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Mechanical doping of ZnO powders

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ABSTRACT

Massive $Zn_{1-x}Fe_xO$ ternary oxides were prepared by mechanical milling from different starting materials as Fe_2O_3, α-Fe or FeO. The influence of different preparation conditions, such as initial concentrations, atmosphere and milling times on final products was investigated. The structure evolution and dopant incorporation in the wurtzite crystalline structure with milling time was analyzed by means of X-ray diffraction. The sample's magnetic character investigated by measurements in a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer consists of two superimposed signals, a ferromagnetic and a paramagnetic one.

1. Introduction

Wide bandgap semiconductor ZnO with the addition of small quantities of magnetic atoms (Mn, Co, Fe and Ni) constitute a new promising material for spintronic applications [1]. The prediction of ferromagnetism at or above room temperature makes these new materials very attractive for use at the integration of photonic, electronic and magnetic devices on a single substrate [2,3]. Moreover, wide synthesized methods were reported in order to obtain both thin films and bulk doped semiconductors. Among them solid state reaction constitutes a versatile approach for this goal being mechanical milling an efficient room temperature process [4]. This technique was previously applied to obtained Co-doped ZnO [5] and Fe-doped ZnO [6–8] where their structural and magnetic properties were analyzed. In the last case, also Mössbauer spectroscopy was applied but no magnetic structures were found in the studied composition range. Fe atom is a particular dopant since it presents two different oxidation states which allow us to vary the starting materials: Fe_2O_3, α-Fe or FeO, while Co is isovalent to Zn. In the present work, comparative magnetic properties of $Zn_{1-x}Fe_xO$ ternary oxides synthesized by mechanical milling from different initial precursors are studied. The influence of different preparation conditions, such as initial concentrations, atmosphere and milling times on final products was investigated. The structure evolution and dopant incorporation in the wurtzite crystalline structure with milling time was analyzed by means of X-ray diffraction. The sample's magnetic character was investigated by measurements in a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer. Our aim is contribute to the comprehension of the origin of ferromagnetism in these novel materials.

2. Experimental

2.1. Sample preparation

Samples from mixtures of ZnO (Alfa Aesar, Johnson Matthey Co., 99.99) with 5 and 10 at% of α-Fe (Merk, 99.5) or FeO (Sigma–Aldrich, 99.9, −10 mesh) or Fe_2O_3 (Johnson Matthey Co., 99.99, −15 mesh) powders were prepared. Samples were manipulated in a Controlled Atmosphere Chamber (O_2 content less than a few ppm), introduced in a cylindrical steel milling chamber together with one steel ball (ϕ = 12 mm), filled with Ar at 0.2 MPa and sealed with an O ring. Mixtures with Fe_2O_3 were also prepared at open air. The ball to sample mass ratio was 11.5:1 and progressive milling was carried on using a horizontal oscillatory mill Retsch, at a fixed oscillation frequency of 32 Hz.

2.2. Characterization techniques

The obtained powders were characterized by X-ray diffraction (XRD) using a Philips PW 1710 with Cu K_α radiation in the $20^\circ \leq 2\theta \leq 80^\circ$ range at 0.02°/s.

The magnetic properties of the samples were measured by a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer at different temperatures.

3. Results and discussion

Fig. 1 shows the diffractograms obtained for ZnO + 10 at% Fe and 10 at% FeO at different milling times. The characteristic diffraction peaks of α-Fe and FeO, still present after 1 h of milling, progressive disappeared with milling time. As milling proceeds broadening

