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Research Article

FMR Study of the Porous Silicate Glasses with Fe_3O_4 Magnetic Nanoparticles Fillers

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The results of research on new magnetic materials for biomedical applications are discussed. These materials are porous silicate glasses with magnetic fillers. To ensure the smallest number of components for subsequent removal from the body, the magnetic fillers are bare magnetite nanoparticles (Fe_3O_4). The magnetic properties of these materials have been investigated using the ferromagnetic resonance method (FMR). The FMR analysis has been complemented by scanning electron microscope (SEM) measurements. In order to examine the effect of time degradation on filling the porous glass with bare magnetite nanoparticles the FMR measurement was repeated five months later. For the samples with high degree of pore filling, in contrast to the samples with low degree of pore filling, the FMR signal was still strong. The influence of different pH values of magnetite nanoparticles aqueous suspension on the degree of filling the pores of glasses is also discussed. The experimental results are supported by computer simulations of FMR experiment for a cluster of N magnetic nanoparticles locked in a porous medium based on a stochastic version of the Landau-Lifshitz equation for nanoparticle magnetization.

1. Introduction

The ferrimagnetic magnetite (Fe_3O_4) nanoparticles are considered among the promising materials for biotechnological and medical applications because of their biocompatibility and low toxicity [1, 2]. An obstacle in the direct use of bare magnetite nanoparticles is their tendency to degradate their magnetic properties with time when exposed to atmospheric air. Therefore, it is necessary to cover the magnetic nanoparticle's surface with a nonmagnetic protective layer. On the other hand, in some medical applications such as magnetic nanocapsules for drug delivery, it is more desirable to use materials with the smallest number of components for subsequent removal from the body. Taking this into account, the study of magnetic properties of bare magnetic nanoparticles for different nonmagnetic matrices is an important goal of research.

In the following, we show that bare magnetite nanoparticles can be fillers of a porous silicate glass without the need for additional protective layer of nanoparticles. In this case, the nonmagnetic porous surrounding of the magnetic nanoparticles acts as a protective layer and magnetic properties of such materials may remain unchanged for a long time. In order to determine the magnetic properties of the samples under consideration we use the method of ferromagnetic resonance (FMR) [3]. It is known that FMR spectroscopy is a very efficient tool to study the magnetic properties of magnetic agglomerates in nonmagnetic matrices [4, 5]. Recently, magnetic nanopowders placed in various nonmagnetic polymer matrices have been proposed as the new types of smart materials which combine mechanical properties of polymer matrix and magnetic response of nanoparticles, for example, in hyperthermia treatment, in magnetic nanocapsules for drug targeting or intracellular manipulation, and so

Table 1: Parameters of the porous glass texture.

Parameter	Glass B	Glass D
Specific area, m^2/g	28.9	5.9
Pore volume, cm^3/g	0.44	0.47
Average diameter, nm	45	320
Porosity, %	50	48

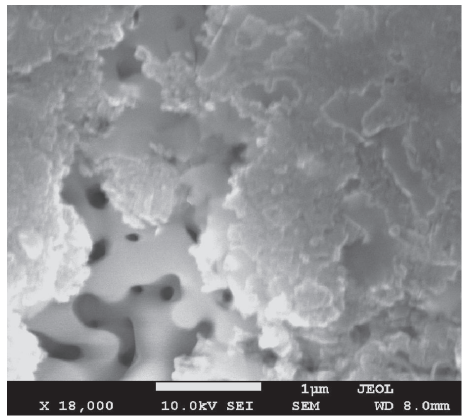

Figure 1: SEM visualisation of the porous silicate glass surface area (sample D).

forth (e.g., [6, 7]). The silica-based materials are currently implemented in medical and biotechnological applications such as bone-repairing devices and drug delivery systems [8, 9].

2. Experimental

Two types of porous silica glass samples (B and D) were studied and they were obtained as a leaching product from one sodium-borosilicate glass with a chemical composition as follows: 90–91% SiO_2, 8.3–8.7% B_2O_3, 0.3–0.6% Na_2O (%mol). For phase separation glass B was heated at 490°C for 165 hours and glass D was heated at 650°C for 100 hours. All the samples were etched in hydrochloric acid and rinsed in deionized water. Then both types of glasses were immersed in KOH [10]. The texture of obtained porous glasses was essentially different (Table 1). In Figure 1 the example of a pore structure in the case of sample D is shown.

