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Magnetic, electric and crystallographic properties of diluted magnetic $InSe_{(1-x)}Fe(Co)_x$ semiconductor

Karimat El-Sayed [a,*], Z.K. Heiba [a,b], K. Sedeek [c], H.H. Hantour [c]

[a] X-Ray Diffraction Unit, Physics Department, Faculty of Science, Ain Shams University, Egypt
[b] Department of Physics, Faculty of Science, Taif University, 888 Taif, Saudi Arabia
[c] Physics Department, Faculty of Science, Girls Branch, Al-Azhar University, Egypt

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ABSTRACT

The structural, magnetic and electric properties of Fe or Co doped InSe system has been studied. The X-ray diffraction patterns of the doped samples indicate the presence of $InSe_{0.9}Fe_{0.1}$ or $InSe_{0.9}Co_{0.1}$, together with a non-magnetic minor phase of In_4Se_3. The $InSe_{0.9}Fe_{0.1}$ system is ferromagnetic with high Curie temperature of 870 K. In contrast, the $InSe_{0.9}Co_{0.1}$ system is antiferromagnetic with different Neel temperatures. Crystallite sizes of the different phases show anisotropy along different crystallographic directions, they vary from 9 to 40 nm. The largest size is along the [0 0 *l*] direction normal to the staking layers planes. The random model was applied to explain the origin of ferromagnetic properties of Fe doped sample. The non-magnetic phase In_4Se_3 played a major role in the high temperature ferromagnetic properties of $InSe_{0.9}Fe_{0.1}$ and the polarization of magnetic spins. The electrical conductivity increased by an order of magnitude of 2 and 1.5 in the case of Fe and Co doped samples, respectively, suggesting that the incorporation of Fe or Co creates new band configuration and hence a modification of electronic density of states of the samples studied. The anomaly in the electrical properties after doping with Fe or Co may suggest that these doped samples may be used as spintronics materials.

1. Introduction

There is an increasing interest in the III–VI materials, which have applications in optoelectronic, photovoltaic industries, and photo electrochemical solar cell devices [1]. Some solar cell devices perform efficiency of 16.4% [2]. The materials also draw attention for their switching and memory effects [3]. InSe is an n-type semiconductor, belonging to the III–VI layered semiconductor family [4]. It has a direct optical band gaps in the range of 1.42–1.62 eV, and indirect band gaps varying from 0.83 to 1.29 eV [5]. It has a potential application as an absorber layer in photovoltaic devices [6]. Its high absorption coefficient as well as its optimum energy band gap, makes it suitable for solar energy conversion [7]. The structure has strong covalent bonding within the layer planes and weak Vander Waals bonding between planes inducing easy cleavage [8].

Diluted magnetic semiconductors (DMSs) are semiconductors to which typically small percentage of a magnetic impurity has been intentionally introduced [5]. They attracted considerable attention forming a class of materials with both semiconducting and magnetic properties. DMS materials have wide application prospects in spintronic devices, which simultaneously exploit the charge and spin properties of electrons. Accordingly, the search for room temperature ferromagnetic DMS materials is in progress in recent years, and many such materials were reported [9]. It is widely expected that new functionalities for electronics and photonics are produced if the injection, transfer, and detection of carrier spin can be controlled at room temperature [10].

A successful operation of spintronic devices requires more than ferromagnetic semiconductor. It requires the support of spin-polarized transport so that spin-polarized charge carriers can be injected into a non-magnetic semiconductor [11]. There are two major criteria for selecting the most promising semiconductor spintronic materials. First, the ferromagnetism is retained to practical temperatures (300 K), and second, it is applicable in an existing technology [12]. Until now, no work has been carried out on InSe as modified by incorporating magnetic atoms, namely Fe or Co; thus, their classification as diluted magnetic semiconductors with spintronic character is still to be determined. In the present work, structural, magnetic and electrical properties of InSe doped with Fe or Co has been investigated. The objective is twofold: (i) identify the best conditions for preparing $InSe_{1-x}M_x$ (M for Fe or Co and $x = 0.0, 0.1$), and (ii) correlate the magnetic and electrical properties of doped samples with its microstructures characterization.

