



Local investigation of hyperfine interactions in pure and Co-doped ZnO

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ABSTRACT

In the present work bulk samples of pure as well as Co-doped ZnO with different concentrations were prepared by sol–gel method from highly pure metallic Zn (99.9999%) and Co (99.9999%). The samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray microanalysis (EDS) and perturbed gamma–gamma angular correlation (PAC) spectroscopy. Carrier-free ¹¹¹In nuclei were introduced during preparation of the samples and used as probe nuclei at Zn sites for PAC measurements. PAC results show that both pure and Zn_{1-x}Co_xO ($x \leq 0.15$) samples have the same electric quadrupole frequency when Co-doped samples are annealed in air, argon or nitrogen atmosphere at 1173 K. SEM and EDS results showed that Co-doped samples are homogeneous without any secondary Co phases. These observations indicate that Co ions are substituted for Zn ions and have a similar electronic structure of Zn ions. A weak local magnetism was observed at temperatures below about 300 K for Co concentration of 10% when sample was annealed in Nitrogen.

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1. Introduction

Recently, ZnO has been recognized as a promising candidate for a diluted magnetic semiconductor (DMS) when doped with transition metal (TM) elements showing room temperature ferromagnetism with a large magnetization [1]. Theoretical calculations have indicated that ZnO when doped with Co or Mn should present ferromagnetism at room temperature [2,3]. While many experimental studies confirm this, several others do not observe magnetic order in these compounds. An important issue is whether the ferromagnetic order is intrinsic or is due to extrinsic magnetic phases of the dopant. Most recent studies conclude that defects as well as temperature and atmosphere used for annealing the samples play an important role in the magnetic behavior of TM-doped ZnO [4]. Conclusions are in general based on macroscopic experimental results that are unable to provide information about the local environment of the dopant. Knowledge of the local structure around the dopant is essential to understand the mechanisms that induce magnetic order in these compounds [5,6]. In the present work samples of pure and Co-doped ZnO were prepared by a sol–gel technique. Compounds prepared by sol–gel method can be obtained in nanoparticle size as well as bulk and are precursor material for thin film samples. Perturbed gamma–gamma angular correlation (PAC) spectroscopy using ¹¹¹Cd as probe nuclei was used to

characterize the sample in order to follow steps of the preparation as well as to observe the local magnetism in Co-doped samples.

The PAC method is based on the observation of hyperfine interaction of nuclear moments with extra-nuclear magnetic fields (B_{hf}) or an 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 [7,8]. The perturbation factor $G_{22}(t)$ of the correlation function contains detailed information about the hyperfine interaction. Measurement of $G_{22}(t)$ allows the determination of the Larmor frequency $\omega_L = \mu_N g B_{hf} / \hbar$, the nuclear quadrupole frequency $\nu_Q = eQV_{zz}/h$ as well as the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, where V_{xx} , V_{yy} and V_{zz} are the components of the electric field gradient tensor in its principal axis system. Consequently, from the known g -factor and quadrupole moment Q of the 245 keV state of ¹¹¹Cd the magnetic hyperfine field B_{hf} the major component V_{zz} of efg and its asymmetry parameter η can be determined. PAC measurements offer the possibility to follow changes such as local magnetism, phase transition, local symmetry, trapping of defects, etc., as a function of temperature [8–10].

2. Experimental

Undoped as well as Co-doped ZnO samples were prepared by a wet chemical route based on sol–gel methodology. Polycrystalline samples of ZnO were prepared from pure Zn (99.9999%), which was dissolved in concentrated acid to obtain the zinc salt solution.

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In order to test the procedure, pure ZnO samples were prepared by using hydrochloric, nitric, and sulfur acid. Metallic Co (99.9999%) was dissolved in nitric acid to obtain cobalt nitrate solution. The Co-doped samples were prepared by mixing the dissolved zinc and cobalt nitrate solutions, with Co concentrations varying from 5% to 15%.

