Materials Science-Poland, Vol. 23, No. 4, 2005

Temperature dependence of the FMR spectra of Fe_3O_4 and Fe_3C nanoparticle magnetic systems in copolymer matrices

T. BODZIONY[1*], N. GUSKOS[1, 2], J. TYPEK[1], Z. ROSLANIEC[3], U. NARKIEWICZ[4], M. KWIATKOWSKA[3], M. MARYNIAK[1]

[1]Institute of Physics, Szczecin University of Technology, al. Piastów 17, 70-310 Szczecin, Poland

[2]Solid State Section, Department of Physics, University of Athens, Panepistimiopolis, 15 784, Greece

[3]Institute of Material Engineering, Szczecin University of Technology, al. Piastów 17, 70-310 Szczecin, Poland

[4]Department of Chemical Engineering, Szczecin University of Technology, al. Piastów 17, 70-310 Szczecin, Poland.

A binary magnetic nanoparticle system, consisting of Fe_3O_4 (35 wt. %), Fe_3C (29 wt. %), and C (36 wt. %) filling in a PTMO–block–PET polymer at low concentration (0.3 %), has been synthesized. X-ray and SEM analyses have been carried out. The temperature dependence of the FMR spectrum of this system has been investigated. At higher temperatures resonance from Fe_3O_4 nanoparticles dominates the FMR spectrum, while at lower temperatures a more intense line from Fe_3C is recorded. The temperature dependence of the FMR spectrum confirms that the nanoparticles of Fe_3O_4 reach the ordered state faster than Fe_3C nanoparticles. In both cases, the spin-glass state is observed below 50 K.

Key words: *magnetite; iron carbide; magnetic resonance*

1. Introduction

Although magnetite (Fe_3O_4) has been well known since an early period of human civilization, its magnetic and electrical properties are still intensively studied at different scales, from macro- to nanoscopic [1–6]. After the discovery of magnetic resonance, magnetite was one of the first materials studied by the magnetic resonance technique [7]. Iron carbide (Fe_3C) is one of the most important components used in

* Corresponding author, e-mail: Tomasz.Bodziony@ps.pl

metallurgy. The ferromagnetic resonance (FMR) spectra of iron carbide nanoparticle agglomerates in a carbon matrix have been shown to exhibit very interesting behaviour [6, 8, 9]. The resonance absorption signal arises from agglomerates of iron carbide with strong magnetic interactions and is significantly influenced by the concentration of magnetic nanoparticles in a non-magnetic matrix. Polymers traditionally have been considered as excellent host matrices for composite materials. Several advanced polymer nanocomposites with magnetic particles dispersed in organic or inorganic matrices are of great interest due to their various applications [10]. Nano-size magnetic materials have attracted the attention of many researchers, because magnetic nanoparticles exhibit such unusual chemical and physical properties as superparamagnetism and quantum tunnelling of magnetization [11]. Therefore it would be very interesting to study the binary magnetic system of iron carbide and iron oxide in a non-magnetic matrix. Moreover, magnetite exhibits extraordinary behaviour near T_c = 125 K (the Verway transition) [2], and this temperature decreases with a diminishing size of the magnetic particles.

The aim of this work is to report the preparation of a binary system of Fe_3O_4 and Fe_3C magnetic nanoparticles dispersed at low concentration (0.3 wt. %) in a PTMO–block–PET polymer, its characterization (by XRD and SEM), and a study of the temperature dependence of its FMR spectra.

