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Hydrogenation induced transformation of paramagnetism to room-temperature ferromagnetism in co-doped TiO_2 ceramics

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Abstract Effects of $Co_xTi_{1-x}O_{2-\delta}$ on the sinterability and the ferromagnetism properties of Co_2O_3/TiO_2 ($0.0 < x < 0.06$) ceramics are investigated in this paper. It is found that the Co-doped TiO_2 ceramics transform from paramagnetism to room-temperature ferromagnetism (RTFM) after hydrogenation. With annealing temperatures at 600°C and 1000°C, these as-prepared samples present anatase and rutile structures respectively, which are analyzed with X-ray diffraction (XRD). After hydrogenation, the relation between temperature variations and the magnetic susceptibility for the hydrogenated samples were measured under zero-field-cooled and field-cooled conditions by using SQUID magnetometer. And the hysteresis loops are observed. These ferromagnetism resonance data suggest that the observed RTFM is at least partly due to the Cobalt nano-particles in our hydrogenated samples.

Keywords Ceramics · Room-temperature ferromagnetism · Nanoparticle · Hydrogenation

1 Introduction

Due to the development of the epitaxial technology, it is possible to study the magnetic properties of the ultra thin magnetic films. Matsumoto et al. [1] first reported the room temperature ferromagnetism (RTFM) in semiconducting anatase Co-doped TiO_2 films, which is obtained with pulsed laser deposition (PLD). Soon after, several groups have used different technique methods in experiments, such as oxygen plasma assisted molecular beam epitaxy (OPA-MBE) (anatase films) [2], reaction sputtering [3], pulsed laser deposition techniques [4], ion implantation [5] (rutile films), and spin-on technique [6] (anatase and rutile films). Though with various samples showing unambiguous ferromagnetic properties at 300 K or above, researchers found it difficult to avoid the formation of Co clusters. Consequently, it is improper to attribute the observed magnetism to Co-substituted TiO_2.

It is shown that the thin films have several phases, such as (a) the anti-ferromagnetic phase with surface spins parallel to the external magnetic field, (b) the anti-ferromagnetic phase with surface spins anti-parallel to magnetic field, (c) a surface spin flop phase and (d) a bulk spin flop phase [7]. Magnetic thin films, such as stacked magnets or magnets on superlattices, have shown properties different from those of bulks [8]. It is expected that Co-doped TiO_2 bulk system shows the behaviors, which exist in both the one-dimensional nanowire system and the two-dimensional thin films system. It is important to choose and prepare the room temperature ferromagnetism (RTFM) for semiconducting targets. In this work, we report on the magnetic and structural properties of Co-doped TiO_2 nano-particles prepared by the solid-state reaction.

2 Experiment

The 6% Co-doped TiO_2 samples were prepared by solid-state reaction. The precursor specimens consist of 99.5% pure Co_2O_3 and 99.8% pure TiO_2 powders with an equivalent molar ratio. The powders were first mixed and ball-milled together for ten hours. The resulting mixture was then calcined at 600°C and 1000°C for 12 h, followed by cooling at the ambient temperature. The powder was then milled, made block

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and sintered for 12 h. The prepared ceramic samples were then annealed in atmosphere at 600°C and 1000°C respectively. The above ceramics were then hydrogenated at 600°C for 1 h and 3 h respectively. The ambient gas was mixed with hydrogen and argon. The ratio of the hydrogen pressure to the argon pressure is 1:9. The samples were found to transform from paramagnetism to room temperature ferromagnetism (RTFM) after hydrogenation.

X-ray diffraction (XRD) is used to measure the hydrogenated samples to analyze the material structures. The temperature dependence of magnetic susceptibility and magnetic field variations of magnetization for the hydrogenated samples were measured by using the superconducting quantum interference device (SQUID) magnetometer. The as-prepared samples annealed at 600°C and 1000°C were also studied for comparison.