* Corresponding author. Tel.: +20 2 22601742, fax: +20 2 26842123.
E-mail address: elkarimat@yahoo.com (K. El-Sayed).

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2. Experimental

2.1. Syntheses

InSe, $InSe_{0.9}Fe_{0.1}$ and $InSe_{0.9}Co_{0.1}$ compounds were prepared by solid-state reaction techniques, using very highly pure elements (99.999%). The proper amounts of In, Se, Fe and Co weighed on a sensitive microbalance. The steps of the preparation process are as follows:

(i) The proper amount of elements were mixed together and then grounded in a mill for 60 min in the presence of argon gas, then placed in a cleaned silica tube which was then evacuated to 10^{-4} Torr.
(ii) Heating up at 1000 °C (±5 °C) for 10 h, then decreasing the heating temperature to 660 °C, for 7 days. The molten mass was occasionally, shaken to ensure complete mixing of the constituents.
(iii) The molten mass allowed to cool down to room temperature to get an ingot. These steps were repeated for the samples of InSe, $InSe_{0.9}Fe_{0.1}$ and $InSe_{0.9}Co_{0.1}$. As the melting point of Fe and Co is very high (1535 °C and 1495 °C, respectively), substitution by diffusion through the as prepared binary systems are used.

2.2. Measurements

X-ray diffraction data were collected using a Philips X'pert MPP diffractometer with a goniometer type PW3050/10. Rietveld's powder diffraction profile-fitting technique was employed for refining the structure and microstructure parameters obtained from the different samples.

The magnetic properties were investigated by using the squid magnetometer. Oxford Cryostat connected to an automatic temperature controller and a 617 Kiethley electrometer were used to measure the electrical conductivity. Flat samples cut from the ingot perpendicular to the axis parallel to the axis of the test tube, the flat cut was then wet polished and then prepared as disk of 1–2 mm thickness. Good contact achieved by painting the opposite faces of the sample by carbon dag. The ohmic behavior of the metallic contact was characterized by measuring the (I–V) characteristics. The DC conductivity is calculated from the formula:

$$\sigma = \left(\frac{1}{R}\right)\left(\frac{L}{A}\right) \quad (1)$$

where σ is the DC conductivity of the sample, R is its resistance, L is the distance between the two electrodes, and A is the cross-section area of the applied electrode.

3. Results and discussion

3.1. XRD and microstructure analysis

Fig. 1 shows the diffraction patterns of the InSe, $InSe_{0.9}Fe_{0.1}$ and $InSe_{0.9}Co_{0.1}$ samples. It can be seen that the InSe sample is a single phase matching the ICDD card no (34-1431) with the hexagonal space group $P6_3/mmc$. For the samples modified by Fe or Co, two phases are identified; the main phase (InSe) and a minor phase

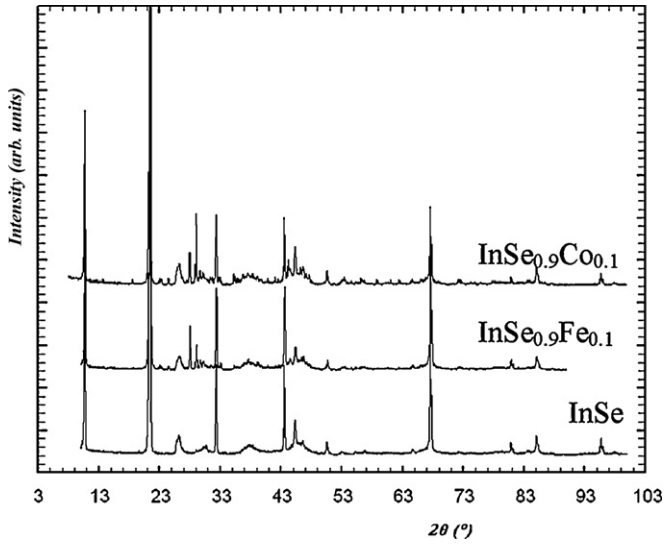

Fig. 1. The diffraction patterns of InSe, $InSe_{0.9}Fe_{0.1}$ and $InSe_{0.9}Co_{0.1}$ samples.

