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Effect of argon annealing method on structural and ferromagnetic properties in Fe-doped SnO_2 powders

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Abstract. Nanocrystalline powders of Fe-doped SnO_2 ($Sn_{1-x}Fe_xO_2$) (x = 0.00, 0.01, 0.03, 0.05) were synthesized by a hydrothermal method. The powders were calcined in argon atmosphere at 600 ºC for 2 h, causing phase transition from diamagnetic and weak ferromagnetic behavior to a ferromagnetic state. No trace and other magnetic impurity phases was detected in the samples with Fe content up to 3%. The magnetic properties of the calcined samples of Fe-doped SnO_2 exhibited ferromagnetic behavior at room temperature with highest magnetization values of 22.54, 383.47 and 434.07 memu/g at 15 kOe for x = 0.01, 0.03 and 0.05, respectively. The room temperature ferromagnetism of samples originated from oxygen vacancies that occurred in the argon calcination process. In particular, oxygen vacancy shows a significant role in ferromagnetic coupling corresponding to *F*-center interaction.

Introduction

SnO_2 as a n-type semiconductor with a wide bandgap (E_g = 3.6 eV) has elicited much interested due to transparency and sensitivity to its reducing gases. SnO_2 as a n-type semiconductors have a wide range of applications in gas sensors [1], optoelectronic devices [2], dye-based solar cells [3], and secondary lithium batteries electrode materials [4]. Recently, transition-metal doped semiconducting oxides have attracted much attention due to their room temperature ferromagnetism. This kind of material called diluted magnetic semiconductors (DMSs), is of great interest for spintronic applications [5]. Because of its excellent electronic and optical properties, the performance of SnO_2 has been improved considerably by doping with Fe [6], Co [7], Ni [8] or Mn [9]. Some studies have reported that the calcination process had effects on the ferromagnetic behaviour of the transition metal doped SnO_2 system [10, 11]. Therefore, it is important to study the influence of the calcination process on ferromagnetic properties of Fe-doped SnO_2 under an atmosphere that is lacking in oxygen.

In this study, Fe-doped SnO_2 ($Sn_{1-x}Fe_xO_2$) nanocrystalline powder was prepared with x = 0.00, 0.01, 0.03 and 0.05 by a hydrothermal method, and the prepared samples of powder were calcined at 600 ºC under argon atmosphere for 2 h. The calcined samples were then characterized for crystal phase identification by X-ray diffraction (XRD). The particle size and morphology were characterized by

transmission electron microscopy (TEM). The magnetic measurements were performed at room temperature using a vibrating sample magnetometer (VSM).

2. Experimental procedure

In this study, Fe-doped SnO_2 nanocrystalline powder was synthesized by a hydrothermal method. $SnCl_2 \cdot H_2O$ (99.99%, Aldrich) and $Fe_3O_9 \cdot 9H_2O$ (99.99%, Aldrich) were used as initial materials. The precursor materials were dissolved in 15 ml deionized water and 5 ml ethanol was added with continuous stirring at 50 ºC for 3 h and then adjusted to pH 11 with sodium hydroxide (NaOH). The homogeneous solution was transferred into a Teflon-lined stainless-steel autoclave, sealed and maintained at 180 ºC for 24 h. After the autoclave was cooled to room temperature, the precipitate was collected and washed several times with deionized water and ethanol separately. Then the product was dried by vacuum oven at 70 ºC for overnight. The sample powder was calcined at 600 ºC under argon atmosphere for 2 h. The calcined samples were characterized for crystal phase identification by powder X-ray diffraction (XRD) using a Philips X-ray diffractometer (PW3710, The Netherlands) with CuKα radiation (λ = 0.15406 nm). The particle size and morphology of Fe-doped SnO_2 samples were characterized by transmission electron microscopy (TEM) (Hitachi H8100 200 kV). The magnetic measurements were performed at room temperature using a vibrating sample magnetometer (Versa Lab VSM, Quantum Design).

