Design and Fabrication of Optical Devices based on New Polyfunctional Photo-thermo-refractive Glasses

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Abstract: Novel optical elements and devices (holographic volume Bragg gratings, gradient optical elements, optical and plasmonic waveguides, hollow structures, thermo-and biosensors, phosphors for LEDs, down-converters for solar cells) have been designed and fabricated based on new polyfunctional photo-thermo-refractive glasses. Some technologies (photo-thermo-induced crystallization, holograms recording, laser treatment, ion exchange, chemical etching) have been used. Shown that photo-thermo-refractive glasses can be used as a basic optical material for many photonics applications with the characteristics comparable with other commercially available materials.

1 INTRODUCTION

The current stage of development of optical, photonic and plasmonic devices calls for new and most likely miniature optical elements that cannot be fully implemented on the basis of traditional materials and technologies. Therefore, the great attention is being paid worldwide to the development of novel optical materials.

The novel fluorine, chlorine and bromine photo-thermo-refractive (PTR) glasses developed in ITMO University (St. Petersburg, Russia) are very promising optical materials for optical, photonic and plasmonic applications (Nikonorov et al., 2010). PTR glass is a multicomponent photosensitive sodium-zinc-aluminosilicate glass doped with halogens (fluorine, chlorine or bromine) and also antimony, cerium, and silver (Dubrovin et al., 2014). The PTR glass changes its refractive index after an exposure to the near UV radiation followed by thermal treatment at temperatures close to the glass transition one (Tg). For example, in case of fluorine PTR glass, that results in the precipitation of nano-crystalline phases of NaF in glass host and negative increment of RI ($\Delta n = - 1000$ ppm). In other words, it results in decrease of RI in UV irradiated area in comparison with unirradiated area of glass. In case of chlorine and bromine PTR glasses that results in growth of AgCL and AgBr nanocrystals and positive increment of RI ($\Delta n = + 1500$ ppm).

The sizes of NaF, AgCL and AgBr nanocrystals are relatively small (10-20 nm), that is why PTR glasses exhibit rather a low level of scattering. The fluorine PTR glass is successfully used for the fabrication of holographic optical elements (HOEs) that dramatically enhance properties of numerous laser systems and spectrometers. It shows high photosensitivity, high thermal stability of the recorded phase holograms, and high tolerance to optical and ionizing irradiation. Basic optical and spectral properties of fluorine PTR glass are described in (Glebova et al., 2008; Efimov et al., 2011). The HOEs recorded in the fluorine PTR glass reveal high chemical stability, thermal, mechanical and optical strength, and from this point of view practically reveal no difference with the commercial optical glass BK7 (Schott). The optical and spectral parameters of the HOEs and GRIN-elements do not change after its multiple heating to the high temperature (500ºC). The important advantages of the fluorine PTR glass as the optical medium are following: (i) high optical uniformity (the refraction index fluctuations across the glass volume have the scale of some 10^{-5}), (ii) reproducibility of its parameters during the starting glass synthesis and during the photo-thermo-induced crystallization, (iii) similarity to optical glass BK7, the PTR glass can be

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subjected to various methods of mechanical processing like grinding and polishing as well as various formation technologies like molding, aspheric surface production, and drawing fiber, (iv) one can fabricate the PTR glass both in laboratory (some hundreds grams) and in industrial (some hundreds kilograms) conditions with the use of simple and non-toxic technology. The chemical reagents, which are necessary for glass fabrication, are commercially available and not too expensive. One has also to note some features of the fluorine PTR glass, which are unusual for recording media. For example, such media can be subjected to the ion-exchange technology, that providing the possibility to fabricate the ion-exchanged optical or plasmonic waveguides and the surface strengthening to improve the mechanical strength, chemical stability, thermal and optical strength of the PTR glass. Moreover, the photoetchable technology can be used in PTR glass to provide the possibility to fabricate "lab-on-a-chip" systems and optical microfluidic devices. PTR glass doped with rare earth ions reveals good laser characteristics (Aseev and Nikonorov, 2008; Glebova et al., 2011).Recording the Bragg gratings in laser PTR glass opens up a possibility to develop lasers with distributed feedback. In (Hofmann et al., 2013), possibilities to draw optical fibers from PTR glass and record the Bragg gratings in the fiber are shown.

