

# High-temperature magnetic-field-induced activation of room-temperature ferromagnetism in $\text{Ce}_{1-x}\text{Ni}_x\text{O}_2$

A. Thurber, K. M. Reddy, and A. Punnoose<sup>a)</sup>

*Department of Physics, Boise State University, Boise, Idaho 83725-1570*

(Presented on 11 January 2007; received 31 October 2006; accepted 19 November 2006; published online 16 April 2007)

We report room-temperature ferromagnetism in nickel doped ceria ( $\text{Ce}_{1-x}\text{Ni}_x\text{O}_2$ ) powders prepared using the sol-gel process. Magnetometry studies on as-prepared samples reveal a weak ferromagnetic (FM) behavior in the range  $0 < x < 0.04$  ( $8.6 \times 10^{-4} \mu_B/\text{Ni}$  ion for 4%). For  $x > 0.04$ , the FM magnetization steadily decreases for increased dopant concentration. The weak FM behavior of the samples improved dramatically after undergoing high-temperature ( $\leq 500$  °C) activation in the presence of an external magnetic field ( $H \leq 1$  T). The magnitude of the improvement, which was very reproducible, was strongest for 10% Ni doped  $\text{CeO}_2$  with saturation magnetization  $M_s$  increasing by 600 times. Curie temperatures of the activated samples varied in the 597–646 K range depending on the Ni concentration and preparation conditions. X-ray diffraction studies did not reveal any noticeable structural changes as a result of the activation process. © 2007 American Institute of Physics. [DOI: [10.1063/1.2709413](https://doi.org/10.1063/1.2709413)]

## I. INTRODUCTION

Recent reports on several metal oxide materials doped with transition metals resulting in room-temperature ferromagnetism<sup>1–7</sup> (RTFM) led to studies on the magnetic properties of doped cerium oxide. The authors have recently reported on weak ferromagnetic (FM) behavior in Ni doped  $\text{CeO}_2$ ,<sup>8</sup> observing an increase in the RTFM up to 4% Ni, followed by a decrease in RTFM with increased doping. However, in a recent study, Tiwari *et al.* have reported a giant magnetic moment of  $8.2 \mu_B/\text{Co}$  ion for Co doped  $\text{CeO}_2$ .<sup>9</sup> The weak RTFM found in Ni doped ceria powders annealed at 450 °C needed to be further improved to verify the intrinsic FM behavior of the doped system and to reach levels of RTFM that would be practically useful. A recent attempt to determine the Curie temperatures of these samples using high-temperature magnetization measurements in the presence of an externally applied magnetic field resulted in a surprising observation of increased FM behavior after cooling to 300 K. No such enhanced magnetic behavior was observed when the samples were subjected to the same heat treatments without an external field. Based on these results, the authors explored the effects of the activation on several Ni doped  $\text{CeO}_2$  samples, details of which are presented in this paper.

## II. EXPERIMENTAL DETAILS

The  $\text{Ce}_{0.9}\text{Ni}_{0.1}\text{O}_2$  samples were prepared in nanocrystalline powder form for use in these studies. The sol-gel synthesis process was used to precipitate a metal hydroxide complex from  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  precursors using  $\text{NH}_4\text{OH}$  solution to control the pH. A predetermined ratio of precursors was used to obtain the molar ratio

$x = [\text{Ni}] / ([\text{Ni}] + [\text{Ce}])$ . The precipitate was dried for 12 h at 50 °C and then ground prior to annealing in the range of 150–900 °C for 3 h. The annealed samples have been characterized using x-ray diffraction (XRD) and magnetometry to determine correlations between structural and magnetic properties as the Ni concentration varies for a fixed annealing temperature (450 °C) and as the annealing temperature varies for 10% Ni. XRD studies were conducted on a Philips X'pert x-ray diffractometer in Bragg-Brentano geometry with a  $\text{Cu K}\alpha$  source ( $\lambda = 1.5418$  Å). For activation, an applied field of  $H = 3$  kOe was present during heating to 500 °C, at which temperature the samples were exposed to a 10 kOe magnetic field. The field was then shut off and the system cooled to room temperature. The choice of this activation process was initially the result of attempting to determine the Curie temperatures using high-temperature magnetization measurements on the weak FM samples, which, after cooling down to 300 K, showed strong RTFM. The activation process was conducted on a vibrating sample magnetometer (VSM, LakeShore model 7407) equipped with a high-temperature oven. Samples mounted inside the oven were packed into a boron nitride cup, and the atmosphere inside the oven was purged with nitrogen during the experiments to prevent oxidation of the oven walls. The frequency of vibration was a constant, 82 Hz. Temperature and magnetic field treatment was accomplished by loading 50–100 mg of powder sample into the high-temperature VSM setup.

