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Dilute magnetism in $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ nanocrystals grown in a glass template

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A B S T R A C T

$\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ dilute magnetic nanocrystals (NCs) were synthesized by fusion method in a glass template and annealed post-growth. Magnetism and quantum confinement of incorporated Mn-ions were confirmed by magnetic force microscopy (MFM), Raman scattering (RS) and electron paramagnetic resonance (EPR). A blueshift in the RS spectra were clear signatures of Mn$^{2+}$ incorporation in the dot structure which were monitored as a function of increasing doping concentration, $x$. The EPR spectra showed six lines associated to the $S = 5/2$ spin half filled d-state, characteristic of Mn$^{2+}$ ions.

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1. Introduction

The electronic and magnetic properties associated with the fraction of cations replaced by transition metals in diluted magnetic semiconductors (DMS) have attracted considerable attention in recent years because they display enhanced magneto-optical properties which can be useful [1]. These structures are also good candidates for quantum computation, spin filters and quantum information, and other spintronic devices [2–4]. In this context, ZnTe and ZnMnTe are key materials, operating in the deep UV frequency range, which could be used, in the near future, for transparent single-electron field-effect transistors, lithography and surface modification [11]. Thus, new processes that allow controlled growth of these nanomaterials are always welcome [12].

2. Experimental details

2.1. Sample preparation

Dilute magnetic $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ dots were synthesized in an PZABP matrix with a nominal composition of 65P$_2$O$_5$·14ZnO·1Al$_2$O$_3$·10BaO·10PbO (mol%) to which 1Te (wt.%), and Mn at doping concentration ($x$) varying with Zn content from 0% to 10% were added. Samples were prepared by first melting powder mixtures in alumina crucibles at 1300 °C for 30 min. Next, thermal annealing of the melted glass was carried out at 450 °C for 10 h in order to enhance the diffusion of Zn$^{2+}$, Mn$^{2+}$, and Te$^{2-}$ species into the host matrix. Finally, as a result of the thermal annealing, dilute $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ NCs were formed in the PZABP matrix. Other details on the nanoparticles growth in glass matrices by the fusion method can be found in literature [3,13–15].

2.2. Instrumentation

The $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ samples were investigated by available techniques: magnetic force microscopy (MFM), Raman scattering (RS) and electron paramagnetic resonance (EPR). The MFM images were obtained with a Shimadzu Scanning Probe Microscope (SPM-9600). Tapping-mode was used to obtain the topography of sample surfaces and lift-mode was used for magnetic phase.

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the tip-sample distance varied by tens to hundreds of nanometers. These images were recorded to confirm the formation of magnetic nanoparticles in the PZABP glass matrix. Raman spectra were excited with the 514.5 nm line of an Argon laser. Room temperature modifications in the electronic structure, induced by Mn$^{2+}$-ion incorporation in ZnTe dots of identical size (2.1 nm), were examined by EPR using a high sensitivity Bruker ESP-300 spectrometer operating in the X-band microwave frequency (9.75 GHz). For all these characterizations, glass samples in form of blades was subjected to a meticulous polishing process for a long time in order to assure that the glass surface roughness is smaller than that nanocrystal sizes and the sides are parallel. In particular, this is appropriate polishing process in order to obtain necessary AFM image showing regular distribution of dots on the flat nanosurface of the matrix. In addition, the glass sample is cleaned immediately before the AFM measurement, in order to avoid incorporation of any contaminants on the polished surface, which could reduce the image quality. By using only the average height of the particles in order to avoid tip convolution effects, we evaluate the average dot radius. All characterizations were performed at room temperature.

3. Results and discussion

3.1. MFM Images

Figure 1 shows MFM images from the UV transparent PZABP matrix containing Zn$_{1-x}$Mn$_x$Te NCs grown with concentrations $x=0$ (Figure 1A), $x=0.005$ (Figure 1B), and $x=0.05$ (Figure 1C). Each panel in Figure 1 shows a topographic image (2D and 3D), a corresponding magnetic phase image (right panel) and a typical profile used to estimate the sizes of NCs isolated from Zn$_{1-x}$Mn$_x$Te.

