Seminar: Structural characterization of photonic crystals based on synthetic and natural opals

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July 19, 2005

Abstract

Novel class of dielectric structures with a refractive index which exhibits spatially periodic modulation is known as photonic crystals. Photonic crystals do not occur naturally, except for a well-known gemstone natural opal with brilliance light scattering in the visible range. Both natural and synthetic opals are made up of closely packed uniformly sized SiO_2-spheres with diameter on the scale of a micrometer. In the present work AFM and optical spectroscopic comparison studies of the both types of opals are carried out. We found Bragg diffraction spectral bands of the natural opals to be significantly narrower as compared to that of unfilled synthetic materials. Numerical calculations were performed within the model of a planar periodic layered medium making use of the transfer matrix technique, which indicate that the voids between SiO_2-spheres in the natural opals are filled with glass-like rock. From the spectra observed the information about real structure of synthetic opals has been extracted with an account of anisotropic shrinkage and sintering of SiO_2-spheres.

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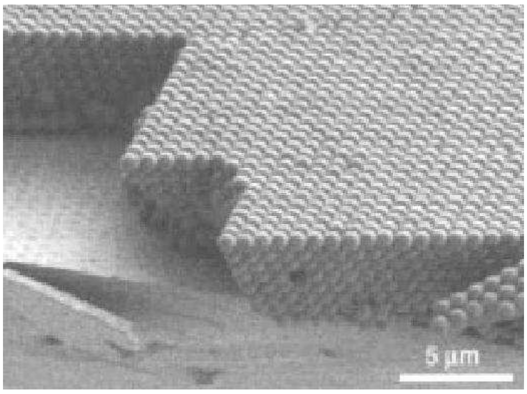

Figure 1: Image of synthetic opal obtained by SEM method

1 Introduction

1.1 Natural and synthetic opals

The photonic crystals are artificially fabricated structures with spatially modulated dielectric constant. This material exhibits frequency ranges where electromagnetic wave can not propagate. These are so called photonic band gaps. The reason of a band gap origination is Bragg reflection of electromagnetic waves on periodical system of crystal layers.

The investigation done at a laboratory of a Solid state spectroscopy at the Ioffe Physico-technical Institute was devoted to natural and synthetic opals. Synthetic opals now became a model object for photonic crystals investigations. Opal structure is the basis for creating a variety of new photonic crystals. Synthetic opal consists of hexagonal layers of closely packed marbles of SiO_2 (i.e. nanosized glasses balls).

Natural opal is one of the most known and expensive gemstones. Its name originated from a Sanscrit word and in Latin it means a “jewel stone”. People know opals and use them as jewelry for more than 2200 years. Now jewelers differ about 10 sorts of a gemstone opal. The beauty of a gemstone opal depends on its optical properties. Natural opals consists of nanosized marbles of SiO_2 and the pores between the marbles are filled with amorphous glass. The intensity of light diffracted by a crystal of opal is defined by optical properties of spheres (marbles) and pores. Gemstone opals have a weak contrast of indexes of refraction between SiO_2 spheres and pores and consist of many different microcrystals so we may enjoy such a wonderful phenomenon as opalescence is.

1.2 Technology of synthetic opals growth

Most of the samples of synthetic opals are purchased commercially. In order to study physics we chose the samples of the best quality fabricated using a certain technological process. At first step the monodisperse suspension of SiO_2 spheres were synthesized. The diameter of spheres varies from 300 up to 800 nm. The standard deviation of the spheres diameter is about 5that the spheres were resuspended in distilled water and this suspension was left undisturbed in a cuvette for a long period (about several months). The spheres in the cuvette slowly settled down and formed a self-organized a three-dimensionally periodic structure. Finally the ordered sediment is annealed at hydrothermal conditions to provide hardness of a sample.

