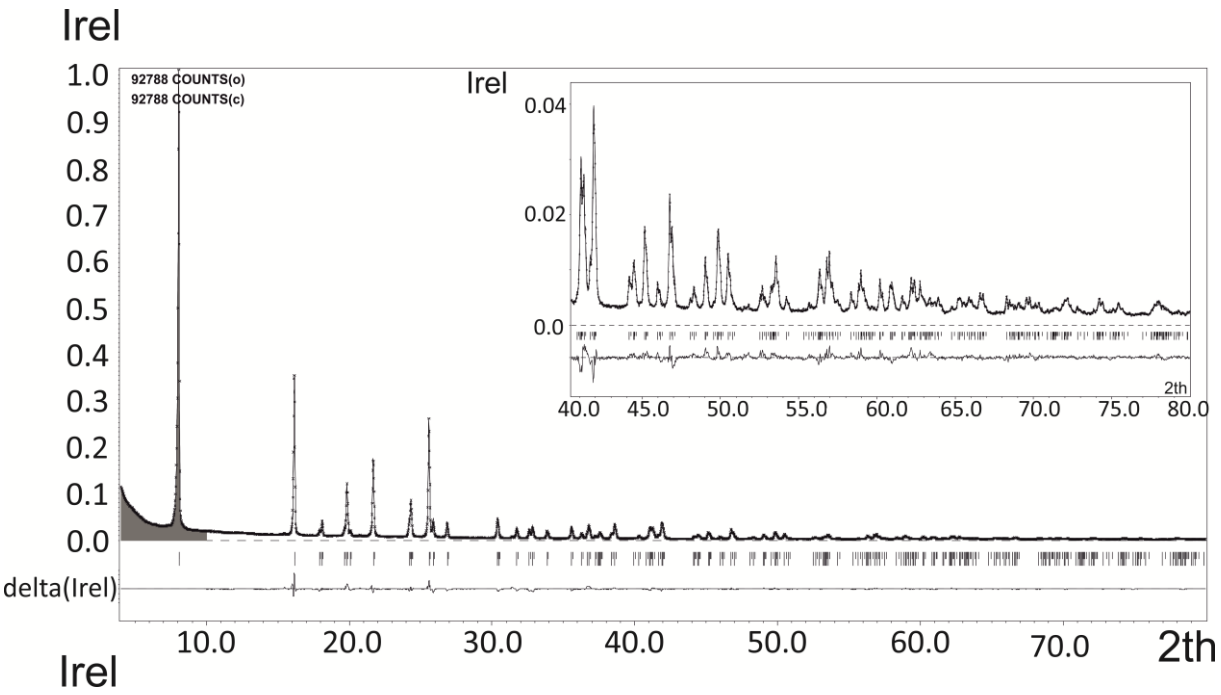
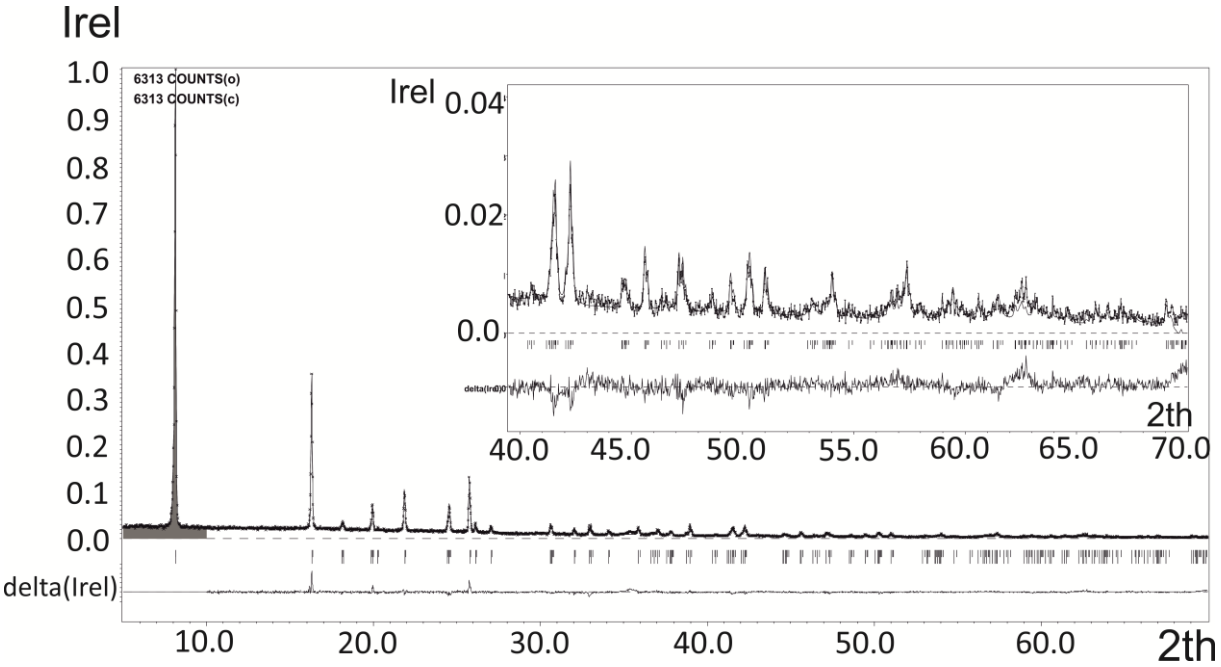
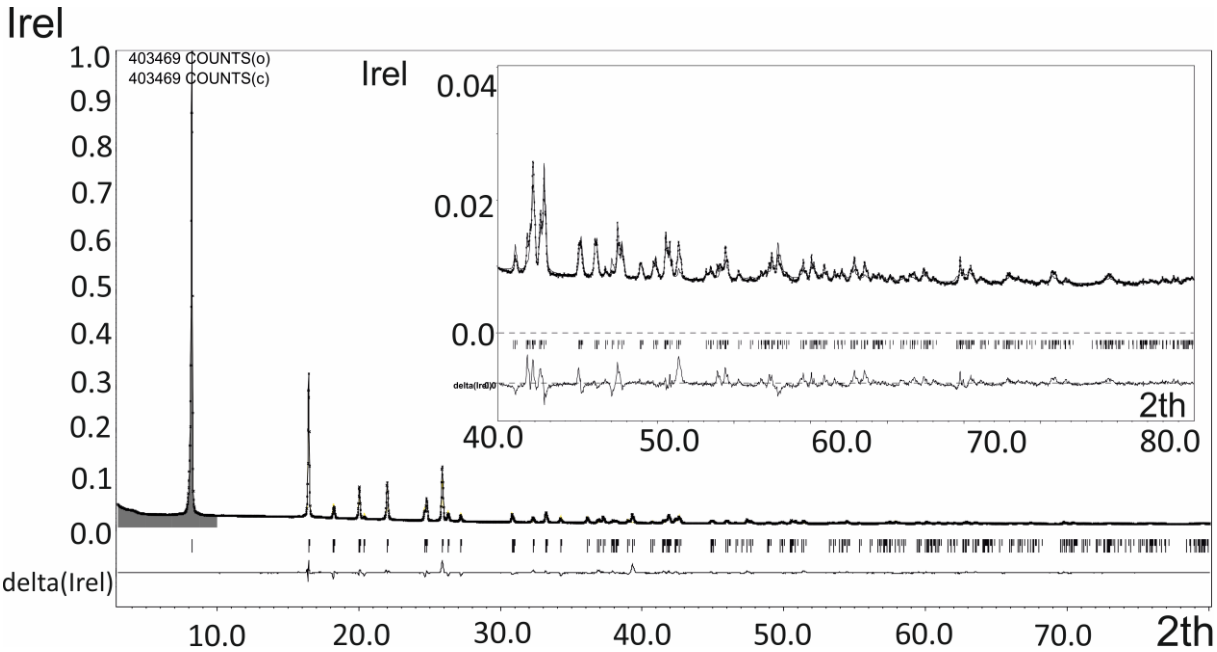


