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Globular and optically transparent photonic crystals based on 3D-opal matrix and REE

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Abstract

By repeatedly filling the octahedral and tetrahedral pores of 3D-silica opal matrices with silica sol doped with rare-earth elements with subsequent heat treatment globular photonic crystals filled with mesoporous glass and optically transparent photonic crystals (quantytes) containing 10-30 ppm REE were produced, depending on the annealing temperature. Voids of fcc lattice formed by amorphous spherical globules of SiO_2 in globular photonic crystals are filled (up to 70%) by mesoporous glass doped with rare earth elements. Pores in the transparent photonic crystals disappear during sintering of globules of silica and mesoporous glass, but the periodic arrangement of REE-enriched silica areas (quantum dots) is retained. The reflection and luminescence spectra of photonic crystals filled with sols doped with europium Eu^{3+} and terbium Tb^{3+} were experimentally studied. A significant increase in the photoluminescence intensity of Eu^{3+} ions at the approach of the spectral position of the transition $^5D_0 \rightarrow {}^7F_2$ to the edge of the bandgaps of the photonic crystal was determined. The authors come to the conclusion that a lowering of the threshold for lasing transitions in ions of rare elements is possible.

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*Keywords:*opal matrix; silica sol; photonic crystals; band gaps; REE; luminescence

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1. Introduction

The synthesis of superfine materials with the desired properties of the sol-gel technique (Alain C. Pierre (1998), C.J. Brinker et. al. (1990), Iler R.K. (1979)) allows for a variety of materials based on colloidal silica: macro- and mesoporous silica gels for catalysts, protective films and membranes, superfine powders and porous glasses and also ordered planar and opal-like three-dimensional structures. Usually different alkoxides and silicon halides are used as reagents in the sol-gel method. The hydrolytic decomposition of these reagents results in the successive formation of the serial sol, and the gel of silicic acid. By means of dehydration of the latter highly dispersed forms of silica are formed. Despite the seeming simplicity and universality of the scheme of the sol-gel process the properties of the resulting oxide material are very sensitive to the choice of the initial reagents, as well as to their ratio and the reaction conditions.

Special attention is given to the ordered planar and three-dimensional structures: photonic crystals based on opal matrices (OM) with an fcc-lattice of globules of amorphous SiO_2 with rare earth elements (REE), as they operate as optical media with a periodic change in the refractive index on a scale comparable to the wavelength of visible light and near-infrared ranges (D.A. Kurdyukovet. al. (2012), X. Yang et. al.(2009), A.I.Artamonov et. al.(2005), Gruzintsev A.N.et. al.(2010), S.V. Gaponenko et. al.(1999), Romanov, S.G et. al.(2000), A. Chiappiniet. al.(2007), A. Chiappiniet. al.(2009)).The Opal-like structures with REE are either prepared by impregnation with solutions of inorganic salts and organic complexes of rare earth elements (Gruzintsev A.N.et. al.(2010), S.V. Gaponenko et. al.(1999), Romanov, S.G et. al.(2000), A. Chiappiniet. al.(2007)) or by synthesizing the inverted samples on a polystyrene template (A. Chiappiniet. al.(2009)). By filling pores of GFC by REE compounds materials with luminescent properties are formed (A. Chiappiniet. al.(2009)). Studies of the photoluminescence spectra showed promising perspectives on injection of europium (Eu^{3+}) and terbium (Tb^{3+}) in the pores of the glass and GFC (Gruzintsev A.N.et. al.(2010), S.V. Gaponenko et. al.(1999), Romanov, S.G et. al.(2000), A. Chiappiniet. al.(2009), Ivicheva S.N. et. al. (2013)), since the phosphors based on them are characterized by high stability and stable emission characteristics in comparison to organic phosphors. However, a single cycle of filling OM with highly concentrated solutions or sols of REE does not allow for complete filling of the pores and may lead to concentration quenching of luminescence.

The purpose of this study was to obtain ordered 3D-nanocomposites based on opal matrices and REE by repeatedly filling the pore space of the OM by sols of silica doped with salts or oxides of rare earth elements, the study of the spectral position of the band gaps and the photoluminescence spectra of two kinds of ordered photonic crystals: globular and transparent (quantytes), obtained by heat treatment of identical opal matrices at 800 and 1200°C.

2. Object and method of studies

Composites based OM and REE were obtained by repeated (up to 8 times) impregnation of OM with a concentrated (25% SiO_2) silica sol doped with rare-earth elements with subsequent heat treatment for a given procedure. Monodisperse spherical particles of silica were obtained by hydrolysis of tetraethoxysilane (TEOS; 0.28 mol/l) in ethyl alcohol taking account of the dependency of the size of the silica spheres on the concentration of water and ammonia in the C_2H_5OH-NH_3-H_2O system (Ivicheva S.N. et. al. (2013), Ivicheva S.N. et. al. (2011), Ivicheva S.N. et. al. (2012), Ivicheva S.N. et. al. (2009), Ivicheva S.N. et. al. (2014)), and the quality of TEOS (Ivicheva S.N. et. al. (2014)). The opal matrix was obtained by sedimentation followed by heat treatment at 800°C in a special procedure. The stable concentrated (up to 25-27% SiO_2) acidic (pH 2) sols were prepared according to the previously described method (Ivicheva S.N. et. al. (2014)). Rare earth oxide (Eu_2O_3, Tb_2O_3) was injected into the sol in the form of a hydrochloric acid solution (of 0.3 wt. % relative to SiO_2). The sols were structured in the OM pores at room temperature followed by gelatination in an oven at 50°C. Heat treatment at 500°C facilitated the transition of the gel into the OM pores to mesoporous xerogel and at 800°C to mesoporous glass with a uniform distribution of REE ions (in particular Europium). Some samples of nanocomposites were annealed at 1200°C. Further, composites based on OM filled with Eu-doped silica sol are labeled as OM/nSolEu (GFC/REE), where n designates the number of times of impregnation, and transparent FC with europium as TFC/Eu.

The study of the reflectance spectra were carried out on the experimental apparatus with a quartz light guide with