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Formation of luminescent centers in CeO_2 nanocrystals

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ABSTRACT

The nature of luminescence centers in CeO_2 nanocrystals with varied oxygen stoichiometry has been investigated. It was shown that the luminescence of CeO_2 is caused by the radiative relaxation in two different optical centers: the first one is Ce^{4+}–O^{2-} charge transfer state and the second one is Ce^{3+} ions. The ratio of Ce^{4+}/Ce^{3+} centers depends on the amount of oxygen vacancies, therefore the variation of ceria stoichiometry allows changing the concentration of Ce^{4+}–O^{2-} and Ce^{3+} luminescence centers. Analysis of splitting of the excitation bands of Ce^{3+} luminescence has shown that oxygen vacancies in CeO_2 nanocrystals are formed at the nearest-neighbor position to the cerium ion.

1. Introduction

Cerium dioxide CeO_2 has found application in different technology fields. Ceria is widely used for catalysts, gas sensors, electrochromic and UV-protective coatings. [1–4]. The last ten years are characterized by sufficient interest to CeO_2 nanocrystals due to possible applications in the fields of electroluminescent devices, integrated optics and biomedicine [5–8]. As was shown in [9,10], ceria nanocrystals possess strong antioxidative activity associated with reversible $Ce^{4+} \leftrightarrow Ce^{3+}$ reduction/oxidation processes facilitated by high degree of non-stoichiometry of CeO_2 nanocrystals. CeO_2 has fluorite-type structure with FCC cubic lattice, each cerium cation is coordinated by eight oxygen anions. [11,12]. For ceria the formation of range of non-stoichiometric oxides CeO_{2-x} (with $x=0\ldots0.4$) 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. [1].

Optical properties of stoichiometric and oxygen-deficient ceria have been investigated previously [13,14]. The theoretical calculations of energy-band structure of CeO_2 were performed in [15,16]. In [17–19] the luminescent properties of CeO_2 nanocrystals doped with different rare-earth ions (Eu^{3+}, Sm^{3+}, Yb^{3+}–Er^{3+}) have been shown. In recent years some results concerning the luminescence properties of pure (undoped) CeO_2 have been obtained [19–22]. Luminescence of pure CeO_2 is usually assigned to crystal lattice defects formed by oxygen vacancies [9], but the obvious experimental evidences of this assumption are absent.

In this paper we have clarified the nature of luminescence in stoichiometric and oxygen-deficient CeO_2 nanocrystals and determined the microscopic feature of Ce^{3+} luminescent centers.

2. Experimental

CeO_2 nanocrystals were obtained by the Pechini method [23]. 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. To determine whether the luminescence of CeO_2 is connected with oxygen vacancies, the nanocrystals were annealed during 2 h in different atmospheres – oxidative (air), neutral (argon) and reducing (hydrogen) at 1000 °C. The corresponding samples are marked later as CeO_2(air), CeO_2(Ar) and CeO_2(H_2).

Luminescence spectra were obtained using spectrofluorimeter based on the grating monochromator, luminescence was excited by He–Cd laser with $\lambda_{exc}=325$ nm. Excitation spectra in 3.7–25 eV range were obtained at SUPERLUMI setup (DESY) in Hamburg,

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Germany using synchrotron radiation. The excitation spectra below the operation region of the SUPERLUMI station (3.7 eV) were measured using LUMINA fluorescence spectrometer by Thermo Scientific (USA). Decay curves were measured by the method of time-correlated single photon counting using Fluo-Time200 picosecond spectrofluorimeter (PicoQuant, Germany). Investigations were carried out at 300 K, 77 K and 10 K.

3. Results and discussion

X-ray diffraction patterns of obtained CeO_2 nanocrystals are shown in the Fig. 1. 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. According to X-ray and TEM data (Fig. 2) the average size of nanocrystals was about 50 nm.

Ceria is dielectric with band gap of about 6 eV with valence band formed by 2p oxygen energy states and conduction band formed by 5d and 6s cerium energy states [24,25]. Meanwhile, in the band gap of CeO_2 there is a narrow subband (from 0.5 to 1 eV, according to various authors) formed by 4f states of Ce^{4+}.

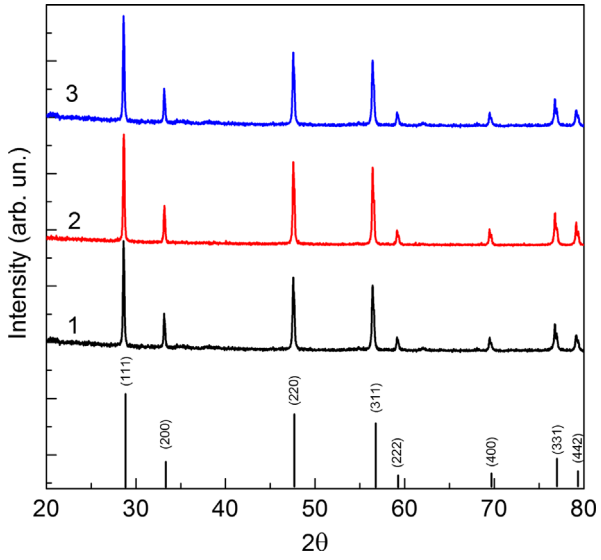

Fig. 1. XRD patterns of CeO_2 nanocrystals. 1 – CeO_2(Air); 2 – CeO_2(Ar); 3 – $CeO_2(H_2)$.

