

One step aqueous solution preparation of nanosize iron-doped tin oxide from $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ gel

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Abstract

Nanosized iron-doped tin oxide solid solution was prepared by mixing tin oxide gel $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ with a boiling solution of iron nitrate. The XRD data of the as-prepared and annealed sample at 773 K show that the patterns are indexed to the rutile phase without any trace of an extra phase. SEM and TEM results performed on different selected area of the samples reveal a homogeneous composition of 8 at.% of Fe content and a size of about 2 nm of the particles. The particles size was found to increase slightly with temperature; about 7 nm after 24 h at 773 K. Structural and magnetic results seem to indicate that Fe^{3+} substitute for Sn^{4+} on the as-prepared sample. The system presents some weak ferromagnetic character at room temperature.

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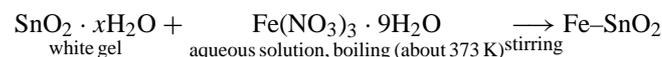
1. Introduction

Tin oxide, SnO_2 , solid solution has many industrial applications such as catalysis and sensing of toxic materials. M-doped tin oxides (where M: d-transition metals such as Fe, Co, Ni, Mn, etc.), the so-called dilute magnetic semiconductors (DMS), are the subject of recent interest for their promising spintronics applications since they have some degree of freedom for both the charge and the spin [1–5]. In general, the preparation of such doped oxides were carried out by two main methods. The first is the standard solid-state reaction method and is based on high-temperature synthesis. The second one is a low-temperature based technique and known as soft chemistry method or chimie douce. This latter method is preferred because other than being easy and cheap, also presents several advantages such as the formation of nanosized particles of pure phases associated with a high surface area, which can change their physical properties and improve their chemical reactivity. Recently, the solid solution of iron-doped tin oxide was prepared by different soft chemistry techniques as co-precipitation method [6]; mechanochemical processing [7]; and hydrothermal technique [8]. Different contents of iron were incorporated into the tin

oxide lattice. However, maximum solubility of iron in tin oxide lattice remains imprecise. We have recently demonstrated [9] that nanosized tin oxide powder can be obtained by a simple aqueous solution method at low temperature. The particles were found to agglomerate, in contrast with the wet tin oxide gel $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ that present a highly dispersed nanosized particles which could increase their reactivity as compared to their bulk counterpart powder. In the present study, the wet tin oxide gel was used to prepare iron-doped tin oxide nanoparticles at normal pressure and low temperature, also its structural and magnetic properties were reported.

2. Experimental

Iron tin oxide solid solution was obtained by mixing nanosized wet gel $\text{SnO}_2 \cdot x\text{H}_2\text{O}$, obtained according to the procedure recently reported [9], with a boiling solution of iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (from BDH Chemical Ltd., Poole, England).



This mixture of about 30% of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was stirred for 40 min (at $T = 373$ K), and soon after allowed to cool down slowly. The light-brown gel product obtained was washed with

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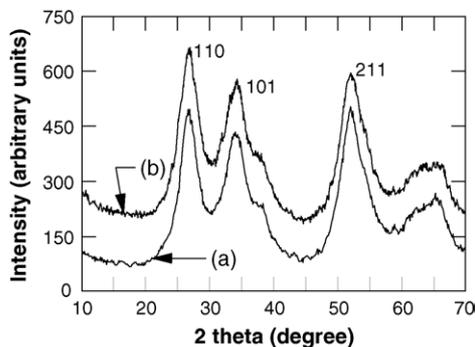


Fig. 1. XRD patterns of as-prepared: (a) SnO₂ and (b) Fe–SnO₂.

