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Structural, optical and magnetic properties of Cr-substituted CeO_2 nanoparticles

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HIGHLIGHTS

- $Cr_xCe_{1-x}O_2$ ($0 \leq x \leq 0.3$) nanoparticles were prepared by microwave refluxing method.
- Chromium addition caused blue shift for optical absorption peaks of CeO_2.
- All the samples exhibited room temperature ferromagnetic behavior.
- Ferromagnetic behavior was a function of concentration of Cr.

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ABSTRACT

Nanocrystalline $Cr_xCe_{1-x}O_2$ ($0 \leq x \leq 0.3$) samples were synthesized by a microwave refluxing method. These samples were characterized by X-ray diffractometer, Transmission electron microscope, Raman spectroscopy, UV-Vis spectrometer, Photoluminescence, and X-ray photoelectron spectroscopy. The XRD and TEM analyses indicates the formation of single phase in them. UV-vis spectroscopy results displayed blue shift of absorption peaks with increased Cr content. Magnetic measurements showed initial increase followed by decrease of saturation magnetization (M_S) with increasing doping concentration. The M_S value of $x = 0.05$ is nearly four times larger than that of undoped CeO_2. This initial enhancement of M_S has been attributed to the creation of oxygen vacancies. The decrease in M_S at higher concentrations, has been corroborated with the appearance of antiferromagnetic interaction above a threshold value of Cr^{3+} content which is lying between $x = 0.05$ and 0.1.

1. Introduction

The report of combined semiconducting, optical and ferromagnetic properties exhibited by dilute magnetic semiconductors (DMSs) or dielectrics (DMDs) has led to intense research for spintronic and magneto-optic applications [1–3]. Existence of room temperature ferromagnetism (RTFM) in some metal oxides with or without doping of transition metal ions has opened up novel ways of using them for newer applications. Such oxides include CeO_2, Al_2O_3, ZnO, InO_3, TiO_2, HfO_2 or SnO_2 which are diamagnetic in nature. However, they display ferromagnetic nature when their crystallite size is reduced to nanometer scale [4–9]. Though, many researchers have focused on the exploration of RTFM in DMSs or DMDs but only a few of them have proposed the formation of oxygen vacancies at the surface as the crucial reason for the RTFM behavior [10]. In contrast, Coey et al. interpreted such a behavior in terms of F-center exchange mechanism [11]. This refers to trapping of an electron in F-center leading to exchange interaction between transition metal ions.

The nanostructured cerium oxide (CeO_2) has assumed its importance in the field of electronic devices owing to (i) display of well above room temperature ferromagnetism, and (ii) transparency to visible light. Further, it has capability to absorb and release oxygen without altering its fluorite structure. Hence, it is found suitable for catalytic and solid-oxide fuel cell applications. The wide bandgap of CeO_2 ($E_g = 3.19$ eV, bulk material) enables more active in ultraviolet (UV) region. It is well known that the bandgap can be varied with particle size and doping.

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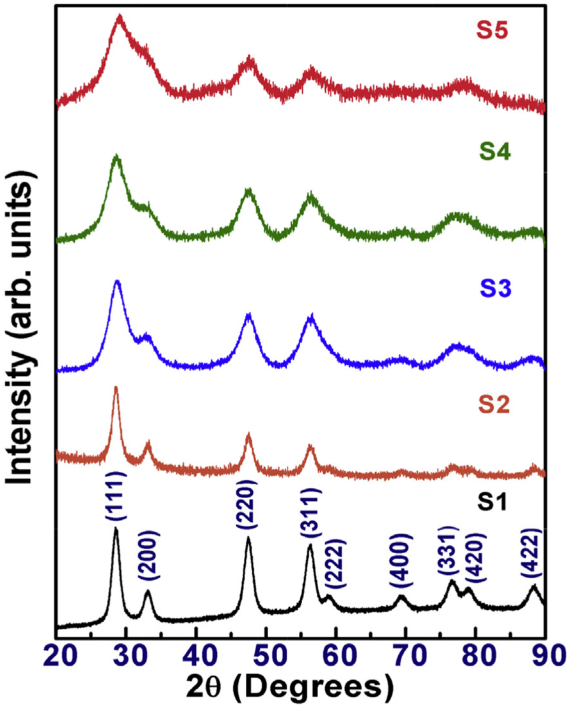

Fig. 1. XRD pattern of $Cr_xCe_{1-x}O_2$ (x = 0, 0.05, 0.1, 0.2 and 0.3) nanoparticles.