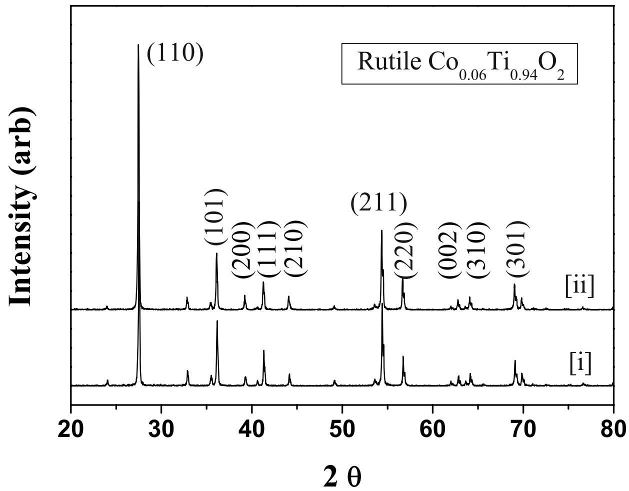

Fig. 2 XRD patterns for the rutile samples, which are annealed at 1000°C, [i] as-prepared sample, and [ii] sample hydrogenated at 600°C for 1 h

3 Experimental results and discussion

The XRD measurement results of the as-prepared and the post-hydrogenated 6% Co-doped TiO_2 ceramic samples are shown in Figs. 1 and 2. The annealing temperature in Fig.1 is 600°C, and both Co_3O_4 and anatase TiO_2 can be found in the as-prepared sample (shown as [i] in Fig. 1). After hydrogenation for 1 h and 3 h ([ii] and [iii] in Fig. 1, respectively), weakly Cobalt peak, instead of Co_3O_4 peak, can be observed.

In Fig. 2, the annealing temperature of the samples is 1000°C. The pure stable rutile TiO_2 is found in both the as-prepared sample ([i] in Fig. 2) and the sample hydrogenated at 600°C for 1 h ([ii] in Fig. 2). Both Co_3O_4 and Cobalt peaks are not observed in the above two XRD patterns.

The magnetism characteristics of the as-prepared and post hydrogenated specimens have been measured with the SQUID magnetometer. The temperature dependence of magnetic susceptibility of the as-prepared sample is shown in Fig. 3. The sample is annealed at 600°C, and the applied field is 100 Oe in the measurement. The sample presents paramagnetism at room temperature, and the magnetic susceptibility follows Curie-Weiss law in the range from 10 K to 300 K. The measured data are fitted with equation: $\chi = \chi_0 + C/(T + \theta)$, in which $\chi_0 = 0.025\ (0.015) \times 10^{-3}$ emu/g Oe, $C = 0.423\ (0.023)10^{-3}$ emu K/g Oe and $\theta = 5.005\ (0.436)$ K. The fitting results are shown as the solid line in Fig. 3. The field dependence of magnetization of the as-prepared sample is also shown as the inset in Fig. 3 to confirm the paramagnetism of measured sample at 300 K.

The temperature dependence of the magnetization for the specimen, which is annealed at 600°C and hydrogenated at

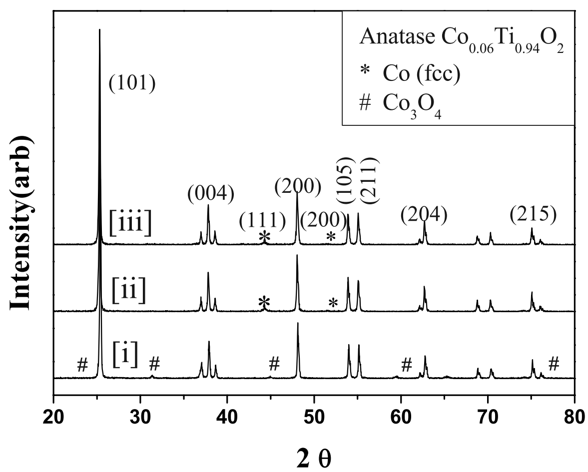

Fig. 1 XRD patterns for the anatase samples, which are annealed at 600°C, [i] as-prepared sample, [ii] sample hydrogenated at 600°C for 1 h, and [iii] sample hydrogenated at 600°C for 3 h

