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# Diluted Magnetic Semiconductors Nanocrystals: Saturation and Modulation

*Anielle C.A. Silva, Amanda I.S. Barbosa, Alessandra S. Silva, Elisson A. Batista, Thaís K. de Lima Rezende, Éder V. Guimarães, Ricardo S. Silva and Noelio O. Dantas*

## Abstract

Diluted Magnetic Semiconductor (DMS) nanocrystals are a new class of materials formed by doping the semiconductor with transition metals (TM), which gives interesting magneto-optical properties. These properties are attributed to the exchange interaction between the pure semiconductor's sp-electrons and the localized TM d-electrons. This book chapter shows exciting results of new DMS developed by the group, both in powder form and embedded in glassy systems. Depending on the concentration of doping ions, saturation of the incorporation of substitutional and interstitial sites in the nanocrystal structure may occur, forming other nanocrystals. In this context, we investigated the doping saturation limit in nanopowders of DMS  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  NCs and  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ ,  $\text{Zn}_{0.99-x}\text{Mn}_{0.01}\text{Co}_x\text{Te}$ , and  $\text{Bi}_{2-x}\text{Co}_x\text{S}$  NCs synthesized in glassy matrices. Thus, the sites' saturation into the crystalline lattice of nanocrystals is a topic little reported in the literature, and we will comment on this work. Therefore, we will show results from the group about the modulation and saturation in diluted magnetic semiconductors nanocrystals in this work.

**Keywords:** Diluted magnetic semiconductor, Nanocrystals, Saturation, Modulation, Doping, Transition metal

## 1. Introduction

The doping of semiconductors with small concentrations of transition metals (TM) ions, such as  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ , allows the formation of new types of materials that have interesting spin-dependent electrical, optical, magnetic, and structural properties [1–3]. These new properties are attributed to the sp-d exchange interactions that involve the d-sub-levels of transition metal (TM) ions and the sp-electrons of the conduction band and/or holes in the host semiconductor valence band [4, 5]. These materials are called diluted magnetic semiconductors (DMS) and present great possibilities for technological applications such as the production of light-emitting diodes (LEDs) [6], spin transistors [7], lasers [8], supercapacitor [9], among others.

DMS materials, when developed under the quantum confinement regime, form nanocrystals (NCs) with smaller dimensions than the bulk material [10]. These DMS NCs have chemistry and physical properties dependent on their shape and size. These materials are obtained from a controlled process known as thermal diffusion of precursor ions to form DMS NC under the requirement of thermodynamic equilibrium.

The substitutional and interstitial sites' saturation in the nanocrystals structure may occur depending on the dopant concentration, and other nanocrystals types are formed. This system is called a nanocomposite and can have several exciting physical, chemical, and biological properties [11].

In this context, we investigated the doping saturation limit in nanopowders of DMS  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  NCs [12] and  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  [13],  $\text{Zn}_{0.99-x}\text{Mn}_{0.01}\text{Co}_x\text{Te}$  [14], and  $\text{Bi}_{2-x}\text{Co}_x\text{S}$  [15] NCs synthesized in glassy matrices by the fusion method. The properties of the nanomaterials were investigated by experimental techniques of photoluminescence (PL), UV-Vis spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (MET). The theoretical study applying the crystalline field theory and UV-Vis spectroscopy data allows identifying the tetrahedral (Th) or octahedral (Oh) location that the TM ions occupy in the crystalline structure of the semiconductor nanocrystal.

## 2. Diluted magnetic semiconductors in Nanopowders and embedded in glassy matrices

### 2.1 Synthesis of Nanopowders and nanocrystals and embedded in glassy matrices

ZnO NCs were synthesized by precipitation method using zinc nitrate and sodium hydroxide (NaOH,  $\geq 98\%$ ) as precursors. In this work, the aqueous solution (1 M) of zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 98%) and the solution (2 M) of NaOH were mixed at room temperature. The NaOH solution was slowly added into zinc nitrate solution under vigorous stirring, which resulted in the formation of a white suspension. The white product was centrifuged at 6000 rpm for 5 min and washed several times with distilled water until the pH of the solution is around 7. The obtained samples were dried at  $100^\circ\text{C}$  for 24 hours. The samples were not subjected to temperatures above  $100^\circ\text{C}$  to avoid diffusion of  $\text{Mn}^{2+}$  ions from the nucleus to the surface of the ZnO NCs [15], since this is not the focus of this work. The  $\text{ZnO}:x\text{Mn}$  NCs were synthesized using the same procedure as ZnO NCs, but with the manganese (II) chloride ( $\text{MnCl}_2$ , 98%) solution during the synthesis process. The  $x\text{Mn}$ - concentration was determined based on the mass percentage of Zn present in ZnO (wt%), for  $x = 0.1; 0.3; 0.5; 0.7; 0.9; 1.0; 3.0; 5.0; 7.0$  and  $9.0$ . All reagents are nearly pure and purchased from Sigma-Aldrich Company.