In the experimental stage, which refers to filling the pores of porous glass by magnetic nanoparticles, glass samples (with dimensions $10 \times 10 \times 0.5\,mm^3$) were immersed in an aqueous suspension of magnetite nanoparticles (Fe_3O_4) for about 48 hours. The experiment was repeated for different values of pH of the aqueous solution. The glass samples were filled with magnetite nanoparticles as a result of a diffusion process from the magnetic suspension. The initial pH value of the water solution with the nanoparticles was adjusted by adding an appropriate amount of the hydrochloric acid or sodium hydroxide. In this work, five samples of porous glass filled with magnetic nanoparticles at different pH values were selected for investigation. They were denoted as sample 1, sample 2, sample 3 (glass type B, pH values 7.92, 8.78, 9.04, resp.), and samples 4 and 5 (glass type D, pH values 7.90 and 7.94, resp.). Samples 4 and 5 were filled with magnetic nanoparticles at approximately the same pH value but sample 5 was subjected to an external constant magnetic field from a permanent magnet ($B_{sat} \sim 0.5\,T$) during the filling process.

The nanoparticles were synthesized according to the Massart's method [11]. Their diameter was smaller than 20 nm. The size of the magnetic nanoparticles has been measured by using semicontact Ntegra Aura system (Scanning Probe Microscope) with a $100 \times 100 \times 10\,\mu m$ closed-loop sample scanner. In Figure 2, two images on the sample of Fe_3O_4 nanoparticles, which has been presented on the fresh mica surface by using drop-coating method after being dispersed into ethanol solvent, are shown. In (a), a small $2.0 \times 2.0\,\mu m$ area has been shown with many tiny magnetic nanoparticles and two of them have been chosen for a detailed investigation in (b). A Si cantilever was used in these measurements with a force constant of $\sim$ 2.0 N/m and a resonance of ~120 kHz. The curvature of the Si tip is 10 nm. Two representative magnetic nanoparticles have dimensions of 14.94 nm and 12.82 nm.

For measurements of FMR spectra of the samples of porous glass filled with magnetic nanoparticles the glass plates were broken into pieces with average dimensions $2 \times 2 \times 0.5\,mm^3$. Next, these pieces were subjected to FMR measurements. The FMR spectra were recorded using X-band ($f \sim 9.4\,GHz$) EPR spectrometer of the SE/X-2013 type (RADIOPAN, Poznań, Poland), operating in high-frequency (100 kHz) modulation mode of magnetic field at room temperature. In addition to FMR measurements the morphology of the porous glass samples has been investigated using the scanning electron microscope (SEM) JEOL 7600F with the energy-dispersive X-ray spectroscopy (EDS) system integrated into it to examine both sample's surface and interior. The latter was the cross-section of the samples after they have been broken in smaller pieces.

3. Discussion of Results

Our method of filling the porous glass is a direct immersion of the samples of porous glasses in an aqueous suspension of magnetic nanoparticles. The filling takes place at a given pH value of the water solution and pH value is one of the most important parameters for controlling the process of diffusion of magnetic nanoparticles from the solution to the pores of glasses and their adsorption into them. It is known that both magnetite nanoparticles and porous glass samples possess a pH-dependent surface charge after contacting aqueous solution. The charge is positive for pH < PZC, where PZC represents the point of zero charge and the charge is negative otherwise. The values of PZC for the silicate glass samples (PZC_g) and magnetite nanoparticles (PZC_m) are substantially different, $PZC_m \sim 7.9$ (in the literature PZC_m ranges from 6.3 to 7.9 [12–15]) whereas $PZC_g \sim 1.8$ for the silicate glasses [16, 17]. In our case, the process of filling the pores by magnetic nanoparticles was carried out for pH > PZC_g for both pH < PZC_m and pH > PZC_m. This means that

