

Spectral-luminescent properties of siliceous films and powders activated with $[\text{Ce}^{3+}\text{O}_8\text{H}:\text{Tb}^{3+}]$ nanoparticles

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Nano- and microparticles of cerium dioxide having a cubic lattice with space group $Fm3m$, whose Ce^{4+} ions are partially substituted for Tb^{4+} and Tb^{3+} ions, are formed in the siliceous films and powders obtained with the help of the sol-gel technique. It is shown that saturation of the media with hydrogen leads to efficient sensitized luminescence from the 5D_4 state of Tb^{3+} ions due to the transfer of excitations from Ce^{3+} ions.

Keywords: cerium dioxide nanoparticles, luminescence, transfer of excitations.

1. Introduction

Glassy media activated with Tb^{3+} ions are promising for producing of various cathodoluminescent screens and optical reradiators [1–3]. In the last case, the main disadvantage of the media is a small light output at near UV excitation because of the high-frequency occurrence of intense absorption bands caused by the $4f^8 \rightarrow 4f^7({}^8S_{7/2})5d^1(T_2)$ and $4f^7({}^8S_{7/2})5d^1(E)$ interconfigurational transitions and a relatively low efficiency of excitation transfer from the known luminescence sensitizers in the disordered matrixes. For example, when Ce^{3+} [4, 5] and Sn^{2+} [6] are used as luminescence sensitizers of Tb^{3+} ions in the glasses, the efficiency of excitation transfer does not exceed 40 and 20%, respectively. Recently [7], it has been shown that co-doping of oxygen-vitrified silica gel-glasses with Ce and Tb can lead to formation of some share of complicated $\text{Ce}^{4+}\text{-Tb}^{3+}(\text{Tb}^{4+})$ -centers that represent cerium dioxide nanoparticles whose Ce^{4+} ions are partially replaced by Tb^{3+} or Tb^{4+} ions. These centers are characterized by an efficient intra-center transfer of excitations from labile photoreduced $(\text{Ce}^{4+})^-$ ions to Tb^{3+} ions in the 5D_4 state and quenching of the luminescence from this state by $\text{Ce}^{4+}\text{-O-Ce}^{3+}$ clusters [8, 9] and Tb(IV) oxo complexes [7] absorbing in the visible range of spectrum. Taking into account the fact

that the coordination number of Ce atoms is equal to 8 in the nanoparticles, we mark them as $[\text{Ce}^{4+}\text{O}_8:\text{Tb}^{3+}(\text{Tb}^{4+})]$. A hydrogen saturation of the glasses may be accompanied by complete suppression of the quenching factors due to the reduction of Ce^{4+} and Tb^{4+} ions in the triply-charged state and leads to a significant increase in the quantum yield of the sensitized luminescence of Tb^{3+} ions which can be close to 100%. Such high value of the yield after the saturation is caused by conservation of structure of the nanoparticles indicated above with inherent to them Ce–O–Tb chains with a nearly collinear configuration that provides a maximum overlap of “optical” orbitals of energy donors and energy acceptors. That permits us to mark the nanoparticles as $[\text{Ce}^{3+}\text{O}_8\text{H}:\text{Tb}^{3+}]$. At the same time, silica gel–glasses do not allow to form a large concentration of the nanoparticles into the ones that limit their applications, while the films and powders obtained by the sol–gel method allow to achieve this goal. Therefore the main aims of present work are to form both the $[\text{Ce}^{3+}\text{O}_8\text{H}:\text{Tb}^{3+}]$ nanoparticles in heavy doped siliceous films and powders prepared by the sol–gel method and to investigate their spectral-luminescent properties. Similar activated films and powders are promising for obtaining different reradiating screens and tubes as well as luminescent marks.

2. Materials and experimental procedure

The process of obtaining the films and powders included the preparation of sols by hydrolyzing tetraethylorthosilicate in a water-alcohol solution in the presence of hydrochloric acid as a catalyst. Then the prepared sols were aged and subsequently nitrate salts of cerium and terbium were dissolved in them in the concentration of 30 and 4 wt%, respectively. The co-doped sols were layer-by-layer deposited on silica substrates by spin-coating with following annealing in oxygen and hydrogen (for preparation of the luminescent films) or were dehydrated and subsequently treated with heat in oxygen and hydrogen (for preparation of the luminescent powder).

