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Origin of Room Temperature Ferromagnetism in Cobalt-doped TiO_2 powder

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Abstract

Cobalt doped anatase TiO_2 powders were synthesized with different concentration of dopant using the sol-gel method. Morphology of the prepared samples was analyzed by micrograph obtained from Scanning Electron Microscopy (SEM). Particles are observed to have almost spherical shape. To study the room temperature magnetic response of synthesized samples, the measurements were performed using vibrating sample magnetometer (VSM). It is perceived that synthesized Cobalt-doped anatase TiO_2 nanopowders reveal room temperature ferromagnetism (RTFM). The saturation magnetizations (M_s) of 3.8×10^{-3}, 9.0×10^{-3} and 11.6×10^{-3} emu/g, for samples having dopant concentration 2.5, 5.0 and 7.5%, respectively. The coercive forces (H_c) varies from 230 to 730 Oe. The saturation magnetizations increase with Cobalt concentration in the host material TiO_2.

Keywords: TiO_2, Anatase, RTFM

1. INTRODUCTION

There are many oxides such as ZnO, SnO_2, CeO_2 etc. have been studied since last two decades to observed RTFM and origin for the same. The transition metal oxide TiO_2 is one them and has tremendous properties like high stability, non-toxicity, biocompatibility etc. owing to its low cost. Doping of suitable element in host material TiO_2 increases its importance in various fields. Its prominence enhances for solar cells, antibacterial activities, sensors etc.[1]. Further, it is also reported in the literature that the dilute doping of impurities decreases the band gap of the host materials and improves its importance as a visible light active photocatalyst [2]. Doping of suitable dopant in TiO_2 not only increases its photo-activity, but also increases magnetism in it. Thus, it shows ferromagnetic behavior along with semiconductor in nature and such materials are named as spintronic. Many researchers worked after the ignition by Matsumoto *et. al.* [3] on TiO_2 for the improvement of room-temperature ferromagnetic behavior and origins of the same. Still, there are a lot of requirements to enlighten the origin for the RTFM in TiO_2 after doping of transition metal ions. Most of the work are focused on the thin films [3-5] and few works are reported on nanopowder in the literature [1]. Also, there is contradictions for the origin of RTFM in transition metal-doped TiO_2. Hence, the origin of RTFM is still under debate. From the controversial results observed in the literature, it might be concluded that RTFM is very sensitive towards the synthesis processes and conditions. Therefore, these facts motivated to study the effect of dopant concentration on the variation of RTFM and to analyze the origin of it. Cobalt doped TiO_2 is one of such material which has been found applicability in spintronic devices. Cobalt doped TiO_2 have been studied in the form of thin films to modify the magnetism and origin of which are suggested to be related with p–d exchange interaction, bound magnetic polaron interaction theory (BMP), hole-mediated interaction and the presence of structural defects [6,7].

2. EXPERIMENTAL DETAILS

Doped and undoped TiO_2 nano crystalline were prepared by a sol-gel method using Titanium Tetrabutoxide ($Ti(OC_4H_9)_4$) and Cobalt Acetate Tetrahydrate ($Co(C_2H_3O_2)_2 \cdot 4H_2O$) as a precursor. The glacial acetic acid is preferred as a solvent. The stirring was performed for one hour at room temperature to get the homogeneous solution of the precursors and solvent dissolved in proper stoichiometry ratio to get 0.0, 2.5, 5.0 and 7.5 % doping concentration. The solution obtained was kept in an oven at 80^{o}C to get the gel and further to dry it. The final powder obtained after grinding was annealed in a furnace at 600 ^{o}C for 2 hours. The synthesized sample are marked A, B, C and D for doping concentrations 0.0,2.5, 5.0 and 7.5 respectively in the figures for SEM and VSM results. The morphology analysis of all samples was studied using micrograph obtained from SEM. The hysteresis curve is obtained from VSM to study the magnetic behavior of the samples.

3. RESULT AND DISCUSSION

The morphology of the doped and undoped TiO_2 powder as obtained by sol-gel technique were characterized by micrograph obtained from SEM as shown in fig.1(A-D). The SEM images indicating the cluster formation in the samples with a particles size of few hundred nanometers. Particles are almost of spherical in nature.

