

Room-Temperature Synthesis and Characterization of Highly Monodisperse Transition Metal-Doped ZnO Nanocrystals

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ABSTRACT

Recent verifications of intrinsic room-temperature (RT) ferromagnetism in transition metal doped-ZnO have increased its attractiveness as promising material for nano-optoelectronic and spintronics-based devices. A control over dopant speciation and the determination of the size-dependence of the properties at the nanoscale, become then indispensable. We present here the conditions for the room-temperature synthesis in ethanol and characterization of bare, Mn- and Co-doped ZnO nanocrystals. The results evidenced the viability on producing highly monodisperse nanocrystals (5-8nm) with no need for any further thermal treatment. However, the formation of the ZnO structure was delayed when dopant ions co-existed with Zn in starting solutions; well-crystallized doped nanoparticles were produced only after their aging in mother liquors. SQUID measurements on doped nanocrystals evidenced a weak, though noticeable RT-ferromagnetism, or paramagnetism, depending on synthesis conditions.

Keywords: zinc oxide, nanocrystals, room-temperature synthesis, diluted magnetic semiconductors, spintronics

1 INTRODUCTION

The prediction of room temperature ferromagnetism [1, 2] in transition metal doped II-VI nonmagnetic semiconductors leads to a number of magnetic, magneto-optical, magneto-transport and optical properties, which make these structures ideal candidates for spintronic-based devices. Sato et al [3] have suggested the possibility of room temperature ferromagnetism in transition metal-doped ZnO structures, where Mn and Co were found to be suitable dopants. In this regard, ferromagnetism with Curie temperature above 280 K in thin films [4] and large magneto-optic effect [5] has been reported for ZnCoO. Moreover, the recent experimental verifications of the intrinsic ferromagnetism above room temperature in transition metal doped-ZnO nanostructures [6-8] enable these types of materials to be considered for nano-optoelectronic and spintronics-based applications. Accordingly, the control over dopant speciation and the determination of the size-dependence of functional properties at the nanoscale become indispensable.

Nowadays, the production of ZnO-based structures has been attempted through different physical and chemical

means. Among them, solution processing routes are based on low-cost, environmental friendly and easily scalable methods. This option also permits the control of the solid formation rate leading to the production of metastable phases, tailored phase compositions and well-tuned particle size at the nanoscale. On these bases, the present work is focused on the synthesis in ethanol solutions of bare and Mn- or Co-doped ZnO nanocrystals at room temperature. The influence of the concentration of dopant species in starting solutions on the stability conditions of the host oxide structure is discussed. Furthermore, the structural, optical and magnetic characterization of the highly monodisperse nanocrystals synthesized by the selected method is also presented.

2 EXPERIMENTAL

2.1 Materials

All reagents were of analytical grade and were used without further purification. Required weights of the acetate salts of zinc and manganese or cobalt were dissolved in anhydrous ethanol at 65°C to produce a solution with a total concentration of metal ions of 0.01M. A solution of LiOH monohydrate in ethanol was used as the precipitating agent. N-heptane was used to coagulate nanocrystals from their suspensions in ethanol.

2.2 Synthesis of Nanocrystals

Doped ZnO nanocrystals were synthesized by conventional precipitation in ethanol solutions as reported by Spanhel and Anderson for bare ZnO [9]. In our case, the syntheses were carried out under ambient-temperature conditions. When the synthesis of doped-ZnO was attempted, the metal ions solutions were prepared for a specific fraction of dopant coexisting with Zn ions in starting solutions, 'x'. The metals and the hydroxide solutions in ethanol were mixed at room temperature under vigorous stirring for 10 minutes ('contact stage'). In order to follow the progress of the oxide formation, the suspension of nanocrystals were aged in their mother liquors at room temperature and without stirring ('aging stage'). Nanocrystals prepared in this way were recovered by successive coagulation/redispersion cycles using n-heptane/fresh ethanol and submitted for characterization. The present synthesis procedure is simple and permits a very fast

nucleation with minimum aggregation of the crystals at a temperature as low as 25°C. Ethanol was selected not only as a suitable solvent but, specifically, because of its dehydrating property. This dehydrating capability plays an essential role in the removal of coordinated water from the precursor compound (basic zinc acetate) that promoted the formation of anhydrous oxide structures at room-temperature.

2.3 Products Characterization

Dried powders were submitted for characterization by using XRD, FT-IR, and SQUID techniques. UV/Vis absorbance spectra were obtained from suspensions of nanocrystals in ethanol. HRTEM was used to determine the size and crystallinity of produced crystals.

