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Synthesis, characterization, and magnetic properties of monodisperse CeO₂ nanospheres prepared by PVP-assisted hydrothermal method

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Abstract

Ferromagnetism was observed at room temperature in monodisperse CeO₂ nanospheres synthesized by hydrothermal treatment of Ce(NO₃)₃·6H₂O using polyvinylpyrrolidone as a surfactant. The structure and morphology of the products were characterized by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy, high-resolution transmission electron microscopy, and field-emission scanning electron microscopy (FE-SEM). The optical properties of the nanospheres were determined using UV and visible spectroscopy and photoluminescence (PL). The valence states of Ce ions were also determined using X-ray absorption near edge spectroscopy. The XRD results indicated that the synthesized samples had a cubic structure with a crystallite size in the range of approximately 9 to 19 nm. FE-SEM micrographs showed that the samples had a spherical morphology with a particle size in the range of approximately 100 to 250 nm. The samples also showed a strong UV absorption and room temperature PL. The emission might be due to charge transfer transitions from the 4*f* band to the valence band of the oxide. The magnetic properties of the samples were studied using a vibrating sample magnetometer. The samples exhibited room temperature ferromagnetism with a small magnetization of approximately 0.0026 to 0.016 emu/g at 10 kOe. Our results indicate that oxygen vacancies could be involved in the ferromagnetic exchange, and the possible mechanism of formation was discussed based on the experimental results.

Keywords: CeO₂, Nanospheres, Dilute magnetic oxide, Ferromagnetism, Oxygen vacancies, Valence states

Background

Oxide-dilute magnetic semiconductors (O-DMSs) such as ZnO, TiO₂, SnO₂, and In₂O₃ doped with transition metal (TM) ions have recently attracted much attention due to their potential use in magneto-optoelectronic applications [1-3]. These O-DMSs are optically transparent and exhibit ferromagnetism (FM) at room temperature (RT) and even well above RT. Recently, TM-doped CeO₂ have been also reported to exhibit ferromagnetism at and above room temperature [4-10]. Unlike other O-DMSs, CeO₂ has a cubic structure with a lattice parameter $a = 0.54113$ nm [11] that will facilitate the integration of spintronic devices with advanced silicon microelectronic devices.

Early work on CeO₂-based O-DMSs was focused on thin films [4-6] and only a few works have been carried out on powders, bulk, or nanocrystalline form [9-12]. Tiwari et al. [4] firstly discovered room temperature ferromagnetism (RT-FM) in Ce_{1-x}Co_xO_{2-δ} ($x \leq 0.05$) films deposited on a LaAlO₃ (001) substrate by pulsed laser deposition (PLD) technique. These films are transparent in a visible regime and exhibit a very high Curie temperature (T_C) at approximately 740 to 875 K with large magnetic moments of 6.1 ± 0.2 to $8.2 \pm 0.2 \mu_B/\text{Co}$. Following the work by Tiwari et al., Song et al. [5] reported successful fabrication of Ce_{1-x}Co_xO_{2-δ} ($x = 0.03$) thin films with (111) preferential orientation deposited on a Si (111) substrate by a PLD technique. Their deposited films show RT-FM with large magnetic moment of $5.8 \mu_B/\text{Co}$ and coercivity of 560 Oe. The authors also showed that the films could be deposited on glass but with smaller magnetic moment and coercivity. These

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results suggested that the FM in Co-doped CeO₂ depend not only on the doping concentration of transition element, but also on the microstructure of film, including its crystallization, defects, vacancies, etc. Vodungbo et al. [6] also reported FM in Co-doped CeO₂ thin films grown by PLD on SrTiO₃ and Si substrate. The films were ferromagnetic with a T_C above 400 K. These authors found that the amount of structural defects had a little effect on FM, but the presence of oxygen during the growth or annealing reduced drastically the FM, suggesting that oxygen vacancies played an important role in the magnetic coupling between Co ions, while Wen et al. [9] reported the ferromagnetism observed in pure and Co-doped CeO₂ powders. The RT-FM in pure CeO₂ originated from oxygen vacancies while a slight Co doping in CeO₂ caused a nearly two-order enhancement of saturation magnetization (M_s) to 0.47 emu/g as compared with the pure sample. The authors suggested that the large RT-FM observed in Co-doped CeO₂ powder originated from a combination effect of oxygen vacancies and Co doping. Similarly, Ou et al. [10] reported RT-FM for Ce_{1-x}Co_xO₂ (0 < x < 0.10) nanorods prepared by electrodeposition route. The nanorods were ferromagnetic with a high T_C of about 870 K and the largest M_s of 0.015 emu/g. They suggested that the RT-FM observed in Co-doped CeO₂ nanorods was adjusted by the structural defects including oxygen vacancies. The same behavior was found in nanoparticles of Fe-doped CeO₂ [11] with an M_s value of 0.0062 emu/g in 3 at % Fe prepared by a sol-gel method and Fe-doped CeO₂ [12] with an M_s value of 0.10 emu/g in 1 at % Fe prepared by the proteic sol-gel process. The authors suggested that the RT-FM originated from an exchange of F-center, which involved a combination of oxygen vacancies and TM doping.

Surprisingly, the researchers report RT-FM of undoping in different oxides, such as thin films of HfO₂ [13], TiO₂ and In₂O₃ [14], and nanoparticles of CeO₂, Al₂O₃, ZnO, In₂O₃, and SnO₂ [15], while the corresponding bulk samples are diamagnetic. Most recently, there are some studies reporting ferromagnetism observed in pure CeO₂ on powders, nanocrystalline, or cubes [16-18]. Liu et al. [16] studied the size-dependent ferromagnetism in CeO₂ powders synthesized by precipitation route. They found that ferromagnetism was observed only in sub-20-nm powders with an M_s value of 0.08 emu/g. Similarly, Chen et al. [17] reported RT-FM in CeO₂ nanoparticles prepared by thermal decomposition method with an M_s value of 0.12 emu/g. The authors showed that its crystallite size in nanometers would be ferromagnetic because of the large value of the surface-to-volume ratio, leading to the exchange interactions between electron spin moments that resulted from oxygen vacancies at the surface [4]. Recently, Ge et al. [18] observed

ferromagnetism in CeO₂ nanocubes with an M_s value of 0.0057 emu/g (an average size of 5.3 nm) prepared by a chemical method. They suggest that oxygen vacancy is essential for the formation of FM in CeO₂ nanocubes.

However, magnetic properties of monodisperse nanospheres of pure CeO₂ have not yet been reported. In this work, we report the ferromagnetism observed in monodisperse CeO₂ nanospheres with a particle size of approximately 200 nm synthesized by hydrothermal treatment of Ce(NO₃)₃·6H₂O using polyvinylpyrrolidone (PVP) as a surfactant. The technique of preparation and the effect of the type of cerium source on the crystallinity and morphology were investigated. The prepared samples were characterized by X-ray diffraction (XRD), Raman spectroscopy, field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), UV and visible spectroscopy (UV-vis), and photoluminescence (PL). The valence states of Ce ions were also investigated by using X-ray absorption near edge spectroscopy (XANES), and the magnetic properties of the samples were determined using a vibrating sample magnetometer (VSM). The origin of RT-FM in this pure CeO₂ is also discussed.