## III. RESULTS AND DISCUSSION

The authors recently investigated the effect of Ni dopant concentration on  $\text{CeO}_2$ .<sup>8</sup> A weak FM behavior was developed with Ni doping showing a maximum for 4% Ni having a saturation magnetization of 1.2 memu/g ( $8.6 \times 10^{-4} \mu_B/\text{Ni}$  ion). Above this dopant concentration, the FM properties gradually diminished with increasing  $x$  as shown in Fig. 1(a).<sup>8</sup> This result qualitatively followed the model proposed

<sup>a)</sup>Author to whom correspondence should be addressed; FAX: 208-426-4330; electronic mail: [apunnoos@boisestate.edu](mailto:apunnoos@boisestate.edu)

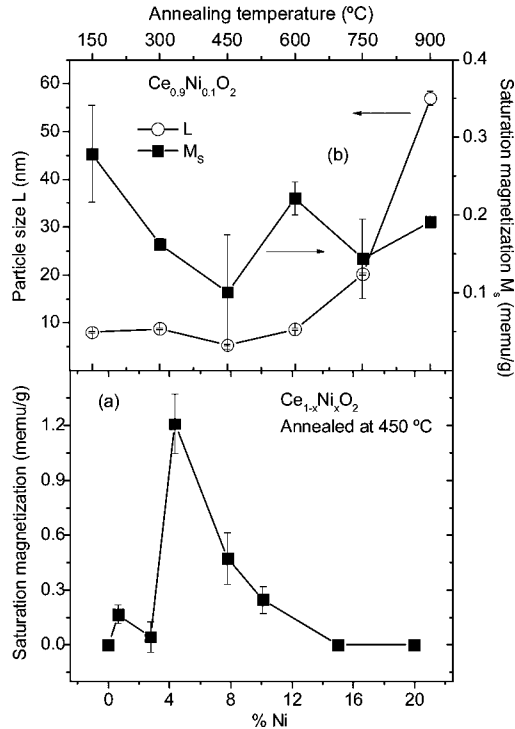


FIG. 1. (a) Saturation magnetization  $M_s$  of  $Ce_{1-x}Ni_xO_2$  annealed at 450 °C as a function of  $x$  and (b) particle size  $L$  estimated from XRD and saturation magnetization  $M_s$  of  $Ce_{0.9}Ni_{0.1}O_2$  as a function of annealing temperature.

by Coey *et al.*,<sup>2</sup> in which doping above a cation percolation limit will diminish the FM behavior due to antiferromagnetic interaction. Figure 1(b) shows the particle size and saturation magnetization variation for  $Ce_{0.9}Ni_{0.1}O_2$  annealed at different temperatures.

Figure 2 shows how the magnetic-field-induced high-temperature activation process affects the magnetic properties of the Ni doped  $CeO_2$  powders. Figures 2(a)–2(c) show panels indicating the changes in (i) saturation magnetization, (ii) coercivity and remanence, and (iii) the resulting Curie temperature  $T_C$  for 450 °C annealed  $CeO_2$  powders containing 4%, 8%, and 10% Ni. All of these samples show increases in their saturation magnetizations by several orders of magnitude after the activation process. The resulting saturation magnetizations were 0.10, 0.095, and 0.050  $\mu_B$ /Ni ion for 4%, 8%, and 10% Ni, respectively. With the 8% and 10% Ni doped samples, the coercivity and remanence also show significant enhancement after the activation process. The Curie temperatures of the activated samples were 612, 597, and 632 K for 4%, 8%, and 10% Ni doped samples, respectively.

XRD measurements were carried out on the  $Ce_{0.9}Ni_{0.1}O_2$  samples to investigate the role of any structural or chemical phase change. Figure 3(a) shows the XRD data of 450 °C annealed  $Ce_{0.9}Ni_{0.1}O_2$  collected before and after the activation process. No new peaks or changes in the XRD pattern were observed as a result of the activation process.

In order to investigate the role of temperature, 10% Ni doped  $CeO_2$  precipitate was annealed at six different temperatures of 150, 300, 450, 600, 750, and 900 °C without any externally applied magnetic field. The XRD patterns shown in Fig. 3(b) demonstrate gradual changes in the peak intensity and width with increasing annealing temperatures.