3 RESULTS AND DISCUSSION

3.1 XRD Analyses

As evidenced by the XRD patterns shown in Figure 1, ZnO having a wurtzite structure was rapidly formed in ethanol even without need of aging ($t=0$ min). Furthermore, the broadness of the XRD peaks reveals the nanocrystalline nature of the powders. The average crystallite size was estimated to be ~ 6 nm using Scherrer's equation. Although there was not a noticeable sharpening of the ZnO peaks for aged samples, initially clear suspension of nanocrystals turned out whitish with time, which could be attributed to the growth and/or aggregation of ZnO crystals.

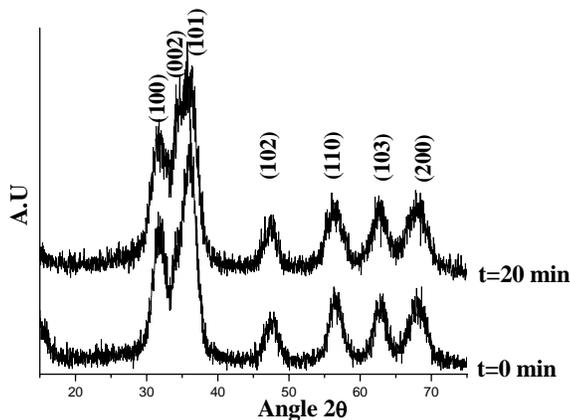


Figure 1: XRD patterns for ZnO powders produced in ethanol after 0 minutes (i. e., no aging) and 20 minutes of aging at 25°C.

XRD analyses also evidenced that the presence of dopant species ('impurities') delayed the formation of the host ZnO structure. Figures 2 and 3 show the XRD patterns for Mn- and Co-doped ZnO powders aged for 30 minutes and 24 hours, respectively, and different fractions of dopant species in starting solutions ('x' values). In both cases it was found that the higher the 'x' values, the more stable the

basic zinc acetate intermediate (marked with ▼ in the corresponding figures).

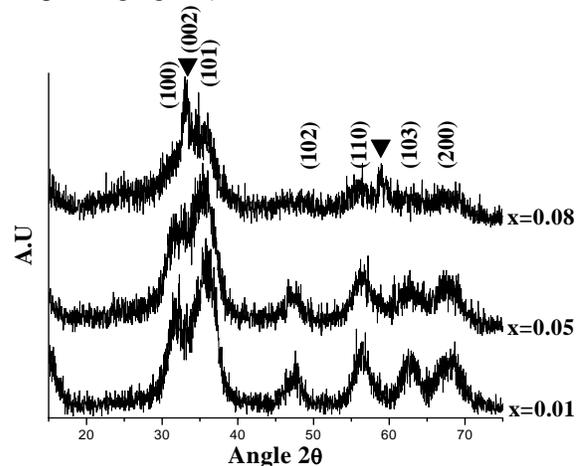


Figure 2: XRD patterns for ZnO powders produced for different fractions of Mn ions in starting solutions, 'x', and 30 minutes of aging at 25°C.

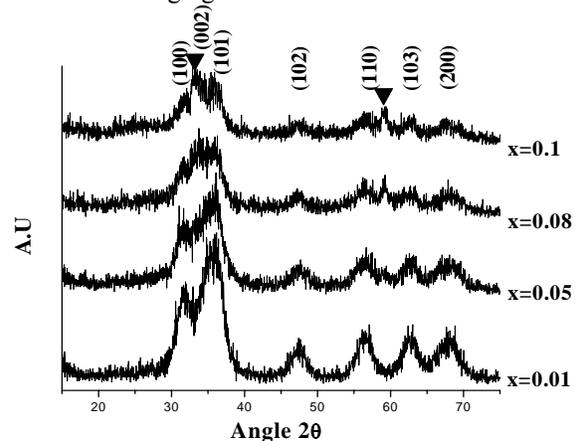


Figure 3: XRD patterns for ZnO powders produced for different fractions of Co ions in starting solutions, 'x', and 24 hours of aging at 25°C.

In doped systems, the complete conversion of the intermediate phase into the host ZnO structure could be achieved after aging of the suspension of nanocrystals. The duration of the aging stage was dependent on the fraction of dopants; longer aging times were required for higher 'x' values. For instance, Co-doped ZnO nanocrystals ($x=0.01$) had to be aged for 30 minutes to develop the oxide structure. In the Mn-doped ZnO system ($x=0.08$), the complete conversion of the intermediate into the oxide phase was only possible after 24 hours of aging. Dopant species trying to get incorporated into the ZnO lattice would have generated internal stresses and some lattice distortion. This incorporation will make the oxide structure unstable retarding its formation: *a pure phase always forms faster than an impure one*. Long enough aging times will favor the atomic rearrangement and dehydration conducive to the formation of the oxide structure at room temperature.