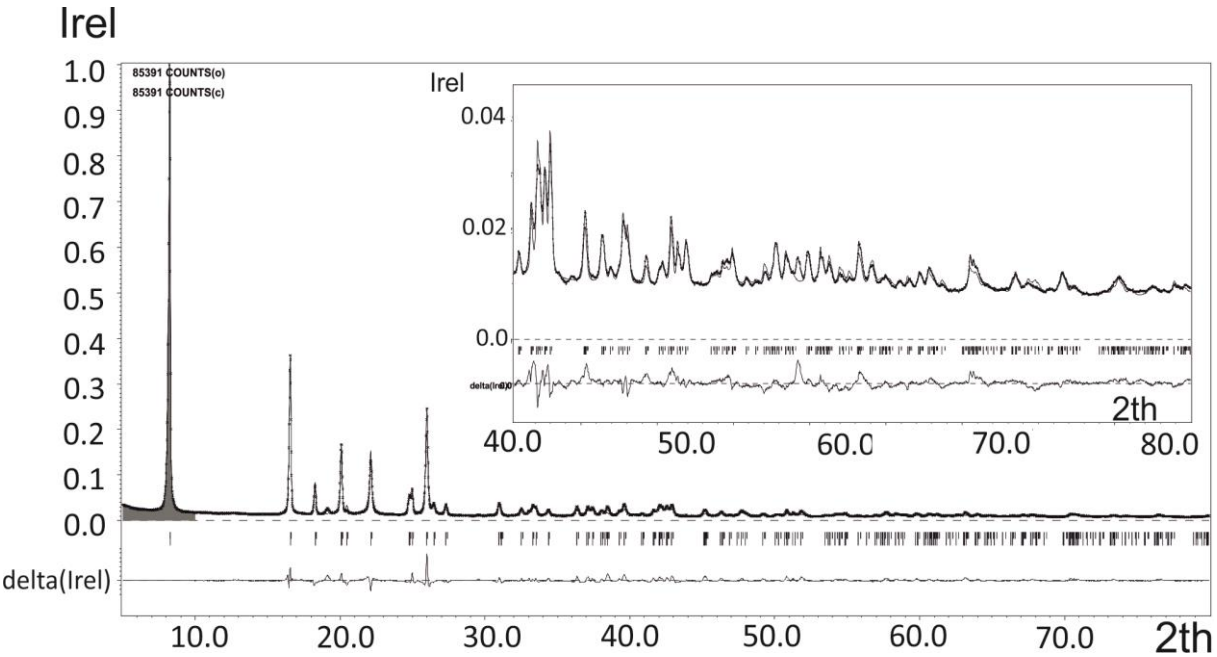
SI.Fig. 1 Rietveld plot for (MXDA)$MnSO_4$. The insets show two theta ranges from 40–80˚ 2θ.



