Study of the magnetic and structural properties of Mn-, Fe-, and Co-doped ZnO powder

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A B S T R A C T
A study of the magnetic and structural properties of Zn$_{1-x}$M$_x$O powder (where $x=0$ or 0.01, and M=Mn, Fe or Co) produced by the proteic sol–gel process was undertaken. The sample crystal structure was analyzed by XRD and magnetic measurements were carried out in a SQUID magnetometer. Of the XRD analysis, all samples had hexagonal wurtzite crystal structure with P63mc space group, and no secondary phase was observed. It is observed of the $M(H)$ measures at 2 K, that the Co- and Mn-doped ZnO displayed saturation magnetizations ($M_s$) of approximately 2 and 3.2 emu/g, respectively, and no remanence ($M_r$) was observed, indicating a superparamagnetic behavior in these samples. However, the Fe-doped sample showed a ferromagnetic behavior with $M_s$ $\sim$ 0.34 emu/g, $M_r$ $\sim$ 0.05 emu/g, and coercivity ($H_c$) $\sim$ 1090 Oe. Already at room temperature, the $M(H)$ measurements reveal a purely paramagnetic behavior for Mn- and Fe-doped ZnO, indicating that the Curie temperature ($T_C$) is below 300 K. However, a weak superparamagnetic behavior was observed in the Co-doped sample, indicating that $T_C > 300$ K.

1. Introduction

There is great interest in spintronics with semiconductors due to the possibility of combining their electrical and magnetic characteristics (i.e., current control by manipulation of spin, non-volatility), resulting in diluted magnetic semiconductors (DMS). Two materials intensively studied for DMS systems were GaMnAs [1,2] and InMnAs [3,4], however, their highest reported Curie temperatures ($T_C$) are only 170 K for GaMnAs and 35 K for InMnAs. Thus, there have been many research efforts into finding new DMS materials with Curie temperatures at or above room temperature to achieve a greater practical applicability. One of the most promising and extensively studied systems is transition-metal-doped ZnO [5]. However, there is heated debate regarding the ferromagnetism of this material, because several studies attribute this property to intrinsic phenomena [6,7], whereas others attribute it to extrinsic phenomena [8,9] and still others report the absence of this property in room temperature (300 K) transition-metal-doped ZnO [10,11]. Because of this controversy, many studies that argue intrinsic ferromagnetism in the transition-metal-doped ZnO in 300 K. However, a weak superparamagnetic behavior was observed in the Co-doped sample, indicating that $T_C > 300$ K.

2. Experimental

The samples were prepared using the general reaction

\[(1-x)\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} + x\text{MQ} \cdot y\text{H}_2\text{O} + CW \rightarrow \text{Zn}_{1-x} \cdot x\text{M}_x\text{O}, \text{ where } x=0 \text{ for the pure oxide and } x=0.01 \text{ for the doped oxide, } M=\text{Mn, Fe or Co.} \]
Co, Q = Cl₂ for Mn and Q = (NO₃)₂ for Fe and Co, y = 4 for Mn, 9 for Fe and 6 for Co, and CW = coconut water. These solutions were put in a furnace for 24 h at 100 °C to eliminate excess water and form the xerogel. Next, the xerogel was calcinated at 1100 °C for 1 h to eliminate organic materials and form a powder. The crystalline phases were identified by X-ray diffraction (XRD) measurements with the Bragg–Brentano geometry through CuKα radiation using a Rigaku RINT 2000/PC diffractometer operating with 40 kV/40 mA in the 2θ range of 30–70° with a step rate of 0.004°/s. The M(H) and M(T) magnetic measurements were carried out in a Quantum Design SQUID magnetometer MPMS-XL, using mass 50 mg of each sample.

3. Results and discussion

The XRD measurements of all samples revealed a wurtzite-type hexagonal crystalline structure with the P63mc space group and without spurious phases, as seen in [24]. Only the ZnO phase is present, which indicates either a total insertion of the dopant ions into the ZnO crystal lattice or a secondary phase that is so small that it is unobservable in XRD measurements. The M(H) values at 2 and 300 K for the Mn- and Co-doped ZnO are shown in Figs. 1 and 2, respectively. In both cases, typical superparamagnets behavior is observed at 2 K due to the absence of remanence (M_r) or coercivity (H_c), and the saturation magnetization (M_s) is approximately 3.2 emu/g for Zn_{0.99}Mn_{0.01}O and 2 emu/g for Zn_{0.99}Co_{0.01}O. According to superparamagnetic theory [25], the magnetic relaxation time (τ) of a particle non-interactant in the zero field limit (H = 0) is given by Eq. (1)

\[ τ = τ_0 \exp(K_V V/k_B T) \]

