UDC 535.36

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OPTICAL PHENOMENA IN MATRIX NANOCOMPOSITES BASED ON SYNTHETIC OPALS

The matrix nanocomposites based on synthetic opals with pores filled with various active dielectrics ($Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$, TeO_2, KH_2PO_4, $Pb_5Ge_3O_{11}$) are obtained. The fact of pores filling is proved by the changes in the reflection or transmission spectra. The crystalline state of embedded dielectrics is determined on the base of measured Raman spectra of the obtained nanocomposites. In all cases, Raman spectra of the nanocomposites undergo the changes (appearance of new bands, shift of the bands, spectral intensity redistribution) compared with the spectra of single crystals or polycrystalline powder of corresponding dielectrics. The modification of the photoluminescence spectrum of the opal-$Bi_{12}SiO_{20}$ system is connected with increasing the number of surface states under the restricted volume conditions. The appearance of intense emission in the opal-KH_2PO_4 spectrum under a 532 nm laser excitation is probably assigned to spontaneous parametric down-conversion which becomes observable due to enhancement of the pump field inside synthetic opal.

Keywords: photonic crystals, Raman scattering, luminescence, spontaneous parametric down-conversion.

Получены матричные нанокомпозиты на основе синтетических опалов, поры которых заполняются различными активными диэлектриками ($Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$, TeO_2, KH_2PO_4, $Pb_5Ge_3O_{11}$). Факт заполнения пор подтверждается изменениями в спектрах отражения или пропускання. На основании измеренных спектров комбинационного рассеяния света полученных нанокомпозитов устанавливается кристаллическое состояние введенных диэлектриков. Во всех случаях спектры комбинационного рассеяния света нанокомпозитов претерпевают изменения (появление новых полос, смещение полос, перераспределение спектральной интенсивности) по сравнению со спектрами монокристаллов или поликристаллических порошков соответствующих диэлектриков. Модификация спектра фотолюминесценции системы опал-$Bi_{12}SiO_{20}$ связывается с увеличением поверхностных состояний в условиях ограниченного объема. Появление интенсивного свечения в спектре опал-KH_2PO_4 при лазерном возбуждении на длине волны 532 нм связывается со спонтанным параметрическим рассеянием света, которое становится наблюдаемым вследствие усиления поля накачки внутри синтетического опала.

Ключевые слова: фотонные кристаллы, комбинационное рассеяние света, люминесценция, спонтанное параметрическое рассеяние света.

Отримані матричні нанокомпозити на основі синтетичних опалів, пори яких заповнені різними активними діелектриками ($Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$, TeO_2, KH_2PO_4, $Pb_5Ge_3O_{11}$). Факт заповнення пор підтверджується змінами у спектрах відбивання чи пропускання. На підставі виміряних спектрів комбінаційного розсіяння світла отриманих нанокомпозитів встановлюється кристалічний стан введених діелектриків. У всіх випадках спектри комбінаційного розсіяння світла нанокомпозитів зазнають змін (поява нових смуг, зсув смуг, перерозподіл спектральної інтенсивності) порівняно зі спектрами монокристалів або полікристалічних порошків відповідних діелектриків. Модифікація спектру фотолюмінесценції системи опал-$Bi_{12}SiO_{20}$ пов'язується із зростанням поверхневих енергетичних станів, що відповідають дефектам або домішкам, за умов обмеженого об'єму. Поява інтенсивного світіння у спектрі опал-KH_2PO_4 за лазерного збудження на довжині хвилі 532 нм пов'язується із спонтанним параметричним розсіянням світла, яке стає можливим спостерігати внаслідок посилення поля накачки усередині синтетичного опала.

Ключові слова: фотонні кристали, комбінаційне розсіяння світла, люмінесценція, спонтанне параметричне розсіяння світла.

Introduction

The creation and investigation of the matrix nanocomposites with active dielectrics attracts a great attention in physics of low-dimensional systems. Physical properties of nanocrystals of active dielectrics should be essentially different from those of bulk crystals because of the quantum-size effects in electronic and vibrational spectra [1]. On the other hand, in case of periodical arrangement of the nanocrystals, the effects attributed to the photonic crystals should be also expected. Thus, such structures have to enlarge our opportunities in the light flows controlling [2].