$\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  and  $\text{Zn}_{0.99-x}\text{Mn}_{0.01}\text{Co}_x\text{Te}$  were synthesized by fusion method in a glass matrix and annealed post-growth. The fusion method consists of two sequential melting-nucleation processes that produce ensembles of nearly spherical nanoparticles embedded in a glass matrix. In the first step, the PZABP glass matrix with a nominal composition of  $65\text{P}_2\text{O}_5 \cdot 14\text{ZnO} \cdot 1\text{Al}_2\text{O}_3 \cdot 10\text{BaO} \cdot 10\text{PbO}$  (mol %) adding 2Te (wt %), and Mn and/or Co at doping  $x$  content varying with Zn content from 0 to 80 (wt %), were synthesized by fusion in alumina crucibles at  $1300^\circ\text{C}$  for 30 minutes. Next, these melted mixtures were quickly cooled to room temperature forming a glass system doped with the precursor ions needed for nanoparticle growth. In the second step, the glass samples were thermally annealed at  $500^\circ\text{C}$

for 10 hours to enhance the diffusion of  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$  and/or  $\text{Co}^{2+}$  and  $\text{Te}^{2-}$  ions throughout the host PZABP matrix and induce the growth of  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}/\text{Zn}_{0.99-x}\text{Mn}_{0.01}\text{Co}_x\text{Te}$  NCs. The physical properties of the glass samples were studied by optical absorption (OA), recorded with a model UV-3600 Shimadzu UV-VIS-NIR spectrometer, operating between 190 and 3300 nm; Photoluminescence (PL), using a 405 nm ( $\sim 3.06$  eV) continuous wave laser; Transmission electron micrographs (TEM JOEL, JEM-2100, 200 kV) and electron paramagnetic resonance (EPR), using a high sensitivity Bruker ESP-300 spectrometer (operating at X-band  $\sim 9.75$  GHz and at Q-band  $\sim 34$  GHz).

$\text{Co}^{2+}$ -doped  $\text{Bi}_2\text{S}_3$  NCs were synthesized in a glass matrix with nominal composition of  $45\text{SiO}_2$ ,  $30\text{Na}_2\text{CO}_3$ ,  $1\text{Al}_2\text{O}_3$ ,  $24\text{B}_2\text{O}_3$  (mol%) adding 2S (wt%), 2Bi (wt%) and  $x = 0, 1$  and 5% of Cobalt (Co), as a function of Bismuth (Bi) concentration. Samples were produced with the powder mixture added in an alumina crucible, and placed in a furnace at 1200 C for 30 min, followed by a fast cooling of the melted mixture down to room temperature, which formed a host glass. Thermal annealing was the next step: The previously-melted glass matrix, as-growth, was then heated at 500 C for 2, 10 and 24 h to enhance the diffusion of  $\text{Bi}^{3+}$ ,  $\text{Co}^{2+}$ , and  $\text{S}^{2-}$  ions precursors within the hosting matrix, resulting in the formation of DMS  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs.

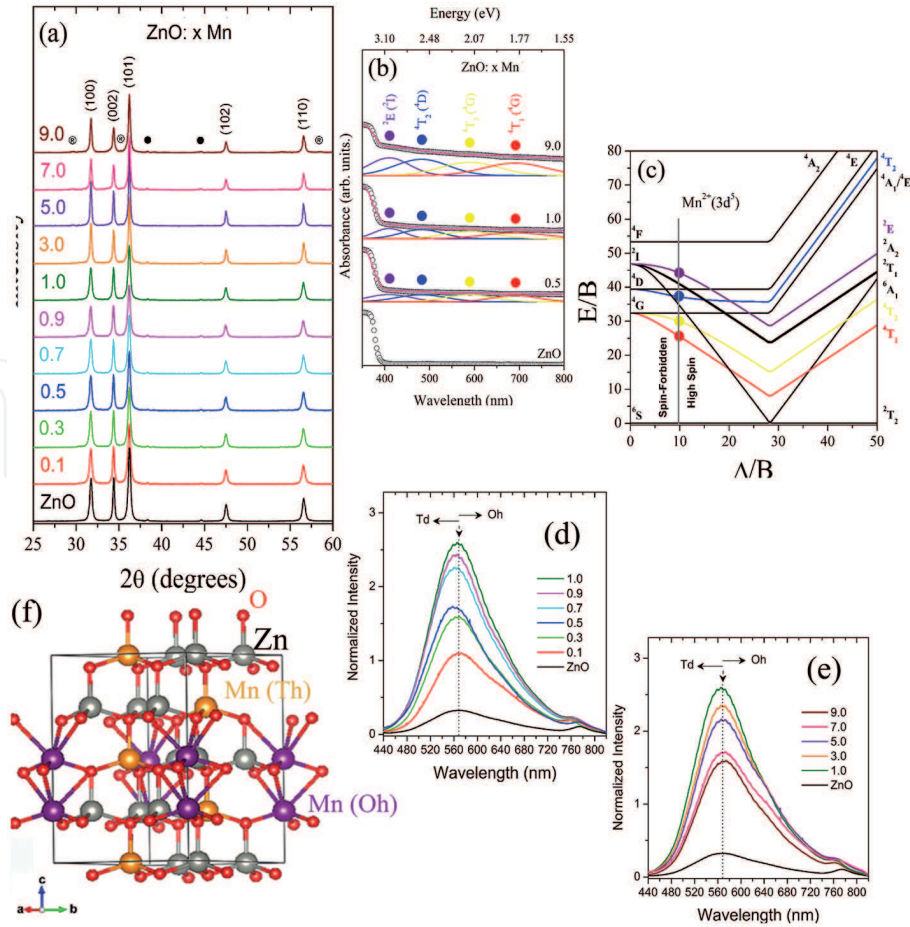
## 2.2 A study in function of Mn concentration in ZnO nanocrystals: Solubility and $\text{Mn}^{2+}$ ions localization

The zinc oxide (ZnO) is a semiconductor with several interesting physical and biological properties such as ultraviolet absorption and bactericidal and antitumor properties [16]. Depending on the ions incorporated in the crystalline structure of ZnO nanocrystals (NCs) one can intensify or generate new and interesting properties. Dantas et al. demonstrated that doped ZnO nanocrystals' bactericidal and antitumor properties are potentiated or inhibited with the concentration and type of dopant [17]. The ZnO is a semiconductor of family II-VI that has a bandgap of 3.44 eV [18]. Due to its wide bandgap range, ZnO is suitable for technological applications of photonic devices operating in the blue and ultraviolet region, fabrication of nanodevices electronics [16, 19].

