

INVESTIGATION OF MAGNETITE FORMATION IN THE PRESENCE OF HYDRAZINE DIHYDROCHLORIDE

D. GINGASU^a, I. MINDRU^a, L.A. PATRON^{a,*}, J. M. CALDERON-MORENO^a,
L. DIAMANDESCU^b, F. TUNA^{a,c}, T. POPESCU^b

^a*Ilie Murgulescu Institute of Physical Chemistry, Splaiul Independentei 202, Bucharest 060021, Romania*

^b*National Institute of Materials Physics, P.O. Box MG-7, Bucharest-Magurele, 077125, Romania*

^c*University of Manchester, School of Chemistry, Manchester M13 9PL, Lancs England*

Fe₃O₄ nanoparticles were synthesized by a wet chemical method using Fe(III)/Fe(II) – hydrazine dihydrochloride systems. The structure, morphology, and magnetic properties of magnetite were examined by X-ray powder diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), Mössbauer spectroscopy and superconducting quantum interference device (SQUID). Almost all the particles exhibit superparamagnetic like properties at room temperature. This behavior can be correlated with the size of the particles which ranged between 20-70 nm.

(Received May 26, 2011; Accepted June 21, 2011)

Keywords: Magnetite; Hydrazine dihydrochloride; X-ray diffraction; SEM; Magnetic measurements

1. Introduction

Discovered more than 2000 years ago, magnetite (Fe₃O₄), a ferromagnetic ore oxide, is the oldest magnetic known material. Because of its natural magnetic properties, magnetite has been of great interest in a multitude of applications, including magnetic storage media, magnetic sensors, catalysts, pigments, magnetic ink and toner, magnetic paper [1-11]. There are also promising *in vivo/in vitro* biomedical applications [12-21]. For all of these applications the quality of magnetite was a research challenge over the years. However, still now, attention has been focused to develop simple and reproducible syntheses methods of Fe₃O₄ with controlled structure and morphology which strongly affect the properties of the magnetic material.

The most common synthesis method of Fe₃O₄ known from 1900 was the coprecipitation of an aqueous solution of ferrous and ferric ions by a base [22-24].

A non-conventional coprecipitation named “the wet ferritization method” was proposed by Japanese researchers [25,26]. A simple hydrothermal method to obtain polycrystalline magnetite particles has been proposed later [27]. In order to obtain ultrafine Fe₃O₄ nanoparticles, various methods were developed, such as hydrothermal route [28-30], sol-gel synthesis [31,32], thermal decomposition [33], microwave synthesis [34], chemical precipitation from microemulsion [35], electron and ultrasound irradiation [36,37].

It is well known that magnetite (Fe₃O₄) is not thermodynamically stable under oxidizing conditions and it will be oxidized to α-Fe₂O₃ [38]. For this reason, in order to protect the magnetic precipitates, argon or other inert gas must be employed to eliminate the oxygen in the reaction

* Corresponding author: Luminita_Patron@yahoo.com

system. This difficulty could be eliminated by introducing an oxidant-resistant reagent. Among the reductants, hydrazine hydrate has received much attention because of its strong reducing ability, low cost and environmental friendliness [24, 28, 30, 38-41]. In the same time, hydrazine reduces the diameter of magnetite nanoparticles and makes perfect its crystallinity [42].

There are many reports on the synthesis of Fe₃O₄ nanoparticles, most of them through hydrothermal reaction by using hydrazine hydrate (N₂H₄·H₂O) as a reductant [24,28,29,39,40].

In this paper, we propose a very simple precipitation route to synthesize magnetite (Fe₃O₄) nanoparticles, by using hydrazine dihydrochloride (N₂H₄·2HCl) instead of hydrazine hydrate (N₂H₄·H₂O).

2. Experimental

2.1. Synthesis

Iron(III) nitrate (Fe(NO₃)₃·9H₂O), iron(II) sulfate (FeSO₄·7H₂O), iron(III) chloride (FeCl₃·6H₂O), iron(II) chloride (FeCl₂·4H₂O) and hydrazine dihydrochloride (N₂H₄·2HCl) were used as starting materials. All reagents used were of analytical grade without further purification.

