Paramagnetism in single-phase $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ dilute magnetic semiconductors

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Transition metal (TM) Co doped SnO$_2$ dilute magnetic semiconductor (DMS) in both nano- and bulk state are prepared by solvothermal and mechanosynthesis route, respectively. Contraction in unit cell volume of tetragonal rutile SnO$_2$ after Co doping and redshift in energy band gap compared to that of undoped SnO$_2$ ensures the incorporation of smaller Co$^{2+}$ ions replacing larger host cations Sn$^{4+}$. Vibrating sample magnetometer measurements show that paramagnetism is the intrinsic magnetic property in single-phase Sn$_{1-x}$Co$_x$O whereas non-DMS related ferromagnetism is associated only with the corresponding nanostructures. Paramagnetism is also confirmed by thermal dependence of magnetization $M$ (T) and magnetic susceptibility ($\chi$) measurement in between 80 $\leq$ T $\leq$ 350 K.

I. INTRODUCTION

The existence of combined magnetic and transport properties in dilute magnetic semiconductors and potential technological applications leads to an emerging field of research since last two decades. Transition metal (TM) doped conventional semiconductors are reported to show the room temperature ferromagnetism while the existence of ferromagnetism in TM doped semiconducting oxides such as SnO$_2$, ZnO TiO$_2$, HfO$_2$, etc., remains controversial from both experimental and theoretical point of view. In fact, different controversial results, such as paramagnetism, ferromagnetism, antiferromagnetism, superparamagnetism, and spin glass behaviors have been observed in TM doped semiconducting oxides. But only paramagnetic contributions of substituted TM ions have been detected by x-ray magnetic circular dichroism (XMCD) study even it was reported to show ferromagnetism. This leads to the fact that TM 3d electrons are not responsible for the origin of ferromagnetism. In most of the cases, small amount of metallic and intermetallic impurity secondary phases or defects is accounted for the origin of observed ferromagnetism. Straumal et al. suggested that grain boundaries and related vacancies are the intrinsic origin for room temperature (RT) ferromagnetism in Mn doped ZnO whereas Liu et al. reported that ferromagnetism in V: ZnO powders is highly correlated with the structural defects. Therefore, the study of magnetism in these materials must be accompanied by a careful identification of the phases and microstructures present in order to overcome the contradiction in these dilute magnetic semiconducting oxides. Recently, we reported only paramagnetism in single phase Zn$_{1-x}$Co$_x$O. Tin-dioxide (SnO$_2$) also belongs to these oxide semiconductor class and it presents special properties, such as transparency or remarkable chemical and thermal stabilities, with direct application for photodetectors, catalysts for oxidation and hydrogenations, solar cells, semiconducting gas sensors, liquid crystal displays, and protective coatings. Here, we have studied the magnetic properties of Sn$_{1-x}$Co$_x$O$_2$ in both bulk and nanostate simultaneously prepared by mechanosynthesis (MS) and solvothermal route, respectively. It is found that the Sn$_{1-x}$Co$_x$O$_2$ dilute magnetic semiconductor show paramagnetism in bulk state where as the ferromagnetism is associated only with its corresponding nanostructures.

II. EXPERIMENTAL DETAILS

A. Solvothermal synthesis (SS)

As rod-shaped magnetic semiconductors are more desirable structure for applications in spintronics, we attempted to prepare rod-shaped Sn$_{1-x}$Co$_x$O$_2$ ($x$=0.02 and 0.04) nanostructures by solvothermal technique. For synthesis we have prepared two precursors (i) 0.05 M SnCl$_4$, 5H$_2$O and 0.0005 M CoCl$_2$, 6H$_2$O in 30 ml ethanol and (ii) 0.2 M NaOH in 30 ml ethanol. After 15 min of stirring each precursor separately, the precursor (i) is poured slowly in precursor (ii). This mixture is stirred again for 30 min. It is transferred to an 80 ml teflon-lined stainless steel autoclave. Then the autoclave is heated at 200 °C for 10 h. A reddish-brown precipitate is washed repeatedly by water and ethanol, and then dried in air at 80 °C for 24 h to obtain the required rod-shaped samples. In order to make bulk samples, these nanorods were sintered at high temperatures 800 °C.

