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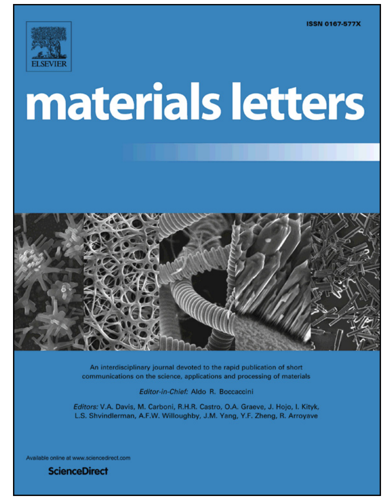

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Magnetic After-effects in Ni Ferrite Nanoparticles

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ABSTRACT

Magnetic after-effects in ferrite nanoparticles have been measured with magnetic disaccommodation technique. For higher annealing temperature multidomain formation is detected with low temperature relaxation process similar to single crystal and polycrystalline $NiFe_2O_4$. As expected, no room temperature processes are observed due to low vacancy content. On the other hand, logarithmic relaxations are observed at lower annealing temperatures, revealing monodomain character.

KEYWORDS

Ferrites
Nanoparticles
Magnetic materials
Magnetic disaccommodation

1. Introduction

Ferrite nanoparticles are at present the subject of increasing interest, as the materials with low dimensionality possess unique physical properties regarding bulk materials, especially in the case of magnetic properties, **of great interest in nanoscale electronic devices [1, 2]**. The reason arises in the increased fraction of surface atoms, in which several factors as coordination number or symmetry of environment, differ from bulk atoms. Among them, nickel ferrite is an intensively studied soft magnetic material due to their excellent properties as good electromagnetic performance and chemical stability. For this reason it can be used in various applications, as in data storage, magnetic resonance imaging, microwave devices, transformer cores, or sensors [3]. Time dependent effects are of considerable relevance to both magnetic recording media and permanent magnet materials [4]. This topic is especially important in the case of employing nanoparticles, where the particle size near the superparamagnetic limit strongly affect the magnetization reversal, and hence the hysteretic behavior of the material. Magnetic after-effect consists in the time variation of the magnetic properties after a shock. In magnetic viscosity, time decay of magnetization is measured after a sudden change of the magnetic field, obtaining a logarithmic dependence with time due to thermal activation of pinned domain walls over energy barriers [4]. In magnetic disaccommodation technique, time evolution of the reversible magnetic permeability is measured after sample demagnetization, usually with an exponential decay behavior. This is a very sensitive technique in the detection of small amounts of impurities, ferrous cations and lattice vacancies as shown previously in bulk polycrystalline spinel ferrites, garnets and hexaferrites [5, 6]. To our knowledge, there is not any systematic study of magnetic disaccommodation measurement in ferrite nanoparticles. In this work we have carried out for the first time this type of measurement in nanoparticle Ni spinel ferrites.

2. Experimental

Nickel ferrite nanoparticles were prepared by a modified sol-gel technique, with starting components $Fe(NO_3)_3$•$9H_2O$ (iron (III) nitrate nonahydrate), $Ni(NO_3)_2$•6 H_2O (nickel (II) nitrate hexahydrate) and lyophilized coconut oil. This route of preparation has revealed to be one efficient and cheap technique to obtain high quality nickel ferrite nanoparticles. Nitrates were dissolved in a suspension of coconut oil and water excess is removed by keeping the suspension at 75º C during 24 h. Dried samples were annealed in air at different temperatures ranging from 400 to 1200º C during 4 h. Crystallization is obtained by fast cooling to room temperature; finally, samples were milled.

For disaccommodation measurement [6], pressed samples of nanoparticle powders form the core of a coil allowing us to measure the temporal evolution of magnetic permeability after ac demagnetization. The obtained isotherm curves μ (t) obtained in the temperature range 80 K- 420 K are converted into isochronal curves applying the transform:

$$\frac{\mu(t_1,T)-\mu(t_2,T)}{\mu(t_1,T)}(\%) \qquad (1)$$

employing t_1=2 s and t_2=4, 8, 16, 32, 64 and 128 s. When the time window $(t_2 - t_1)$ is of the same order of magnitude as the relaxation time at a specified temperature, this curve exhibits a maximum, in the case of thermally activated processes.

3. Results and discussion

From XRD measurements and Scherrer formula [7], representative figures of particle sizes corresponding to single phase spinel structure for the different annealing temperatures employed are displayed in Table 1. It is noteworthy that even for the lower annealing temperature the samples are out of the superparamagnetic region at room temperature. **We have assumed spherical shape of the samples according to their FMR behaviour [7]**.

