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Towards 3D photonic crystals

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Abstract

Synthesis of artificial opals with the structural and optical properties of three-dimensional (3D) photonic crystals has been carried out. We describe the stages of the uniform silica globules preparation by the multistage build-up method, their packing in the 3D lattice by centrifugation, and their sintering. The correlation between technological parameters used and structural and optical properties of the fabricated opals with the photonic band gap maximum range from 475 to 650 nm is discussed.

Keywords: Artificial opal; Photonic crystal; Colloidal crystal

1. Introduction

The growing interest in fabrication and investigation of the two- and three-dimensional (3D) photonic crystals is determined by the novel optical properties of such materials, due to photonic band gap effect, which has been theoretically predicted by Yablonovitch [1] and John [2]. Opaline structures were found to be a successful solution for 3D periodic modulation of optical properties of medium ensuring the existence of photonic band gaps (PBG) [3–7].

The preparation of opaline material with PBG-properties includes several steps such as: (i) synthesis of monodisperse silica powders; (ii) their 3D packing; and (iii) sintering. Usually, the procedure of 3D periodic packing is realised under the gravitation field (free sedimentation), thus being a time-consuming process. However, a centrifugal acceleration, which is routinely employed for phase separation, seems also attractive in the growth of colloidal crystals.

In this paper, we report on the synthesis of opaline materials using sedimentation of silica globules in centrifugal field. The fabricated opaline colloidal crystals exhibit PBG effect in the visible range.

2. Experimental

To prepare the silica powders a multistage synthesis was used [8]. At first tetraethylorthosilicate (TEOS), ethanol, distilled water and ammonium hydroxide were stirred using a magnetic mixer during 5 h in the Erlenmeyer flask with the ground stoppers [9]. This procedure resulted in synthesis of monodisperse silica powders with less than 10% dispersion of size. Then TEOS and solvent reproducing the original reactionary composition were added into the system, so that the silica concentration did not exceed 16 mg/ml. At higher concentration of silica the essential aggregation of particles was observed.

The packing of silica powders was carried out onto highly polished glass substrate for 3 h at a centrifugal acceleration ranging from 7500 to 9000 m/s^2 depending on the size of particles used. Smaller powders were precipitated at higher accelerations. Sintering of the samples was carried out at a temperature from 800 to 900°C for 2–3 h. Isothermal treatment at temperature of 130°C was used to avoid cracking of samples during evaporation of physically adsorbed liquid. The quality of the fabricated silica powder packings was estimated by SEM-microscopy.

Optical spectra of the opaline samples were recorded using Carry 500 spectrophotometer. Reflection spectra were obtained from the surface of the pieces. To get transmission spectra the samples were impregnated with glycerol.

3. Results and discussion

Statistical analyses of SEM-micrographs reveal that repeated synthesis of the fabricated powders result in reducing of their size variation. It could be understood, considering that the particles of the smaller size have a smaller

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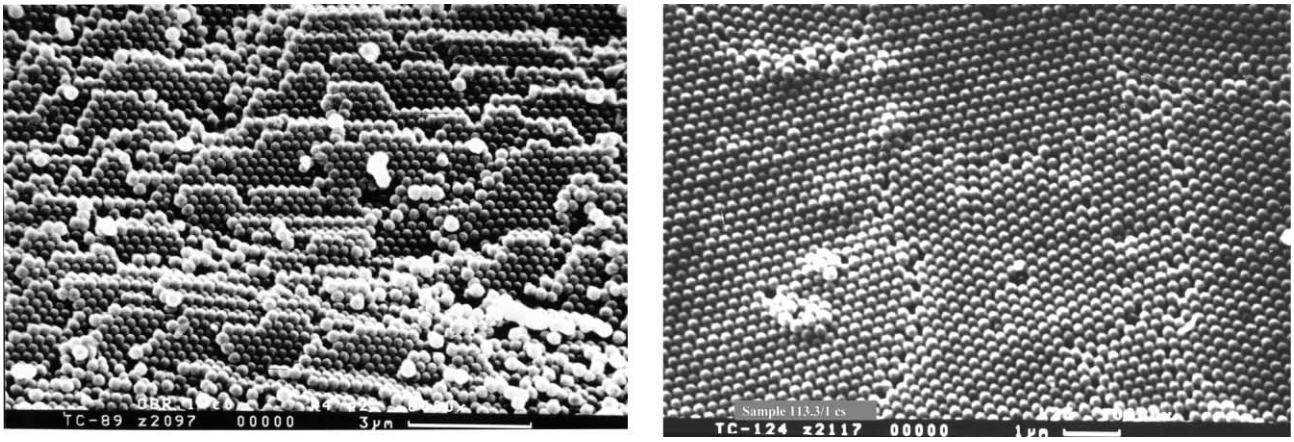

