The object of the study in this paper - silver nanoporous silicate matrix with pore size less than 20 nm. Colloidal silver particles with volume concentration about $10^{-4}$ are formed within free volume of pores of silicate matrix by chemical method. Changes in the attenuation spectra of the investigated object during changing of the refractive index of free volume of pores from 1.0 to 1.5 are reviewed. Comparison of the obtained experimental data with the results of calculations was carried out.

1. Introduction
Nanoparticles of metal silver are of considerable interest in the development of plasmonic materials - artificial nanostructured materials for nanophotonics with unique functional properties that exceed the capabilities of traditional materials and systems. The basic requirements to such materials are: the absence of scattering of containing matrix and a high degree of monodispersion of metal particles. In the studied structure these requirements were achieved by using nanoporous silicate matrix with high transparency in the visible range of the spectrum (the average pore diameter is about 17 nm) and also due to the fact that metal particles are formed in the free volume of pores which are cross-cutting and occupy about 50% of the volume of the sample [1, 2].

Nanoporous silicate matrices are received from the original two-phase glass by processing in the acid and alkali. Samples represent polished plane-parallel plates or disks with the thickness of 1-3 mm. In air-dry condition samples have significant absorption in the short-wave region of the spectrum due to the scattering on porous structure and absorption by the components of the framework. During the introduction of immersion with the refractive index close to the refractive index of the frame into the free volume of pores the sample with the thickness of 1 mm has a high level of transparency in almost entire of the visible spectrum.

2. Experimental methodology
Nanoporous matrices NPM-17 with the thickness of 1 mm with free volume of pores (55±1%) were used in the work, their characteristics are shown on fig.1.

Nanoparticles of silver were formed inside the pores by photolysis of nanoparticles of AgNO$_3$. First, pores of the sample were filled with water solution of AgNO$_3$ with concentration of about one weight percent (1 w. %). Then the sample was briefly washed in distilled water to remove solution from the surface and dried to remove all water from the pores. After this was irradiation of sample by ultraviolet radiation of mercury lamp ($\lambda = 254, 313$ and 365 nm) during two hours. In the course of irradiation full photolysis of AgNO$_3$ to Ag in colloidal state took place. After formation of
nanoparticles of Ag initially colorless sample has orange-red color. Range of optical density has intense peak of absorption in the spectral range from 350 to 500 nm that is caused by the plasmonic resonance of Ag nanoparticles.

At such method of obtaining the maximum size of silver particles is limited and can’t exceed the maximum pore size of silicate matrix (i.e. the diameter of obtained particles doesn’t exceed the values of 20-22 nm). Volume concentration of particles in the samples was of the order of $10^{-4}$. Maximum of plasmonic resonance of such particles is located in the shortwave region of the visible spectrum and its position depends on the refractive index of the containing matrix \[3, 4\].

According to some researchers changing on the refractive index of the medium which contains particles from 1.5 to 2.3 leads to a significant shift of plasmonic absorption band in the long-wave region of the spectrum and its reduction - to a shift in the short-wave region and to increasing of the transparency of the sample in the whole visible range of the spectrum.

We know \[2\] that attenuation of radiation of nanoporous matrices in the shortwave spectral region due to the absorption of components of the silicate framework and to the scattering on porous structure. When filling out with water (n=1.34) free volume of pores compared to air-dry condition of matrix absorption is not changed while scattering reduces significantly and range of attenuation of matrix shifts to the short-wave region (“blue” shift), it is demonstrated on figure 2 (curves 1 and 1’).
During filling out with water free volume of pores of air-dry matrix with colloidal silver particles (figure 2, curves 2 and 2') the shift of attenuation spectrum of matrix to the long-wave region of the spectrum (“red” shift) is explicitly defined.

For a given concentration of silver particles the measurements are possible in the spectral range $\lambda > 550$ nm, where the optical density does not exceed the values of $D = 4$. In this spectral range the absorption of silicate frame and scattering on porous structure is negligible and can be ignored. Thus, the value of the attenuation spectrum caused by the absorption of silver particles, but the maximum values of optical density of the absorption spectrum in this case are impossible to determine.

For obtaining the measured values of the optical density of nanoporous medium with colloidal silver particles were prepared preparation of such medium diluted with water to the necessary concentration - on figure 2, curve 3 attenuation spectrum of such product, investigated silver particles in the water, is shown. As you can see, the maximum of the attenuation spectrum of silver particles in the water is 410 nm.

Table 1 shows the theoretically calculated values of the maximum of the spectrum of attenuation of colloidal silver particles at different values of index of refraction of the medium that surrounds the particle. The calculations were made according to the methodology described in work [5] for silver particles with the same geometric parameters. As you can see, there is good coincidence between the experimental data and theoretical calculations in the case of using water as well as oil immersion.

| Filler | Air (vacuum) | Water | Oil (cedar) | Immersion |
|--------|--------------|-------|-------------|-----------|
| $n_f$  | 1.0          | 1.34  | 1.48        | 1.7       | 2.2       |
| $\lambda$ | 370         | 410   | 430         | 460       | 520       |
The experimental data obtained during changing of the refractive index of free volume of pores are shown on Fig 3.

**Figure 3.** Attenuation spectra of nanoporous medium with colloidal silver particles during changing the filler of the free volume of pores.

As a filler are used: air, water, oil (cedar). The data presented on fig.3 demonstrate increasing of «red» shift when increasing of refractive index of the filler.

**Table 2.** The shift of attenuation spectra of nanoporous matrices with colloidal silver particles, (Δλ), during changing filler of free size of pores of the matrix, n.

| Conditions of measurements | Air-water | Water-oil |
|----------------------------|----------|-----------|
| 1                          | D = 2    | 80        | 20        |
| 2                          | D = 3    | 80        | 20        |
| 3                          | Calculation on Dmax | 40 | 20 |

Table 2 shows the qualitative results of the definition of observed shifts in the experiments. Because the shift of the maximum can’t be determined experimentally the measurements of the shift of wavelength of radiation at changing of the refractive index of the filler at different levels of optical density (D=2 and D=3) were carried out. Experimental values of the shift of the side sections of the spectrum, of course, exceed the value of the shift of the maximum of the spectrum.

3. **Conclusion**

Researching of influence of the filler of free size of pores of nanoporous silicate matrix on the parameters of the attenuation spectrum of colloidal silver particles formed inside the free size of pores of this matrix is carried out. The presence of long-wavelength, «red», shift of plasmonic resonance of silver particles during increasing refractive index of free volume of pores is shown. A good coincidence between the experimental results and theoretical estimates is received.

This effect can be used for evaluation:
effective refractive index of the medium surrounding the particle of silver;
refractive index of the medium directly surrounding the particle of silver;
the structural parameters of nanocomposites with particles of colloidal silver.

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