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Weak ferromagnetism in Mn^{2+} doped Bi_2Te_3 nanocrystals grown in glass matrix

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ABSTRACT

We observed weak ferromagnetism in $Bi_{2-x}Mn_xTe_3$ nanocrystals grown in a glass matrix. Magnetization measurements at 5 K showed an increase in the coercive field that was proportional to Manganese concentration. Transmission Electron Microscopy images showed the formation of $Bi_{2-x}Mn_xTe_3$ nanocrystals with an average size of 5.0 nm. X-ray diffraction measurements revealed the hexagonal structure of the $Bi_{2-x}Mn_xTe_3$ nanocrystals and confirmed the replacement of Bi^{3+}-ions with Mn^{2+}-ions at different x_{Mn}-concentrations. Electron Paramagnetic Resonance of these Mn-doped Bi_2Te_3 nanocrystals showed six lines associated with the S = 5/2 spin half-filled *d*-electrons that are characteristic of Mn^{2+} ions.

1. Introduction

Transition metal (TM) doped nanocrystalline semiconductor structures have attracted great interest due their unique properties caused by exchange interactions between the *sp*-band electrons in the semiconductor with the *d*-electrons of the TM ions [1–3]. The optical, structural, and magnetic properties of these materials are controlled by the size, shape, and TM-concentration of the crystalline nanostructures, with potential applications in solar cells [4], medicinal drugs [5], and quantum computing [6]. These materials are called dilute magnetic semiconductors (DMS), in which a small number of spins trapped in semiconductor structures can be manipulated by external magnetic fields, that may allow applications in future spintronic devices [7,8].

Ferromagnetism (FM) in DMS nanostructures such as $Cd_{1-x}Mn_xS$ [9], $Sn_{1-x}Fe_xO_2$ [10], InSe: Co [11] and $Zn_{1-x}Cr_xS$ [12] results from *sp-d* exchange interactions. Theoretical models of the DMS crystalline zinc-blend structure $Ga_{1-x}Mn_xAs$ show that the ferromagnetic ordering results from the substitution of TM ions (Mn) in place of cations in the crystal structure (Ga) [13]. Therefore, Mn-doped Bi_2Te_3 NCs grown in a glass matrix could be candidates for manifold applications given that the transparent host material is robust and provides excellent stability for the DMS nanomaterials [14]. In literature, is report the ferromagnetism in DMS $Bi_{2-x}Mn_xTe_3$ nanoplates [15] and crystals [16–19] results from the substitution of Bi^{3+} ions with Mn^{2+} ions, allowing possible applications in the manufacture of magneto-optic devices.

In this paper, we investigated the magnetic properties of DMS $Bi_{2-x}Mn_xTe_3$ NCs in glass matrix by the fusion method in function of x_{Mn}-concentration. The borosilicate glass is an amorphous matrix that generally exhibits a diamagnetic behavior. DMS $Bi_{2-x}Mn_xTe_3$ NCs embedded in host glass show a ferromagnetism behavior, being attributed by incorporation of the Mn^{2+} ions in place of Bi^{3+} ions in the crystalline structure of Bi_2Te_3 NC. DMS $Bi_{2-x}Mn_xTe_3$ NCs evidence both magnetic ordering and topological states within the same material and have the potential for development in future nanodevices with applications in spintronics. To study these novel properties of the DMS $Bi_{2-x}Mn_xTe_3$ NCs

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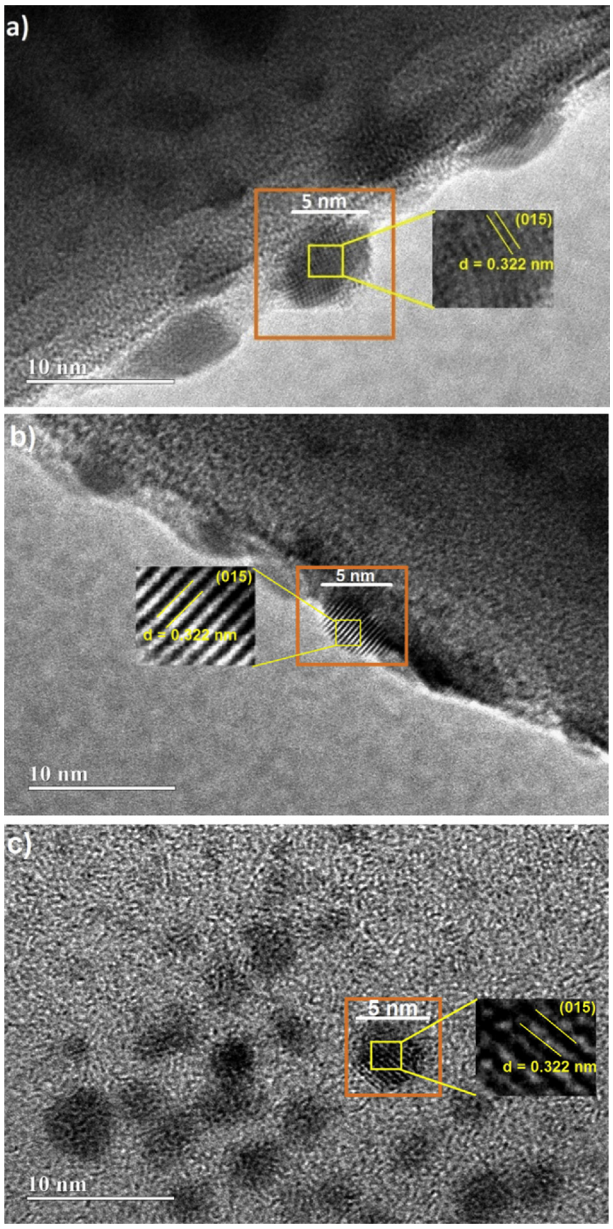

