

## Formation of Luminescence Centers in Oxygen-Deficient Cerium Oxide Nanocrystals

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In this work the peculiarities of oxygen vacancies formation in cerium oxide nanoparticles for different external influences have been investigated by spectroscopic methods.

The features of oxygen vacancies and therefore non-stoichiometric cerium oxide formation in CeO<sub>2</sub> nanocrystals depending on the atmosphere of high temperature treatment were investigated. Stimulation of oxygen vacancies formation in reducing and neutral atmospheres was revealed. Occurrence of two different luminescence centers (viz. the charge-transfer complexes formed by Ce<sup>4+</sup> and O<sup>2-</sup> ions, and Ce<sup>3+</sup> ions stabilized by vacancies) after cerium oxide nanoparticles annealing in a neutral atmosphere has been observed.

**Keywords:** Cerium oxide nanoparticles, Oxygen vacancies, High temperature treatment.

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### 1. INTRODUCTION

Nanocrystalline cerium dioxide is a promising material which have found a wide application in different high-tech branches of industry.

Cerium dioxide is widely used in protective UV absorbing coatings, as the main component of the polishing compounds, in electrochromic coatings, etc. Use of nanocrystalline CeO<sub>2</sub> for biomedical applications also seems perspective.

Literature data on the structure and properties of nanosized CeO<sub>2-x</sub> often contradict each other. Moreover, most of the properties of nanocrystalline CeO<sub>2-x</sub>, remain almost unexplored.

### 2. MATERIALS AND METHODS

CeO<sub>2</sub> nanocrystals were synthesized by means of colloidal precipitation method.

Luminescence spectra of CeO<sub>2</sub> nanocrystals have been obtained by means of the spectrofluorimeter based on grid monochromator. Reciprocal linear dispersion of monochromator was equal to 1.6 nm / mm. Registration of spectra was carried out by photomultiplier tube operating in photon counting mode. Luminescence was excited by helium-cadmium laser at 325 nm. Possibility of temperature variation was obtained by placing of the sample in the cryostat.

### 3. RESULTS AND DISCUSSION

Cerium dioxide has the fluorite structure, which consists of a simple cubic oxygen sub-lattice with the cerium ions occupying alternate cube centres. In the perfect ceria the oxygen ions have a formal charge of 2-; the anions are tetrahedrally coordinated to the cerium ions and octahedrally coordinated to the surrounding oxygen atoms. The cerium ions have a formal charge of 4+ (the electronic structure is [Ne]5d10) and are coordinated to eight oxygen ions.

Cerium with a 4f<sup>2</sup>5d<sup>0</sup>6s<sup>2</sup> electron configuration can

exhibit both the +3 and +4 oxidation states, and intermediate oxides with composition in the range between Ce<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> can be formed. Thermodynamic data indicate that cerium is unstable in the presence of oxygen and that Ce<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> are easily formed [1]

Due to the low value of oxidation-reduction potential of the Ce<sup>4+</sup>/Ce<sup>3+</sup> pair (1.61 eV) cerium dioxide is able to attach and release oxygen rather easily (due to Ce<sup>3+</sup>-Ce<sup>4+</sup> transition). At high temperatures and low oxygen pressure cerium dioxide tends to reduce Ce<sup>4+</sup> ions to Ce<sup>3+</sup> ones and forms a continuous series of oxygen-deficient, nonstoichiometric oxides (CeO<sub>2-x</sub>). These oxides are characterized by disordered arrangement of oxygen vacancies. At the same time at low temperatures these oxides have a highly organized fluorite structure CeO<sub>2</sub>. [2, 3].

CeO<sub>2</sub> belongs to a class of materials whose optical properties are determined by the charge-transfer transitions. The formation of the charge transfer complexes is a common phenomenon for all rare-earth ions. Such transitions can be identified by broad bands in the absorption or excitation spectra. However, most of the rare-earth ions do not exhibit CT-luminescence due to nonradiative relaxation from the CT-state. Another typical feature of the CT luminescence is a very low temperature quenching.

As was already mentioned, cerium can exhibit both the +3 and +4 oxidation states, and oxygen deficient nonstoichiometric oxides with composition in the range between Ce<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> can be formed. In this case there is a significant dependence of the stoichiometry of the sample from 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<sub>2</sub> crystalline phase. So the processes of oxygen vacancies formation in CeO<sub>2</sub> crystals can be controlled by changing the atmosphere of high-temperature treatment.

In addition, increased role of the surface for CeO<sub>2</sub>

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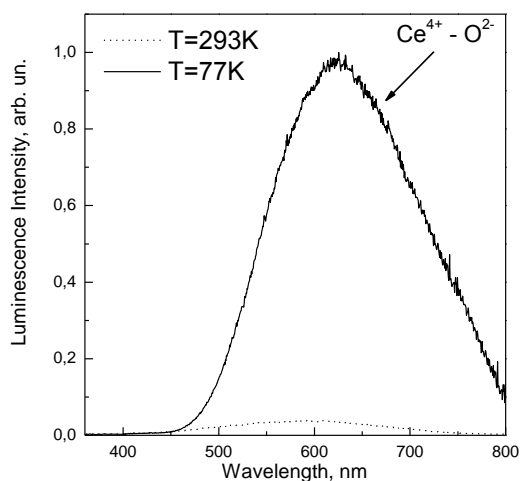
nanocrystals compared to the bulk should stimulate the formation of oxygen vacancies, that may lead to the nonstoichiometrical structure even in the absence of a reducing atmosphere.