Methods

In this study, cerium (III) nitrate hexahydrate, Ce(NO₃)₃·6H₂O (99.99% purity; Kanto Corporation, Portland, OR, USA); cerium (III) acetate hydrate, Ce(CH₃CO₂)₃·xH₂O (99.9% purity; Sigma-Aldrich Corporation, St. Louis, MO, USA); cerium (III) chloride heptahydrate, CeCl₃·7H₂O (99.9% purity; Sigma-Aldrich Corporation); cerium (III) sulfate octahydrate, Ce₂(SO₄)₃·8H₂O (99.999% purity; Sigma-Aldrich Corporation); and PVP (Sigma-Aldrich Corporation) were used as starting materials. In a typical procedure, one gram of PVP was mixed with 40 mL of deionized water under vigorous magnetic stirring at room temperature (27°C) until a homogeneous solution was obtained. Subsequently, 3 mmol of cerium source was slowly added to the PVP solution under vigorous stirring at room temperature for 2 h, in order to obtain a well-dissolved solution. Throughout the whole process described, no pH adjustment was made. The homogeneous solution was transferred into a Teflon-lined stainless steel autoclave of 50-mL capacity and prepared at 160°C and 200°C for 12 h and 160°C and 200°C for 24 h. After the autoclave was cooled naturally to room temperature, the precipitate was collected and washed several times with distilled water. The final product was then dried in a vacuum at 80°C overnight. In addition, the as-prepared samples were also annealed in argon atmosphere at 400°C for 2 h to study the effect of oxygen vacancies on magnetic properties of the annealed samples.

The prepared samples were characterized using XRD, Raman spectroscopy, FE-SEM, TEM, HRTEM, UV-vis, PL, XANES, and VSM. A Philips X-ray diffractometer (Philips Tecnai, Amsterdam, The Netherlands) with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm) was used to study the phases of the pure CeO_2 samples. The 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, France). The morphology of the sample was obtained from TEM (JEM 2010 200 kV, JEOL Ltd., Akishima, Tokyo, Japan). FE-SEM was performed using a JEOL JSM-6335 F (JEOL Ltd.). The optical absorption spectrum was measured in the range of 200 to 800 nm using a UV-3101PC UV-vis-NIR scanning spectrometer (Shimadzu Corporation, Nakagyo-ku, Kyoto, Japan). PL was carried out on a luminescence spectrometer (PerkinElmer LS-55B, PerkinElmer Instrument, Waltham, MA, USA), using a Xenon lamp as the excitation source at room temperature. The Ce L_3 XANES spectrum was studied using XANES in transmission mode at the BL4 Station at Siam Photon Laboratory (Synchrotron Light Research Institute (Public Organization), SLRI) in Nakhon Ratchasima, Thailand. The magnetic measurements were performed at room temperature using a vibrating sample magnetometer (VSM 7403, Lakeshore, Westerville, OH, USA).

Results and discussion

XRD analysis

The XRD patterns of the samples prepared by hydrothermal reaction at 160°C for 12 h are shown in Figure 1a. The sample obtained with $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ as the starting agent shows no XRD peaks, indicating that it is amorphous, whereas the sample from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ exhibits XRD peaks that correspond to the (111), (200), (220), (311), (222), and (400) planes, which are consistent with the face-centered cubic fluorite structure of CeO_2 in the standard data from the Joint Committee on Powder Diffraction Standards (JCPDS) 34-0394, indicating that pure CeO_2 was successfully synthesized via these procedures.

In this study, we found that the type of cerium source has a great effect on the morphology of the final product. The cerium source from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ shows that the sample consisted of sphere-like particles with diameters of 100 to 250 nm (Figure 1b), whereas other cerium sources such as $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, and $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ resulted in irregular shapes and agglomerated particles as shown in Figure 1c,d,e, respectively. Therefore, it is clearly seen that cerium source from nitrate is most favorable for the formation of uniformly sized CeO_2 nanospheres. It is possible that the absorption of PVP molecules on various crystallographic planes of cerium source played a major role in determining the product morphology, due

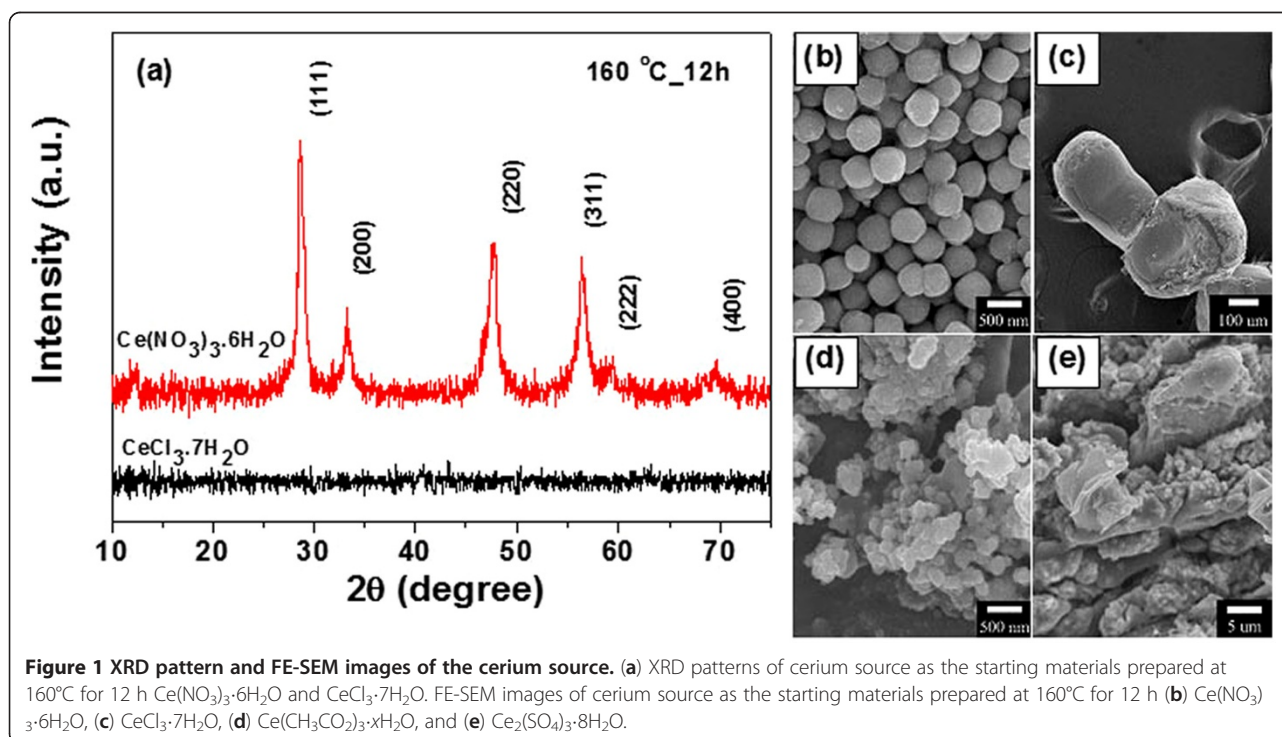
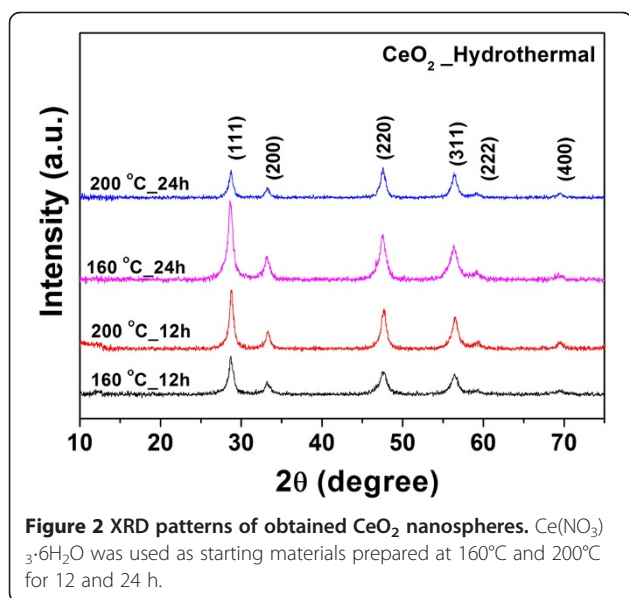


