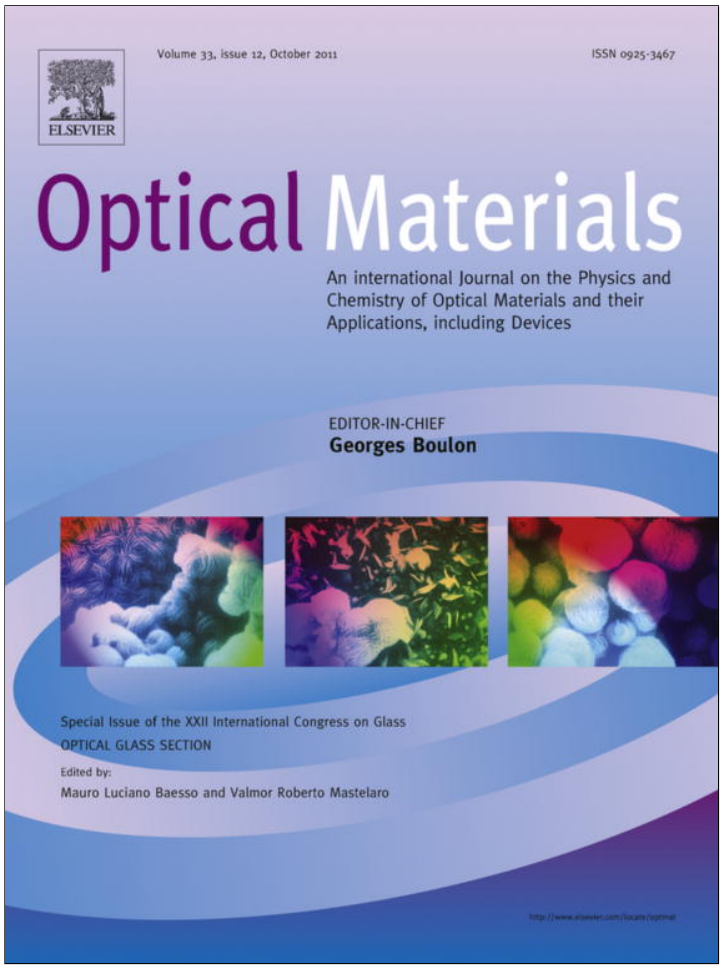

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Photo-thermo-refractive glass co-doped with Nd^{3+} as a new laser medium

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ABSTRACT

Photo-thermo-refractive (PTR) glass demonstrates refractive index change after exposure to UV radiation followed by a thermal treatment that enables recording of high efficiency holographic optical elements. This work demonstrates feasibility of function of this material as a complex optical medium which possesses both photosensitive and luminescent properties and paves a way for creation of monolythic solid state lasers where resonator components can be holographically recorded inside of a laser medium. It was found, that incorporating of Nd^{3+} ions in PTR glass does not affect photosensitivity required for hologram recording. It was demonstrated that emission wavelength, spectral width, and cross section of Nd^{3+} luminescence in PTR glass are typical for silicate laser glasses and Nd-doped PTR glass can be considered as a promising laser medium for monolithic solid state lasers.

1. Introduction

Extensive development of laser systems used in harsh environment dictates a number of extremely challenging requirements for such fine optical devices. These requirements include minimizing weight and volume, increasing of power and brightness, high tolerance to mechanical and acoustic vibrations, high tolerance to ionizing radiation. The solid state lasers provide the best parameters which are necessary for free space optical communications, remote sensing, micromachining, etc. However, all such lasers require fine alignment and, therefore, are very sensitive to vibrations, shocks, thermal gradients, etc. The ideal situation would be if all laser elements would be incorporated in the volume of a gain medium. There are several problems preventing the development of such laser systems. Thus, the semiconductor lasers, which are all-solid-state by design, cannot accumulate energy and, therefore, cannot produce high energy laser pulses. The solid state lasers, which have the dielectric mirrors, deposited on the facets of a gain medium, do not provide any spectral or angular selection and, therefore, do not provide high quality narrow band radiation. The fiber lasers can provide successful monolithic solutions for the CW lasers but cannot enable generation of high energy pulses.

A completely new approach to the problem was announced in Ref. [1]. It was said that extending of photosensitive properties of PTR glass toward lasing properties of gain media by doping this glass with a luminescent agent such as Nd, could enable fabrication of a monolithic solid state laser with holographic feedback mirrors recorded inside of a gain media (Fig. 1). In this case, all alignment could be done in the process of recording of the holographic mirrors, and no misalignment would be possible in any conditions of exploitation.

