

Interplay of Structural, Optical and Magnetic properties in Gd doped CeO₂

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Abstract. In this research work systematic investigation on the synthesis, characterization, optical and magnetic properties of Ce_{1-x}Gd_xO₂ (where x=0.02, 0.04, 0.06, and 0.10) synthesized using the Solid-state method. Structural, Optical and Magnetic properties of the samples were investigated by X-ray diffraction (XRD), UV-VIS-NIR spectroscopy and VSM. Fluorite structure is confirmed from the XRD measurement on Gd doped CeO₂ samples. Magnetic studies showed that the Gd doped polycrystalline samples display room temperature ferromagnetism and the ferromagnetic ordering strengthens with the Gd concentration.

Keywords: Gd-CeO₂ polycrystalline, RTFM, SQUID, Structural and Optical properties..

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INTRODUCTION

Dilute magnetic semiconductors (DMSs) have attracted wide research attention due to their potential application in Spintronics and microelectronics [1]. Research interests were triggered by reports of robust enhancement in their magnetization at 300K upon their hydrogenation [2]. Defects, especially, the oxygen vacancies and their link to ferromagnetism, have been focus of recent research in magnetic semiconductors. It is proposed that oxygen vacancies form donor impurity band that assist in establishing exchange coupling in ZnO, TiO₂, SnO₂ etc[3]. Besides these semiconductors, some dielectrics/insulators like CeO₂ are also found to show the room temperature ferromagnetism (RTFM) [4]. However, the exchange mechanism in them is expected to be different than that in the magnetic semiconductors. Many studies on transition metal doped CeO₂ have been reported. Tiwari *et al.* [5] showed that the Co-doped CeO₂ displays room temperature ferromagnetism with high magnetic moment (8.2μ_B/Co) and Curie temperature (725 K).

In this research paper, we have carried out a systematic study of the Gd doped CeO₂ polycrystalline samples prepared by solid-state reaction method with the help of XRD, UV-VIS-NIR Spectroscopy, and VSM techniques.

Polycrystalline samples in the series Ce_{1-x}Gd_xO₂ (where x = 0.02, 0.04, 0.06 and 0.10) were prepared using the solid-state reaction route. In solid-state reaction route of preparation, the powders were calcinated for 15 hours at 500 °C in a microprocessor controlled furnace to obtain the polycrystalline precursors. Then the powder were pressed into Pellets (12 mm diameter and 1 mm thickness) using a hydraulic pressure of nearly 5 tons and then sintered at 900 °C in Ar atmosphere.

The phase purity and crystalline structure of the samples were determined by powder X-ray diffraction. Rietveld profile refinements of the XRD patterns were carried out using the FULLPROF Program. Optical absorption spectra were studied using a Perkin-Elmer Lambda 750 UV-VIS-NIR spectrophotometer with pre-aligned Tungsten, Halogen and Deuterium sources. The magnetic properties were studied on a VSM.

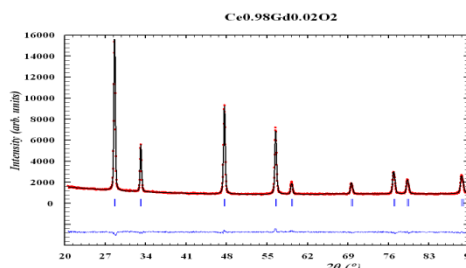


FIGURE 1. XRD Pattern of Ce_{1-x}Gd_{0.02}O₂ sample.

EXPERIMENTAL DETAILS

RESULTS AND DISCUSSION

XRD Spectra of Gd doped CeO₂ samples

Figure 1 shows the XRD pattern of Ce_{1-x}Gd_xO₂ (where x=0.02, 0.04, 0.06, and 0.10) samples, all diffraction peaks corresponds to CeO₂ fluorite structure. No secondary phase was detected within the sensitivity of XRD. It is clear from the XRD spectra that all the exhibited peaks are consistent with the face centered cubic fluorite structure of CeO₂ in the space group of *Fm-3m*, in which Ce is located at 4*a* position, surrounded by eight O (located at 8*b*) positions. The XRD patterns indicate that the cubic fluorite structure of the CeO₂ samples is not altered by Gd substitution as none of the diffraction peaks corresponding to cluster formation of Gd and Gd₂O₃ type related impurity phases have been observed in the Gd-doped CeO₂ samples, which further confirmed the formation of a single phase of Ce_{1-x}Gd_xO₂ and also confirmed the substitution of Gd at Ce sites. Rietveld profile refinements of all the samples have been carried out and the results are listed in Table 1. Gd doping at Ce-site in CeO₂ leads to monotonic enhancement in the lattice parameter in comparison to undoped CeO₂. This change is possibly due to the replacement of the smaller Ce⁺⁴ ions (0.97 Å) by the larger Gd⁺³ ions (1.053 Å) into the crystal lattice

