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Characterization of Sm-doped CeO_2 nanoparticles and their magnetic properties

Ekaphan Swatsitang [a], Sumalin Phokha [b,*], Sitchai Hunpratub [b], Santi Maensiri [c]

[a] Integrated Nanotechnology Research Center and Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[b] Department of Physics, Faculty of Science, Udon Thani Rajabhat University, Udon Thani 41000, Thailand
[c] School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

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ABSTRACT

Cubic phase Sm-doped CeO_2 nanoparticles ($Ce_{1-x}Sm_xO_2$, $x=0$, 0.05, 0.10, 0.15 and 0.20) were synthesized by the polymer pyrolysis method. X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and vibrating sample magnetometer (VSM) were employed to characterize the phase, morphology, valence states and magnetic properties of the samples. The samples were calcined at the low temperature of 600 °C which resulted in crystallite sizes of 10–20 nm. Raman and XPS spectra showed the presence of Ce^{4+}, Ce^{3+} and Sm^{3+} ions and oxygen vacancies in the samples. Magnetization curves obtained from all samples exhibited ferromagnetic behavior at room temperature (RT-FM) with a maximum value of 0.012 emu/g for $x=0.15$. The data exhibited a good fit to bound magnetic polaron (BMP) model curves which account for the RT-FM behaviour by having sufficient concentrations of electrons bound to oxygen vacancies to facilitate a long-range exchange interaction between Ce^{3+} ions. However, the relatively low values obtained for the BMP concentrations suggest that other mechanisms may also be at play.

1. Introduction

Transition metal (TM) doped oxide semiconductors such as ZnO, TiO_2, SnO_2, CeO_2 and In_2O_3, have been studied due to their novel magnetic, magneto-optical and magneto-electrical properties [1,2]. These materials are referred to as dilute magnetic oxides (DMOs) and offer the possibility of controlling charge transport by using the spin degree of freedom [1,2]. Among them, Cerium oxide (CeO_2) has attracted considerable interest in the past decade due to their potential for applications in catalysis, electrochromic devices, gas sensors and ultraviolet radiation detectors [3,4]. Moreover, it exhibits a cubic structure with a lattice parameter close to that of Si, offering the possibility that CeO_2 devices might be integrated with conventional silicon-based electronic circuits [3–9].

Room temperature (RT) ferromagnetism (FM) of pure and/or TM-doped CeO_2 has been reported in thin films [6–8] and powders [9–22], for example Wen et al. [9] have reported RT-FM in undoped and cobalt doped CeO_2 powders. In their study they measured a two orders of magnitude enhancement of the magnetization (M_s) following cobalt doping, to a value of 0.47 emu/g. The same behavior was found in nanoparticles of Fe-doped CeO_2 prepared by a sol–gel method, with a very low M_s value of 0.0026 emu/g for CeO_2 increasing to 0.03 emu/g when 3% Fe-doped [5]. The authors suggested that both TM doping and oxygen vacancy creation were key factors in inducing the magnetic ordering described by the bound magnetic polaron (BMP) model. Ferromagnetic behavior with large magnetic moments was also observed in CeO_2 doped with rare earth metals such as Nd, Sm or Pr [23–25], for example Dimri et al. [23] have reported that rare earth (Sm and Tb) doped CeO_2 bulk samples exhibited enhanced RT-FM behavior due to the enhancement of oxygen vacancy numbers. These studies have suggested that structural crystal defects can play an important role in determining the ferromagnetic behavior of these materials.

In this work we have investigated the RT-FM properties of $Ce_{1-x}Sm_xO_2$ nanoparticles ($x=0$, 0.05, 0.10, 0.15 and 0.20) prepared by the polymer pyrolysis method. The structural properties of the nanoparticles were studied using X-ray diffraction and high resolution transmission electron microscopy, which showed that the Sm-doped CeO_2 exhibited a single cubic phase. Magnetic measurements showed that all samples exhibited weak FM behavior at RT with the $x=0.15$ Sm sample having the maximum saturation magnetization.

* Corresponding author.
E-mail address: sumalinphokha@gmail.com (S. Phokha).

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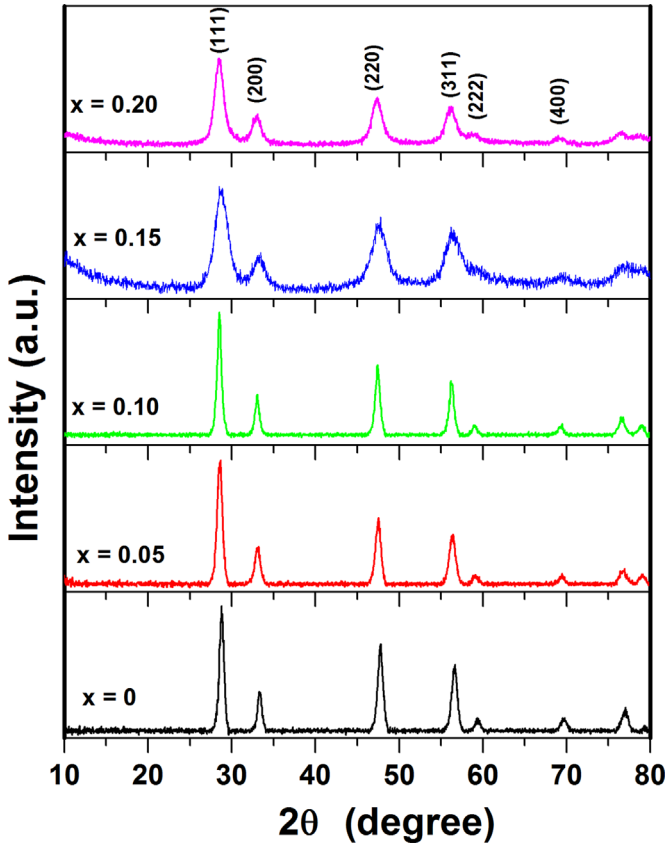

Fig. 1. XRD patterns obtained from $Ce_{1-x}Sm_xO_2$ samples calcined at 600 °C.

