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A simple method to obtain Fe-doped CeO_2 nanocrystals at room temperature

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ABSTRACT

$\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ nanocrystals ($0 < x < 0.05$) have been synthesized at room temperature using the coprecipitation method. The samples were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and magnetization measurements as a function of field. The XRD results and Rietveld refinement analysis show that all particles have a crystalline structure isomorphous to the host structure (CeO_2), with average size of 9 nm. This information was also confirmed by TEM images in which it is shown that the particles present spherical-like shape. The magnetic measurements indicated that the Fe-doped samples exhibit a weak ferromagnetism at room temperature, which increases with the increasing of the Fe content.

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1. Introduction

In the last years, oxide semiconductors doped with 3d transition metals have attracted much attention from the scientific community. The interest in the so-called diluted magnetic semiconductor (DMS) is associated to the appearing of both magnetic and semiconductor properties causing these materials have great potential for application in magneto-electronic devices [1,2]. Recently, it has increased the interest in the diluted magnetic oxide semiconductors (DMOS) due to simplicity to obtain it when compared to $(\text{Ga}_{1-x}\text{Mn}_x)\text{As}$ alloy. In this class of materials, the ZnO belongs to the list of the most suitable candidates for spintronics application. Therefore, the CeO_2 arise as a possible candidate to the DMOS because presents a band gap near to the ZnO. On the other hand, these materials can be applied only if they exhibit a ferromagnetic behavior at room temperature. Therefore, the origin of ferromagnetism in these materials is still under debate. Some groups defend the idea of the existence of magnetic clusters on the semiconductor host due to segregation of the ferromagnetic phase [3,4]. Nevertheless other authors show through theoretical calculations the possibility that the ferromagnetic ordering can be related to the localized impurity magnetic moments. These moments are induced by indirect exchange (RKKY) interaction mediated through p-type free carriers in some transition-metal doped semiconductors [5,6]. All these discussions show that the growth process of the DMS can play an important role to control the ferromagnetic behavior.

In this sense, several methods have been studied to make DMOS nanoparticles including sol-gel synthesis [7], thermal decomposition [8], hydrothermal method [9], microemulsion [10]. However, few works are devoted to the preparation of CeO_2 nanoparticles doped with transition metals. Moreover, these methods use high temperature sintering and there is no control of the particle size distribution and particle shape.

Here, we describe a simple route to make Fe-doped CeO_2 single nanocrystals for different iron concentrations obtained at room temperature. The structural and magnetic properties have been studied in detail by X-ray diffraction (XRD) and Rietveld analysis, infrared spectroscopy (IR), transmission electron microscopy (TEM) and DC magnetization measurements.

2. Experimental

2.1. Preparation of $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ nanocrystals

Fe-doped CeO_2 nanocrystals (NC's) were prepared by coprecipitation method at room temperature using $(\text{CeCl}_3 \cdot 6\text{H}_2\text{O}, \text{FeCl}_3 \cdot 6\text{H}_2\text{O}; \text{sigma-aldrich})$ as starting materials. This method consists in dissolving salts under stoichiometric proportions in de-ionized water. In this solution was added slowly a 1 mol/L NaOH solution under vigorous stirring until the pH value 9 is reached. The precipitated material was collected after washed and centrifuged any times in order to completely remove ionic impurities. The precipitated was collected and dried into a dry box at room temperature by 72 h.

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2.2. Characterization methods

The XRD data were collected using a Panalytical X'Pert MRD diffractometer (with $\text{CuK}\alpha$ radiation operated at 40 kV, 40 mA). Rietveld refinement was carried out by DBWS9807 with interface dbwstools using pseudo-voigt function as profile function [11,12]. From these analyses, it has been extracted information on the cell parameters and full width at half maximum (FWHM). The latter was used to estimate the mean microstrain and crystallite size calculated from the Williamson–Hall plot based on the equation