Figure 1 XRD pattern and FE-SEM images of the cerium source. (a) XRD patterns of cerium source as the starting materials prepared at 160°C for 12 h $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. FE-SEM images of cerium source as the starting materials prepared at 160°C for 12 h (b) $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, (c) $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, (d) $\text{Ce}(\text{CH}_3\text{CO}_2)_3 \cdot x\text{H}_2\text{O}$, and (e) $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$.

to the fact that the supersaturation degree has a significant influence on the crystal nucleation rate and crystal growth rate [19]. However, the real reason for the morphology variation of the cerium source and surfactants has yet to be fully understood.

Figure 2 shows the XRD patterns of the pure CeO₂ from cerium nitrate at various hydrothermal treatment durations and temperatures. All the samples exhibited six typical peaks corresponding to the (111), (200), (220), (311), (222), and (400) planes, which are consistent with the face-centered cubic fluorite structure of CeO₂ in the standard data from JCPDS 34–0394, and this is in agreement with the selected area electron diffraction (SAED) patterns shown in Figure 3d. The values of the lattice constant calculated from the XRD spectra are shown in Table 1. The average crystallite size of all the samples was calculated from X-ray line broadening of the peaks at the (111), (200), (220), and (311) planes using Scherrer's equation, (as listed in Table 1). We observed that the lattice parameter decreases with increasing crystallite size. This decrease is possibly due to the introduction of Ce³⁺ ions into the crystal lattice. Ce³⁺ ions have a higher ionic radius (1.034 Å) compared with the Ce⁴⁺ ions (0.92 Å) and introduce oxygen vacancies. Therefore, the concentration of Ce³⁺ ions increases, and there is also an increase in the number of oxygen vacancies. It is observed that the pure CeO₂ nanoparticles experience considerable lattice distortion, which is in good agreement with earlier reports on CeO₂ nanoparticles [9,20], which indicated that this causes a change in the Ce-O bond length (lattice distortion) and the overall lattice parameter.



Raman analysis

The formation of a cubic structure in the CeO₂ nanospheres was further supported by the Raman spectra. Figure 4 shows typical spectra of CeO₂. The Raman active modes are shifted from 458 to 461 cm⁻¹ for the CeO₂ samples heated at 160°C to 200°C. These Raman active modes are attributed to a symmetrical stretching mode of the Ce-8O vibrational unit, and therefore, they are very sensitive to any disorder in the oxygen sublattice that resulted from thermal, doping, or grain size [21-24]. The effect of the microstructure of CeO₂ on the shape of the Raman spectra was observed by the broadening of the line and by increases in its asymmetry, which are attributed to the reduction of the phonon lifetime in the nanocrystalline regime [25, 26]. The particle size of the CeO₂ sample can be also estimated from the Raman line broadening using the following Equation 1 [23, 24, 27]:

$$\Gamma(\text{cm}^{-1}) = 10 + \frac{124.7}{D_R}, \quad (1)$$

where $\Gamma(\text{cm}^{-1})$ is the full width at half maximum of the Raman active mode peak and D_R is the particle size of a CeO₂ sample. This relation can be used to determine the crystal size of the CeO₂ samples as shown in Table 1. This calculated crystal size is near that obtained from X-ray line broadening.

FE-SEM, TEM, and HRTEM analyses

The morphology and structure of CeO₂ nanospheres were investigated by FE-SEM and TEM as shown in Figure 3. TEM bright field images show that the samples contain monodisperse nanospheres with a narrow size distribution. The high-magnification TEM image of a single particle (Figure 3b) indicates that the sphere has a diameter of about 218 nm. This result is similar to the work reported by Zhou et al. [28], in which spherical CeO₂ crystallites assembled by nanoparticles were synthesized by hydrothermal treatment because small nanoparticles of CeO₂ aggregated and gradually evolved into a spherical assembly, achieving a low surface energy. The corresponding SAED patterns (inset in Figure 3d of the products show spotty ring patterns indicative of a face-centered cubic structure of CeO₂ (JCPDS 34–0394), which is in agreement with the XRD results. The HRTEM images of the CeO₂ sample prepared at 200°C for 12 h and the CeO₂ sample prepared at 200°C for 12 h followed by annealing in Ar at 400°C for 2 h, are shown in Figure 5a,b, respectively. The *d* spacings of the lattice fringes of approximately 0.30 and 0.31 nm for the CeO₂ sample prepared at 200°C for 12 h (Figure 5a) calculated from the HRTEM images correspond to

