

Effect of argon annealing method on structural and ferromagnetic properties in Fe-doped SnO₂ powders

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Abstract. Nanocrystalline powders of Fe-doped SnO₂ (Sn_{1-x}Fe_xO₂) (x = 0.00, 0.01, 0.03, 0.05) were prepared by a hydrothermal method. The powders were calcined in argon atmosphere at 600 °C 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 calcined samples of Fe-doped SnO₂ revealed the room temperature ferromagnetism with highest magnetization values of 434.07 memu/g at 15 kOe for x = 0.05. 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.

1. Introduction

Nanostructures of tin dioxide (SnO₂), as a n-type semiconductor with a wide bandgap ($E_g = 3.6$ eV) has elicited much interested due to their potential for a wide range of applications [1-4]. Recently, diluted magnetic semiconductors (DMSs) have attracted much attention due to their novel magnetism and potential application in spintronics [5]. In addition, SnO₂ has an excellent electronic and magneto-optical properties. The performance of SnO₂ 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 SnO₂ system [10, 11]. Therefore, it is important to examine the effect of the calcination process on ferromagnetic behaviour of Fe-doped SnO₂ under an atmosphere that is lacking in oxygen.

In this study, Fe-doped SnO₂ (Sn_{1-x}Fe_xO₂) 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 °C under argon atmosphere for 2 h. The calcined samples were then examined for crystal structure via X-ray diffraction (XRD). The particle size and shape were characterized by transmission electron microscopy (TEM). The ferromagnetic measurements were performed at 300 K using a vibrating sample magnetometer (VSM).

2. Experimental procedure

Fe-doped SnO₂ nanocrystalline powders were prepared via a hydrothermal method. SnCl₂•H₂O (99.99%, Aldrich) and FeN₃O₉•9H₂O (99.99%, Aldrich) were used as initial materials. The precursor materials were dissolved in 15 ml deionized water (DI water) and 5 ml ethanol was added with continuous stirring at 50 °C for 3 h and then adjusted to pH 11 with sodium hydroxide (NaOH). The mixed solution was changed to a Teflon-lined stainless-steel autoclave with heating treatment at 180 °C for 24 h. The precipitates were picked by centrifugation and washed many times with DI water and ethanol separately, then dried the powders at 70 °C for overnight. The powders were calcined at 600 °C under argon atmosphere for 2 h. The crystal structure of the samples was examined by X-ray diffraction (XRD) using a Philips X-ray diffractometer (PW3710, The Netherlands). Size and shape of Fe-doped SnO₂ samples were performed by transmission electron microscopy (TEM) (Hitachi H8100 200 kV). The ferromagnetic behaviour was examined at 300 K by a vibrating sample magnetometer (Versa Lab VSM, Quantum Design).

3. Results and discussion

Figure 1(a) presents the XRD patterns of the SnO₂ and Sn_{1-x}Fe_xO₂ (x = 0.00, 0.01, 0.03, 0.05) samples. The diffraction peaks observed for the SnO₂ and Sn_{1-x}Fe_xO₂ samples can be indexed to the pure phase of tetragonal structure (JCPDS No. 41-1445). The XRD patterns of the SnO₂ and Sn_{1-x}Fe_xO₂ 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 Fe₂O₃ [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 Sn⁴⁺ ions within the lattice. Therefore, the synthesis of Sn_{1-x}Fe_xO₂ by this hydrothermal method is limited by the solubility Fe ions instead of Sn⁴⁺ 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 Fe₂O₃ and other compounds in the structure (figure 1(b)). This indicates that calcining at 600 °C under argon provides reaction conditions that allows Fe³⁺ ions to be inserted in the structure of SnO₂. Moreover, after being calcined, the samples showed intensity increased and decrease peak width, which indicated more crystalline properties [14, 15].

