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# On the agent role of $\text{Mn}^{2+}$ in redirecting the synthesis of $\text{Zn}(\text{OH})_2$ towards nano-ZnO with variable morphology†

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One of the simplest routes to prepare polycrystalline  $\text{Zn}(\text{OH})_2$  is by coprecipitation, with zinc nitrate as a cation source. However, the addition of even minute amounts of manganese nitrate to the precursors used to prepare pure  $\text{Zn}(\text{OH})_2$  results in  $\text{Mn}^{2+}$  doped nanostructured ZnO. The comparison with other  $\text{Mn}^{2+}$  doped metal hydroxides prepared by the same coprecipitation method, involving metal nitrates precursors, shows that this behavior is unique, pertaining only to  $\text{Zn}(\text{OH})_2$ . A systematic study of the samples prepared without and with variable amounts of  $\text{Mn}^{2+}$  ions, in the 1 to 5000 ppm nominal concentrations range showed that the re-routing of the reaction takes place even for the lowest nominal dopant concentration of 1 ppm. According to X-ray diffraction, transmission electron microscopy and Fourier transform infrared spectroscopy investigations, both crystallite size and morphology of the resulting nanostructured ZnO samples varied with the  $\text{Mn}^{2+}$  nominal concentration. Moreover, quantitative electron paramagnetic resonance investigations showed that the incorporation rate of the  $\text{Mn}^{2+}$  ions at different sites in the nanostructured ZnO depended on the nominal  $\text{Mn}^{2+}$  concentration. The results are discussed in terms of the coordination properties of the  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  ions and the nature of the reaction precursors.

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## 1. Introduction

Doped nanocrystalline zinc oxide (nano-ZnO) is one of the most studied semiconductors, many investigations being focused on tailoring the material properties for applications in spintronics, nano- and/or optoelectronics, by changing/adjusting the nature and concentration of the dopant ions.<sup>1–4</sup> Doping nanocrystals, typically grown using colloidal synthesis, is still an experimental challenge and the progress in controlling and understanding the incorporation of impurities in semiconductor nanocrystals has been slow.<sup>5–7</sup> Thermally induced decomposition of doped precursors has proved to be an alternative efficient way to obtain doped nano-ZnO. Thus, as shown in the case of the  $\text{Mn}^{2+}$  doped hydrozincite (ZCB) –  $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$  precursor, with proper adjustment of the annealing temperature and atmosphere conditions it was possible to control the size and size distribution of the resulting  $\text{Mn}^{2+}$  doped ZnO ( $\text{ZnO}:\text{Mn}$ ) nanoparticles.<sup>8,9</sup>

Zinc hydroxide –  $\text{Zn}(\text{OH})_2$  has attracted a lot of interest during the last years as a precursor in the synthesis of nano-ZnO

with controlled size and morphology.<sup>10–14</sup> Moreover, as in the case of the ZCB,<sup>8,15</sup> doped  $\text{Zn}(\text{OH})_2$  was expected to be also a valuable precursor for doped nano-ZnO. However, our attempts to prepare  $\text{Zn}(\text{OH})_2$  by coprecipitation in the presence of  $\text{Mn}^{2+}$  ions failed to produce the expected  $\text{Mn}^{2+}$  doped  $\text{Zn}(\text{OH})_2$ .<sup>13</sup> Every sample prepared in these conditions resulted in nano-ZnO:Mn, independent of the  $\text{Mn}^{2+}$  ions concentration. To our knowledge, this is the first observation of a redirection of the  $\text{Zn}(\text{OH})_2$  synthesis towards nano-ZnO by doping instead of by modifying essential synthesis or post-synthesis parameters (*i.e.* temperature, pressure, stirring), as previously reported (*e.g.* ref. 10–14 and 16).

In an effort to understand the extent of the manganese effect on the reaction products and to determine the  $\text{Mn}^{2+}$  concentration threshold for the synthesis redirection to take place, we performed a systematic study of the samples prepared without and with a  $\text{Mn}^{2+}$  source, varying the nominal  $\text{Mn}^{2+}$  ions concentration from 1 to 5000 ppm. Structural and morphological studies have been performed by X-ray diffraction (XRD), transmission electron microscopy (TEM) and Fourier transform infrared (FTIR) spectroscopy. The localization and distribution of the  $\text{Mn}^{2+}$  ions in the  $\text{Zn}(\text{OH})_2$  and ZnO samples were determined by multifrequency electron paramagnetic resonance (EPR) spectroscopy, which we successfully employed to investigate various  $\text{Mn}^{2+}$  doped semiconducting nanostructures.<sup>8,9,13,17–19</sup> We have shown that EPR spectroscopy is a sensitive and reliable, statistically relevant technique (as it

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measure the whole volume of the sample), which can offer accurate information concerning the localization of the paramagnetic  $\text{Mn}^{2+}$  ions in the volume and at the surface/interface of the nanostructures, the configuration of their neighboring ligands and the local structural/bonding modifications induced by thermo-chemical treatments.

The discussion of the results takes into consideration the role played by the  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  ions, their favored coordination and the nature of the reaction precursors in redirecting the  $\text{Zn}(\text{OH})_2$  synthesis towards nano-ZnO.