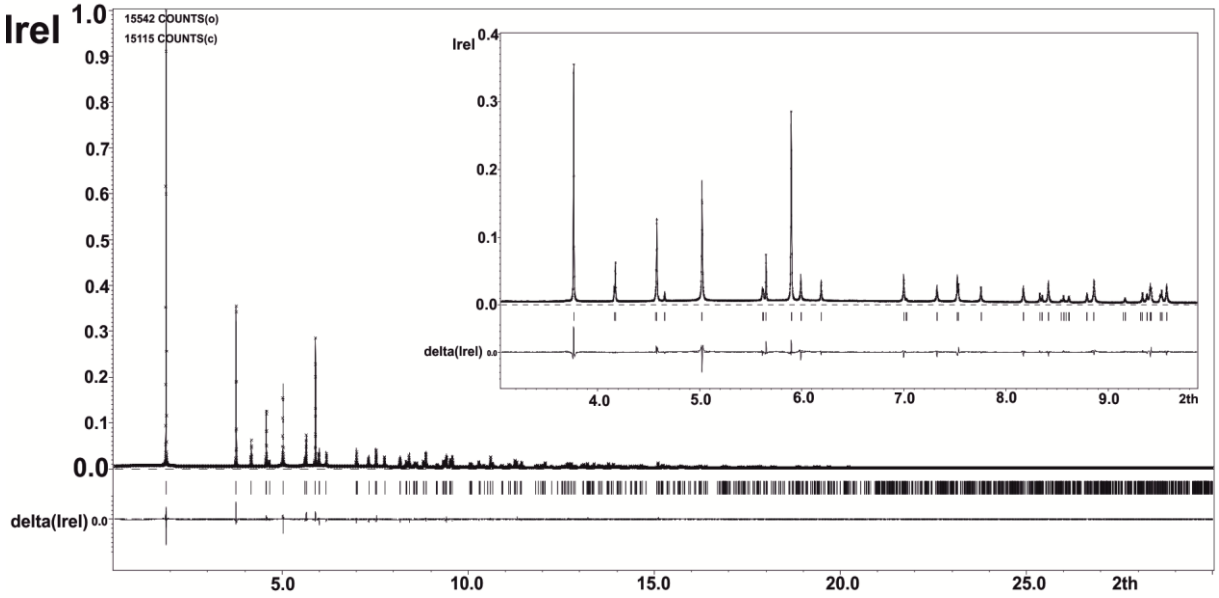
SI.Fig. 2 Rietveld plot for (MXDA)$FeSO_4$. The insets show two theta ranges from 40–70˚ 2θ.



