Luminescence of F^0 centers in CeO$_2$ nanocrystals

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In the paper luminescent properties of CeO$_{2-x}$ (ceria) nanocrystals are discussed. Ceria nanocrystals with different oxygen non-stoichiometry were obtained using sol-gel method and subsequent annealing in oxidizing or reducing atmosphere. Luminescence spectra of ceria nanocrystals reveal three types of luminescent centers. Beyond previously observed 4f-5d luminescence of Ce^{3+} ions and charge transfer (CT) luminescence determined by radiative relaxation in Ce^{4+}-O^{2-} complexes, wide luminescence band formed by F^0 centers was revealed. Ratio between luminescent centers of different types can be varied by variation of treatment atmosphere. Luminescence of Ce^{3+} ions is the most intensive in reducing atmosphere due to highest content of oxygen vacancies, and, correspondingly, of Ce^{3+} ions. As CT luminescence of Ce^{4+}-O^{2-} complexes, so luminescence of F^0 centers demonstrate strong quenching with temperature increase; however CT luminescence quenching is more pronounced than quenching of luminescence for F^0 centers.
Keywords: ceria; F-centers; luminescence; nanocrystals.

В статье обсуждаются люминесцентные свойства нанокристаллов CeO$_{2-x}$ (диоксида церия). Нанокристаллы диоксида церия с различной кислородной нестехиометрией были получены при помощи золь-гель метода с последующим отжигом в окислительной или восстановительной атмосфере. Спектры люминесценции нанокристаллов диоксида церия демонстрируют наличие центров люминесценции трех типов. Помимо ранее наблюдаемой 4f - 5d люминесценции ионов Ce^{3+} и полосы с переносом заряда (CT), обусловленной излучательной релаксацией Ce^{4+} - O^{2-} комплексов, выявлена широкая полоса, формируемая F^0 центрами. Соотношение между содержанием центров люминесценции разных типов можно изменять путем варьирования атмосферы отжига. Люминесценция ионов Ce^{3+} наиболее интенсивна при обработке в восстановительной атмосфере благодаря высокой концентрации кислородных вакансий и, соответственно, ионов Ce^{3+}. Как CT люминесценция Ce^{4+} - O^{2-} комплексов, так и люминесценция F^0 центров демонстрирует сильное тушение с возрастанием температуры, однако температурное тушение CT люминесценции выражено сильнее, чем тушение люминесценции F^0 центров.
Ключевые слова: диоксид церия; F-центры; люминесценция; нанокристаллы.

В даній статті обговорюються люмінесцентні властивості нанокристалів CeO$_{2-x}$ (діоксиду церію). Нанокристали діоксиду церію з різною кисневою нестехіометрією були отримані за допомогою золь-гель методу з подальшим відпалом в окислювальній або відновлюючій атмосфері. Спектри люмінесценції нанокристалів діоксиду церія демонструють наявність центрів люмінесценції трьох типів. Окрім 4f - 5d люмінесценції іонів Ce^{3+} та смуги з переносом заряду (CT), обумовленої випромінювальною релаксацією Ce^{4+} - O^{2-} комплексів, що спостерігалися раніше, виявлена широка смуга, сформована F^0 центрами. Співвідношення між вмістом центрів люмінесценції різних типів можна змінювати шляхом варіювання атмосфери відпалу. Люмінесценція іонів Ce^{3+} найбільш інтенсивна при обробці в відновлювальної атмосфері завдяки високій концентрації кисневих вакансій і, відповідно, іонів Ce^{3+}. Як CT люмінесценція Ce^{4+} - O^{2-} комплексів, так і люмінесценція F^0 центрів демонструє сильне гасіння зі зростанням температури, однак температурне гасіння CT люмінесценції виражено сильніше, ніж гасіння люмінесценції F^0 центрів.
Ключові слова: діоксид церію; F-центри; люмінесценція; нанокристали.

Introduction

High oxygen storage capacity and ability to switch between Ce^{4+} and Ce^{3+} oxidation states recently has turned the attention of leading material scientists to ceria (CeO$_{2-x}$) powders and nanocrystals [1-3]. Low Ce^{4+}→Ce^{3+} reduction energy and high concentration of oxygen vacancies in ceria lattice seem to be the main prerequisites for the specific properties of nanoceria, so variation of co-dopants and treatment conditions allow obtaining ceria nanocrystals with different oxygen storage and antioxidant properties[4,5].

