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Impurity Effect on Magnetic Properties in Pure and TM-Doped Nanophase-SnO_2 Synthesized by Facile Co-Precipitation Method

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Abstract: ***Samples of ferromagnetic $Sn_{1-x}Fe_x$ O_2 (x=0, 0.2, 0.4, 0.6 and 0.8) nanoparticles were prepared by a facile co-precipitation method using stannic chloride pentahydrate and ferric chloride tetrahydrate. Magnetic properties were studied using vibrating sample magnetometer. It was observed that impurity controls the magnetic properties significantly. The magnetic coercive field ranged from 142.122Oe to 1622.674Oe, mostly increasing with doping concentration, and maximizing at a concentration of 6% of Fe. The retentivity increased 10-17 times, and saturation magnetization 2-6 times, by controlling doping concentration. It is the finding of the experiment that at a dilute impurity of 2%, the sample shows the maximum retentivity with saturation magnetization, and a coercive field of 216.36 Oe.***

Keywords: Fe: SnO_2 nanoparticles, dilute impurity effect, magnetic behaviour, ferromagnetism

1. Introduction

Stannic dioxide is a wide band gap semiconductor with transparent and chemically stable configurations useful in solar cell, gas sensing, catalytic and spintronics applications. Such materials doped with TM show magnetic properties and form basis of spintronics (Rai B. C., Kumar S., Raj R., Kumari N., Monalisa et al (2016)). These can be synthesized by various methods such as spray pyrolysis or flame spray synthesis (Sahm et al. 2004) laser removal process (Lu et al. 2006), mini arc plasma (Fujihara et al. 2004), hydrothermal (Shaikh et al. 2018 & Bhagwat et al. 2003), amorphous citrate route (Gnanam & Rajendram, 2010), wet chemical method (Li et al. 2002), solid state reaction (Hench & West 1990), sol-gel (Wang et al. 2017 & Lu G et al.2012), co-precipitation (Raj R, et al. 2022 & Kumari et al, 2022), etc. Literature exhibits that oxides often have oxygen vacancies, working as shallow donors, which are different from III-V systems, where these come from magnetic ions acting as donors or acceptors. Also thermally excited hot carriers can participate in ordering. Magnetic clusters, percolation of magnetic polaron and RKKY interactions may lead to magnetism (Liu & Wang 2020). However, there is no general unique source of magnetic behaviour of nanoparticles (Calderon M.J. & Sarma SD. (2007)), and reasons may be specific to materials and methods of synthesis. Lack of conclusive evidences of magnetic source in such materials creates a research gap and opens the subject for investigation.

We synthesized nanophase samples of pure and Fe-doped stannic dioxide semiconductor at room temperature, characterized and studied its magnetic properties and impurity effect using experiment on vibrating sample magnetometer.

2. Experimental Method

Chemicals of analytic grade were procured and used directly. For preparing the samples, chemicals of Sn and Fe sources were taken in molar ratios determined by x values (**Kumar et al, 2023**). Samples were prepared as reported earlier. Following samples were obtained (Table 1).

Table 1: Samples Prepared

Fe(x-values)	Sample formula	Temperature lower	Calcination Temperature	Lab symbol of sample
0.00	SnO_2	35°C	120°C	S00
0.02	$Sn_{0.98}Fe_{0.02}O_2$	35°C	120°C	S02
0.04	$Sn_{0.98}Fe_{0.02}O_2$	35°C	120°C	S04
0.06	$Sn_{0.98}Fe_{0.02}O_2$	35°C	120°C	S06
0.08	$Sn_{0.98}Fe_{0.02}O_2$	35°C	120°C	S08

Results of Magnetic studies of samples using VSM

Magnetization of samples in various magnetizing fields were studied using Vibrating Sample Magnetometer. Table 2 shows the sample mass and annealing temperatures used in calculating per gram values of magnetizations.