Table 1
The refined lattice parameters (a and c) (Å), Z-fractional coordinate of In and Se, unit cell volume V (Å^3), the anisotropic crystallite size D (nm), the microstarin e and the reliability factors: R_{wp} and R_p (%) obtained from Rietveld analysis of the powder XRD patterns of all the samples.

	InSe	$InSe_{0.9}Fe_{0.1}$	$InSe_{0.9}Co_{0.1}$
a (Å)	4.0037 (14)	3.9915 (15)	4.0022 (12)
c (Å)	16.644 (23)	16.640 (15)	16.6440 (13)
V (Å^3)	231.06	229.59	230.97
Z (In)	0.1679 (22)	0.167 (20)	0.168 (72)
Z (Se)	0.0900 (32)	0.0903 (27)	0.0921 (14)
$D_{(h00)}$ (nm)	21	19	14
$e_{(h00)}$	15×10^{-5}	0.003	0.002
$D_{(00l)}$ (nm)	39.5	47.5	39.8
$e_{(00l)}$	83×10^{-5}	84×10^{-4}	28×10^{-4}
$\langle D\rangle_{(10l)}$ (nm)	10.0	11.0	10.0
$e_{(10l)}$	0.0172	0.019	0.020
InSe (%)	100	91.5	93.5
In_4Se_3 (%)	0	8.5	6.5
R_{wp} (%)	16	17	18
R_p (%)	13	13	14

(In_4Se_3) matching ICDD card no (83-0039) with the orthorhombic space group $Pnnm$.

During Rietveld analysis, a preferred orientation along the [0 0 l] direction as shown in Tables 1 and 2, which could not be avoided during measurements in spite of back-loading and fine grinding the sample. This preferred orientation was mainly due to the presence of the stacking layers aligned on top of each other along the [0 0 l] direction [4]. Fig. 2 shows the staking layers of the (0 0 l) planes. Fig. 3 is a zoom-in part of the InSe pattern where anisotropic broadening is obvious for different peaks. For example the broadenings for the (1 0 l) reflections is due to the high strain (0.0175) and the smaller crystallite size (10 nm) along (1 0 l] compared with the other crystallographic direction in the structure as shown in Tables 1 and 2.

The structural parameters obtained from Rietveld refinement for the $InSe_{1-x}Fe_x(Co_x)$ are shown in Table 1. Fig. 4 shows the profile fitting resulting from Rietveld refinement. During analysis, the only trial that gives reasonable good R-factors is by accommodating the magnetic atoms substituting for Se in InSe as intended during preparation. With the incorporation of Fe or Co, small changes in unit cell parameters and fractional atomic coordinates of the InSe phase are also detected. This is another proof that the Fe or Co is incorporated in the InSe phase only.

Table 2 shows large anisotropy values in crystallite size and microstrains along different crystallographic directions, especially along the (1 0 l] direction. This anisotropy results in rather large

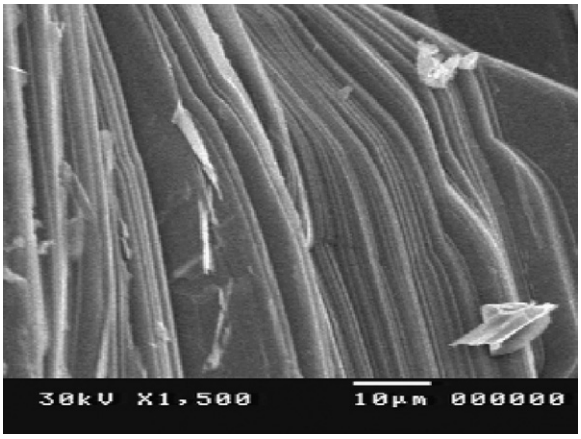

Fig. 2. The scanning electron micrograph of $InSe_{0.9}Fe_{0.1}$ showing deformed stacking layers.