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Three-Dimensional Quantum Photonic Crystals and Quantum Photonic Glasses

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Abstract—The structure and optical properties of quantum-dot photonic crystals (quantytes) were studied. Such crystals have the so-called band gaps, which leads to a strong reflection of electromagnetic waves from the crystal surface. It was shown that in certain spectral regions the refractive index has a negative sign, and the group velocity of electromagnetic waves essentially decreases. The applications of quantytes as optical information recording and rewriting devices, negative refractive optical elements, selective mirrors, narrow-band filters, and others were discussed.

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INTRODUCTION

The physical properties of a great number of identical quantum objects arranged in a definite order in the environment radically differ from those of single objects in a free space. In particular, this relates to periodically arranged quantum objects [1–3]. It was found that the characteristics of spontaneous emission of atoms and molecules in periodic structures are much different from those of emission in a free space. In the emission spectrum of spatial periodic structures there are so-called stop bands, where the intensity of spontaneous emission sharply decays. By contrast, at the edges of the band gaps the emission intensity sharply enhances as a result of density anomalies of photonic states.

The works [1–3] formed the theoretical basis for the development of a new field of physics, associated with the so-called photonic crystals [4, 5]. In a broad sense, the term "photonic crystals" relates to any spatially ordered structures whose crystal lattice period may much exceed atomic dimensions. Of particular interest are photonic crystals, the crystal lattice period of which compares with the visible wavelength.

In the forbidden photonic band gap, light can hardly propagate through the material medium because of its anomalously strongly reflection from sample surface. This property allows photonic crystals to be used as high-efficiency light filters, high-Q resonators, selective mirrors, and nonlinear optical elements [6, 7]. One-, two, and three-dimensional photonic crystals are recognized. Three-dimensional (3D) photonic crystals are exemplified by the mineral opal ($SiO_2 \cdot nH_2O$) and synthetic opal matrices called globular photonic crystals. Natural opal crystals have a cubic face-centered lattice formed by amorphous silicon dioxide globules 200–1000 nm in size [6].

An opal matrix having pores filled with quantum objects periodically arranged in space is a 3D quantum photonic crystal [8, 9]. If the long-range order in the arrangement of quantum objects is disturbed, we can speak about a quantum photonic glass. An important property of quantum photonic crystals is that the quantum objects with a disordered spatial arrangement are identical. Therewith, the role of a "carrier" both for quantum photonic crystals and for quantum photonic glasses can be played both an opal matrix and a quasi-uniform condensed medium (amorphous silicon dioxide, leucosapphire, etc.). The quantum objects that form quantum photonic crystals and quantum glasses can be quantum dots (semiconductor, metal, magnetic), as well as atoms, ions, molecules, etc. Along with known quantum objects (atoms, molecules), much recent interest has been attached to quantum dots, quantum cuts, nanotubes, and nano-surfaces, i.e. "quantum shells." The characteristic dimensions of such quantum objects (1–10 nm). By present production technologies for monodisperse

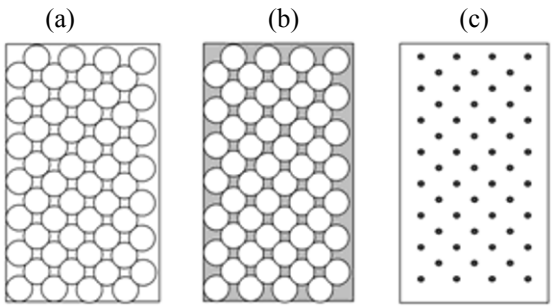

Fig. 1. Nanostructures of 3D photonic crystals: (a) initial synthetic opal; (b) opal impregnated with a saturated salt solution; and (c) quantite structure.

semiconductor quantum dots (silicon, cadmium selenide, zinc oxide, etc.), metal quantum dots (copper, gold, silver, etc.), carbon nanotubes, graphene, as well as magnetic and ferroelectric quantum dots have been developed.

The present work reports on certain properties of 3D quantum photonic crystals and quantum glasses fabricated on the basis of opal matrices or isotropic condensed media with embedded quantum objects. Possible applications of quantum photonic crystals and quantum photonic glasses in optical devices are also analyzed.

Fabrication of Opal-Based Photonic Crystals

Synthetic opals after some engineering processing (drying, annealing, etc.) have a face-centered cubic lattice of silicon dioxide nanoglobules with tetrahedral and octahedral voids between them. Annealing the starting opal matrices at 600°C in air leads to an almost complete oxidation of carbon in organic compounds used for sedimentation of silica nanoparticles in the process of fabrication of the matrices. After annealing pores of the starting opal contain nothing but air.

