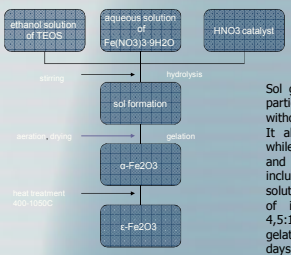
ICAME 2009

SYNTHESIS AND MAGNETIC PROPERTIES OF HEMATITE NANOPARTICLES

Marija Perović, Ana Mraković, Marin Tadić, Dragana Marković, Vojislav Spasojević,
The Vinca Institute of Nuclear Science, Condensed Matter Physics Laboratory POB 522, 11001 Belgrade, Serbia

Conventional sol-gel procedure resulted in formation of hematite nanoparticles, embedded in porous silica matrix. TEM studies confirmed that the average particle size of hematite is around 15 nm, with narrow size distribution. Selected area electron diffraction (SAED) showed the formation of the hematite phase.
X-ray diffraction and Mössbauer measurements confirmed formation of alpha phase of iron oxide nanoparticles with the same average size .
Magnetic measurements using SQUID magnetometer showed typical behavior for superparamagnetic nanoparticle systems such as blocking temperature, irreversibility of zero-field cooled (ZFC) and field cooled (FC) curves and emergence of magnetic hysteresis below blocking temperature. Magnetization behavior was measured in both regimes: blocked and superparamagnetic. Magnetic moments of nanoparticles were determinate by comparing obtained data with values predicted by Langevin model. Experimental results are in good agreement with numerical calculations of ZFC and FC magnetization based on the superparamagnetic blocking model. Calculated values for anisotropy constants are in predicted extent for hematite nanoparticle samples.
Superparamagnetic relaxation phenomena were investigated by Mossbauer spectroscopy in wide range of temperatures, from 10K to 295K. Although weak ferromagnetism was expected in the whole temperature range due to absence of Morin transition, the coexistence of two sextet components appeared in the Mossbauer spectrum.
.

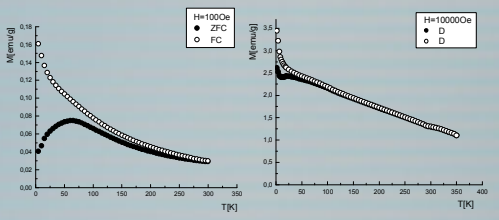
Preparation route:



Sol gel method is very useful for obtaining particles of well defined shape and size, without significant interparticle interactions. It allows control of size and interactions, while silica matrix ensures uniform ordering and geometry of vacancies. Preparation included several stages: mix of etanol solution of tetraetoxysilan with water solution of iron nitrate Fe(NO3)3·9H20 in ratio 4,5:1:19. mixture homogenization 1h, gelation process on air, drying of gel, few days on 55°C and heat treatment 4h, 200 °C

α-Fe_2O_3 nanoparticles (15nm) in a silica matrix containing 45 wt.% of hematite

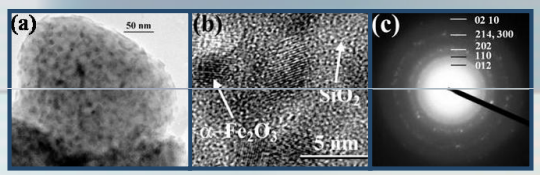
SQUID measurements:



	TB (K)	Tirr (K)	K (10^5erg/cm^3)
M100Öe	62	290	1,21
M500Öe	60,5	270	1,18
M1000Öe	56	240	1,13
M10000Öe	20	50	0,39

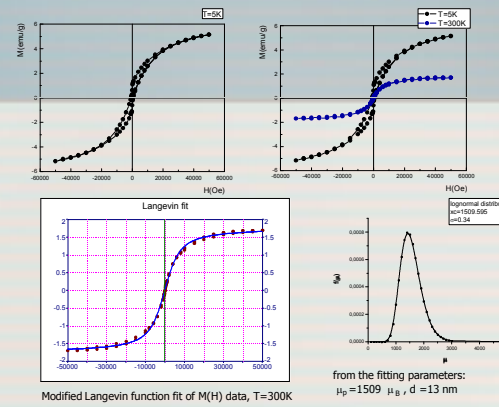
Magnetization as a function of temperature was measured for the different fields: H=100Oe, 500Öe, 1000Öe i 10000Öe.
There is no observation of Morin transition in the whole range of temperatures, which is expected for nanoparticles of ~15nm mean diameter. Blocking temperature is found to be on 62K. From the relation KV = 25kBTB effective anisotropy constant was derived. Comparison of value K=(1,2±0,1)·10^5 erg/cm3 to bulk value K=8·10^4 erg/cm3 suggested important contribution of surface anisotropy in the case of hematite nanoparticle sample.
Temperature of irreducibility Tirr=290K for the measurement in field of 100 Öe points on progressive blocking of superparamagnetic nanoparticle moments.
Measurements on α-Fe2O3 30% samples showed that probably presence of weak interactions in our sample caused increase of blocking temperature.

TEM:



Transmission electron micrograph of α–Fe_2O_3/SiO_2 (a) silica grain with embedded α–Fe_2O_3 nanoparticles (b) high resolution image of selected grain region (c) the SAED pattern of the same region

The occurrence of hematite particles embedded and well dispersed into the SiO2 is confirmed by TEM observations. SAED pattern of the same area confirmed α-phase of iron oxide. Narow size distribution of particles with mean diameter d≈13nm was observed, with no particle agglomeration.



