Influence of Sm and Y molar fractions on the properties of electrospun (Fe, Sm) and (Fe, Y) oxides

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Zagreb, Croatia

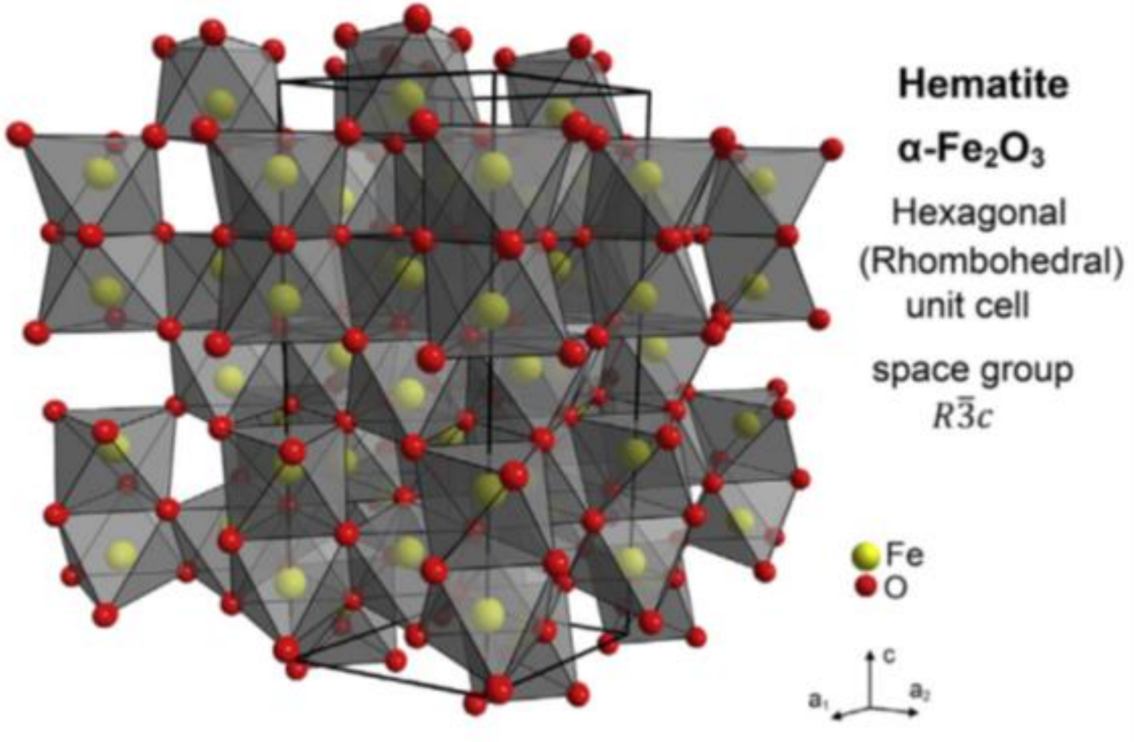
Ruđer Bošković Institute

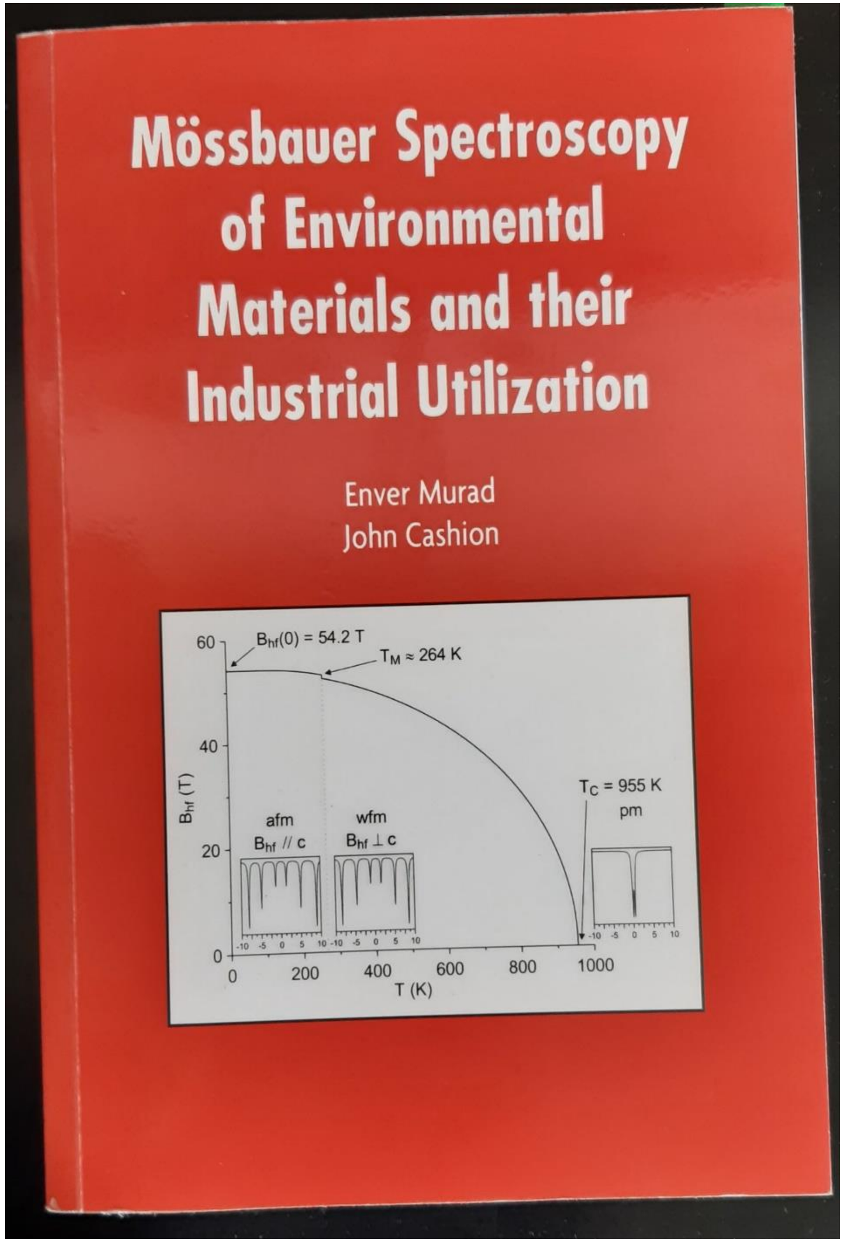
Hematite

- α-Fe_2O_3
- Crystal structure: rhombohedral system (hexagonal)
- Magnetic properties: WFM at RT, AF below 264 K
- Mössbauer: one sextet (RT)
- Applications: catalysis, photocatalysis, pigment
- Tuning hematite properties: doping, synthesis procedures, particle size

S. Krehula et al. / Journal of Alloys and Compounds **695** (2017) 1900e1907
R. M. Cornell, U. Schwertmann: The Iron oxides, Structure, Properties, Reactions, Occurrences and Uses

Hematite





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Maghemite

- γ-Fe_2O_3
- Crystal structure: cubic
- Magnetic properties: ferrimagnetic at RT
- Mössbauer: can be approximated with one sextet (RT)

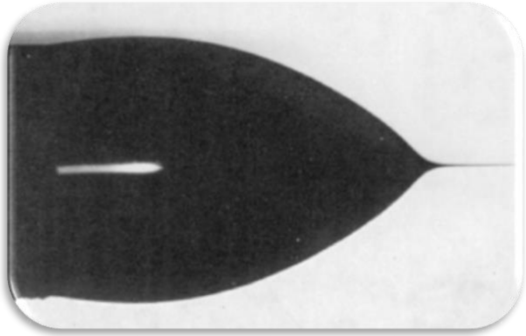
  usually has 2 sextets (tetrahedral and octahedral iron)
- Applications: magnetic pigment, recording media, medicine

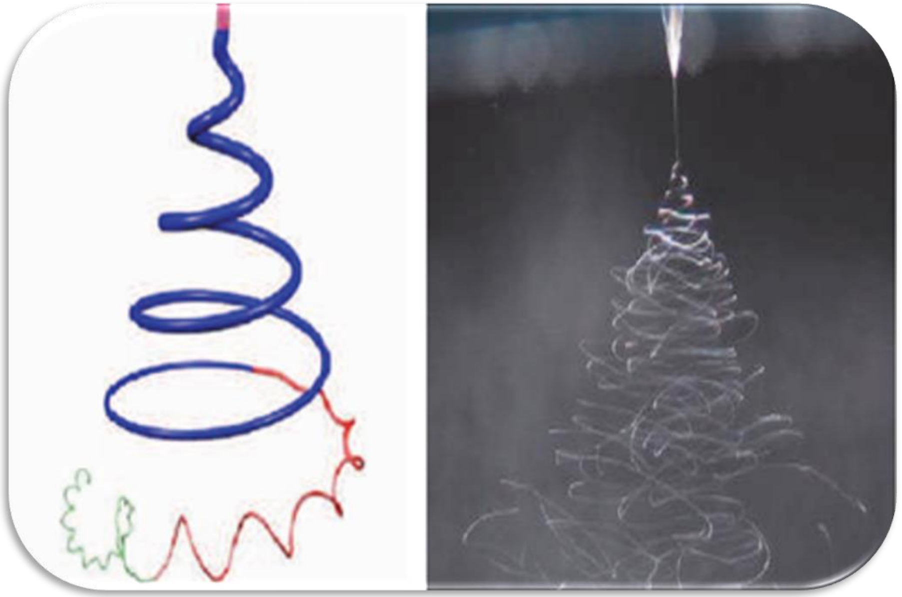
R. M. Cornell, U. Schwertmann: The Iron oxides, Structure, Properties, Reactions, Occurrences and Uses

Electrospinning
History

1902.-first patent (J.F. Cooley)
→Apparatus for electrically dispersing fluids (patent US692631)

1964.-1969. - G.I.Taylor
→Taylor conus

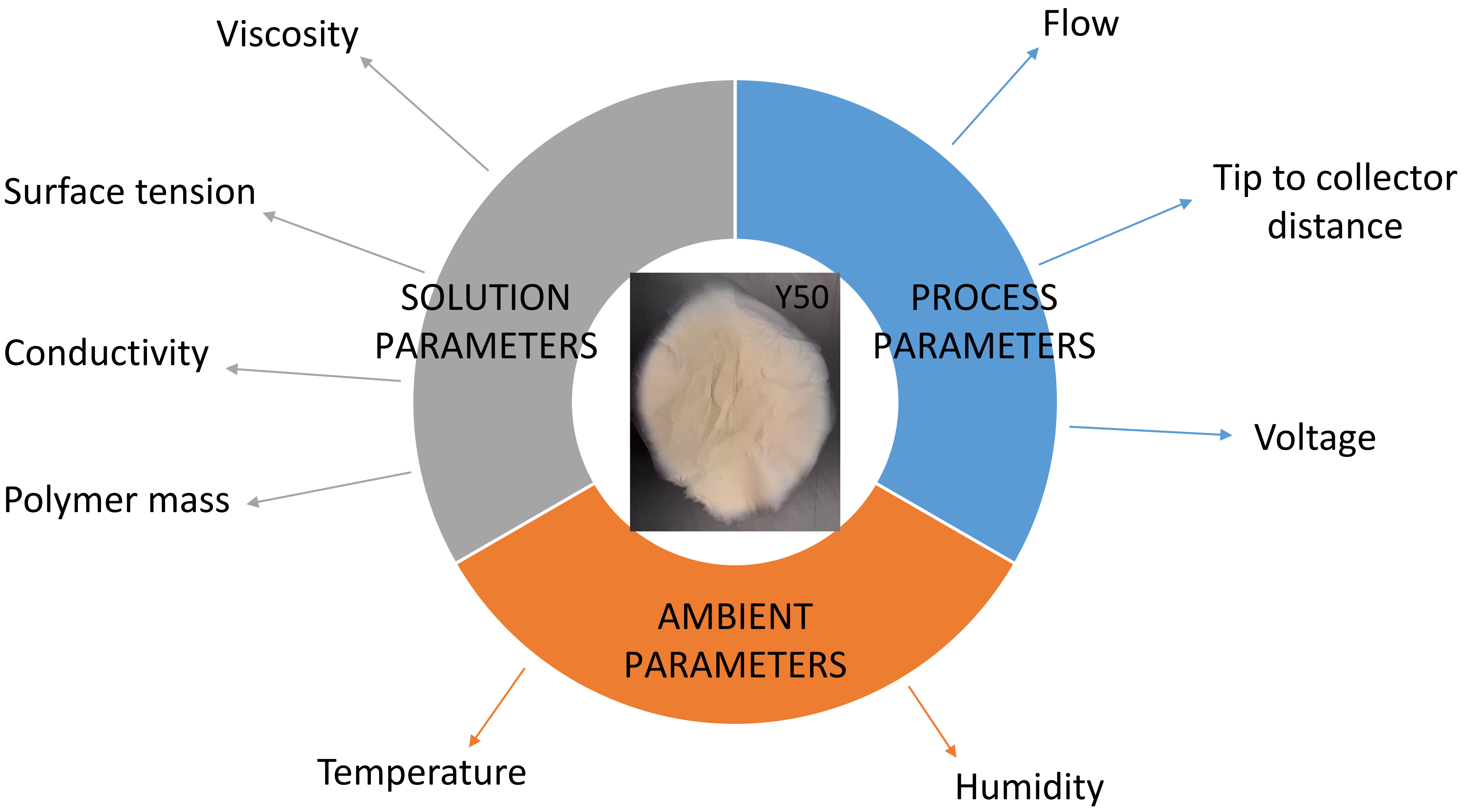




G. Taylor, Electrically driven jets, Proc. Roy. Soc. Lond. A. **313** (1969) 453-475

S. Petrík, Industrial Production Technology for Nanofibers, *ELMARCO s.r.o, Czech Republic*

Electrospinning parameters



N. Bhardwaj, S. C. Kundu, Electrospinning: A fascinating fiber fabrication technique **28** (2010) 325-347

Sample synthesis

Solution preparation

Electrospinning

Composition

PVP (1 300 000)

EtoH (abs)

H_2O (miliQ)

Glacial acetic acid

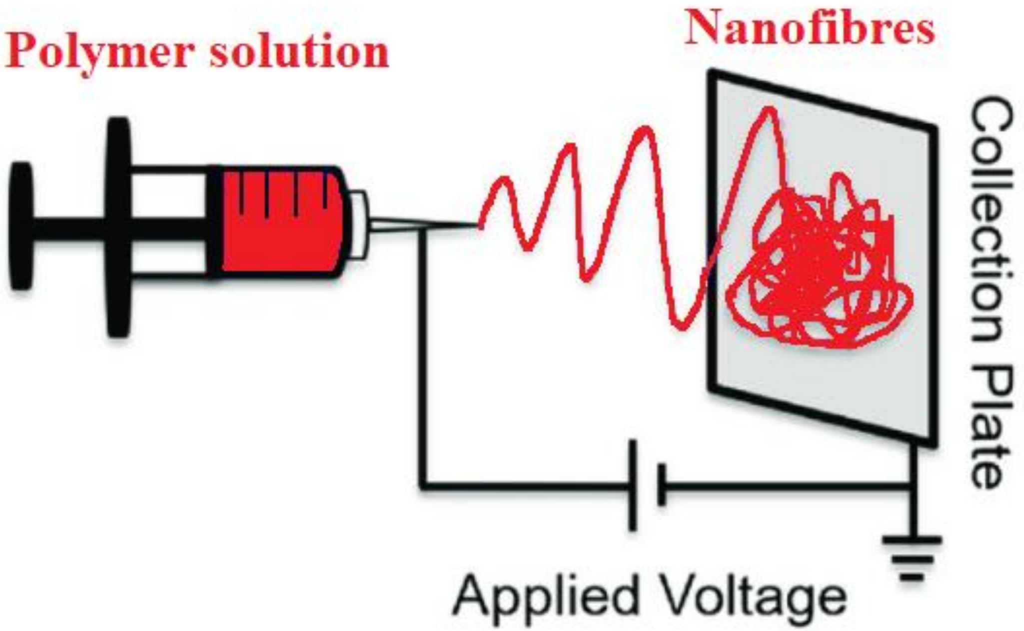
base

Fe (III) nitrate

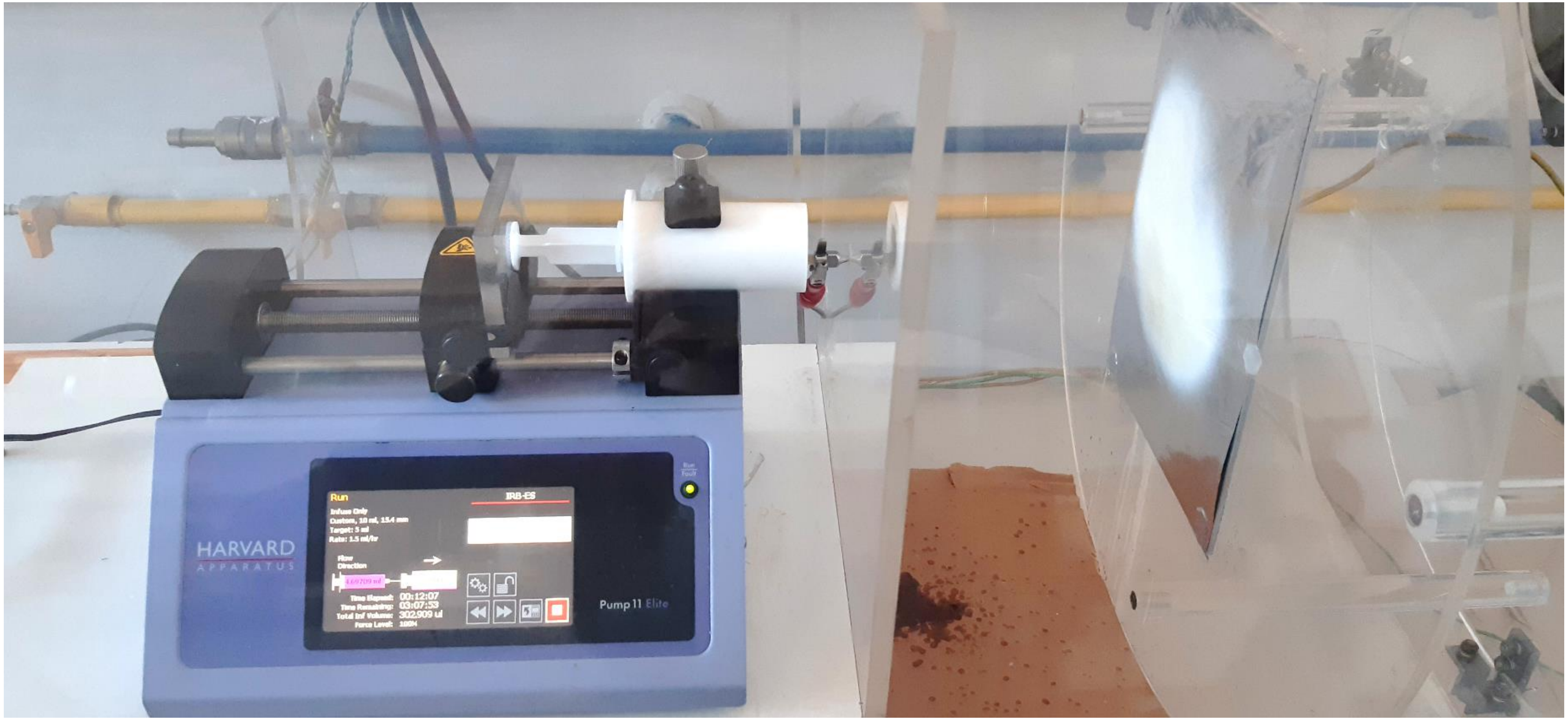
Sm (III) nitrate

Y (III) nitrate

metal cation

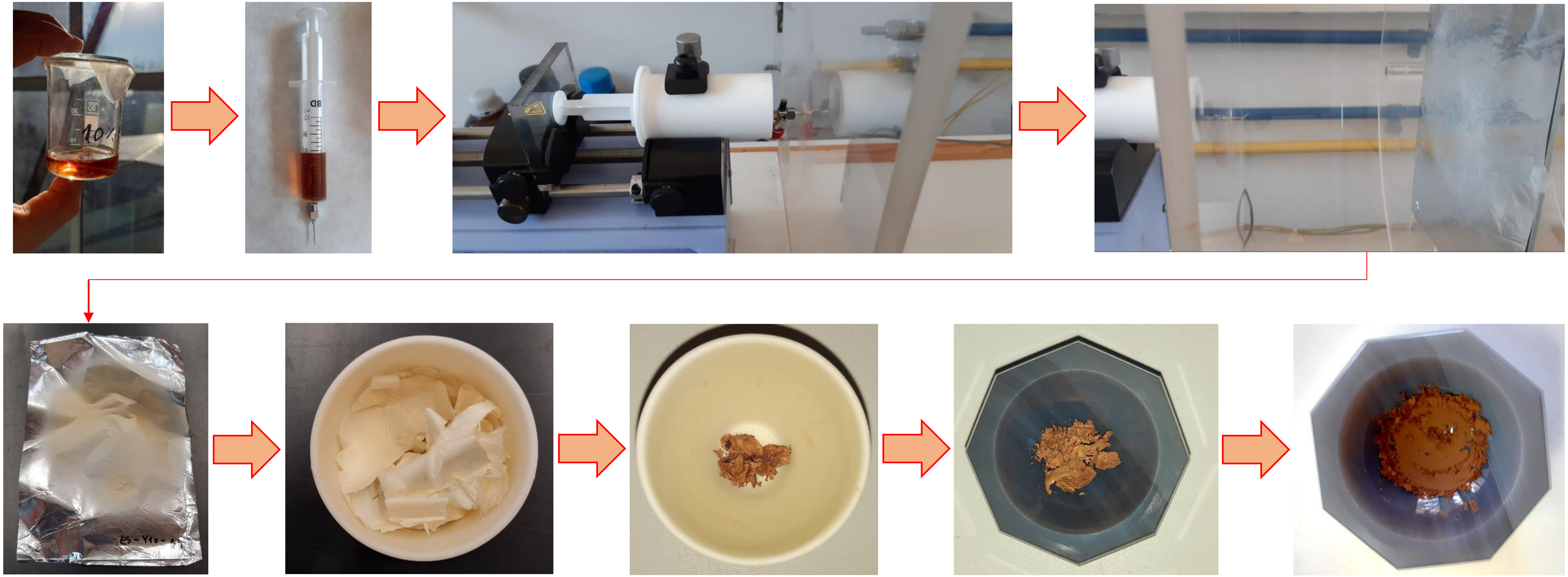


Sample synthesis-apparatus



Electrospinning (Y10, hybrid fibres)

Sample synthesis-procedure



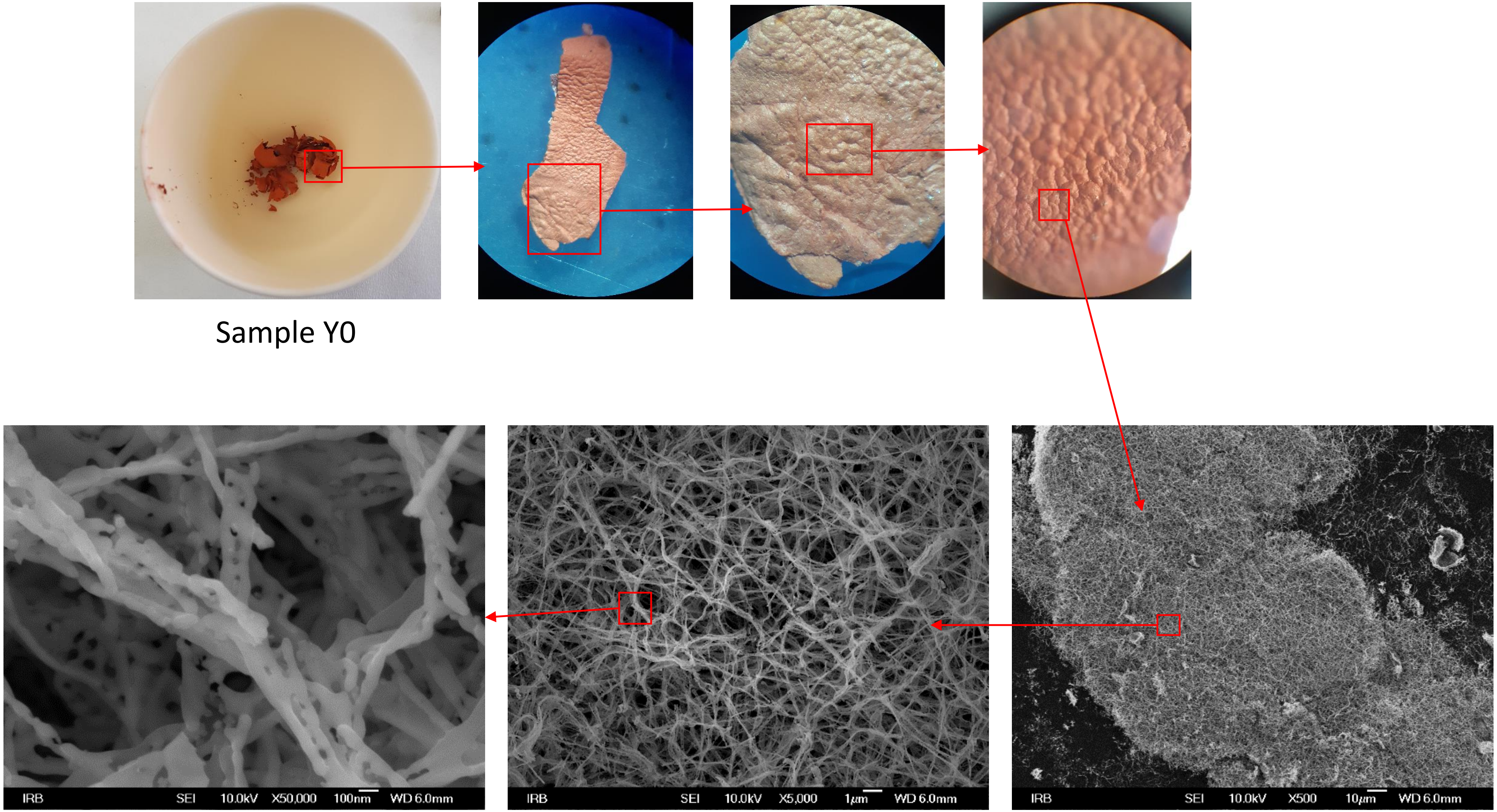
composite (hybrid)
Y10 fibres

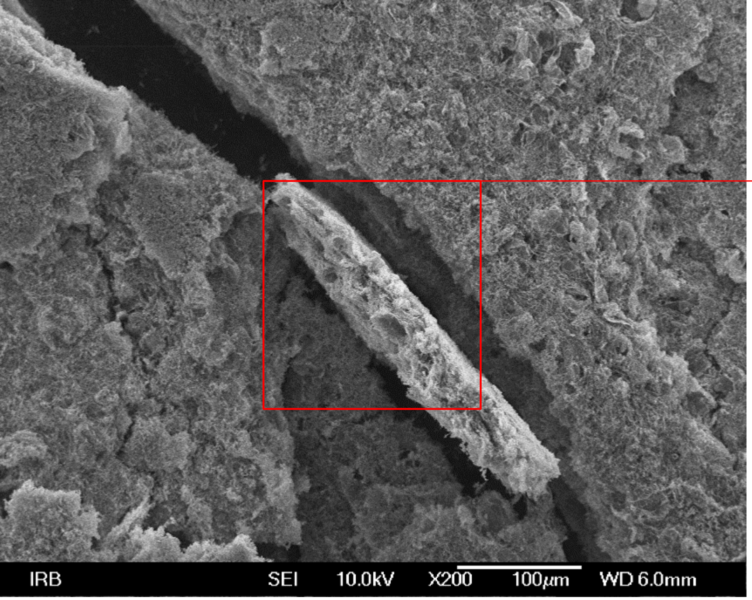
Y10

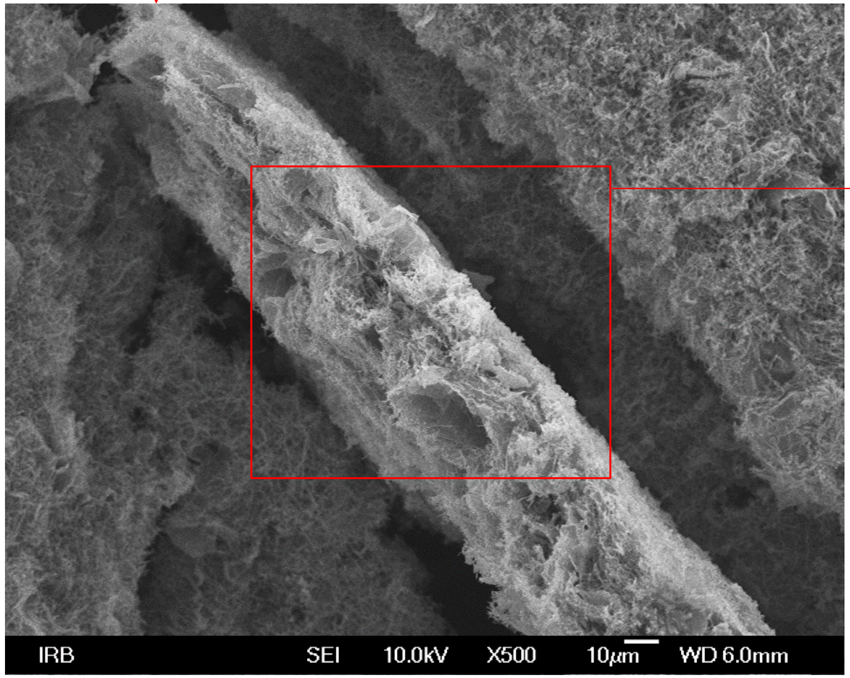
Sample synthesis-composite fibre mat

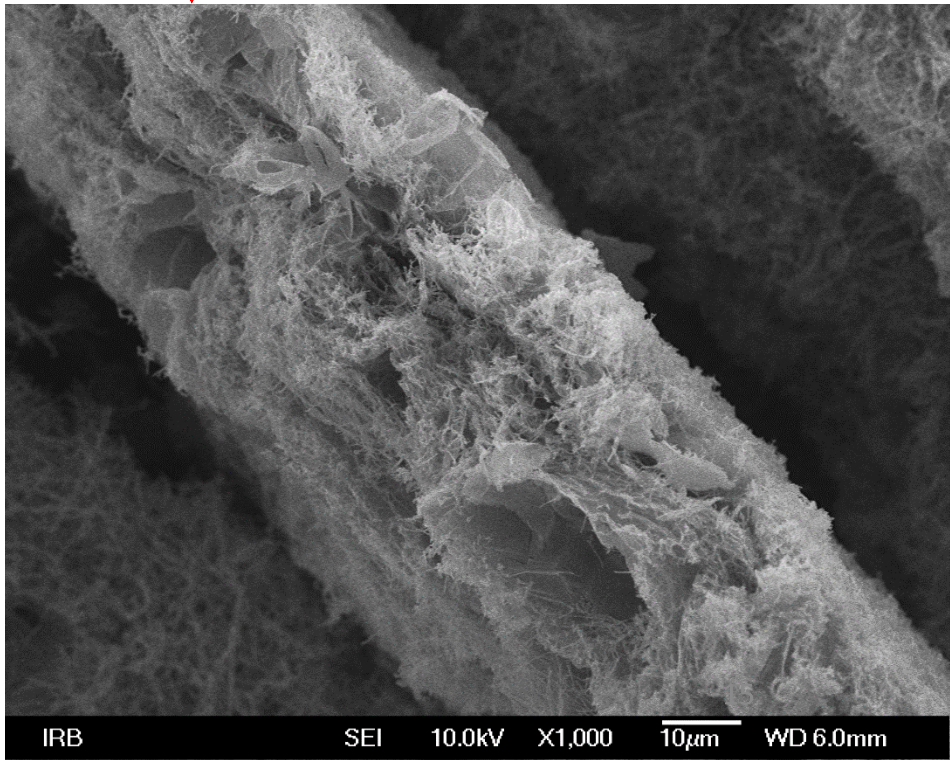
Thin hybrid fibre mat (Y1)

