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Absence of room temperature ferromagnetism in transition metal doped ZnO nanocrystalline powders from PAC spectroscopy

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Abstract Local structural and electronic environment around ^{111}In probe atoms in transition metal doped $Zn_{1-x}T_xO$ (T=Mn, Co, V and Ni; x = 0.01, 0.02, 0.05) and Cu co-doped $Zn_{1-x}Co_xCu_{0.01}O$ (x = 0.01–0.04) have been monitored on an atomic scale by Perturbed Angular Correlation (PAC) spectroscopy. Single phase nanocrystalline powders were synthesized at low annealing temperatures by sol-gel method. PAC measurements exhibited the well known quadrupole interaction frequency, $\nu_Q =$ 31 MHz, which have been attributed to the substitutional incorporation of ^{111}In in ZnO matrix. PAC results did not reveal any evidence of magnetic ordering down to 77 K in pure and doped ZnO, which is consistent with the recent observation of paramagnetic behavior in transition metal doped ZnO with synchrotron based studies.

Keywords ZnO · Perturbed angular correlation · Magnetism

1 Introduction

Recently, ZnO has been recognized as a promising candidate for a dilute magnetic semiconductor when doped with transition metal elements with possibilities of presenting room temperature ferromagnetism with large magnetization [1]. Theoretical calculations have indicated that ZnO doped with Co or Mn should present ferromagnetism at room temperature [2]. However, results obtained did not prove to be consistent: some studies reported observation of room-temperature ferromagnetism [3] whereas others reported the total absence of ferromagnetism in these materials

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[4, 5]. The effect of Cu co-doping, a possible pathway for inducing ferromagnetism has also been observed in transition metal-doped ZnO [6]. It is therefore still questionable whether transition metal doped ZnO is really ferromagnetic at room temperature! Another important issue is to understand whether the ferromagnetic behavior comes from the interaction proposed by Dietl (based on Zener model) [1] or from extrinsic magnetic dopant phases. Recent studies have also brought considerable attention to the important role of intrinsic defects, annealing temperatures and annealing atmosphere in achieving room temperature ferromagnetism. Conclusions are, in general, based on macroscopic experimental results that are unable to provide information about local environment. Knowledge of the local structure around dopants is important in order to better understand the mechanisms that induce magnetic ordering in these compounds. In this context, the present work makes use of Perturbed Angular Correlation technique, which is able to provide local information about the chemical nature of intrinsic and extrinsic defects.

2 Experimental procedure

Samples were prepared by a wet chemical route based on sol-gel Pechini methodology. Stoichiometric samples of ZnO were prepared from pure Zn (99.9999%), which was dissolved in concentrated HCl to obtain a zinc chloride solution. High purity doping elements (99.9999%), like Co, Mn, V and Ni, were also dissolved in the same way. Doped ZnO samples were prepared by mixing solutions of zinc chloride with dopant chloride. Approximately 20 μCi of $^{111}InCl_3$ solution was added to this sol-gel, which was evaporated to dryness on a hot plate at 80°C. The gel was then heated at 350°C for 10 h. The resulting powder was sintered at 500°C. Another set of samples was prepared using the same procedures but without radioactive ^{111}In for X-ray diffraction (XRD) measurements. The PAC data was acquired for these samples using a spectrometer consisting of four conical BaF_2 detectors with a conventional slow-fast coincidence set-up. The well known γ-cascade of 172–245 keV, populated from the decay of ^{111}In with an intermediate level with spin $I = 5/2^+$ at 245 keV ($T_{1/2} = 84.5$ ns) in ^{111}Cd, was used to investigate the hyperfine interactions. The PAC method is based on the observation of hyperfine interaction of nuclear moments with extra-nuclear magnetic field (B_{hf}) or electric field gradient (EFG). The technique measures the time evolution of the γ-ray emission pattern caused by hyperfine interactions. A description of the method as well as details about the PAC measurements can be found elsewhere [7].

3 Results and discussion

XRD measurements on samples indicated a single phase ZnS-type structure with $P6_3mc$ space group symmetry. PAC measurements were taken for ZnO doped samples at room temperature after 500°C annealing procedure in nitrogen atmosphere. PAC spectra generated from coincidence counts for various samples are shown in Fig. 1. A visual inspection of these spectra clearly reveals the presence of only pure electric quadrupole interaction. The environment of ^{111}In probe atoms in the ZnO