Some characteristics of fluorine PTR-glass and VBGs are demonstrated in Table 1.

Table 1: Characteristics of fluorine PTR-glass.

Transparency range, nm	350-3000
Photosensitivity spectral range, nm	280-350
Photosensitivity, mJ/cm2	50
RI change, Δn	1×10^{-3}
RI modulation amplitude, δn	5×10^{-4}
Induced optical loss, cm-1 - visible range - near IR range	 0.1 0.001
Space frequency, mm-1	up to 5000
Diffraction efficiency, %	95
Hologram thickness, mm	0.1-10
Angular selectivity, ang. min	<1
Bandwidth FWHM, nm	0.1
Size, mm	up to 25×25
VBGs are completely stable at temperature, °C	200

2 DESIGN AND FABRICATION OF OPTICAL DEVICES

2.1 Holographic Optical Elements

2.1.1 Volume Bragg Gratings for Laser Diodes

Wide spread of laser diodes connected with its high energy conversion efficiency, small size, simplicity of use and low cost. However, as it well known laser diodes has wide emission spectra and absence of spectral stability caused by temperature shifts during operation. This problem can be solved by mean of VBG, due to high spectral selectivity of recorded holograms implementation of such grating inside external cavity of laser diode can significantly narrow the output spectra. On the picture below is shown emission of laser diode with and without grating. As one can see grating narrows emission spectra from 6nm down to 6pm. Furthermore, due to high transparency of HOE on PTR glass there's almost no losses in resulting output power. Moreover, gratings can provide tunability for such lasers. By simple rotation of the element one can change output wavelength in a wide range. As experiments shows such laser can be tuned in the whole range of diode gain spectral range, which is about 10 nm.

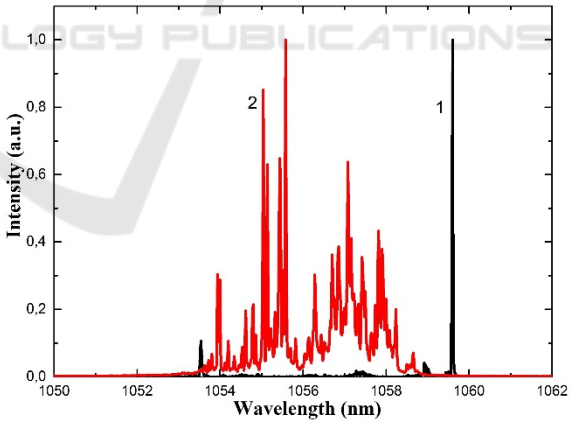

Figure 1: Emission spectra of laser diode source with (1) and without (2) grating.

2.1.2 Imaging Holograms for Collimator Sight

High transparency of novel material in visible range (above 90% without AR) opens a new field of applications with strict requirements to transmission in observation channel such as collimator sight. Application of PTR glass can solve problem of mark

image stabilization, which is necessary due to the instability of laser diode source used in such scopes. To date this problem is solved by addition in optical scheme achromatizing diffraction elements such as additional thin gratings, complex two-cavity mirrors or compound objectives. Wavelength shift, caused by laser diode temperature changes, can be nullified by spectral selectivity of thick hologram recorded on PTR glass. While the central wavelength of laser diode shifts, recorded hologram continues to reconstruct image of mark on proper angle – thus maintaining the position of mark in target plane. Moreover, redistribution of energy in diode output spectra leads to insignificant lowering of intensity of the mark that can be easily leveled by diode power output adjustment. Since the diffraction efficiency of holograms on PTR glass can achieve values of 99%, intensity required for mark observation is pretty low. Worth noting that up to date materials used for mark recording are vulnerable to external impact such as moisture and mechanical damage, that leads to need in additional cover for holograms. With application of PTR glass, since it is high resistant to external impacts, there is no need in additional protection of observation channel. In Figure 2 observable image of holographic mark is demonstrated.

