Synthesis and Characterization of Nanocrystalline Zn$_{1-x}$M$_x$O (M=Co or Mn) by Proteic Sol-Gel Process

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Abstract – We present in this work a study on the magnetic properties of Mn- Co-doped ZnO obtained by proteic sol-gel process. It accomplishes analysis of XRD, Rietveld refinement through the program GSAS and magnetic measures using a magnetometer VSM. The samples of Zn$_{0.9}$M$_{0.1}$O (M = Co or Mn) present single phase with wurtzite structure (hexagonal) and space group P6$_3$mc. The Zn$_{0.9}$Co$_{0.1}$O and Zn$_{0.9}$Mn$_{0.1}$O presented, at room temperature, a behavior of a soft ferromagnetic with a coercive field (Hc) of 336 Oe and 1240 Oe, a remanence (Mr) of 0.005 and 0.0025 emu/g, respectively.

The existence of ferromagnetism at room temperature in Co-doped ZnO it yet is not understood completely and thus a careful investigation of the structural features are required. Apart from the possibility of intrinsic ferromagnetism from Zn$_{1-x}$Co$_x$O, the existence of cobalt oxide crystals could be an additional source of ferromagnetism [1]. We present in this work a study on the magnetic properties of the nanopowders of Mn-, Co-doped ZnO obtained by proteic sol-gel. The samples were prepared though of the general reaction (1-x)Zn(NO$_3$)$_2$ ·6H$_2$O + xMO·yH$_2$O + CN → Zn$_1$-xM$_x$O [where x = 0 for the pure oxide or x = 0.1 for the doped oxide; M = Co or Mn; Q = (NO$_3$)$_2$ for Co or Q = Cl$_2$ for Mn; y = 6 for Co or y = 4 for Mn; CN = coconut water]. Those solutions were put in a greenhouse by 24h at 100°C for that all the water evaporated remaining the xerogel. Soon afterwards, the xerogels were calcinated at temperatures between 600 and 1200 ºC, during 1h for to eliminate the organic materials and completely oxidize the salts. The magnetics hysteresis were measurement using a commercial VSM magnetometer and the crystalline phases were identified by X-ray diffraction (XRD) measurements using Cu-α radiation at 40 kV/40 mA on a Bragg-Bretano geometry in the 2θ range of 30º to 70º, in steps of 0.02º, and a counting time of 5 s per step. The XRD pattern of the Zn$_{0.9}$Co$_{0.1}$O and Zn$_{0.9}$Mn$_{0.1}$O calcined at 900°C are shown in Fig. 1. Neither spurious peak was encountered indicating that zinc oxide was doped with cobalt and manganese ions. On the other hand, little clusters of cobalt oxide or manganese can have formed in very low concentration that were not detecting by X-ray diffractometry. The samples calcined below 900°C presented the phases of CoO and Mn$_2$O$_3$. The field dependence of the magnetization (M versus H) curve at room temperature is shown in Fig. 2, where the paramagnetic contribution was subtracting of the loops. It is clearly seen hysteresis loops with a coercive field (Hc) of 336 Oe and 1240 Oe, a remanence (Mr) of 0.005 and 0.0025 emu/g for Zn$_{0.9}$Co$_{0.1}$O and Zn$_{0.9}$Mn$_{0.1}$O, respectively. The saturation field (Hs) was 7.5 kOe for both samples. The Zn$_{0.9}$Co$_{0.1}$O loop showed a small exchange bias field (Heb = 80 Oe), indicating a coupling ferro/antiferromagnetic, formed by CoO clusters round of the doped ZnO (Zn$_{0.9}$Co$_{0.1}$O/CoO). The exchange bias phenomenon and the dependency of the ZnO magnetization as a function of the metal concentration and calcination temperature will be published elsewhere. The proteic sol-gel process showed to be a good alternative path to synthesize Zn$_{0.9}$Co$_{0.1}$O and Zn$_{0.9}$Mn$_{0.1}$O presenting soft ferromagnetic behavior at room temperature.

References