Self-ignition of Sm0 hybrid fibres at 225 °C during calcination


Sample Y0
IRB SEI 10.0kV X50,000 100nm WD 6.0mm
IRB SEI 10.0kV X5,000 1μm WD 6.0mm
IRB SEI 10.0kV X500 10μm WD 6.0mm


IRB
SEI
10.0kV
X200
100µm
WD 6.0mm


IRB
SEI
10.0kV
X500
10µm
WD 6.0mm

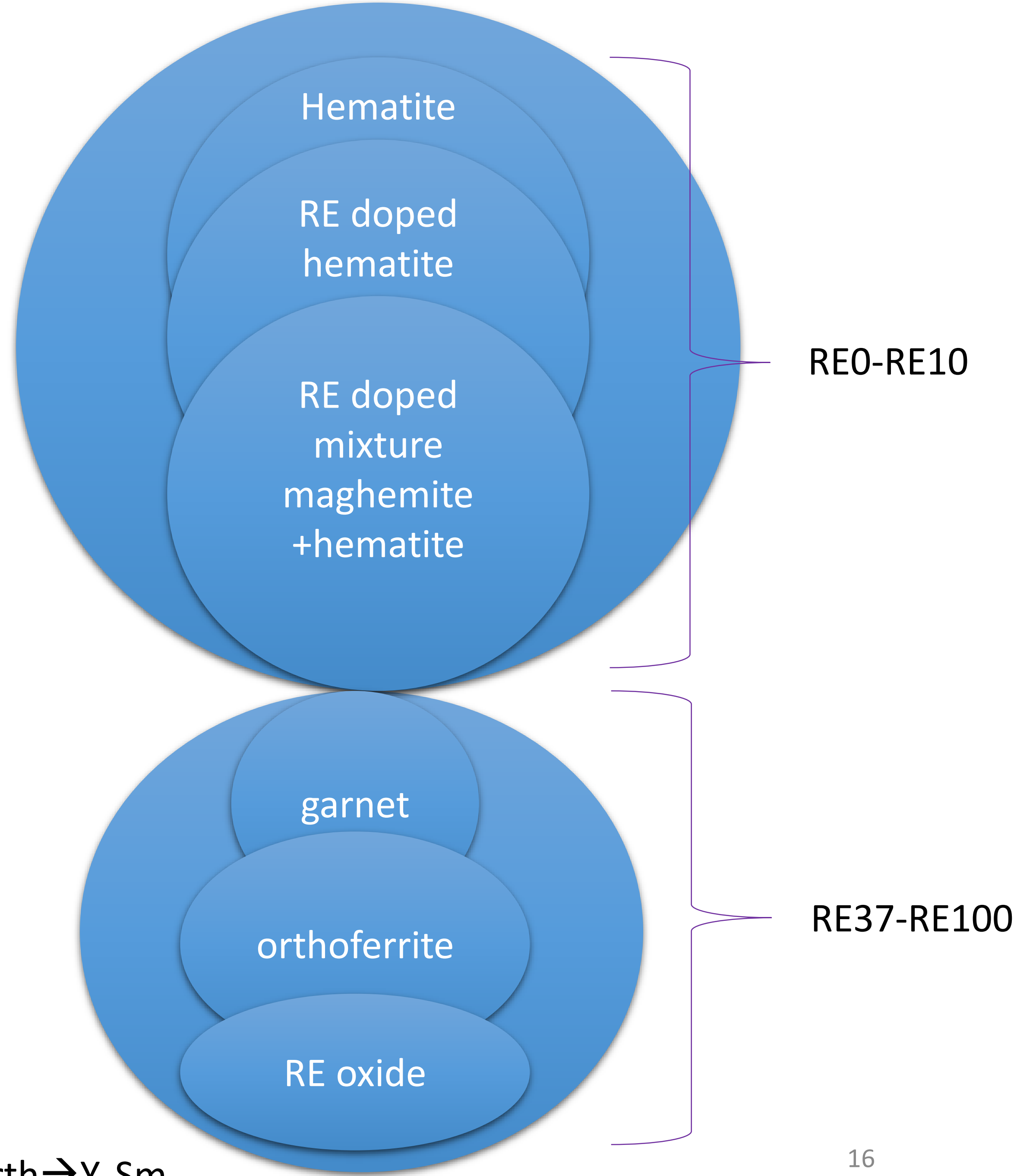

IRB
SEI
10.0kV
X1,000
10µm
WD 6.0mm

Y10 fibres

The main concept

- By varying amount of yttrium in electrospinning solution we can simply prepare wide range of metal oxides!

- In this study sample composition is examined in the whole range of yttrium presence in electrospinnng solution

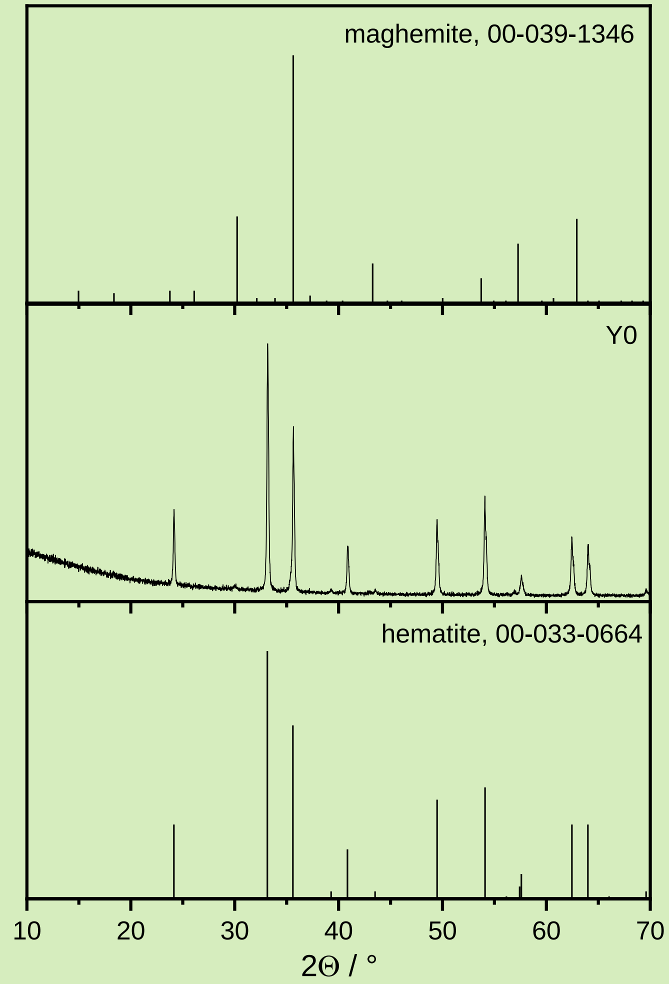


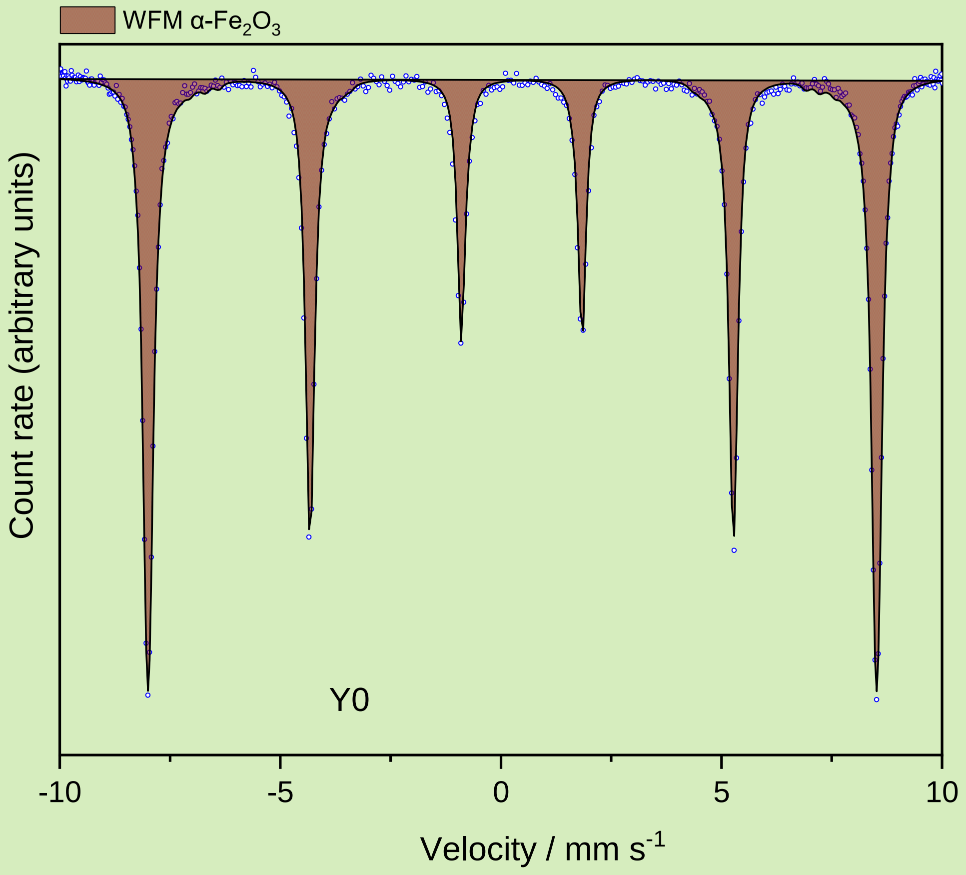
RE=rare earth→Y, Sm

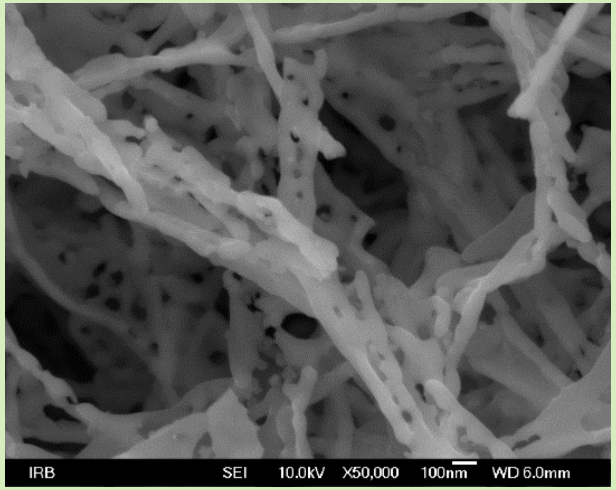
YTTRIUM

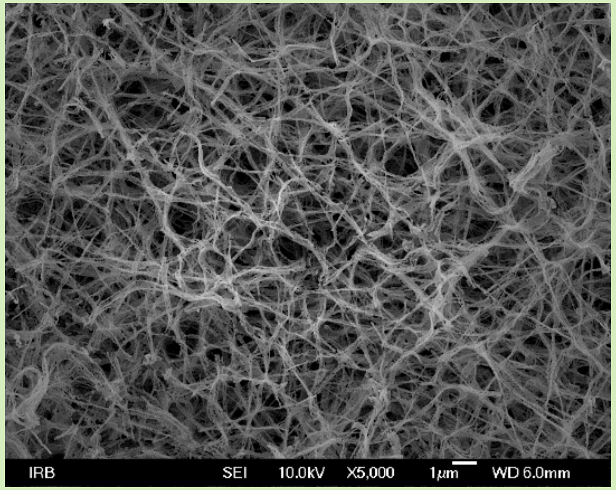
Y0

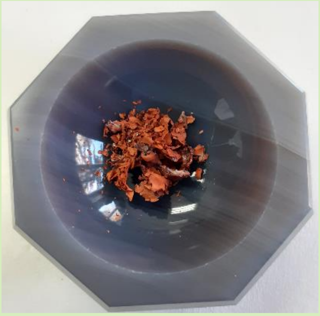
BET→surface area:
115.3400 ±5.0544 m^2/g





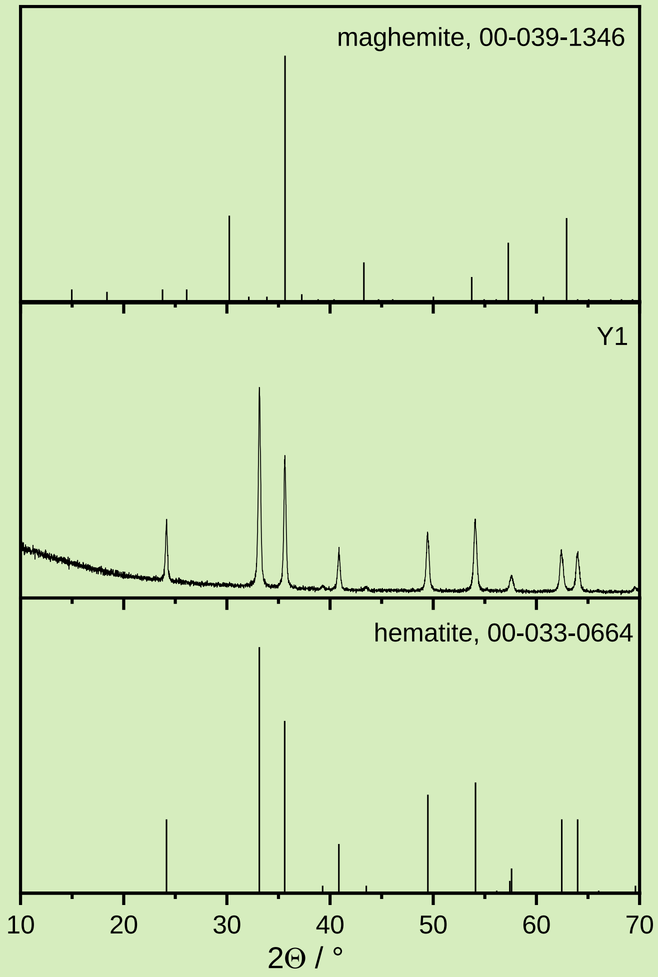


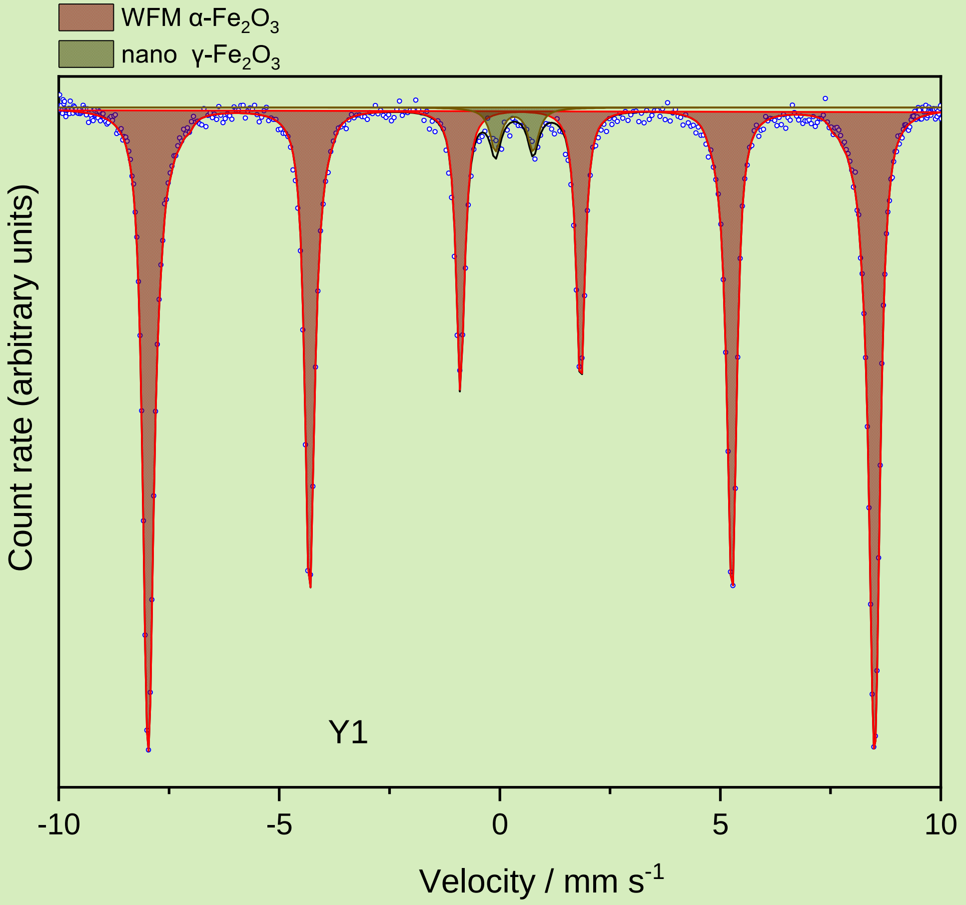


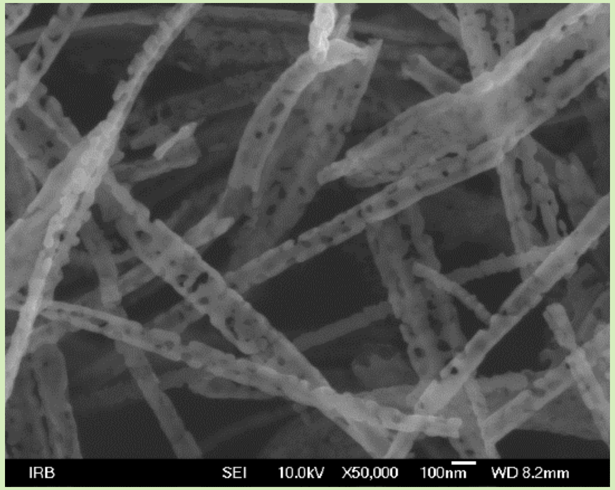


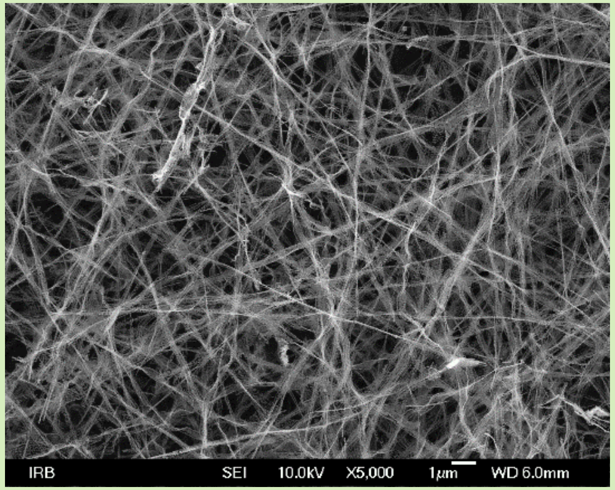
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y0	sextet	0.37	-0.21	51.0*	0.21	100.0	WFM α-Fe_2O_3

Y1



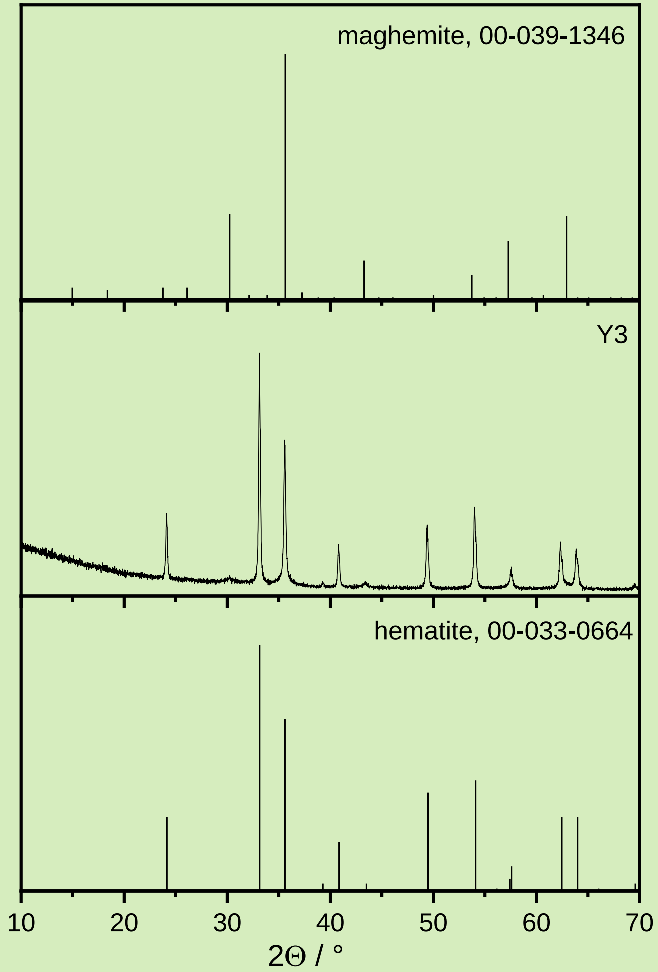


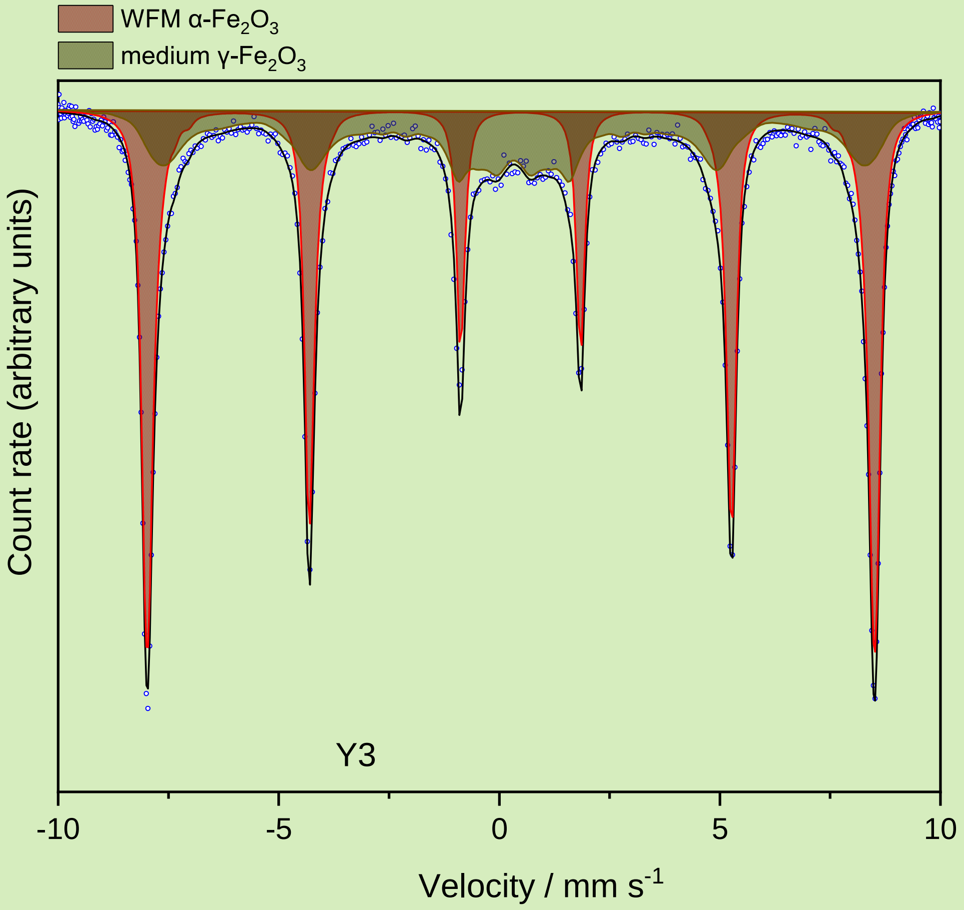


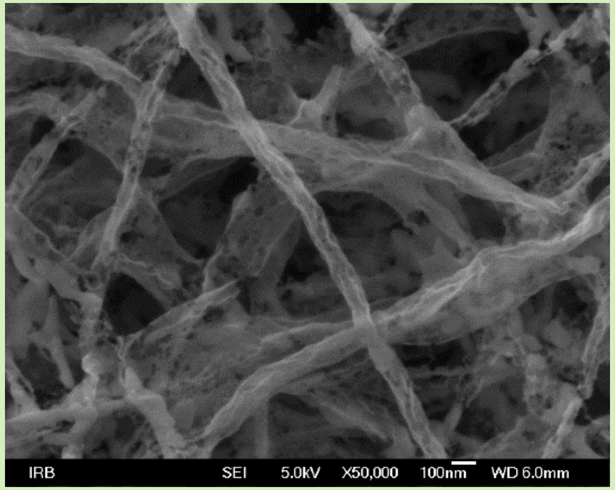


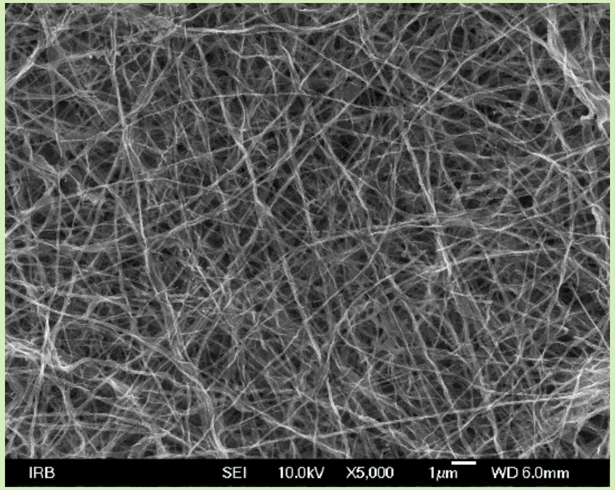
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y1	sextet	0.37	-0.22	50.9*	0.22	96.7	WFM α-Fe_2O_3
	doublet	0.33 (f)	0.86	-	0.30(f)	3.3	nano γ-Fe_2O_3