Photo-thermo-refractive (PTR) glass is a $Na_2O–K_2O–ZnO–Al_2O_3–SiO_2$ glass doped with cations Ce^{3+}, Ce^{4+}, Ag^{+}, Sb^{3+}, and Sn^{4+}, and anions F^{-} and Br^{-}. Amplitude photosensitivity of this class of glasses (induced absorption and scattering) resulted from photoinduced thermal crystallization was discovered by Stookey in 1949 [2] while phase photosensitivity (induced refractive index change) was demonstrated 40 years later [3]. Sensitivity of this glass to UV radiation is determined by Ce^{3+} cations, introduced in the glass composition, which are ionized by near UV radiation and release free electrons, which subsequently used for photoreduction of $Ag^{+} \rightarrow Ag^{0}$. Atomic silver, in turn, serves as a main component of photo-induced nucleation centers at elevated temperature (Fig. 2) [2,4]. Further heat treatment results in precipitation of NaF crystals on such nuclei. This feature allows for formation of a photo-controlled crystallization in the bulk of glass, which causes of a refractive index change in UV-exposed areas of a glass volume [3,5,6]. Such controllable refractive index change in PTR glass enables fabrication of phase volume holographic optical elements in PTR glass, including external feedback mirrors in laser resonators [1].

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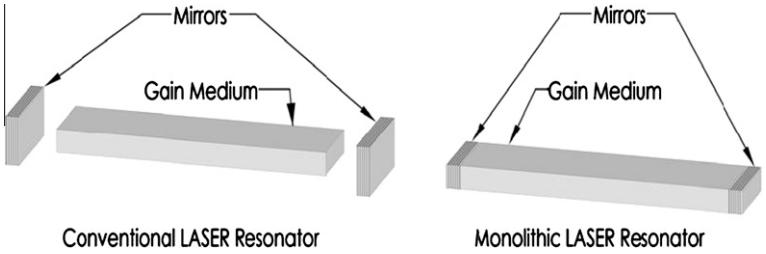

Fig. 1. Comparative geometry of conventional and monolithic laser resonators.

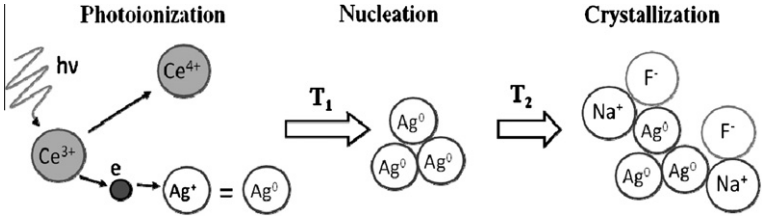

Fig. 2. Photo-thermo-induced crystallization.

Oxide-silicate and fluoride-silicate glasses doped with different rare earth ions were the most common materials for solid state lasers for many years of the initial laser development [7]. These materials demonstrate wide absorption spectra convenient for flash lamp pumping, low losses at lasing wavelengths, high quantum efficiency, low concentration quenching enabling high doping concentrations, and high enough gain coefficients for a number of laser applications, especially for high power, large aperture laser systems. Nowadays, the most common fiber lasers are based on silica doped with different rare earth ions, such as Nd, Yb, Er, Ho, and Tm. However, there are no evidences that silicate glasses can demonstrate simultaneously high efficiency of luminescence enabling fabrication of lasers and high phase photosensitivity enabling fabrication of holographic optical elements.

In this work the conventional PTR glass, which is extensively used for the holographic optical elements, has been co-doped with Nd^{3+} ions (NdPTR) in order to obtain sufficient luminescence, which will allow for using this new material as a gain medium. It is important to note that to obtain such a level of the luminescence, the concentration of the luminescent agent (Nd) has to be about 100 times higher than the concentration of the photosensitive agent (Ce). The presence of both components, having similar chemistry in the host glass, could result in destroying the photo-induced crystallization, which is a key to recording of volume holograms. Therefore, for both the NdPTR and conventional the PTR glasses, we have been studied absorption and luminescence along with photo-induced crystallization and photo-thermo-induced refractive index variations in order to demonstrate an opportunity of a successful combination of photosensitive and luminescence properties.

