Preparation, characterization and application of magnetic sorbents based on the CeO_2/Fe_2O_3

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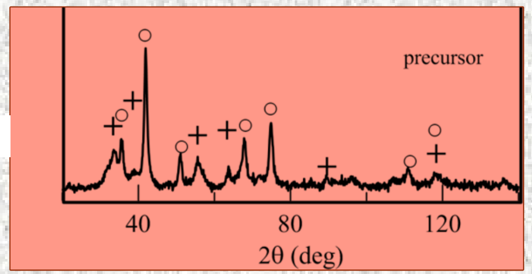
Outline

- **Introduction of research team**
- **Motivation**
- **CeO_2/Fe_2O_3 sorbents**
  - Preparation
  - Applications
  - Microstructure
  - Mössbauer spectroscopy
  - Magnetic measurements

Introduction of research team

Dr. Yvonna Jirásková, Dr. Jiří Buršík
Institute of Physics of Materials ASCR Brno

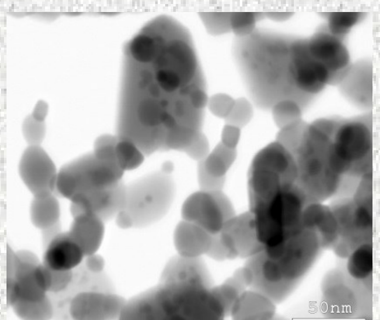
X-ray diffraction (XRD)



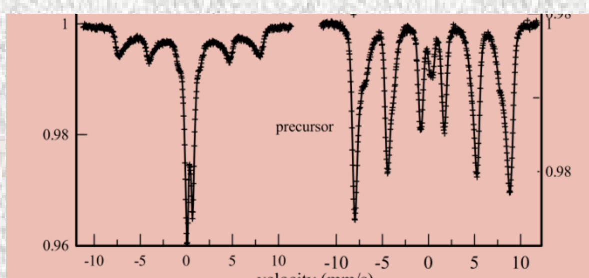
prof. Pavel Janoš
University of J. E. Purkyně
Ústí nad Labem

Sorbent preparation,
chemical analysis and applications

Scanning and transmission
electron microscopy
(SEM, TEM)



Room- and low-temperature
transmission Mössbauer
spectroscopy



prof. Jiří Luňáček
VŠB-TU Ostrava

Room- and
low-temperature
magnetic properties
(VSM, PPMS)

Motivation

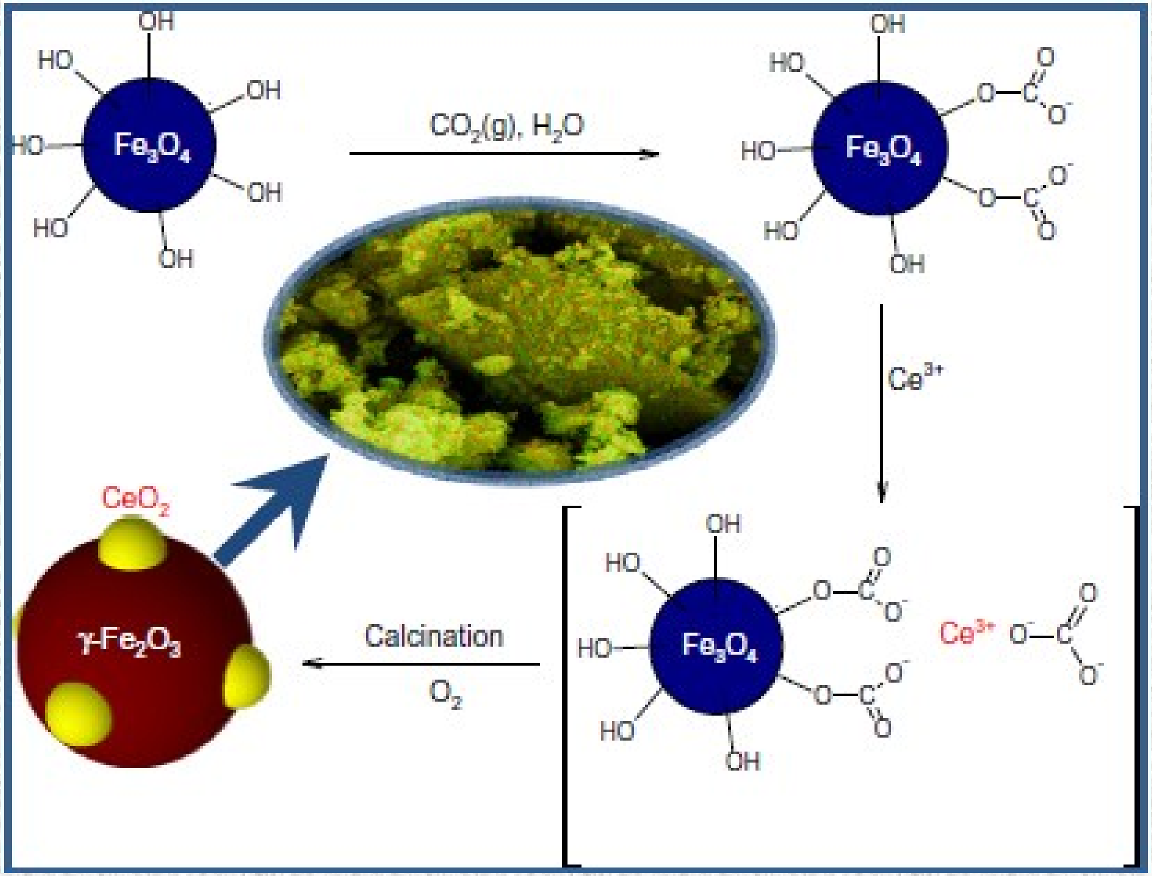
Iron oxides (magnetite – Fe_3O_4, hemätite – α-Fe_2O_3, maghemite – γ-Fe_2O_3):

