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Co²⁺ and Fe³⁺ EPR study of magnetic ZnO nanoparticles for its potential use in cancer cell treatment

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Introduction

Nanoparticles are being increasingly recognized for their potential use in biological applications including nanomedicine for cancer treatment. The response of normal human cells to ZnO nanoparticles under different signaling environments was investigated previously and compared to the response of cancerous cells. As a result, ZnO nanoparticles exhibit a strong preferential ability to kill cancerous T cells, compared to normal cells [1, 2]. This ability is enhanced with transition metal ions doping. Therefore careful investigation of local environment and magnetic state of these ions is very important in the study of potential use of ZnO nanoparticles for cancer cell treatment.

Experimental results

An EPR study of ZnO nanoparticles, doped with Fe ions, prepared using acetate method, was recently carried out [3]. Here we present the results of EPR investigations on two types of ZnO nanoparticles, prepared using chemical hydrolysis methods, in diethylene glycol (NL), and in denatured ethanol solutions (QJ), respectively, doped with 0.5 – 10 % Fe³⁺ and Co²⁺, which were carried out at X-band (9.5 GHz) at 5 K. To interpret the experimental results. EPR spectra were simulated by exact diagonalization of the spin-Hamiltonian matrix, in order to identify the presence of Fe³⁺ and Co²⁺ ions at different magnetically active sites in these samples. The simulation of EPR spectra for NL samples revealed that they contained (i) Fe³⁺ and Co²⁺ ions, which substituted for Zn²⁺ ions, exhibiting axial Co²⁺ EPR spectrum in crystalline ZnO; (ii) low intense EPR signals in the samples with Co concentration more than 0.5% and less than 5%; (iii) EPR spectrum due to surface oxygen defects; and (iv) FMR (ferromagnetic resonance) from ferromagnetically (FM) ordered area in ZnO nanoparticles. The EPR spectra for QJ samples are similar to those for NL samples, however FMR signal is found more intense. No EPR signals due to surface oxygen defects were observed in QJ samples, as well as no low intense EPR signals. The ferromagnetism and EPR spectra are found to vary with differences in the surface morphology of nanoparticles.

Origin of ferromagnetism

Recently, Coey et al. [4] suggested new mechanism for ferromagnetism nature, based on charge transfer in defected oxides. They involved the model of Stoner ferromagnetism

for explanation of ferromagnetism origin. In this model paramagnetic impurity ions are not ordered and ferromagnetism arises due to defect band electron structure of semiconducting ZnO. In this model, Fe³⁺ and Co²⁺ ions and ferromagnetically ordered area exist separately. This model can be applied to semiconducting ZnO.

Conclusion

The main conclusions of our EPR investigations of ZnO nanoparticles are as follows:

(i) The observed EPR spectra provide clear evidence for the presence of both paramagnetic localized Fe³⁺ and Co²⁺ ions exhibiting sharp lines, as well as FMR lines, due to ferromagnetically coupled area, producing very broad signal. Fe³⁺ and Co²⁺ EPR lines are broadened due to wide distribution of oxygen defects near surface. Both the paramagnetic Fe³⁺ and Co²⁺ ions and the ferromagnetic components are present in NL and QJ samples. EPR linewidth of Co²⁺ in QJ samples is much larger, than in NL samples.

(ii) EPR signal, due to surface oxygen defects, was clearly observed in NL samples, but not in QJ samples. This explains the smaller magnetic moment observed in NL samples, where not all oxygen defects involved in ferromagnetic ordering. QJ samples, on the other hand, exhibit intense FM resonance signals, suggesting that all oxygen defects in them are magnetically coupled. This accounts for their stronger ferromagnetism.

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