As a base matrix for obtaining these structures the synthetic opals are widely used. Regular arrangement of cavities and channels in initial synthetic opals allows for getting 3D periodical structures for a wide range of organic and inorganic compounds. A typical embedding procedure is a soaking of initial opal into the compound solution at temperatures close to room temperature or into the melt of compound with the following crystallization by cooling [3, 4]. In this case, a solid phase of embedded compound is formed under the other conditions than as usual. These special conditions are the high temperature, the limited volume of pores and the lack of atmosphere into interior pores.

The present work is devoted to the obtaining of matrix nanocomposites based on synthetic opals whose pores were filled with active dielectrics ($Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$, TeO_2, KH_2PO_4, $Pb_5Ge_3O_{11}$), to their characterization with the use of reflection (or transmission) and Raman spectroscopy technique and to the study the secondary emission spectra of the obtained structures.

The obtaining and characterization of samples

Bulk opals were grown by slow crystallization of a colloidal solution of monodisperse SiO_2 globules synthesized by modified Stöber method [5]. After drying in air the obtained precipitate was annealed at 125 ^{0}C for 1 h, then at 750 ^{0}C for 2 h. The opal structure was a face-centered cubic lattice formed by hexagonal close-packed layers of monodisperse globules. To determine the structural parameters of opal matrix (globules diameter D and interplanar distance d) and, consequently, to estimate the geometrical sizes of pores the Bragg diffraction spectra in the reflected beams have been measured. According to the Bragg law, a spectral position λ_m of the reflection peak is connected with an interplanar distance d as follows

$$\lambda_m(\theta) = 2\mathrm{d}\sqrt{\varepsilon_{eff} - \sin^2\theta} \tag{1}$$

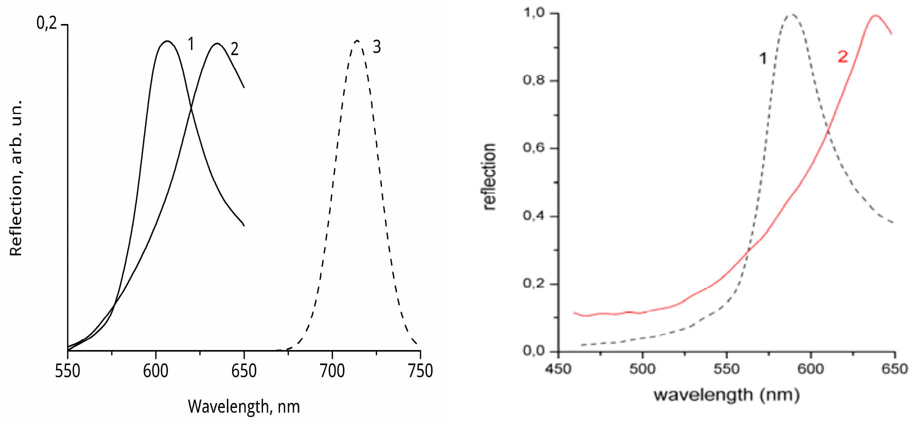
where θ is an incident angle of light beam on system of the {111} planes, ε_{eff} is an effective dielectric constant. The latter is determined by the dielectric constants ε_i of substances which form the composite and the volume part of substance f_i as follows

$$\varepsilon_{eff} = 0.74 \cdot \varepsilon_{SiO_2} + \sum_i f_i \cdot \varepsilon_i\ ,\ \sum_i f_i = 0.26 \tag{2}$$

The connection between D and d is determined by the geometry of globules arrangement and, in our case, is simply as $D = d\sqrt{3/2}$. For different opal samples in study the values of diameter D and interplanar distance d were varied between 250 – 270 nm and 204 – 220 nm, respectively. An average linear size of pores was about of 70 nm.

The filling of opal pores was carried out by melting-in a fine dispersive polycrystalline powder of corresponding dielectrics. (The exception was made in case of KH_2PO_4 (KDP), when the infiltration was performed by a multiple soaking of opals in supersaturated water – KDP solutions at room temperature.) For this purpose, a thin uniform layer of the substance powder was placed on the surface of synthetic opal (or under the surface) and the whole system was held in the resistance furnace at temperatures above the substance melting temperature for 15 – 30 min. After this the samples were cooled down room temperature with the average cooling rate of 3 ^{0}C/min.