Embedding quantum objects into opal pores is performed in different ways [10, 11]. One of the most accessible of them involves impregnation of opal with suspensions of small quantum dots, which are present in liquids used to wet silica. Annealing such samples at 400–500°C forms condensed phases of quantum dots inside photonic crystal pores (Figs. 1a and 1b). In the case of high-temperature annealing (up to 1200°C), amorphous silicon dioxide globules soften and merge with each other. As a result, a transparent isotropic matrix is formed, which contains periodically arranged nanoclusters of refractory components of quantum dots. When the clusters are a few nanometers in size, the inclusions are quantum dots in nature, and the crystal structure that forms is classified as a quantum photonic crystal, specifically quantite (see Fig. 1c). If the long-range order of quantum dots is not preserved, a quantum glass is formed.

When opal is annealed in a noble gas atmosphere at 600–700°C, organic compounds used for sedimentation of silica nanoparticles decompose to form free carbon which deposits on the spherical surface of amorphous silica globules as a single-layer shell or spherical graphene (Fig. 2a). In this case, the quantum component is fairly large spheres (radius 100–150 nm) coated by carbon–graphene shells. Spherical graphene is similar in electrical characteristics to planar graphene, i.e. spherical graphene has a fairly high conductivity.

Ultrathin carbon (spherical graphene) quantum shells should exhibit the quantum confinement effect. Therewith, carbon quantum spheres also exhibit galvanic anisotropy.

Another example of quantum photonic crystals is provided by synthetic opals with a little refractory dielectrics (ZrO_2, Eu_2O_3, $LiNbO_3$, $BaTiO_3$, etc.) embedded in their pores. The properties of ferroelectric and magnetic quantum photonic crystals may radically differ from those of bulk ferroelectrics and magnetics.

Such refractory components as noble metals (gold, platinum, palladium), too, can be embedded in opal pores. Noble metal salts are introduced into pores of an opal and then subjected to reductive decomposition to form a noble-metal quantum shell on quartz globules (Fig. 2b).

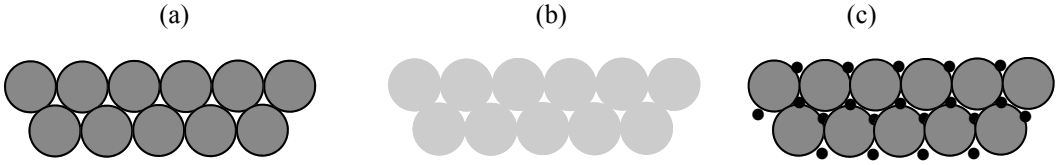

Fig. 2. A portion of a 3D photonic crystal with "quantum shells" from (a) carbon and (b) noble metals and (c) with embedded solid quantum dots.

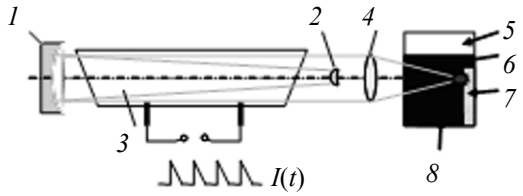

Fig. 3. Scheme of preparing a sol of nanoparticles by laser ablation and their embedding into a globular photonic crystal: (*1, 2*) mirrors of the unstable resonator of a copper vapor laser; (3) active element (copper vapor); (*4*) lens; (*5*) parallel-sided cell; (*6*) liquid (water, ethanol); (*7*) solid sample; and (*8*) photonic crystal.

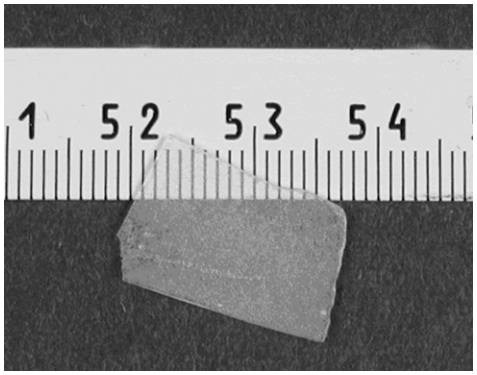

Fig. 4. Image of a transparent opal–zirconium oxide–carbon composite sample. Plate thickness 0.7 mm.

