Preparation and properties of Fe and Fe_3O_4 nanoparticles embedded in ZrO_2 matrix

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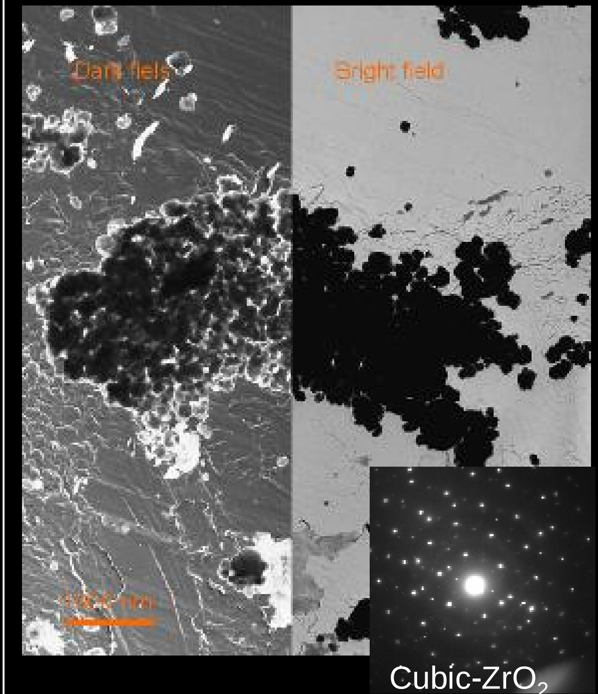
Aim

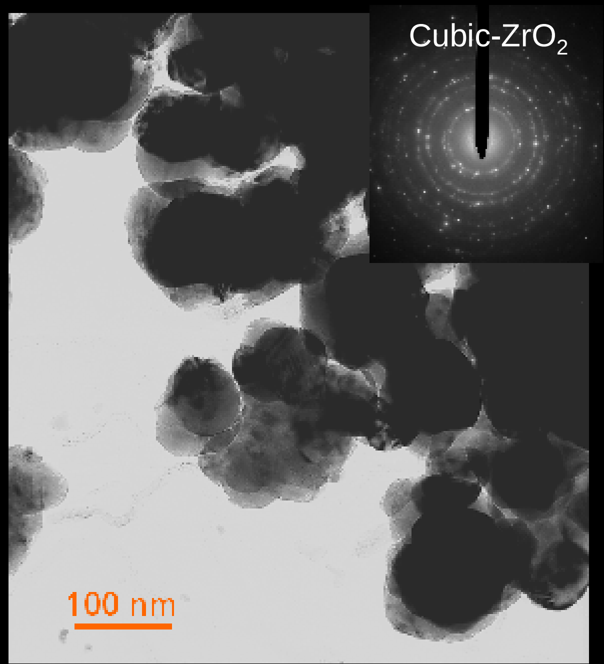
- Preparation of the nanocomposite in the form of α-Fe and Fe_3O_4 nanoparticles embedded in ZrO_2 matrix.
- Magnetic properties and phase composition of the composite.
- Determination of activation energy of transformation of iron oxide particles to α Fe by annealing in hydrogen.

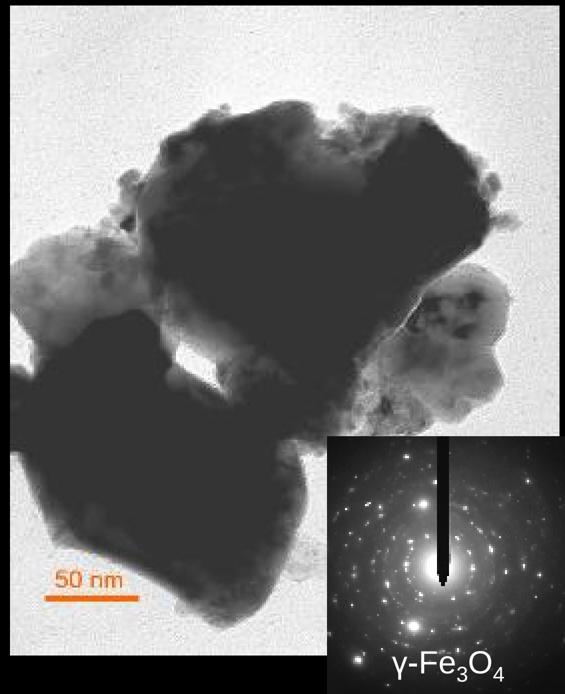
Experimental details

- The samples of the nanocomposite were prepared by mixing of nanocrystalline Fe_3O_4/Fe_2O_3 (~30 nm) or Fe_2O_3 (>100 nm) and ZrO_2 or ZrH_2 (~60÷110 nm) in agate mortar.
- Magnetic measurements were carried out using vibrating sample magnetometer (VSM) during a measurement in high temperature (at 293÷1093K), in the vacuum (10^{-2} Pa) and in the pure hydrogen (5N) atmosphere.
- ^{57}Fe Mössbauer spectra (MS) were collected by a standard transmission method at room temperature using $^{57}Co/Rh$ source.
- XRD was performed using CoKα radiation.
- Temperature dependence of the magnetic moment were measured for determination of critical temperatures of magnetic transition and isothermal transformation. The points corresponding to 50% of isothermal transformation were selected for the calculation of general rate of diffusion transformation in hydrogen by means of Arhenius equation.

