

Magnetic Property Study in Eu Doped TiO₂ Nanoparticles

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Abstract—Doped TiO₂ is among the diluted oxide base magnetic semiconductor with potential uses such as in spintronic devices and magneto-optical devices. Oxygen vacancies play an important role in promoting long-range ferromagnetic (FM) ordering in doped TiO₂. In our work Europium (Eu) doped TiO₂ nanoparticles have been synthesized using simple sol-gel technique. The structural characterisation of the nanoparticles were performed by X-ray diffraction and transmission electron microscopy. In the present investigation at low concentration of dopant (Eu³⁺) ions, the material shows ferromagnetic behavior. However as the concentration is increased, transition to paramagnetic phase is noticed. The electronic configuration of Eu is Xe4f⁷6s². At higher concentration because of the shielding of the 4f shell by 6s5d electrons, the interaction of these unpaired electrons is anticipated to be very weak. These noninteracting and localized magnetic moment of the Eu³⁺ ions induces the observed paramagnetism.

1. INTRODUCTION

Diluted magnetic semiconductors (DMSs) and Diluted Magnetic Oxides (DMOs) are very interesting class of materials studied over last few decades or so. Most of the wide band-gap oxide semiconductors such as ZnO, In₂O₃, TiO₂, SnO₂, CuO, HfO₂ although are non-magnetic but injection of spin in these DMOs have been made possible by utilising them as the host matrix for the magnetic ions such as transition metal ions to visualize ferromagnetism. Although bulk TiO₂ has been found to be non-magnetic in nature, induction of magnetism has been made successful by the incorporation of magnetic ions in the TiO₂ matrix or by inducing crystalline defects in its crystalline structure such as oxygen vacancies. Hence choice of growth conditions and synthesis technique plays an important role in determining the magnetism.

TiO₂ is a transparent wide band gap semiconductor. Rare earth doping has been proposed not only to introduce magnetism in TiO₂ nanoparticles but also avail the excellent luminescence of these elements. Nguyen Hoa Hong et.al. observed room temperature ferromagnetism in undoped TiO₂, HfO₂ and In₂O₃ thin films [1]. Soack Dae Yoon et.al. detected oxygen defect

induced magnetism in semiconducting anatase TiO₂ films[2]. S k Pandey and R J Choudhary reported that oxygen vacancies formation due to creation of defects don't induce appreciable magnetism but doping of non-magnetic ions do[3]. In the present work, the effect of incorporating Eu³⁺ ions in TiO₂ matrix on its magnetic properties has been investigated by employing Vibratory Sample Magnetometer (VSM). However Choudhury et.al. found paramagnetic behavior of Gd³⁺ doped TiO₂ under room temperature conditions[4]. Their samples exhibited negative Curie-Weiss temperature which has been believed due to exhibition of antiferromagnetic interaction.

The electronic configuration of Eu is [Xe]4f⁷6s² with unpaired electrons in the 4f shell. The 4f electronic transitions make rare earth elements special. In transition metal, magnetic moment arises from partially filled outermost 3d electrons, whereas in rare earth ions magnetic moment arises from the inner 4f incomplete sub-shell. Shielding effect reduces the probability of interaction of the unpaired electrons with the dopant ions. In rare earth ions, the 4f electrons are shielded by the 5d6s electrons and the strength of spin-orbital coupling is much greater than the crystal field energy whereas the reverse is the fact in case of transition elements with partially filled d-orbital [4].

2. EXPERIMENTAL DETAILS

2.1 Preparation of Eu doped TiO₂

Specimen	Average crystallite size (nm)
Undoped TiO ₂	7.775
1Eu:TiO ₂	6.151
3Eu:TiO ₂	6.147
5Eu:TiO ₂	5.510

Synthesis of Eu-doped TiO₂ nanoparticles has been accomplished by employing the most exploited sol-gel technique. Synthesis has been carried out with three different europium concentrations 1, 3 and 5%. In a typical synthesis 5 ml of titanium isopropoxide was added to 15 ml of 2-propanol under constant stirring. After 15 min of stirring, 1 ml of water was added to initiate the hydrolysis reaction. Then europium

nitrate pentahydrate $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with the aforementioned concentration, was slowly added to the hydrolysed mixture under vigorous stirring. Once all dopant solutions were added, the mixture was stirred for 5 h. During this time of the reaction, first a sol was formed, which ultimately transformed into gel. After this time period the stirring was stopped, and the gel was left in ageing condition for 12 h. The prepared material was dried in air at 80°C and then heat treated at 450°C to get the desired Eu^{3+} -doped TiO_2 nanoparticles.

