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# Characterization of ZnO and $Zn_{0.95}Co_{0.05}O$ prepared by sol-gel method using PAC spectroscopy

**M. E. Mercurio · A. W. Carbonari · M. R. Cordeiro · R. N. Saxena**

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**Abstract** The measurement of the electric field gradient (efg) with PAC spectroscopy was used to follow the heat treatment during the preparation of ZnO samples using sol-gel method. In particular, the investigation was carried out on samples of intrinsically n-type II-VI wurtzite semiconductor ZnO and Co-doped $Zn_{0.95}Co_{0.05}O$ samples prepared by sol-gel methodology from pure metallic Zn(99.9999%). Carrier-free $^{111}$In nuclei were introduced in the samples by thermal diffusion. $^{111}$In solution was added to the precursor sol-gel solution prior to the formation of gel material. PAC measurements were carried out to follow the formation of the ZnO. Two undoped ZnO samples, which were heated in air and argon atmosphere, show different results. PAC measurements were also used to follow the $^{111}$In diffusion in a commercially purchased ZnO (99.99%) sample as well as to compare the results with the measurements taken with sol-gel prepared samples. The results show that samples prepared by sol-gel process followed by heating in argon produce better quality ZnO samples. The results also show that the Co atoms in $Zn_{0.95}Co_{0.05}O$ are in substitutional sites.

**Keywords** ZnO · Perturbed angular correlation · Diluted magnetic semiconductor · Electric field gradient

## 1 Introduction

The ZnO is a wide-bandgap (3.437 eV at 2 K) semiconductor that has many technological applications, such as piezoelectric transducers, varistors, phosphors, and electroluminescent device [1]. Recently, ZnO has been recognized as a promising candidate for a diluted magnetic semiconductor (DMS) when doped with transition

M. E. Mercurio · A. W. Carbonari (✉) · M. R. Cordeiro · R. N. Saxena
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, São Paulo, Brazil
e-mail: carbonar@ipen.br

metal (TM) elements showing room temperature ferromagnetism with a large magnetization [2]. Theoretical calculations have indicated that ZnO when doped with Co or Mn should present ferromagnetism at room temperature [3, 4]. While many experimental studies confirm this, several others do not observe magnetic order in such compounds. Most recent studies conclude that defects play an important role in the magnetic behavior of TM-doped ZnO. The doping with a 3D magnetic impurity is more efficient and precise and therefore produces high quality samples if a chemical sol-gel process is used. However, some parameters like temperature and atmosphere used for annealing in this process are not well established yet.

In the present work samples of ZnO and $Zn_{0.95}Co_{0.05}O$ 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. PAC spectroscopy using $^{111}$Cd as probe nuclei was used to characterize the sample in order to follow steps of the preparation.

## 2 Experimental procedure

Undoped as well as Co-doped ZnO samples were prepared by a wet chemical route based on sol-gel methodology. Stoichiometric polycrystalline samples of ZnO were prepared from pure Zn (99.9999%), which was dissolved in concentrated $H_2SO_4$ to obtain a zinc sulfate solution. Metallic Co (99.9999%) was dissolved in $HNO_3$ to obtain cobalt nitrate solution. The Co-doped samples were prepared by mixing the zinc sulfate and cobalt nitrate solutions. In order to obtain the sol-gel, known amounts of citric acid and ethylene glycol were added to the zinc sulfate solution and the mixture of zinc sulfate and cobalt nitrate solutions. 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 450°C for 10 h. The resulting powder was sintered at 900°C, pressed into a small pellet and heated again at 900°C.

One more set of samples were prepared using the same procedures but without radioactive $^{111}$In for X-ray diffraction measurements. The samples were measured by perturbed gamma-gamma angular correlation (PAC) technique using a spectrometer consisting of four conical $BaF_2$ detectors with a conventional fast-slow coincidence set-up. The well known gamma 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. Measurements were performed in the temperature range of 295–1,075 K

The PAC method is based on the observation of hyperfine interaction of nuclear moment with extra-nuclear magnetic field ($B_{hf}$) or electric field gradient. The technique measures the time evolution of the $\gamma$-ray emission pattern caused by hyperfine interactions. A description of the method as well as details about the PAC measurements can be found else where [5, 6].