distilled water and dried at room temperature. The structure, microstructure and average size of the particles were analyzed with powder X-ray Philips 1710 diffractometer, JEOL JSM-5600LY scanning electron microscope with an Oxford EDAX detector, and JEOL 1234 transmission electron microscope. The magnetization was measured with a DMS 1660 vibrating sample magnetometer (VSM) in a magnetic field up to 13 kOe, and the temperature range 77–700 K. The VSM was calibrated using pure nickel ($M_s = 54.9$ emu/g). The Mössbauer spectrum was recorded at 300 K using ⁵⁷Co/Rh source with the spectrometer in the transmission mode.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of as-prepared iron-doped tin oxide dried at room temperature. The XRD pattern of pure tin oxide, obtained after drying the wet tin oxide gel at room temperature, is also displayed for comparison. Pure tin oxide has a white color, whereas the doped one presents light brown colors, which indicates the presence of iron. The diffraction patterns of the two samples are found to be identical; it is worth noting that no trace of iron oxides is detected in the limit of XRD sensitivity.

The TEM analysis (Fig. 2) shows homogenous agglomerate particles with a very fine particles size of about 2 nm. The average particles size (Δ) is also calculated from XRD patterns, by using the usual Scherrer equation [$\Delta = 0.9\lambda / \Delta(2\theta) \cos \theta_0$], and is found to be around 2.1, 1.6 and 1.9 nm as determined from

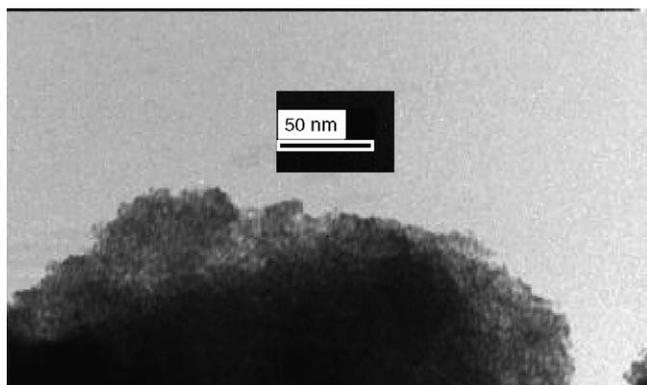


Fig. 2. TEM picture of as-prepared Fe–SnO₂ sample.

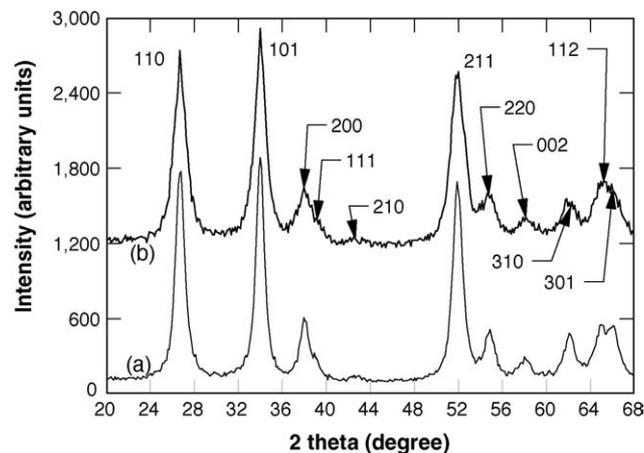


Fig. 3. XRD pattern of annealed samples at 773 K for 24 h: (a) SnO₂ and (b) Fe–SnO₂.

the main peaks (1 1 0), (1 0 1) and (2 1 1), respectively. This is consistent with TEM result confirming also the size and the spherical shape of the particles.

In order to estimate the amount of iron present in the as prepared sample, EDAX detector connected to scanning electron microscope was used. EDAX data taken at a number of selected areas throughout the as-prepared sample revealed an Fe content of 8 at.%, which could be incorporated into the tin oxide lattice. This reflects a uniform composition of the sample. In order to investigate the presence of any iron oxides or iron aggregate in Fe–SnO₂, not detected at room temperature, the sample was subjected to annealing at 773 K for 24 h. Such procedure would improve the crystallinity of any existing amorphous or nanocrystalline iron-oxide phase. The pure SnO₂ sample was also annealed under the same conditions, for comparison. The XRD patterns of the annealed SnO₂ and Fe–SnO₂ samples are displayed in Fig. 3.

