

Influence of CeO₂ 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 CeO₂ nanocrystals has been investigated. Changes in concentration of oxygen vacancies were determined by two independent indicators: intensity of $5d \rightarrow 4f$ luminescence of Ce³⁺ ions and ratio between ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ luminescence bands of Eu³⁺ ions incorporated into ceria nanocrystals as structural probes. It was shown that for CeO₂ 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 Ce³⁺ ions, while for CeO₂:Eu³⁺ nanocrystals it leads to lowering of symmetry for Eu³⁺ 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 CeO₂. Для определения изменения концентрации кислородных вакансий использовано два независимых показателя — интенсивность $5d \rightarrow 4f$ люминесценции ионов Ce³⁺ и отношение между ${}^5D_0 \rightarrow {}^7F_1$ и ${}^5D_0 \rightarrow {}^7F_2$ люминесцентными полосами ионов Eu³⁺, введенных в нанокристаллы в качестве структурных зондов. Показано, что для нанокристаллов CeO₂ уменьшение размера (от 75 до 20 нм) приводит к возрастанию в 1,5 раза интенсивности полосы, связанной с ионами Ce³⁺, стабилизированными кислородными вакансиями, тогда как для нанокристаллов CeO₂:Eu³⁺ уменьшение размеров приводит к понижению симметрии центра Eu³⁺ и соответствующего снижению 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 CeO₂.

Вплив розміру на процеси формування вакансій у нанокристалах CeO₂, встановлений за допомогою спектроскопічних методів. *П.О.Максимчук, В.В.Семінко, І.І.Беспалова, А.О.Масалов.*

Досліджено вплив розміру на процеси формування кисневих вакансій у нанокристалах CeO₂. Для визначення зміни концентрації кисневих вакансій використано два незалежні показники — інтенсивність $5d \rightarrow 4f$ люмінесценції іонів Ce³⁺ та відношення між ${}^5D_0 \rightarrow {}^7F_1$ та ${}^5D_0 \rightarrow {}^7F_2$ люмінесцентними смугами іонів Eu³⁺, введених у нанокристали в якості структурних зондів. Показано, що для нанокристалів CeO₂ зменшення розміру (від 75 нм до 20 нм) призводить до зростання у 1,5 рази інтенсивності смуги, пов'язаної з іонами Ce³⁺, стабілізованими вакансіями, тоді як для нанокристалів CeO₂:Eu³⁺ зменшення розмірів призводить до зниження симетрії центра Eu³⁺ 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 наночастках CeO₂.

1. Introduction

Ceria (CeO₂) 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 Ce³⁺–Ce⁴⁺ oxidation/reduction processes determined by low energy of oxygen vacancies formation in this material (formation of the complex defect Ce³⁺–O_v–Ce³⁺ with the vacancy situated at NN site to Ce³⁺ ion requires only 0.26 eV) [5]. Creation of each oxygen vacancy is accompanied by transition of two Ce⁴⁺ ions to Ce³⁺ ones, so oxygen vacancy concentration and Ce³⁺/Ce⁴⁺ ratio are directly proportional to each other. Extremely high concentrations of the oxygen vacancies (and correspondingly, Ce³⁺ ions) in ceria nanoparticles were recently determined by EMR (about 18 % of Ce³⁺ ions for 3 nm nanoparticles) [6] and XPS investigations (17 % of Ce³⁺ 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 Ce³⁺ ions that was confirmed spectroscopically in [8]. As was shown [8], luminescent properties of CeO₂ nanocrystals are determined by two different luminescent centers formed by Ce³⁺ ions and Ce⁴⁺–O²⁻ charge transfer (CT) states. $5d \rightarrow 4f$ Luminescence intensity of Ce³⁺ ions increases strongly with increase of concentration of the oxygen vacancies that allows to considerate this intensity as a measure of the oxygen vacancies concentration in ceria nanocrystals. Incorporation of trivalent (for instance, rare-earth) ion instead of Ce⁴⁺ 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 Gd³⁺ 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 Gd³⁺ (such as Eu³⁺ ions) the vacancy is repelled to NNN (next to nearest-neighbor) position. According to these predictions the surrounding of Eu³⁺ ion must preserve O_h symmetry and only

