Magnetic Properties of Zn-Ferrites Obtained From Multilayer Film Deposited by Sputtering

K. L. Salcedo Rodríguez[1], F. Golmar[2,3], and C. E. Rodríguez Torres[1]

[1]IFLP y Departamento Física, Facultad de Ciencias Exactas, Universidad Nacional de la Plata-CCT, La Plata CONICET, CP 1900, La Plata, Argentina

[2]CIC nanoGUNE Consolider, 20018 Donostia-San Sebastián, Basque Country, Spain

[3]I.N.T.I.-CONICET, B1650JKA San Martín, Bs As, Argentina

Epitaxial $ZnFe_2O_4$ thin films were deposited on monocrystalline MgO substrate by dc-sputtering. Ferrites were grown from Zn-O and Fe-O multilayers starting from metallic targets in oxygen atmosphere. The number and thickness of layers were varied holding constant the total thickness (50 nm) and sample stoichiometry (Fe/Zn $= 2$). The samples were structural and magnetically characterized by X-ray diffraction and magnetic measurements, respectively. Thin film fabricated using 20 bilayers of thickness 3 nm present a magnetic behavior similar to bulk $ZnFe_2O_4$, with a Néel temperature $T_N = 10.5$ K. The magnetic behavior of those films obtained from thicker bilayers (6 and 10 nm) is characterized by the coexistence of antiferro and ferromagnetic regions. This is probably due to the inhomogeneities in Zn and Fe distributions caused by an incomplete interdiffusion process prevented by the relatively large multilayer thickness. These inhomogeneities probably generate zinc-iron position replacements and interrupt the long-range antiferromagnetic order, giving rise to ferromagnetic clusters coexisting with the antiferromagnetic component.

***Index Terms*—Diluted antiferromagnetism (DAFF) system, dc-sputtering, ferrite film, magnetic analysis.**

NOWADAYS, transition metal oxide films generate great interest because they may behave as insulators, semiconductors, superconductors or metallic conductors, depending on several factors controllable during the synthesis process. In particular, variables as deposition pressure and temperature of the substrate play an important role on the resulting film properties [1].

Many recent studies focus on bulk and nanostructured zinc ferrite due to the capability of changing their properties by modifying the cation distribution [2]–[4]. Bulk zinc ferrite has a normal spinel structure. Tetrahedral A sites are occupied by Zn^{+2} ions and octahedral B sites are occupied by magnetic ions Fe^{+3}. The inverse spinel occurs when all divalent ions occupy B sites and trivalent cations occupy sites A and B. Magnetically, it behaves as an antiferromagnet (AF) with a Néel temperature of $T_N = 10.5$ K. However, when normal spinel ferrite becomes nanosized it presents a net magnetization at room temperature [3]–[5]. Several works have suggested that, in such a case, the ferrite displays a nonequilibrium cation distribution among A and B sites that alters its long-range magnetic ordering. As a consequence, the magnetic response is drastically enhanced. In addition, several authors reported the clear dependence of magnetic response on the preparation process, apart from the particle size [6], [7].

In this paper, we present a preliminary study of the magnetic properties of a structurally homogeneous compound of zinc ferrite fabricated by starting from thin film deposited by dc-magnetron sputtering. Ferrites were fabricated from Zn-O and Fe-O multilayers. We varied the number and the thickness of layers maintaining constant the total thickness and sample stoichiometry. Samples were characterized using X-ray diffraction (XRD) and magnetic measurements.

The motivations of this study are mainly to explore the possibility of obtaining ordered Zn ferrite from dc sputtering, starting from metallic targets, and also to prepare Zn ferrite with inhomogeneous concentration of Zn and Fe in order to study the influence of inhomogeneities in magnetic properties. We observed that the deposition of multilayers in oxygen atmosphere, with a hot MgO (001) substrate (973 K), low deposition rate and very thin monolayers, results in structurally homogenous zinc ferrites. However, magnetic results indicate that some inhomogeneities (probably nonhomogenous Fe and Zn distribution) break antiferromgnetic order giving room temperature ferromagnetism in the cases of samples obtained from thicker monolayers.

