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# The Effect of Eu Doping on the Growth, Structure and Red-Ox Activity of Ceria Nanocubes

Oleksii Bezkrovnyi<sup>a</sup>, Małgorzata A. Małecka<sup>a</sup>, Radoslaw Lisiecki<sup>a</sup>, Volodymyr Ostroushko<sup>b</sup>, Andrew G. Thomas<sup>c</sup>, Sandeep Gorantla<sup>d</sup>, Leszek Kepinski<sup>a</sup>

a. W. Trzebiatowski Institute of Low Temperature and Structure Research Polish Academy of Sciences, Wroclaw, Poland

b. NSC "Kharkov Institute of Physics and Technology", Kharkov, Ukraine

c. School of Materials and the Photon Science Institute, The University of

Manchester, M13 9PL, UK

d. Wrocław Research Centre EIT+, Wroclaw, Poland

corresponding authors: <u>O.Bezkrovnyi@int.pan.wroc.pl</u>; L.Kepinski@int.pan.wroc.pl



Figure S1. Magnified part of the XRD patterns ((200) reflection) of  $Ce_{1-x}Eu_xO_2$ nanocubes with x = 0 and 0.4.

A magnified part of the XRD patterns of  $Ce_{1-x}Eu_xO_2$  (Figure S1) clearly shows the shift of the (200) reflection to lower 2 $\theta$  angle as the result of  $Eu^{3+}$  substitution for  $Ce^{4+}$  in the cation sub-lattice of ceria.



Figure S2. Experimental (red), calculated black) and difference (blue - bottom) XRD patterns of Ce<sub>0.6</sub>Eu<sub>0.4</sub>O<sub>2</sub> particles. Positions of ceria and Eu(OH)<sub>3</sub> reflections are also shown.

X-ray diffraction (XRD) patterns of the large  $Ce_{0.6}Eu_{0.4}O_2$  particles (Figure S2.) display the characteristic reflections of fluorite-type  $CeO_2$  and weak reflections from  $Eu(OH)_3$ . The (0 1 0)  $Eu(OH)_3$  reflection at 16.1 is strongly enhanced due to texture. The whole pattern fitting analysis gave the amount of  $Eu(OH)_3$  phase in this sample ~1 mol. %.



Figure S3. STEM HAADF images and corresponding EDS elemental maps of Ce, O and Eu distribution in  $Ce_{0.96}Eu_{0.04}O_2$  nanocubes.



Figure S4. XPS spectra of Ce<sub>0.98</sub>Eu<sub>0.02</sub>O<sub>2</sub> nanocubes

The results of XPS analysis are shown in Fig. S5. The characteristic Ce 3d spectrum is quite complex due to final state effects, but its shape indicates that Ce is present mostly as Ce<sup>4+</sup> [1] with some amount of Ce<sup>3+</sup>. The Eu  $3d_{5/2}$  signal at 1135 eV indicates that europium in the CeO<sub>2</sub> lattice exists as Eu<sup>3+</sup> ions [1].



Figure. S5. The dependence of the  ${}^{5}D_{0}-{}^{7}F_{2}/{}^{5}D_{0}-{}^{7}F_{1}$  bands ratio on the Eu concentration in Ce<sub>1-x</sub>Eu<sub>x</sub>O<sub>2</sub> nanocubes. Typical photoluminescence spectrum of Ce<sub>1-x</sub>Eu<sub>x</sub>O<sub>2</sub> nanoparticles is shown as inset.

