

## Nanocrystals of $\text{Zn}_{1-x}\text{M}_x\text{O}$ ( $\text{M} = \text{Co}, \text{Mn}$ ) by proteic sol-gel process

**D A A Santos, A D P Rocha, J G S Duque and M A Macedo**

Physics Department, Federal University of Sergipe  
49100-000 - São Cristóvão – SE - Brazil

E-mail: mmacedo@ufs.br

**Abstract.** We present in this work a study on the magnetic properties of nanocrystals of Mn- or Co-doped ZnO obtained by a proteic sol-gel process. Analysis of these nanocrystals is accomplished using x-ray diffraction (XRD), the Rietveld refinement through using the General Structure Analysis System (GSAS) program, and magnetic measurements using a vibrating sample magnetometer (VSM). The samples of  $\text{Zn}_{0.9}\text{M}_{0.1}\text{O}$  ( $\text{M} = \text{Co}$  or  $\text{Mn}$ ) possess single phase crystals with a wurtzite structure (hexagonal) and a P6<sub>3</sub>mc space group. The  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  and  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$  samples presented, at room temperature, the behavior of a soft ferromagnetic with a coercive field ( $H_c$ ) of 336 Oe and 1240 Oe, respectively, and a remanent magnetization ( $M_r$ ) of 5 and 2.5 memu/g, respectively.

### 1. Introduction

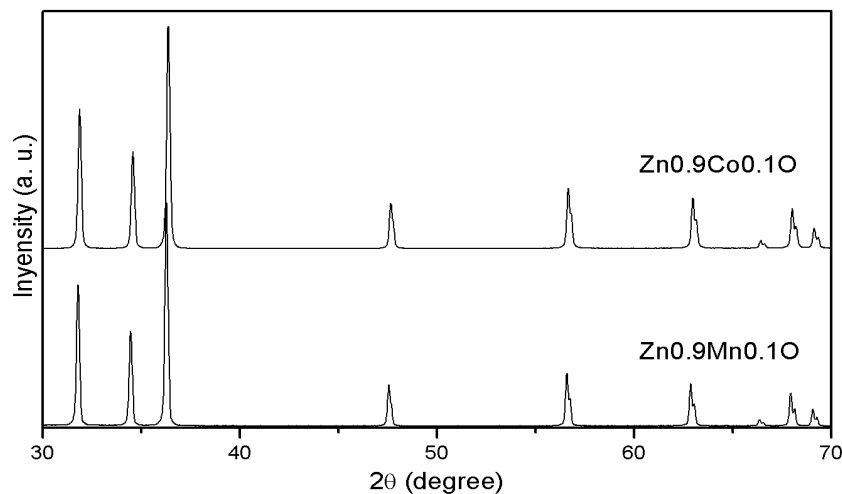
Diluted magnetic semiconductors (DMS), in which transition metal atoms are introduced into the cationic sites of the semiconducting host lattice, have recently attracted increasing attention because of their potential use in spin electronic (or spintronic) devices [1]. A key factor in the realization of spintronic devices is the development of ferromagnetic DMS with a Curie temperature greater than room temperature. Interest in ZnO-based DMS was initially generated by the theoretical prediction [2, 3] that greater than room temperature ferromagnetism is possible in ZnO-based DMS. The existence of ferromagnetism at room temperature in Co-doped ZnO is not completely understood, and thus a careful investigation of the structural features is required. Apart from the possibility of intrinsic ferromagnetism from  $\text{Zn}_{1-x}\text{Co}_x\text{O}$ , the existence of cobalt oxide crystals could be an additional source of ferromagnetism [4]. Kim et al. [5] found that the ferromagnetism resulted from the formation of cobalt microclusters in  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  thin films grown by pulsed laser deposition. Lee et al. [6] and Rode et al. [7] reported intrinsic ferromagnetic behavior of Co-doped ZnO films with a Curie temperature of approximately 350 K. Many reports further support the possibility of having intrinsic ferromagnetism in Co-doped ZnO [8, 9]. Further support for the absence of ferromagnetism in Co-doped ZnO is reported by various groups [10-12]. Jayakumar et al. [13] report the magnetism of Mn-doped ZnO nanocrystalline particles obtained by a co-precipitation method. We present in this work, a study of the magnetic properties of nanopowders of Mn- and Co-doped ZnO obtained by an innovative process known as proteic sol-gel [14], and the use of the Rietveld refinement using the GSAS program [15] to determine the parameters of the crystalline structure.

