Latest Achievements in Chemical Composition Optimization of Photo-Thermo-Refractive Glass and Its Applications

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Keywords: Hologram, Refractive Index, Volume Bragg Gratings, VBG, Photo-Thermo-Refractive Glass, PTR Glass, Photo-Thermo-Inducted Crystallization, PTI Crystallization.

Abstract: Review on latest modification applied to chemical composition of PTR glass was made. Advancements of updated chemical composition of PTR glass was shown in comparison with commercially produced glass. Such properties as refractive index change, optimal exposition and optical losses in visible range for the glass with recorded hologram was studied. In work samples of two chemical compositions were studied. Conditions of matching included equal regimes of thermal treatment and expose dosages as well as optimized parameters for each composition. Also the study of holograms received at optimal parameters for each glass was made on three different wavelengths. Moreover several new applications for holograms on a modified PTR glass were tested: such as holographic marks in telescopic systems and complex linked holograms. Due to high transparency in visible range, PTR glass now can be applied for creating holographic marks in telescopic systems. Studies show transparency of 92% with Fresnel losses. Also it is found that spectral selectivity is maintained for such holograms, thus it is opening a new way of optical solutions in telescopic systems. As it was measured, spectral selectivity of recorded hologram corresponds to 400mkm efficient thickness according to calculations. Though, it needs further studies to increase the effective thickness of such holograms as well as investigations of different Bragg angles at recording step. Complex (linked) holography is another way of multiplexing inside a bulk glass. It leads to combination of reflecting and transmitting Bragg gratings as a unite element with proper functions. This, for instance, can provide positive feedback for complexes of laser diode crystals on a small size site. Simultaneously, such element can combine emission from all emitting surfaces in one beam. This study may lead to creation of high power coherent diode laser sources at small size site with ultra-narrow emitting bandwidth and high quality spatial beam characteristics.

1 INTRODUCTION

Not as long ago as a holographic medium was mostly used thin mediums, efficient thickness of hologram for those was below 1mm. Such restrictions had place due to low homogeneity as well as incapability of achieving thick photosensitive layers. For complex elements with high spatial and wavelength selectivity, it is necessary to record holograms at high deep. It's necessary, first of all, because selectivity of Bragg grating depends from efficient thickness of hologram and this dependence is linear. For instance, selectivity of grating with 500mkm thickness is twice lower than such for 1000mkm one. Due to this fact, such material as a photo-thermo-refractive (PTR) glass, which allows recording of holograms with high efficient thickness, keep getting more and more popular as a material for amplitude-phase hologram and diffraction elements creation (Adibi, Buse, and Psaltis, 2001). PTR glass is manufactured by several companies: Corning(USA), Optigrate(USA), PD-LD(USA) and University ITMO(Russia). On the basis of commercially produced (classical) PTR glass a variety of holographic diffractive optical elements can be produced: spectral and spatial selectors, narrow-filters intracavity Bragg mirrors, Bragg chirped gratings for compression of light pulses, combiners for powerful laser beams, etc. (Efimov et al, 1999).

Ivanov S., Nikonorov N. and Ignatiev A..
Latest Achievements in Chemical Composition Optimization of Photo-Thermo-Refractive Glass and Its Applications.
DOI: 10.5220/0005334400780084
In *Proceedings of the 3rd International Conference on Photonics, Optics and Laser Technology* (PHOTOPTICS-2015), pages 78-84
ISBN: 978-989-758-092-5

2 RECORDING PROCESS

PTR glass is a multicomponent material which includes such components as glass formers and modifiers Na_2O, $A1_2O_3$ and ZnO as well as different dopants. $Ce^{3+}$is a donor of photoelectrons which defines the photosensitivity of material. Ions of Sb^{5+} and Sn^{4+}, at first, act as photoelectron acceptors and trap photoelectrons from cerium, at second, act as donors of electron for silver ions, during the process of thermal treatment. Silver ions are responsible for formation of colloidal particles, which are becoming a core for the crystalline phase growth. Halides and bromides are crystalized on the silver cores, during the process of thermal treatment, which leads to refractive index change.