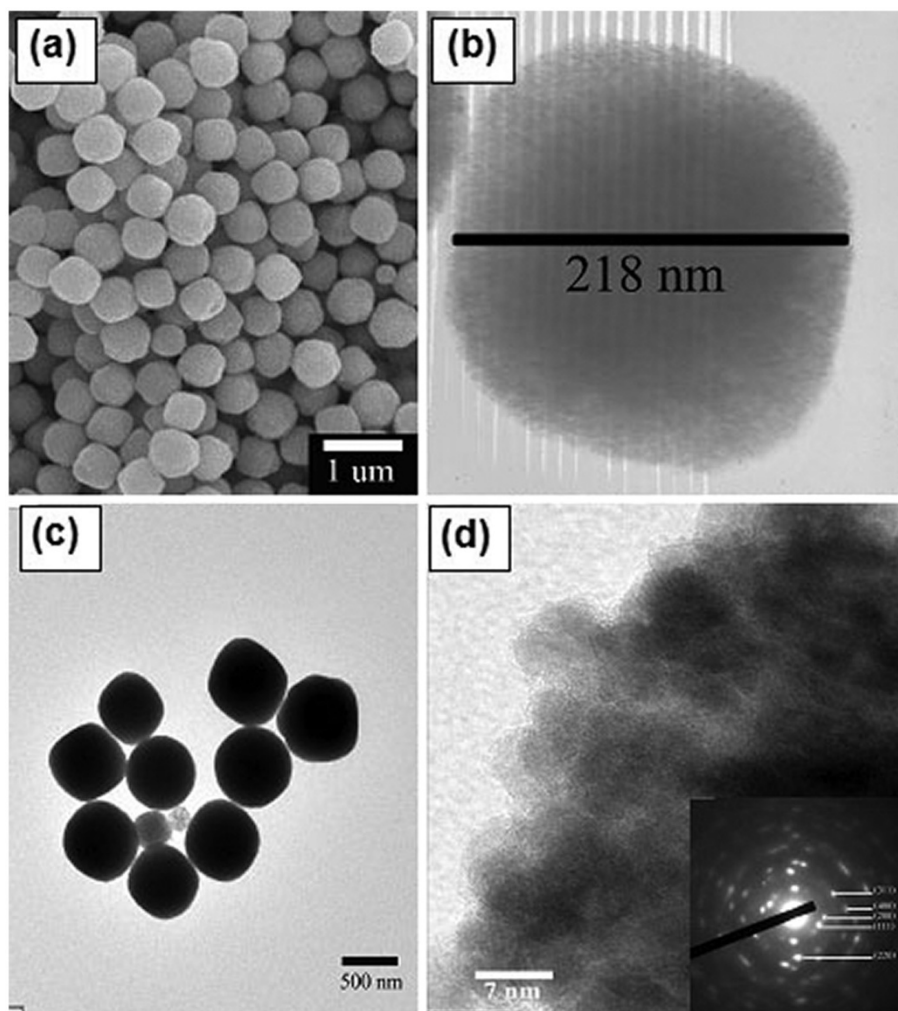


Figure 3 FE-SEM and TEM bright field images of CeO₂ nanospheres. (a) FE-SEM images of CeO₂ nanospheres prepared at 200°C for 24 h; (b) TEM bright field images of CeO₂ nanospheres prepared at 160°C for 12 h; (c) and (d) are TEM bright field images with corresponding SAED patterns (insets) of CeO₂ nanospheres prepared at 200°C for 12 h.

the (111) plane of CeO₂, whereas the *d* spacings of approximately 0.31 and 0.32 nm (Figure 5b) for the CeO₂ sample prepared at 200°C for 12 h followed by annealing in Ar at 400°C for 2 h match with (111) plane of CeO₂. This is in good agreement with the standard data (JCPDS 34–0394).

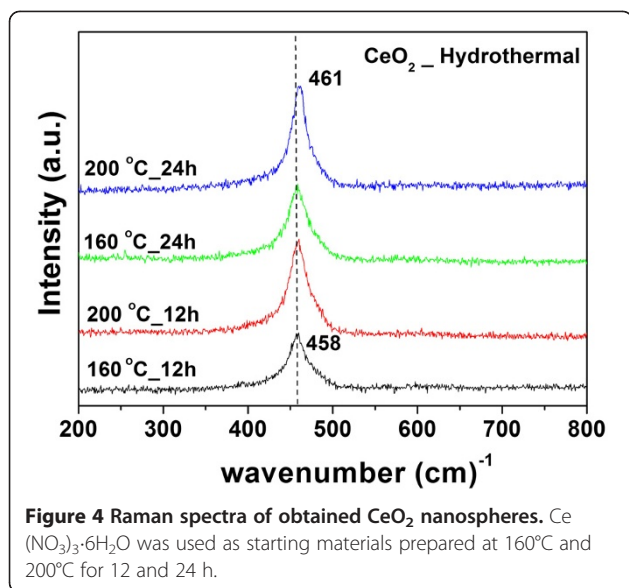
Optical properties

The UV–vis absorption spectra of the pure CeO₂ nanospheres are shown in Figure 6a. All the samples show a strong absorption below 400 nm (3.10 eV) with a well-defined absorbance peak at approximately 302 nm (4.10 eV). The direct bandgap energy (*E_g*) is determined

Table 1 Summary of crystallite sizes, lattice constant, bandgap, and magnetization of pure CeO₂ nanospheres

Sample	Crystallite size from XRD (nm)	Lattice constant <i>a</i> (nm)	<i>E_g</i> (eV)	Crystallite size from Raman spectroscopy (nm)	<i>M_s</i> at 10 kOe (emu/g)	
					Before Ar annealing	After Ar annealing
CeO ₂ at 160 °C for 12 h	9.43 ± 0.41	0.5430 ± 0.0021	3.00	7.39	-	-
CeO ₂ at 200 °C for 12 h	19.6 ± 0.53	0.5420 ± 0.0003	3.04	8.21	0.0026	0.011
CeO ₂ at 160 °C for 24 h	12.2 ± 0.13	0.5430 ± 0.0003	3.06	9.23	0.0053	0.0026
CeO ₂ at 200 °C for 24 h	15.6 ± 0.20	0.5428 ± 0.0006	3.10	12.28	0.016	0.015

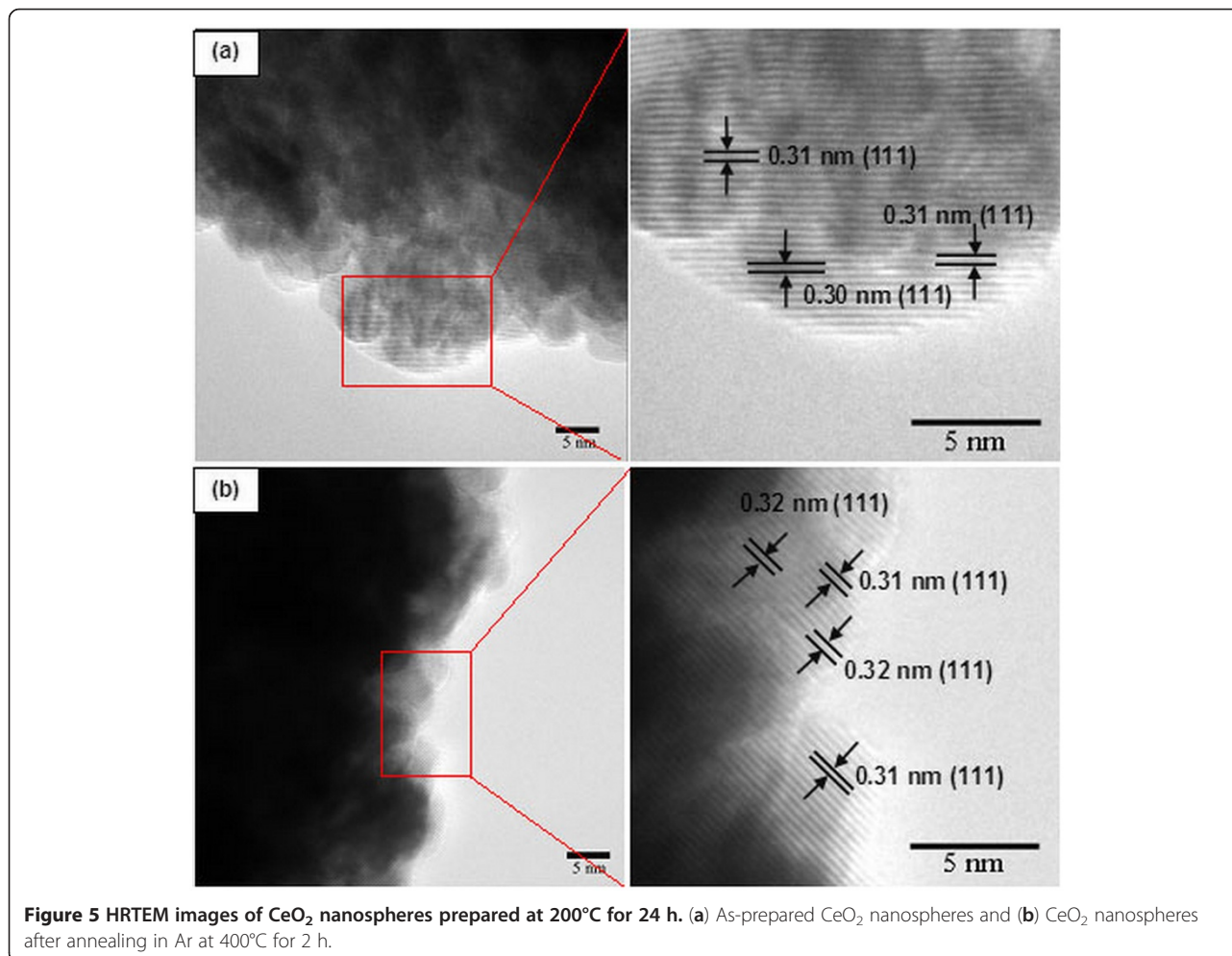
E_g, bandgap energy; *M_s*, saturation magnetization. Data of magnetization of pure CeO₂ nanospheres is before and after Ar annealing.