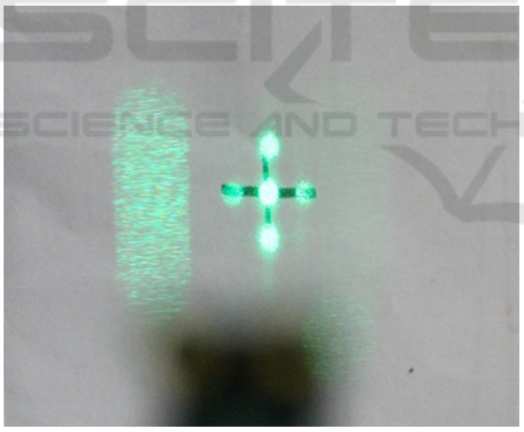

Figure 2: Photo of a reconstructed image of a volume holographic mark.

2.2 Optical Amplifiers

We have demonstrated an optical amplification in the laser PTR glass doped with rare earth ions (Er^{3+} and Yb^{3+}). The concentration of ytterbium ions was equaled to 17.8×10^{20} cm^{-3}. The concentration of erbium ions was varied from 0 to 2.26×10^{20} cm^{-3}. The introducing rare earth ions into the virgin PTR glasses did not change its photosensitive properties.

The experimental spectral dependences of the gain/loss coefficient for various pump power are shown in Fig. 3.

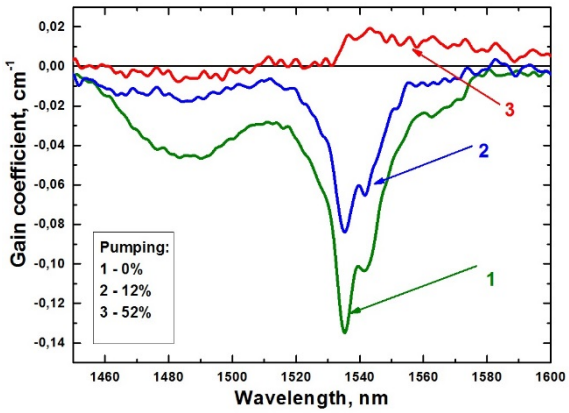

Figure 3: Gain/loss spectrum of PTR glass ceramics with various pump power. $N_{Er}=0.26\times10^{20}$ cm^{-3}, $N_{Yb}=17.6\times10^{20}$ cm^{-3}.

As the pumping power increases, the absorption spectrum transforms into a gain spectrum. The gain coefficient at wavelength of 1.55 μm was close to commercial Yb-Er silicate glass and achieved $g=0.016$ cm^{-1}. The gain is obtained on the samples with a minimum erbium-ion concentration $N_{Er}=0.26\times10^{20}$ cm^{-3} and $N_{Er}=0.56\times10^{20}$ cm^{-3}. Increasing the erbium-ion concentration reduces the gain.

The combination of laser and holographic photorefractive properties into the laser PTR glass substrate allowed us to realize a monolithic integration of optical amplifier with Bragg grating playing a role of spectral flattening filter.

2.3 Optical Waveguides

The virgin PTR glass contains 15-20 mol % of Na_2O. That fact allowed us to consider the PTR glass as ion-exchangeable medium and use an ion-exchange technology for optical and plasmonic waveguides fabrication. The optical waveguides have been prepared with the use of exchange of $Na^+_{(glass)}\leftrightarrow Ag^+$, K^+, Rb^+, $Cs^+_{(salt)}$ from melt of corresponding nitrate. In the case of $Na^+_{(glass)}\leftrightarrow Ag^+_{(salt)}$ optical waveguides reveal no birefringence and RI increment caused by differences in the polarizabilities of cations exchanged achieves $\Delta n=0.014$. In case of replacing the sodium ions in glass by other alkali cations (potassium, rubidium, and cesium), the refractive index profile in waveguides formed by not only differences of ions' in the polarizabilities of ions under exchange but also due to the photoelastic effect arising at the expense of the compressive mechanical

