Luminescent properties of nanocomposite - Bi$_{12}$SiO$_{20}$, filled with C$_6$H$_9$EuO$_6$ × H$_2$O

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Abstract. The work presents the results of the study of the photoluminescence spectra of the (111) growth surface of an opal - Bi$_{12}$SiO$_{20}$ matrix nanocomposite filled with europium (III) acetate hydrate (C$_6$H$_9$EuO$_6$ × H$_2$O). An increase in the integral luminescence intensity of the matrix composite opal - Bi$_{12}$SiO$_{20}$: Eu$^{3+}$ compared to composite opal: Eu$^{3+}$ was found. The measured photoluminescence spectra of the Bi$^{3+}$ ions in the opal pores indicate its participation in optical processes as a co-activator of luminescence. A change in the character of the splitting of the main luminescence bands of Eu$^{3+}$ ions in the region of 575–635 nm and the integral luminescence intensity after dehydration of the crystalline hydrate in opal pores has been established.

1. Introduction
The fabrication and research of the optical properties of new luminescent materials on the basis of synthetic opals is of both fundamental and practical interest. In [1-3] it is shown that erbium (Er$^{3+}$), europium (Eu$^{3+}$) and terbium (Tb$^{3+}$) are promising materials for filling opal pores. Of particular interest from the scientific and practical points of view are opal nanocomposites - active dielectric activated by fluorescent centres.

This work is devoted to the study of the influence of nanocrystalline behavior and photonic crystal effects on the photoluminescence spectra of opal - Bi$_{12}$SiO$_{20}$ nanocomposite infiltrated with salt europium (III) acetate hydrate (C$_6$H$_9$EuO$_6$ × H$_2$O).

Bulk synthetic opals were grown by slow crystallization of monodisperse colloidal suspension of globules α-SiO$_2$ synthesized by the modified Stober method [4]. The hydrolysis of tetraethoxysilane was carried out in an aqueous-alcoholic medium in the presence of ammonia as a catalyst. The molar ratio of the components in the reaction mixture was: NH$_4$OH : H$_2$O : C$_2$H$_5$OH : Si(OCH$_3$)$_4$ = 1 : 3 : 19-21 : 11 : 0.14. Synthetic opals were obtained by the method of natural sedimentation under isothermal conditions at T = 20°C. In this work, samples of bulk synthetic opals consisting of monodisperse α-SiO$_2$ globules forming a face-centered cubic (FCC) lattice were studied. The size of bulk samples averaged 7×7×1.5 mm$^3$. A typical view of the initial globules (transmission electron microscope) and the surface of samples of synthetic opal after high-temperature annealing at T = 850°C (Electron Probe Microanalyzer JEOL - JXA-8200) are presented in figure 1.
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Figure 1. The photograph of the initial globules (a) and the photograph of the surface of the initial opal after high-temperature annealing at T=850°C (b).

As can be seen from figure 1, (b) after high-temperature annealing of the opal sample, the globules are sintered and acquire a hexagonal shape, while the pore size decreases. For samples of the initial opals used in the work, the values of the diameter of the globules and the interplanar distance were D = 300 nm d = 245 nm. The spectral position of the center of the photon stop-band for the samples of the initial opals was 602 nm (θ = 20°) according to the measurement results. The fabrication of opal - Bi$_{12}$SiO$_{20}$ nanocomposite was carried out by filling the pores of opal samples with the melt of single crystal Bi$_{12}$SiO$_{20}$ (BSO) under the action of capillary forces. The fact of filling the pores of opal with melting was detected by the shift of the band maximum of a Bragg reflection in the wavelength region. Due to the high refractive index of BSO crystals (n = 2.54; λ = 632.8 nm). To detect the peak of the Bragg diffraction of light in the visible region of the spectrum, large reflection angles were used (60°). The spectral position of the photonic stop-band for the opal matrix nanocomposite Bi$_{12}$SiO$_{20}$, according to the measurement results, was 615 nm (θ = 60°). Based on the comparison the position of the maximum of the measured reflection spectrum of nanocomposite sample and the calculated value of $\lambda_{m}$, under the condition of 100% filling of the pores with BSO melt, the percentage of filling the pores was determined, which was ~ 50% of volume.