Table 2: Sample Masses used in VSM at 300 K

Samples	Formula	Mass (mg)	Annealing temperature(°C)
S00	SnO2	9.5	120
S02	Sn0.98Fe0.02O2	5.43	120
SO4	Sn0.96Fe0.04O2	3.37	120
S06	Sn0.94Fe0.06O2	5.08	120
S08	Sn0.92Fe0.08O2	7.33	120

Table 3 shows magnetic parameters of samples corresponding to applied field H not more than 5 kOe in magnitude.

Table 3: Results: Mean of Readings Mr, Ms and Hc at different impurities

TM-impurity, x	Annealing temp(°C)	Np size (nm)	Coercive field Hc(Oe)	Retentivity, Mr(emu/g)	Saturation magnetization, Ms (emu/g)
0.00	120	2.81	142.7953	0.001060872	0.0071773486
0.02	120	2.37	216.3566	0.017787533	0.0453555751
0.04	120	4.05	142.7953	0.001791045	0.0165422886
0.06	120	2.95	1622.674	0.014618086	0.0226777875
0.08	120	7.09	1549.113	0.010199737	0.0185491659

3. Discussion

Table 3 summarizes the magnetic properties of pure and Fe-doped SnO_2 nanoparticles that were annealed at 120°C. With a saturation magnetization (Ms) of 0.0072 emu g^{-1}, a remanent magnetization (Mr) of 0.0011 emu g^{-1}, and a coercive field (Hc) of 142.8 Oe, pure SnO_2 nanoparticles show very mild ferromagnetism. Intrinsic defects, especially oxygen vacancies, which produce localized magnetic moments, are responsible for the room-temperature ferromagnetism in undoped SnO_2.

The magnetic behaviour is significantly altered by even dilute Fe doping. Enhanced ferromagnetic ordering is indicated by the highest saturation magnetization (Ms = 0.0454 emu g^{-1}) and remanence (Mr = 0.0178 emu g^{-1}) in as- low- as 2% Fe-doped sample. The findings show that Fe inclusion modifies crystallite size, defect concentration, and magnetic exchange interactions, all of which have a substantial impact on SnO_2's magnetic behaviour. The VSM-measured values of coercive fields, magnetization- saturation and retentivity in Table 3 show that the coercive field Hc depends upon the impurity concentration. It ranges from 142.122Oe to 1622.674Oe, almost increasing with doping concentration. Such a behaviour was also observed in [S. Ferrari et al., 2016]. The maximum coercive field corresponds to an impurity concentration of 0.06.

The bound magnetic polaron (BMP) model provides an explanation for this improvement. Magnetic polarons are created when electrons trapped at oxygen-vacancy sites interact with the localized magnetic moments of Fe^{3+} ions. Long-range ferromagnetic coupling is created when these polarons overlap, increasing magnetization.

The saturation magnetization gradually drops from 0.0165 to 0.0185 emu g^{-1} when the Fe concentration increases from 4% to 8%, but it is still much lower than that of the 2% Fe-doped sample. This trend implies that ferromagnetism is not continuously enhanced by excessive Fe incorporation. Higher dopant concentrations cause nearby Fe ions to be closer together on average, which encourages antiferromagnetic super-exchange interactions (Fe^{3+}–O^{2-}–Fe^{3+}), which oppose and diminish ferromagnetic BMP interactions. Additionally, the uneven distribution of Fe ions and oxygen vacancies may lessen magnetic polaron overlap, resulting in weaker long-range ferromagnetic ordering. The coercivity exhibits a substantial increase with Fe doping. While pure SnO_2 shows a coercivity of approximately 143 Oe, the 6% and 8% Fe-doped samples display significantly higher coercive fields of 1622.7 and 1549.1 Oe, respectively. The enhanced coercivity can be attributed to increased magneto-crystalline anisotropy induced by Fe incorporation, as well as defect-related pinning of magnetic domain walls. The 8% Fe-doped sample may further contribute to the increase in magnetic anisotropy and coercive field due to structural disordering,