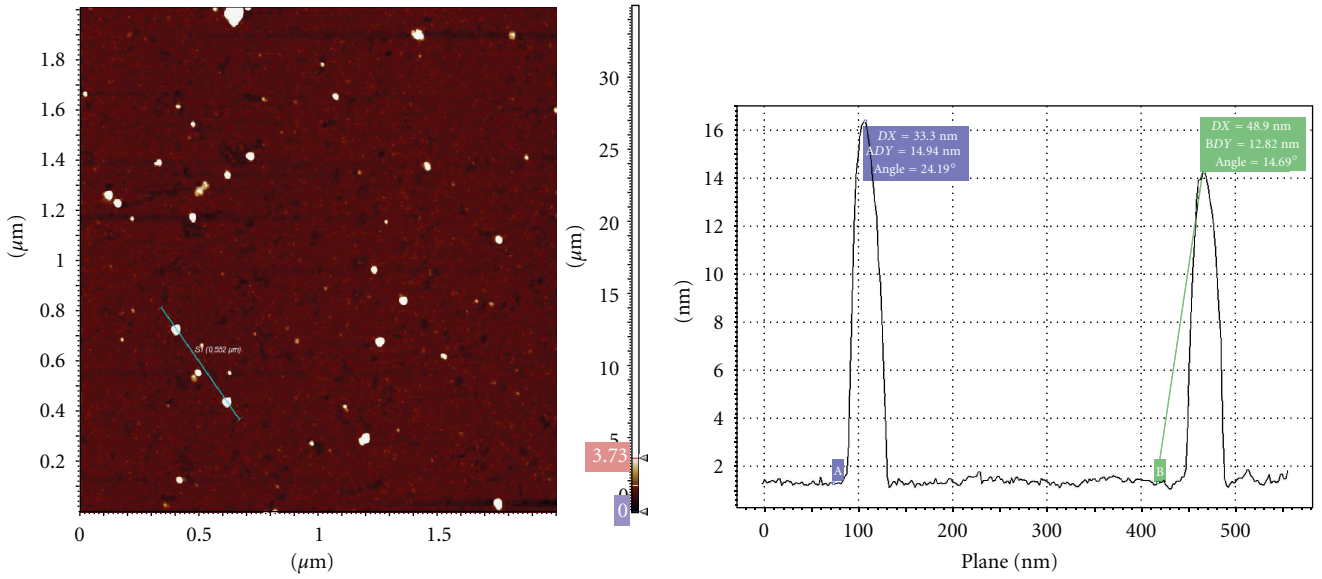

Figure 2: Investigation of Fe_3O_4 nanoparticle by Ntegra Aura system (Scanning Probe Microscope): (a) sample of Fe_3O_4 nanoparticles in $2.0 \times 2.0\,\mu$m scanning area, (b) two nanoparticles have been measured and the dimensions are 14.94 nm and 12.82 nm.

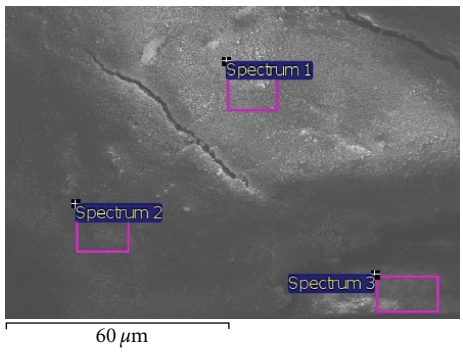

Figure 3: SEM visualisation of a large surface fragment of the sample 2 (glass of type B), where three rectangular areas were selected for whom EDS analysis was carried out (Table 2).

Table 2: Elements identified by SEM on the surface of sample 1 in three regions denoted as Spectrum 1, Spectrum 2, Spectrum 3 in Figure 3.

	Element	Weight%	Atomic%
Spectrum 1	O K	25.48	54.41
	Fe K	74.52	45.59
Spectrum 2	O K	28.20	56.27
	Si K	4.73	5.38
	Fe K	67.07	38.35
Spectrum 3	O K	55.08	68.28
	Si K	44.92	31.72

porous glass surface was always negatively charged whereas the surface charges of magnetic nanoparticles were positive or negative unless pH = PZC_m. We have observed that the best filling of glasses of type B takes place when pH $\gtrsim$ PZC_m, that is, when the surface charge of magnetic nanoparticle is positive. Close to pH $\sim$ PZC_m the electrostatic repulsion between the magnetic nanoparticles weakens and magnetic dipolar forces causes them to aggregate. The filling process appeared to be inefficient for glasses of type D at pH $\sim$ PZC_m. It is interesting that in the latter case we have observed the improving of the degree of pore filling after the magnetic nanoparticles were exposed to a weak external magnetic field, which introduces an additional aggregation of magnetic nanoparticles. Note that the average pore diameter for samples D is several times larger than the average diameter of the synthesized magnetite nanoparticles opposed to type B samples. In the case of type B samples the external magnetic field prevented insertion of nanoparticles inside the pores of the glass because the size of the magnetic aggregations that have been created exceeded the pore diameter.