Magnetic disaccommodation spectra of Ni ferrite nanoparticles are represented in Fig. 1. The effect is small but detectable with our system, initially developed for analysis of bulk polycrystalline ferrites (the sample annealed at 1000º C show the signal to noise ratio of our measurement system). At lower annealing temperatures we observe an almost linear increase of the disaccommodation with temperature in the range available in our experimental setup, reaching maximum values when annealing at 600º C. On the other hand, sample annealed at 1200º C behaves in a very different way: we can observe a relaxation process at low temperatures that vanishes at 200 K. Sample annealed at 1000º C, which marks the frontier of the above mentioned behaviors, do not show detectable disaccommodation.

Due to the low amplitude of DA figures, we haven't performed fitting, hence we will proceed with a qualitative discussion of the results that allow us to obtain interesting findings. It is well known that the origin of magnetic disaccommodation processes in multidomain polycrystalline ferrites lie in the reorientation of anisotropic structural or point defects, i.e. electronic hopping or vacancy mediated ionic diffusion within the Bloch walls, and is usually observed by exponential decay of magnetic permeability, with a time constant strongly temperature dependent [5, 6], thus promoting typical peaks in isochronal spectra. In this case we are dealing with a magnetic nanoscale system composed of assemblies of magnetic nanoparticles, whose size is small enough to be considered single domain, and hence without domain walls, so that magnetic disaccommodation due to the above mentioned mechanism cannot take place. However, we observe an almost linear variation in the whole temperature range, and equidistant isochronal curves for different window times, thus pointing to a logarithmic variation of permeability with time, in a similar way to viscosity measurements [4].

This result is not very surprising, as magnetic disaccommodation and magnetic viscosity refer to similar after-effect processes, and both measurements give similar results when the applied field in viscosity measurements is low enough [8,9]. In addition, Swartzendruber work [4] also show the small negative viscosity after ac demagnetization in iron nanoparticles with similar size than our samples, so that this effect, despite its low amplitude, is not negligible, and their origin has to be discussed. As mentioned above, the magnetic properties depend strongly on the size and shape of the nanoparticles, the size dispersion and the particle interaction. With decreasing particle size, the shell exhibit different coordination of the atoms, broken bonds that alter the magnetic exchange, and different concentration and type of defects than the core promoting a disordered spin structure in the surface that result usually in reduced magnetization and increased magnetocrystalline anisotropy, that can be up to two orders of magnitude higher than bulk counterpart. Then, the origin of observed disaccommodation lies in the slow relaxation towards local energy minimum of the magnetic moments pinned in the shell in the demagnetization stage. The effect of increasing temperature in after-effect measurement produces a decrease of anisotropy in the shell, promoting a higher rate of unpinned spins during the measurement time and hence a higher disaccommodation rate. Comparing with viscosity measurements, our results are similar both qualitatively and quantitatively than the calculated temperature evolution in viscosity coefficient of single domain nanoparticles with comparable sizes [10]. With increasing sintering temperature, Ni ferrite nanoparticles grow, both the core and the shell, and the higher crystallinity weakens the surface anisotropy, thus increasing the amount of unpinned moments. A further increase in crystal size promote that the relative surface area decreases and hence the defects in the shell. This fact can eventually produce an annealing temperature range in which the size is small enough to have single domain particles but high enough to minimize the spin disorder in the shell, reducing the effective anisotropy and minimizing the amount of pinned spins so that disaccommodation reduces and finally vanishes at the onset of multidomain formation.

This effect could be a general trend, as it has also been observed by us in similar ferrite nanoparticle systems. **Variation of coercivity in the samples analyzed, presented in Table 1, supports this discussion.**

Finally, the behavior observed for the sample annealed at 1200º C is understandable in terms of multidomain formation. In Fig. 2, which show the temperature evolution of the magnetic permeability in the analyzed samples, we can observe a qualitatively different, higher permeability of this sample. This qualitative difference is also observed in microwave absorption measurements in this system [7]: increased particle size finally allow the presence of domain walls. Vacancy related after-effect processes observed at room temperature in polycrystalline Ni ferrites [11] are not present due to the stoichiometry of sample and annealing conditions, as vacancies are not expected. On the other hand, the observed relaxation process at low temperature has also been obtained in polycrystalline samples as well as in Ni ferrite single crystals, represented in Fig. 3. This process, **with activation energies up to 0.2 eV,** has been attributed to thermally activated electron hopping [11], in a broad temperature range due to strong Anderson electron localization induced by the presence of Ni cations. **Electron hopping can take place among Fe^{3+} in octahedral sites where there are states just above Fermi level so that electronic transitions are allowed with this range of energies [12]. Nevertheless, some amount of Fe^{2+} can also be considered**. The disaccommodation amplitude in nanoparticle system is lower due to both the small amount of domain walls regarding polycrystals and the lower vacancy content regarding single crystal and polycrystalline ferrites, but is a clear proof of the appearance of Bloch walls, **supported with the decrease of coercive field** in the sample annealed at 1200º C.