Another method of forming quantum photonic crystals involves direct embedding of quantum dots into opal pores (Fig. 2c) via channels linking neighboring silica globules. To this end, the starting photonic crystal is placed into a liquid containing nanoparticles generated by one of presently known techniques, in particular, laser ablation [12] (Fig. 3). A solid is placed into a neutral liquid and subjected to intense pulse laser radiation focused on the solid surface. Laser pulses induce laser ablation processes, specifically, ejection of nanoparticles from the solid body into the liquid, which is accompanied by formation of hot bubbles. If the formed solid nanoparticles are no larger than channels between photonic crystal globules (5–10 nm), these particles are capable of entering pores of the photonic crystal.

Nanoparticles can also be embedded into the bulk of photonic crystal from a nanoparticle sol under the accelerating field of pulse laser radiation. This method was classified as laser implantation.

It is known that, along with 3D photonic crystals, under certain conditions of growth of synthetic opals the long-range order of globules is not retained, and the material is characterized by a disordered globular configuration. If the dimensions of individual globules are retained, the resulting material is classified as photonic glass. An opal photonic glass with quantum objects embedded in its pores is referred to as quantum photonic glass.

Optical Properties of ZrO_2 Quantum-Dot Photonic Crystals

Let us first dwell on the synthesis of quantum photonic crystals (quantites) with ZrO_2–carbon complexes as quantum dots [6, 7].

The opal matrices (silica particles) were synthesized by the hydrolysis of tetraethoxysilane in alcoholic aqueous ammonia (this technology was described in detail in [8, 9]). The resulting matrices were impregnated with aqueous $ZrOCl_2 \cdot 8H_2O$ with the zirconium oxochloride concentrations correspond-ing to 1.5–10 wt % of zirconium dioxide in the SiO_2–ZrO_2 system. The impregnated matrix was treated with ammonium hydroxide for a day. As a result, $Zr(OH)_4$ precipitated in pores of the opal matrix. The matrix was dried and annealed at ~500°C; during this process zirconium hydroxide decomposed to form zirconium oxide.

To introduce carbon into opal, the starting matrices are impregnated by aqueous solutions of organic compounds. The impregnated matrices are dried and annealed under argon at 600–650°C; as this takes place, organic compounds decompose into carbon inside the opal matrix. The final stage involves sintering at 1200°C for 30 h, after which the samples are subjected to a vacuum at 1500°C for 2 h to obtain a transparent opal–ZrO_2–C composite (Fig. 4).

Figure 5 illustrates the surface microstructures of the starting opal matrix and the sample filled with ZrO_2–C quantum dots. In our work, the microstructure of the quantum photonic crystal was studied by a Zeiss Supra 50 VP high-resolution scanning electron microscope (1.3 nm at the accelerating voltage 20 kV and working distance 2 mm). The accelerating voltage was varied from 100 V to 30 kV, maximum magnification ×900000.

The band-gap analysis of the obtained crystals was performed by the optical fiber technique. The light source in the measurement of reflection and transmission spectra was a halogen lamp which produces a continuous spectrum in the visible range.

(a) (b)

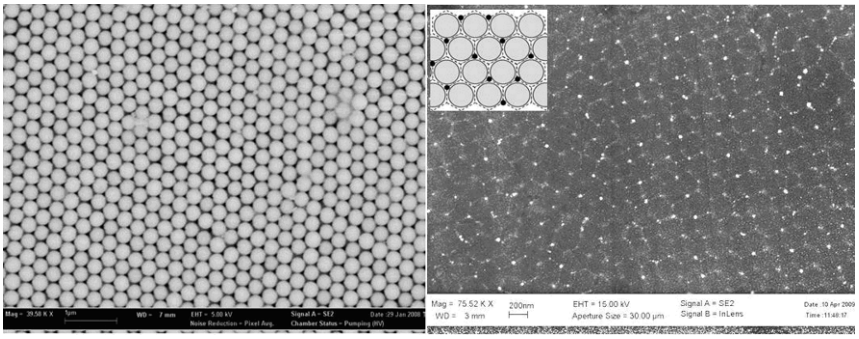

Fig. 5. Images of the surfaces of the (a) initial photonic crystal, (111) plane, and (b) opal− ZrO_2−C nanocomposite. The insert in Fig. 5b shows a scheme of the honeycomb structure of the opal (111) plane.