I. Experimental Details

Ferrite thin films were grown on MgO (001) from Zn-O and Fe-O multilayers, starting from Zn and Fe metal targets in oxygen atmosphere by dc magnetron sputtering. The multilayer films were grown with a base pressure of 2×10^{-7} Torr and operation pressure of 2×10^{-2} Torr under Ar and O_2 atmosphere, which were flowed at 22 and 3 ml/min, respectively. Supplied dc power was 200 Watts. Deposition was carried out at a substrate temperature of 973 K in order to favor the interlayer diffusion. Deposition rates were 0.10 and 0.74 Å/s for Fe-O and Zn-O monolayers, respectively. Z5, Z10 and Z20 samples consist of 5, 10 and 20 bilayers of Zn-O and Fe-O respectively. In all cases final thickness is around 50 nm. The estimated individual thickness of each layer (if no interdiffusion process occurs) is presented in Table I. The thicknesses were chosen in such way to maintain a ratio Fe/Zn equal to 2 in each bilayer such as in $ZnFe_2O_4$ compound.

Bulk ferrite in powder was prepared by conventional solid state reaction. Fe_2O_3 and ZnO in ratio 1:1 were mixed in an

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TABLE I
THICKNESS OF INDIVIDUAL LAYERS AND DEPOSITION TIMES

Sample	Thickness Fe [nm]	Thickness Zn [nm]	Deposit time Fe/Zn [s]
Z5	6	4	600/54
Z10	4	2	400/27
Z20	2	1	200/13.5

agate mortar. The mixture was calcinated at 1000 C for 12 h. The process was repeated three times.

The structural characterizations were performed using XRD. The XRD spectra were recorded using the $\theta - 2\theta$ scan with CuKα radiation (0.15406 nm).

Measurements of magnetic moment (M) versus applied field parallel to thin film plane (H) and zero field cooling (ZFC) and field cooling (FC) were performed using a Quantum Desing MPMS superconducting quantum interference device (SQUID) magnetometer.

II. RESULTS

Fig. 1(a) presents the XRD patterns of samples Z5, Z10 and Z20. The patterns show only (400) reflection of Zn ferrite closed to (200) MgO peak. These patterns indicate the epitaxial growth of zinc ferrite (400) on MgO (001) substrate. The fact that the main component of the XRD pattern in all the samples is (400) reflection of Zn ferrite indicates that the thin films are structurally homogenous and the monolayers' interdiffusion is almost complete. Diffraction pattern of Z5 also showed very weak reflections of ZnO and Fe_3O_4 [see Fig. 1(b)]. Taking into account the relative areas of the reflections peaks, we estimated that the relative amount of magnetite is less than 0.5 at. %. The presence of impurity phases (with very low concentration) is probably due to the incomplete interdiffusion between layers of Fe-O and Zn-O in minority regions during deposit process.

M versus H curves measured at different temperatures are shown in Fig. 2, after discounting the diamagnetic contribution from the substrates. The curves corresponding to bulk $ZnFe_2O_4$ (in powder) are also included. At room temperature (c), Z20 presents only a paramagnetic component with very low susceptibility as it is observed for the bulk ferrite (d). As the number of layers decreases (and consequently their thickness increases), the high field paramagnetic susceptibility increases and a ferromagnetic-like component appears with almost zero remanence and coercivity. A similar result has been obtained at 100 K (b). At 10 K (a), all samples present hysteretic ferromagnetic component with coercivities of 0.032_5, 0.034_7, 0.018_4 T for Z5, Z10 and Z20, respectively. The ferromagnetic component is more notorious in Z5 and Z10.

