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Luminescent photonic crystals

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Angular distribution of photoluminescence of trivalent rare earth ions included inside three-dimensional opal and inverse opal photonic crystals is experimentally shown to be strongly modulated for the emission frequencies near the first and higher photonic stop-bands. Numerical simulations of fractional density of optical states also predict highly directional emission from photonic crystals with perfect structure. Experimental results are shown to be in a good agreement with calculated angular dependences. However, better agreement between experimental and theoretical data requires smoothing of calculated dependences, which can be attributed to the presence of structural imperfections in real photonic crystal samples.

Экспериментально показано, что угловое распределение люминесценции трехвалентных редкоземельных ионов, введенных в фотонные кристаллы трехмерных опалов и инвертных опалов, сильно модулировано для частот излучения, близких к первой и высших фотонных стоп-зон. Численное моделирование фракционной плотности оптических состояний также предсказывает высоконаправленное излучение из фотонных кристаллов совершенной структуры. Показано, что экспериментальные результаты хорошо согласуются с расчетными угловыми зависимостями люминесценции. Однако для лучшего согласования экспериментальных данных с теоретическими необходимо сглаживание расчетных зависимостей, что можно объяснить наличием структурных несовершенств в реальных образцах фотонных кристаллов.

Photonic crystals (PCs) are periodic dielectric materials exhibiting photonic band gaps (PBGs), where light of certain energies cannot propagate inside PC. In the case of three-dimensional PC, a complete PBG is possible where light cannot propagate in any direction. However, in practice, due to symmetry limitations, low refractive index contrast, and structure imperfections, PCs typically possess only stop-bands corresponding to the prohibition of light propagation only in some defined directions. As a result, the emission of luminescence centers from such PCs undergoes strong spatial modulation.

In thin PC films (of thickness less than the mean free path of photons $l \sim 20$ μm), the emission directionality can be described using an approach based on calculation of the angle-dependent or fractional density of optical states (FDOS) [1, 2]. According to simulation results employing this approach, the emission of active centers from opal and inverse opal films may be highly directional [3, 4]. In this work, the results of FDOS calculations are compared with experimental data on angular dependences of photoluminescence intensity obtained for opal and inverse opal thin films doped with rare earth ions Eu^{3+} and Tb^{3+}.

The opal films were grown using the vertical deposition method [5]. The samples consisted of 410 nm polystyrene microspheres self-assembled in a face-centered

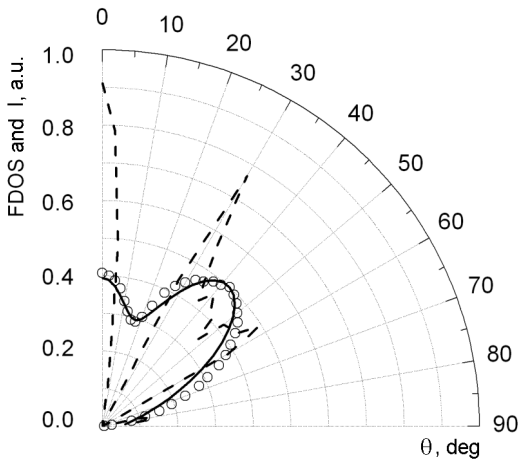

Fig. 1. Calculated FDOS angular dependences for Mg_2SiO_4 inverse opal prior to (dashed curve) and after smoothing (solid curve) in comparison with experimental dependence of photoluminescence intensity (circles) for 617 nm Eu^{3+} emission peak from the same inverse opal film. The normal direction is [111], the angle counts from this axis to [11$\bar{1}$].

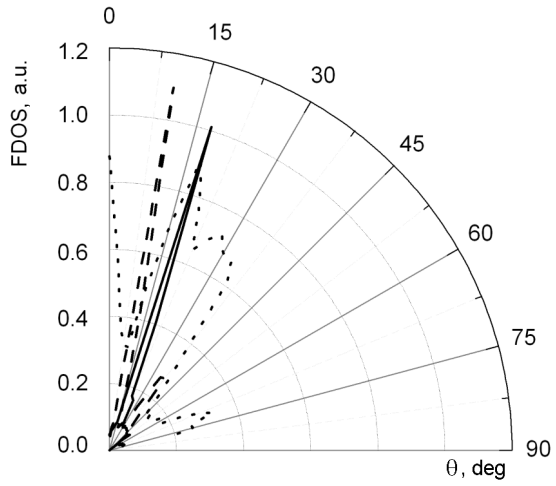

Fig. 2. Calculated FDOS angular dependences for emission bands of Tb^{3+} ions in the perfect opal film. Emission wavelengths: solid curve, 620 nm; dashed curve, 585 nm; dotted curve, 544 nm.

cubic structure with (111) surface orientation. Some of such grown films were used as templates for the synthesis of inverse opal samples based on Mg_2SiO_4. Briefly, colloidal crystal films were impregnated with a mixture of tetraethoxysilane ($Si(OC_2H_5)_4$), magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$), ethanol, hydrochloric acid, dried in air for 24 h, and annealed at 500C for 10 h resulting in the removal of polystyrene microspheres and obtaining a porous magnesium silicate framework. The average diameter of spherical voids in the inverse opals was 360 nm. Finally, the samples were impregnated with water-alcohol solutions of rare earth complexes with 2-pyrazinecarboxylic acid, $Re(pyca)_3{\cdot}xH_2O$ (Re = Tb or Eu) known to possess a high efficiency of excitation. Narrow emission lines of rare earth ions were quite suitable to investigate the luminescence directionality from PCs. The microstructure of PCs was studied using laser diffraction [6]. For all samples, relatively large areas of several thousand μm^2 with one predominant crystallographic orientation have been found. The diameter of UV exciting spot from a xenon arc-lamp was about 80 μm.

