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PAPER

## Suppression of inherent ferromagnetism in Pr-doped CeO<sub>2</sub> nanocrystals

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Ce<sub>1-x</sub>Pr<sub>x</sub>O<sub>2-δ</sub> (0 ≤ x ≤ 0.4) nanocrystals were synthesized by self-propagating method and thoroughly characterized using X-ray diffraction, Raman and X-ray photoelectron spectroscopy and magnetic measurements. Undoped CeO<sub>2</sub> nanocrystals exhibited intrinsic ferromagnetism at room temperature. Despite the increased concentration of oxygen vacancies in doped samples, our results showed that ferromagnetic ordering rapidly degrades with Pr doping. The suppression of ferromagnetism can be explained in terms of the different dopant valence state, the different nature of the vacancies formed in Pr-doped samples and their ability/disability to establish the ferromagnetic ordering.

### Introduction

Among the rare-earth oxides, nanostructured cerium oxide (CeO<sub>2</sub>) has recently emerged as one of the most interesting oxides due to its exceptional properties which make it useful for various applications. It is an important catalyst for automotive catalytic converters, production of hydrogen, crude oil refining and the water–gas shift reaction<sup>1–4</sup> and is widely used as electrolyte in solid oxide fuel cells due to its high ionic conductivity.<sup>5</sup> These applications of nanocrystalline CeO<sub>2</sub> mostly stem from its remarkable oxygen-storage capability, which is especially pronounced on a particle surface, *i.e.* ability to absorb oxygen in oxygen-rich environment and release oxygen in an oxygen-poor environment without changing its fluorite structure.

Since the report of Matsumoto *et al.*<sup>6</sup> that TiO<sub>2</sub> doped with Co shows room-temperature ferromagnetism (RTFM), there were a lot of reports about oxide semiconductors and insulators such as TiO<sub>2</sub>, SnO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, ZnO, HfO<sub>2</sub> or CeO<sub>2</sub> which become ferromagnetic at RT when they were in the nanophase.<sup>7–12</sup> The FM in these nanostructures can be enhanced through doping with small amount of transition metals (TM) such as Cr, Mn, Fe, Co, Ni or Cu.<sup>10,13</sup> These diluted magnetic oxides (DMO) are intensively explored, since they challenge our understanding of the FM. The generally accepted picture of the exchange mechanisms between nearest-neighbors is inadequate to explain the FM in these materials. The FM ordering in DMO can be established far below the percolation threshold (sometimes with only 1% of dopant atoms), with Curie temperatures well in excess of RT. In some cases the achieved moment per dopant atom can exceed the maximum possible moment for the individual dopant atoms. The

FM in DMO is different from the FM in III–V diluted magnetic semiconductors such as Mn doped GaAs, for which Dietl *et al.* gave an explanation of the FM interaction in the framework of the Zener model of hole-mediated ferromagnetism.<sup>14</sup> The origin of the FM in DMO is still under investigation, but it is widely believed that the oxygen vacancies play a crucial role. It has been shown that there is a strong correlation between the presence of oxygen vacancies and ferromagnetism.<sup>9,15–19</sup> One of the frequently used models to explain the FM ordering in DMO is the F-center exchange mechanism, proposed by Coey *et al.*<sup>20,21</sup> According to this mechanism, an electron trapped in an oxygen vacancy (F center) acts as a coupling agent between magnetic ions.

These materials have become very interesting nowadays, especially for spintronic applications. In this respect, CeO<sub>2</sub> attracts great attention since it has a high dielectric constant ( $\epsilon = 26$ ) and almost perfect crystal lattice constant matching with silicon single crystals, making it very suitable for epitaxial growth of various silicon based structures. RTFM in CeO<sub>2</sub> thin films and nanopowders has been extensively studied both experimentally and theoretically. In the majority of previous experimental reports the attention was paid to the influence of TM doping or oxygen vacancies on the FM.<sup>9,15–19,22–28</sup> To the best of our knowledge, there are few papers dealing with RTFM in rare-earth doped ceria nanocrystals<sup>29,30</sup> but none with Pr as dopant. In most of the papers dealing with CeO<sub>2</sub> doped with rare earth elements,<sup>31–39</sup> research was mostly focused on structural, optical, electronic or catalytic properties. In the present work our objective was to investigate the influence of Pr dopant, as an f element, on the magnetic properties of nanostructured CeO<sub>2</sub> and to explore the role played by oxygen vacancies on the magnetic properties.

### Experimental

Nanocrystalline powders of pure CeO<sub>2</sub> and doped with 1, 3, 5, 10, 15, 20, 30 and 40 at.% of praseodymium were prepared by a