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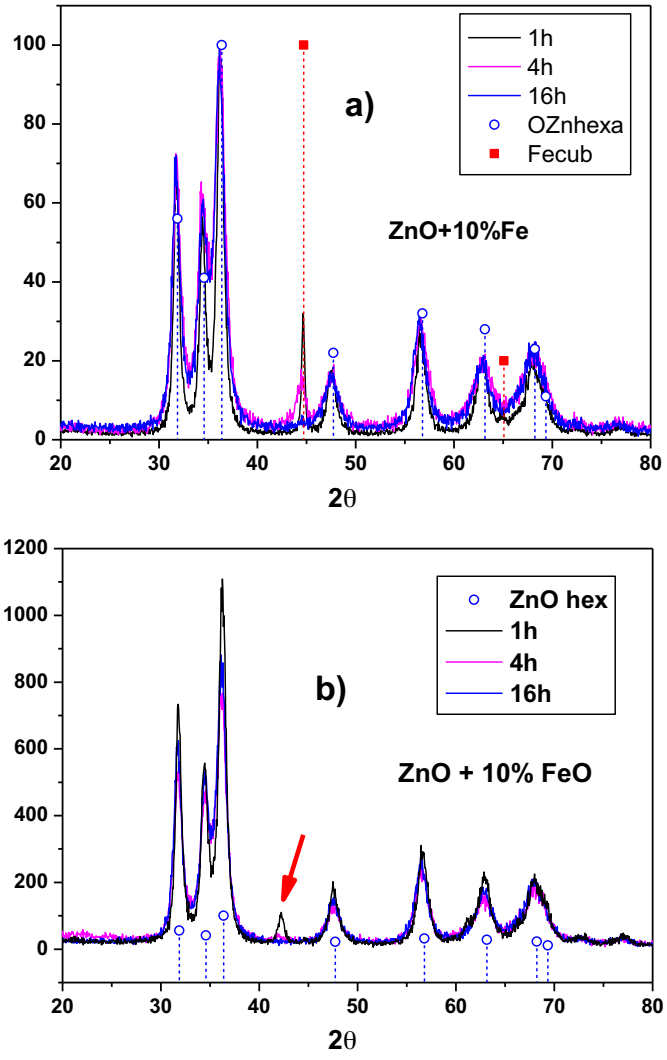

Fig. 1. X-ray diffraction patterns for ZnO powders milled with 10 at% Fe (top) and 10 at% FeO (bottom).

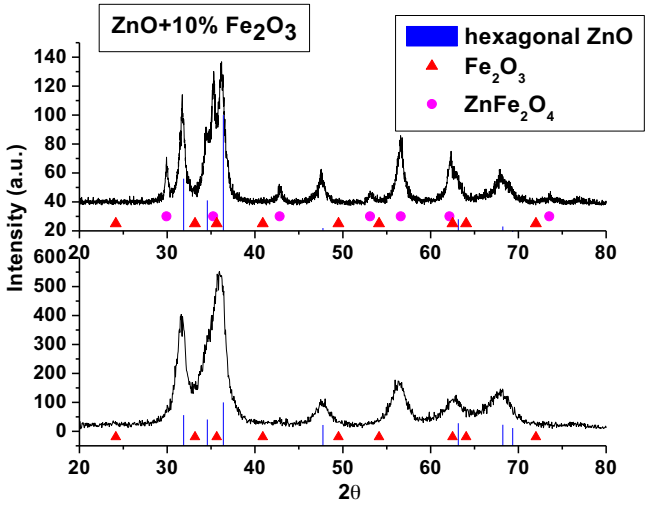

Fig. 2. X-ray diffraction patterns for ZnO powders milled with 10 at% of hematite at different atmospheres: in air (top), under controlled Ar atmosphere (bottom).

of diffraction peaks is observed due to grain size reduction. After 16 h of mechanical work the ZnO hexagonal structure (P63 mc) is observed for both samples. Similar features were observed for samples doped with 5 at% of both starting materials [8].

The evolution with milling time of those mixtures with hematite depends on atmosphere. While after prolonged (16 h) mechanical milling in air the spinel structure $ZnFe_2O_4$ forms, under Ar, the wurtzite structure is obtained (Fig. 2). However, for this last case, after the final milling step a slight contribution of Fe_2O_3 still remains [8].

A peak broadening, associated to a decrease in grain size, is observed in all samples. From these results crystallite sizes were evaluated from Rietveld refinements yielding a final value of around 20 nm for all doped samples [7,8]. As an example, in Fig. 3 the resulting fit for ZnO + 10 at% Fe after 16 h of milling is shown, at the inset the obtained straight lines corresponding to the Full Width at Half Maximum (FWHM) vs 2θ are also shown.

In order to analyze the influence of milling time on magnetic properties on these systems, those samples with 10 at% Fe were investigated. Fig. 4 shows the magnetization curves for 4 and 16 h of milling at different measuring temperatures with a maximum applied field of 10 kOe. Also shown are the ZFC–FC curves. As milling proceeds, Fe contribution to magnetization decreases while a paramagnetic (PM) contribution becomes important. This result is consistent with X-ray diffraction results were a progressive incorporation of Fe into the wurtzite-type structure with time of milling is observed.

From the ZFC–FC curves a shift of the blocking temperature with milling towards low values, around 40 K for the sample milled 16 h, can be appreciated.

