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Transition from N-Type to P-Type Destroys Ferromagnetism in Semiconducting $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ and $\text{Sn}_{1-x}\text{Cr}_x\text{O}_2$ Nanoparticles

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Abstract

This work reports strong correlations between the structural, magnetic and electronic properties of room temperature ferromagnets (RTFM) $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ and $\text{Sn}_{1-x}\text{Cr}_x\text{O}_2$ for $x = 0$ to 0.1. The samples prepared by the sol-gel chemical method show RTFM for $x < x_L$ with the limiting concentration $x_L = 0.01$ for Co doping and $x_L = 0.025$ for Cr doping. As doping level x is increased from $x = 0$, the magnetic moment per ion, μ , increases and the lattice volume V_L decreases up to $x = x_L$. For $x > x_L$, μ dramatically decreases toward zero and V_L increases, the latter suggesting interstitial doping. Thermoelectric measurements showed that the samples are n-type for $x < x_L$ and p-type for $x > x_L$, suggesting that the RTFM is intrinsic and it is electron mediated.

1. Introduction

Tin dioxide (SnO_2) is a transparent semiconductor with a band gap $E_g \simeq 3.6$ eV. In a number of recent studies of transition metal doped SnO_2 , room temperature ferromagnetism (RTFM) has been reported for dilute dopings of Fe [1,2], Co [3-6] and Cr [7]. Search for an n-type transparent semiconductor with RTFM has been stimulated by the theoretical work as well as by the potential uses of such materials in spintronics and optoelectronic devices [8, 9]. Most popular potential hosts for transition metal doping for RTFM have been TiO_2 [10-12] and ZnO [13, 14]. The mechanism for producing RTFM has often been related to carrier-mediated exchange coupling between the transition metal ions [8, 9]. In this paper, we report the observation of a clear correlation between the presence of RTFM, carrier-type and doping concentrations for Cr- and Co-doped SnO_2 systems. Details of these results and their discussion are presented below.

2. Materials and Methods

The synthesis of the bulk powder samples of $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ and $\text{Sn}_{1-x}\text{Cr}_x\text{O}_2$ for x up to 0.1 using the sol-gel method has been described in earlier papers [5, 7]. Both sets of samples were characterized by room temperature x-ray diffraction (XRD) after annealing the as-prepared samples at 600°C. Magnetic measurements (magnetization M vs. the applied field H) were carried out using a vibrating sample magnetometer (VSM).

An important contribution in this work is the determining of charge carrier-type in the doped SnO_2 samples by the hot-probe method which is known to accurately determine semiconductor carrier-type [17]. For these measurements, the powder samples were pressed into 15 mm diameter pellets using an 8 ton press. Two electrical copper contacts were made across from each other on the pellet face with silver paste for voltage measurements. One side of a contact end on the pellet was heated with a hot probe to about 150°C whereas the other contact end was at room temperature. The direction of the voltage measured determined whether the sample is n-type or p-type.

3. Results and Discussion

In Fig. 1, we show the XRD patterns for both sets of samples for $0 \leq x \leq 1$. In $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$, the tetragonal form of SnO_2 (cassiterite) is the dominant phase with only minor contamination from the orthorhombic form of SnO_2 . However for $\text{Sn}_{1-x}\text{Cr}_x\text{O}_2$, the orthorhombic phase is comparatively stronger but the tetragonal phase is still dominant. Recent studies have shown the formation of the orthorhombic phase of SnO_2 under a variety of synthesis methods [15,16]. It is important to note that in the samples reported here for $x \leq 0.1$, the presence of Co_3O_4 and Cr_2O_3 are not observed in $\text{Sn}_{1-x}\text{Co}_x\text{O}_2$ and $\text{Sn}_{1-x}\text{Cr}_x\text{O}_2$ respectively. XRD studies of the pelletized

powders show no change in the crystal structure. The lattice parameters a and c of the dominant tetragonal phase were determined using the strong (110) and (220) peaks [7]. The particle sizes determined from the Scherrer XRD line broadening showed a decrease from 70 nm for pure SnO₂ to about 40 ± 10 nm for 5% doped SnO₂ [7], and were further confirmed by TEM.

