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Luminescence Spectra of $C_6H_9EuO_6$ x H_2O Doped Synthetic Opals Matrix Containing Bi-Active Dielectrics

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Abstract

This paper presents the results of experimental studies for the luminescence spectral intensity redistribution of opal photonic crystals containing various active dielectrics - $Bi_{12}SiO_{20}$, opal - Bi_2TeO_5 and opal - $NaBi(MoO_4)_2$ matrix nanocomposites and filled with europium $C_6H_9EuO_6$ x H_2O salt. Ultraviolet excitation was provided by semiconductor laser operating at wavelengths of 400nm and 100 mW average power. An increase in the integral luminescence intensity of the matrix composite opal - $Bi_{12}SiO_{20}$: Eu^{3+} was found. The possibility of the participation of bismuth ions as a co-activator and luminescence concentrator also is analyzed. It has been proposed to use opal-$Bi_{12}SiO_{20}$ nanocomposite filled with europium as a potentially attractive material to improving the solar cell efficiency.

Keywords: Photoluminescence, Synthetic Opals, Matrix Nanocomposite, Solar Cell

1. Introduction

In the recent years the nanotechnologies related to the fabrication and application of nano-structural photonic-crystals active dielectrics doped is of fundamental interest for the physics of low-dimensional systems. The investigation of optical properties for new luminescent materials on the basis of synthetic opals which represent a class of 3D photonic crystals and offer a potentially opportunities to investigate the effect of spontaneous emission, low-threshold lasing, information processing and transferring (Joannopoulos, Villeneuve, & Fan, 1997). In (Aliev et al., 2002; Li et al., 2007; Gorelik, Lepnev, & Litvinova, 2017) it is shown that erbium (Er^{3+}), europium (Eu^{3+}) and terbium (Tb^{3+}) are perspective materials for filling opal pores. Special interest from the scientific and practical points of view represents nanocomposites opal-active dielectric, which activated by luminescent centres. The present work is devoted to study the influence of nanocrystalline structure of europium ions and photonic - crystal effects on the photoluminescence spectra matrix nanocomposites of opal-$Bi_{12}SiO_{20}$ opal - $NaBi(MoO_4)_2$, and opal - Bi_2TeO_5, infiltrated with europium $C_6H_9EuO_6$ x H_2O salt. The aim of present work is to clarify the nature of emission and comparing spectra of essential opal and dielectrics-infiltrated synthetic opals with europium.

2. Experimental Setup

Bulk synthetic opals crystals were grown through slow crystallization from monodisperse colloidal suspension of globules α - SiO_2 synthesized by modified Stöber method (Stöber, Fink, & Bohn, 1968). For different samples the values of the diameter of the globules and the interplanar distance was varied in the range D = 295 - 306nm d = 241 - 250nm. The spectral position of the photon stop -zone for the samples of essential opals corresponded to the range 593 - 614nm in the direction (111). The fabrication of nanocomposites was carried out by filling the pores of opal samples with the melt of single crystals $Bi_{12}SiO_{20}$ (BSO), $NaBi(MoO_4)_2$ (NBMO) and Bi_2TeO_5 (BTO) under the influence of capillary forces. The fact of filling the pores of opal with melting were detected by shift of the band maximum of a Bragg reflection in the wavelength region. Due to the high refractive index of crystals ($n_{BSO} = 2.54$; $n_{NBMO} = 2.25$; $n_{BTO} = 2.36$; $\lambda = 632.8$nm) to detect the peak of the Bragg diffraction of light in the visible region of the spectrum, large reflection angles were used (60^0). Based on comparison the position of the maximum of the measured reflection spectrum of nanocomposite sample and the calculated value of λ_m, under the condition of 100% filling of the pores with melt, the percentage of filling the pores was determined, which was ~ 50% of volume. For all nanocomposites, it was found that the substance in the opal pores is in the crystalline state. This is confirmed by the characteristic form of the measured X-ray diffractgrams (X-ray diffractometer PW3040/60).

Next we carried out impregnation of the samples of the nanocomposite in an aqueous solution of salt $C_6H_9EuO_6$ x H_2O (99.9%). 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 λ_{ex} = 405nm. The spectra were recorded in (111) ($\theta = 0$) direction and for $\theta = 30^o$ and 60^o angles with (111) axis by a modified laser spectrometer based on the DFS-12 double monochromator (Figure 1).

