

Gadolinium substitution effect on the thermomagnetic properties of Ni ferrite ferrofluids

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Abstract

This work is focused on the characterization of Ni-ferrite nanocrystals and their subsequent doping with Gd, in an attempt to explore Gd inclusion in the thermomagnetic properties of prepared ferrofluids.

Spinel ferrites NiFe_2O_4 , and $\text{NiFe}_{1.88}\text{Gd}_{0.12}\text{O}_4$ were prepared by the auto-combustion method. The substituted sample is obtained with a small amount of Gd inclusion and the excess appears as GdFeO_3 . The smallest nanoparticles of both samples were properly coated and dispersed in kerosene. Thermal conductivities of the produced ferrofluids were measured at 25 °C in a magnetic field. There is a significant enhancement in thermal conductivity of the ferrofluid prepared with NiGd ferrite with respect to the one with Ni ferrite, in presence of a magnetic field. This effect is directly related to the well-known magnetocaloric effect of Gd.

Keywords: substituted ferrites, nickel ferrites, gadolinium, thermomagnetic properties, ferrofluid.

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1. Introduction

Spinel ferrites are among the most widely used magnetic materials [1] because of their low cost, high electrical resistivity and high Curie temperature. Many basic and applied investigations on the frequency behavior of ferrites have been carried out. The studies of electrical and magnetic properties of ferrites are useful for their applications in electronics [2-6]. The semiconducting properties of nickel ferrite have also been discussed in detail [7]. The electrical conductivity and magnetic properties of ferrites are mainly governed by the Fe-Fe interaction (spin coupling of the 3d electrons) and also by Ni^{2+} ions. The electromagnetic properties of Ni-ferrites may be modified by the doping with rare earth (R) cations [8] which play an important role in determining magnetocrystalline anisotropy in the 4f-3d intermetallic compounds [9]. From Relescu's studies [10] it is known that R atoms with a large radius and a stable valence of 3+ (such as Gd in Gd_2O_3) produce the best modification in ferrites' structure and properties. In a previous work, we investigated the structure of R-doped Ni-Zn ferrites [11] finding an increment in the cell parameter with increasing R content, indicating that R had been incorporated within the spinel structure. Sileo *et al.* [12] reported that an orthorhombic phase appears, for low Gd substitution, when samples are calcined at 1000°C. Notwithstanding, Gd inclusion was confirmed by an increase in cell parameters of Ni ferrite as Gd content increased while electromagnetic properties.

On the one hand, Gd inclusion in MnZn ferrites has been explored by O-Peralez-Perez *et al.* [13-14]. They related an improvement in thermomagnetic properties in these compounds and the displacement of Fe ions from B sites to A sites as a consequence of Gd inclusion. In turn, the fact that Gd-ferrite exhibits a Curie temperature T_C as low as 298 K and high pyromagnetic coefficient [14] could open the possibility to tune T_C in Mn-Zn ferrites by a controlled incorporation of this R element into the ferrite structure.

On the other hand, there is wide experimental demonstration of Gd magnetocaloric effect, mostly when pure or in alloys [15], and to the best of our knowledge, it has not yet been reported the influence of Gd in Gd-doped Ni ferrite compounds for ferrofluids.

The magnetocaloric effect is a phenomenon in which a temperature change is produced in a material by applying a magnetic field. In this process, a change in the magnetic field intensity allows the magnetic moments to orient or disorient with respect to the magnetic field, by thermal energy variation of the phonons inside the material. The temperature variation produced by the magnetocaloric effect is described by: $\Delta T = - \int_{H_1}^{H_2} \left(\frac{T}{C_p(T,H)} \right) \left(\frac{\partial M(T,H)}{\partial T} \right) dH$, where T is the temperature, H the applied field, and C_p and M are the isobaric heat capacity and the magnetization of material, respectively.