It can be seen from Fig. 3 that the structure remains rutile-type. The peaks become sharper reflecting an increase of the particles size, but no sign of extra phase is detected. The intensity of some peaks of Fe–SnO₂ slightly changes (the peak 1 0 1 slightly increases, in opposite the peak 2 1 1 slightly decreases), which may indicate the incorporation of Fe in SnO₂-rutile structure. Also, Fe–SnO₂ diffraction peaks are slightly broader than

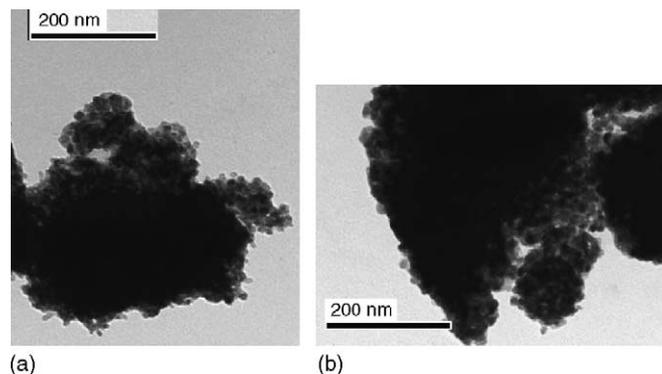


Fig. 4. TEM pictures of the annealed samples at 773 K for 24 h: (a) Fe–SnO₂ and (b) SnO₂.