(PLACE FIGURE 1 APPROX. HERE)

(PLACE FIGURE 2 APPROX. HERE, after Figure 1)

Fig. 2 summarizes the results of the variations in lattice volume V_L , the saturation magnetization M_s and the carrier-type with respect to concentrations of the two dopants, Cr and Co, varied between zero and 10%. M_s is the measured magnetization at $H = 10$ kOe after subtracting out the linear component from the M vs. H plots. In Fig. 3, M vs. H plots obtained from samples with dopant concentrations of x_L , and one representative plot for the $x < x_L$ and $x > x_L$ ranges are shown for both Co and Cr doped SnO₂. Seebeck coefficients estimated from the hot-probe experiment are shown in Fig. 4. For Cr doped SnO₂ samples, the Seebeck coefficient ranges from 23mV to -20mV whereas for the Co doped SnO₂ samples, it varies in the 126mV to -100mV range. Here, a positive coefficient represents n-type conductivity and a negative coefficient indicates p-type. In Fig. 2, it is evident that for $x = 0$ (pure SnO₂), the material is n-type (see Fig. 4) and $M_s = 0$. As doping level is increased, the lattice contracts for both Co and Cr, and M_s increases. For Co doping, both the contraction and M_s increase rapidly, reaching maximum values at $x_L = 0.01$. Our next data point at $x = 0.03$ yields $M_s = 0$ and the lattice expands to nearly the original value. For larger Co dopings of 5 and 8%, the material switches to p-type (shown in Fig. 4) with $M_s = 0$. So, for Sn_{1-x}Co_xO₂, RTFM is lost for $x > x_L = 0.01$ and material becomes p-type. For Sn_{1-x}Cr_xO₂, the behavior is qualitatively similar except that $x_L = 0.025$ is higher. The important point is that RTFM is observed only for the range $0 < x \leq x_L$ with slightly different values of x_L for Co and Cr doping and that n-type conductivity is essential for RTFM.

(PLACE FIGURE 3 APPROX. HERE)

(PLACE FIGURE 4 APPROX. HERE, after 3)

Considering that the charge on the dopant ions is lower than that of the Sn⁴⁺ they substitute for, the charge balance requirements dictate that substitution should lead to oxygen vacancies at neighboring sites. These oxygen vacancies can trap electrons and form F-centers. This explains the observed n-type conductivity for $x < x_L$. For $x > x_L$, we suggest that doping occurs interstitially producing p-type conductivity and observed lattice expansion. This argument also suggests that RTFM likely results from exchange coupling between the dopants mediated somehow by electrons trapped by oxygen vacancies. Recent paper by Fitzgerald et al [18] on the magnetism in doped SnO₂ discusses various possible explanations for the observed RTFM including the bound magnetic polarons formed by overlapping Bohr-like F-center orbitals. However, none of the models considered can explain the high Curie temperatures observed in these systems. Non-uniform magnetism as the source of high T_c in doped SnO₂ (also TiO₂ and ZnO) has also been suggested [19]. Overall, it can be stated that a satisfactory theoretical explanation for the various observations of RTFM in so lightly doped SnO₂ and other semiconductors is not yet available. It is hoped that strong correlations reported here between the structural, magnetic and electronic properties of Cr and Co doped SnO₂ would provide an impetus for further theoretical investigations of the mechanism for the observed RTFM.

4. Conclusion

In the results presented here, it has been shown that in Sn_{1-x}M_xO₂ (M=Co, Cr), n-type conductivity and room temperature ferromagnetism coexist for lighter dopings for $x < x_L$. However, for $x > x_L$, the materials become p-type and room temperature ferromagnetism is lost. This association of n-type conductivity with room temperature ferromagnetism provides a strong motivation for developing a suitable theoretical mechanism for these observations.

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