magneto-dipole transitions of Eu³⁺ (such as $^5D_0 \rightarrow ^7F_1$) are possible [10]. However, in [9] it was shown that in CeO₂:Eu³⁺ there are up to four additional positions of Eu³⁺ ion with symmetry lower than O_h that manifests itself in occurrence of electro-dipole $^5D_0 \rightarrow ^7F_2$ transition (forbidden for Eu³⁺ centers in O_h positions) in luminescence spectra of Eu-doped ceria. Moreover, the number of Eu³⁺ ions in distorted states increases strongly with Eu concentration and calcination temperature increase [11]. As was supposed in [11], Eu³⁺ 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 Eu³⁺ content increase) leads to sufficient increase of the number of Eu³⁺ ions in distorted positions. So, the relative content of Eu³⁺ 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 Ce³⁺ ions and the ratio between intensities of $^5D_0 \rightarrow ^7F_1$ (symmetry insensitive) and $^5D_0 \rightarrow ^7F_2$ (symmetry sensitive) transitions of Eu³⁺ as indicators that allow to determine the change of the oxygen vacancies concentration in CeO₂ nanocrystals depending on their size and to estimate the correspondent concentrations of the oxygen vacancies in these nanocrystals.

2. Experimental

CeO₂ nanocrystals were obtained by Pechini method, CeO₂:Eu³⁺ (0.2, 2, 6 and 10 at.%) nanocrystals were synthesized by colloidal precipitation method. CeO₂ 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 $r = 9\eta 2g(\rho - \rho_0)Ht$, where η is viscosity coefficient, ρ and ρ_0 are densities of precipitant and water, respectively, H/t is deposition rate. Luminescence of all samples was excited by He–Cd laser ($\lambda_{exc} = 325$ nm). Luminescence spectra of CeO₂ nanocrystals were taken at 77 K, spectra of CeO₂:Eu³⁺ nanocrystals were taken at 300 K.

3. Results and discussion

As was recently shown in [8], optical properties of CeO₂ nanocrystals are deter-

mined by presence of two different optical centers formed by Ce³⁺ ions and Ce⁴⁺-O²⁻ charge transfer states. Luminescence spectra of CeO₂ nanoparticles (shown in Fig. 1) consist of two spectral bands with maximums 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 [8] to $5d \rightarrow 4f$ transitions of Ce³⁺ ions. In reducing atmosphere concentration of the 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. 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 Ce⁴⁺-O²⁻ complex. 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 ceria nanocrystals with different sizes. In the Fig. 1 the luminescence spectra of CeO₂ 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 $5d \rightarrow 4f$ luminescence of Ce³⁺ ion. Intensity of this band is directly proportional to Ce³⁺ concentration and, correspondingly, to concentration of oxygen vacancies in the nanocrystal. 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.

Eu³⁺ ion is widely used for determination of local structure of cationic centers in different crystal matrices [12]. It is connected with high sensitivity of electro-dipole $^5D_0 \rightarrow ^7F_2$ transition of Eu³⁺ ion to presence or absence of inversion center of symmetry. Contrary to $^5D_0 \rightarrow ^7F_2$ transition, intensity of magneto-dipole $^5D_0 \rightarrow ^7F_1$ transition of Eu³⁺ ion is practically independent on the symmetry of cationic center. So the ratio between the intensities of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions provides an information about local symmetry of the Eu³⁺ surrounding symmetry.

