INFLUENCE OF COORDINATION ENVIRONMENT AND DIELECTRIC CONTRAST ON THE SPECTRAL-LUMINESCENT PROPERTIES OF EUROPIUM IONS IN THE PORES OF FILM OPALS

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The photoluminescence spectra of the inorganic salt of europium $C_6H_9EuO_6 \times H_2O$ in the pores of film opals, with globule diameter $D \approx 300$ nm on a glass substrate, were measured. In the measured spectra the radiative transitions in the energy spectrum of Eu^{3+} $^5D_0 \to {}^7F_0$, $^5D_0 \to {}^7F_1$, and $^5D_0 \to {}^7F_2$ were observed at wavelength 580 nm, 592 nm and 617 nm, respectively. The presence in the luminescence spectra of the maximum possible number of components of the Stark structure of the $^5D_0 \to {}^7F_J$ (J=1–2) transitions, equal to $2J+1$, and the high intensity of the $^5D_0 \to {}^7F_0$ transition indicate that the symmetry of the luminescence centers is low, not higher than C_3. The dependence of the luminescence spectra on the additional impregnation of the samples with glycerol was established: smoothing of the Stark structure and broadening of the $^5D_0 \to {}^7F_2$ band were observed, as well as a decrease in the ratio of integrated intensities $I(^5D_0 \to {}^7F_2) / I(^5D_0 \to {}^7F_1)$ from 3.6 to 1.9.

Keywords: photonic crystal, film opals, inorganic salt of europium, hypersensitive transition, photoluminescence spectra, Stark effect, dielectric contrast.

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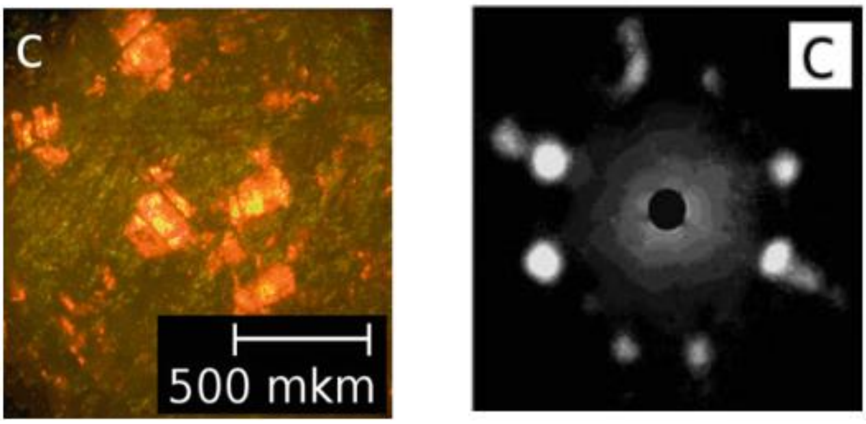
1. Introduction

Synthetic opals are widely used as three-dimensional space-periodic structures with a face-centered cubic lattice to create regular matrix nanocomposites based on them. Due to the periodic modulation of the permittivity, they have band gaps for photons. The creation and study of the optical properties of new luminescent materials based on synthetic opals and rare earth elements are of both fundamental and practical interest. Such materials combine the photonic-crystal properties of synthetic opals [1] and narrow bands in the luminescence spectra of rare-earth ions [2], which makes it possible to create new efficient light sources as well as luminescent sensors of pressure, temperature, and humidities. Erbium (Er^{3+}), europium (Eu^{3+}), and terbium (Tb^{3+}) are shown to be promising materials for filling opal pores with both regular (photonic crystal) and random distribution of silicon dioxide globules (photonic glass) [3]. In the latter case, due to intense multiple scattering, the light is retained in the active medium consisting of rare-earth ions, and omnidirectional laser radiation can be generated [4, 5].

This work is devoted to studying the influence of the dielectric contrast and the structure of the coordination environment of europium ions in the pores of film opals on the photoluminescence spectra.

2. Experiment

In this work, films of synthetic opals were used as initial matrices. The film preparation process consisted of two stages. At the first stage, by the method of slow alkaline hydrolysis of tetraethoxysilane (TEOS) in a water-alcohol medium [6], spherical particles of amorphous silica (α-SiO_2) of a given diameter were obtained ($\approx$ 300 nm). The reaction of formation of the lot of polysilicon acids and the subsequent formation of material from them, close in composition to stoichiometric α-SiO_2, stopped when using TEOS. At the second stage, to prepare film opals from a suspension of monodisperse silicon dioxide globules, we used the method of globule deposition in the region of a movable meniscus onto a vertical glass substrate during solvent evaporation. Typical defects and polydomain structures of film opals are clearly visible in an optical microscope and appear on the optical diffraction patterns of film opals (Fig. 1) [7].



a b

Fig. 1. Photos of the surface (a) and the optical diffraction pattern (b) of the same area (C) of film opal [7].