Magnetocaloric compounds are of special interest for applications in industrial heat transfer devices, for which high thermal conductivity and low heat capacity ferrofluids are required. Keeping this in mind, the purpose of this work is the structural and magnetic characterization of Gd-doped Ni ferrite nanoparticles (NPs) and the preparation of a ferrofluid for applications in heat transfer devices. Kerosene-based ferrofluids were investigated and a thermomagnetic characterization of the prepared fluids was performed. In order to investigate if the magnetocaloric effect of Gd in Ni-ferrite also influences the ferrofluid behavior, their thermal conductivities as a function of magnetic field and heat capacity were studied.

2. Experimental

Spinel ferrites of nominal composition NiFe_2O_4 (labeled S-Ni) and $\text{NiFe}_{1.88}\text{Gd}_{0.12}\text{O}_4$ (labeled S-NiGd) were prepared according to Ref. [12] from Fe(III), Gd(III) and Ni(II) citrates. X-Ray diffractograms were measured in a Philips diffractometer using $\text{Cu K}\alpha$ radiation. Diagrams were collected in the 2θ range 25-75°, with a step-size of 0.02°, at a counting rate of 4 seconds per step. The crystallite sizes of the samples were estimated from the line width of the (311) peak. The morphology of precursors and calcined samples was examined by Scanning and Transmission Electronic Microscopy (SEM and TEM). The magnetic properties of the

samples compacted in 1-2mm thick disks were measured at room temperature (RT) in a vibrating sample magnetometer LakeShore 7200 with a maximum applied field of 15 kOe.

Kerosene-based ferrofluids were prepared by coating the NPs with oleic acid and dispersing them in kerosene during ultrasound treatment. Two fractions were separated by centrifugation from an initial ferrofluid previously sonicated in order to select the smallest particles. Mean particle diameters were explored by SEM and TEM. Kerosene-based ferrofluids were prepared with S-Ni and S-NiGd particles at two concentrations (5% and 10%), and were named F-Ni and F-NiGd, respectively. These fluids showed good stability for 24 hours.

For investigating the thermal variables of the prepared fluids and evaluating their properties, a specific device was used. It was designed, constructed and calibrated exclusively for this purpose in our laboratory and it is based on the transient hot wire method [16-18]. It allows measuring temperature vs. time under applied magnetic fields while heating a cylindrical container with the tested fluid.

3. Results and Discussion

3.1 Structural characterization

Figure 1 shows the diffractograms of the studied samples.

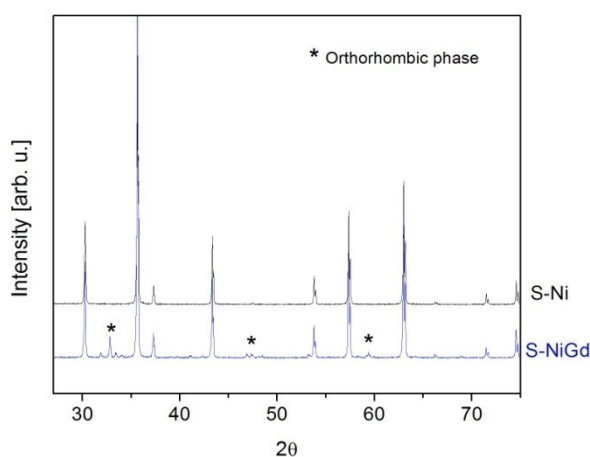


Figure 1: X-Ray diffractograms of the powders S-Ni and S-NiGd. The peaks corresponding to the orthorhombic phase $GdFeO_3$ are indicated.

The peaks in the spectra indicate that S-Ni has the cubic structure of spinel ferrite with no extra reflections. Small variations in the peak positions of the ferrite-phase are observed. However, a gadolinium ferrate orthorhombic phase ($GdFeO_3$) is well detected in sample S-NiGd with a fraction of 13%. These results indicate that Gd ions cannot totally enter into the ferrite lattice, probably because of the larger radii of Gd ions relative to Fe ions. Some Gd ions may reside at grain boundaries and form oxides. Rietveld analysis and Mössbauer studies reported by us on this sample [12] support the previous hypothesis. The cell parameter of Ni-ferrite increases from 8.3359(1) Å to 8.3384(1) Å (Table I) with the incorporation of Gd ions. For sample S-NiGd the calculated ferrite composition indicates a smaller degree of Gd-for-Fe substitution, this fact agrees with the slight increase in lattice parameter. For this substitution, 13% $GdFeO_3$ is segregated. Crystallite size slightly decreases with Gd inclusion.