2. Experimental

The fusion of magnetite with small amounts of Al_2O_3 and CaO (3 wt.%) was first used in the preparation of the sample. The material obtained after the fusion was cooled to room temperature, crushed and sieved (the 1.2–1.5 mm fraction was taken), and reduced in hydrogen at temperatures in the range of 620–770 K. Nanocrystalline iron was obtained after reduction, while the promoter oxides remained in the oxidized state and their role was to stabilize a well-developed nanocrystalline iron structure. To avoid oxidation after reduction, the sample was passivated with nitrogen containing traces of water vapour. The mean size of iron crystallites was determined by using the XRD method; the size was estimated to be about 17 nm. The sample of nanocrystalline iron was carburised with a CO–CO_2 mixture (98 vol. % CO) at 720 K in a glass flow reactor. The carburising gas mixture was obtained via the Boudouard process ($C + CO_2 = 2CO$), passing carbon dioxide through the bed of active carbon at 1370 K. The analysis of the gas at the inlet and outlet of the carburisation reactor was performed using gas chromatography (Hewlett Packard, 4890D). 5 A molecular sieves of were used as a column filling. After carburisation the samples were characterised using XRD (Philips X Pert, $CoK_{\alpha 1}$), TOC (total carbon, Multi N/C, equipped with an Eltra HFT-540 oven, Analytik Jena), and SEM (DSM-962, LEO, Zeiss Jena) methods. The specific surface area and pore distribution were measured using low temperature nitrogen adsorption (Micromeritics, ASAP).

The composite used in our experiments consisted of a PTMO–block–PET polymer filled at low concentration (0.3 %) with the nanoparticle mixture: Fe_3O_4 (35 wt. %), Fe_3C (29 wt. %) and C (36 wt. %). The composite was carefully mixed manually, poured out into the mould and hardened thermally.

The nanocomposite samples were obtained by introducing the filler into the reaction mixture and synthesizing multiblock poly(ether–ester) copolymers based on polyoxytetramethylene and poly(ethylene terephtalate) (PET). An appropriate amount of filler was dispersed in 1,4-ethanediol by ultrasonication in a Sonoplus-Homogenisator HD2200. The synthesis of the multiblock copoly(ether–ester) was a two-stage process, carried out in an acid-resistant steel reactor. The transesterification of dimethyl terephthalate (DMT) with ED was the first stage process. The reaction was carried out at temperatures between 420 and 460 K, under atmospheric pressure, until the 90% conversion was measured by the amount of distilled methanol with respect to the theoretical amount. In the next stage, the transesterification of di(2-hydroxytetramethylene) terephthalate with α, ω-dihydroxy-polyoxytetramethylene (PTMEG) was performed. Polycondensation was carried out at 460–500 K, with the pressure decreasing step by step down to 0.1 hPa. The progress of the reaction was determined on the basis of the amount of distilled ED and the increase in the torque of the stirrer. The polymer was extruded from the reactor using compressed nitrogen.

Magnetic resonance absorption measurements were carried out with a conventional X-band (ν = 9.43 GHz) Bruker E 500 spectrometer and 100 kHz magnetic field modulation. The samples, each containing around 20 mg of the material, were placed in quartz tubes 4 mm in diameter. Prior to measurements, the samples were magnetized by a steady 1.6 T magnetic field in order to saturate any domain structure. The measurements were performed in the range from room to helium temperature, with $\Delta T = \pm 1.0$ K stability, using an Oxford cryogenic system.

3. Results and discussion

The sample was characterized using XRD and SEM. Figure 1 presents an XRD pattern for a binary system of magnetic nanoparticles in carbon. According to the XRD and TOC methods, after carburisation and before polymerisation the sample contained: Fe_3O_4 (35 wt. %), Fe_3C (29 wt. %), and C (36 wt. %). A SEM micrograph (Fig. 2) shows that the grains of the magnetic binary system in carbon are distributed almost homogeneously in the PTMO–block – PET polymer matrix. The two magnetic phases are contained in one grain, with carbon being the environment. Over 95% of all grains had a radius below 100 nm.

Figure 3 presents an FMR spectrum of the investigated sample at various temperatures. At higher temperatures, an intense, slightly asymmetric resonance line centred at $g_{\text{eff}} = 2.204(1)$ is observed. With decreasing temperature, the intensity of the FMR spectrum strongly decreases, the linewidth increases, and the resonance field shifts towards lower magnetic fields (Fig. 3).

