Synthesis and study of magnetic properties of Co-doped anatase TiO$_2$ nanoparticles

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Abstract. Anatase phase Ti$_{0.97}$Co$_{0.03}$O$_2$ nanoparticles were synthesized using two different preparation methods. The prepared samples were investigated by X-ray diffraction (XRD), X-ray fluorescence (XRF) analysis, and magnetization measurements. The particle diameters were controlled by adjusting the annealing temperature, and they ranged from 4.2–7.0 nm for Ti$_{0.97}$Co$_{0.03}$O$_2$ encapsulated in amorphous SiO$_2$, and from 14–61 nm for Ti$_{0.97}$Co$_{0.03}$O$_2$ that was not encapsulated in amorphous SiO$_2$. Magnetization measurements were performed on the 7.0-nm sample from the former sample set, and on the 14-nm sample from the latter sample set, and both these samples exhibited an identical crystal structure and an equal number of magnetic ions, as confirmed by XRF and XRD measurements. The magnetization curves for the two samples indicated their ferromagnetic behavior at room temperature. However, the magnetic parameters of saturation magnetization $M_S$ and coercive force $H_C$ were clearly different for these two samples. We attribute this difference in magnetic properties between these samples to magnetic impurities present due to the different degrees of solubility of Co ions in the TiO$_2$ lattice.

1. Introduction

Diluted magnetic semiconductors (DMSs) have been studied because of their potential application in spintronics devices [1]. In this light, Co-doped anatase TiO$_2$ thin films, which are a class of DMSs, are reported to exhibit Curie temperatures ($T_C$) that are above room temperature [2]. Subsequently, extensive research has been carried out on Co-doped anatase TiO$_2$ thin films [2-6]. However, in contrast to thin films, few studies have focused on nanoparticles. It is noteworthy that current methods for preparing Co-doped anatase TiO$_2$ thin films are complicated, and they require the use of special techniques such as molecular beam epitaxy, pulsed laser deposition, chemical vapor deposition, and sputtering. In addition, certain preparation methods require special conditions such as vacuum conditions and a reductive atmosphere in order to achieve room-temperature ferromagnetism [7-10]. Moreover, it is known that the magnetic properties of DMSs depend on the preparation method and conditions [10].

In our previous studies, we prepared magnetic nanoparticles, including those of 3$d$ transition metals such as metal oxides and hydroxides, and investigated their magnetic [11, 12] and thermal properties [13, 14] along with their structural analyses [15, 16]. In this study, we prepared Co-doped anatase TiO$_2$ nanoparticles using two simple and novel preparation methods. We investigated the magnetic properties of these materials, and we observed their room-temperature ferromagnetic behavior.
2. Experimental

2.1. Sample preparation

Co-doped anatase TiO\(_2\) (Ti\(_{0.97}\)Co\(_{0.03}\)O\(_2\)) nanoparticles were synthesized using two different methods.

Method 1: Aqueous solutions of TiCl\(_4\) and CoCl\(_2\) • 6H\(_2\)O were mixed, and the pH of the mixture was adjusted to about 6.8 using aqueous ammonia to obtain precipitates. The molar ratio of the prepared reagent was Ti:Co = 0.97:0.03. The obtained precipitates were washed several times with distilled water and dried at 330 K in a thermostat. The as-prepared samples were subjected to heat treatment in a furnace in air at annealing temperatures between 723 K and 873 K for 10 hours.

Method 2: Aqueous solutions of TiCl\(_4\), CoCl\(_2\) • 6H\(_2\)O, and Na\(_2\)SiO\(_3\) • 9H\(_2\)O were mixed, and the pH of the mixture was adjusted to about 6.8 using aqueous ammonia to obtain precipitates. The molar ratio of the prepared reagent was Ti:Co:Si = 0.97:0.03:1.00. Subsequent to mixing the solutions, the obtained precipitates were washed and dried in the same manner as in method 1. The as-prepared samples were subjected to heat treatment in a furnace in air at annealing temperatures between 873 K and 1073 K for 10 hours.

2.2. Property analysis

Each sample was examined using CuK\(_\alpha\) X-ray diffraction (XRD, \(\lambda = 0.154\) nm) and X-ray fluorescence analysis (XRF). The average sample diameters were analyzed by fitting the theoretical 101 diffraction peak of the anatase phase to the measured diffraction peak of each sample. The theoretical diffraction patterns were calculated using the Stokes & Wilson method [16] by means of crystallite size distribution analysis software (Ver. 1.3, Rigaku Corporation, Japan). Magnetization measurements were carried out at 300 K under a magnetic field of \(\pm 50\) kOe using a SQUID magnetometer.

Chemical analysis was performed in order to confirm the molar ratio of the ions in each of the obtained samples. The X-ray fluorescence analysis patterns of the samples prepared via the two methods are shown in figure 1. Subsequently, the actual Ti and Co content was determined by using fundamental parameter method. The molar ratio of the sample obtained via method 1 was Ti:Co = 0.969:0.031, and that of the sample obtained via method 2 was Ti:Co = 0.967:0.033. We confirmed that the Ti and Co ions present in each sample as charged quantities contained no impurity ions. Actual Ti and Co content is summarized in Table 1.