B. Mechanosynthesis (MS)

For the preparation of bulk Sn$_{1-x}$Co$_x$O$_2$ by mechanical milling process, we have used Fritsch make (Germany) Pulverisette-7 mill which have hard-metal tungsten carbide (WC) vials and WC balls of diameter 10 mm. Commercial SnO$_2$ powder having tetragonal crystal structure (with lattice parameter as $a=b=4.74$ Å and $c=3.19$ Å) and CoO with 99.99% purity were used as the starting materials. A mixture of 5 g of SnO$_2$ and CoO powders were taken in the vials with rotational frequency of 800 rpm. The mixtures were milled for 12 h with powder: ball ratio as 1:10 by weight. After that the compounds are sintered in air at 700 °C for 1 h to obtain
the single-phase samples. Thus, we have synthesized bulk Sn$_{1-x}$Co$_x$O$_2$ dilute magnetic semiconductor with different Co concentration $x$=0.02, 0.05, and 0.08.

The samples are characterized by x-ray diffraction (XRD) using Cu $K_\alpha$ radiation ($\lambda=1.540\ 598$ Å), UV-visible spectroscopy, transmission electron microscopy (TEM), and vibrating sample magnetometer (VSM) (Lake Shore Cryotronics) for magnetic measurements within $80$ K $\leq T \leq 300$ K.

III. RESULTS AND DISCUSSION

The XRD patterns of Sn$_{1-x}$Co$_x$O$_2$ ($x=0$, 0.02, and 0.04) nanorods prepared by SS are shown in Fig. 1. All XRD peaks correspond to tetragonal (rutile cassiterite) SnO$_2$, indicating no other impurity phases like metallic Co, CoO, or Co$_3$O$_4$ present in our samples. The XRD peaks of as-prepared samples also show the large full width at half maximum (FWHM) which indicates the formation of nanostructures. But the samples sintered at $800$ °C have relatively small FWHM and consequently larger particle size close to bulk state. We have also prepared bulk Sn$_{1-x}$Co$_x$O$_2$ ($x=0.02$, 0.05, and 0.08) samples by MS route and the corresponding XRD pattern are presented in Fig. 2(a). The lattice parameters of the undoped and Co doped SnO$_2$ are estimated from the XRD peak positions using the Bragg’s law $2d \sin \theta=n\lambda$, where $\theta$ is the peak position, $\lambda$ is the wavelength of x-rays and $d$ is the interplaner spacing defined as $1/d^2=(h^2+k^2)/a^2+l^2/c^2$ for tetragonal crystal structures, where (h, k, and l) the miller indices of the crystallographic planes, a and c are the lattice parameters of the tetragonal structures. The variation in lattice volumes of the Co doped samples is shown in the inset of Fig. 2(b). It is important that the lattice volume decreases considerably for doped samples prepared by both processes. This contraction in lattice volume with the increase in Co concentration can be understood by the incorporation of smaller Co$^{2+}$ ions (0.58 Å) replacing larger Sn$^{4+}$ ions (0.69 Å) in tetragonal host semiconducting SnO$_2$ lattice structure in agreement with what reported for Co doped with other semiconducting oxides.\[15,16\]

The crystallite sizes (\(t\)) are also estimated for all the samples using the Debye–Sherrer formula and presented in Table 1. It is noticeable that the crystallite sizes are increased significantly after sintering the as-prepared nanostructures prepared by SS which indicates a transformation from nanostate to corresponding bulk state which is also obvious from the TEM micrographs in Fig. 3. It shows TEM images of Fig. 3(a) undoped SnO$_2$ and Fig. 3(c) Sn$_{0.98}$Co$_{0.02}$O$_2$ nanorods and SEM images of their corresponding bulk state obtained by high temperature (800 °C)

![XRD pattern of as-prepared and sintered (800 °C) SnO$_2$ and Sn$_{1-x}$Co$_x$O$_2$ obtained by SS.](image1.png)

**FIG. 1.** XRD pattern of as-prepared and sintered (800 °C) SnO$_2$ and Sn$_{1-x}$Co$_x$O$_2$ obtained by SS.

![XRD pattern of bulk SnO$_2$ and Sn$_{1-x}$Co$_x$O$_2$ prepared by mecha-no synthesis route and (b) variation in unit cell volume (Å$^3$) for Sn$_{1-x}$Co$_x$O$_2$ obtained by both solvothermal SS and MS route with Co concentration in at. wt %.](image2.png)

**FIG. 2.** (a) XRD pattern of bulk SnO$_2$ and Sn$_{1-x}$Co$_x$O$_2$ prepared by mechano synthesis route and (b) variation in unit cell volume (Å$^3$) for Sn$_{1-x}$Co$_x$O$_2$ obtained by both solvothermal SS and MS route with Co concentration in at. wt %.