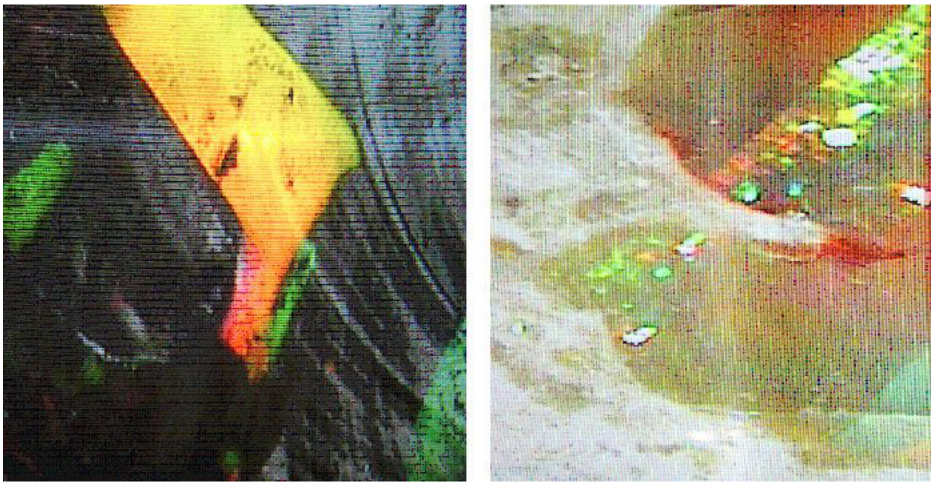

Figure 2: Enlarged photo of natural gemstone opals (field of Mexico)

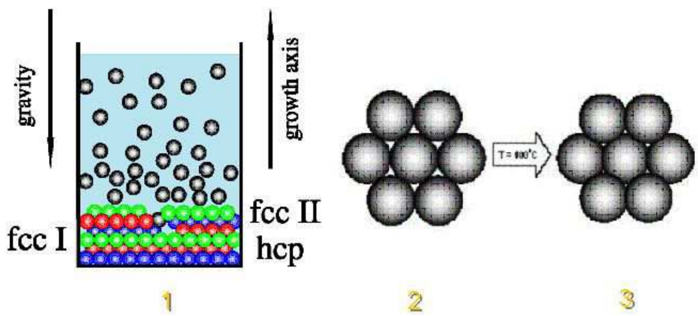

Figure 3: Technology of synthetic opals growth

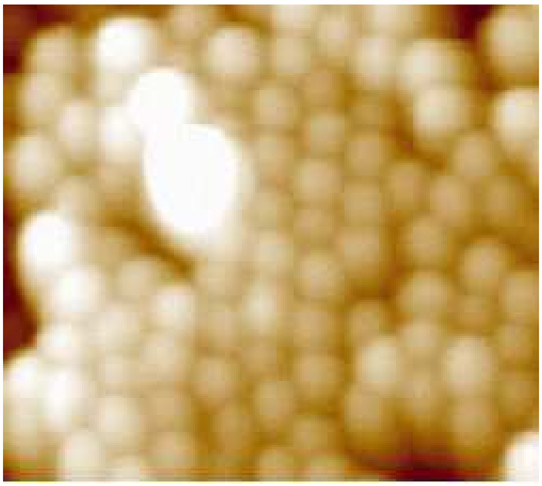

Figure 4: Growth surface of synthetic opal

2 Characterization of synthetic opals by atomic force microscopy method

One of the methods we used for opal parameters investigation was the atomic force microscopy (AFM). The fig. 4 shows growth surface of a sample of synthetic opal obtained by AFM. A real size of this peace of opal is about 3.5 micrometers. The data obtained let us to estimate the lattice constant of our sample of synthetic opal.

3 Bragg reflection spectroscopy

3.1 Scheme of spectroscopic plant

The main method of characterization our samples was Bragg reflection spectroscopy. The spectroscopic measurements were distinguished at this spectroscopic plant. A beam of light from the source L_0 propagated forward through the polarizer P and was focused by collimation system L_1 at a surface of our sample. The sample fixed at a goniometer G was rotated around the axis perpendicular to a plane of a screen. The light reflected the surface of a crystal propagated though the system of lenses L_2, L_3 and directly to input slot of the monochromator. The robotizing system was used so we obtained a spectrum in a digital form with a computer.

Our main task was to find out the parameters of opal-based photonic crystals. To solve it we registered Bragg reflection spectra of the most ordered surface of opal that is a surface of crystal growth. Spectra were measured at different angles (10, 20, 30 and 40 degrees)of light incidence at the growth surface. The spectral position of a stop zone depends on an angle of light incidence according to the Bragg law. So the more is the angle the shorter is the Bragg wavelength.