stresses under the exchange of ions with various ionic radii. Such mechanical stresses can improve physicochemical properties of glass surface (mechanical strength, microhardness, thermal stability, and optical durability). For example, our measurements showed an increase in Vickers microhardness of PTR glass from 554 MPa before the potassium IE to 655 MPa after the IE (temperature and duration being 350°C and 6h). The RI increment reaches 0.01 for K^+-waveguides, 0.025 for Rb^+-waveguides and 0.05 for Cs^+-waveguides. The optical losses of the waveguides do not exceed 0.5 dB/cm. Thus, we made a conclusion that the ion-exchangeable properties of the PTR glass are comparable with ones of commercial optical glass of BK7 used for optical waveguides fabrication. In case of Ag^+-waveguides the silver ions can be transformed into silver metallic nanoparticles by thermal treatment in reducing atmosphere. This technology allowed us to fabricate plasmonic waveguides with a strong surface plasmon resonance used for chemical and biological sensors.

2.4 Photoetchable Media for Microfluidic, MEMS and MOEMS Devices

A technology of chemical etching of the fluorine PTR glass has been developed for the first time. The rate of etching of the crystalline phase is much higher than one for the glass host by factors of 6-10.

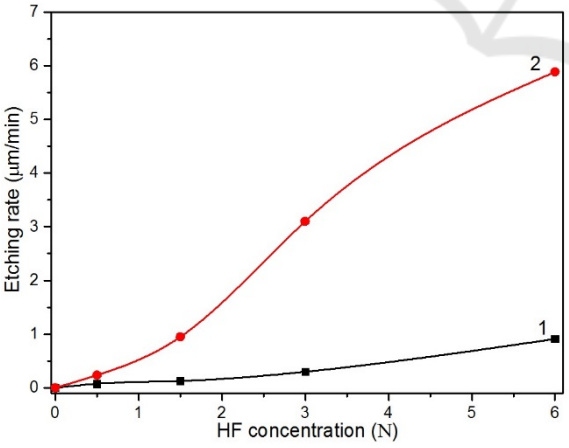

Figure 4: Dependences of etching rates for PTR glass (1) and fluorine glass ceramics (2) on the HF concentration in aqueous solution.

In Fig. 4 are shown dependences of etching rate on the HF concentration in aqueous solution for glass and fluorine glass ceramics. It's obvious that glass ceramics reveal the higher etching rate than the unirradiated fluorine PTR glass. So, the fluorine PTR glass can be compared with well known photoceramics of Foturan™ (Schott, Germany), Fotoform™ (Corning, USA) and PEG3™ (Hoya, Japan) with etching rates of 15-20 between the crystalline phase and the glass host, that are successfully used for fabrication of 3D hollow microstructures, microfluidic devices, micro-total analysis systems (μTAS), micro-electro-mechanical systems (MEMS) and micro-opto-electro-mechanical systems (MOEMS). At the same time holographic properties of the Foturan™ and PEG3™ (Kösters et al., 2005) greatly concede ones of the PTR glass.

To demonstrate photostructable properties of the PTR glass the Russian abbreviation of the ITMO University was chemically etched.

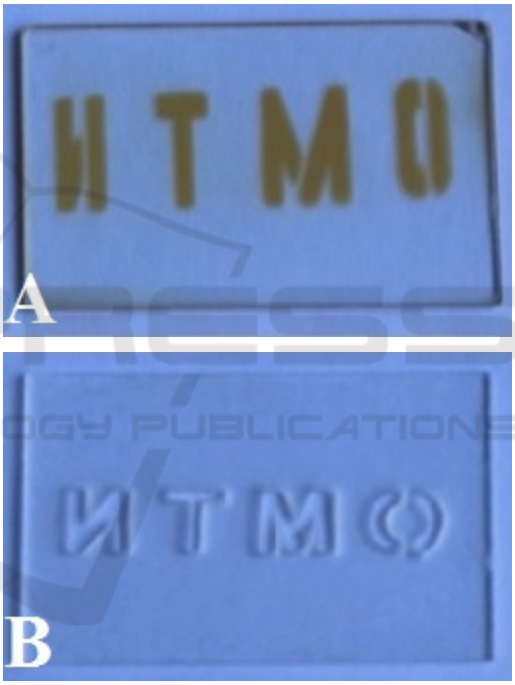

Figure 5: UV irradiated through mask and heat treated 1 mm PTR glass (A). Subsequently chemically etched PTR glass (B).