The structural and optical properties are shown in **Figure 1**. The characteristic diffraction patterns of ZnO crystals with wurtzite structure (JCPDS n° 36–1451) were observed in the X-ray patterns of samples (**Figure 1a**). The presence of additional diffraction peaks for concentrations above 3.0 Mn (%wt) corresponding to the phase  $\text{ZnMn}_2\text{O}_4$  (JCPDS n° 24–1133), indicating the formation of the second phase (open circles). The closed circles are identified by the aluminum sample holder. Thus, this new crystal formation is associated with the saturation of the substitutional and interstitial sites in the ZnO crystal structure.

In order to identify the symmetrical environment in which the  $\text{Mn}^{2+}$  ions may be found in the ZnO NCs, adjustments will be made to the optical absorption spectra of the samples (ZnO, 0.5Mn, 1.0Mn and 9Mn) shown in **Figure 1(b)**. These adjustments are made in the positions of absorption of  $\text{Mn}^{2+}$  ions, making possible the use of the crystalline field theory (CFT) based on the crystalline field strength parameters  $\Delta$  and Racah B, both calculated with help of Tanabe– Sugano diagram (**Figure 1(c)**) [20]. From the OA spectra of the NCs of Zn: xMn, based on the Tanabe-Sugano diagram, the energies of the characteristic electronic transitions of  $\text{Mn}^{2+}$ :  ${}^6\text{A}_1 ({}^6\text{S}) \rightarrow {}^4\text{T}_1 ({}^4\text{G})$  (691 nm),  ${}^6\text{A}_1 ({}^6\text{S}) \rightarrow {}^4\text{T}_2 ({}^4\text{G})$  (590 nm),  ${}^6\text{A}_1 ({}^6\text{S}) \rightarrow {}^4\text{T}_2 ({}^4\text{D})$  (482 nm), and  ${}^6\text{A}_1 ({}^6\text{S}) \rightarrow {}^2\text{E} ({}^2\text{I})$  (410 nm) (**Figure 1b**) subtly permitted by spin-orbit coupling were effectively described by the Racah B parameter ( $559 \text{ cm}^{-1}$ ) and the crystalline field division ( $\Delta = 5464 \text{ cm}^{-1}$ ) [21, 22].





**Figure 1.**

(a) X-ray diffractograms (b) As adjusted curves represent the experimental energies of the transitions prohibited by spin  ${}^6A_1(S) \rightarrow {}^4T_1(G)$ ,  ${}^4T_2(G)$ ,  ${}^4T_2(D)$ ,  ${}^2A_2(I)$  e  ${}^2E(I)$ . (c) Tanabe-Sugano diagram for the electronic configuration of the  $Mn^{2+}(3d^5)$  ( $C/B = 4.5$ ) with vertical solid line in  $\Delta/B = 9.77$ ,  $\Delta = 5464 \text{ cm}^{-1}$ , and  $B = 559 \text{ cm}^{-1}$ , PL spectra from 440 to 820 nm for concentrations of (d) 0.1 to 1.0 of Mn and (e) of 1.0 to 9.0 of Mn, (f) wurtzite structure of ZnO NCs with coordination geometry in which the  $Mn^{2+}$  ions are, represented by tetrahedral sites (Td) and octahedral sites (Od).

The results from  $\Delta$  and  $B$  show that the  $Mn^{2+}$  dopants incorporated mainly at octahedral sites in the hexagonal structure of ZnO, for the sample with low concentration, and in the tetragonal structure of  $ZnMn_2O_4$ . Thus, the excited states of the  $Mn^{2+}$  in the binder field reside in the host semiconductor energy gap [21, 22].

Fluorescence spectra of the nanocrystals of ZnO: x Mn where the band at 570 nm are assigned to vacancies [23] are shown in **Figure 1(d, e)**. Luminescence intensification and *blue shift* to a concentration of 0.5 Mn. This result confirms the incorporation of  $Mn^{2+}$  ions into the tetrahedral sites of ZnO NCs (inside nanocrystal). However, there is a contribution to incorporating  $Mn^{2+}$  ions into the octahedral sites (surface nanocrystal). It is noteworthy that the band widening around 570 nm is due an overlapping characteristics bands of oxygen vacancies and d-d ( ${}^4T_1 \leftarrow {}^6A_1$ ) of  $Mn^{2+}$ -ions in ZnO NC host [23, 24].

As the concentration increases from 0.5 to 1.0 Mn, the band's position remains, confirmed the half-height with  $x_{Mn}$ -concentration, which is related to the presence of the formation of the  $ZnMn_2O_4$  NCs and that the  $Mn^{2+}$  are incorporated in the octahedral sites of the crystal structure saturation of the sites present in the ZnO NCs.

In order to visually check how these are coordination geometry, **Figure 1(f)** shows the wurtzite structure of ZnO NCs, which the  $Mn^{2+}$  ions are in tetrahedral sites (Td) and/or octahedral sites (Od).

