

Mapping ferromagnetism in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$: Role of preparation temperature (200–900 °C) and doping concentration ($0.00015 \leq x \leq 0.1$)

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Based on the conflicting reports in the literature, an extensive investigation to map room-temperature ferromagnetic regimes in the $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ system has been undertaken by studying 70 different sol-gel synthesized nanopowder samples by systematically varying x and/or annealing temperatures T_A in the $0.00015 \leq x \leq 0.1$ and 200–900 °C ranges, respectively. The evolved map demonstrates interesting roles of x and T_A resulting in localized regions and pockets of ferromagnetic behavior ($\leq 0.32\mu_B$) which changes gradually to larger nonferromagnetic regions. In general, the ferromagnetic regimes occur at higher Co concentrations as T_A increases. X-ray diffraction studies showed a gradual decrease in temperature range at which the anatase-to-rutile transformation occurs in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ as x increased from 0 to 0.1. Co doping also lowered the band gap energy. © 2007 American Institute of Physics. [DOI: 10.1063/1.2712020]

Ever since the discovery of room-temperature ferromagnetism (FM) by Matsumoto *et al.*,¹ in Co doped TiO_2 in 2001, there has been tremendous attention toward developing possible dilute magnetic semiconductors (DMSs) using TiO_2 and other oxide semiconductor systems to provide efficient injection of spin polarized carriers for spintronics applications. Research on Co doped TiO_2 material is largely carried out utilizing thin film techniques,^{2–8} in addition to a few studies on samples prepared by chemical methods.^{9,10} However, the employed Co dopant levels and preparation temperatures were somewhat random in these studies and a comprehensive investigation to identify the ferromagnetic regimes by systematically varying these parameters has not been conducted yet. For example, Griffin *et al.*¹¹ have reported the intrinsic FM in sputter deposited insulating Co doped TiO_2 with 2 at. % Co incorporation with a substrate temperature of 550 °C. A review article by Fukumura *et al.*¹² compared the FM behavior found in nine recent reports on FM in Co doped TiO_2 prepared with Co concentrations in the 0% to 15% range, grown using techniques such as PLD, MBE, sputtering, and metal-organic chemical vapor deposition (MOCVD) at growth temperatures in the 250–750 °C range. These studies, however, did not clearly reveal any systematic dependence of the FM with doping level or growth temperature. Evidence of FM due to intrinsic $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ (Refs. 6, 8, and 11) as well as Co clusters^{5,13,14} have been reported in these studies. The intrinsic nature of FM in materials prepared using deposition techniques in reducing atmospheres is difficult to confirm due to the possible segregation of magnetic dopants especially when used in high concentrations exceeding the solubility limits. The TiO_2 matrix has 2%–3% solubility limit for transition metal (TM) dopants.¹⁵ Higher cobalt concentration might create impurity phases such as Co metal, CoO, or CoTiO_3 . Cobalt distribution in the films is strongly dependent on the growth condi-

tions and solubility of the host matrix, which in turn affects the structure-property relationship of the host system.

In bulk form, the rutile phase is the most stable one at room temperature. However, when prepared in the nanoparticle form, other phases also might stabilize at room temperature.¹⁶ TiO_2 is known to undergo phase transformation with increasing temperatures through one of the sequences: anatase to rutile, anatase to brookite to rutile or brookite to anatase to rutile. In doped TiO_2 , these phase changes and sequences will also depend on the dopant concentration and reaction temperature.^{17,18}

Based on the conflicting reports on the magnetic behavior of Co doped TiO_2 , we investigate in this paper the room-temperature FM, optical properties, and structural changes using 70 samples of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles prepared by a sol-gel mediated hydrolysis method^{19,20} by varying x in the $0.00015 \leq x \leq 0.1$ range and annealing the reaction precipitate in the 200–900 °C range for each x explored. The sol-gel based synthesis intrinsically eliminates the possible formation of metallic clusters due to its aerobic nature.

A total of 70 powder samples of $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ —with Co doping percentages of 0.015, 0.03, 0.075, 0.15, 0.3, 0.6, 1.2, 3, 5.6, and 10—each annealed in air at temperatures 200, 300, 450, 600, 750, and 900 °C for 3 h, were studied in this work. XRD patterns were recorded on all the samples to confirm the structure and a few representative patterns are presented in Fig. 1. Low temperature annealings produce anatase phase which gets converted to rutile phase gradually at higher temperatures. The phase composition of the samples was obtained from the following equation:²¹ $x_A = 1/[1 + 1.26(I_R/I_A)]$, where x_A is the weight fraction of anatase in the mixture and I_A and I_R are the peak intensities of the anatase (101) and rutile (110) diffractions, respectively. Co doping accelerates the anatase to rutile phase transformation process, as shown in Fig. 2(a). With increasing Co concentration, the rutile phase started appearing at relatively lower temperatures. When the Co% increases, additional peaks due to the CoTiO_3 impurity phase started appearing at