We have prepared PCs so that opal films had fundamental gap and inverse opals had second and third stop-bands in the visible spectral region. Consequently, angular dependences of luminescence recorded for these samples were different. Fig. 1 shows a comparison of FDOS angular dependence with the experimental data on photoluminescence intensity for one of inverse opal films containing $Eu(pyca)_3{\cdot}xH_2O$. Zeroing of FDOS at 10–20° corresponds to overlapping of 617 nm Eu^{3+} emission band with the first stop-band of PC. Smoothing of calculated dependence (see solid curve) is necessary to achieve its good agreement with experimental data. The physical meaning of this smoothing is the presence of various structural imperfections and defects in self-assembled PCs causing differences in surroundings of emitting centers.

Fig. 2 shows calculated FDOS dependences for three wavelengths corresponding to different emission bands of Tb^{3+} ions embedded inside opal film made of polystyrene microspheres. High and sharp solid (λ = 620 nm) and heavy dashed (λ = 585 nm) peaks at about 20° and 10°, respectively, correspond to the low energy edge of the second photonic stop-band, while second heavy dashed peak at about 36° corresponds to the high energy edge. The solid curve clearly demonstrates the possibility of highly directional emission from the opal film under the influence of the second photonic stop-band.

A comparison of FDOS dependences with real data on emission from polystyrene opal film with $Tb(pyca)_3{\cdot}xH_2O$ is shown in Fig. 3. In this case, smoothing of FDOS depend-

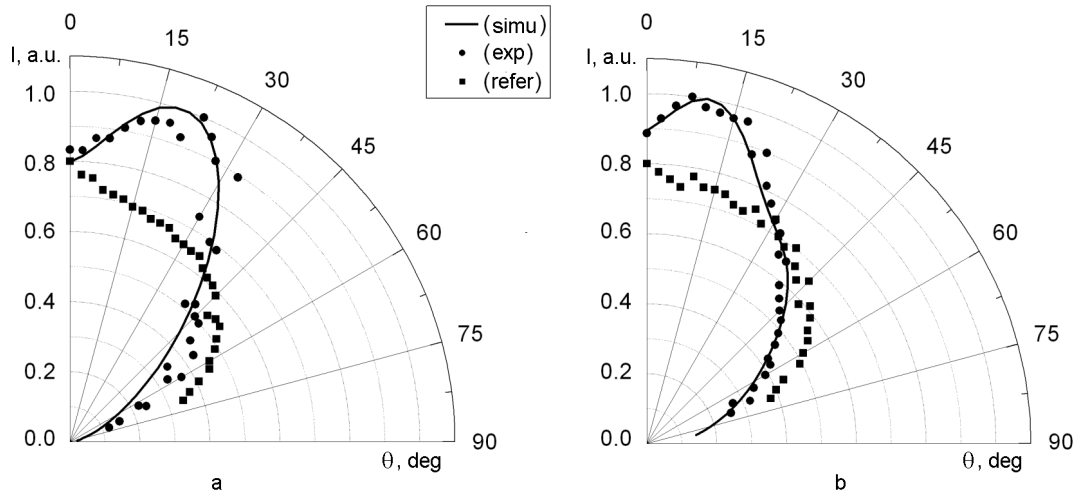

Fig. 3. Angular dependencies of photoluminescence intensity for Tb^{3+} emission bands from polysterene opal film (circles), from reference film witout photonic band structure (squares) and corresponding FDOS dependencies after smoothing (lines). Emission wavelegths: a – 620 nm, b – 585 nm.

ences to achieve accordance with experimental data is also necessary.

As a result, FDOS calculations prove that high directionality of luminescence is possible for thin films with perfect opal structure, especially in the energy range of second photonic stop-band. However, structure imperfections result in a reduced directionality of luminescence from the real samples.

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Люмінесцентні фотонні кристали

С.О.Климонський, А.С.Синицький, В.В.Абрамова, С.В.Єлісєєва, Ж.Лі, П.Чжанг, М.Лі, Ж.І.Чжоу, Ю.Д.Третьяков

Експериментально посвідчено, що кутовий розподіл люмінесценції тривалентних рідкісноземельних іонів, введених у фотонні кристали тривимірних опалів та інвертних опалів, є сильно модульованим для частот випромінювання, близьких до першої та вищих фотонних стоп-зон. Числове моделювання фракційної густини оптичних станів також завбачає високонапрямне випромінювання з фотонних кристалів досконалої структури. Показано, що експериментальні результати добре узгоджуються з розрахунковими кутовими залежностями люмінесценції. Однак для кращого узгодження експериментальних даних з теоретичними необхідним є згладжування розрахованих залежностей, що можна пояснити присутністю структурних недосконалостей у реальних зразках фотонних кристалів.