### 2.3 Solubility of manganese and cobalt in ZnTe nanocrystals embedded in $P_2O_5$ - ZnO - $Al_2O_3$ - BaO - PbO glassy matrix

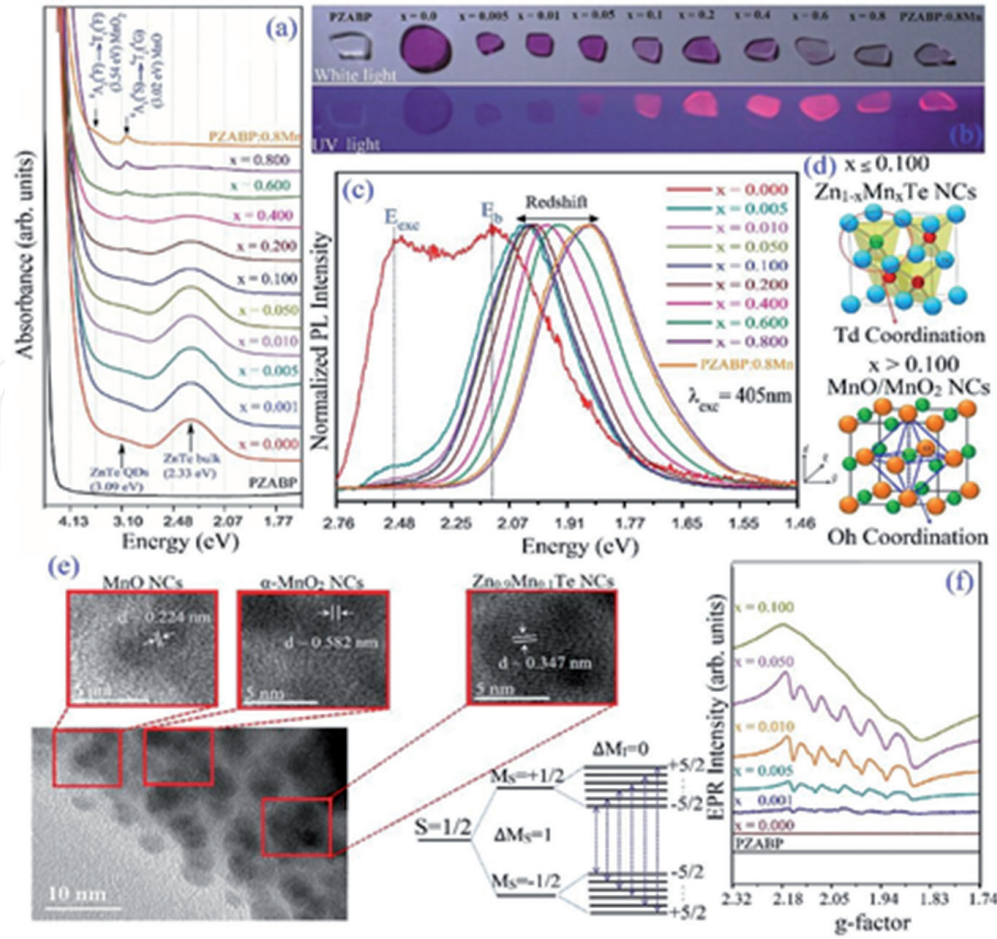
The incorporation of magnetic ions into the crystal structure of ZnTe semiconductor nanocrystals, which grow in glassy systems, has become very interesting due to the various applications in spintronics are governed by sp-d spin interaction between carriers and magnetic ions [25]. Some possible applications require nanoparticles to be embedded in highly stable, robust, and transparent host materials, as glassy systems [26]. The present study reports on the investigation of the solubility/saturation of  $Mn^{2+}$  ions in  $Zn_{1-x}Mn_xTe$  [13, 26, 27] and competition between  $Co^{2+}$  and  $Mn^{2+}$  ions into  $Zn_{0.99-x}Mn_{0.01}Co_xTe$  [14, 28] nanosized DMS embedded in a glassy system with a wider Mn/Co concentration range ( $x = 0.000$ – $0.800$ ). According to the literature, the  $Mn^{2+}/Co^{2+}$  ion can be thermodynamically incorporated into II-VI semiconductors up to its solubility limit [29, 30]. Above this limit, saturation occurs, and  $Mn^{2+}/Co^{2+}$  ions tend to be expelled toward the semiconductor nanocrystal surface [30].

**Figure 2** presents OA (a) and PL (c) spectra and photographs (b) of the samples containing  $Zn_{1-x}Mn_xTe$  NCs, with Mn-concentrations ranging from  $x = 0.000$  to  $x = 0.800$ , and with PZABP ( $65P_2O_5 \cdot 14ZnO \cdot 1Al_2O_3 \cdot 10BaO \cdot 10PbO$  (mol %)) glassy matrix doped only 80Mn (% wt of Zn). The OA spectra show absorption bands centered attributed to  $Zn_{1-x}Mn_xTe$  NCs (quantum dots (QDs) and bulk NCs) and the incorporation of  $Mn^{2+}$  ions. This substitutional incorporation is confirmed from the EPR spectra (**Figure 2(f)**) that showed six lines associated to  $S = 5/2$  spin half-filled d-state, characteristic of  $Mn^{2+}$  ions (as detailed in the energy diagram) [26]. For  $x > 0$ , additional bands are observed.