Cerium compounds in which the valence of cerium is 4+ have no luminescence in contrast to trivalent cerium compounds, which has an intense 4f-5d transition in the blue region of the luminescence spectrum. Thus, by the intensity of the 4f-5d luminescence it is possible to make conclusions about the presence of the  $Ce^{3+}$  ions, and therefore the degree of nonstoichiometry of the structure of the nanocrystals.

In this work the peculiarities of oxygen vacancies formation in cerium oxide nanoparticles for different external influences have been investigated by spectroscopic methods.

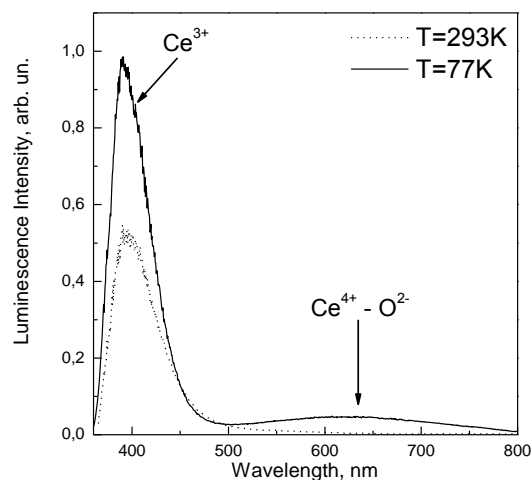
In order to explore the features of the formation of oxygen vacancies in the nanocrystals  $CeO_2$ , we have carried out studies of the luminescence spectra after high temperature treatment in different atmospheres. High-temperature annealing was carried out in an oxidizing (air), inert (Ar) and reducing (hydrogen) environments at 1000°C for 2 hours. The measurement of luminescence spectra was carried out at room temperature (293 K) and liquid nitrogen (77 K) temperatures.

All three spectra are characterized by an intense luminescence band with maximum at 625 nm. This luminescence band can be attributed to the charge-transfer (CT) transition, which occurs due to electron transfer from the ligand to the cerium ion. CT-transitions in the absorption spectra have been observed for almost all rare-earth ions [4, 5]. In [6, 7] it was shown that the luminescence of cerium in the crystal  $Sr_2CeO_4$  is also caused by charge transfer transitions. The fact that the luminescence in  $CeO_2$  nanocrystal belongs to CT - transition is also confirmed by the study of low-temperature spectra. In the luminescence spectrum of nanocrystals heat-treated in an oxidizing environment (Fig. 1) only luminescence band at 625 nm related to charge-transfer transition is present. The absence of luminescence of trivalent cerium indicates that the number of oxygen vacancies in the nanocrystal is small, so that the structure of the nanocrystal is close to the stoichiometric  $CeO_2$ .



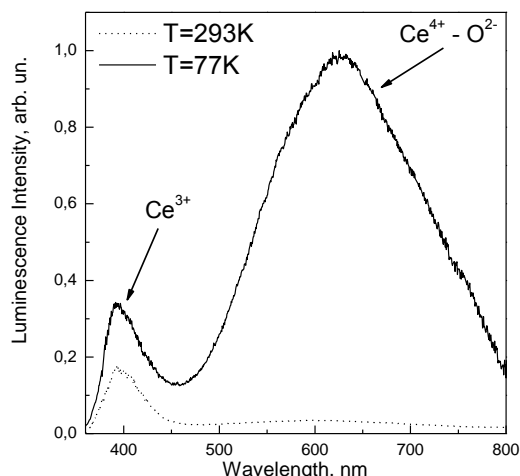
**Fig. 1** – Luminescence spectrum of  $CeO_2$  nanocrystals heat-treated in an oxidizing environment

In a reducing environment (Fig. 2) in addition to the charge transfer band an intense luminescence band with maximum at 390 nm is observed. This band can be clearly attributed to 4f-5d transition of trivalent cerium. Occurrence of this band confirms the statement that the reducing environment stimulates the formation of a large number of vacancies in the crystal structure of  $CeO_2$ , which leads to a high degree of stoichiometry and formation of  $Ce^{3+}$  ions. The transition of some of the cerium ions to the trivalent state in a reducing atmosphere has been shown previously for the bulk crystal. However, such a transition was observed only at sufficiently high pressures. Thus, the transition from bulk to nanoscale crystals stimulates the formation of oxygen vacancies in the crystal lattice.



**Fig. 2** – Luminescence spectrum of  $CeO_2$  nanocrystals heat-treated in a reducing environment

Even more significant evidence of this statement was the presence of additional band in the luminescence spectra of  $CeO_2$  nanocrystals after high temperature treatment in an inert atmosphere (Fig. 3).



**Fig. 3** – Luminescence spectrum of  $CeO_2$  nanocrystals heat-treated in an inert environment

As in the case of a reducing atmosphere this band can be attributed to 4f-5d transition of trivalent cerium. The formation of a significant number of oxygen vacancies in the absence of a reducing atmosphere is not typ-

ical for bulk CeO<sub>2</sub> crystals and, thus, this effect is a manifestation of the increased role of the surface in nanocrystals.

#### 4. CONCLUSION

Thus, peculiarities of oxygen vacancies formation in cerium oxide nanoparticles for different external influences have been investigated by spectroscopic methods. Features of oxygen vacancies and therefore

non-stoichiometric cerium oxide formation in CeO<sub>2</sub> nanocrystals depend on the atmosphere of high temperature treatment. Reducing and neutral atmospheres stimulates oxygen vacancies formation. Occurrence of two different luminescence centers (viz. the charge-transfer complexes formed by Ce<sup>4+</sup> and O<sup>2-</sup> ions, and Ce<sup>3+</sup> ions stabilized by vacancies) after cerium oxide nanoparticles annealing in a neutral atmosphere has been observed.

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