The average size of ZnTe and Zn$_{1-x}$Mn$_x$Te quantum dots, estimated from the AFM/MFM topographical images, is $R=2.16$ nm. Already, for the ZnTe and Zn$_{1-x}$Mn$_x$Te NCs with bulk properties, the estimated from the AFM/MFM topographical images average size of R is estimated at approximately 6.5 nm given that from $R=5.39$ nm, ZnTe NCs begin to exhibit bulk properties [15]. It can be seen that NC size did not change with increasing concentrations $x$ of Mn.

MFM images in Figure 1B and C, regarding magnetic phase, present some contrasts that correspond to magnetic nanocrystalline structures observed in the topographic images (left panels). These contrasts do not appear in the magnetic phase image Figure 1A for the sample containing only the ZnTe NCs. This observation can be attributed to the fact that samples containing magnetic ions respond magnetically when induced by tip magnetization. Thus, the dark (light) contrasts shown in the MFM images, Figures 1B and 2C, indicate that Zn$_{1-x}$Mn$_x$Te NCs are magnetic in a direction parallel (antiparallel) to tip magnetization [16,17]. These results strongly indicate the formation of magnetized Zn$_{1-x}$Mn$_x$Te nanoparticles in the PZABP glass matrix.

3.2. Raman spectra

Raman spectroscopy is another optical technique that is highly sensitive to Mn-incorporation and which can probe the phonon spectrum changes of the nanostructure.

Figure 2 shows Raman spectra recorded for the same samples discussed in Figure 2. Here, the peaks near 215, 323 and 428 cm$^{-1}$ correspond, respectively, to: (i) a first order process involving one longitudinal optical phonon (1LO) [18,19], (ii) a second order process involving combined transversal/longitudinal optical plus one acoustical longitudinal mode (TO/LO + LA) [24]
and finally, (iii) a process involving two longitudinal optical phonon modes (2LO) of bulk ZnTe [20].

It should be noted that Raman scattering, associated to the 1LO process, demonstrates blue-shift for increasing magnetic ion concentration, as shown in Figure 3. The inset shows that the resonant peak changes from 215.3 cm\(^{-1}\) in undoped ZnTe to 217.3 cm\(^{-1}\) for dots doped with a concentration \(x = 0.1\). The origin of this blue-shift is related to the different atomic mass of Mn(55) < Zn(65). Thus, in addition to expected increase in phonon mode frequencies with increasing Mn concentration, this replacement may also induce small distortions into the zincblende crystalline structure of ZnTe [18].

### 3.3. EPR Spectra

In order to analyze the magnetic properties of dilute ZnMnTe NCs, using the same samples discussed earlier, EPR spectra changes with increasing Mn-concentration were studied, as shown in Figure 4. To simulate these transitions the Hamiltonian of the Eq. (1) was used:

\[
H = H_0 + H_z,
\]