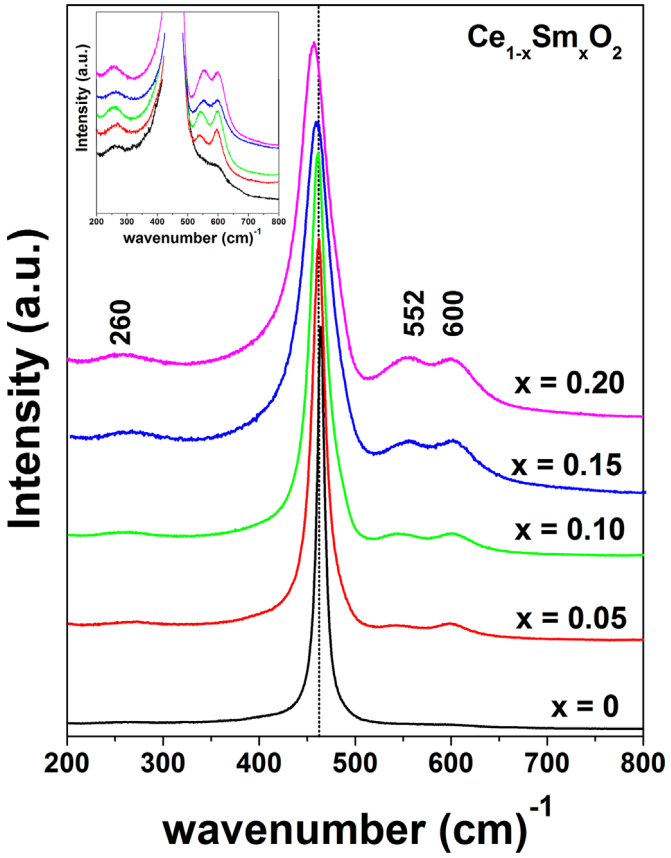

Fig. 2. Raman spectra obtained from $Ce_{1-x}Sm_xO_2$ samples calcined at 600 °C.

Table 1
Summary of average crystallite sizes calculated from XRD peak line broadening, lattice parameters (a) and saturated magnetizations (M_S) at RT for $Ce_{1-x}Sm_xO_2$ nanoparticles calcined for 3 h in air at 600 °C.

Sm mole fractions in $Ce_{1-x}Sm_xO_2$	Average crystallite size (nm)	Lattice parameter a (nm)	M_S (emu/g)
$x=0$	15 ± 0.5	0.5375 ± 0.0004	0.0085 ± 0.00005
$x=0.05$	13 ± 0.4	0.5416 ± 0.0002	0.0068 ± 0.00005
$x=0.10$	15 ± 1	0.5425 ± 0.0001	0.0110 ± 0.00005
$x=0.15$	20 ± 0.7	0.5387 ± 0.0002	0.0120 ± 0.00005
$x=0.2$	10 ± 1	0.5421 ± 0.0008	0.0030 ± 0.00005

2. Experimental

Stoichiometric amounts of $Ce(NO_3)_3\cdot6H_2O$ (99.99%, Kanto), $Sm(NO_3)_3\cdot6H_2O$ (99.99%, Aldrich) and acrylic acid ($C_3H_4O_2$) were dissolved in deionized water to promote polymerization after which the precursor solution was stirred and heated at 30 °C until dry. The final product was pre-calcined for 2 h in air at 200 °C in an electric furnace to form the polyacrylate salt and was further calcined for 3 h in air at 600 °C to obtain the cubic phase of $Ce_{1-x}Sm_xO_2$.

All samples were characterized using XRD, Raman, TEM, XPS and VSM. A Bruker D2 Phaser X-ray diffractometer using Cu Kα radiation ($\lambda=0.154184$ nm) was used to study the phases of the $Ce_{1-x}Sm_xO_2$ samples and Raman spectra were recorded at room temperature using a triple spectrometer (Jobin Yvon/Atago-Bussan T-64000, HORIBA Jobin Yvon S.A.S., Chilly-Mazarin). TEM images and selected area electron diffraction patterns were collected (Ziess, EM902) to allow the morphology and crystal structure of the samples to be determined. XPS spectra were obtained using monochromatic Al $K_{\alpha1,2}$ radiation at 1.4 keV (AXIS Ultra DLD). The magnetic properties of the nanoparticles at room temperature were studied using VSM (Versa Lab VSM, Quantum Design).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the XRD patterns obtained from the $Ce_{1-x}Sm_xO_2$ samples with $x=0$, 0.05, 0.10, 0.15 and 0.20. All samples exhibit peak positions consistent with the face-centered cubic structure (space group $Fm3m$) of CeO_2 according to the JCPDS 34-0394 standard and no additional peaks suggesting impurity phases are observed. The broadening of the peaks with increasing Sm content is consistent with the smaller crystallite size in these samples. The average crystallite size (D) in each sample were calculated from the X-ray line broadening of the (111), (200), (220) and (311) peaks using Scherrer's equation and were found to be 15 ± 0.5, 13 ± 0.4, 15 ± 1, 20 ± 0.7 and 10 ± 1 nm for samples with $x=0$, 0.05, 0.10, 0.15 and 0.20, respectively. These results are similar to the 9–13 nm reported for 10–20% Sm-doped CeO_2 [26]. The lattice parameters (a) of the samples ranged between 0.5375 nm and 0.5425 nm and were decreasing with increasing Sm content as shown in Table 1.