by fitting the absorption data to the direct transition as shown in Equation 2:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (2)$$

where α is the optical absorption coefficient, $h\nu$ is the photon energy, E_g is the direct bandgap, and A is a constant [29]. The extrapolation of the linear portions of the curves towards absorption equal to zero ($y=0$) gives E_g for direct transitions (Figure 6b). The estimated direct bandgaps of all the samples are shown in Table 1. The bandgap of CeO₂ reported in this work is lower than that reported in the literature. Chen and Chang [30] reported direct bandgap values ranging from 3.56 to 3.71 eV for CeO₂ nanoparticles synthesized by precipitation method. Maensiri et al. [21] reported direct bandgap values ranging from 3.57 to 3.61 eV for CeO₂ nanoparticles synthesized by the sol-gel method using egg white. Similarly, Masui et al. reported direct bandgap values of 4.1 and 2.6 nm for CeO₂ nanoparticles prepared using reverse micelles to be 3.38 and 3.44 eV [31],



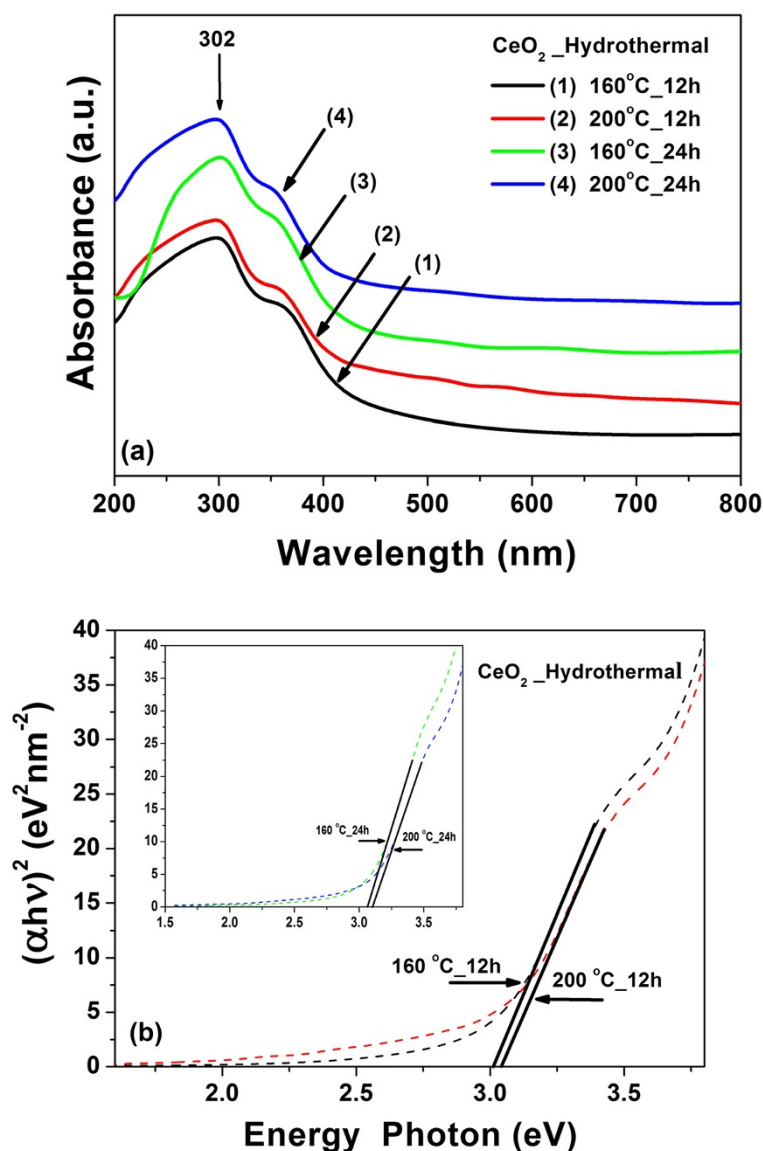


Figure 6 Room temperature optical absorbance spectra of CeO₂ nanospheres and plot of $(\alpha h\nu)^2$. (a) Room temperature optical absorbance spectra of CeO₂ nanospheres using Ce(NO₃)₃·6H₂O as starting materials. (b) Plot of $(\alpha h\nu)^2$ as a function of photon energy for the CeO₂ nanospheres.

respectively, due to quantum confinement effect [32]. This phenomenon has been well explained for particle sizes down to less than a few nanometers, but for our results, the bandgaps increased with increasing crystal size, which exhibit blueshifts in the UV absorption spectra inferred from the bandgap calculated for pure CeO₂ nanospheres. This blueshift has been reported to be an electrostatic potential effect due to a cerium valence change when the particle size is larger than a few nanometers (e.g., ≥8 nm). The Ce⁴⁺ ions coexist with Ce³⁺ ions, and these ions can be attributed to oxygen vacancies at the surface [33]. Therefore, in our work, the bandgaps increased with increasing crystal

size. The crystallite size is in the range of 9 to 19 nm as indicated by the existence of the blueshift for our CeO₂ nanospheres.