where \(H_z = \mu_e \vec{S} \cdot \vec{g}_e \vec{B}\) describes the Zeeman interaction with \(\mu_e\), \(\vec{g}_e\), and \(\vec{B}\) representing the Bohr magneton, the Landé \(g\)-factor and the magnetic field strength, respectively [3,13,21–24]. The term, \(H_0 = D(S^2 - 3/3) + E(S_e^2 - S^2) + A \vec{S} \cdot \vec{I}\) includes the zero magnetic field fine interaction (terms proportional to \(D\) and \(E\)) between the electron spin and the crystal field. This contribution introduces non-zero spin splitting only in crystalline environments with symmetries lower than cubic. Finally, the term \(A \vec{S} \cdot \vec{I}\) represents the hyperfine interaction between the electron spin and the nuclear spin of Mn-ions. In the presence of the hyperfine interaction, each Mn sextet level, associated to the magnetic numbers \(M_s = \pm 5/2, \pm 3/2, \pm 1/2\) splits into an additional six levels identified by the nuclear magnetic quantum numbers, \(M_I = \pm 5/2, \pm 3/2, \pm 5/2\). The six strongest lines observed in the EPR spectra of Figure 4 are due to the resonance associated to the dipole-allowed \(\Delta M_s = \pm 1\) with \(\Delta M_I = 0\) [3], as shown schematically in the inset of Figure 4 where \(S = 1/2\). Certainly, these resonances attest to Mn\(^{2+}\) incorporation in the core region of the ZnTe NCs. In addition, it is possible to observe weaker kinks in the Raman spectra which are produced by fine and hyperfine resonance from magnetic ions located near the dot surface. This can be seen in the Zn\(_{1-x}\)Mn\(_x\)Te samples with concentrations between \(x = 0.001\) and \(x = 0.05\). For the sample where \(x = 0.1\), both fine and hyperfine structures are too weak and result in only a broad EPR spectrum resembling a free-like state for \(S = 1/2\) and magnetic spin quantum number \(M_s = \pm 1/2\). The magnetic ions inside a dot generated an EPR signal \(S_1\) and ions located near the surface produced an EPR signal \(S_2\) shown in Figure 5 [25]. The simulated \(S_1\) and \(S_2\) EPR spectra as well as their combined effects for dipole-allowed transitions \(\Delta M_s = \pm 1\) with \(\Delta M_I = 0\) were compared to the experimental spectrum recorded for the Zn\(_{0.995}\)Mn\(_{0.005}\)Te dot dilute sample. The hyperfine constant and \(g\)-factor used to generate these two EPR spectra for a carrier with \(g_I = 2.0097\) interacting with Mn-ions with electronic and nuclear spins \(S = 5/2; I = 5/2\) are: \(A_s = 9.3\) mT, for Mn ions in the ZnTe dot core (signal \(S_1\)), and \(A_s = 9.7\) mT and \(g_I = 2.0300\) for Mn-ions at or near the dot surface (signal \(S_2\)). It can also be seen that possible distortions in the cubic lattice caused by Mn-incorporation are negligible since the simulated spectra did not

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**Figure 2.** Raman spectra of Zn\(_{1-x}\)Mn\(_x\)Te NCs embedded in the UV transparent matrix containing dots with concentrations: \(x = 0\), \(x = 0.001\), \(x = 0.005\), \(x = 0.01\) and \(x = 0.1\).**

**Figure 3.** Raman spectra of Zn\(_{1-x}\)Mn\(_x\)Te NCs embedded in a UV transparent substrate for dilute samples with Mn-concentrations: \(x = 0\), \(x = 0.001\), \(x = 0.005\), \(x = 0.01\) and \(x = 0.1\). The inset shows the dependence of the (1LO) resonant phonon frequency on Mn-concentration at room temperature. The dashed-line is a polynomial fitting for this phonon mode frequency.
display any dramatic change for variations in the crystal field parameters $D = 3.7 \text{ mT}$ and $E = 1.3 \text{ mT}$. Thus, for the samples analyzed, the ZnMnTe dilute dots ($x < 0.1$) retain their zincblende structure. Agreement between the mode of the main aspects of the experimental EPR lines provided further evidence for Mn-incorporation and magnetic ion presence at the core and surface of the ZnMnTe dots.

4. Conclusion

In summary, dilute magnetic Zn$_{1-x}$Mn$_x$Te nanocrystals were successfully grown in UV transparent PZABP substrates. Incorporation of Mn-ions in the dot structure was investigated by available techniques: AFM/MFM, Raman scattering and EPR. The blueshift observed in the (1LO) Raman peak as a function of increasing Mn-concentration provided strong evidence for the presence of Mn$^{2+}$ ions in ZnTe NCs. Besides AFM/MFM images show strong clues about the formation of these DMS NCs, in the glass matrix PZABP. Further confirmation was obtained from EPR spectra, where the presence of Mn-ions was detected inside the dot structure and near the dot surface. These key wide-gap materials could be utilized in lithography, surface modification, single-electron field-effect transistors and other device applications.

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