$$\beta = \frac{\lambda}{t \cos \theta} + 4\varepsilon \tan \theta$$

where β is FWHM, λ is the wavelength, t is the crystallite size, θ is the Bragg angle and ε is the microstrain. Details as to calculate the equation above can be found in reference [13]. Measurements of IR were performed using a Perkin Elmer Spectrum 100 instrument ($3000\text{--}500\text{ cm}^{-1}$, applying to the samples dispersed in KBr). Magnetic measurements as a function of the field at room temperature were carried out using a SQUID magnetometer (Quantum Design MPMS evercool system). To visualize the morphology and crystallite size, we have used a transmission electron microscopy (TEM–HR JEOL 3010) operated at 300 kV.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the calculated and experimental X-ray diffraction patterns for all samples studied in this work. Differently of Li et al., which have obtained similar systems at high temperatures [14], all our XRD results show that the samples present only one phase with identical structure to the cubic CeO_2 with the $Fm\text{--}3m$ space group. From Rietveld refinement analysis, we have estimated the mean crystallite size of nearly 9 nm for all samples as

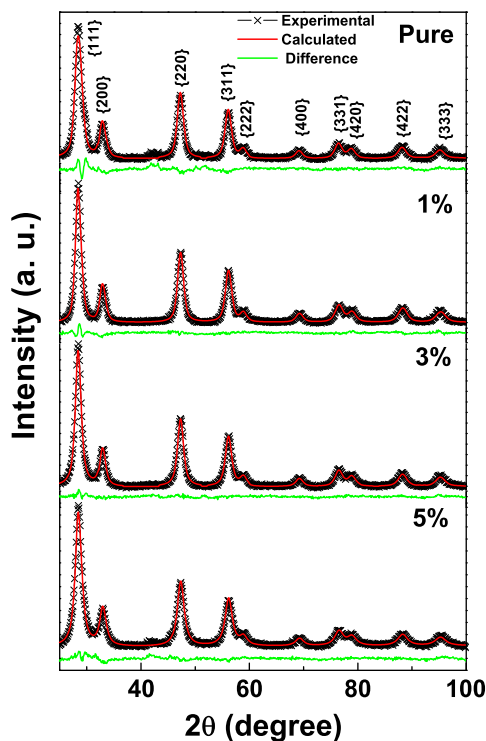


Fig. 1. Calculated and experimental XRD patterns for samples pure and Fe-doped CeO_2 for different concentrations of Fe.

Table 1

The mean particle sizes and cell parameters to Fe-doped CeO_2 at different concentrations of Fe estimated from Rietveld refinement data.

Sample	Size (nm)	a (Å)	Microstrain (%)
Pure	9(1)	5.412(1)	0.25
1%	11(1)	5.420(3)	0.83
3%	9(1)	5.412(2)	0.63
5%	9(1)	5.411(2)	0.47

Note: $9(1)=9 \pm 1$

shown in Table 1. Although the ionic radii of Ce^{4+} (1.01 Å) at an octahedral arrangement is larger than the Fe^{3+} (0.69 Å), we have not verified any change in lattice parameters ($a=5.410\text{ Å}$) except for samples with lowest Fe concentration (1%). The microstructural analysis shows that the microstrain does not follow a systematic (see Table 1) trend. These results suggest that the incorporation of Fe in CeO_2 host is not ordered.

In order to analyze the shape and particle size, we have done analysis using transmission electron microscopy (TEM) for Fe-doped CeO_2 samples. Fig. 2 clearly shows the formation of crystallites which agglomerates with a spherical-like shape, highly crystalline and with particle sizes of nearly $8(2)\text{ nm}$. They are in good agreement with the average crystalline size determined by Williamson–Hall analysis of the X-ray diffraction for doped samples.

The FTIR spectra have been performed to investigate the effect of Fe doping on the O–Ce–O bonding. The results presented in Fig. 3 show the presence of the characteristic vibration of CeO_2 at 1090 cm^{-1} [15]. The absorption bands observed around 1550 and 1635 cm^{-1} are attributed to the stretching mode hydroxyl associated with the existence of water molecules. The peaks at 1383 and 856 cm^{-1} are due to the vibrations associated with the nitrate groups, and at 2366 cm^{-1} the characteristic vibration of CO_2 molecules.