## 2. Experimental section

### 2.1. Synthesis

The starting materials used in the synthesis were analytical grade zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  – 99% purity), manganese nitrate tetrahydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  – 99.98% purity) and sodium hydroxide ( $\text{NaOH}$  – 97% purity) from Alfa Aesar, without further purification. Pure crystalline  $\text{Zn}(\text{OH})_2$  was prepared by coprecipitation of an aqueous solution of zinc nitrate with sodium hydroxide (in excess) by a procedure described elsewhere.<sup>13</sup> The syntheses in the presence of  $\text{Mn}^{2+}$  ions were made by a similar procedure, which consisted in mixing the corresponding amounts of 0.19 M  $\text{Zn}(\text{NO}_3)_2$  and 0.02 M  $\text{Mn}(\text{NO}_3)_2$  aqueous solutions at 50 °C to obtain Mn/Zn ratios of 1, 5, 50, 100, 500, 1000 and 5000 ppm (0.5 at%). Afterwards, an aqueous solution of 2.4 M  $\text{NaOH}$  was added dropwise using a peristaltic pump under continuous stirring. The resulting precipitates were then centrifuged, washed several times with bi-distilled water and finally with absolute ethanol and dried at 60 °C (in air) in a similar way as the pure  $\text{Zn}(\text{OH})_2$ .

In order to ascertain the role of the precursor materials in the reactions leading to the final product, several other compounds were synthesized by the same procedure. Thus, to investigate the role of the  $\text{Zn}^{2+}$  ions in obtaining ZnO:Mn instead of  $\text{Mn}^{2+}$  doped  $\text{Zn}(\text{OH})_2$ , other metal hydroxides such as  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Cd}(\text{OH})_2$  were synthesized in both pure and manganese doped forms, with  $\text{Mn}^{2+}$  nominal concentrations of 1000 ppm. Also, taking into account the possibility that the anionic part of the precursors (*i.e.* the nitrate) may be responsible for the observed turn of the reactions, several syntheses were performed starting from M(II) chlorides/acetates (where  $\text{M(II)} = \text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ ).

### 2.2. Characterization methods

XRD investigations were performed with a Bruker D8 Advance X-ray diffractometer, in the  $\theta$ - $\theta$  geometry, with Cu anode and Ni filter ( $\lambda = 1.54184 \text{ \AA}$ ). The lattice parameters of the identified crystalline phases and the average crystallites size were determined by Rietveld refinement of the experimental data using the Topas v. 3 software from Bruker.

TEM/HRTEM morphology and structure investigations at low and high magnifications were performed with an atomic resolution analytical JEOL ARM 200F electron microscope operated at 200 kV, on specimens prepared by crushing the as

grown powder in ethanol, dispersing it by sonication, dropping it on lacey carbon grids and drying it at room temperature (RT).

Weighted amounts of pure and Mn doped powdery samples were inserted in calibrated pure fused silica EPR sample tubes of 2 mm and 3 mm inner diameter. The X (9.5 GHz)- and Q (34 GHz)-band EPR measurements were performed at RT with the Bruker ELEXSYS-E580X and -E500Q spectrometers, respectively, from the Center for advanced ESR/EPR techniques (CetRESav – <http://www.cetresav.infm.ro/>). The X-band spectrometer, equipped with the calibrated Super High QE cylindrical cavity resonator (ER 4123SHQE), was also employed for quantitative determinations of the  $\text{Mn}^{2+}$  ions concentration in the investigated samples. The absolute spin quantitation routine (based on the double integration of the spectra), included in the XEPR software from Bruker, was used. The spin Hamiltonian (SH) parameters of the observed paramagnetic centers were determined using a two-steps procedure<sup>20</sup> based on the lineshape simulation of the EPR spectra with the EASYSPIN v.5.0.12 software.<sup>21</sup>

FTIR spectra were recorded on several selected samples with a Spectrum BX II (Perkin Elmer) spectrometer in the 4000–350  $\text{cm}^{-1}$  spectral range, with 128 scans and 4  $\text{cm}^{-1}$  resolution. The ZnO:Mn samples were embedded/diluted in KBr pellets.

## 3. Results and discussion

### 3.1. XRD results

The XRD pattern of the undoped sample (Fig. 1 – bottom) shows the presence of a single phase  $\epsilon$ - $\text{Zn}(\text{OH})_2$  with orthorhombic ( $P2_12_12_1$ ) structure [JCPDS card no. 38-0385]. The resulting lattice parameters (Table S1 from ESI†) are similar with those previously reported.<sup>13</sup>

In the case of the  $\text{Mn}^{2+}$  doped samples, the analysis of the XRD patterns evidences the formation of a single phase of nanocrystalline hexagonal ZnO [JCPDS card no. 89-1397] in all samples, even for the lowest  $\text{Mn}^{2+}$  nominal concentration of 1 ppm. Fig. 1 presents only the XRD patterns of the samples

