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Defect-induced room temperature ferromagnetism in mechanically milled nanocrystalline In_2O_3 powder

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ABSTRACT

Although bulk In2O3 is diamagnetic, recent studies reported that In_2O_3 nanowires and thin *films how ferromagnetic* behavior at room temperature due to the defects induced during the preparation. This research work shows that mechanical milling is an effective approach to induce defects in ground materials. Structural, optical and magnetic properties of as-received and milled In_2O_3 powders have been studied. Magnetic characterization showed that milled In_2O_3 for 40 h became totally ferromagnetic with a hysteresis loop at room temperature; having a saturation magnetization of 0.05 emu/g due to intrinsic defects *induced during* milling process. XRD analysis confirms the absence of any impurities or secondary phases which can induce ferromagnetism ordering.

1. Introduction

Diluted magnetic semiconductors (DSMs) have been investigated extensively as potential candidate for spintronics, because of their unique properties where a semiconducting oxide becomes ferromagnetic (small magnetization in the range of few memu/g) by doping the original oxide by a foreign metal (usually transition metal or/and rare earth). Many doped oxides have been investigated as DMSs, such as ZnO [1–3], TiO_2 [4], HfO_2 [5], etc. Similarly, In_2O_3 has been doped with various metals, but most of the reported studies are related to the electrical, optical and gas-sensing properties as thin films [6,7]. Bulk In_2O_3 oxide is known as diamagnetic, but recent reports showed room–temperature ferromagnetism (RTFM) in un-doped In_2O_3 films. Tien et al. observed a *ferromagnetic behavior in un-doped In_2O_3 nanowires attributed to* the intrinsic defects [8]. Sun et al. also reported that oxygen and indium vacancies induced ferromagnetism in n- and p-type In_2O_3 thin films [9]. *Some research* works in the literature have reported the appearance of ferromagnetism for un-doped and non-magnetic oxides such as ZnO, TiO_2, CeO_2 [10–12]. The origin of RTFM remains controversial. Both experimental and fundamental studies suggested that the origin of ferromagnetism in un-doped non-magnetic oxides is due to intrinsic defects mainly related to metal or oxygen vacancies.

The aim of this research work consists on using mechanical milling for inducing RTFM in diamagnetic In_2O_3 bulk powder. It is important to highlight that particles refinement, creation of defects and lattice strain can be achieved by milling. Micro-sized In_2O_3 powder has been milled in a planetary ball mill with zirconia grinding tools (bowl, lid and balls) in order to avoid any contamination with magnetic impurities during the sample preparation. Magnetic measurement showed that In_2O_3 powder becomes ferromagnetic after 40 h of milling associated with the defects induced by milling. A detailed characterization by XRD, SEM, UV–vis and VSM will be presented.

2. Experimental part

Commercial In_2O_3 powder (purity: 99.9%) has been milled in a planetary ball mill for 40 h and balls-to-powder mass ratio fixed to 10:1. Zirconia grinding medium has been used in order to avoid any contamination with magnetic impurities during milling. Structural characterization was performed using Bruker D8

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Discover diffractometer (θ–2θ) equipped with Cu-Kα radiation (λ=1.5406 Å). The average crystallites size is calculated from the Williamson-Hall Eq. (1):

$$B\cos\theta=\frac{K\lambda}{D}+4\epsilon\sin\theta \quad (1)$$

where D is the coherent scattering length (crystallite size); K is a constant depending on the shape of particles (crystallites) usually taken as 0.9; B the integral width of the sample (in rad) and ε is the inhomogeneous internal strain (in %). Morphological observations were carried out using Sigma Carl Zeiss field emission scanning electron microscopy (FESEM). Magnetic characterization was carried out using a vibrating sample magnetometer (VSM) type MicroMag Model 3900. Perkin Elmer Lambda 950 spectrophotometer was employed to measure the absorption spectra over the range 300–600 nm.

3. Results and discussion

Fig. 1 shows the x-ray diffraction patterns for In_2O_3 as-received and 40 h milled powders. The pattern of un-milled In_2O_3powder shows a series of strong and narrow peaks characteristic for high crystalline powder, and indexed within the body centered cubic *bcc*-phase of In_2O_3 (bixbyite-type, space group Ia3) in agreement with JCPDS card no. 06-0416. After milling, the diffraction peaks become *broader and* their relative intensity decreases drastically (by almost three fold), which is a typical behavior of materials after milling. This is attributed usually to the reduction of crystallite size (grain refinement) and the lattice strain due to the defects occurring simultaneously during milling.

The lattice constant can be estimated using the following Eq. (2):

$$a=\frac{\lambda\sqrt{h^2+k^2+l^2}}{2\sin\theta} \quad (2)$$

The value obtained for milled powder (a=10.10 Å) is slightly higher than the standard value of 10.09 Å (JCPDS card no 06-0416), which is due may be to the effect of milling leading to the expansion of the lattice.

Moreover, no additional peaks can be detected for milled powder, suggesting that there is no secondary phase or impurities generated from the grinding medium.

