

Optically Detected Effect of Size on the Oxygen Vacancies Concentration in Cerium Oxide Nanocrystals

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In this work effect of the size on the oxygen vacancies concentration in cerium oxide nanocrystals have been investigated by means of luminescence spectroscopy techniques. For determination of changes of oxygen stoichiometry intensity of 5d-4f luminescence of Ce^{3+} ions were used. It was shown that for CeO_2 nanocrystals decrease of the size from 50 nm to 2 nm manifests itself in 8 times increase of the band intensity associated with vacancy-stabilized Ce^{3+} ions. The same effects have been observed at atmosphere variation from oxidizing to reducing and are connected with significant increase of concentration of oxygen vacancies. Obtained results allow to determine that decrease of the size stimulate formation of oxygen vacancies in cerium oxide nanocrystals.

Keywords: Luminescence spectroscopy, Cerium oxide nanoparticles, Oxygen vacancies.

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1. INTRODUCTION

In recent years, several authors have demonstrated that the size of the nanocrystal can greatly affect the oxygen non-stoichiometry of oxide material. Dependence of oxygen non-stoichiometry on the particle size most clearly manifested for nanosized cerium dioxide [1-6]. Cerium dioxide CeO_2 has found application in different technology fields. Ceria is widely used for catalysts [7], fuel cells [8, 9], oxygen sensors [10], ultraviolet blocks [11], and luminescent materials [12, 13]. Recently, ceria nanoparticles have attracted attention within the biomedical research community as a potential agent to inhibit cellular aging [14, 15].

As was shown in [5], 1.9 nm is the critical size of cerium dioxide nanoparticles, at which all of cerium ions in the crystal lattice of CeO_{2-x} are triple-charged. According to existing ideas, oxygen non-stoichiometry defines basic biomedical properties of cerium oxide - the ability to participate in redox processes taking place in the organism [16, 17]. Extremely high concentrations of oxygen vacancies (and correspondingly, Ce^{3+} ions) in cerium oxide nanocrystals were recently determined by XPS investigations (17 % of Ce^{3+} ions for 30 nm and up to 44 % for 3 nm nanoparticles) [18] and EMR (about 18 % of Ce^{3+} ions for 3 nm nanoparticles) [19]. Literature data on the structure and properties of nanosized CeO_{2-x} often contradict each other. Moreover, most of the properties of nanocrystalline CeO_{2-x} , remain almost unexplored.

The main goal of the present work was to find a way to determine the oxygen vacancies concentration in the CeO_{2-x} nanocrystals of different size using optical spectroscopy. The optical spectroscopy techniques used were fluorometry, to measure the luminescence spectrum of the CeO_{2-x} nanocrystals. These techniques are widely used to characterize semiconducting materials [20], but have not been extensively used for CeO_{2-x}

nanocrystals. One advantage of these techniques is that the optical spectroscopy systems are inexpensive and have fast data acquisition.

2. MATERIALS AND METHODS

CeO_2 nanocrystals were obtained by two methods: Pechini method [21, 22] and colloidal precipitation method [23]. Using of two methods of synthesis allow to obtain CeO_2 nanocrystals of different sizes (2 nm and 10 nm for colloidal precipitation method; 50 nm for Pechini method). Sizes of nanocrystals were controlled by TEM (Fig. 1).

Stoichiometry of the nanocrystal depends on the atmosphere in which high-temperature treatment is carried out. Reducing atmosphere stimulates the formation of oxygen vacancies and, consequently, the formation of nonstoichiometric oxides. In the oxidizing atmosphere number of oxygen vacancies in the crystal is much lower thus leading to formation of CeO_2 crystalline phase. To obtain a different degree of stoichiometry, nanocrystals synthesized using Pechini method were annealed during 2 hours in different atmospheres - oxidizing (air), neutral (argon) and reducing (hydrogen) at 900 °C.

X-ray diffraction patterns of obtained CeO_2 nanocrystals are shown in the Fig. 2 (curve 1-50 nm cerium dioxide nanocrystals, curve 2-10 nm cerium dioxide nanocrystals and curve 3-2 nm cerium dioxide nanocrystals). The structure of the samples corresponds with JCPDS card No.34-0394, so the nanocrystals are characterized by FCC fluorite-type lattice and formation of any additional phases at these conditions can be excluded.

