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Influence of the 3d-metal doping on the magnetic properties of SnO_2 nanoparticles

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Abstract – The magnetic properties of metal -doped SnO_2 nanoparticles fabricated by a polymer precursor method is reported in this work. X-ray diffraction patterns indicate the formation of single phase for metal contents below ~10%. Magnetization isotherms obtained at 5K indicate only a paramagnetic behavior for the Co-doped sample. Moreover, for samples doped with Ni and Cr a ferromagnetic order is observed in the low doping range (<3%). Above that content, a gradual trend to a paramagnetic behavior is determined. Susceptibility vs. temperature curves follow the Curie-Weiss law and suggest the presence of Ni^{2+}, Co^{2+} and Cr^{3+} ions for the metal-doped samples.

The oxide semiconductor SnO_2 doped with transition metals has attracted considerable attention due to the possibility of obtaining the ferromagnetic Curie temperature (T_C) above room temperature which is important for spintronic applications. Fe- and Cr-doped SnO_2 systems of rutile structure have been reported as ferromagnetic materials with T_C above room-temperature. Unfortunately, due to the complex solid-state chemistry involved in the preparation the resulting properties depend on the conditions and preparation technique. In spite of the intense research there is still a lot of controversy mainly related to the origin of the magnetic order in the transition-metal doped SnO_2 semiconductor. In this work, we present the study of the structural and magnetic properties of SnO_2 nanoparticles doped with Cr, Co and Ni, which were produced by a polymer precursor method.

X-ray diffraction patterns indicate the formation of only the rutile phase for samples with low metal content (below 10%). Above ~30% Ni, additional Bragg reflections corresponding to a second phase is determined. Undoped SnO_2 nanoparticles show an average particles size of ~13nm which decreases when the content of metal is increased (see Fig. 1). The crystalline size is further corroborated by Transmission Electron Microscopy experiments. It is determined that in samples with very low metal content a solubility regime occurs, but when the metal content is increased a regime of surface segregation is determined [2]. That segregation is thought to cause a decrease in the surface energy and, therefore, an increase in the surface area. Magnetization measurements indicate a paramagnetic behavior in the whole range of doping for Co doped samples (see Fig. 2); however, in samples doped with Ni and Cr, a ferromagnetic order has been observed for metal content below ~3mol% and a paramagnetic behavior for higher dopant content. Those results are related to the metal segregation which occurs on the particles surface and to the second phase nucleation observed in samples with high metal content.

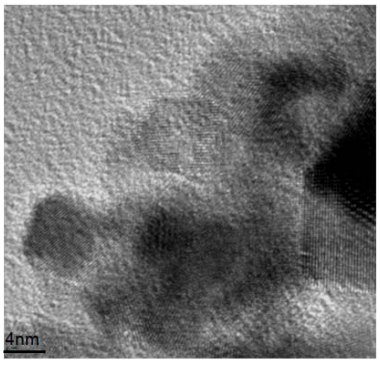

Figure 1: HRTEM image of SnO_2 doped with 5mol% Cr.

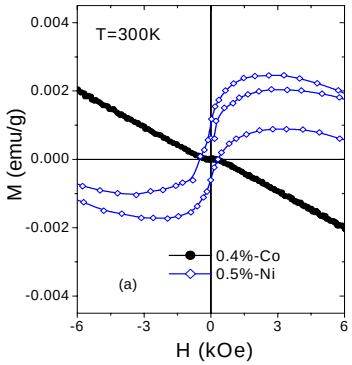

Figure 2: M vs. H curves obtained at 5K for SnO_2 doped with 10mol% Co and Ni.

[1] W. Wang, Z. Wang, Y. Hong, J. Tang, and M. Yu, J. Appl. Phys. 99 (2006) 0M115
[2] P. Hidalgo, R. H. R. Castro, A. C. V. Coelho, and D. Gouvêa, Chem. Mater. 17 (2005) 4149.