Y3



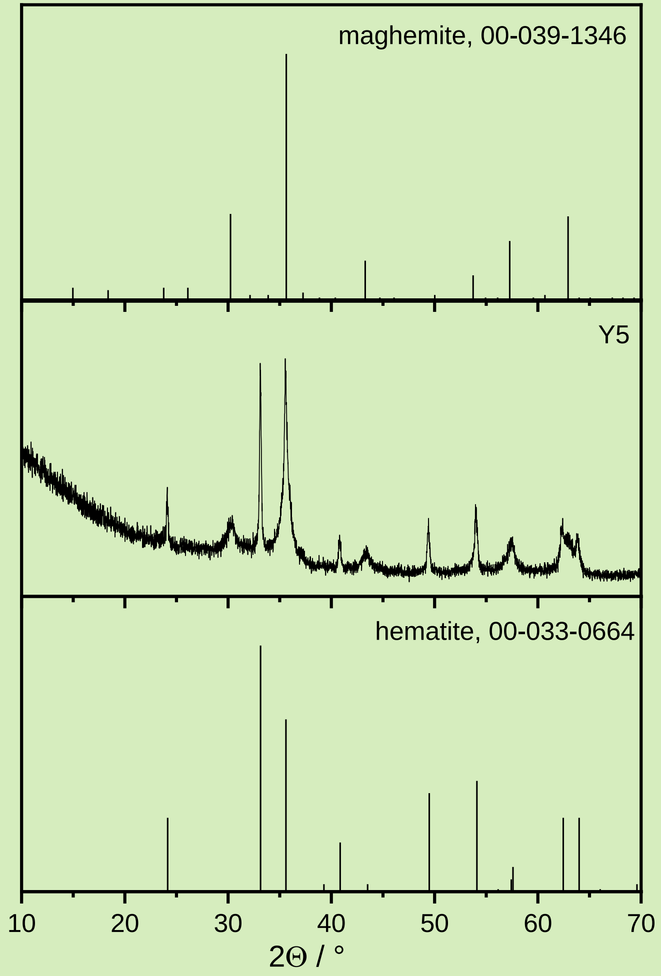


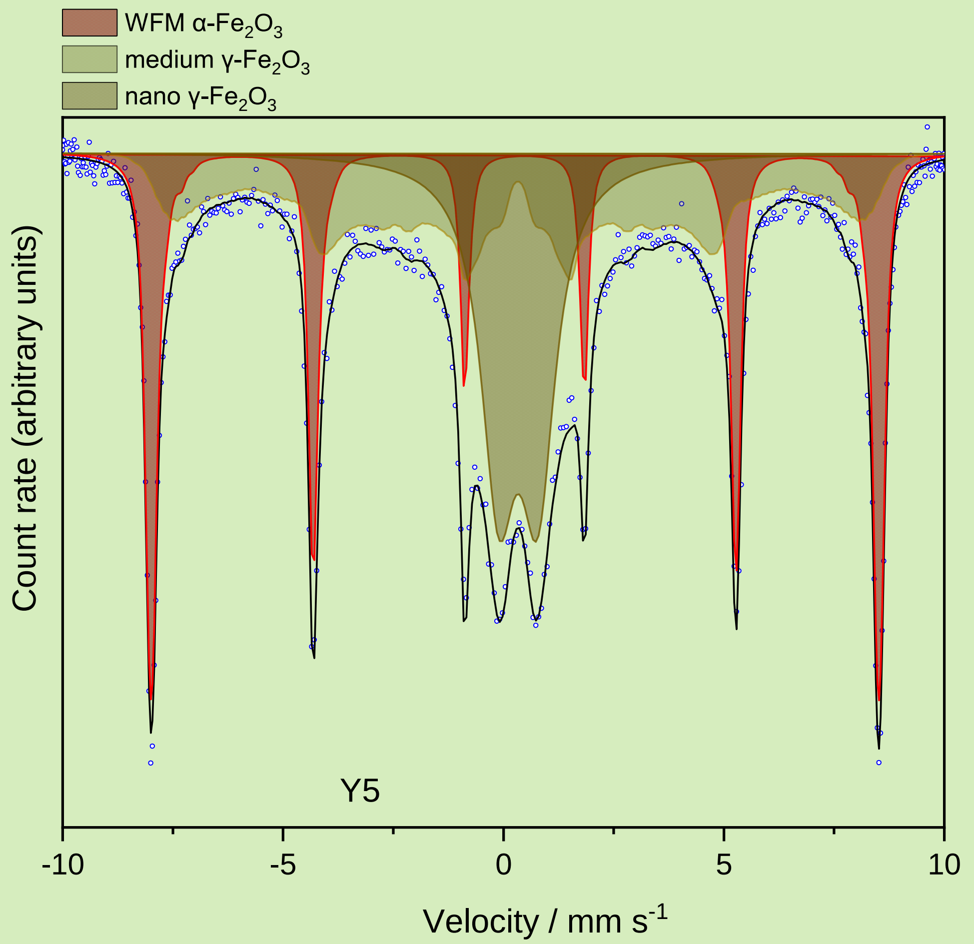


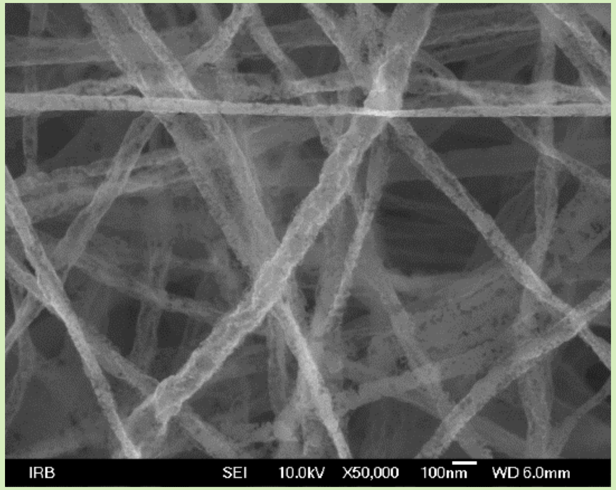


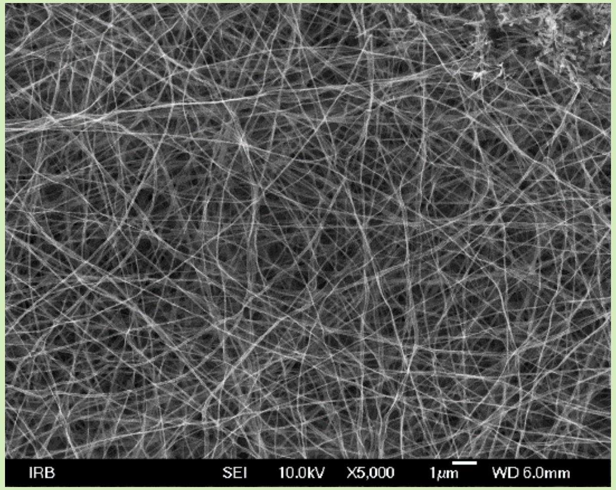
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y3	sextet	0.37	-0.22	51.2*	0.21	60.7	WFM α-Fe_2O_3
	sextet	0.33(f)	0.00(f)	34.2*	0.35	39.3	medium γ-Fe_2O_3

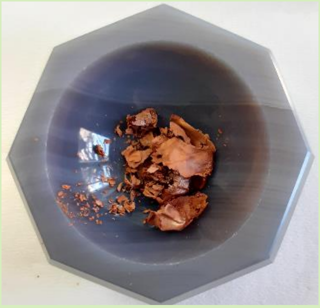
Y5







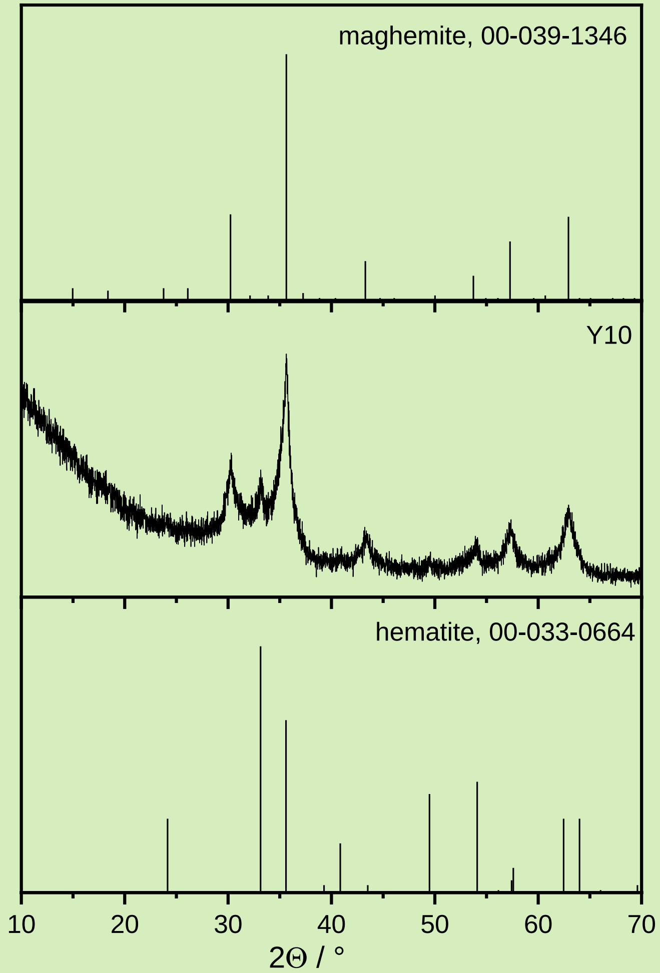


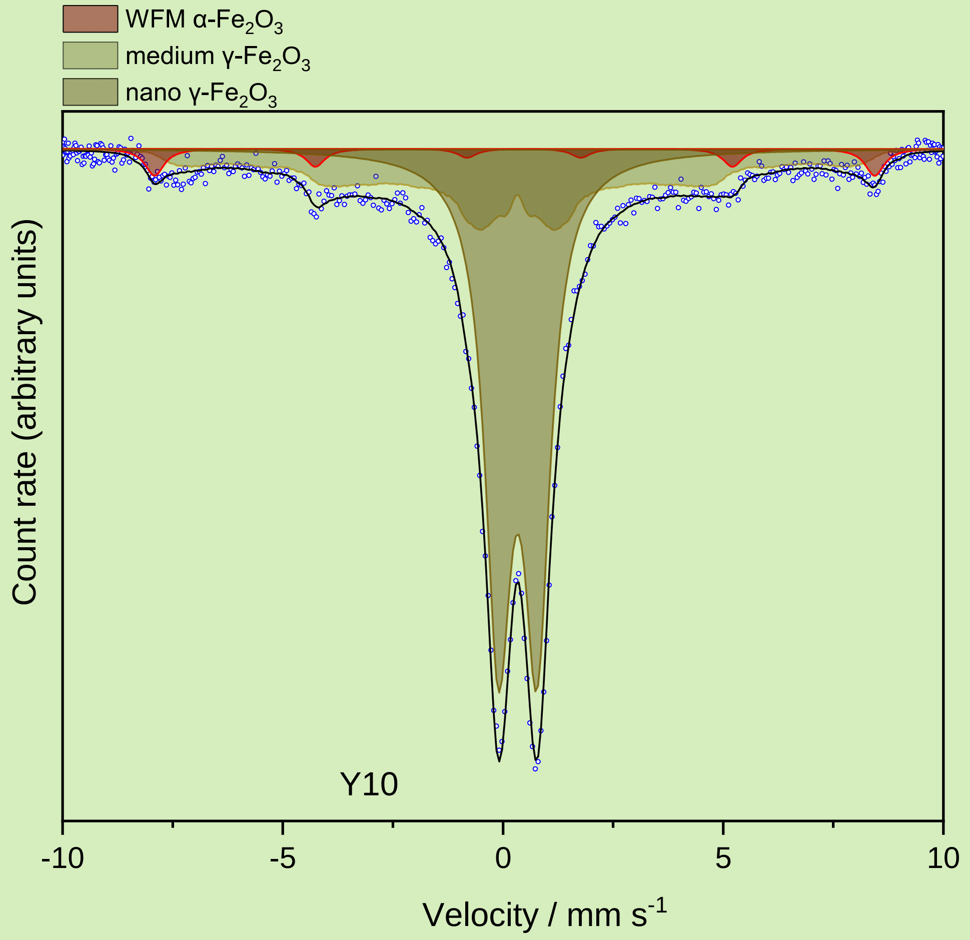


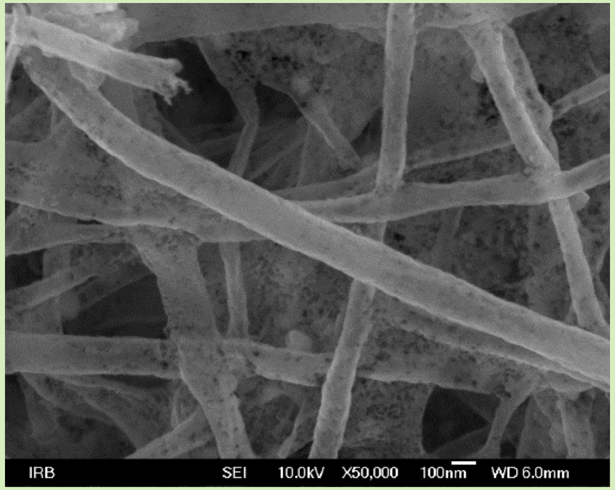
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y5	sextet	0.37 (f)	-0.22	51.1*	0.22	32.7	WFM α-Fe_2O_3
	sextet	0.33(f)	0.00(f)	32.8*	0.24	36.9	medium γ-Fe_2O_3
	doublet	0.33	0.89	-	0.97	30.4	nano γ-Fe_2O_3

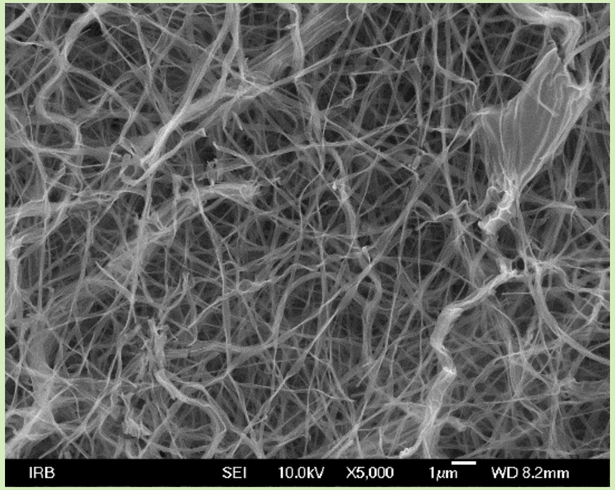
Y10

BET→surface area:
67.1153 ± 0.7675



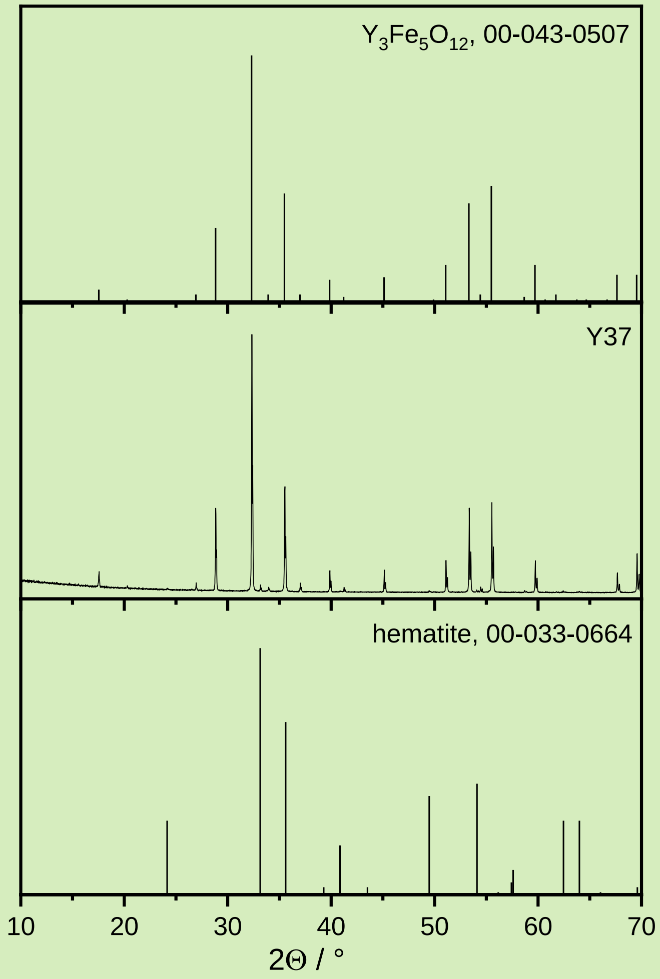


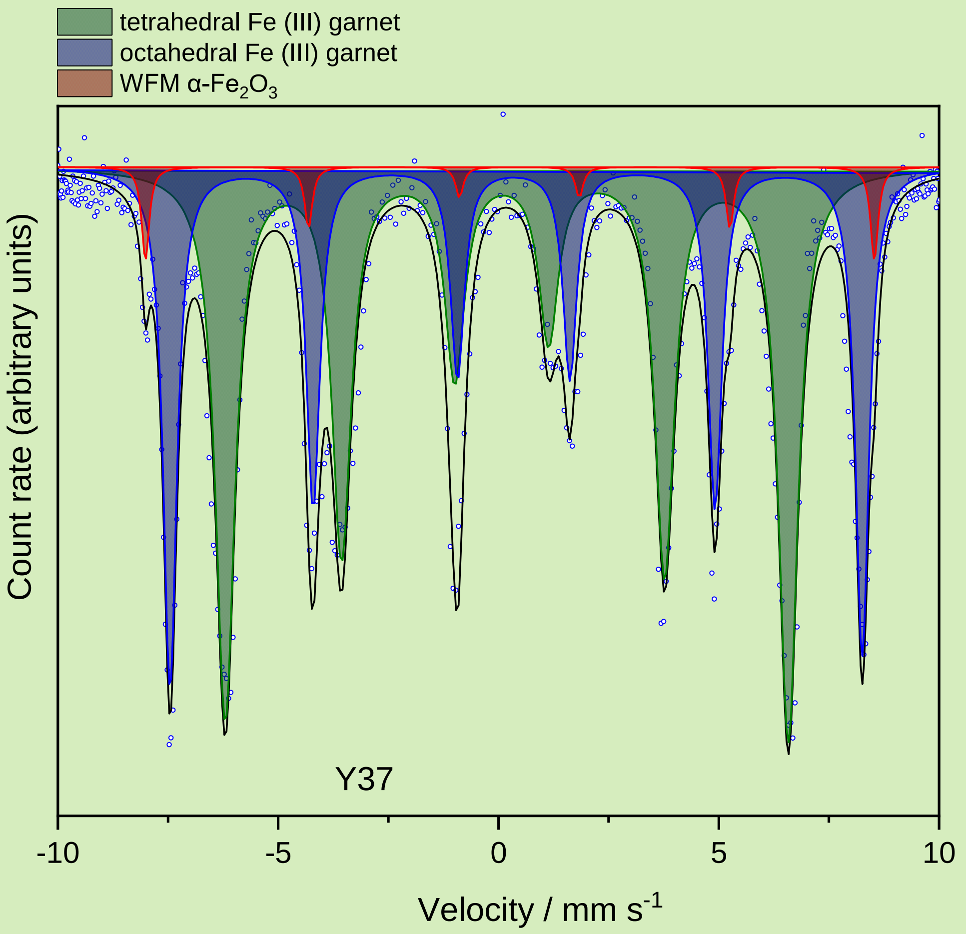


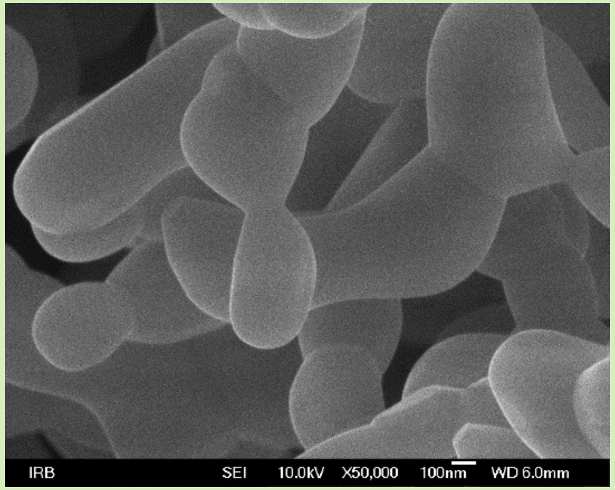


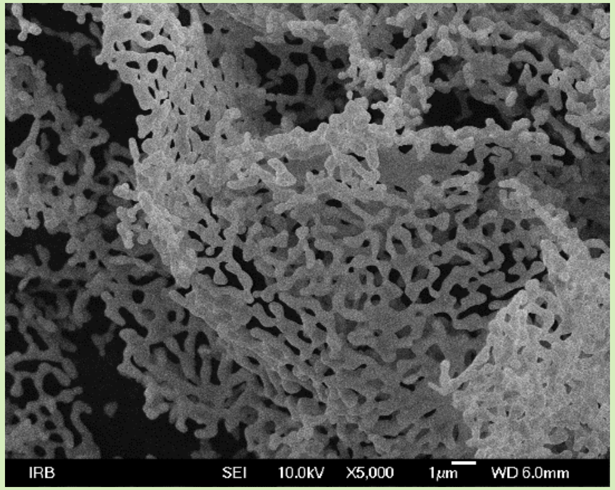
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y10	sextet	0.37 (f)	-0.21(f)	50.8	0.52	5.1	WFM α-Fe_2O_3
	sextet	0.33	0.00(f)	25.5*	0.22	33.2	medium γ-Fe_2O_3
	doublet	0.34	0.88		0.73	61.7	nano γ-Fe_2O_3

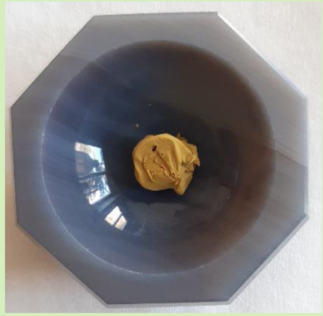
Y37





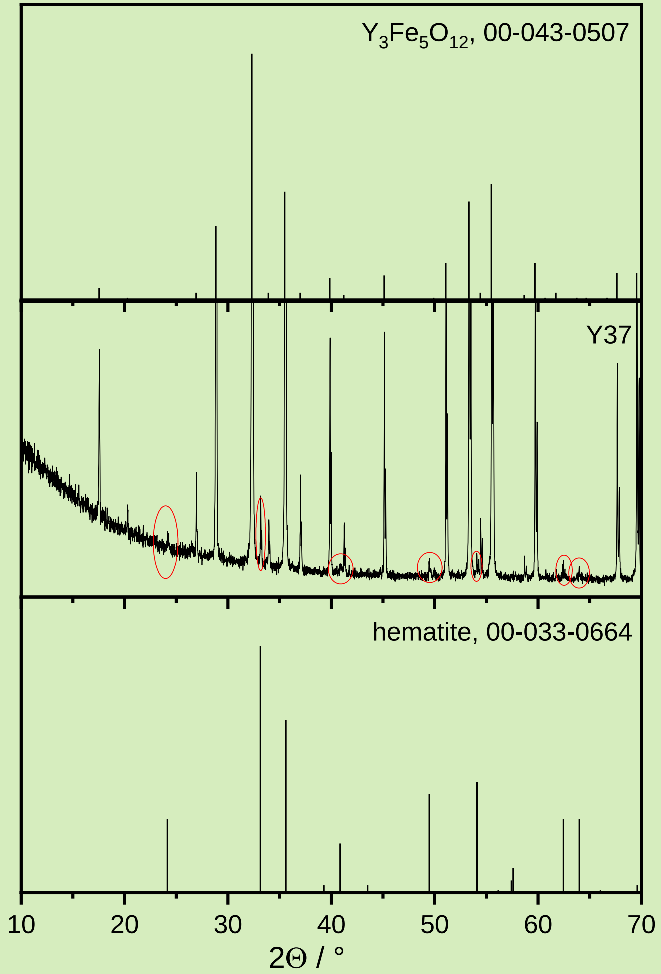


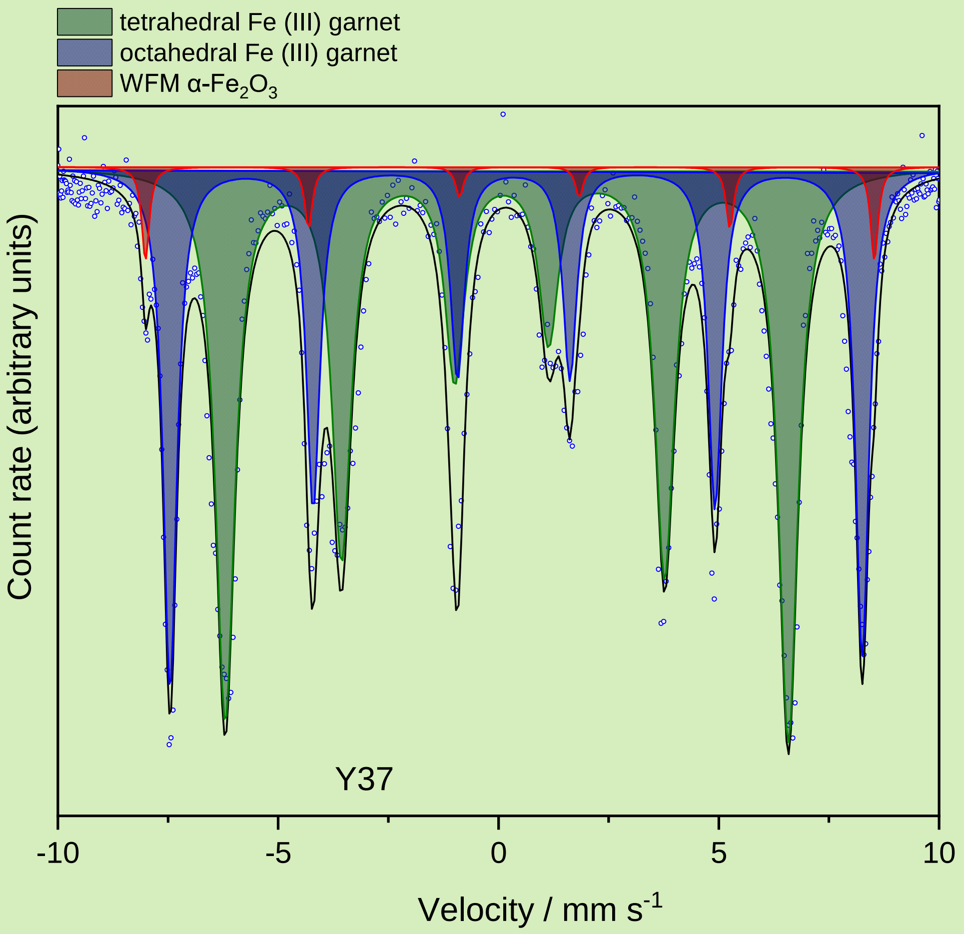


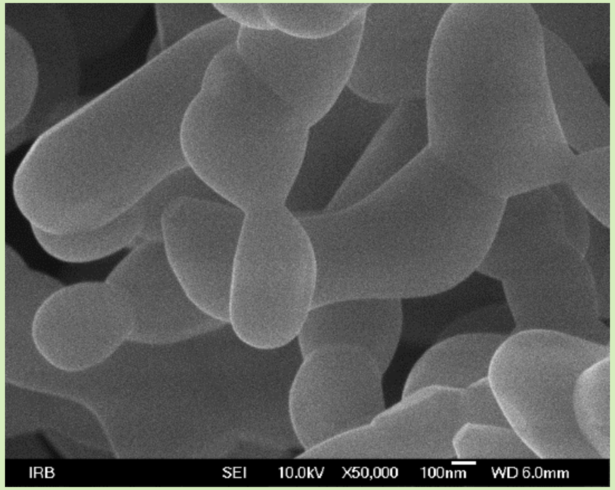


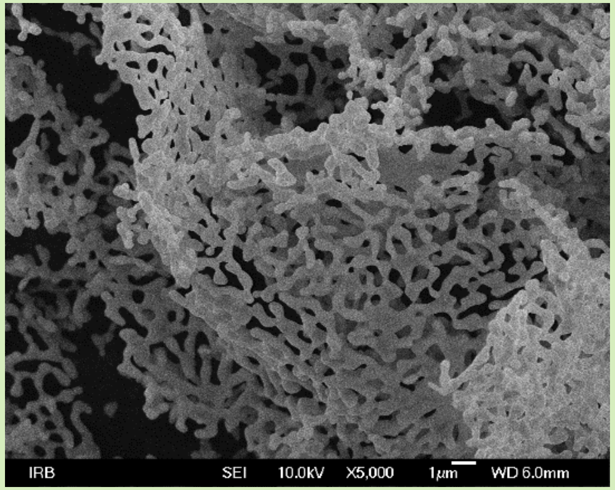
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y37	sextet	0.38	0.07	48.9	0.38	37.8	^{VI}Fe(III) in $Y_3Fe_5O_{12}$ (O)
	sextet	0.13	0.16	39.6	0.54	58.5	^{IV}Fe(III) in $Y_3Fe_5O_{12}$ (T)
	sextet	0.37(f)	-0.21(f)	51.4	0.21(f)	3.7	WFM α-Fe_2O_3