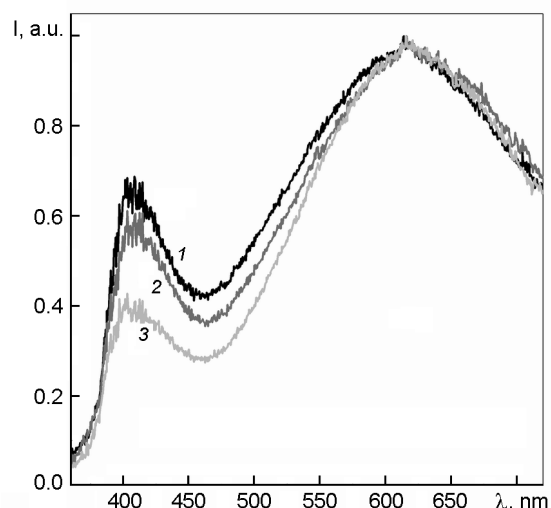


Fig. 1. Luminescence spectra of CeO₂ nanocrystals (1 — 20 nm, 2 — 50 nm, 3 — 75 nm).

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 $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ intensities of Eu³⁺ ion can be used. Formation of the oxygen vacancy near Eu³⁺ 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_{3v} or lower. As was shown in [11] increase of Eu³⁺ concentration (and, correspondingly, of the oxygen vacancies) leads to proportional increase of the number of centers with non-cubic symmetry determined by change of $^5D_0 \rightarrow ^7F_1 / ^5D_0 \rightarrow ^7F_2$ ratio. The influence of the atmosphere treatment on the vacancies concentration can be determined in the same way. In our experiment the concentrations of Eu³⁺ in CeO₂ were very low (about 0.2 at.%, $C_{vac} = 0.05$ %) to exclude from consideration the vacancies created by incorporation of Eu³⁺ ion instead of Ce⁴⁺ and to deal mostly with the vacancies provided by change of the atmosphere treatment.

Luminescence spectra of CeO₂:Eu³⁺ nanocrystals (10 nm) at treatment atmosphere variation are shown in the Fig. 2. It consist of characteristic $^5D_0 \rightarrow ^7F_1$ and

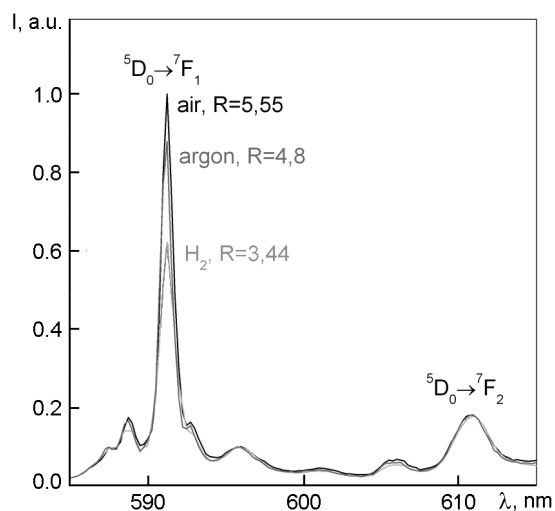


Fig. 2. Luminescence spectra of CeO₂:Eu³⁺ nanocrystals (10 nm) treated in oxidizing (air), neutral (Ar) and reducing (H₂) atmosphere.

$^5D_0 \rightarrow ^7F_2$ 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 Eu³⁺ ion and surrounding of Eu³⁺ ion preserve cubic symmetry. While the radius of Eu³⁺ ion is bigger than radius of Gd³⁺ 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 Eu³⁺ 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 Eu³⁺ 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 — Eu³⁺" associates and distortion of O_h symmetry can be suggested [9].