- use as nanomaterials, easy availability, low-cost production
- minimization into nanometer dimensions – new materials with various applications, e.g. in drug delivery, manipulation of biological objects, removal of industrial pollutants from water, gas sensors, mixed oxides, etc.

Cerium dioxide (CeO_2):

- biomedical and pharmacological use, porous glass-ceramics, enhance thermal stability of pure oxides
- in a form of nanoparticles – RT ferromagnetic behaviour
- exchange interactions between localized electron spin moments resulting from the oxygen vacancies at the surface of nanograins

Sorbent preparation



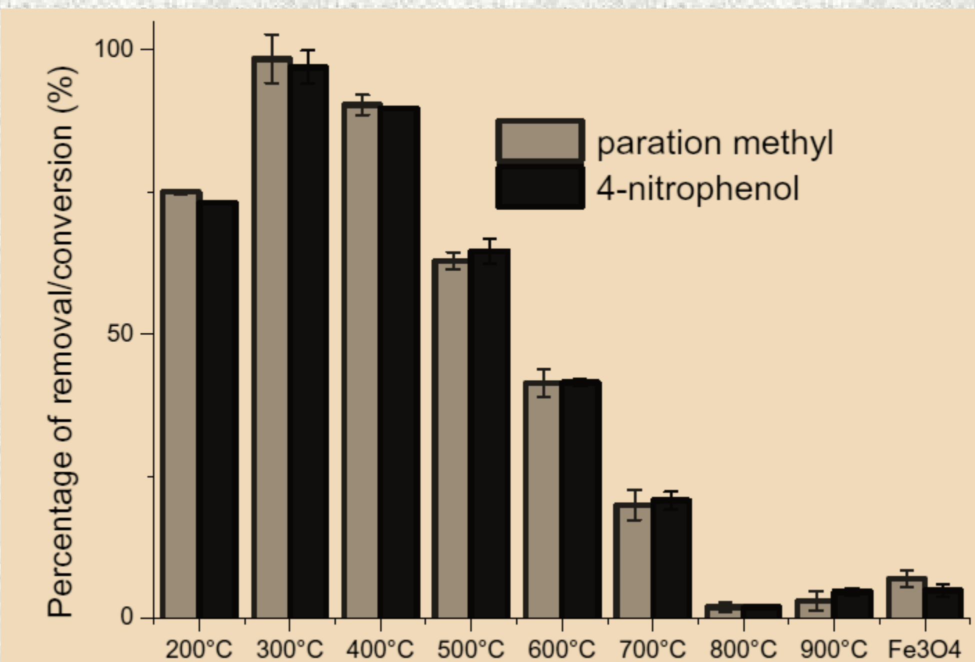
Magnetite core prepared by reversed co-precipitation method:

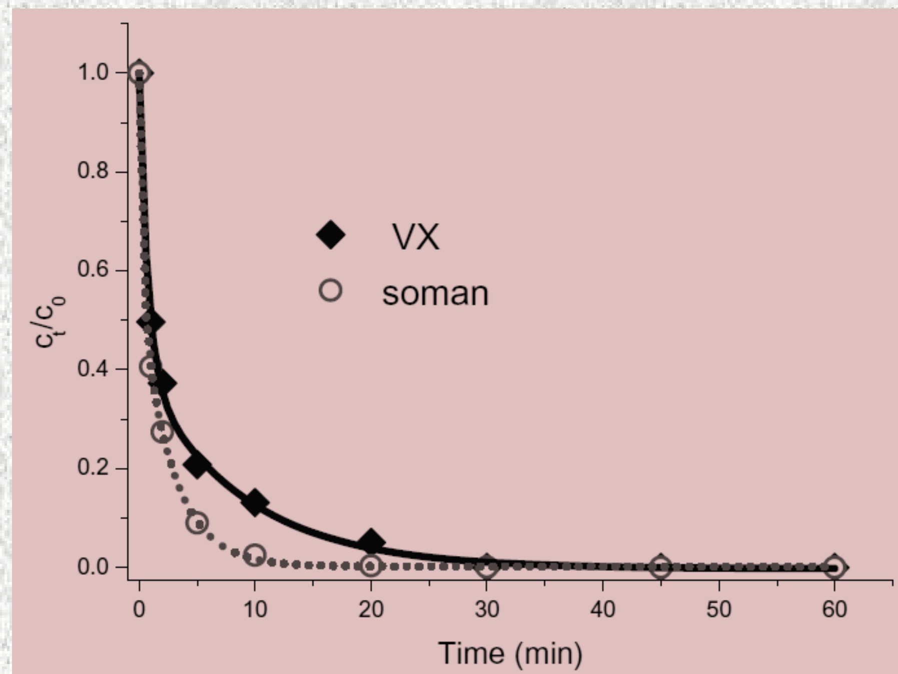
- Fe^{2+}/Fe^{3+} salts mixed with aqueous ammonia
- gaseous CO_2 introduced until the PH dropped to 7.5
- magnetite grains coated with cerium carbonate, separated using a permanent magnet, washed with deionised water and dried at 105 °C
- reactive sorbents prepared by calcination in a muffle furnace for 2 h at **temperatures ranging from 573K to 1173K**