where τ_0 is a factor related to the natural frequency of the gyromagnetic precession time and can be found theoretically or experimentally, K_V is the anisotropic energy density or anisotropy constant, V is the particle volume, k_B is the Boltzmann constant, and T is the absolute temperature. Therefore, according to Eq. (1), the thermal energy supplied \((k_B T)\) to the Zn_{0.99}Mn_{0.01}O and Zn_{0.99}Co_{0.01}O samples at 2 K is sufficient to overcome the energy barrier (K_V V) and allow the rotation of the particle spins such that there is no remanence for H = 0. In other words, the relaxation time of these particles is smaller than the measure time (t_m) at 2 K. In Fig. 1, a purely paramagnetic behavior is observed at 300 K, indicating that the Curie temperature (T_C) of this material is below room temperature. Whereas the included graph in Fig. 2 shows a weak superparamagnetic behavior at 300 K with an M_s value of approximately 0.0003 emu/g, indicating that T_C is above room temperature. Figs. 3 and 4 show the M(T) curves of the Zn_{0.99}Mn_{0.01}O and Zn_{0.99}Co_{0.01}O samples under a DC field of 1000 Oe. Both samples demonstrate typical Langevin-paramagnetism behavior, in which the DC susceptibility (\(\chi_{DC} = M/H_{DC}\)) is a function that decreases rapidly with increasing temperature. In addition, no blocking temperature (T_B) is observed, which reinforces the argument made earlier that τ < t_m and that the particles are in the superparamagnetic state. However, both graphs of (\(\chi_{DC}^2(T)\)) (included in Figs. 3 and 4) obtained from ZFC curves show Langevin paramagnetic behavior (solid line) and Curie–Weiss ferromagnetic behavior (dashed line), indicating that the dopant ions of these samples also interact ferromagnetically with each other. However, the number of interacting atoms is so small that it was not possible to verify the remanence in the M(H) curves at 2 K (Figs. 1 and 2), suggesting that the atoms of Mn and Co are well diluted in the ZnO matrix. A similar analysis was carried out by Martínez [26] to explain the antiferromagnetic behavior in a Co-doped ZnO sample. Fig. 5 shows M(H) measurements of the Fe-doped ZnO at 2 and 300 K. Ferromagnetic behavior is observed at 2 K with M_s, M_r, and H_c values of approximately 0.34 emu/g, 0.05 emu/g, and 1090 Oe, respectively.
In this case, there are magnetic interactions between particles, which impede the rotation of spins and give rise to the remanence, in addition to the energy barrier $K_a V$ (Eq. (1)). Thus, it is necessary to supply extra energy through the application of the coercive field $H_c$ to demagnetize the material. Fig. 5 also shows purely paramagnetic behavior at 300 K, indicating that the Curie temperature ($T_c$) of this material is also below room temperature. Fig. 6 shows the $M(T)$ curve of the Zn$_{0.99}$Fe$_{0.01}$O sample under a DC field of 1000 Oe. As expected, a blocking temperature ($T_B$ $\approx$ 15 K), characterized by a maximum in the ZFC curve, is observed, indicating a ferro-superparamagnetic or ferro-paramagnetic transition. In this case, $T_B$ corresponds to the ferro-superparamagnetic transition because it is below $T_c$, however, if the two temperatures were equal, then it would correspond to the ferro-paramagnetic transition. In the Zn$_{0.99}$Fe$_{0.01}$O sample, the particles are in the ferromagnetic state below $T_B$ and are called blocked because the energy supplied is insufficient to allow the rotation of spins, and thus $\tau > t_m$. However, the particles are in the superparamagnetic state above $T_B$ ($\tau < t_m$). Magnetic irreversibility temperature ($T_{irr}$ $\approx$ 10 K) is also observed, characterized by the separation of the ZFC and FC curves. This observation indicates either a spin glass behavior or the presence of secondary crystalline phases. However, the decrease in FC value with decreasing temperature (Fig. 6) from 15 to 10 K (i.e., $T_B$ to $T_{irr}$) suggests the presence of a small antiferromagnetic phase not visible in the XRD analysis. This finding is confirmed by the analysis of the graphs $\chi_{dc}(T)$ (inset in Fig. 6), which shows Curie-Weiss antiferromagnetic (solid line) and ferromagnetic (dashed line) behavior. Therefore, total insertion of the Fe ions in the ZnO crystal lattice does not occur, leading to the formation of a small secondary antiferromagnetic phase (e.g., Fe$_2$O$_3$ or FeO), which explains the low $M_s$ value of this sample.

4. Conclusion

All samples had hexagonal wurtzite crystal structures with the P63mc space group and no secondary phase, as observed via XRD. At 2 K the Co- and Mn-doped ZnO presented a superparamagnetic behavior, whereas the Fe-doped sample showed a ferromagnetic behavior. However, at 300 K, the Mn- and Fe-doped ZnO revealed a purely paramagnetic behavior indicating that $T_c$ is below room temperature and the Co-doped sample showed a weak superparamagnetic behavior (i.e., $T_c$ $\approx$ 300 K). A detailed magnetic analysis suggests the presence of small spurious antiferromagnetic phase in the Zn$_{0.99}$Fe$_{0.01}$O sample, which was not observed via XRD.

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References