TEM

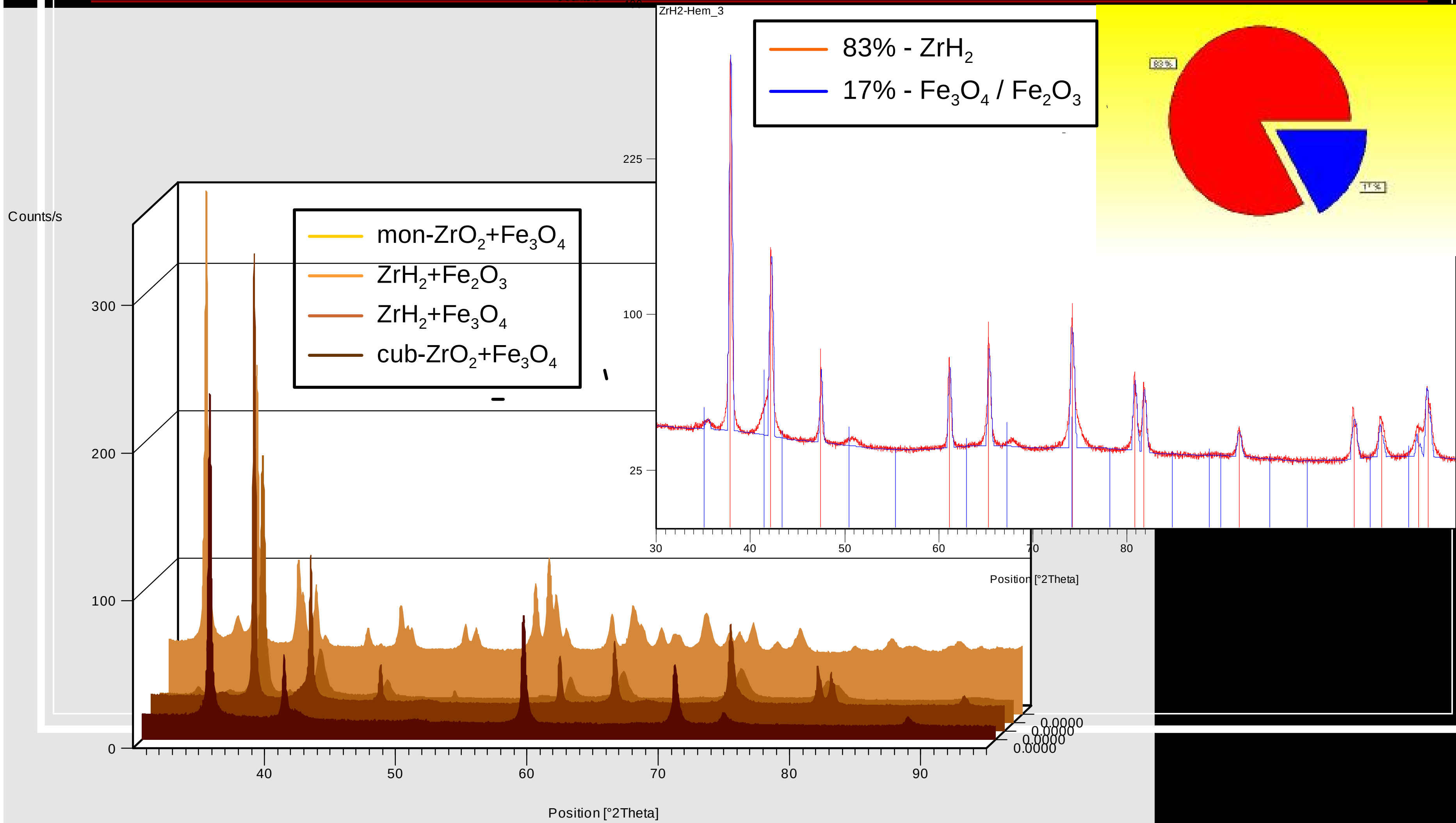




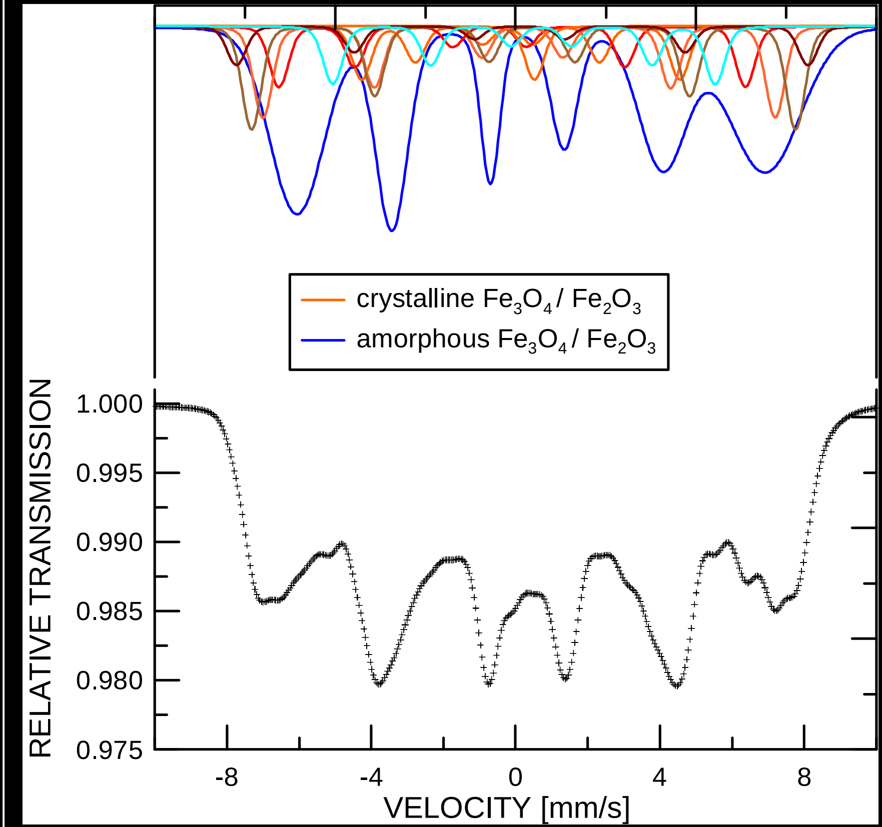


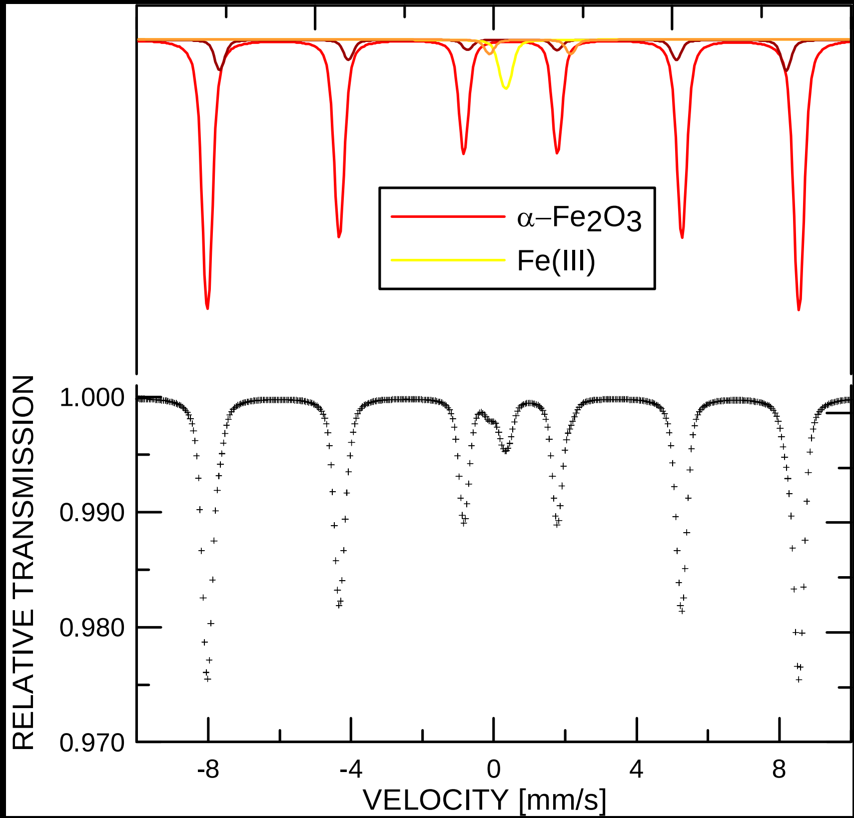
Selected area diffraction pattern from fine particles was identified as cubic form of ZrO_2. The clusters of Fe_3O_4 are disseminated in zirconia matrix.

