Manganese-Doped Zirconia Nanocrystals

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In recent theoretical work, it was predicted that transition-metal-doped zirconia (ZrO$_2$) can be ferromagnetic at room temperature with a dependence on the metal dopant and its oxidation state and concentration.[1] For experimental verification of these predictions, manganese-doped ZrO$_2$ nanoparticles were synthesized. The synthesis was achieved by the benzyl alcohol route, which led to high-quality nanocrystals with uniform size and shape. The obtained particles present a homogeneous distribution of the magnetic ion. The crystallographic phase was studied by XRD, electron diffraction, and high-resolution TEM. The doping efficiency was determined at the macroscopic level by chemical analysis and at the nanoscale level by electron energy loss spectrometry. The local structure of the manganese ions in the ZrO$_2$ matrix was characterized by electron paramagnetic resonance. Finally, the magnetic properties of the obtained nanocrystals were investigated by susceptibility measurements.

Introduction

Materials based on zirconia (ZrO$_2$) display good thermal stability and interesting acid–base and redox properties, and they also have the advantage of a very low cost. As a consequence, zirconia is a leading material used in industry with applications in catalysis, ceramics, and in solid-oxide fuel cells.[2–4] ZrO$_2$ can crystallize in a monoclinic, cubic, or tetragonal phase.[5] One of the major challenges is therefore to control and tune the crystallographic phase. In view of its applications, the cubic phase is the most suitable. Although this phase is metastable, it can be stabilized by the addition of another cation in the structure, mainly yttrium, but also magnesium, calcium, gadolinium, and cadmium; moreover, the concentration of the cation plays an important role.[6–11] In the literature, many studies have centered on the local environment of the stabilizing ion by means of electron paramagnetic resonance (EPR).[12–14] Interestingly, doped ZrO$_2$ was rarely considered as a potential material for its electronic properties. Furthermore, the study of the magnetic properties of zirconia doped with magnetic ions (e.g., Mn, Co, Fe, etc.) was almost completely neglected. Indeed, one study only reported the magnetic properties when zirconia was doped with manganese.[15]

Recently, the field of transition-metal-doped oxides was dominated by the quest for high-temperature ferromagnetic semiconductors, so called diluted magnetic semiconductors (DMS). Most of the theoretical and experimental studies focused on zinc oxide or gallium nitride. These materials gave rise to further investigation on very large bandgap semiconductors, as they were predicted ferromagnetic above room temperature when doped with magnetic ions. Materials possessing the required characteristics are scarce. As recently predicted by Ostanin et al.[1] doped ZrO$_2$ should be considered as one of the few suitable materials.

In this manuscript, we present a benzyl-alcohol-based synthesis[16–19] of highly crystalline and monodisperse ZrO$_2$ nanoparticles that are doped with up to 5% of Mn. This synthetic approach in general leads to nanosized particles that are well suited for decent characterization by various techniques including high-resolution TEM, EELS, and EPR. The synthesized particles are presented here as an ideal system for studying the effect of Mn doping on the magnetic properties of the material. This is of special interest in view of recent theoretical investigations aimed at the prediction of new DMS materials.

Results and Discussion

The condensation reaction leading to the formation of zirconia is an ether elimination occurring between zirconium isopropoxide and benzyl alcohol,[20] similarly to what was found previously for the formation of HfO$_2$.[21] In the case of zirconia, the particles exhibit a uniformly spherical morphology with a narrow size distribution of 3–4 nm and particles can be produced in multigram-scale quantities.[17,20,22] Doping of ZrO$_2$ was performed by the addition of a quantity of manganese(II) acetate or, alternatively, of manganese(III) acetylacetonate to the reaction mixture. In
both cases, pale-brown powders were obtained. The doping concentration after the synthesis was monitored by ICP-AES measurements and was found to range from 1 to 5% (Table 1). The effectiveness of the doping is elevated, and it ranges from around 80% for Mn(ac)$_2$ to 90% in the case of Mn(acac)$_3$.