We also measured Bragg reflection spectra of natural opals. It was done for the first time, no one measured it before. The main feature of reflection peaks of natural opals is a narrow half-width. They are much narrower than reflection peaks of synthetic opals without filling showed on the fig. 6. The reason of overlapping of spectral positions of stop zones is that the crystal consists of many microcrystals.

We filled our sample of synthetic opal with distilled water and isopropyl alcohol to characterize the opal completely. These liquids were chosen because the value of index of refraction is near to opal's index of refraction. It's easy to see that the half width of reflection spectra

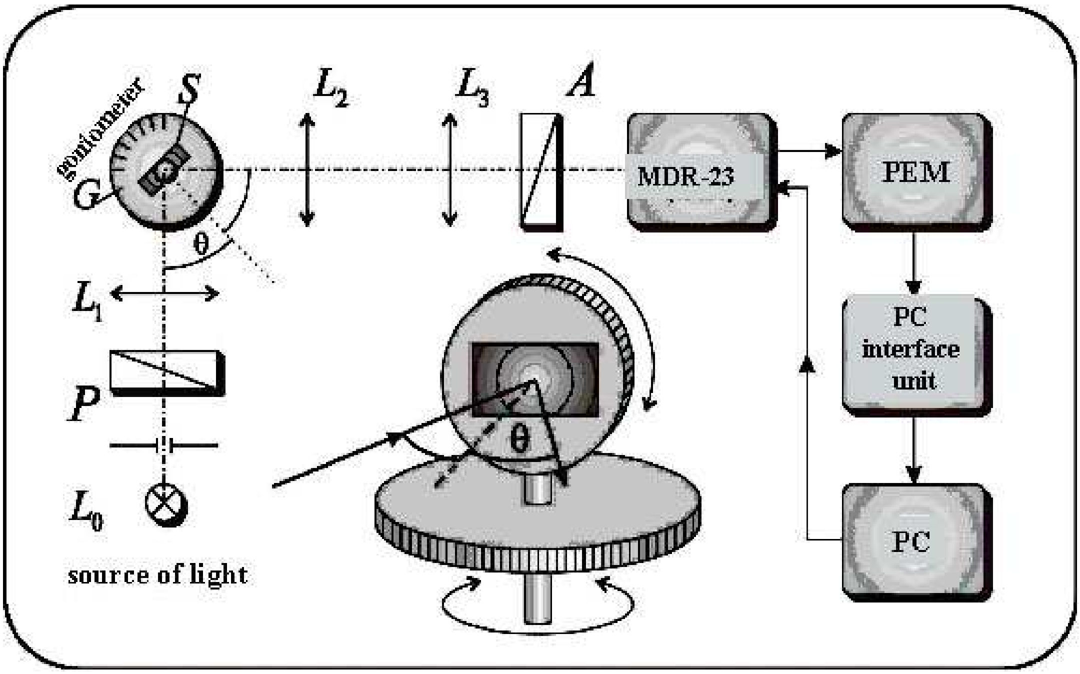

Figure 5: Scheme of spectroscopic plant

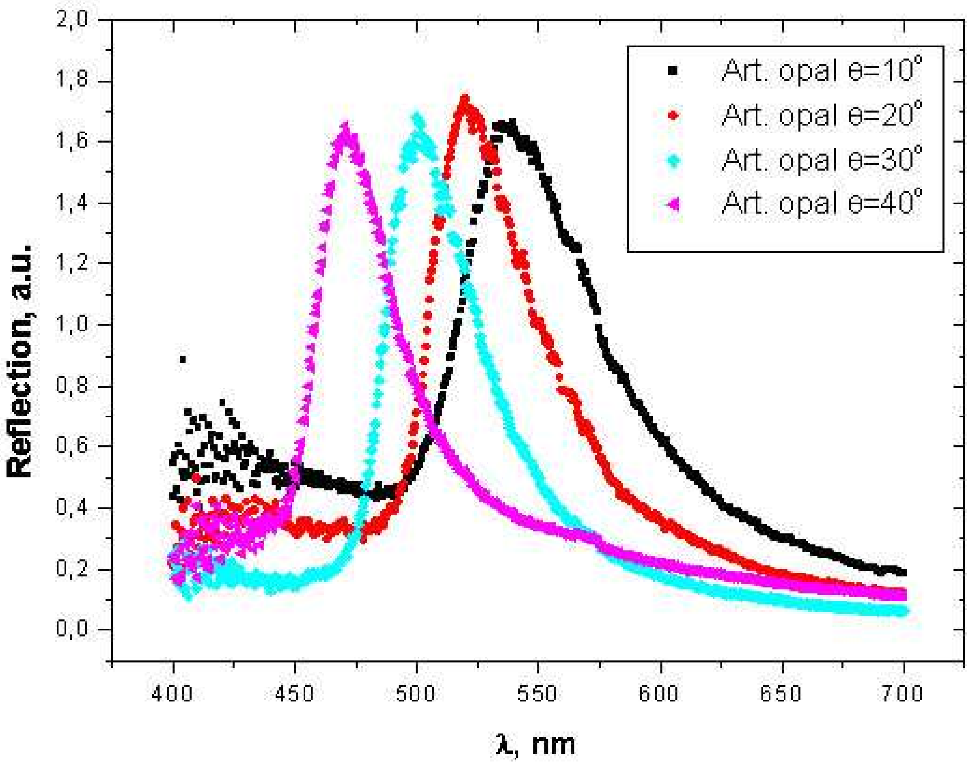

Figure 6: Bragg reflection spectra of synthetic opals

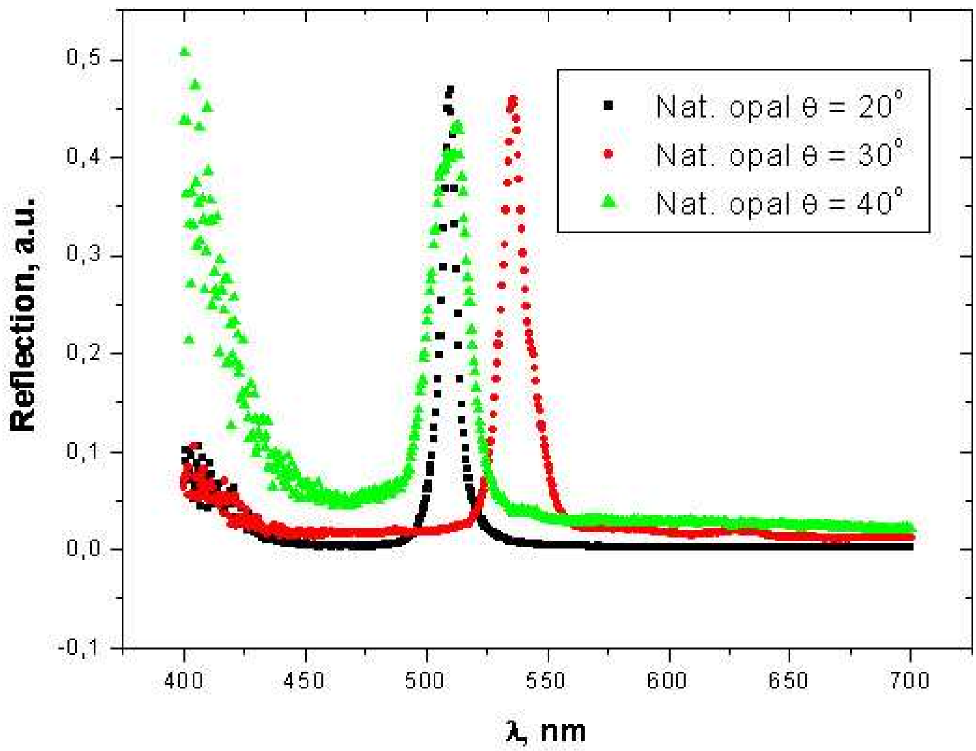

Figure 7: Bragg reflection spectra of natural opals

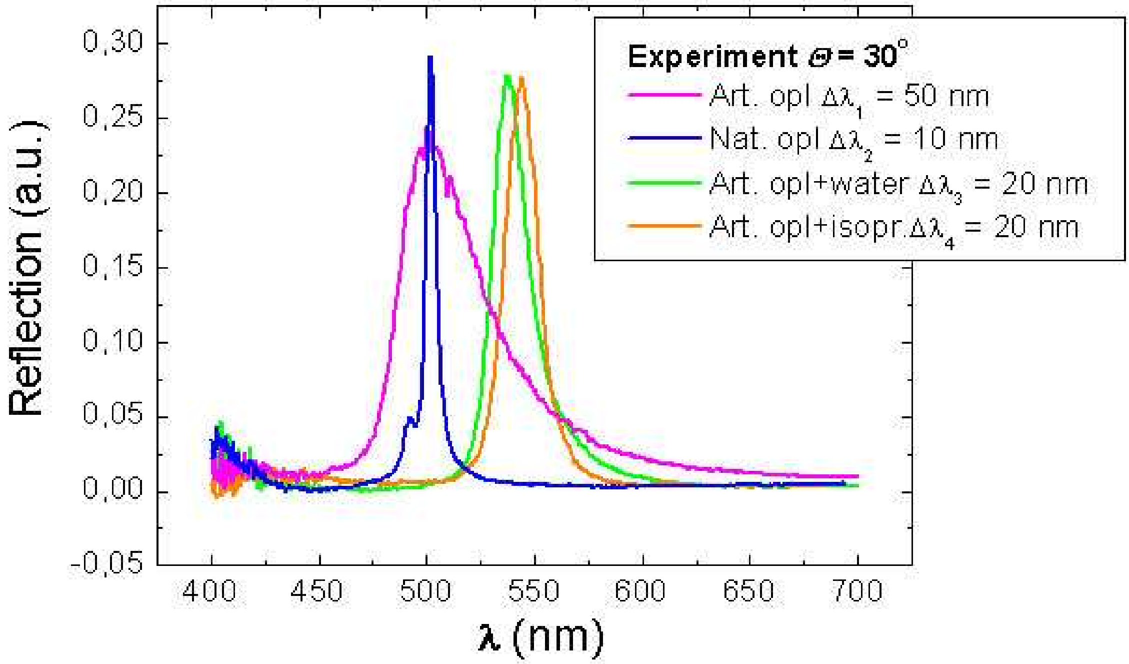

