Role of shallow electronic traps formed by oxygen vacancies in formation of luminescent properties of CeO_{2-x} nanocrystals

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In the paper methods of thermoluminescence (TSL) and time-resolved spectroscopy were used for investigation of shallow electron traps near edge of $4f^0$ band in CeO_2 and nonstoichiometric CeO_{2-x} nanocrystals. It was shown that presence of the electronic traps located about 0.2 eV lower than the bottom of $4f^0$ band leads to sufficient modification of $O2p$–$Ce4f$ excitation relaxation processes due to excitation retrapping. Strong dependence of TSL signal on the stoichiometry of nanocrystal allows to suppose that electronic defects are associated with oxygen vacancies and are formed by F^+ centers.

Методами термолюминесценции и время-разрешенной спектроскопии исследованы мелкие электронные ловушки вблизи края $4f^0$ зоны в нанокристаллах CeO_2 и CeO_{2-x}. Показано, что наличие электронных ловушек, расположенных на 0,2 эВ ниже края $4f^0$ зоны, приводит к существенному изменению процессов релаксации $O2p$–$Ce4f$ возбуждения, что обусловлено высокой вероятностью перезахвата возбуждения. Существенная зависимость сигнала термолюминесценции от стехиометрии нанокристалла позволяет предположить, что электронные дефекты связаны с кислородными вакансиями и, вероятнее всего, образованы F^+-центрами.

Роль неглибоких електронних пасток, сформованих кисневими вакансіями, у формуванні люмінесцентних властивостей нанокристалів CeO_{2-x}. *П.О.Максимчук, В.В.Семінько, І.І.Беспалова, А.О.Масалов.*
Методами термолюмінесценції та розподіленої у часі спектроскопії досліджено неглибокі електронні пастки поблизу краю $4f^0$ зони у нанокристалах CeO_2 і CeO_{2-x}. Показано, що наявність електронних пасток, розташованих на 0,2 еВ нижче краю $4f^0$ зони, призводить до істотної зміни процесів релаксації $O2p$–$Ce4f$ збудження, що зумовлено високою ймовірністю перезахоплення збудження. Істотна залежність сигналу термолюмінесценції від стехіометрії нанокристала дозволяє припустити, що електронні дефекти пов'язані з кисневими вакансіями і, найімовірніше, утворені F^+-центрами.

1. Introduction

Cerium oxide (CeO_2) recently has attracted much attention as a material that can be effectively applied for catalysis [1], fuel cells [2, 3] and oxygen sensors [4] due to its high oxygen sensitivity and oxygen storage capacity provided by facile Ce^{4+}/Ce^{3+} redox cycles. As was shown in [5, 6], reversible $Ce^{4+} \leftrightarrow Ce^{3+}$ reduction/oxidation processes are facilitated for CeO_2 nanocrystals as compared to correspondent bulk materials that is determined by the high degree of non-stoichiometry of ceria nanoparticles.

Cerium dioxide has the fluorite structure with FCC cubic lattice, which consists of a simple cubic oxygen sub-lattice with cerium

ions occupying alternate cube centers [7, 8]. Formation of range of non-stoichiometric CeO_{2-x} oxides (with $x = 0...0.4$) was also observed. Non-stoichiometry of CeO_{2-x} is determined by oxygen vacancies in the lattice. In spite of the high concentration of vacancies the fluorite-type structure is preserved for the all range of oxides while the part of Ce^{4+} ions is reduced to Ce^{3+} ones [9].

Luminescent properties of CeO_2 nanocrystals were investigated in the number of papers recently [10–12]. As was shown, luminescence of ceria is connected strongly with stoichiometry of nanocrystals and is determined by different F-centers (F^0, F^+ and F^{2+}) [11], subsurface defects [10] and Ce^{3+} ions (for non-stoichiometric ceria nanocrystals) [12]. In our recent paper [12] Ce4f–O2p charge transfer (CT) luminescence of both stoichiometric and non-stoichiometric CeO_2 nanocrystals was observed as well. Dependence of luminescence characteristics of ceria on the method of synthesis, treatment atmosphere and size of nanocrystals complicates sufficiently the assignment of the bands observed in the spectrum to the peculiar centers.

As was shown both theoretically [13] and experimentally [11] oxygen vacancy in CeO_2 can capture an electron (or two electrons) remained after oxygen release thus forming F^+ or F^0 centers. Position of electronic levels of all F centers are close to the bottom of empty 4f^0 band so one can suppose that these centers can act also as electronic traps for electrons from 4f^0 band. So the sufficient influence of concentration of oxygen vacancies on the relaxation processes of O2p–Ce4f excitations, and, correspondingly, on the luminescence properties of ceria nanocrystals can be expected.