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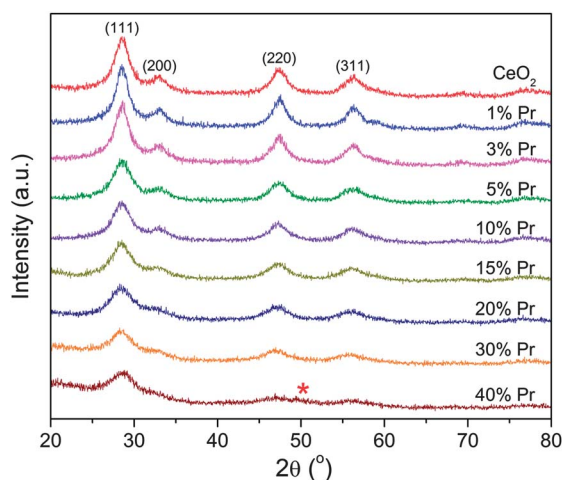
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self propagating room temperature (SPRT) synthesis method<sup>40</sup> using  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Acros Organics) and  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Merck) as the precursors. The purity of cerium nitrate salt was 99.5%. The major impurities were rare earth oxides and some other impurities ( $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{SO}_4$ ), without any magnetic ion impurity (such as  $\text{Fe}$ ,  $\text{Co}$  etc.). The purity of Pr salt was 99.9%. The structural characteristics of the samples were determined by powder X-ray diffraction (XRD) at room temperature on a Siemens D5000 diffractometer using filtered  $\text{Cu K}\alpha$  radiation. XRD patterns were collected in the  $2\theta$  range from 20 to  $80^\circ$  using a position sensitive detector with an  $8^\circ$  acceptance angle. Raman scattering measurement was performed using a TriVista 557 Spectrometer in triple subtractive configuration and a nitrogen-cooled charge coupled device detector. The  $\text{Ar}^+$  laser line of 514.5 nm was employed as an excitation source. Micro-Raman spectra of the samples were collected at room temperature. The incident laser power on the samples was kept low in order to prevent heating effects. X-ray photoelectron spectroscopy (XPS) was used for the oxidation state and atomic ratio analysis. XPS was carried out on a PHI Quantera equipment with a base pressure in the analysis chamber of  $10^{-9}$  Torr. The X-ray source was monochromatized  $\text{Al K}\alpha$  radiation (1486.6 eV) and the energy resolution was 0.7 eV. The spectra were calibrated using the C 1s line (284.8 eV) of the adsorbed hydrocarbon on the sample surface. The magnetic properties of the samples were measured with a vibrating sample magnetometer in a high field measuring system (HFMS, Cryogenic Ltd).

## Results and discussion

XRD patterns of the  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$  ( $0 \leq x \leq 0.4$ ) nanocrystalline samples are shown in Fig. 1. It can be seen that diffraction patterns of the samples exclusively correspond to a fluorite-like structure. None of the samples in the compositional range up to  $x = 0.4$  show any evidence of phase separation. In the case of  $x = 0.4$  sample there is an indication (marked with an asterisk) of a  $\text{Pr}_2\text{O}_3$  phase. This finding is in accordance with Luo *et al.* who have noticed the onset of a secondary  $\text{Pr}_6\text{O}_{11}$  phase for  $x \geq 0.5$  in the case of Pr doped ceria.<sup>39</sup>

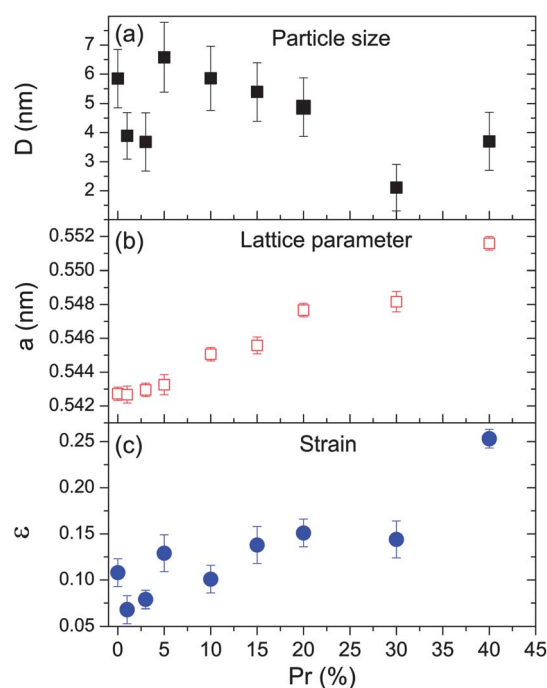


**Fig. 1** XRD patterns of undoped and Pr-doped  $\text{CeO}_2$  nanocrystalline powders. The appearance of  $\text{Pr}_2\text{O}_3$  phase is indicated with an asterisk.

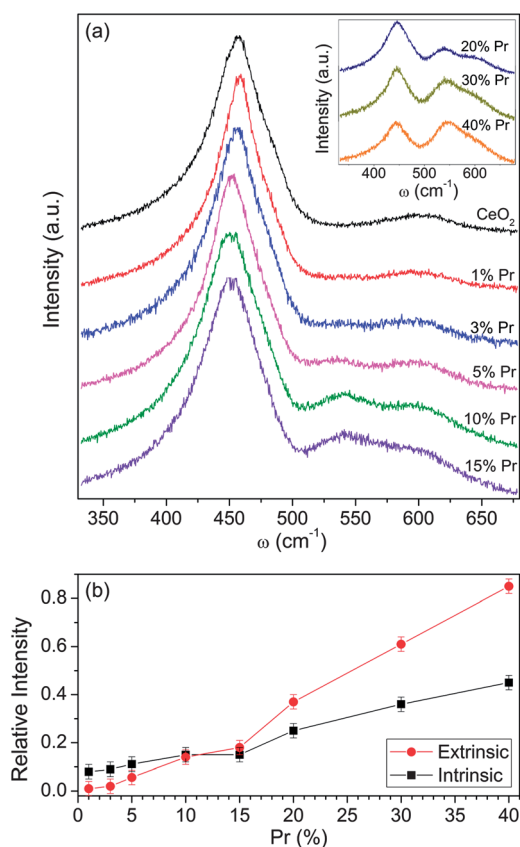
The average particle size ( $D$ ), lattice parameter ( $a$ ) and lattice strain ( $\epsilon$ ) were obtained after Rietveld data refinement. Fig. 2a shows particle size change with Pr doping. The general tendency is particle size decrease with Pr doping, especially for higher doping concentrations. This suggests that Pr doping hinders crystallite growth similarly to TM-doped metal oxide systems.<sup>25,41,42</sup>