Sorbent applications

- degradation of paration methyl in organic solvent heptan
- degradation product – 4-nitrophenol

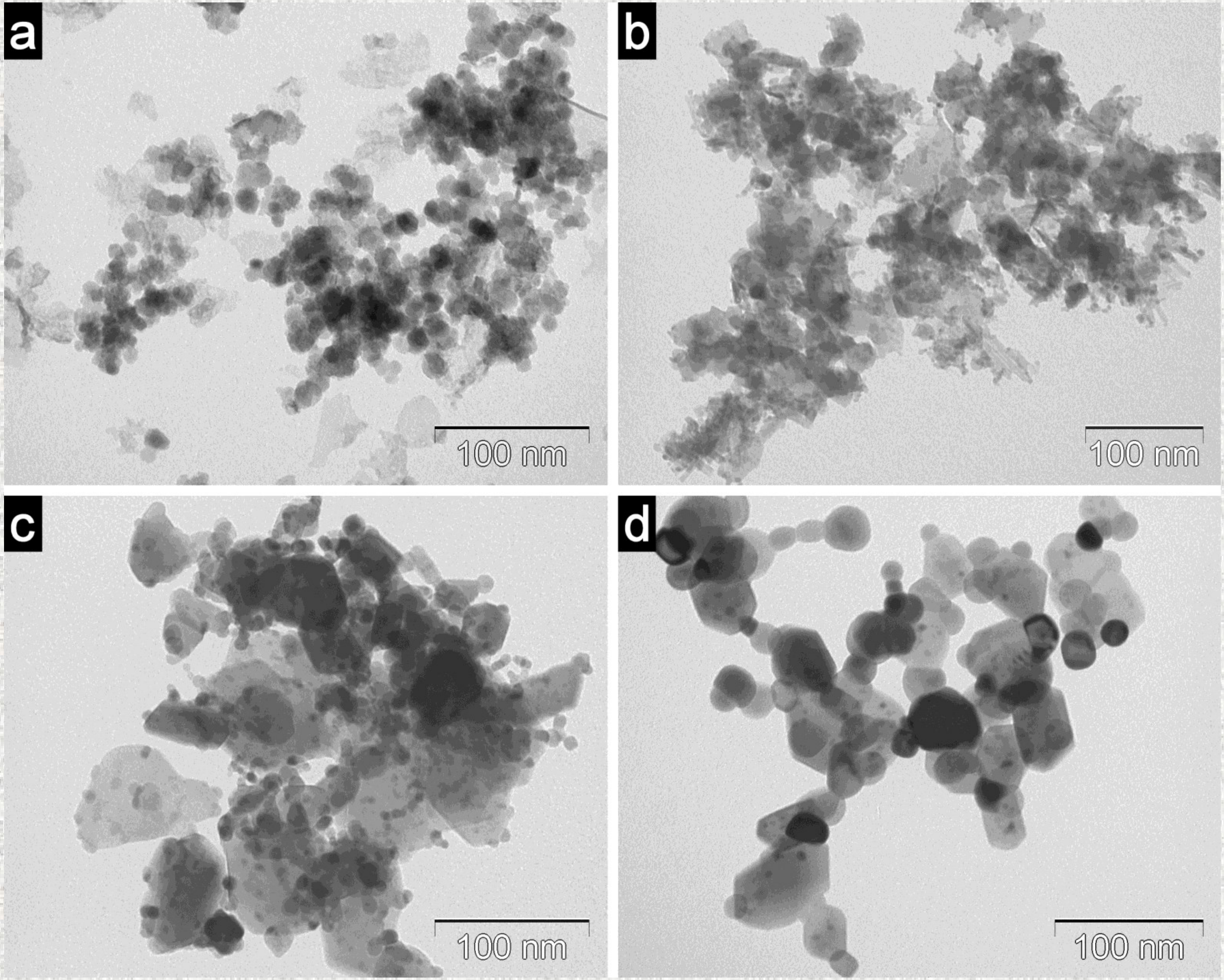
- degradation of dangerous nerve agents using the 300 °C annealed sorbent, reactions performed in nonane