## 3 Results and discussion

X-ray measurements on the samples indicated a single phase ZnS-type structure with $P6_3mc$ space group. The first sample S1 was a commercial ZnO powder pressed

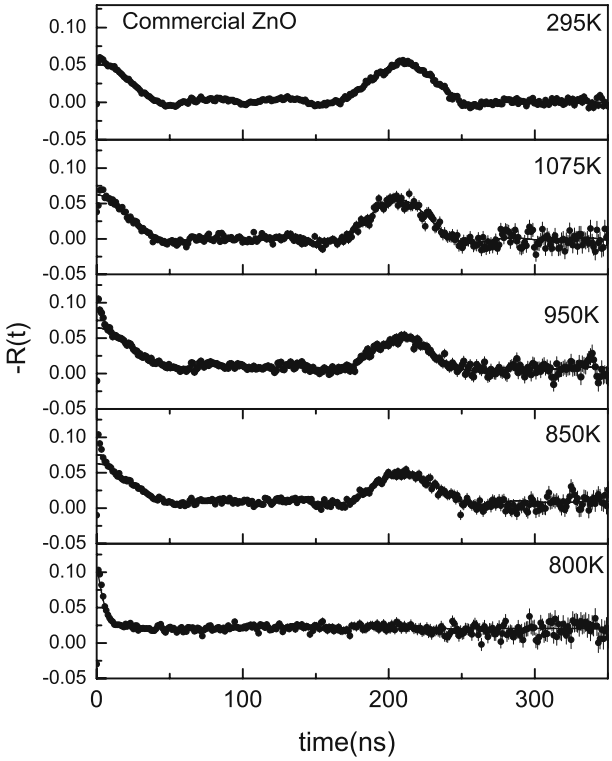


**Fig. 1** PAC spectra at indicated temperatures for sample S1

in to a small pellet on which a few drops of $^{111}InCl_3$ solution were deposited. The pellet was sealed in a quartz tube under argon atmosphere. The diffusion of $^{111}In$ was followed by PAC measurements taken at different temperatures. The PAC spectra at some of the temperatures are shown in Fig. 1. It can be seen that $^{111}In$ starts diffusing above around 850 K. All the spectra above 850 K show two fractions, the major fraction corresponds to $^{111}In$ probes substituting Zn ions (as reported in [7] and [8]) with a well defined frequency for example at 850 K the major fraction (53%) has $\nu_Q = 31.6(1)$ MHz and the minor fraction with highly distributed frequency probably due to probes occupying vacancies or interstitial sites. The major fraction increased to 84% at 1,075 K. The spectra at 295 K taken after cooling the sample to room temperature was characterized by a major fraction (85%) with $\nu_Q = 31.8(1)$ MHz.

The second sample S2, was the undoped ZnO prepared by sol-gel method. The resulting pellet was sealed in a quartz tube under argon atmosphere. The diffusion of $^{111}In$ was then followed by PAC measurements as a function of temperature. Figure 2 shows some of the spectra taken at different temperatures. The results indicate a highly distributed interactions at temperatures below around 800 K and a high frequency at higher temperatures where the amplitude of the oscillation drops to almost zero value indicating a dynamic interaction. After the diffusion the quartz tube was opened and the pellet was found to have strongly reacted with quartz tube walls. A small part of the sample removed from the tube was again measured at room temperature (Fig. 2) and indicated a single fraction with a very well defined frequency of $\nu_Q = 31.5(1)$ MHz, corresponding to $^{111}Cd$ substituting Zn in ZnO