The magnetic ordering of Fe-doped SnO_2 nanoparticles is mostly determined by the concentration and distribution of oxygen vacancies, as seen by the change in magnetic characteristics with Fe content. The BMP mechanism states that ferromagnetic interaction between Fe ions is mediated by oxygen vacancies. Thus, to increase ferromagnetism, an ideal concentration of Fe ions and oxygen vacancies is required. Higher Fe concentrations promote competitive antiferromagnetic interactions and decrease total magnetism, while the 2% Fe-doped sample's improved magnetic performance indicates the presence of such an ideal defect–dopant equilibrium [Mudarra et al (2015)].

Overall, the magnetic results verify that defect-mediated exchange interactions, mainly controlled by oxygen vacancies and associated magnetic polarons, are the source of room-temperature ferromagnetism in Fe-doped SnO_2 nanoparticles. The 2% Fe-doped sample exhibits the highest ferromagnetic response, whereas greater Fe concentrations cause enhanced coercivity but decreased saturation magnetization because of defect chemistry changes and the commencement of antiferromagnetic coupling.
The retentivity, Mr, depends on concentration of impurity element. It has increased 10-17 times upon doping. The saturation magnetization, Ms, depends on the impurity percentage. It has increased 2-6 times upon doping. It is observed that the dilute impurity of 2% shows a minimum size, the maximum retentivity and saturation magnetization. The coercive field at this value of Fe was found 216.36 Oe.

Result: Hysteretic Loops as FM evidence
Using VSM measurement, the loops of M (H) curves were observed, which are characteristic for ferromagnetic materials, and clearly indicate successful synthesis of a ferromagnetic sample of pristine and doped SnO_2. Thus, the dilute magnetism is successfully observed.

Impurity control of loops: The hysteresis loops change by controlling the doping concentration. Table 4 shows the variation in loop area with doping concentration.

Table 4: Impurity Effect on Hysteresis loop area

Sample	Impurity (%) (Fe)	Annealing Temperature(°C)	Loop area (emu.Oe g^{-1})
S00	0.00	120	11.9
S002	2	120	28.83
S004	4	120	7.18
S006	6	120	11.09
S008	8	120	16.68

Smaller loop area means smaller energy loss per cycle. Such materials are energy efficient in cyclic field systems like transformers.

Result of High field effect and discussion

We see that above about 5kOe field, the tails of loops become lines, with negative slopes.

In impurity-controlled magnetism in nanoparticles, there may arise increment in orbital contribution with a diamagnetic effect, fall in exchange interaction, or spin frustration at higher external fields.

4. Conclusion

Magnetic properties measured by VSM indicate hysteresis loop, which shows that both pure and doped samples are ferromagnetic at room temperature. Their hysteretic loop areas, coercive fields, saturation magnetization and retentivity are also measured, and found in consistent range. The coercive field is low at less than 5% Fe concentration, and maximum at 6% [**Ferrari S, et al, 2016**]. It remains high at 8% also. Retentivity (in m emu/g) are observed to be 1.06 (for pure), 17.78 (for 2% Fe), 1.79 (for 4% Fe), 14.6 (for 6%Fe), and 10.2 (for 8% Fe). It is maximum at 2% of dilute impurity. The saturation-magnetization values are (in 10^{-3} emu/g) 7.17 (for pure), 45.35 (for 2% Fe), 16.54 (for 4% Fe), 22.68(for 6% Fe) and 18.54 (for 8% Fe). The maximum magnetization occurs for 2% doping, a dilute impurity in deed, with a coercive field of 216.36 Oe and a maximum retentivity. Although the magnetic properties can be defect and lattice strain induced [**Monalisa et al, 2021**], field dependence at higher values, as well as impurity control, may require more studies (**Zutic I, Fabian J. and Sarma Das S. (2004)**).

The impurity controls magnetism more effectively at dilute level, and materials prepared are suitable for magnetic and microelectronic applications.

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