In this paper we have used the methods of thermoluminescence to determine whether the electronic traps are present in sol-gel obtained CeO_2 nanocrystals; their nature, depth and dependence on the stoichiometry of nanocrystal were determined as well. Also the influence of shallow electron traps on the processes of charge transfer excitation relaxation was shown.

2. Methods and materials

CeO_2 nanocrystals were obtained by Pechini method [14]. Cerium oxide CeO_2 (99.999 %, Sigma-Aldrich) was dissolved in the mixture of nitric acid HNO_3 and hydrogen peroxide H_2O_2 (in 1:1 volume ratio). The solution of 0.75 g of citric acid and 1 ml of ethylene glycol was added to 20 ml of cerium nitrate $Ce(NO_3)_3$ ($c = 1$ mol/l) solution. The resulting mixture was treated at 80°C during 10 h and then hydrolyzed by means of 10 mass.% NH_3 water solution. The precipitate was dried at 120°C during 5 h and then dehydrated at 250°C during 4 h. Stoichiometry of the nanocrystal depend 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 were annealed during 2 h in different atmospheres — oxidizing (air) and reducing (hydrogen) at 900°C.

Luminescence spectra were obtained using spectrofluorimeter based on the grating monochromator, luminescence was excited by He–Cd laser with $\lambda_{exc} = 325$ nm. Decay curves were measured by the method of time-correlated single photon counting using FluoTime200 picosecond spectrofluorimeter (PicoQuant, Germany). Investigations were carried out at 293 K and 77 K. The thermoluminescence glow curves were obtained by linear heating from 50 to 290 K at the heating rate of 2 K/s after irradiation with He–Cd laser ($\lambda_{exc} = 325$ nm) for 15 min. The radiation of samples was detected by R9110 Hamamatsu photomultiplier tube.

X-ray diffraction patterns of obtained stoichiometric and nonstoichiometric CeO_2 nanocrystals are shown in the Fig. 1. All the diffraction peaks in these patterns can be indexed to a fluorite cubic phase of CeO_2 (JCPDS 34-0394) (Fig. 1). There are diffraction angles of 28, 33, 47, 56, 59, 69 and 76, which are corresponding to ceria (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (3 3 1), respectively. So the structures of the samples are characterized by FCC fluorite-type lattice and formation of any additional phases at these conditions can be excluded.

The average size of nanocrystals was about 50 nm that was confirmed by TEM data (Fig. 2).

3. Results and discussion

Ceria is wide band gap (~6 eV) material with valence band formed by O2p and conduction band by Ce5d states. In the band gap of stoichiometric CeO_2 narrow sub-band
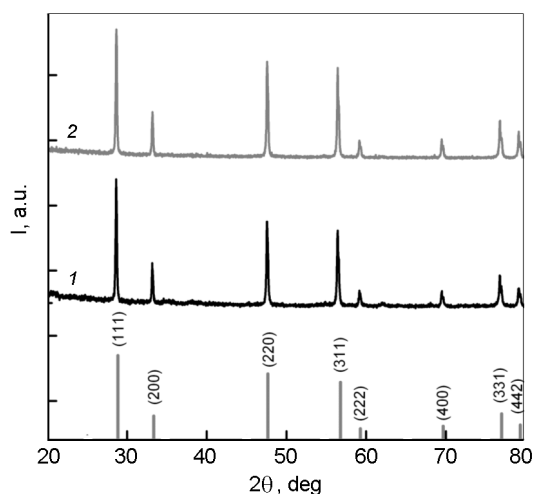
Fig. 1. XRD patterns of CeO_2 nanocrystals (*1* — CeO_2 treated in oxidizing atmosphere; *2* — CeO_2 treated in reducing atmosphere).

Fig. 2. TEM image of CeO_2 nanocrystals.

is present formed by empty $4f^0$ states of Ce^{4+} ion. For non-stoichiometric CeO_{2-x} splitting of this band to the empty $4f^0$ and filled $4f^1$ sub-bands occurs. $Ce^{4+} \rightarrow Ce^{3+}$ transition providing filling of $4f^1$ state can occur as via formation of oxygen vacancy and subsequent capture of excess electron by Ce^{4+} ion, so by charge transfer from oxygen ion at $O2p \rightarrow Ce4f$ excitation. As was shown in [12] both charge transfer (Ce^{3+}+hole) and vacancy-stabilized (Ce^{3+}+vacancy) states form separate luminescent centers which ratio can be controlled by atmosphere of treatment.