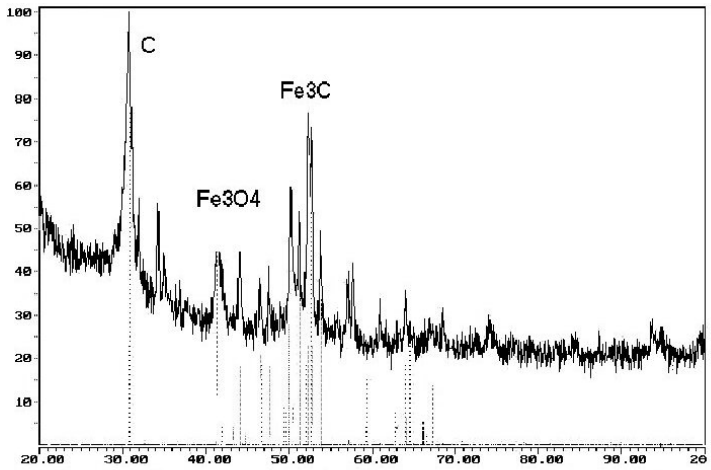

Fig. 1. The XRD pattern for a binary system of magnetic nanoparticles in carbon

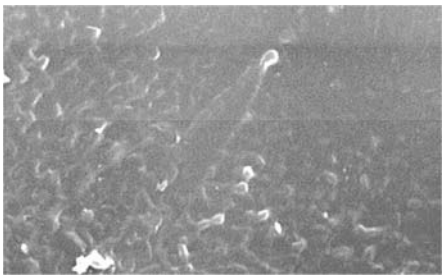

Fig. 2. The SEM micrograph of a magnetic binary system in carbon in a polymer matrix

The FMR study of the Fe_3O_4 + Fe_3C magnetic nanoparticle system dispersed in epoxy resin has revealed a resonance line that could be fitted by two separate Lorentzian functions [12]. A similar procedure has been successfully used for the present sample. The line shape asymmetry observed at higher temperatures can be explained assuming the spectrum is a superposition of two separate Lorentzian-shaped lines, including the tail of the resonance absorption at negative fields due to the linearly polarized radio frequency radiation.

Figure 4 presents, as an example, the FMR spectra registered at two temperatures, 33.1 K and 263.1 K, together with the fitted Lorenztian curves. The dotted line and the dashed line show the first (narrow) and second (broad) component Lorentzian lines, respectively. The solid line shows the best fit of the resonance spectrum by assuming a superposition of two Lorenztian lines. The FMR spectrum at room temperature (T = 295 K) consists of two lines with the following g-factors and peak-to-peak linewidths: g = 2.250(1) and ΔH_{pp} = 142 mT for the first component, and the second being centred near zero resonance magnetic field with the linewidth of ΔH_{pp} = 365 mT. On the basis of our earlier studies of a Fe_3O_4 + Fe_3C magnetic nanoparticle system dispersed in epoxy resin and PTMO–block–PET polymer at a higher concen-

tration (0.5 %) [13], we were able to make the assumption that the narrow and more intense component observed in the FMR spectrum at higher temperatures arises from the magnetite, while the broader line is due to iron carbide.

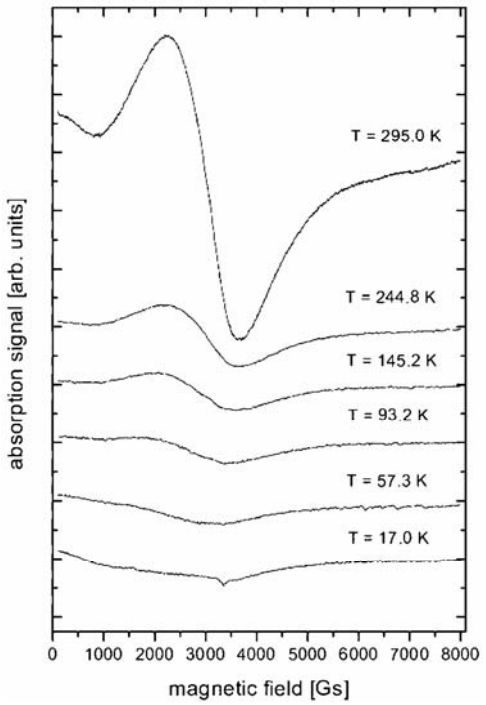

Fig. 3. An example of an FMR spectrum for 0.3% (Fe_3O_4 + Fe_3C)/C in a polymer matrix at different temperatures