<table>
<thead>
<tr>
<th>Synthesis process</th>
<th>Samples</th>
<th>Lattice parameters</th>
<th>Crystallite sizes (nm)</th>
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<tr>
<td></td>
<td></td>
<td>$a=b$</td>
<td>$c$</td>
</tr>
<tr>
<td>SS</td>
<td>SnO$_2$</td>
<td>$4.74 \pm 0.005$</td>
<td>$3.19 \pm 0.005$</td>
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<tr>
<td></td>
<td>Sn$<em>{0.98}$Co$</em>{0.02}$O$_2$</td>
<td>$4.73 \pm 0.005$</td>
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<tr>
<td></td>
<td>Sn$<em>{0.96}$Co$</em>{0.04}$O$_2$</td>
<td>$4.72 \pm 0.005$</td>
<td>$3.18 \pm 0.005$</td>
</tr>
<tr>
<td>MS</td>
<td>SnO$_2$</td>
<td>$4.74 \pm 0.005$</td>
<td>$3.19 \pm 0.005$</td>
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<td>Sn$<em>{0.98}$Co$</em>{0.02}$O$_2$</td>
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<td>Sn$<em>{0.96}$Co$</em>{0.04}$O$_2$</td>
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<td>$4.72 \pm 0.005$</td>
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</tr>
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</table>

**TABLE I.** Some typical estimated values of lattice parameters (Å), lattice volumes (Å$^3$), and crystallite sizes (nm) for undoped SnO$_2$ and Sn$_{1-x}$Co$_x$O$_2$ samples prepared by SS and MS.
Sn$_{0.96}$Co$_{0.04}$O$_2$ nanorods. Similar results are also obtained for as-prepared norods forms near spherical particle of micrometer size. Where $h$ is Planck's constant and $/H_9271/ \times 10^{-3}$, estimated according to the formula $\alpha h v = \text{const} (h v - E_g)^{1/2}$, where $h$ is Planck's constant and $v$ is the frequency of the incident photon. The estimated values of bang gap ($E_g$), obtained by extrapolating the Tauc plot $(\alpha h v)^2$ versus $h v$ curves, and are provided in the inset of Fig. 4. The estimated energy band gap for undoped SnO$_2$ is $E_g \approx 3.85$ eV and is in agreement with that reported in literature. But in case of Co doped samples this energy band gap ($E_g$) decreases which signifies the influence of incorporated Co on the electronics states, as reported earlier. The amount of decrease in band gap is also depends on the Co concentration. This observed redshift in energy band gap can be explained on the basis of the $sp$-$d$ exchange interactions between the band electrons and the localized $d$ electrons of the Co$^{3+}$ ions substituting Sn$^{4+}$ ions. The $s$-$d$ exchange interactions give rise to a negative correction to conduction-band edge whereas the $p$-$d$ exchange interaction lead to a positive correction to the valence band edges, resulting a decrease in band gap.