The hologram recording process is divided on two steps. First is UV expose at 325nm wavelength, which is close to absorption band of Ce^{3+} (λ max ≈ 310 nm). During the expose cerium gives away electron with oxidation (figure 1a) according to following reaction:

$$Ce^{3+} + h\nu \rightarrow e^- + [Ce^{3+}]^+$$

Approximately 20% of photoelectrons gained at photo ionization process are trapped by ions of silver, which create molecular clusters (Ag_2^+, Ag_3^{2+}et al.) rest of them are accepted by ions of tin and antimony (figure 1b):

$$e^- + Sb^{5+} \rightarrow [Sb^{5+}]^-$$

$$e^- + Sn^{4+} \rightarrow [Sn^{4+}]^-$$

Subsequent thermal treatment at temperatures around 300ºC leads to discharge of tin and antimony and formation of molecular clusters and colloidal particles of silver $Ag^o n$ (figure 1c):

$$[Sb^{5+}]^- \rightarrow [Sb^{5+}]^- + e^-$$

$$[Sn^{4+}]^- \rightarrow [Sn^{4+}]^- + e^-$$

$$nAg^+ + ne^- \rightarrow nAg^o$$

Further temperature increase leads to the shell growth on the colloidal particle of silver (figure 1.d). And finally crystalline phase NaF grows on the shell (Pierson and Stookey, 1999) (figure 1.e).

The UV dose defines concentration of colloidal particles and thus concentration of microcrystals. Then temperature and duration of thermal treatment defines the size of microcrystals and their volume fraction. As a result, difference in refractive index, between exposed and unexposed parts of glass, appears. In exposed part refractive index is defined by refractive index of crystalline phase and its volume fraction as well as refractive index of residual glass phase from which fluorite and sodium are crystallized. In unexposed part refractive index doesn't change compare to virgin glass (Pierson and

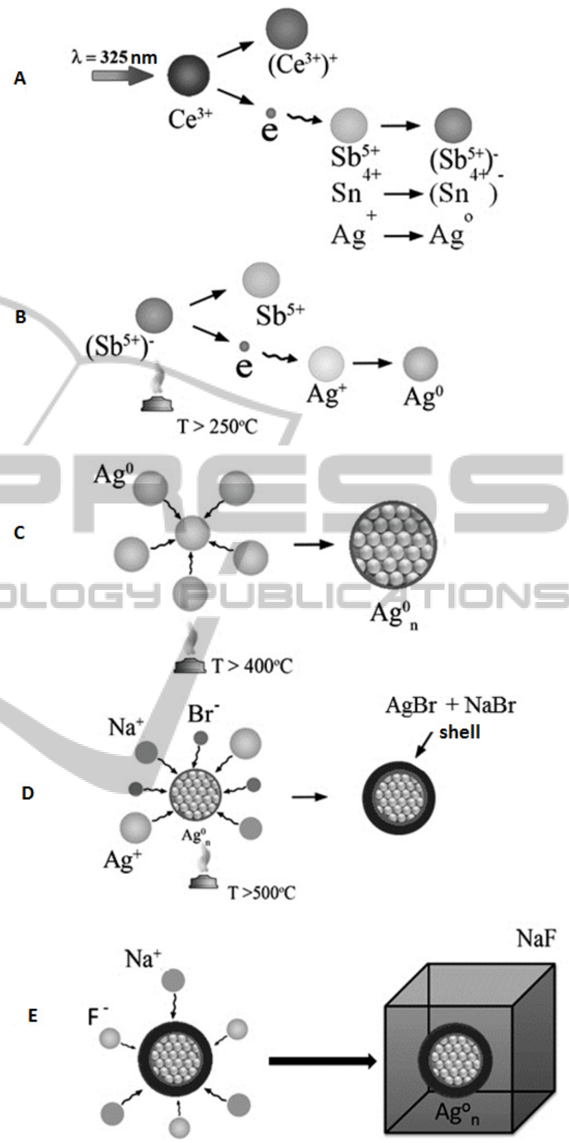


Figure 1 photo-thermo-inducted crystallization of PTR glass:

A) Cerium photoionization and accept of electrons by Sb and Sn ions;
B) Discharge electrons by Sn and Sb and accept with Ag ions with formation of neutral silver;
C) Colloidal particles formation at heating up to 400 ºC;
D) Shell growth (Ag,Na)Br on colloidal particle of silver T>500ºC;
E) Growth of microcrystals NaF T>500 ºC.