For the 16 h milled sample with 10 at% of FeO (shown in Fig. 5) the magnetization curves display a paramagnetic behavior, with a small ferromagnetic signal at 150 and 300 K and a very week one at 5 K where no saturation is yielded in the full magnetic field observed range. No blocking temperature was observed.

The measured hysteresis loop at room temperature may be interpreted in terms of two magnetic contributions:

$$M(H) = \frac{2M_S}{\pi} \arctan\left[\left(\frac{H \pm H_C}{H_C}\right) \tan\left(\frac{\pi M_R}{2M_S}\right)\right] + N_C \mu L\left(\frac{\mu H}{k_B T}\right) \quad (1)$$

The first term describes the hysteretic part and the second one is a Langevin function. M_S is the saturation magnetization, H_C the coercivity, M_R the remanence, N_C the number of PM clusters, μ an average value of their magnetic moment, k_B the Boltzmann constant and T the absolute temperature [9].

The results of the fittings are also shown in Figs. 4 and 5 for both samples: after the last milling step two superimposed signals are proposed: (i) very weak ferromagnetic almost independent of temperature, incompatible with superparamagnetic particles and suggesting long range coupling between magnetic moments; (ii) paramagnetic dominating at low temperature (5 K). The presence of this last signal is responsible for the straight tails at high field at 5, 150 and 300 K in both samples.

These overall results are in agreement with previous Mossbauer studies where different paramagnetic and magnetic signals were observed [7,8].

Complementary magnetic measurements are now in course to a better understanding of the magnetic behavior of these samples.

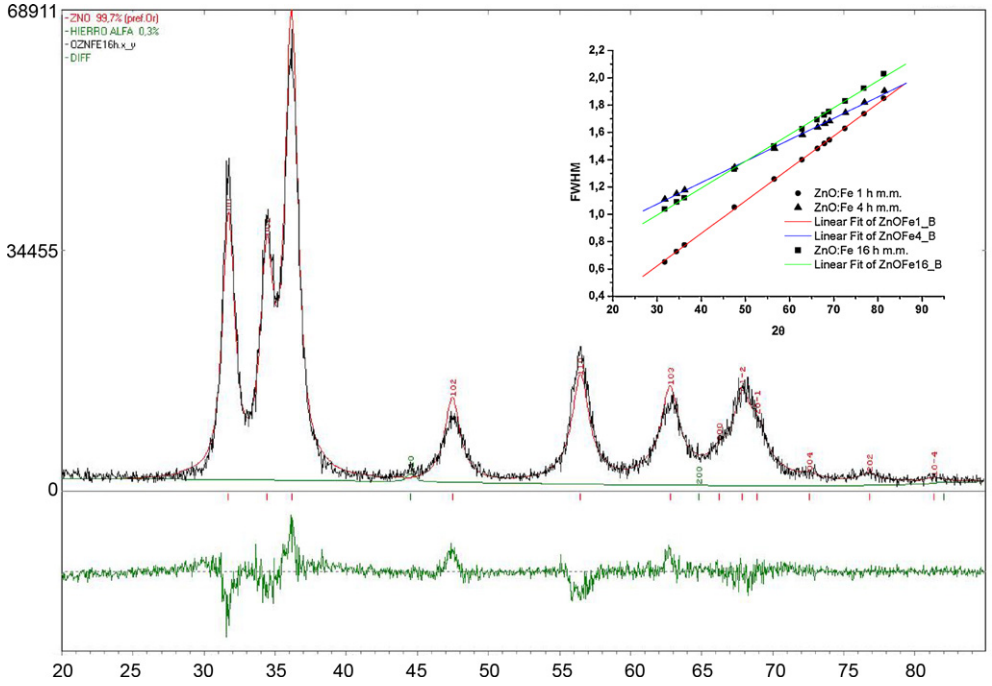

Fig. 3. Rietveld refinement of ZnO + 10 at% Fe X-ray diffraction pattern after 16 h of milling. Insert: FWHM vs. 2θ and least squared fittings for all milling times from where the grain size were calculated.