Photoluminescence (PL) spectroscopy is an effective method to determine the optical properties of materials and the defect chemistry associated with these properties. In the  $Ce_{1-x}Eu_xO_2$  solid solution the luminescent center –  $Eu^{3+}$ , can be used as a spectroscopic probe for study the local environment of cationic centers [2,3].  $CeO_2$  crystallizes in a cubic fluorite-type structure with space group Fm3m. In this lattice, the point-group symmetry of Ce sites is ideally  $O_h$ . It is well-known, that the  ${}^5D_0{}^{-7}F_2$  transition in  $Eu^{3+}$  is hypersensitive, while the  ${}^5D_0{}^{-7}F_1$  transition is weakly sensitive to the crystal field environment. In sites with an inversion symmetry, the magnetic dipole transition  ${}^5D_0{}^{-7}F_2$  electronic transition becomes the strongest one [4]. Therefore, a measurement of the intensity ratio of  ${}^5D_0{}^{-7}F_2$  to  ${}^5D_0{}^{-7}F_1$  transitions is a convenient method to evaluate the

Eu site symmetry. It may thus be used to study local environment of Eu<sup>3+</sup> ions in the CeO<sub>2</sub> matrix. The presence of oxygen vacancies in the europium coordination sphere can effectively increase the intensity of  ${}^{5}D_{0}{}^{-7}F_{2}$  band, and thus the  ${}^{5}D_{0}{}^{-7}F_{2}/{}^{5}D_{0}{}^{-7}F_{1}$  ratio. Fig. S6 presents the dependence of the ratio of the intensities of  ${}^{5}D_{0}{}^{-7}F_{2}$  and  ${}^{5}D_{0}{}^{-7}F_{1}$  bands on the europium content for ceria nanocubes. Due to strong concentration quenching, only samples with Eu content  $x \le 0.1$  could be studied. It can be discerned, that in the case of the lowest europium concentrations (x=0-0.02) the value of  ${}^{5}D_{0}{}^{-7}F_{1}$  intensity ratio is undefined. For these samples the total europium emission is rather weak due to quite low Eu<sup>3+</sup> concentration. Nevertheless, the emission spectra are dominated by the  ${}^{5}D_{0}{}^{-7}F_{1}$  transition, showing that the impact of doping ions on the crystal structure and/or creation of oxygen vacations is insufficient. On the other hand observed rise of the of  ${}^{5}D_{0}{}^{-7}F_{1}{}^{-5}D_{0}{}^$ 



Figure S6. Normalized Raman spectra of ceria nanocubes with different europium content.

Figure S6 depicts the Raman spectra of the ceria nanocubes with different europium content. The main Raman peak near 465 cm<sup>-1</sup> is assigned to  $F_{2g}$  mode that appears due to the symmetrical stretching of oxygen ion situated in a tetrahedron formed by four Ce<sup>4+</sup> ions in the fluorite structure of CeO<sub>2</sub> [5,6]. The observed Raman peak at 545cm<sup>-1</sup> is directly related to oxygen vacancies [7]. Intensity of oxygen vacancy related peak increases with increasing europium content which is in good agreement with photoluminescence data (See Fig. S5). The phonon mode near 605 cm<sup>-1</sup> appears due to the insertion of a M<sup>3+</sup> (M = lanthanide, including Ce) ion into the fluorite structure, with formation of a MO<sub>8</sub> -type complex [7]. The occurrence of 605 nm<sup>-1</sup> peak for pure ceria nanocubes confirms the presence of small amount of Ce<sup>3+</sup> ions in the nanocubes. Intensity of the peak increases with the europium content due to growing number of MO<sub>8</sub> complexes.



Figure S7. Typical TM images of Eu doped nanoparticles without (x=0.04) and with (x=0.1-0.3) superstructure fringes due to oxygen vacancies ordering.

## Table S1

Crystal structure model of  $Ce_{0.80}Eu_{0.20}O_2$  with oxygen vacancies ordering. Space group *Ia*-3 (206), a = 1.086 nm.

