Opal-Matrix Nanocomposites Containing Metallic Nanoparticles
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Abstract—A method has been proposed for the fabrication of three-dimensional photonic crystals based on ordered opal matrices (OMs), with pores containing iron group metal (M = Ni, Co, Fe) nanoparticles. The core of the method is the reduction of salts and oxides of these metals with supercritical isopropanol. The phase composition of OM/M composites depends on the composition of the starting salts (nitrates or chlorides): the use of ferric chloride leads to the formation of nanoparticles of solid solutions based on nickel metal, α-cobalt, or β-cobalt (Ni–Fe and Co–Fe systems) in opal pores; with the corresponding nitrates, we obtain OM/NiCo (cubic solid solution), OM/Fe, OM/Ni3Fe, OM/NiFe, OM/CoFe, and OM/NiCoFe nanocomposites. We have measured broadband reflection spectra of the (111) surface of the photonic crystals using a fiber-optic technique for taking reflection spectra. The intensity peak in the reflection (band gap) spectrum of the OM/M (M = Fe, Co, Ni) nanocomposites is shown to be shifted to longer wavelengths.

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INTRODUCTION
Recent years have seen rapid growth of nanotechnologies related to the fabrication and practical application of ordered three-dimensional nanostructures—three-dimensional photonic crystals [1–5]. Typical examples of such nanostructures are opal matrices (synthetic opal) built up of close-packed amorphous quartz (silica) spheres 200 to 600 nm in size. The crystal structure of such opal photonic crystals has a face-centered cubic lattice. Between the close-packed nanospheres in opal, there are tetrahedral and octahedral pores (voids). The volume fraction of the pores in opal is about 0.26. The relative radii (relative to the radius of the \( \text{SiO}_2 \) spheres) of spherical nanoparticles that can be embedded in the opal pores are 0.23 and 0.41 for the tetrahedral and octahedral pores, respectively.

The opal pores can be filled with a variety of substances. The simplest approach is to impregnate synthetic opal with liquids that wet quartz: water, alcohols, acetone, and others. Filling the opal pores with saturated solutions of salts or aromatic compounds in such liquids, followed by evaporation of the solvent in the opal pores, leads to the precipitation of the respective compounds: salts, aromatic substances, etc. [6]. Attempts to fill opal pores with metals or oxides pose more serious problems [7]. Iron-group metal nanoparticles can be prepared by a variety of methods: thermolysis of metalorganic compounds [8–10], electrochemical [11] and chemical deposition [12, 13], and in colloidal chemical systems with reverse micelles as micro- and nanoreactors [14, 15] that can be used for embedding in mesoporous silica. In particular, nickel nanoparticles can be embedded in mesoporous silica using inorganic and organic salts (nickel nitrates, sulfates, chlorides, bromides, amine chlorides, and amine nitrates, as well as nickel acetate, acetylacetonate, and citrate) [16]. Ni nanowires in channels of anodized aluminum oxide can be produced by metal electocrystallization at a constant potential [17]. Cobalt-containing nanocomposites can be prepared using cobalt carbonyl and various salts: \( \text{Co}_2(\text{CO})_8 \), \( \text{Co(NO}_3)_2 \), and \( \text{Co(AC)}_2 \). Cobalt is introduced in the form of cobalt-containing compounds or preprepared metal nanoparticles during the synthesis of a mesoporous matrix, by impregnating it with salt solutions, followed by reduction in the liquid phase [18]. Magnetic nanocomposites containing filamentary iron and iron oxide nanoparticles in a mesoporous silica matrix are commonly prepared by embedding iron pentacarbonyl, acetylacetonate, or citrate into the hydrophobic or hydrophilic part of \( \text{SiO}_2 \)/template composite micelles, followed by crystallization in flowing hydrogen at temperatures from 250 to 700°C [19]. Fe–Co and Fe–Ni solid solution nanoparticles can be prepared by reducing solutions of their salts with hydrazine hydrate in an alkaline medium [12, 20, 21]. FeNi3 nanoparticles were prepared by a hydrothermal process [22]. There are also reports on the preparation of monodisperse spherical iron particles [23], Co dendrites [20], magnetite tetrapods [24], multi-
layer FeCo structures [25], and core/shell bimetallic particles [26].

Liquid metals can be infiltrated into synthetic opal pores at high pressures and temperatures by magnetron sputtering [27], ultrasonic processing [28], laser ablation [29], chemical deposition [8, 30], and electrolysis [31]. With these techniques, however, substances are only incorporated into a thin surface layer of opal crystals.

Refractory metals and oxides can be incorporated into opal pores by reducing appropriate salts in opal with alcohols in a supercritical state [32–35]. As shown in experimental studies [32–35], reactions of supercritical alcohols with salts and oxides have a reducing character, ensuring the formation of refractory metal or oxide nanoparticles in opal pores.