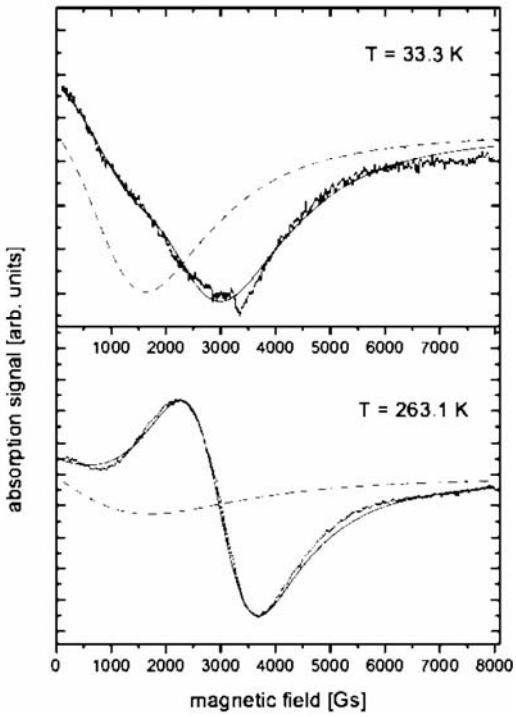

Fig. 4. An example of an FMR spectrum for T = 33.1 K and T = 263.1 K. The solid line shows the best fit of the resonance spectrum using two Lorenztian lines. The dotted and dashed line show the first (narrow) and second (broad) Lorentzian lines originating from magnetite and iron carbide, respectively

Figures 5 and 6 present the temperature dependences of the resonance field H_r, peak-to-peak linewidth ΔH_{pp}, and integrated intensity I arising from magnetite (Fig. 5) and iron carbide (Fig. 6). At high temperatures (55 K < T < 300 K), this type of temperature dependence has been frequently observed in the FMR spectra of iron oxide nanoparticles and suggests the presence of superparamagnetic phenomena [14–17]. The gradual suppression of the averaging effect of thermal fluctuations and interparticle interaction or the emergence of spin-glass like freezing with decreasing temperature for magnetite nanoparticles could essentially influence the FMR spectrum at higher temperatures, at which it is dominated by the signal from magnetite.

Figure 7 shows the temperature dependence of the g parameter from room temperature to about 20 K, computed from the best fit of the resonance spectra for the

broader Lorentzian line (Fig. 7a), and for the narrower component (Fig. 7b), originating from iron carbide and magnetite, respectively. The FMR line from iron carbide displays an abrupt change in its g parameter at temperatures between 93.2 K and 118.5 K (Fig.7a). This effect should be expected in the behaviour of a Lorentzian line arising from magnetite, which undergoes a structural phase transition at T_c = 125 K for bulk material, known in literature as the Verwey transition [2]. The temperature dependence of the *g* parameter for the narrower component (arising from magnetite) at temperatures from 57.3 K to room temperature was fitted with a Curie–Weiss curve (Fig. 8).

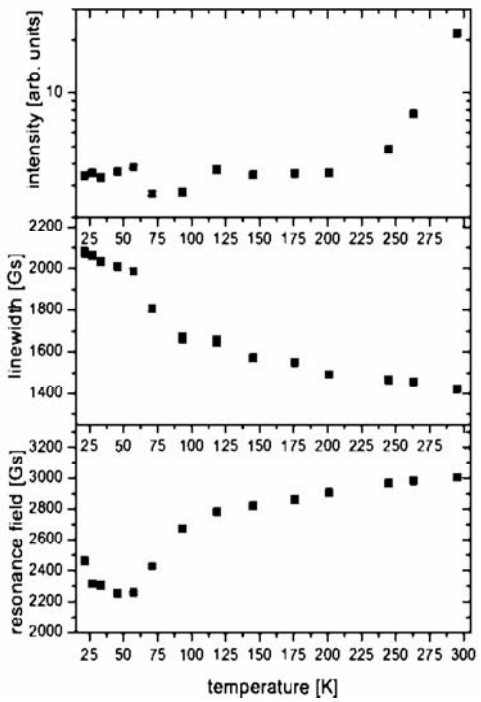

Fig. 5. Temperature dependence of FMR intensity, peak-to-peak linewidth, and resonance field for the narrow component originating from magnetite