4. Conclusions

It has been demonstrated the possibility of carry out magnetic disaccommodation measurements, initially devoted to bulk polycrystalline samples, to nanostructured samples, obtaining logarithmic results for single domain nanoparticles, and evidence of multidomain formation for bigger ones, hence allowing us to obtain the critical size in a nanoparticle system.

Acknowledgements

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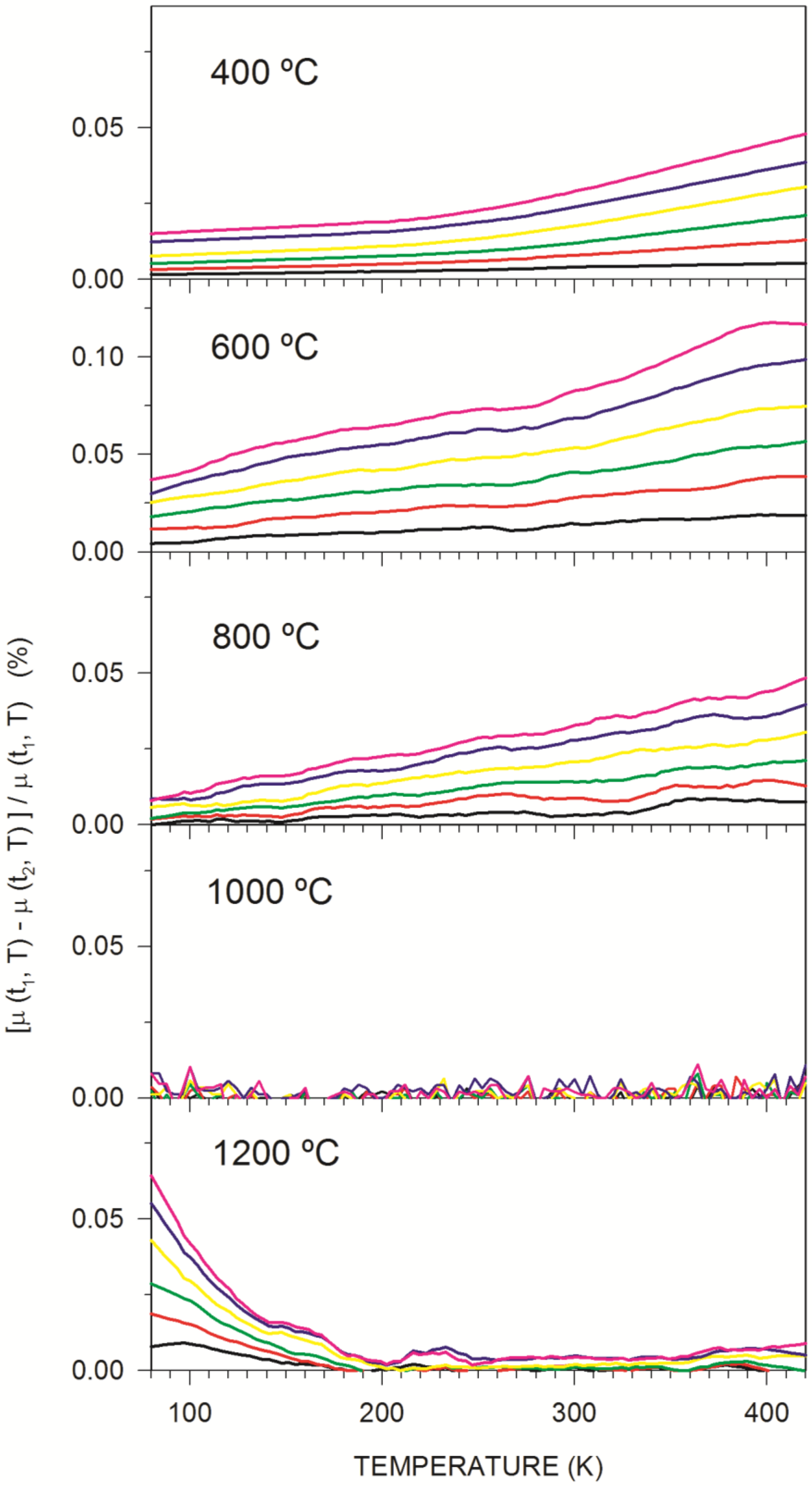
FIGURE AND TABLE CAPTIONS