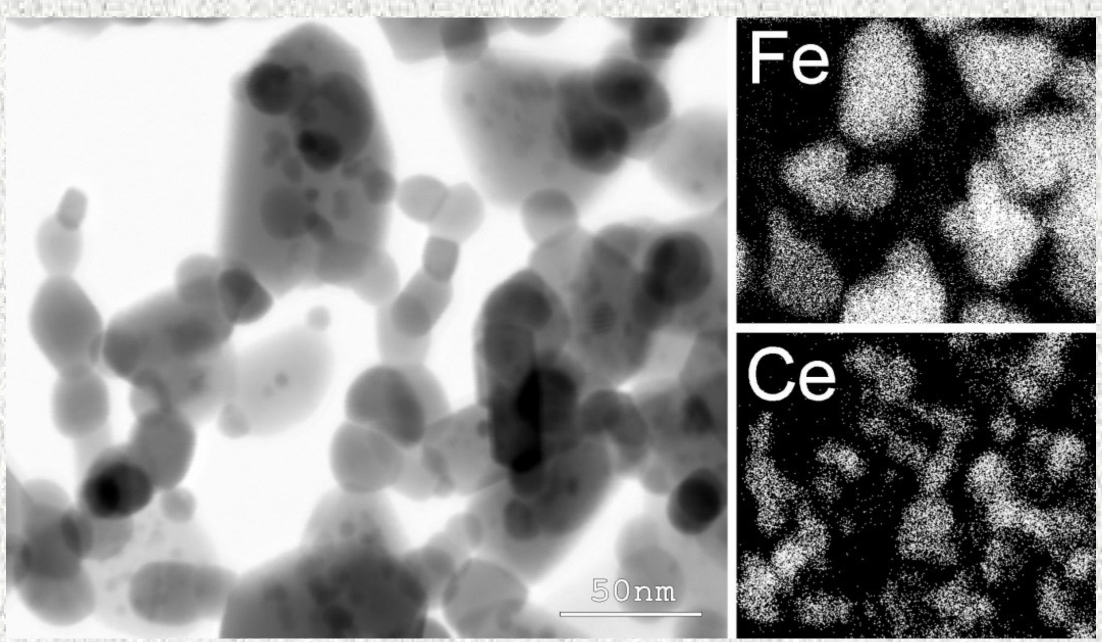
Microstructure - TEM

Pre-cursor **773K**

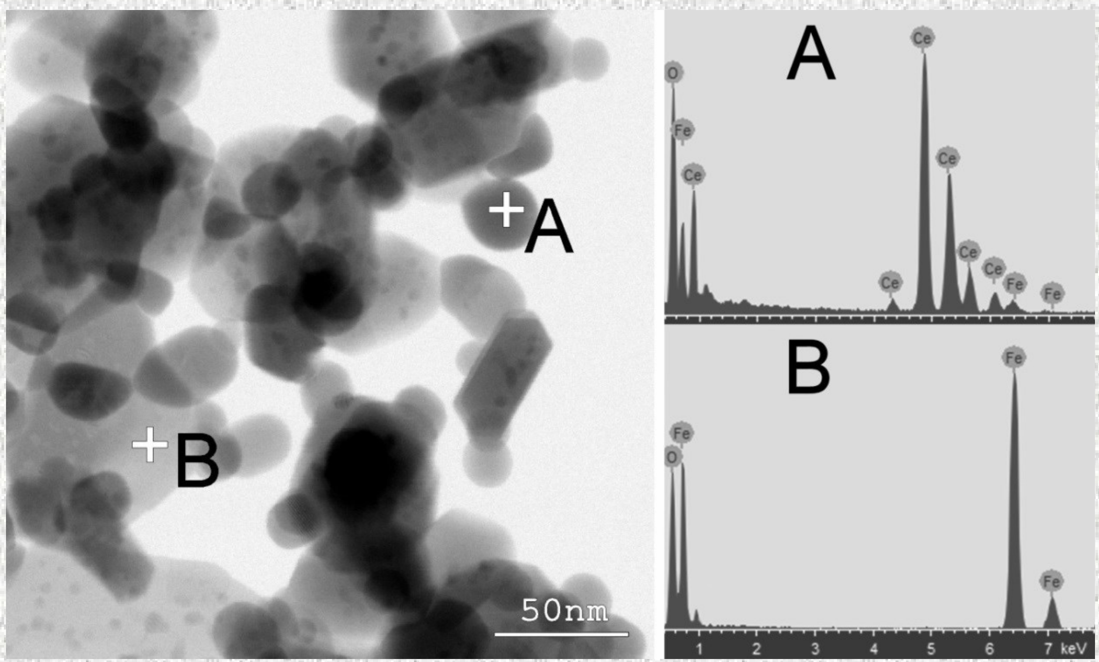


873K **973K**

Microstructure - TEM

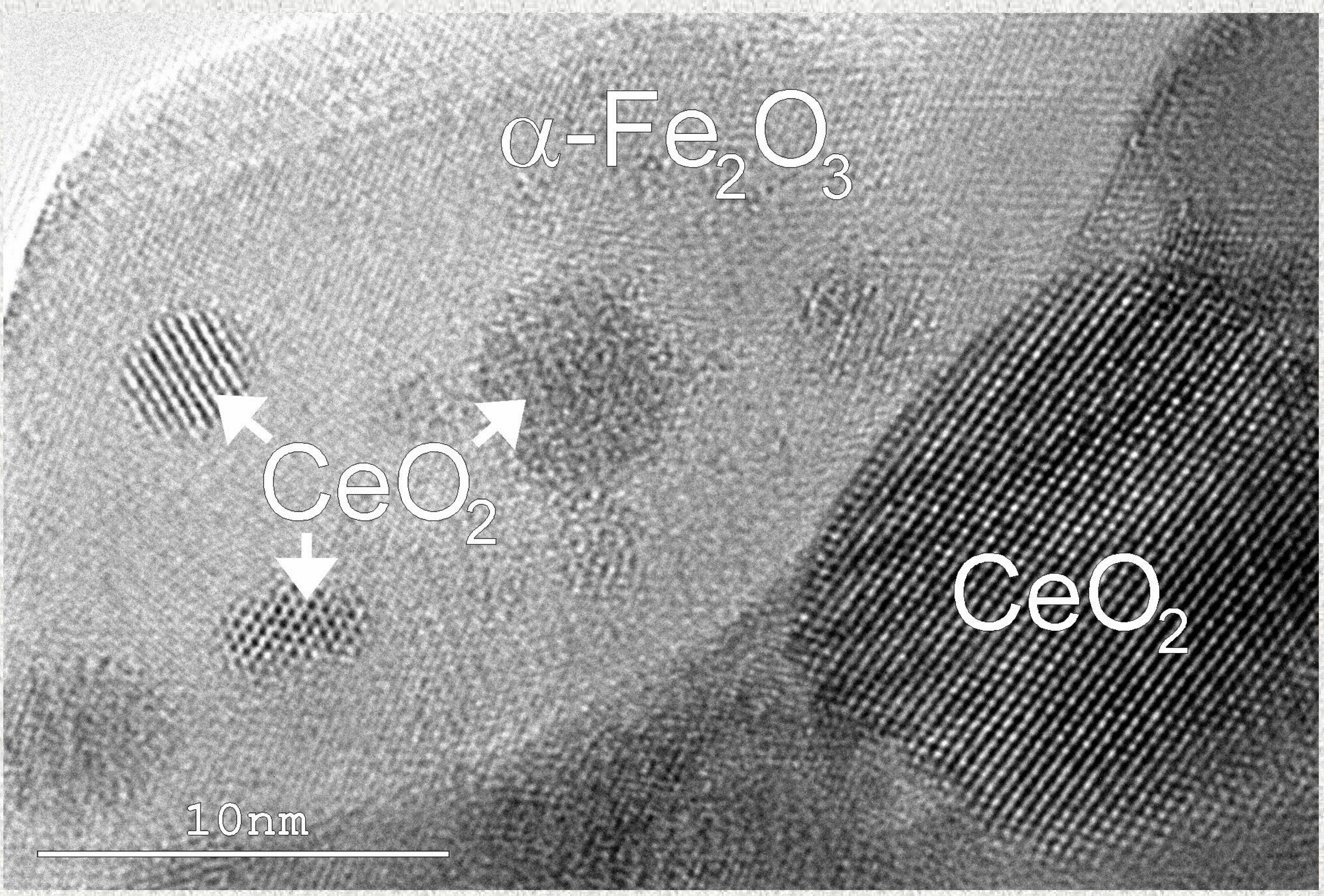