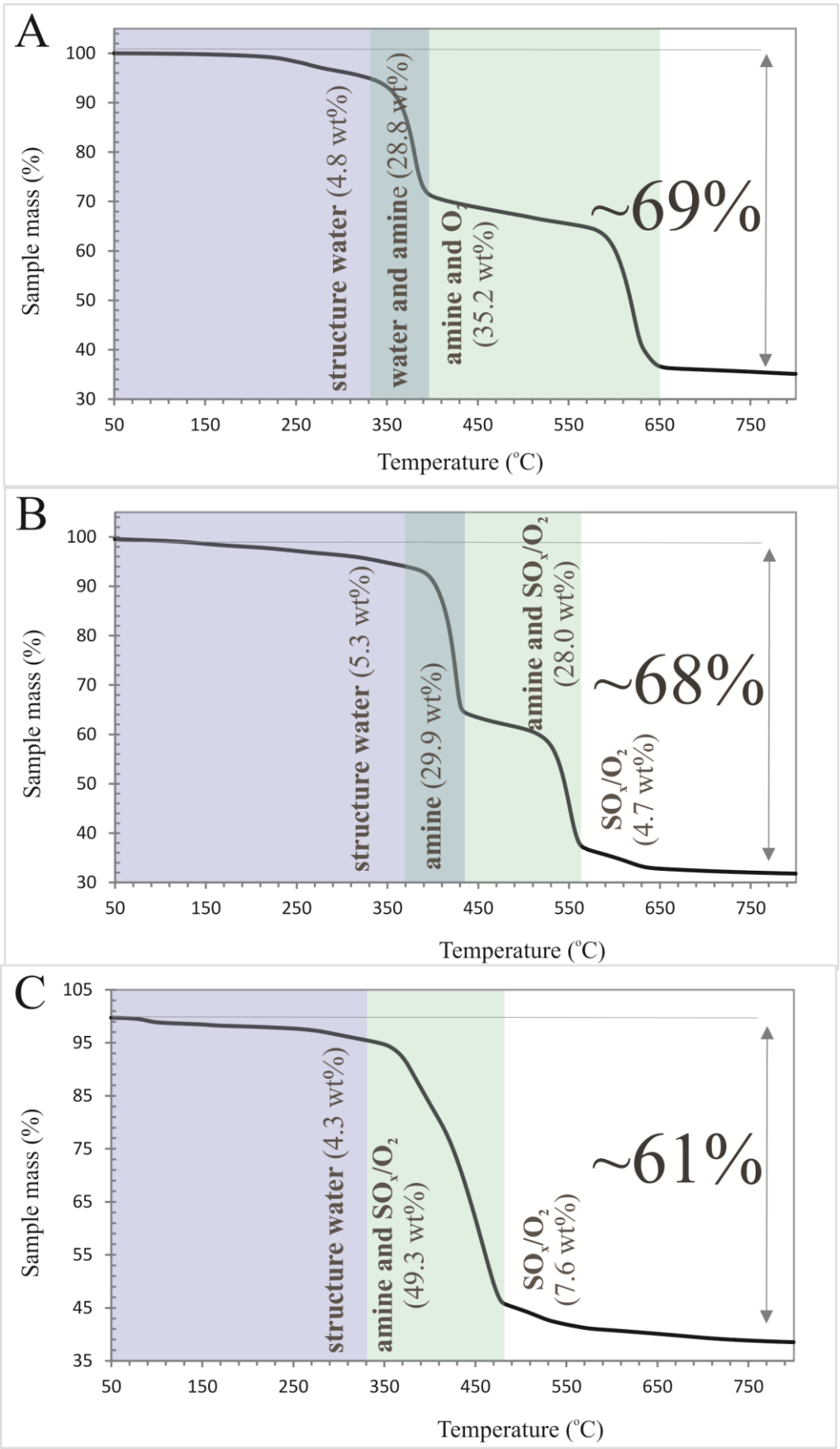
SI.Fig. 3 Rietveld plot for (MXDA)$CoSO_4$. The insets show two theta ranges from 40–80˚ 2θ.



SI.Fig. 4 Rietveld plot for (MXDA)$NiSO_4$. The insets show two theta ranges from 40–80˚ 2θ.



SI.Fig. 5 Rietveld plot for (MXDA)$CoSO_4$ - synchrotron data. The insets show two theta ranges from 4–10˚ 2θ.



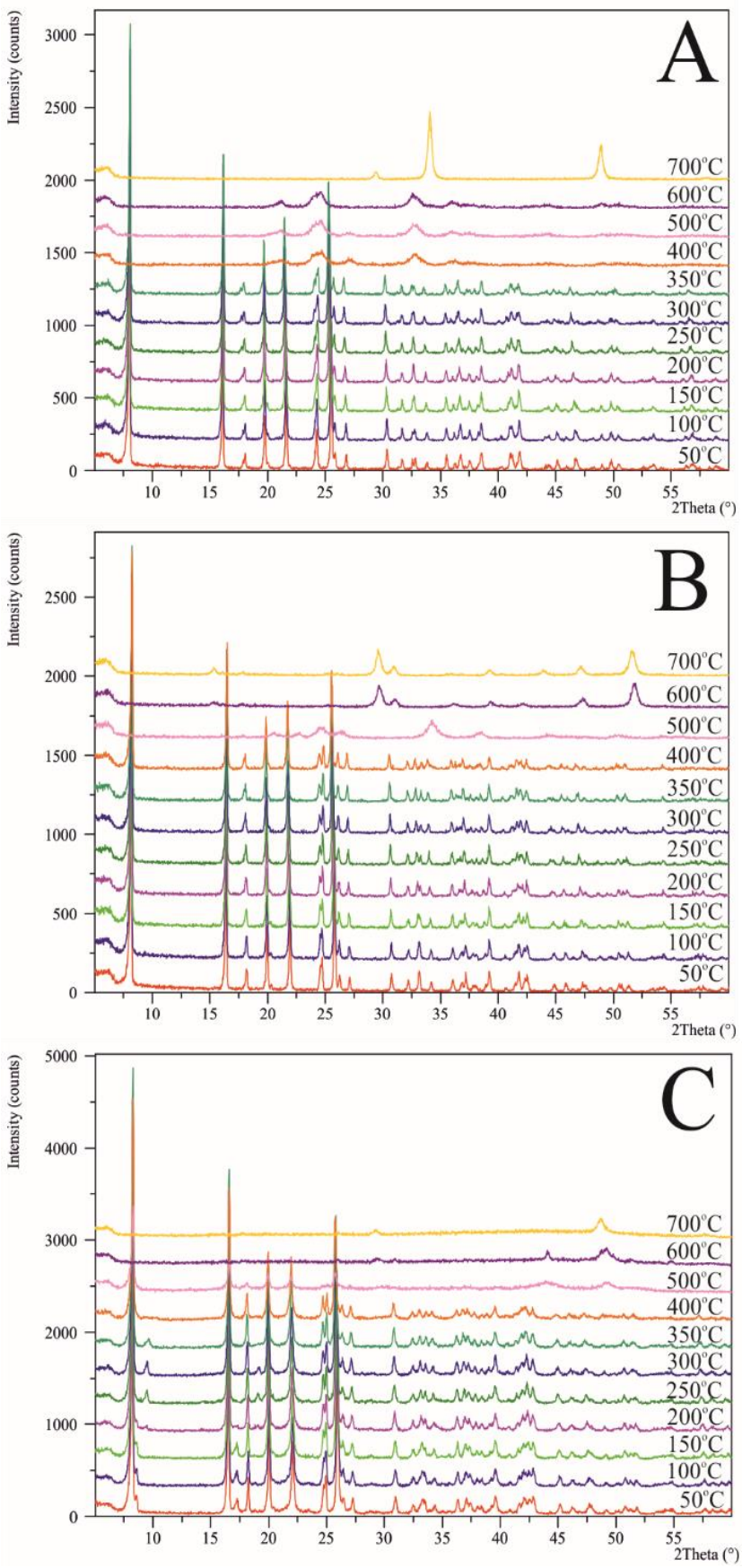
SI.Fig. 6. TG results in nitrogen atmosphere for samples A) (MXDA)$MnSO_4$, B) (MXDA)$CoSO_4$, C) (MXDA)$NiSO_4$

