Influence of CeO$_2$ nanocrystals size on the vacancies formation processes determined by spectroscopic techniques

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In the paper influence of the size on the processes of oxygen vacancies formation in CeO$_2$ nanocrystals has been investigated. Changes in concentration of oxygen vacancies were determined by two independent indicators: intensity of 5$d$ $\rightarrow$ 4$f$ luminescence of Ce$^{3+}$ ions and ratio between $^5D_0\rightarrow^7F_1$ and $^5D_0\rightarrow^7F_2$ luminescence bands of Eu$^{3+}$ ions incorporated into ceria nanoparticles as structural probes. It was shown that for CeO$_2$ nanocrystals decrease of the size (from 75 nm to 20 nm) manifests itself in 1.5 times increase of the band intensity associated with vacancy-stabilized Ce$^{3+}$ ions, while for CeO$_2$:Eu$^{3+}$ nanocrystals it leads to lowering of symmetry for Eu$^{3+}$ centre and correspondent decrease of $^5D_0\rightarrow^7F_1$/$^5D_0\rightarrow^7F_2$ intensity ratio. It was shown that decrease of the size stimulates formation of the oxygen vacancies in ceria nanoparticles.

Исследовано влияние размера на процессы формирования кислородных вакансий в нанокристаллах CeO$_2$. Для определения изменения концентрации кислородных вакансий использованы два независимых показателя — интенсивность 5$d$ $\rightarrow$ 4$f$ люминесценции ионов Ce$^{3+}$ и отношение между $^5D_0\rightarrow^7F_1$ и $^5D_0\rightarrow^7F_2$ люминесцентными полосами ионов Eu$^{3+}$, введенных в нанокристаллы в качестве структурных щедр. Показано, что для нанокристаллов CeO$_2$ уменьшение размера (от 75 до 20 нм) приводит к возрастанию в 1.5 раза интенсивности полосы, связанной с ионами Ce$^{3+}$, стабилизированными кислородными вакансиями, тогда как для нанокристаллов CeO$_2$:Eu$^{3+}$ уменьшение размеров приводит к повышению симметрии центра Eu$^{3+}$ и соответствующего уменьшения значения отношения $^5D_0\rightarrow^7F_1$/$^5D_0\rightarrow^7F_2$. Полученные результаты позволяют определить, что уменьшение размера стимулирует формирование кислородных вакансий в наночастицах CeO$_2$.

Влияние размера на процессы формирования вакансий в нанокристаллах CeO$_2$, установленный за допомогою спектроскопичних методів. П.О.Максимчук, В.В.Семинко, І.І.Беспалова, А.О.Масалов.

Досліджено вплив розміру на процеси формування кисневих вакансій у нанокристаллах CeO$_2$. Для вивчення зміни концентрації кисневих вакансій використано два незалежні показники — інтенсивність 5$d$ $\rightarrow$ 4$f$ люминесценції йонів Ce$^{3+}$ та відношення між $^5D_0\rightarrow^7F_1$ та $^5D_0\rightarrow^7F_2$ люминесцентними сплінами йонів Eu$^{3+}$, введенних у нанокристалли в формі структурних щедр. Показано, що для нанокристалів CeO$_2$ зменшення розміру (від 75 нм до 20 нм) призводить до зростання у 1.5 разів інтенсивності сплін, пов'язаної з іонами Ce$^{3+}$, стабілізованими вакансіями, тоді як для нанокристалів CeO$_2$:Eu$^{3+}$ зменшення розміру призводить до зниження симетрії центра Eu$^{3+}$ та відповідного зниження значення відношення $^5D_0\rightarrow^7F_1$/$^5D_0\rightarrow^7F_2$. Отримані результати дозволяють визначити, що зменшення розміру стимулює формування кисневих вакансій у наночастинах CeO$_2$.
1. Introduction

Ceria (CeO\textsubscript{2}) is well-known material which is widely used for creation of ionic conductors, fuel cells and UV-protective coatings [1–3]. Recently it was successfully applied in biology as an effective ROS (Reactive Oxygen Species)-defending agent similar in its properties to catalase protein [4]. Unique properties of ceria are connected with effective Ce\textsuperscript{3+}–Ce\textsuperscript{4+} oxidation/reduction processes determined by low energy of oxygen vacancies formation in this material (formation of the complex defect Ce\textsuperscript{3+}–O\textsubscript{y}–Ce\textsuperscript{3+} with the vacancy situated at NN site to Ce\textsuperscript{3+} ion requires only 0.26 eV) [5]. Creation of each oxygen vacancy is accompanied by transition of two Ce\textsuperscript{4+} ions to Ce\textsuperscript{3+} ones, so oxygen vacancy concentration and Ce\textsuperscript{3+}/Ce\textsuperscript{4+} ratio are directly proportional to each other. Extremely high concentrations of the oxygen vacancies (and correspondingly, Ce\textsuperscript{3+} ions) in ceria nanoparticles were recently determined by EMR (about 18 \% of Ce\textsuperscript{3+} ions for 3 nm nanoparticles) [6] and XPS investigations (17 \% of Ce\textsuperscript{3+} ions for 30 nm and up to 44 \% for 3 nm nanoparticles) [7].