2.2 Characterisation Details

The structure of all the samples are determined using Rigaku Miniflex CD 10041 XRD unit with copper target and $\lambda = 0.154 \text{ nm}$ at a scanning rate of $1^\circ/\text{min}$ and in the scanning range of $10\text{--}80^\circ$. High resolution transmission electron microscope images for morphology and particle size determination are observed with JEM-2100, 200 kV JEOL. The elemental compositions are known from energy dispersive X-ray analysis (EDX) equipped with a JEOL JSM 6390 LV scanning electron microscope (SEM). Magnetic measurements are carried out in a vibrating sample magnetometer (VSM) using a selection of Varian and Walker electromagnets.

3. RESULTS AND DISCUSSIONS

3.1. Structural and morphological analysis

The XRD pattern of the specimens are shown in Fig.1. A close observation of the plot shows that compared to undoped TiO_2 the most intense peak (101) is slightly shifted to the lower angle side which is due to the incorporation of europium ions in the doped sample. The average particle size has been calculated using the Scherrer equation.

$$d = \frac{0.9\lambda}{\beta \cos\theta}$$

Where λ = wavelength of the X-ray source used; β = full width at half maximum (FWHM); θ = Bragg diffraction angle.

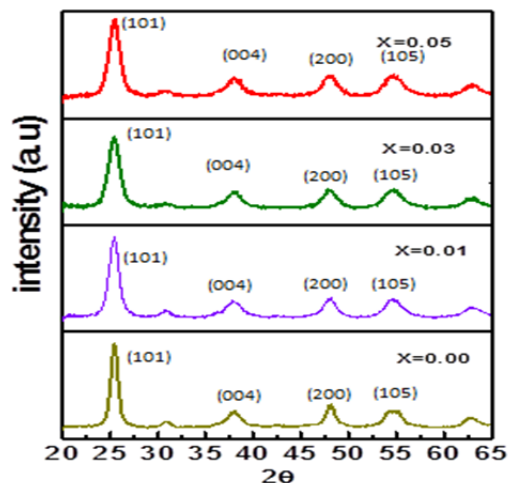


Fig. 1: X-ray diffraction pattern of all the samples.

The average crystallite is shown in Table 1

Table 1: Average crystallite size calculated using Scherrer's formula

Specimen	Average crystallite size (nm)
Undoped TiO_2	7.775
1Eu: TiO_2	6.151
3Eu: TiO_2	6.147
5Eu: TiO_2	5.510

Due to the large size incongruity with Ti^{4+} (0.68 \AA), Eu^{3+} (1.07 \AA) ions cannot inhabit the sites in the lattice of TiO_2 [5]. The particles reside on the particle surface and on the grain boundaries and thereby produces strain in those regions. As a result of this the repulsive interaction between the Eu^{3+} ions increases and in turn prevents the coalescence of nanocrystallites by forming Eu-O-Ti bonds [4].

The transmission electron microscope images of the undoped and Gd doped TiO_2 nanoparticles are shown in Fig 2(a-d). The TEM image shows that the particle size for undoped TiO_2 is 15-20 nm while for doped TiO_2 it is 7-9 nm. A nanoparticle of polycrystalline aggregates is composed of different size grains. Scherrer's formula determines the size of rationally diffracting grain size. In addition the size determined by Scherer's formula is affected by instrumental broadening, crystalline strain, defects, etc. TEM, on the other hand provides unswerving evidences of the nanoparticle size, shape. It is to be mentioned that due to the polycrystalline nature containing several grain sizes the crystallite size is not generally same as the particle size [4].

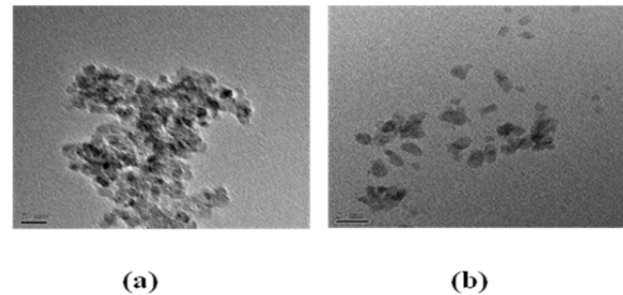


Fig. 2: TEM image of (a) undoped (b) doped samples

3.2. Elemental Compositional analysis

The compositional analysis of ($x=0.05 \text{ mol}$) is performed with EDX analysis. The spectrum is marked with the signals obtained from Ti, O, Eu is shown in Fig.3