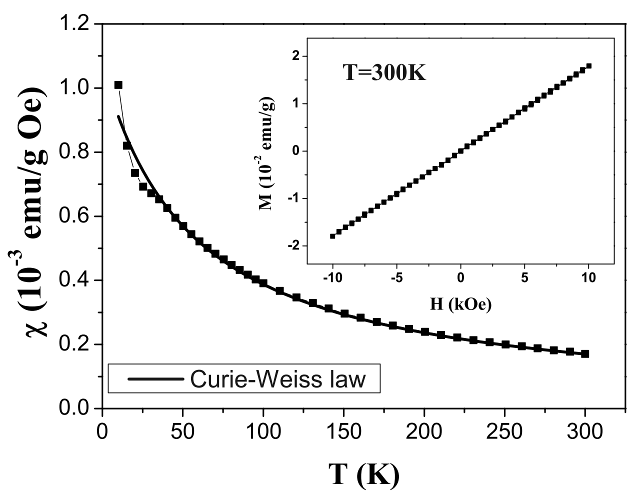

Fig. 3 Temperature variation of the magnetic susceptibility of the as-prepared sample annealed at 600°C. The inset gives the field dependence of magnetization of the as-prepared sample measured at 300 K.

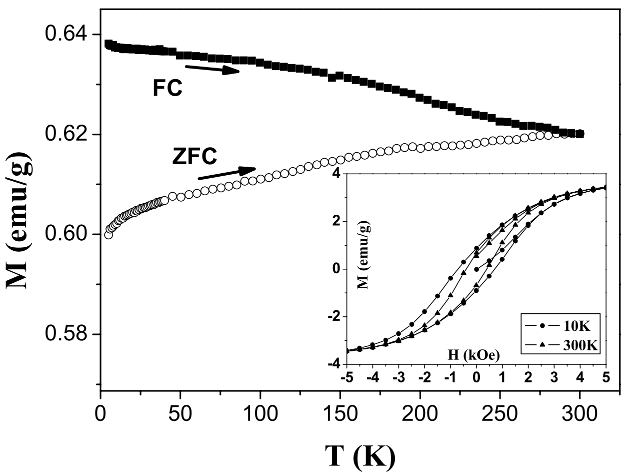

Fig. 4 Temperature variations of the magnetization for the hydrogenated anatase Co-doped TiO_2 sample in both ZFC and FC cases. The sample is annealed at 600°C and hydrogenated at 600°C for 3 h. The inset shows the hysteresis loop of the specimen under both 10 K and 300 K

600°C for 3 h is shown in Fig. 4. The sample is measured from 5 K to 300 K under both zero field cool (ZFC) and field cool (FC) conditions. The external field is 100 Oe for the measurements. The inset in Fig. 4 shows the hysteresis loop of the hydrogenated sample.

The field dependence of the magnetization for the sample, which is annealed at 1000°C and hydrogenated at 600°C for 1 h, is shown in Fig. 5. The hysteresis loop can be

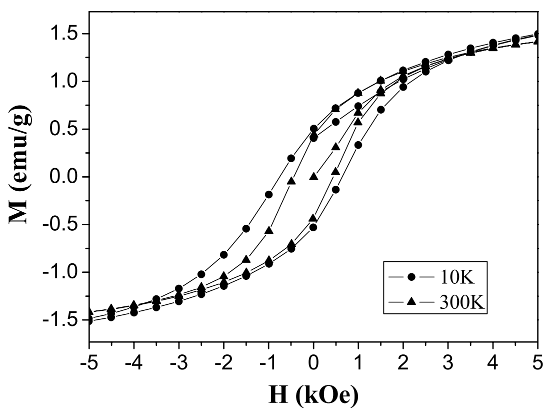

Fig. 5 The hysteresis loop of the hydrogenated rutile Co-doped TiO_2 sample under both 10 K and 300 K. This sample is annealed at 1000°C and hydrogenated at 600°C for 1h

observed under both 10 K and 300 K. According to the XRD measurement results, the post-hydrogenated samples, both with rutile Co-doped TiO_2 (annealed at 1000°C) and anatase Co-doped TiO_2 (annealed at 600°C), are observed to be room temperature ferromagnetism. This phenomenon suggests the origin of the ferromagnetism has no business with the material structure. The substituted cobalt ions become nano particles after the hydrogenation. The ferromagnetism properties are determined by the Co-Co interaction.

4 Conclusions

In this work, the Co-doped TiO_2 ceramic samples are prepared by solid state reaction method. The as-prepared samples are observed to be paramagnetism, and the post-hydrogenated samples are ferromagnetism. After hydrogenation, both the rutile Co-doped TiO_2 and the anatase Co-doped TiO_2 are observed to be room temperature ferromagnetism. The hysteresis loop is observed under both low temperature and room temperature. The ferromagnetism is assumed to be caused by the Cobalt nano particles, which are induced by the hydrogenation of the samples.

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