Fig. 1. TEM images of $Bi_{2-x}Mn_xTe_3$ nanocrystals for x_{Mn}-concentration of (a) 0.00, (b) 0.05, and (c) 0.10 with size around of 5.0 nm. The interplanar distance correspond the crystalline plane (015).

embedded in a borosilicate glass host the synthesized samples were investigated by techniques of Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Electron Resonance Paramagnetic (EPR), and Magnetization.

2. Experimental details

DMS $Bi_{2-x}Mn_xTe_3$ NCs were synthesized by the fusion method in a glass matrix with the following nominal composition: $45SiO_2 \cdot 30Na_2CO_3 \cdot 5Al_2O_3 \cdot 20B_2O_3$ (mol %). The DMS $Bi_{2-x}Mn_xTe_3$ NCs were prepared by adding $2Bi_2O_3$ and 1Te as a weight percent of the glass matrix mass and nominal x content of Mn (x = 0, 0.05, and 0.10) as a function of bismuth concentration. All chemical reagents used in the synthesis process were nearly 99% pure and procured from the Sigma-Aldrich company. The powder mixture of the glass and NC precursors were mixed together and melted in an alumina crucible at 1200 °C for 30 min and cooled at room temperature. The resulting samples were then thermally treated at 500 °C for 10 h to provide the energy and time needed for the diffusion of the Bi^{3+}, Te^{2-}, and Mn^{2+} ions throughout the host matrix and the growth of DMS $Bi_{2-x}Mn_xTe_3$ NCs. Finally, the samples were characterized by TEM, XRD, EPR, and SQUID Magnetometry. Transmission Electron Microscopy micrographs were acquired with a JEM-2100 (JEOL, 200 kV) and used to investigate the formation, size, shape, and growth of the heat-treated DMS $Bi_{2-x}Mn_xTe_3$ NCs. The crystalline structure of the nanostructures was revealed by X-Ray Diffraction patterns obtained at room temperature with an XRD-6000 (Schimadzu) using the Cu-$K_{\alpha 1}$ radiation line. Magnetic electronic states of the manganese ions in the structure of the magnetic doped NCs were investigated at room temperature via EPR techniques using an ST ER4102 spectrometer (Bruker EMX spectrometer) with a rectangular cavity, microwave frequency of 9.75 GHz (X-band), microwave power of 20 mW, and 100 kHz field modulation. The magnetization measurements were performed using a SQUID sensitive Magnetic Property Measurement System (MPMS3 by Quantum Design).

3. Results and discussion

Transmission Electron Microscope images show the formation of $Bi_{2-x}Mn_xTe_3$ NCs in the glass matrix heated at 500 °C for 10 h (Fig. 1, x_{Mn}: (a) 0.00, (b) 0.05 and (c) 0.10). The nanocrystals have an average size of 5.0 nm and an interplanar distance of 0.322 nm that is attributed to the hexagonal phase of the crystalline plane (015) of Bi_2Te_3 [14]. The average size and interplanar distance of the $Bi_{2-x}Mn_xTe_3$ nanocrystals were analyzed by

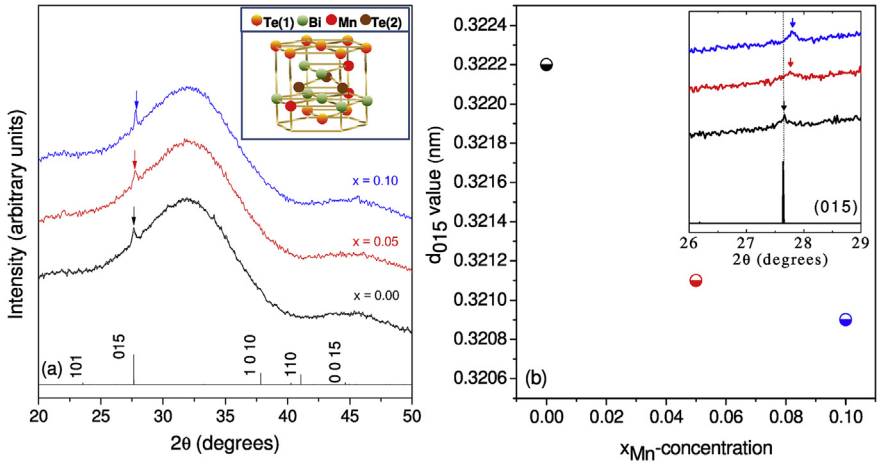

Fig. 2. (a) XRD pattern of $Bi_{2-x}Mn_xTe_3$ nanocrystals embedded in borosilicate glass matrix with the presence of (015) peak characterized of the hexagonal structure (inset) and (b) The magnitudes of the observed shift with applying Bragg's law to the (015) peaks for different x_{Mn}-concentration.