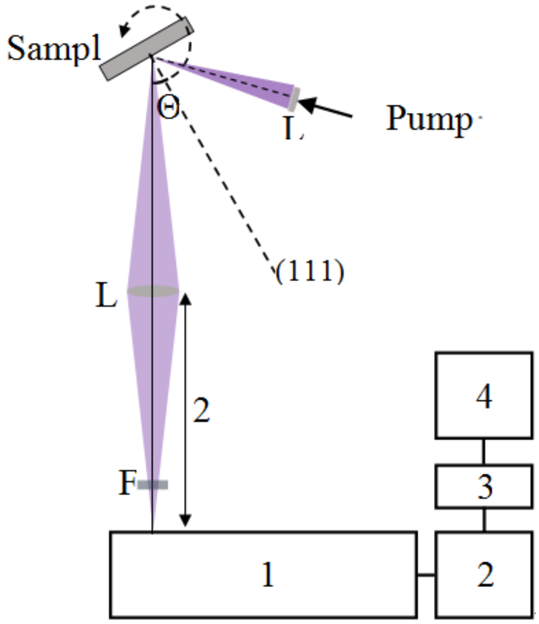

Figure 1. Optical scheme of sample excitation and photoluminescence registration system: 1 - monochromator DFS-12; 2 - FEU-79; 3 - ADC; 4 - PC

3. Results and Discussions

According to the results of X-ray phase analysis of opal nanocomposite - $Bi_{12}SiO_{20}$ (Figure 2), the dominant presence of bismuth $Bi_4Si_3O_{12}$ orthosilicate nanocrystals in pores of opals was established (Liu & Kuo, 1997).

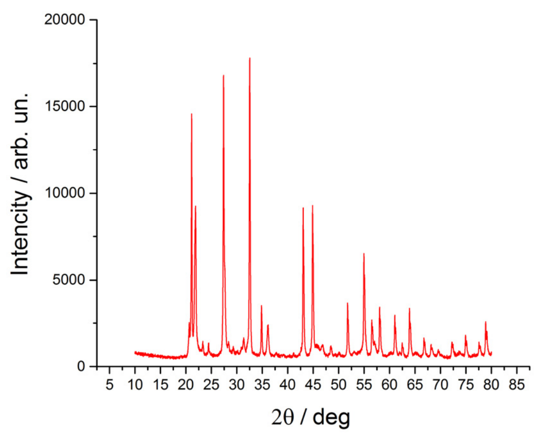

Figure 2. X - ray diffractogram (Cu K_α - radiation) of the opal-$Bi_{12}SiO_{20}$ sample, on which the most intense peaks correspond to the crystal phase $Bi_4Si_3O_{12}$ (Liu & Kuo, 1997)

In Figure 3 shows the measured photoluminescence spectra of matrix nanocomposites infiltrated with europium salt. For comparison, the photoluminescence spectra of the salt solution and the essential opal infiltrated with $C_6H_9EuO_6$ x H_2O were measured.

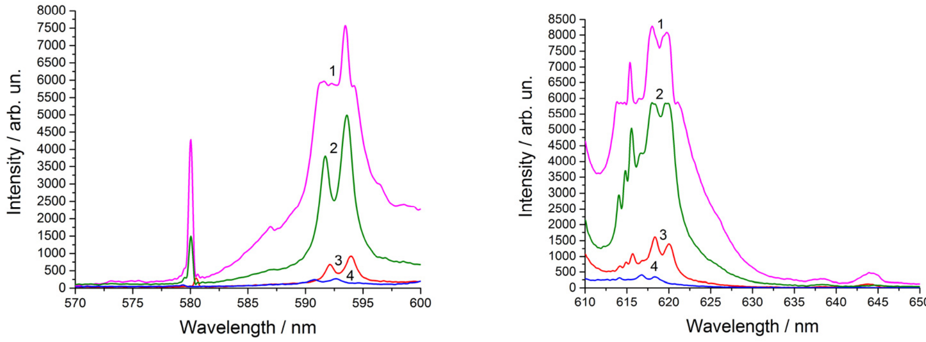

Figure 3. Photoluminescence spectra of an essential opal (2), nanocomposite opal - ($Bi_{12}SiO_{20}$, $Bi_4Si_3O_{12}$) (1), nanocomposite opal - $NaBi(MoO_4)_2$ (3), nanocomposite opal - Bi_2TeO_5 (4), infiltrated with $C_6H_9EuO_6$ x H_2O, measured in the (111) direction

In typical luminescence bands spectra the energy spectrum of europium ions $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, and $^5D_0 \rightarrow {}^7F_2$ were observed for wavelengths of 580nm, 592nm and 619nm, respectively. The following regularities were established:

a) The red shift of the photoluminescence spectrum of Eu^{3+} ions in the opal and nanocomposite pores by 3nm compared to the luminescence spectrum of the salt solution;

b) The increase in the integrated intensity of emission of europium ions in the pores of the nanocomposite opal - $Bi_{12}SiO_{20}$, $Bi_4Si_3O_{12}$ and its decrease for nanocomposites opal - $NaBi(MoO_4)_2$ and opal - Bi_2TeO_5 (Figure 3);

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 λ_{max} = 580nm (Figure 4).