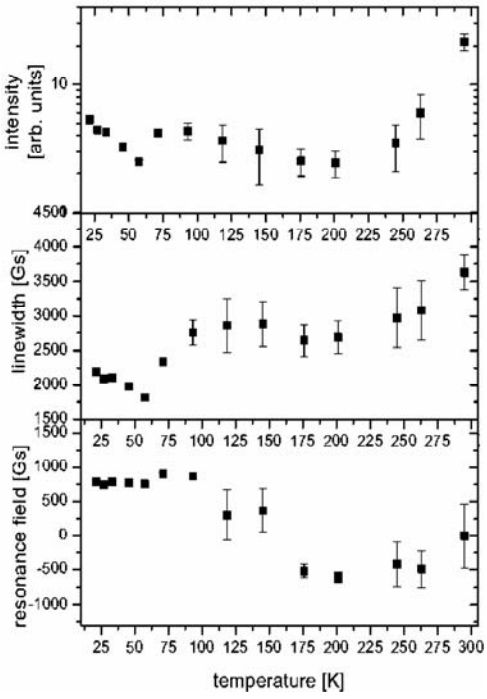

Fig. 6. Temperature dependence of FMR intensity, peak-to-peak linewidth, and resonance field for the broad component originating from iron carbide

Figure 9 shows the temperature dependence of the integrated intensity ratio of the lines, $I_{\text{iron carbide}}/I_{\text{magnetite}}$, expressed in %. The temperature dependence of this ratio varies between 60% and about 160%.

In order to understand the behaviour of the FMR spectrum of a binary magnetic system, we have to remember that the internal magnetic field acting on a mono-domain nanometer-size ferromagnetic particle can be formed by the following components [8]:

$$B_{\text{tot}} = B_{\text{dem}} + B_{\text{app}} + B_{\text{dip}} + B'_{\text{dip}} \tag{1}$$

where B_{dem} is the demagnetisation field, B_{app} is the applied external magnetic field, B_{dip} is the dipole field from the neighbouring nanoparticles, and B'_{dip} is the dipole –dipole interaction between aggregates. The collective spins of aggregates or agglomerates could recognize an additional magnetic field, and this could broaden the FMR spectrum and shift it towards lower magnetic fields.

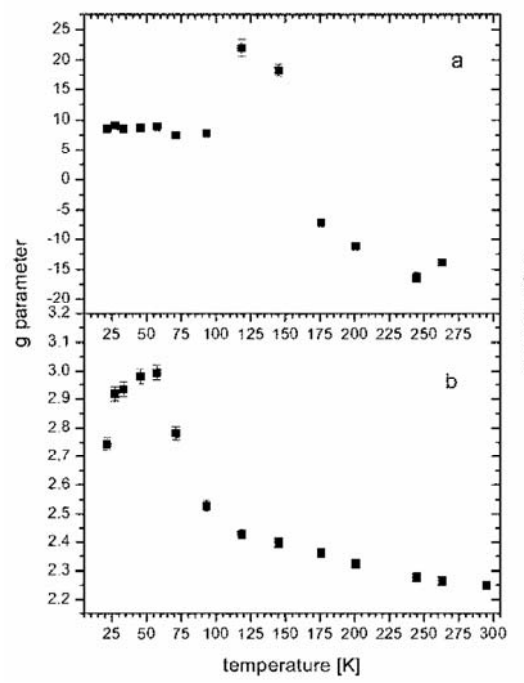

Fig. 7. Temperature dependence of the *g* parameter computed from the best fit to the resonance spectrum for the broad Lorentzian line (a), and for the narrow Lorentzian line (b), originating from iron carbide and magnetite, respectively