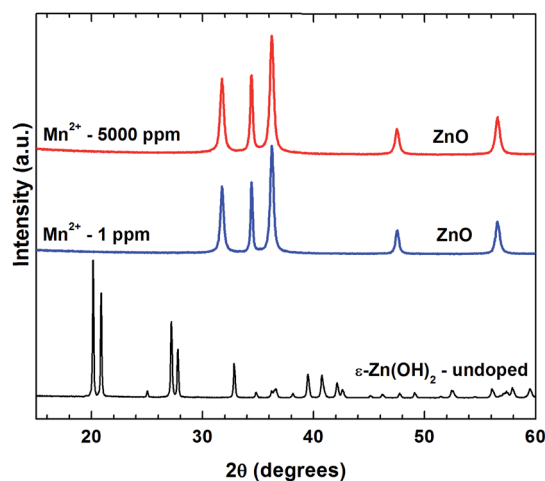
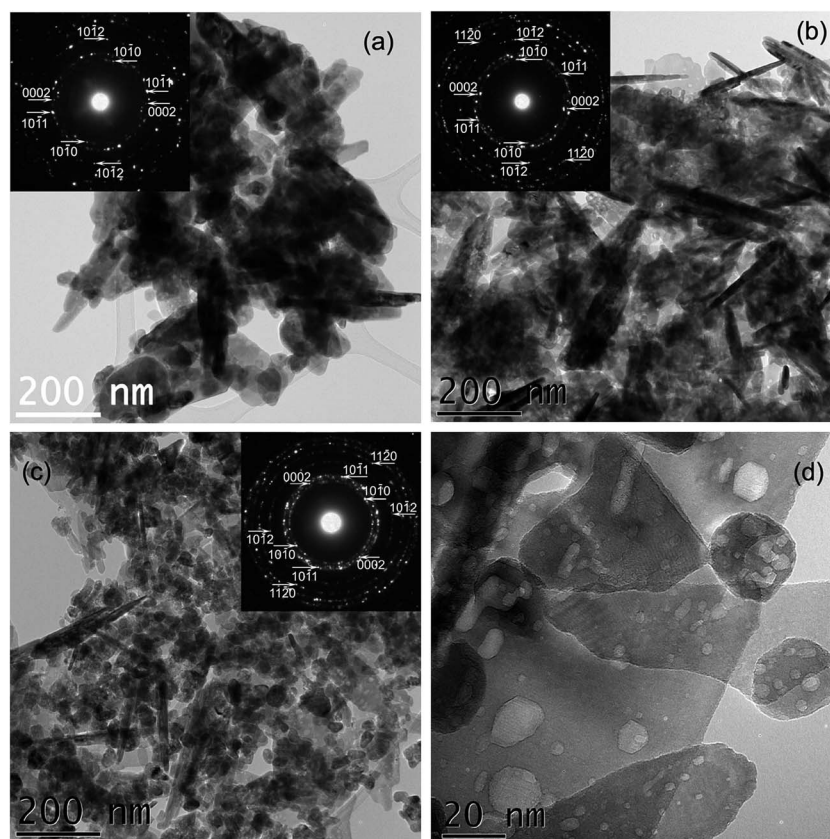


Fig. 1 XRD diffractograms of the undoped (bottom) and  $\text{Mn}^{2+}$  doped (upper) samples.



There are several mechanisms proposed to explain the inhibition of the ZnO crystallites growth by the presence of impurities.<sup>23–25</sup> The reduced diffusivity in ZnO due to Zn concentration decrease in the doped samples suppresses the grain growth. Also, the presence of impurities produces a retarding force on the grain boundaries, impeding the grain

The TEM images in Fig. 2 illustrate the changes in the morphology of the resulting ZnO samples doped with  $\text{Mn}^{2+}$  ions of increasing nominal concentrations. According to Fig. 2a the sample prepared with 1 ppm  $\text{Mn}^{2+}$  nominal concentration consists of large nanoparticles (30–200 nm), most of them with lamellar and rod shapes. It is interesting to note that the pure  $\text{Zn}(\text{OH})_2$  sample exhibits the same morphology, but the crystallites are much larger (one order of magnitude on the average). In the case of the sample prepared with 1000 ppm



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$\text{Mn}^{2+}$  nominal concentration (Fig. 2b) the lamellar nanoparticles are smaller, while the rods remain of the same size as in the sample prepared with 1 ppm  $\text{Mn}^{2+}$ .

Finally, in the case of the sample prepared with 5000 ppm  $\text{Mn}^{2+}$  nominal concentration, Fig. 2c shows that the majority of the nanoparticles exhibits a rather uniform morphology with smaller, 20–60 nm size, although some nanorods and lamellar nanoparticles are still present. Therefore, the increase in the  $\text{Mn}^{2+}$  nominal concentration leads to the formation of ZnO nanoparticles with much more uniform morphology and smaller dimensions. All the corresponding electron diffraction (ED) patterns in the insets of Fig. 2a–c were indexed with the ZnO structure. The HRTEM image (Fig. 2d) reveals additional details of the sample prepared with 5000 ppm nominal concentration of  $\text{Mn}^{2+}$  ions. The morphology of the nanocrystals is indeed polyhedral. Voids with dimensions of 1–16 nm are observed on each nanocrystallite. It looks like a degassing effect took place during their synthesis. Note that the presence of these voids can be also observed in Fig. 2a, in regions where the large crystallites are not overlapped, suggesting that their presence is not related to an increase in the nominal concentration of  $\text{Mn}^{2+}$  ions in the solution, but to the synthesis process itself. These voids were observed only in the  $\text{Mn}^{2+}$  doped nano-ZnO, independent of the Mn concentration, and not in the undoped  $\text{Zn}(\text{OH})_2$ , as one can see in Fig. S1 from ESI.†

### 3.3. EPR results

**3.3.1.  $\text{Mn}^{2+}$  paramagnetic centers.** Fig. 3 presents the Q-band EPR spectra of selected samples, showing significant differences. Each spectrum was recorded in the multiscan mode, increasing the number of scans at 0.16 mW microwave power and 1 G modulation amplitude values from 1 up to 100 scans, from the maximum to the minimum  $\text{Mn}^{2+}$  nominal concentrations, respectively, in order to enhance the signal to

noise ratio. The EPR spectra were further normalized to the same amplitude of the  $\text{Mn}^{2+}(\text{c})$  center spectrum (Fig. 3), to better follow the lineshape changes.