3. Results and discussion

The XRD patterns of the SnO_2 and $Sn_{1-x}Fe_xO_2$ (x = 0.00, 0.01, 0.03, 0.05) samples are shown in figure 1(a). The SnO_2 and $Sn_{1-x}Fe_xO_2$ samples exhibit peaks that correspond to the (110), (101), (200), (211), (220), (310), (112), (301) and (321) planes with the tetragonal structure when compared to the standard data (JCPDS No. 41-1445). The XRD patterns of the SnO_2 and $Sn_{1-x}Fe_xO_2$ with x = 0.01 and 0.03 samples with no contaminated phase or magnetic impurity phase are detected. The exception is the sample of x = 0.05, which reveals an extra peak at 2θ ~ 32.86, 37.15 and 50.29 which can be an index as the Fe_2O_3 [12]. The detection of contaminated phase in the structure of this sample, reveals that of the Fe ions cannot completely insert into the position of the Sn^{4+} ions within the lattice. Therefore, the synthesis of $Sn_{1-x}Fe_xO_2$ by this hydrothermal method is limited by the solubility Fe ions instead of Sn^{4+} ions within the lattice being less than 5% [13]. After the samples were calcined in argon, the samples did not demonstrate a contaminated phase of Fe_2O_3 and other compounds in the structure (figure 1(b)). This indicates that calcining at 600 ºC under argon provides reaction conditions that allows Fe^{3+} ions to be inserted in the structure of SnO_2. Moreover, after being calcined, the samples showed intensity increased and decrease peak width, which indicated more crystalline properties [14, 15].

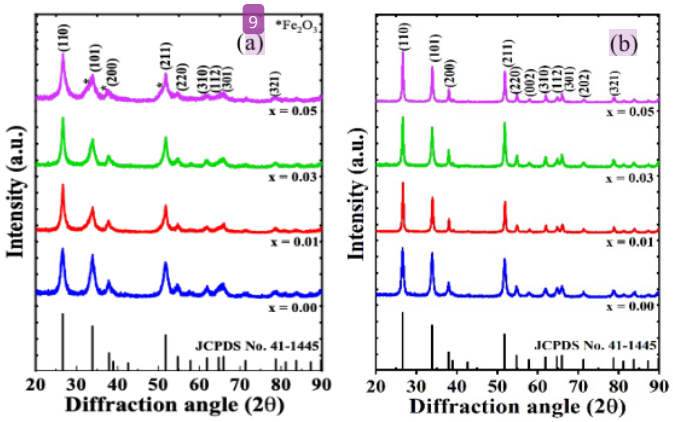

Figure 1. XRD patterns of (a) pre-calcined $Sn_{1-x}Fe_xO_2$ and (b) $Sn_{1-x}Fe_xO_2$ were calcined in argon.

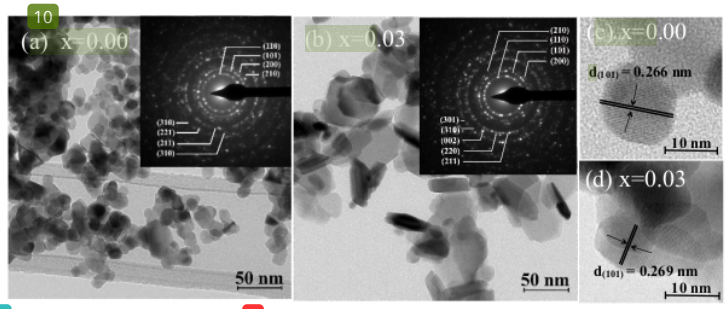

Figure 2. (a) and (b) are TEM images with corresponding selected area electron diffraction (SAED) patterns (inset), (c) and (d) are high-resolution TEM images and lattice fringe of $Sn_{1-x}Fe_xO_2$ calcined in argon.