TG (in nitrogen) analysis

(MXDA)$MnSO_4$ in nitrogen: Three clearly visible losses of weight are present. The first, Δm~4.8 wt%, is related to the structure water removed from the structure; the second to amine released Δm~28.8 wt%. The third is a consequence of combined amine and O_2 removal, Δm~35.2 wt%. The total loss of weight is Δm~69.5 wt% (calc. 69.68 wt%); the final product is MnS (COD 9005930).

(MXDA)$CoSO_4$ in nitrogen: The first loss of weight is related to the structure water release (Δm~5.3 wt.%). Next, sole amine is removed (Δm~29.9 wt%) At about 430°C, the process of SO_x/O_2 creation is initiated. At 560°C all amine is removed and only SO_x/O_2 is still being released (Δm~4.7 wt.%). The total loss of weight is Δm~68 wt.%; the final products were identified as CoO (COD 1541662) and Co_9S_8 (COD 1011206).

(MXDA)$NiSO_4$ in nitrogen: First the structure water is removed (Δm~4.3 wt%). Next, amine is removed up to 420°C; then the process of SO_x/O_2 release begins. Starting at 480°C, only SO_x/O_2 are removed. The total loss of weight is Δm~61 wt%; the final products were identified as Ni_3S_2 (COD 9000564) and Ni (COD 2102278).



SI.Fig. 7. XRD vs temperature of the compounds A) **(1)** – (MXDA)$MnSO_4$, B) **(3)** – (MXDA)$CoSO_4$, C), **(4)** – (MXDA)$NiSO_4$

PXRD vs. temperature analysis (in nitrogen)

(MXDA)$MnSO_4$

At 400°C, as the result of amine removal from the analysed material, two phases, namely α-$MnSO_4$ (PDF 00-029-0898) and MnO_2 (PDF 00-059-0633) were formed. All were stable up to 700°C, when MnS (PDF 04-007-3621) appears as the only phase. The grain size of the final phase is ca.20 nm.