3.2. Magnetic properties

Fig. 4 shows the M vs H curves at 300 K for $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ samples with $x=0.01$ and $x=0.03$ with the lower-field regions shown in the inset. These results were normalized after subtracting the diamagnetic contribution due to the CeO_2 host. The obtained hysteresis at room temperature supports the fact that the samples present a weak ferromagnetic behavior and not a superparamagnetic one as observed in several magnetic nanoparticles. For pure sample, we have not observed a ferromagnetic behavior (not shown here), differently of Fernandes et al. [16]. The inset shows the detail of the low field region with $H_C=10\text{ Oe}$ and $M_R=2.7 \times 10^{-4}\text{ emu/g}$ for doped sample with 1% of Fe and $H_C=50\text{ Oe}$ and $M_R=1.4 \times 10^{-4}\text{ emu/g}$ for doped sample with 3% Fe. Although the values of H_C and M_R can be considered small, our results are in good agreement with those obtained for on CeO_2 nanoparticles with sizes near to 7 nm [17,18]. We have also observed that the $\text{Ce}_{0.99}\text{Fe}_{0.01}\text{O}_2$ sample presents a magnetization greater than that obtained for $\text{Ce}_{0.97}\text{Fe}_{0.03}\text{O}_2$ sample. Sheera et al. have observed a similar behavior when they compared the Cu-doped CeO_2 nanoparticles with 2.5 and 5% of doping and they have associated this behavior with the presence of impurities of iron oxides phases [17]. In this sense, these results suggest the formation of ferromagnetic clusters due to the unhomogeneity of Fe ions in the CeO_2 host lattice, which they corroborate with the microstructural analysis.

4. Conclusions

A simple and easy route has been employed to synthesize $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ nanocrystals ($x=0, 0.01, 0.03, 0.05$) at room temperature