![Figure 1](image-url)  
**Figure 1.** X-ray fluorescence analysis patterns of samples prepared by two different methods.

**Table 1.** Actual Ti and Co content, as determined by XRF.

| Sample obtained | Ti content (%) | Co content (%) |
|-----------------|---------------|---------------|
| Method 1        | 96.9          | 3.1           |
| Method 2        | 96.7          | 3.3           |
3. Results and Discussion

3.1. X-ray diffraction
The X-ray diffraction patterns of samples obtained via two methods are shown in figures 2 and 3. Figure 2 shows the XRD patterns of samples prepared via method 1 (sample set 1). In the case of the sample that was annealed at 723 K, all the detectable peaks can be indexed as those corresponding to the anatase phase. The peaks corresponding to the rutile phase and CoTiO$_3$ were clearly detected in addition to the peaks corresponding to the anatase phase in the samples annealed at 773 and 873 K. The average diameters were estimated to be 14, 31, and 61 nm for the samples annealed at 723, 773, and 873 K, respectively. Figure 3 shows the XRD patterns of samples prepared via method 2 (sample set 2). In the case of the samples annealed at 873 K, 923 K, and 973 K, all the detectable peaks can be indexed as those corresponding to the anatase phase. The peaks corresponding to the rutile phase appeared in the sample annealed at 1023 K, and all the detectable peaks can be indexed as those corresponding to the rutile phase and the SiO$_2$ crystal in the sample annealed at 1073 K. The average diameters of the samples obtained via method 2 were estimated to be 4.2, 6.0, 7.0, and 13 nm at annealing temperatures of 873, 923, 973, and 1023 K, respectively. Figure 4 shows the relationship between the particle diameter and the annealing temperature for each sample set. From these results, we determined that the average diameter of Ti$_{0.97}$Co$_{0.03}$O$_2$ nanoparticles could be controlled by adjusting the temperature of the annealing process. The results of the XRD analysis indicated the following:

1. Samples prepared via method 2 exhibit a higher anatase-to-rutile-phase transition temperature when compared with that for samples prepared via method 1.

2. The particle sizes of the samples in set 2 were smaller than those of the samples in set 1 when they were annealed at the same temperature, and the particle sizes in the case of the set 2 samples grew more slowly than those of the set 1 samples.

3. The CoTiO$_3$ peak was not detected in the set 2 samples regardless of the annealing temperature.

It has been speculated that Ti$_{0.97}$Co$_{0.03}$O$_2$ nanoparticles prepared by method 2 are encapsulated in amorphous SiO$_2$ [15]. It has been previously reported that TiO$_2$ encapsulated in SiO$_2$ leads to the suppression of the anatase-to-rutile transition [17]. Even in our study, anatase-to-rutile-phase transition was suppressed, and as a result, a higher anatase-to-rutile-phase transition temperature was observed. In addition, the presence of amorphous SiO$_2$ contributed towards nanometer-level control of particle sizes of the samples in set 2. Furthermore, the XRD results show that the CoTiO$_3$ peak was detected in sample set 1. We speculate that this could be due to the fact that Co ions may not be completely soluble in the TiO$_2$ lattice.
**Figure 2.** X-ray powder diffraction patterns of samples prepared via method 1 and annealed at 723, 773, and 873 K in an air atmosphere.

**Figure 3.** X-ray powder diffraction patterns of samples prepared via method 2 and annealed at 873, 923, 973, 1023, and 1073 K in an air atmosphere.
3.2. Magnetization measurements

At this stage of the study, the two types of anatase structures prepared via the two above-mentioned methods were compared in terms of magnetization measurements. Figure 5 shows the magnetization curves at room temperature (300 K) of the sample annealed at 723 K via method 1 (named “sample A”) and the sample annealed at 973 K via method 2 (named “sample B”). Both samples exhibit an identical crystal structure and an equal number of magnetic ions, as confirmed by XRF and XRD measurements. It was found that both samples exhibited ferromagnetism at room temperature. For sample A, the saturation magnetization per Co ion, $M_S$, was $0.8 \times 10^{-3} \mu_B$, and the magnetic coercive force, $H_C$, was 32.5 Oe. In the case of sample B, the saturation magnetization per Co ion, $M_S$, was $2.5 \times 10^{-3} \mu_B$, and the corresponding $H_C$ value was 71 Oe. Remarkably, both the samples exhibited different magnetic parameter values regardless of the fact that they possessed the same crystal structure and the same number of magnetic ions. In the case of sample A (method 1), we speculate that Co ions might not be completely soluble in the TiO$_2$ lattice; a CoTiO$_3$ peak was detected for samples annealed at high temperatures. Co ions that did not dissolve in the TiO$_2$ lattice may have led to the formation of oxidative products such as CoO, Co$_3$O$_4$, and CoTiO$_3$, which exhibit Néel temperatures of $T_N = 291, 33, 38$ K, respectively. These impurities might contribute to the decrease in the magnetic moment of Co per ion in this sample.