The EPR spectrum of the undoped sample (Fig. 3 – bottom), recorded with 100 scans, corresponds to paramagnetic impurity levels of less than 1 ppm. It consists of a dominant set of six lines with almost equal intensity, separation ( $\sim 9.2$  mT) and linewidth, characteristic for the central hyperfine allowed ( $M_s: -1/2 \leftrightarrow 1/2, \Delta M_I = 0$ ) transitions of the  $\text{Mn}^{2+}$  ions ( $S = 5/2, I = 5/2$ ) in a polycrystalline lattice host.<sup>20</sup> A few additional lines from other paramagnetic defects are also present in the EPR spectrum, as previously reported.<sup>13</sup>

The EPR spectra of the  $\text{Mn}^{2+}$  doped samples differ from the EPR spectrum of the undoped sample, due to the different host lattice. These spectra are dominated by six similar groups of three close lying lines, with a  $\sim 7.8$  mT separation between the groups, typical for  $\text{Mn}^{2+}$  in ZnO.<sup>26</sup> Another sextet of lines, with a larger  $\sim 9$  mT separation, belonging to a different  $\text{Mn}^{2+}$  center, can be observed. The relative intensities of the two sextets are different in the five different  $\text{Mn}^{2+}$  doped samples (Fig. 3).

The SH parameters of the  $\text{Mn}^{2+}$  centers, determined by simulation and lineshape fitting of the X- and Q-band spectra of the undoped and doped samples, are given in Table S2 from ESI.† In the undoped sample the SH parameters of the paramagnetic center called  $\text{Mn}^{2+}(\text{a})$  are identical with those previously reported for the substitutional  $\text{Mn}^{2+}$  ions in  $\text{Zn}(\text{OH})_2$ .<sup>13</sup> The localization of the  $\text{Mn}^{2+}$  in the  $\epsilon\text{-Zn}(\text{OH})_2$  lattice at tetrahedrally, four-fold coordinated  $\text{Zn}^{2+}$  cation sites resulted from the analysis of the multifrequency EPR spectra, recorded on as grown and annealed polycrystalline  $\epsilon\text{-Zn}(\text{OH})_2$ .<sup>13</sup> One could thus explain why during the thermal decomposition of the polycrystalline  $\epsilon\text{-Zn}(\text{OH})_2$  into nano-ZnO, the observed paramagnetic  $\text{Mn}^{2+}$  centers transformed into  $\text{Mn}^{2+}$  centers consisting of  $\text{Mn}^{2+}$  ions localized substitutionally at  $\text{Zn}^{2+}$  sites in the ZnO lattice.<sup>13</sup> The substitutional localization of the  $\text{Mn}^{2+}$  impurity ions in  $\epsilon\text{-Zn}(\text{OH})_2$  at  $\text{Zn}^{2+}$  cation sites fourfold coordinated by hydroxyl ligands was further confirmed by the observed changes in the  $\text{Mn}^{2+}$  ions hyperfine splitting during the three-steps thermal decomposition of the  $\epsilon\text{-Zn}(\text{OH})_2$  shell of cubic ZnS nanocrystals with core-shell structure into a ZnO shell.<sup>19</sup> The hyperfine splitting changes reflected the sequential dehydration of the four nearest neighbor hydroxyl ligands.

The complex sextet in the EPR spectrum of the  $\text{Mn}^{2+}$  doped samples is generated by two types of  $\text{Mn}^{2+}$  paramagnetic centers, called  $\text{Mn}^{2+}(\text{c})$  and  $\text{Mn}^{2+}(\text{d})$  (see Fig. 3 and 4). Their SH parameters (Table S2 – ESI†) are very close to those previously reported for the  $\text{Mn}^{2+}(\text{c})$  and  $\text{Mn}^{2+}(\text{d})$  centers in the nanostructured ZnO resulted from the thermal decomposition of ZCB,<sup>8</sup> which consist of  $\text{Mn}^{2+}$  ions substitutionally localized at tetrahedrally coordinated  $\text{Zn}^{2+}$  sites in ZnO nanocrystals and disordered ZnO phase, respectively. The very small differences (less than 2%) in the hyperfine parameters of the  $\text{Mn}^{2+}$  centers localized in ZnO (see Table S2 – ESI†) can be explained by slightly different average coordination numbers of the  $\text{Mn}^{2+}$  ions,<sup>9,27</sup> associated with small variations in samples stoichiometry. Such variations could appear due to the particularities of the synthesis routes.

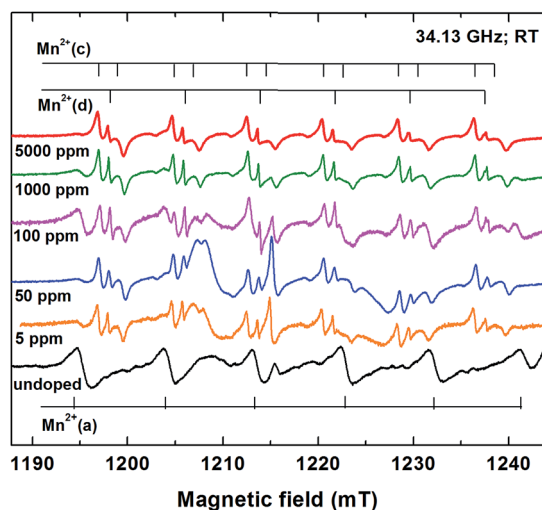


Fig. 3 Multiscan Q-band EPR spectra for the undoped (bottom) and  $\text{Mn}^{2+}$  doped (upper) samples. The six hyperfine lines/doublet-lines of the  $\text{Mn}^{2+}(\text{a})$ ,  $\text{Mn}^{2+}(\text{d})/\text{Mn}^{2+}(\text{c})$  paramagnetic centers are marked with vertical bars.



