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Magnetic properties of nanosized $MgFe_2O_4$ powders prepared by auto-combustion

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Abstract. Targets were prepared to be used for magnetron sputtering and laser ablation and their microstructural and magnetic properties were investigated. The base material was nanosized $MgFe_2O_4$ powder produced by citrate auto-combustion synthesis. The auto-combusted powders were annealed at temperatures in the range 600 - 1000^{o}C in air to study the effect of temperature on thofe formation $MgFe_2O_4$. The saturation magnetization M_s was 24.30 emu/g at room temperature.

1. Introduction

In this paper we describe the synthesis of $MgFe_2O_4$ nanoparticles by auto-combustion and present their structural and magnetic characteristics. Among the different ferrites, magnesium ferrite enjoys special attention because of its various applications in high-density recording media, heterogeneous catalysis, adsorption, sensors and magnetic technologies [1, 2]. The $MgFe_2O_4$ powder is used to prepare targets for thin films deposition by magnetron sputtering and laser ablation. This is one of the reasons why the structural and magnetic properties of this material are being studied, since from technological and theoretical points of view it is important to know if a transfer takes place of the structural and physical properties between as synthesized nanoparticles powder, pressed targets and deposited films. The second most important reason why $MgFe_2O_4$ is studied is that it is present as a second phase during synthesis of multiferroic Y-type hexaferrites, such as $Ba_2Mg_2Fe_{12}O_{22}$ [3]. The presence of $MgFe_2O_4$ in

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these hexaferrites may affect their magneto-electric properties, which makes the study of magnesium ferrite magnetic properties important. It is well known that the properties of $MgFe_2O_4$ depend on the method of synthesis. The preparation methods that have usually been used are a solid-state reaction [4], co-precipitation [5, 6], microemulsion [7], sol-gel and auto-combustion [8-10]. In our study, the $MgFe_2O_4$ powder was obtained by citrate auto-combustion synthesis.

2. Experiment

$Fe(NO_3)_3$. $9H_2O$, $Mg(NO_3)_2.6H_2O$ and citric acid all with analytical grade purity were used as starting materials. The molar ratio of metal nitrates to citric acid was fixed at 1:3. The metal nitrates were dissolved together in a minimum amount of de-ionized water to obtain a clear solution. A citric acid solution was slowly added to the mixed solution of nitrates as a chelating agent. The solution was slowly evaporated to form a gel. This gel was dehydrated at 120^{o}C to obtain the barium-magnesium-iron citrate precursor. During the dehydration process the gel turned into a fluffy mass and was burnt in a self-propagating combustion manner. The as prepared auto-combusted powders were annealed at temperatures in the range 600 – 1000 ºC in air to study the effect of the temperature on the $MgFe_2O_4$ formation.

The powders were characterized using X-ray diffraction analysis on a Bruker D8 Advance diffractometer with CuKa radiation and LynxEye detector within the 15 - 120 deg. 2θ range with a constant step of 0.02 deg. 2θ. The evaluation of the X-ray powder diffraction pattern of $MgFe_2O_4$ sample heated at 1100 ^{o}C was performed using the FullProf software. The magnetization was measured by a homemade low-frequency (3.6 Hz) vibrating sample magnetometer (VSM) [11] at 4, 50, 78, 150, 220 and 300 K. The AC magnetization (ACM) measurement was performed on a Physical Properties Measurement System (PPMS) in an *ac* magnetic field with amplitude 10 Oe and frequency 1 kHz. The sample was first cooled down to 4 K without magnetic field and the ACM was measured as the temperature was increased up to 300 K.

3. Results and discussion

The XRD spectra of the powders after auto-combustion and heat treatment at different temperatures are presented in figure 1, a). The material is predominantly amorphous after the auto-combustion process. Small and broad peaks of $MgFe_2O_4$ and Fe_2O_3 (hematite) could be seen on this diffraction pattern indicating the poor crystalline state of the phases formed at this stage of the synthesis. The spectrum of the samples annealed at 600ºC shows that the powder is already crystalline but is not single phase. Besides the $MgFe_2O_4$ peaks, there are lines of a second phase of hematite (Fe_2O_3). The XRD patterns show that the peaks become sharper and narrower as the sintering temperature is increased, indicating that the crystallinity of the samples is improving with the sintering temperature. The spectrum of the sample obtained at 850ºC shows that the main phase in the material is $MgFe_2O_4$. The second phase of hematite continues to be present, but the peaks intensity is lower in comparison with those of the sample obtained at 600 ºC. The XRD spectrum of the sample synthesized at 1100ºC shows the presence of $MgFe_2O_4$ only.