As was shown in the number of papers [6,7], formation of oxygen vacancies in ceria is accompanied by capture of two electrons by Ce^{4+} ions, which turn in this way to Ce^{3+} ones. However, some recent publications suggested that

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electrons can be captured not only by Ce^{3+} ions, but by oxygen vacancies as well, leading to formation of so-called F-centers [8]. Presence of different kinds of F-centers in nanoceria was confirmed in [9] both by EPR and optical spectroscopy methods. Moreover, recently in [10] a new phenomenon of room temperature ferromagnetism for undoped ceria films and nanocrystals was shown and exchange interactions between F-centers were proposed to be the cause of this effect [11]. F-centers can be formed as a result of capture of one (F^+), two (F^0) or no (F^{++}) electrons by oxygen vacancies. While each of these centers has its distinct magnetic and spectroscopic features, clear distinction between F-centers can be made.

Spectroscopic properties of ceria nanocrystals depend on the presence of both Ce^{3+} ions and defect centers. Undoped ceria is a dielectric material with band gap of about 6 eV with valence band formed by 2p states of oxygen, and conduction band formed by mixed 6s+5d states of cerium [12, 13]. Inside the band gap of ceria a narrow band formed by empty $4f^0$ states of Ce^{4+} ions is observed. The distance between the top of the valence band and the bottom of $4f^0$ band is about 3.15 eV.

Steady state and time-resolved luminescence studies shown in our previous papers [14] enable us to distinguish clearly two types of optical centers in undoped ceria nanocrystals formed by Ce^{3+} ions which charge is compensated by oxygen vacancies in NN positions, and Ce^{4+}-O^{2-} charge transfer (CT) complexes, respectively. Also it was determined that ratio between intensities of Ce^{3+} 5d→4f luminescence and CT luminescence in Ce^{4+}-O^{2-} complex depended strongly both on the atmosphere of treatment and size of nanocrystal [15]. Increase of the content of oxygen vacancies either due to treatment in reduction atmosphere or decrease of nanocrystal size led to corresponding increase of Ce^{3+} luminescence intensity as compared to CT band. However, presence of alternative paths of electron behavior after oxygen vacancy formation besides localization on cerium ions, such as formation of F-centers, can complicate sufficiently this rather simple picture. In this paper we show that F-centers (namely, F^0 centers) are inevitably formed in ceria lattice even at treatment in oxidative atmosphere leading to formation of alternative luminescence centers.

Experimental

CeO_2 nanocrystals were obtained by Pechini method [16]. 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 (corresponding pH change was from 3 to 7). The precipitate

was dried at 120 °C during 5 h and then dehydrated at 250 °C during 4 h. CeO_2 nanocrystals were annealed in oxidative (air) and reducing (hydrogen) atmospheres at 1000°C during 2 h. The corresponding samples are marked in the paper as CeO_2 (Air), and $CeO_2(H_2)$. Average size of nanocrystals was estimated from TEM images and was about 50 nm for all 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 were obtained using spectrofluorimeter based on the grating monochromator, luminescence was excited by He-Cd laser (λ_{exc} = 325 nm), diode-pumped solid state laser (λ_{exc} = 457 nm), Ar^+ laser (488 nm) and YAG:Nd laser (532 nm) Investigations were carried out at 293 K and 77 K.

Results and discussion

CeO_2 nanocrystals obtained by the method described in previous section were treated at 1000°C in different atmospheres in order to obtain nanoceria with different concentration of oxygen vacancies, and so, with different content of structural defects. In fig. 1 the luminescence spectra of CeO_2 (Air), and $CeO_2(H_2)$ at 77 K under excitation in the charge-transfer (CT) band (λ_{exc} = 325 nm) are shown. The band with maximum of about 400 nm was observed only for $CeO_2(H_2)$ and as was shown in our previous paper [14] this band is determined by 5d→4f luminescence of Ce^{3+} ions stabilized by oxygen vacancies. Both excitation
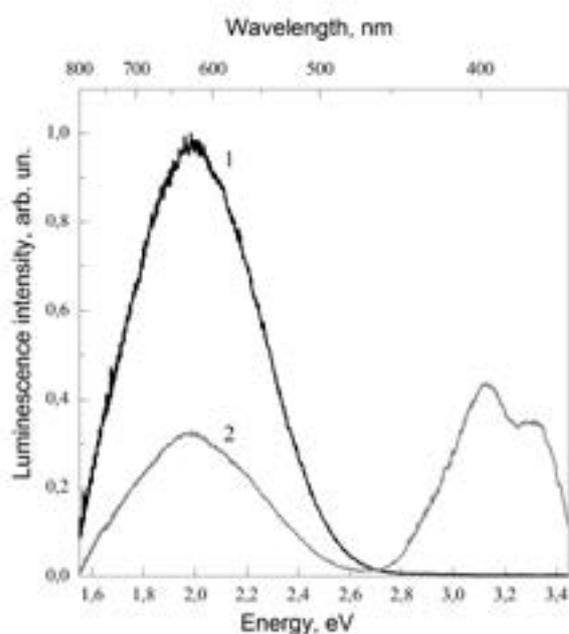