Fig. 2b shows the lattice parameter change in  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$  samples. The lattice parameter of pure  $\text{CeO}_2$  nanocrystalline samples (0.5427 nm) is higher in comparison with bulk counterpart (0.541 nm) as a consequence of the increased presence of oxygen vacancies and  $\text{Ce}^{3+}$  ions.<sup>43–45</sup> The lattice parameter linearly increases with increasing Pr content according to Vegard's law. The ionic radius of  $\text{Pr}^{4+}$  (96 pm) is slightly smaller than the  $\text{Ce}^{4+}$  radius (97 pm), so if  $\text{Ce}^{4+}$  is replaced by  $\text{Pr}^{4+}$  no significant change of the lattice parameter is expected. The presence of  $\text{Pr}^{3+}$  ions in ceria lattice will cause a lattice expansion because of the larger  $\text{Pr}^{3+}$  ionic radius (112.6 pm). Therefore, from the lattice parameter change we can conclude that, with doping, the content of  $\text{Pr}^{3+}$  ions increases. From Fig. 2c it can be seen that the undoped  $\text{CeO}_2$  sample has a moderate strain. This is in agreement with other reports on nanosized  $\text{CeO}_2$  particles.<sup>43</sup> The strain originates from the presence of  $\text{Ce}^{3+}$  ions and oxygen deficiency in the host matrix. In doped samples, the strain increases because of the higher content of  $\text{Pr}^{3+}$  ions. With increasing amount of Pr the diffraction peak widths also increase due to the crystallite size decrease and lattice strain increase.

The Raman spectra of  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$  samples are shown in Fig. 3a. The Raman spectra of highly doped samples ( $x > 15\%$ ) are given in the inset of Fig. 3a for clarity. The most prominent feature in the spectra is the  $\text{F}_{2g}$  mode characteristic of a fluorite crystal structure, which is positioned around  $456 \text{ cm}^{-1}$  in



**Fig. 2** Particle size (a), lattice parameter (b) and strain (c) of pure and Pr-doped  $\text{CeO}_2$  nanocrystals.



**Fig. 3** (a) Raman spectra of pure and Pr-doped ceria samples and (b) the intensity of the intrinsic–extrinsic vacancy modes relative to the  $F_{2g}$  mode intensity, as a function of Pr concentration. Inset: Raman spectra of highly doped  $Ce_{1-x}Pr_xO_{2-\delta}$  samples ( $x > 15\%$ ).

nanocrystalline  $CeO_2$ . This mode in the nanocrystalline  $CeO_2$  sample experiences a red shift and an asymmetrical broadening in comparison with its bulk counterpart.<sup>46</sup> Phonon confinement, inhomogeneous strain and the presence of defects cause the observed changes of the Raman spectra.<sup>47,48</sup> In Pr-doped ceria samples, the lattice expands with increased concentration of  $Pr^{3+}$  ions, leading to the shift of the  $F_{2g}$  mode energy to lower frequencies. In the samples with higher Pr content (15% and more) the  $F_{2g}$  mode becomes slightly broader due to the increased strain. The systematic shift and small broadening of the  $F_{2g}$  mode with increasing Pr content shows that Pr has incorporated into the ceria lattice forming solid solutions.<sup>36,38,49</sup>

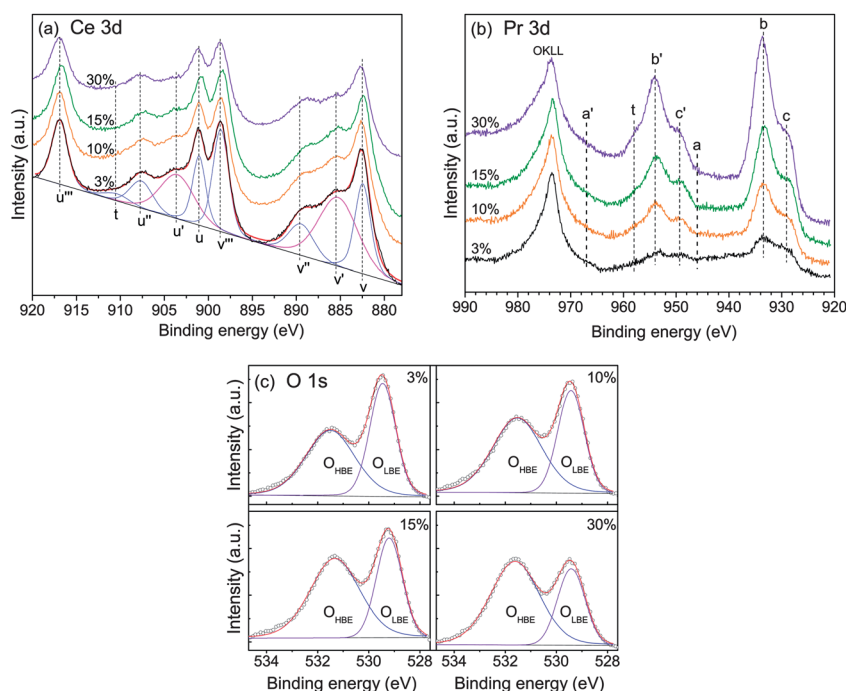
Besides the  $F_{2g}$  mode, in the Raman spectra of Pr-doped samples there are two additional modes positioned at  $\sim 540\text{ cm}^{-1}$  and  $\sim 600\text{ cm}^{-1}$ . These modes are related to the local vibrations of different oxygen vacancy ( $V_O$ ) complexes. The mode at  $600\text{ cm}^{-1}$  originates from the existence of  $Ce^{3+}-V_O$  complexes in the ceria lattice. This mode is referred to as the intrinsic vacancy mode.<sup>50</sup> The extrinsic vacancy mode appears in doped samples and mostly originates from different types of oxygen vacancy complexes formed by doping.<sup>38,50</sup> This mode is positioned around  $540\text{ cm}^{-1}$  in our Pr-doped samples. The intensity change of these two modes relative to the  $F_{2g}$  mode intensity is given in Fig. 3b. With increasing Pr content, the intensity of the extrinsic vacancy mode increases much faster than the intensity of the intrinsic

vacancy mode, implying faster increase of the extrinsic vacancy concentration with doping. From this behavior we can conclude that the concentrations of both kinds of defect complexes increase and at certain point, defect complexes introduced by Pr doping surpass the  $Ce^{3+}-V_O$  complexes.