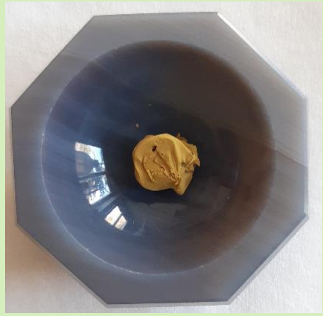
Y37





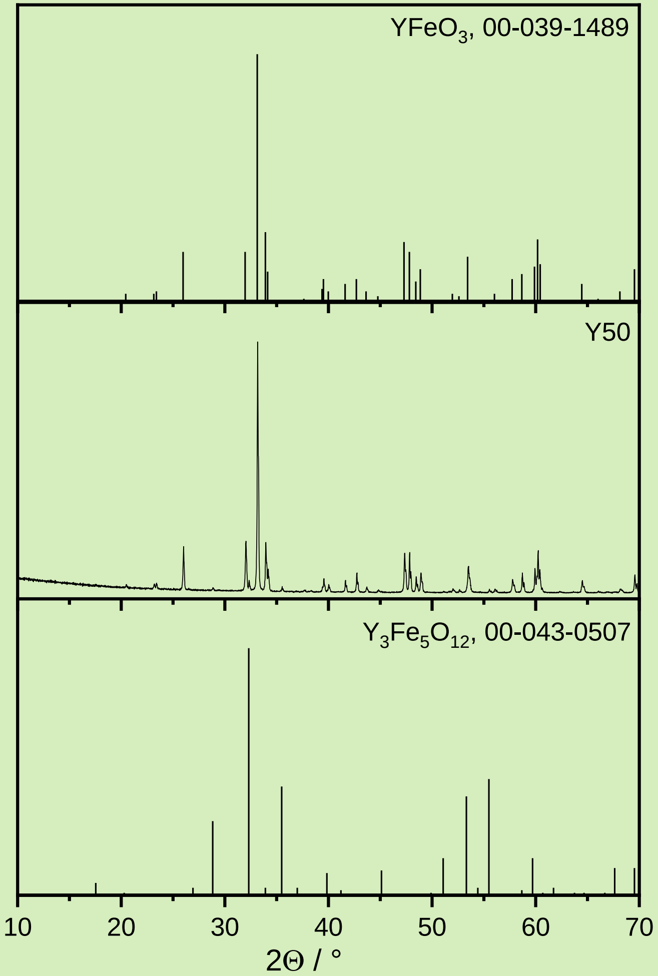


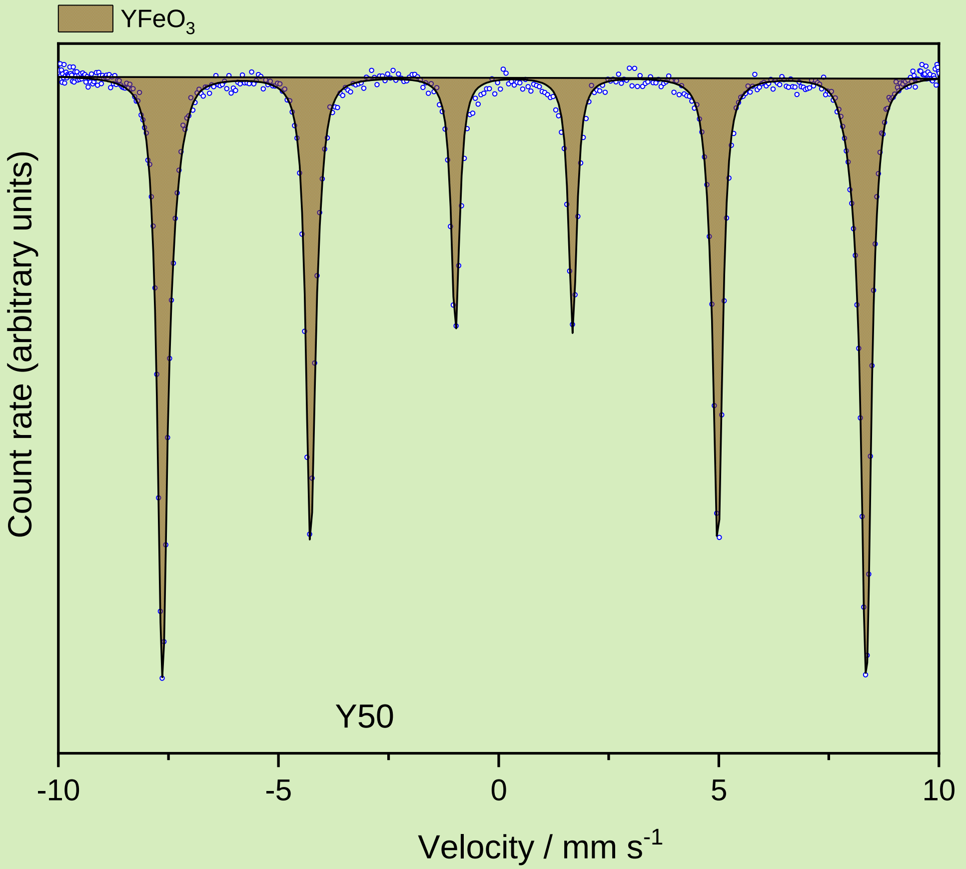


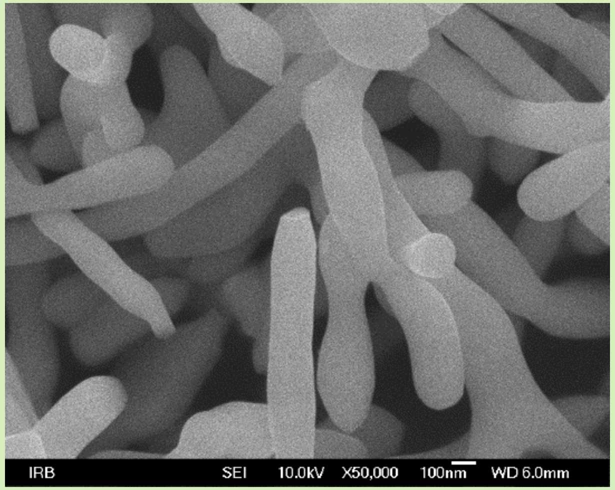


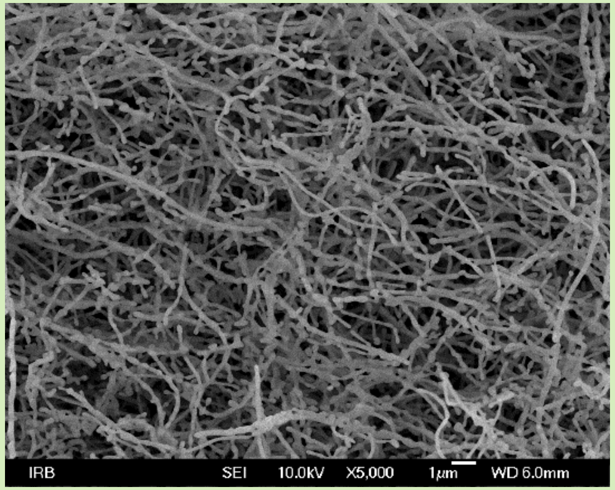
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y37	sextet	0.38	0.07	48.9	0.38	37.8	^{VI}Fe(III) in $Y_3Fe_5O_{12}$ (O)
	sextet	0.13	0.16	39.6	0.54	58.5	^{IV}Fe(III) in $Y_3Fe_5O_{12}$ (T)
	sextet	0.37(f)	-0.21(f)	51.4	0.21(f)	3.7	WFM α-Fe_2O_3

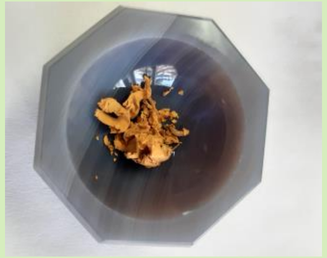
Y50





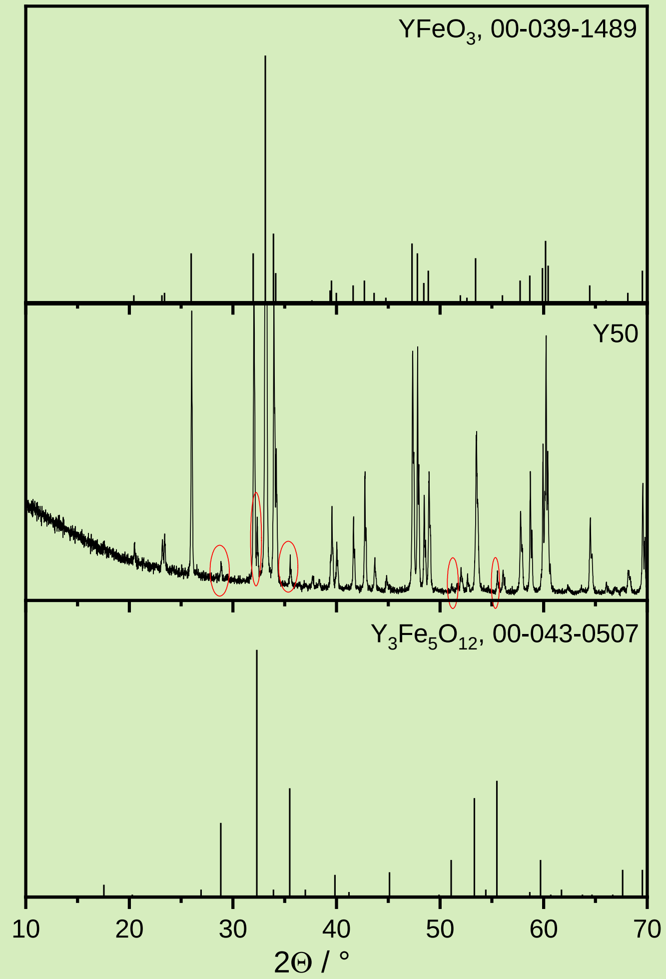


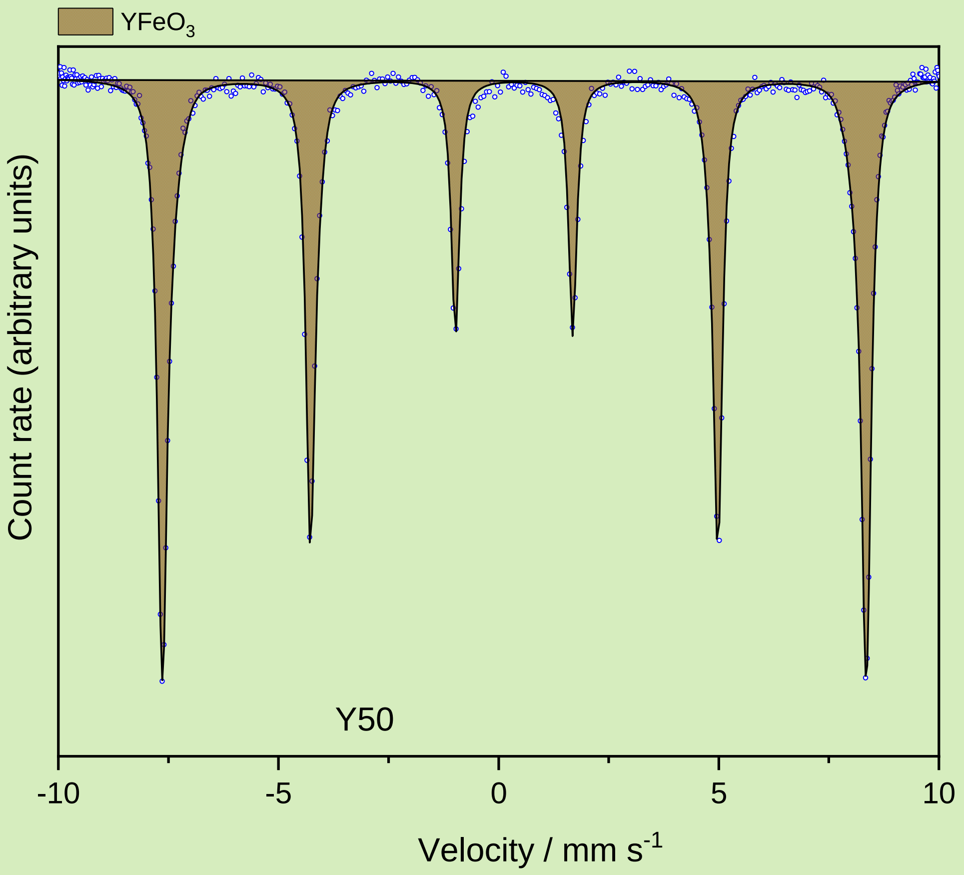


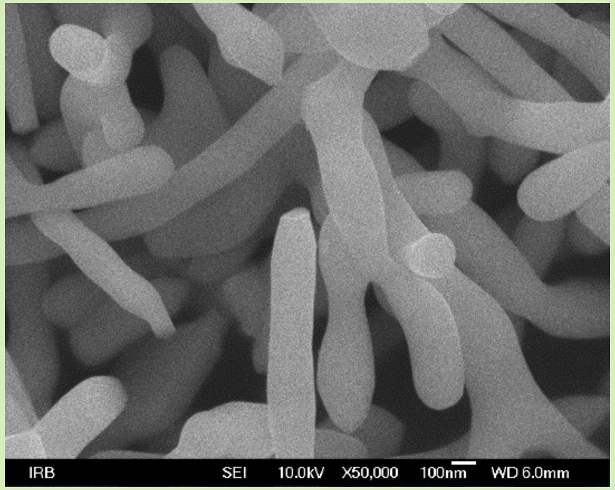


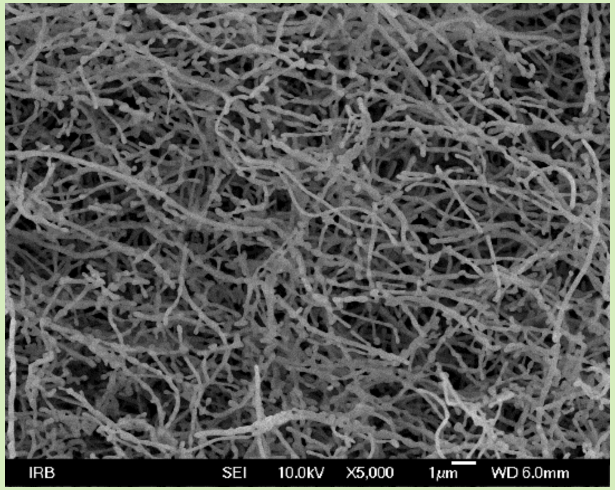
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y50	sextet	0.36	0.00	49.5	0.21	100.0	YFeO$_3$

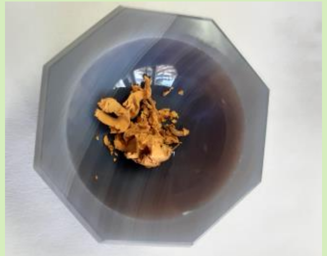
Y50





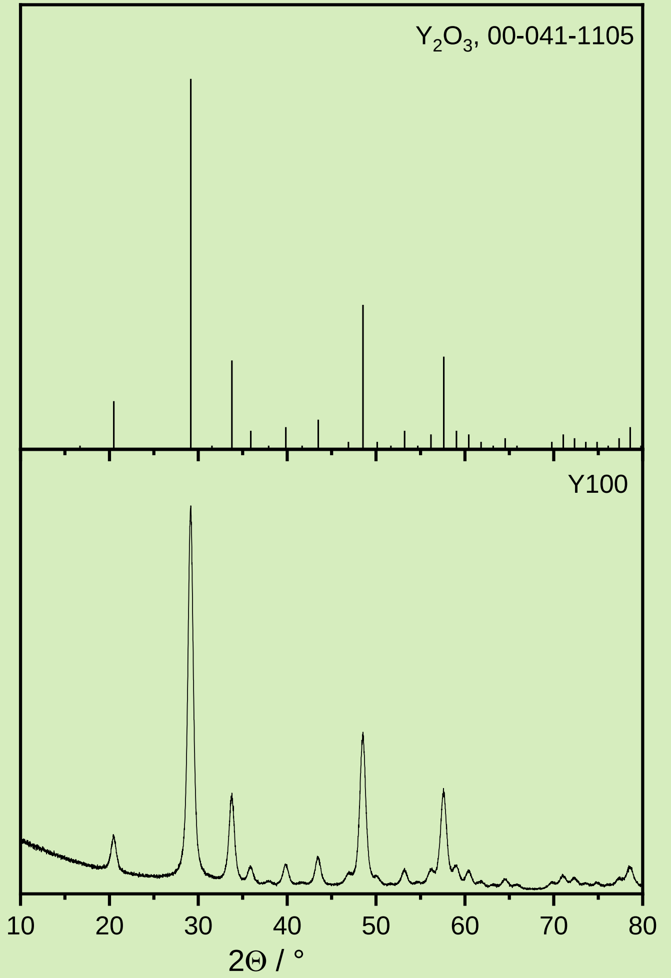


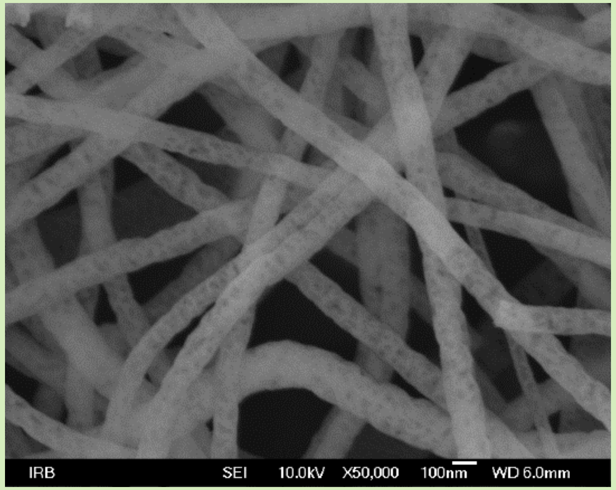


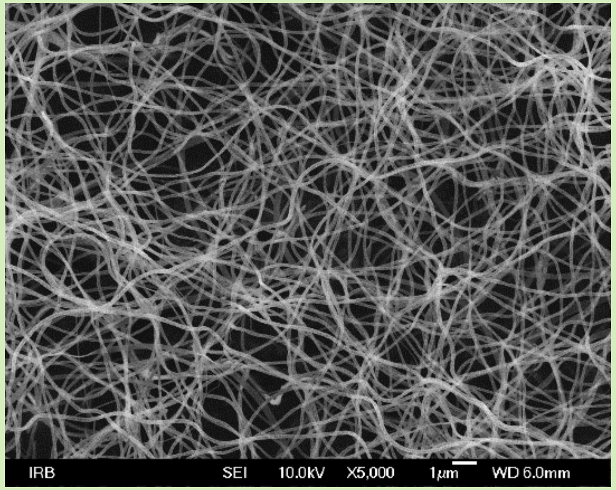


Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Y50	sextet	0.36	0.00	49.5	0.21	100.0	$YFeO_3$

Y100


Y_2O_3, 00-041-1105
Y100
10
20
30
40
50
60
70
80
2Θ / °


IRB
SEI 10.0kV X50,000 100nm WD 6.0mm

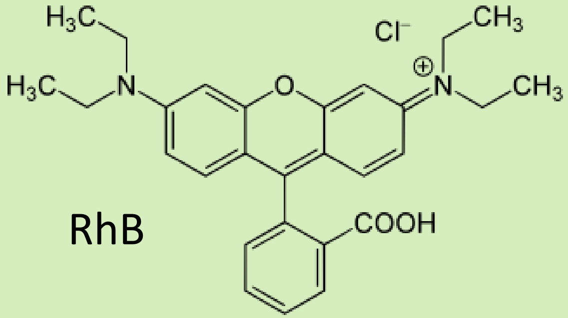

IRB
SEI 10.0kV X5,000 1μm WD 6.0mm

Y series
Composition

Sample	Phase composition
Y0	hematite
Y1	hematite (+ 3.3 % maghemite)
Y3	Hematite+maghemite
Y5	hematite + maghemite
Y10	maghemite + hematite
Y37	garnet + hematite (minor phase)
Y50	orthoferrite + garnet (minor phase)
Y100	yttrium oxide

