Magnetic Properties of Cobalt Doped Ceria Nanoparticles

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Abstract— *Cobalt doped ceria nanoparticles are synthesized by chemical precipitation technique. Latiice parameter and grain size of the as-prepared and annealed samples are calculated from XRD. Lattice parameter decreases and grain size increases with increase in annealing temperature.VSM measurements are carried out to understand the magnetic properties.*

Keywords— *Nanoparticles, XRD, Magnetic Properties*

I. Introduction

DILUTED magnetic semiconductors (DMS) are currently being explored with a strong drive to find room temperature ferromagnetic materials (RTFM) for possible technological applications. DMS are experimentally obtained by doping the oxide matrix with a small amount of magnetic transition metal ions such as Fe^{3+}, Co^{2+}, Mn^{3+} etc. This procedure may introduce ferromagnetism in otherwise non magnetic materials and open up feasibility of applications in spintronics and magneto optical devices [1]. Spintronics has vast potential in the storage, processing, transmission of digital information and optical and magnetic sensors. Many promising compounds such as: Transition Metals (TM) doped ZnO, TiO_2, CeO_2 and HfO_2 have been observed to show RT-FM, but intrinsic origin of the FM is still under debate. Therefore, these controversial results give an indication that FM in DMS is very sensitive to preparation methods and preparation conditions. Most of the room temperature ferromagnetics -DMS materials discovered so far have noncubic crystal symmetry. The RTFM in cubic systems will facilitate the integration of spintronic devices with advanced silicon based microelectronic devices. Among the materials with cubic symmetry, cerium oxide is an interesting candidate for advanced multifunctional devices. The recent discovery of RTFM in pure and/or doped CeO_2 nanoparticles and thin films give realization of future spintronic devices.

II. Experimental

A. Synthesis

The synthesis of cobalt doped cerium oxide nanoparticles was carried out by hydrolysis assisted precipitation techniques as follows: Aqueous solutions of cerium chloride ($CeCl_3.7H_2O$) and Cobalt chloride ($CoCl_3$) were taken in a flask fitted with a Liebig's condenser. The mixed solution was heated at 120 ^{0}C in an electric oven and the evaporated solution was condensed back to the flask by the Liebig's condenser. This process of hydrolysis was carried out for 72 hours [2]. An appropriate amount of ammonium hydroxide was added to the hydrolyzed solution and the obtained precipitate was washed many times with doubly distilled water to remove the remaining ammonia solution and then dried at 100 ^{0}C for 1 h.

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B. Characterizations

X-ray diffraction studies were carried out for the as-prepared and annealed samples using a Rigaku Ultima-III X-ray diffractometer using Cu $K\alpha_1$ radiation in the 2θ range from 20^0 to 80^0 at 30 kV, 20 mA at a scanning rate of 3^0/min. Magnetic measurements were carried using a Lakeshore 7404 vibrating sample magnetometer (VSM).

III. Results And Discussions

Grain size of the as-prepared and annealed samples is calculated from XRD data using Scherrer's formula

$$\text{Average grain size } t_{xrd} = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

where λ is the wavelength of the incident X-rays (1.5406 Å) β is Full Width Half Maximum and θ the diffraction angle.

Table 1**:** Variation of lattice parameter and grain size with annealing temperature

Sample		Lattice parameter (Å)	Grain size (nm)
$Ce_{0.95}Co_{0.05}O_{2-\delta}$	As-prepared	5.38	6.8
	Annealed at 600^{0}C	5.37	8.4
	Annealed at 900 ^{0}C	5.36	19.5
$Ce_{0.85}Co_{0.15}O_{2-\delta}$	As-prepared	5.41	5.0
	Annealed at 600 ^{0}C	5.39	6.9
	Annealed at 900 ^{0}C	5.38	18.4

Lattice parameter is found to be decreasing with increase in annealing temperature because annealing removes the defect states in the samples. Grain size is found to be increasing with increase in annealing temperature due to the enhancement of crystallinity. With the increase of annealing temperature, the growth rate of particles increases more rapidly than the nucleation rate does, and the aggregation trend of particles becomes stronger. Therefore, the average size of CeO_2 particles increases with increase in annealing temperature.