We examined the surface of five samples of silica glass with magnetic fillers, samples 1–5 which have been defined in Section 2, using SEM (scanning electron microscope). We have observed that large areas of the surface of the porous glass samples with linear dimensions of micrometers have been coated with a homogeneous layer of magnetic nanoparticles. In Figure 3, it has been shown the surface of sample 2, where three rectangular areas were selected for whom EDS analysis was carried out (Table 2). It is evident from the SEM data in Table 2 that there are large surface areas occupied by magnetic nanoparticles, like the one in a window called Spectrum 1.

Using the SEM/EDS visualisation we obtained also information concerning the filling of pores of porous glass in the range of a few micrometers below the surface layer of glass.

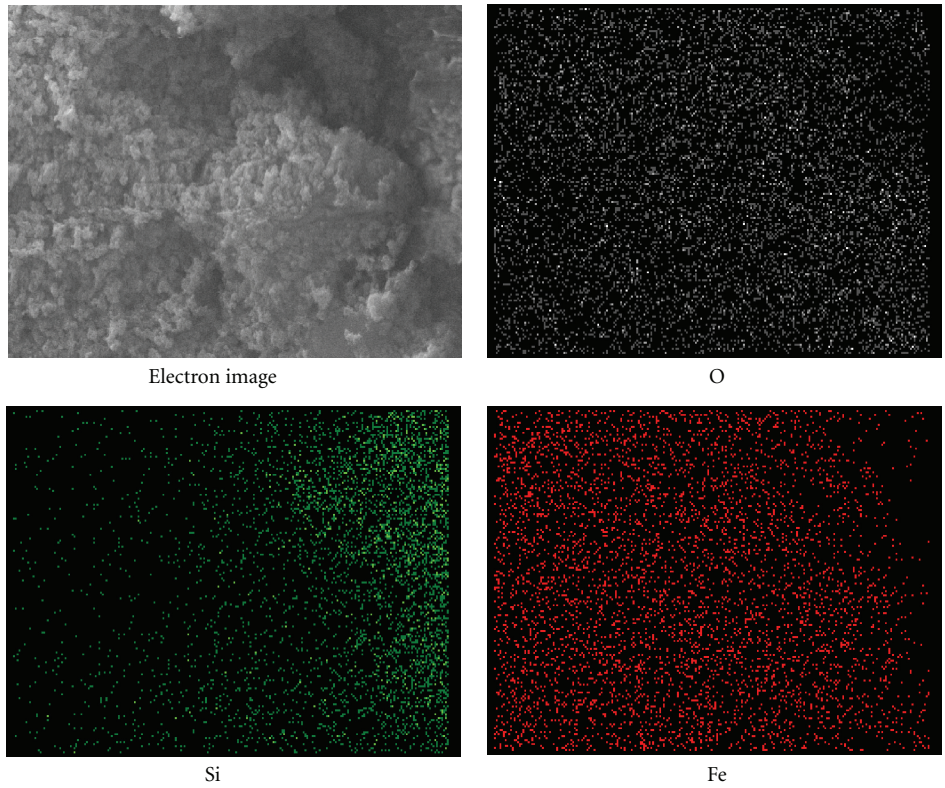

Figure 4: SEM/EDS images of the surface of the cross-section ($4.5 \times 6.0\,\mu$m) of porous silicate glass sample which was obtained after breaking the sample. The first photo shows an SEM visualization of the cross-section surface. The remaining three photos represent space distribution of different elements, Si, O, Fe, identified in this cross-section with the respective color saturation corresponding to the actual density of the identified elements.

This has been done by breaking the glass sample and observing the distribution of elements in the resulting cross-sections. The results of this analysis have been shown in Figure 4 and it is evident that the inner layers of the porous glass are very homogeneously filled with the magnetite nanoparticles.

