Spectroscopically Detected Formation of Oxygen Vacancies in Nano-Crystalline CeO$_{2-x}$

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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$_2$ 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^{4+} and O^{2-} ions, and Ce^{3+} 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.

1. INTRODUCTION

One of the most important functional rare earth oxides, cerium dioxide (CeO₂), has attracted much attention for promising applications in catalysts [1], fuel cells [2, 3], oxygen sensors [4], mechanical polishing [5], ultraviolet blocks [6], and luminescent materials [7, 8.] due to its oxygen storage capacity via facile Ce^{4+} / Ce^{3+} redox cycles, high mechanical strength, and optical properties.

Cerium dioxide is a wide bandgap semiconductor that has been synthesized and studied in both thin-film [9, 10] and nanoparticle form [11-13]. As a thin-film, cerium oxide has unique properties such as a high refractive index, a high dc dielectric constant and a lattice constant similar to Si, making it suitable as an insulating material in Si device technology [14]. These properties make cerium oxide useful for applications in microelectronics and optics.

Recently, ceria nanoparticles have attracted attention within the biomedical research community as a potential agent to inhibit cellular aging [15, 16]. Mixed brain cell cultures have been shown to have an increased lifespan when a solution containing ceria nanoparticles is introduced into their environment. The likely mechanism for the longevity increase is the scavenging of free radical species in the cells that would normally damage the cell, causing the cell to age [17]. The scavenging effect is attributed to the presence of Ce^{3+} ions that reduce the free radical species as the Ce^{3+} ions are oxidized to Ce^{4+}.

Literature data on the structure and properties of nanosized CeO$_{2-x}$ often contradict each other. Moreover, most of the properties of nanocrystalline CeO$_{2-x}$, remain almost unexplored.

The main goal of the work was to find a way to determine the oxygen vacancies concentration in the cerium dioxide nanoparticles using optical spectroscopy. The optical spectroscopy techniques used were spectrophotometry, to measure the excitation spectrum of the samples, and fluorometry, to measure the luminescence spectrum of the cerium dioxide nanoparticles. These techniques are widely used to characterize semiconducting materials [18], but have not been extensively used on ceria nanoparticles. One advantage of these techniques is that the optical spectroscopy systems are inexpensive and have fast data acquisition.

2. MATERIALS AND METHODS

By means of Pechini-type sol-gel process cerium dioxide samples with an average diameter of 40 nm and narrow size distribution were synthesized (Fig. 1).
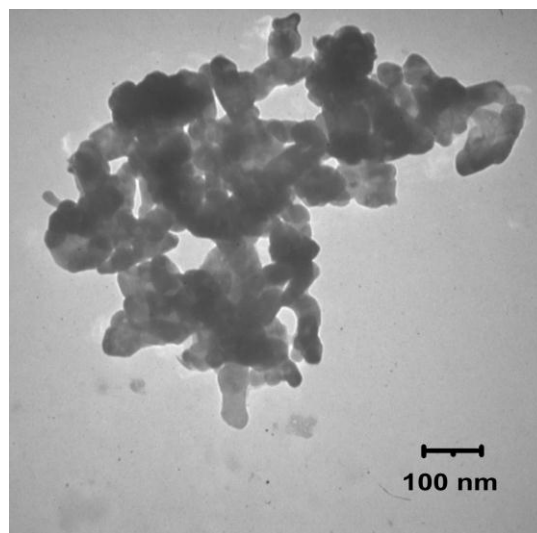

Fig. 1 – TEM image of synthesized CeO$_2$ nanocrystals

The structural characteristics of nanocrystalline samples were examined from X-ray diffraction (XRD) (Fig. 2). All the diffraction peaks in these patterns can be indexed to a fluorite cubic phase of CeO$_2$ (JCPDS 34-0394) (Fig. 2). There are diffraction angles of 28, 33, 47,