2.1.1. Systems $Fe^{2+} : 2Fe^{3+} : nN_2H_4 \cdot 2HCl$ (where $n = 4; 8$)

Iron(III) nitrate and iron(II) sulfate were dissolved in minimum amount of distilled water. Then an aqueous solution of hydrazine dihydrochloride was added. We have chosen two molar ratios of metal ions and hydrazine dihydrochloride 1:2:4 and 1:2:8, respectively. This solution was stirred, followed by the slow addition of NH₄OH 25% solution until pH of 10-11 was reached. The solution color could be seen to alter from orange to black, leading to a black crystalline magnetic powder. The precipitate thus obtained was filtered, washed with water (until the pH~7) and dried on P₄O₁₀ (Magnetite 15 is magnetite obtained from the system Fe²⁺ : 2Fe³⁺ : 4N₂H₄·2HCl; Magnetite 16 is magnetite obtained from the system Fe²⁺ : 2Fe³⁺ : 8N₂H₄·2HCl).

2.1.2. System $Fe^{2+} : 3N_2H_4 \cdot 2HCl$

Ferrous chloride was dissolved in a minimum amount of distilled water, to which hydrazine dihydrochloride aqueous solution was added. The molar ratio of metal ion and hydrazine dihydrochloride was 1:3. The pH was reached to 10-11 by addition of NH₄OH 25% solution, under continuous stirring. The solution turned from green to black, indicating the formation of magnetite. The precipitate was filtered and washed with water for several times (until the pH~7) and dried on P₄O₁₀ (Magnetite 18).

2.2. Physical measurements

The phase content was examined using the Bruker D8 Advance X-ray powder diffractometer with CuK_α radiation ($\lambda = 1.5406 \text{ \AA}$).

Scanning Electron Microscopy (SEM) was used to examine the surface morphology, using a Zeiss EVO LS10 environmental SEM microscope.

The IR spectra of the magnetic powders were recorded on KBr pellets with a JASCO FTIR 4100 spectrophotometer in the 4000–400 cm⁻¹ range.

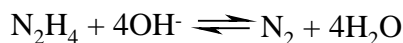
Mössbauer spectra were recorded at room temperature with WissEl Mössbauer spectrometer using a 20 mCi ⁵⁷Co(Rh) source. The sample thickness was ~7 mg Fe/cm².

Magnetic data were obtained with a Quantum Design MPMS SQUID susceptometer.

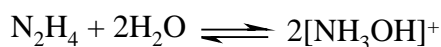
3. Results and discussion

It is well known that in alkaline medium, hydrazine can serve either a reducer or an oxidant [28,29,39,40]:

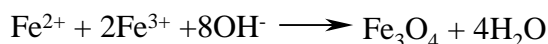
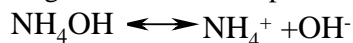
As a reducer:



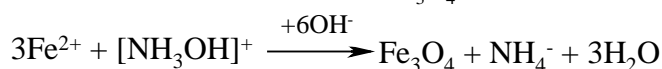
As an oxidant:



In reaction system containing NH_4OH and N_2H_4 , there are two processes forming magnetite. In the first process:



In the second process, hydrazine acting as an oxidant can form $[\text{NH}_3\text{OH}]^+$; the $[\text{NH}_3\text{OH}]^+$ cations can also react with Fe^{2+} to form Fe_3O_4 :



In the same time, by these reactions, the hydrazine eliminates oxygen from the system, protecting Fe^{2+} ions. The synthesis takes place at high pH level. The key factor that influences the magnetite formation is the amount of alkali.

Taking account both the hydrazine behavior in alkaline medium and the lack of data regarding the obtaining of magnetite in the presence of the hydrazine dihydrochloride, we studied the systems:



Magnetite nanoparticles are successfully obtained from all these systems.