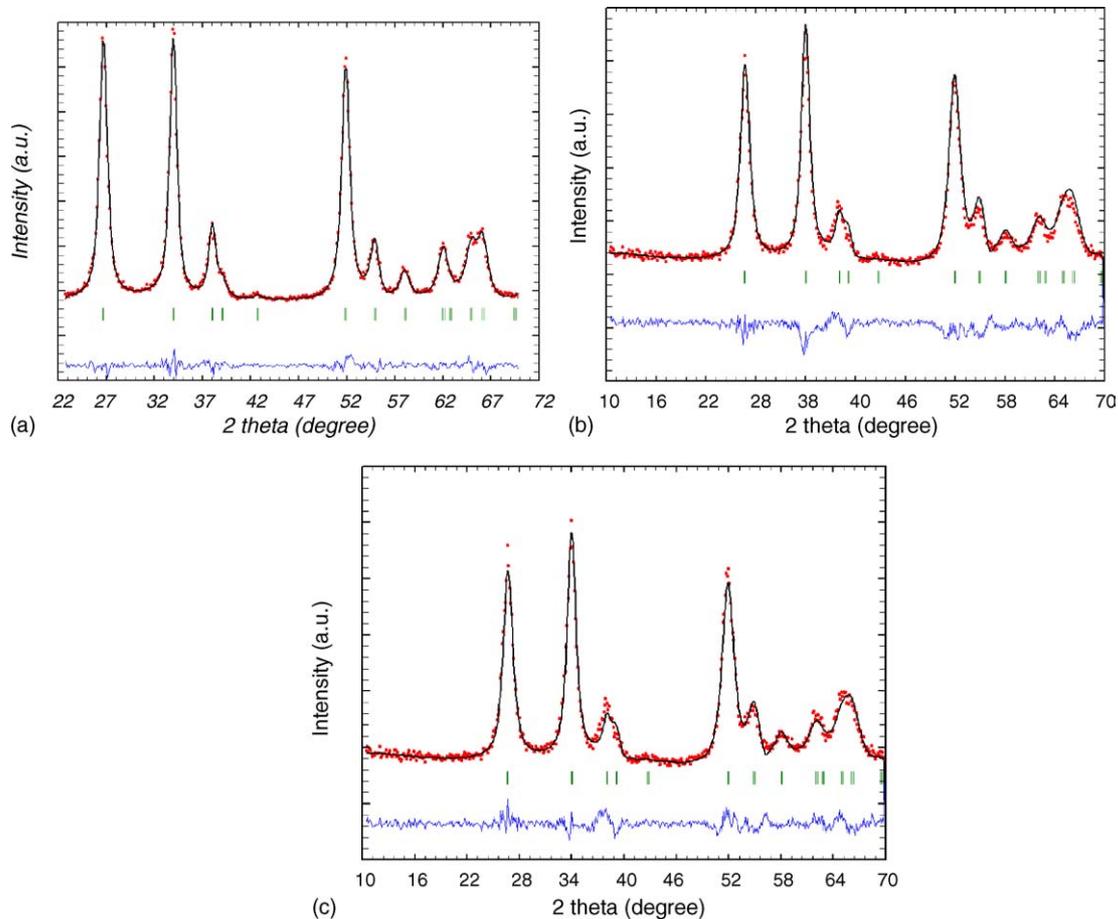


Fig. 5. XRD experimental and calculated pattern based on the Rietveld refinement of the samples: (a) pure annealed SnO_2 ; (b) annealed Fe-SnO_2 , calculation based on undoped SnO_2 ; (c) annealed Fe-SnO_2 , calculation based on Fe-doped SnO_2 . The difference between the experimental and the corresponding calculated patterns are also displayed.

that of pure annealed SnO_2 . The particles size of the annealed Fe-SnO_2 sample is estimated from TEM measurements to be about 7 nm (Fig. 4) slightly smaller than that of SnO_2 , which is consistent with the above XRD data. The crystallite size measurement using the Scherrer equation is also similar; it shows the particle size of iron-doped tin oxide is 1–2 nm smaller than the particle size of pure tin oxide. Previously published work [6–8] had reported that incorporation of iron in the tin oxide lattice prevents the growing of tin oxide particles under thermal treatment.

The EDAX analysis of the annealed Fe-doped SnO_2 revealed the same atomic content of Fe (8 at.%). The Rietveld refinement of the XRD patterns of the annealed SnO_2 and Fe-SnO_2 samples are carried out using Fullprof program [10]. The results are reported in Fig. 5. An acceptable agreement between the calculated and experimental spectra of the pure SnO_2 (Fig. 5(a)) is obtained with the parameters $R_p = 6.27$ and $R_{wp} = 8.38$. The refinement of the annealed Fe-SnO_2 sample (Fig. 5(b)) is first based of the non-doped SnO_2 leading to $R_p = 11.7$ and $R_{wp} = 13.3$. The XRD refinement is improved by considering the substitution of the iron for tin sites with fixed occupancy as determined from EDAX analysis (Fig. 5(c)) associated with the new value of the parameters $R_p = 8.81$ and $R_{wp} = 10.4$. This result supports the fact that iron substitutes for tin in the lattice.

Furthermore, a distortion of the crystalline structure is observed (based on XRD Rietveld refinement) due presumably to the difference in ionic radius of Fe^{3+} and Sn^{4+} . The distortion of the octahedral polyhedron SnO_6 of the annealed Fe-SnO_2 sample is well reflected in the value of the bonds with two bonds of 1.844 Å and two others slightly longer of 2.186 Å. In contrast, pure tin oxide presents almost a regular octahedral polyhedron with approximately similar bond: two bonds of 1.987 Å and two others of 2.092 Å.

From this study it is evident that iron substitutes for tin in the rutile structure in the annealed Fe-doped SnO_2 sample. To ensure that iron ion substitutes for tin in the lattice of the as-prepared sample before annealing, we have prepared a sample containing nanosized SnO_2 (obtained by drying the wet $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ at room temperature) and commercial $\alpha\text{-Fe}_2\text{O}_3$ with the same proportion as the doped Fe-SnO_2 sample (8 at.% of Fe). The mixture $\alpha\text{-Fe}_2\text{O}_3\text{-SnO}_2$ was stirred in small volume of acetone for 1 h and dried at room temperature. XRD patterns at room temperature and annealed (at 773 K for 24 h) of $\text{Fe}_2\text{O}_3\text{-SnO}_2$ mixture are shown in Fig. 6. Both XRD patterns exhibit clearly $\alpha\text{-Fe}_2\text{O}_3$ related reflections, which were absent in the as-prepared Fe-SnO_2 samples.