Some information on the magnetic properties of the silica glass filled with nanoparticles can be obtained from the analysis of the absorption lines in FMR experiment. They represent the imaginary part χ'' of the complex ac magnetic susceptibility

$$\chi = \chi' - i\chi''. \tag{1}$$

In the FMR experiments, the absorption lines derivatives, $d\chi''/dH_{\mathrm{dc}}$, with respect to the external dc magnetic field are measured instead of direct measuring of χ''. It is always the case that H_{dc} is transverse to an external ac magnetic field H_{ac} which is rotating with a frequency f. The ferromagnetic resonance condition takes place when

$$f = \frac{\gamma}{2\pi} H_{\mathrm{eff}}, \tag{2}$$

where $\gamma = 2.21 \times 10^5\ \mathrm{s}^{-1}\,(\mathrm{A/m})^{-1}$ denotes the gyromagnetic ratio and H_{eff} represents the net magnetic field experienced by a magnetic moment of magnetic nanoparticle.

The FMR experiment technique [3] is one of the basic methods for determining the magnetic properties of magnetic agglomerates dispersed in nonmagnetic matrices. Usually, the main peak corresponding to the uniform resonance mode in the FMR spectra is accompanied by a series of other peaks which originate both from a spin-wave exchange model [18, 19] and dipolar interparticle interactions and they can as well be coupled with the magnetoelastic phenomena. The latter case has been discussed in [20] in the case of the γ-Fe_2O_3 ferrimagnetic nanoparticles embedded in a multiblock poly(ether-ester) copolymer nonmagnetic matrix. The results suggested that some additional peaks in low temperatures originate from the orientational anisotropy of frozen polymer blocks. The same interpretation of the presence of additional peaks in the case of materials with random agglomerates of magnetic nanoparticles can be found in theoretical papers, for example, [5, 21], where the stochastic version of the Landau-Lifshitz equation [22, 23] has been used to model the ferromagnetic resonance. In the papers, there is a discussion on the shape of the ferromagnetic resonance spectra for the ensemble of the randomly distributed magnetic anisotropy axes and their dependence on temperature. In particular, it is observed the multimodal FMR signal and its broadening for the randomly distributed magnetic anisotropy axes as compared to the magnetic nanoparticles which all have the same orientation of the

magnetic anisotropy. These theoretical models adequately can explain the asymmetric and multimodal FMR spectral line shape which we have received for the agglomerates of magnetite nanoparticles in porous glasses in the case of Figures 5 and 6. Note that qualitatively the same topology of the FMR signal, as in Figures 5 and 6, has been shown in Figure 7, which is a result of the computer simulation of the random clusters consisting of $N = 80$ and $N = 200$ magnetic nanoparticles, respectively. In the same figure, there have been also plotted the spectral lines of the single chains consisting of $N = 40$ magnetic nanoparticles. The single chains were oriented in the direction of the field H_{dc} (dot-dashed line in the figure) and transversely to it (dashed line in the figure), respectively. The simulation results suggest that in the case of the silica glass filled with magnetic nanoparticles (Figures 5 and 6) there are large magnetic agglomerates inside them which have the orientation of anisotropy axis aligned with the direction of the field H_{dc} and there are also large clusters where the orientation is set transversely to the direction of the H_{dc}. In the computer simulations, the dc magnetic field has been chosen into z-direction ($H_z = H_{dc}$) and the ac magnetic field into x-direction ($H_x = H_{ac} = H_{ac}^0 \cos(2\pi f)$)). In this case, the components of the complex ac susceptibility (1) have been calculated by performing the Fourier transform on the time averaged x-component of the magnetization, that is,

$$\chi = \frac{1}{\tau H_{ac}^0} \int_0^\tau dt M_x(t) e^{-i2\pi f t}, \tag{3}$$

where $\tau = 1/f$. The values $M_x(t)$ are calculated with the help of the Landau-Lifshitz equation ([5, Equation (12)]) describing the magnetic nanoparticle magnetization dynamics in the case of the frozen orientation of its magnetic anisotropy axis.