3.1. XRD characterization

The XRD patterns show that the samples are pure Fe_3O_4 without impurity phases and match well with the standard pattern of Fe_3O_4 [JCPDS nr. 79-0419] (Fig. 1). The lattice parameters given by Rietveld refinements and the average particle sizes are listed in Table 1.

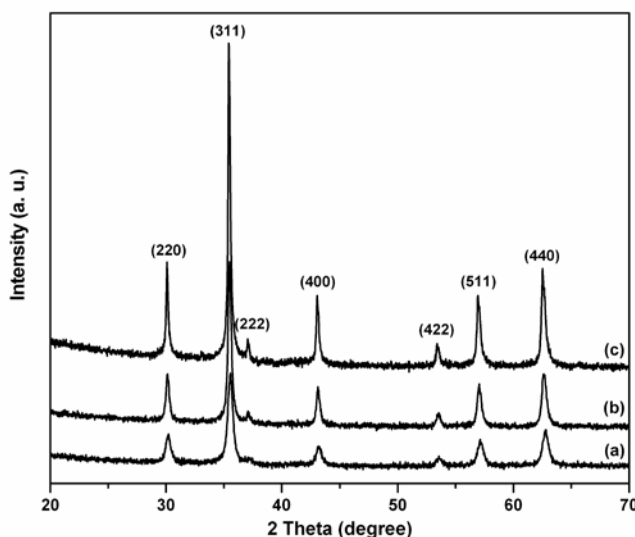


Fig. 1. XRD patterns of: (a) Magnetite15; (b) Magnetite16; (c) Magnetite18

Table 1. Rietveld refinement parameters and saturation magnetizations for Fe_3O_4 obtained from the systems Fe(III)/Fe(II)-hydrazine dihydrochloride

Sample	Lattice parameter A (Å)	Particle dim. All reflections (nm)	Saturation magnetization M_s ($emu \cdot g^{-1}$)
Magnetite15	8.3709	23	74.70
Magnetite16	8.3853	39	79.85
Magnetite18	8.3930	70	79.45

3.2. SEM of nanoparticles

The SEM measurements shown in Fig. 2, revealed homogeneous nanopowders with particle sizes in the range 20-70 nm.

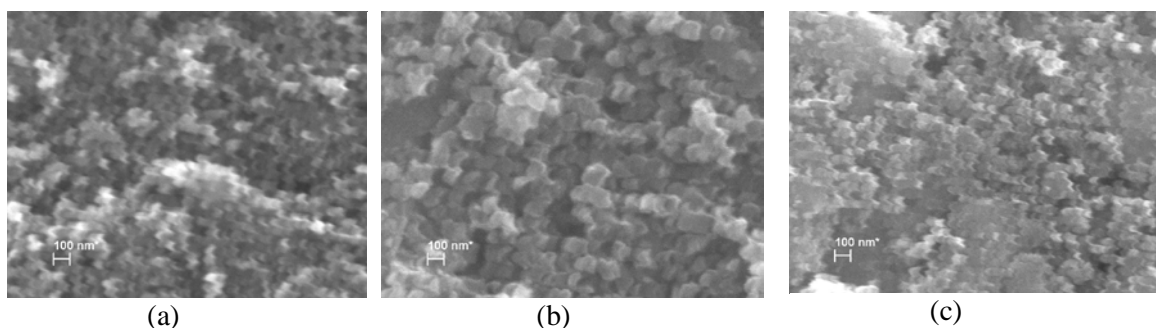


Fig. 2. SEM image of: (a) Magnetite15; (b) Magnetite16; (c) Magnetite18

3.3. IR spectra of Fe_3O_4

The IR spectra of the samples exhibit a broad intense band around 560-570 cm^{-1} , assignable to the Fe-O of the Fe_3O_4 [43, 44]. In Fig. 3 is presented the IR spectrum for sample Magnetite 18.