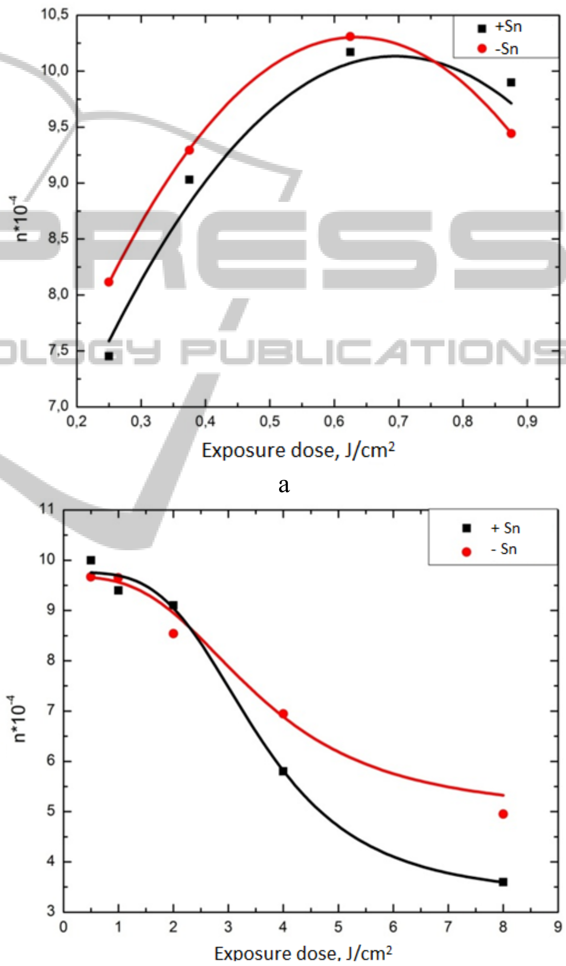
Stookey, 1999). Summary, the refractive index change in PTR glass depends from UV exposure dose and temperature and time of thermal treatment and known to reach values of $\Delta n = 5 \times 10^{-4}$. With high efficient thickness of holograms, such value is enough for achieving 99% diffraction efficiency. In addition, lifetime of such elements is nearly unlimited due to high stability of NaF crystals. Holograms recorded in PTR glass are high resistant to mechanical and chemical treatment almost like BK7 glass. Optical breakdown for PTR glass is 1kJ/cm^2 at $\lambda = 1.06\mu m$. Optical and spectral characteristics of holograms are stable with heating up to 450 ºC.

An important advantage of PTR glass as a material for hologram recording is its high homogeneity (refractive index fluctuations in the order of 10^{-5}) and reproducible characteristics of the glass. PTR glass, like BK7 optical glass, allows traditional methods of machining - grinding and polishing, as well as a variety of forming techniques (e.g., sagging and aspheric surfaces creation). It is worth noting that the glass itself is flexible material and allows various ways for composition modification, for example, it can be doped with rare earth ions, or it can be ion exchanged for waveguide structures creation or material strength increase. Production of PTR glass can be carried out both in the laboratory (600 g) and industrial (300 kg) scales using simple and non-toxic technology. Wherein the chemical reagents required for the synthesis of glass are commercially available and inexpensive.

To date, the properties of PTR glass still are actively studied and improved. One of the important aspects is the study of influence of different modifications of the chemical composition on the holographic properties of the glass.