Table 1: Details of XRD data Analysis

<i>Samples Ce_{1-x}Gd_xO₂</i>	<i>x=0.00</i>	<i>x=0.02</i>	<i>x=0.04</i>	<i>x=0.06</i>	<i>x=0.10</i>
<i>Lattice Parameter - a (Å)</i>	5.4025(7)	5.4038(5)	5.4088(4)	5.4127(6)	5.4135(6)
<i>Unit Cell Volume - V(Å³)</i>	157.66(3)	157.80 (2)	158.23(2)	158.58(3)	158.65(2)
<i>R_p</i>	2.78	2.61	3.42	2.86	3.01
<i>R_{wp}</i>	3.56	3.32	4.56	3.70	3.85
<i>R_{exp}</i>	2.98	2.86	3.08	3.58	3.55
<i>χ²</i>	1.43	1.34	2.19	1.07	1.18
<i>R_{Bragg}</i>	4.35	5.51	8.18	3.89	3.38

Table 2: The calculated optical band gap values and refractive index

<i>S.No.</i>	<i>Name of the sample</i>	<i>Optical band gap in eV</i>	<i>Refractive index (n)</i>
1	<i>Ce_{1-x}Gd_xO₂(x=0.02)</i>	3.09	2.37
2	<i>Ce_{1-x}Gd_xO₂(x=0.04)</i>	3.11	2.368
3	<i>Ce_{1-x}Gd_xO₂(x=0.06)</i>	3.14	2.360
4	<i>Ce_{1-x}Gd_xO₂(x=0.10)</i>	3.17	2.352

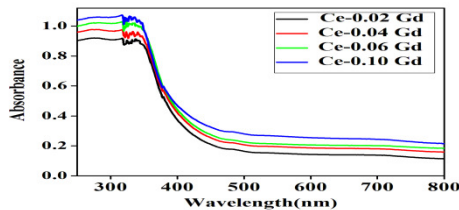


FIGURE 2. Absorption spectra of 2%, 4%, 6% and 10% Gd doped bulk CeO₂

Optical properties of Gd doped CeO₂ samples

Figure 2 shows the UV-visible optical absorption spectra of 2, 4, 6 and 10% Gd doped bulk CeO₂. The samples show a strong absorption below 400 nm with an absorbance peak in the UV range, due to charge-transfer transition from O²⁻ (2p) to Ce⁴⁺ (4f) orbital's in CeO₂, which indicate that the charge transfer transition of Ce⁴⁺ overlaps with the 4f¹-5d¹ transition of Ce³⁺ [6], it is also known as f-f spin orbit splitting of the Ce 4f state [7]. The band gap energies of Gd doped CeO₂ have been calculated from their absorption curves, using Tauc's relation. The refractive index of bulk CeO₂ has been calculated by using the equation (1). Where n is the refractive index of the material and E_{opt.} is the optical band gap. We can see that the calculated values of refractive index for Gd doped bulk Ceria is found to decrease with increasing doping concentration of Gd ion in Ceria.

Form the calculated values of optical band gap it is clear that as the doping concentration of Gd increased in bulk CeO₂ band gap energy is also increased. This indicates blue shift due to increasing the doping concentration. At the outermost CeO₂ surface, Ce⁴⁺ ion coexist with Ce³⁺ ions.

Magnetic Measurements

The magnetization (M) of Ce_{1-x}Gd_xO₂ (where x=0.02, 0.04, 0.06, and 0.10) polycrystalline samples as a function of magnetic field (H) measured at room temperature using VSM. The well defined exhibited hysteresis loops, readily reveal an unmistakable RTFM ordering in the samples. We can see that the magnetization of Ce_{1-x}Gd_xO₂ samples increases with Gd content. As seen from the figure 3 the doped

sample is the superposition of two components; one is paramagnetic and second is ferromagnetic.