Fig. 1. Luminescence spectra of CeO_2 nanocrystals treated in oxidizing (1) and reducing (2) atmospheres (λ_{exc} = 325 nm), T=300 K.
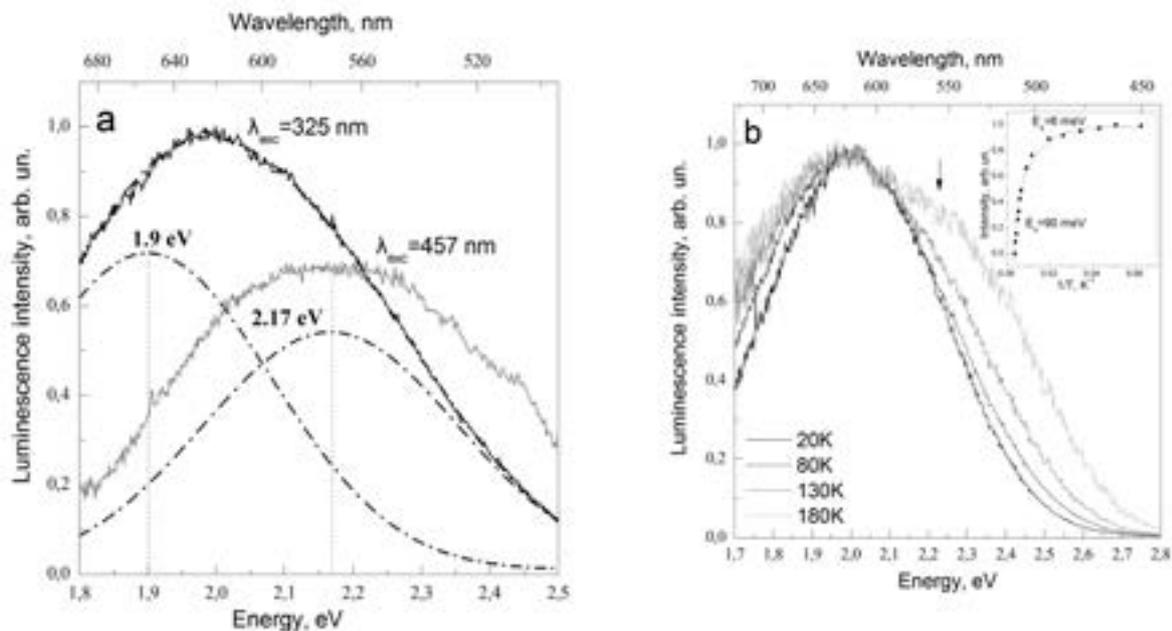
Fig. 2. a) Luminescence spectra of CeO$_2$ nanocrystals treated in oxidizing atmosphere at λ_{exc} = 325 nm and 457 nm; fitting of luminescence spectrum at λ_{exc} = 325 nm by two Gaussian profiles is also shown. b) Luminescence spectra at λ_{exc} = 325 nm at variation of temperature in the range from 20 K to 180 K normalized by the intensity of 650 nm band. In the inset – temperature dependence of intensity of 570 nm band at 457 nm excitation.

spectrum and typical for Ce^{3+} 5d→4f luminescence decay times in nanosecond range clearly confirm this attribution [14]. At the same time as for stoichiometric, so for non-stoichiometric ceria, wide band with maximum at 620 nm was observed. In [14] it was shown that this band can be attributed to CT-luminescence of Ce^{4+}-O^{2-} charge transfer complex.