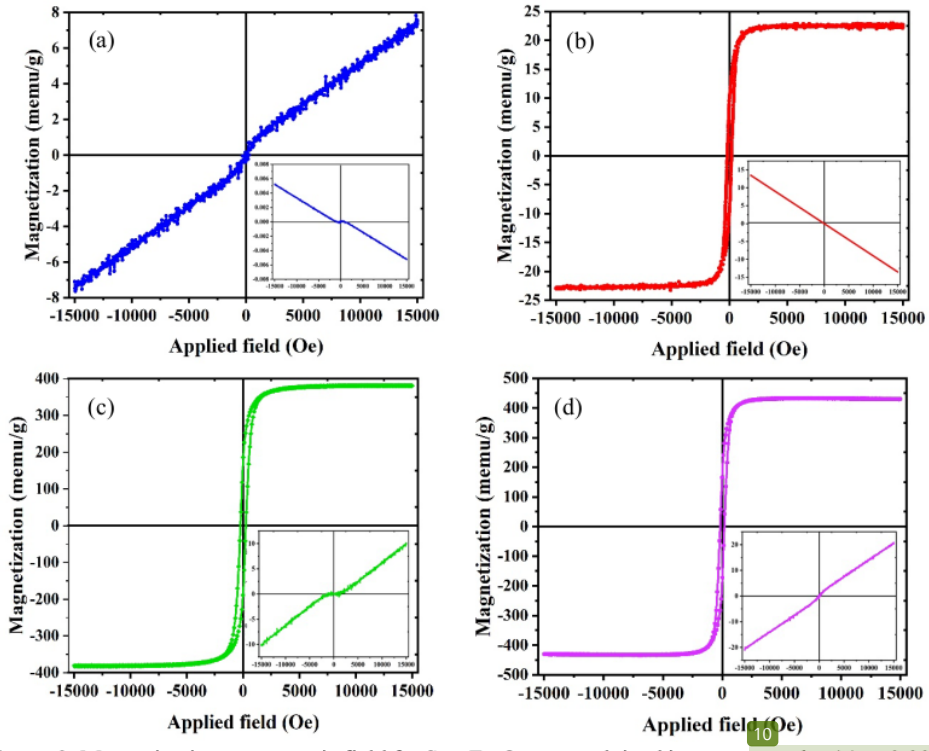

Figure 3. Magnetization vs magnetic field for $Sn_{1-x}Fe_xO_2$ were calcined in argon samples (a) x=0.00, (b) x=0.01, (c) x=0.03 and (d) x=0.05. Inset bottom right shows the magnetic behavior for pre-calcined samples.

The morphology of the SnO_2 and 3% Fe-doped SnO_2 calcined in argon were examined by TEM. Figure 2(a) and (b) reveal TEM bright field images with the corresponding selected area of electron diffraction (SAED) patterns of SnO_2 and 3% Fe-doped SnO_2 samples. TEM bright field images show the agglomerated nanoparticles with particle size ~15-23 nm. The SAED patterns of SnO_2 and 3% Fe-

doped SnO_2 samples in the inset of figure 2 reveal pure phase of tetragonal structure without magnetic impurity phases of Fe, Fe_2O_3 or Fe_3O_4, which is in agreement with the XRD results. The high resolution TEM images shown in figure 2(c) and (d) indicate the presence of the lattice fringe in the samples of SnO_2 and 3% Fe doped SnO_2. The lattice distance of 0.266 and 0.269 nm indicated in these figures corresponded to the (101) crystalline plane.

The field dependence of magnetization (M-H curve) of SnO_2 and $Sn_{1-x}Fe_xO_2$ samples obtained from VSM measurement at room temperature are shown in Figure 3. The SnO_2 sample (figure 3(a)) reveals weak ferromagnetic behaviour after the sample was calcined under argon. All of the samples doped with Fe exhibited ferromagnetic behaviour. The magnetization of Fe-doped SnO_2 samples increased with increasing concentration of dopant. In addition, after doped samples were calcined in argon, the magnetization value are also increased. The doped samples showed ferromagnetic behaviour at room temperature with magnetization values of 22.5, 383.5 and 434.1 memu/g and coercivity of 183.8, 239.9 and 171.6 Oe for x = 1, 3 and 5%, respectively. These results suggest that the Fe content and calcination process play an important role on magnetism for the SnO_2 nanocrystalline system. However, pre-calcined samples doped with 1% Fe exhibited diamagnetic properties while the samples doped with 3 and 5% Fe show weak ferromagnetic properties with the magnetization of 0.6 and 2.2 memu/g. The observed difference between ferromagnetism for pre-calcined and calcined samples is directly related to the concentration of defects in the crystal structure. Mehraj *et al*. [10] observed the annealing temperature on magnetization for SnO_2 nanoparticles to be 0.75 emu/g and found that the concentration of oxygen vacancies was important for magnetism. Therefore, the variation of magnetization in our samples is possibly attributed to their difference in oxygen content. The plausible mechanism, which has been proposed to explain ferromagnetism in SnO_2 is an *F*-center exchange interaction [6]. An electron trapped in oxygen vacancy constitutes an *F*-center, where the electron occupies and orbital with overlap the d-shells of nearest neighbors. In Fe-doped SnO_2 samples, we expect that Fe^{3+}-□-Fe^{3+} groups will share a common structure, where -□- denotes an oxygen vacancy [6]. Based on Hund's rule and the Pauli Exclusion Principle, spin orientations of the trapped electrons and two neighboring Fe ions should be parallel in the same direction, thus ferromagnetism is achieved.

4. Conclusion

Nanocrystalline powders of SnO_2 and Fe-doped SnO_2 as diluted magnetic semiconductors have been synthesized by a hydrothermal method. The calcination process in argon improved the ferromagnetism in the samples. All of doped samples showed ferromagnetic-like ordering with the highest magnetization of 434.1 memu/g at room temperature. The ferromagnetic-like ordering is due to the defect of oxygen vacancies in the structure. The magnetization value is directly related to the content of oxygen vacancies and crystallite size of SnO_2 nanocrystalline powder as a function of calcination process. This study showed that the ferromagnetism in SnO_2 compound can be improved by calcination process under an oxygen deficient atmosphere.

Acknowledgments

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