PL analysis

Figure 7 shows the room temperature PL spectra obtained using a Xenon laser of 290 nm as the excitation source of the CeO₂ nanospheres. The spectra of all the samples are almost identical and mainly consist of five emission bands: a strong blue emission band at 422 nm (2.93 eV), a weak blue band at 446 nm (2.78 eV), a blue band at 460 nm (2.69 eV), a strong blue-green band at 485 nm (2.55 eV), and a green band at 529 nm

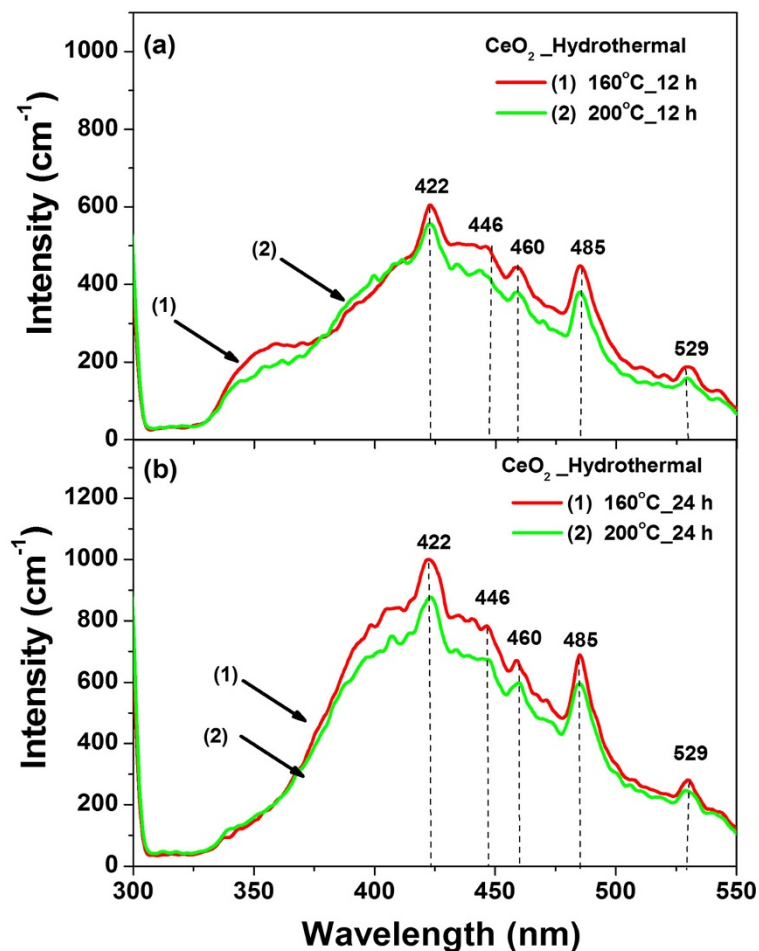


Figure 7 Room temperature photoluminescence spectrum of CeO₂ nanospheres using Ce(NO₃)₃·6H₂O as starting materials. The sample was dispersed in methanol and the excitation wavelength used in PL measurement was 290 nm.

(2.35 eV). Our results are consistent with that reported for CeO₂ in the literature. The strong emission peak at 410 nm [34] and 422 nm [35] observed for CeO₂ nanoparticles as-prepared at $\lambda_{\text{ex}} = 290$ nm. Maensiri et al. [21] reported a blue band at approximately 443 nm, along with a green band at 529 nm for 400°C to 500°C calcined sample, and a strong UV emission band at 392 nm for 600°C calcined sample. The dependence of the PL blue-shift peak on CeO₂ particle concentration has also been observed by Sathyamurthy et al. [34] for CeO₂ nanoparticles synthesized by a reverse micelle route. This phenomenon has been explained by charge transitions from the 4*f* band to the valence band of the CeO₂ in both nanoparticles and thin films [36]. In addition, it is well known that the emission energy from the 4*f* band to the valence band energy gap of CeO₂ is about 3.0 to 3.38 eV, as determined from the calculation of the electronic structure of CeO₂ [35,37]. Therefore, the emission in our CeO₂ samples could be assumed to be the transition from the Ce 4*f* band to the O 2*p* band (valence

band) in CeO₂. The broad PL band ranging from 300 to 550 nm of all the samples could be the result of defects, including oxygen vacancies in the crystal with electronic energy levels below the 4*f* band [38]. This is confirmed by the enhanced absorption tail below 3 eV in nonstoichiometric CeO₂ that was previously observed and attributed to the presence of oxygen vacancies [39].

XANES analysis

The valence state of Ce in pure CeO₂ nanospheres was determined by XANES spectra measured at Ce L₃ edge. Figure 8a shows the edge energies of the Ce (NO₃)₃·6H₂O standard and CeO₂ standard. The standard Ce(NO₃)₃·6H₂O has a single peak illustrated by one intense white line at approximately 5,726.8 eV, which can be associated with the final state of $2p4f^15de_gL$, where \underline{L} denotes an oxygen ligand 2*p* hole, corresponding to the Ce³⁺ valence state [40]. In the standard CeO₂, there are four peaks comprising high energy peak A, main peak B, low energy peak C,