Moreover, combination of photoetchable and ion exchangeable properties of the PTR glass could open new prospects for developing new microfluidic and plasmonic devices. It's well known that first application of the ion exchange technology was a glass strengthening (Nordberg et al., 1964). In (Razzaghi et al., 2013) was shown that silver ion exchange also can impart the hydrophobic properties to glass surface. So it's possible to improve chemical durability, microhardness and hydrophilicity of microfluidic channels formed in the PTR glass

substrate. Besides that, silver ions in the ion exchange layer can be transformed into either luminescent silver molecular clusters or plasmonic silver nanoparticles that allows developing integrated microfluidic-plasmonic sensors.

For example, we realized luminescent clusters and plasmonic nanoparticles inside of the hollow structures in volume of the PTR glass by ion exchange of $Na^{+}_{(glass)} \leftrightarrow Ag^{+}_{(salt)}$ and following thermal treatment.

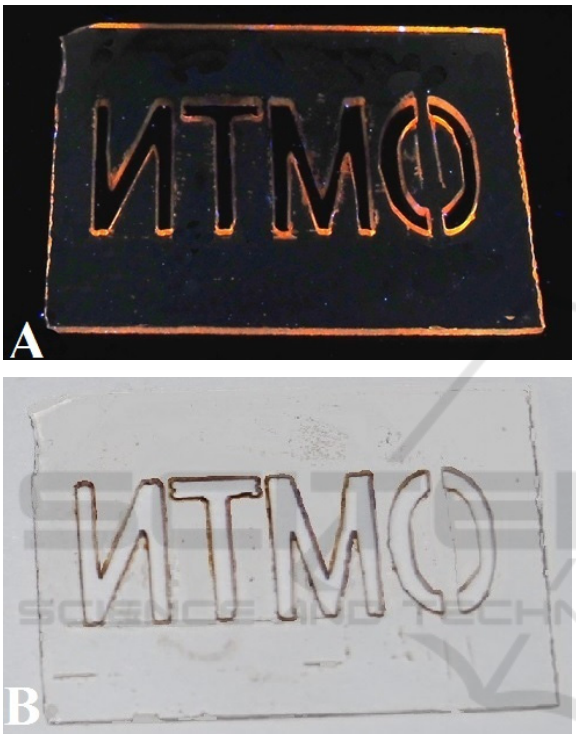

Figure 6: Luminescent silver clusters (A) and plasmonic silver nanoparticles (B) formed by silver ion exchange and subsequent heat treatment inside of the hollow structures in volume of the fluorine PTR glass.

2.5 Phosphors for LEDs and Down-converters for Solar Cells

Luminescent silver molecular clusters and complicated complexes like “silver-bromine” or “silver-chlorine” can be precipitated in the PTR glasses by using ion-exchange technique or can be embedded in glass host during glass synthesis. These clusters and complexes have a broadband luminescence in the visible and NIR ranges under UV) excitation (Dubrovin et al., 2014).

In the same time luminescent properties of the PTR glasses have a strong dependence on glass composition and treatments (UV irradiation, heat treatment) parameters (Fig. 7).

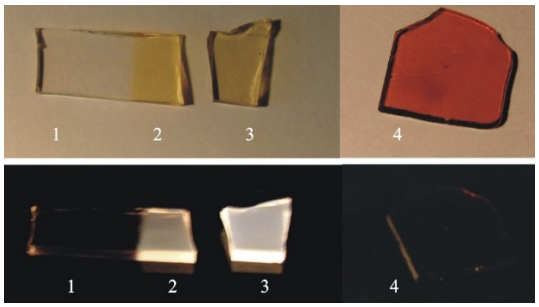

Figure 7: Chlorine PTR glass samples and effects caused by their treatment. (1) virgin glass, (2) UV irradiated glass, (3) sample after the UV irradiation and heat treatment at T = 400°C for 3 h and (4) sample after the UV irradiation and heat treatment at T = 500°C for 3h. Excitation wavelength is 360nm.