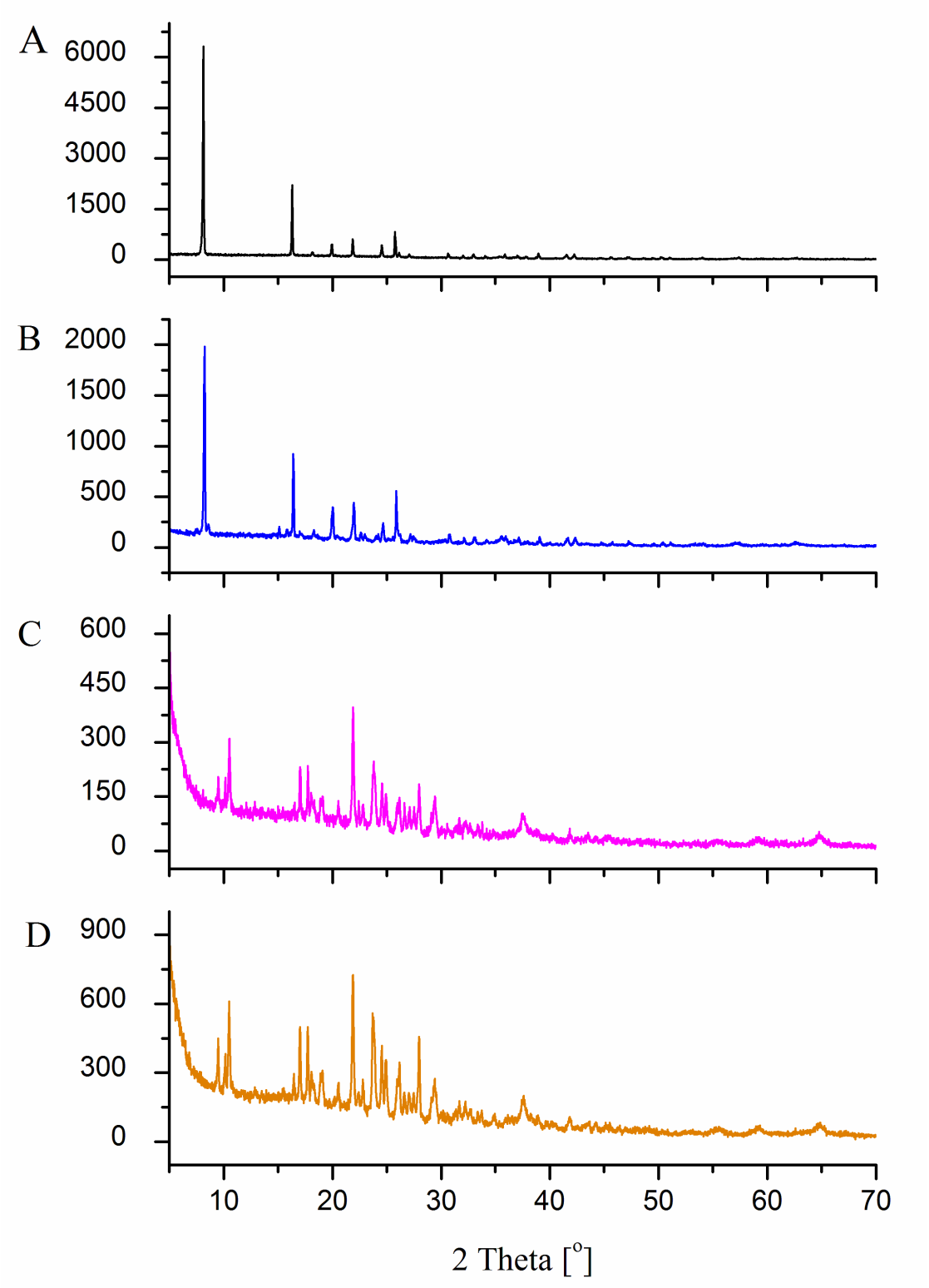
(MXDA)$CoSO_4$

In the case of (MXDA)$CoSO_4$, the sample is stable up to 400°C. At 500°C the only phase present is β-$CoSO_4$ (PDF 00-011-0305), with a grain size of about 7 nm. At 600°C, Co_9S_8 (PDF 04-007-1251) and CoO (PDF 01-076-3830) are formed. Co_9S_8 remains stable up to 700°C, whereas CoO is no longer present. The grain size of Co_9S_8 is about 15 nm and does not change significantly during heating.

