



# Nanocrystalline tin oxide: Possible origin of its weak ferromagnetism deduced from nuclear magnetic resonance and X-ray photoelectron spectroscopies



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## ABSTRACT

Nanocrystalline tin oxide was fabricated, with molar ratio O/Sn determined as 1.40, 1.55, 1.79, 1.92 and 1.96 from X-ray photoelectron spectroscopy. They displayed weak ferromagnetism, the sample with O/Sn = 1.55 showing the maximum saturation magnetization reaching almost  $8 \times 10^{-3}$  emu/g at room temperature.  $^{119}\text{Sn}$  nuclear magnetic resonance allowed the deduction, based on four resolved resonance peaks, that their Sn ions had four possible coordination numbers, namely 3, 4, 5 and 6. The relative fraction of 4-coordinated cations was the one found to bear positive linear correlation with saturation magnetization of the sample. It is surmised that magnetism in tin oxide results mainly from 4-coordination Sn ions, of valance about +3, as estimated from the binding energies of their 3d photoelectron emission levels.

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## 1. Introduction

Tin dioxide as a wide bandgap and non-stoichiometric semiconductor has found applications as material for transparent conducting electrodes [1–4] and gas sensors [5–7]. It has a rutile crystal structure, in which the Sn(IV) cation sits within an oxygen octahedron and so has a coordination number 6 [8–11]. As tin exhibits heterovalency, existing also as Sn(II), anion vacancies are the most common type of intrinsic lattice defects [12,13]. Oxygen deficient  $\text{SnO}_{2-x}$  has been studied and first-principles calculations predict a homologous series of  $\text{Sn}_{n-1}\text{O}_n$  ( $n = 2-6$ ) in which oxygen vacancies arise on (101) planes [14,15].

Recently, not only the bulk material doped with transition metals [16–18] but also its pristine films and nanoparticles [19–22] have been observed to display magnetism at room temperature. Processing of the undoped film in ambient oxygen significantly affects its magnetic ordering, suggesting that lattice defects, low dimensionality or both are probable mechanisms [23]. Indeed, theoretical calculations [24,25] show that neutral cation vacancies induce ferromagnetism in the dioxide. Golovanov et al. [26] propose

that the ferromagnetism derives from oxygen di-vacancies, due to magnetic moments on surrounding fourfold-coordinated Sn cation and O anions, that arise from hole-mediated s-p exchanges between cations.

This paper offers our experimental evidence to verify whether 4-coordinated Sn and O vacancies in the tin oxides are responsible for magnetism. Tin oxide nanoparticles have been prepared under different conditions, and their magnetization curves measured. After deducing their O/Sn molar ratios and fractions of 3-, 4-, 5- and 6-coordinated cations from various spectroscopic measurements, we establish positive linear correlation between their saturation magnetization and their concentrations of 4-coordinated Sn ions, whose valance is about +3, which accords well with theoretical prediction.

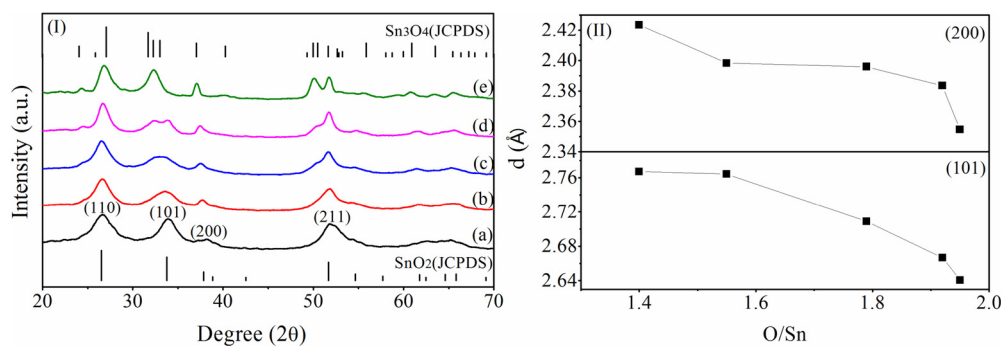
## 2. Experimental

Five types of nanocrystalline tin oxides were prepared from  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ . These precursors,  $\geq 99\%$  in purity, were supplied by Alfa Aesar and Shanghai No. 4 H.V. Chemicals respectively. They had been stored in dry boxes but used without further purification. Ammonia (28% w/w) and sodium hydroxide (0.5 M) served as reactants, and absolute methanol and ethanol were used as cleaning agents; all of analytical grade and sourced from Nanjing Reagents.

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**Fig. 1.** (I) XRD patterns of (a) Pt400, (b) AN120, (c) HF120, (d) HF180 and (e) pH2, marked with peak positions for SnO<sub>2</sub> and for Sn<sub>3</sub>O<sub>4</sub>; (II) *d*-spacings of (101) and (200) peaks vs. O/Sn ratio in various samples.

### 2.1. Synthesis via precipitation

A clear solution of tetrachloride hydrate dissolved in methanol (typically 3.5 g in 100 ml) was mixed with ammonia (4 ml), slowly but under vigorous stirring in a magnetic stirrer. The resulting white precipitate was filtered, thoroughly washed with methanol, then dried at 80 °C for 10 h. Calcination at 400 °C for 2 h in atmosphere produced nanocrystals, which variety of sample will be referred to as “Pt400”.