973K annealed sample with elemental maps of constituent elements



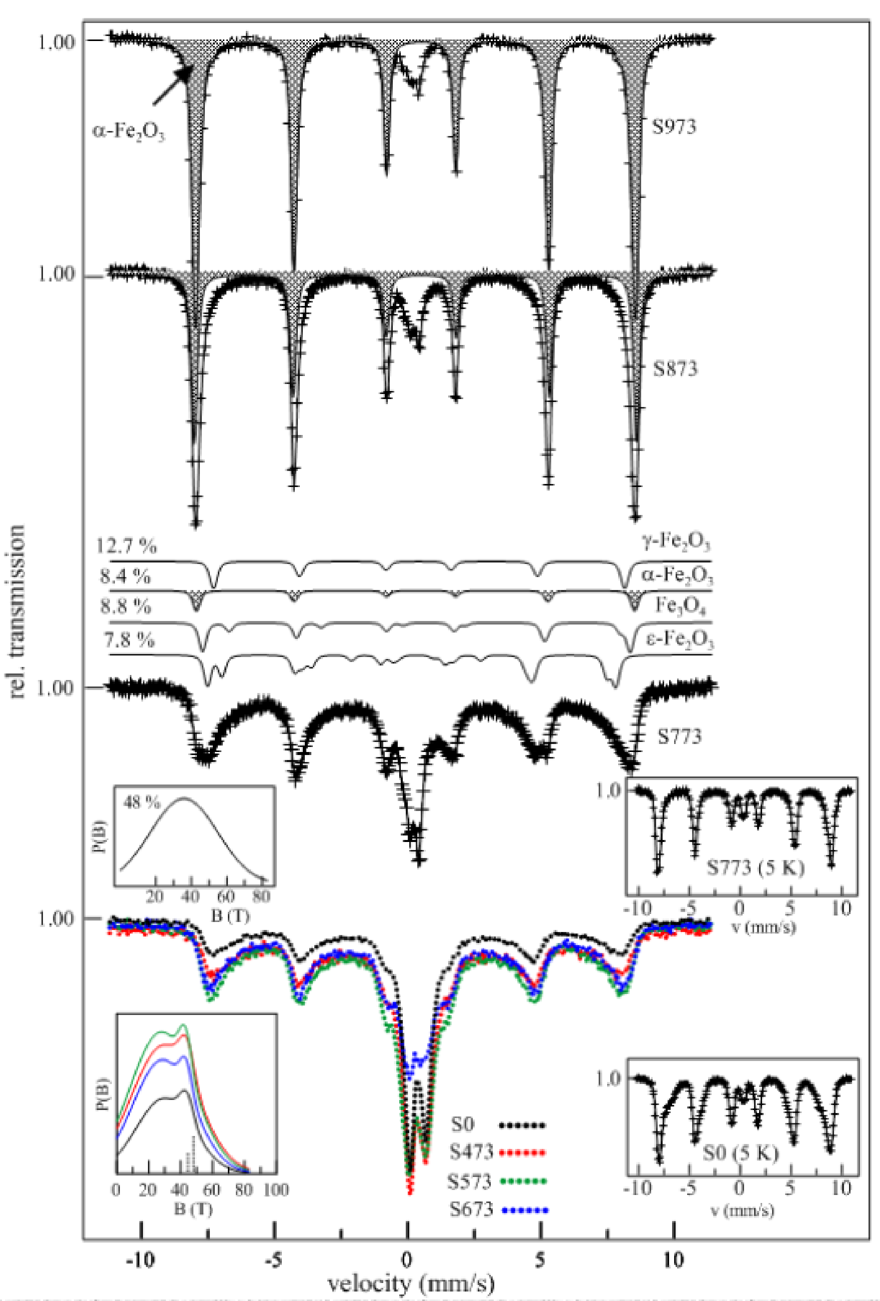
973K annealed sample with EDXspectra of Ce-rich (A) and Fe-rich (B) particles