The filling of opal pores with active dielectrics resulted in shifting Bragg reflection peak to the longer wavelengths, if the refractive indexes of embedded dielectrics were higher than that of SiO_2 globules ($n_{SiO2} = 1.47$). The reason for it is the increase of ε_{eff} by enlarging the value of the latest part of sum in expression (2). Some results corresponding to this case are presented in Fig. 1. In case of the close values of the refractive indexes of opal matrix and embedded substance, e.g. for opal-KDP system ($n_{KDP} = 1.49$), any significant shift was not observed, but the halfwidth of the Bragg reflection (or non-transmission) peak became smaller with an each next infiltration cycle (Fig. 2). It can be explained by diminishing the optical contrast in such system.



a) **b)**

Fig. 1. The reflection spectra of initial opals (curves 1 in both parts) at $\theta = 7^0$ and the same opals after filling with $Bi_{12}SiO_{20}$ (curve 2 in the part a) and with TeO_2 (curve 2 in the part b) at $\theta = 60^0$ and 70^0, respectively. The curve 3 is the calculated reflection spectrum of opal-$Bi_{12}SiO_{20}$ system at $\theta = 0^0$.

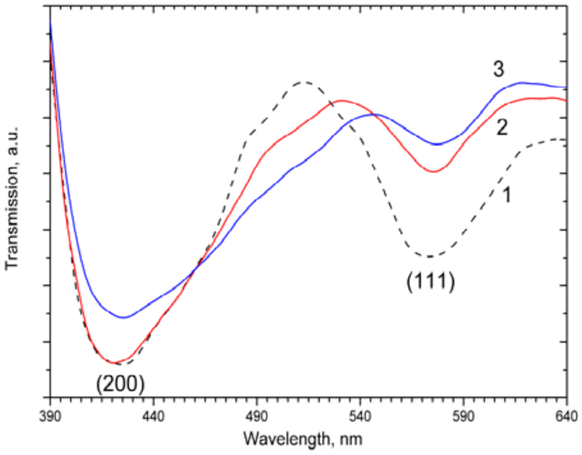


Fig. 2. The transmission spectra of initial opal (curves 1 in both parts) at $\theta = 7^0$ and the same opal filled with KH_2PO_4 after one (2) and two (3) soaking cycles.

Raman spectra of the obtained nanocomposites demonstrate clearly the crystalline state of embedded dielectrics in the opal pores (Fig. 3 - 5). According to results of our previous study, one can exclude an admixture of initial opal Raman spectrum from the further consideration. The reason for this is that the intensities of wide diffuse bands in its Raman spectrum are very small compared with those in the powder and nanocomposite spectra. We can also neglect the influence of photonic stop-band as it is situated far from the studied spectral region. The most features of Raman spectra of the obtained nanocomposites in comparison with the spectra of corresponding polycrystalline powder are the following: 1) an appearance of new bands; 2) a spectral redistribution mostly within a low- and medium-frequency range; 3) a total enhancement of Raman spectrum in case of nanocomposites.

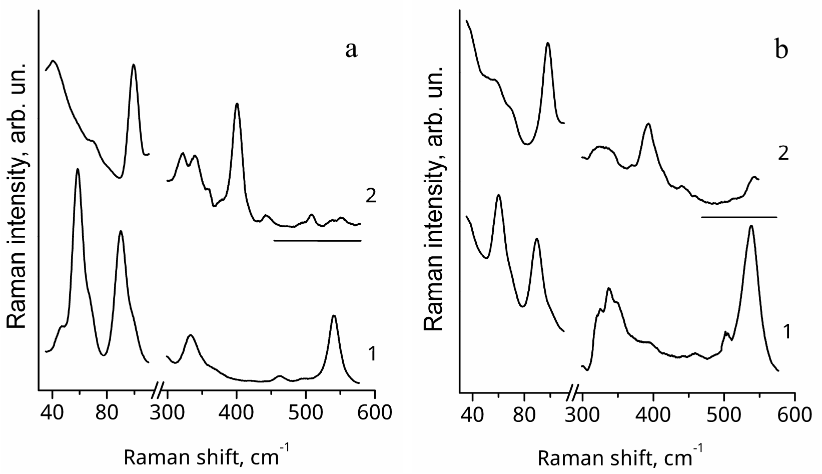


Fig. 3. Raman spectra of polycrystalline powders of $Bi_{12}SiO_{20}$ (1a), $Bi_{12}GeO_{20}$ (1b) and nanocrystals of $Bi_{12}SiO_{20}$ (2a), $Bi_{12}GeO_{20}$ (2b) in opal pores.