Spectra of CeO_2 nanocrystals treated in oxidizing atmosphere (1) and reducing atmosphere (2) at 77 K are shown in the
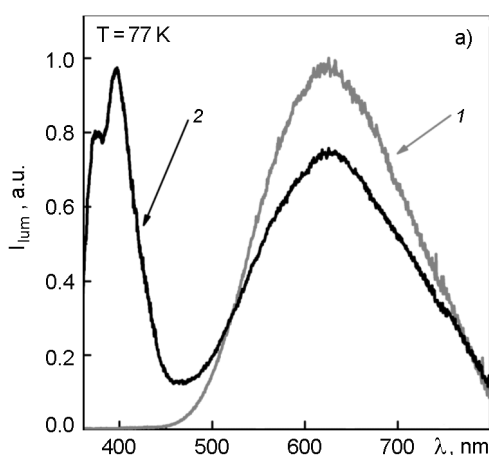
Fig. 3a. Luminescence spectrum of CeO_2 nanocrystals treated in oxidizing atmosphere consists of one band with maximum at 630 nm, while spectrum of non-stoichiometric CeO_2 nanocrystals consists of two bands with maxima at 390 nm and 630 nm. As was shown previously, 630 nm band is determined by radiative relaxation in Ce^{4+}–O^{2-} charge transfer state (CT-luminescence), 390 nm band is determined by Ce^{3+} ion luminescence and corresponds to electronic transition from excited $5d^1$ state to the ground $4f^1$ state of Ce^{3+} ($^2F_{7/2}$ and $^2F_{5/2}$ terms) [12, 15].

Presence of shallow electronic traps usually modifies the processes of excitation relaxation at sub-band gap excitation. In CeO_2 nanocrystals luminescence band at 390 nm originates from $5d^1$ electronic state of Ce^{3+} ion, while 630 nm band — from

Fig. 3. a) Luminescence spectra of CeO_2 nanocrystals treated in oxidizing atmosphere (*1*) and reducing atmosphere (*2*), λ_{exc} = 325 nm. T = 77 K. b) Decay curves of CeO_2 nanocrystals treated in reducing atmosphere (*1* — λ_{reg} = 390 nm; *2* — λ_{reg} = 630 nm), λ_{exc} = 330 nm, T = 77 K.
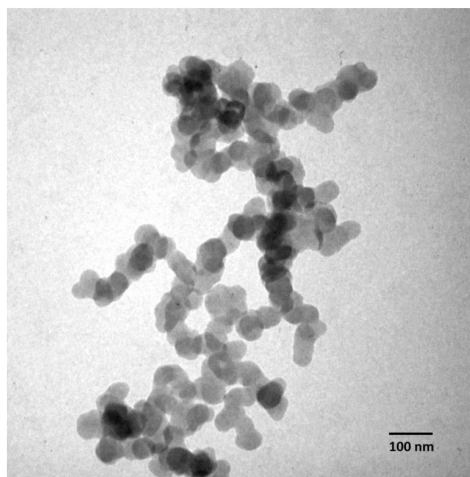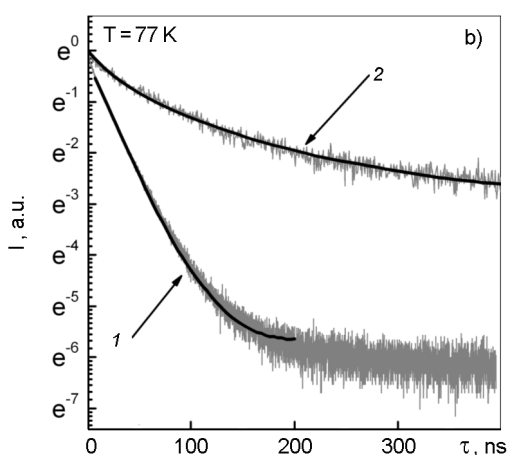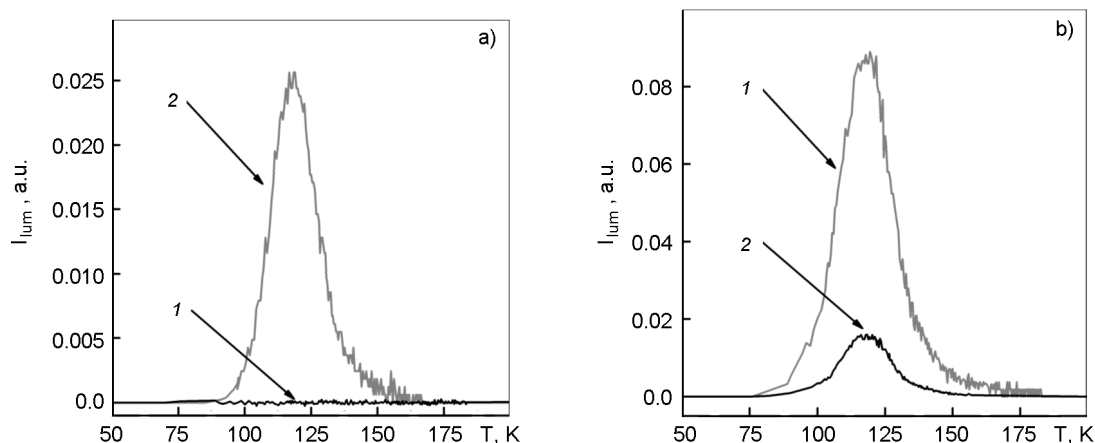
Fig. 4. a) TSL glow curve of CeO_2 nanocrystals treated in reducing atmosphere (*1* — λ_{reg} = 390 nm, *2* — 630 nm); b) TSL glow curve of CeO_2 nanocrystals treated in reducing atmosphere (*1*) and in oxidizing atmosphere (*2*) (λ_{reg} = 630 nm).