In order to obtain the sol–gel, a known amounts of citric acid and ethylene glycol were added to the zinc solution and to the mixture of zinc and cobalt nitrate solutions. Approximately 20 μCi of $^{111}\text{InCl}_3$ solution was added to this sol–gel, which was evaporated to dryness on a hot plate at 353 K (step 1 of procedure). The gel was then heated in air in a muffle furnace at temperatures not higher than 723 K, depending on the sample (step 2). The resulting powder was sintered at 773 K in a tubular furnace with a controlled atmosphere (step 3), pressed into a small pellet and heated again following the same conditions (step 4). In order to better diffuse the radioactive ^{111}In , each sample was sealed in a quartz tube under vacuum and heated to 1173 K.

One more set of each sample was prepared using the same procedures but without radioactive ^{111}In . The pellets resulting from the annealing at 773 K in the tubular furnace were broken into several pieces in order to perform EDS and scanning electron microscopy (SEM) measurements. One piece of each sample was also used for PAC measurements where a drop of $^{111}\text{InCl}_3$ solution was deposited on its surface and diffused by sealing the sample in a quartz tube under vacuum and heating to 1173 K.

The samples were measured by perturbed gamma–gamma angular correlation technique using a four conical BaF_2 detectors spectrometer. Measurements were performed in the temperature range of 50–1075 K.

3. Results and discussion

Results of X-ray measurements (see in Fig. 1) indicated that all pure ZnO samples as well as Co-doped samples with Co

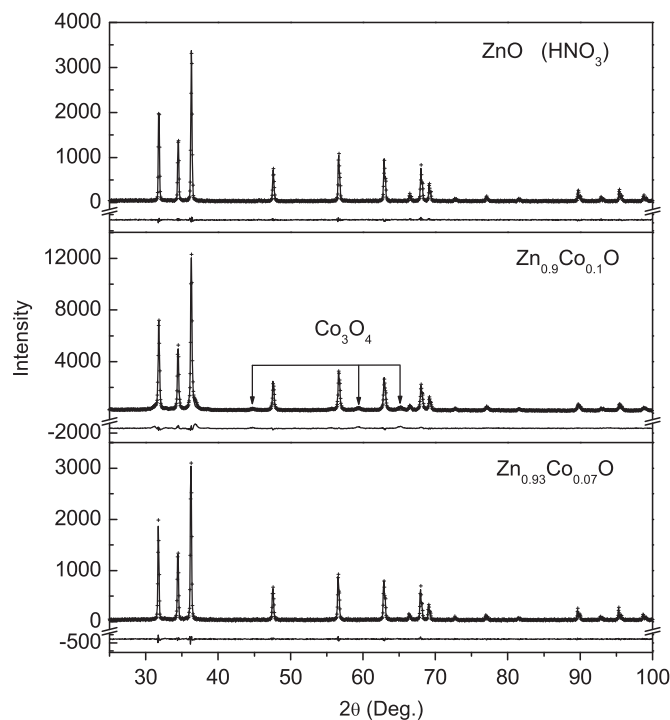


Fig. 1. The observed X-ray powder-diffraction spectra for pure and Co-doped ZnO. The solid lines represent the calculated pattern with the Rietveld method. The residuals are shown in the lower part of each spectra.

concentration less than 10% have a single phase ZnS-type structure with $P6_3mc$ space group. Samples with Co concentration of 10% and 15% presented a very small fraction (higher in 15% Co concentration sample) of Co_3O_4 .

In order to compare the sample preparation procedures a commercial ZnO powder (alpha-acesar, 99.99%) was pressed into a small pellet on which a few drops of $^{111}\text{InCl}_3$ solution were deposited. The pellet was sealed in a quartz tube under low-pressure argon atmosphere. The diffusion of ^{111}In was followed by PAC measurements taken at different temperatures and results showed that ^{111}In starts diffusing above around 850 K [11]. The results also showed two fractions, a major fraction corresponding to ^{111}In probes substituting Zn ions (as reported in Refs. [12,13]) with a well defined frequency and the minor fraction with highly distributed frequency ($\nu_Q = 151(5)$ MHz and $\eta = 0.6(1)$) probably due to probes occupying vacancies or interstitial sites. The spectra at 295 K taken after cooling the sample to room temperature were characterized by a major fraction (85%) with $\nu_Q = 31.8(1)$ MHz. These spectra are shown in Fig. 2 along with room-temperature spectra for ZnO made from metallic Zn dissolved in three different acids using the procedure described above. For all these three spectra a major fraction (higher than 95%) with $\nu_Q = 31.7(1)$ MHz has been observed indicating a good quality ZnO samples.