An increase in luminescence intensity of the PTR glass after UV irradiation is caused by transform of silver ions Ag^{+}, and charged molecular clusters Ag_n^{+m} to neutral state during UV irradiation and also by increasing neutral silver clusters number and size during subsequent heat treatment. Formation of silver nanoparticles results to decreasing luminescence intensity. Absolute quantum yield of silver clusters formed in bulk of PTR glass reaches 50%.

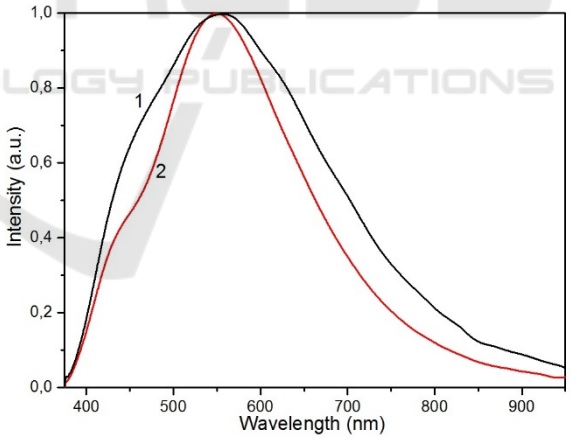

Figure 8: Luminescence spectra of heat treated at 400°C for 3h PTR glasses with silver clusters formed in the bulk (1) and in ion exchanged layer (2), λ_{ex}=360nm.

Thin layers with high concentration of luminescent silver molecular clusters can be formed by the silver ion exchange. Intensity, shape and efficiency of the luminescence strongly depends on the temperature and duration of subsequent heat treatment. Luminescence efficiency grows with increasing heat treatment temperature up to 450°C that can be associated with increasing concentration

of silver molecular clusters. Heat treatment at temperature higher than the glass transition temperature (464°C) results to formation of silver nanoparticles and luminescence quenching in the visible. Concentration of reducing agents (Ce^{3+}, Sb^{3+}) existing in the PTR glass also significantly effects on the luminescence efficiency. Increasing CeO_2 or Sb_2O_3 concentration in the PTR glass composition leads to luminescence quenching that can be caused by the formation of larger clusters that have weak luminescence in the visible and/or concentration quenching. Ion exchanged PTR glasses with silver molecular clusters reveal white light emission and high absolute quantum yield (up to 63%).

As conclusion, the PTR glass can be successfully used as phosphors for white LEDs or down-converters for solar cells. It should be pointed out, that these luminescent clusters and complexes can be formed in defined local spot of the PTR glass substrate by laser radiation. It allowed us to create complicated light architecture from luminescent centers.

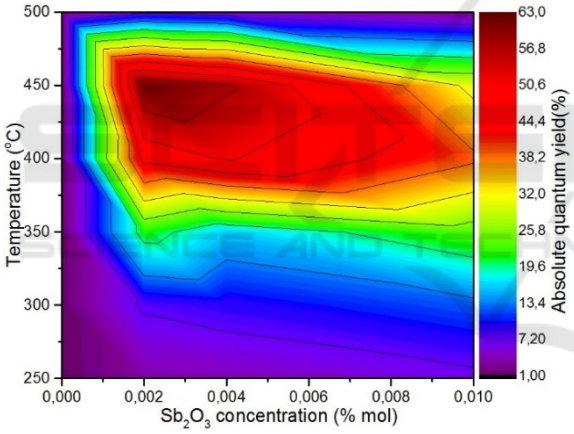

Figure 9: Dependence of absolute quantum yield on the antimony oxide concentration in PTR glass composition and temperature of heat treatment.