In [5] it was shown that oxygen vacancies in ceria are formed preferentially in the nearest-neighbor (NN) position to Ce\textsuperscript{3+} ions that was confirmed spectroscopically in [8]. As was shown [8], luminescent properties of CeO\textsubscript{2} nanocrystals are determined by two different luminescent centers formed by Ce\textsuperscript{3+} ions and Ce\textsuperscript{4+}–O\textsuperscript{2−} charge transfer (CT) states. 5d \rightarrow 4f Luminescence intensity of Ce\textsuperscript{3+} ions increases strongly with increase of concentration of the oxygen vacancies that allows to consider this intensity as a measure of the oxygen vacancies concentration in ceria nanocrystals. Incorporation of trivalent (for instance, rare-earth) ion instead of Ce\textsuperscript{4+} leads to formation of the oxygen vacancies required for compensation of excess negative charge. Relative position of the oxygen vacancies and rare-earth (RE) ions in RE-doped ceria nanocrystal was investigated recently in the few papers [9]. In [10] it was theoretically shown that for ions with radius smaller than radius of Gd\textsuperscript{3+} ion the oxygen vacancy is localized preferentially on the NN position to the RE ion, while for the ions with radius bigger than radius of Gd\textsuperscript{3+} (such as Eu\textsuperscript{3+} ions) the vacancy is repelled to NNN (next to nearest-neighbor) position. According to these predictions the surrounding of Eu\textsuperscript{3+} ion must preserve O\textsubscript{h} symmetry and only magneto-dipole transitions of Eu\textsuperscript{3+} (such as \textsuperscript{5}D\textsubscript{0} \rightarrow \textsuperscript{7}F\textsubscript{1}) are possible [10]. However, in [9] it was shown that in CeO\textsubscript{2}:Eu\textsuperscript{3+} there are up to four additional positions of Eu\textsuperscript{3+} ion with symmetry lower than O\textsubscript{h} that manifests itself in occurrence of electro-dipole \textsuperscript{5}D\textsubscript{0} \rightarrow \textsuperscript{7}F\textsubscript{2} transition (forbidden for Eu\textsuperscript{3+} centers in O\textsubscript{h} positions) in luminescence spectra of Eu-doped ceria. Moreover, the number of Eu\textsuperscript{3+} ions in distorted states increases strongly with Eu concentration and calcination temperature increase [11]. As was supposed in [11], Eu\textsuperscript{3+} ions in ceria can act as traps of the oxygen vacancies located in the NN positions to the ion and increase of the vacancy concentration (due to annealing temperature or Eu\textsuperscript{3+} content increase) leads to sufficient increase of the number of Eu\textsuperscript{3+} ions in distorted positions. So, the relative content of Eu\textsuperscript{3+} ions in positions with non-cubic symmetry also can be a measure of the oxygen vacancies concentration in nanocrystals.

In this paper we have used the intensity of 5d \rightarrow 4f luminescence of Ce\textsuperscript{3+} ions and the ratio between intensities of \textsuperscript{5}D\textsubscript{0} \rightarrow \textsuperscript{7}F\textsubscript{1} (symmetry insensitive) and \textsuperscript{5}D\textsubscript{0} \rightarrow \textsuperscript{7}F\textsubscript{2} (symmetry sensitive) transitions of Eu\textsuperscript{3+} as indicators that allow to determine the change of the oxygen vacancies concentration in CeO\textsubscript{2} nanocrystals depending on their size and to estimate the correspondent concentrations of the oxygen vacancies in these nanocrystals.