Fig. 1. Typical micrographs of opaline samples: cross-section (left), top surface (right).

curvature radius and large surface energy. Thus, the products of reaction are deposited first on the smaller particles. On the other hand, the smallest powders are diluted during prolonged mixing and, in its turn, it results in the additional growth of the other particles. At the multistage building up of the particles the powders varying less than 4% in size were prepared.

Thermal treatment of SiO_2 particles (20–800°C) in air leads to the change of phase composition of the powders. The results of X-ray phase analysis demonstrate that, thermal treatment at 800°C causes transformation of about 50% of initially amorphous particles into crystalline phase with β-crystoballite crystallites about 5 nm in size.

SEM-analyses of the colloidal packings obtained after centrifugation reveal their polycrystalline structure with the monocrystalline blocks about 0.1 mm in size. Preliminary isothermal treatment of the samples results in their toughening without failure of the structure (Fig. 1).

The presence of stop-band in certain position of transmission spectra of samples also specifies the quality of packing. A long-ordered packing of silica globules could not be obtained at low acceleration of centrifuge. It is confirmed by the comparison of the transmission spectra of the samples prepared from the same silica powder with different values of acceleration (Fig. 2a). A pronounced dip at transmission spectra was observed only in the case of packing of the globules at high accelerations. Thus, the sample formed at acceleration of 8750 m/s^2 and sintered at 800°C reveals a well-resolved dip in reflection spectra centred from 420 to 540 nm depending on the incidence angle (Fig. 2b).

In conclusion, opal-like colloidal crystals exhibiting PBG in visible range were fabricated by sedimentation at centrifugal field followed by sintering in air. It was found that the quality of the packing could be improved by using higher acceleration (about 8750 m/s^2 in our case). It was detected by both the optical transmission and reflection analyses. Recently, we observed the partial inhibition of terbium photoluminescence (PL) from titania xerogel, embedded in such a colloidal crystal [10], following the previous study of Tb PL in titania xerogel [11].

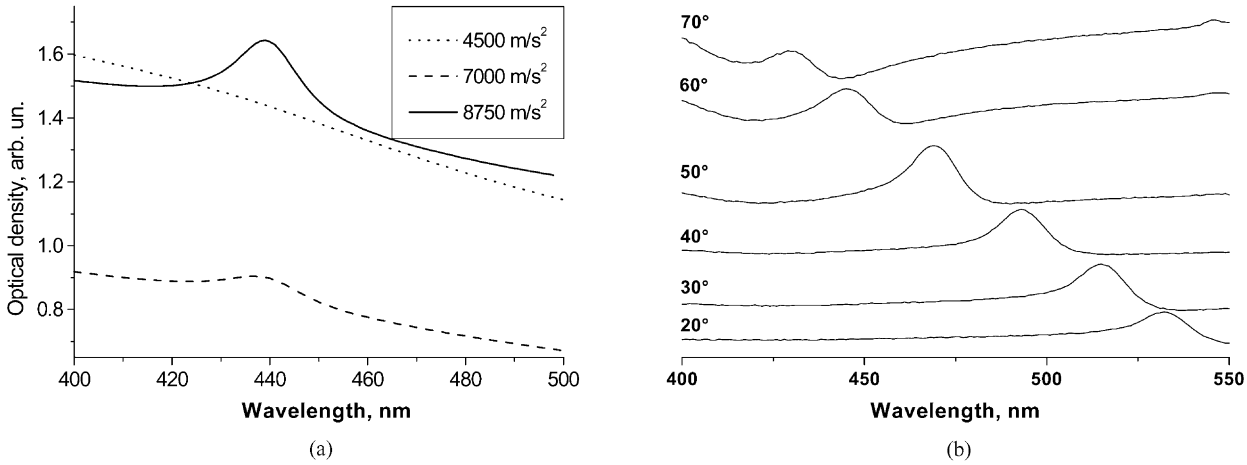

Fig. 2. Optical spectra of the opaline samples: transmission spectra of the samples in glycerol prepared with the same powder at different centrifugal accelerations (a); stop-band position vs. angle of incident light on reflection spectra of opaline sample (b).

Acknowledgements

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