2.6 Media for Optical Information Storage

The bright luminescence of neutral silver molecular clusters in PTR glasses makes possible to record optical information in them by UV nanosecond laser irradiation. If the PTR glass was preliminary irradiated by the UV radiation into the absorption band of Ce^{3+} ions the UV nanosecond laser irradiation results in the silver clusters luminescence quenching (Fig. 10A). If the PTR glass was not preliminary irradiated by the UV radiation into the absorption band of Ce^{3+} ions the UV nanosecond laser irradiation results in the neutral silver clusters luminescence appearance (Fig. 10B). The subsequent thermal treatment above the glass transition temperature results in the silver nanoparticles growth in the irradiated zones. The described effects can be used for the optical information recording by the local change of glass luminescence or absorption.

Figure 10: Negative and positive luminescent images in PTR glass plates irradiated through the mask by the UV nanosecond laser radiation with (A) and without (B) the preliminary irradiation by the UV mercury lamp.

2.7 Luminescent Thermo-sensors

PTR glasses can be successfully use for fabrication of luminescent thermo-sensors. The effect of temperature on the luminescence of neutral MC in PTR glasses is illustrated in Fig. 11. As seen, the shape and location of the luminescence maximum on the wavelength scale remain intact under an increase in temperature (Fig. 11A), whereas the intensity of luminescence decreases. In particular, an increase in temperature from -10 to +250°C causes a decrease in the integrated intensity of luminescence by a factor of 25. Notably, the temperature dependence of the luminescence intensity shows no hysteresis and can be multiply reproduced. Such properties of PTR glasses make them promising materials for the luminescent temperature sensors. The temperature dependence of luminescence intensity of PTR glass in -10 - +250 °C temperature range can be approximated quite satisfactorily (see Fig. B) by empirical function as follows:

$$I=0.9(0.55*\exp(-T/25))+0.25*\exp(-T/150) \quad (1)$$

the former term being responsible for the low-temperature section of the dependence and the latter term for the high-temperature one. Complex nature of the function is associated with the presence of several types of MC in a glass.

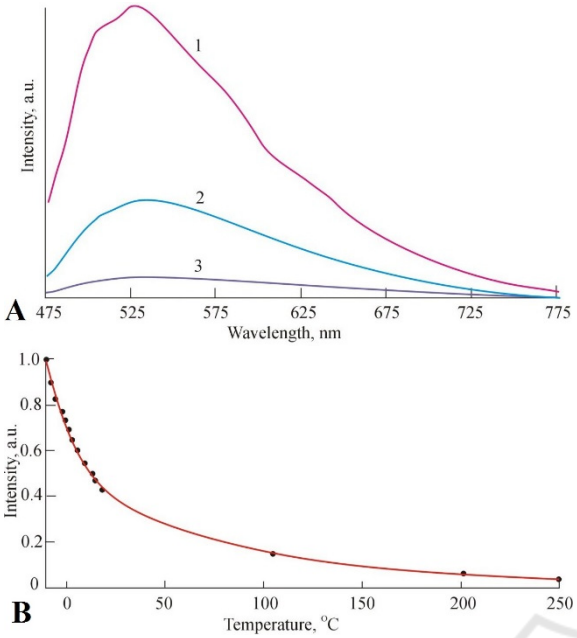

Figure 11: The effect of temperature on the luminescence of PTR glass subjected to the UV irradiation and subsequent heat treatment. A: The luminescence spectra recorded at temperatures of (1) -10°C, (2) +25°C and (3) +200°C. B: Normalized dependence of the integrated intensity of luminescence on temperature.

Also the fluorine PTR glasses doped with rare earth ions (for example, Er^{3+}) can be used for fabrication of luminescent thermo-sensors operating in a wide temperature range (from - 200°C up to +500°C). In this case, several effects can be used for measurement of temperature: (i) temperature dependence of erbium luminescence life time, (ii) temperature deformation of profile of luminescence spectra, and (iii) change of luminescence peaks of thermo-coupling levels.

2.8 Plasmonic Sensors

Some technologies of control of concentration, size and shape of silver metallic nanoparticles in bulk of the PTR glass and on its surface (Fig. 12) have been developed for plasmonic sensors. The technologies allowed us to precipitate high concentration of silver nanoparticles with size of 4-8 nm in the PTR glass host. The absorption coefficient of the plasmonic pick achieves more than 1000 cm^{-1}. These silver nanoparticles can have different shape: spherical, ellipsoidal and cubical. These metallic particles can be covered by dielectric (NaF) or semiconductor (AgCl, AgBr) shells. Some applications of the material have been demonstrated: chemical and biological sensors based on localized surface plasmon resonance.