2. Results

For the opal - Bi$_{12}$SiO$_{20}$ matrix nanocomposite, it was found that the substance in the opal pores is in the crystalline state. This is confirmed by both, the characteristic form of the measured Raman spectra (LabRam HR800 confocal Raman microscope with radiation $\lambda = 632.8$ nm) and x-ray diffractogram (X-ray diffractometer PW3040/60) (figure 2). According to the Raman spectra and x-ray diffraction analysis in addition to Bi$_{12}$SiO$_{20}$, the phase of bismuth orthosilicate (Bi$_4$Si$_3$O$_{12}$) was revealed in the opal pores. Comparison of our results with literature data on Raman spectra [5, 6] and X-ray diffraction analysis [7, 8] allowed to establish a dominant presence in the pores of opals nanocrystals of bismuth orthosilicate Bi$_4$Si$_3$O$_{12}$, which is formed in the pores of the opal due to the interaction of the BSO melt with the structure of SiO$_2$ globules.
Next, we carried out the impregnation of the samples of the nanocomposite in an aqueous solution of salt $\text{C}_6\text{H}_9\text{EuO}_6 \times \text{H}_2\text{O}$ (99.9%) (SIGMA-ALDRICH) with subsequent drying at a temperature of 23°C. Excitation of photoluminescence spectra was carried out in the geometry of "reflection" from the plane (111) of the sample by radiation of a semiconductor laser with $\lambda_{\text{ex}} = 405$ nm. The spectra were recorded in [111] ($\theta = 0°$) direction and for $\theta = 30°$ and $60°$ angles with [111] axis by a modified laser spectrometer based on the DFS-12 double monochromator (figure 3). The signal from the photomultiplier tube (FEU-79) after preamplification was recorded in the one-electron pulse counting

Figure 2. The Raman spectra (a) and X-ray diffractogram (CuKα – radiation) of the opal - Bi$_{12}$SiO$_{20}$ sample, on which the most intense peaks correspond to the crystal phase Bi$_4$Si$_3$O$_{12}$ (b)
with accumulation mode. For comparison, the photoluminescence spectra of the salt solution and the essential opal infiltrated with C₆H₉EuO₆ × H₂O were measured.

![Optical scheme of sample excitation and photoluminescence registration system](image)

**Figure 3.** Optical scheme of sample excitation and photoluminescence registration system: 1 - monochromator DFS-12, 2 - FEU-79, 3 - ADC, 4 - PC.

In figure 4 the measured photoluminescence spectra of Eu³⁺ ions under different conditions are presented.

![Photoluminescence spectra](image)

**Figure 4.** Photoluminescence spectra of an aqueous solution of salt (1), essential opal (2), and nanocomposite opal - Bi₁₂SiO₂₀, Bi₄Si₃O₁₂ (3), infiltrated with C₆H₉EuO₆ × H₂O, measured in the [111] direction.

In the measured spectra, radiative transitions in the energy spectrum of europium ions ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₁, and ⁵D₀ → ⁷F₂ were observed for wavelengths of 580 nm, 592 nm, and 619 nm, respectively. The following regularities were established: a) the redshift of the photoluminescence spectrum of Eu³⁺ ions in the opal and nanocomposite pores by 3 nm compared to the luminescence spectrum of the salt solution; b) the increase of the integrated intensity of luminescence of europium
ions in the pores of the nanocomposite (figure 4); c) the dependence of the intensity of the glow from the direction of observation. The strongest angular dependence was demonstrated by the forbidden electrodipole transition with $\lambda_{\text{max}} = 580$ nm (figure 5).

![Figure 5](image)

**Figure 5.** The dependence of the photoluminescence spectra of the nanocomposite opal - Bi$_{12}$SiO$_{20}$, Bi$_4$Si$_3$O$_{12}$, infiltrating by salt C$_6$H$_9$EuO$_6$ $\times$ H$_2$O from the direction of observation: 1 $- \theta = 0$, 2 $- \theta = 30^\circ$, 3 $- \theta = 60^\circ$.

The salt C$_6$H$_9$EuO$_6$ $\times$ H$_2$O introduced into the opal pores forms a crystalline hydrate in which the water molecule is coordinated with the europium cation Eu$^{3+}$. After annealing the sample at 150°C for 1 hour, the dehydration resulted in the decomposition of the crystalline hydrate. The coordination environment of the europium ion changed. In this case, the photoluminescence spectra acquired the form shown in figure 6.

![Figure 6](image)

**Figure 6.** The photoluminescence spectra of the opal nanocomposite - Bi$_{12}$SiO$_{20}$, Bi$_4$Si$_3$O$_{12}$, infiltrated with salt C$_6$H$_9$EuO$_6$ $\times$ H$_2$O, measured in the [111] direction before (1) and after decomposition of the crystalline hydrate (2).