The phase analysis of the obtained samples was controlled on a DRON-2.0 X-ray diffractometer using Cu $K\alpha$ radiation. The nanostructure was examined with the LEO-1420REM scanning electron microscope. The spectra of steady-state luminescence and its excitation spectra were detected on an SFL-1211A spectrofluorimeter and corrected with regard to the spectral sensitivity of the recording system and spectral density distribution of the exciting radiation. These spectra were normalized by reducing their maximum to unity and presented in the form of the dependence of the number of quanta per unit interval of wavelengths $dN/d\lambda$ on the wavelength. The quantum yield of luminescence η was determined by the established procedure based on the comparison of the areas under the corrected luminescence spectra of the experimental samples and the standard, with allowance for the refraction indices and the fraction of exciting radiation absorbed by the samples. As a standard, we used the Sn-containing glass for which the value of η was determined by the direct method [8]. All spectral measurements were performed at $T = 298$ K.

3. Results and discussion

Figure 1 shows the micrographs of Ce–Tb-containing siliceous powder annealed in oxygen during 1 h at $T = 1000\text{ }^{\circ}\text{C}$. It is seen that the powder represents agglomerates with sizes of about $1\text{ }\mu\text{m}$ and more of individual particles with sizes $\sim 100\text{--}300\text{ nm}$ (see Fig. 1a). Relatively large sizes of the particles can be connected with the high temperature of their annealing. It is interesting to note that this powder includes some portion of ideal spherical particles with diameter of about $3\text{ }\mu\text{m}$ (see Fig. 1b) which, perhaps, arise from a colloidal aggregation of some oxides.

Figure 2 shows the X-ray diffraction pattern of Ce–Tb-containing siliceous powder whose micrographs are below. As can be seen, the pattern exhibits a large number of clear peaks among which the peaks at the angles $2\theta \approx 28.4^{\circ}$, 33.0° , 47.3° , 56.1° , 76.6° and 88.3° with relative intensities 1.0, 0.39, 0.62, 0.55, 0.22 and 0.20 are notable. These data are in satisfactory fit with the locations and intensities in the JCPDS-1996

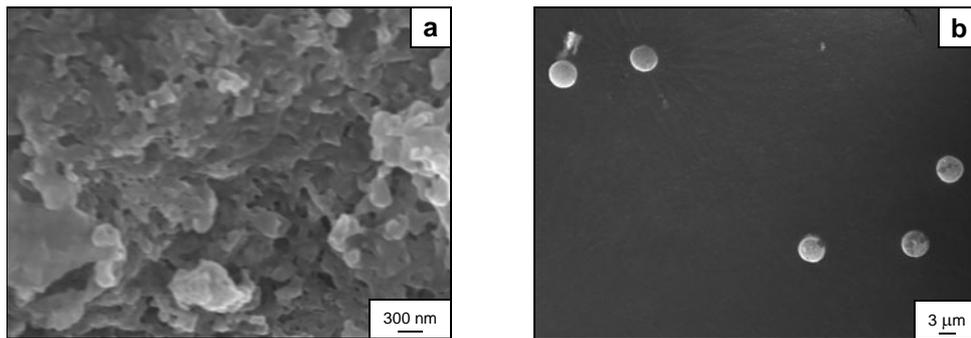


Fig. 1. Micrograph of Ce–Tb-containing siliceous powder.

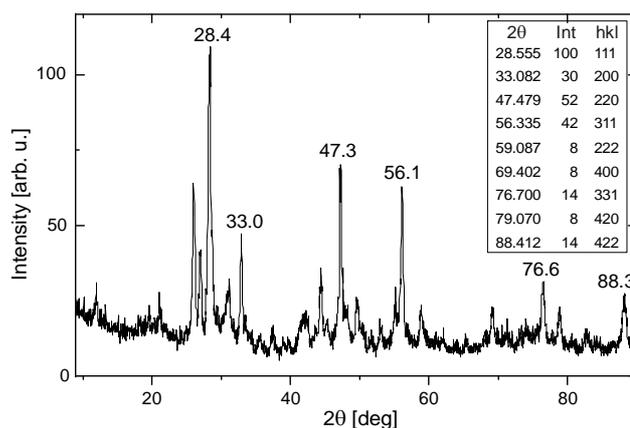


Fig. 2. X-ray diffraction patterns of Ce–Tb-containing siliceous powder and data of JCPDS-1996 Powder Diffraction File No. 34-0394 (inset).