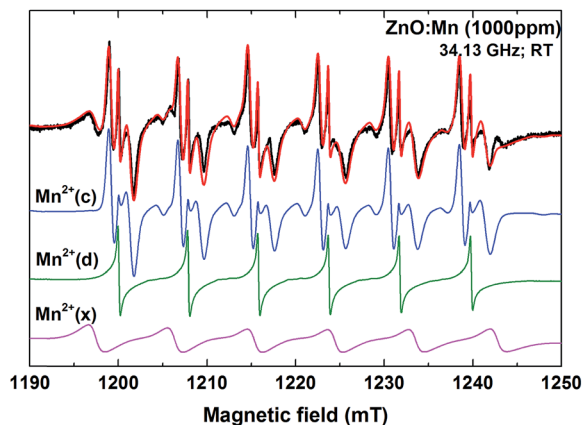


Fig. 4 Experimental (black) and simulated (red) Q-band EPR spectrum of the ZnO sample with 1000 ppm  $\text{Mn}^{2+}$  nominal concentration. Contributions to the simulated spectrum of the  $\text{Mn}^{2+}$  ions localized in crystalline ( $\text{Mn}^{2+}(\text{c})$  – blue) and disordered ( $\text{Mn}^{2+}(\text{d})$  – green) ZnO environment, and in the unknown disordered phase ( $\text{Mn}^{2+}(\text{x})$  – magenta) are shown below.

The third  $\text{Mn}^{2+}$  center in the EPR spectrum of the  $\text{Mn}^{2+}$  doped samples, with larger hyperfine separation, called  $\text{Mn}^{2+}(\text{x})$  (Fig. 4), is better observed in the EPR spectrum of the sample with 100 ppm Mn nominal concentration (see Fig. 3). The SH parameters of the  $\text{Mn}^{2+}(\text{x})$  center, presented in Table S2 from ESI,<sup>†</sup> indicate the localization of the  $\text{Mn}^{2+}$  ions in a disordered environment, different from ZnO.

**3.3.2. Quantitation of the  $\text{Mn}^{2+}$  paramagnetic centers.** The absolute number of spins in each doped nano-ZnO sample was determined by the quantitation of the X-band EPR spectra recorded for weighted amounts of the samples. The resulting spin concentrations correspond to the total concentrations of  $\text{Mn}^{2+}$  ions in the samples. In order to determine the distribution of the  $\text{Mn}^{2+}$  ions at different sites, the X- and Q-band EPR spectra were submitted to deconvolution procedures, thus separating the component spectra corresponding to the different centers. As an example, the deconvolution of the Q-band EPR spectrum of the sample with 1000 ppm  $\text{Mn}^{2+}$  nominal concentration is shown in Fig. 4.

The evolution of the concentrations of the three  $\text{Mn}^{2+}$  centers with the nominal concentration increase, as determined from the deconvoluted spectra, is presented in Table 1.

Unsurprisingly, the total concentration of incorporated isolated  $\text{Mn}^{2+}$  ions is much lower than the nominal concentration, in agreement with the low doping efficiency observed in Mn doped II–VI nanostructures.<sup>6,7,28–31</sup> For the samples with nominal concentrations lower than 100 ppm the low incorporation efficiency resulted in very low intensity X-band spectra, and, therefore, in unreliable quantitation results.

One can notice that the percentage of  $\text{Mn}^{2+}(\text{c})$  centers from the total concentration  $C_t$  of isolated  $\text{Mn}^{2+}$  ions in the sample increases as the  $\text{Mn}^{2+}$  nominal concentration increases. This behavior seems to be correlated with the morphology changes observed by TEM vs.  $\text{Mn}^{2+}$  nominal concentration increase, in agreement with theoretical studies which show that the doping efficiency varies with the morphology and size of nanocrystals.<sup>5,32</sup>

Assuming a uniform distribution of the  $\text{Mn}^{2+}$  ions in the sample material, the relative concentrations of the three paramagnetic centers would reflect the proportions of their host structural phases in the sample volume. According to the data in Table 1, the concentration of the  $\text{Mn}^{2+}(\text{x})$  centers is quite high in all samples, which would correspond to the presence of a large amount of the unknown disordered X phase in the samples. However, no trace of such a secondary phase has been detected by XRD (Fig. 1) or TEM (Fig. 2), meaning that the amount of the disordered X phase is below the detection limit (1–2%). Therefore one concludes that the  $\text{Mn}^{2+}$  ions distribution is not uniform in the sample and that the considerably large percentage of  $\text{Mn}^{2+}$  ions localized in the disordered phases reflects a segregation process of the  $\text{Mn}^{2+}$  ions outside the ZnO nanocrystals. This segregation process diminishes as the nominal concentration of  $\text{Mn}^{2+}$  ions increases.