In order to characterize the samples of film opals, reflectance spectra were measured. The spectra were measured in reflected light at an angle of incidence with respect to the film plane (111) $\theta \approx 15^{O}$. To eliminate the influence of the glass substrate, the measured reflection spectrum was divided by the spectrum of the lamp. Weak reflection maxima with a half-width of 70 – 100 nm were observed. No interference spectrum of light reflected from the two surfaces of the film was observed. This indicates a weakly pronounced stop-band due to its filling with defective states [8]. The position of the center of the stop-band (λ_C) and the diameter of the globules (D) were determined from the reflection spectra using the Bragg law: $\lambda_C = 2d/k\ [n^2(\lambda) - sin^2\theta]^{1/2}$, where $n = n_{SiO2}(\lambda) \times f_{SiO2} + n_{air} \times (1 - f_{SiO2})$, $n_{SiO2} \approx 1.36$, $f_{SiO2} = 0.74$, $d = D\ (2/3)^{1/2}$.

Next, we carried out the impregnation of the film opals samples in an aqueous solution of salt $C_6H_9EuO_6 \times H_2O$ (99.9%) (Sigma-Aldrich) with subsequent drying at a temperature of 23°C. Electron microscopic studies have established that the salt in the polycrystalline state is deposited in a thin layer on the inner surface of the pores [9].

To reveal photonic-crystal effects in the luminescence spectra of europium ions in the pores of film opals, the region of the film infiltrated with salt was additionally impregnated with an aqueous solution of glycerol to reduce the dielectric contrast $(n_1^2)/(n_2^2)$, $(n_1 > n_2)$. In this case, the dielectric contrast decreased from 1.85 to 1.13.

The photoluminescence spectra of the inorganic europium salt $C_6H_9EuO_6 \times H_2O$ were measured in the initial state in an optical cell and in the pores of film opals with a globule diameter of $D \approx 300$ nm on a glass substrate. The excitation of the samples was carried out in the "reflection" geometry from the (111) plane by the radiation of diode-pumped solid-state laser with $\lambda_{ex} = 532$ nm in the absorption band $^5D_1 \leftarrow {}^7F_1$ (*hypersensitive transition*). The spectra were measured using a DFS-12 double monochromator and a recording system in the photon counting mode with accumulation (Fig. 2). At the first stage, the luminescence spectra of the initial salt in the free state were measured (Fig. 3).

On the spectrum of the starting salt ($C_6H_9EuO_6 \times H_2O$) (Fig. 3) there are distinctive europium lines at 580 nm, 593 nm and 618 nm, which correspond to the typical transitions of this rare-earth element, such as $^5D_0 \rightarrow {}^7F_J$, where $J = 0, 1, 2$ [2]. The presence in the luminescence spectra of the maximum possible number of components of the Stark structure of the $^5D_0 \rightarrow {}^7F_J$ ($J = 1–2$) transitions, equal to $2J+1$, and the high intensity of the $^5D_0 \rightarrow {}^7F_0$ transition indicate that the symmetry of the luminescence centers is low, not higher than C_{2v}.

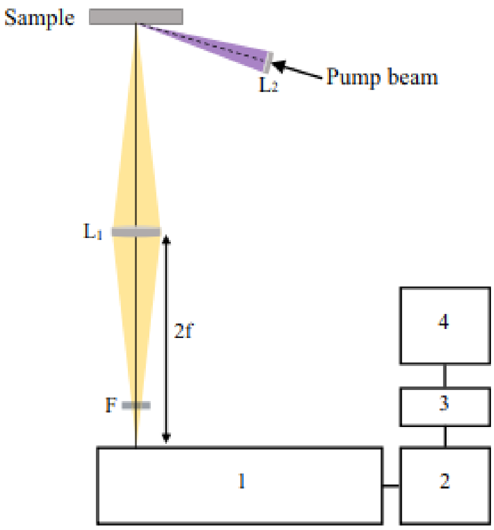


Fig. 2. Optical scheme of sample excitation and photoluminescence registration system: 1 – monochromator DFS-12, 2 – photomultiplier tube FEU-79, 3 – analog-to-digital converter, 4 – PC.