Table I: Notation, crystallite sizes and lattice parameters of the synthesized samples.

Sample	Crystallite size, D [nm]	Lattice parameter, a [Å]
S-Ni	58	8.3359 (1)
S-NiGd	43	8.3384 (1)

Nickel ferrite has an inverse spinel structure, with the following cation distribution: $(\text{Fe}^{3+})_A[\text{Ni}^{2+}\text{Fe}^{3+}]_B\text{O}_4$. When Gd^{3+} is introduced in the lattice, some of the Gd ions may occupy octahedral sites (B), resulting in a migration of Fe^{3+} ions to tetrahedral sites (A). This migration is related to changes in M_s .

The microstructure of the synthesized powders was studied by scanning electron microscopy (SEM). Figure 2 a) shows agglomerated particles of S-Ni with a wide size distribution centred in 270 nm, while Figure 2 b) corresponds to S-NiGd particles, with a mean size of 250 nm.

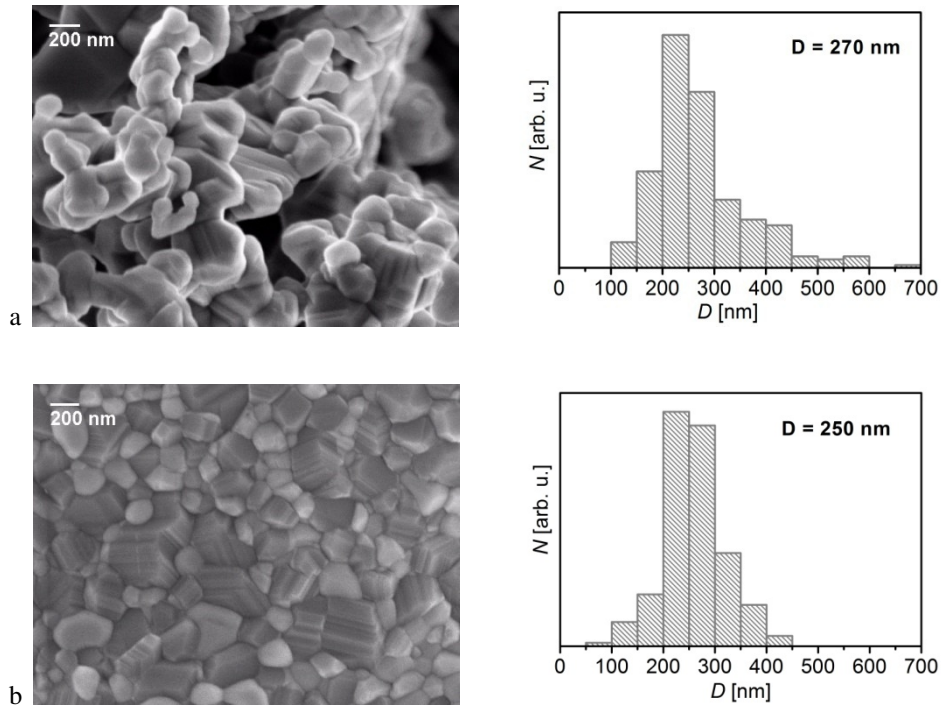


Figure 2: SEM images of samples S-Ni (a) and S-NiGd (b) and the particle size histogram corresponding to each sample.

As the stability of ferrofluids increases as particle size diminishes, suspended particles were centrifuged and separated in order to keep the fraction of the smallest particles. Figure 3 a) and b) show the morphology of the particles used to prepare the studied ferrofluids.