### 2.2. Hydrothermal synthesis I

Dichloride hydrate was dissolved in 1:1 admixture of deionized water and ethanol (2.36 g in 620 ml of solvent), stirred for 5 min, before ammonia (45 ml) was added slowly with continuous stirring. The homogeneous solution, transferred to a Teflon-lined stainless steel autoclave, was sealed and heated at 120 °C for 13 h. The residue was washed several times with ethanol, and the final product dried in vacuum at 50 °C overnight. This is sample “HF120”. Further annealing in oxygen at 200 °C for 4 h produced sample “AN120”. A third variant was obtained when initially 5 ml ammonia had been added and the solution heated at 180 °C for 8 h; It is named “HF180”.

### 2.3. Hydrothermal synthesis II

Dichloride hydrate dissolved in distilled water (8.12 g in 60 ml) was mixed with NaOH until its pH value reached 2.0, then stirred for 2 h before its transfer into a Teflon-lined autoclave. After its treatment at 150 °C for 24 h, the residues were washed with ethanol three times, dried in vacuum at 50 °C overnight. This is sample “pH2”.

### 2.4. Characterization

All five kinds of samples had their structures and properties determined with the help of powder X-ray diffractometry (XRD), high-resolution transmission electron microscopy (HR-TEM), inductively coupled plasma optical emission spectrometry (ICP-OES), superconducting quantum interference device (SQUID) magnetometry, scanning X-ray photoelectron spectrometry (XPS), and solid-state magic-angle nuclear magnetic resonance (NMR) spectrometry. Instruments used included XRD-6000 Shimadzu diffractometer equipped with a Cu-K $\alpha$ 1 radiation (0.15406 nm) source, JEOL JEM-200CX operated under the accelerating potential of 200 kV, ICP-OES (Optima 5300DV), and Quantum Design SQUID (MPMS-XL-7). XPS spectra were recorded in a PHI Versa II microprobe under raster-scanned micro-focussed Al K $\alpha$  X-ray (1486.7 eV) beam, and analysed by XPSPEAK41 software. NMR measurements were performed in a Bruker AV-300 spectrometer, whose rotor

**Table 1**

Molar ratio of O/Sn calculated from XPS peaks areas, and saturation magnetization  $M_S$  from SQUID measurements.

Sample	O/Sn	$M_S$ (emu/g)
pH2	1.40	$1.59 \times 10^{-4}$
HF180	1.55	$7.67 \times 10^{-3}$
HF120	1.79	$3.55 \times 10^{-3}$
AN120	1.92	$1.97 \times 10^{-3}$
Pt400	1.95	$2.68 \times 10^{-4}$

spun at 10 kHz during acquisition of <sup>119</sup>Sn spectra utilising solid-echo pulse sequence with a delay of 110 s, that were analysed by Topspin 2.1 and DMFIT (2010) software.

### 3. Results

Fig. 1 presents our XRD results. Peak matching with the Powder Diffraction File establishes that pattern (a) was SnO<sub>2</sub> phase (JCPDS 41-1445), whereas (e) was Sn<sub>3</sub>O<sub>4</sub> (JCPDS 16-0737). Patterns (b), (c) and (d) suggest coexisting tetragonal SnO<sub>2</sub> and triclinic Sn<sub>3</sub>O<sub>4</sub> phases, as they include both the (101) and (211) diffraction peaks of the former, and the (121) and (301) peaks at 32.31° and 50.09° respectively, that belong to the latter. The (101) and (200) peaks move perceptively to lower angles in patterns (a) to (e), indicative of increasing *d*-spacings. The O/Sn molar ratio is ideally 2 in Pt400, and  $4/3 \approx 1.33$  in pH2, but has been determined from XPS data (see Table 1 below) for all five samples, so that this trend can be rendered quantitative in Fig. 1(II).

Typical electron micrographs are depicted in Fig. 2. Pt400 crystallized as irregular polyhedra, of around 5 nm in diameter. AN120 and HF120 had a flake-like morphology, mixed with some thicker particles. HF180 and pH2 were also found as flakes, which had larger areas and some of which spontaneously convoluted to minimise surface energy. It is seen that the samples existed in quite different morphologies.

ICP-OES gave an iron concentration of  $13 \pm 1$  ppm in samples obtained from precipitation, and  $7 \pm 1$  ppm in those via hydrothermal method. Among the iron oxides, FeO, Fe<sub>3</sub>O<sub>4</sub> and nanocrystalline  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are not ferromagnetic; bulk  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at the 13 ppm level could contribute the maximum of  $0.7 \times 10^{-3}$  emu/g.

Fig. 3 plots magnetic induction in all five samples vs. external magnetic field, at room temperature and with induction corrected after subtraction of the contribution from diamagnetic holder. Their small but distinct hysteresis loops signify weak ferromagnetism, the best in HF180 with saturation magnetisation of  $7.67 \times 10^{-3}$  emu/g at coercivity field of 80 Oe, but the weakest in pH2 with corresponding values of  $1.59 \times 10^{-4}$  emu/g and 77 Oe.

In the wide scan XPS shown in Fig. 4, where binding energies have been calibrated by reference to C1s, peaks from only C, O and

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