2. Experimental

Two glasses have been prepared for this study – the regular photo-thermo-refractive glass (PTR) as a reference, and the Nd-doped photo-thermo-refractive glass (NdPTR). PTR glass has the following composition: $15Na_20{-}5ZnO{-}4Al_2O_3{-}70SiO_2{-}5NaF{-}x$KBr (mol%) doped with Ce, Ag, Sn and Sb in amount of 0.01 mol%. NdPTR glass of the same composition as above was doped with 0.12 at.% of Nd in a form of oxide. The batches of both glasses were prepared using high purity chemicals with the level of impurities equal or lower than 2 ppm. These glasses were prepared with the same basic procedure as the one used for a standard PTR glass. They were melted in 0.5 liter platinum crucible at 1460 °C for approximately 5 h. The melt was continuously stirred with a platinum stirrer for 2 h. After melting, each glass was annealed from T_g down to the room temperature for the period of 20 h. Both melts demonstrated good optical homogeneity with refractive index fluctuations below 10^{-4}, high transparency (near IR absorption at the level of 10^{-4} cm^{-1}) and no spontaneous crystallization was obtained during cooling to the room temperature.

The absorption spectra were recorded with Shimadzu UV–Vis–NIR spectrophotometer. The temperature of crystallization and T_g were obtained by Differential Scanning Calorimetry (DSC) using TA Instrument Q10 calorimeter. The crystalline phase was studied by X-ray Difractometry (XRD) using Rigaku Miniflex II diffractometer. The luminescence spectra of NdPTR glass were measured by using excitation by a 100 W Xe lamp with 400 nm cutoff filter to prevent photo-ionization of Ce^{3+}, projecting excited area of a glass sample to a multimode fiber, and detecting the signal by means of ANDO optical spectrum analyzer. Measurement of a luminescence lifetime (τ_{rad}) was produced by irradiation of a sample by pulses of a laser diode operating at 808 nm with pulse rise time about 10 μs and pulse duration time about 1 ms. Intensity of luminescence was detected by a photodiode. The luminescence decay curve was fitted by the Forster Dexter model [8] and the radiation lifetime of Nd luminescence in NdPTR glass was calculated.

The measured luminescence spectra and the emission lifetime were used to calculate the emission cross section (σ_{em}). We used the following formula [9]:

$$\sigma_{em}(\lambda) = \frac{\lambda}{8\pi c n^2 \tau_{rad}} \times \frac{I(\lambda)}{\int I(\lambda) d\lambda} \quad (1)$$

where λ is the wavelength, c is the speed of light, n the glass refractive index and $I(\lambda)$ the emission intensity.

The photosensitivity of both glasses was measured as a refractive index change caused by the photo-induced crystallization after the UV irradiation by means of a He–Cd laser emitting at 325 nm with different dosages from 1 J/cm^2 to several tens of J/cm^2, and a subsequent thermal treatment. The refractive index change was measured using the shearing interferometer [10].

3. Results

Since the main goal of this work was a development of a new material, which is retaining the photosensitive properties of a

regular PTR glass along with the new ability of efficient luminescence, we have studied the optical properties and the photo-induced crystallization of a NdPTR glass in comparison with a conventional PTR glass.

3.1. Absorption

The absorption spectra of PTR and NdPTR glasses are shown in Fig. 3. Absorption spectra of both glasses are identical in the UV spectral region and the Ce^{3+} absorption band with maximum at 305 nm, which is used for excitation during the hologram recording in conventional PTR glass (325 nm), is not masked by other bands in NdPTR glass. It means that the conventional excitation at 325 nm for hologram recording in NdPTR glass is also possible. It can be seen in these spectra that absorption band of Nd at 808 nm, which is widely used for a optical pumping by diode lasers, is not covered by other peaks of the host glass. This is a good fact that the diode pumping of NdPTR laser is achievable as well.

3.2. Photo-thermo-induced crystallization

This crystallization was studied by DSC and XRD techniques. In Fig. 4, the DSC curves of irradiated and virgin samples of NdPTR glass are shown. The DSC curves for a conventional PTR glass are the same and are not shown here. Since the only irradiated sample has a crystallization peak with maximum at 625 °C, it means that we deal only with the photo-induced crystallization. The unexposed area is not crystallized after a thermal development, which is at ca. 500 °C, and such parasitic crystallization does not smear the hologram. Fig. 5 represents comparative XRD curves of PTR and NdPTR glasses after an irradiation and a thermal treatment. As it was determined by this analysis, NdPTR glass has the same, cubic NaF, crystals and in relatively the same amount. It also supports the idea about the similarities of both glasses in terms of their photosensitivity (see Fig. 6).