3 CHEMICAL COMPOSITION IMPROVEMENTS

A study of tin influence on holographic characteristics was held. It was found that the addition of Tin in the glass composition adversely affects characteristics of the recorded diffraction elements. In the course of this work, was compared several key parameters of holographic gratings for different glass compositions. These parameters were efficient thickness of the hologram, and refractive index modulation amplitude (RIMA). RIMA is a quantity equal value to half of the refractive index change resulting from the process of photo-thermo-inducted (PTI) crystallization. During the hologram recording process in the glass sinusoidal distribution of the refractive index is formed. While the two amplitudes of the distribution fall within the dynamic range of refractive index change (corresponds to refractive index change caused by PTI crystallization process). Thus, by measuring the RIMA at the optimum recording conditions, it is possible to obtain data on the maximum dynamic range of the refractive index change. A study, based on a comparison of the RIMA for the glass composition with different tin concentration, showed that the presence of tin does not affect the dynamic range of the refractive index change (figure 2a).

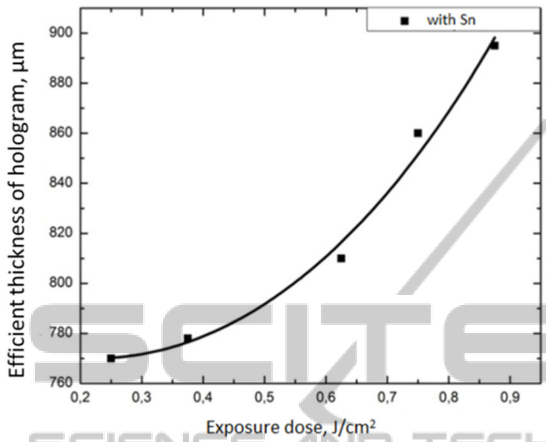


a

b

Figure 2: amplitude of the refractive indexmodulation with respect to exposure dose in optimal exposure range (a) and over-exposure range (b).

RIMA curves for the investigated glass were almost identical. The difference in the maximum value of the refractive index change is actually missing. Further studies revealed that in range of over-exposure (figure 2.b), beyond the optimal dose of UV irradiation, the fall of the RIMA is different. We suppose that it’s connected with scattering difference at the recording step. This assumption was confirmed by comparison of efficient thickness of obtained holographic gratings. Gratings, recorded in the glass containing tin, had a smaller efficient thickness compare to the gratings in the glass without tin, at the same doses of UV irradiation and thermal treatment regime.



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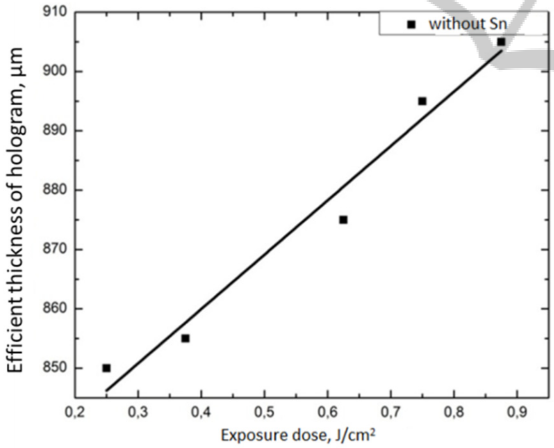


b

Figure 3: efficient thickness with respect to exposure dose sample with tin (a) and without (b).

Moreover, the efficient thickness dependence of exposure for the composition containing tin differs from linear (figure 3 a), whereas for glass without tin dependence is strictly linear (figure 3 b). Exclusion of tin from composition of the modified PTR glass, allows reducing of stray formation of silver clusters in the unexposed areas of interference pattern, i.e. reducing scattering of recorded holograms, as well as adjusting growth kinetics of silver particles in the irradiated areas.