Figure 8: Bragg reflection spectra of synthetic opals filled with water and isopropyl alcohol and natural opals

decreased. So the difference between half widths of synthetic opal and natural opal is not so significant. The reason of narrow reflection peak of natural opals is a weak dielectric contrast in these opals.

4 Estimation of synthetic opals parameters

4.1 Structural parameters of synthetic opals

Let's now speak about structural parameters of opals. These parameters characterize the crystal lattice of synthetic opals: eps-dielectric constant; a_{00}-lattice constant; h-axial ratio; f_0-filling fraction of spheres; f_{00}-filling fraction of point-contacted spheres; χ-sintering coefficient of α -SiO_2 particles. It was possible to estimate these values by the shape and spectral position of Bragg reflection line. Some calculations were carried out. The main formulas: the Bragg law and the filling fraction calculating. The eps is a complex value, it includes imaginary part describing damping of a spectral line.

In Fig. 10 there is a result of a processing of dependence of spectral position of Bragg line on angle of light incidence. According to the Bragg law there should be a linear dependence of λ^2 on $sin^2\ \theta$. Actually our experimental data are well approximated by straight lines. That's true for opals with 3 kinds of filling. Lattice parameter D may by estimated out of approximation.

Fig. 11 shows reflection spectra of synthetic opals again. The processing of shape of Bragg reflection peak was carried out the model of periodical planar medium approximation. At this model three dimensional periodical dielectric constant of a crystal is averaged over the plane of crystal growth. As you can see the approximation within the framework of this model is

$$\lambda^2 = \frac{8}{3} D^2 (\varepsilon_0 - \sin^2 \theta), \ where \ D = a_{00}\eta$$

$$\varepsilon_0 = f_0 \varepsilon_a + (1 - f_0)\varepsilon_b$$

$$f_0 = f_{00} \frac{1 - 3\chi^2 (3 - \chi)}{(1 - \chi)^3}, \ where \ f_{00} = \frac{\pi}{3\sqrt{2}} \approx 0.74$$

Figure 9: Calculation of filling fraction and dielectric constant of synthetic opals