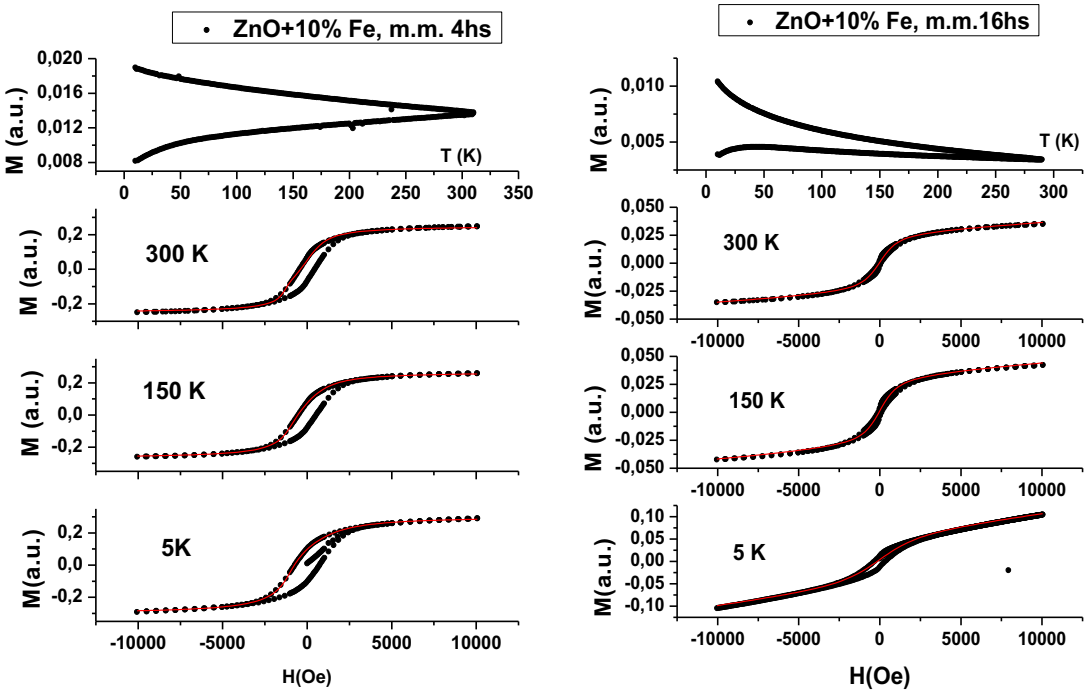

Fig. 4. Magnetization curves at different measuring temperatures for ZnO + 10 at% Fe, milled 4 h (left) and 16 h (right) at a maximum field of 10 kOe. Also shown are the ZFC–FC curves. Full line indicates the result of least squared fitting to function [1].

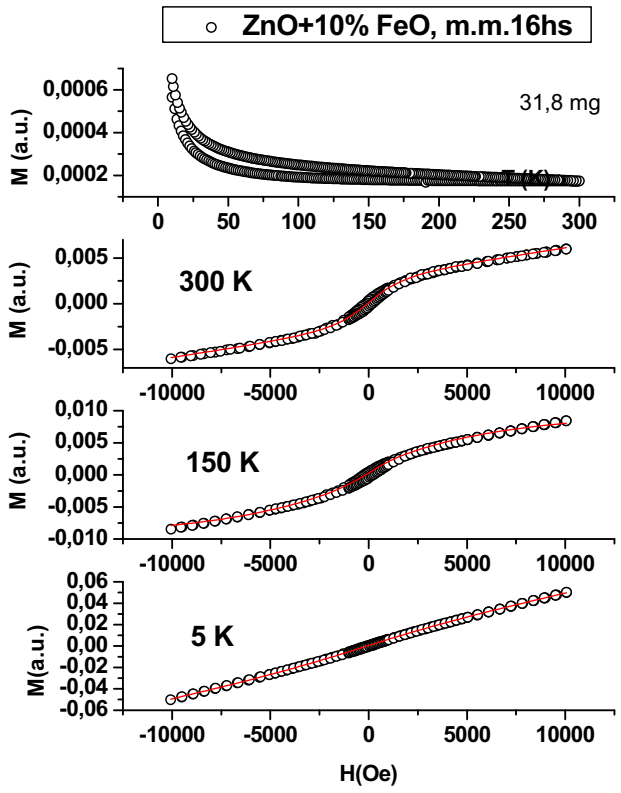

Fig. 5. Magnetization curves at different measuring temperatures for ZnO + 10 at% FeO, milled 16 h at a maximum field of 10 kOe. Also shown is the ZFC–FC curve. Full line indicates the result of least squared fitting to function [1].

4. Conclusion

High energy milling work leads to total or partial cation substitution in the wurtzite ZnO structure. As was previously reported, milling conditions (starting materials, atmosphere, etc.) are important for the obtained final phases. Magnetic measurements indicate that two magnetic phases are present, with a ferromagnetic one dominating at high temperatures. The relative contribution of each other may depend on starting materials while for the case of hematite, atmosphere is a relevant parameter.

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