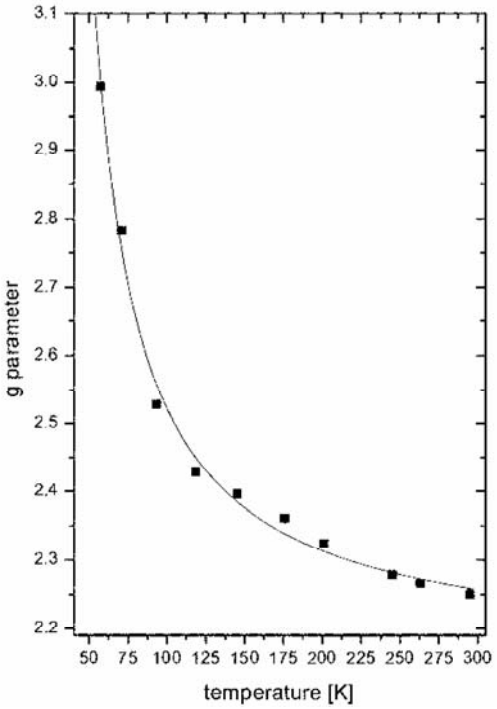

Fig. 8. A fragment of temperature the dependence of the *g* parameter for the narrow Lorentzian line originating from magnetite, and a fitted Curie–Weiss curve

The magnetic nanoparticles are distributed in the PTMO–block–PET polymer matrix almost homogenously, as evidenced by the SEM micrograph (Fig. 2), so only the exchange interaction of the neighbouring magnetic nanoparticles must be taken into account, while the interaction between agglomerates (or aggregates) can be neglected. The influence of neighbouring magnetic nanoparticles on the FMR spectrum could be observed by a closer inspection of the temperature dependence. The same binary magnetic system but in greater concentration in the epoxy resin matrix showed a resonance line significantly broader than in the polymer matrix [12]. The behaviour of the peak-to-peak linewidth and integrated intensity (Figs. 5 and 6) suggests that in the

case of a Fe_3O_4 + Fe_3C binary magnetic system dispersed at low concentration (0.3 %) in the PTMO–block–PET polymer, the magnetic field B_{dip} – the dipole field from neighbouring nanoparticles – can be small or even negligible. This may be the consequence of a low concentration of magnetic nanoparticles in a non-magnetic matrix and of a situation in which particular nanoparticles are rather isolated from their neighbours.

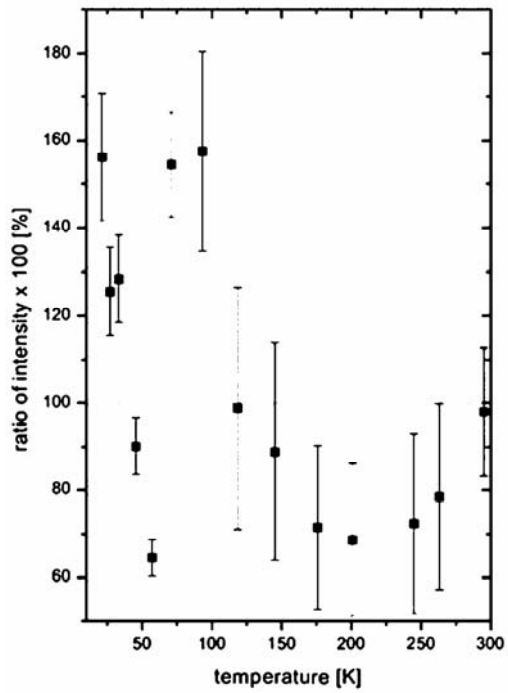

Fig 9. Temperature dependence of the ratio of FMR intensity of the broad Lorentzian component to that of the narrow Lorentzian component

The behaviour of the *g* parameter for lines originating from magnetite and iron carbide is rather interesting. In the case of the *g* parameter for iron carbide, an abrupt change in the temperature range between 93.2 K and 118.5 K can be seen. Such an effect should be expected in the behaviour of this line due to the Verwey transition. It might be supposed that the inner layer of a nanoparticle is made of iron carbide and surrounded by magnetite, and that the outer layer is formed by carbon [13]. An anomaly in the FMR spectra recorded below 50 K could suggest some parts of the sample may be in the spin-glass state.