The absorption band centered at 3.54 eV is attributed at  $MnO_2$ , and the bands centered at 3.02, and 2.43 eV is attributed at MnO [31]. The TEM images in **Figure 2(e)** (for  $x = 0.100$ ), revealed interplanar distances corresponding to  $Zn_{0.9}Mn_{0.1}Te$  NCs ( $d \sim 0.347$  nm) [32], MnO ( $d \sim 0.224$  nm) [33] and  $MnO_2$  ( $d \sim 0.582$  nm) NCs [34]. This result can be confirmed by the PL spectra, on what the observed redshift shows that it was possible to tune Mn emission energy from orange to near-infrared as a function of concentration. These results confirm the successful inclusion of  $Mn^{2+}$  ions in the  $Zn_{1-x}Mn_xTe$  up to the nominal solubility limit of  $x = 0.100$ . Above this solubility limit, one can observe Mn's saturation, forming MnO and  $MnO_2$  NCs, as represented in **Figure 2(d)**. Thus, one of the main motivations for studying semiconductors doped with transition metals, especially  $Mn^{2+}$  ions, is for applications in luminescent devices.

**Figure 3** presents OA (a), PL (b) and EPR (c) spectra and photographs (between OA and PL spectra) of the samples containing  $Zn_{0.99-x}Mn_{0.01}Co_xTe$  NCs, with Co-concentrations ranging from  $x = 0.000$  to  $x = 0.800$ . **Figure 3(d)** presents the energy diagram of all transitions related to OA and PL data, and **Figure 3(e)** shows the transitions satisfying the selection rules  $\Delta M_S = \pm 1$  and  $\Delta M_L = 0$ . The AO spectra, besides the bands attributed to  $Zn_{1-x}Mn_xTe$  QDs and bulk NCs, as previously presented in **Figure 3**, four characteristic bands in the visible spectrum for all doped samples with cobalt. These four are due to the spin-allowed transitions:  $^4A_2(F) \rightarrow ^2T_1(P)$  (2.13 eV); and spin-forbidden transitions:  $^4A_2(F) \rightarrow ^2A_1(G)$  (2.33 eV),  $^4A_2(F) \rightarrow ^4T_1(G)$  (1.95 eV) and  $^4A_2(F) \rightarrow ^2E(G)$  (1.91 eV) [14]. These bands show the substitutional incorporation of  $Co^{2+}$  ions in tetrahedral  $Zn^{2+}$  ions sites. The PL spectra show emissions from two NC groups: QDs ( $E_{exc} \sim 2.53$  eV) and bulk NCs ( $E_b \sim 2.21$  eV); defects related to zinc vacancies ( $E_{VZn} \sim 2.53$  eV) and oxygen centers ( $E_o \sim 1.91$  eV) [14, 27].

The emission centered at approximately 2.03 eV and 1.89 eV corresponds to tetrahedrally (Td) and octahedrally (Oh) coordinated  $Mn^{2+}$  ions. Already, when the



**Figure 2.**

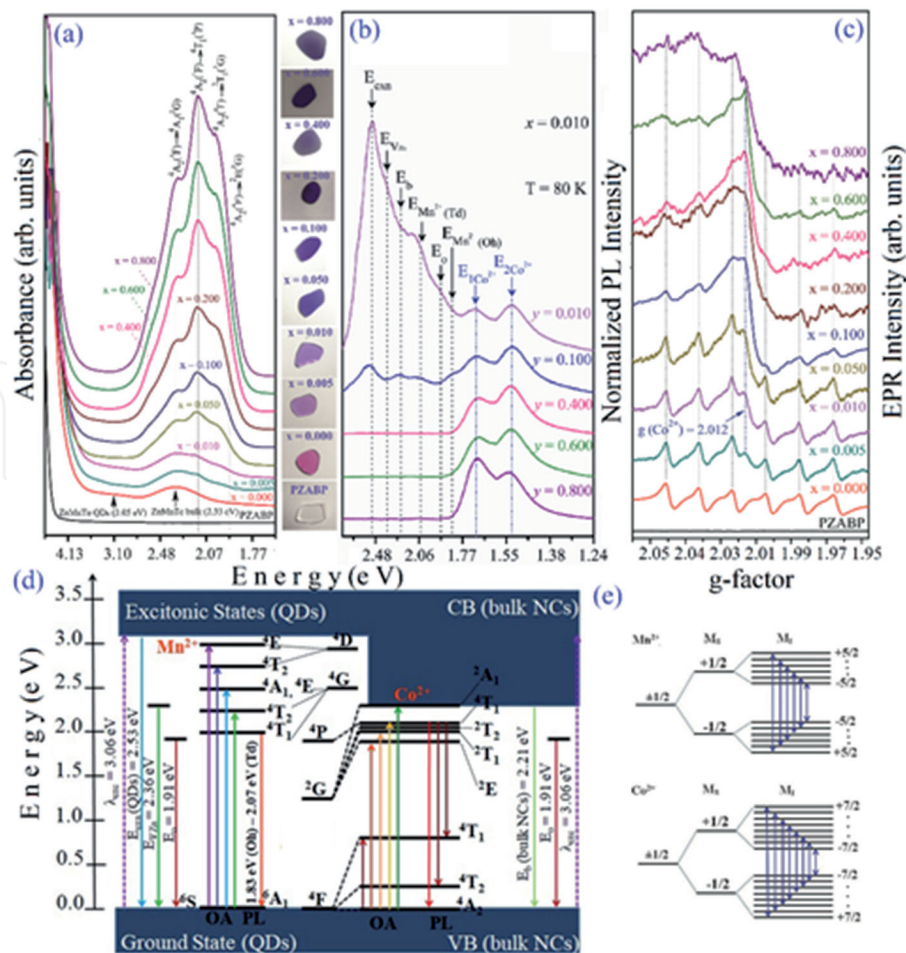
OA (a) and PL (c) spectra and photographs (b) of samples containing  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  NCs, with Mn-concentrations ranging from  $x = 0.000$  to  $x = 0.800$ . In (d)  $\text{Mn}^{2+}$  ions located in tetrahedral sites (td) of  $\text{ZnTe}$  NCs (concentration  $x < 0.100$ ) and  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  located in octahedral sites (oh) of  $\text{MnO}$  and  $\text{MnO}_2$  NCs (concentration  $x \geq 0.100$ ); (e) TEM images for concentration  $x = 0.100$ ; (f) EPR spectra of  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$  NCs with Mn concentrations varying from  $x = 0.00$  to  $x = 0.100$  and selection rules  $\Delta M_S = \pm 1$  and  $\Delta M_I = 0$  (next to).