2. Experimental

CeO\textsubscript{2} nanocrystals were obtained by Pechini method, CeO\textsubscript{2}:Eu\textsuperscript{3+} (0.2, 2, 6 and 10 at.\%) nanocrystals were synthesized by colloidal precipitation method. CeO\textsubscript{2} nanocrystals were dispersed in water and fractions with different sedimentation rates were taken and placed on the quartz. The average sizes of nanocrystals taken from each fraction was determined from equation \( r = 9 \eta \nu g(\rho - \rho_0)Ht \), where \( \eta \) is viscosity coefficient, \( \rho \) and \( \rho_0 \) are densities of precipitant and water, respectively, \( H/t \) is deposition rate. Luminescence of all samples was excited by He–Cd laser (\( \lambda_{\text{exc}} = 325 \text{ nm} \)). Luminescence spectra of CeO\textsubscript{2} nanocrystals were taken at 77 K, spectra of CeO\textsubscript{2}:Eu\textsuperscript{3+} nanocrystals were taken at 300 K.

3. Results and discussion

As was recently shown in [8], optical properties of CeO\textsubscript{2} nanocrystals are deter-
minded by presence of two different optical centers formed by Ce$^{3+}$ ions and Ce$^{4+}$–O$^{2-}$
charge transfer states. Luminescence spectra of CeO$_2$ nanoparticles (shown in Fig. 1) consist of two spectral bands with max-
imums at 390 nm and 620 nm accordingly. The band at 390 nm is temperature-independent but its intensity increases strongly
at atmosphere variation from oxidizing to reducing. This band was ascribed in [6] to 5$d$ → 4$f$ transitions of Ce$^{3+}$
ions. In reducing atmosphere concentration of the oxygen vacancies and, correspondingly, of Ce$^{3+}$ 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. The band at
620 nm exhibit strong quenching with temperature increase and slightly depends on the atmosphere of treatment. It was
ascribed to charge-transfer luminescence of Ce$^{4+}$–O$^{2-}$ complex. As CT luminescence is independent on the vacancy concentration, relative intensity of Ce$^{3+}$ 5$d$–4$f$ luminescence can be used as a measure of Ce$^{3+}$ (and oxygen vacancies) concentration in ceria nanocrystals with different sizes. In the
Fig. 1 the luminescence spectra of CeO$_2$
nanocrystals ($\lambda_{exc}$ – 325 nm) with sizes of about 20 nm, 50 nm and 75 nm are shown. Decrease of the size from 75 nm to 20 nm
leads to increase in 1.5 times of intensity of
390 nm band associated with 5$d$ → 4$f$ luminescence of Ce$^{3+}$ ion. Intensity of this band is directly proportional to Ce$^{3+}$ concentration and, correspondingly, to concentration of oxygen vacancies in the nanocrystal. So, it can be concluded that decrease of the size of the ceria nanoparticles from 75 nm to 50 nm and from 50 nm to 20 nm leads to
1.25 and 1.5 times increase of the oxygen vacancy concentration.

Eu$^{3+}$ ion is widely used for determination of local structure of cationic centers in differ-
et crystal matrices [12]. It is connected with high sensitivity of electro-dipole $^5D_0$→$^7F_2$ transition of Eu$^{3+}$ ion to presence or absence of inversion center of symmetry. Contrary to $^5D_0$→$^7F_2$ transition, intensity of magneto-dipole $^5D_0$→$^7F_1$ transition of Eu$^{3+}$ ion is practically independent on the symmetry of cationic center. So the ratio between the intensities of $^5D_0$→$^7F_1$ and
$^5D_0$→$^7F_2$ transitions provides an information about local symmetry of the Eu$^{3+}$ sur-
rounding symmetry.

Due to incorporation of trivalent ions instead of tetravalent the treatment in reducing
atmosphere must lead to formation of additional oxygen vacancies in the ceria lattice. To trace the process of oxygen vacancies formation during the high-temperature treatment in different atmospheres ratio between $^5D_0$→$^7F_1$ and $^5D_0$→$^7F_2$ intensities of Eu$^{3+}$ ion can be used. Formation of the oxygen vacancy near Eu$^{3+}$ ion must lead to sufficient change of its ligand surrounding. If the vacancy is located outside the first coordination sphere the surroundings of doped ion must preserve $O_h$ symmetry point group, if the vacancy is located in the first coordination sphere of doped ion, the symmetry of cation center changes to $C_{2v}$ or lower. As was shown in [11] increase of Eu$^{3+}$ concentration (and, correspondingly, of the oxygen vacancies) leads to proportional increase of the number of centers with non-cubic symmetry determined by change of $^5D_0$→$^7F_1$/$^5D_0$→$^7F_2$ ratio. The influence of the atmosphere treatment on the vacancies concentration can be determined in the same way. In our experiment the concentrations of Eu$^{3+}$ in CeO$_2$ were very low (about 0.2 at.%, $C_{vac} = 0.05\%$) to exclude from consideration the vacancies created by incorporation of Eu$^{3+}$ ion instead of Ce$^{4+}$ and to deal mostly with the vacancies provided by change of the atmosphere treatment.