relaxed Ce^{4+}–O^{2-} charge transfer state located in the close vicinity to edges of empty $5d^0$ and $4f^0$ electronic bands, respectively. So an effective transport of electrons from luminescent centers to electron traps and vice versa can be predicted. So if the electronic traps are present near edges of either $5d^0$ or $4f^0$ electronic bands they must reveal itself in changing of excitation relaxation patterns and correspondent modification of luminescence decay curves can be expected.

The luminescence decay curves taken at 390 and 630 nm are shown in Fig. 3b. The decay curve of 390 nm emission band is monoexponential with decay time of $\tau \approx 25$ ns that is typical for $5d \rightarrow 4f$ transitions of Ce^{3+} ions [16]. Monoexponential form of decay curve definitely demonstrates that either the electronic traps are absent near band edge of $5d^0$ band or at least they are rather ineffective. Decay curve of 630 nm emission band has non-exponential pattern and can be approximated by hyperbolic law $I = I_0/(1 + pt)^\alpha$ with $p = 0.02$ and $\alpha = 1.17$. Such type of luminescence decay curve is typical for decay in the presence of shallow traps. According to [17] $\alpha = 1.17$ corresponds to about 30 acts of excitation re-trapping on the electronic traps during excitation lifetime.

To confirm the presence of shallow electrons traps thermally stimulated luminescence (TSL) glow curves of CeO_2 nanoparticles with different stoichiometry were investigated. Each thermoluminescence peak corresponds to the release of an electron or hole from a particular trapping level during heating of the material [18]. The thermoluminescence was registered in the maximum of Ce^{3+} $5d \rightarrow 4f$ luminescence (390 nm) and in the maximum of Ce^{4+}–O^{2-} luminescence (630 nm) after irradiation of the CeO_2 nanocrystals with He–Cd laser (λ_{ex} = 325 nm).

Fig. 4a shows the thermally stimulated luminescence glow curves between 50 K and 200 K for CeO_2 nanocrystals treated in reducing atmosphere registered at 390 and 630 nm. No peaks were observed in the TSL glow curve registered at 390 nm (Ce^{3+} band). This result agrees well with results obtained from decay curve and shows that there are no shallow electronic traps near $5d^0$ band of ceria. TSL curve of CeO_2 registered at 630 nm has one peak at ~120 K (2). Presence of only one maximum in the curve indicates the presence of only one type of electron traps [18]. So, the Ce^{4+}–O^{2-} charge transfer complexes are the recombination centers for de-trapped charge carriers and carriers escape thermally from the traps to the CT-band before their radiative recombination.

Thermoluminescence peak shape and methods of calculation of energy trap parameters are determined by the type of kinetics of recombination processes [18]. It is known [18, 19], the kinetics of thermoluminescence may be of the first or the second order due to different probability of charge carriers retrapping.