Further study of chemical composition allowed complex optimization of components, with main goal to decrease optical losses in visible spectral range caused by absorption band of colloidal silver (Ivanov et al, 2014). Concentration optimization undergone following elements: halides (fluorides and bromides), responsible for the growth of microcrystalline shell and crystalline phase; Antimony ions, which play a key role in the acceptance and donation of the photoelectrons received upon irradiation of cerium and subsequent thermal treatment of PTR glass; also was lowered the concentration of impurities capable of photoelectrons capture. In work, mainly was compared RIMA and induced losses spectra in the visible range. As well as comparison between the value of the optimal exposure for the classic and improved glass was made. During the work, we also had to upgrade the regime of thermal treatment, because the new glass composition reveals its potential in other regime than classic PTR glass composition. As a result was improved a number of parameters exceeding commercially produced material. First of all, problem with absorption in visible spectral range was solved, resulting in great reduction of induced optical losses caused by colloidal silver. The new composition of PTR glass after the FTI crystallization process shows no absorption band of the colloidal particles in the optical losses spectra of PTR glass with recorded hologram (figure 4).

The absence of the absorption band in visible spectral range allows production of pure phase volume holographic gratings, which positively affects the characteristics of the following elements, and as a consequence the quality of the diffracted beam.

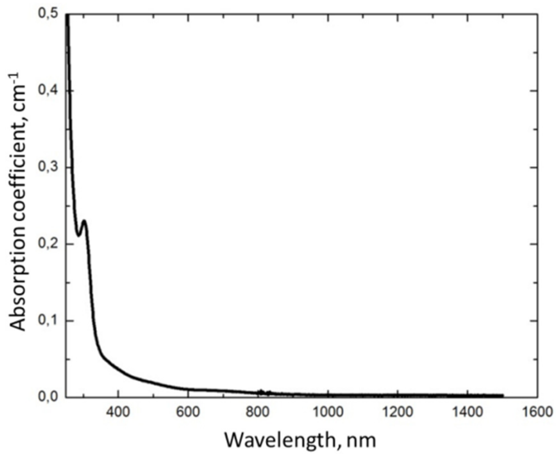


Figure 4: Absorption coefficient spectra of modified PTR glass with recorded hologram.

Thus, the absence of the induced losses in the visible spectrum allows usage of the elements on this material in schemes with high requirements for transmission in optical channel. Because holograms are purely phase, i.e. they lack the contribution of the amplitude component; contours of angular and spectral selectivity have good quality and symmetry (figure 5) that positively affects the optical quality of the beam in diffracted order. In addition, chemical composition optimization increased RIMA up to $n_1 = 10.2\times10^{-4}$ which means that refractive index dynamic range of the new PTR glass has value of 2×10^{-3}.

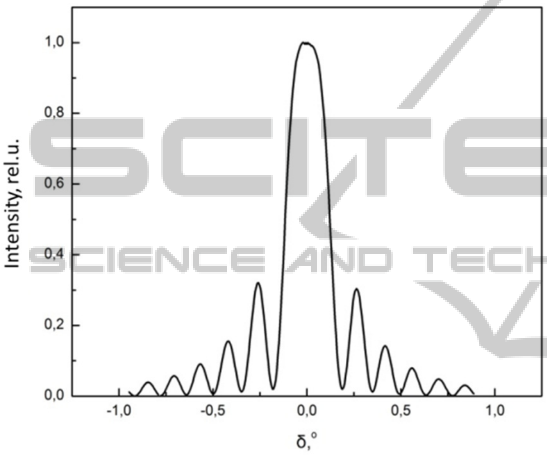


Figure 5: Contour of angular selectivity of hologram recorded on modified PTR glass.

Optimization of antimony concentration led to shift of optimal exposition towards shorter times (figure 6), i.e. for modified PTR glass maximum RIMA is achieved with 4 times lesser recording times than that for a commercially produced material and lays in range of $0.5 J/cm^2$.