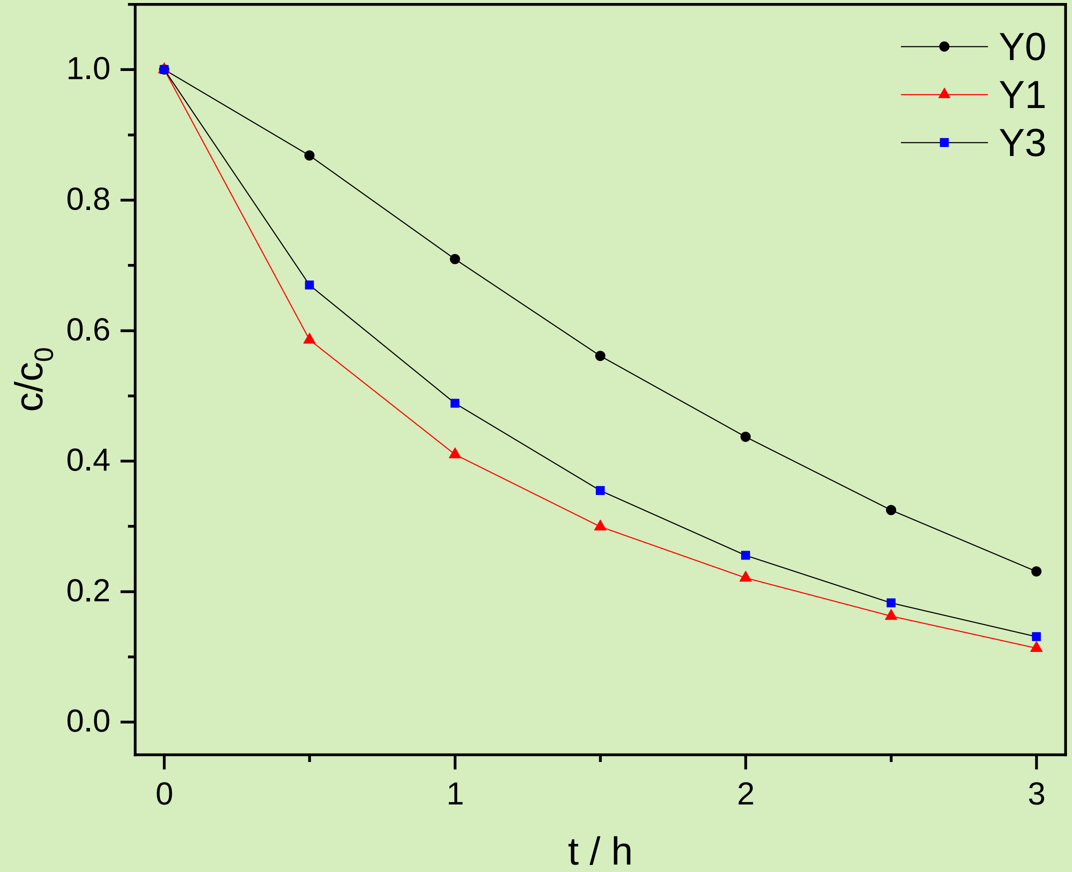
Y series

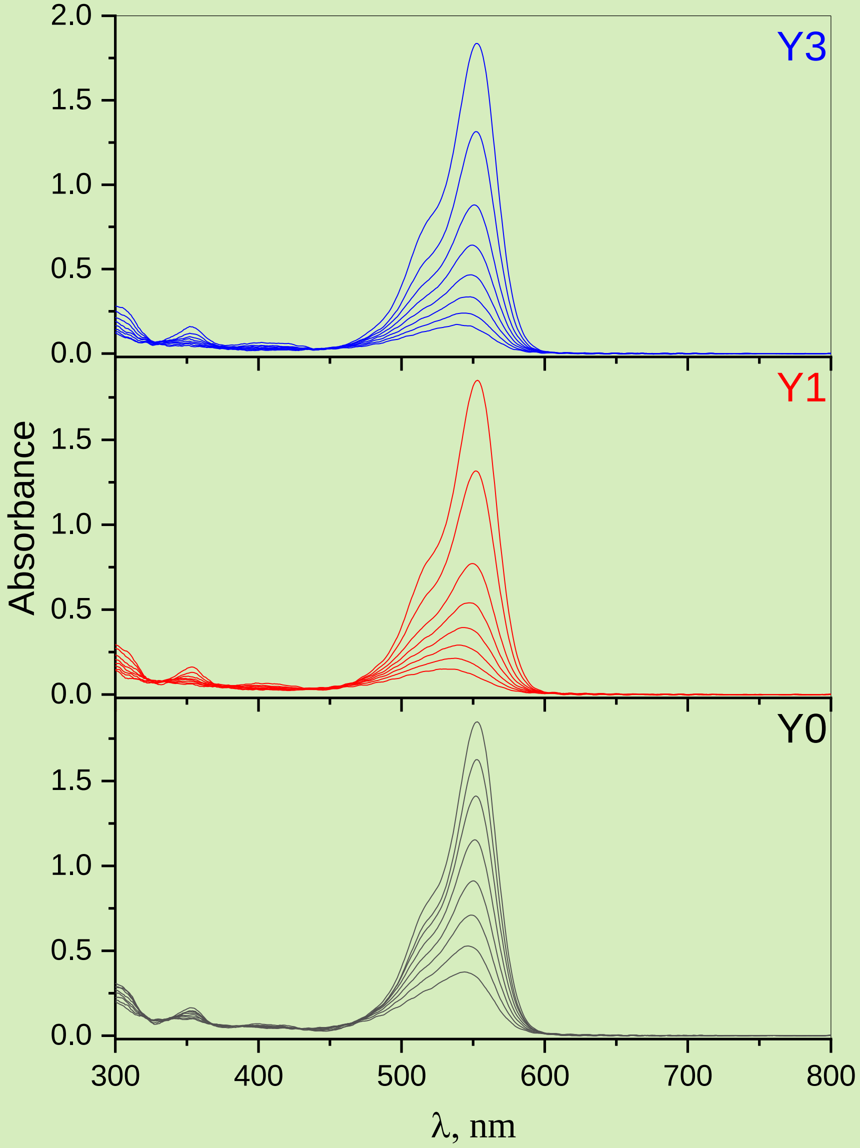
Potential applications



RhB

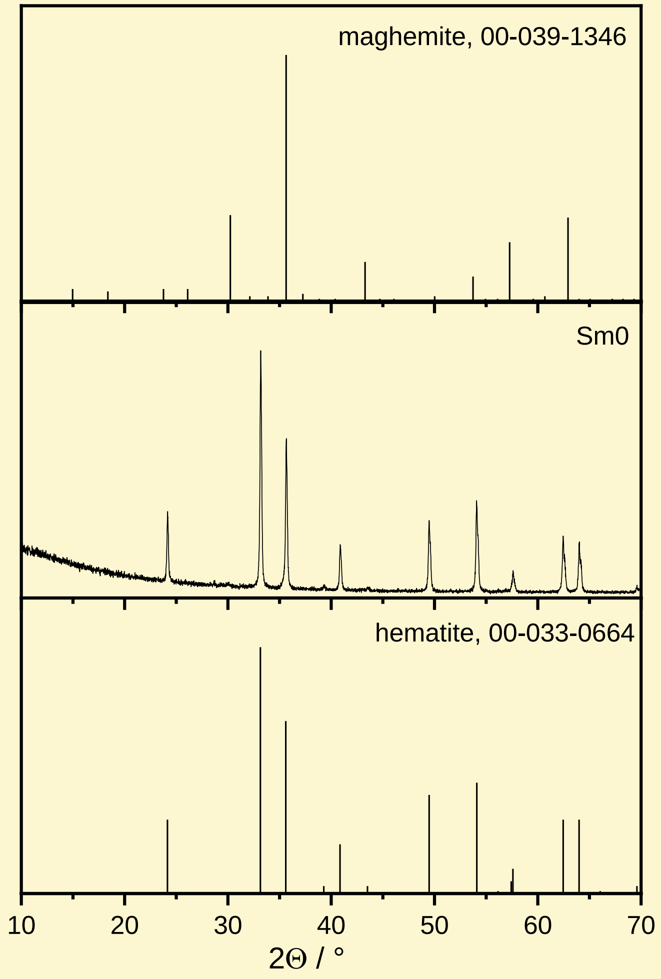
Preliminary results in photocatalysis

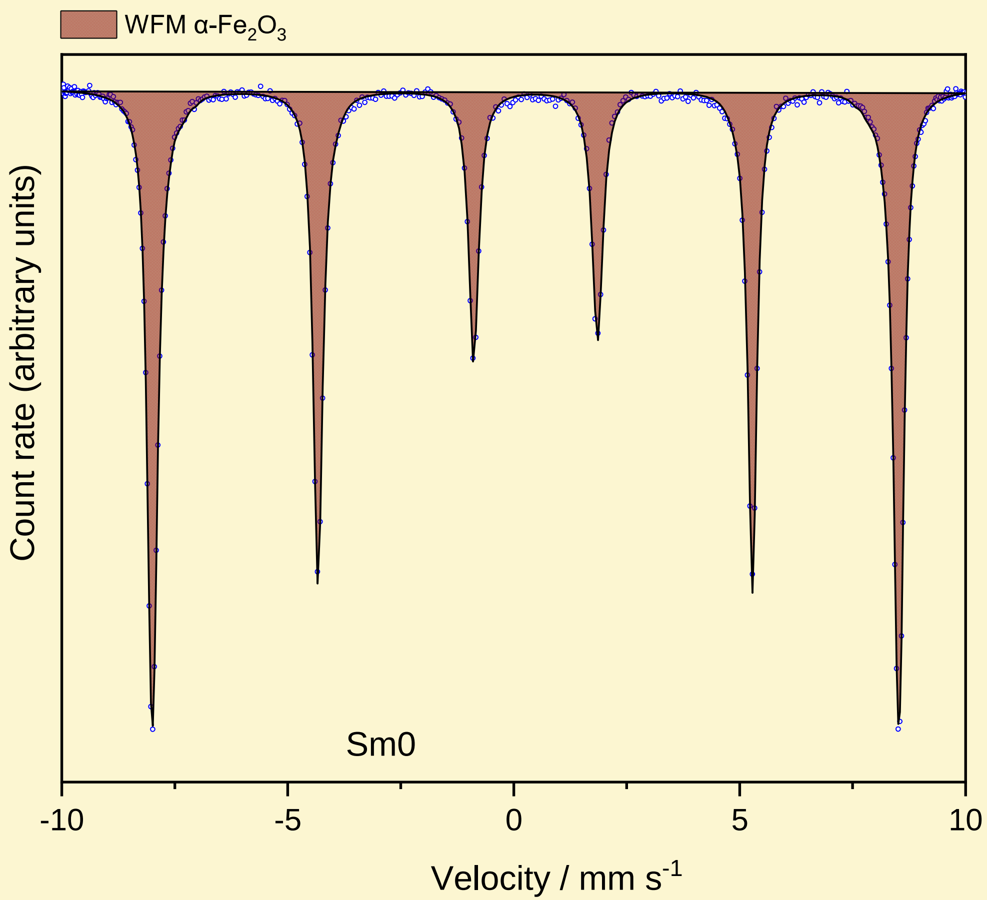


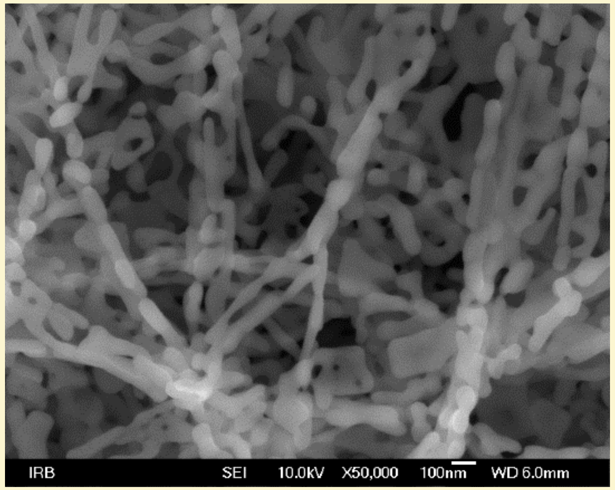


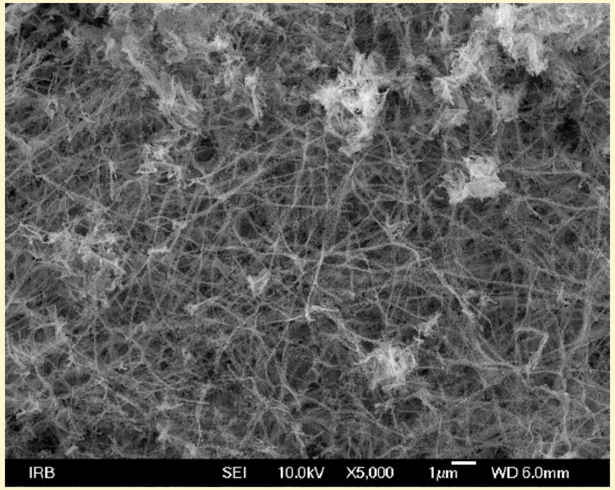
SAMARIUM

Sm0



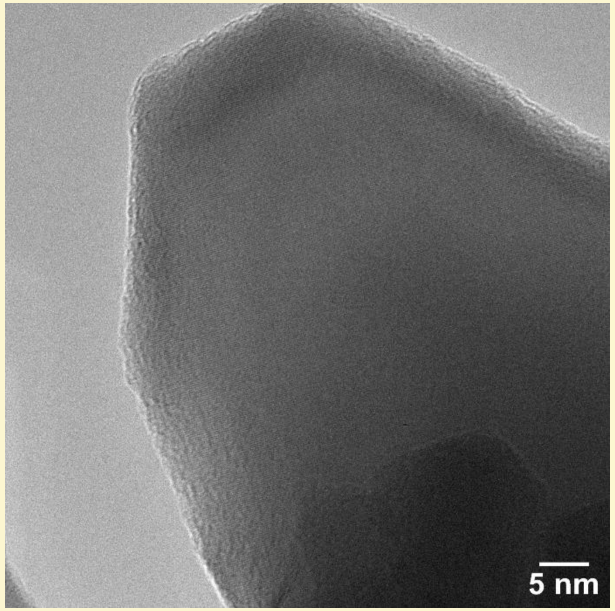


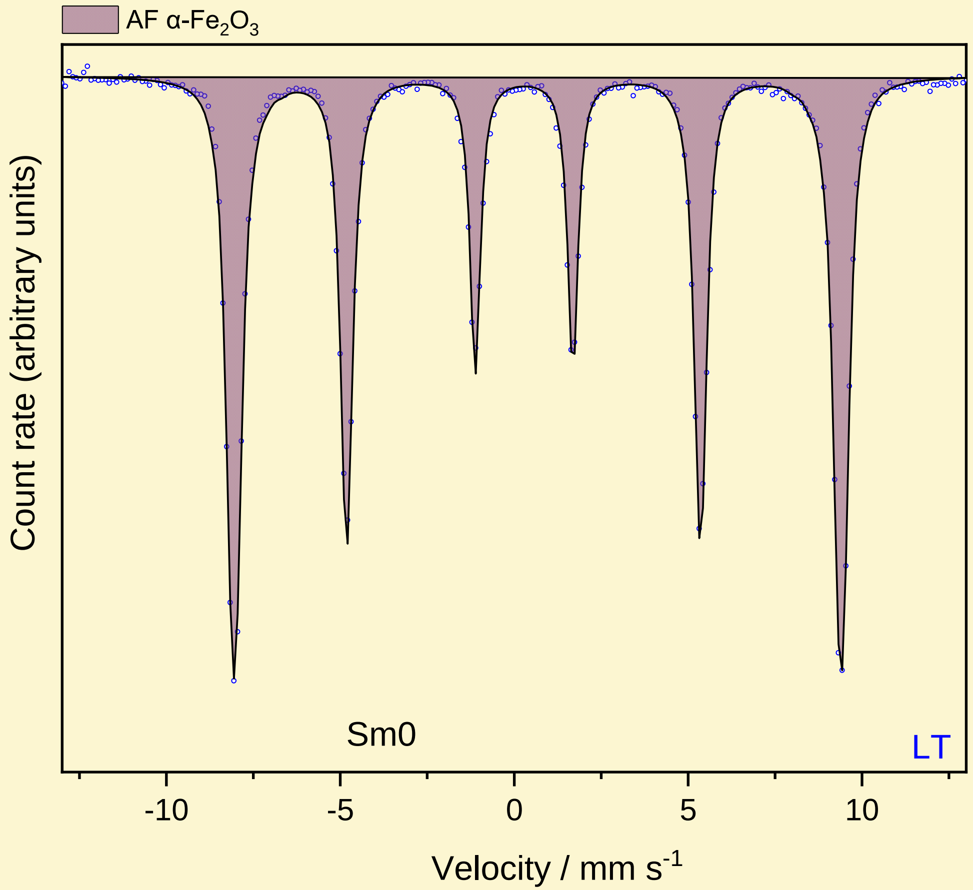


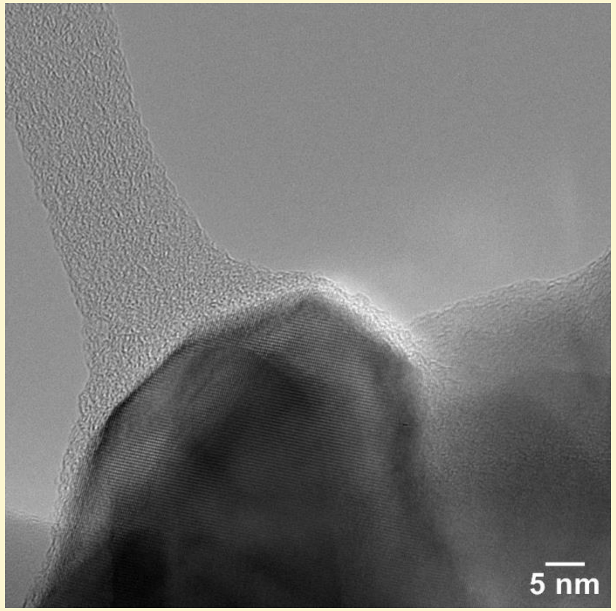


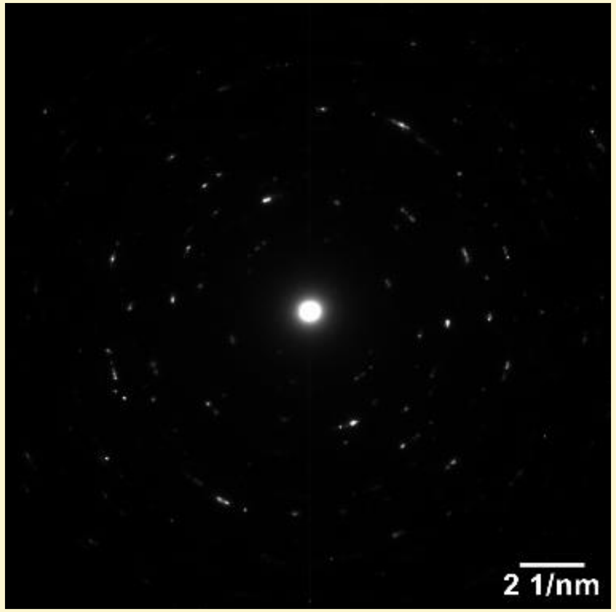
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 0	sextet	0.37	-0.22	51.2*	0.22	100.0	WFM α-Fe_2O_3

Sm0



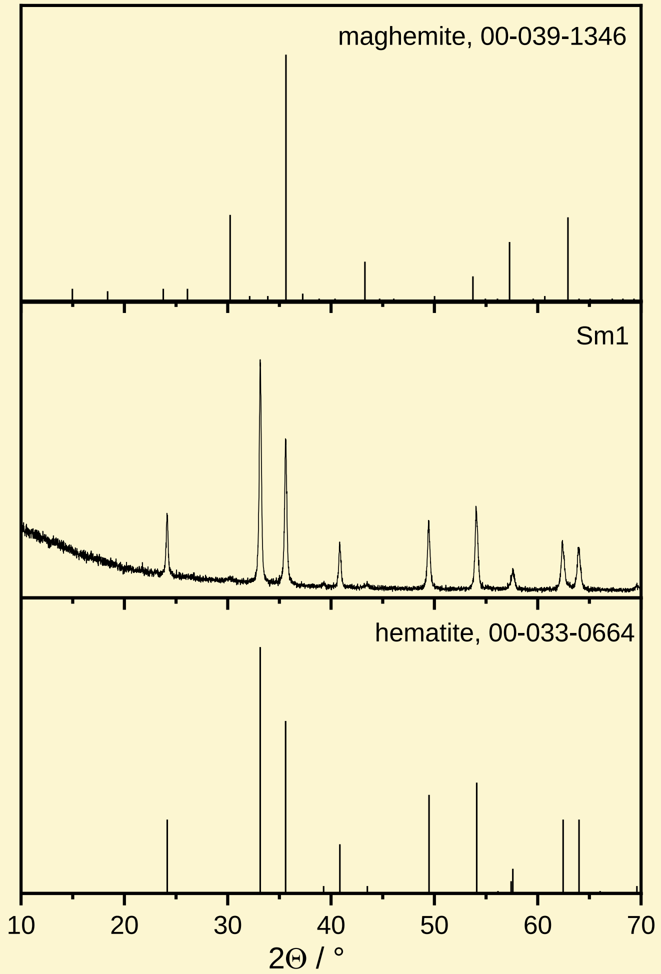


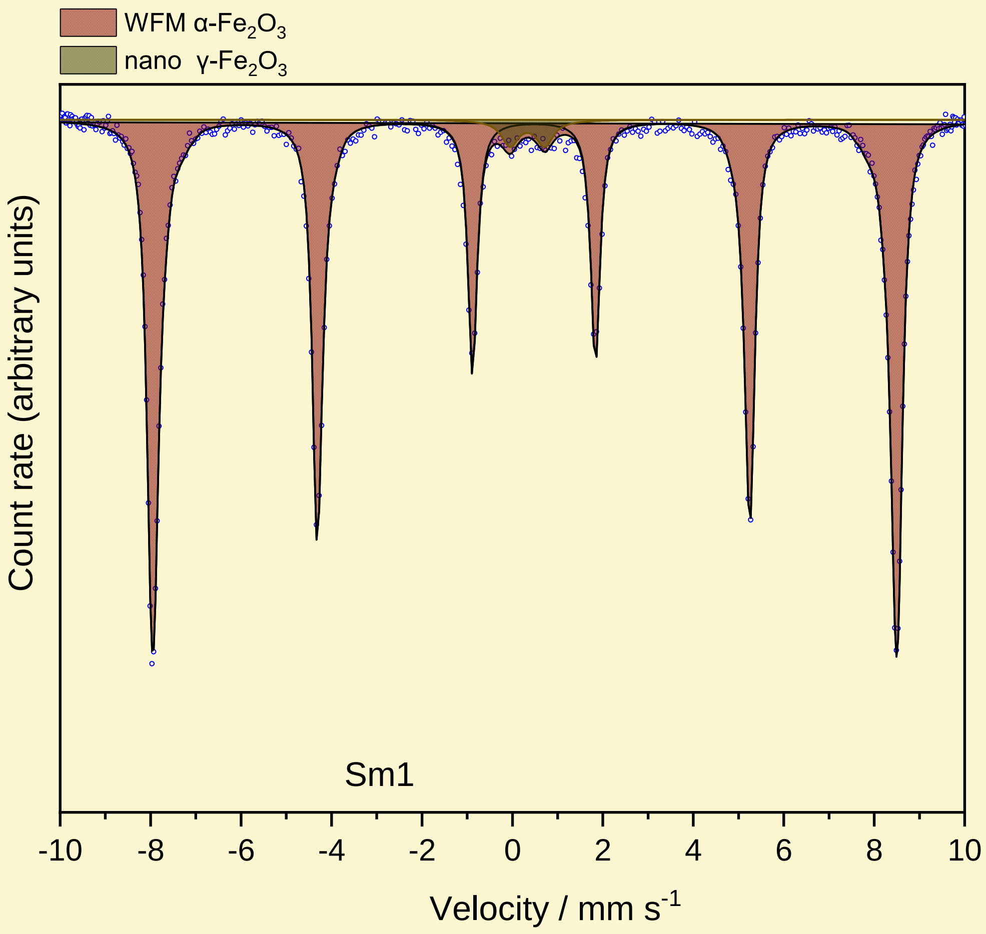


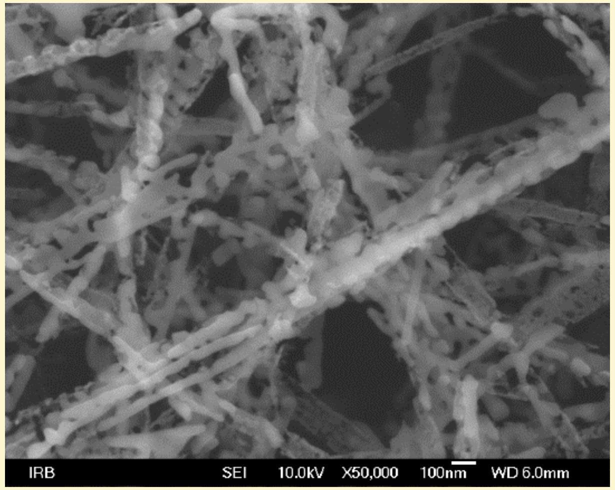


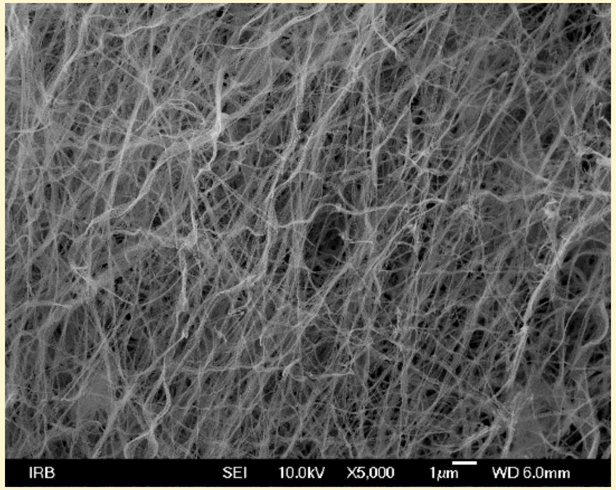
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 0	sextet	0.47	0.40	54.2*	0.34	100.0	AF α-Fe$_2$O$_3$

Sm1



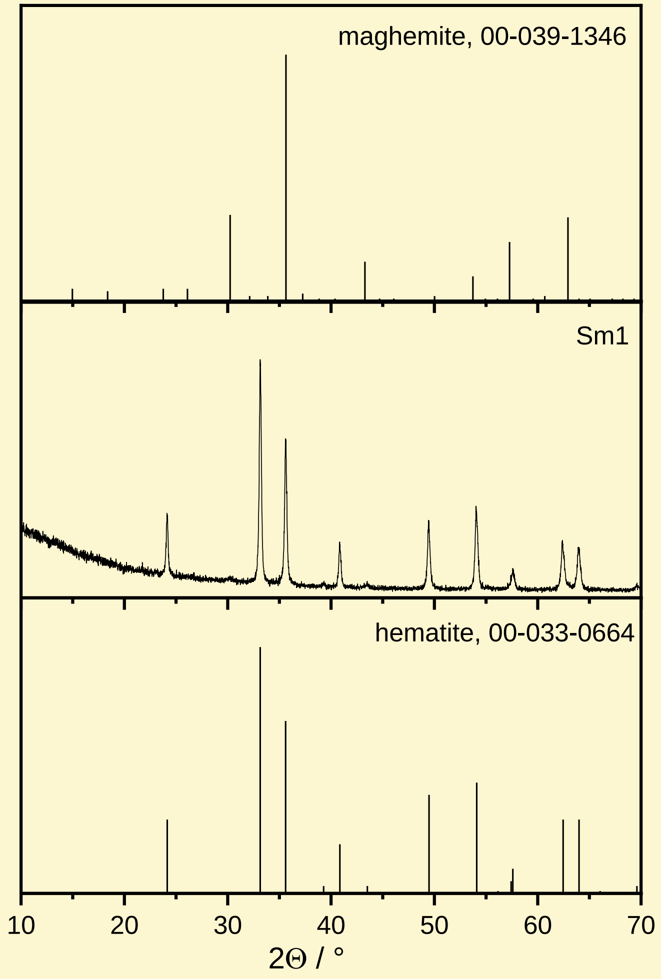


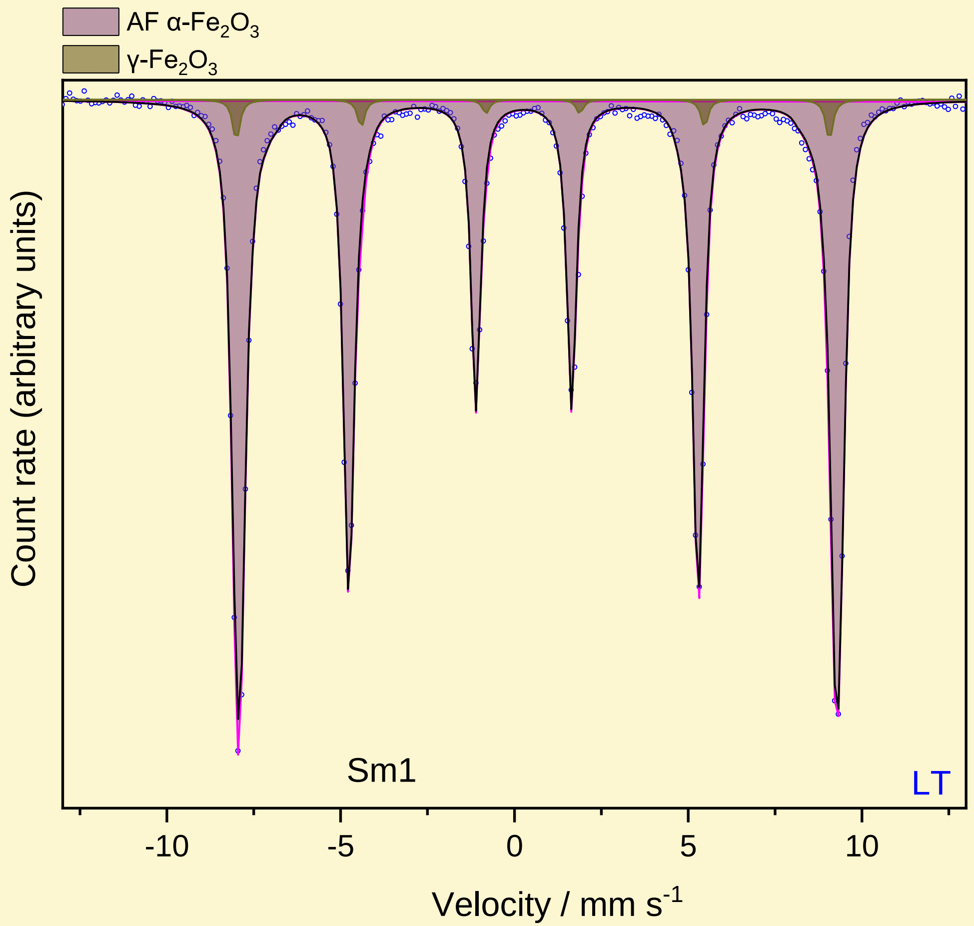


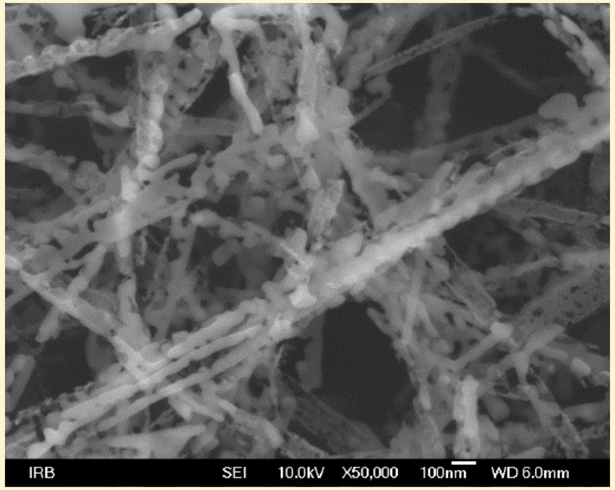


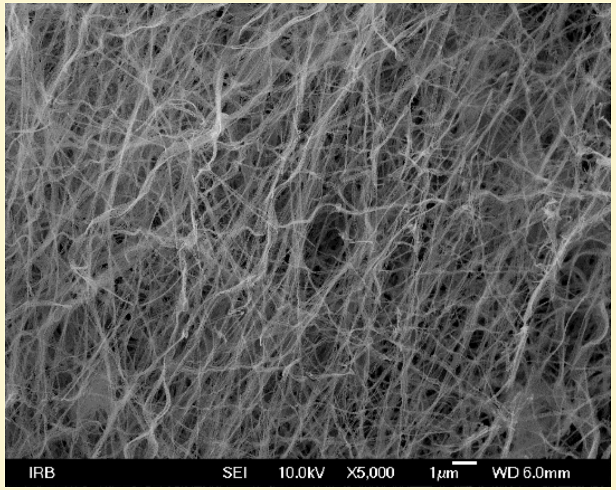
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 1	sextet	0.37	-0.21	50.9*	0.23	96.7	WFM α-Fe_2O_3
	doublet	0.33(f)	0.77	-	0.45(f)	3.3	nano γ-Fe_2O_3

Sm1



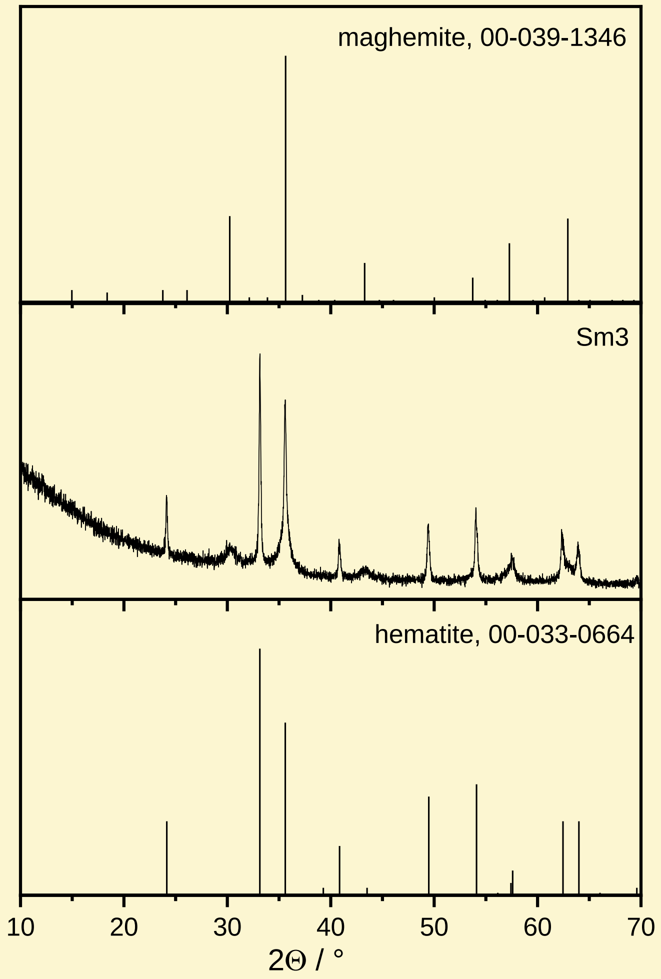


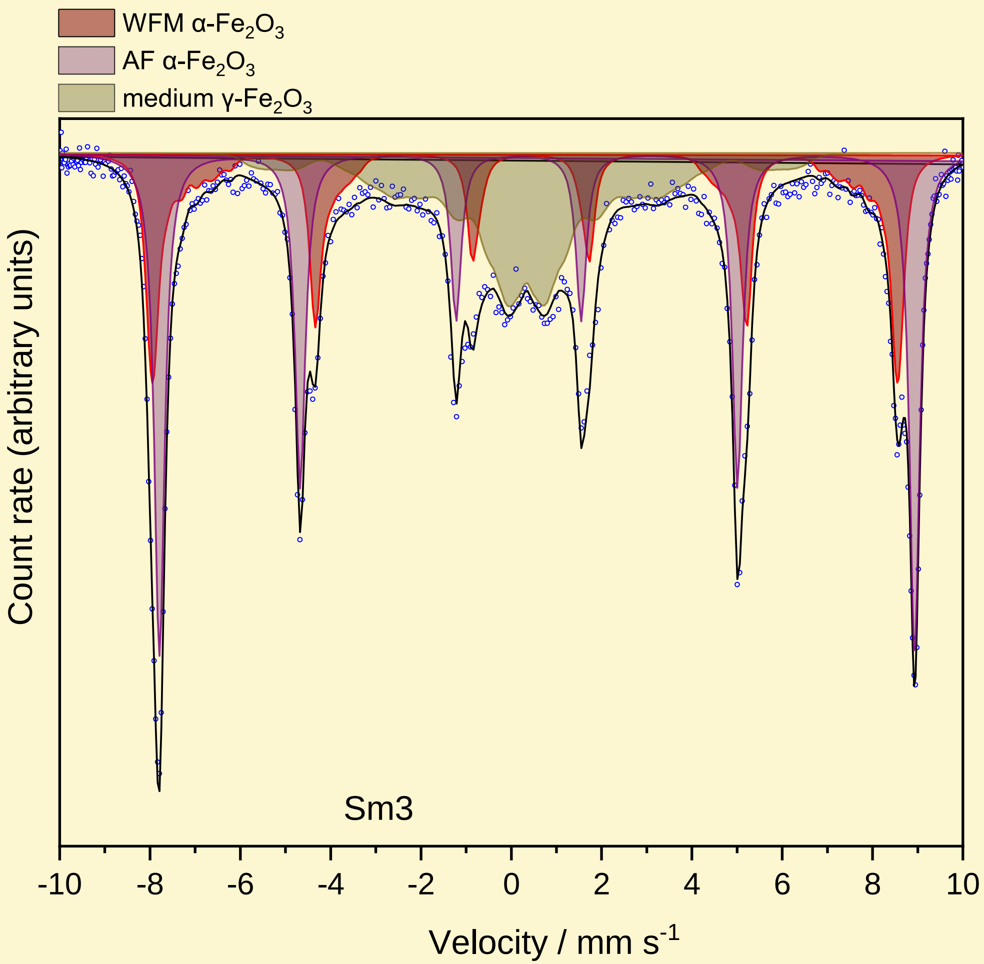


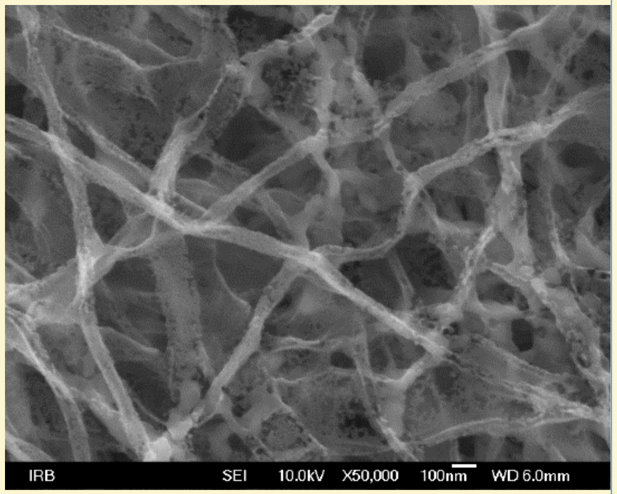


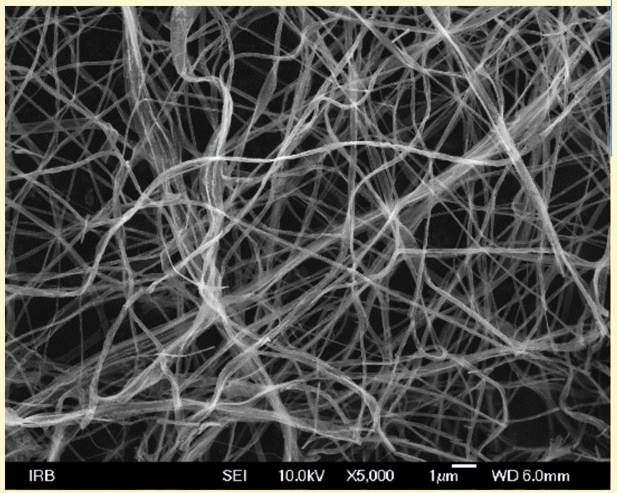
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm1	sextet	0.47	0.40(f)	53.4*	0.32	96.5	AF α-Fe_2O_3
	sextet	0.53(f)	0.00(f)	53.0	0.24	3.5	γ-Fe_2O_3

