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 термolumинесценции и време-разрешенной спектроскопии исследованы мелкие электронные ловушки ближайшие краю 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 термolumинесценции от стехиометрии нанокристалла позволяет предположить, что электронные дефекты связаны с кислородными вакансиями и, вероятно, всего, образуют F$^+$-центры.

Роль неглубоких электронных пасток, сформированных кислородными вакансиями, у формованных люминесцентных властивостей нанокристалів CeO$_{2-x}$ P.O.Mаксимчук, \(В.В.Семінкo, И.И.Беспалова, А.А.Масалов.

Методами термolumинесценции и разрешенной в часі спектроскопії досліджено неглибокі електронні пастки біля краю 4f$^0$ зони в нанокристаллах 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 термolumинесценции від стехіометрії нанокристалла дозволяє припустити, що електронні дефекти пов’язані з кислородними вакансіями і, найімовірніше, утворені F$^+$-центрими.

1. Introduction

Ceircon 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$^{4+}$ ↔ 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.

Ceircon 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 fluoride-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] Ce$^{4f}$–O$^{2p}$ 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 O$^{2p}$–Ce$^{4f}$ 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$_2$O$_2$ (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 $\lambda_{\text{exc}}$ = 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 ($\lambda_{\text{exc}}$ = 325 nm) for 15 min. The irradiation 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 O$^{2p}$ and conduction band by Ce$^{5d}$ states. In the band gap of stoichiometric CeO$_2$ narrow sub-band
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 $4f^{2}$ 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 O2$p$ $\rightarrow$ Ce4$f$ 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. 1. XRD patterns of CeO$_{2}$ nanocrystals (1 — CeO$_{2}$ treated in oxidizing atmosphere; 2 — CeO$_{2}$ treated in reducing atmosphere).](image)

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 5$d^{1}$ state to the ground 4$f^{1}$ state of Ce$^{3+}$ ($^{2}F_{7/2}$ and $^{2}F_{5/2}$ 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 5$d^{1}$ electronic state of Ce$^{3+}$ ion, while 630 nm band — from

![Fig. 2. TEM image of CeO$_{2}$ nanocrystals.](image)

![Fig. 3. a) Luminescence spectra of CeO$_{2}$ nanocrystals treated in oxidizing atmosphere (1) and reducing atmosphere (2), $\lambda_{\text{exc}} = 325$ nm, $T = 77$ K. b) Decay curves of CeO$_{2}$ nanocrystals treated in reducing atmosphere (1 — $\lambda_{\text{red}} = 390$ nm; 2 — $\lambda_{\text{red}} = 630$ nm), $\lambda_{\text{exc}} = 330$ nm, $T = 77$ K.](image)
relaxed Ce$^{4+}$–O$_2^-$ charge transfer state located in the close vicinity to edges of empty 5$d^0$ and 4$f^0$ electronic bands, respectively. So an effective transport of electrons from luminescence centers to electron traps and vice versa can be predicted. So if the electronic traps are present near edges of either 5$d^0$ or 4$f^0$ 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 monoeponential with decay time of $\tau = 25$ ns that is typical for 5$d \rightarrow 4f$ transitions of Ce$^{3+}$ ions [16]. Monoeponential form of decay curve definitely demonstrates that either the electronic traps are absent near band edge of 5$d^0$ 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 electronic 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$^{3+}$ 5$d \rightarrow 4f$ luminescence (390 nm) and in the maximum of Ce$^{4+}$–O$_2^-$ luminescence (650 nm) after irradiation of the CeO$_2$ nanocrystals with He–Cd laser ($\lambda_{ex} = 325$ nm).

Fig. 4a shows the thermally stimulated luminescence glow curves between 50 K and 290 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 5$d^0$ 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 $[1/T, \ln(t)]$ coordinates (slope of 120 K TSL peak is shown).

The 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 O$_2$p–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.

References