In order to clarify the mechanism for increasing the integral intensity of europium ions emission in the pores of the nanocomposite, we measured the photoluminescence spectra of the Bi$_{12}$SiO$_{20}$ crystal.
and the control sample Bi$_4$Si$_3$O$_{12}$. A control sample of the crystalline phase Bi$_4$Si$_3$O$_{12}$ was obtained by melting polycrystalline Bi$_{12}$SiO$_{20}$ powder at a temperature of 996°C, followed by recrystallization under the same temperature conditions in which the BSO melt was filled into the opal pores. Figure 7 (a) shows the photoluminescence spectra of the Bi$_{12}$SiO$_{20}$ crystal and the control sample Bi$_4$Si$_3$O$_{12}$, and figure 7 (b) shows the photoluminescence spectrum of Bi$_{12}$SiO$_{20}$ and Bi$_4$Si$_3$O$_{12}$ in opal pores.

![Figure 7](image)

Figure 7. Photoluminescence spectra of a Bi$_{12}$SiO$_{20}$ crystal (1) and a control sample of Bi$_4$Si$_3$O$_{12}$ (2) (a) and photoluminescence spectra of the nanocomposite opal - (Bi$_{12}$SiO$_{20}$, Bi$_4$Si$_3$O$_{12}$) with the results of decomposition into spectral components (b). All spectra are given to the same amount of substances.

As can be seen from figure 7, a photoluminescence spectrum of Bi$_4$Si$_3$O$_{12}$ is shifted towards short wavelengths and has a markedly lower intensity. The photoluminescence spectrum of the nanocomposite opal - (Bi$_{12}$SiO$_{20}$, Bi$_4$Si$_3$O$_{12}$), is the total contribution to the luminescence from Bi$_{12}$SiO$_{20}$ and Bi$_4$Si$_3$O$_{12}$. At the same time, the position and intensity ratio of the spectral components in the spectrum of the composite opal (Bi$_{12}$SiO$_{20}$, Bi$_4$Si$_3$O$_{12}$) differs from the photoluminescence spectra of the original Bi$_{12}$SiO$_{20}$ and Bi$_4$Si$_3$O$_{12}$ crystals (Figure 7 (b)). The reason for this may be the nanocrystalline state of substances formed in the pores of the opal. The electronic properties of nanocrystals have a number of features associated with quantum-size effects and the large contribution of electronic states localized at the interfaces. In addition, as established in the present work, the dominant presence of bismuth orthosilicate nanocrystals in the opal pores occurs. The observed spectra can be attributed to the luminescence of Bi$^{3+}$ ions, which occupy an isolated position in the structure of crystals [9, 10]. The results of measurements of the absorption and luminescence spectra of Eu$^{3+}$ ions in glasses [11, 12] demonstrate absorption at the $^7F_{0.1} \rightarrow ^5D_1$ (520-545 nm) and $^7F_0 \rightarrow ^5D_0$ (580 nm) transitions. In this case, both photoluminescence spectra of Bi$_{12}$SiO$_{20}$ and Bi$_4$Si$_3$O$_{12}$ in the pores of opal overlap the absorption region of europium ions. Thus, it can be assumed that the increase in the integral intensity of emission of europium ions in the pores of the nanocomposite opal - (Bi$_{12}$SiO$_{20}$, Bi$_4$Si$_3$O$_{12}$) (figure 4) is due to the participation in the optical processes of Bi$^{3+}$ ions as a coactivator of luminescence of Eu$^{3+}$ ions.

3. Conclusions

The method for introducing the Bi$_{12}$SiO$_{20}$ melt into the pores of bulk synthetic opals was developed. It provides the filling of pores up to 50 vol. % on average over the sample volume per cycle. It was established that as a result of crystallization of the melt, nanocrystals Bi$_{12}$SiO$_{20}$ and Bi$_4$Si$_3$O$_{12}$ are formed in the pores of the opal. The amount of Bi$_4$Si$_3$O$_{12}$ in the pores of opal is dominant. The results of measurements of the photoluminescence spectra of the matrix nanocomposite opal - Bi$_{12}$SiO$_{20}$ and initial opal infiltrated with an aqueous solution of the CaH$_2$EuO$_6 \times$ H$_2$O salt showed an increase in the nanocomposite integral intensity of the bands at wavelengths of 592 nm and 619 nm in 3 and in 2 times respectively. It is established that the observed increase in the integral intensity is due to the
additional energy transfer to Eu\(^{3+}\) ions from Bi\(^{3+}\) ions, which are the coactivator luminescence. This is confirmed by direct measurements of the photoluminescence spectra of the matrix nanocomposite opal - Bi\(_{12}\)SiO\(_{20}\). It was found that after dehydration of crystallohydrate C\(_6\)H\(_9\)EuO\(_6\) × H\(_2\)O in opal pores at 150°C the spectral distribution of the photoluminescence intensity changes and the integral intensity decreases. This is due to the change in the coordination environment of the Eu\(^{3+}\) ion as a result of splitting the water molecule from the europium ion.

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