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56, 59, 69 and 76, which are corresponding to ceria (111), (200), (220), (311), (222), (400) and (331) respectively. No impurity is observed, indicating that pure CeO_2 is synthesized by a Pechini-type sol-gel process.
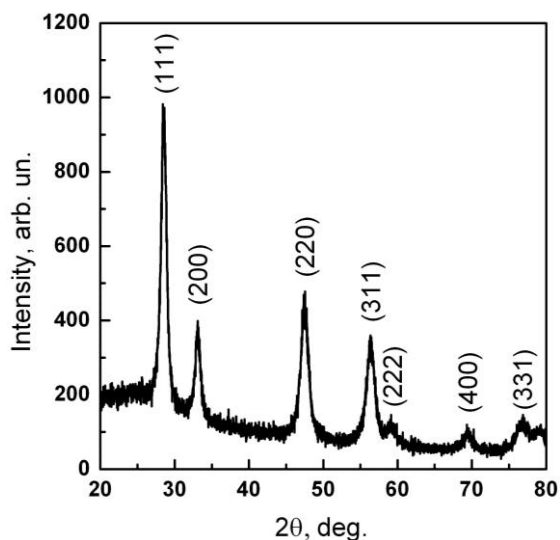

Fig. 2 – XRD of the synthesized CeO_2 nanocrystals

Luminescence spectra of CeO_2 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 (Fig. 3). 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.
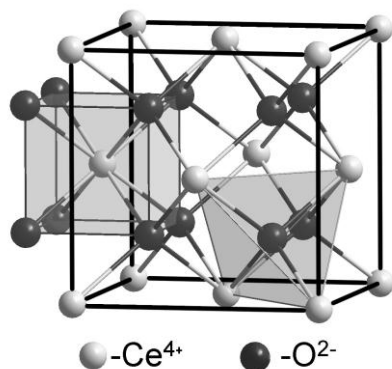

Fig. 3 – Structure of cerium dioxide

Cerium with a $4f^25d^0f6s^2$ electron configuration can exhibit both the + 3 and + 4 oxidation states, and in-

termediate oxides with composition in the range between Ce_2O_3 and CeO_2 can be formed. Thermodynamic data indicate that cerium is unstable in the presence of oxygen and that Ce_2O_3 and CeO_2 are easily formed [19].

Due to the low value of oxidation-reduction potential of the Ce^{4+}/Ce^{3+} pair (1.61 eV) cerium dioxide is able to attach and release oxygen rather easily (due to Ce^{3+}-Ce^{4+} transition). At high temperatures and low oxygen pressure cerium dioxide tends to reduce Ce^{4+} ions to Ce^{3+} ones and forms a continuous series of oxygen-deficient, nonstoichiometric oxides (CeO_{2-x}). 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_2 [20, 21]. Oxygen nonstoichiometry defines basic biomedical properties of cerium oxide – the ability to participate in redox processes taking place in the organism.

CeO_2 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 nonradioactive 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 non-stoichiometric oxides with composition in the range between Ce_2O_3 and CeO_2 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_2 crystalline phase. So the processes of oxygen vacancies formation in CeO_2 crystals can be controlled by changing the atmosphere of high-temperature treatment.

In addition, increased role of the surface for CeO_2 nanocrystals compared to the bulk should stimulate the formation of oxygen vacancies that may lead to the nonstoichiometric 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 nonstoichiometric 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 [22, 23]. In [24, 25] it was shown that the luminescence of cerium in the crystal Sr_2CeO_4 is also caused by charge transfer transitions. Such transitions can be identified by broad bands in the excitation spectra. The broad band in the excitation spectrum of CeO_2 nanocrystals heat-treated in an oxidizing environment comes from the charge transfer (CT) transition from O^{2-} to Ce^{4+} (Fig. 4). The fact that the luminescence in CeO_2 nanocrystal belongs to CT-transition is also confirmed by the study of low-temperature spectra.
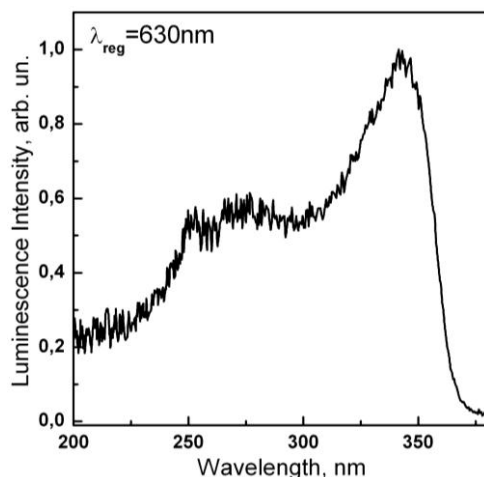

Fig. 4 – Excitation spectrum of CeO_2 nanocrystals heat-treated in an oxidizing environment

In the luminescence spectrum of nanocrystals heat-treated in an oxidizing environment (Fig. 5) 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.