The crystal morphology and size were observed by scanning electron microscopy and the results, shown in Fig. 3 (top) for Co concentrations of 15%, indicate that the samples are homogeneous with Co substituting Zn in ZnO compound and do not present any other significant Co phases. The EDS results also shown in Fig. 3 (bottom) indicate that no other elements but Zn, Co and O are present in the samples. The small Pt peak appearing in the spectrum is due to the coating of the sample surface required for the measurements.

The ZnO sample doped with 10% Co with radioactive $^{111}\text{InCl}_3$ added to the mixed solution during preparation was annealed in a flux of Nitrogen during steps 3 and 4. The resulting pellet was sealed in a quartz tube under vacuum and heated to 1173 K. After cooling, the sample was measured with PAC at 295 K and the results showed a major fraction (75%) with $\nu_Q = 31.2(1)$ MHz and a minor fraction with highly distributed frequency $\nu_Q = 151(5)$ MHz and $\eta = 0.6(1)$, also observed in the pure ZnO samples. This fraction was assigned to ^{111}In occupying interstitial or vacancy sites. The sample was then cooled and PAC measurements were taken at different temperatures starting with 50 K up to 295 K. Spectra for some temperatures are shown in Fig. 4.

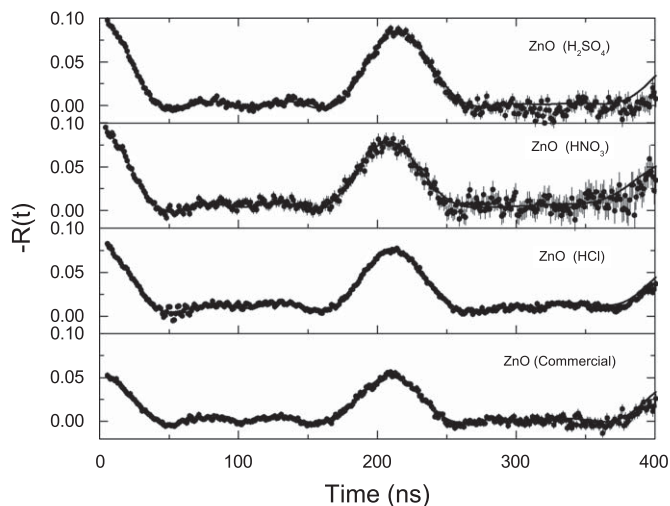


Fig. 2. PAC spectra measured at room temperature with ^{111}Cd for commercial undoped ZnO and sol–gel prepared undoped ZnO.

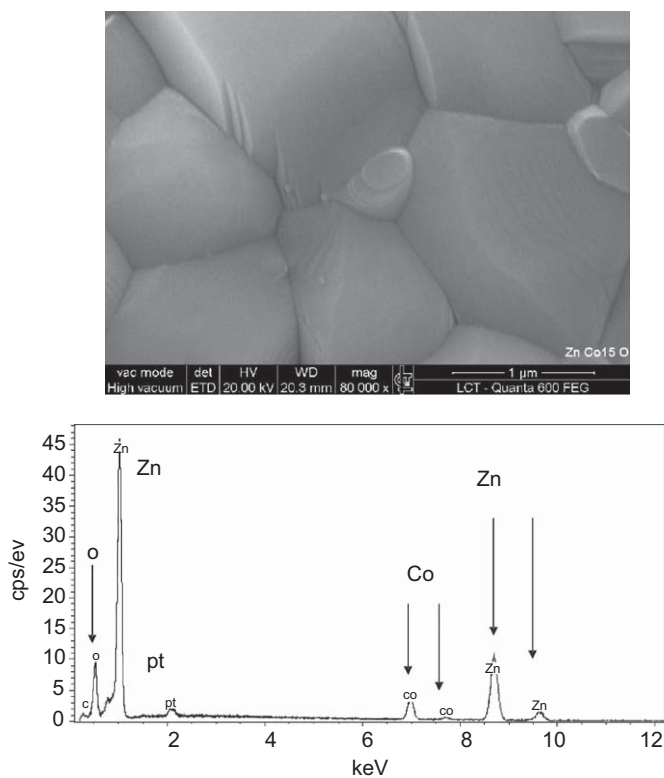


Fig. 3. SEM images of $\text{Zn}_{0.85}\text{Co}_{0.15}\text{O}$ sample (top) with corresponding EDS results (bottom).