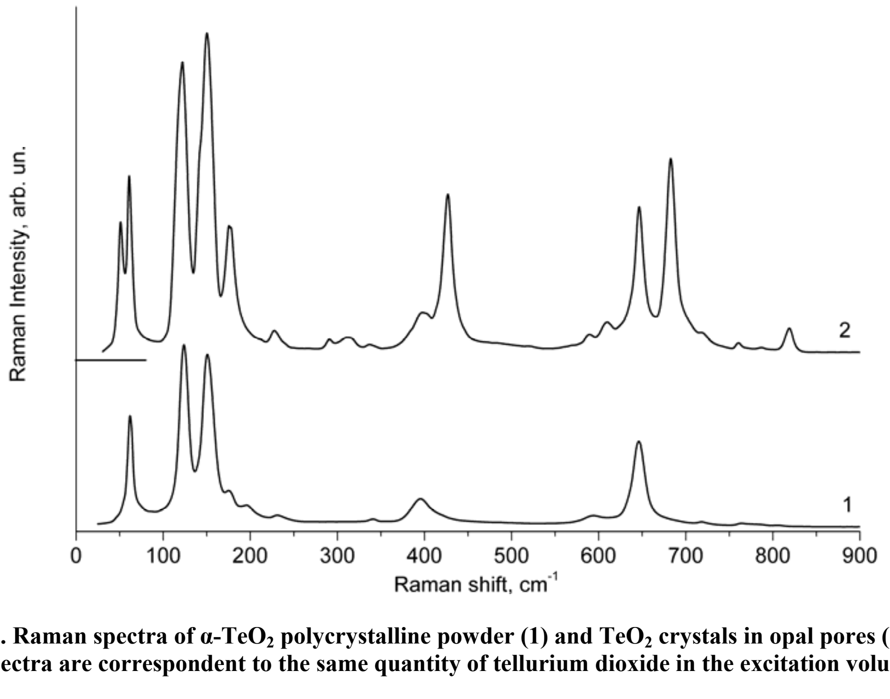


Fig. 4. Raman spectra of α-TeO_2 polycrystalline powder (1) and TeO_2 crystals in opal pores (2). The spectra are correspondent to the same quantity of tellurium dioxide in the excitation volume.

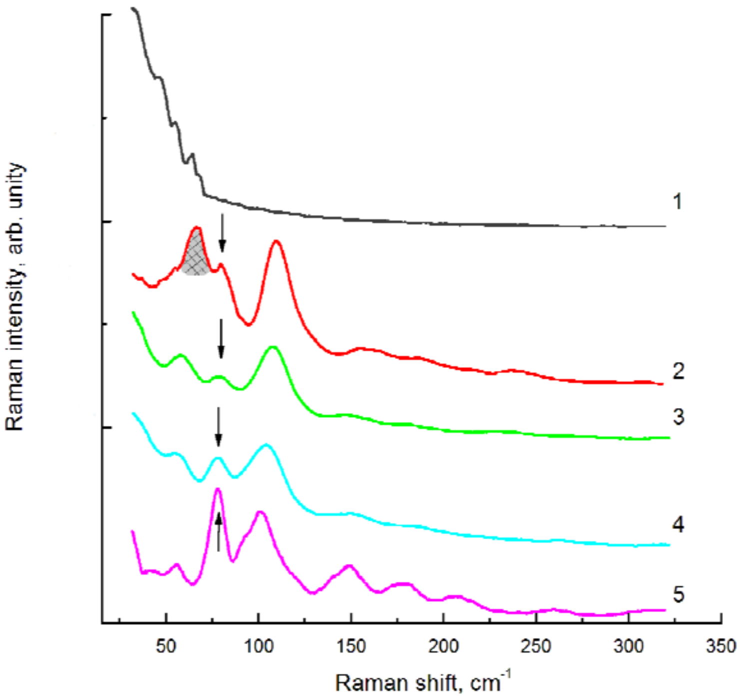


Fig. 5. Raman spectra of "opal - $Pb_5Ge_3O_{11}$" system from different volumes of sample (1 - 4) and single $Pb_5Ge_3O_{11}$ crystal (5).