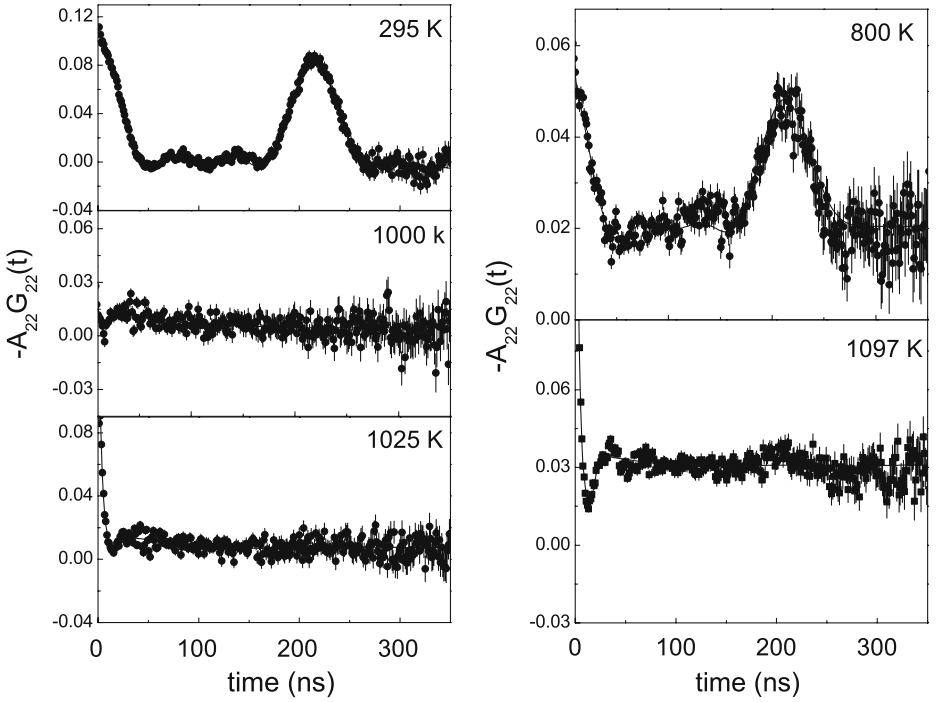


**Fig. 2** PAC spectra at indicated temperatures for sample S2 (*left*) and S3 (*right*)

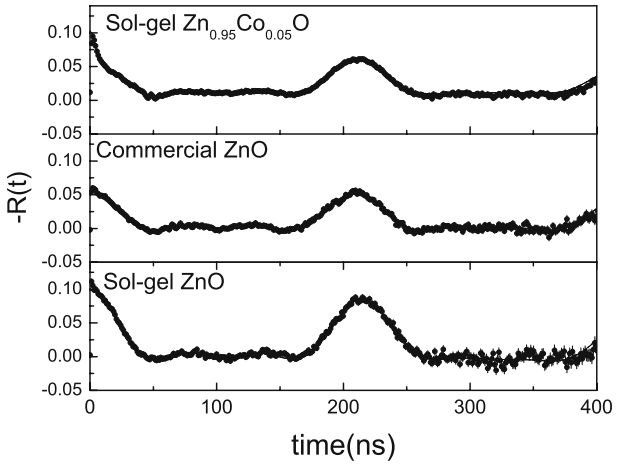


**Fig. 3** PAC spectra measured at room temperature with $^{111}$Cd for Co-doped ZnO (*top*), commercial undoped ZnO (*middle*) and sol-gel prepared undoped ZnO (*bottom*)

structure. The dynamic interaction was probably due to after-effects from electron capture decay of $^{111}$In in the compound resulting from the reaction of ZnO with quartz or any electronic rearrangemet in such a compound due to defect complex [9].

The third sample S3, was a sol-gel undoped ZnO also prepared by sol-gel method where the powder before the annealing was placed in an open quartz tube and

the PAC measurements were carried out in air as a function of temperature. The results (Fig. 2) show that $^{111}$In starts diffusing at lower temperature around 800 K. However at higher temperature the spectra showed a widely distributed pattern. We believe that the diffusion in air at temperatures higher than 800 K favors the formation of a complex Zn-In oxide.

The fourth sample S4, was a sol-gel Co-doped ZnO. The resulting powder was annealed in an alumina boat under Argon flux at 900°C for 12 h. The powder was then pressed in to a pellet and annealed again in the alumina boat under Argon flux at 900°C for 12 h. The PAC spectrum for this sample measured at room temperature is shown in Fig. 3. The fitting yields a major fraction (85%) with a well defined frequency of $\nu_Q = 31.5(1)$ MHz. The results of commercial and sol-gel undoped ZnO are also shown in this figure for comparison. The results therefore show that Co at this concentration fully substitute for Zn in ZnO.

In conclusion, PAC characterization of undoped and Co-doped ZnO shows that ZnO reacts with silica when annealed in a sealed quartz tubes, Co ions are in substitutional Zn sites for 5% Co-doped ZnO and that the sol-gel method used for sample preparation can produce very good quality ZnO.

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