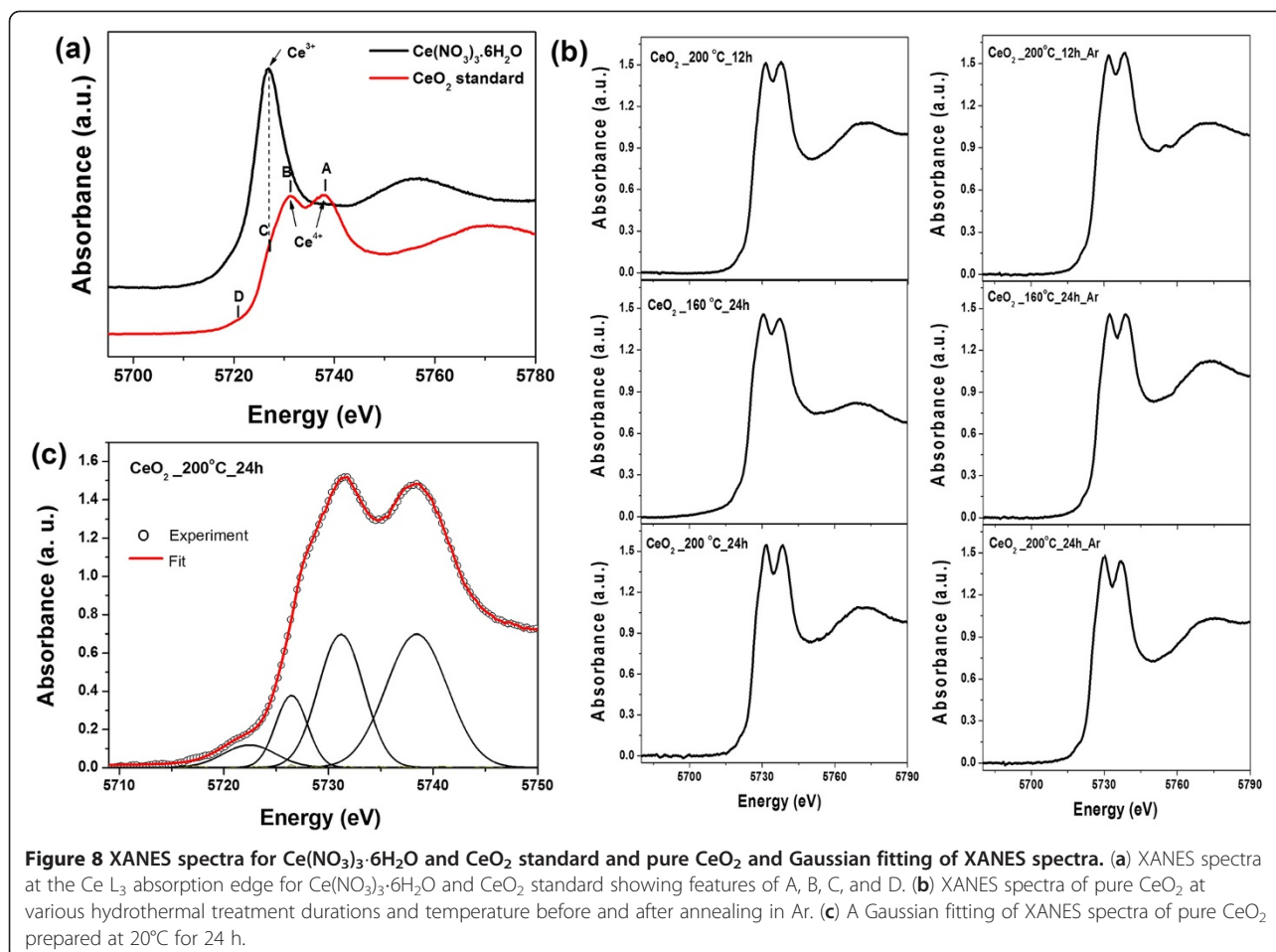


Figure 8 XANES spectra for Ce(NO₃)₃·6H₂O and CeO₂ standard and pure CeO₂ and Gaussian fitting of XANES spectra. (a) XANES spectra at the Ce L₃ absorption edge for Ce(NO₃)₃·6H₂O and CeO₂ standard showing features of A, B, C, and D. (b) XANES spectra of pure CeO₂ at various hydrothermal treatment durations and temperature before and after annealing in Ar. (c) A Gaussian fitting of XANES spectra of pure CeO₂ prepared at 20°C for 24 h.

and pre-edge peak D, which have been reported and assigned previously [41-43]. Peaks A and B are shifted to higher energies at approximately 5,737.9 and 5,731.3 eV, respectively, and were assigned as being due to a mixture of the multi-electron with the final state of $2p4f^05d$ and $2p4f^15d_{gL}$, respectively, which characterizes the Ce in the Ce⁴⁺ valence state [40]. Peak C, at approximately 5,726.8 eV, is observed at the same energy as the white line of a typical Ce (NO₃)₃·6H₂O standard, corresponding to the Ce³⁺ valence state. Peak D is assigned to the final states of $2p5d$ with a delocalized *d* character at the bottom of the conduction band due to the cubic crystal-field splitting of Ce 5*d* states [44].

Figure 8b shows the XANES spectra of pure CeO₂ for various hydrothermal treatment durations and temperatures before and after annealing in Ar. The quantitative analysis of the valence state of Ce in each of the three states of the CeO₂ nanospheres was performed using multi-peak Gaussian fitting obtained from the XANES spectra, as shown in Figure 8c. The analysis shows that Ce in the samples is in a mixed

valence state of Ce³⁺ and Ce⁴⁺. From these results, we can obtain the valence state of Ce according to the fitting parameters of the peak positions and areas listed in Table 2. It is observed that the percentage of Ce³⁺ ranges from 7% to 13.7% in the pure CeO₂ samples. These results provide confirmation of the formation of oxygen vacancies on the surface of the CeO₂ samples. It is possible that the concentration and distribution of oxygen vacancies play an important role in the magnetism of our CeO₂ nanospheres. The highest percentage of Ce³⁺ is 13.7% for CeO₂ prepared at 200°C for 24 h, with the increase in the number of oxygen vacancies, leading to the highest *M_s* values. The concentration of Ce³⁺ in our pure CeO₂ sample is higher than the values reported in the literature for CeO₂. Zhang et al. [41] reported the average Ce³⁺ concentration of 10- and 6-nm CeO₂ nanoparticles prepared by mixing cerium nitrate and hexamethylenetetramine in aqueous solution at room temperature to be 1% and 6.5%, respectively. Chen et al. [17] reported that the concentration of Ce³⁺ was higher than 21% for CeO₂ nanoparticles

Table 2 Gaussian fitting for percentage of Ce³⁺ of pure CeO₂ nanospheres before and after Ar annealing

Sample	Peak position (eV)		Peak area (eV)		Percentage of Ce ³⁺ (%)	
	Before Ar annealing	After Ar annealing	Before Ar annealing	After Ar annealing	Before Ar annealing	After Ar annealing
CeO ₂ at 200 °C for 12 h	5737.881	5738.471	5.128	5.672	7.8	12.4
	5730.733	5731.222	3.791	3.603		
	5724.617	5725.931	0.761	1.308		
CeO ₂ at 160 °C for 24 h	5737.245	5738.888	6.734	4.703	9.8	10.4
	5729.911	5731.695	3.549	3.427		
	5726.128	5726.769	1.013	0.949		
CeO ₂ at 200 °C for 24 h	5738.440	5736.924	5.154	5.713	13.7	13.3
	5731.205	5729.691	3.799	3.741		
	5726.465	5724.987	1.427	1.445		

synthesized by the thermal decomposition method, which is higher than the value for pure CeO₂ nanospheres reported in this study.

Magnetic properties

Figure 9a,b shows the field dependence of the specific magnetization (*M-H* curve) of pure CeO₂ samples prepared at 160°C and 200°C for 12 h and prepared at 160°C and 200°C for 24 h, respectively, obtained from room temperature VSM measurements. The sample of CeO₂ prepared at 160°C for 12 h exhibits mixed behaviors of ferromagnetism and diamagnetism having hysteresis loops at low field. The samples that were prepared at 200°C for 12 h showed weak RT-FM with magnetization (*M*) of approximately 0.0026 emu/g, and the samples that were prepared at 160°C and 200°C for 24 h showed weak RT-FM with saturation magnetization (*M_s*) of approximately 0.0053 and 0.016 emu/g, respectively (as listed in Table 1). These values are higher than the *M_s* values reported in the literature for pure CeO₂ nanospheres [15,17]. Sundaresan et al. [15] reported an RT-FM with an *M_s* value of approximately 0.0019 emu/g for CeO₂ nanoparticles with an average size of approximately 15 nm. Ge et al. [18] reported weak ferromagnetic behavior at an ambient temperature with an *M_s* value of approximately 0.0007 emu/g for pure CeO₂ nanoparticles with an average size of approximately 100 nm obtained commercially from Sigma-Aldrich Corporation (purity of 99.9%). However, magnetic behavior (*M_s* of approximately 0.0057 emu/g) was also observed in monodisperse CeO₂ nanocubes with an average size of approximately 5.3 nm prepared by a chemical method. The results obtained here (experimental and theoretical) provide evidence that pure CeO₂ samples can indeed have a magnetic moment due to oxygen

vacancies. This direct ferromagnetic coupling is called *F*-center exchange (FCE) [45], as cerium can have both variable valence states (Ce⁴⁺/Ce³⁺) and oxygen vacancies on the surface of the CeO₂ nanoparticles. It is possible that oxygen vacancies can create magnetic moments on neighboring Ce ions [46]. In this work, the effect of Ar annealing at 400°C for 2 h on the magnetic properties was also performed to confirm the effect of oxygen vacancies on magnetic properties of the annealed samples. However, this effect was clearly observed only on the CeO₂ sample prepared at 200°C for 12 h and followed by annealing in argon atmosphere at 400°C for 2 h, as its magnetization increased from 0.0025 emu/g to 0.010 emu/g as (see inset of Figure 9b). It is noted that for the samples prepared at 160°C and 200°C for 24 h, annealing did not affect much their magnetic behavior due to the short time of annealing.

