



Effect of indium doping on magnetic properties of cerium oxide nanoparticles

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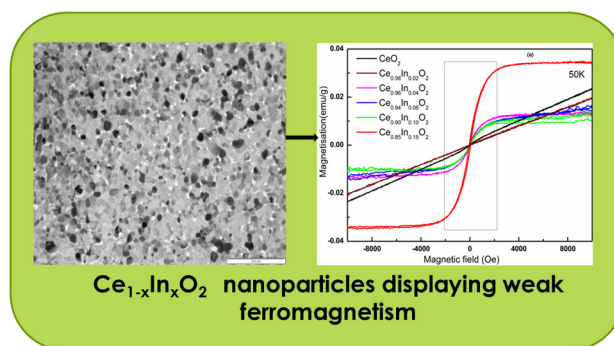
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HIGHLIGHTS

- Pristine and In doped CeO₂ nanoparticles prepared by sol-gel method.
- Doped samples display super-paramagnetic behaviour.
- XPS confirmed the mixed valence state of Ce³⁺/Ce⁴⁺.
- Nano-size and associated defects are responsible for the observed magnetism.

GRAPHICAL ABSTRACT



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ABSTRACT

Ce_{1-x}In_xO₂ (x = 0.0, 0.02, 0.04, 0.06, 0.10 and 0.15) nanoparticles have been successfully synthesized by sol gel method using citric acid as a gelling agent. The gel obtained was characterised using DG-DTA analysis. The XRD confirmed the fluorite phase formation and purity of the compounds. Morphological studies revealed the flaky and porous nature as seen from SEM images. TEM showed that the average particle size obtained is less than 20 nm. The existence of Ce³⁺/Ce⁴⁺ oxidation states is confirmed from XPS data which in turn results in the oxygen deficiency in the system. The Electrical studies displayed the typical semiconductor nature of the nano-particles. The dilute magnetic property has been studied using VSM where the existence of very weak room temperature ferromagnetism is seen in pristine sample which is found to be enhanced on indium doping where for Ce_{0.85}In_{0.15}O₂ composition showed a super-paramagnetic nature with negligible coercivity (*H_c*), in magnetisation v/s field studies. The saturation magnetisation (*M_s*) and coercivity (*H_c*) are further found to be enhanced at 50 K. When compared with the bulk sample the magnetism here was found to be lowered or reduced. This suggests that the oxygen vacancies and defects in the nanostructure are responsible for the observed magnetic behaviour in the prepared compounds.

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1. Introduction

Dilute magnetic semiconductors (DMS), exhibiting room temperature ferromagnetism (RTFM) have been the significant topic of research for last couple of decades owing to their applications in

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the field of spintronics [1–4]. Several non-magnetic semiconductor oxides, when doped with transition metals display room temperature ferromagnetism. Cerium oxide is one of the metal oxides screened for DMS property. Cerium oxide (CeO_2) is a well-known rare earth oxide used in various applications, which majorly includes catalysis [5–8] and solid oxide fuel cells [9–11]. The presence of redox equilibrium ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$), electronic structure and mobility of vacancies govern most of its properties [12]. These properties also make it a potential candidate for DMS. Several reports are available on pristine [13,14] and transition metal doped cerium oxide nanoparticles revealing their magnetic properties [15–24]. Ferromagnetism (FM) origination from magnetic ions mediated by oxygen vacancies is reported for Co and Ni doped ceria [13,25]. R. A. Kumar et al. also reports ferromagnetism in pristine and Fe, Gd co doped cerium oxide nanoparticles [26].

The influence of oxygen vacancies (V_o) on FM in Co doped CeO_2 was revealed by Q.Y. Wen [27] and Y.Q. Song et al. [28]. S.Y. Chen et al. showed that Cr^{3+} incorporation in CeO_2 promotes FM by reducing the distance between magnetic Ce^{3+} and increasing the defect density [29]. Ferromagnetism originating from F centre has also been shown by S. Phokha et al. in Cr doped Samples [30]. The ferromagnetism in rare earth doped cerium oxide bulk samples has been investigated by M.C. Dimri et al., the Nd and Sm doped compounds showed RT FM whereas in La, Tb, Gd, Er and Dy it was found to be absent. Here the FM is attributed to oxygen vacancies and not surface defects owing to the presence of FM in bulk sintered samples also [31].

Effect of non-magnetic dopant (Ca^{2+}) on the magnetic property of CeO_2 was studied by X. Chen et al. [32]. While there are several reports available which attribute the observed ferromagnetism to oxygen vacancies (V_o) in doped as well as pristine as mentioned above [13,14,33], at the same time Y. Liu et al. reveals no linkage between observed FM in pristine CeO_2 and V_o but attributes it to the smaller particle size [34]. Recent paper by S. Sonsupapa et al. displayed ferromagnetism in Fe doped CeO_2 nano-fibers originating from V_o defects where calcinations increases the FM ordering which is attributed to the increased participation of Fe^{3+} ions in exchange mechanism [35]. More than some few reports are also exist on pure CeO_2 exhibiting FM at room temperature [36,37]. The nano-particle size, defects in structures and the doped impurities are the probable explanations given so far for the origin of observed ferromagnetism.