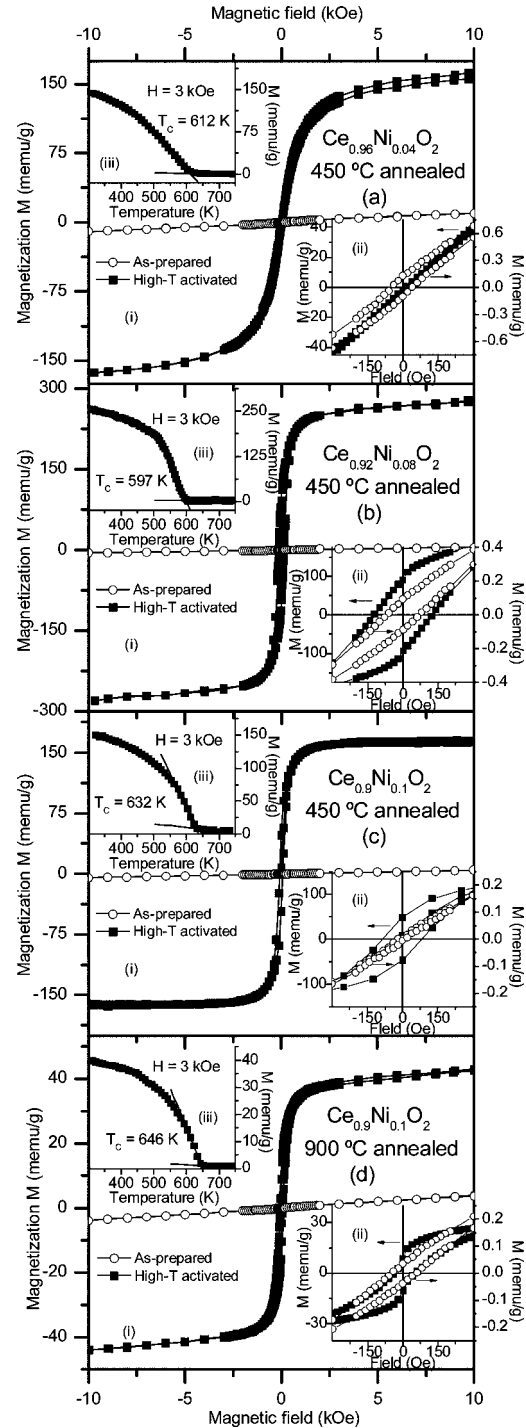


FIG. 2. As-prepared and activated magnetic data from powder samples showing (i) full-scale room temperature  $M$  vs  $H$  displaying change in saturation, (ii) low field region  $M$  vs  $H$  displaying changes in coercivity and remanence, and (iii)  $M$  vs  $T$  after activation for (a)  $Ce_{0.96}Ni_{0.04}O_2$ , (b)  $Ce_{0.92}Ni_{0.08}O_2$ , and (c)  $Ce_{0.9}Ni_{0.1}O_2$  annealed at 450 °C and (d)  $Ce_{0.9}Ni_{0.1}O_2$  annealed at 900 °C.

The average particle size estimated from the XRD data using the Scherrer relation, shown in Fig. 1(b), increases from 8 nm at 150 °C to 57 nm at 900 °C. Figure 1(b) also shows the variation in saturation magnetization for 10% Ni as the annealing temperature is varied, producing values in the 0.1–0.3 memu/g range with no apparent correlation to the annealing temperatures. This suggests that the rapid increase in average particle size does not result in discernible changes

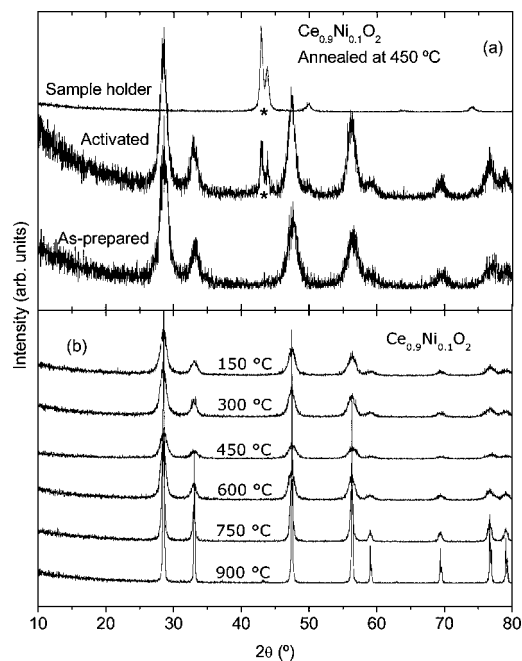


FIG. 3. X-ray diffraction on powder samples of  $\text{Ce}_{0.9}\text{Ni}_{0.1}\text{O}_2$  displaying (a) the effect of high-temperature activation of ferromagnetism on the structure and (b) the change in peak width as annealing temperature changes. Also shown in (a) is the XRD sample holder background, since the holder background appears in the activated sample due to the small amount of powder used in activation. Asterisk (\*) indicates peaks from background.

in the magnetization. The cubic  $\text{CeO}_2$  lattice parameter estimated from these data was  $5.41 \pm 0.01 \text{ \AA}$  showing no systematic variation with annealing temperature.