Modified Langevin function fit of M(H) data, T=300K

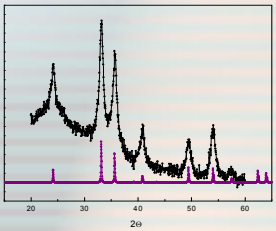
Magnetization as a function of field was measured for several temperatures: T=5K, 40K, 250K, 300K. Above blocking temperature, there is no hysteresis That is characteristic for superparamagnetic systems.
Hysteresis, measured on 5K showed lack of saturation. Coercive field and remanent magnetization were Hc=700Öe i Mr=0,61emu/g due to weak ferromagnetism of hematite nanoparticles.
With the assumption that weak interparticle interactions are negliable, curve M(H) on 300K was fitted by Langevin functions including log normal distribution of particle size.
From the fitting parameters, magnetic moment and mean particle diameter were derived: μp =1465 μB i d=14 nm. Results showed good agreement with particle size derived by XRD and TEM techniques. Also parameters of distrubion functions were obtained.

$$M(H,T) = N \int_{\mu_{min}}^{\mu_{max}} \mu L\left(\frac{\mu H}{k_B T}\right) f(\mu) d\mu$$

$$f(\mu) = \frac{A}{\mu\sigma\sqrt{2\pi}} \exp\frac{\left(\log\left(\frac{\mu}{x_c}\right)\right)^2}{2\sigma^2}$$

from the fitting parameters:
μ_p =1509 μ_B , d =13 nm

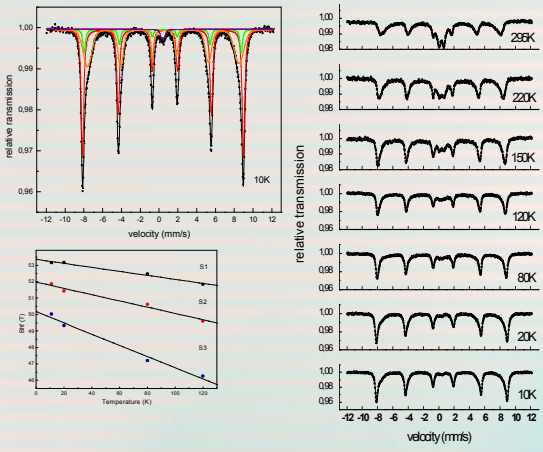
XRD:



X-ray diffraction spectra of iron oxide particles embedded in a silica matrix

The XRD spectrum of the sample showed well-defined hematite diffraction pattern. No iron-containing impurity phases were observed. The average particle size was obtained from the line broadening of the diffraction peaks using the Scherrer formula , where is the wavelength (CuKα=1,54181A) and θ is the Bragg angle. Assuming spherical shape the particle diameter d was obtained from the FWHM line breadth β by setting =0,916. Amorphous pattern of silica is visible. Mean particle diameter is found to be d=15nm.

Mössbauer spectra:



Mössbauer absorption spectra were obtained in a standard transmission geometry, using a source of ^{57}Co in rhodium. Calibration was performed using a 25 μm thick natural iron foil; the isomer shift values are referred to α- Fe. The spectra were fitted with a simple model with two or three sextets and one or two doublets. The fitted hyperfine parameters of the components clearly correspond to hematite.

Although weak ferromagnetism was expected in the whole temperature range due to the absence of Morin transition, the coexistence of two sextet components appeares in the Mossbauer spectrum. One of the possible explanations can be found in the fact that hematite particles certainly have a great number of iron atoms at their surface, which are likely to interact with the silica network. Particle-matrix interactions might involve either the presence of Fe-O-Si bridges at the interface of the two oxides or the replacement of tetrahedral Fe(III) sites in the iron oxide phase by Si(IV). There is no evidence by XRD or TEM for formation of some other iron containing compound .
There are suggestions that additional component can be attributed to grain boundaries and interfacial regions, while the first one accounts for the core of grains. The first component in the low temperature spectrum, corresponding to core grains atoms, shows hyperfine field smaller than those of the corresponding bulk phase, because of the nanocrystalline character of the particles. Additional decrease of hyperfine field was observed in the second component. The decrease of the mean hyperfine field in this case must be connected with those grain boundaries and interfacial regions with higher degree of disorder.
At intermediate temperatures, the sextet and doublet coexist. Collapse of the sextet is due to superparamagnetic relaxation of the particles. Sextets are not fully collapsed till T=296K. It can be suggested that the apparent higher blocking temperature could be caused by an increase in the superparamagnetic relaxation time due to higher anisotropy energy constant. Such an effect could be related to the influence of adsorbed molecules on the surface anisotropy. Another explanation can be found in the fact that interparticle interactions can cause similar behavior, but in the case of samples prepared by sol gel method that is very unlikely.
The average hyperfine fields, $B_{hf}(T)$ at low temperatures, where no doublet is present, were used to determine an effective anisotropy constant, K.

$$B_{hf} = B_{hf0}\left(1 - \frac{kT}{2KV}\right)$$

literature:

1. P. Kaushik et al., Colloids and Surfaces A 293 (2007) 162-166
2. V. Chhabra et al., Materials Letters 26 (1996) 21-26
3. J. M. Florez et al. Hyperfine Interactions (2005) 165: 253–259
4. G. Ennas et al., *Chem. Mater.*, (1998), 10 (2), 495-502
5. S.Morup, C. Ostenfeld, *Hyperfine Interactions* 136 (2001), 125–131,
6. F. Bødker, S. Mørup, *Europhys. Lett.*, 52 (2) (2000), pp. 217–223
7. M. F. Hansen, C. B. Koch, S. Morup, Phys. stat. sol. (a) 173, (1999),305
8. G. Rixecker , R. Birringer , U. Gonser , and H. Gleiter
9. J.-M. Greneche, *Hyperfine Interactions* 148/149: 79–89, 2003.
10. J.M. Greneche, A. Slawska-Waniewska, J. Mag. Mag. Mat. 215/216 (2000) 264-267