Luminescence spectra of CeO$_2$:Eu$^{3+}$
nanocrystals (10 nm) at treatment atmos-
phere variation are shown in the Fig. 2. It consist of characteristic $^5D_0$→$^7F_1$ and

![Fig. 1. Luminescence spectra of CeO$_2$
nanocrystals (1 – 20 nm, 2 – 50 nm, 3 – 75 nm).](image-url)
$^5D_0 \rightarrow ^7F_2$ bands at 590 nm and 610 nm, respectively. The ratio between $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ bands is about 5.6 for oxidizing atmosphere, 4.8 for neutral atmosphere and 3.4 for reducing atmosphere. Low intensity of $^5D_0 \rightarrow ^7F_2$ band as compared to $^5D_0 \rightarrow ^7F_1$ band for all atmospheres allows to determine that vacancies are located preferentially outside the first coordination sphere of Eu$^{3+}$ ion and surrounding of Eu$^{3+}$ ion preserve cubic symmetry. While the radius of Eu$^{3+}$ ion is bigger than radius of Gd$^{3+}$ ion, it corresponds well with predictions [10] that such ions must have a charge compensating defect in the NNN but not NN positions. At the same time for reducing atmosphere the portion of Eu$^{3+}$ centers with $O_h$ symmetry is the lowest as compared to ones obtained after treatment in oxidizing and neutral media. However the relative intensity of $^5D_0 \rightarrow ^7F_1$ band is still higher than the one of $^5D_0 \rightarrow ^7F_2$ band, so even for reducing atmosphere most of Eu$^{3+}$ ions do not have a vacancy on the NN position. As a cause of increase of the portion of non-cubic centers for neutral and reducing atmosphere, increase of oxygen vacancies content leading to formation of vacancy — Eu$^{3+}$ associates and distortion of $O_h$ symmetry can be suggested [9].

Luminescence spectra of CeO$_2$:Eu$^{3+}$ nanocrystals of different sizes (10 nm, 25 nm and 50 nm) are shown in the Fig. 3. For all sizes the ratio between $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ bands depends on the atmos-

![Figure 2](image2.png)

**Fig. 2.** Luminescence spectra of CeO$_2$:Eu$^{3+}$ nanocrystals (10 nm) treated in oxidizing (air), neutral (Ar) and reducing (H$_2$) atmosphere.

![Figure 3](image3.png)

**Fig. 3.** Luminescence spectra of CeO$_2$:Eu$^{3+}$ nanocrystals treated in oxidizing (air), neutral (Ar) and reducing (H$_2$) atmosphere (a — 10 nm, b — 25 nm, c — 50 nm).
phere of treatment and for reducing atmosphere the value of this ratio is the smallest. The values of \( ^5D_0 \rightarrow \ ^7F_1/ ^5D_0 \rightarrow \ ^7F_2 \) ratio for nanocrystals with different sizes are summarized in Table. Decrease of the size from 50 nm to 10 nm leads to increase of the portion of non-cubic sites formed after treatment in reducing atmosphere. So it can be supposed that concentration of the vacancies in smaller CeO\(_2\) nanoparticles is more than in the bigger ones.

For estimation of the oxygen vacancies concentration in CeO\(_2\):Eu\(^{3+}\) nanocrystals of different sizes the dependence of \( ^5D_0 \rightarrow \ ^7F_1/ ^5D_0 \rightarrow \ ^7F_2 \) ratio on the concentration of the vacancies was determined. Introduction of two Eu\(^{3+}\) ions instead of Ce\(^{4+}\) ones into stoichiometric CeO\(_2\) lattice leads to formation of one oxygen vacancy required for compensation of excess negative charge. So, in CeO\(_2\):Eu\(^{3+}\) treated in the oxidizing atmosphere the oxygen vacancies concentration will be proportional to the concentration of Eu\(^{3+}\) ions and particular ratio between \( ^5D_0 \rightarrow \ ^7F_1 \) and \( ^5D_0 \rightarrow \ ^7F_2 \) bands can be assigned to the particular vacancy concentration.