The Rietveld refinement procedure was performed on the $MgFe_2O_4$ sample synthesized at 1100ºC. The results of the refinement are summarized in table 1. The Rietveld plot is shown in figure1, b). The tetrahedral and octahedral distances obtained are 1.933(2) Å and 2.031(2) Å, respectively. The mean crystallite size was evaluated at about 270 nm.

Table 1. Structural parameters of the $MgFe_2O_4$ sample. The refined unit cell parameter a = 8.3852(1) Å. Reliability factors: R_{exp}=7.07, R_{wp}=9.95, GOF=1.85, R_{Bragg}=4.14.

Site	Position	X	y	z	Ion	Occupancy	B_{izo}
Tetrahedral	8a	1/8	1/8	1/8	Fe	0.863(4)	0.62(3)
					Mg	0.137(4)	0.62(3)
Octahedral	16d	½	1/2	1/2	Mg	0.863(4)	0.64(3)
					Fe	1.137(4)	0.64(3)
Oxygen	32e	0.2581(2)	0.2581(2)	0.2581(2)	O	4	1.31(7)

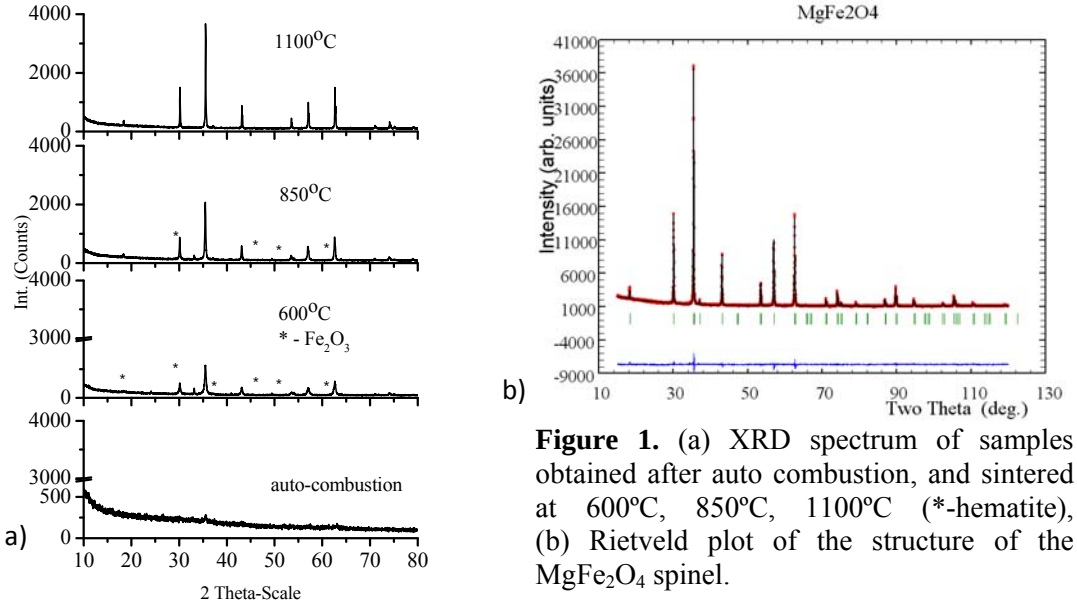

Figure 1. (a) XRD spectrum of samples obtained after auto combustion, and sintered at 600ºC, 850ºC, 1100ºC (*-hematite), (b) Rietveld plot of the structure of the $MgFe_2O_4$ spinel.

Figure 2 shows a SEM image of the sample immediately after the completion of the auto-combustion process. A typical porous structure is observed formed during the burn process, with the pores on the surface having a smaller size than those within the core. The $MgFe_2O_4$ sample heated at 1100ºC is homogeneous with respect to the particles size and shape. It is also seen that the particles have an approximately spherical shape.

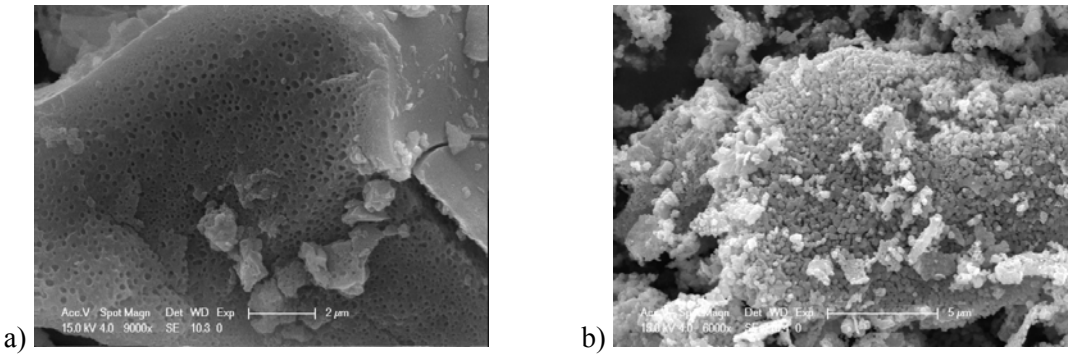

Figure 2. SEM images of samples obtained after auto-combustion (a) and at 1100ºC (b).