More detailed analysis of this band reveals its complex nature (fig. 2a). Fitting of luminescence spectrum obtained at 325 nm excitation at 77 K by two Gaussian profiles reveals two peaks at 1.9 eV (650 nm) and 2.17 eV (570 nm). At 457 nm excitation (with energy lower than the difference between the top of the valence band and bottom of 4f^0 band) the 650 nm sub-band disappears and spectrum consists of the band with maximum at 570 nm. The same luminescence spectra as for 457 nm excitation were observed at different excitations with energies below optical gap (488 nm and 532 nm). The fact that 650 nm sub-band can be excited only at 2p^6→4f^0 excitation allows to attribute it to CT-luminescence of Ce^{4+}-O^{2-} charge transfer complex, while 570 nm band must have some different origin. These sub-bands exhibit sufficiently different temperature dependences (fig. 2b) – intensity of 650 nm band is comparable with intensity of 570 nm one only at low temperatures (less than ~100 K), while at room temperature its contribution to total intensity of complex 620 nm band is negligible. The 570 nm sub-band also exhibit temperature quenching but this quenching is

sufficiently weaker than for 650 nm one. So, it must be concluded that 620 nm band consists of two sub-bands with different origin – while luminescence band at 570 nm can be excited as via CT excitation band, so directly by 457
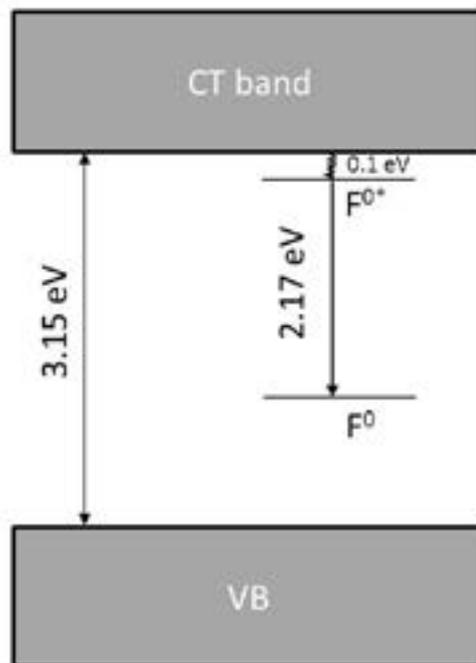

Fig. 3. Energy scheme for CeO$_2$ showing the positions of F^0 and F^{0*} levels in the band gap of ceria (VB – valence band, CT – charge transfer (4f^0) band).

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nm excitation and probably has the defect-related nature, luminescence band at 650 nm can be excited only via CT band and so can be ascribed to luminescence in Ce^{4+}-O^{2-} charge transfer complex.

Fitting the temperature dependence of 570 nm (defect-related) band intensity by $I = I_0(1 + B_1 e^{-\frac{E_1}{kT}} + B_2 e^{-\frac{E_2}{kT}})^{-1}$ (fig.2b, inset) allows determining the activation energy in the low and high-temperature ranges: 6 meV and 90 meV, respectively. These values are in good agreement with the correspondent values of activation energy for F^0 centers in ceria nanocrystals obtained by precipitation method in [9]. Also the maximum of luminescence band for F^0 centers determined in [9] (2.1 eV) is close to the maximum of defect band for our nanocrystals (2.17 eV). So, the 570 nm band is most probably related to transitions in F^0 centers ($F^{0*} \rightarrow F^0$).

The most probable pathway of $F^{0*} \rightarrow F^0$ luminescence quenching is the one with participation of the bottom of $4f^0$ (CT) band. So the activation energy of 570 nm band luminescence quenching at room temperature (90 meV) can be associated with energy difference between F^{0*} level and the bottom of $4f^0$ band. This supposition allows us placing F^0 and F^{0*} levels in the band gap of ceria (fig.3).

Conclusions

1. Luminescence spectra of ceria nanocrystals at 325 nm excitation consist of two luminescence bands: the first one is determined by 4f-5d luminescence of Ce^{3+} ions and second one is complex consisting of two sub-bands: charge transfer (CT) luminescence band and luminescence band formed by F^0 centers.

2. Both CT luminescence band and F^0 luminescence band are temperature-dependent, however temperature quenching of F^0 luminescence band is less pronounced, than temperature quenching of CT luminescence which at room temperature almost disappear.

3. Temperature quenching of F^0 luminescence is realized with participation of the bottom of $4f^0$ band. Energy difference between excited F^{0*} level and bottom of $4f^0$ band is about 0.1 eV.

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