Fig. 4a shows the Ce 3d XPS spectra of  $Ce_{1-x}Pr_xO_{2-\delta}$  samples for  $x = 3, 10, 15$  and 30% Pr content. The fitting of the spectra was done using Gaussian Lorentzian profiles and the overall fit is presented for the 3% Pr-doped sample. The deconvolution of the spectra gives four spin-orbit doublets ( $3d_{5/2}$  and  $3d_{3/2}$ ) labeled  $v-v''$  and  $u-u''$  using the notation of Ce peaks introduced by Burroughs *et al.*,<sup>51</sup> and a small extra satellite feature labeled as  $t$  which could be a contribution from multiplet splitting effect. The position of the peaks and their binding energies (BE) are summarized in Table 1. Doublets  $u/v$ ,  $u''/v''$  and  $u'''/v'''$  belong to  $Ce^{4+}$ , while  $u'/v'$  belong to  $Ce^{3+}$ . The relative concentration of  $Ce^{3+}$  ions can be calculated from the integrated areas ( $A_i$ ) of the respective peaks as  $[Ce^{3+}]/[Ce^{3+} + Ce^{4+}] = (A_{u'} + A_{v'}) / (A_u + A_v + A_{u'} + A_{v'} + A_{u''} + A_{v''} + A_{u'''} + A_{v'''})$ , and the obtained values are listed in Table 2. It can be seen that the relative concentration of  $Ce^{3+}$  ions is almost constant, indicating that the Pr doping does not significantly change the  $Ce^{3+}/Ce^{4+}$  ratio in the samples.

In the Pr 3d spectra, shown in Fig. 4b, the most prominent features are two spin-orbit doublets labeled  $c/c'$  and  $b/b'$  with approximate energies of *ca.* 929/949 eV and 933/954 eV respectively. These doublets represent the  $3d_{5/2}$  ( $c, b$ ) and  $3d_{3/2}$  ( $c', b'$ ) components of the spectra. An additional structure  $t$  is present in the  $3d_{3/2}$  component and can be explained by a multiplet effect.<sup>52</sup> The characteristic oxygen Auger peak labeled OKLL is also present in the spectra. Contrary to the Ce 3d spectra, for the Pr 3d spectra there is no precise and reliable method for quantitative analysis of the oxidation states by deconvolution of the spectra. Doublets  $c/c'$  and  $b/b'$  are present in both  $PrO_2$  and  $Pr_2O_3$  compounds<sup>53</sup> and hence cannot be exclusively assigned to  $Pr^{4+}$  or  $Pr^{3+}$ . On the other hand, in the XPS spectra of the  $PrO_2$  compound exists a doublet  $a/a'$  with energies of *ca.* 946/967 eV. This doublet feature is exclusively characteristic of the  $PrO_2$  compound.<sup>34,52–56</sup> The position of the peak  $a$  at 946 eV is very close to the stronger  $c'$  peak and is hardly observable. On the contrary, the peak  $a'$  at 967 eV is very distinctive and can be used for qualitative assessment of the  $Pr^{4+}$  presence.<sup>34,53–55</sup> The expected positions of these peaks are also indicated in Fig. 4b. As can be seen from the Pr 3d spectra, the peak  $a'$  is absent and the overall look of the spectra is more similar to the spectra of  $Pr_2O_3$  than to  $PrO_2$ .<sup>52,53</sup> This analysis indicates that in the nanoparticles' surface layer, most of the Pr ions are in the  $Pr^{3+}$  state, although a small amount of  $Pr^{4+}$  cannot be completely ruled out.

In order to estimate the relative amount of Pr and Ce in the samples, the total areas of Pr 3d and Ce 3d peaks were divided and corrected for the atomic sensitivity factors taken from the literature.<sup>57</sup> The obtained values are given in Table 2. It should be emphasized that these values correspond to the samples' surface layer of about 1 nm to which the XPS technique is the most sensitive. The estimated and nominal sample composition is in quite good agreement at higher Pr content. For the lowest Pr content (3% Pr) the measured Pr atomic fraction is much higher than the nominal one. This indicates that for low Pr content there is a higher tendency of Pr segregation in the surface layer of nanocrystals.



**Fig. 4** The XPS spectra of (a) Ce 3d, (b) Pr 3d and (c) O 1s region for several  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$  nanocrystalline samples. Deconvolution of Ce 3d spectra is presented for the 3% Pr-doped sample for clarity, whereas for the O1s region it is given for the investigated samples. The positions of additional features  $a/a'$  expected for  $\text{PrO}_2$  and the oxygen Auger peak (OKLL) are also marked.