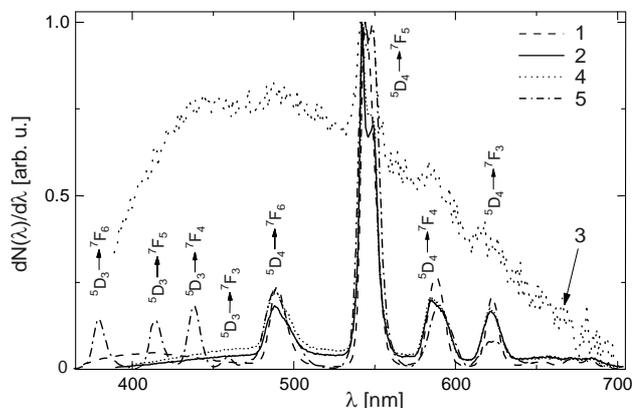


Fig. 3. Corrected and normalized luminescence spectra of siliceous powder (1) and films (2–5) doped with terbium (1–5) and co-doped with cerium (1–4) after annealing in air (5), hydrogen (4), oxygen (1–3) and additional annealing in hydrogen (1, 2); $\lambda_{\text{exc}} = 330$ nm (1–4) and $\lambda_{\text{exc}} = 220$ nm (5); $\Delta\lambda_{\text{exc}} = 5\Delta\lambda_{\text{rec}} = 5$ nm.

Powder Diffraction File No. 34-0394 for the CeO_2 cubic lattice with the space group $Fm\bar{3}m$ (see inset) that permits us to conclude about the formation of an essential share of the CeO_2 micro- and nanocrystals. The other relatively clear peaks at $2\theta \approx 26.0^\circ$ and 27.0° in the pattern are probably caused by some cerium silicate. According to Warren procedure [10], we estimated the average crystal particle size from the line broadening at $2\theta \approx 28.4^\circ$ which appeared to be equal to 300 nm, which is in good agreement with the micrographs data. For the siliceous film with the identical to the powder composition, X-ray diffraction pattern corresponds to the amorphous phase having only one very weak peak at $2\theta \approx 28.4^\circ$. It can testify to the absence of the conditions for formation of sufficiently large crystalline nanoparticles in the film.

Figure 3 shows the luminescence spectra of Ce–Tb-containing siliceous powder (curve 1) and an 8-layered film (curve 2), prepared by the methods indicated in the section 2, at excitation in the $4f^1 \rightarrow 4f^05d^1$ interconfigurational transition of Ce^{3+} ions ($\lambda_{\text{exc}} = 330$ nm). By comparison, the luminescence spectra of similar films before annealing in hydrogen (curve 3) and annealed in hydrogen without annealing in oxygen (curve 4) are displayed too. In addition, the luminescence spectrum (curve 5) of air-annealed film obtained from the sol doped only by terbium nitrate with concentration of Tb the same as the one in the co-doped film at excitation in the interconfiguration transition of Tb^{3+} ions ($\lambda_{\text{exc}} = 220$ nm) is shown here. It is seen that the oxygen-annealed Ce–Tb-containing film, before annealing in hydrogen, is characterized by a broad band caused by luminescence of residual Ce^{3+} ions from the lower $5d$ -sublevel and a series of narrow bands, in the broad band long-wavelength side, caused by luminescence of residual Tb^{3+} ions from the 5D_4 state. The powerful noise in the spectrum testifies about very weak intensity of the bands that we can connect with quenching of the luminescence of both ions by the $\text{Ce}^{4+}\text{--O--Ce}^{3+}$ clusters [8, 9] and Tb(IV) oxo complexes. After annealing of the film in hydrogen, the Tb^{3+}

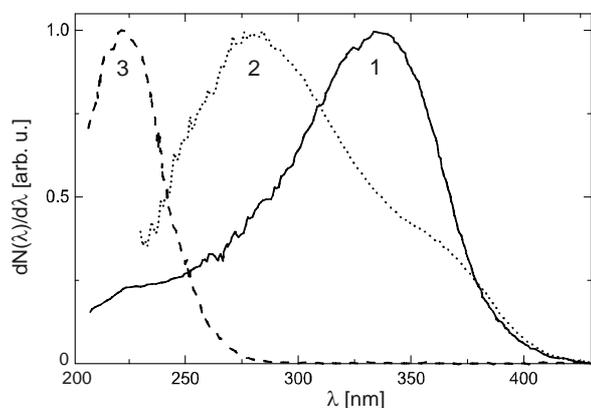


Fig. 4. Corrected and normalized luminescence excitation spectra of siliceous films (1, 3) and powder (2) doped with terbium (1–3) and co-doped with cerium (1, 2) after annealing in air (3) and in oxygen (1, 2) with additional annealing in hydrogen; $\lambda_{\text{rec}} = 545$ nm.