Fig. 3 shows M versus T curves after zero field cooling (ZFC) and after field cooling (FC) measured at applied field of 500 Oe. The corresponding curves of bulk Zn ferrite (powder) are also included for comparison purposes. The thin film curves present a bifurcation of ZFC and FC below a temperature (T_{irr}) which is a typical trait of ferromagnetic materials, spin glass, superparamagnetic (SPM) or diluted antiferromagnetism (DAFF) in a field behavior. T_{irr} is around 30 K for Z5 and Z10 and 15 K for Z20. ZFC curves present a peak at around 15–20 K with similar

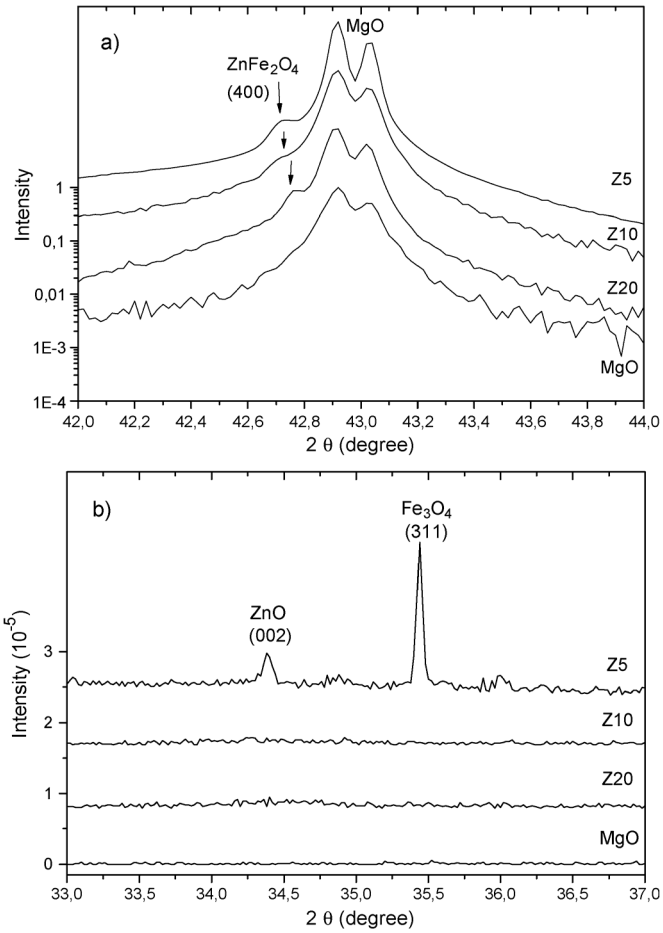

Fig. 1. XRD patterns of samples Z5, Z10, Z20 and MgO substrate. (a) Region between $42 < 2\theta < 44$ degree (plotted in log scale). (b) Region between $33 < 2\theta < 37$ degree (plotted in linear scale). Note that ZnO and Fe_3O_4 reflections are three orders of magnitude smaller than the $ZnFe_2O_4$ one.

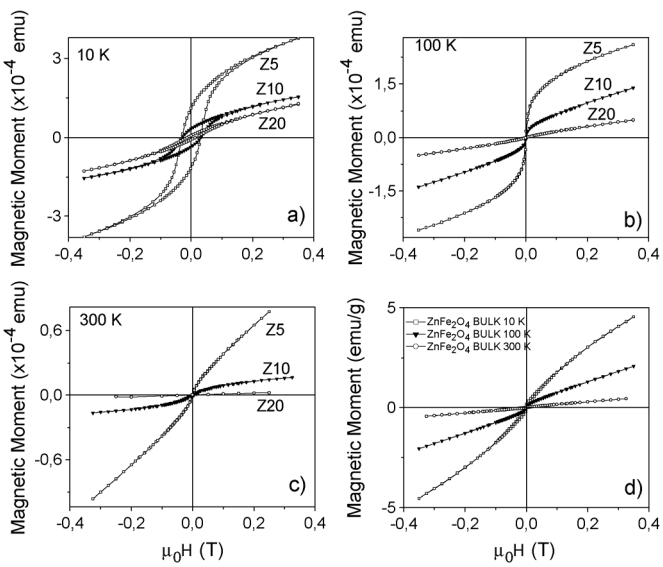

Fig. 2. Magnetic moment versus applied field curves for samples Z5, Z10 and Z20 measured at (a) 10 K, (b) 100 K, and (c) 300 K. (d) M versus H curves of bulk $ZnFe_2O_4$ powder recorded at 10 K, 100 K, and 300 K.

