Origin of high-coercivity in nanocomposites by single-precursor sol-gel method

J Poltierova Vejpravova 1 P Brazda 2 A Mantlikova 1 D Niznansky 3 J Rohovec 4
1 Charles University Prague, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 – Prague 2, Czech Republic
2 Institute of Inorganic Chemistry, Academy of Sciences of the CR, 250 68 - Rez near Prague, Czech Republic
3 Charles University Prague, Faculty of Sciences, Department of Inorganic Chemistry, Hlavova 2, 121 16 – Prague 2, Czech Republic
4 Institute of Geophysics, Academy of Sciences of the CR, Rozvojova 269, 16500 – Prague 6, Czech Republic

E-mail: jana@mag.mff.cuni.cz

Abstract. We have fabricated high-coercivity nanocomposites constituted of Fe2O3 or CoFe2O4 nanocrystals embedded in amorphous silica matrix by a single-molecule precursor sol-gel method. Our approach enables smooth variation of the Fe(Co) : Si ratio up to 40 weight % of the magnetic phase, resulting in high density nanocomposite. Final crystallite size and phase composition was adjusted by subsequent heat treatment. The Fe2O3/SiO2 samples annealed at 1000 and 1100 °C revealed coercivity, \( H_c \sim 2 \) T at 300 K due to formation of the metastable \( \varepsilon \)-Fe2O3 phase. The CoFe2O4/SiO2 composites exhibit enhancement of the \( H_c \) value with increasing annealing temperature. Origin of the large coercivity in the two types of the magnetically hard nanocomposites will be discussed.

1. Introduction
Magnetic nanomaterials have been intensively studied as promising candidates for high-density magnetic storage media, ferrofluid technologies, and biomedical applications [1-3]. Their functionality is often conditioned by large coercivity \( (H_c) \) values. The most promising candidate is the \( L1_0 \) FePt phase, which exhibits \( H_c \sim 2.2 \) T; however, the nanocrystals must be protected against rapid oxidation, that introduces additional technological treatment [4]. Our aim was to create a smart method for preparation of high-concentration nanocomposites and provide air-resistant materials with sufficient magnetic characteristics for high-density magnetic storage. In this paper, we report on magnetic properties of the two series of oxide-based nanocomposites: Fe2O3/SiO2 and CoFe2O4/SiO2.

Published under licence by IOP Publishing Ltd
Figure 1. Typical TEM (left) and SEM (right) images of the high-density composite (Fe1000 sample).

Figure 2. X-ray diffraction patterns. The solid lines correspond to the fit. Vertical lines mark positions of the Bragg reflections of the phases included in the Rietveld analysis. From top row to bottom row: epsilon – maghemite - hematite for Fe900 and Fe1100, and CoFe$_2$O$_4$ - hematite for CoFe800 and CoFe1100, respectively. The broad peak at around 20° is originated by the amorphous SiO$_2$.

2. Experimental details – synthesis, characterization and magnetic measurements

2.1. Synthesis
The samples were obtained by smart sol-gel method, where a single molecule serves as a source of the silica matrix and the nanocrystals. Details of the precursor molecule synthesis are described in [5]. For purpose of this work, the Fe : Si molar ratio was fixed to 1 : 2. Wet gels were obtained by hydrolysis of the precursor molecule. The gel was left for ageing at 50°C for two days, and then it was
progressively heated up to 300°C in vacuum. The obtained xerogels were divided into several batches and each was annealed up to 800, 900, 1000 and 1100 °C, respectively, on air for 1 hour. Annealing times above 1 hour did not reveal significant changes in sample constitution. The nanocomposites were labeled according to the final treatment temperature as Fe800 – Fe1100 for the Fe₂O₃/SiO₂ and CoFe800 – CoFe1100 for the CoFe₂O₃/SiO₂.

2.2. Characterization
Final products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). The SEM analysis revealed morphology of the powders, while the TEM observations served for determination of the size, shape and packing of the nanocrystals in the silica matrix. The XRD data were treated by Rietveld analysis in order to refine lattice parameters, atomic positions and apparent crystallite size corresponding to the volume of the coherently scattering domain of a nanocrystal [6]. Only spherical shape of the crystallites was considered in the model.