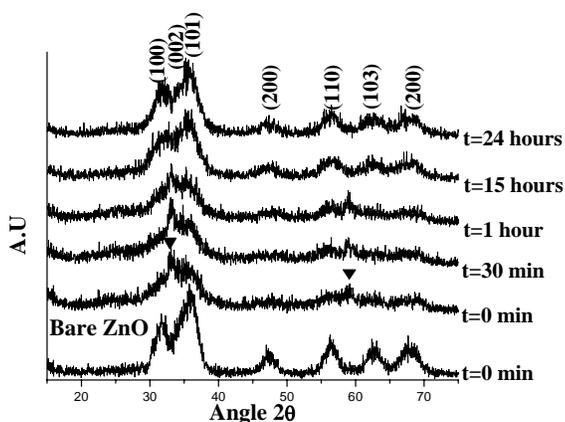


Figure 4: XRD patterns for Mn-doped ZnO powders produced at different aging times ('t' in minutes or hours) and $x = 0.08$.

3.2 FT-IR Analyses

Figure 5 shows the FT-IR spectra of Mn-ZnO crystals ($x=0.08$) aged for different times. The systematic increase in the intensity of the band at 525cm^{-1} , assigned to the stretching vibrations of the Zn-O bonds, indicated the favorable effect of aging on the development of the host ZnO structure. In turn, the bands at 1342cm^{-1} , 1420cm^{-1} and 1574cm^{-1} can be assigned to the stretching vibration of C=O, C=C and C-H groups in acetate species. The acetate species were detected even after intensive washing of the solids with ethanol, suggesting their presence as adsorbed species.

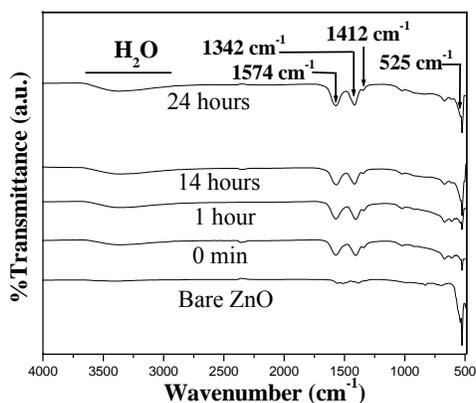


Figure 5: FT-IR spectra for Mn-doped ZnO powders produced at different aging times and $x = 0.08$. The spectrum for bare ZnO corresponds to a micron-size commercial powder.

3.3 HRTEM Observations

Figure 6 show the high resolution TEM pictures of ZnO nanocrystals after 4 weeks of aging at room temperature. Darker particles show stronger diffraction due to orientation effect. The nanoparticles were highly monodisperse, with sizes between 6 and 8 nm, and well-crystallized. Nanometric sizes of the particles are attributed to the very

fast nucleation rate capable to be reached during synthesis in ethanol. Also, adsorbed acetate species must have provided a negative charge to the surface of the nanocrystals that prevented their aggregation.

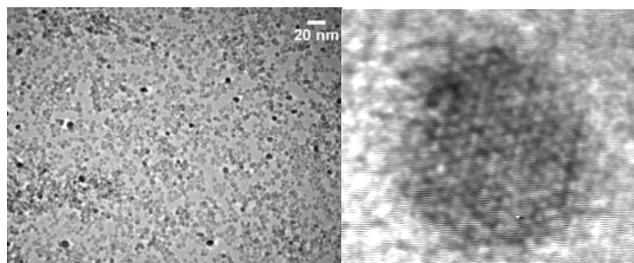


Figure 6: HRTEM pictures of ZnO nanocrystals produced after 4 weeks of aging.

3.4 UV-Vis Measurements

The red shift in absorption peak with aging observed in the room temperature UV-Vis absorption measurements for ZnO nanocrystals, (Figure 7), was attributed to crystal growth. Indicated wavelengths correspond to $\lambda_{1/2}$ values, from which the values of the band gap energy of the inset were estimated. All band gap energy values were above 3.28 eV (for bulk ZnO), evidencing the nanocrystalline nature of aged particles. The end of the growth process is evidenced by the minimum shift in the UV-Vis spectra after 48 hours of aging.