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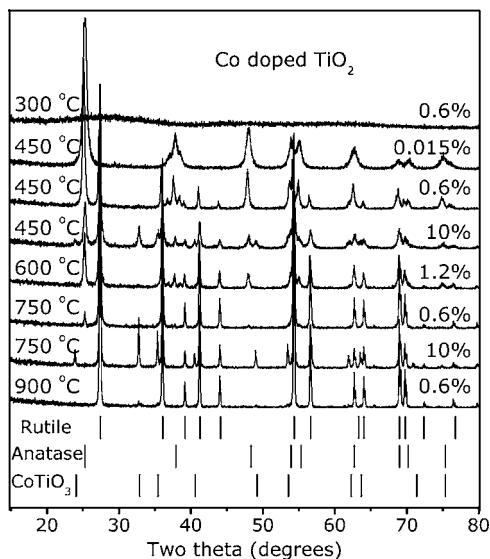


FIG. 1. Representative powder x-ray diffraction patterns of Co doped TiO_2 samples showing the doping percentages and annealing temperatures.

annealing temperatures $\geq 450^\circ\text{C}$ [Fig. 2(b)]. Average particle size of the nanoparticles, shown in Fig. 2(c), was estimated from the XRD data using the Scherrer formula.¹⁹ At any given annealing temperature, the particle size of the $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles increased with increasing dopant concentration. As the annealing temperature increases, the <10 nm anatase (closed data points) $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles observed in 200°C annealed samples changed to 30–60 nm rutile (open data points) particles in 900°C annealed samples.

Zhang and Banfield²² investigated the phase transformation of TiO_2 from anatase to rutile and it was argued to be a nucleation and growth process. This occurs through the nucleation of rutile phase within the anatase phase and it grows gradually in size with increasing temperature, at the expense of the surrounding anatase. The observed changes in the particle size in this study are in agreement with the results of Zhang and Banfield. The anatase phase is thermodynamically more stable when the particle size is small. However, with increasing particle size it transforms to rutile phase. The Co doping clearly increases the particle size and accelerates this phase transformation process in agreement with other reports also.²³ Because of the variation in the effective ionic radii of Ti^{4+} (0.645 \AA) and Co^{2+} (0.72 \AA) in octahedral coordination and the differences in the charges, Co incorporation might lead to significant lattice strain. This might cause lattice modifications and lower the activation energies which facilitate the anatase to rutile phase transformation.

To study the Co doping effect on the optical properties of TiO_2 , diffuse reflectance spectrophotometry was employed. Figure 3 presents the diffuse reflectance spectra of selected Co doped TiO_2 samples annealed at different temperatures and with varying Co concentration. The band edges for the samples annealed at $\leq 600^\circ\text{C}$ are observed at around 350 nm, while the band edges of samples annealed at higher temperatures were near 380 nm in accordance with band gap energies of 3.3 and 3.1 eV for anatase and rutile phases of

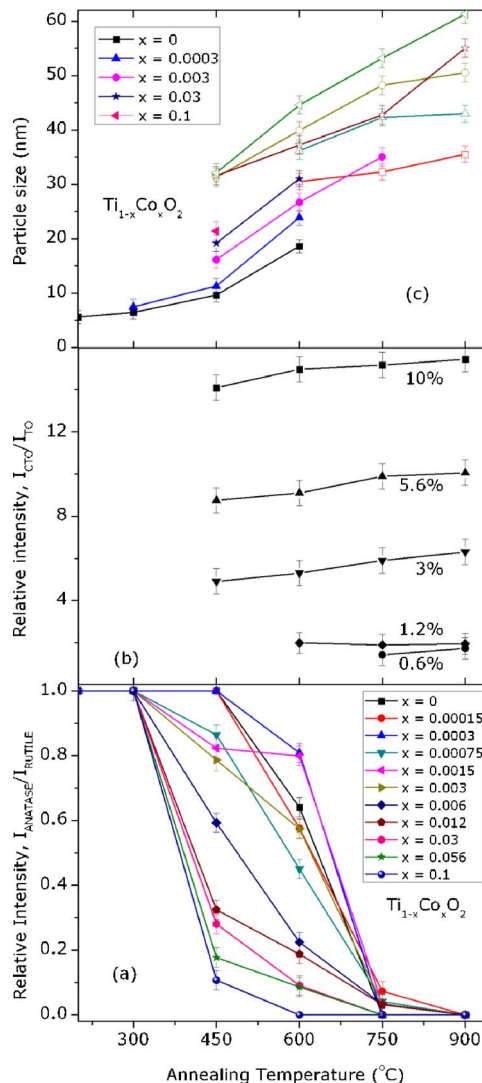


FIG. 2. (Color online) Plots showing the (a) effect of cobalt doping and annealing temperature on the anatase to rutile phase transformation plotted using the peak intensities of the (101) peak of anatase TiO_2 (I_{anatase}) and (110) peak of rutile TiO_2 (I_{rutile}), (b) ratio of CoTiO_3 to TiO_2 phase with annealing temperature plotted as the ratio of the peak intensities of the (104) peak of CoTiO_3 (I_{CTO}) and (110) peak of rutile TiO_2 (I_{TO}), and (c) particle size of anatase (closed data points) and rutile (open data points) $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ nanoparticles as a function of annealing temperature.