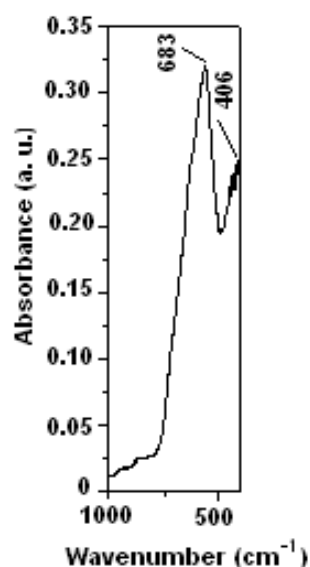


Fig. 3. Infrared spectrum of Magnetite18

3.4. Magnetic properties analysis

Above the Verwey temperature, $T_V = 120$ K, magnetite has a cubic spinel structure, space group 227 - $Fd3m$, with lattice parameter $a = 8.3910$ Å and the oxygen atoms arranged in a face centered-cubic lattice. In the tetrahedral sites (A) the lattice can hold Fe^{3+} while in the octahedral positions (B) there are both Fe^{3+} and Fe^{2+} ions. Due to a fast electron hopping between iron ions in octahedral sites, only two magnetic sextets can be observed in the room temperature Mössbauer spectra of bulk magnetite with the characteristic magnetic fields of 491 kOe for tetrahedral positions and 453 kOe for octahedral ones [27].

Sample Magnetite 15 exhibits a six line pattern with strongly distorted (non lorentzian) lines suggesting a hyperfine distribution due to the corresponding particle size distribution (Fig. 4a). The best fit was obtained in a model of hyperfine filed distributions where the minimum value is close to 21.9 kOe and the maximum value of about 48.1 kOe. The values are lower than corresponding for bulk magnetite in agreement with XRD results that gives a mean particle size of about 23 nm.

The best fit for sample Magnetite 16 was obtained taking into account two magnetic sublattices corresponding to tetrahedral and octahedral positions of iron ions in the magnetite lattice (Fig. 4b). The hyperfine fields given by the fit with Lorentzian lines are 486 kOe for tetrahedral sites and 453 kOe for octahedral ones. This behaviour suggests a higher particle size as confirmed by XRD measurements (~ 39 nm).

Sample Magnetite 18 displays nearly the characteristic pattern of the bulk magnetite sample (Fig. 4c). However the hyperfine magnetic field of about 485 kOe for the tetrahedral sites is a little bit lower than of the standard magnetite (491 kOe). For the octahedral site the value of 455 kOe is close to the standard magnetite (453 kOe).