Sm3



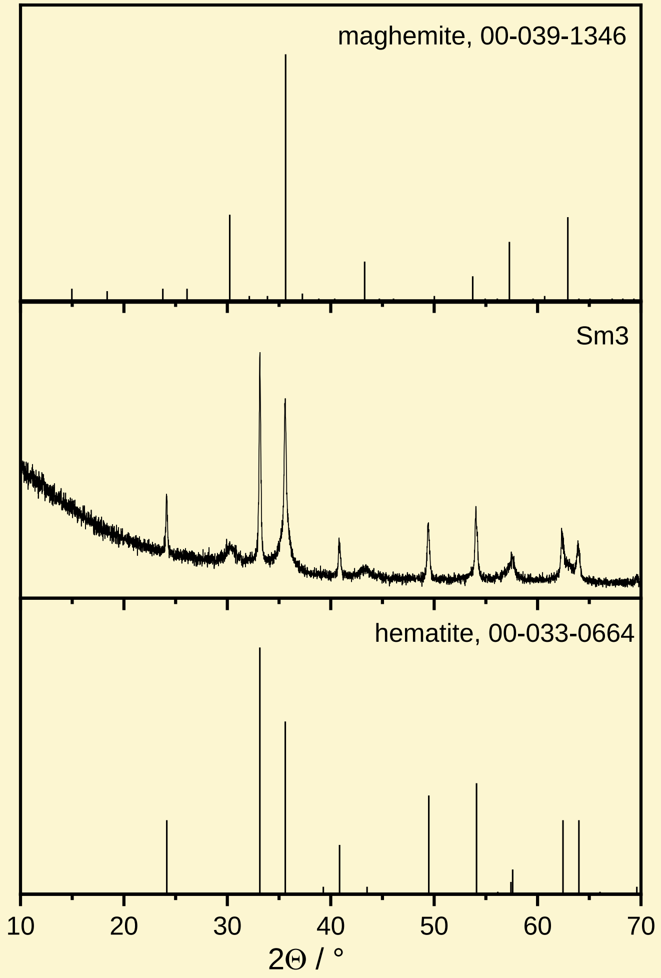


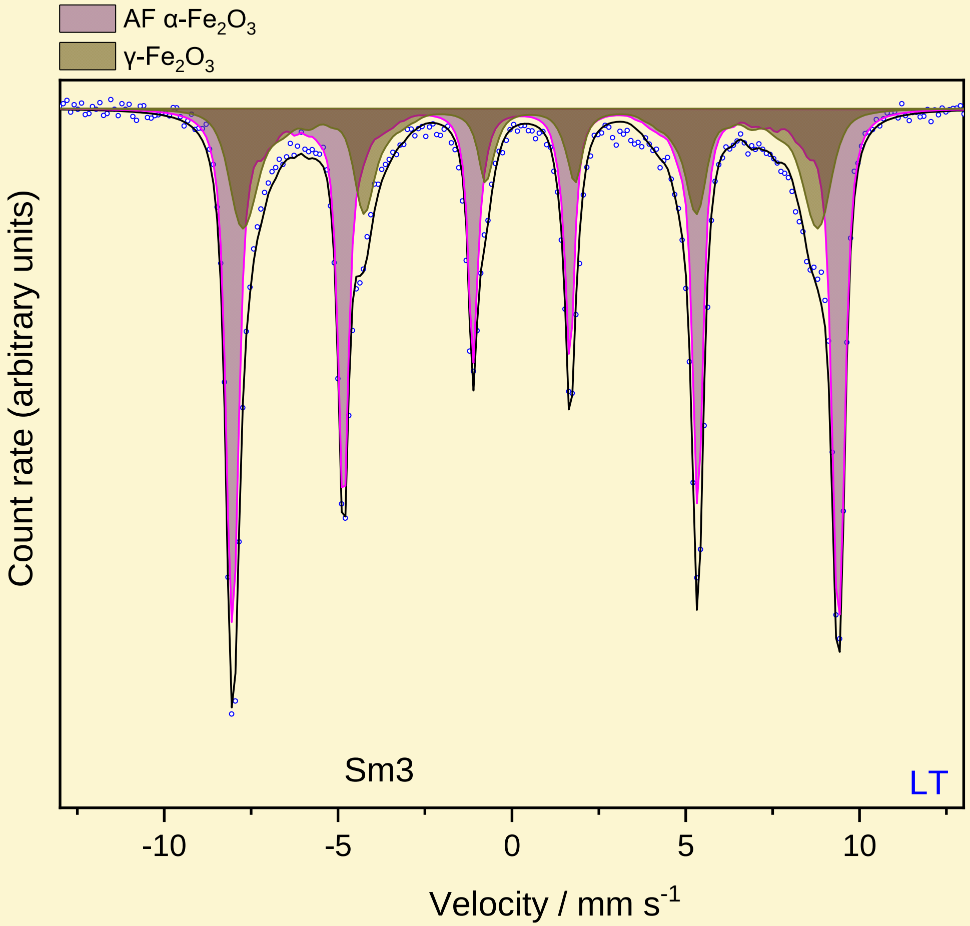


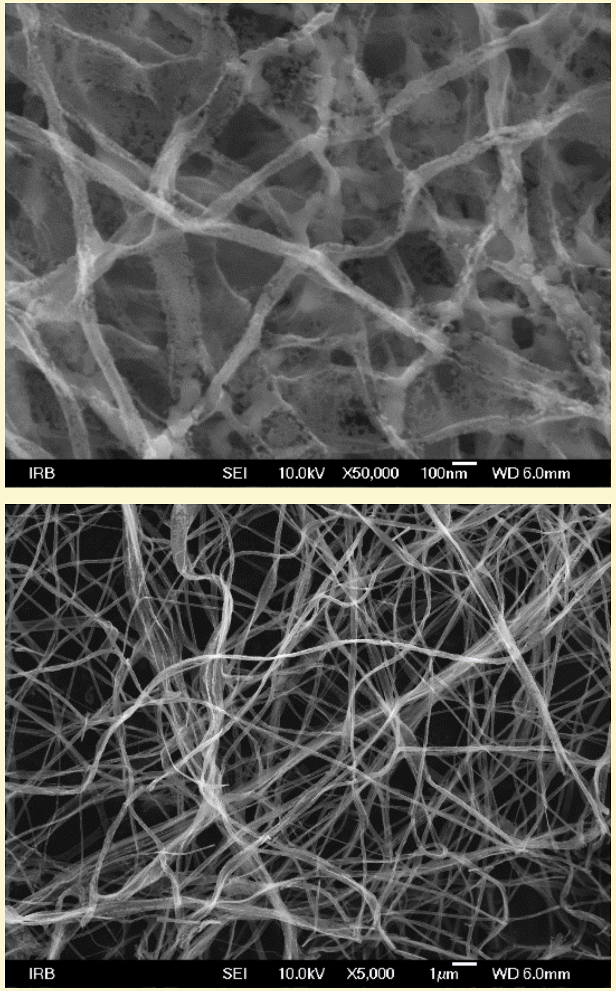


Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 3	sextet	0.37(f)	-0.13	49.6*	0.26	29.8	WFM α-Fe_2O_3
	sextet	0.37	0.40	52.0	0.28	41.0	AF α-Fe_2O_3
	sextet	0.34	0.01	15.0*	0.30(f)	29.2	medium γ-Fe_2O_3

Sm3

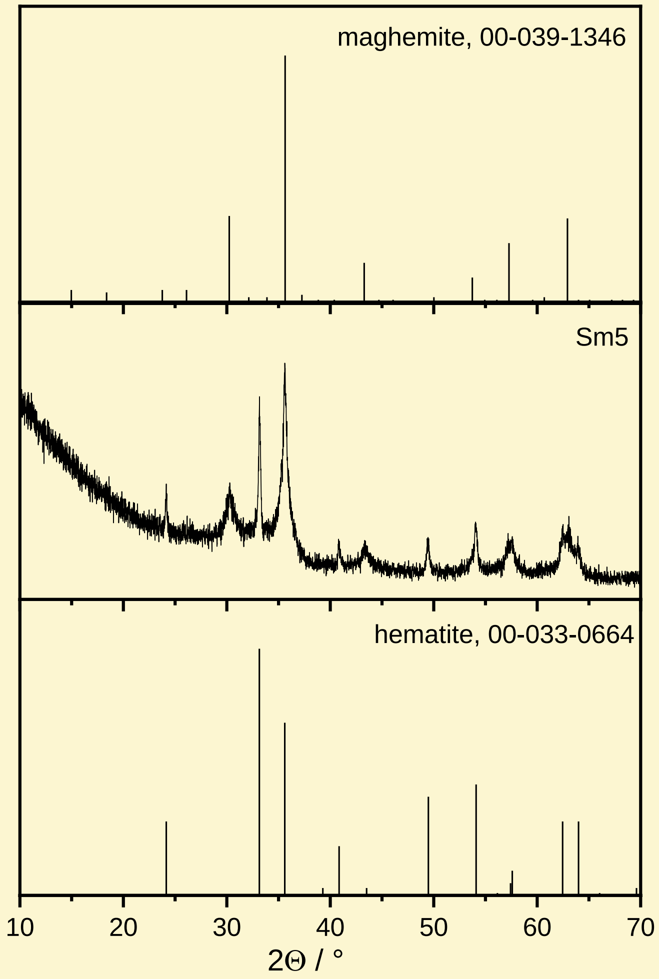


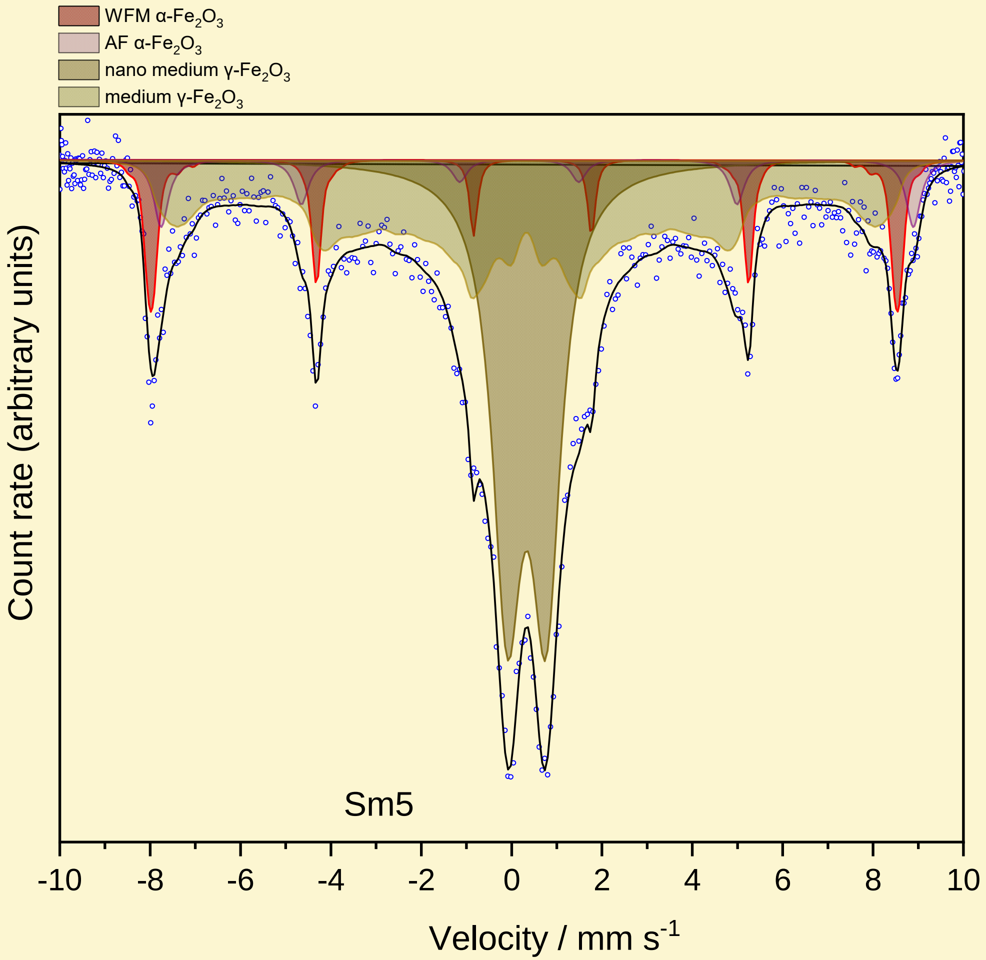


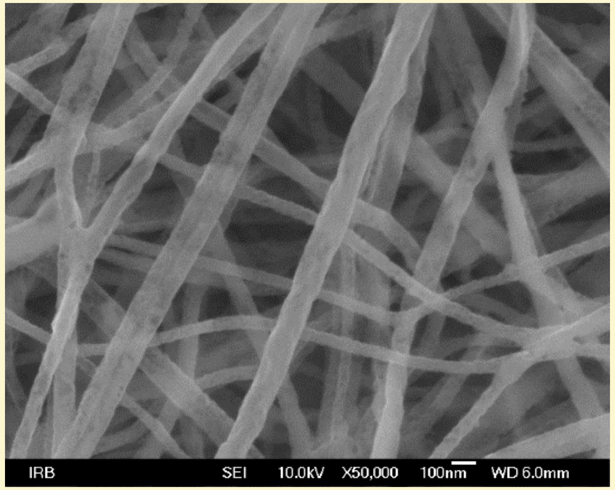


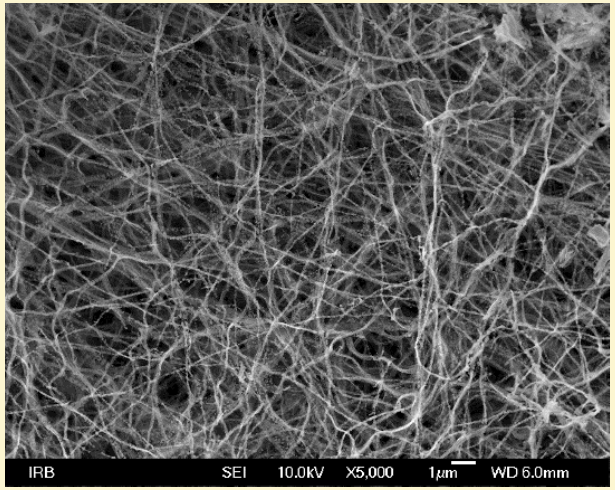
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm3	sextet	0.47(f)	0.40	53.1*	0.31	67.1	AF α-Fe_2O_3
	sextet	0.53(f)	0.00(f)	49.4*	0.47	32.9	γ-Fe_2O_3

Sm5



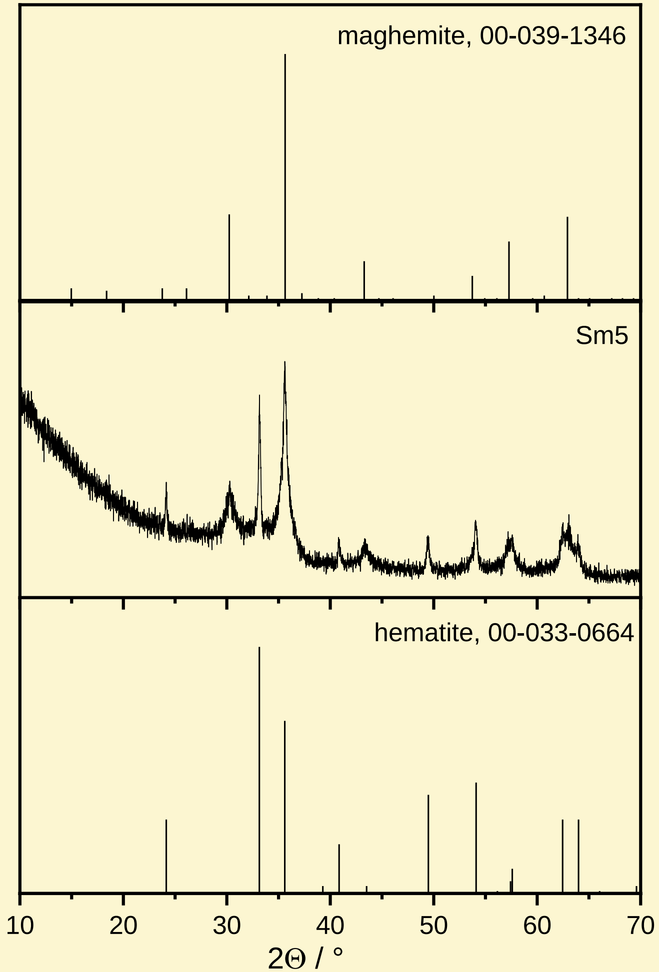


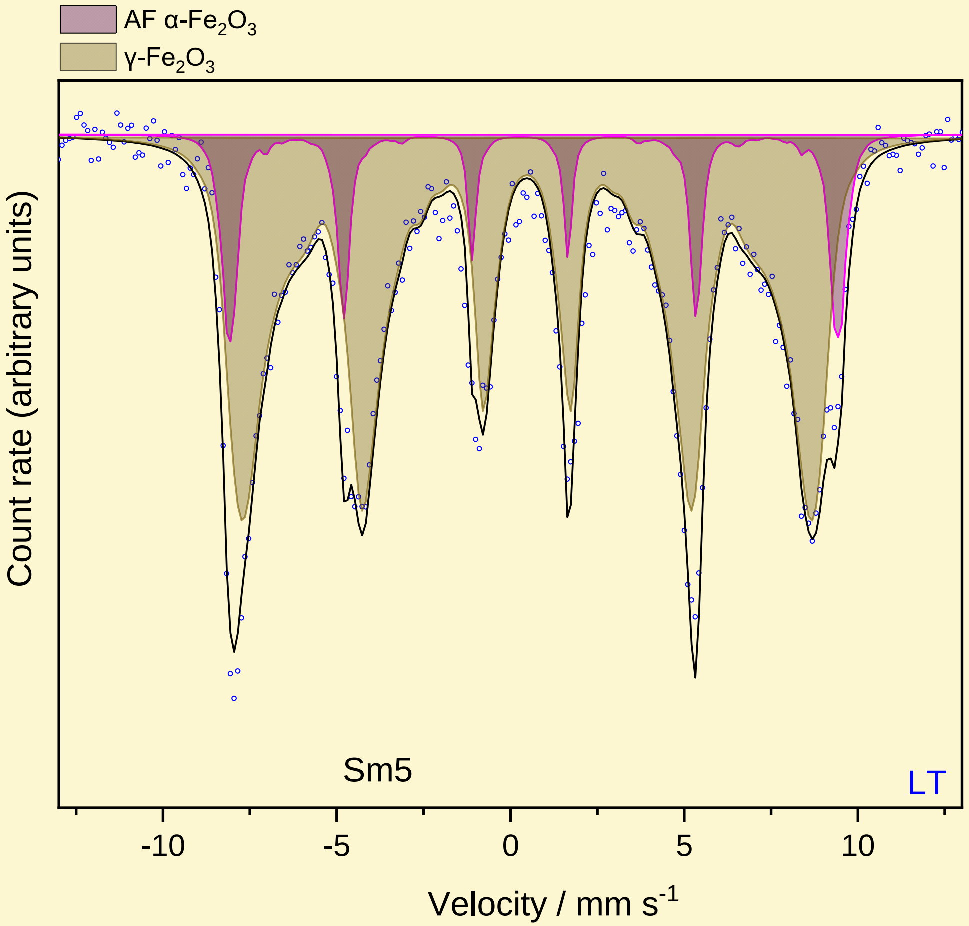


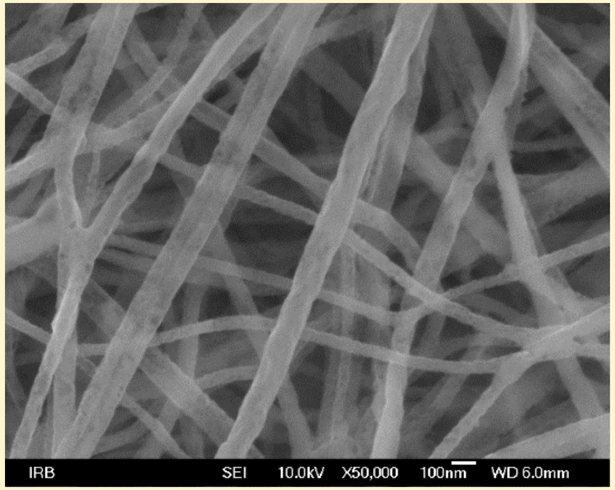


Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 5	sextet	0.37(f)	-0.18	51.2*	0.19	10.7	WFM α-Fe_2O_3
	sextet	0.37(f)	0.40(f)	51.8	0.39	6.1	AF α-Fe_2O_3
	sextet	0.33(f)	0.00(f)	30.1*	0.31	44.6	medium γ-Fe_2O_3
	doublet	0.33	0.86	-	0.79	38.7	nano γ-Fe_2O_3

Sm5



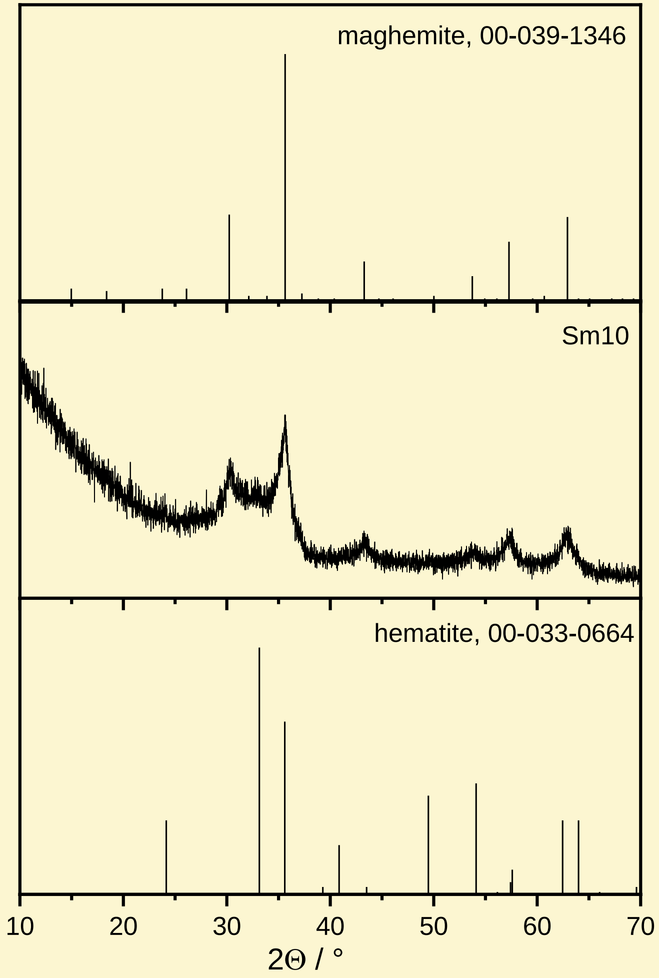


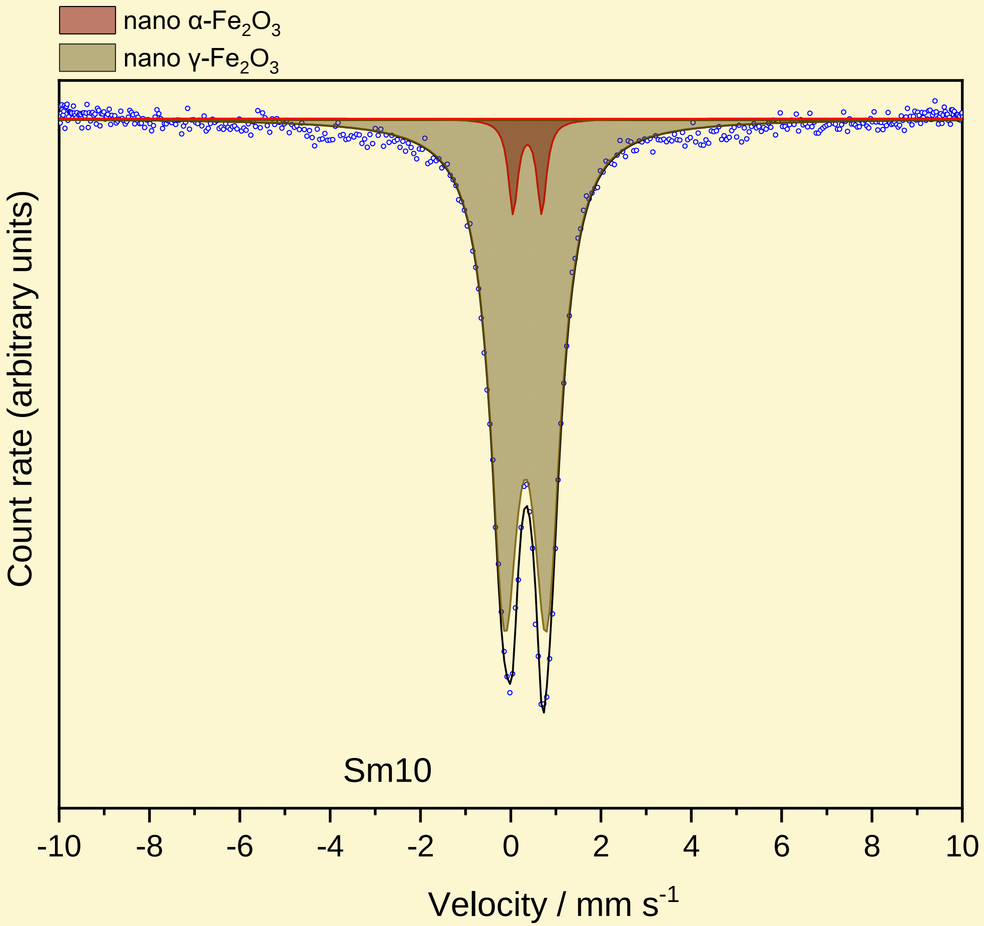


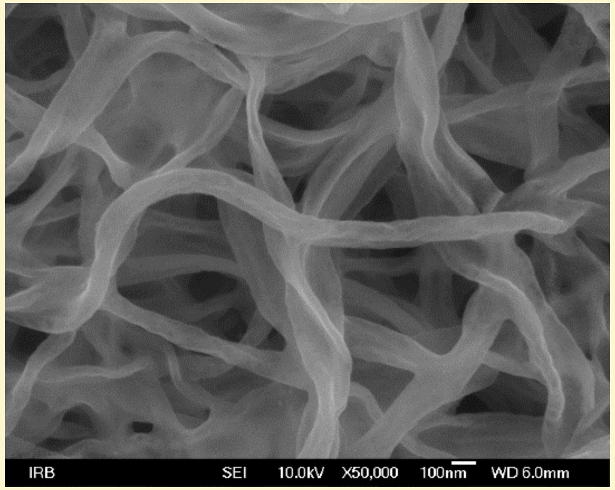
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm5	sextet	0.47(f)	0.40(f)	53.5*	0.24	16.9	AF α-Fe_2O_3
	sextet	0.48(f)	0.00(f)	46.7*	0.53	83.1	γ-Fe_2O_3