2.3. Magnetic measurements
Magnetic properties of the nanocomposites were measured using SQUID magnetometer (MPMS by Quantum Design) in the temperature range 2 – 400 K and magnetic fields up to 7 T. To avoid rotation of the crystallites when applying magnetic field, the powders were fixed by glue in gelatine capsules. The specific magnetization data were determined relative to the mass of the magnetic oxide phase, obtained from the EDX analysis.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. Fe₂O₃/SiO₂ nanocomposites
The typical constitution of the nanocomposites as observed by the TEM and SEM methods is demonstrated in Figure 1. The composites are formed of well-isolated crystallites embedded in the
amorphous silica. The average crystallite size, determined from the XRD profile analysis increases with increasing annealing temperature; it ranges from 5 nm to 29 nm for the Fe900 – Fe1100 samples, respectively, as presented in Table 1. The molar ratio of the Fe, Si and O, obtained by the EDX analysis corresponds to the nominal stoichiometry. The key observation is the influence of the annealing temperature on the phase composition of the samples. While the Fe800 contains only the maghemite phase with defect spinel structure, the sample Fe900 revealed two phases, the maghemite and the orthorhombic ε-phase [7,8]. The nanocrystals in the Fe1000 and Fe1100 are mostly single-phase ε- Fe2O3; the Fe1100 contains below 5% of the rhomboedic hematite phase and both also samples include small amount of a very rare variant of the Fe2O3, the β- phase [9]. The resulting lattice parameters and the average crystallite size for the Fe900 - 1100 samples is summarized in the Table 1.

3.1.2. CoFe2O4/SiO2 nanocomposites
The morphology and constitution of the CoFe2O4/SiO2 nanocomposites is almost identical to the Fe2O3/SiO2 samples, shown in the Figure 1. The crystallites appear to be spherical, as expected when considering the cubic symmetry of the ferrite (inverse spinel) structure. The average crystallite size, determined from the XRD profile analysis also increases with increasing annealing temperature from 3 nm to 13 nm in the CoFe800 – CoFe1100 samples, respectively, while the lattice parameter a remains intact (see Table 1). The required elemental ratio was confirmed by the EDX method. The lower particle size in comparison to the Fe2O3/SiO2 composites can be explained as follows. There is limited intermixing of the cations (Co2+, Fe3+) into the silica matrix, which influences its viscosity and hence formation of the pores and crystallite growth during annealing. Also the degree of compaction of the starting xerogels can be different for the two types of composites.

3.2. Magnetic measurements

3.2.1. Fe2O3/SiO2 nanocomposites
The typical hysteresis loops of the composites measured at the room temperature and at 10 K are presented in Figure 3. It is evident, that the hysteresis parameters significantly differ with respect to the phase composition of the samples, as summarized in the Table 1. The Fe900 reflects a typical trend expected for superparamagnetic maghemite nanoparticles with weak inter-particle interaction; the 10 K – loop shows moderate coercivity $H_c = 0.07$ T, which decreases down to 0.01 T at 300 K. Considering the fact, that the 5 nm maghemite nanoparticles should be in paramagnetic state at the room temperature [10], the low coercivity observed can be attributed to inter-particle interaction of dipolar origin. In contrast, the Fe1100 sample exhibit $H_c = 0.7$ T at 10 K, but enhancement of the value at 300 K up to 2.1 T. The observation can be explained by the typical features of the ε- Fe2O3 phase, which exhibits order-to-order magnetic phase transition at 150 K from the high-temperature high-coercivity magnetic phase to the low-coercivity ground-state magnetic phase [8]. The Fe1000 sample follows the expected behavior of the hybrid between the Fe900 and Fe1100 samples.