## 2. Experimental

The samples were prepared through the general reaction:  $(1-x)\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + x\text{MQ} \cdot y\text{H}_2\text{O} + \text{CW} \rightarrow \text{Zn}_{1-x}\text{M}_x\text{O}$ ; where  $x = 0$  for the pure oxide or  $x = 0.1$  for the doped oxide,  $\text{M} = \text{Co}$  or  $\text{Mn}$ ,  $\text{Q} = (\text{NO}_3)_2$  for  $\text{Co}$  or  $\text{Q} = \text{Cl}_2$  for  $\text{Mn}$ ,  $y = 6$  for  $\text{Co}$  or  $y = 4$  for  $\text{Mn}$ , and  $\text{CW} = \text{coconut water}$ . These solutions were put in a furnace for twenty-four hours at  $100^\circ\text{C}$  in order to ensure excess water was evaporated from the xerogel. Then, the xerogels were calcinated at temperatures between  $600$ - $1200^\circ\text{C}$  for one hour to eliminate organic materials and completely oxidize the salts. Using a commercial VSM magnetometer, the magnetic hysteresis was measured and the crystalline phase was identified by XRD measurements using  $\text{CuK}\alpha$  radiation at  $40 \text{ kV}/40 \text{ mA}$  on a Bragg-Bretano geometry in the  $2\theta$  range of  $30^\circ$ - $70^\circ$ , in steps of  $0.02^\circ$ , and a counting time of  $5 \text{ s}$  per step.

## 3. Results and discussion

The XRD patterns of the  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  and  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$  calcined at  $900^\circ\text{C}$  are shown in figure 1. It can be seen from this figure that no spurious peak was encountered, which indicates that the zinc oxide was doped with ions of cobalt and manganese. Furthermore, small clusters of cobalt oxide or manganese may have formed in very low concentrations that were not detected by XRD.



**Figure 1.** XRD pattern for  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  and  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$  calcined at  $900^\circ\text{C}$ .

The samples calcinated below  $900^\circ\text{C}$  presented the phases of  $\text{CoO}$  and  $\text{Mn}_2\text{O}_3$ . The results of the Rietveld refinement are showed in table 1. All of the analyzed powders, either pure  $\text{ZnO}$  or doped, presented a wurtzite structure (hexagonal) with a  $\text{P6}_3\text{mc}$  space group and there are no impure phases. The size of the crystallites was estimated in the directions parallel ( $P_{\parallel}$ ) and perpendicular ( $P_{\perp}$ ) to the anisotropy of growth, using the following formulas of GSAS:

$$P_{\perp} = (18000 \cdot k \cdot \lambda) / (\pi \cdot \text{LX}) \quad (1)$$

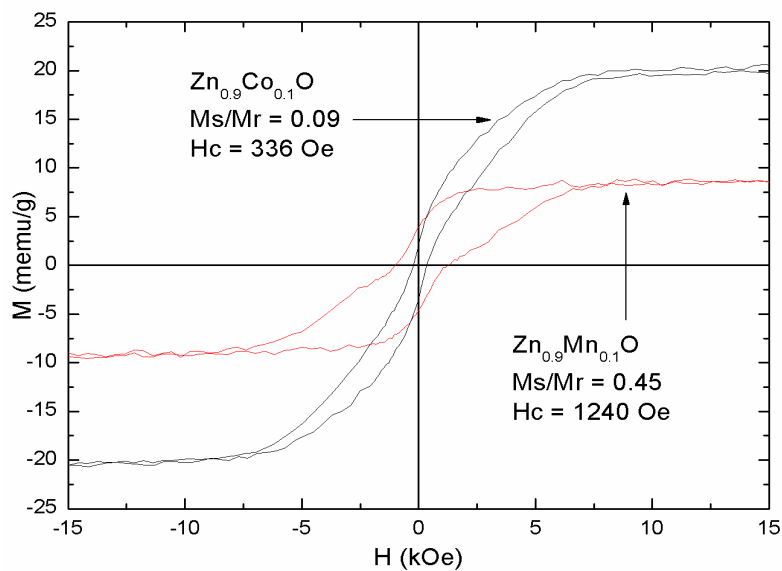
$$P_{\parallel} = (18000 \cdot k \cdot \lambda) / \pi \cdot (\text{LX} + \text{PTEC}) \quad (2)$$