Microstructure - TEM



CeO_2 particles on a large α-Fe_2O_3 grain

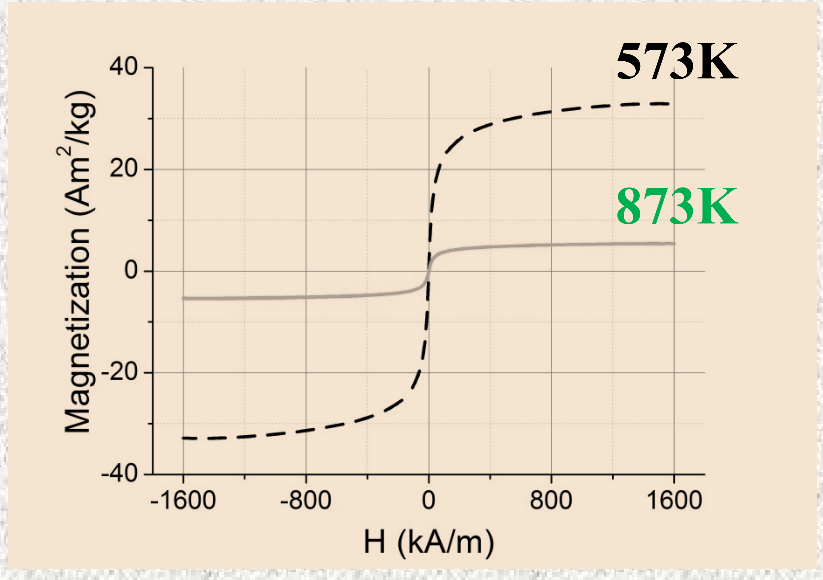
Mössbauer spectroscopy

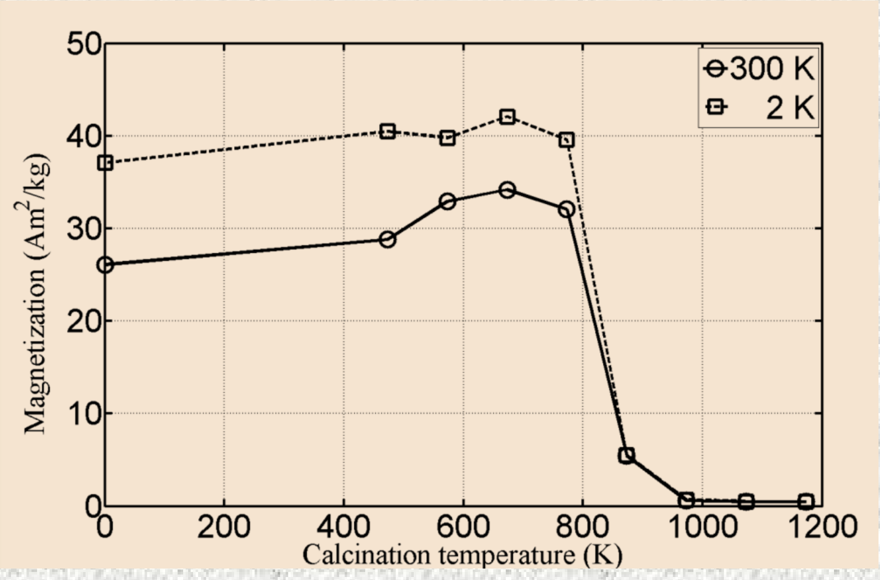


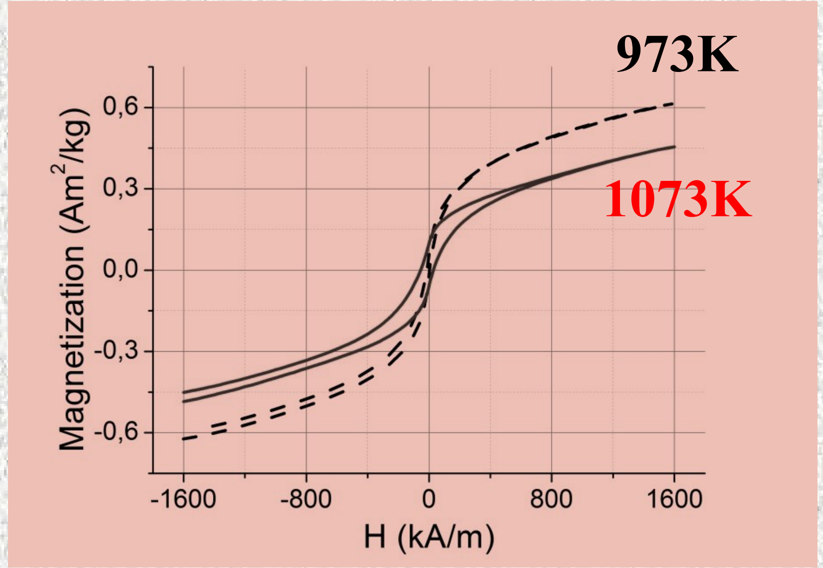
Relative area, *A*, hyperfine induction, *B*, isomer shift/quadrupole splitting, δ/Δ. Estimated exp. errors: *A*: ± 0.8 %; *B*: ± 0.2 T; δ: ± 0.01 mm/s; Δ: ±0.01 mm/s.

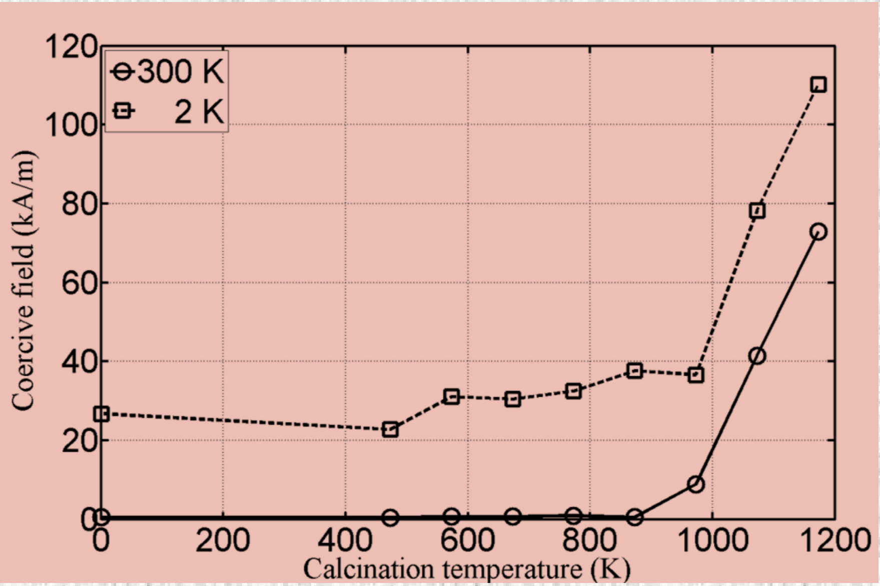
T_a (K)		773			873			973		
Phase	*T* (K)	*A* (%)	*B* (T)	δ Δ (mm/s)	*A* (%)	*B* (T)	δ Δ (mm/s)	*A* (%)	*B* (T)	δ Δ (mm/s)
γ-Fe$_2$O$_3$	300	12.7	47.8	0.30 – 0.01						
	5	18.3	51.6	0.48 – 0.01						
		4.2	48.1	0.41 0.00						
ε-Fe$_2$O$_3$	300	4.0	44.9	0.39 – 0.32	2.2	44.9	0.44 – 0.31			
		1.6	39.9	0.11 – 0.05	1.7	39.8	0.36 – 0.01			
		2.2	25.9	0.32 – 0.17	1.1	26.8	0.12 0.09			
	5	2.4	45.9	0.33 0.31	4.6	48.8	0.42 – 0.04			
		10.9	51.5	0.25 0.02						
α-Fe$_2$O$_3$	300	8.4	50.9	0.39 – 0.21	76.3	51.1	0.39 – 0.22	94	51.1	0.39 –0.21
	5	19.2	53.9	0.46 0.23	77.9	53.9	0.47 0.27	96	54.2	0.51 0.39
Fe$_3$O$_4$	300	4.1	49.7	0.39 – 0.13	5.3	49.6	0.39 – 0.07			
		4.7	45.7	0.52 0.05	5.0	46.7	0.56 – 0.13			
	5	32.3	53.3	0.46 – 0.17	14.0	53.2	0.46 0.06			
		6.0	49.7	0.58 – 0.37						
Interfacial	300	48.0	35.2	0.40 – 0.05						