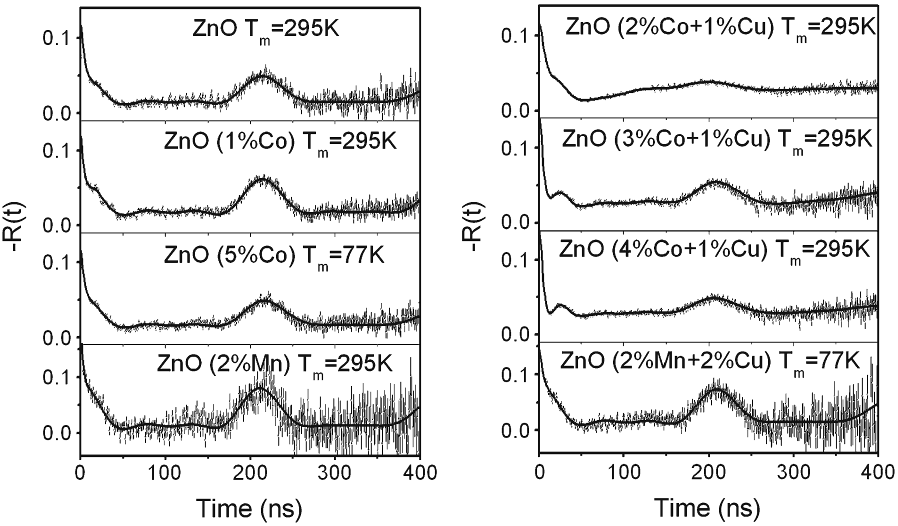


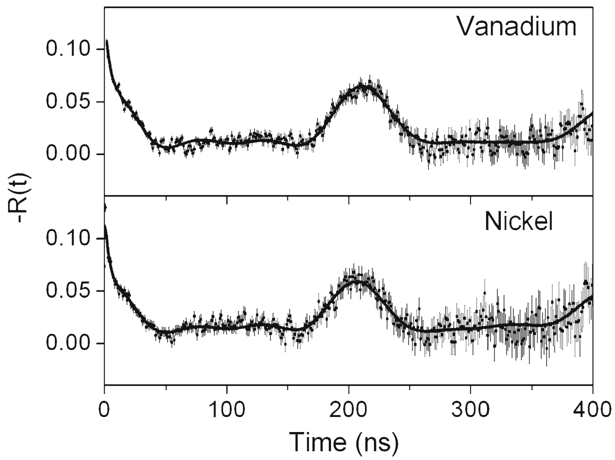
Fig. 1 Least squares fitted PAC spectra for pure and doped ZnO with ^{111}In probes

lattice is characterized by two quadrupole interaction frequencies[1]: The first one is a well defined quadrupole interaction frequency of $\nu_Q = 31.5$ MHz which has been extensively reported in literature [8] and corresponds to ^{111}In probes occupying substitutional Zn-sites in ZnO matrix. The second one is a large quadrupole interaction frequency with large distribution of EFGs, which indicates that probe atoms were incorporated in a non-unique crystalline environment. The associated large distribution of EFGs is quite usual for nano sized particles where surface to volume ratio is relatively large. This behavior has already been observed in previous measurements on ZnO [9], and has been associated to probe atoms that did not diffuse properly through sample, residing mostly on nanoparticle surfaces as well as on grain boundary sites.

The measured quadrupole interaction frequencies correspond to symmetric EFGs (i.e., $\eta = 0$) in pure and doped ZnO, which was expected for crystal symmetry of Wurtzite type structure. We did not observe any signature of magnetic hyperfine interaction either at room temperature or at liquid nitrogen temperature (77 K). This behavior has also been observed for other transition metal dopants (like nickel and vanadium) for which the PAC spectra are shown in Fig. 2. The absence of magnetic hyperfine interaction in doped samples indicates that dopants are homogeneously distributed in ZnO lattice ruling out the possibility of the presence of contaminant phases like Co_3O_4, Mn_2O_3or metallic clusters rather dopants substitute Zn sites without causing significant deformation in the crystal structure of the ZnO lattice. These results are consistent with the previous results for cobalt doped ZnO [9] which showed that for concentrations at least up to 15% no other phases are observed.

[1]The quadrupole interaction frequency is $\nu_Q = \frac{eQV_{zz}}{h}$. The V_{zz} is the strongest component of EFG tensor and Q is the nuclear electric quadrupole moment of the probe.

Fig. 2 Least squares fitted PAC spectra for ZnO doped with Ni and V (5%) at 77 K



4 Conclusion

ZnO samples doped with transition metals were synthesized by means of a sol-gel procedure. PAC measurements using ^{111}In probes, which provide information on an atomic scale, revealed no evidences of magnetic ordering at room temperature rather well defined quadrupole interactions were observed in pure and doped samples of ZnO. These results cast doubt on the possibilities of achieving ferromagnetism for these materials, as well as the role of transition metal doping elements as responsible for ferromagnetic interactions. The present PAC results are consistent with the recent observation of paramagnetic behavior in transition metal doped ZnO using synchrotron based measurements [10]. Therefore, more detailed measurements are needed in order to verify the real suitability of these materials as potential candidates for future spintronic devices.

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