where  $k = 0.9$  is the constant of Scherrer,  $\lambda = 1.54056 \text{ nm}$  is the wavelength of  $\text{Cu}$ ,  $\text{LX}$  is a function of Lorentz for the crystallite size and  $\text{PTEC}$  is an index related to the anisotropy of crystallite size.

**Table 1.** Data of the refinement.

	<b>ZnO</b>	<b>Zn<sub>0.9</sub>Co<sub>0.1</sub>O</b>	<b>Zn<sub>0.9</sub>Mn<sub>0.1</sub>O</b>
<b>T(°C)</b>	900	900	900
<b>a=b(Å)</b>	3.249587	3.254061	3.253373
<b>c (Å)</b>	5.203588	5.205724	5.209253
<b>V(Å<sup>3</sup>)</b>	47.587	47.738	47.750
<b>P<sub>⊥</sub>(nm)</b>	93.41(6)	133.73(5)	150.51(7)
<b>P<sub>∥</sub>(nm)</b>	93.41(3)	130.54(4)	144.34(4)
<b>ρ(g/cm<sup>3</sup>)</b>	5.700	5.665	5.644
<b>Rwp</b>	0.0579	0.0680	0.0672
<b>χ<sup>2</sup></b>	1.134	1.166	1.162
<b>Rp</b>	0.0391	0.0474	0.0479

The field dependence of the magnetization (M versus H) curve at room temperature (figure 2) was measured by subtracting the loops from the paramagnetic contribution where the paramagnetic contribution was subtracting of the loops. The subtraction paramagnetic phase aimed to measure the actual contribution of Ms, Mr and Hc of the ferromagnetic phase. These measurements showed clear hysteresis loops with an Hc of 336 Oe and 1240 Oe and a Mr of 5 and 2.5 memu/g for the Zn<sub>0.9</sub>Co<sub>0.1</sub>O and Zn<sub>0.9</sub>Mn<sub>0.1</sub>O samples, respectively.



**Figure 2.** Magnetization as a function of field at room temperature of Zn<sub>0.9</sub>Co<sub>0.1</sub>O and Zn<sub>0.9</sub>Mn<sub>0.1</sub>O calcined at 900°C.

The saturation field (Hs) was 7.5 kOe for both samples. The Zn<sub>0.9</sub>Co<sub>0.1</sub>O loop showed a small exchange bias field (Heb = 80 Oe), indicating a ferro/antiferromagnetic coupling, formed by CoO round clusters in the doped ZnO (Zn<sub>0.9</sub>Co<sub>0.1</sub>O/CoO) sample. Belghazi *et al.* obtained a similar result in

a Co-doped ZnO thin film with 10% Co [16]. For the  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$  sample no exchange bias on the magnetization was observed, which is a strong indication of total doping of Mn in ZnO. The origin of the magnetism in the samples was not identified and it can therefore not be determined whether the magnetism is intrinsic or extrinsic. However, our results contradict several works of literature that reported the absence of ferromagnetism in Co or Mn-doped ZnO [10-12]. The origin of the magnetism in the samples, the exchange bias phenomenon, and the dependency of the ZnO magnetization with the concentration of the metal and the temperature of calcination will be presented in a future publication.

#### 4. Conclusion

The proteic sol-gel process has been shown to be a good alternative method for obtaining DMS doped with transition metals. The  $\text{Zn}_{0.9}\text{Co}_{0.1}\text{O}$  and  $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$  samples presented, at room temperature, the behavior of a soft ferromagnetic with an  $H_c$  of 336 Oe and 1240 Oe and a  $M_r$  of 5 and 2.5 memu/g, respectively.

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