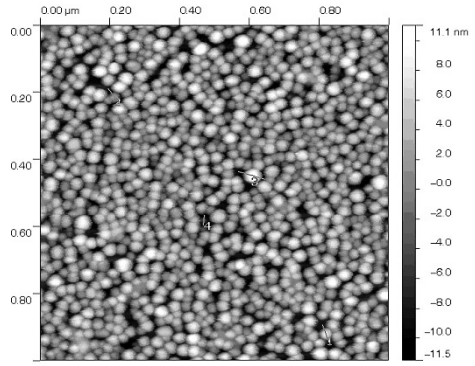

Figure 12: AFM-image of silver nanoparticles on surface of the PTR glass.

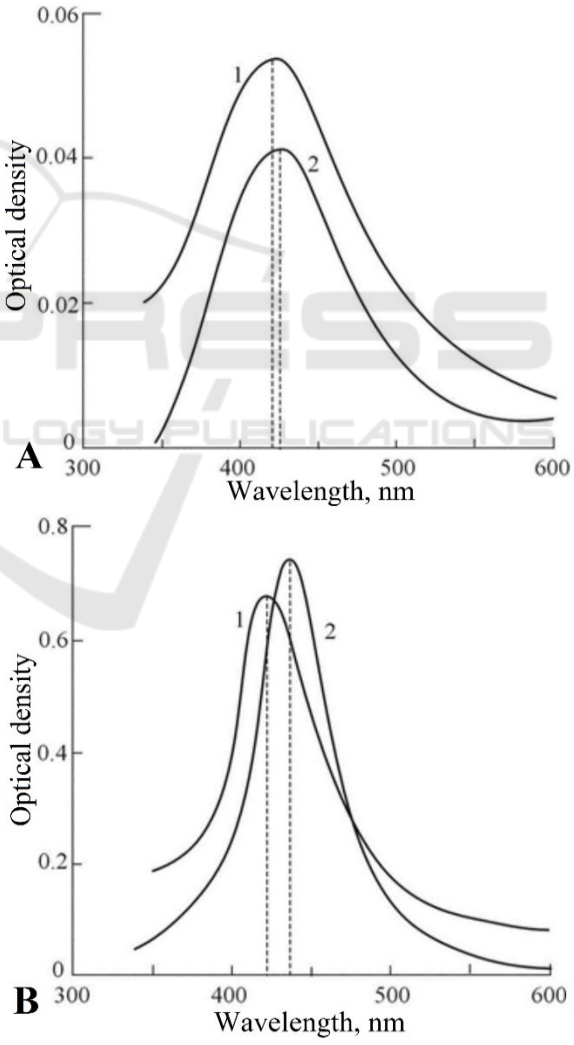

Figure 13: Spectral position of the plasmon resonance peaks for the silver nanoparticles with (a) and without (b) dielectric shell on a PTR glass surface in air (1) and in water (2).

Silver nanoparticles can be formed on the surface of PTR glasses by the thermal treatment in the reducing atmosphere or by the laser ablation of the surface of PTR glass. In the last case silver nanoparticles are covered by the SiO_2 shell 3-5 nm thick. Figure 13 shows the spectral position of the plasmon resonance peaks for the silver nanoparticles with (a) and without (b) dielectric shell on a PTR glass surface in air and in water. In the first case the plasmon resonance spectral shift is 6 nm, in the second case – 13 nm. It is enough for the application in the sensors for the environment refraction index measurements.

3 CONCLUSIONS

We have demonstrated some examples of design and fabrication of optical, photonic and plasmonic devices based on new fluorine, chlorine and bromine PTR glasses: holographic volume Bragg gratings for diode lasers, optical amplifier, optical and plasmonic waveguides, hollow structures, thermo- and biosensors, phosphors for LEDs and down-converters for solar cells.

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