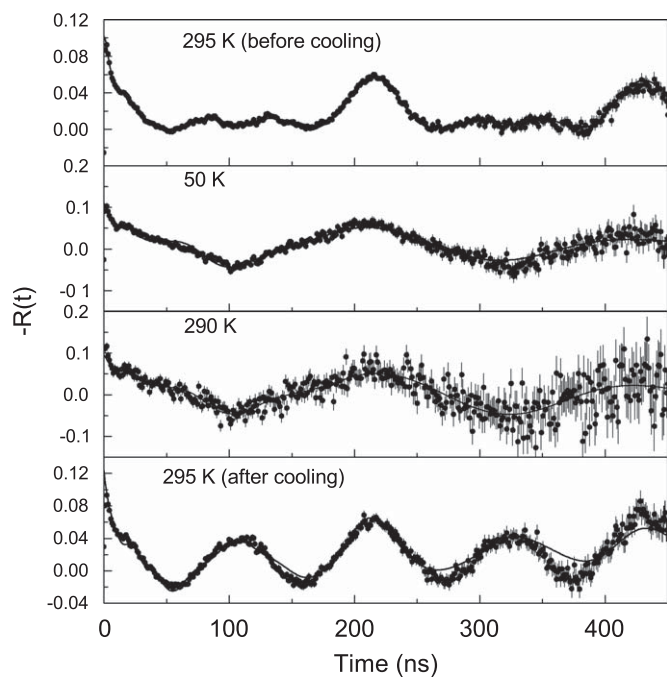


Fig. 4. PAC spectra measured at indicated temperature with ^{111}Cd for ZnO doped with 10% of Co.

For all these temperatures, PAC results show a major fraction with combined magnetic dipole plus electric quadrupole interaction. The corresponding spectra are each characterized by a major quadrupole frequency ($\nu_Q \sim 31.5$ MHz) and a temperature dependent well-defined magnetic dipole interaction. The

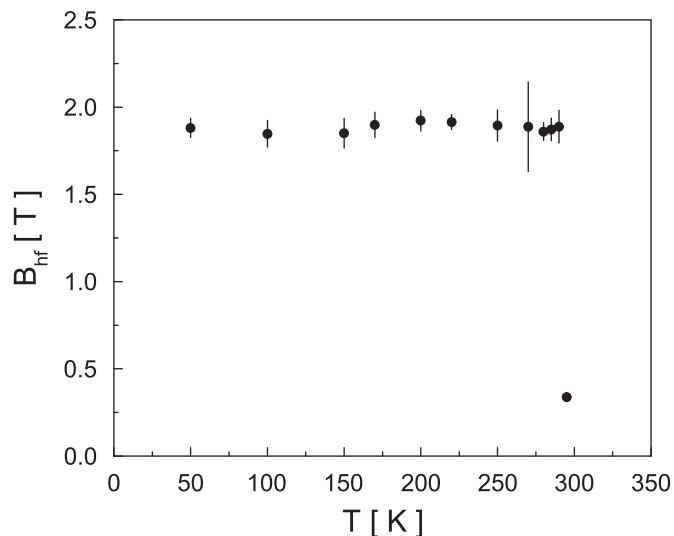


Fig. 5. Temperature dependence of the magnetic hyperfine field for ^{111}Cd probe nuclei in ZnO doped with 10% Co.

temperature dependence of the magnetic hyperfine field associated with the major interaction for each compound is shown in Fig. 5. The magnetic hyperfine field practically does not vary with temperature ($B_{hf} \sim 1.9$ T) except at 295 K for which $B_{hf} = 0.337(5)$ T. These results strongly indicated a first-order ferromagnetic transition around $T_C \sim 300$ K.

The PAC spectra at room temperature for Co-doped ZnO samples for all concentrations showed major fractions with frequencies which have almost the same value as those obtained for undoped sample. The results therefore suggest that Co atoms do not form other phases or clusters and substitutes Zn sites without causing any deformation in the crystal structure nor modifying the electronic structure.

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