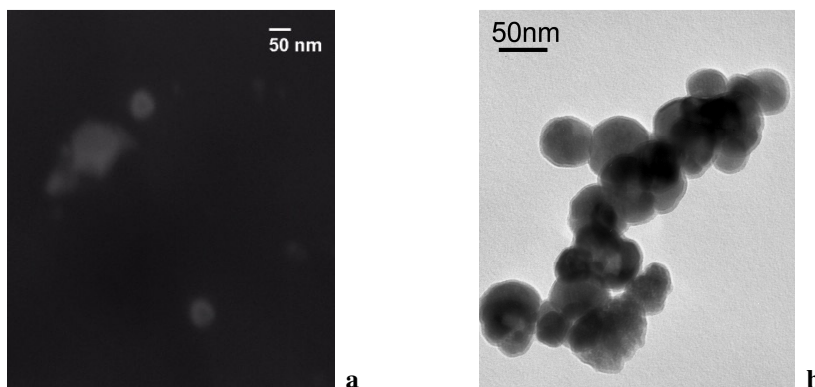


Figure 3. SEM (a) and TEM (b) images of the smallest selected nanoparticles of S-NiGd, after coating with oleic acid.

3.2 Magnetic measurements

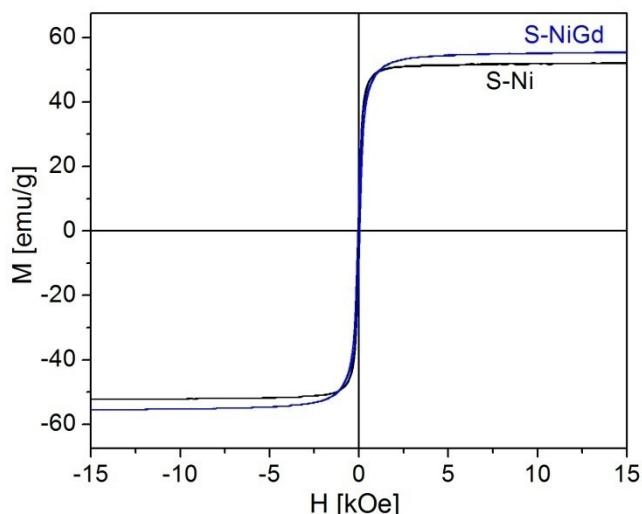


Figure 4: Hysteresis loops M vs. H at room temperature for samples S-Ni and S-NiGd, after correcting for Gd ferrate.

Figure 4 shows the hysteresis loops at room temperature of the studied samples. Sample S-Ni shows the expected ferrimagnetic behavior of spinel ferrites, reaching saturation at relatively low fields (6 kOe) with a saturation magnetization value (M_s) of 52 emu/g. Sample S-NiGd is not single phase, since a fraction of 13% $GdFeO_3$ was determined from X-Ray results [12]. This phase is paramagnetic, with a magnetization value of 1.5 emu/g at 15 kOe [19] and its contribution can be subtracted from the measured data in order to keep only the ferrimagnetic contribution from the spinel phase. The corrected hysteresis loop for S-NiGd is shown in Figure 4. Gd inclusion in the spinel lattice of Ni ferrite increases saturation magnetization approximately 5%. Coercivity (H_c) is very small, with values < 50 Oe in both samples.

3.3 Thermomagnetic characterization of ferrofluids

The ferrofluids prepared with S-Ni and S-NiGd were labeled F-Ni and F-NiGd, respectively.