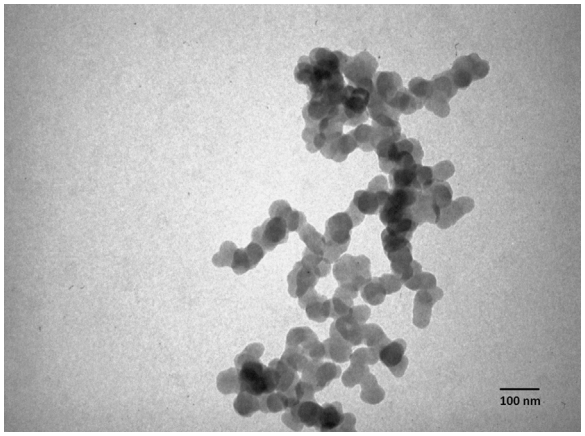

Fig. 2. TEM of CeO_2 nanocrystals.

Therefore, the optical gap in CeO_2 is only about 3.2 eV and optical properties of ceria are determined by charge transfer from 2p oxygen states to the empty 4f shell of Ce^{4+} [14].

In Fig. 3a luminescence spectra of CeO_2(air) at 77 K and 300 K under excitation in the charge-transfer (CT) band (3.8 eV) are shown. At 300 K the spectrum consists of the weak band with maximum at 600 nm. Temperature decrease to 77 K leads to sufficient increase of band intensity and shift band maximum to 630 nm. The width of the band is about 4000 cm^{-1} at 77 K. Approximation of temperature

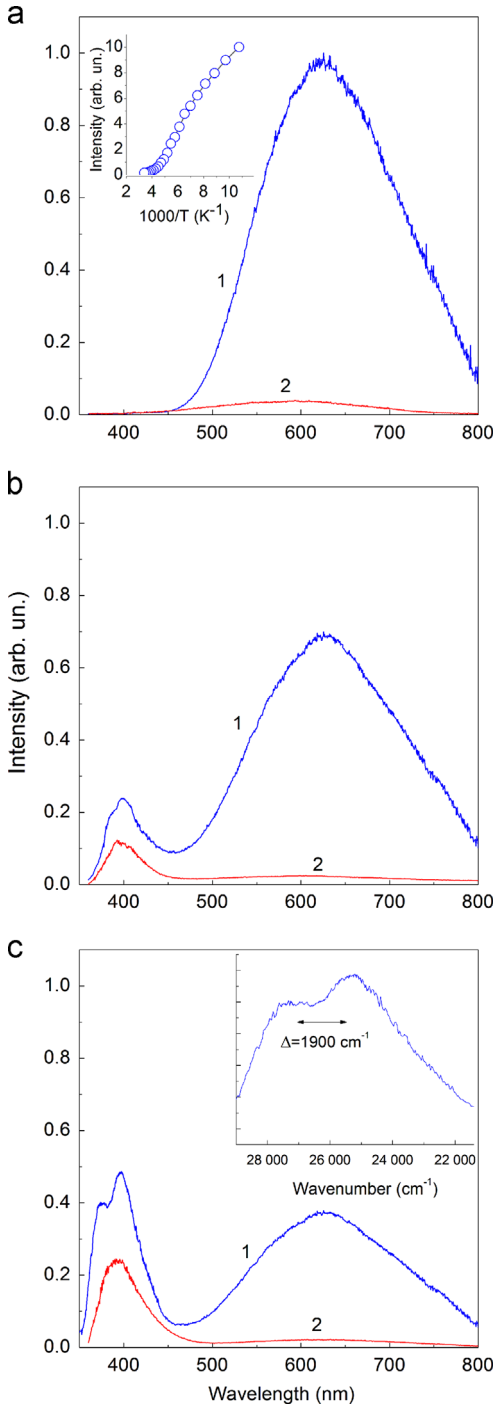

Fig. 3. Luminescence spectra of CeO_2(Air) (a), CeO_2(Ar) (b) and $CeO_2(H_2)$ (c) nanocrystals, λ_{exc}= 325 nm. 1 – T=77 K; 2 – T=300 K. Spectra are normalized on the luminescence intensity of CeO_2 (air) sample. The insets represent: (a) the Arrhenius plot of temperature dependence of band at 630 nm; (c) the part of luminescence spectrum of $CeO_2(H_2)$ at 77 K in cm^{-1}.