spin-allowed transitions centred around 1.69 eV ( ${}^4\text{T}_1({}^4\text{P}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ , named  $\text{E}_{1\text{Co}^{2+}}$ ) and 1.52 eV ( ${}^4\text{T}_1({}^4\text{P}) \rightarrow {}^4\text{T}_2({}^4\text{F})$ , named  $\text{E}_{2\text{Co}^{2+}}$ ) [14]. The energy diagram in **Figure 3(d)** shows these OA and PL spectra transitions. The EPR spectra, besides proving the substitutional incorporation of  $\text{Mn}^{2+}$  in  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ , as justified by **Figure 3(f)**, also reveals that as the Co doping, an intense central line with  $g = 2.012$  attributed to interacting  $\text{Co}^{2+}$  [14]. For both  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  ions the transitions observed satisfy the selection rules  $\Delta M_S = \pm 1$  and  $\Delta M_I = 0$  (**Figure 3(e)**). Thus, the EPR spectra suggest a kind of competition between  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  ions to substitute  $\text{Zn}^{2+}$  ions, controlled by the Co concentration.

## 2.4 Effects of symmetry and concentration of cobalt-doped $\text{Bi}_2\text{S}_3$ nanocrystals embedded in host glass matrix

$\text{Bi}_2\text{S}_3$  semiconductor nanocrystals (NCs) present radioactive recombination of electron-hole carriers adjustable according to the temperature, time, and concentration of doping ions in the system [15, 35–37]. The occupation of vacancies in the  $\text{Bi}_2\text{S}_3$  orthorhombic network by  $\text{Co}^{2+}$  ions (0.72 Å) replacing  $\text{Bi}^{3+}$  ions (1.03 Å) can reduce intrinsic point defects and consequently increase the efficiency of semiconductor nanocrystals, for applications in solar cells [38], photocatalytic devices of visible light [39], thermoelectric [40] and spintronic [41]. Therefore, the control of the magnetic saturation of the energy states located of the  $\text{Co}^{2+}$  ions in the  $\text{Bi}_2\text{S}_3$  NCs





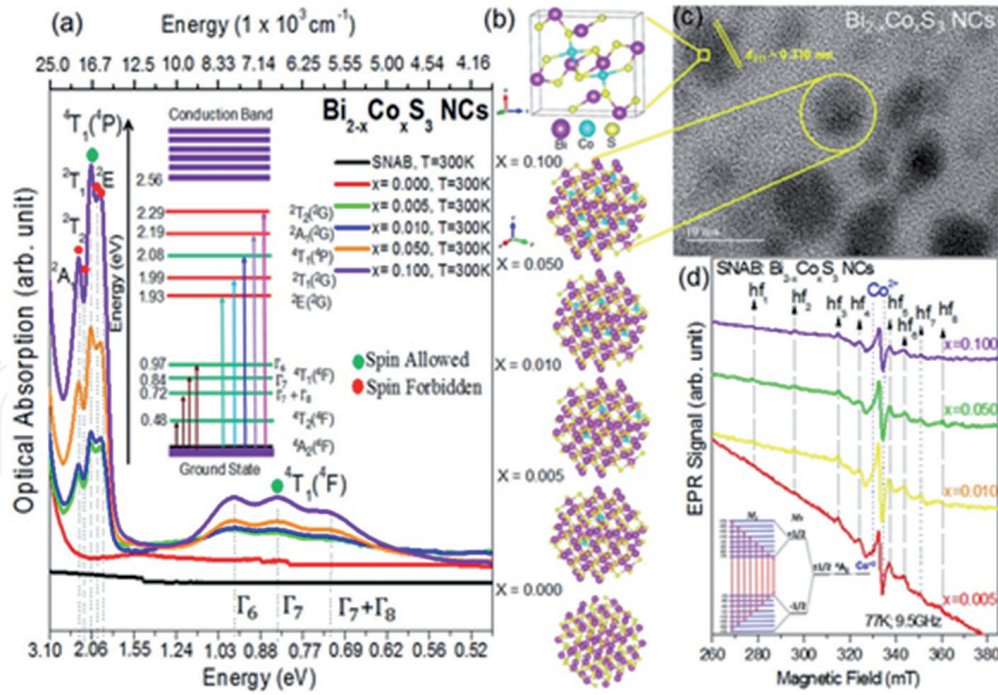
**Figure 3.** OA (a), PL (b) and EPR (c) spectra and photographs (between OA and PL spectra) of the samples containing  $\text{Zn}_{0.99-x}\text{Mn}_{0.01}\text{Co}_x\text{Te}$  NCs, with Co-concentrations ranging from  $x = 0.000$  to  $x = 0.800$ . Energy diagram of all transitions related to OA and PL data (d). Transitions satisfying the  $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$  selection rules  $\Delta M_S = \pm 1$  and  $\Delta M_L = 0$  (e).