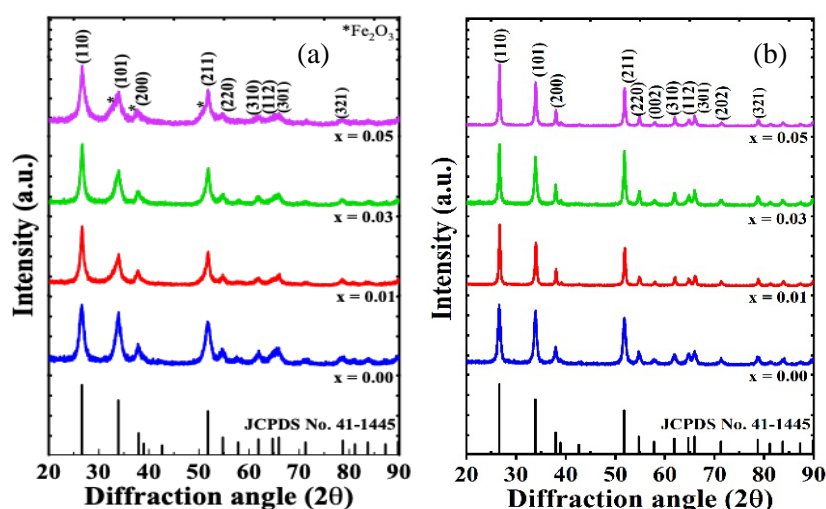


Figure 1. XRD patterns of (a) pre-calcined Sn_{1-x}Fe_xO₂ and (b) Sn_{1-x}Fe_xO₂ were calcined in argon.

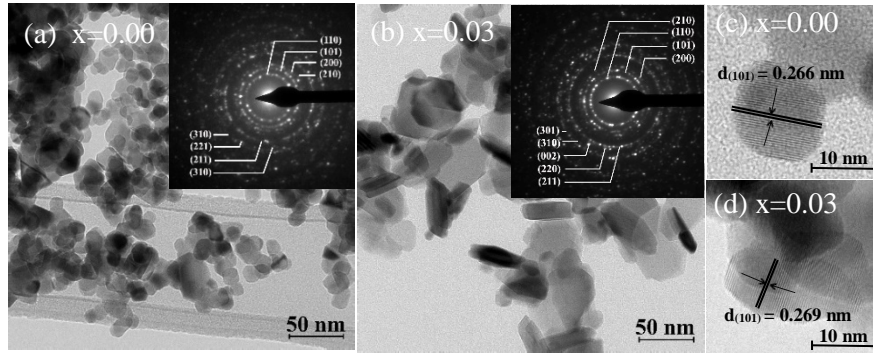


Figure 2. Images of Fe-doped SnO₂ samples: (a) TEM image with the corresponding SAED patterns (inset) for $x=0.00$, (b) TEM image with the corresponding SAED patterns (inset) for $x=0.03$, (c) and (d) HRTEM images of the samples.