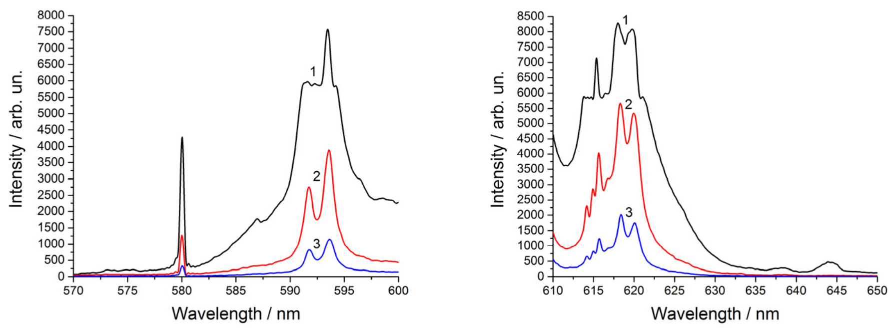

Figure 4. The dependence of the photoluminescence spectra of the nanocomposite opal - $Bi_{12}SiO_{20}$, $Bi_4Si_3O_{12}$, infiltrating with salt $C_6H_9EuO_6$ x H_2O, from the direction of observation. 1 - θ = 0, 2 - θ = 30°, 3 - θ = 60°

It is assumed that the increase in the integral intensity of emission of europium ions in the pores of the nanocomposite opal - ($Bi_{12}SiO_{20}$, $Bi_4Si_3O_{12}$) (Figure 3) is due to the participation in the optical processes of Bi^{3+} ions as a co-activator of luminescence of Eu^{3+} ions. This is confirmed by direct measurements of the luminescence spectra of bismuth-containing materials (Jung, Park, Seeta Rama Raju, Jeong, & Moon, 2011; Peng & Wondraczek, 2010; Murphy, Stevens, Garces, Moldovan, Giles, & Hallibur-ton, 1999).

The observed effects are proposed to be used to create an active mirror for solar cells (Yevchik, Moiseyenko, Dergachov, & Shvets, 2014) based on opal matrix nanocomposites - $Bi_{12}SiO_{20}$: Eu^{3+} to provide an effective "down" - conversion of the shortwave part of the solar spectrum to the area of fundamental silicon absorption. A solar cell design was proposed in which the nanocomposite layer performs “down” conversion of solar radiation and provides effective illumination of its active layer from below (Figure 4) (Peng & Wondraczek, 2010). Additionally, for uniform illumination of the solar element, regardless of the position of the sun above the horizon, a regular layer of millimeter-scale quartz globules is located on its surface.

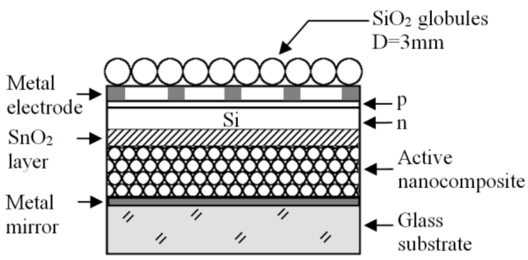

Figure 5. The design of a solar cell with an active reflective layer based on an matrix nanocomposite opal - active dielectric (Derhachov, Moiseienko, Kutseva, Abu Sal, Holze, Pliaka, & Yevchyk, 2018)

4. Conclusions

The method for introducing the $Bi_{12}SiO_{20}$, Bi_2TeO_5 and $NaBi(MoO_4)_2$ melt into the pores of bulk synthetic opals was developed. It provides 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 $Bi_4Si_3O_{12}$ Bi_2TeO_5 and $NaBi(MoO_4)_2$ are formed in the pores of the opal. 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 $C_6H_9EuO_6 \times H_2O$ salt showed an increase in the nanocomposite integral intensity of the bands at wavelengths of 592nm and 619nm 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 co-activator luminescence. The design of a solar cell with an active mirror based on a BSO opal nanocomposite has been proposed.

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Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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