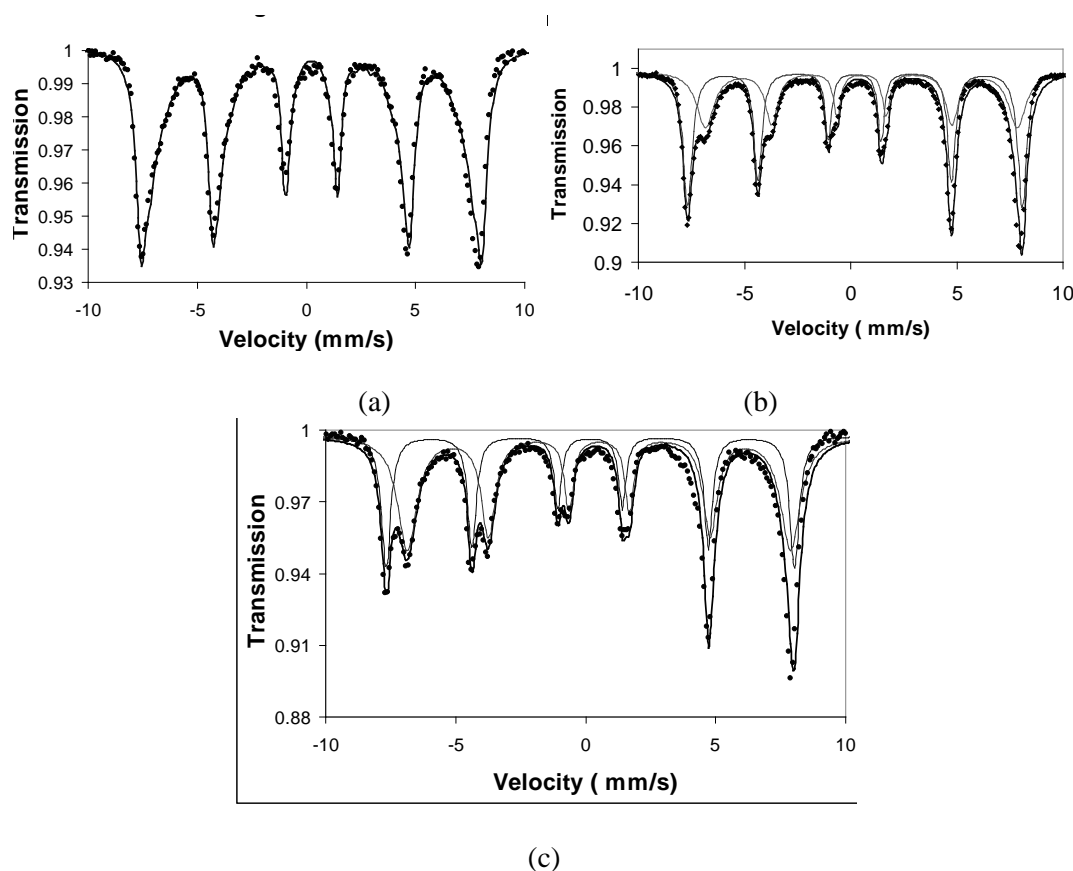


Fig. 4. Mossbauer spectra of: (a) Magnetite15; (b) Magnetite16; (c) Magnetite18

Figs. 5-7 show the hysteresis loops of the magnetite samples at 300 K and 5K. Almost all the particles display superparamagnetic like properties at room temperature since the remanence of the particles is equal to zero and the coercivity is almost negligible in the absence of an external magnetic field. This behaviour can be correlated with the size of the particles, which ranged between 23 nm and 70 nm. Morrish and Yu [45] have shown that Fe_3O_4 particles single domain appeared when their diameter is ~ 50 nm or less. The saturation magnetization (M_s) of the samples (Table 1) is smaller than that of the Fe_3O_4 bulk materials ($M_s \sim 92 \text{ emug}^{-1}$) [29,46].

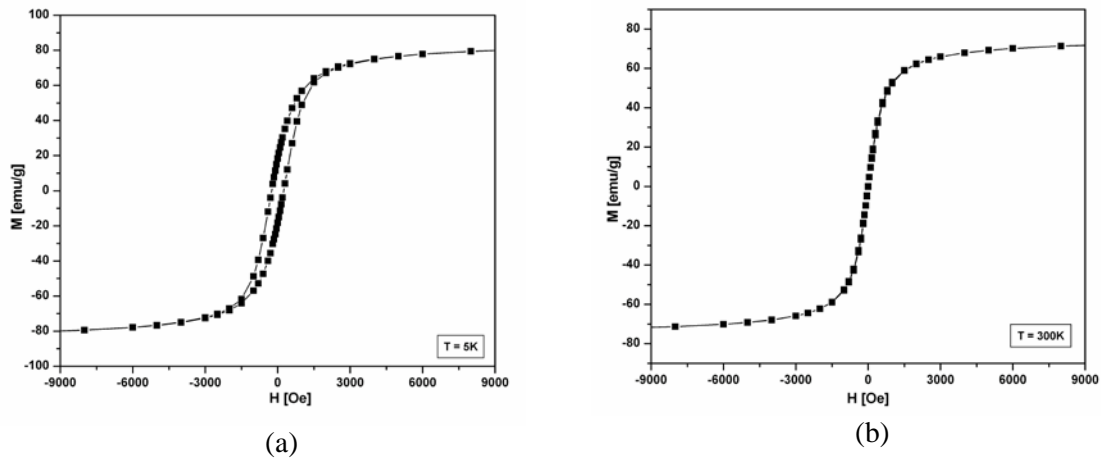


Fig. 5. Hysteresis loops of Magnetite15 registered at temperature: (a) 5K and (b) 300K