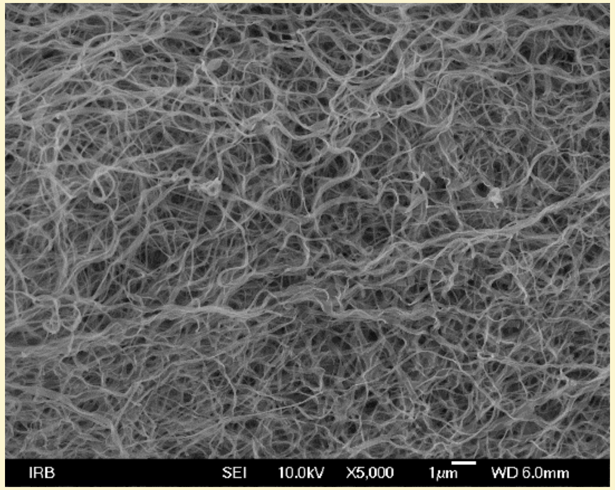
Sm10

BET→surface area:
64.2848 ± 0.4187





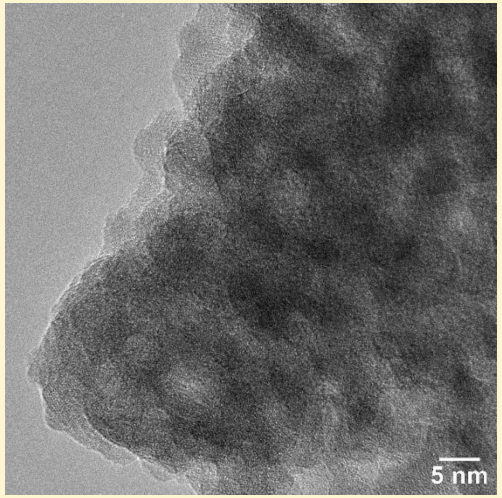


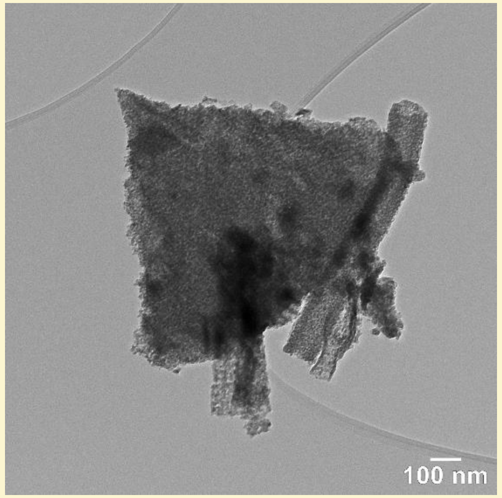


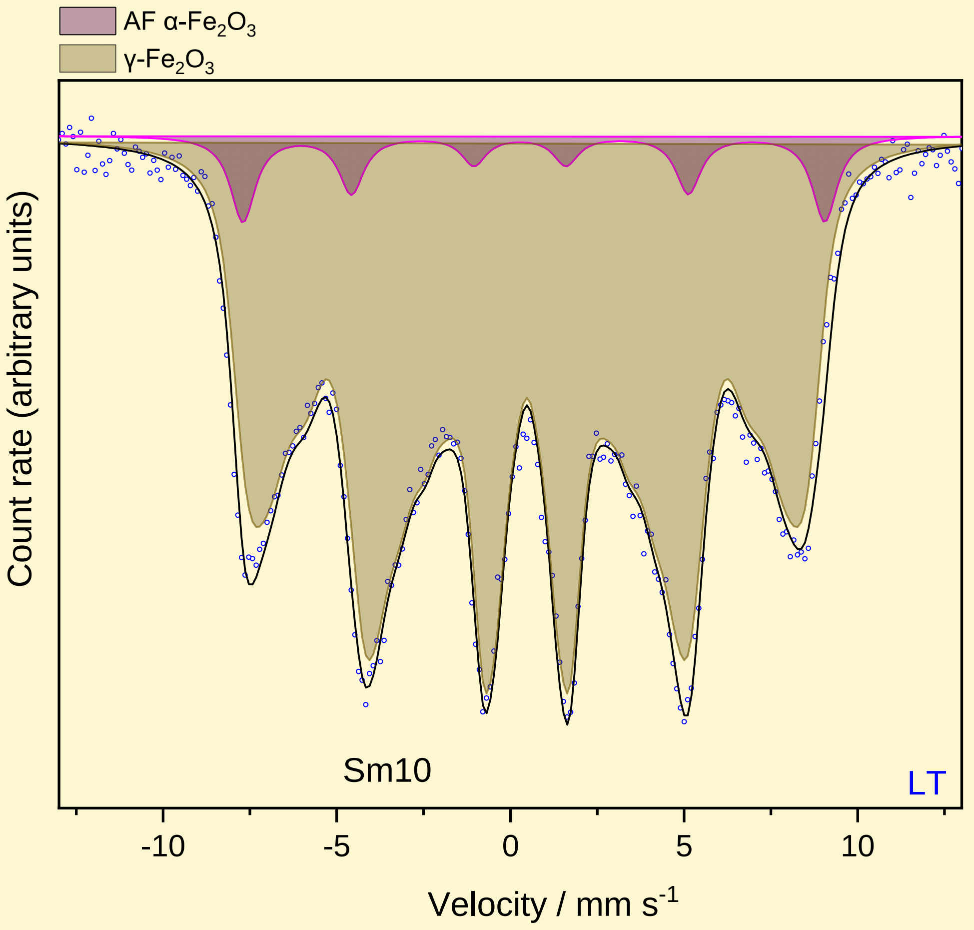
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 10	doublet	0.37(f)	0.63	-	0.26	6.5	nano α-Fe_2O_3
	doublet	0.33	0.93	-	0.76	93.5	nano γ-Fe_2O_3

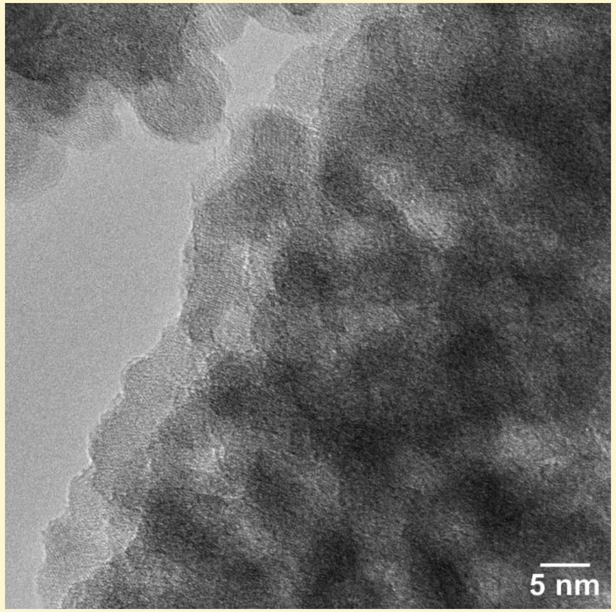
Sm10

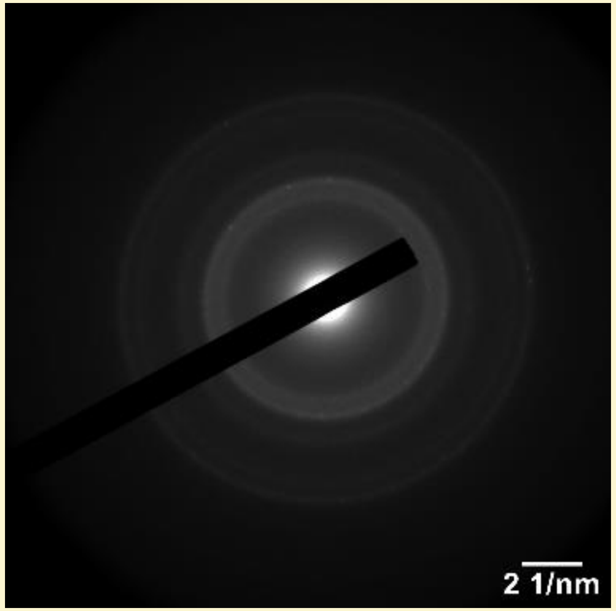
BET→surface area:
64.2848 ± 0.4187 m^2/g





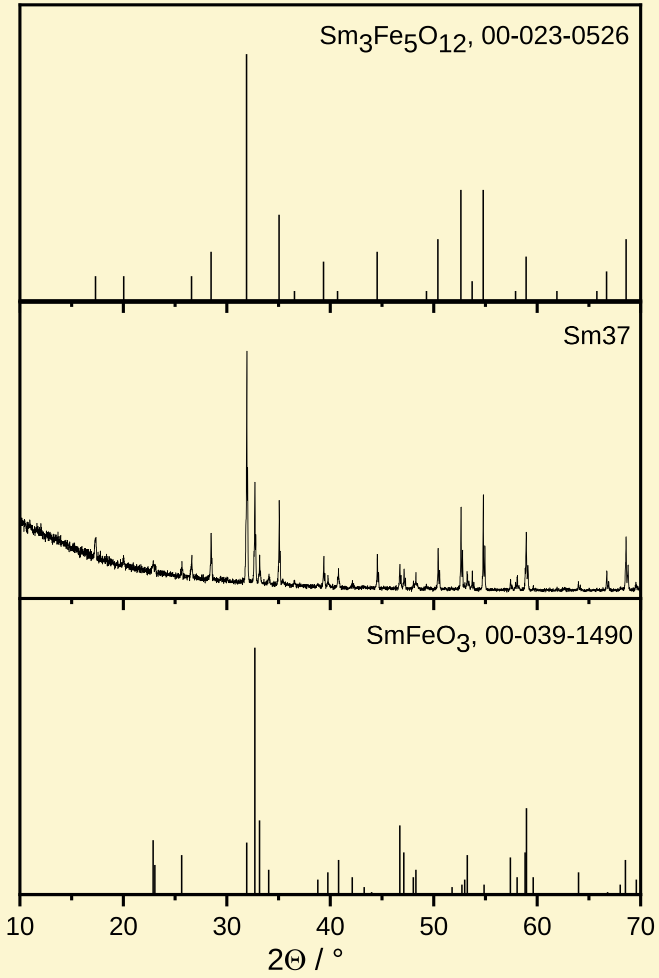


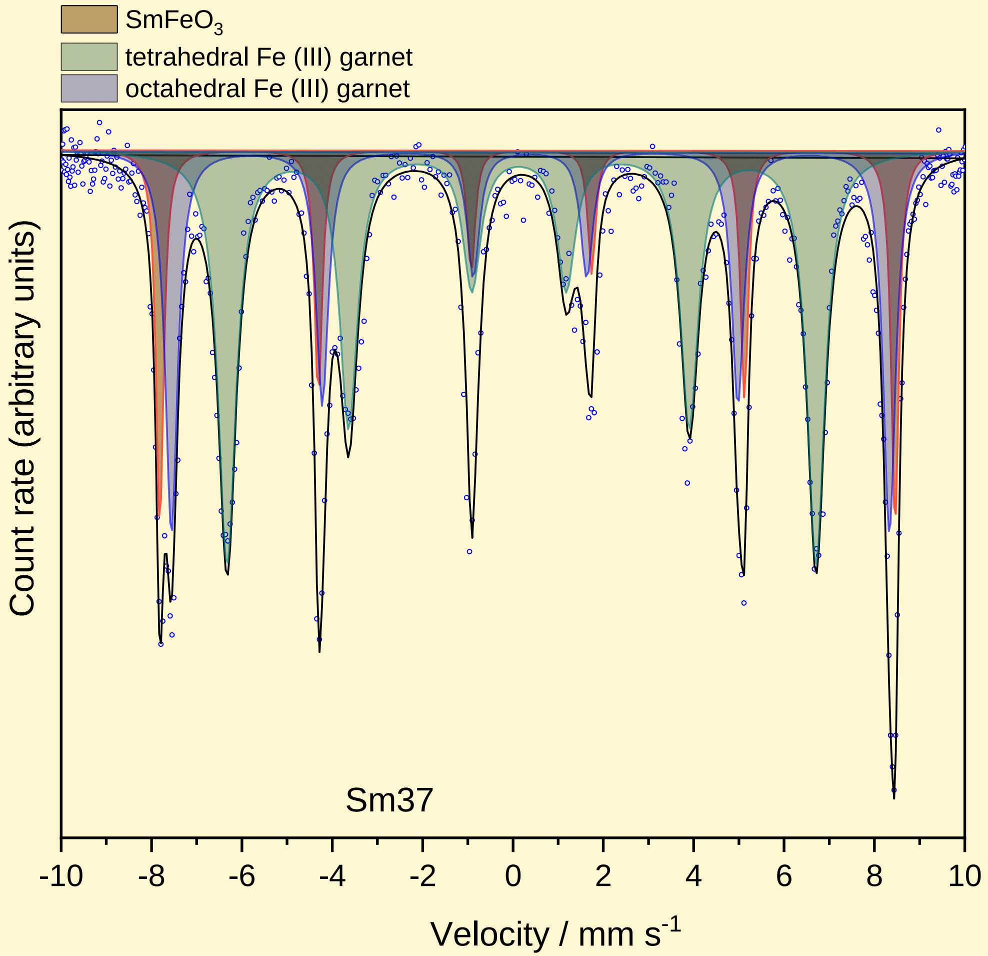


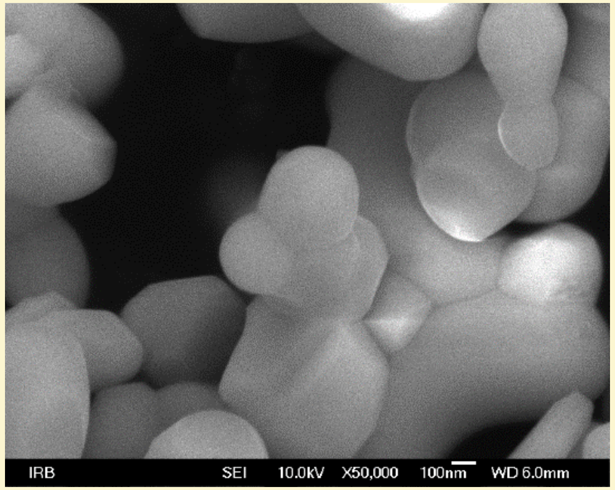


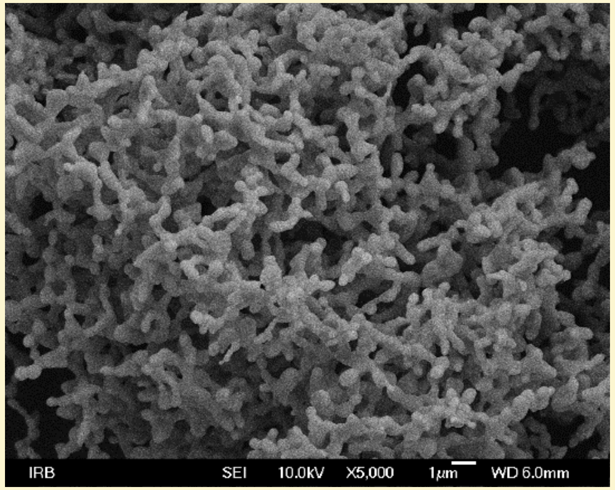
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm10	sextet	0.47(f)	0.40(f)	52.1	0.87	6.5	AF α-Fe_2O_3
	sextet	0.48(f)	0.00(f)	36.57*	0.72	93.5	γ-Fe_2O_3

Sm37



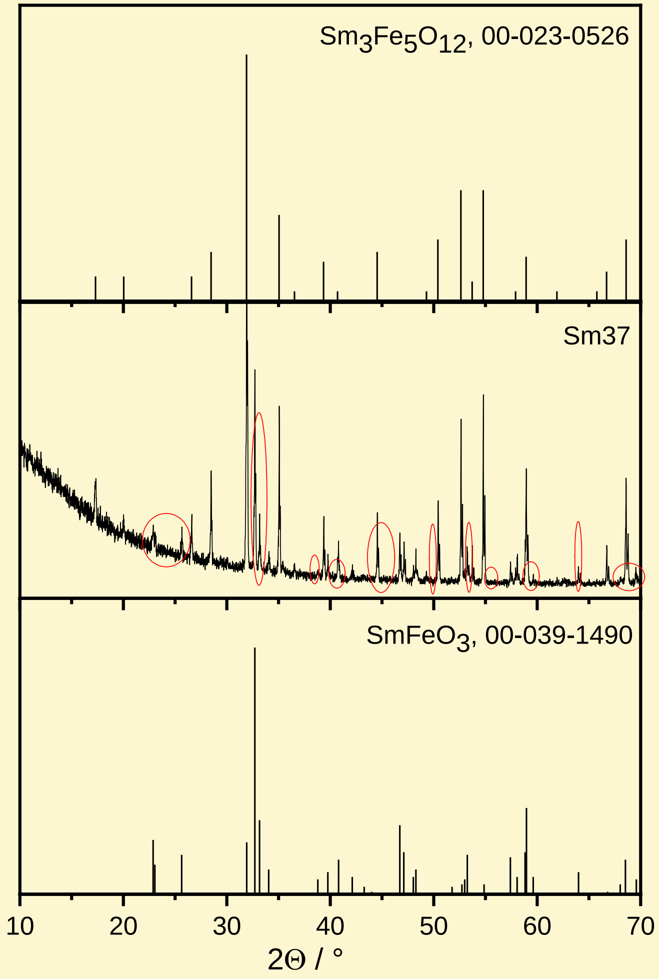


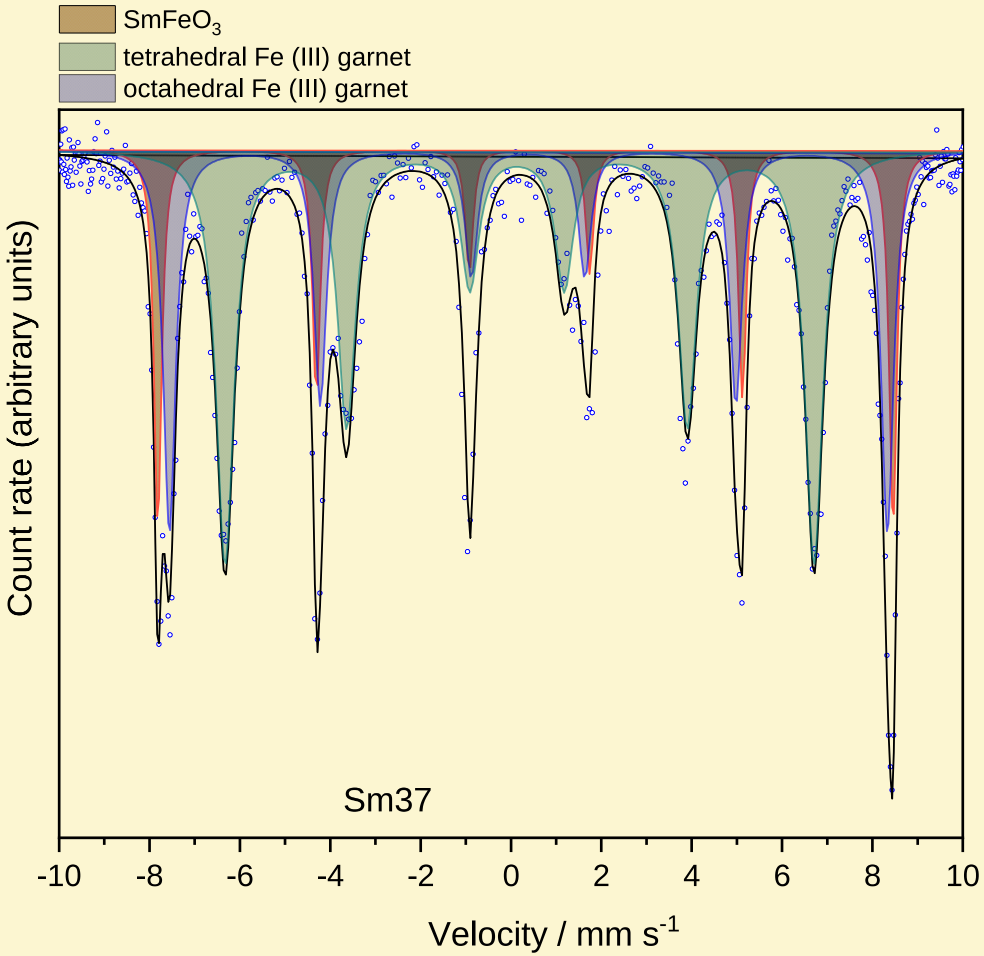


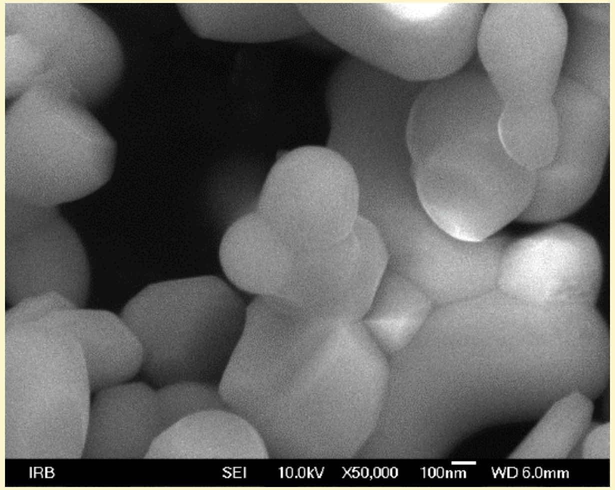


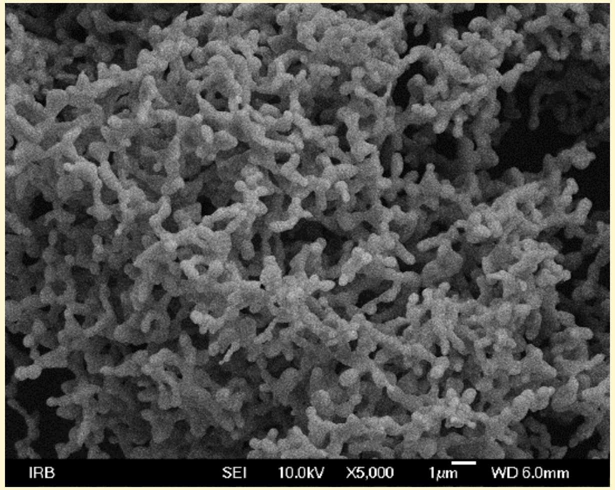
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 37	sextet	0.38	0.01	49.4	0.33	31.6	^{VI}Fe(III) in $Sm_3Fe_5O_{12}$ (O)
	sextet	0.16	0.06	40.5	0.49	49.4	^{IV}Fe(III) in $Sm_3Fe_5O_{12}$ (T)
	sextet	0.36	-0.09	50.6	0.21	19.0	$SmFeO_3$

Sm37







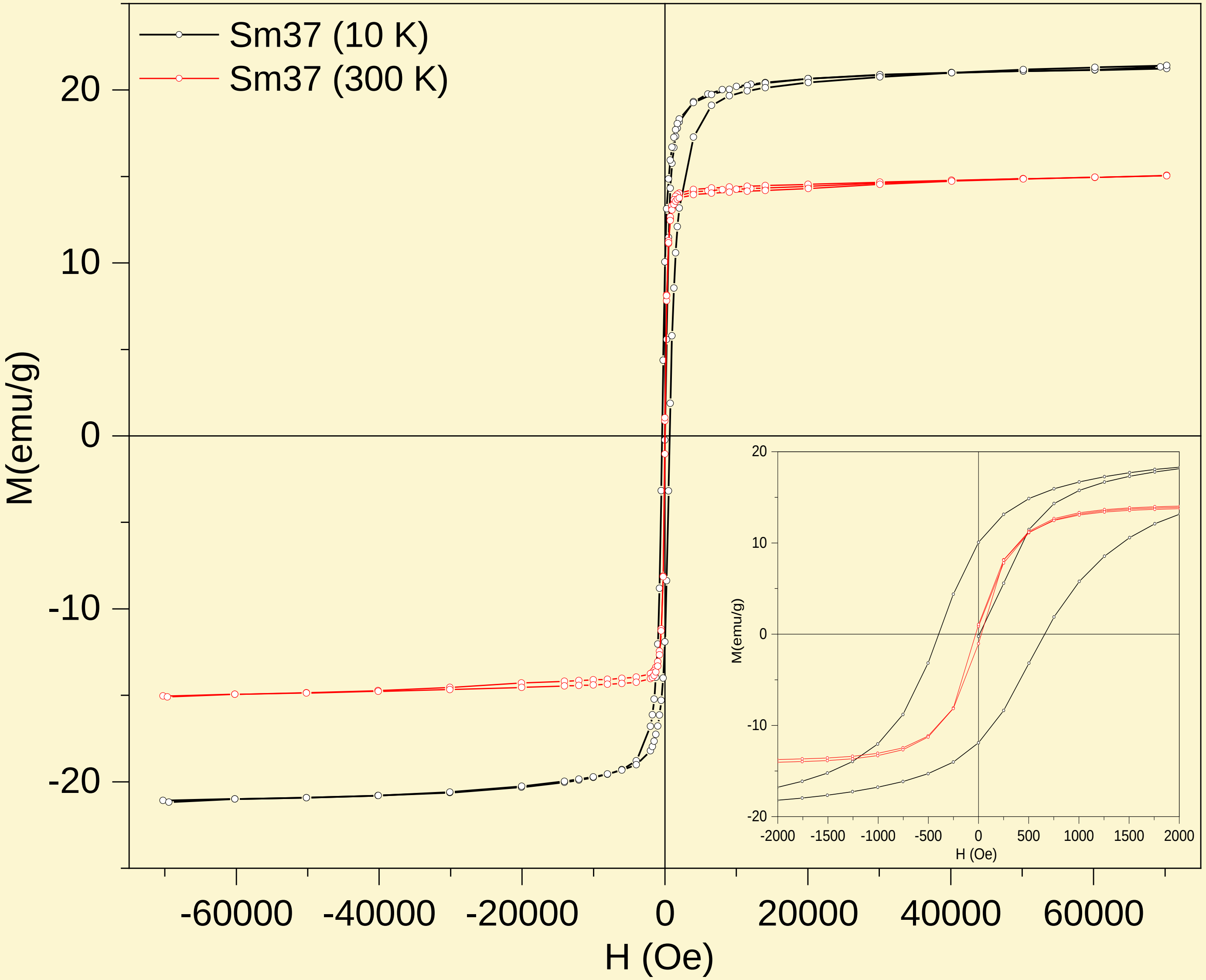


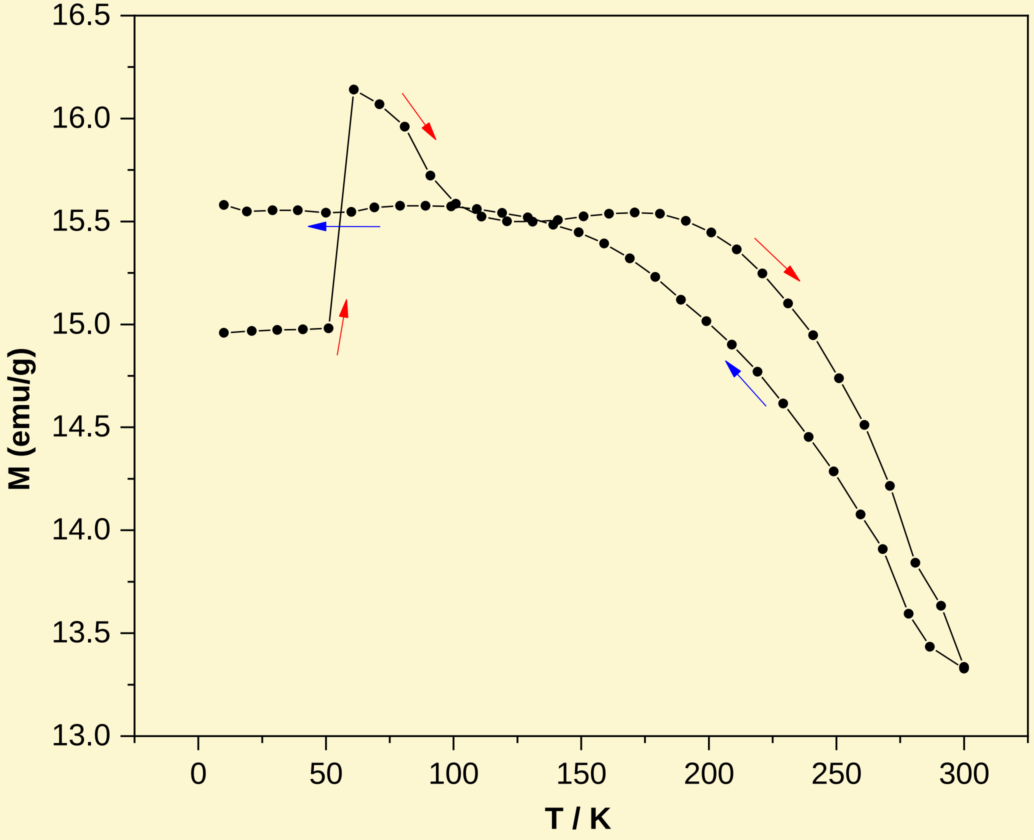
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm 37	sextet	0.38	0.01	49.4	0.33	31.6	^{VI}Fe(III) in $Sm_3Fe_5O_{12}$ (O)
	sextet	0.16	0.06	40.5	0.49	49.4	^{IV}Fe(III) in $Sm_3Fe_5O_{12}$ (T)
	sextet	0.36	-0.09	50.6	0.21	19.0	$SmFeO_3$