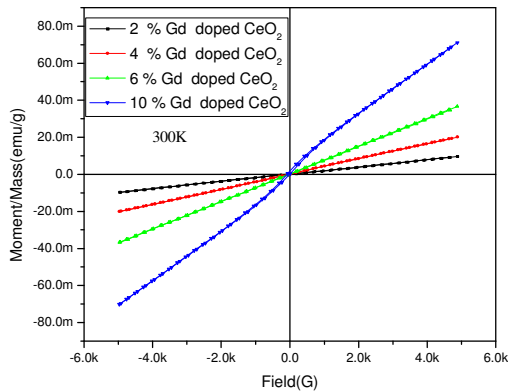


FIGURE 3. Field dependent magnetization M (H) measurements of Gd doped CeO_2 sample.

In nature, 2% Gd doped sample shows an approximate linear M-H behavior, which indicates that a dominant paramagnetic ordering is present in the sample, which is superimposed with ferromagnetic ordering but in the case of 10% Gd-doped sample, a curvature is observed near the origin, which indicates that a ferromagnetic component is superimposed over the strong paramagnetic background at room temperature. Bulk Gd is ferromagnetic with Curie temperature $\sim 300\text{K}$, but in our sample it has been observed that for the low concentration of Gd-ions could not be able to enhance the ferromagnetism in the sample at room temperature but for 10% Gd-doped sample a small change in the strong paramagnetic to ferromagnetic behavior at RT is seen. Similarly Dimri et al. reported ferromagnetic behavior with some linear paramagnetic behavior at room temperature for 20% Nd and Sm doped CeO_2 and ferromagnetism originated due to phase purity and oxygen vacancies which may be created due to rare earth doping, but 10% Gd doped CeO_2 bulk sample could not exhibit room temperature ferromagnetism in their sample [8]. In our sample the RT-FM has been achieved as trivalent Gd ion concentration increased in CeO_2 sample, which may be due to oxygen vacancies and the defect formation on cluster sites. The direct ferromagnetic coupling is called F-centre exchange (FCE) mechanism. In FCE mechanism, the magnetic ions and oxygen vacancy give the ferromagnetic ordering. As the CeO_2 can have variable valence states like Ce^{+3} or Ce^{+4} , so it is possible that oxygen vacancy can create magnetic moment on neighboring Ce-ions of $\text{Ce}^{+3}\text{Ce}^{+3}$, where denotes the oxygen vacancy. When trivalent Gd ion is doped in CeO_2 sample, according to the FCE mechanism F centre consists of an electron trapped in oxygen vacancy with two Gd

ions (i.e. $\text{Gd}^{+3}\text{Gd}^{+3}$). The electron trapped in oxygen vacancy occupies an orbital which overlaps the d-shell of neighboring Gd ions. According to the Hund's rule and Pauli principle the trapped electrons spin should have direction parallel to two neighboring Gd ions, which results in ferromagnetic ordering. The ferromagnetic ordering in our sample is associated with FCE coupling between Gd ions and oxygen vacancy. The XRD spectra of the sample show that Gd^{+3} ion is substituted in CeO_2 and Ce ion in +3 state (with $4f^1$ configuration), which can be ascribed to the oxygen vacancy in Gd doped CeO_2 sample. Therefore, FCE mechanism in complex structure of $\text{Gd}^{+3}\text{Gd}^{+3}$ shows RT-FM in the sample. This F-centre exchange coupling between oxygen defect and Gd ions forms BMP's (bound magnetic polarons), these neighboring BMP's can overlap and give result in the long range Gd-Gd ferromagnetic coupling in doped CeO_2 sample.

The effect of Gd doping on the crystal structure, optical and magnetic properties of CeO_2 have been investigated systematically. As the concentration of Gd ion is increased in the sample, therefore this long range magnetic ordering exists in between the different states of Gd ions and oxygen ion. Therefore, RTFM in the sample may be arising due to F-centre exchange coupling between oxygen defect and the overlapping of BMP's formed by Gd ions.

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