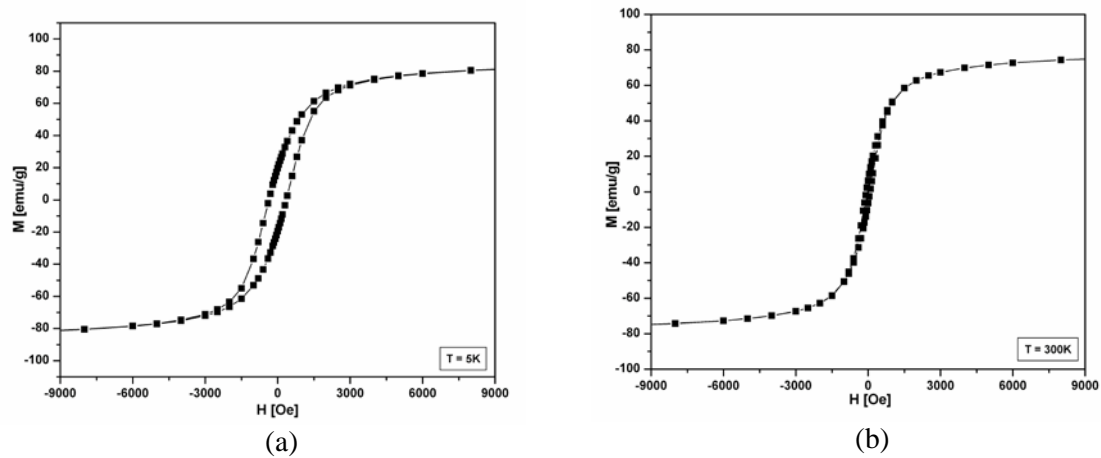


Fig. 6. Hysteresis loops of Magnetite16 registered at temperature: (a) 5K and (b) 300K

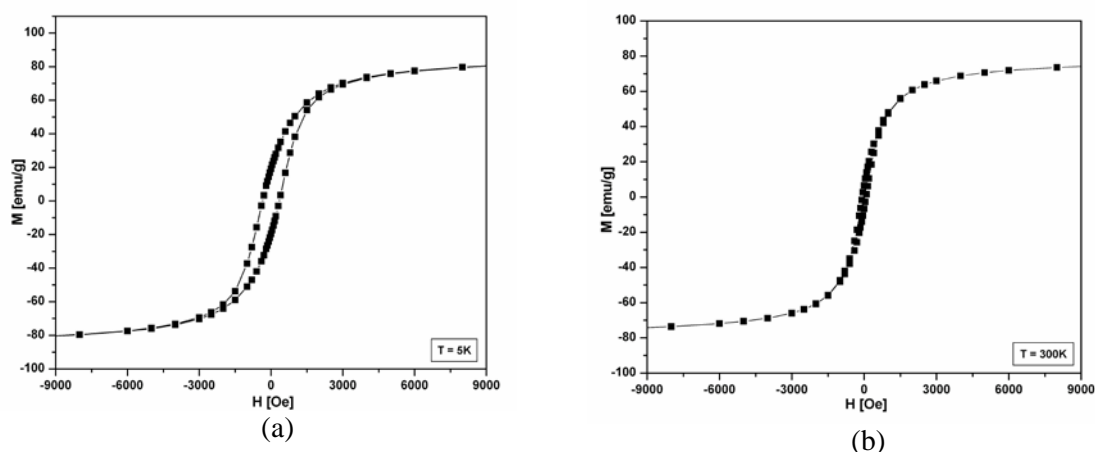


Fig. 7. Hysteresis loops of Magnetite18 registered at temperature: (a) 5K and (b) 300K

4. Conclusions

Magnetite nanoparticles were synthesized by a wet method using the systems Fe(III)/Fe(II) – hydrazine dihydrochloride. The XRD patterns showed pure Fe_3O_4 , only. The M_s of the magnetite nanoparticles is lower than that of bulk value. Almost all the particles possess superparamagnetic like properties. The size of the particles ranged between 20-70 nm.