4. Conclusions

The binary magnetic system of (Fe_3O_4 + Fe_3C)/C in a non-magnetic matrix of PTMO–block–PET polymer has been prepared. FMR measurements have shown that the spectrum at higher temperatures is dominated by a magnetite signal, while at

lower temperatures it transforms into the FMR spectrum of iron carbide. The complex structure of nanoparticles in these binary magnetic systems could consist of an inner layer made of iron carbide surrounded by magnetite, and an outer layer made of carbon. Below 50 K, the spin-glass state may be formed.

Acknowledgements

This work was partially supported by the grant PBZ-KBN-095/TO8/2003.

References

[1] CHAINANI A., YOKOYA T., MORIMOTO T., TAKAHASHI T., TODO S., Phys. Rev., B51 (1995), 17976.
[2] WALZ F., J. Phys.: Condens. Matter, 14 (2002), R285.
[3] OWENS F.J., J. Phys. Chem. Solids, 64 (2003), 2289.
[4] HIRANO S., YOGO T., SAKAMOTO W., YAMADA S., NAKAMURA T., YAMAMMTO T., UKAI H., BANNO K., NAKAFUKU T., ANDO Y., J. Sol-Gel Sci. Technol., 26 (2003), 35.
[5] ZHANG X.Y., CHEN Y.J., J. Magn. Magn. Mat., 271 (2004), 184.
[6] GUSKOS N., TYPEK J., NARKIEWICZ U., MARYNIAK M., AIDINIS K., Rev. Adv. Mater. Sci., 8 (2004) 34.
[7] BICKFORD L.R., Phys. Rev., 78 (1950), 449.
[8] NARKIEWICZ U., GUSKOS N., ARABCZYK W., TYPEK J., BODZIONY T., KONICKI W., GASIOREK G., KUCHAREWICZ I., ANAGNOSTAKIS E.A., Carbon, 42 (2004), 1127.
[9] GUSKOS N., ANAGNOSTAKIS E.A., GASIOREK G., TYPEK J., BODZIONY T., NARKIEWICZ U., ARABCZYK W., KONICKI W., Mol. Phys. Rep., 39 (2004), 58.
[10] XIAOTUN Y., LINGGE X., CHOON N.S., HARDY C.S.O., Nanotechnology, 14 (2003), 624.
[11] TANGO T., HATSUTA T., MIYAJIMA K., KISHADA M., TASHIRO S., WAKABAYASHI K., J. Am. Ceram. Soc., 85 (2002), 2188.
[12] GUSKOS N., ANAGNOSTAKIS E.A., LIKODIMOS V., BODZIONY T., TYPEK J., MARYNIAK M., NARKIEWICZ U., KUCHAREWICZ I., WAPLAK S., J. Appl. Phys., 97 (2005), 024304
[13] BODZIONY T., GUSKOS N., TYPEK J., ROSLANIEC Z., NARKIEWICZ., KWIATKOWSKA M., MARYNIAK M., Rev. Adv. Mater. Sci., 8 (2004), 86
[14] GAZEAU F., SHILOV V., BACRI J.C., DUBOIS E., GENDRON F., PERZYNSKI R., RAIKHER YU.L., STEPANOV V.I., J. Magn. Magn. Mater., 202 (1999), 535.
[15] BERGER R., CLIAVA J., BISSEY J.C., BAIETTO V., J.Appl. Phys., 87 (2000), 7389.
[16] BERGER R., BISSEY J.C., CLIAVA J., DAUBRIC H., ESTOURNES C., J. Magn. Magn. Mater., 234 (2001), 535.
[17] KOSKAROV YU.A., PANKRATOV D.A., GUBIN S.P., KOSOBUDSKY I.D., BELTRAN M., KHODORKOVSKY Y., TISHIN A.M., J. Appl. Phys., 89 (2001), 2293.

Received 12 November 2004
Revised 17 March 2005