Figure 6 shows the normed visible transmission and reflection spectra of the quantite. The transmission spectrum of the quantum photonic crystal shows strongly intensity decay at 570 nm. Thus, there are all grounds to suggest that here we deal with a well-defined photonic band gap. The transmission spectrum contains a maximum at 510 nm. At lower wavelengths, transmission strongly decreases, which is associated with the intrinsic absorption of the composite.

The reflection spectrum looks like a fairly narrow band with a maximum at 577 nm. The spectral width of the reflection band (less than 10 nm) relates to the band-gap width of the quantum photonic crystal.

Figure 7 illustrates the emission spectrum of a white light diode and the reflection spectrum of the same light from the [111] plane of the quantite. As seen, the reflection intensity in the maximum (575 nm) of the reflection spectrum is higher than the incident intensity at this wavelength, i.e. the effective reflection coefficient is higher than 1. This effect is explained by the conversion of the rest part of the white light spectrum into a quasi-monochromatic light (secondary light maximum at 575 nm). Evidence for this explanation comes from the spectra in Fig. 8, which show that the short-wave radiation at 368, 385, and 410 nm converts into a Bragg peak at 575 nm. As seen from Fig. 8, the intensity of the converted light increases as the exciting light wavelength gets closer to the photonic band-gap edge. Upon light conversion in the elementary process of inelastic reflection, the exciting light quantum loses part of energy via its transfer to photonic crystal. Inelastic reflection of light quanta with different energies gives rise to a light

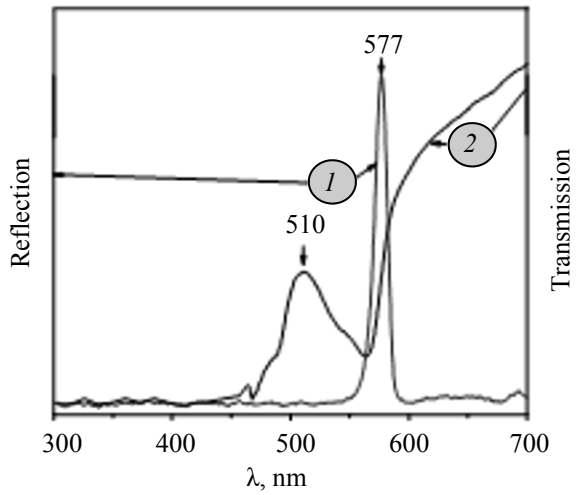

Fig. 6. Normed (*1*) transmission and (*2*) reflection spectra of the opal–ZrO_2–C nanocomposite. Light source: a halogen lamp.

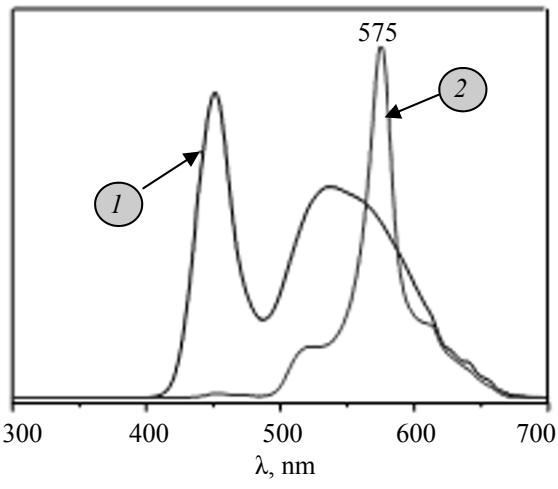

Fig. 7. (*1*) Emission spectrum of a white light diode and (*2*) secondary emission spectrum excited in the opal–ZrO_2–C quantite by the white light diode by the "reflection" scheme.