3.2.2. CoFe2O4/SiO2 nanocomposites
The hysteretic behavior of the CoFe2O4/SiO2 nanocomposites is demonstrated in the Figure 3 and the important parameters (coercivity, $H_c$ and remanence, $M_r$) are summarized in the Table 1. As the particle size increases, the $H_c$ and the $M_r$ values increase when comparing the CoFe800 – CoFe1100 samples at the same temperature. Also the $H_c$ and $M_r$ decrease with increasing temperature as expected for an ensemble of nanosized particles, which usually exhibit superparamagnetic phenomena [11,12]. Due to rather high density of the composites, additional inter-particle interactions are expected to occur and hence the values of the $H_c$ can be arbitrary enhanced due to them. When comparing the values to those obtained on CoFe2O4/SiO2 nanocomposites with lower density (10 weight % of the magnetic oxide), prepared by conventional sol-gel approach, they are very similar. Therefore, the dipolar interactions are of equal importance regardless the concentration of the nanocrystals in the matrix.
4. Conclusions
We have prepared high-concentration nanocomposites constituted of magnetic oxide nanocrystals (Fe$_2$O$_3$ and CoFe$_2$O$_4$) embedded in amorphous silica matrix using a smart sol-gel method. The single-molecule precursor technology can be easily utilized in production of corresponding thin films and coatings down to nm thickness and enables smooth variation of the magnetic phase-to-silica ratio. The final particle size and hence the magnetic properties of the composites can be easily controlled by annealing of the dry gels at temperatures from 800 °C to 1100 °C. The most important is the appearance of the 2 T-coercivity at room temperature in the Fe$_2$O$_3$/SiO$_2$ nanocomposite annealed at 1100 °C due to presence of the ε-phase, which designates it as a suitable candidate for magnetic storage and bio-sensing devices.

5. Acknowledgments
This work was supported by the Czech Science Foundation, project no. 202/08/P006 and Grant Agency of the AS CR, project no. 40010065.

Table 1. Summary of the lattice parameters ($a$, $b$, $c$) and average particle size ($d$) obtained from the Rietveld analysis. Only results obtained for the majority phase are presented (ε-Fe$_2$O$_3$ and CoFe$_2$O$_4$ in the Fe and FeCo series, respectively). The coercivity values ($H_c$) at 2 K and 300 K are also shown.

|       | $d$ (nm) | $a$ (pm) | $b$ (pm) | $c$ (pm) | $H_c$ (T) $T=10$ K | $H_c$ (T) $T=300$ K |
|-------|----------|----------|----------|----------|---------------------|-----------------------|
| Fe900 | 5±2      | 512±2    | 880±3    | 938±3    | 0.07                | 0.01                  |
| Fe1000| 11.6±2.5 | 508.5±0.2| 876.1±0.2| 943.1±0.1| 0.20                | 0.40                  |
| Fe1100| 29.0±9.1 | 508.6±0.1| 876.2±0.2| 943.2±0.2| 0.70                | 2.10                  |
| CoFe800| 3.0±0.8 | 837.0±0.3| -        | -        | 0.85                | 0.008                 |
| CoFe900| 3.9±0.7 | 837.2±0.4| -        | -        | 0.95                | 0.014                 |
| CoFe1000| 13.2±0.6| 837.9±0.3| -        | -        | 1.83                | 0.044                 |
| CoFe1100| 12.0±1.2| 837.3±0.3| -        | -        | 1.53                | 0.090                 |

6. References

[1] Tartaj P, Morales M P, Veintemillas-Verdaguer S, Gonzales-Carreno T and Serna C Synthesis, properties, and biomedical applications of magnetic nanoparticles, in Handbook of Magnetic Materials, edited by Buschow K H J, Elsevier 2006
[2] Tartaj P, Current Nanosci 2006 2 43
[3] Weller D and Moser A 1999 IEEE Trans Magn 35 4423
[4] Sun S, Murray C B, Weller D, Folks L and Moser A 2000 Science 287 1989
[5] Brazda P, Niznansky D, Rehspringer J L and Poltierova Vejpravova J 2009 J. Sol Gel Sci 83 826
[6] Microstructure Analysis from Diffraction, edited by Snyder R L, Bunge H J, and Fiala J, International Union of Crystallography, 1999
[7] Jin J, Hashimoto K and Ohkoshi S 2005 J. Mater. Chem. 15 1067
[8] Kurmoo M, Rehspringer J L, Hutlová A, D’Orléans C, Vilminot S, Estournès C and Nižňanský D 2005 Chem. Mater. 17 1106
[9] Zbořil R, Mashlan M and Petridis D 2002 Chem. Mater. 14 969
[10] Fiorani D, Testa A M, Lucari F, D’Orazio F and Romero H 2002 Physica B 320 122
[11] Cao X and Gu L 2005 Nanotechnology 16 180
[12] Hutlová A, Nižňanský D, Rehspringer J L, , Estournès and Kurmoo M 2003 Adv. Mater. 15 1622