### 3.4. FTIR measurements

The FTIR spectra recorded for the manganese doped ZnO samples (with 1, 50, 1000, and 5000 ppm Mn nominal concentrations) exhibit similar features, with small differences related to the intensities and positions of certain absorption bands (Fig. 5). The sharp and very intense absorption bands in the 560–400  $\text{cm}^{-1}$  spectral range correspond to the presence of a dominant ZnO phase. The positions and number of these absorption bands, characteristic to the  $\nu(\text{Zn-O})$  stretching vibration modes, depend on the particles morphology.<sup>33,34</sup> Thus, spherical ZnO particles usually show a single distinct IR absorption band, while for ZnO particles with different

Table 1 Concentrations of the three  $\text{Mn}^{2+}$  paramagnetic centers (in ppm and % of the total concentration  $C_t$  of incorporated  $\text{Mn}^{2+}$  ions) in doped ZnO samples<sup>a</sup>

$\text{Mn}^{2+}$ nominal concentration	$C_t$ [ppm]	$\text{Mn}^{2+}(\text{c})$ concentration		$\text{Mn}^{2+}(\text{d})$ concentration		$\text{Mn}^{2+}(\text{x})$ concentration	
		[ppm]	[% $C_t$ ]	[ppm]	[% $C_t$ ]	[ppm]	[% $C_t$ ]
100 ppm	4	1	25	0.5	13	2.5	62
500 ppm	18	5	29	4	22	9	49
1000 ppm	26	11	44	5	19	10	37
5000 ppm	49	25	50	8	16	16	34

<sup>a</sup> The error was estimated to be 25–30%.



morphologies this band splits in characteristic ways.<sup>33,34</sup> Following the profiles of these IR bands in Fig. 5, one can notice that, by increasing the Mn nominal concentration, the positions, number and intensities of the  $\nu(\text{Zn-O})$  bands change in agreement with the morphologic changes of the nanostructured ZnO phase, from the dominant lamellar towards the dominant polyhedral shape. These variations in the nanostructured ZnO morphology with the Mn doping concentration, reflected in the FTIR spectra, are in agreement with the TEM results.

Several medium to weak intensity absorption bands observed in the  $1460\text{--}760\text{ cm}^{-1}$  spectral range, assigned to the vibration modes for nitrate ions ( $\text{NO}_3^-$ ), indicate the presence of a secondary phase which contains nitrate groups in its chemical composition.<sup>35</sup> The vibration modes observed at  $\sim 3420\text{ cm}^{-1}$  and  $\sim 1640\text{ cm}^{-1}$  are attributed to the presence of hydroxyl ions, which can originate from adsorbed water or a hydroxide compound.<sup>36</sup> The FTIR results are in agreement with the EPR data, confirming the coexistence in these samples of a dominant ZnO phase (nanocrystalline + disordered) and a secondary X phase (disordered) which, according to FTIR data, is expected to contain nitrate groups. Such a secondary phase could be incorporated between the aggregated ZnO nanoparticles during the final drying step, similar to the case of the cZnS nanoparticles synthesis.<sup>37</sup> Table S3 from ESI† summarizes the most important absorption bands maxima observed in the infrared spectra and their assignments for the investigated ZnO:Mn samples.

Although the change in the morphology of the nanostructured ZnO with increasing  $\text{Mn}^{2+}$  concentration, observed by TEM and FTIR, is not a new phenomenon, a recently published review<sup>38</sup> regarding the influence of ionic impurities on the phase and growth/morphology of semiconductor nanocrystals shows that, despite intensive research, there are fundamental issues still unsolved. Previous articles have reported morphological changes of the ZnO nanomaterials associated with the doping process,<sup>39–43</sup> which could be connected to specific structural and coordination properties, as further

explained. The crystallographic plane with the minimum surface free energy determines the preferential growth direction. For semiconductors, the surface free energy depends on the hybridized orbit. In the tetrahedrally coordinated ( $\text{sp}^3$  hybridized orbit) ZnO, with wurtzite structure, the (001) plane has the minimum surface free energy, resulting in a preferential growth along the  $c$ -axis, *i.e.* a (001) “self-texture”.<sup>44</sup> The impurities, once added, become involved in the nucleation and growth processes, influencing thus the surface free energy and therefore the morphology and size of a given crystallite. For example, doping induced morphology changes were reported in the case of the ZnO nanorods, with the different shapes depending on the nature of the impurities: better-formed nanorods (Li, Na doped ZnO), petal-like particles (Mg doped ZnO), both rods and irregular shaped particles with a tendency to agglomeration (Cu doped ZnO), spherical particles ( $\text{Pr}^{3+}$  doped ZnO).<sup>39</sup> Moreover, doping with  $\text{Fe}^{3+}$  ions was reported to induce important changes in the morphology of nanostructured ZnO, ranging from nanowires to nanorods and then to nanoparticles, only by increasing the dopant concentration.<sup>41</sup> Also, in Ni/Fe mono- or co-doped ZnO nanomaterials, the morphology changed from highly crystalline nanorods at low dopant concentration ( $<5\%$ ) towards well dispersed plate-like nanoparticles at higher dopant concentration.<sup>42</sup> The explanation offered for these effects was that the replacement of the  $\text{Zn}^{2+}$  ions by  $\text{Fe}^{2+}/\text{Ni}^{2+}$  ions could affect the local charge density, polarity and potential energy of specific crystal planes, thus resulting in changes of the growth orientation with the Fe/Ni dopant concentration increase.<sup>42</sup>

Yang *et al.*<sup>40</sup> have shown that ZnO faceted nanocrystals changed into nano-tetrapods when doped with a few percent of divalent Mg, Cd, Ni or Mn ions. At high doping concentrations ( $>30\%$ ), the tetrapods changed into nanowires. They experimentally found that the dopants play an important role in the primary growth stage, resulting in initial growth seeds with diverse crystallographic structures, which are critical for the generation of doped nanocrystals with different shapes. Further investigations dedicated to Mn doped nano-ZnO<sup>45</sup> explored the growth mechanism of doped ZnO with an interesting shape transition from tetrapods to spherical nanoparticles by increasing the reaction time and temperature, without changing the dopant concentration. However, it was shown<sup>38,40,45</sup> that the growth mechanism is not simple and further experiments and theoretical simulations are required for specific growth conditions.