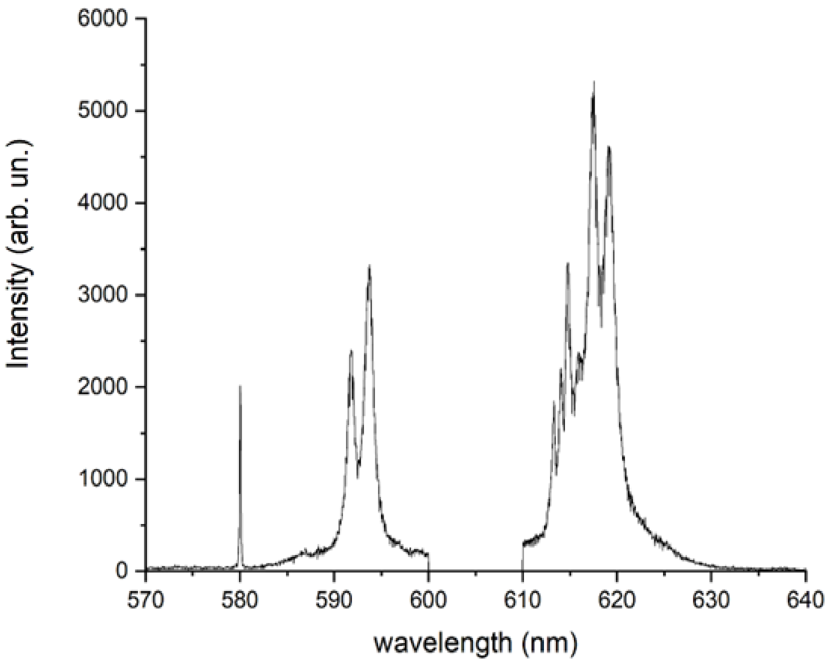


Fig. 3. Photoluminescence spectrum of the starting salt Europium (III) acetate hydrate ($C_6H_9EuO_6 \times H_2O$) in polycrystalline state in an optical cell.

3. Results and discussions

The photoluminescence spectrum of the film opal samples infiltrated by europium there are distinctive europium lines at 580 nm, 593 nm and 618 nm, which correspond to the typical transitions of this rare-earth element, such as $^5D_0 \rightarrow {}^7F_J$, where J = 0, 1, 2 (Fig. 4 and Fig. 5).

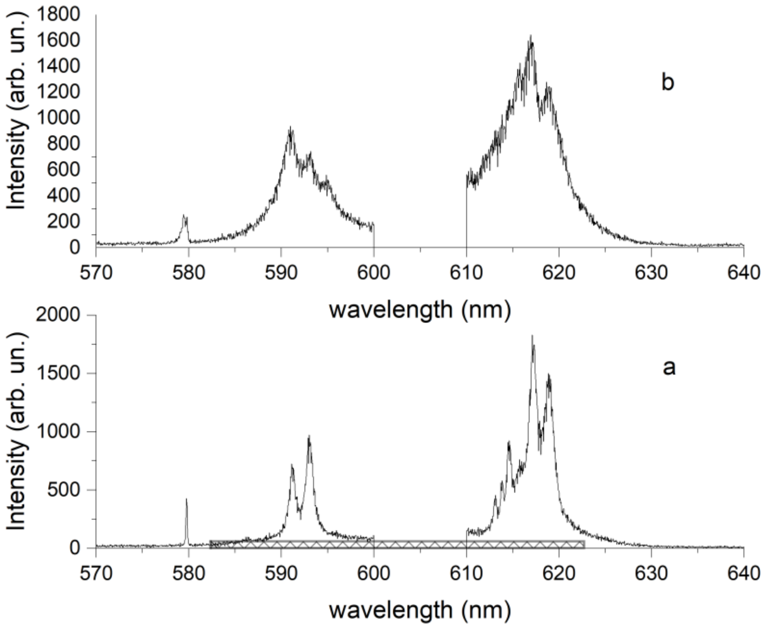


Fig. 4. Photoluminescence spectrum of the film opal with λ_C = 613 nm and *D* = 301 nm: a – salt in the pores in the polycrystalline state; b – after additional impregnation of salt infiltration area with glycerol; the shaded strip on the wavelength scale is the position and width of the stop-band.