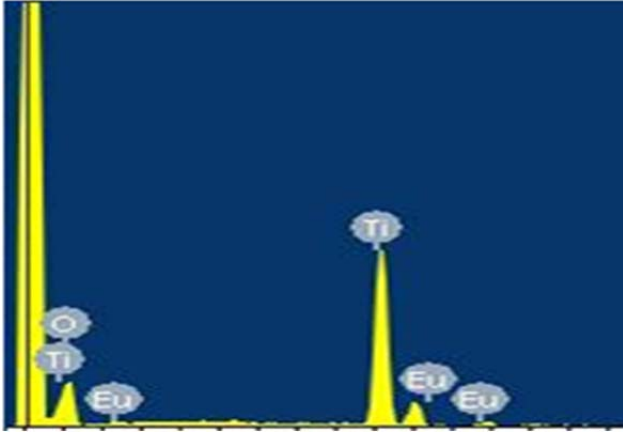


Fig. 3: EDX analysis of doped samples

3.3. Magnetic study of the samples

Fig.4 shows the M-H curve doped samples ($x=0.01, 0.05$). At low concentration of dopant (Eu^{3+}) ions, the material shows ferromagnetic behavior. However as the concentration is increased, transition to paramagnetic phase is noticed. The electronic configuration of Eu is $\text{Xe}4f^76s^2$. At higher concentration because of the shielding of the 4f shell by $6s5d$ electrons, the interaction of these unpaired electrons is anticipated to be very weak. These noninteracting and localized magnetic moment of the Eu^{3+} ions induces the observed paramagnetism.

From the M-H curve it is seen that dopant concentration of 0.01 mol is showing ferromagnetic behavior while 0.05 mol shows paramagnetic behavior. The ferromagnetism may be due to the substitution of Ti^{4+} ions by the Eu^{3+} ions. Europium ions on substituting Ti^{4+} creates oxygen vacancies. These oxygen vacancy with single trapped electron (F^+ center) behaves like a 1s hydrogenic type orbital. This F center may couple with the nearest Ti or Eu 4f orbital and form bound magnetic polaron (BMP). When the size of the bound magnetic polaron is large enough to percolate through the lattice, long range ferromagnetism could be realized. However with the increase in Eu concentration upto 0.05 mol the number of Eu ions in the interior of TiO_2 lattice is comparatively less than that on its surface or on the grain boundary. Only those Eu ions are allowed to enter the lattice that are permissible by the host and the rest are expelled. Doping at higher level decreases the separation among Eu^{3+} ions. These largely separated ions undergo super-exchange interaction with each other via O^{2-} ions and results in antiparallel alignment of the magnetic spins of Eu 4f shell present in the nearest neighbor. Thus it is anticipated that higher dopant concentration tends to destroy the observed ferromagnetism in Eu doped TiO_2 nanoparticles.

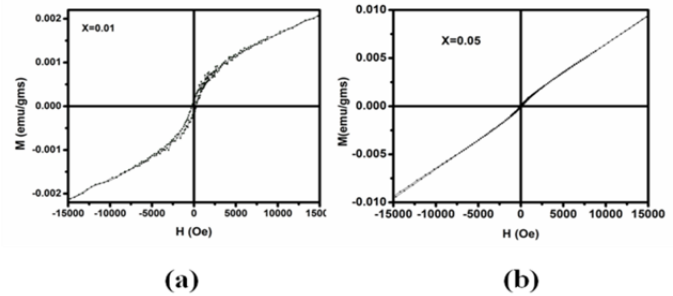


Fig. 4: M-H curve of 0.01 mol and 0.05 mol Eu doped TiO_2 samples

4. CONCLUSION

In summary, we have prepared Eu doped TiO_2 nanoparticles employing a simple sol-gel method. XRD and TEM study reveals that the dopant ions interferes with the growth of the nanoparticles by sitting on the surface or on the grain boundaries. Magnetic study shows that higher dopant concentration destroy the observed ferromagnetism behavior and induces paramagnetism in the samples.

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REFERENCES

- [1] Hong,N.H., S, Joe, Poirot,N, B, Virginie Room-temperature ferromagnetism observed in undoped semiconducting and insulating oxide thin films, *Phys Rev B* , 13, April 2006, 132404.
- [2] Yoon,D,S.,Chen.Y,Yang,A,Goodrich,T.L.,Zuo,X, Arena,A,D, Zimer,K, Vittoria, C, Harris,V.JYoon Oxygen-defect-induced magnetism to 880 K in semiconducting anatase $\text{TiO}_{2-\delta}$ films, *J.Phys.: Condens. Matter*, 23 June 2006, L355-L361
- [3] Pandey,S.K , Choudhary, R J Effect of non-magnetic impurities on the magnetic states of anatase TiO_2 , *J. Phys.: Condens. Matter* 23, 21 June 2011, 276005 (5pp).
- [4] Paul,S,Choudhury,B,Choudhury,AMagnetic property study of Gd doped TiO_2 nanoparticles *J.Alloys and Compounds* , 601, 22 Feb 2014, 201-206.
- [5] Mukherjee.S,Sudarsan,V,Vasta,R.K,Tyagi,A.K, Luminescence studies on Lanthanide ions (Eu^{3+} , Dy^{3+} and Tb^{3+}) doped YAG: Ce nanophosphors *J.Luminescence* , 129, 27 Aug 2008 , 69-72