The magnetic properties are measured using a VSM in the temperature range $80 \leq T \leq 350$ K. Figure 5 shows room temperature magnetization curves for Fig. 5(a) as-prepared and sintered Sn$_{0.98}$Co$_{0.02}$O$_2$, Fig. 5(b) as-prepared and sintered Sn$_{0.96}$Co$_{0.04}$O$_2$, Fig. 5(c) as-prepared SnO$_2$, and Fig. 5(d) sintered SnO$_2$ prepared by SS. It is seen that the $M$ ($H$) curves of as-prepared Co doped SnO$_2$ nanorods show ferromagnetic behavior with hysteresis loop having coercivity ($H_C$) $\sim 140$ Oe; saturation magnetization ($M_s$) $\approx 12 \times 10^{-3}$ emu/g for Co concentration x=0.02 and $H_C \sim 100$ Oe; $M_s \approx 40 \times 10^{-3}$ emu/g for x=0.04. At the same time even the as-prepared SnO$_2$ nanorods are also showing a ferromagnetic behavior with low magnetic moment $\sim 6 \times 10^{-3}$ emu/g which is in agreement of the results reported by Sundaresan et al. On the other hand ferromagnetism is suppressed in SnO$_2$ with $\sim 500$ nm particle size due to sintering at $800$ °C for 1 h and they exhibits a linear M ($H$) curve, a diamagnetic [Fig. 5(d)] behavior as normally expected in case of SnO$_2$. Therefore, ferromagnetism is observed in SnO$_2$ nanostructure whereas the corresponding bulk samples are diamagnetic. Similarly, the ferromagnetism of Sn$_{1-x}$Co$_x$O$_2$ nanostructures also vanishes in bulk samples obtained by sintering at same temperature ($800$ °C) and show a linear paramagnetic behavior. To check this paramag-

FIG. 3. (a) TEM images of undoped SnO$_2$ and (c) Sn$_{0.98}$Co$_{0.02}$O$_2$ nanorods and SEM images of their corresponding bulk phases obtained by high temperature ($800$ °C) sintering in (b) and (d), respectively.

FIG. 4. Relative absorption (%) vs wavelength of incident photons for Sn$_{1-x}$Co$_x$O$_2$ samples using UV-visible absorption spectroscopy. Inset: Tauc plot of $(\alpha h v)^2$ as a function of photon energy ($h v$).

FIG. 5. Magnetization curves for (a) as-prepared and sintered Sn$_{0.98}$Co$_{0.02}$O$_2$, (b) as-prepared and sintered Sn$_{0.96}$Co$_{0.04}$O$_2$, (c) as-prepared SnO$_2$, and (d) sintered SnO$_2$ prepared by SS.
netic behavior of the bulk state we have also prepared bulk
Sn$_{1-x}$Co$_x$O$_2$ samples prepared by SS. As no impurity
peaks are detected in XRD pattern, any impurity or secondary
phase is not present. These nanostructures seem to be similar to
those in thin films resulting from thin film growth conditions. 25
Ferromagnetic impurity, vacancies, interstitials, and other
defects and/or disorders at surfaces, interfaces, grain bound-
daries or inside of samples. As no impurity peaks are detected
in XRD pattern, any impurity or secondary phase is not present.
The Room temperature M (H) curve for x=0.08 shows linear
behavior in the higher field region whereas an “S” shaped M
(H) curve [inset of Fig. 2(a)] is observed in the low field region.
Careful observation shows that there is no such significant coercivity present. It
is also interesting that this effect is absent when we measured M
(H) curve at low temperature (80 K) which shows perfectly linear behavior. One possible reason might be presence of some nonequilibrium states in room temperature due to higher Co concentration and one might need relatively higher sintering temperature (700 °C) to obtain the required equilibrium state. The magnetic moments of the Co doped samples increases quite linearly with increasing Co concentration which demonstrates linear insertion of Co ions replacing the Sn$^{4+}$ ions. As no other secondary or impurity phases are detected in XRD pattern [Fig. 2(a)] within the detection limit of the x-ray diffractometer, paramagnetism is the results of insertion of Co ions replacing the Sn$^{4+}$ ions.

The thermal dependence of magnetization at constant
magnetic field H=1 kOe is measured for all Co doped
samples prepared under different conditions. The M (T)
curves for bulk Sn$_{1-x}$Co$_x$O$_2$ samples prepared by SS
and bulk samples obtained by high temperature sintering
prepared by solvothermal route are shown in Figs. 7(a)
and 7(c), respectively. It is seen that they can be fitted well according
to the magnetization for paramagnetic materials (Curie’s law)
for low field and high temperature limit, defined as
$M = N g^2 \mu_B^2 H J(J+1)/3k_B T = CH/T$, where
$C = N g^2 \mu_B^2 J(J+1)/3k_B$, the Curie constant, N is the number of interacting
Co$^{2+}$ ions with total angular momentum J, g is the spectroscopic splitting factor (g=2.0023 for free-electrons), $\mu_B$ is