Sm37

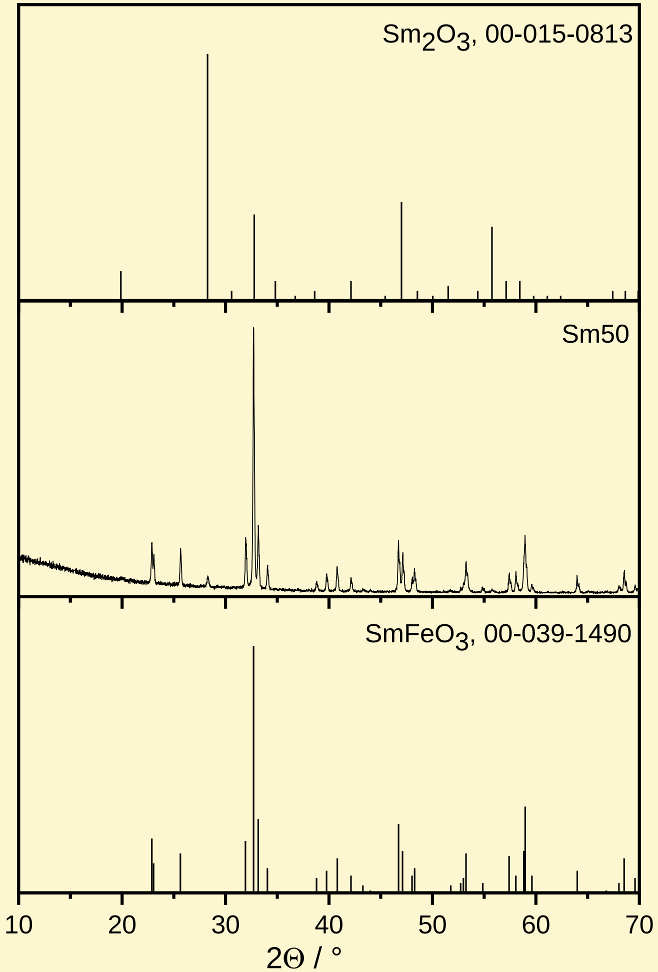
magnetic measurements

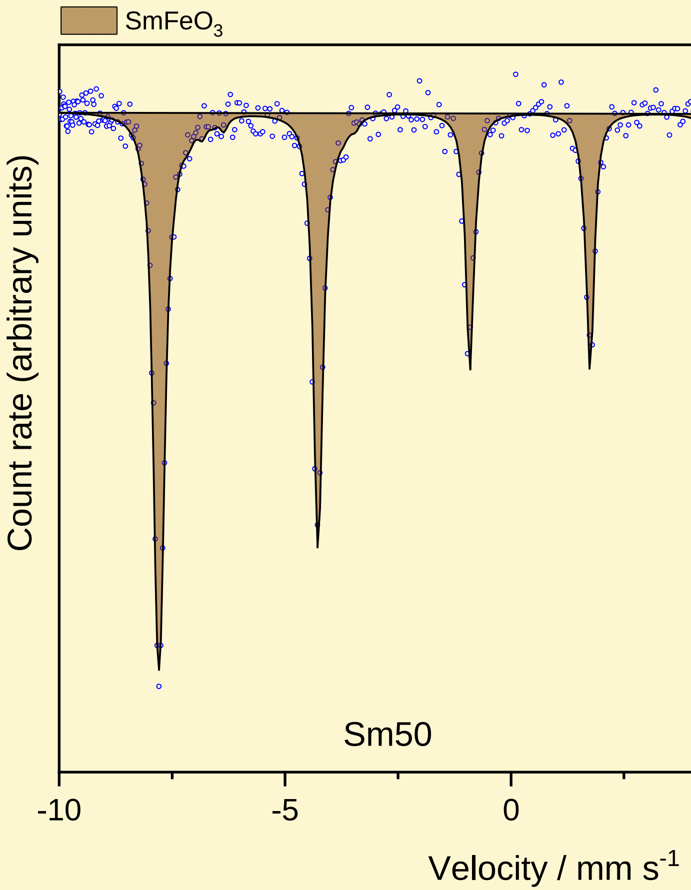
T / K	H_c /Oe	M_r / emu g^{-1}	M_s/ emu g^{-1}
	coercivity	saturation remanence	saturation magnetization at 7 T
10	396.7	10.1	21.2
300	28.7	1.1	15.0

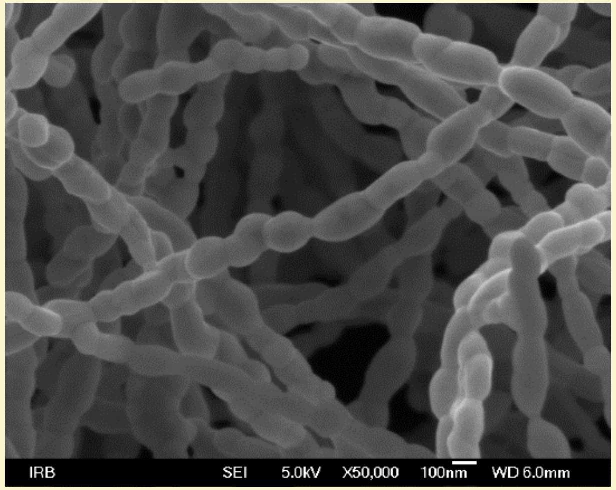


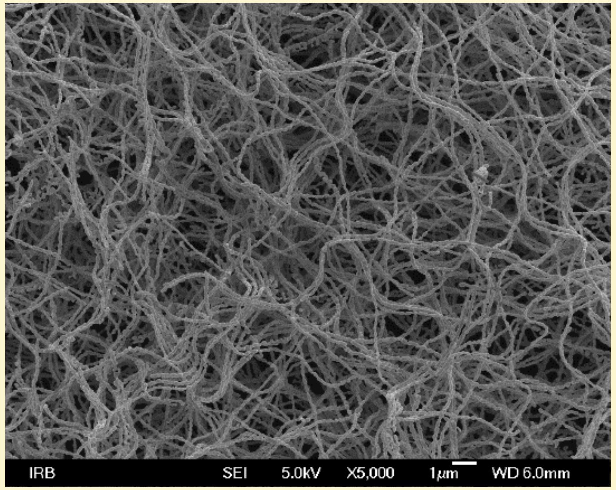


Sm50



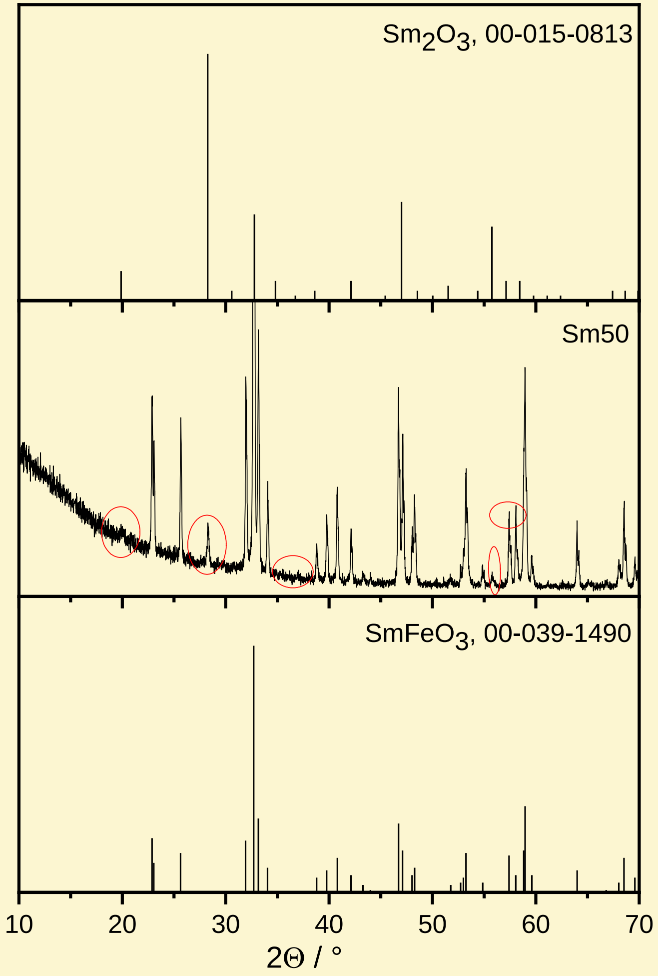


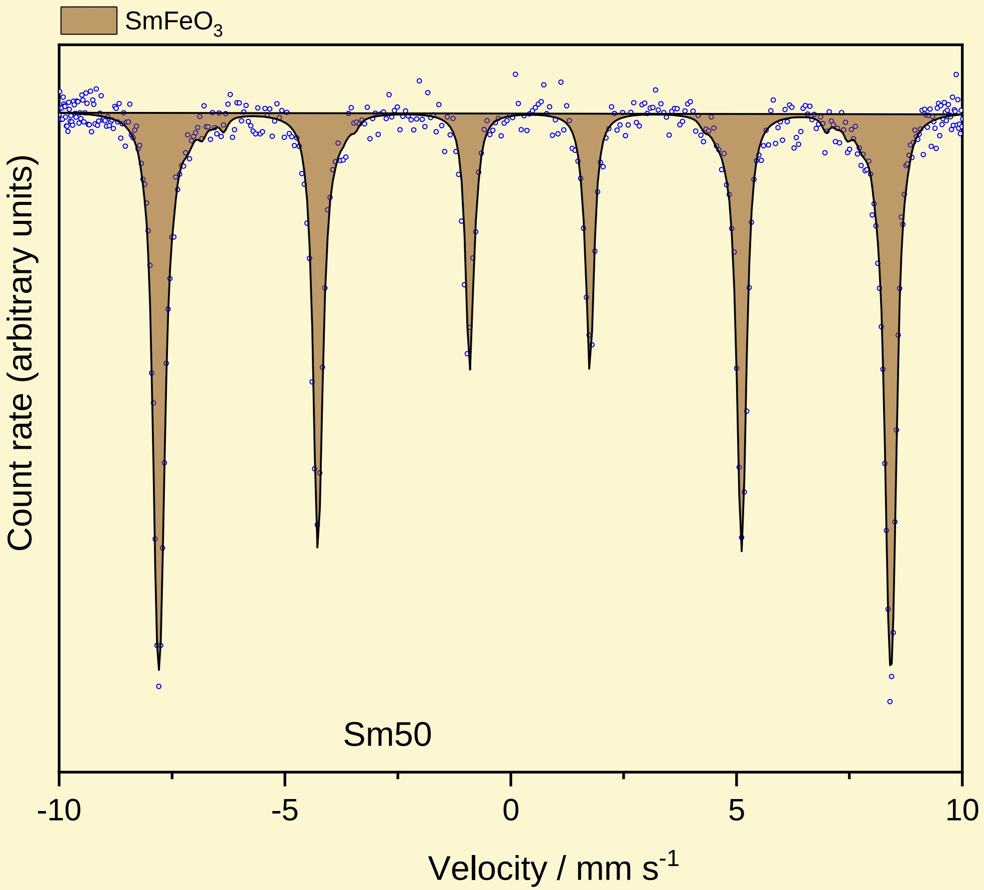


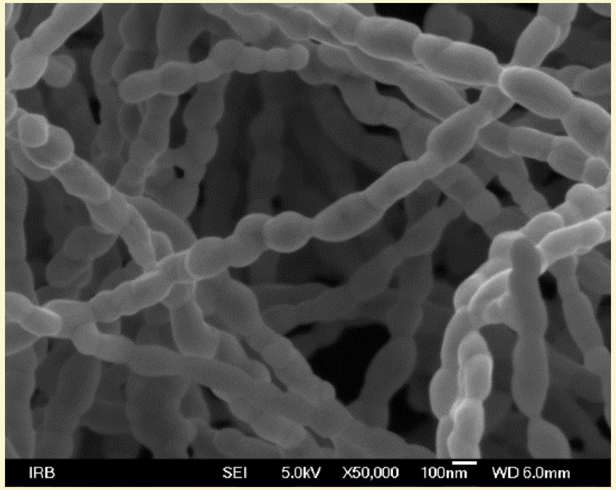


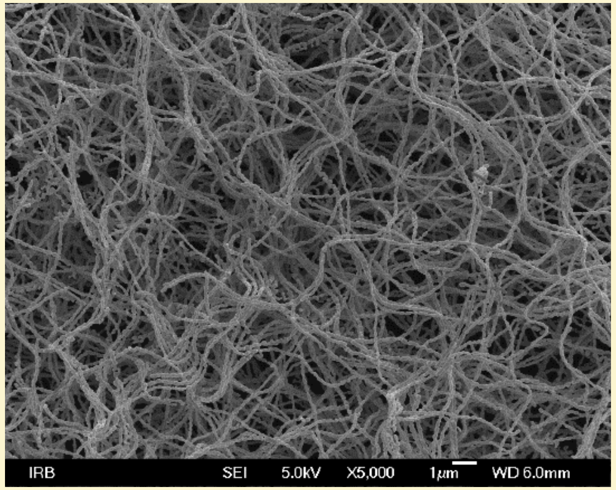
Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm50	sextet	0.37	-0.11	49.9*	0.20	100.0	$SmFeO_3$

Sm50



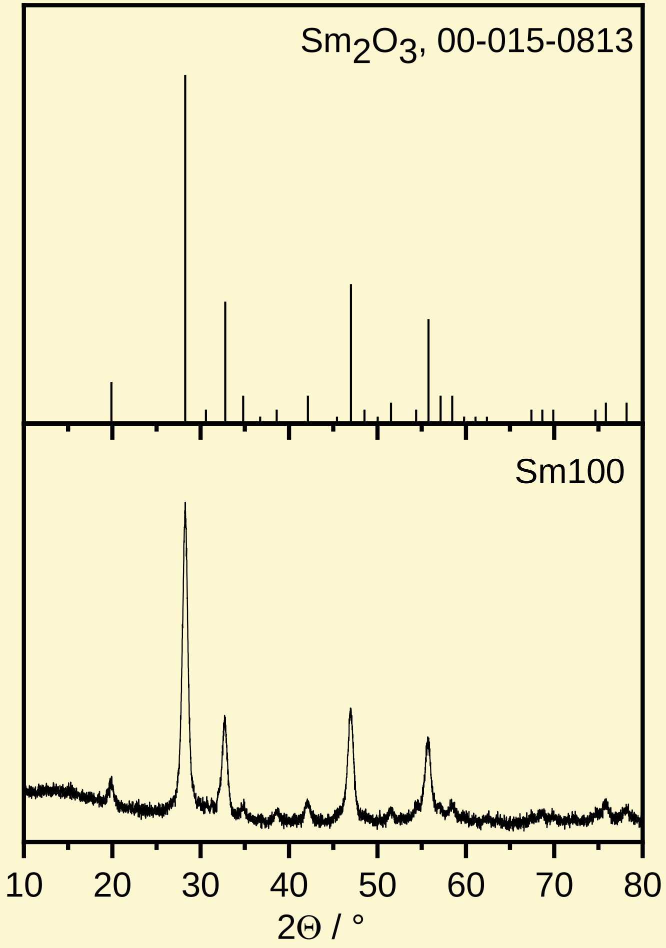




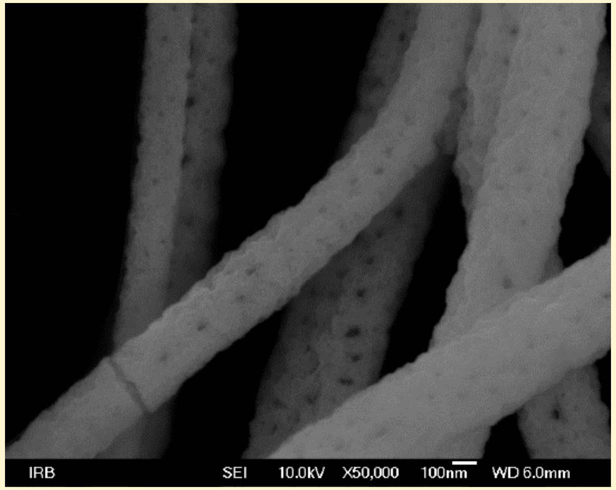


Sample	Spectral component	δ (mm s^{-1})	2ε or Δ (mm s^{-1})	$\langle B_{hf} \rangle$ (T)	Γ (mm s^{-1})	Area (%)	Phase
Sm50	sextet	0.37	-0.11	49.9*	0.20	100.0	SmFeO$_3$

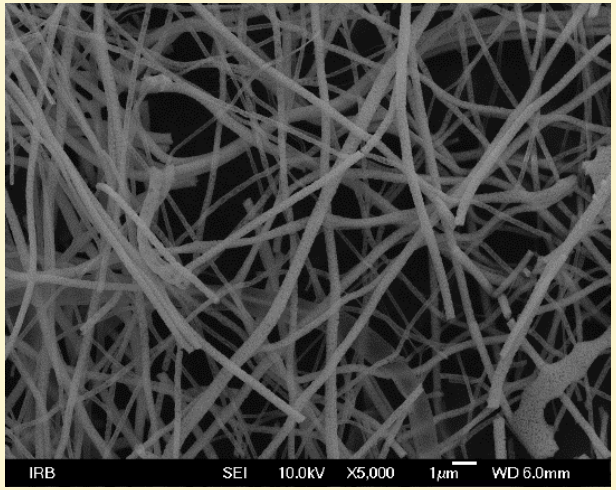
Sm100



Sm_2O_3, 00-015-0813
Sm100
10 20 30 40 50 60 70 80
2Θ / °



IRB SEI 10.0kV X50,000 100nm WD 6.0mm



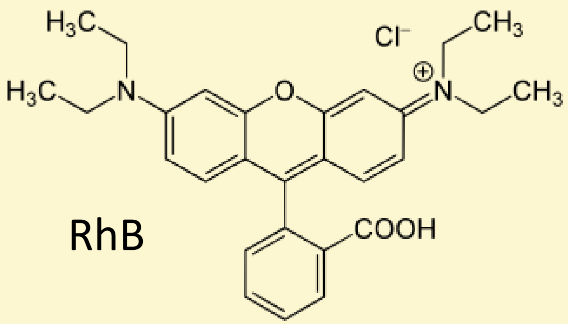
IRB SEI 10.0kV X5,000 1µm WD 6.0mm

Sm series
Composition

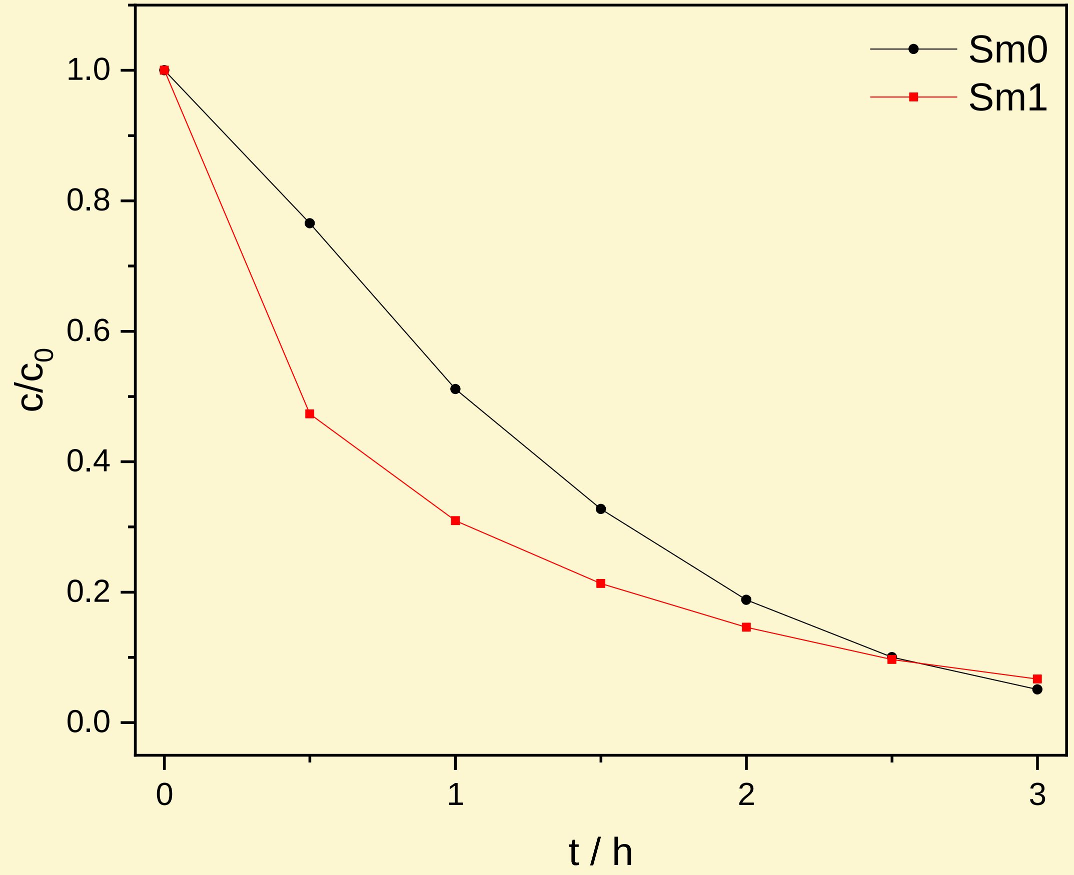
Sample	Phase composition
Sm0	hematite
Sm1	hematite (+3.5% maghemite)
Sm3	hematite + maghemite
Sm5	hematite + maghemite
Sm10	maghemite + hematite
Sm37	garnet + orthoferrite (19%)
Sm50	orthoferrite + samarium oxide
Sm100	samarium oxide

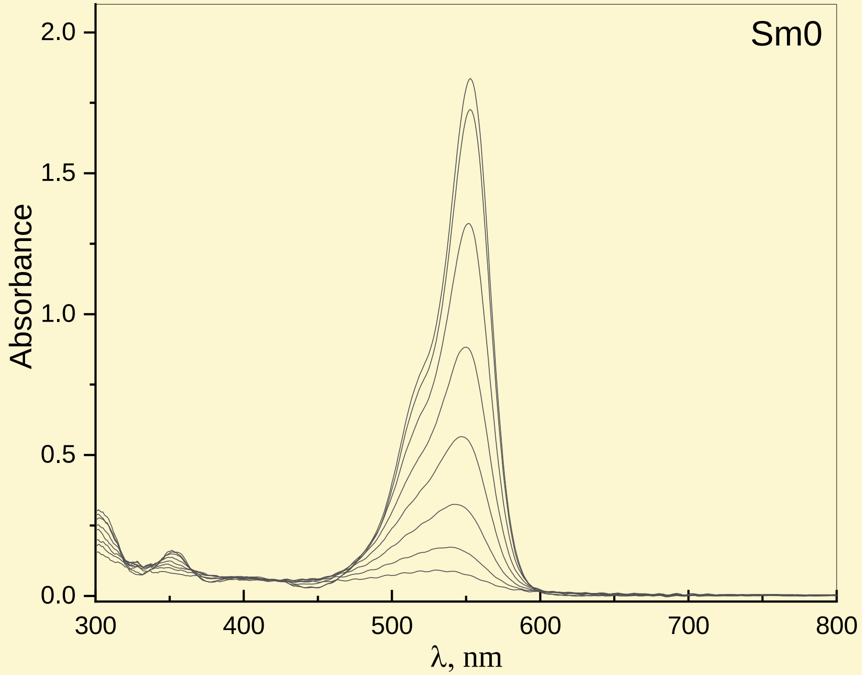
Sm series

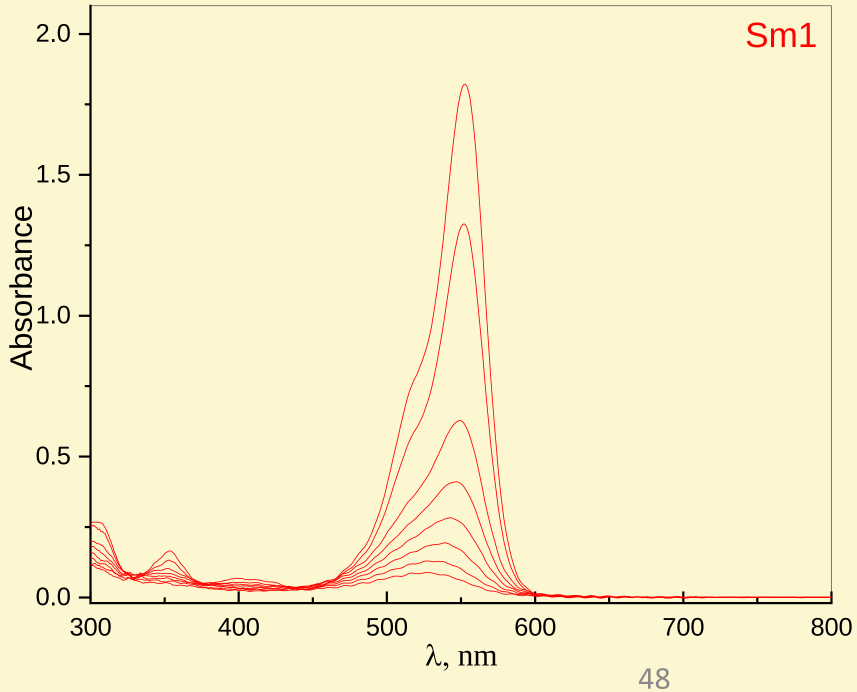
Potential applications



Preliminary results in photocatalysis







Conclusion

Concept

- XRD
- FE SEM
- Mössbauer
- Photocatalysis

Conclusion

XRPD results

- RE affected the phase composition drastically

- With increasing RE content:

  a) XRD lines broadening

  b) maghemite fraction gradually increased

- Samples were not very crystalline in general

Conclusion

FE SEM

- Fibres morphology can be preserved if composite fibres are calcinated at relatively low temperatures 600-900°C

- Garnet samples lost fibre morphology (sintering)

- According to FE SEM fibers had on average 50-200 nm in cross-section

Conclusion

Mössbauer

- Mössbauer was ~~very useful~~ **essental** for
- A) amorphous sample analysis
- B) magnetic properties

- Sm3 → antiferromagnetic hematite

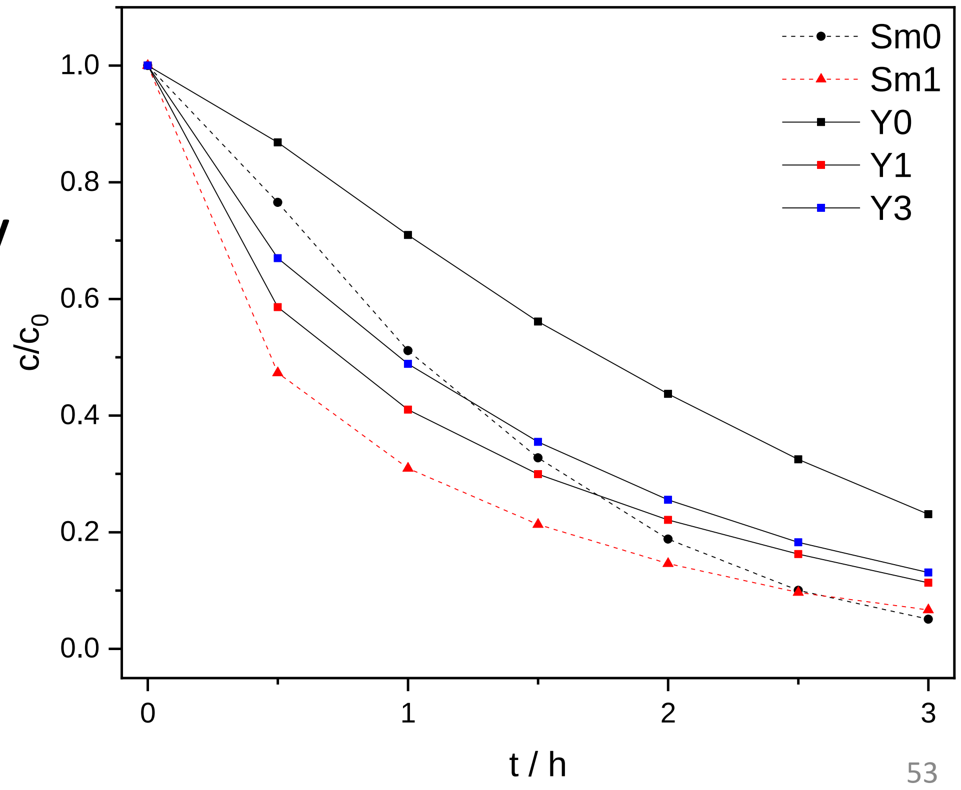
Conclusion

Photocatalysis-preliminary results

Doped samples→better results

- Sm1 shown better photocatalytic activity compared to Sm0

- Y1 shown better photocatalytic activity compared to Y3 and Y0



Conclusion

in general

- higher RE content (RE0-RE10)

→higher maghemite content (nano size)

- Various oxides are prepared by simple method,
  only by varying the RE:Fe ratio
  (hematite, maghemite, orthoferrites, garnets, RE oxides)

- Garnets and orthoferrites synthesized were not pure (contamination)

- Preliminary tests- samples are useful in photocatalysis

- Samarium can also increase Morin transition temperature (besides platinum group)

Thanks

→ my research group

- Svetozar Musić and Stjepko Krehula-mentoring and leadership
- Mira Ristić-the project idea
- Nina Popov-moral support and experience exchange

Special thanks

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→Petre Badica, Andrei Alexandru-Dinu, Andrei Kuncser

- I wish to thank colleagues in Hungary on low-temperature Mössbauer measurements:

→Zoltán Homonnay, Ernő Kuzmann

Special thanks

…to my office colleague Nikol Bebić for the magnetic experiments shown on the right

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Thank you for your kind attention!!