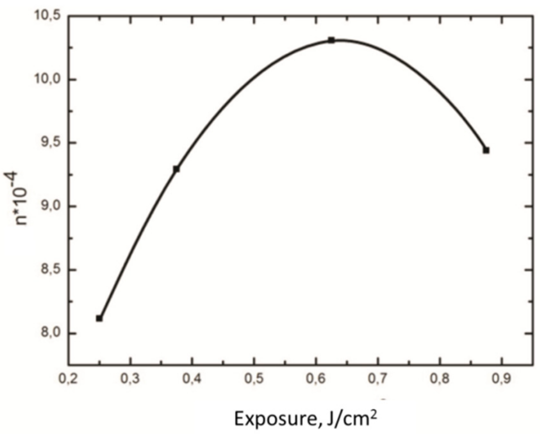


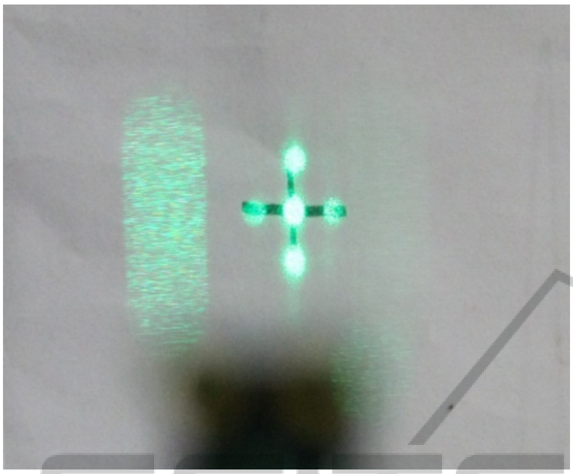
Figure 6: amplitude of the refractive indexmodulation with respect to exposure dose.

This is beneficial for the quality of obtained diffractive elements, because the process of hologram recording is very sensitive to air turbulence and vibrations of the optical scheme, high recording times are extremely undesirable and lead to decrease of contrast in the interference pattern. Synthesis of modified PTR glass from high purity reagents allowed to lower impurities concentration (mainly iron oxide), which are responsible for capturing and irretrievable loss of photoelectrons, required during PTI crystallization process. Also, it's improved the transmission of the virgin glass in the UV optical range.

4 NEW APPLICATION

All the above optimizations led to the new field of application for PTR glass as a holographic medium for holographic marks for telescoping systems (Ivanov et al, 2014). Since transmission of glass, containing hologram, is above 90% without AR coating, it can took its place in problems 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. And redistribution of energy in diode output spectra leads to insignificant lowering of intensity of the mark which 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. Important to note that current 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 pictures below are photo of reconstructed image of mark (figure 7 a) and spatial shift of central dot in the mark image with respect to wavelength change (figure 7 b).



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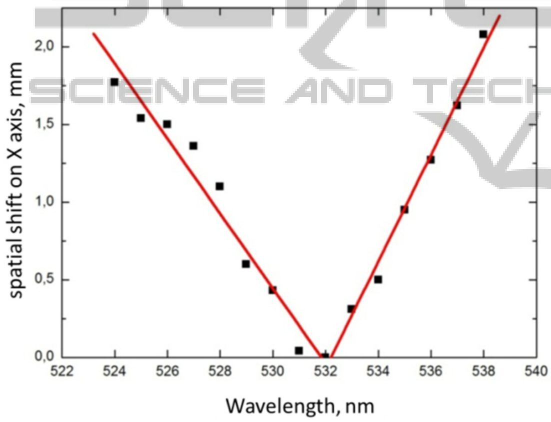


b

Figure 7: photo of reconstructed image of mark in target plane at 180 cm (a) and spatial shift of central dot in the mark image with respect to wavelength (b).

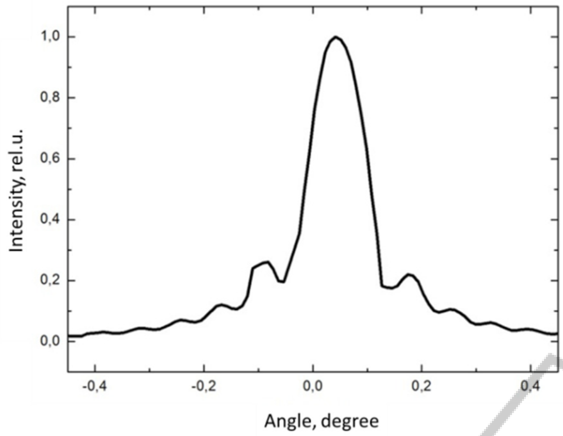
Due to the complexity of measuring spectral selectivity of image hologram, in the experiment was measured spatial shift of central dot in the mark image. From that spatial shift spectral selectivity of recorded hologram was calculated. Spectral selectivity matches theoretical predictions and corresponds to 400µm efficient thickness of recorded hologram. Such a low thickness is a result of huge losses of intensity during recording process, what means that expose times should be readjusted to achieve desirable spectral selectivity and spatial stability of mark image.