the magnitude of Bohr magneton, $k_B$ is the Boltzmann constant,
and T the temperature in Kelvin. The magnetic susceptibilities of these samples are estimated and the temperature variation in inverse susceptibility $(1/\chi)$ is plotted in Figs. 7(b) and 7(d). The linear fitting of the inverse susceptibility passing through origin versus temperature confirms the paramagnetic interaction between the Co ions. These results are in agreement with the results reported for Co doped ZnO. 14,23 The effective magnetic moment of Co$^{2+}$ ions inside the Sn$_{1-x}$Co$_x$O$_2$ are also estimated using $\mu_{\text{eff}}^2 = 3k_B T \chi^\prime / N$, where $\chi^\prime$ is magnetic susceptibility at temperature T. For Sn$_{0.95}$Co$_{0.05}$O$_2$, putting $N = 2.04 \times 10^{20}$, $k_B = 1.38 \times 10^{-16}$ erg K$^{-1}$, $\chi^\prime = 1.96 \times 10^{-6}$ emu cc$^{-1}$ Oe$^{-1}$ at T = 300 K, we have obtained effective magnetic moment $\mu_{\text{eff}} = 3.72 \mu_B$/Co$^{2+}$ which is much less than that of full magnetic moment of Co$^{2+}$ (6.63 $\mu_B$) with L=3 and S=3/2. In fact, it is close to the theoretical value 3.87 $\mu_B$/Co$^{2+}$ ion if only the spin contribution of Co$^{2+}$ ($J=S=3/2$) is considered. This leads to the phenomenon of quenching of orbital angular momentum. Similar observations are also observed for 2% and 8% Co doped SnO$_2$. This quenching of orbital angular momentum might possible due to crystal field splitting of 3$d^5$ levels of Co$^{2+}$ ions with 3$d^5$ high-spin configuration under the crystal field formed by neighboring O$^{2-}$ ions which is also observed for Co doped ZnO. 14,24

Therefore, the ferromagnetism in these Co doped SnO$_2$
dilute magnetic semiconductor oxides is associated with only
the nanostructure of these materials whereas the corresponding bulk state are paramagnetic which is intrinsic. Even the much expected diamagnetic material SnO$_2$ show ferromagnetism in its nanophase. The origin of ferromagnetism in these nanostructures seems to be similar to that in thin films of TiO$_2$, HfO$_2$, and In$_2$O$_3$ where the oxygen deficiency results from thin film growth conditions. 15,26 Ferromagnetic signature may also come from different sources such as ferromagnetic impurity, vacancies, interstitials, and other defects and/or disorders at surfaces, interfaces, grain boundaries or inside of samples. As no impurity peaks are detected in XRD pattern, any impurity or secondary phase is not responsible for observed ferromagnetism in SnO$_2$ and
Sn_{1-x}Co_xO_2 nanorods prepared by SS. Additionally this ferromagnetism is suppressed when the particular nanostructure is being converted to micrometer-sized particle by sintering at 800 °C. This observation helps to understand that the origin of ferromagnetism exists in the formation of nanostructure and it is possible that the unpaired electron spins responsible for ferromagnetism in the nanorods have their origin in the oxygen vacancies, especially on the surface of the nanorods. Although the nature of exchange interaction is not clear at present, one may except that electron trapped in oxygen vacancies are polarized to give room temperature ferromagnetism.27

IV. CONCLUSIONS

In conclusion, we have successfully prepared Sn_{1-x}Co_xO_2 dilute magnetic semiconductor in both nanostate and bulk state with different Co concentration by solvothermal and MS route, respectively. We found that the paramagnetism is an intrinsic magnetic property in Co doped SnO_2 whereas ferromagnetism associated only with the nanostructure. The magnetization curve, thermal dependence of magnetization, and magnetic susceptibility confirmed the paramagnetic interaction between the Co ions in the bulk samples. The ferromagnetism assumed to be associated with the oxygen vacancies in corresponding nanostructure. Therefore it is not possible to obtain ferromagnetism in single-phase Co doped SnO_2 with its high structural perfection.