Let us consider the reasons for these features by using the opal-tellurium dioxide Raman spectrum as an example. An appearance of new bands may testify the changes in crystalline structure. It is really, the frequencies of new bands appeared in opal-tellurium dioxide Raman spectrum (Fig. 4), except for a 51 cm^{-1} band, are well coincident with the majority of bands frequencies in the γ-TeO_2 spectrum [6]. Thus, one can conclude that both α-phase and γ-phase are formed in tellurium dioxide crystals grown into synthetic opal pores. As for a 51 cm^{-1} band, which is absent in the spectra of both crystalline phases, its appearance may be connected with the folding up of acoustic phonons branch by decreasing the Brillouin zone for TeO_2 nanocrystals in opal pores. The spectral redistribution within a 100 – 180 cm^{-1} range is probably due to the appearance of new γ-TeO_2 band at 142 cm^{-1} which enlarges the total intensity within a 140 – 180 cm^{-1} range.

The total enhancement in Raman spectra of the obtained nanocomposites can be explained by multiple reflections of exciting photon from disordered elements in synthetic opal structure which result in increasing a temporal interval of radiation-substance interaction.

Secondary emission spectra of the obtained nanocomposites

The obtained active matrix nanocomposites may be involved in the process of the optical radiation conversion due to their emission properties. The spectrum conversion into the volume of these nanocomposites occurs in processes of famous optical phenomena, such as photoluminescence and spontaneous parametric down-conversion.

In photoluminescence spectrum of the opal-$Bi_{12}SiO_{20}$ system a "red" shift of the luminescence band and an essential increase of integral intensity are observed in comparison with that spectrum of single $Bi_{12}SiO_{20}$ crystal (Fig. 6).

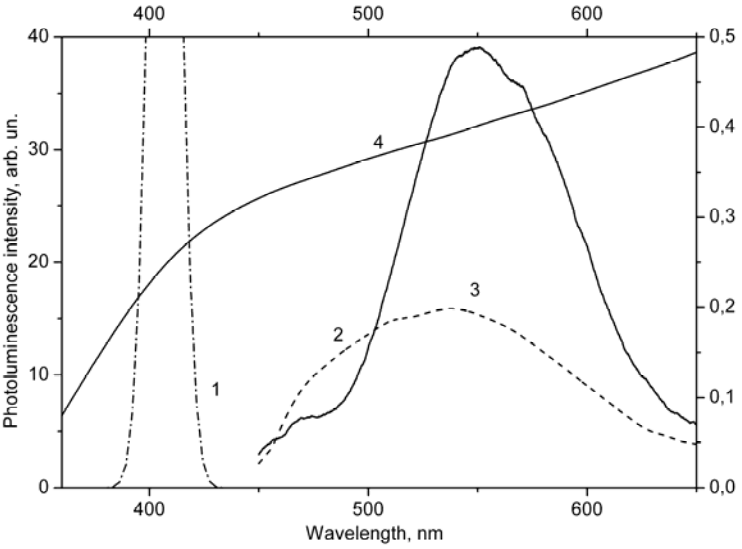


Fig. 6. Spectral shape of the 407 nm exciting line (1), photoluminescence spectra of single $Bi_{12}SiO_{20}$ crystal (2) and of opal-$Bi_{12}SiO_{20}$ system (3) with the spectral response of the typical Si solar cell (4). The photoluminescence spectra are correspondent to the same $Bi_{12}SiO_{20}$ quantity in the excited volume.

The reason of shift is most probably the rebuilding of the $Bi_{12}SiO_{20}$ energy spectrum under restricted volume conditions. The total intensity enhancement is caused both by the Bragg reflection of photons by system of the {111} planes at the larger incident angles with the following output along the [111] direction and by increasing a temporal interval of radiation-substance interaction due to the multiple scattering of light into nanocomposites volume.

The secondary emission spectra of the opal-KDP system under different excitation are presented in Fig. 7.

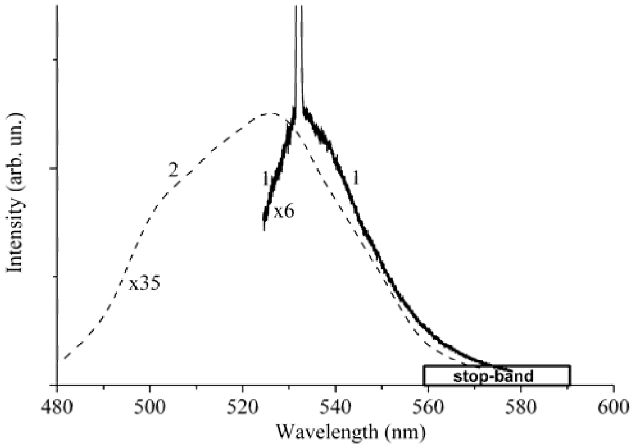


Fig. 7. The secondary emission spectral of the opal - KDP system under a 532 nm laser excitation (1) and a 400 nm LED excitation (2).