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Figures 1 and 2 shows the magnetization curves of 5% and 15% cobalt doped CeO_2 in the as-prepared and annealed conditions. The hysteresis loops indicate that all the nanoparticles have clear RTFM. The RTFM in Co doped samples also can be explained on the basis of FCE mechanism. The Cobalt ions that entered substitutionally in place of Ce^{4+} in the lattice produce oxygen vacancies and FM behaviour. Each oxygen vacancy site easily traps an electron from adsorption species forming an F centre. The exchange interaction between the Co^{2+} ions and singly charged vacancy enables indirect FM coupling known as F-centre exchange coupling (FCE). Magnetization is not saturated due to the presence of antiferomagnetic or paramagnetic components [3].

When a divalent or trivalent Co ion is substituted in CeO_2, an oxygen vacancy is naturally formed to ensure charge neutrality. An oxygen vacancy in CeO_2 traps an electron to form F-centers. This F-centre with two Co ions constitutes a Co^{2+} - Vo- Co^{2+} group, where Vo denotes the oxygen vacancy. The electron trapped in the oxygen vacancy occupies an orbital which overlaps the d shells of both Co ion neighbours. Based on Hund’s rule and Pauli’s exclusion principle, spin orientations of the trapped electrons and the two neighbouring Co ions should be parallel in the same direction, thus ferromagnetic ordering is achieved [4].

The M-H curve of the 900 0C annealed sample shows a well defined hysteresis loop with a coercive field of ∽200 Oe and magnetisation of Ms∽0.07 emu/g. On annealing FM increases and saturation magnetization is observed in Co doped ceria due to high crystallinity and lower surface disorder. Annealing provides thermal energy and crystal lattice reconfirmation happens to form high quality nanocrystals. So

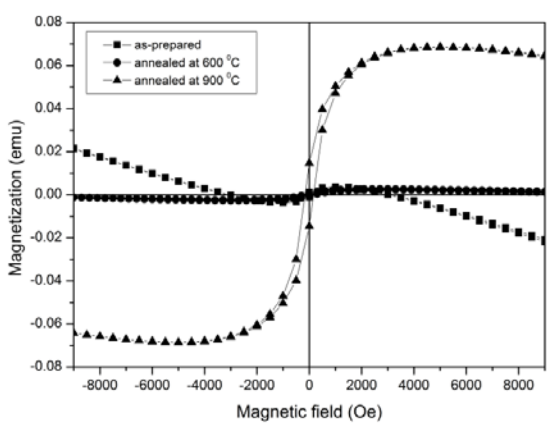

Figure 1:Hysteresis loops for $Ce_{0.95}Co_{0.05}O_{2-\delta}$

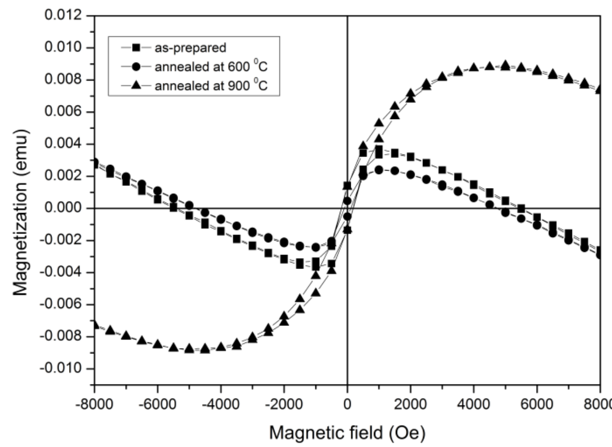

Figure 2: Hysteresis loops for $Ce_{0.85}Co_{0.15}O_{2-\delta}$

FM increases because of lowering of surface spin disorder of larger magnetic nanoparticles [5].

IV. CONCLUSION

Room temperature ferromagnetism (RTFM) has been observed in nanocrystalline cobalt doped CeO_2 powders, which is synthesised using a surfactant free, simple hydrolysis assisted chemical precipitation technique with cerium chloride and ammonia as precursors. The shape of the hysteresis loops indicates the presence of a diamagnetic component in addition to the ferromagnetic one. In the 15% cobalt doped ceria the magnetization is less than that in the 5% Co doped ceria due to higher concentrations of paired cobalt ions. In these samples, however magnetization increases with increase in annealing temperature due to lower surface spin disorder arising from better crystallinity of larger particles formed as a result of annealing.

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