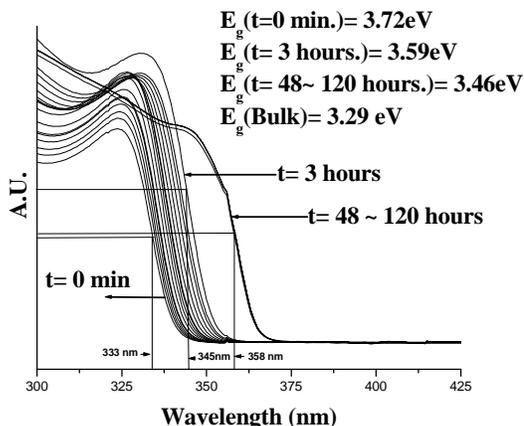


Figure 7: UV/Vis spectra for suspensions of ZnO nanocrystals aged at room temperature.

The crystal growth observed during aging could be stopped by coagulating the nanocrystals with n-heptane and subsequent redispersion in fresh ethanol. To verify the restriction on crystal growth, UV-Vis absorption measurements were carried out on redispersed nanocrystals coagulated after 5 minutes, 1.5 hours and 3 hours of aging (Figure 8). Each curve in this figure corresponds to five observations performed in 15 minutes intervals. The inhibition in crystal growth was evidenced by the invariable position of the absorption peak for each sample.

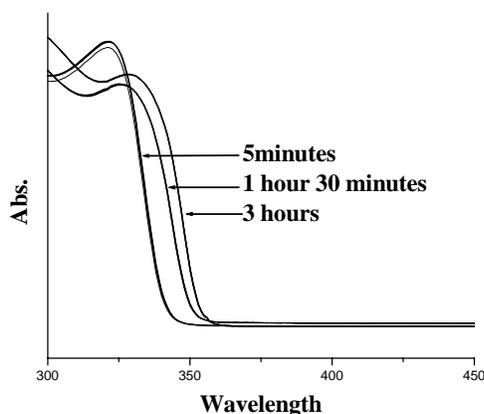


Figure 8: UV/Vis spectra for ZnO nanocrystals coagulated after 5 minutes, 1.5 hours and 3 hours of aging and redispersed in fresh ethanol.

3.5 SQUID Measurements

The results of SQUID analyses suggested the actual incorporation of Mn ions into the otherwise diamagnetic ZnO structure. The Mn-doped ZnO nanocrystals ($x=0.05$, 24 hours aging) exhibited a room temperature paramagnetic behavior, whereas a very weak coercivity ($\sim 150\text{Oe}$) was observed at 5K. In good agreement with observed behavior no blocking temperature was observed within 2K and 300K in ZFC/FC measurements under an applied field of 1000Oe. Similar characteristics were observed in other Mn-ZnO samples synthesized for different 'x' values.

Figure 9 shows the M-H curves at 300K corresponding to as-synthesized Co-doped ZnO nanocrystals ($x = 0.01$, 30 min aging). The inset is a magnification of the same figure and shows a small, though noticeable, coercivity which suggests a weak ferromagnetism at room temperature. More recent results have evidenced room temperature ferromagnetism in as-synthesized free-standing nanocrystals with a coercivity as high as 150Oe. Detailed work will be published elsewhere.

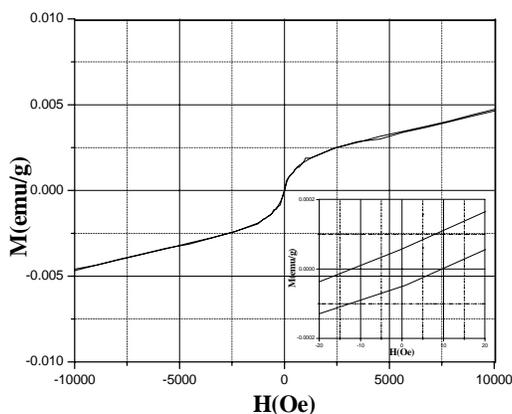


Figure 9: M-H curve for as-synthesized Co-doped ZnO nanocrystals ($x = 0.01$, 30 min aging). The inset is a magnification of the same figure.

4 CONCLUDING REMARKS

ZnO, Mn- and Co-doped ZnO nanocrystals were synthesized in ethanol solutions at room temperature. XRD characterization showed the tight relationship between the stability of the host ZnO oxide structure, the fraction of dopants in starting solutions and the length of aging at room temperature. The high monodispersity and crystallinity of ZnO nanoparticles was also confirmed by HRTEM observations. The growth of the nanocrystals during aging was revealed by UV-Vis measurements, though a fast coagulation of nanocrystals by n-heptane interrupted the growth process. SQUID analyses suggested the actual incorporation of Mn and Co ions into otherwise diamagnetic ZnO structure. Doped nanocrystals exhibited a predominant paramagnetic behavior at room-temperature, although a small coercivity became evident for the as-synthesized Co-ZnO nanocrystals. Ongoing works are focused on the synthesis of doped ZnO crystals having different sizes and verification of the crystal size dependence of ferromagnetism for a particular composition.

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