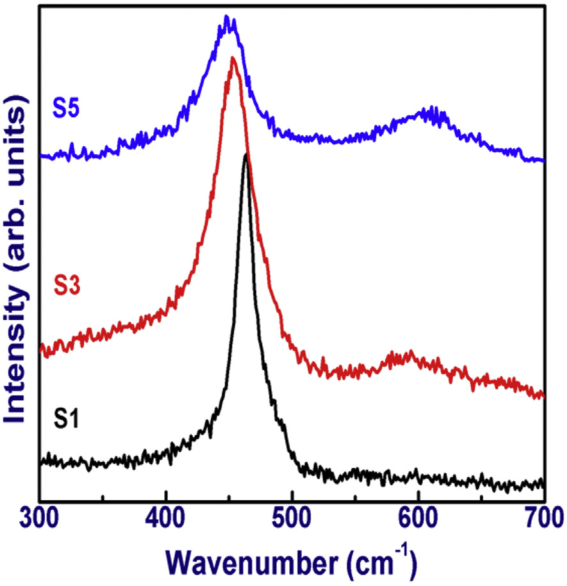

Fig. 2. Raman spectra of $Cr_xCe_{1-x}O_2$ (x = 0, 0.1 and 0.3) nanoparticles.

Nanocrystalline CeO_2 exhibits blue shift of UV absorbance spectra. This can be explained on the basis of quantum size effect [12]. Doping with a selected element into nanostructured CeO_2 causes decrease in a bandgap i.e red shift of UV spectra. This is because of formation defect states between valence band and conduction band [13]. While, blue shift causes by doping of an element in CeO_2 can be explained by Burstein-Moss band filling effect [14,15]. There are numbers of methods reported for the synthesis of undoped and doped CeO_2 nanostructures. They refer to hydrothermal [16], co-precipitation [17], sol-gel [18], hydrolysis [19], self-assembly processes [20], pulsed laser deposition [21], sonochemical [22], combustion synthesis [23] and thermal decomposition [24]. Some of these help control shape and size of crystallites.

The magnetic properties of nanocrystalline powders or thin films of doped cerium oxides ($M_xCe_{1-x}O_2$, M = Co, Fe, Cu, Ca, Cr, Pr and Ni) are extensively studied [25–31]. It is noteworthy to mention that saturation magnetization (M_S) value changes with variety of dopants in such systems. For instance, thin films of Fe or Pr doped CeO_2 show a systematic decrease in M_S value with increased doping concentration [29,30]. In case of 3 and 15 at % doping of Cu into CeO_2 thin films lead to increase in M_S values. Phokha et al. observed that M_s value is varied with dopant concentration in Cr doped CeO_2 particles [32]. Ferreira et al. found that 1, 3 and 5 at% of doping in $CeO_{2-\delta}$ exhibits RTFM and increased Cr concentration improves the M_s value of $CeO_{2-\delta}$ [28,33]. Furthermore, Thurber et al. reported systematic increase in M_S value up to 4 at % of Ni in CeO_2. Following this, there was decrease in M_S value with increased Ni content [31]. Hence, tailoring of saturation magnetization by different elements and varying their concentration has become an important way of manipulating M_S values and RTFM characteristics. The shape and size, of course, give additional parameters for M_S and T_c modifications.

Chromium and its main oxidation product (Cr_2O_3) are antiferromagnetic and they do not contribute to RTFM in such systems. Thus, the doping of Cr may be helpful in interpreting RTFM in doped CeO_2. In the literature it is reported that RTFM was observed in upto 7 at% of Cr doped CeO_2 particles prepared by solid state reaction [32]. They have also observed that different magnetization values with increased Cr content. Based on the results, they have suggested that incorporation of Cr-ions into CeO_2 lattice facilitates long range ferromagnetic ordering and decrease in magnetization because of anti-ferromagnetic interaction between Ce- and Cr-ions. However, more detailed investigation is necessary to interpret effect of Cr doping on magnetic properties of CeO_2. In addition, effect of Cr doping on optical properties not yet reported. Hence, we systematically studied the effect of higher concentration (up to 30 at % substitution on cerium site) of Cr on the structural, optical and magnetic properties of CeO_2 that were synthesized by microwave refluxing method.

2. Experimental details

All chemicals used in this study were of AR grade. $CrCl_3.6H_2O$ (≥98%), NaOH pellets, Ethylene Glycol (Merck, Mumbai, India) and $Ce(NO_3)_3.6H_2O$ (99.99%, Loba Chemie, Mumbai, India) were used as precursors. The stoichiometric amounts of all these precursors

Table 1
The variation of lattice parameter, coherently scattered domain size (crystallite size), bandgap and saturation magnetization with Cr concentration.

Cr concentration x	Lattice parameter (Å)	Crystallite size (Å)	Bandgap (eV)	Saturation magnetization (Am^2/kg)
0	5.419	10	2.97	0.018
0.05	5.420	8	3.01	0.080
0.1	5.389	6	2.98	0.010
0.2	5.380	5	2.99	0.008
0.3	5.360	<5	3.02	0.007