Figure 1. Magnetic disaccommodation spectra of Ni ferrite nanoparticles annealed at 400º C; 600º C, 800º C, 1000º C, and 1200 ºC. Figures are obtained with equation (1) by using t_1=2 s and t_2= 4, 8, 16, 32, 64 and 128 s (plots from bottom to top in each graph)

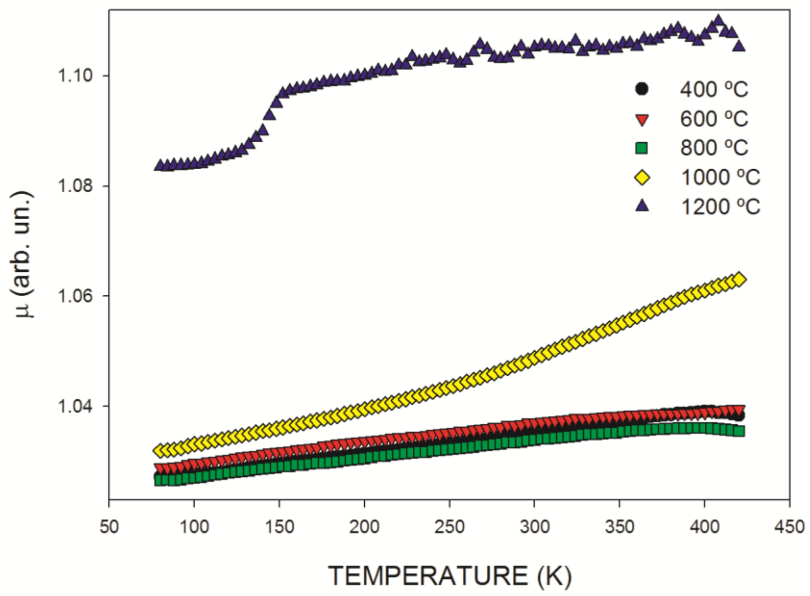
Figure 2. Magnetic permeability of Ni ferrite nanoparticles.

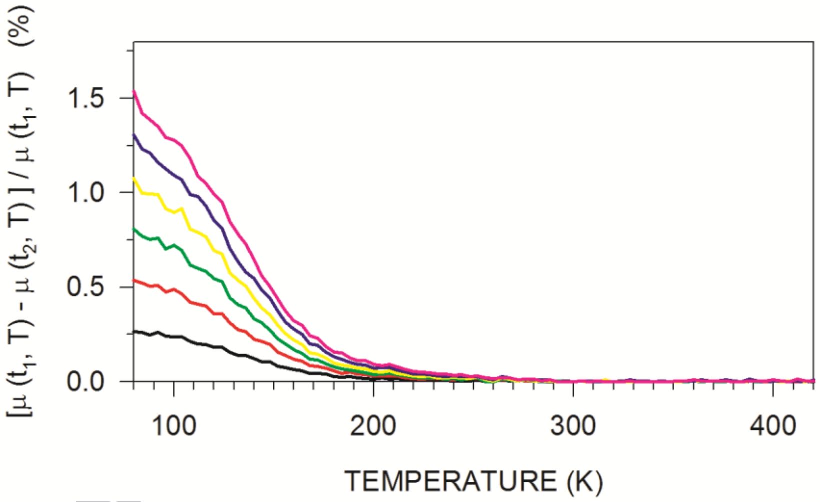
Figure 3. Magnetic disaccommodation spectra of $NiFe_2O_4$ single crystal.

Table 1. Particle sizes and coercivities of prepared Ni ferrite nanoparticles



400 ºC
600 ºC
800 ºC
1000 ºC
1200 ºC
0.00
0.05
0.10
[μ (t$_1$, T) - μ (t$_2$, T)] / μ (t$_1$, T) (%)
100
200
300
400
TEMPERATURE (K)





Annealing temperature	Particle size (nm)	Coercive Field (Oe)
400º C	13±2	131.2
600º C	40±4	127.3
800º C	75±7	170.8
1000º C	120±11	111.6
1200º C	138±14	51.9

Highlights

Magnetic disaccommodation in Ni ferrite nanoparticles have been measured for the first time

Different behaviour for monodomain and multidomain nanoparticles

Logarithmic relaxations observed arise from increased magnetocrystalline anisotropy in the core

Graphical Abstract