bandgap allows assigning new magnetic and optoelectronic properties. In this context, we investigated the effect of the molar fraction and the coordination symmetry of  $\text{Co}^{2+}$  ions in cobalt-doped  $\text{Bi}_2\text{S}_3$  NCs embedded in a host glass matrix ( $\text{SNAB} - 45\text{SiO}_2 \cdot 30\text{Na}_2\text{CO}_3 \cdot 5\text{Al}_2\text{O}_3 \cdot 20\text{B}_2\text{O}_3$ ) (mol%).

**Figure 4(a)** shows the UV-VIS-NIR optical absorption spectrum (OA) of the  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs embedded in a SNAB glass matrix, at temperature (300 K), as a function of the increasing concentration of doping  $x\text{Co}$  ions ( $x = 0.000$ ;  $0.005$ ;  $0.010$ ;  $0.050$ ;  $0.100$ ). The OA spectrum of the SNAB matrix is transparent in the spectral region where the  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs can absorb and emit a photon. The OA spectrum of the samples shows energy bands of the exciton charge carrying states and the d-d transitions of the  $\text{Co}^{2+}$  ions in the  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs. The structure of the absorption bands is due to that of the ligand field of  $\text{S}^{2-}$  ions in distorted tetrahedral sites around the  $\text{Co}^{2+}$  ions. Such bands of electronic level transitions have increased due to the increasing concentration of  $\text{Co}^{2+}$  ions in the  $\text{Bi}_2\text{S}_3$  NCs structure.

Furthermore, the p-d and spin-orbit interactions in an asymmetric tetrahedral coordination complex  $[\text{CoS}_4]^{6-}$  provide a higher intensity for 3d-3d transitions [14, 15, 20, 42]. Therefore, the exotic properties of these new materials called diluted magnetic semiconductors (DMS) NCs are linked to the nature of the sp-d exchange interaction that occurs between the charge carriers of the  $\text{Bi}_2\text{S}_3$  semiconductor bands around the electrons in the central metal ion orbital ( $\text{Co}^{2+}$ ) with  $3d^7$  electronic configuration (spin)  $3d^7$  ( $S = 3/2$ ) [15, 20, 36, 42].





**Figure 4.**

(a) Optical absorption spectra at room temperature of  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs ( $x = 0.000; 0.005; 0.010; 0.050; 0.100$ ) embedded in the SNAB glass matrix annealed for 2 h at  $500^\circ\text{C}$ . for comparison purposes, the absorption spectrum of the SNAB glass matrix is represented on the black bottom line. The inset shows the energy level diagram for  $\text{Co}^{2+}$  ( $3d^7$ ) in a tetrahedral site and the respective spin allowed and forbidden transitions. (b)  $\text{Bi}_2\text{S}_3$  orthorhombic unit cell and  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  quantum dots with the interstitial replacement of  $\text{Bi}^{3+}$  ions by  $\text{Co}^{2+}$  at distorted tetrahedral sites. (c) TEM image of  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs ( $x = 0.100$ ). (d) EPR spectra (77 K) of  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs ( $x = 0.005; 0.010; 0.050; 0.100$ ) embedded in the SNAB glass matrix.

For  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs, the spin allowed transitions  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{F})$  and  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{P})$  are obtained with the energy value of the barycenter for a normal distribution of the bands observed in the spectrum absorption in the range of 0.62–1.24 eV and 1.70–2.60 eV. The bands observed in the OA spectrum of **Figure 4(a)** correspond to the spin allowed and forbidden transitions,  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{F})$  (0.84 eV),  $^4\text{A}_2(^4\text{F}) \rightarrow ^2\text{E}(^2\text{G})$  (1.93 eV),  $^4\text{A}_2(^4\text{F}) \rightarrow ^2\text{T}_1(^2\text{G})$  (1.99 eV),  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{P})$  (2.08 eV),  $^4\text{A}_2(^4\text{F}) \rightarrow ^2\text{A}_1(^2\text{G})$  (2.19 eV) and  $^4\text{A}_2(^4\text{F}) \rightarrow ^2\text{T}_2(^2\text{G})$  (2.29 eV). Such identified 3d-3d transitions are attributed to the crystal field strength ( $\Delta = 3882 \text{ cm}^{-1}$ ) and the electronic repulsion parameter (Racah,  $B = 772 \text{ cm}^{-1}$ ), based on the crystal field theory and the Tanabe-Sugano diagram  $d^7$ , tetrahedral for  $C/B = 4.5$  [20, 43, 44]. The wide absorption band in the infrared is due to a spin-orbit coupling interaction that split the excited state  $^4\text{T}_1(^4\text{F})$  into three energy sub-states:  $\bar{\text{A}}_6$  (0.97 eV),  $\bar{\text{A}}_7$  (0.84 eV) e  $\bar{\text{A}}_7 + \bar{\text{A}}_8$  (0.72 eV) [12, 13]. Therefore, the excited states of the  $\text{Co}^{2+}$  ions are located in the energy gap (2.65 eV) of electrons and holes confined between the ground state and the conduction band of the  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs. The energy level diagram of  $\text{Co}^{2+}$  ions ( $3d^7$ ) in a ligand field of  $\text{S}^{2-}$  ions at tetrahedral coordination sites  $[\text{CoS}_4]^{6-}$  is shown in the inset in Figure x (a). The energy band associated with the spin allowed transition  $^4\text{A}_2(^4\text{F}) \rightarrow ^4\text{T}_1(^4\text{F})$  (0.48 eV) does not appear in the OA spectrum (**Figure 4a**) due to the low intensity and energy [15, 43].