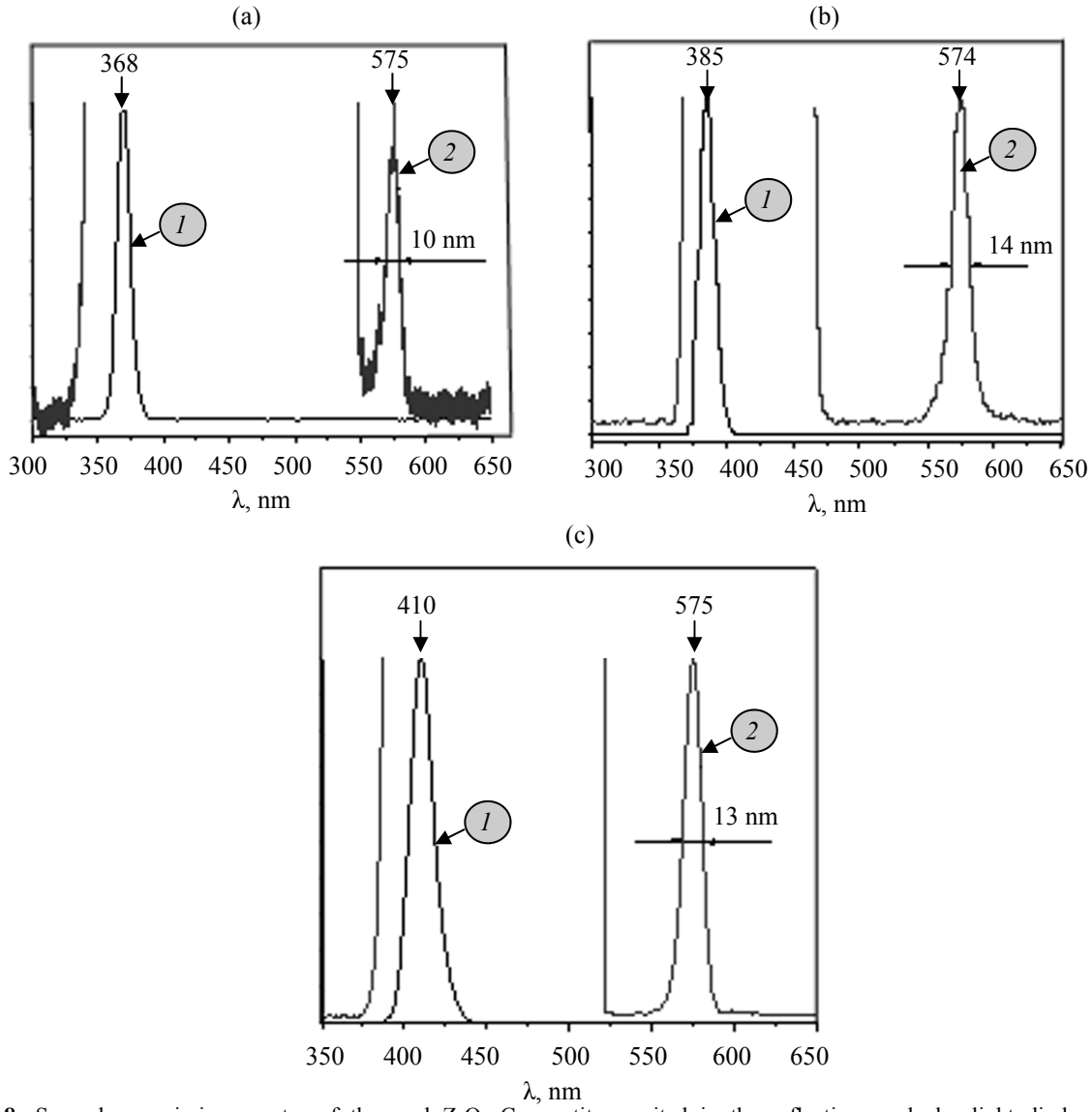

Fig. 8. Secondary emission spectra of the opal–ZrO_2–C quantite, excited in the reflection mode by light diodes with the wavelengths (a) 368, (b) 385, and (c) 410 nm: (*1*) Exciting light band and (*2*) secondary emission band.

quantum with the same energy which is close to the photonic band-gap energy.

Opal matrices with embedded zirconium oxide were annealed at a high temperature in air to obtain transparent and mechanically strong SiO_2–ZrO_2 quantite samples. In the experiments on broad-band light reflection from the (111) surface of these samples, we observed band gap–related reflection peaks only in certain regions smaller than 1 mm.

Figure 9 shows the reflection spectra of the broad-band light of a halogen lamp and a white light diode from such regions of the (111) surface of the SiO_2–ZrO_2 sample. The reflection spectrum contains a narrow band corresponding to a band gap. Thus, here we deal with nothing more than clusters of a quantum photonic crystal in a matrix of a quantum photonic glass.

The presence of narrow band gaps in quantites opens up a way to their application as narrow-band filters which are of interest, in particular, for Raman spectroscopy. Such filter is set after the scattering substance, and it selectively reflects the exciting light and transmits both Stokes and anti-Stokes Raman signals.