(MXDA)$NiSO_4$

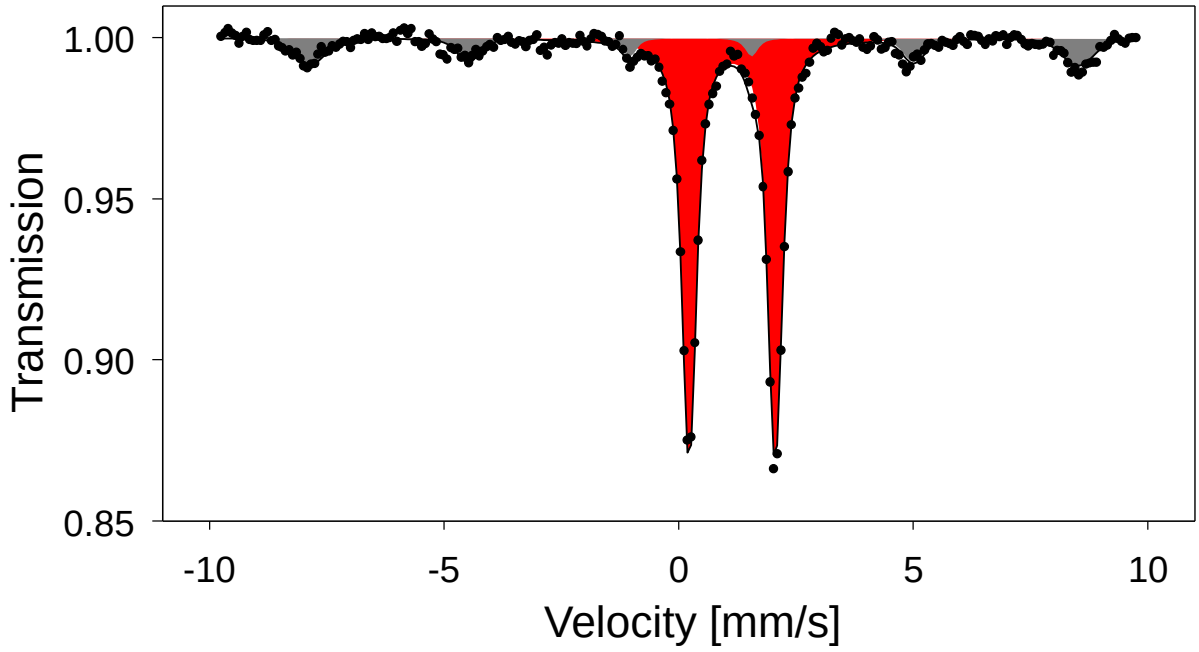
A slightly different situation is observed for the (MXDA)$NiSO_4$ sample. In this case, directly after the removal of amine from the structure (between 400 and 500°C), NiO (PDF 04-007-8202) and $Ni_{1.5}S$ (PDF 04-004-1264) are formed. Thus, no sulphate intermediate phase is observed. Both phases are stable up to 600°C; at 700°C only $Ni_{1.5}S$ is left. Grain size increases with heating; in the case of $Ni_{1.5}S$ it increases from 8 (500°C) to 12 nm (700°C), in the case of NiO from 4 (500°C) to 24 nm (600°C).

In all above cases, the detailed analysis of the diffraction patterns was performed in order to found changes related to dehydration of structures. However, no significant changes in comparison to data measured in room temperature was found, which confirm that the molecule of water is disordered and the average structure is observed.