XRD *(as-prepared samples)*



MS

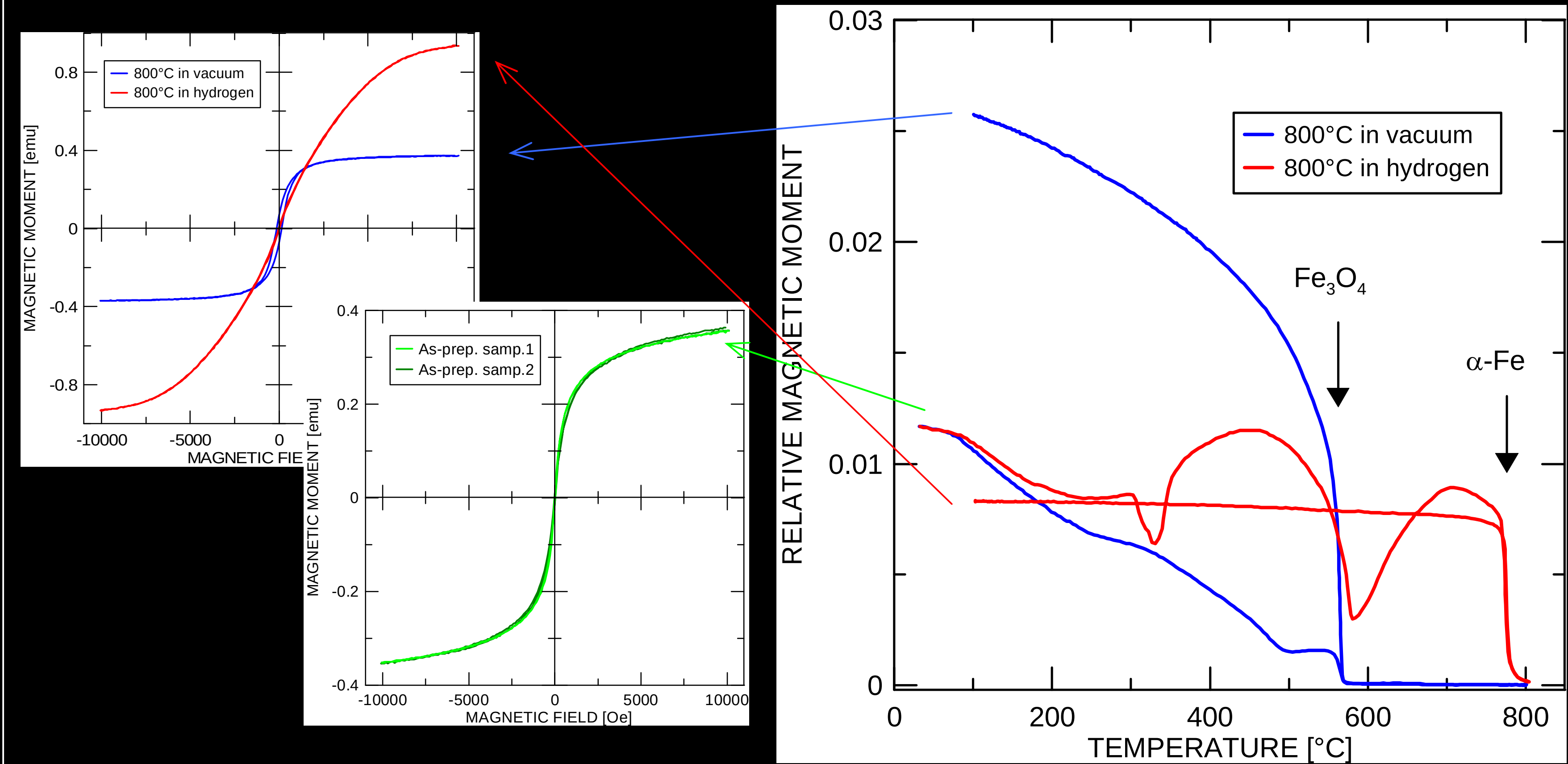

crystalline Fe_3O_4 / Fe_2O_3
amorphous Fe_3O_4 / Fe_2O_3
RELATIVE TRANSMISSION
1.000
0.995
0.990
0.985
0.980
0.975
-8
-4
0
4
8
VELOCITY [mm/s]


α–Fe_2O_3
Fe(III)
RELATIVE TRANSMISSION
1.000
0.990
0.980
0.970
-8
-4
0
4
8
VELOCITY [mm/s]