Luminescence spectra of CeO₂:Eu³⁺ 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-

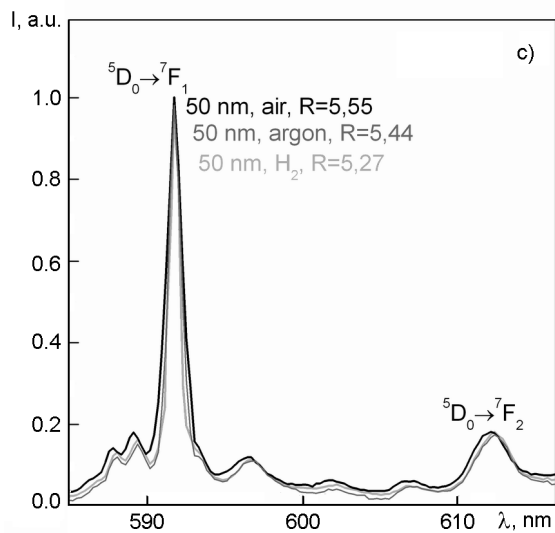
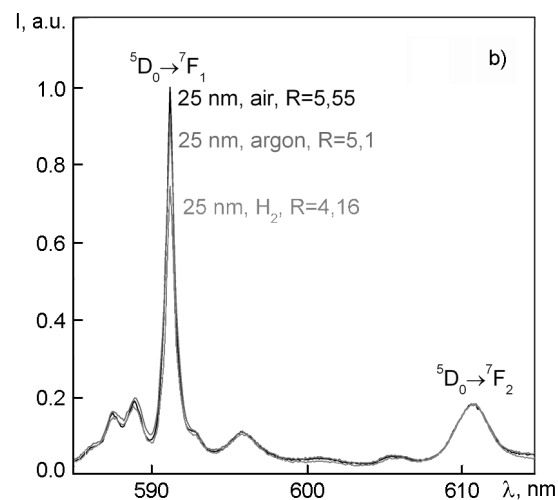
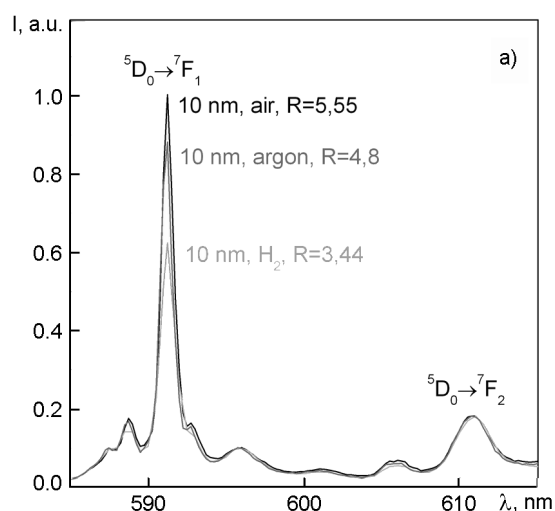


Fig. 3. Luminescence spectra of CeO₂:Eu³⁺ nanocrystals treated in oxidizing (air), neutral (Ar) and reducing (H₂) atmosphere (a — 10 nm, b — 25 nm, c — 50 nm).

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 CeO₂ nanoparticles is more than in the bigger ones.

For estimation of the oxygen vacancies concentration in CeO₂:Eu³⁺ 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 Eu³⁺ ions instead of Ce⁴⁺ ones into stoichiometric CeO₂ lattice leads to formation of one oxygen vacancy required for compensation of excess negative charge. So, in CeO₂:Eu³⁺ treated in the oxidizing atmosphere the oxygen vacancies concentration will be proportional to the concentration of Eu³⁺ 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 CeO₂:Eu³⁺ nanocrystals with different Eu³⁺ concentrations are shown in Fig. 4. Increase of Eu³⁺ concentration from 2 at.% to 10 at.% leads to decrease of intensity of ${}^5D_0 \rightarrow {}^7F_1$ luminescence band. So the number of Eu³⁺ centers with O_h symmetry also decreases with increase of Eu³⁺ concentration in agreement with results obtained in [11]. Preferential formation of Eu³⁺ centers with the symmetry lower than O_h for high Eu³⁺ concentrations is determined by high concentrations of the oxygen vacancies required for compensation of additional charge of doped ions and formation of the Eu³⁺-oxygen vacancy associates [9].