ions luminescence increases many times, whereas the share of quanta radiated by the Ce^{3+} ions significantly decreases. A similar situation takes place for the similarly subsequently annealed Ce–Tb-containing powder too. That testifies to the effective transfer of excitations from Ce^{3+} to Tb^{3+} , which can be realized in the $[\text{Ce}^{3+}\text{O}_8\text{H}:\text{Tb}^{3+}]$ nanoparticles indicated above. On the other hand, the relatively small increase in the quanta share for the film annealed only in hydrogen (*cf.* curves 2 and 4) may be caused by small Ce–Tb distance due to the large lanthanides concentration and, correspondingly, by an effective sensitization of the Tb^{3+} luminescence too. Judging from the absence in the spectra 2 and 1 of luminescence bands from the 5D_3 state of Tb^{3+} ions, which is present in the spectrum of the Tb-containing film (see curve 5 at $\lambda < 470$ nm), the excitations transfer occurs to the 5D_4 state. At the same time, relative intensities of the individual ${}^5D_4 \rightarrow {}^7F_j$ bands and the position of the broad band visibly differ in the spectra 1 and 2. It permits us to conclude that there is a difference in the complicated Ce–Tb-centers structure in the powder and film.

Figure 4 shows the luminescence excitation spectra of Ce–Tb-containing siliceous an 8-layered film (curve 1) and powder (curve 2), prepared by the methods indicated in the section 2, at recording in the ${}^5D_4 \rightarrow {}^7F_5$ band ($\lambda_{\text{rec}} = 545$ nm). By comparison, the same name spectrum of air-annealed film obtained from the sol doped only by terbium with the concentration equal to one in the co-doped film is displayed too (curve 3). It is seen that the spectrum of the latter film is characterized by an intense broad band at $\lambda \approx 225$ nm caused by the $4f^8 \rightarrow 4f^7({}^8S_{7/2})5d^1(E)$ interconfigurational transition of Tb^{3+} whose intensity more than two orders of magnitude exceeds the intensity of these ions parity-forbidden intraconfigurational transitions situated in the region 300–380 nm. A new relatively long-wavelength, more intense band caused by the $4f^1 \rightarrow 4f^05d^1$ interconfigurational transition of Ce^{3+} ions arises in the spectra of the Ce–Tb-containing samples. It is notable that the position and shape of the new band essentially differs for the powder and film (*cf.* curves 1 and 2), which is

an additional confirmation of the above conclusion concerning the differences in structure of Ce–Tb optical centers in the powder and film. Here, it should be noted that the excitation spectra of Ce–Tb-containing film and powder are superimposed on the ${}^7F_6 \rightarrow {}^5D_3$ absorption band lying at 380 nm. This leads to the transfer of excitations from the lowest Ce^{3+} excited state only to the 5D_4 state of Tb^{3+} ions.

These results should be supplemented by the information that quantum yield of luminescence of the oxygen-annealed film co-doped with cerium and terbium after annealing in hydrogen exceeds 90%. Such high value of η in spite of the removal of $\text{Ce}^{4+}\text{--O--Ce}^{3+}$ clusters and Tb(IV) oxo complexes is possible only at the absence of Tb–O–Tb chains with inherent to them cross-relaxation quenching of luminescence. Apparently, the $[\text{Ce}^{4+}\text{O}_8]$ nanoparticles do not allow to form the chains at replacement of Ce by Tb.

4. Conclusions

Siliceous films and powders heavy doped with Ce and Tb have been prepared by the sol–gel method. The $[\text{Ce}^{4+}\text{O}_8:\text{Tb}^{3+}(\text{Tb}^{4+})]$ cubic nano- and microparticles with the $Fm\bar{3}m$ space group are formed in the media. It has been shown that the particles, after the transformation to the $[\text{Ce}^{3+}\text{O}_8\text{H}:\text{Tb}^{3+}]$ particles at saturation of the media with hydrogen, display an effective sensitized luminescence of their Tb^{3+} ions. The complicated Ce–Tb optical centres structure is not completely identical in the films and powders.

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