To explain the origin of the ferromagnetic contribution in the CeO₂ nanostructures, the following arguments are proposed. The annealing of samples in an Ar atmosphere at 400°C for 2 h could possibly increase the number of oxygen vacancies and Ce³⁺ ions in the samples. The high concentration of Ce³⁺ (approximately 13.3% Ce³⁺ for the sample prepared at 200 °C for 24 h) suggests that defects could be present in the majority of the samples, which activate more coupling between the Ce ions, leading to an increase in *M_s*. Wen et al. [9] reported the variation of RT-FM in oxygen and H₂ (10%)/Ar (90%) annealed samples of 1% Co-doped CeO₂ powder. They found that the sample showed little hysteresis loop after O₂ annealing and that the FM signal decreased significantly, while the H₂ (10%)/Ar (90%) annealed sample showed an enhanced FM with *M_s* of about 0.4 emu/g. However, further work is needed to achieve a thorough understanding, and this will be of

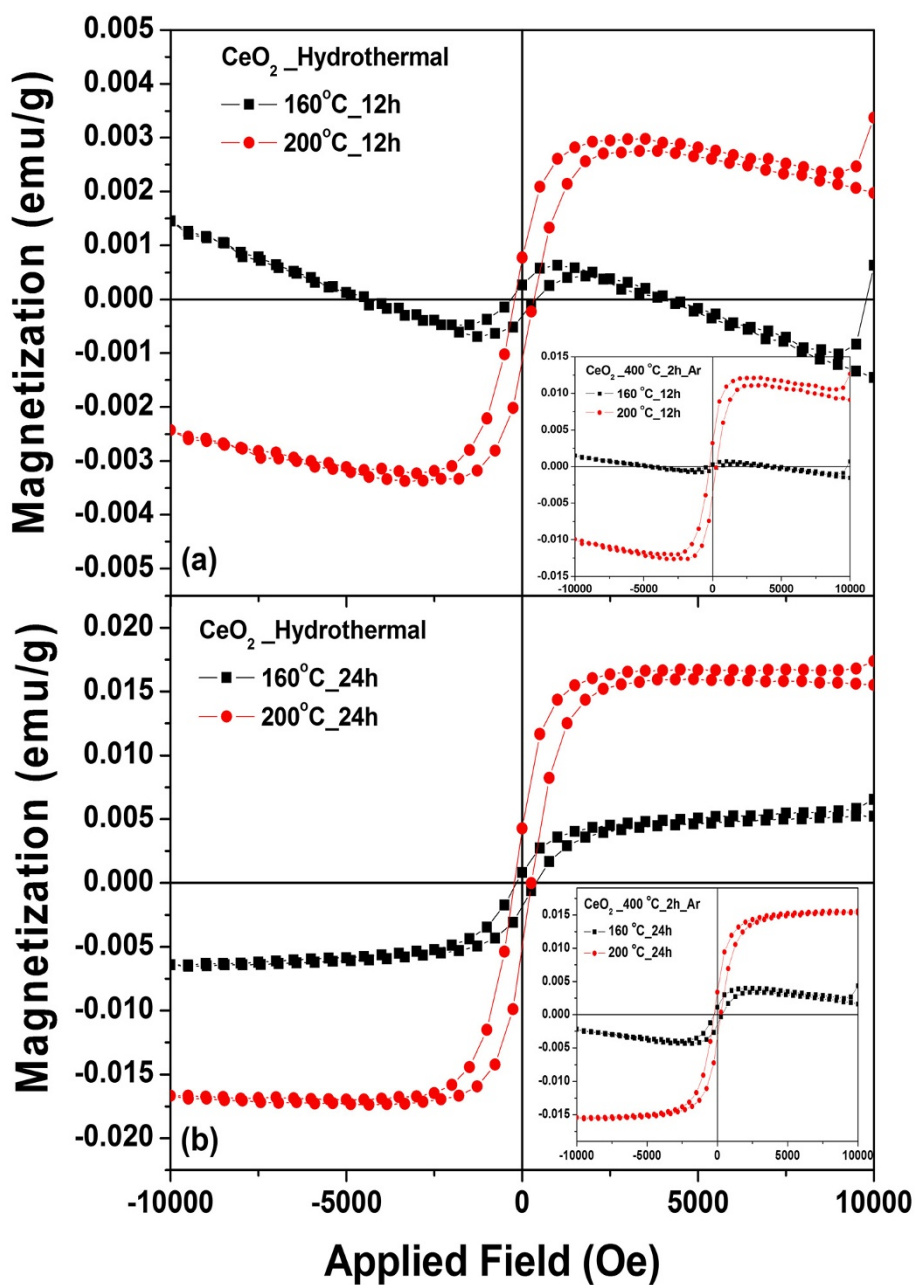


Figure 9 Magnetic properties of monodisperse CeO₂ nanospheres. Prepared at (a) 160°C and 200°C for 12 h and (b) 160°C and 200°C for 24 h. Inset shows CeO₂ samples after annealing in argon atmosphere at 400°C for 2 h.

great interest to researchers in the field of dilute magnetic oxides.

Conclusions

In summary, spheres of pure CeO₂ with Ce(NO₃)₃·6H₂O using PVP as a surfactant have been successfully synthesized by hydrothermal method, and their structures, valence state, and magnetic properties were investigated. The XRD and Raman spectroscopy results suggested the formation of CeO₂ cubic fluorite structures in the CeO₂

samples, which was in agreement with the SAED patterns. It is observed that there is a decrease in the lattice parameters with increasing crystallite size, possibly due to the formation of structure defects/oxygen vacancies in the CeO₂ lattice. The bandgaps of our CeO₂ nanospheres increased with increasing crystal size indicated by the existence of a blueshift due to a cerium valence change, and this can be attributed to oxygen vacancies at the surface. The surface defects in the CeO₂ nanospheres play an important role in the PL properties of

our sample. The XANES results reveal that a fraction of the Ce ions are in the 3+ state, and these cause the samples to show weak RT-FM with an M_s value of 0.0026 to 0.016 emu/g. A ferromagnetic exchange mechanism in the pure CeO₂ samples is discussed by FCE, and the M_s of samples was shown to change, as well as the proportion of oxygen vacancies.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

SP designed and carried out all the experiments and data analysis, and participated in preparing the draft of the manuscript. SP co-supervised the research and offered technical support for TEM. PC and YP offered technical support for XANES measurement and analysis. SM, the project coordinator, supervised the research, designed the experiments, participated in preparing the draft of the manuscript, and revised the manuscript. All authors read and approved the final manuscript.

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