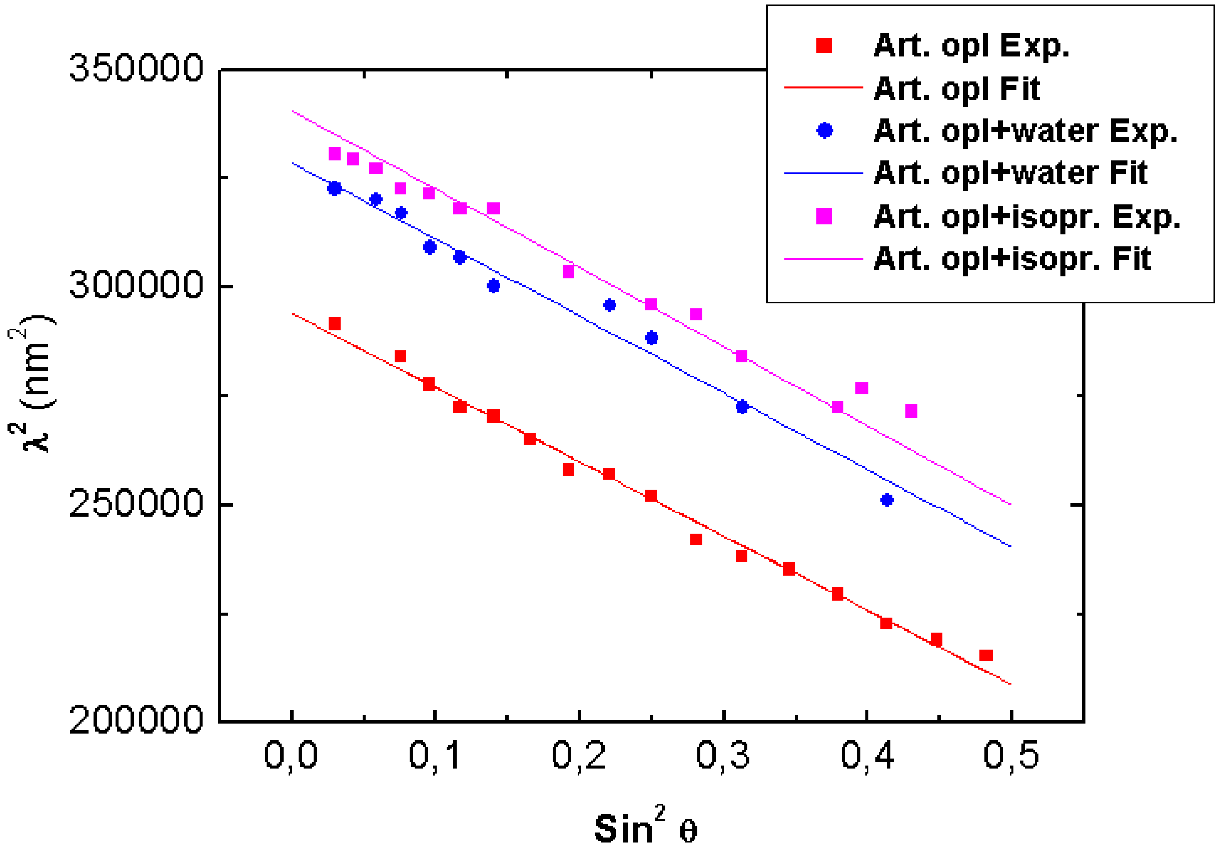

Figure 10: The dependence of the squared Bragg wavelength on the squared sine of the light incidence angle