In a reducing environment (Fig. 6) in addition to the charge transfer band an intense luminescence band with maximum at 390 nm is observed.

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.
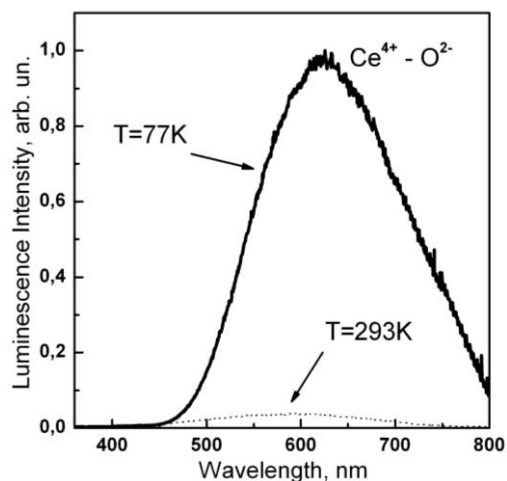

Fig. 5 – Luminescence spectrum of CeO_2 nanocrystals heat-treated in an oxidizing environment
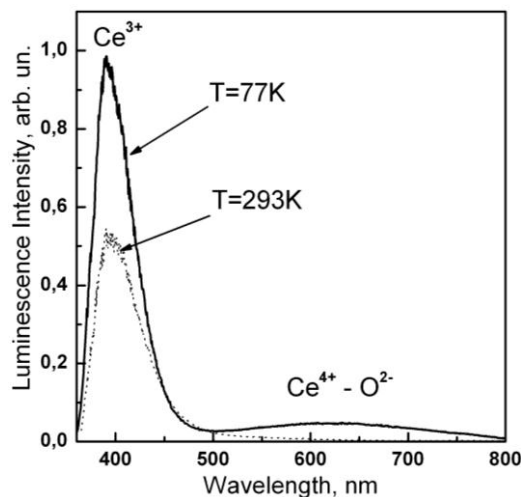

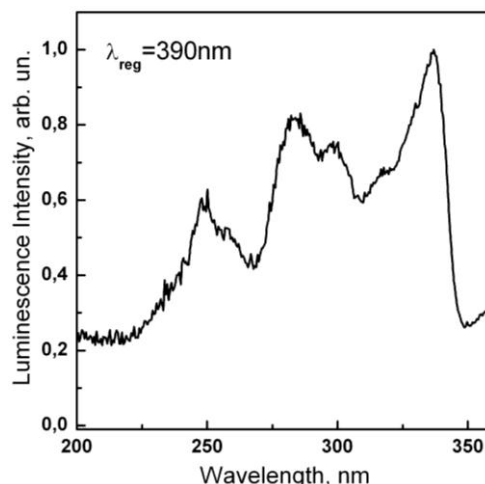**Fig. 6** – Luminescence spectrum of CeO_2 nanocrystals heat-treated in a reducing environment

Fig. 7 – Excitation spectrum of CeO_2 nanocrystals heat-treated in a reducing environment

The excitation spectrum of the band at 390 nm is significantly different from the charge transfer complex excitation band (Fig. 7).

The excitation spectrum contains characteristic bands corresponding to 4f-5d transitions of the Ce^{3+} ion. This band can be clearly attributed to 4f-5d transition of trivalent cerium.