It is known that the key property of photonic crystals is the presence of band gaps, which are responsible for the anomalous reflection of electromagnetic radiation from the surface of a three-dimensional photonic crystal in the spectral region corresponding to the position of a band gap. At typical sizes of spheres in synthetic opal (200–400 nm), the band gaps of opal crystals fall into the visible range.

Gorelik [5, 36] and Voinov et al. [37] developed an effective technique for obtaining the spectrum of the band gaps of photonic crystals with high spatial resolution using fiber optics. It involves a local analysis of broadband reflection spectra of the (111) surface of a three-dimensional photonic crystal at normal incidence of light on this surface and in backscattering geometry. Such experiments, with the use of a halogen or deuterium lamp as a broadband light source, allow one to determine characteristics of the first and second band gaps in the [111] crystallographic direction of the photonic crystal.

The objectives of this study were to produce new types of opal-matrix (OM) nanocomposites containing iron-group refractory metal (M = Ni, Co, Fe) nanoparticles prepared by reducing appropriate salts or oxides with supercritical alcohols [32–35] and to obtain broadband reflection spectra of the (111) surface of the photonic crystals using a fiber-optic technique developed previously [5, 36, 37] for measuring reflection spectra, in order to find characteristics of the band gaps of the nanocomposites.

**EXPERIMENTAL**

**Fabrication of opal-matrix composites containing iron group metal nanoparticles.** The starting chemicals used to prepare the solutions to be infiltrated into opal were the crystalline hydrates Ni(NO$_3$)$_2$·6H$_2$O (analytical grade), Co(NO$_3$)$_2$·6H$_2$O (analytical grade), Fe(NO$_3$)$_3$·9H$_2$O (analytical grade), and FeCl$_3$·6H$_2$O (analytical grade). Opal/metal nanocomposites had the form of opal matrices consisting of SiO$_2$ spheres, with opal pores containing 3d transition metal nanoparticles (Fe, Co, Ni, and their binary and ternary combinations: alloys and solid solutions) synthesized as described previously [32–35]. Opal crystals containing nanoparticles of various metals were prepared as described elsewhere [38]. Opal consisting of monodisperse silica spheres 270–280 nm in size was infiltrated with concentrated (50%) water–alcohol solutions of Co, Ni, and Fe(III) salts (nitrates and chlorides) and with mixed solutions of iron group metal salts in various proportions for the Co: Ni, Co: Fe, and Ni: Fe binary systems and in the Co: Ni: Fe (1: 1: 1) ternary system. The samples thus prepared were dried at room temperature ($T_R$) and then heat-treated at 450°C to a preset schedule. Next, the samples were exposed to supercritical isopropanol at temperatures from 250 to 300°C and a pressure on the order of 10 MPa in 200-cm$^3$ steel autoclaves.

The phase composition of the unfilled opal and nanocomposites was determined after each processing step by X-ray diffraction on a Shimadzu XRD 6000 diffractometer ($\lambda_{Cu}=1.54184$ Å). The crystallite size ($D_c$) of crystalline phases in the X-ray amorphous opal was evaluated from X-ray diffraction data using the Scherrer formula. Unit-cell parameters were determined by least squares extrapolation. The phases present were identified using JCPDS–ICDD PDF data (release 2003) [39].

The morphology and size of the nanoparticles in the opal matrix were assessed by scanning electron microscopy (SEM) on a Carl Zeiss Model NVision 40 and a JEOL JSM-7001F electron microscope equipped with Oxford Instruments X-ray microanalysis systems.

**Fiber-optic technique for local analysis of the spectrum of band gaps in the nanocomposites.** In this study, we used as-prepared opal consisting of monodisperse spheres about 270 nm in diameter. The opal had the form of 2- to 4-mm-thick plane-parallel plates ~1 cm$^2$ in area, with (111)-oriented faces. Figure 1 shows a block diagram of the experimental setup used. Spectra were analyzed in backscattering (180°) geometry. Broadband radiation from a radiation source ($I$) (halogen lamp) was delivered by an optical fiber ($2$) secured in a probe ($4$) to the (111) surface of a sample under study ($5$). A diaphragm ($6$) ensured localization of the radiation under study on a small surface area of the nanocomposites being investigated. Another optical fiber ($3$) was used to deliver the reflected light to an FSD8 minispectrometer, which was connected to a computer ($8$). From the minispectrometer, reflection spectra in digital form were fed to the computer through a USB cable. The optical and spectral characteristics of the spectrometer ensured high sensitivity in spectral measurements. The spectra were obtained at exposure times from 100 μs to 32 s.

The fiber-optic setup built for measurements of local reflection spectra enabled parameters of the band gaps of opal crystals to be determined with a 0.2-mm