*The average crystallite size and microstrain are obtained from Williamson-Hall method (*Fig. 1 b and c*) for the as received and milled sample. The values of crystallite size are respectively* 60 nm *and* 22 nm, *while the microstrain is* 0.63% *and* 1.57%.

SEM images of powders before and after milling are displayed in Fig. 2. It is clear that un-milled powder shows undefined shaped particles with broad size distribution. After milling, the particles tend to be more spherical in shape with narrow size distribution. In addition, it can be observed the formation of agglomerates of cauliflower-like morphology, composed of very fine particles within the nanoscale range. Thus, it can be concluded that milling for 40 h has led to an important microstructural modification; i.e. particle size reduction and accumulation of microstrain.

Fig. 3-shows UV–vis absorption spectra for as-received and 40 h milled powders. As expected, both powders show a good absorption in the region 300–350 nm. It can be seen also that there is a shift to higher wavelengths and a decrease in the absorbance for milled powder; which can be associated with the reduction of the crystallite size induced by milling. The optical band gap value was estimated by plotting $(\alpha h\nu)^2$ as a function of photon-energy ($h\nu$) using Tauc relation [13]. The linear intercept with the $h\nu$-axis gives the value of the band gap energy (E_g). The determined values are

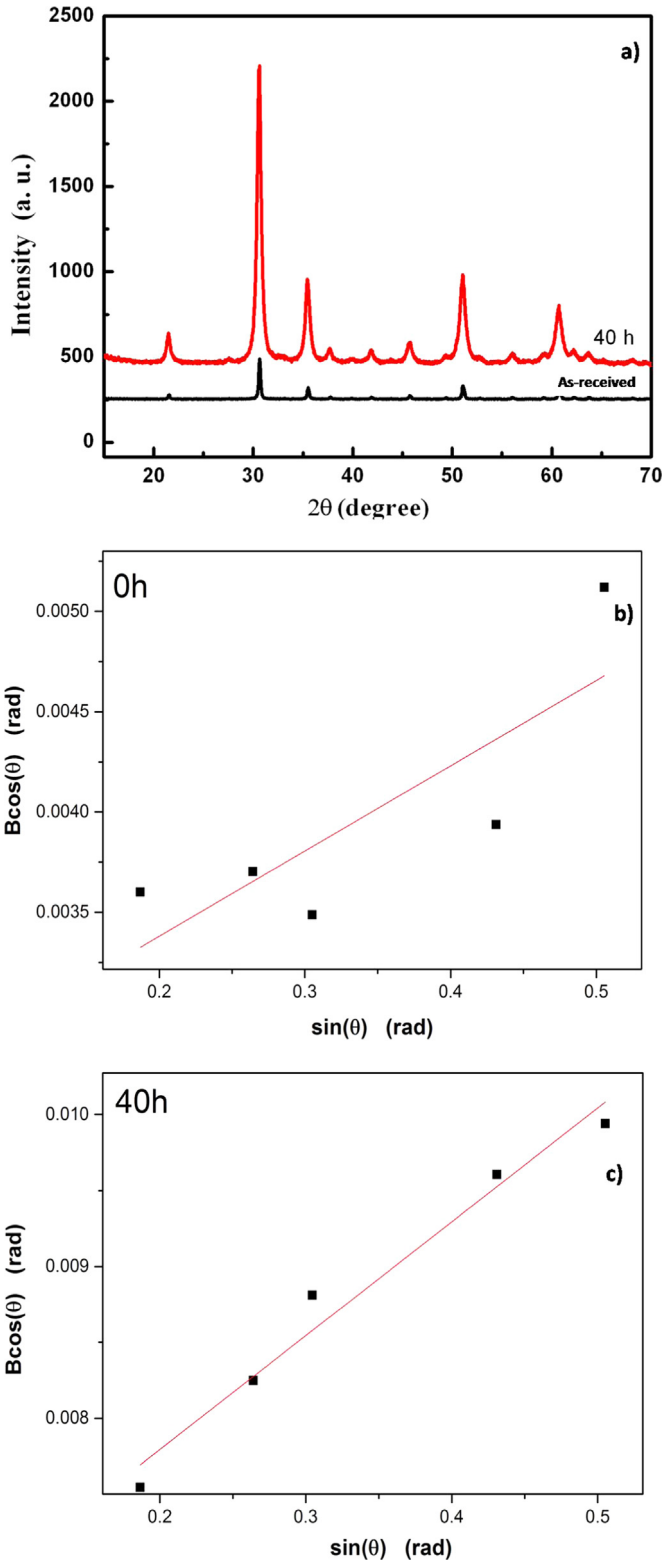

Fig. 1. (a) XRD patterns of In_2O_3 as-received and 40 h milled powders. (b) Williamson-Hall plot for the sample as received and (c) milled for 40 h.

3.88 and 3.91 eV (Fig. 3-b) for as-received and milled powders, respectively. *The value of* E_g is found to increase slightly after milling due to crystallite size reduction leading to a shift to the shorter wavelengths. This is in good agreement with the well-known *property of nanostructured* semiconductors: the energy band gap increases with decreasing the crystallite size due to