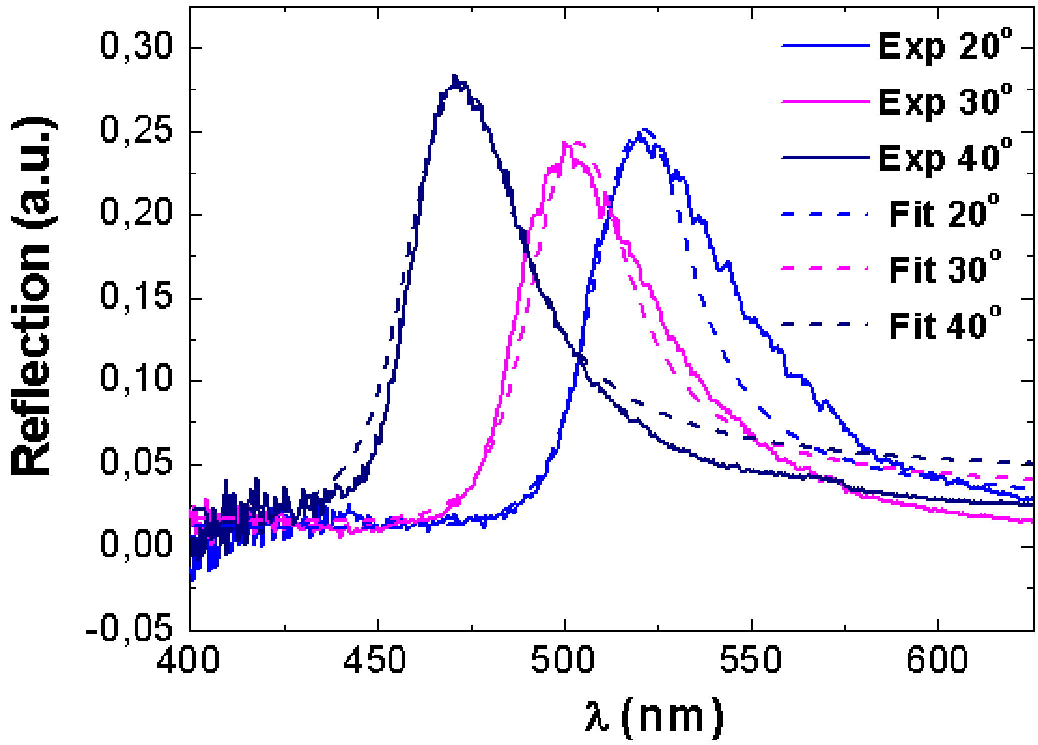

Figure 11: Bragg reflection spectra of synthetic opals: the experimental curves and calculated curves

quite exact.

4.2 Calculated parameters of synthetic opals

The results of the approximation are represented on the Fig. 12. The upper table contains the value of lattice distant of opals (synthetic opals) estimated with three ways: different optical methodics and microscopy. Optical means proceeding of reflection spectra and Bragg law and microscopy means AFM method. All results are of good agreement. A sintering coefficient from lower table is of great importance. Knowing the value of this lattice parameter we calculated the filling fraction of opal pores. And real value of filling fraction is 8than it used to consider for an ideal FCC structure.

The ideal FCC structure means that synthetic opal consists of ideal point-contacted spheres. In this case the filling fraction is equal to 74 per cent and the dielectric constant is defined this way. And to consider a real crystal structure of opals one should include a sintering effect of shrinkage. A sintering coefficient of our structure was equal 0.035 and real filling fraction of our sample was 82 per cent. So the dielectric constant should be defined this with the equation showed on the Fig. 14.

5 Conclusions

1. In the present work AFM and optical spectroscopic investigation and comparison of natural opals and synthetic opals with different fillings were carried out. 2. It was shown that natural

Lattice distance of opals	Reflection spectra	Bragg low	AFM data
a_{00} (nm)	270 nm	275 nm	280 nm

Angle θ, degrees	Sintering coefficient, χ, a. u.	Imaginary part of dielectric constant, ε''
20	0,030	0,07
30	0,040	0,07
40	0,030	0,07

Figure 12: Structural parameters of synthetic opals: spectroscopy + AFM

$$f_{00} = \frac{\pi}{3\sqrt{2}} \approx 0.74$$

$$\varepsilon_0 = 0.74\varepsilon_a + 0.26\varepsilon_b$$

Figure 13: Structural parameters of synthetic opals in point-contact balls approximation

$$\chi \approx 0.035$$

$$f_0 = f_{00} \frac{1-3\chi^2(3-\chi)}{(1-\chi)^3} \approx 0.82$$

$$\varepsilon_0 = 0.82\varepsilon_a + 0.18\varepsilon_b$$

Figure 14: Structural parameters of synthetic opals: real structure including the sintering effect

opals consist of an α -SiO^2 microcrystals. The microcrystals are differently orientated inside of a sample. 3. Half-width of the Bragg reflection peak of natural opals is small because of a weak dielectric contrast in opal/filling (α -SiO^2) system. 4. A set of structural parameters of synthetic opals was defined including a filling fraction. The meaning of a filling fraction of our samples is 82 per cent. It means the 8 per cent decreasing a volume of pores of the sample as a result of a shrinkage during a process of opals growth. 5. The data obtained by optical spectroscopic investigation and AFM method are of good agreement.