10% Ni doped  $\text{CeO}_2$  annealed at  $900 \text{ }^\circ\text{C}$  was also subjected to the activation process to investigate the effect of particle size and annealing process to temperature. The data shown in Fig. 3(d) demonstrate a somewhat similar improvement in magnetization compared to the  $450 \text{ }^\circ\text{C}$  annealed samples. This shows that the higher annealing temperature and the resulting larger particle size do not have a significant role in the activation process. However, the Curie temperature of the  $900 \text{ }^\circ\text{C}$  annealed sample with 10% Ni was the highest at 646 K.

In summary, Ni doped  $\text{CeO}_2$  samples show RTFM after high-temperature activation with some dependencies on the preparation conditions and Ni concentration. The enhancement effect was strongest with an increase of  $\sim 600$  times on  $\text{Ce}_{0.9}\text{Ni}_{0.1}\text{O}_2$  annealed at  $450 \text{ }^\circ\text{C}$ , while a maximum saturation magnetization ( $0.10 \mu_B/\text{Ni}$  ion) is observed for  $\text{Ce}_{0.94}\text{Ni}_{0.04}\text{O}_2$  after activation. The FM behavior of

$\text{Ce}_{1-x}\text{Ni}_x\text{O}_2$  samples and the observed enhancement in magnetization resulting from magnetic-field-induced high-temperature activation are not due to the presence of any impurity phases for the following reasons: (i) The weak FM in as-prepared samples shows very systematic variation, and random impurities will not lead to a systematic variation of magnetization. (ii) Impurities due to precipitation of the dopants would result in the magnetization increasing with  $x$ , which is not the case. (iii) The magnetic-field-induced activation is not expected in any of the known possible impurity phases. (iv) The activation is a reproducible effect, observed in several samples with different  $x$  and annealing temperatures. (v) The Curie temperature depends on the dopant concentration and preparation conditions, and the estimates for some of the samples are higher than that of bulk Ni metal and the Néel temperature of bulk NiO. Interestingly, the authors<sup>10</sup> have earlier reported on a magnetic-field-induced metamagnetic transition in Co doped  $\text{SnO}_2$ . Archer *et al.*<sup>11</sup> have also reported on activation of RTFM in Ni doped  $\text{SnO}_2$  nanoparticles. To understand the mechanism of the observed magnetic-field-induced high-temperature activation in  $\text{Ce}_{1-x}\text{Ni}_x\text{O}_2$  samples, more detailed studies are required, and this will be the subject matter of future investigations. With the ability to create Ni doped ceria with better magnetization at room temperature, it is a promising material for use in possible spintronic devices.

This research was supported in part by grants from NSF-Idaho-EPSCoR program (EPS-0447689), Research Corporation, NSF-CAREER program (DMR-0449639), and the DOE-EPSCoR program (DE-FG02-04ER46142) at Boise State University.

<sup>1</sup>A. H. MacDonald, P. Schiffer, and N. Samarth, *Nat. Mater.* **4**, 195 (2005).

<sup>2</sup>J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, *Nat. Mater.* **4**, 173 (2005).

<sup>3</sup>S. A. Chambers and R. F. C. Farrow, *Mater. Res. Bull.* **28**, 729 (2003).

<sup>4</sup>J. Hays, A. Thurber, K. M. Reddy, A. Punnoose, and M. H. Engelhard, *J. Appl. Phys.* **99**, 08M123 (2006).

<sup>5</sup>P. V. Radovanovic and D. R. Gamelin, *Phys. Rev. Lett.* **91**, 157202 (2003).

<sup>6</sup>A. Punnoose, J. Hays, A. Thurber, M. H. Engelhard, R. K. Kukkadapu, C. Wang, V. Shutthanandan, and S. Thevuthasan, *Phys. Rev. B* **72**, 054402 (2005).

<sup>7</sup>S. B. Ogale *et al.*, *Phys. Rev. Lett.* **91**, 077205 (2003).

<sup>8</sup>A. Thurber, K. M. Reddy, V. Shutthanandan, M. H. Engelhard, C. Wang, J. Hays, and A. Punnoose, *Phys. Rev. B* (submitted, 2007).

<sup>9</sup>A. Tiwari, V. M. Bhosle, S. Ramachandran, N. Sudhakar, J. Narayan, S. Budak, and A. Gupta, *Appl. Phys. Lett.* **88**, 142511 (2006).

<sup>10</sup>A. Punnoose and J. Hays, *J. Appl. Phys.* **97**, 10D321 (2005).

<sup>11</sup>P. I. Archer, P. V. Radovanovic, S. M. Heald, and D. R. Gamelin, *J. Am. Chem. Soc.* **127**, 14479 (2005).