In the present study In^{3+} doped CeO_2 nano-particles have been prepared, characterised and its magnetic properties have been evaluated. To the best of knowledge this is the first report on $\text{Ce}_{1-x}\text{In}_x\text{O}_2$ compositions and their magnetic properties.

2. Experimental

$\text{Ce}_{1-x}\text{In}_x\text{O}_2$ ($x = 0.0, 0.02, 0.04, 0.06, 0.10$ and 0.15) nano-particles were prepared by sol gel method [38]. The metal nitrate to citric acid ratio was maintained to 1:3. The starting materials used were $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (sd fine chem. Ltd. 99%), In_2O_3 (Sigma Aldrich 99.9%) and citric acid (Thomas baker 99.7%). In typical synthetic procedure stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in minimum amount distilled water, to this In_2O_3 (dissolved in dilute HNO_3) was added followed by citric acid and the mixture was homogenised by stirring. It was then concentrated on a hot plate. Evaporation of water takes place which proceeds in the formation of a gel. The gel undergoes decomposition in a highly exothermic reaction giving the fine powder which was then sintered at 600°C for 5 h.

The decomposition of the gel was studied on Thermogravimetric–differential thermal (TG–DTA) analyzer (NETZSCH TG–DSC STA 409PC) in air from 30 to 700°C . The

structural characterization was carried out by X-ray diffraction using a RIGAKU MINIFLEX diffractometer with $\text{Cu-K}\alpha$ radiation, in steps of 0.02° . Morphological characterization was carried out by taking images on JEOL model 5800LV Scanning electron microscope (SEM). Particle size and shape was determined using PHILIPS CM 200 transmission electron microscope (TEM), operating at an accelerating voltage of 200 kV . The valence state of the elements were identified by X-ray photoelectron spectroscopy (XPS) where the sample was excited using $\text{Mg-K}\alpha$ radiations ($h\nu = 1254.6\text{ eV}$) and the spectra were analyzed using a VG make CLAIM2 analyzer system in the energy range 0 – 1000 eV . For electrical resistivity studies the samples were pelletized and the measurements were carried out using two probe techniques from 100 to 500°C . The contacts were made directly by touching the probe to pellet to achieve ohmic contact, no special material was used to make contacts. The magnetic measurements were performed using QUANTUM DESIGN PPMS vibrating sample magnetometer (VSM). The magnetisation with varying magnetic field up to 3 KOe was measured at 300 and 50 K and magnetisation with varying temperature was studied at applied field of 500 Oe .

3. Results and discussion

3.1. TG/DTA analysis

The sol-gel method using citric acid was used for the synthesis of $\text{Ce}_{1-x}\text{In}_x\text{O}_2$ compounds. The TG–DTA curves of $\text{Ce}_{0.90}\text{In}_{0.10}\text{O}_2$ gel obtained during the process are presented in Fig. 1. The initial weight loss is about 50% corresponding to loss of water molecules. TG shows a gradual weight loss in this region attributed to the loss of physisorbed and coordinated water accompanied by a sharp endothermic peak at 100°C and slight shoulder around 135°C . The decomposition of the gel proceeds via two steps, around 10% more weight loss is observed in the temperature region of 175°C – 255°C , with an exothermic peak at 207°C . Further, a sudden drop in weight is observed at 278°C with more weight loss of around 23% . This is the temperature at which the gel is completely decomposed producing the desired compound and the oxides of carbon are released. A sharp exothermic peak is distinct at 294°C characteristic of the decomposition process. Further only the calcination takes place by removing any carbonaceous material leftover. The compound is highly stable beyond 310°C , no variation in weight was observed beyond this temperature as seen in Fig. 1.

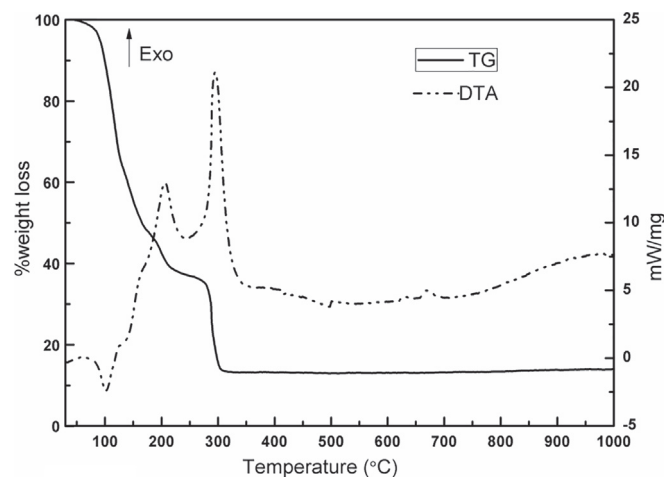


Fig. 1. TG-DTA curves of $\text{Ce}_{0.90}\text{In}_{0.10}\text{O}_2$ gel.

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