In Fig. 4c is presented the O 1s region of the XPS spectra, where two peaks can be clearly resolved. The peak with lower BE = 529.2 eV is labeled as  $O_{\text{LBE}}$ , and the peak with higher BE = 531.1 eV is labeled as  $O_{\text{HBE}}$ . It can be seen that the  $O_{\text{HBE}}$  peak increases with Pr doping. The relative increase of the  $O_{\text{HBE}}/O_{\text{LBE}}$  ratio is also given in Table 2. The  $O_{\text{LBE}}$  peak originates from  $\text{O}^{2-}$  ions in the lattice.<sup>34,58–60</sup> The  $O_{\text{HBE}}$  peak is controversial, as it has been assigned to the oxygen in the form of OH group,  $\text{O}^{\delta-}$  species, CO or  $\text{CO}_2$ .<sup>34,59,61</sup> This peak can be also associated with the presence of oxygen vacancies.<sup>17,22,58,60,62,63</sup> For example, Shah *et al.*<sup>17</sup> concluded that the  $O_{\text{LBE}}$  peak belongs to the oxygen in the  $\text{O}-\text{Ce}^{4+}$  bond, whereas the  $O_{\text{HBE}}$  originates from the oxygen in the  $\text{O}-\text{Ce}^{3+}$  bond. Therefore, the  $O_{\text{HBE}}$  peak can be correlated with  $\text{Ce}^{3+}$  ions and oxygen vacancies. Our XPS results are completely compatible with such an explanation. In our samples, the  $O_{\text{HBE}}$  peak partially originates from the oxygen in  $\text{O}-\text{Ce}^{3+}$  bonds and partially from the oxygen in  $\text{O}-\text{Pr}^{3+}$  bonds, whereas the  $O_{\text{LBE}}$  peak is due to the oxygen in the  $\text{O}-\text{Ce}^{4+}$  and  $\text{O}-\text{Pr}^{4+}$  bonds. This means that  $O_{\text{HBE}}/O_{\text{LBE}}$  ratio reflects the  $[\text{Ce}^{3+} + \text{Pr}^{3+}]/[\text{Ce}^{4+} + \text{Pr}^{4+}]$  ratio. The  $O_{\text{HBE}}$  peak can be less pronounced,<sup>17,58,62</sup> often showing as a shoulder in the O 1s spectra. In our Pr-doped samples this peak is very strong

**Table 2** Atomic fractions of the Ce and Pr ions of several Pr-doped ceria samples. The last column presents the  $O_{\text{HBE}}/O_{\text{LBE}}$  ratio. The estimated relative errors for the atomic fraction are about 10%

Sample	Pr	Ce	$[\text{Ce}^{3+}]/[\text{Ce}^{3+} + \text{Ce}^{4+}]$	$O_{\text{HBE}}/O_{\text{LBE}}$
3% Pr	9.5	90.5	33.3	53.3
10% Pr	13.0	87.0	36.4	59.2
15% Pr	17.0	83.0	34.8	62.4
30% Pr	31.0	69.0	31.7	68.0

even for small concentrations of Pr, due to the significant contribution of  $\text{O}-\text{Ce}^{3+}$  bonds. As we have seen, doping with Pr does not significantly change the concentration of  $\text{Ce}^{3+}$  ions so the contribution from  $\text{O}-\text{Ce}^{3+}$  and  $\text{O}-\text{Ce}^{4+}$  bonds is approximately constant. We have also seen that at the nanoparticles' surface, most of the Pr ions are in the  $\text{Pr}^{3+}$  state whereas the presence of  $\text{Pr}^{4+}$  ions is negligible, meaning that  $[\text{Ce}^{4+} + \text{Pr}^{4+}]$  content is also approximately constant. Therefore, the increase of the  $O_{\text{HBE}}$  peak with Pr doping basically reflects the  $\text{Pr}^{3+}$  and oxygen vacancies concentration increase, what is in complete agreement with our previous XRD and Raman scattering analysis.

**Table 1** Binding energies (eV) of individual peaks in the Ce 3d spectrum for several Pr-doped nanocrystalline samples

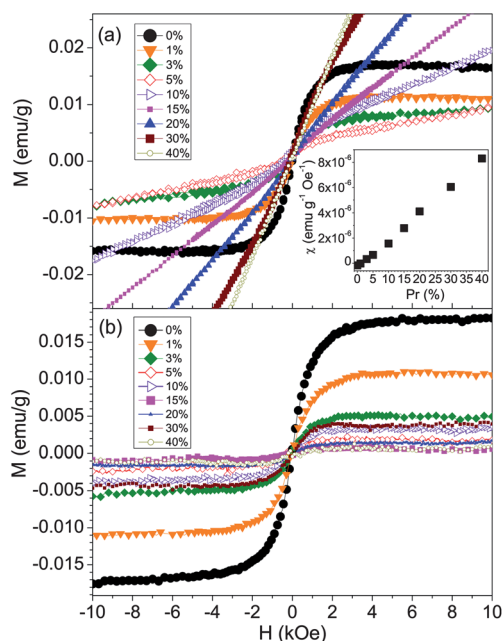
Sample	$3d_{5/2}$				$3d_{3/2}$				
	$v$	$v'$	$v''$	$v'''$	$u$	$u'$	$u''$	$u'''$	$t$
3% Pr	882.4	885.2	889.4	898.5	901.0	903.5	907.6	916.8	910.4
10% Pr	882.5	885.5	889.0	898.5	901.0	903.4	907.7	916.9	911.0
15% Pr	882.2	885.2	889.0	898.3	900.8	903.4	907.6	916.6	910.8
30% Pr	882.5	885.4	889.1	898.5	901.1	903.2	907.6	916.9	911.2