Luminescence spectra of CeO_2 nanocrystals have been obtained by means of the spectrofluorimeter based on grid monochromator. Registration of spectra was carried out by photomultiplier tube operating in photon counting mode. Luminescence was excited by helium-

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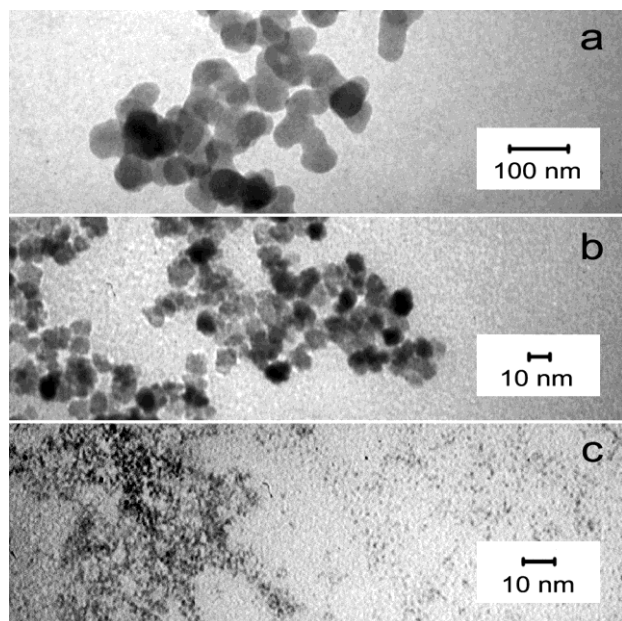


Fig. 1 – TEM images of CeO₂ nanocrystals of different sizes: a – 50 nm nanocrystals obtained by Pechini method, b – 10 nm nanocrystals obtained by colloidal precipitation method, c – 2 nm nanocrystals obtained by colloidal precipitation method

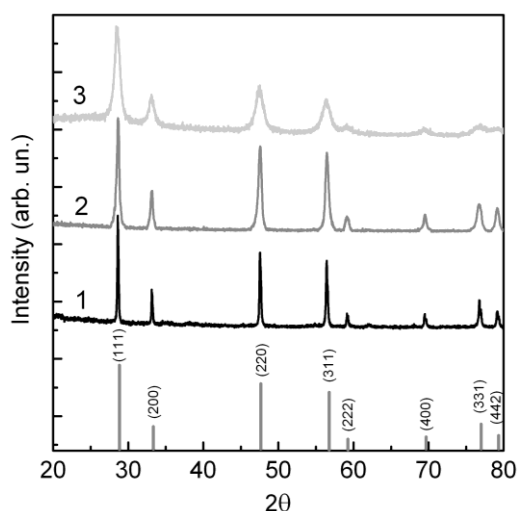


Fig. 2 – XRD patterns of CeO₂ nanocrystals of different sizes: 50 nm (curve 1), 10 nm (curve 2) and 2 nm (curve 3).

cadmium laser at 325 nm. Possibility of temperature variation was obtained by placing of the sample in the cryostat.

3. RESULTS AND DISCUSSION

Ceria is wide band gap (~ 6 eV) material with valence band formed by O2p and conduction band by Ce5d states [24, 25]. In the band gap of stoichiometric CeO₂ narrow sub-band is present formed by empty 4f⁰ states of Ce⁴⁺ ion. For non-stoichiometric CeO_{2-x} splitting of this band to the empty 4f⁰ and filled 4f¹ sub-bands occurs [26].

Spectra of CeO₂ nanocrystals ($\lambda_{exc} = 325$ nm) treated in oxidizing atmosphere (curve 1), neutral atmosphere (curve 2) and reducing atmosphere (curve 3) at 77 K are shown in the Fig. 3.

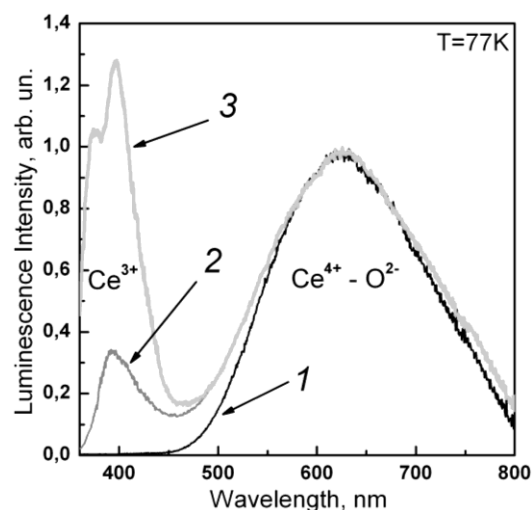


Fig. 3 – Luminescence spectra of CeO₂ nanocrystals treated in oxidizing atmosphere (curve 1), neutral atmosphere (curve 2) and reducing atmosphere (curve 3). $\lambda_{exc} = 325$ nm, $T = 77$ K.