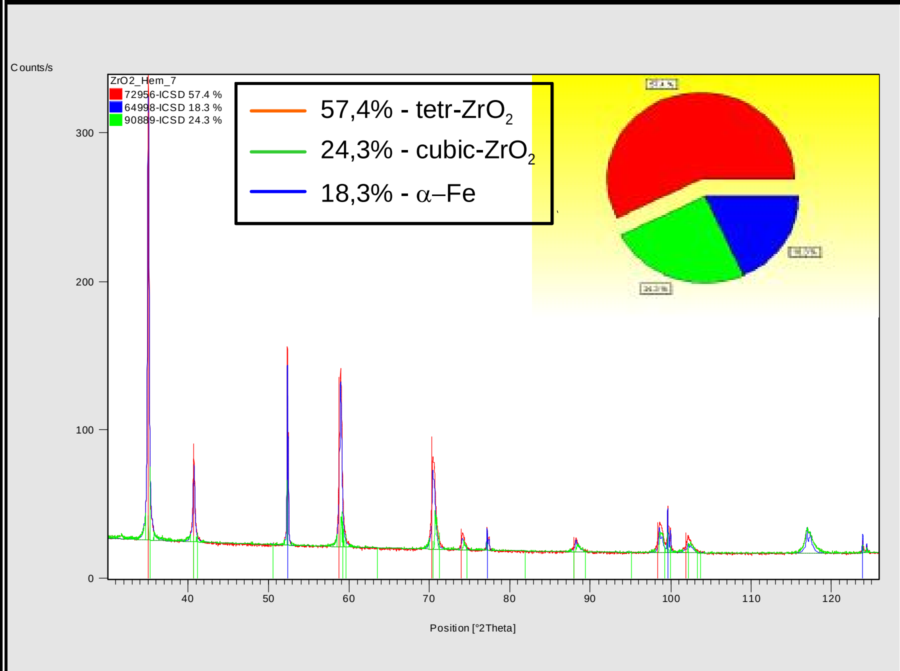
XRD Data

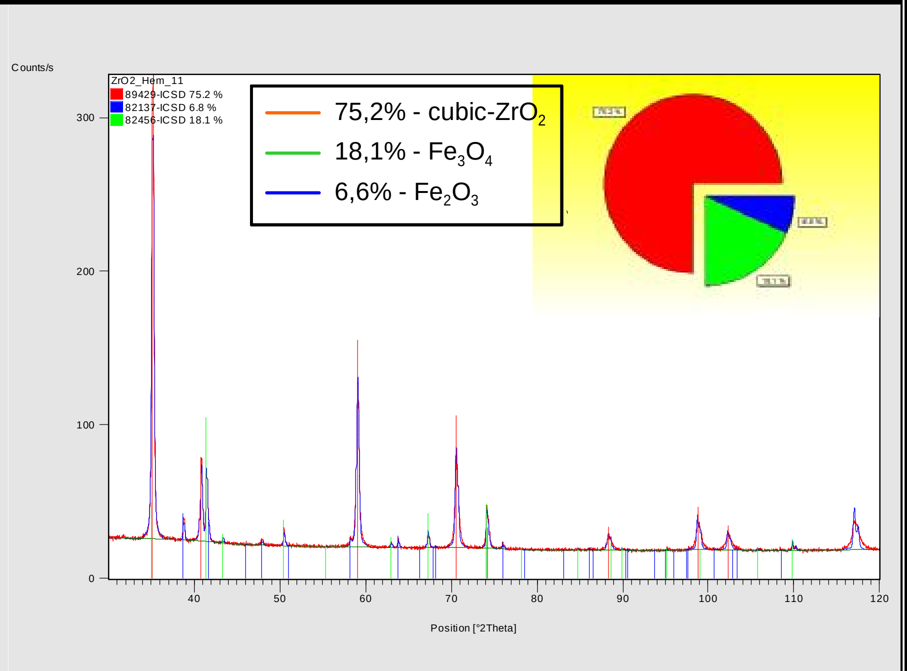
phase composition/ mean size of particles	as prepared	annealing at 800°C in vacuum
ZrH_2 + Hematite	ZrH_2 - 43%, Hematite - 57%	FeO-30%, ZrO_2m-20%, Magnetite -20%, Zr-20%,Fe-10%
	ZrH_2 - 110 nm, Hematite - 90 nm	FeO-42nm, ZrO_2m-23nm, Fe_3O_4-36nm, Zr-25nm,Fe-45nm
ZrH_2 + Magnetite	ZrH_2 - 98%, Magnetite - 2%	FeO-15%, ZrO_2m-45%, Fe-15%, ZrO_2t-25%
	ZrH_2 - 108 nm, Magnetite - 30 nm	FeO-51nm, ZrO_2m-38nm, Fe-16nm, ZrO_2 t-22nm
Monoclinic-ZrO_2 + Magnetite	ZrO_2m - 99%, Magnetite - 1%	Magnetite - 42%, ZrO_2m - 53%, Hematite - 5%
	ZrO_2 - 30 nm, Magnetite - 30 nm	Magnetite - 42 nm, ZrO_2m - 25 nm, Hematite - 41 nm
Cubic-ZrO_2 + Magnetite	ZrO_2c - 98%, Magnetite - 2%	Magnetite - 18%, ZrO_2c - 75%, Hematite - 7%
	ZrO_2 - 34 nm, Magnetite - 33 nm	Magnetite - 42 nm, ZrO_2c - 35 nm, Hematite - 51 nm

Temperature dependence of the magnetic moment and hysteresis loops of the as prepared powder (before and after TM)