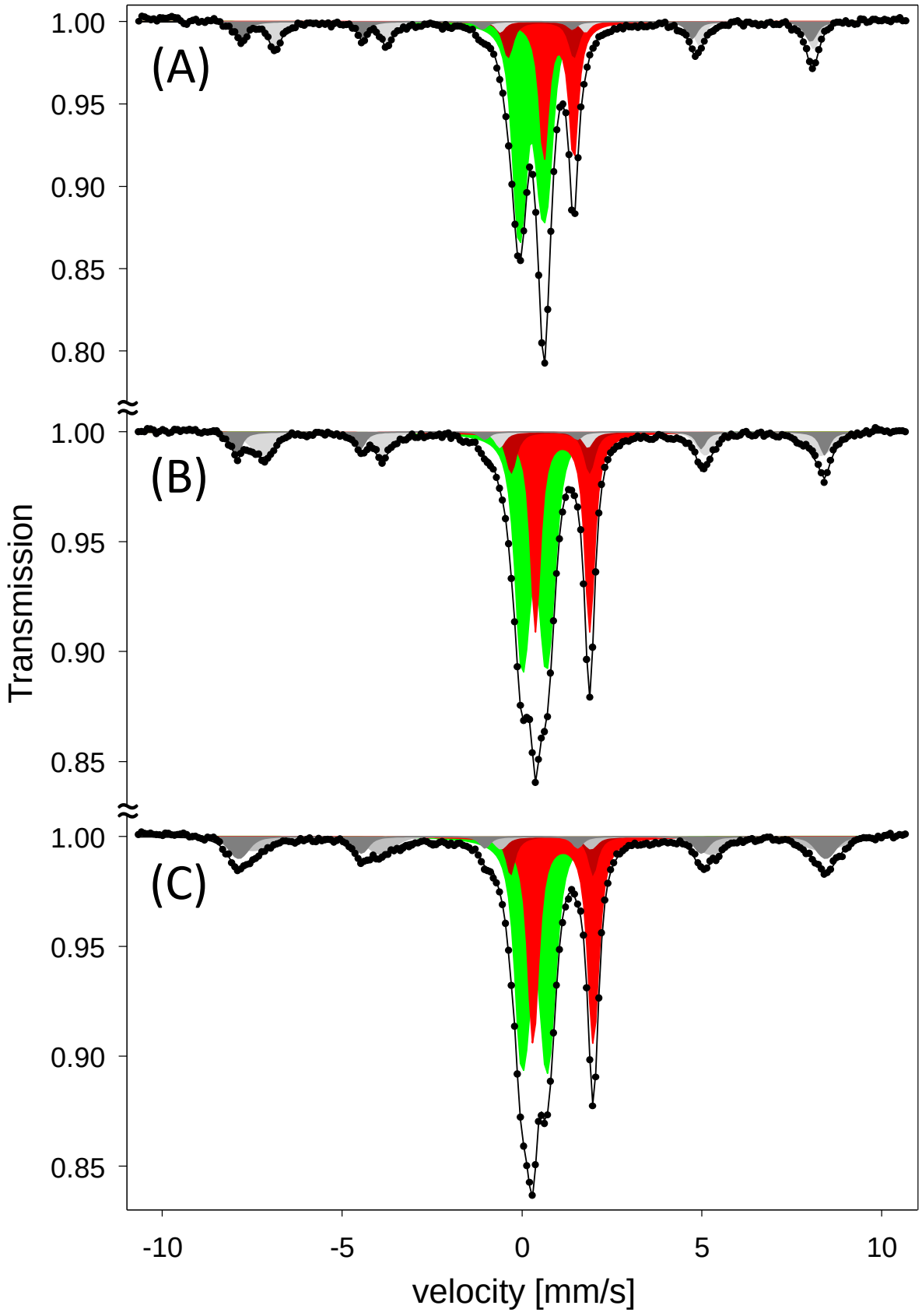


SI.Fig. 8. XRD patterns of (MXDA)$FeSO_4$ A) immediately after synthesis, B) after 3 days, C) after 60 days, D) after 90 days.

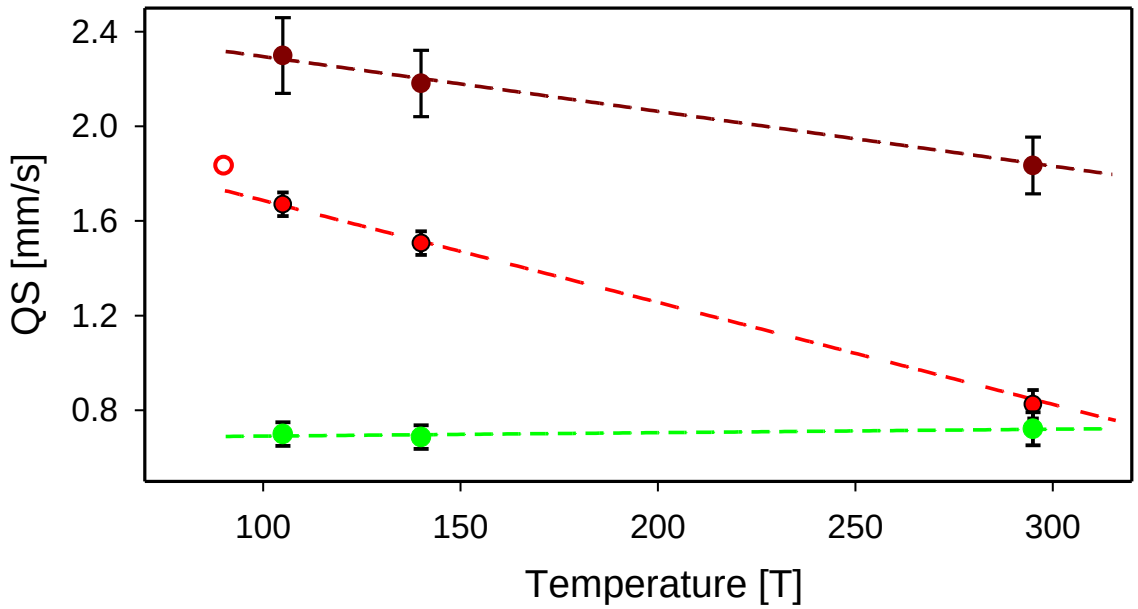
In the diffraction pattern (3 days after synthesis) the hybrid compound is still present in the sample. However, numerous small diffraction maxima's near strong lines appeared which can be assigned to the second phase obtain as a result of decomposition of main phase. (Similar situation was confirmed also several dozen minutes after synthesis). That suggest high instability of hybrid compound with iron. Such effect was not observed for other family members.



SI.Fig. 9. Mössbauer spectrum of (MXDA)$FeSO_4$ in toluene, measured at 90 K, 8 h after synthesis. Colour code of spectral components: Grey- magnetite below Verwey transition; Red – high spin Fe(II).



SI.Fig. 10. Mössbauer spectra of (MXDA)$FeSO_4$, dried, measured at 295 K (A), 140 K (B) and 105 K (C), 14 days after synthesis. Colour code of spectral components: Grey and light dark grey- tetrahedral and octahedral Fe in magnetite, respectively; Red and dark red – high spin Fe(II), Green - high spin Fe(III)



SI.Fig. 11. Temperature dependence of quadrupole splitting derived from the Mössbauer spectra. Colours correspond to those of the spectral component in SI.Fig. 5. Empty circle corresponds to Fe(II) in SI.Fig. 4.

SI. Table 1. Crystallographic data for (MXDA)$CoSO_4$

Compound	**(MXDA)$CoSO_4$**
Empirical formula	$CoSO_4C_8H_{12}N_2$
Formula weight /g·mol^{-1}	291.2
Crystal system	orthorhombic
Space group	*P2$_1$ma*
a/Å	9.72817(13)
b/Å	10.78331(10)
c/Å	4.87797(7)
V/Å^3	511.708(11)
R_p	5.96
R_{wp}	8.00
R_F	12.0
Colour	violet