The luminescence spectra of CeO\(_2\):Eu\(^{3+}\) nanocrystals with different Eu\(^{3+}\) concentrations are shown in Fig. 4. Increase of Eu\(^{3+}\) concentration from 2 at.% to 10 at.% leads to decrease of intensity of \( ^5D_0 \rightarrow \ ^7F_1 \) luminescence band. So the number of Eu\(^{3+}\) centers with \( O_h \) symmetry also decreases with increase of Eu\(^{3+}\) concentration in agreement with results obtained in [11]. Preferential formation of Eu\(^{3+}\) centers with the symmetry lower than \( O_h \) for high Eu\(^{3+}\) concentrations is determined by high concentrations of the oxygen vacancies required for compensation of additional charge of doped ions and formation of the Eu\(^{3+}\)-oxygen vacancy associates [9].

As was mentioned before, for CeO\(_2\):Eu\(^{3+}\) nanocrystals treated in oxidizing atmosphere the oxygen vacancies concentration is proportional to the concentration of Eu\(^{3+}\) ions (for instance, 0.2 at.% of Eu\(^{3+}\) ions corresponds to 0.05 % of oxygen vacancies). So, dependence of \( ^5D_0 \rightarrow \ ^7F_1/ ^5D_0 \rightarrow \ ^7F_2 \) ratio on the concentration of Eu\(^{3+}\) ions can be considered as dependence of this ratio on the concentration of the oxygen vacancies ions as well. This dependence is shown in Fig. 5. The values of \( ^5D_0 \rightarrow \ ^7F_1/ ^5D_0 \rightarrow \ ^7F_2 \) ratio for CeO\(_2\):Eu\(^{3+}\) nanocrystals with different sizes and treated in different atmospheres (determined from Fig. 3) are shown by asterisks. Comparison of the values of \( ^5D_0 \rightarrow \ ^7F_1/ ^5D_0 \rightarrow \ ^7F_2 \) ratio for nanocrystals with the different sizes and with the different concentrations of Eu\(^{3+}\) ions allows to determine that concentration of the oxygen vacancies increases with decrease of the size of nanocrystals: from 0.07 % (50 nm) to 0.125 % (10 nm) at treatment in neutral atmosphere and from 0.08 % (50 nm) to 0.33 % (10 nm) at treatment in reducing atmosphere (Table). Such increase of the oxygen vacancies concentration can be explained by the higher surface/volume ratio and decrease of an activation energy for the small CeO\(_2\):Eu\(^{3+}\) nanocrystals [13].

![Image](image_url)

**Fig. 4. Luminescence spectra of CeO\(_2\):Eu\(^{3+}\) nanocrystals (0.2, 2, 5 and 10 at. %).**

<table>
<thead>
<tr>
<th>Size</th>
<th>( R(\text{air}) )</th>
<th>( R(\text{Ar}) )</th>
<th>( R(H_2) )</th>
<th>( C_v, % ) (air)</th>
<th>( C_v, % ) (Ar)</th>
<th>( C_v, % ) (H(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 nm</td>
<td>5.55</td>
<td>4.8</td>
<td>3.44</td>
<td>0.05</td>
<td>0.125</td>
<td>0.33</td>
</tr>
<tr>
<td>25 nm</td>
<td>5.55</td>
<td>5.1</td>
<td>4.16</td>
<td>0.05</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>50 nm</td>
<td>5.55</td>
<td>5.44</td>
<td>5.27</td>
<td>0.05</td>
<td>0.07</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Table. Values of \( ^5D_0 \rightarrow \ ^7F_1/ ^5D_0 \rightarrow \ ^7F_2 \) ratio and concentration of oxygen vacancies for CeO\(_2\):Eu\(^{3+}\) nanocrystals with the different sizes and treated in different atmospheres.
4. Conclusions

In the paper an influence of the size on the processes of oxygen vacancies formation in CeO$_2$ nanocrystals has been investigated by means of spectroscopic techniques using intensity of $5d \rightarrow 4f$ luminescence of Ce$^{3+}$ ions and $^5D_0 \rightarrow ^7F_1/^5D_0 \rightarrow ^7F_2$ ratio of Eu$^{3+}$ bands as indicators of the oxygen vacancies concentration. Both methods allow to determine sufficient increase of the vacancy concentration with decrease of the size of nanocrystal. Increase in 1.5 times of $5d \rightarrow 4f$ luminescence intensity of Ce$^{3+}$ ions corresponding to the same increase in the vacancies concentration with decrease of the size from 75 nm to 20 nm was shown for undoped CeO$_2$ nanocrystals. For CeO$_2$:Eu$^{3+}$ nanocrystals it was shown that decrease of the size of nanocrystal from 50 nm to 10 nm leads to increase of the oxygen vacancies concentration in 1.8 times for nanocrystals treated in neutral atmosphere and in 4 times for nanocrystals treated in reducing atmosphere.

References