Symbol	Wyckoff	X	У	Z	Occupation
Ce	8b	0.250	0.250	0.250	0.800
Eu	8b	0.250	0.250	0.250	0.200
Ce	24d	0.994	0	0.250	0.800
Eu	24d	0.994	0	0.250	0.200
Ο	48e	0.379	0.131	0.376	1.000
Ο	16c	0.375	0.375	0.375	0.800



Figure S8. Experimental (red), calculated (blue) and difference (red - bottom) XRD patterns of Ce<sub>0.80</sub>Eu<sub>0.20</sub>O<sub>2</sub> particles. Calculated XRD pattern was generated on the

#### basis of the crystal structure model in Table S1.



Figure S9. Simulated TEM images of Ce<sub>0.8</sub>Eu<sub>0.2</sub>O<sub>2</sub> slab with ordered oxygen vacancies for following thicknesses: 5, 10, 60 nm.

On the figure S9 we present the simulated TEM images of  $Ce_{0.8}Eu_{0.2}O_2$  slabs with  $1/4\{220\}_F$  superstructure fringes occurring due to doubling of the fluorite cell, as a result of the oxygen vacancy ordering. As can be seen from this figure, the visibility the superstructure fringes diminishes with increasing slab thickness. Therefore, we assume that the vacancy ordering occurs in both small and large ceria particles at higher Eu content, but was difficult to be noticed in large particles (> 50 nm).

## Table S2

Hydrogen consumption	and amount of Ce	<sup>4+</sup> reduced to Ce <sup>3-</sup>	<sup>+</sup> ions calculated from
H <sub>2</sub> -TPR data for Ce <sub>1-x</sub> Eu	$_{x}O_{2}$ (x=0-0.4) nand	ocubes at differen	t temperature regions.

Sample	Hydro			gen consumption $\mu$ mol H <sub>2</sub>				
	300°C	400°C	500°C	600°C	700°C	800°C	900°C	
CeO <sub>2</sub>	-0.20	0.40	4.56	12.88	23.76	44.52	73.09	
Ce <sub>0.96</sub> Eu <sub>0.04</sub> O <sub>2</sub>	0.28	0.67	4.04	12.28	24.45	48.61	74.23	
Ce <sub>0.90</sub> Eu <sub>0.10</sub> O <sub>2</sub>	-0.14	1.05	6.68	16.94	33.87	58.16	78.44	
$Ce_{0.60}Eu_{0.40}O_2$	0	1.32	6.47	17.21	29.56	42.79	55.22	
	Percentage of Ce <sup>4+</sup> ions reduced to Ce <sup>3+</sup>							
		Р	ercentage (	of Ce <sup>4+</sup> ions	s reduced t	o Ce <sup>3+</sup>		
	300°C	P 400°C	ercentage ( 500°C	of Ce <sup>4+</sup> ion: 600°C	s reduced t	o Ce <sup>3+</sup> 800°C	900°C	
CeO <sub>2</sub>	300°C 0	P 400°C 0.14	ercentage of 500°C 1.57	of Ce <sup>4+</sup> ion: 600°C 4.43	s reduced t 700°C 8.18	o Ce <sup>3+</sup> 800°C 15.33	900°C 25.16	
CeO <sub>2</sub> Ce <sub>0.96</sub> Eu <sub>0.04</sub> O <sub>2</sub>	300°C 0 0.1	P 400°C 0.14 0.24	ercentage ( 500°C 1.57 1.45	of Ce <sup>4+</sup> ions 600°C 4.43 4.41	s reduced t 700°C 8.18 8.77	o Ce <sup>3+</sup> 800°C 15.33 17.45	900°C 25.16 26.64	
$CeO_{2}$ $Ce_{0.96}Eu_{0.04}O_{2}$ $Ce_{0.90}Eu_{0.10}O_{2}$	300°C 0 0.1 0	P 400°C 0.14 0.24 0.40	ercentage ( 500°C 1.57 1.45 2.56	of Ce <sup>4+</sup> ions 600°C 4.43 4.41 6.49	s reduced t 700°C 8.18 8.77 12.98	o Ce <sup>3+</sup> 800°C 15.33 17.45 22.30	900°C 25.16 26.64 30.07	



Figure S10. TEM images of  $CeO_2$  nanocubes annealed at different temperatures

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