By our best knowledge this report is the first one obtaining magnetite nanoparticles in the presence of hydrazine dihydrochloride. This method is expected to be generally applicable for the preparation of other nanoferrites.

References

- [1] D. C. Culita, G. Marinescu, L. Patron, Magnetita – eterna enigma, MatrixRom, Bucuresti (2009).
- [2] L. Rossi, A. D. Quach, Z. Roserweig, Anal. Bioanal. Chem. **380**, 606 (2004).
- [3] G. Istamboulie, S. Andreescu, I. L. Marty, T. Noguier, Biosens. Bioelectron. **23**, 506 (2007).
- [4] H. Jung, J. W. Kim, H. Choi, J. H. Lee, H. G. Hur, Appl. Catal. B: Environmental **83**, 208 (2008).
- [5] F. J. Beltran, F. J. Rivas, R. Montero de Espinoza, Water Res. **39**, 3553 (2005).
- [6] G. A. Waychunas, C. S. Kim, J. F. Bonfiel, J. Nanopart. Res. **7**, 409 (2005).
- [7] L. R. Miranda, L. Sathler, R. Noguiera, S. L. Brasil, Mater. Corros. **51**, 182 (2000).
- [8] J. Bohacek, J. Subrt, T. Hanslik, J. Mater. Sci. **28**, 2827 (1993).
- [9] M. E. Mang, H. Chang, M. L. Grande, G. A. Minagawa, Patent 1821153 A1, 22.08.2007.
- [10] D. Canetti, J. R. Correa, J. Ulalde, C. Toledo, L. C. Otero-Diaz, Acta Microscopica **16**, 132 (2007).
- [11] J. A. Carrazana-Garcia, M. A. López-Quintela, J. Rivas-Rey, Colloid Surface A **121**, 61 (1997).
- [12] A. Ito, M. Shinkai, H. Honda, T. Kobayashi, J. Biosci. Bioenerg. **100**, 1 (2005).
- [13] A. K. Gupta, M. Gupta, Biomaterials **26**, 3995 (2005).
- [14] C. C. Berry, A. S. G. Curtis, J. Phys. D: Appl. Phys. **36**, R198 (2003).
- [15] T. Kubo, T. Sugita, S. Shimose, Y. Nitta, T. Murakami, Int. J. Oncol. **18**, 121 (2001).
- [16] H. Sasaki, S. Niimi, M. Akiyama, T. Tanaka, A. Hazato, S. Kurozumi, S. Fukushima, M. Fukushima, Cancer Res. **59**, 3919 (1999).
- [17] M. Timko, M. Koneracká, N. Tomasovicová, P. Kopcanský, V. Závísová, J. Magn. Magn. Mater. **300**, e191 (2006).