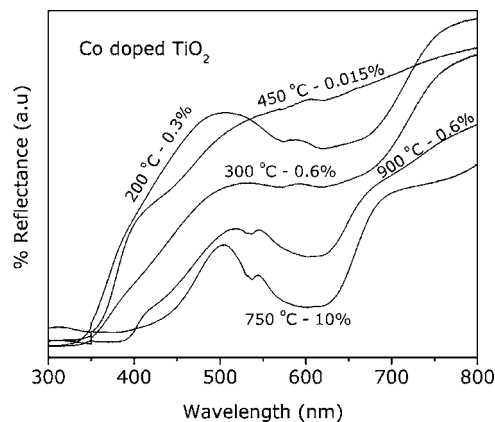


FIG. 3. Diffuse reflectance spectroscopy patterns of cobalt doped TiO_2 nanoparticles annealed at different temperatures.

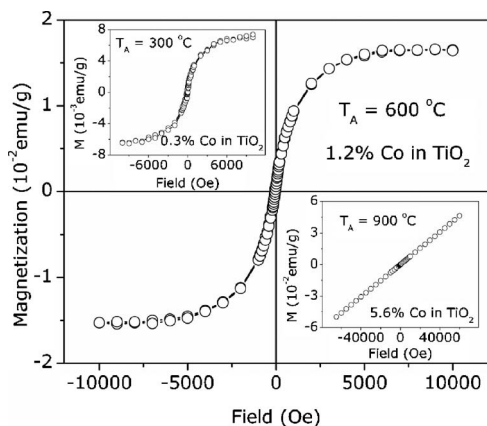


FIG. 4. Room-temperature hysteresis loop from 1.2% Co doped TiO_2 prepared at 600°C . The inset (top) shows the hysteresis loop obtained from 0.3% Co doped TiO_2 annealed at 300°C and (bottom) the loop from 5.6% Co in TiO_2 annealed at 900°C .

TiO_2 , respectively.²⁴ Upon increasing the Co concentration, the band edge shifted to higher wavelengths (lower band gap energies). However, when Co concentration in the TiO_2 matrix increased above 0.6%, characteristic electronic transitions in 500–700 nm range due to tetrahedral Co^{2+} species were observed. This is likely due to the Co^{2+} ions doped in TiO_2 ²⁵ and/or in the impurity phase CoTiO_3 phase.^{26,27}

Figure 4 shows the room-temperature hysteresis loops from 1.2% Co doped TiO_2 sample annealed at 600°C with a saturation magnetization of 15 memu/g. Two inset panels show the room-temperature magnetization data of 0.3% Co doped TiO_2 annealed at 300°C and 5.6% Co doped TiO_2 annealed at 900°C . Based on similar magnetization data collected on the entire sample set, a map of the FM regimes as a function of Co concentration and annealing temperature is presented in Fig. 5.

FM regimes clearly exist both in anatase and rutile samples based on the data shown in Fig. 5. This is in agreement with existing literature that the reported FM in both anatase and rutile forms of TiO_2 . The CoTiO_3 phase is also not seem to play a significant role since FM is present in samples with low Co concentrations and when prepared at lower annealing temperature. Formation of CoTiO_3 phase

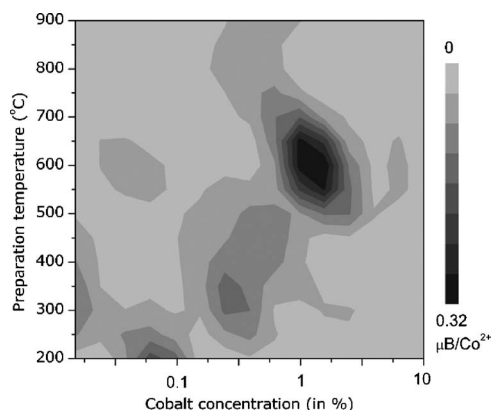


FIG. 5. A map of ferromagnetic regimes observed at room temperature in cobalt doped TiO_2 nanoparticles, demonstrating the effect of Co concentration and preparation temperatures.

will reduce the actual concentration of Co in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ phase from the intended levels. This may be an important factor since Coey²⁸ has shown that FM occurs in TM doped oxide semiconductors when the dopant concentration is below their cation percolation limit and the oxygen vacancy concentration is greater than the polaron percolation limit. Our results (Fig. 5) show that, in general, FM regimes occur at higher x for samples prepared at higher annealing temperatures. A possible reason for this may be evident from Fig. 2(b) which indicate the formation of an increasing concentration of CoTiO_3 phase as T_A and x increase. Thus, the relative concentration of CoTiO_3 phase, oxygen vacancies, and the actual dopant concentration in the $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ fraction of the samples seem to be the controlling factors that define the FM regimes.

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