characteristics of ZFC curve corresponding to bulk ferrite one that is a bulk regular AF. For a regular AF a peak both in the

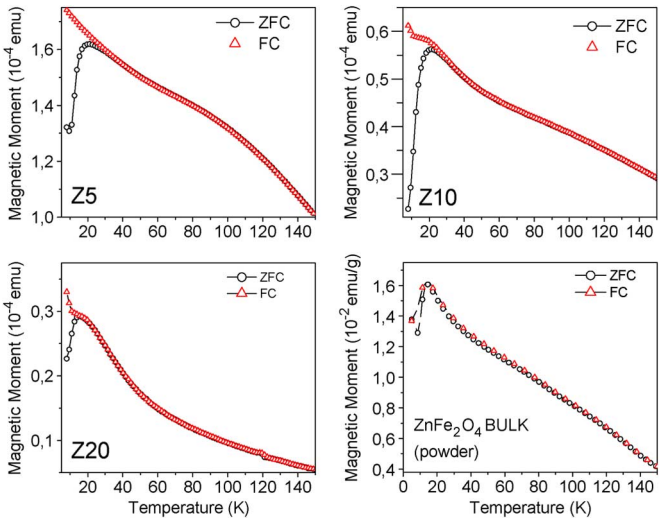

Fig. 3. M versus T curves measured after zero field cooling ZFC and after field cooling FC measured at applied field of 500 Oe.

ZFC and FC curve is expected, when the field is applied along the anisotropy direction. The inflection point left to the peak position marks the critical temperature T_N [8]. Instead, often in literature, the peak position itself is used to mark the critical temperature [9], [10]. T_N estimated as the inflection point for bulk $ZnFe_2O_4$ powder (Fig. 3) is 11 K in coincidence with reported Néel temperature (10.5 K) for this compound. T_N determined from ZFC curves for Z5, Z10 and Z20 are 12.5, 11.5 and 10.7 K respectively, values that are around the transition temperature of bulk $ZnFe_2O_4$. The peak position of bulk ferrite is 14.6 K and corresponding to Z5, Z10 and Z20, 21, 21.5 and 15 K, respectively. It can be seen that obtained values of T_N (inflection point or peak position) coincide with bulk ferrite ones. Then, taking into account M versus H and M versus T results, we infer that Z20 is the sample that magnetically has more similarities to the bulk ferrite.

Z5 and Z10 samples present a major ferromagnetic contribution. The magnetic behavior of these samples is similar to the reported one for the case of DAFF systems [11]. DAFF systems are usually antiferromagnetic lattices where magnetic ions are randomly substituted by nonmagnetic ions. DAFF exhibits long range order if it is cooled from above T_N in ZFC conditions. However, when the system is cooled in the presence of a magnetic field, a stable domain state without long range order is obtained below a certain temperature [12], [13]. In our case, the inhomogeneity in Fe and Zn distribution is more pronounced in Z5 and Z10 because the nucleus layers are thicker. Inhomogeneous concentrations can generate that zinc atoms occupy otherwise iron positions, causing a break in the antiferromagnetic order. This probably makes possible the emergence of ferromagnetic clusters regions that coexist with the antiferromagnetic component. Complementary magnetic studies are necessary to verify this hypothesis.

III. Conclusion

In summary, we have obtained structurally homogenous epitaxial growth $ZnFe_2O_4$ thin film by dc-sputtering, starting from metallic targets, which to our knowledge, has not been reported before. We characterized magnetically these samples. We found that sample with the highest number of layers have a higher interdiffusion between layers, achieving orderly manufacturing ferrite. For thicker layers there are an inhomogeneity in the distribution of Zn and Fe but structurally the film is homogeneous. The inhomogeneity could derive in DAFF behavior that consists of small ferromagnetic clusters enclosed in an antiferromagnetic matrix.

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