- [18] M. Kusaka, K. Takegami, A. Sudo, T. Yamazaki, J. Kawamura, A. Uchida, *J. Orthop. Sci.* **7**, 354 (2002).
- [19] K. Takegami, T. Sano, H. Wakabayashi, J. Sonoda, T. Yamazaki, S. Morita, T. Shibya, A. Uchida, *J. Biomed. Mat. Res. (Appl. Biomater.)* **43**, 210 (1998).
- [20] G. Cho, Y. Wu, J.L. Ackermann, *Science* **300**, 1123 (2003).
- [21] A. Ito, M. Hayashida, H. Honda, K.I. Hata, H. Kagami, M. Ueda, T. Kobayashi, *Tissue Eng.* **10**, 873 (2004).
- [22] W. C. Elmore, *Phys. Rev.* **54**, 309 (1938).
- [23] J. H. Wu, S. P. Ko, H. I. Liu, S. Kim, J. S. Ju, Y. K. Kim, *Mater. Lett.* **61**, 3124 (2007).
- [24] H. Yan, J. Zeng, C. You, Z. Song, B. Yu, Y. Shen, *Mater. Chem. Phys.* **113**, 46 (2009).
- [25] H. Yosuoaka, A. Hirai, T. Shihjo, M. Kiyama, Y. Bando, T. Takada, *J. Phys. Soc. Jpn.* **22**, 174 (1967).
- [26] T. Sugimoto, E. Matijevic, *J. Colloid Interf. Sci.* **74**, 227 (1980).
- [27] L. Diamandescu, D. Mihaila-Tarabasanu, V. Teodorescu, N. Popescu-Pogrion, *Mater. Lett.* **37**, 340 (1998).
- [28] H. Zhu, D. Yang, L. Zhu, *Surf. Coat. Tech.* **201**, 5870 (2007).
- [29] J. Wang, J. Sun, Q. Sun, Q. Chen, *Mater. Res. Bull.* **38**, 1113 (2003).
- [30] C. Q. Hu, Z. H. Gao, X. R. Yang, *Chem. Phys. Lett.* **429**, 513 (2006).
- [31] L. Duraes, B. F. O. Costa, J. Vasquez, J. Campos, A. Portugal, *Mater. Lett.* **59**, 859 (2005).
- [32] S. Solinas, G. Piccaluga, M. P. Morales, C. J. Serna, *Acta Mater.* **49**, 2805 (2001).
- [33] S. Sun, H. Zeng, D. B. Robinson, S. Raoux, P. M. Rice, S. X. Wang, G. Li, *J. Am. Chem. Soc.* **126**, 273 (2004).
- [34] R. Y. Hong, T. T. Pan, H. Z. Li, *J. Magn. Magn. Mater.* **303**, 60 (2006).
- [35] M. J. Meziani, P. Liu, P. Pathak, J. Lin, S. K. Vajandar, L. F. Allard, Y. P. Sun, *Ind. Eng. Chem. Res.* **45**, 1539 (2006).
- [36] Z. Q. Liu, H. Hashimoto, M. Song, K. Mitsuishi, K. Furuya, *Acta Mater.* **52**, 1669 (2004).
- [37] J. H. Liu, J. Wei, S. M. Li, *Mater. Lett.* **61**, 1529 (2007).
- [38] J. H. Li, R. Y. Hong, H. Z. Li, J. Ding, Y. Zheng, D. G. Wei, *Mater. Chem. Phys.* **113**, 140 (2009).
- [39] D. E. Zhang, W. Wu, S. Z. Li, X. B. Zhang, G. Q. Han, A. Ying, J. Y. Gong, Z. W. Tong, *J. Mater. Sci.* **45**, 34 (2010).
- [40] R. Y. Hong, J. H. Li, H. Z. Li, J. Ding, Y. Zheng, D. G. Wei, *J. Magn. Magn. Mater.* **320**, 1605 (2008).
- [41] R. Y. Hong, S. Z. Zhang, G. Q. Di, H. Z. Li, Y. Zheng, J. Ding, D. G. Wei, *Mater. Res. Bull.* **43**, 2457 (2008).
- [42] Y. Li, H. Liao, Y. Qian, *Mater. Res. Bull.* **33**, 841 (1998).
- [43] R. Y. Hong, J. H. Li, J. Wang, H. Z. Li, *Particuol.* **5**, 186 (2007).
- [44] R. Y. Hong, T. T. Pan, Y. P. Han, H. Z. Li, J. Ding, S. J. Han, *J. Magn. Magn.* **310**, 37 (2007).
- [45] A. H. Morrish, S. P. Yu, *J. Appl. Phys.* **26**, 1049 (1955).
- [46] D. H. Han, J. P. Wang, H. L. Luo, *J. Magn. Magn. Mater.* **136**, 176 (1994).