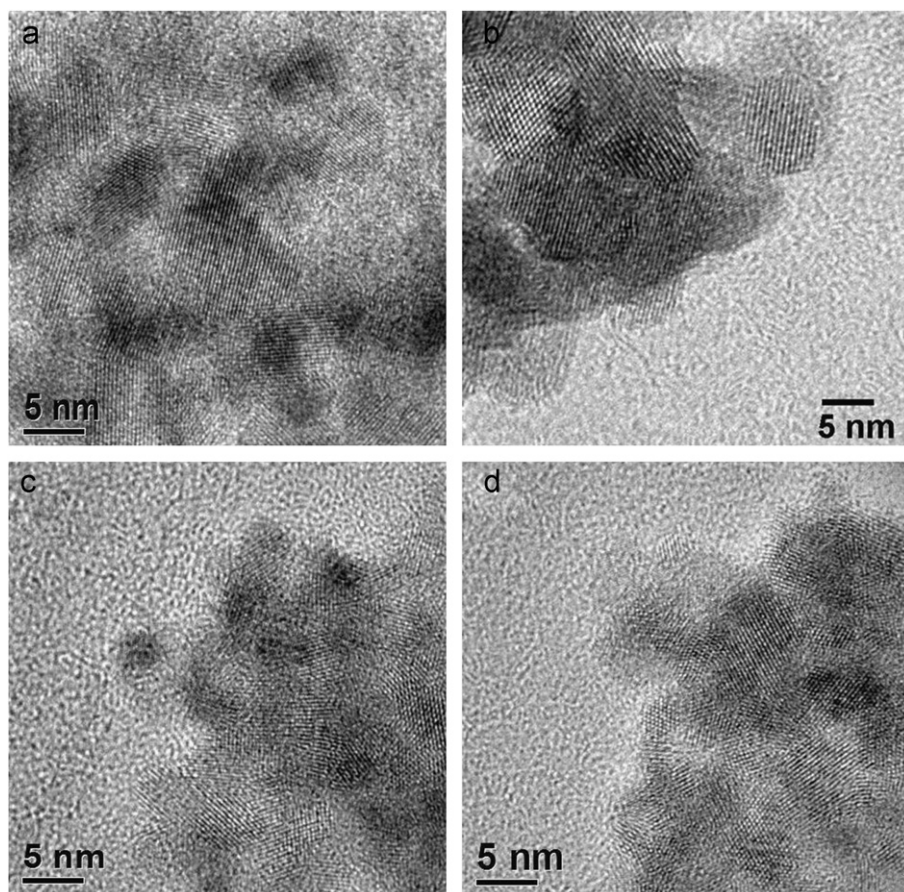


Fig. 2. High resolution TEM images of the Fe-doped CeO_2 samples with (a) pure, (b) 1%, (c) 3% and (d) 5%.

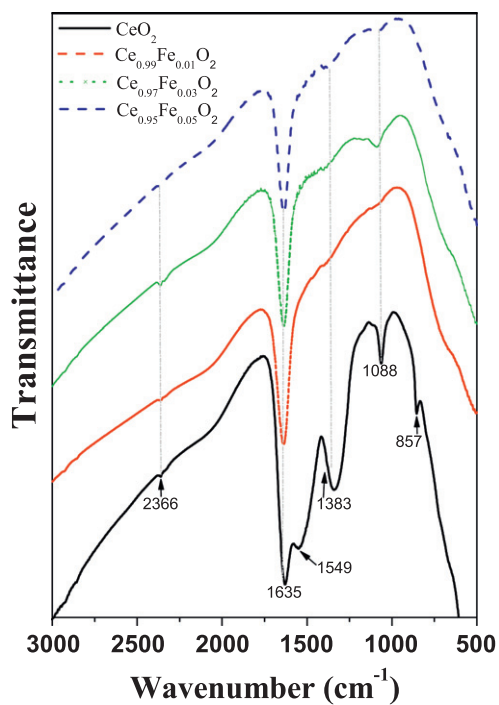


Fig. 3. Infrared spectra of the CeO_2 particles obtained in this work.

by co-precipitation method without the impurity phase confirmed by XRD and Rietveld refinement analyses. The particle size for all samples studied estimated by XRD revealed that the

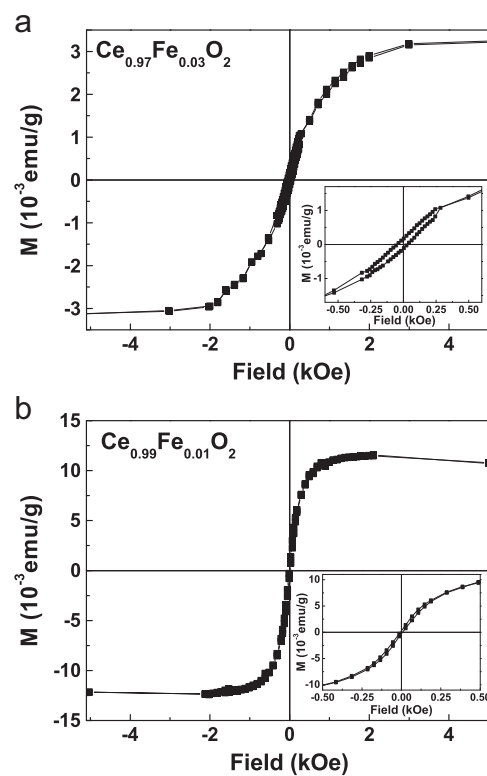


Fig. 4. Magnetization versus magnetic field taken at room temperature for samples (a) $\text{Ce}_{0.97}\text{Fe}_{0.03}\text{O}_2$ and $\text{Ce}_{0.99}\text{Fe}_{0.01}\text{O}_2$, the inset shows the region at a low field.

CeO₂ nanocrystals present mean size nearly to 9 nm with spherical shape confirmed by TEM images. *M* vs *H* results for doped samples show a weak ferromagnetic behavior at room temperature which can be associated with the formation of magnetic clusters.

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