The experimental results in Figures 5 and 6 concern the newly synthesized porous glass and magnetic nanoparticles. In view of the potential applications of such material to the magnetic nanocapsules important is the question of the degradation of the magnetic material in these nanocapsules since magnetite nanoparticles degradate with time if they are exposed to atmospheric air. We have measured the FMR signal from the selected samples of porous glass with magnetic fillers after the expiry of five months. In general, we observed that in the cases where the magnetite nanoparticles are mainly deposited on the surface of porous glass (samples of type D) the FMR signal decreased. The signal from the magnetic nanoparticles inside the glass remained just as strong as five months earlier. These trends are evident in Figures 8 and 9 for samples 1 and 5, respectively. The main resonance amplitudes of the ageing samples decrease and they are shifted towards higher values of the magnetic field H_{dc} as compared with the newly synthesized samples. The ageing of the samples introduces additional averaging of the FMR signal possibly due to the reorientation of magnetic anisotropy axes as it is suggested by computer simulations (Figure 7). This signal averaging effect is greater for sample 5 (Figure 9) with pores of large diameter than for sample 1 (Figure 8)

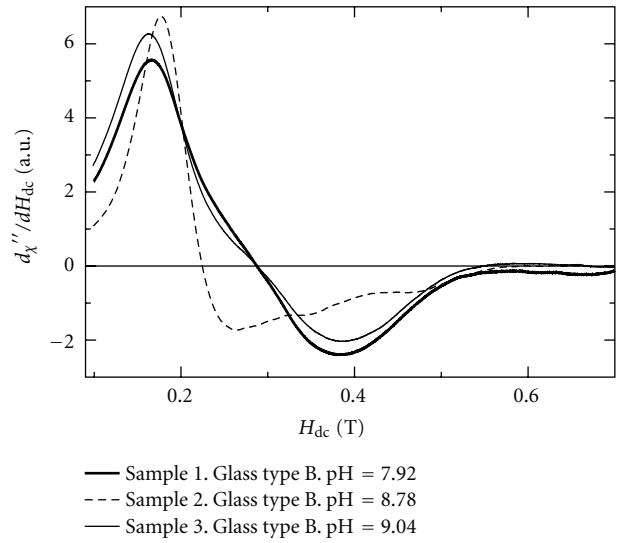

Figure 5: The examples of the dependence of the absorption lines derivatives, $d\chi''/dH_{dc}$, on dc magnetic field H_{dc}. The spectral lines were recorded for three different samples of porous glass of type B in the case when magnetic nanoparticles filling the samples come from the magnetic aqueous suspension with pH value 7.92, 8.78, and 9.04, respectively.

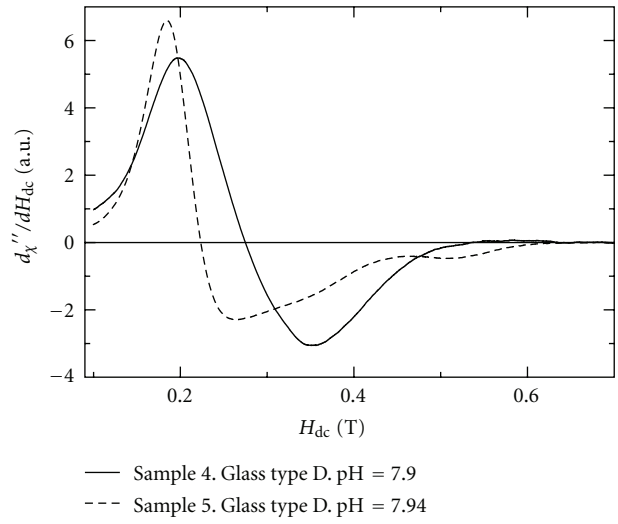

Figure 6: The dependence of the absorption lines derivatives, $d\chi''/dH_{dc}$, on dc magnetic field H_{dc} for two samples of type D. The plot made by dashed line relates to magnetic nanoparticles, which in the course of filling the pores of the porous glass were subjected to an external magnetic field of a permanent magnet ($B_{sat} \sim 0.5$ T). It was not the case for the plot made by continuous line.

with a small pore diameter. The results confirm the importance of porous structure to prevent degradation of the magnetite nanoparticles. This property is promising for using the porous silica glasses filled with magnetite nanoparticles, for example, for the radiofrequency heating applications.