Table 1. Manganese-doped samples studied in this work. The table shows the inorganic precursors used, the atomic concentration of Mn in zirconia [Zr$_{(1-x)}$Mn$_x$O$_y$], and the oxidation state of the manganese as estimated from EPR measurements. Magnetic moments at saturation (Msat) were determined from a Langevin fit of the magnetization curves.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn precursor</th>
<th>$x = %$Mn (ICP-AES)</th>
<th>$%$Mn$^{2+}$ (EPR)</th>
<th>$%$Mn$^{3+}$ (EPR)</th>
<th>Msat [$\mu_B$/Mn]</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Mn(acac)$_3$</td>
<td>1.20</td>
<td>69 ± 2</td>
<td>31 ± 2</td>
<td>4.33</td>
</tr>
<tr>
<td>II</td>
<td>Mn(ac)$_2$</td>
<td>1.39</td>
<td>61 ± 2</td>
<td>39 ± 2</td>
<td>4.27</td>
</tr>
<tr>
<td>III</td>
<td>Mn(ac)$_2$</td>
<td>4.38</td>
<td>9 ± 2</td>
<td>91 ± 2</td>
<td>3.55</td>
</tr>
<tr>
<td>IV</td>
<td>Mn(acac)$_3$</td>
<td>4.85</td>
<td>8 ± 2</td>
<td>92 ± 2</td>
<td>3.40</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns of the as-synthesized pure and doped zirconia particles are displayed in Figure 1. They show broad diffraction peaks due to the nanometric size of the zirconia crystals. No additional reflections of crystalline impurities are observed even for the most doped sample. An average particle size of approximately 3–4 nm, as deduced by the Scherrer formula, is obtained for both pure and doped zirconia particles. As the diffraction peaks are broad, XRD experiments are not suitable to assign univocally the crystalline structure of the nanoparticles. Indeed, lattice parameters of the cubic (JCPDS [27–997]) and tetragonal phase (JCPDS [17–923]) of zirconia are similar, and XRD patterns only differ in a few and very close reflections (cf. vertical bar Figure 1). However, on the basis of Rietveld refinement, it was shown that the synthetic procedure leads to the cubic phase.[20] Contrarily to the bulk phase at the nanoscale, the cubic or tetragonal structure does not need to be stabilized by the addition of another ion.[23–28]

Observation of the synthesized products by transmission electron microscopy (TEM) reveals particles of highly homogeneous size and shape (Figure 2). The spherical particles have an average diameter of 3 to 4 nm and appear at random orientation on the supporting carbon film of the TEM grid. At high magnification, the crystalline particles show lattice fringes. The distances and angles between the corresponding lattice planes were abstracted from the Fourier-transformed high-resolution images. They are in good agreement with the cubic ZrO$_2$ phase for both the Mn-doped and the undoped sample.

Figure 2 shows overview and high-resolution TEM micrographs as well as the power spectra from single particles in the [110] direction. The particles are monocristalline in nature and do not present any core defaults. Because of the small size of the particles, the precision in the measurement of the lattice spacing from high-resolution images is limited. Therefore, slight changes in the lattice spacing that might eventually be induced by the dopant cannot be detected. This was expected, as no shift in the lattice spacing was detected by XRD either. In fact, the amount of Mn in the ZrO$_2$ is too low in order to significantly modify the lattice parameters.

In order to investigate the distribution of manganese, electron energy loss spectrometry (EELS) was applied. EELS is a very sensitive technique and perfectly suitable for analyzing the chemical composition of materials at the nanometer scale. EELS spectra recorded in the energy range covering the oxygen K edge at around 530 eV and
the manganese L2,3 edges at 638 (L3) and 649 eV (L2), respectively, are presented in Figure 3. The spectra were recorded from sample III (high doping) at different regions containing varying numbers of particles in order to draw conclusions about the homogeneity of the Mn distribution (Figure 3, A–C). In all presented spectra, the background was removed and zero-loss deconvolution for the removal of the intensity due to plural inelastic scattering was performed. A clear manganese L2,3 edge is visible in all the obtained spectra; although, according to the ICP-AE measurements, only 4.38% of the zirconium atoms were replaced by manganese. In general, the relative intensities of the Mn L3 and L2 edges and their integrated intensities are a sensible measure for the manganese oxidation state and its quantity. In the present case, the low amount of Mn in combination with the small particle size result in a bad signal-to-noise ratio, which prevents precise determination of these quantities.