Moreover, the room temperature hysteresis loops of the as-prepared Fe-SnO_2 and mixture $\alpha\text{-Fe}_2\text{O}_3\text{-SnO}_2$ have substan-

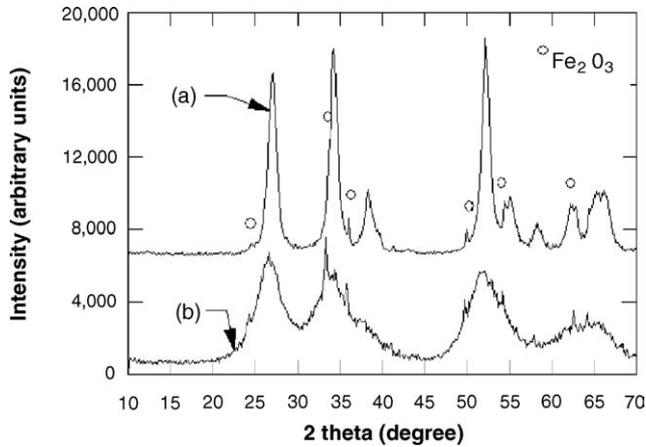


Fig. 6. X-ray diffraction patterns of the mixture α - Fe_2O_3 - SnO_2 : (a) annealed at 773 K for 24 h; (b) room temperature.

tial different behaviors as shown in Fig. 7(a). Clearly, the two curves have different shape. The mixture α - Fe_2O_3 - SnO_2 sample shows a sort of weak ferromagnetism-like characteristic of bulk hematite phase at room temperature with a coercivity of about 500 Oe and remanence ratio (M_r/M_s) of about 0.3, whereas the coercivity of the as-prepared Fe-SnO_2 sample was considerably smaller (~ 75 Oe) and with almost no remanence (inset of Fig. 7(a)). This difference in the magnetic response of the two

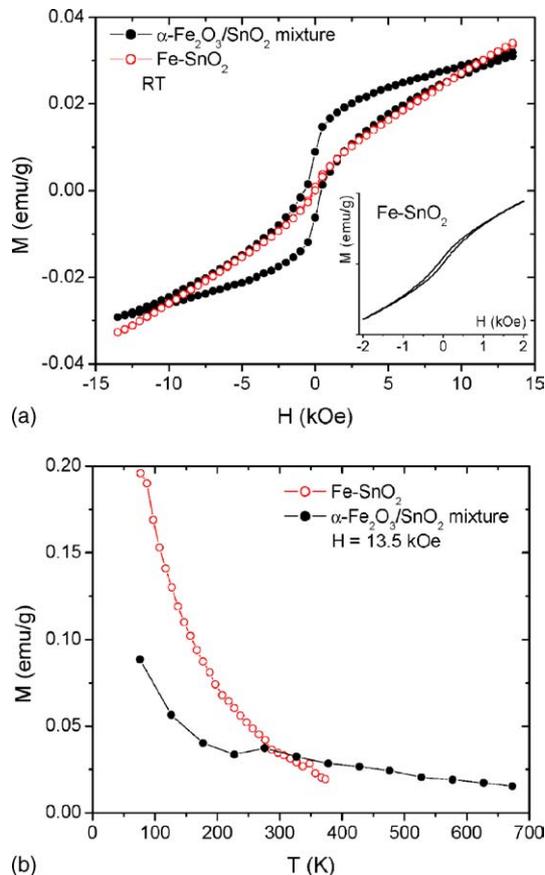


Fig. 7. (a) Room temperature hysteresis loops; (b) the temperature dependence of magnetization.