In both cases, we obtained a wide emission band within a 480 – 600 nm range. The emission intensity decreases within a stop-band region but it does not vanish completely because of the existence of point defects and structural disordering in photonic crystals. Basing on our previous study of nonlinear-optical photonic crystals [7], we assign this emission to the spontaneous parametric down-conversion.

Spontaneous parametric down-conversion is a process of spontaneous disintegration of pump photons ($\hbar\omega_p$, $\boldsymbol{k}_p$) into pairs of signal ($\hbar\omega_s$, $\boldsymbol{k}_s$) and idler ($\hbar\omega_i$, $\boldsymbol{k}_i$) photons. As this process is a second-order nonlinear process it occurs in media with no inversion symmetry. For spatially non-uniform media with regular structures (photonic crystals) a periodic modulation of linear and nonlinear susceptibilities should be considered in general case. By taking into account the $\chi^{(2)}$ periodic modulation the bi-photons spectrum should be determined by an additive sum of single harmonics of $\chi^{(2)}$ susceptibility. In contrast to parametric down-conversion spectrum of spatially uniform sample the bi-photon field spectrum of photonic crystal should be broadened, and the interference effects may appear in its spectral intensity distribution. Spontaneous parametric down-conversion intensity per a unit angle and spectral interval is determined by the value of quasi-synchronism Δ_m for the m-th order nonlinear diffraction. In case of 3D synthetic opal photonic crystals this magnitude is defined by the structure disordering degree, the nonlinear substance filling factor and by the existence of polydomain structure which forms additional superlattice. In our samples typical domain size was about of 70 mkm. Then the phase quasi-synchronism condition becomes true for the greater number of directions and wavelengths.

Conclusions

The technology of embedding active dielectrics into opal pores has been worked out. Active dielectrics have been found to be in the nanocrystalline form. In some cases it is possible the formation of metastable phase. The essential shift of Bragg reflection band towards infrared spectral region has been obtained. In nanocomposites with nonlinear optical dielectrics the multiphoton processes are observed. The effect of enhancement of secondary emission in active matrix nanocomposites on the base of synthetic opals has been found.

Acknowledgments

This work is supported by the Ukrainian–Russian Project No. F53.2/030 “Creation and investigation of active matrix nanocomposites on the base of photonic glasses and crystals for solar cells”.

References

1. **Stroscio M.** Phonons in nanostructures/ M. Stroscio, M. Dutta // New York: Cambridge University Press, 2001. – 320 p.

2. **Joannopoulos, J.** Photonic crystals. Molding the flow of light / J. Joannopoulos, G. Johnson, J. Winn, R. Meade // Princeton and Oxford: Princeton University Press, Second Edition, 2008. – 632 p.

3. **Aliev A.** 2003. Thermal conductivity of opal filled with a $LiIO_3$ ionic conductor/ A. Aliev, N. Akhmedzhanova, V. Krivorotov, I. Kholmanov, A. Fridman //Phys. of the Solid State.– 2003.– V.45. – P.61-68.

4. **Gorelik V.** Optical and dielectric properties of nanostructured photonic crystals loaded by ferroelectrics and metals / V. Gorelik // Phys. of the Solid State. – 2009. – V.51. – P. 1321-1327.

5. **Stöber W.** Controlled growth of monodisperse silica spheres in the micron size range /W.Stöber, A.Fink, E.Bohn // J. Colloid and Interface Sci. – 1968. – V.26. – P.62-69.

6. **Champarnaud-Mesjard J.** Crystal structure, Raman spectrum and lattice dynamics of a new metastable form of tellurium dioxide: γ-TeO_2 / J. Champarnaud-Mesjard, S. Blanchandin, P. Thomas, A. Mirgorodsky, T. Merle-Mejean, B. Frit // J. Phys. and Chem. of Solids.– 2000.– V.61.– P. 1499–1507.

7. **Moiseyenko V.** Quantum Optics Phenomena in Synthetic Opal Photonic Crystals /V.Moiseyenko, M.Dergachov // Quantum Optics and Laser Experiments. Ed. By Sergiy Lyagushyn. - InTech-Open Access Publisher, Croatia, 2012. - P. 87 – 106, ISBN 978-953-307-937-0.

Received 13.07.2013.