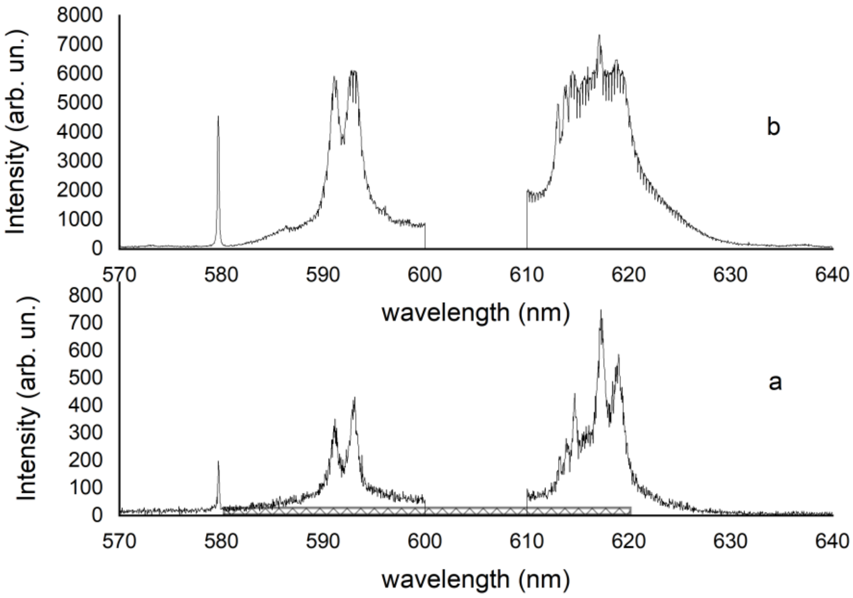


Fig. 5. Photoluminescence spectrum of the film opal with λ_C = 600 nm and *D* = 294 nm: a – salt in the pores in the polycrystalline state; b – after additional impregnation of salt infiltration area with glycerol; the shaded strip on the wavelength scale is the position and width of the stop-band.

Significant photonic-crystal effects were not revealed with a decrease in the dielectric contrast, which may be due to a weakly pronounced stop-band due to its filling with defect states.

The observation of the quite intense $^5D_0 \rightarrow ^7F_0$ transition is an indication that the Eu^{3+} ion occupies a site with C_3 symmetry [2]. Peak splitting for the $^5D_0 \rightarrow ^7F_0$ transition, shows that more than one Eu^{3+} position is present (Fig. 4, b). The splitting value in this case was 12 cm^{-1}. The $^5D_0 \rightarrow ^7F_1$ transition is a magnetic dipole transition. The intensity of a magnetic dipole transition is independent of the environment of the Eu^{3+} ion. The $^5D_0 \rightarrow ^7F_1$ transition directly reflects the splitting of the $^7F_1$ level by the crystal field. In hexagonal, tetragonal, and trigonal crystal fields, the $^7F_1$ level splits into a nondegenerate and doubly degenerate level. In orthorhombic or lower symmetry, the degeneracy is completely removed by the crystal field, which leads to three sublevels for $^7F_1$ [2]. As can be seen from Fig. 4, b, additional impregnation of film opal area infiltrated with europium salt with glycerol lowers the symmetry of the environment of the europium ion. In this case, the splitting value was 54 - 58 cm^{-1}. The $^5D_0 \rightarrow ^7F_2$ transition is a "*hypersensitive transition*". Its intensity is much more influenced by the local symmetry of the Eu^{3+} ion and the nature of the ligands. Instead of absolute intensity of the $^5D_0 \rightarrow ^7F_2$ transition, intensity ratio $I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$ used to detect changes in the environment of the europium ion. Preliminary estimates show that for both samples (Fig. 4 and Fig. 5) the ratio of integrated intensities $I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$ decreases from 3.6 to 1.9 after additional impregnation with glycerol. In addition, a noticeable broadening of the transition band $^5D_0 \rightarrow ^7F_2$ was observed.

4. Conclusions

1. In the luminescence spectrum of europium ions in the composition of salt in the pores of film opals, bands are observed corresponding to the transitions of europium ions $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$. In this case, no significant photonic-crystal effects were revealed.

2. The presence in the luminescence spectra of the maximum possible number of components of the Stark structure of the $^5D_0 \rightarrow ^7F_J$ ($J = 1–2$) transitions, equal to $2J + 1$, and the quite high intensity of the $^5D_0 \rightarrow ^7F_0$ transitions indicates a low symmetry of the luminescence centers, not higher than C_3.

3. With a decrease in the dielectric contrast $(n_1 / n_2)^2$ after additional impregnation of the salt infiltration zone with an aqueous solution of glycerol (85%) from 1.85 to 1.13, a smoothing of the spectrum of the Stark structure of band splitting and noticeable broadening of the transition band $^5D_0 \rightarrow ^7F_2$ were observed.

4. Additional splitting of the band forbidden for electron-dipole transitions ($^5D_0 \rightarrow ^7F_0$) with a value of 12 cm^{-1} was observed, which indicates the presence of two positions of europium ions in the salt structure in the pores of film opal.

5. Additional splitting of the band corresponding to the magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) with a value of 54 – 58 cm^{-1} was observed, which indicates a change in the polarizability of the medium surrounding europium ions in the pores of film opal.

6. The ratio of integrated intensities $I(^5D_0 \rightarrow ^7F_2) / I(^5D_0 \rightarrow ^7F_1)$ decreases from 3.6 to 1.9.

The observed changes may indicate disordering of the ligands in the coordination environment of the europium ion in the pores of film opals after additional impregnation of samples with glycerol.

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