5 COMPLEX MULTIPLEXATION

Another promising application of holograms on PTR glass is complex (linked) multiplexation, which means recording multiply gratings in a single volume, where each grating corresponds to Bragg conditions inside the medium for another grating. Reciprocal gratings combination within the medium can be various, and they can perform their functions simultaneously. For instance, it is possible to create a combination of reflective and transmitting hologram for spatial and spectral filtering at the same time; that can be used to create arrays from emitting diode elements at the small size site. Complex element in such application will provide positive feedback for each emitting area, stabilizing the emission wavelength and adjusting the spatial characteristics of the beam. In one optical path inside the element radiation is directed onto a reflective grating, which has high spectral selectivity. Reflective hologram is responsible for the spectral stabilization. Reflected radiation is directed back into the crystal along the same path. Another path within the complex element is for output. Transmitting grating provides radiation output at the appropriate angle for all emitting areas. Presence of multiple transmitting gratings allows correction of the spatial characteristics of the beam emerging from the system. It is noteworthy that in this implementation is possible to create a single cavity for a large number of emitting semiconductor crystals, this leads to the creation of a coherent high power source of radiation with extremely narrow bandwidth. Due to the large dynamic range of the refractive index change in PTR glass, it is possible to record a plurality of holographic elements in one volume. In pictures below are shown spatial contours of single hologram and complex hologram (figure 8). Gratings period and their spatial orientation within the medium are selected following next conditions: first diffraction order from first grating meets Bragg condition in the medium for the second grating.

6 CONCLUSIONS

These studies, aimed at material characteristics improvement led to: refractive index dynamic range increase; optimal exposure lowering; scattering during recording process and after thermal treatment reduction; and allowed to get rid of the absorption band of the colloidal particles in the visible spectral



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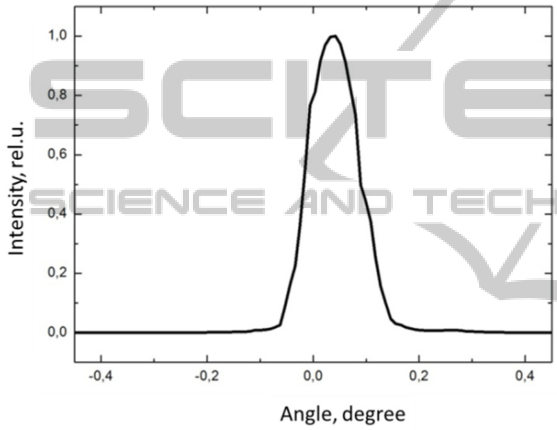

b

Figure 8: angular selectivity contours of usual (a) and complex linked hologram (b).

range. All of the above makes it possible to extend the application area of this material, including such as: recording of holographic marks for telescopic systems; complex elements for semiconductor laser diodes creation and powerful coherent radiation sources based on them; usage the elements on PTR glass as intracavity selectors and filters for pulse Raman lasers.

In summary, PTR glass and optical elements based on it has the following advantages: high refractive index dynamic range ($\Delta n \approx 2\times10^{-3}$); High diffraction efficiency (up to 99%); large efficient thickness of the hologram (above few mm), which allows you to create narrow spectral ($\Delta\lambda \approx 0{,}05$nm) and spatial (0.2degree) filters; unlimited lifetime of hologram (up to ten years), high thermal (up to 450 ° C), mechanical and chemical resistance. Optical breakdown threshold of the hologram on the PTR glass close to the breakdown threshold of commercial optical glass BK7 (1 kJ/cm2 under pulsed irradiation at λ= 1.06μm).

This work was financially supported by Russian Scientific Foundation (Agreement # 14-23-00136).

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