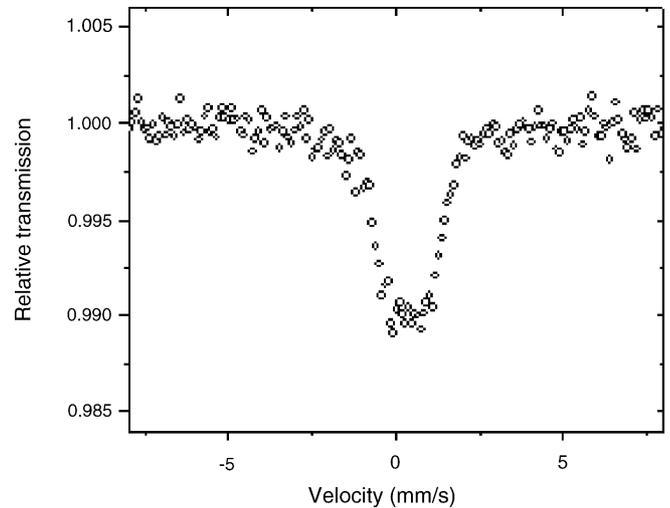


Fig. 8. Mössbauer spectrum at room temperature.

samples is also well reflected in the temperature dependence of the magnetization (Fig. 7(b)). Contrary to the as-prepared Fe-SnO_2 , the temperature dependence of the magnetization of the mixture α - Fe_2O_3 - SnO_2 shows an anomaly at around 263 K characteristic of Morin transition in hematite.

The Mössbauer spectrum at room temperature of the as-prepared Fe-SnO_2 sample is a single paramagnetic doublet with isomer shift characteristic of Fe^{3+} (Fig. 8). The line broadening could be due to a sort of magnetic order, which can be correlated, to the weak ferromagnetism observed in this sample from magnetization measurements.

One of our future objectives is to investigate the effect of Fe content in Fe-doped SnO_2 nanoparticles of about 2 nm on its magnetism. This may shed more light on the mechanism of ferromagnetism observed in this Fe-SnO_2 dilute semiconductor.

4. Conclusion

This method used the wet $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ gel as starting material. A material found to be more reactive than tin oxide powder prepared or commercial. The method leads successfully to prepare nanosize solid solution of iron-doped tin oxide $\text{Fe}_{0.08}\text{Sn}_{0.92}\text{O}_{2-\delta}$ at low temperature. Added to the simplicity of this method; the homogeneity of the doping throughout the sample and the specific weak ferromagnetism-like character of the as-prepared Fe doped SnO_2 sample.

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References

- [1] H. Ohno, Science 281 (1998) 951.
- [2] G.A. Prinz, Science 282 (1998) 1660.
- [3] S.B. Ogale, et al., Phys. Rev. Lett. 91 (2003) 077205.

- [4] C.B. Fitzgerald, M. Venkatesan, A.P. Douvalis, S. Huber, J.M.D. Coey, *J. Appl. Phys.* 95 (2004) 7390.
- [5] A. Punnoose, J. Hays, *J. Appl. Phys.* 97 (2005) 10D321.
- [6] W. Jumbo, Y. Minge, L. Yingmin, C. Licheng, Z. Yan, D. Bingjun, *J. Non-Cryst. Solid* 351 (2003) 228.
- [7] K. Galatsis, L. Cukrov, W. Wlodarski, P. McCormick, K. Kalantar-zadeh, E. Comini, G. Sberveglieri, *Sens. Actuators B* 93 (2003) 562.
- [8] M. Sorescu, L. Diamandescu, D. Tarabasanu-Mihaila, V.S. Teodorescu, B.H. Howard, *J. Phys. Chem. Solid* 65 (2004) 1021.
- [9] K. Melghit, A.K. Mohammed, I. Al-Amri, *Mater. Sci. Eng. B* 117 (2005) 302.
- [10] J. Rodrigues-Carvajal, *Collected Abstracts of Powder Diffraction Meeting, Toulouse, France, 1990*, p. 127.