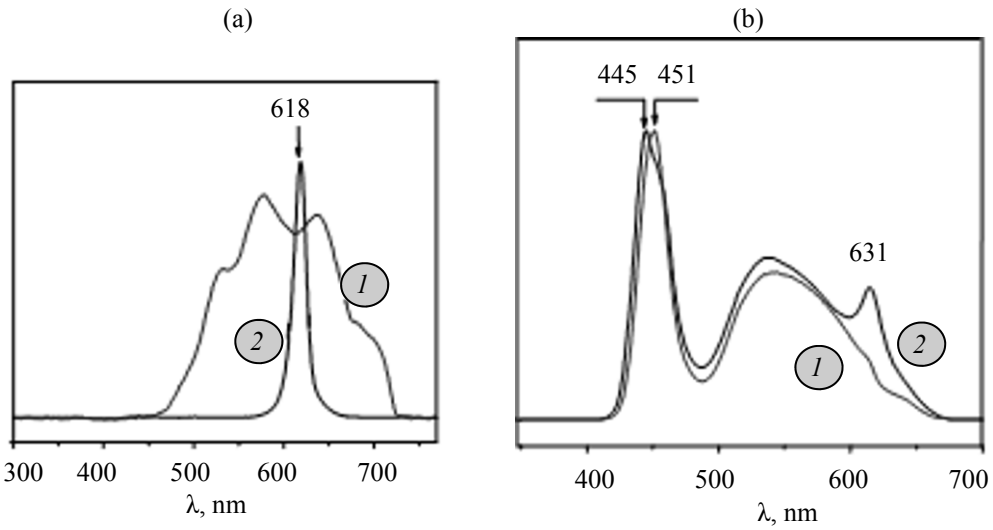

Fig. 9. (*1*) Continuous spectrum of a light source and (*2*) reflection spectrum from the surface of a photonic crystal, viz. a synthetic opal with embedded ZrO_2. Light source: (a) halogen lamp and (b) white light diode.

Another possible use of quantites is associated with quantum holography, a technology for recording and reading optical information. A transparent substrate bearing optical information is introduced into a laser beam. A lens focusing the laser beam onto a small spot on a photonic crystal is used to record this information as a perturbation of the quantum state of quantum dots located in this region. The second lens is used to transmit the recorded information as an image on a display.

Since the quantum information recorded on quantum dots embedded in a quantum crystal is stored for a fairly long time, the image can be reproduced on a display even if the primary information carrier is no longer present in the laser beam.

Photonic crystals can store a large volume of information, the volume dependent on the total number of quantum dots, as well as the spectral and time characteristics of the laser beam. The storage time of the recorded information depends on the relaxation time which, in its turn, depends on the efficiency of interaction of quantum dots with each other, as well as with the photonic crystal matrix, viz. an amorphous silicon dioxide.

Thus, periodically arranged quantum dots embedded in a quantum crystal change the optical properties of the parent synthetic opals, which reveals itself in a shift of the band gap wavelength, emergence of additional resonances in the spectrum of the photonic crystal, selective reflection of electromagnetic radiation, etc.

CONCLUSIONS

Unlike globular photonic crystals on the basis of opal matrices, quantites are crystals optically homogeneous and transparent in the visible spectral range. Such crystals can be used as homogeneous optical media with a negative refractive index for various optical devices. They are also of interest as an alternative for a notch filter. Quantite plates can be used in Raman spectroscopy as filters which selectively reflect the exciting light and transmit both Stokes and anti-Stokes signals. Further on quantites can be used as selective mirrors in laser resonators providing a high degree of monochromatization of laser radiation.

If the energy level of a quantum dot falls within the band gap region, a narrow spectral transmission zone forms in this region. In this case, the so-called resonance photonic crystal is realized, in which the Anderson photon localization, i.e. anomalous light retardation inside the crystal, takes place [12]. As a result, conditions for a considerable decrease of laser generation threshold develop. This phenomenon can be used to create new efficient lasers, where the active medium contains rare-earth elements.

When pulsed laser radiation is focused in the bulk of a resonance quantum photonic crystal, the anomalous retardation of electromagnetic wave may result in nonequilibrium heating of the material medium to a very high temperature required to induce high-temperature phase transformations, chemical reactions,

and other processes that occur at anomalously high temperatures.

Finally, quantum photonic crystals are promising candidates for quantum holography applications.

ACKNOWLEDGMENTS

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