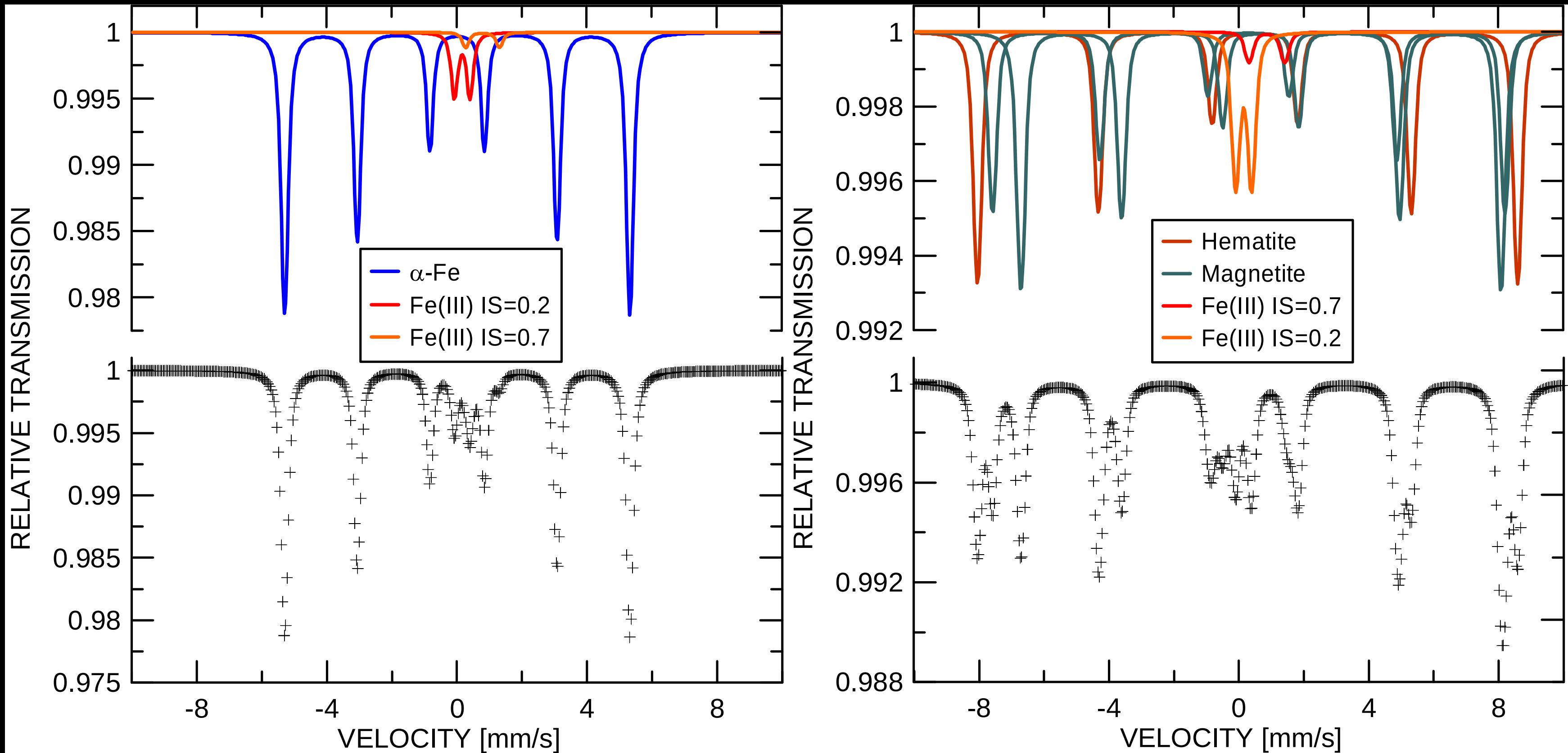


XRD *(annealed in hydrogen and in vacuum)*





MS *(annealed in hydrogen and in vacuum)*

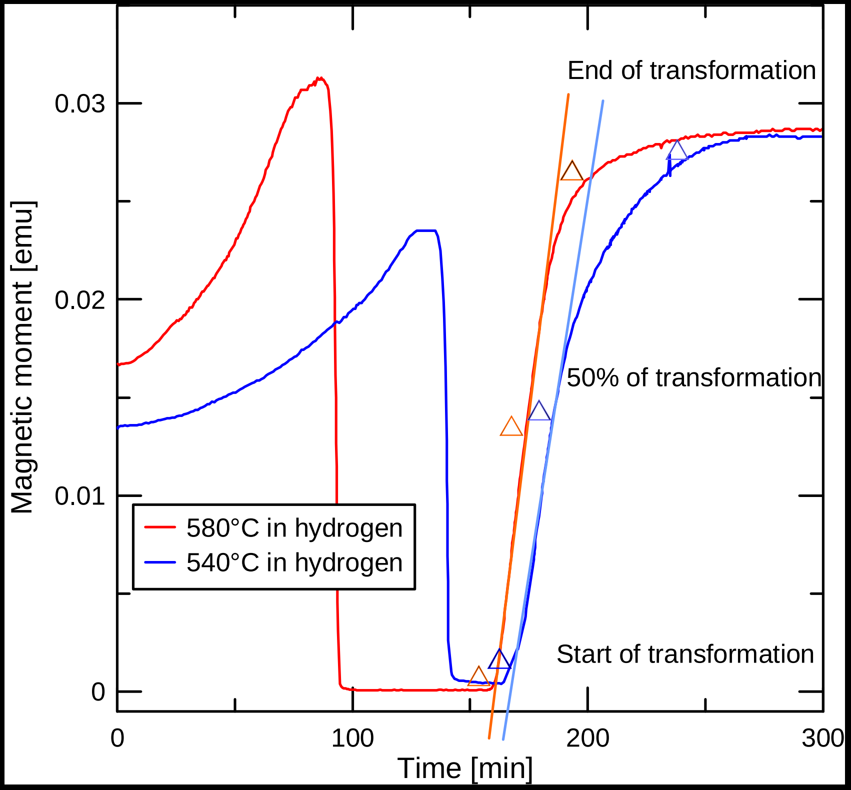


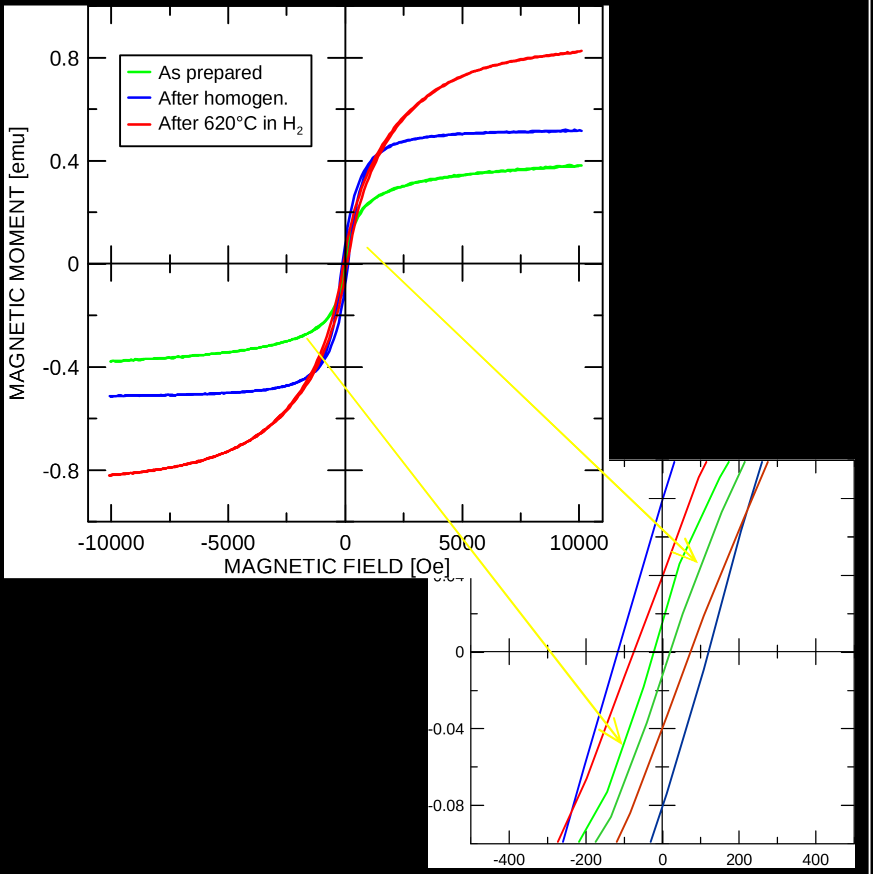
MS and XRD data

Phase composition of the samples (originally cubic ZrO_2 + Fe_3O_4) annealed by measurement of thermomagnetic curve up to 800°C in hydrogen and in vacuum.