![Figure 3](image-url)  
Figure 3. EELS spectra recorded from different agglomerations of 4.38% Mn-doped particles (A), (B), and (C). The TEM images show the amount of particles that have contributed to each spectrum. Scale bars correspond to 50, 10, and 10 nm for A, B, and C, respectively.

Besides the low signal-to-noise ratios, removal of the background and deconvolution are also responsible for most of the observed differences in the spectra. This is due to the fact that both background subtraction and zero-loss deconvolution were done for spectra that were recorded under non-ideal conditions, that is, from regions containing inhomogeneous distributions of particles. Nevertheless, on the basis of the presence of the manganese L2,3 edges in all spectra and independent of the amount of particles from which the signal was recorded, a homogeneous distribution of manganese in the particles is concluded.

The local environment and oxidation state of the Mn ions was probed with electron paramagnetic resonance (EPR) on powder samples. EPR is a sensitive probe and was previously used for the investigation of transition-metal impurities on surfaces or in dilute solid solutions. In the present case, the nanocrystals can be regarded as a collection of diluted spins that are randomly distributed in the oxide matrix. Therefore, EPR measurements provide information about the oxidation state, the local symmetry, and the spin–spin interactions. Figure 4 shows a characteristic EPR spectrum recorded at room temperature. In a set of experiments, the temperature was varied from 300 down to 6 K. No change in the spectrum, except for an increase in the signal amplitude, was observed. In zirconia, the manganese ions can exist or coexist in three different oxidation states (II, III, and IV). Mn2+ and Mn4+ show similar, but discernible resonances, whereas the Mn3+ ion is EPR "silent". The lack of signals for Mn3+ is due to the large value of the zero-field splitting that occurs for most of the local environments (i.e., crystal fields), which shifts the EPR signal out of the energy regime of conventional X-band spectrometers.

![Figure 4](image-url)  
Figure 4. EPR spectrum recorded at room temperature for sample I [1.20% Mn from Mn(acac)3 precursor].

All recorded spectra display two contributions centered at $g = 2.020$ (Figure 4): (1) a broad resonance resulting from magnetic interactions of the Mn ions and (2) a sextet from isolated spins. The observed hyperfine splitting [$A = 86(1)$ Gauss] corresponds to the usual values for Mn2+. The g factor of Mn2+ (3d5, $g_0 = 2.00$) and Mn4+ (3d3, $g_0 = 1.98$) are very close to each other. However, the A value is usually found to be lower in the case of Mn4+ [$A = 78(1)$ Gauss]. By taking into account the $g$ factor and the A value, the EPR signal is then assumed to be mainly dominated by the contribution of Mn2+. This analysis is in agreement with a previous study where EPR analysis revealed isolated Mn2+ in zirconia.

A manganese salt [manganese(II)acetate, hydrated] diluted in a matrix and Mn-doped ZnO were used as references to perform quantitative EPR analysis. Mn-doped zinc oxide is a suitable reference, as it is a DMS itself that contains Mn in a 2+ oxidation state. The nominal content of Mn2+ in ZrO2 was evaluated from the double integral of the respective EPR signals after a baseline correction. In all cases, the amount of Mn2+ was found to be lower than the manganese total concentration derived from ICP-AES measurements. The amount of Mn3+ was therefore deduced by simple subtraction (Table 1).

First order analysis of the data therefore revealed the presence of manganese in two oxidation states (II and III). An interesting point is the relation between the manganese concentration and its oxidation state. For diluted samples I...
and II, Mn$^{II}$ is the predominant species, and its concentration is independent of the oxidation state of the precursor used (Table 1). From this, it follows that for the highly diluted samples each Mn atom in the zirconia matrix should be associated to one oxygen vacancy.