The redshift observed at the OA band edge for the  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs with increasing concentration  $x_{\text{Co}}$ , from  $x = 0.000$  (2.75 eV) to  $x = 0.100$  (2.56 eV) (see **Figure 4a**), are consequences of sp-d exchange interactions between sp. electrons confined in states of quantum dots and localized states partially filled with 3d electrons of the  $\text{Co}^{2+}$  ions [10]. No significant changes occur in the quantum size of the  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs with the incorporation of Co. The TEM image (**Figure 4c**) shows an average size

of 6 nm for  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs ( $x = 0.100$ ) with quantum dot properties. The interplanar distance ( $d_{211} = 0.310$  nm) shows the crystal plane (211) characteristic of the orthorhombic structure of the mineral Bismuthinite. **Figure 4(b)** illustrates the  $\text{Bi}_2\text{S}_3$  orthorhombic structure unit cell doped with  $\text{Co}^{2+}$  ions at distorted tetrahedral sites and the respective  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  quantum dots function of the xCo concentration.

**Figure 4(d)** shows the EPR spectra obtained in the best conditions at 77 K and 9.75 GHz for samples of  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$  NCs embedded in SNAB glass matrix, with xCo concentration ranging from  $x = 0.005$  to 0.100. The intense central signal at ( $g \approx 2.005$ ;  $\Delta H \approx 8$  mT) corresponds to free  $\text{Co}^{+2}$  ions, dispersed in the glass matrix and not incorporated in the  $\text{Bi}_2\text{S}_3$  NCs [2, 10]. The inset in Figure x (d) presents a diagram with the allowed hyperfine lines  $\Delta M_S = \pm 1$  with  $\Delta M_I = 0$ , related to the transition between the levels of fine interaction  $M_S = +1/2 \leftrightarrow -1/2$ . The anisotropic characteristic of the eight lines ( $hf_1$ ;  $hf_2$ ;  $hf_3$ ;  $hf_4$ ;  $hf_5$ ;  $hf_6$ ;  $hf_7$ ;  $hf_8$ ) of the hyperfine interaction between the electron spin ( $S = 3/2$ ) and the nuclear spin ( $I = 7/2$ ) and its similar shapes for all xCo concentrations confirms magnetic doping in distorted tetrahedral sites. The result is compatible with a region where there is a large, inhomogeneous crystal field due to the lack of interface between the host glass matrix and the NCs [42].

### 3. Conclusion

The synthesis and investigation of the DMS NC have allowed the production of new types of materials with possible technological applications in Engineering, Medicine, Environment, Telecommunications, and others. We report the synthesis of the  $\text{Zn}_{1-x}\text{Mn}_x\text{O}$  nanopowders and the  $\text{Bi}_{2-x}\text{Co}_x\text{S}_3$ ,  $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$   $\text{Zn}_{0.99-x}\text{Mn}_{0.01}\text{Co}_x\text{Te}$  NCs in glass by fusion method. The formation of DMS NCs is observed by SEM and MET images. The EPR spectra confirm the incorporation of  $\text{TR}^{2+}$  ions ( $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$ ) in the doped nanocrystals' crystalline structure. The optical properties of these materials were investigated by photoluminescence and Uv-Vis spectroscopy techniques, which show the influence of  $\text{TR}^{2+}$  ions ( $\text{Mn}^{2+}$  and  $\text{Co}^{2+}$ ) on the visible spectrum, altering the optical absorption and photoluminescence bands of undoped naocrystals. In this work, we hope to contribute significantly to the study of DMS NCs and their possible technological applications for society's benefit.

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## Author details

Anielle C.A. Silva<sup>1,2\*</sup>, Amanda I.S. Barbosa<sup>1</sup>, Alessandra S. Silva<sup>5</sup>,  
Elisson A. Batista<sup>3</sup>, Thaís K. de Lima Rezende<sup>4</sup>, Éder V. Guimarães<sup>5</sup>,  
Ricardo S. Silva<sup>5</sup> and Noelio O. Dantas<sup>1</sup>

1 Laboratory of New Nanostructured and Functional Materials, Physics Institute,  
Federal University of Alagoas, Maceió, AL, Brazil

2 Programa de Pós-Graduação da Rede Nordeste de Biotecnologia (RENORBIO),  
Federal University of Alagoas, Maceió, AL, Brazil

3 Physics Institute, Federal University of Uberlândia, Uberlândia, MG, Brazil

4 Chemical Institute, Federal University of Uberlândia, Uberlândia, MG, Brazil

5 Institute of Exact, Natural Sciences and Education (ICENE), Department of  
Physics, Federal University of Triângulo Mineiro, Uberaba, MG, Brazil

\*Address all correspondence to: [aniellechristineas@gmail.com](mailto:aniellechristineas@gmail.com)

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