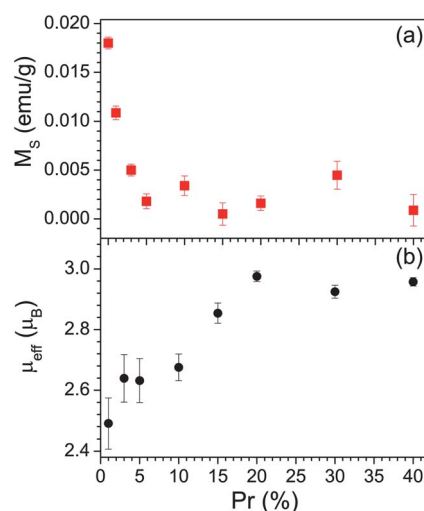
Fig. 5a shows magnetization ( $M$ ) vs. magnetic field ( $H$ ) dependence for undoped and Pr-doped  $\text{CeO}_2$  nanocrystals measured at RT. The doped samples show FM behavior which is significantly weaker than in the undoped sample except for the lowest Pr concentrations. The FM component is superimposed over a linear background which is diamagnetic for the undoped and 1% Pr-doped sample and paramagnetic for the rest of the samples. From the inset of Fig. 5a it can be seen that the susceptibility of this background component linearly increases with Pr content. Stoichiometric  $\text{CeO}_2$  is diamagnetic and the presence of paramagnetic  $\text{Ce}^{3+}$  ions ( $4f^1$ ) in the undoped nanocrystalline sample leads to an increase in susceptibility.  $\text{Pr}^{4+}$  ( $4f^1$ ) and  $\text{Pr}^{3+}$  ( $4f^2$ ) ions are also paramagnetic leading to a further increase in the paramagnetic background with Pr doping.

Fig. 5b presents  $M$  vs.  $H$  dependence for the samples after subtracting the linear background, showing well-defined hysteresis curves. The saturation magnetization ( $M_S$ ) values are plotted in Fig. 6a. In the case of the undoped  $\text{CeO}_2$ , the  $M_S$  takes value of  $0.018 \text{ emu g}^{-1}$ , which is comparable with previous reports on RTFM in  $\text{CeO}_2$  nanoparticles.<sup>9,15,18,26,64</sup> The composition of cerium nitrate precursor excludes the possibility that the FM in the pure  $\text{CeO}_2$  sample originates from the FM impurities such as Fe, Co or Ni, but contains the traces of nonmagnetic impurities such as rare earth oxides. This is in accordance with finding of Ackland *et al.*<sup>64</sup> that the presence of rare earth traces in cerium salt of lower purity (in their case La in 99% pure cerium nitrate) can favor the establishment of the FM, compared to the samples synthesized from 99.999% pure cerium nitrate, for which they found no ferromagnetism.

The obtained value of the saturation magnetization supports the opinion that only a small fraction of the sample volume ( $f$ ) is



**Fig. 5** Room temperature magnetization ( $M$ ) versus field ( $H$ ) dependence of undoped and Pr-doped  $\text{CeO}_2$  nanocrystals: (a) raw magnetization and (b) the magnetization after subtracting the linear background component. Inset: susceptibility of the subtracted background component.



**Fig. 6** (a) The saturation magnetization  $M_S$  of undoped and Pr-doped  $\text{CeO}_2$  nanocrystals. (b) The magnetic moment  $\mu_{\text{eff}}$  per Pr ion calculated using eqn (1).

magnetic,<sup>12,64,65</sup> which is in our case the surface layer of nanoparticles. Using the procedure described by Coey *et al.*<sup>12</sup> and Ackland *et al.*,<sup>64</sup> we estimated that the value of  $f$  is about 0.5% for the undoped  $\text{CeO}_2$ , which is in agreement with their results. Therefore we can conclude that the RTFM is an intrinsic property of nanocrystalline  $\text{CeO}_2$  originating from the surface of the nanoparticles.

The  $M_S$  rapidly decreases with Pr-doping and for 5% of Pr it takes a value of  $0.002 \text{ emu g}^{-1}$  which is almost 10 times lower than for the undoped  $\text{CeO}_2$ . Further increase of Pr content does not change the  $M_S$  significantly. It can be concluded that even a small amount of Pr severely reduces the saturation magnetization and weakens the FM ordering in ceria nanoparticles.

The effective magnetic moment  $\mu_{\text{eff}}$  per Pr ion, given in Fig. 6b is calculated from the susceptibility data according to the equation<sup>66</sup>

$$\mu_{\text{eff}} = \sqrt{\frac{3k_B T M_{\text{mol}} \chi_c}{x N_A}} \quad (1)$$

where  $x$  is Pr content in a formula unit,  $M_{\text{mol}}$  is the molar mass,  $T$  is temperature (300 K),  $k_B$  is the Boltzmann constant and  $N_A$  is Avogadro's number. In the eqn (1),  $\chi_c$  is the corrected value of susceptibility obtained by subtracting the susceptibility of the undoped  $\text{CeO}_2$  nanocrystalline sample from the susceptibility of the doped samples. This is done in order to eliminate the diamagnetic contribution of  $\text{CeO}_2$  and paramagnetic contribution due to  $\text{Ce}^{3+}$  ions and to calculate more correctly the paramagnetism originating from Pr doping. From Fig. 6b it can be seen that with doping the magnetic moment per Pr ion increases from about  $2.49 \mu_B$  to  $2.96 \mu_B$ . For lanthanides, because of the strong LS coupling, the orbital moment is not quenched and the total angular momentum  $J = L + S$  has to be used for the calculation of the magnetic moment:  $\mu_{\text{eff}} = g_J \sqrt{J(J+1)} \mu_B$ , where  $g_J$  is the Lande  $g$ -factor. In the case of  $\text{Ce}^{3+}$  ions (ground state  $^2F_{5/2}$ ,  $S = 1/2$ ,  $L = 3$ ,  $J = 5/2$ ,  $g_J = 6/7$ ) the magnetic moment is  $\mu_{\text{eff}} = 2.54 \mu_B$ . The same is valid for  $\text{Pr}^{4+}$  ions. For  $\text{Pr}^{3+}$  ions

( $^3\text{H}_4$ ,  $S = 1$ ,  $L = 5$ ,  $J = 4$ ,  $g_J = 4/5$ ) the magnetic moment is  $\mu_{\text{eff}} = 3.58 \mu_{\text{B}}$ .<sup>67</sup> Hence, the increase of the magnetic moment per Pr ion with doping implies that with increased Pr content the  $\text{Pr}^{3+}/\text{Pr}^{4+}$  ratio increases. This conclusion is already supported by XRD and XPS results.