An increase in the Mn concentration from 1 to 5 atomic% leads to a decrease in the paramagnetic signal. This can be attributed to the oxidation of some Mn$^{II}$ towards the EPR-silent Mn$^{III}$. The estimated Mn$^{III}$ content is larger than that of Mn$^{II}$ for the most-concentrated samples (Table 1). To confirm this hypothesis, a technique suitable for the characterization of the Mn oxidation state, such as XPS, should be used.

**Magnetic Properties**

After providing evidence for the homogeneity of doping and the absence of any secondary phase, the magnetic properties of the DMS can now be safely discussed. The magnetic measurements were performed at low and high field as a function of manganese concentration and oxidation state of the inorganic precursor used. The susceptibility was investigated by using a zero-field-cooled/field-cooled routine at low field ($\mu_0H = 5.0 \text{ mT}$). Figure 5 shows the results for two different Mn concentrations. The susceptibility and the inverse of the susceptibility are both plotted as a function of temperature. All samples display paramagnetic behavior. For the most-diluted sample (Sample I, 1.20% Mn), the inverse of susceptibility follows a Curie law with a parameter $C = 8.85 \times 10^{-4} \text{emu K}^{-1} \text{Mn}^{-1}$ and a Curie–Weiss temperature of $\theta = (-0.4 \pm 0.2) \text{ K}$. For the sample with the highest Mn concentration (Sample III, 4.38% Mn), the same parameters reach the values of $C = 1.16 \times 10^{-3} \text{emu K}^{-1} \text{Mn}^{-1}$ and $\theta = (-50 \pm 2) \text{ K}$. From the Curie constants, the spontaneous moment per Mn atom can be determined $M_s = 4.4(1)$ and $3.8(1) \mu_B/\text{Mn}$ for Sample I and III, respectively.

As the samples showed a pure paramagnetic behavior at room temperature, additional high-field measurements, $M(H)$, were performed at low temperature ($T = 2 \text{ K}$). The results are plotted in Bohr magnetons per manganese atom ($\mu_B/\text{Mn}$) for the samples synthesized from Mn(ac)$_2$ and Mn(acac)$_3$ in Figure 6a and b, respectively. All doped samples display a hysteresis. The coercive field reaches 1.7 mT for the 4.38 and 4.85% Mn-doped samples and 0.4 mT for the most diluted samples. The observed hysteresis results...
from antiferromagnetic coupling between the manganese atoms. At high field ($\mu_0H = 5$ T), the magnetic moment per atom reaches 3.90 and 3.68 $\mu_B$/Mn for the most diluted samples (Samples I and II) and 2.80 and 2.74 $\mu_B$/Mn for the most concentrated ones (Samples III and IV). As a general trend, the magnetization does not reach saturation even at an applied field of 5 T. The magnetic moments at saturation determined from the fitting of the experimental curves with a Langevin function $M(H, T) = M_T Li(\mu_0H/k_B T)$ are very close to the values determined from Curie constants obtained from susceptibility measurements.

The magnetization of diluted samples (I and II) provides a clear evidence for the presence of a majority of manganese in a low-oxidation state (Mn²⁺, 3d⁵ or Mn³⁺, 3d⁴; the expected effective moments are: Mn²⁺ 5.92 $\mu_B$, Mn³⁺ 4.90 $\mu_B$, and Mn⁴⁺ 3.87 $\mu_B$). In the case of more concentrated samples (III and IV), the magnetization does not allow any conclusion, as the values are lower than that expected for any oxidation state. This result therefore supports the hypothesis of a coexistence of different manganese oxidation states in the zirconia matrix. The low-field and high-field magnetic measurements provide clear evidence for a paramagnetic behavior with antiferromagnetic interactions that increase with the dopant concentrations from ca. 1 to ca. 5%. The manganese oxidation state is difficult to determine from the collected magnetic data. A purely Mn⁴⁺ or Mn⁵⁺ dopant state was already excluded on the basis of EPR measurements. Interestingly, the observed magnetic properties are not sensitive to the nature of the molecular source of manganese, that is, Mn(acac)₂ or Mn(acac)₃. This surprising result may be related to the synthetic route. It was already shown that the synthesis of Mn oxides by the “benzyl alcohol route” always leads to the formation of a secondary phase, which is MnO for the case of Mn₃O₄ and vice versa.⁴⁰ In our case, the presence of Mn²⁺ in the samples synthesized from Mn(acac)₃ can be explained by the soft reducing power of the benzyl alcohol. Furthermore, from quantitative EPR measurements and the derived magnetic moment, it follows that Mn³⁺ is not the only species obtained from the Mn(ac)₂ precursor. As each Mn²⁺ diluted in zirconia requires the generation of one oxygen vacancy, manganese atoms with a higher oxidation state are more likely to substitute a zirconium atom for large concentrations.