The results of the magnetization measurements at room temperature (300 K) in the case of samples obtained via method 2 (two different particle sizes) are shown in figure 6. In the figure, the 7.0-nm-diameter sample is the same as the sample for which the magnetization curve is shown in figure 5. The saturation magnetization per Co ion, $M_S$, for the 4.2-nm-diameter sample was $1.0 \times 10^{-3} \mu_B$, and the magnetic coercive force $H_C$ was 44 Oe. We confirmed that 4.2-nm sample exhibited a decreased ferromagnetic interaction when compared with the 7.0-nm sample. We attribute this variation in magnetic parameters between the 4.2- and 7.0-nm samples to the different degrees of solubility of Co ions in the TiO$_2$ lattice as well as the difference in the magnetization curves of the two samples (figure 5). In order to confirm the impurities existing in above-mentioned samples, XAFS and XPS measurements will be performed in the near future [18].

Figure 4. Average diameters estimated from the 101 X-ray diffraction peaks of samples obtained via methods 1 and 2.
Figure 5. Magnetization curves for samples A and B at 300 K.

Figure 6. Magnetization curves at 300 K for samples obtained via method 2 for particle diameters of 4.2 and 7.0 nm.

4. Conclusion
We successfully prepared Co-doped anatase TiO$_2$ nanoparticles that exhibited ferromagnetism at room temperature via two simple and novel preparation methods. The XRD results showed that the crystal structures of both sample A (obtained via method 1; annealed at 723 K) and sample B (obtained via method 2; annealed at 973 K) are anatase single-phase structures. The magnetic properties of each sample were examined; the magnetic properties of the two sample sets prepared by these methods were dissimilar. Nevertheless, each representative sample exhibited an identical crystal structure and an equal number of magnetic ions, as confirmed by XRF and XRD measurements. We speculate that the solubility of Co ions in the TiO$_2$ lattice depends on the sample preparation method, and that magnetic impurities interfere with the ferromagnetism of Co-doped anatase TiO$_2$. 
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References

[1] Ohno H 1998 Science 281 951–956
[2] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and H. Koinuma 2001 Science 291 854–856
[3] Ohtsuki T, Chainani A, Eguchi R, Matsunami M, Takata Y, Taguchi M, Nishino Y, Tamasaku K, Yabashi M, Ishikawa T, Oura M, Senba Y, Ohashi H and Shin S 2011 Phys. Rev. Lett. 106 047602
[4] Manivannan A, Seehra M S, Majumder S B and Katiyar R S 2003 Appl. Phys. Lett. 83 111–113
[5] Matsumoto Y, Takahashi R, Murakami M, Koida T, Fan X J, Hasegawa T, Fukumura T, Kawasaki M, Koshihara S and Kounuma H 2001 Jpn. J. Appl. Phys. 40 L1204–L1206
[6] Fukumura T, Toyosaki H, Ueno K, Nakano M and Kawasaki M 2008 New J. Phys. 10 055018
[7] Manivannan A, Glaspell G and Seehra M S 2003 J. Appl. Phys. 94 6994–6996
[8] Bryan J D, Heald S M, Chambers S A and Gamelin D R 2004 J. Am. Chem. Soc. 126 11640–11647
[9] Choudhury B, Choudhury A, Maidul Islam A K M, Alagarsamy P and Mukherjee M 2011 J. Magnetism Magnetic Mater. 323 440–446
[10] Li J-G, Büchel R, Isobe M, Mori T and Ishigaki T 2009 J. Phys. Chem. C 113 8009–8015
[11] Ichiyanagi Y, Kubota M, Moritake S, Kanazawa Y, Yamada T and Uehashi T 2007 J. Magnetism Magnetic Mater. 310 2378–2380
[12] Ichiyanagi Y, Uehashi T and Yamada S 2004 Physica Status Solidi (c) 12 3485–3488
[13] Kubota M, Kanazawa Y, Nasu K, Moritake S, Kawaji H, Atake T and Ichiyanagi Y 2008 J. Therm. Anal. Calorim. 92 461–463
[14] Kimura S, Mashino T, Hiroki T, Shigeoka D, Sakai N, Zhu L and Ichiyanagi Y 2012 Thermochimica Acta 532 119–122
[15] Moro Y, Katayanagi H, Kimura S, Shigeoka D, Hiroki T, Mashino T and Ichiyanagi Y 2010 Surf. Interface Anal. 42 1655–1658
[16] Ida T, Shimazaki S, Hibino H and Toraya H 2004 J. Appl. Crystallogr. 36 1107–1115
[17] Suyama Y and Kato A 1978 J. Ceram. Soc. Jpn. 86 119–125
[18] Wei H, Yao T, Pan Z, Mai C, Sun Z, Wu Z, Hu F, Jiang Y and Yan W 2009 J. Appl. Phys. 105 043903