Thermal conductivity of both F-Ni and F-NiGd ferrofluids was measured as a function of magnetic field for concentration values of 5 and 10 % v/v. Magnetic field values ranged from 0 to 2000 Oe. The thermal diffusivity was also calculated with the hot transient method and the obtained results are not shown here for exceeding the purpose of this work. The influence of dispersing the NPs in kerosene on the thermal conductivity was calculated as the increment: $I = (k_F - k_0)/k_0 \cdot 100\%$. In this expression, k_F and k_0 are the FF and the kerosene conductivities, respectively. Heat capacity was also calculated using the expression: $C_p = k/\rho\alpha$, being α the diffusivity and ρ the fluid density, calculated as: $\rho = x\rho_{\text{NPs}} + (1-x)\rho_0$, being x the weight fraction of NPs, and ρ_0 and ρ_{NPs} the base liquid and the NPs densities, respectively. For a better interpretation, the relative heat capacity was calculated as the ratio between FF and kerosene heat capacity values (C_{PF} and C_{P0} , respectively): $C_{\text{Pr}} = C_{\text{P0}}/C_{\text{PF}}$.

In Figure 5, the results of thermal conductivity measurements for F-Ni and F-NiGd with concentrations of 5% and 10% v/v are shown.

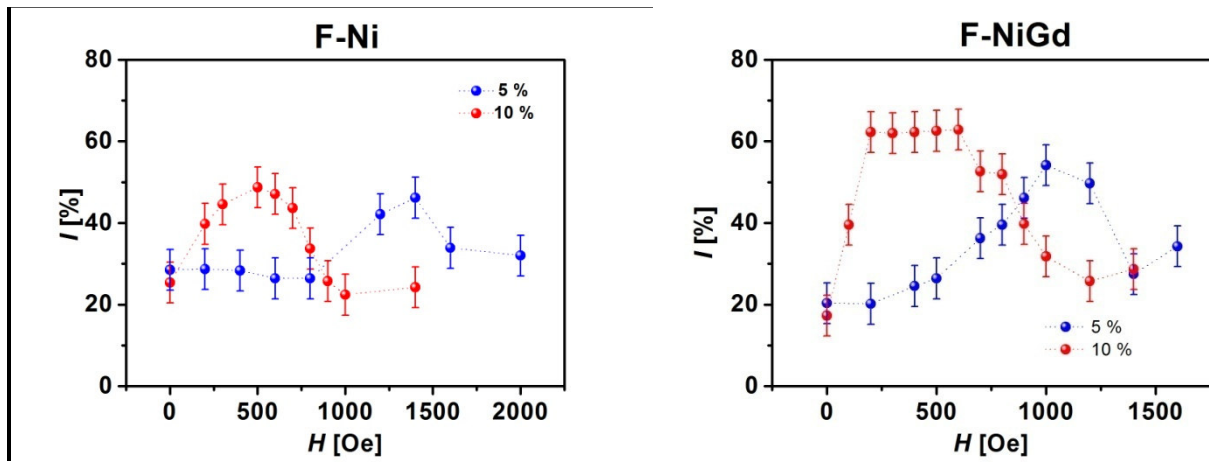


Figure 5: Thermal conductivity increments.

It is clear from Figure 5 that thermal conductivity of the studied FFs is enhanced up to a maximum and then diminishes in every case. At zero applied field, the presence of NPs in the fluid enhances the properties with respect to that of pure kerosene. This behavior of increasing and diminishing in the thermal variables has also been observed by Philip *et al* [20] in water-based ferrofluids prepared with magnetite NPs.

In a FF at room temperature, the NPs magnetic moments are randomly oriented because the thermal energy is higher than the dipolar interaction between the NPs. When applying a magnetic field, the energy corresponding to the dipolar interaction is enough for the formation of particles doublets, triplets and chains –along the field direction– whose lengths become larger while increasing the magnetic field. This thermal conductivity enhancements are well-explained with Phillip’s theory based in percolation [20]. The number of magnetic NPs in the field direction is significantly increased at higher magnetic field intensities and it produces considerable enhancements in the thermal conductivity of kerosene. When the applied magnetic field is high enough, many particle-chains link with another, forming cluster-like structures and larger liquid zones, free of NPs -with lower thermal conductivity- appear, therefore diminishing the FF thermal conductivity.