As was mentioned before, for CeO₂:Eu³⁺ nanocrystals treated in oxidizing atmosphere the oxygen vacancies concentration is proportional to the concentration of Eu³⁺ ions (for instance, 0.2 at.% of Eu³⁺ ions

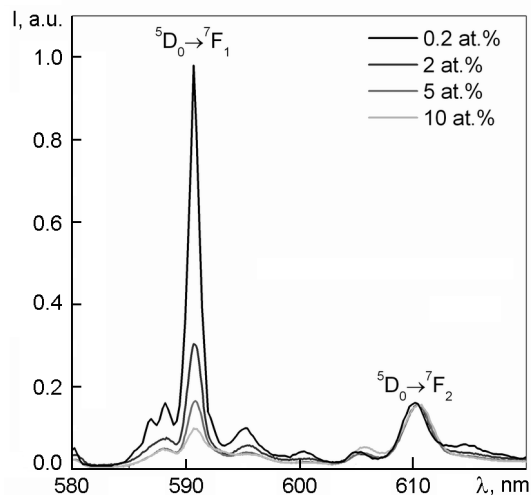


Fig. 4. Luminescence spectra of CeO₂:Eu³⁺ nanocrystals (0.2, 2, 5 and 10 at.%).

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 Eu³⁺ 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 CeO₂:Eu³⁺ 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 Eu³⁺ 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 CeO₂:Eu³⁺ nanocrystals [13].

Table. Values of ${}^5D_0 \rightarrow {}^7F_1 / {}^5D_0 \rightarrow {}^7F_2$ ratio and concentration of oxygen vacancies for CeO₂:Eu³⁺ nanocrystals with the different sizes and treated in different atmospheres

Size	$R(\text{air})$	$R(\text{Ar})$	$R(\text{H}_2)$	$C_v, \% (\text{air})$	$C_v, \% (\text{Ar})$	$C_v, \% (\text{H}_2)$
10 nm	5.55	4.8	3.44	0.05	0.125	0.33
25 nm	5.55	5.1	4.16	0.05	0.1	0.2
50 nm	5.55	5.44	5.27	0.05	0.07	0.08

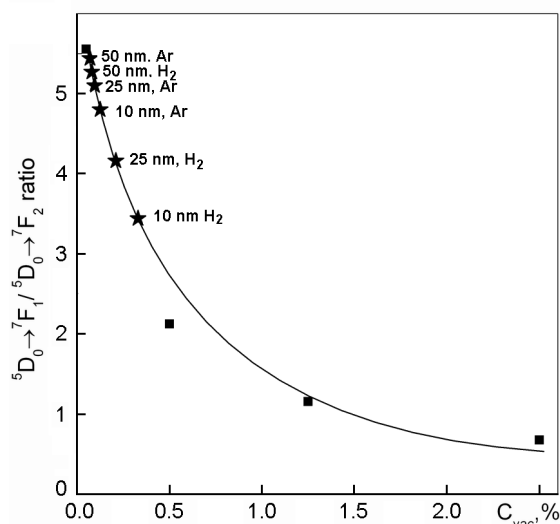


Fig. 5. Dependence of ${}^5D_0 \rightarrow {}^7F_1 / {}^5D_0 \rightarrow {}^7F_2$ ratio on the oxygen vacancies concentration. Values of ${}^5D_0 \rightarrow {}^7F_1 / {}^5D_0 \rightarrow {}^7F_2$ ratio for CeO₂:Eu³⁺ nanocrystals with the different sizes and treated in different atmospheres are shown by asterisks.

4. Conclusions

In the paper an influence of the size on the processes of oxygen vacancies formation in CeO₂ nanocrystals has been investigated by means of spectroscopic techniques using intensity of $5d \rightarrow 4f$ luminescence of Ce³⁺ ions and ${}^5D_0 \rightarrow {}^7F_1 / {}^5D_0 \rightarrow {}^7F_2$ ratio of Eu³⁺ 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 Ce³⁺ 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 CeO₂ nanocrystals. For CeO₂:Eu³⁺ 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.

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