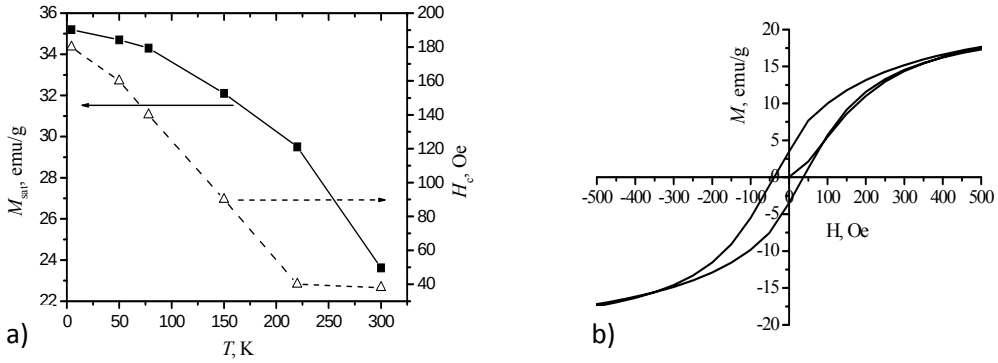

Figure 3. Saturation magnetization at *dc* magnetic field of 1.5 T (filled squares) and coercivity (blank triangles) versus temperature – a); and hysteresis of $MgFe_2O_4$ at 300K – b).

The saturation magnetization M_{sat} and coercivity H_c versus the temperature of the $MgFe_2O_4$ sample synthesized at 1100ºC are shown in figure 3, a). The magnetization value at 1.5 T is assumed to be the saturation magnetization value. As the temperature is raised, the saturation magnetization M_{sat} and coercivity H_c decrease quickly. At room temperature (figure 3, b), the coercivity H_c is only 38 Oe, the saturation magnetization M_s is 24.30 emu/g and the remanence M_R is 3.5 emu/g. The coercivity is too small for such relatively large particles. This could be related to fact that the particles probably consist of only a few domains.

Figure 4 presents the real M' (in phase) and imaginary M'' (out of phase) part of the *ac* magnetization. The in-phase component does not exhibit any transitions, while in the out of phase component one can see a few peaks related to energy losses as the energy of the *ac* magnetic field is absorbed by the sample. The spectrum is typical for polydomain-structured soft magnetic materials and demonstrates a motiont and rotation of the domain walls.

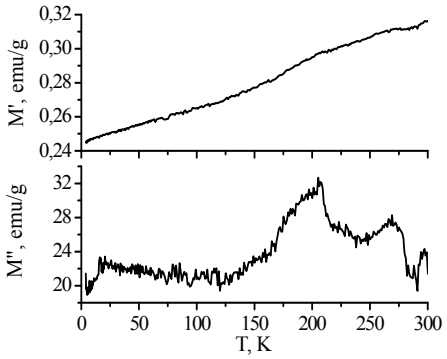

Figure 4. *ac* magnetization (in-phase component of complex magnetization–M' and out of phase component – M'') at *ac* field with amplitude 10 Oe and frequency 1 kHz.

As the temperature is raised, the resonance behavior becomes stronger reaching a maximum at a critical temperature of about 210 K. In this case, the individual particles can be regarded as spherical objects with one or a few domain walls depending of the particles' diameters. Under certain assumptions, the particles could be considered as harmonic oscillators with resonance frequency depending on their diameter. This model gives opportunity to seek a connection between the magnetic properties of the material and the diameter of the particles in the target in the thin film deposition process.

On the other hand, the frequency of maximum dispersion is related to the boundary frequency of the domain wall and is controlled by the attenuation caused by the environment in which the domain wall is moving so that the maximum frequency depends on the anisotropy constant. Further research is needed to study the magnetic dynamics of the particles.

Conclusions

Single phase $MgFe_2O_4$ nanoparticles were synthesized by autocombustion. The mean crystallite size was about 270 nm. The microstructural studies demonstrated that the powders thus produced can be used to form targets for magnetron sputtering and laser ablation. The targets' morphology and magnetic properties were studied systematically, which revealed a polydomain structure with $M''(T)$ value typical for magnetically soft materials. Experiments are being performed on films deposition using these targets, the results of which will be the subject of a future publication.

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