According to criteria of Randall and Wilkins [20] thermoluminescence kinetics of the first order is observed when the probability of re-trapping is negligible compared with the probability of recombination. So, first-order peak is asymmetric with most of the peak area being on the low temperature
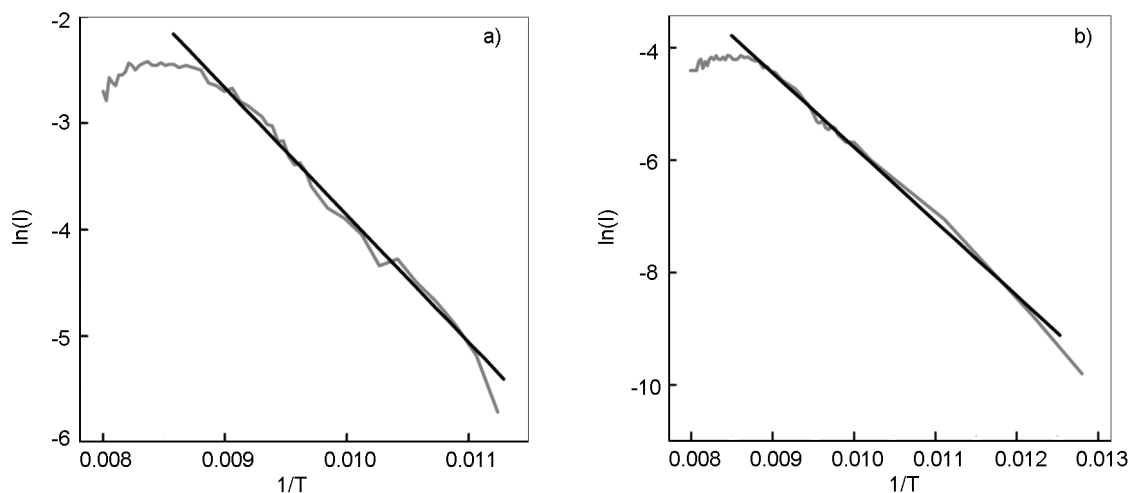
Fig. 5. TSL glow curves of CeO_2 nanocrystals treated in reducing atmosphere (a) and in oxidizing atmosphere (b) in $\{1/T, \ln(I)\}$ coordinates (slope of 120 K TSL peak is shown).

side from the maximum (T_m). The second-order glow curve is observed if the probability of re-trapping is high. Intensity of the second-order glow curve is more in the high temperature side of the peak [21]. Also the second-order TSL curve is more symmetrical than a first-order curve [18].

Fig. 4b shows the thermally stimulated luminescence glow curves between 50 K and 200 K for CeO_2 nanocrystals treated in reducing and oxidizing atmosphere and registered at 630 nm. Position of the maximum in the glow curves for CeO_2 nanocrystals treated as in reducing, so in oxidizing atmosphere is located at 120 K. This suggests the presence of traps of the same nature [18]. Increase of 120 K peak intensity with increase of oxygen deficiency indicates that this peak can be associated with oxygen defects. Both TSL glow are symmetrical, so in both cases second order kinetics of thermoluminescence is observed.

Knowledge of the order of thermoluminescence kinetics allows to determine an activation energy of electronic traps by the initial rise method. This method is known as the most accurate method for the second-order kinetics [18, 22]. In the temperature range of $T < T_m$ TSL intensity is proportional to $\exp(-E/kT)$. This fact provides a simple mean for calculating the activation energy from the slope of $\ln(I)$ vs. $1/T$ plot in the initial rise region [23]. The calculated values of activation energy for both CeO_2 nanocrystals treated in reducing atmosphere and treated in oxidizing atmosphere are equal to 0.2 eV (Fig. 5).

The same thermoluminescence kinetics, position of the maxima and activation energy confirms the suggestion about the same nature of electron traps for CeO_2 nanocrystals treated in reducing and oxidizing atmosphere. Increase of TSL peak intensity with increase of oxygen deficiency indicates that this peak arises from oxygen vacancies. Activation energy of 0.2 eV corresponds well with activation energy of F^+ centers determined earlier from temperature dependence of correspondent luminescence band for CeO_2 nanocrystals obtained by precipitation method [11]. So we can suppose that electronic traps for CeO_2 investigated in our paper also are formed by F^+ ("oxygen vacancy + electron") centers.

4. Conclusions

Influence of shallow electron traps on the processes of $O2p$–$Ce4f$ excitation relaxation was shown by means of time-resolved spectroscopy and thermoluminescence analysis for CeO_2 nanocrystals with different oxygen stoichiometry. It was shown that electron traps in CeO_2 nanocrystals arise from oxygen vacancies and their impact depends strongly on the stoichiometry of nanocrystal. Activation energy of electronic traps calculated by means of the initial rise method for CeO_2 nanocrystals was equal to about 0.2 eV that corresponds well with position of levels of F^+ centers relative to the bottom of $4f^0$ band.

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