Some parameters of interest were defined: the zero field conductivity enhancement ($I(H=0)$), the maximum conductivity enhancement ($I_{\text{máx}}$) and the magnetic field that produces the maximum enhancement (H_k). These parameters are presented in Table II, together with the heat capacity for each FF.

Table II: Ferrofluids concentration, thermal conductivity enhancements at zero and maximum field, field intensities that produce the maximum values, and relative heat capacity.

Fluid	C [% v/v]	$I(H=0)$ [± 5 %]	$I_{m\acute{a}x}$ [± 5 %]	H_k [± 20 Oe]	α ($H = 0$)	C_{Pr}
F-Ni	5	29	46	1400	(1.8 \pm 0.2)	(0.50 \pm 0.05)
	10	25	48	500	(1.4 \pm 0.2)	(0.5 \pm 0.1)
F-NiGd	5	20	54	1000	(1.0 \pm 0.3)	(0.5 \pm 0.1)
	10	18	63	200-600	(2.2 \pm 0.3)	(0.30 \pm 0.05)

In fluids with 10 % v/v concentration, the maximum enhancement is reached at lower intensity fields than for the 5 % v/v concentration, as indicated in Table II. This is due to the increment of NPs amount in a volume unity that favors even more the interaction between particles in presence of a magnetic field, forming chains that enhance the heat conduction with low intensity fields.

The most remarkable aspect is that, according to Table II, the conductivity enhancement produced in F-Ni (without Gd) at zero field are higher, while, in presence of a magnetic field, the enhancement is higher for F-NiGd. This effect is clearly associated to Gd inclusion. Besides, for F-NiGd10 % v/v, a lower field intensity is required for maximizing the increments of conductivity. The maximum increment for F-NiGd 10% v/v reaches 63% for a wide range of low fields (200 – 600 Oe) which are easily produced by commercially available permanent magnets.

From this study, it is evident that Gd inclusion in the Ni-ferrite structure enhances the thermomagnetic properties of kerosene-based FF prepared in the same conditions, while at zero field the FFs prepared with Ni-ferrite NPs gave a better response.

The significant enhancement in conductivity of the fluids F-NiGd with respect to those of F-Ni in presence of magnetic field is straightforwardly related to the well-known magnetocaloric effect of Gd. In order to have a deeper insight into this aspect, the heat capacity relative to kerosene was calculated (see Table II) for F-Ni and F-NiGd.

The heat capacity of kerosene diminishes when incorporating the NPs, as C_{Pr} is less than 1 in every case. Besides, C_{Pr} of F-NiGd is lower than C_{Pr} of F-Ni for 10 % v/v concentration. This decrease in heat capacity of the FF has been recently reported by Angayarkanni et al [21] in other systems, and in our case is directly associated to the Gd magnetocaloric effect. This confirms that doping Ni-ferrite with Gd modifies the heat capacity of the fluids in which the NPs are suspended, and enhance the thermal conductivity. In this sense, the fluid F-NiGd 10 % v/v is the most appropriate candidate for application in heat transfer devices.

4. Conclusions

The influence of Gd ions on structural, magnetic and thermomagnetic properties of Ni-ferrites has been investigated.

- Gd enters the spinel lattice of Ni-ferrite only partially, as a gadolinium ferrate orthorhombic phase ($GdFeO_3$) is well detected.
- Saturation magnetization of the spinel phase slightly increases with Gd content.

- The prepared FF reaches increments of 48% (F-Ni 10%) and 63% (F-NiGd 10%) in thermal conductivity, under applied magnetic fields of 500 and 200 Oe, respectively. This result indicates that Gd induces magnetocaloric effects in Ni-ferrite FF, and the thermal properties of the FF can be optimized by applying a low intensity magnetic field.
- F-NiGd 10 % v/v fluid has a lower heat capacity than F-Ni 10 % v/v, favoring the increase of the magnetocaloric effect at constant magnetic field.
- The magnetocaloric effect of Gd as a dopant in Ni-ferrite is a novel contribution to the state of art in magnetocaloric effect of Gd alloys.

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