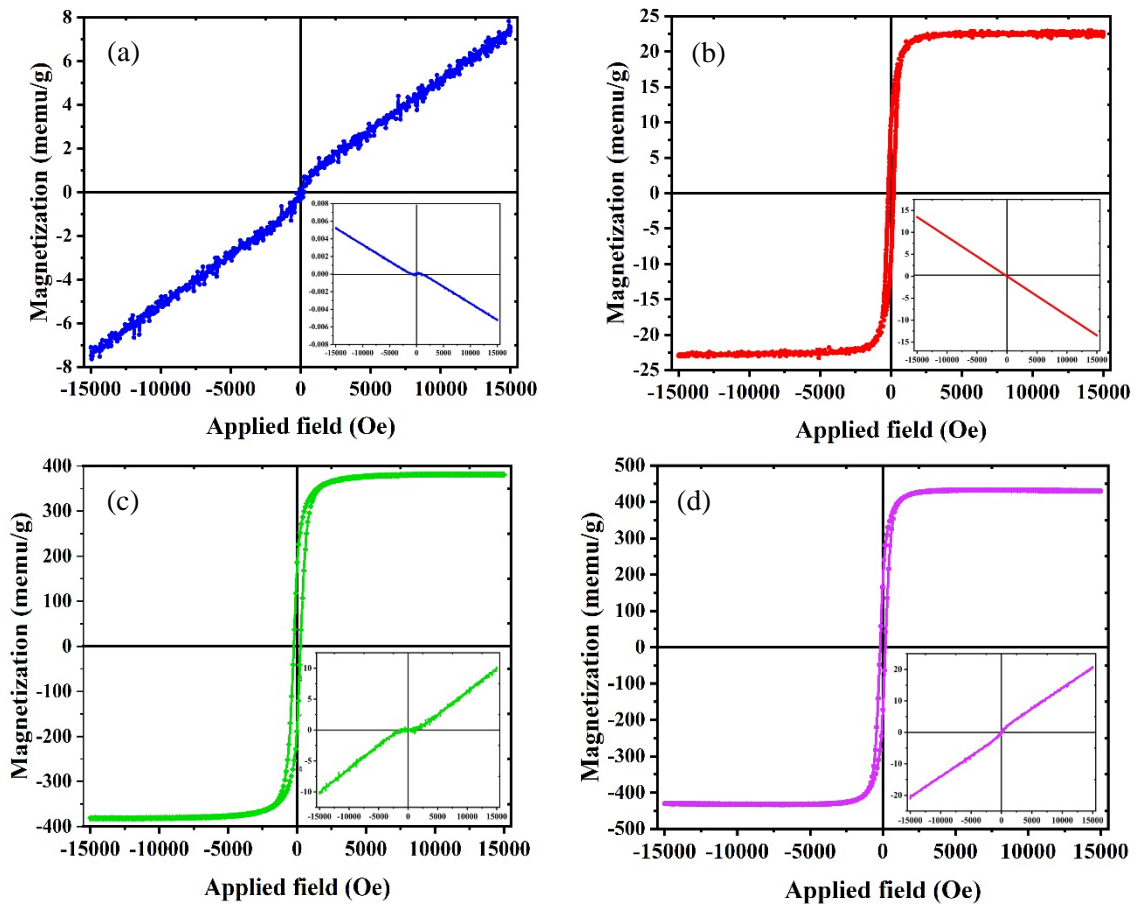


Figure 3. Magnetization vs magnetic field for Sn_{1-x}Fe_xO₂ samples were calcined in argon (a) $x=0.00$, (b) $x=0.01$, (c) $x=0.03$ and (d) $x=0.05$. Inset bottom right shows the magnetic behavior for pre-calcined samples.

The morphology and structure of the SnO₂ and 3% Fe-doped SnO₂ calcined in argon were examined by TEM with the corresponding selected area of electron diffraction (SAED) patterns as presented in figure 2. The particle size of the samples is ~15-23 nm. The SAED patterns of SnO₂ and 3% Fe-doped SnO₂ samples in the inset of figure 2 reveal pure phase of tetragonal structure without magnetic impurity

phases of Fe, Fe₂O₃ or Fe₃O₄, which corresponds to XRD results. The HRTEM images indicate the presence of the lattice fringe in the samples of SnO₂ and 3% Fe doped SnO₂ (figure 2(c) and (d)). The lattice distance of 0.266 and 0.269 nm indicated in these figures corresponded to the (101) crystalline plane.

Figure 3 presents the VSM measurement of field dependence of magnetization for SnO₂ and Sn_{1-x}Fe_xO₂ samples at room temperature. The SnO₂ sample (figure 3(a)) exhibits weak ferromagnetic behavior after the sample was calcined under argon. The magnetization curves of SnO₂ doped with 1, 3 and 5% Fe are shown in figure 3(b), (c) and (d), respectively. All of the samples doped with Fe exhibited ferromagnetic behaviour. The magnetization of Fe-doped SnO₂ 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 SnO₂ 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 SnO₂ nanoparticles to be 0.75 emu/g and found that the concentration of oxygen vacancies was important for magnetic behaviour. Therefore, the difference of magnetization values in Fe-doped SnO₂ samples is possibly allocated to their difference in oxygen content. The plausible mechanism, which has been proposed to explain ferromagnetism in SnO₂ is an F-center exchange interaction [6]. An F-center, an electron in the d-shells trapped in oxygen vacancy, where the electron occupies and overlap with nearest neighbors. We expect that the ferromagnetic coupling of Fe³⁺ and Fe³⁺ ions by an electron trapped in oxygen vacancy, thus ferromagnetism is achieved for Fe-doped SnO₂ samples [6].

4. Conclusion

Nanocrystalline powders of SnO₂ and Fe-doped SnO₂ as diluted magnetic semiconductors have been prepared 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 SnO₂ nanocrystalline powder as a function of calcination process. This study showed that the ferromagnetism in SnO₂ compound can be improved by calcination process under an oxygen deficient atmosphere.

Acknowledgments

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