Systematic studies of magnetic properties of nanosized  $\text{CeO}_2$  and other semiconductor oxide nanostructures demonstrated that oxygen vacancies play a pivotal role in establishing FM in these materials. It has been shown that there is a strong correlation between the concentration of oxygen vacancies and the saturation magnetization.<sup>9,15–19</sup> One of the widely used mechanisms for the explanation of FM ordering in nanocrystalline  $\text{CeO}_2$  is the so called F-center exchange mechanism (FCE).<sup>20,21,28,68</sup> According to this mechanism, an electron trapped in an oxygen vacancy (F center) acts as a coupling agent between magnetic  $\text{Ce}^{3+}$  ions, effectively forming overlapping magnetic polarons. The oxygen vacancy can actually exist in three possible charge states: (a) an  $\text{F}^{2+}$  center with no trapped electrons; (b) an  $\text{F}^+$  center with one trapped electron which can mediate the FM interaction; and (c) an  $\text{F}^0$  center with two trapped electrons which are in the singlet ( $S = 0$ ) state and can only mediate weak antiferromagnetic interactions.<sup>17,21</sup> Theoretical calculations also predict that vacancies tend to migrate from the nanoparticles' interior to the surface.<sup>69</sup> These calculations are supported by many reports which undoubtedly show that the FM originates mostly from the surface layer.<sup>9,15,16,70</sup>

Our results have pointed out that the inherent FM ordering in nanocrystalline  $\text{CeO}_2$  rapidly degrades even with the smallest amount of Pr content. Fig. 7 schematically presents a possible scenario for the degradation of the FM ordering with increased Pr content. In the undoped sample (Fig. 7a), there is a considerable concentration of oxygen vacancies and  $\text{Ce}^{3+}$  ions which are mostly located at the nanocrystals' surface. They are responsible for the establishment of the FM ordering through the F-center exchange mechanism. When  $\text{CeO}_2$  nanocrystals are doped with Pr ions, for lower doping concentrations (Fig. 7b), the Pr ions segregate at the nanocrystals' surface, in the form of  $\text{Pr}^{3+}$  ions. Due to this segregation in the thin surface layer, the  $\text{Pr}^{3+}$  concentration is several times higher than might be expected from the nominal Pr content. The presence of  $\text{Pr}^{3+}$  ions in this layer weakens the FM ordering and drastically reduces the saturation magnetization. With further doping (Fig. 7c),  $\text{Pr}^{4+}$  and  $\text{Pr}^{3+}$  ions enter in the core of the nanocrystals with increasing  $\text{Pr}^{3+}$  portion. The increased concentration of  $\text{Pr}^{3+}$  ions in the surface and core of nanocrystals is responsible for the lattice expansion,  $\text{F}_{2g}$  Raman mode red shift, and increase of susceptibility and magnetic moment per Pr ion. Raman and XPS results

showed that the concentration of oxygen vacancies increased with Pr doping. However, the presence of additional vacancies does not enhance the FM as is usually observed. We believe this is because of the inhibiting effect of  $\text{Pr}^{3+}$  ions which can provoke the conversion of  $\text{F}^+$  centers into  $\text{F}^{2+}$  or  $\text{F}^0$  centers. Doping with Pr can produce different magnetic/nonmagnetic complexes in the ceria lattice. Here we will restrict our attention only to certain types of complexes which can be held responsible for the degradation of the FM ordering.

When an oxygen vacancy is created in a ceria lattice, two electrons are left behind. If one electron localizes on a  $\text{Ce}^{4+}$  ion creating a  $\text{Ce}^{4+}-\text{V}_\text{O}-\text{Ce}^{3+}$  complex, and the other electron is trapped in a hydrogenic orbital around  $\text{V}_\text{O}$ , it will create an  $\text{F}^+$  center responsible for the establishment of the FM. In doped samples, in a similar way, the formation of  $\text{Pr}^{4+}-\text{V}_\text{O}-\text{Ce}^{3+}$  complexes can favour the FM ordering. However, if both electrons are localized on cations then a significant portion of the  $\text{Pr}^{3+}-\text{V}_\text{O}-\text{Ce}^{3+}$  or  $\text{Pr}^{3+}-\text{V}_\text{O}-\text{Pr}^{3+}$  complexes can be formed in the ceria lattice. The vacancies in these complexes turn into  $\text{F}^{2+}$  centers with no trapped electrons and do not mediate the FM ordering any more. In our recent paper<sup>71</sup> we experimentally showed that in highly oxygen deficient nanoceria, electrons are not only localized on  $\text{Ce}^{3+}$  or dopant ions but also on vacancy sites. The incorporation of  $\text{Pr}^{3+}$  ions in the ceria lattice brings additional vacancies and electrons are left behind. If two electrons remain localized on a vacancy then the oxygen vacancy becomes doubly occupied ( $\text{F}^0$  centers). Contrary to the singly occupied oxygen vacancies which mediate the FM, the doubly occupied vacancies can only mediate weak antiferromagnetic exchange.<sup>21</sup> The creation of  $\text{F}^{2+}$  and  $\text{F}^0$  centers would decrease a number of  $\text{F}^+$  centers, and more importantly, would reduce their concentration below the percolation threshold of the related magnetic polarons, preventing the establishment of the long-range FM ordering. Hence, the inhibiting effect of  $\text{Pr}^{3+}$  ions on the FM ordering in a ceria lattice manifests through the appearance of  $\text{F}^{2+}$  and  $\text{F}^0$  centers which do not promote ferromagnetic exchange. Some possible magnetic/nonmagnetic complexes, already discussed, are illustrated in Fig. 8.