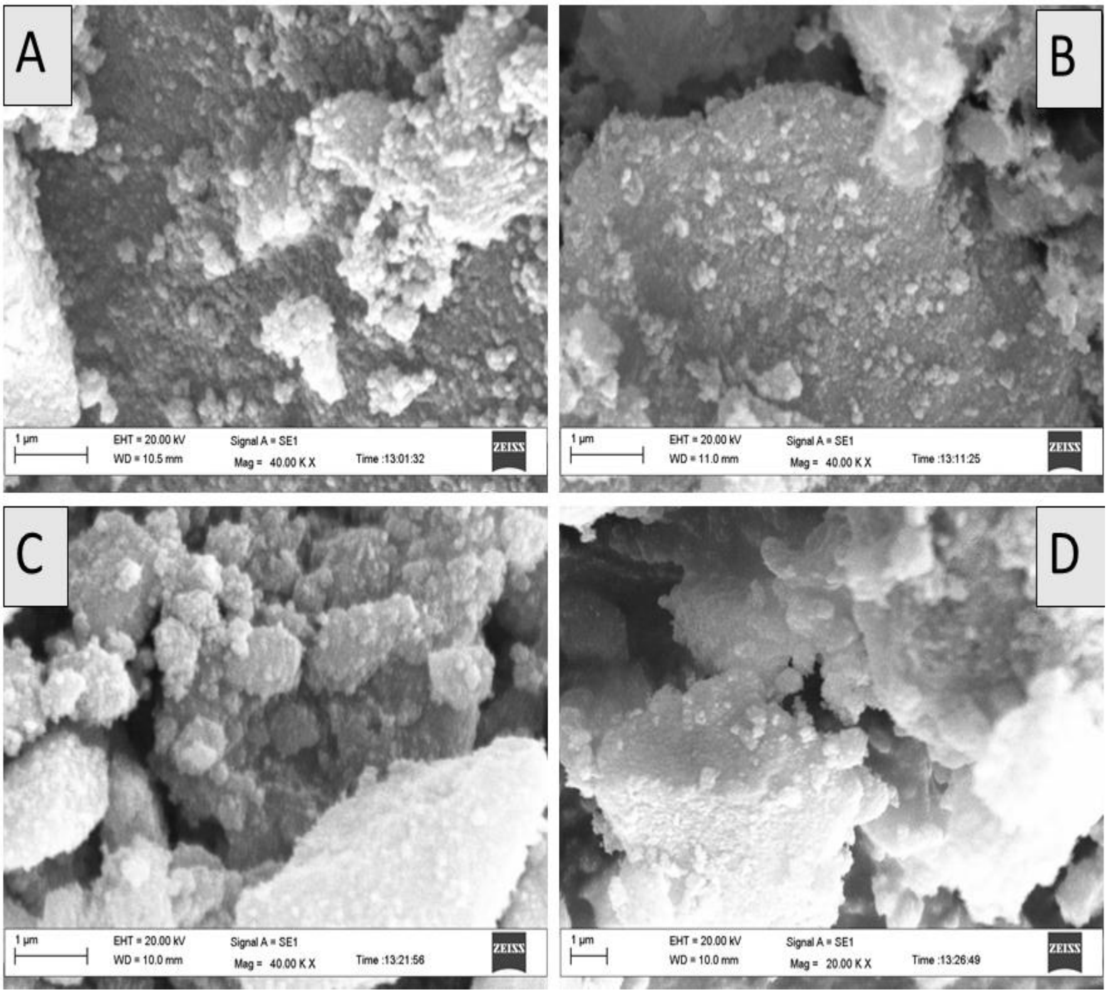

Fig. 1- SEM micrograph for undoped and cobalt doped TiO_2 powder.