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. 8).
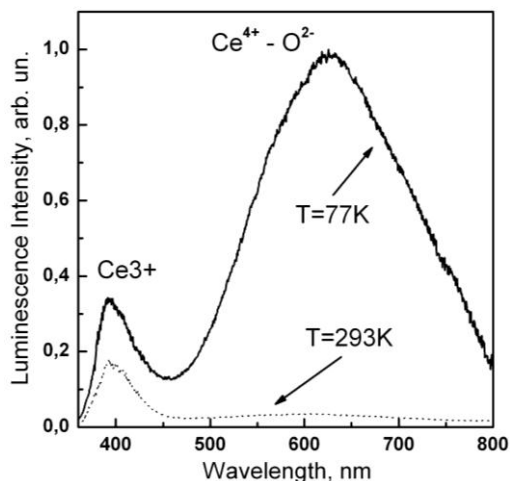

Fig. 8 – Luminescence spectrum of CeO_2 nanocrystals heat-treated in an inert environment

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 typical for bulk CeO_2 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_2 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^{4+} and O^{2-} ions, and Ce^{3+} ions stabilized by vacancies) after cerium oxide nanoparticles annealing in a neutral atmosphere has been observed.

REFERENCES

1. Z. Zhan, S.A. Barnett, *Science* **308**, 844 (2005).
2. D.R. Ou, T. Mori, H. Togasaki, M. Takahashi, F. Ye, J. Drennan, *Langmuir* **27**, 3859 (2011).
3. Z.C. Kang, Z.L. Wang, *Adv. Mater.* **15**, 521 (2003).
4. H. Imagawa, A. Suda, K. Yamamura, S. Sun, *J. Phys. Chem. C* **115**, 1740 (2011).
5. Z. Zhang, L. Yu, W. Liu, *Appl. Surf. Sci.* **256**, 3856 (2010).
6. D.M. Kempaiah, S. Yin, T. Sato, *Cryst. Eng. Comm* **13**, 741 (2011).
7. Y. Yoshida, S. Fujihara, *Eur. J. Inorg. Chem.* **2011**, 1577 (2011)
8. X.J. Yu, P.B. Xie, Q.D. Su, *Phys. Chem. Chem. Phys.* **3**, 5266 (2001).
9. P. Patsalas, S. Logothetidis, L. Sygellou, S. Kennou, *Phys. Rev. B* **68**, 035104 (2003).
10. T. Suzuki, I. Kosacki, H. Anderson, P. Colomban, *J. Am. Ceram. Soc.* **84**, 2007 (2001).
11. S. Tsunekawa, J.T. Wang, Y. Kawazoe, *J. Alloy. Compd.* **408**, 1145 (2006).
12. F. Zhang, S.W. Chan, J.E. Spanier, E. Apak, *Appl. Phys. Lett.* **80**, 127 (2002).
13. T. Sakata, H. Mori, *Chem. Mater.* **9**, 2197 (1997).
14. L. Tye, N.A. El-Masry, *Appl. Phys. Lett.* **65**, 3081 (1994).
15. B. Rzigalinski, *Technol. Cancer Res. T.* **4**, 651 (2005).
16. D. Bailey, L. Chow, S. Merchant, S.C. Kuiry, *Nat. Biotechnol.* **14**, 112 (2003).
17. B.A. Rzigalinski, K. Meehan, R.M. Davis, Y. Xu, W.C. Miles, C.A. Cohen, *Nanomedicine* **4**, 399 (2006).
18. M.D. Sturge, *Phys. Rev.* **127**, 768 (1962).
19. L.R. Morss, *Handbook on the Physics and Chemistry of Rare Earths* (New York: Elsevier Science: 1994).
20. G. Adachi, N. Imanaka, *Chem. Rev.* **98**, 1479 (1998).
21. D.J.M. Bevan, J. Kordis, *J. Inorg. Nucl. Chem.* **26**, 1509 (1964).
22. P. Dorenbos, *J. Phys.: Condens. Mat.* **15**, 8417 (2003).
23. E. Nakazawa, *J. Lumin.* **100**, 89 (2002).
24. A.A. Masalov, O.G. Viagin, I.I. Ganina, *Functional materials* **16**, 442 (2009).
25. O. Viagin, A. Masalov, I. Ganina, *Opt. Mater.* **31**, 1808 (2009).