### 3.5. Comparison with metal hydroxides prepared by the same method

The most interesting and surprising result of this work is the redirection of the  $\text{Zn}(\text{OH})_2$  synthesis towards nano-ZnO even for nominal concentrations of Mn as low as 1 ppm added in the synthesis. However, the manganese doping was successfully achieved in other hydroxide materials such as  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\beta\text{-Ni}(\text{OH})_2$ ,<sup>46–49</sup> without producing structural changes of the host lattice. EPR studies have been performed and the SH parameters of the  $\text{Mn}^{2+}$  paramagnetic centers were determined

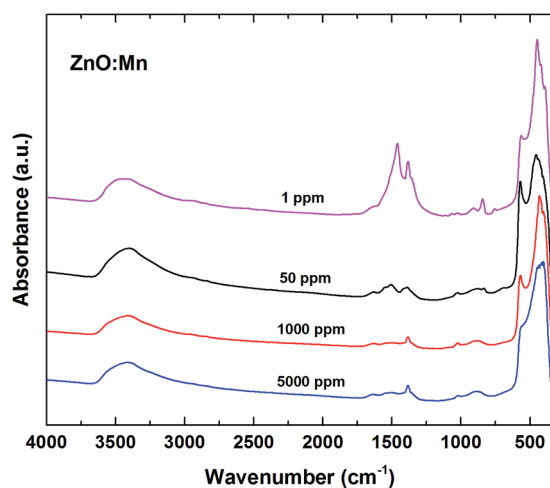


Fig. 5 FTIR spectra for ZnO:Mn samples doped with 1, 50, 1000, and 5000 ppm Mn nominal concentration.



in  $\text{Mg}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  single crystals (SC) doped with significant concentrations of  $\text{Mn}^{2+}$  ions. In contrast, the SH parameters of the  $\text{Mn}^{2+}$  centers in  $\text{Zn}(\text{OH})_2$  were determined only recently in polycrystalline  $\text{Zn}(\text{OH})_2$  containing traces of  $\text{Mn}^{2+}$  ions (<1 ppm).<sup>13</sup> Because the above mentioned results were obtained on doped crystals synthesized by different procedures than the one we used, we decided to prepare several metal hydroxides, pure and doped with Mn, in order to check for a similar redirection of the hydroxide synthesis towards oxide induced by the Mn presence. We used the same preparation procedure and precursors as for  $\text{Zn}(\text{OH})_2$ , replacing the Zn nitrate with nitrates of Mg, Ca and Cd. Fig. 6 presents the XRD patterns of the undoped and Mn (1000 ppm) doped  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Cd}(\text{OH})_2$  samples thus obtained. The XRD diffractograms have been indexed with the  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Cd}(\text{OH})_2$  structures, according to the JCPDS card no. 86-0441, JCPDS card no. 87-0674 and JCPDS card no. 73-0969, respectively. It is obvious that doping with 1000 ppm Mn did not induce structural changes of the  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{Cd}(\text{OH})_2$  lattices, unlike the case of  $\text{Zn}(\text{OH})_2$ .

We have also investigated the possible influence of the anion nature in the starting materials, by replacing the  $\text{M}(\text{II})$  nitrates with  $\text{M}(\text{II})$  acetates and chlorides, where  $\text{M}(\text{II}) = \text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ , and leaving the other parameters of the preparation algorithm unaltered. The synthesis performed in the same conditions using zinc acetate as starting material resulted in a hydroxycarbonate compound, while the one using zinc chloride lead to zinc oxide. On the other hand, there are synthesis conditions (temperature, pH) for which ZnO is obtained from all the precursors, *i.e.* containing nitrate, chloride, sulphate or acetate.<sup>50–53</sup>

The addition of the Mn source in the synthesis procedure did not affect the result in either case. However, as none of the four synthesis procedures performed (acetate/chloride precursors with/without manganese) resulted in  $\text{Zn}(\text{OH})_2$ , they cannot shed light on the cause of the synthesis redirection observed for

nitrate precursors. Therefore this forms a separate subject which can be further studied.