Fig 2(A-D) shows M-H curves measured at room temperature for undoped and Cobalt-doped TiO_2 powder. Results for undoped TiO_2 indicates its diamagnetic nature, while cobalt doped samples clearly showing the room temperature ferromagnetic behavior. With the increase in doping concentration increase in M_s observed. The values of M_s are 3.8×10^{-3}, 9.0×10^{-3} and 11.6×10^{-3} emu/gm for 2.5, 5.0 and 7.5% doping concentration respectively. Karthik *et.al*.[8] reported the similar type if results but here improved results are obtained. Our main aim is to understand the origin of RTFM. Generally, there is two mechanisms i.e. Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions and bound magnetic polarons (BMP), to understand the origin of magnetism. RKKY applicable on the metallic system while BMP on semiconducting or insulating materials. Here, the existence of oxygen vacancies is considered to explain the origin of RTFM. With cobalt doping, the oxygen vacancies attained in the host material. As the dopant concentration increase the oxygen vacancy increases. With the increase of oxygen vacancies the number of F centers increases. The electrons are localized in the oxygen centers i.e. near Co^{2+} which results in exchange interaction named as F center exchange mechanism (FCE). FCE is sub class of bound magnetic polaron (BMP) theory and is suitable to explain the origin of RTFM here [9]. According to this theory, the RTFM arises due to the presence of oxygen vacancies. There are three possible charge states of an oxygen vacancy i.e. F^{2+}, F^{1+} and F^{0+}center with zero, one and two trapped electrons respectively. The F^0 center charge states form a shallow donor level or lie above the conduction band edge. Further, the doped magnetic ions align in ferromagnetic order via an electron trapped in oxygen vacancy. Here, magnetism is observed the due formation of impurity bands when the F^0 center states overlap with the conduction band of the host oxide [9] With the increase in dopant concentration M_S increases, it has been attributed to the good solubility of dopant up to used percentage. Hence, to get stable magnetic semiconductors, there is a requirement of host matrix that has good solubility of magnetic ions [10].

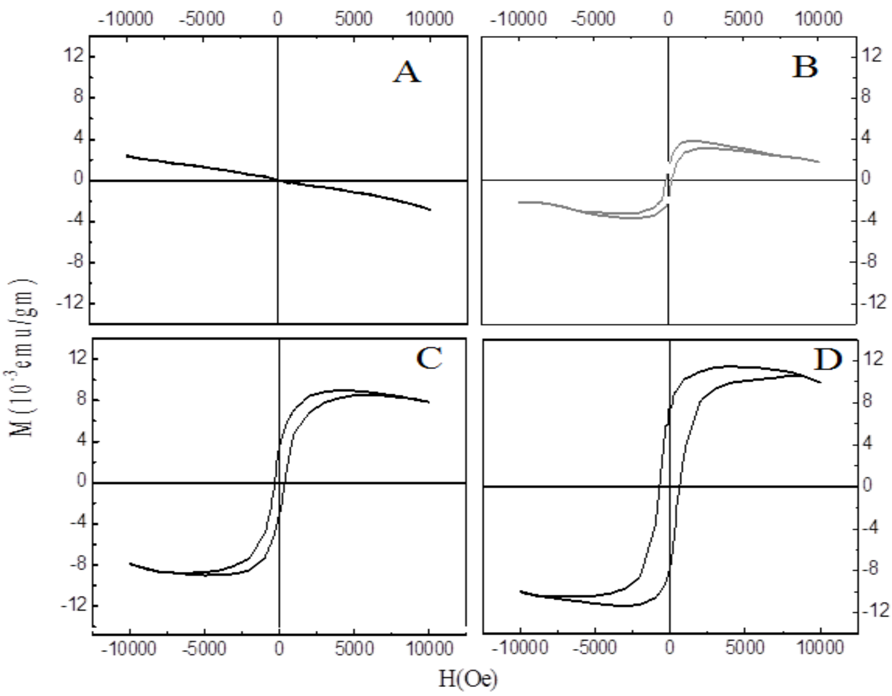

Fig. 2- M-H curves for undoped and cobalt doped TiO_2 powder.

CONCLUSION

Synthesized particle are almost in spherical in shape. Undoped TiO_2 samples are diamagnetic and cobalt doped TiO2 samples shown the RTFM. The saturation magnetization increases with dopant concentration. Origin of magnetism is explained with F center exchange mechanism. The observed RTFM should be exchanged interaction of the Co^{2+} ions via oxygen vacancies.

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