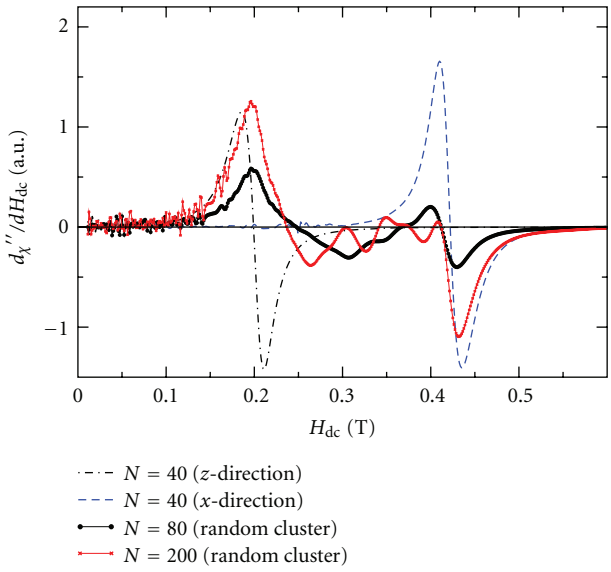

Figure 7: Absorption lines derivatives, $d\chi''/dH_{dc}$, resulting from the computer simulations in the case when magnetic anisotropy axes orientations represent a chain-like structure of $N = 40$ magnetic nanoparticles oriented into z-direction, chain-like structure of $N = 40$ nanoparticles oriented into x-direction, or they represent a random cluster consisting of $N = 80$ and $N = 200$, respectively. The parameters of the computer simulation have only a qualitative meaning and they have been taken the same as in [5].

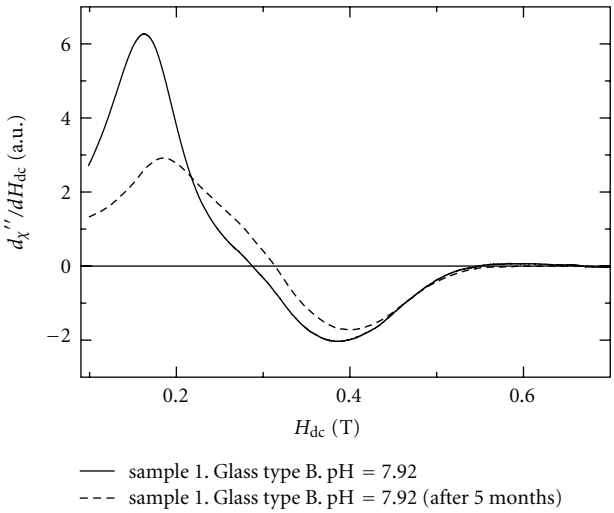

Figure 8: Visualization of the effects of ageing of magnetite nanoparticles in porous silicate glass of type B (sample 1) in terms of the FMR signal for the same samples after the expiration of five months.

4. Conclusions

We have described the procedure of preparation of silica porous glasses filled with magnetite nanoparticles. We have shown that the magnetic nanoparticles do not degradate for long time, and therefore we suggest the possibility of a simple production of such systems for medical purposes, while ensuring no chemical pollutants typical of other methods of coated nanoparticles synthesis. The ability to control the average pore diameter during the synthesis of porous glass provides additional opportunities for specialization of such systems.

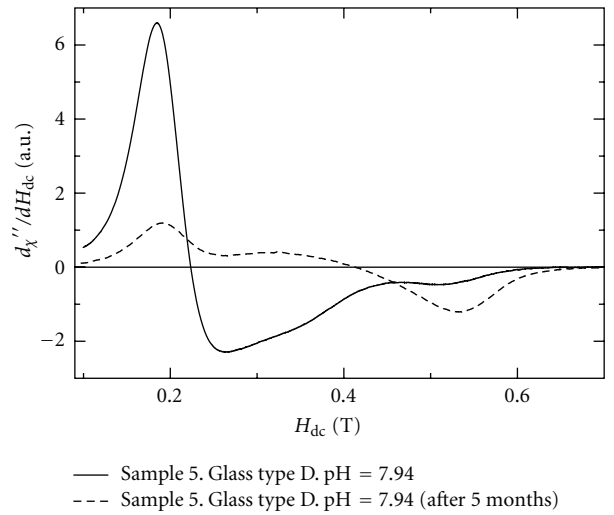

Figure 9: The same as in Figure 8 but for sample 5 of the glass of type D.

Acknowledgments

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