Magnetic measurements

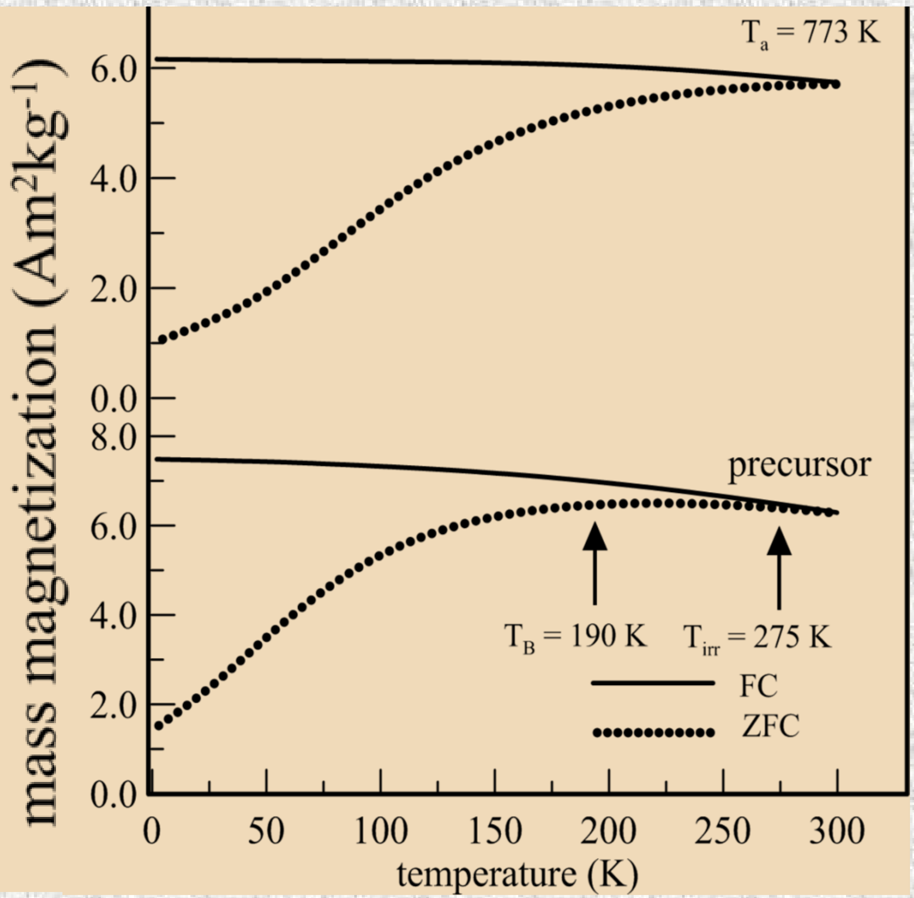


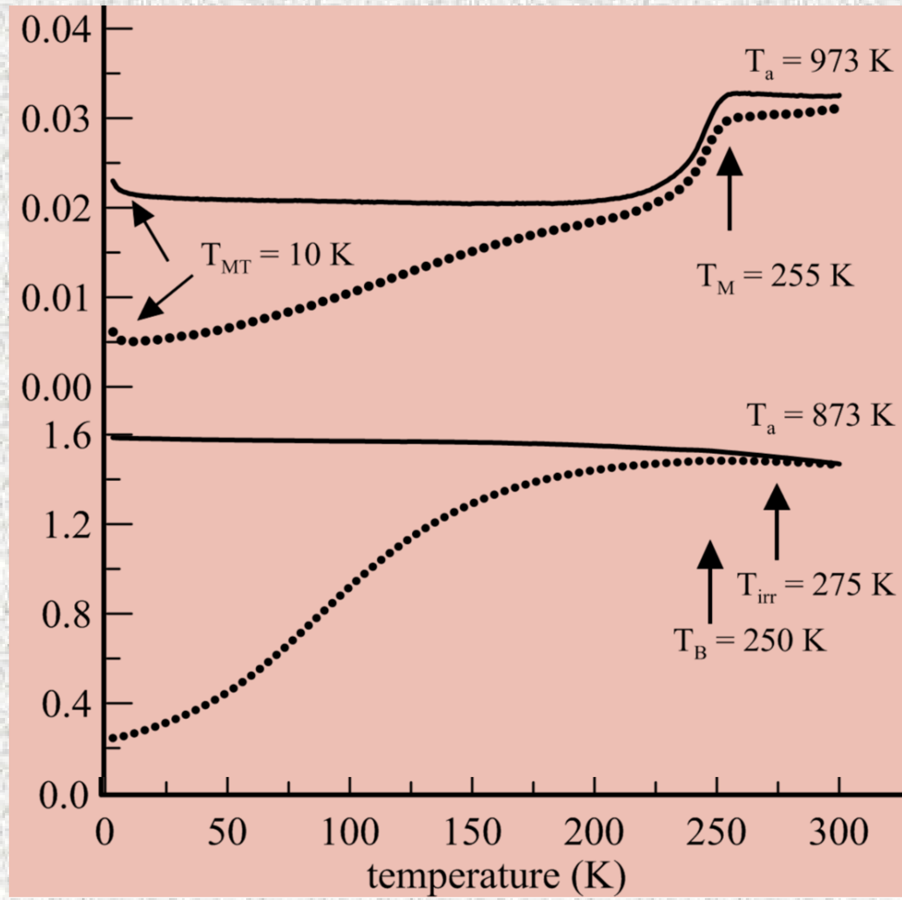






Magnetic measurements





FC/ZFC curves

Conclusions

- Magnetically reactive sorbents were prepared by a simple precipitation/calcination method.
- They destroy toxic organophosphates (pesticides, nerve agents) within less than 1 hour.
- Magnetic properties, microstructure, and degradation efficiency are governed by the calcination temperature.
- Sorbents annealed above 873K own lower degradation efficiency due to transformation of magnetite into hematite.
- Mössbauer spectroscopy reveals transformation of magnetite into hematite over γ-Fe_2O_3 and ε-Fe_2O_3.
- Increase of coercive field and decrease of saturation magnetization is detected at sorbents annealed above 873K.

Thanks for your attention

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