In the case of the other metal hydroxides, we have to take into consideration that zinc itself could be responsible for the observed effect. Indeed, as previously reported,<sup>54–56</sup>  $\text{Zn}^{2+}$  has a different behavior than the other metal ions regarding its preferred coordination number and ligands type. While  $\text{Mn}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$  and  $\beta\text{-Ni}(\text{OH})_2$  exhibit the same  $\text{CdI}_2$  type crystal structure (hexagonal system), where each cation is surrounded by six anions forming a slightly compressed octahedron, in the case of  $\text{Zn}(\text{OH})_2$ , the  $\text{Zn}^{2+}$  ion has a tetrahedral coordination, each cation being surrounded by four anions. This difference in the coordination behavior of  $\text{Zn}^{2+}$  compared to the other  $\text{M}(\text{II})$  ions could lead to a change in the hydroxide host lattice when the  $\text{Mn}^{2+}$  ions enter in  $\text{Zn}^{2+}$  sites, thus leading to the formation of doped ZnO instead of doped  $\text{Zn}(\text{OH})_2$ . A possible explanation is that by forcing the  $\text{Mn}^{2+}$  ions, which prefer an octahedral coordination in almost all compounds, to replace  $\text{Zn}^{2+}$  in tetrahedrally coordinated sites in the  $\text{Zn}(\text{OH})_2$  lattice, a coordinative hindrance appears for manganese. As the specific role played by  $\text{Mn}^{2+}$  is restricted only to  $\text{Zn}(\text{OH})_2$ , it is obvious that the observed effect is based on a fine balance between the  $\text{Zn}^{2+}$  cation, nitrate anion and  $\text{Mn}^{2+}$  dopant, which makes it difficult to give a precise growth mechanism at this stage. The elucidation of the exact reactions which take place during the synthesis necessitates more in-depth/dedicated investigations. Moreover, in spite of extensive studies, it is difficult to propose a definite growth mechanism even for pure ZnO, since there are many factors (such as temperature, pH, water presence) affecting the reactions.<sup>38,57</sup>

## 4. Conclusion

$\text{Zn}(\text{OH})_2$  is one of the valued precursor materials which by a simple thermal annealing results in nanostructured ZnO with controlled size and size distribution. The attempt to add “controlled doping” to the properties of the resulting nano-ZnO lead us to the observation that the simple synthesis by coprecipitation method used for the envisaged  $\text{Mn}^{2+}$  doped  $\text{Zn}(\text{OH})_2$  was redirected and the final product was nano-ZnO:Mn. To our knowledge this is the first observation of the  $\text{Zn}(\text{OH})_2$  synthesis redirection towards ZnO where the agent was a dopant ion instead of a synthesis or post-synthesis parameter such as temperature, pressure or stirring. The systematic investigation of the samples prepared without  $\text{Mn}^{2+}$  and with  $\text{Mn}^{2+}$  ions in a wide nominal concentrations range showed that the synthesis redirection takes place for a  $\text{Mn}^{2+}$  nominal concentration as low as 1 ppm.

We have also found out that this effect takes place only for  $\text{Zn}(\text{OH})_2$ , while the synthesis of other  $\text{M}(\text{II})$  hydroxides ( $\text{M}(\text{II}) = \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cd}^{2+}$ ) by the same procedure is not affected by the presence of a Mn source in the starting material. A possible explanation for the synthesis redirection from  $\text{Zn}(\text{OH})_2$  towards nano-ZnO is based on the different coordination properties of the  $\text{Mn}^{2+}$  and  $\text{Zn}^{2+}$  ions, which could lead to a coordinative hindrance for the  $\text{Mn}^{2+}$  ions.

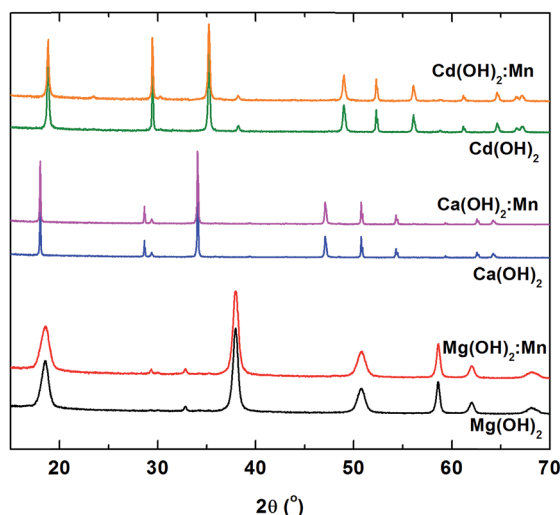


Fig. 6 XRD diffractograms of the pure and Mn (1000 ppm) doped  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ , and  $\text{Cd}(\text{OH})_2$  samples.





We have also examined the extent of the manganese influence on the synthesis products. EPR investigations showed a non-uniform distribution of the  $\text{Mn}^{2+}$  ions in the resulting nano-ZnO samples. Besides the  $\text{Mn}^{2+}$  ions substitutionally localized in tetrahedrally coordinated  $\text{Zn}^{2+}$  sites in nanocrystalline and disordered ZnO, a significant amount of  $\text{Mn}^{2+}$  ions are segregated in a disordered secondary phase. FTIR investigations showed that this secondary phase could consist of rests of nitrate compounds from the precursors, in an amount below the detection limit of XRD. It was also found out that the percentage of segregated  $\text{Mn}^{2+}$  ions from the total concentration of  $\text{Mn}^{2+}$  ions incorporated in the samples decreases with the nominal concentration increase, while the percentage of  $\text{Mn}^{2+}$  ions localized in ZnO nanocrystals increases.

TEM and FTIR investigations evidenced morphological changes of the ZnO nanostructures associated with the Mn concentration increase. This result points to an interesting possibility to control the morphology and size of the ZnO nanostructures by varying the doping concentration, which is important for designing ZnO nanoparticles with high surface area for specific applications, such as catalysis or gas sensing.

We believe that this subject merits further experimental and theoretical investigations not least because, in the end, it provides a simple, cost and time effective, non-toxic method of preparation for manganese doped ZnO, with controlled morphology and particle size.

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