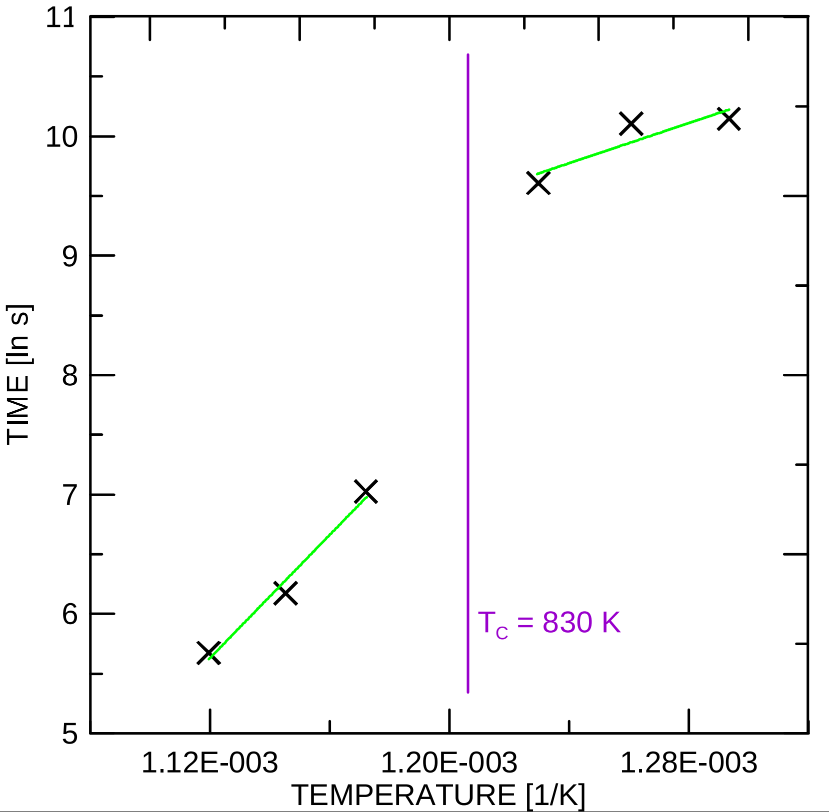
C-ZrO_2+ Fe_3O_4	Mössbauer spectroscopy				XRD		
as-prepared	nanocrystalline or/and amorphous structure of magnetite and maghemite				79% c-ZrO_2	21% Fe_3O_4	
in H_2	90% α-Fe	8%Fe(III) IS=0.2	2% Fe(III) IS=0.7		58% t-ZrO_2	24% c-ZrO_2	18% α-Fe
in vacuum	50% Fe_3O_4	34% Fe_2O_3	11% γ-Fe_2O_3	3%Fe(III) IS=0.2	75% c-ZrO_2	7% Fe_2O_3	18% Fe_3O_4