Conclusions

In search for high-temperature, ferromagnetic, diluted magnetic semiconductors, zirconia doped with up to 5% of manganese was synthesized by the “benzyl alcohol route”. The synthetic approach led to the formation of homogeneously doped single-crystalline nanoparticles with diameters of 3–4 nm. As a positive side effect of the nanoscale, the cubic structure does not need to be stabilized by the addition of another cation. The environment of the manganese diluted into the zirconia matrix was probed by EPR. It was found that Mn²⁺ and Mn³⁺ coexist and that their ratio depends only on the manganese concentration. Magnetic measurements show mainly paramagnetic behavior of the diluted spins in the matrix. For larger Mn concentrations, a small amount of antiferromagnetic interactions was found. The ferromagnetism predicted by the theoretical work of Ostanin et al. was not found even at low temperature. This can be explained by the low oxidation state of the manganese, which, in our case, was estimated to be between (II) and (III). In fact, a higher oxidation state is more likely to give rise to ferromagnetic interactions. Furthermore, the same theoretical study predicts that the Curie temperature increases with the concentration of manganese. To confirm or refute the theoretical results, careful control of the manganese oxidation state and the amount of oxygen vacancies, as well as an increase in the manganese concentration is required. This will be the focal points of future studies.

Experimental Section

Zirconium(IV) isopropoxide 2-propanol complex (99.9%), manganese(II) acetate (98%), manganese(III) acetylacetonate, and benzyl alcohol (99%) were purchased from Aldrich, stored in a glove box, and used as received.

All the syntheses were performed in a glove box. In a typical reaction, a Teflon cup with an inner volume of 45 mL was filled with zirconium(IV) isopropoxide 2-propanol complex (1.29 mmol), benzyl alcohol (20 mL), and an adequate quantity of dopant. The cup was inserted into a steel autoclave, sealed, removed from the glove box, and then heated at 230 °C for 2 d in a furnace. The resulting suspensions were centrifuged, and the resulting precipitates were meticulously washed with ethanol and acetone and then dried in air at 80 °C. The reaction produced nanocrystals of pure ZrO₂ as a white powder with a yield greater than 80% or slightly brown crystals when Mn⁴⁺ and Mn⁵⁺ dopants were added.

The X-ray powder diffraction (XRD) data were collected with an XPERT MPD Philips diffractometer (Cu-Kα, X-radiation at 40 kV and 50 mA). Transmission electron microscopy (TEM) was carried out with a Hitachi H-9000 microscope operating at 300 kV. High-resolution microscopy and EELS measurements were performed with a CM200FEG (Philips) microscope operating at 200 kV and equipped with a field-emission gun. Samples were prepared by depositing a drop of a suspension of particles in ethanol on a copper grid coated with an amorphous carbon film. Inductively coupled plasma–atomic emission spectrometry (ICP-AES) was realized in the Analytical Laboratories of University of Aveiro. The EPR experiments were performed at X band ca. 9.5 GHz with a Bruker ESP300 spectrometer with microwave powers between 0.02 and 200 mW. Temperature studies from 6 to 300 K were carried out by using an Oxford gas-flow cryostat. Magnetic properties were measured with a SuperQuantum Interference Design (SQUID) magnetometer MPMS XL.7 in the temperature range 2–350 K and a field of 0–5 T. The temperature-dependent susceptibility was measured by using the DC procedure. The sample was cooled to 2 K under zero magnetic field, a low magnetic field (5 mT) was then applied and the data collected from 2 K to 350 K (zero-field cooled, ZFC). Field-cooled (FC) measurements were performed from 2 to 350 K with an applied field during the cooling.

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