It should be noted that, besides the FCE mechanism, the band ferromagnetism approach or its variation, the charge transfer model,<sup>65</sup> can also be taken under consideration. Following this approach, if the Fermi level ( $E_{\text{F}}$ ) is near the local maximum of density of states of a band and the Stoner criterion is satisfied, a spontaneous band spin-splitting occurs giving rise to the FM. In such a way, a defect-related band formed due to a high oxygen deficiency can be responsible for the FM in  $\text{CeO}_2$ .<sup>65,71</sup> The influence of Pr doping would manifest as rise in  $E_{\text{F}}$  if Pr ions give

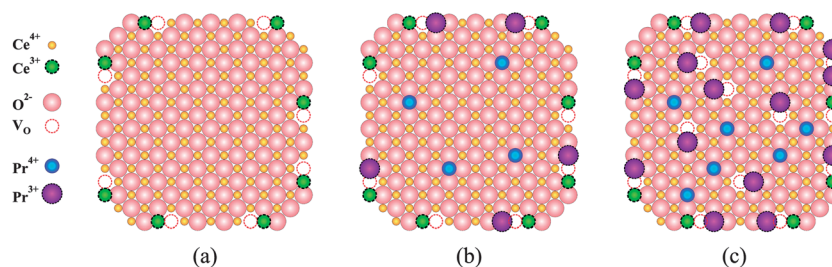
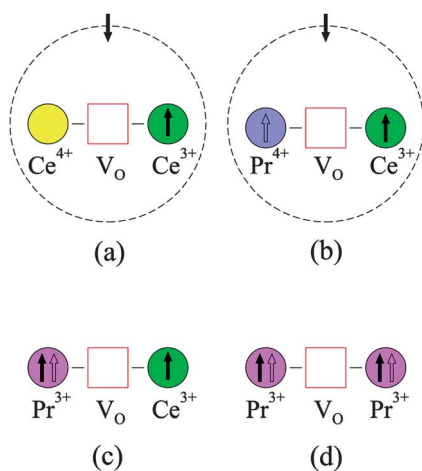


Fig. 7 Schematic representation of  $\text{CeO}_2$  nanocrystals: (a) undoped and doped with (b) lower and (c) higher Pr concentrations.



**Fig. 8** The complexes (a) and (b) mediate FM ordering through  $F^+$  centers, whereas complexes (c) and (d) do not establish long-range FM ordering because of the formation of  $F^{2+}$  centers. Bold arrows indicate the electrons left after oxygen vacancy ( $V_O$ ) creation.

away electrons to the oxygen deficiency band. On the other hand, Pr doping can introduce an unfilled impurity band below the oxygen deficiency band. Electrons from the oxygen deficiency band can transfer to this band, leading to lowering of  $E_F$ , a failure to fulfil the Stoner criterion and the destruction of the FM.

Furthermore, the reduction of the FM ordering in a case of high dopant concentrations can be explained through the nearest-neighbor antiferromagnetic exchange via oxygen anions which would suppress the FM ordering.<sup>21</sup> All of this can have negative effect on the establishment of the ferromagnetism in  $CeO_2$  nanocrystals.

## Conclusions

In summary, we investigated structural, vibrational and magnetic properties of  $Ce_{1-x}Pr_xO_{2-\delta}$  ( $0 \leq x \leq 0.4$ ) nanocrystals, synthesized by the SPRT method, using X-ray diffraction, Raman and X-ray photoelectron spectroscopy and magnetic measurements. The pure nanocrystalline ceria exhibits room-temperature ferromagnetism mediated by oxygen vacancies ( $F^+$  centers). Our results showed that Pr ions enter into ceria lattice in a mixed valence state and segregate at the nanocrystals' surface predominantly in the  $Pr^{3+}$  valence state. The presence of  $Pr^{3+}$  ions in thin surface layer, where oxygen vacancies are mostly located, is responsible for the rapid degradation of ferromagnetism. The formation of different complexes like  $Pr^{3+}-V_O-Ce^{3+}$  or  $Pr^{3+}-V_O-Pr^{3+}$  favors creation of unoccupied oxygen vacancies ( $F^{2+}$  centers) which do not mediate ferromagnetic ordering. Electron localization on vacancies can promote a formation of doubly occupied oxygen vacancies ( $F^0$  centers) which can only mediate weak antiferromagnetic exchange. The creation of  $F^{2+}$  and  $F^0$  centers reduces the number of  $F^+$  centers and suppresses ferromagnetism in Pr-doped ceria samples. For high Pr concentrations, the nearest-neighbor antiferromagnetic exchange via oxygen anions can additionally weaken the ferromagnetic ordering. On the other hand, from the band ferromagnetism point of view, Pr doping can shift the Fermi level away from a

maximum of density of states of defect band leading to a failure to fulfil the Stoner criterion and suppression of ferromagnetism. Our results indicate that room temperature ferromagnetism in diluted magnetic oxides such as  $CeO_2$  can be strongly dependent on the doping element and its valence state, as well as on the type of oxygen vacancies and their ability/disability to mediate ferromagnetism.

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