Isothermal curves + hysteresis loops





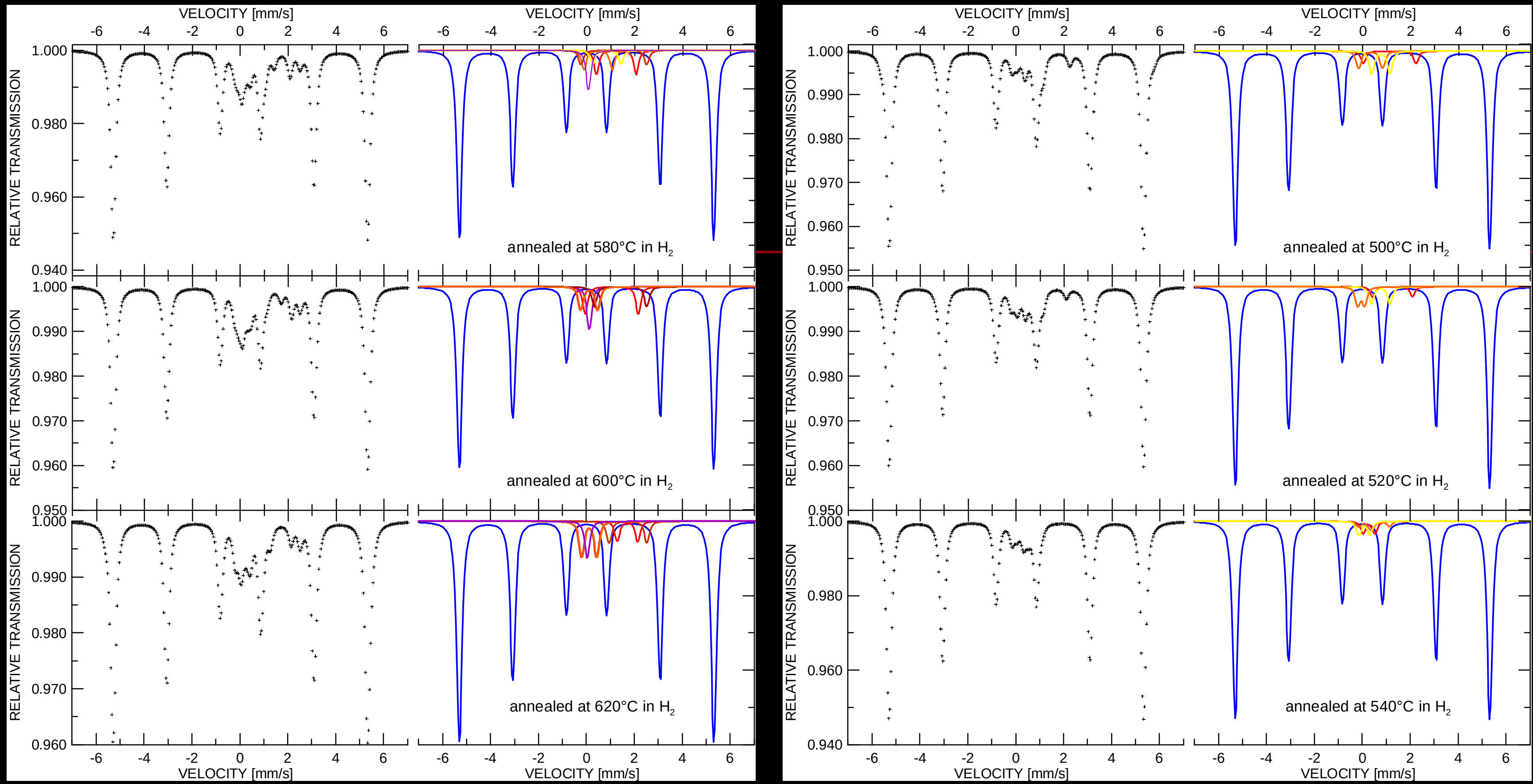
Arhenius equation: *(general rate of diffusion transformation)*



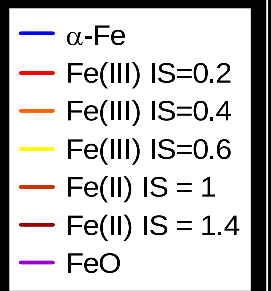
$$y' = A \cdot \exp\left(\frac{-Q}{R \cdot T}\right) \Rightarrow \ln y' = \ln A + \frac{Q}{R} \cdot \frac{1}{T}$$

y´ - rate of decrease magnetic moment
Q - activation energy
A - constant
R - molar gas constant

- Activation energy of magnetic transformation:
- below transition temperature Q = 1 kJ/mol
- above transition temperature Q = 3.1 kJ/mol



		Mössbauer spectroscopy				XRD		
		α-Fe	Fe(III)	FeO	Fe(II)	ZrO2-t	α-Fe	ZrO2-c
1	Annealed at 500°C	90%	7%	-	2%	80%	20%	-
2	Annealed at 520°C	90%	5%	3%	2%	71%	20%	9%
3	Annealed at 540°C	95%	2%	3%	-	79%	21%	-
4	Annealed at 580°C	85%	5%	3%	6%	80%	20%	-
5	Annealed at 600°C	83%	3%	4%	10%	80%	20%	-
6	Annealed at 620°C	84%	7%	3%	6%	81%	19%	-



Conclusions

- The as-prepared powders consist of mixture of Fe_3O_4(30nm), Fe_2O_3 (90 nm), ZrO_2-monoclinic (30 nm) and cubic (35 nm) and ZrH_2 (110 nm) phases.
- The samples annealed in vacuum are formed by particles of FeO (50 nm), Fe_3O_4(45 nm), Fe_2O_3 (50 nm), ZrO_2-monoclinic (25 nm), tetragonal (22 nm) and cubic (35 nm).
- Annealing in hydrogen causes reduction of iron oxides to pure iron particles (180 nm) and clusters of Fe atoms in ZrO_2.
- The magnetic parameters confirm full transformation of iron oxides to α-Fe.
- The activation energy of transformation Fe_3O_4 to α-Fe calclulated using Arhenius equation exhibit different values below (Q_H = 1.0 kJ/mol) and above (Q_H = 3.1 kJ/mol) magnetic transition temperature (Hedvall effect).

Thank you for your attention

- Thank to Dr. N. Pizurová for the TEM analysis.
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