Luminescence spectrum of CeO₂ nanocrystals treated in oxidizing atmosphere consists of one band with maximum at 630 nm, while spectrum of non-stoichiometric CeO₂ nanocrystals consists of two bands with maxima at 390 nm and 630 nm. As was recently shown in [22], optical properties of CeO₂ nanocrystals are determined by presence of two different optical centers formed by Ce³⁺ ions and Ce⁴⁺-O²⁻ charge transfer (CT) states. The band at 390 nm is temperature-independent but its intensity increases strongly at atmosphere variation from oxidizing to reducing. This band is determined by Ce³⁺ ion luminescence and corresponds to electronic transition from excited 5d¹ state to the ground 4f¹ state of Ce³⁺ (²F_{7/2} and ²F_{5/2} terms) [22, 27]. In reducing atmosphere concentration of oxygen vacancies and, correspondingly, of Ce³⁺ ions (that require oxygen vacancies for charge compensation) is much more than in oxidizing atmosphere, so the dependence of this band intensity on the atmosphere of treatment can be easily explained. Thus the ratio of Ce⁴⁺ / Ce³⁺ centers has been shown to be strongly depended on the amount of oxygen vacancies. Therefore, the increasing non-stoichiometry of CeO₂ nanocrystals leads to the enhancement of Ce³⁺ luminescence. The band at 620 nm exhibit strong quenching with temperature increase and slightly depends on the atmosphere of treatment. As was shown previously, 630 nm band is determined by radiative relaxation in Ce⁴⁺-O²⁻ charge transfer state (CT-luminescence). As CT luminescence is independent on the vacancy concentration, relative intensity of Ce³⁺ 5d-4f luminescence can be used as a measure of Ce³⁺ (and oxygen vacancies) concentration in CeO₂ nanocrystals with different sizes.

In the Fig. 4 luminescence spectra of CeO₂ nanocrystals ($\lambda_{exc} = 325$ nm) with sizes of about 50 nm (curve 1), 10 nm (curve 2) and 2 nm (curve 3) are shown.

Decrease of the size from 50 nm to 10 nm leads to increase in 2.5 times of intensity of 390 nm band associated with 5d → 4f luminescence of Ce³⁺ ion. Decrease of the size from 10 nm to 2 nm leads to increase in 3.2 times of intensity of 390 nm band associated with

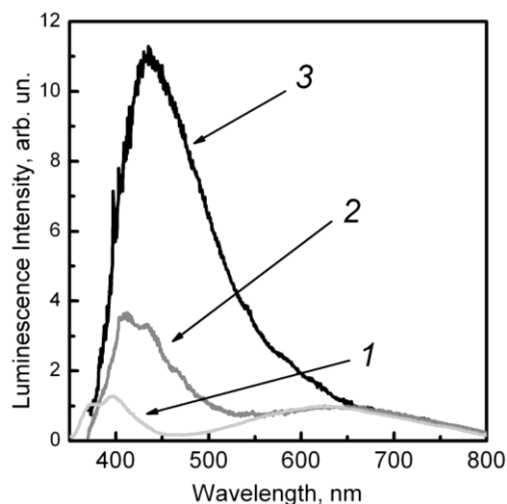


Fig. 4 – Luminescence spectra of CeO₂ nanocrystals of different sizes: 50 nm (curve 1), 10 nm (curve 2) and 2 nm (curve 3). $\lambda_{exc} = 325$ nm, $T = 77$ K.

$5d \rightarrow 4f$ luminescence of Ce³⁺ ion. Intensity of this band is directly proportional to Ce³⁺ concentration and, correspondingly, to concentration of oxygen vacancies in the nanocrystal. The same effects have been observed at atmosphere variation from oxidizing to reducing and

are connected with significant increase of concentration of oxygen vacancies. So, it can be concluded that decrease of the size of cerium dioxide nanoparticles from 50 nm to 10 nm and from 10 nm to 2 nm leads to 2.5 and 3.2 times increase of oxygen vacancy concentration. Obtained results allow to determine that decrease of the size stimulate formation of oxygen vacancies in cerium oxide nanocrystals.

4. CONCLUSIONS

In the paper influence of size on the processes of formation of oxygen vacancies in CeO₂ nanocrystals has been investigated by means of spectroscopic techniques. The ratio of Ce⁴⁺ / Ce³⁺ centers has been shown to be strongly depended on the amount of oxygen vacancies. Therefore, the increasing non-stoichiometry of ceria nanocrystals leads to the enhancement of Ce³⁺ luminescence. Thus, variation of the Ce³⁺/Ce⁴⁺ ratio in CeO₂ allows to control the oxygen non-stoichiometry by luminescence properties of this material. Size dependence of oxygen non-stoichiometry for CeO₂ nanocrystals was shown. For CeO₂ nanocrystals it was shown that decrease of the size from 50 nm to 2 nm leads to 8 times increase of oxygen vacancy concentration.

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