3.3. 3. Photo-thermo-induced refraction

The photo-thermo-induced crystallization results in a refractive index change (Δn) of an irradiated part of glass, this is actually a measure of a photosensitivity of a material. To measure this characteristic, the both glasses were irradiated with different dosages of UV radiation at 325 nm followed by a thermal treatment. Fig. 7 shows the samples of PTR and NdPTR glass samples exposed to 1 mm-wide stripes of UV radiation with Gaussian lateral profile for different dosages. Brown coloration of the stripes is caused by

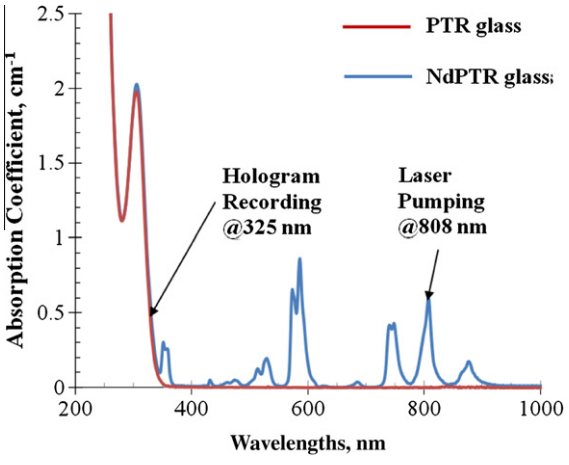

Fig. 3. Absorption spectra of PTR and NdPTR glasses.

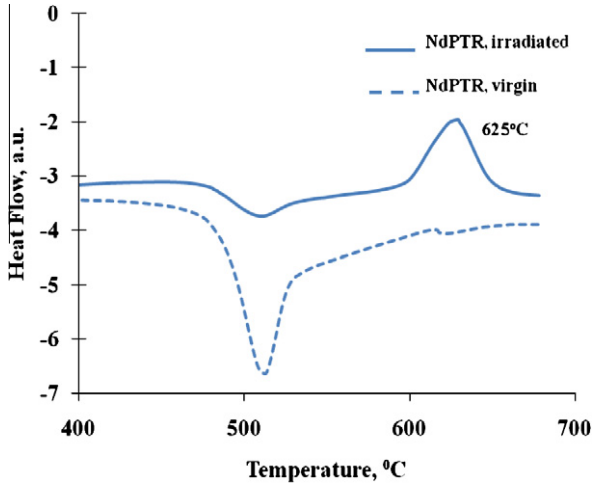

Fig. 4. Differential scanning calorimetry of irradiated and virgin NdPTR glass samples.

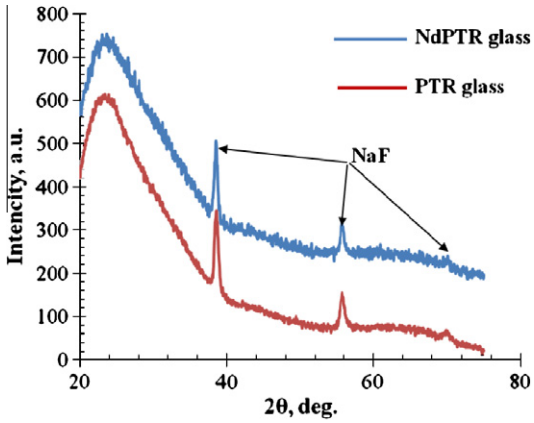

Fig. 5. X-ray diffraction spectra of PTR and NdPTR glasses after UV exposure and thermal development.

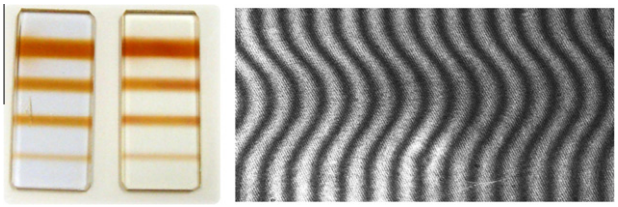

Fig. 6. Photos of the developed samples of NdPTR (left) and PTR (center) glasses exposed to stripes of UV radiation with different dosages and a typical interferogram (right) of a stripe.

formation of silver bromide particles during the development process. Photo-thermo-induced refractive index changes are summarized in Table 1. Such changes, which are in the range of 60–250 ppm, are sufficient for the hologram recording.

3.4. Luminescence spectra of NdPTR glass

Fig. 7 shows luminescence spectra of NdPTR glass. One can see three main emission lines centered at 0.9, 1.06, and 1.32 μm which are typical for all silicate glasses. However, the exact position of the most intensive luminescent band has maximum at 1.055 μm which is shifted to shorter wavelengths compared to those in pure oxide silicate glasses. This effect could be explained by an

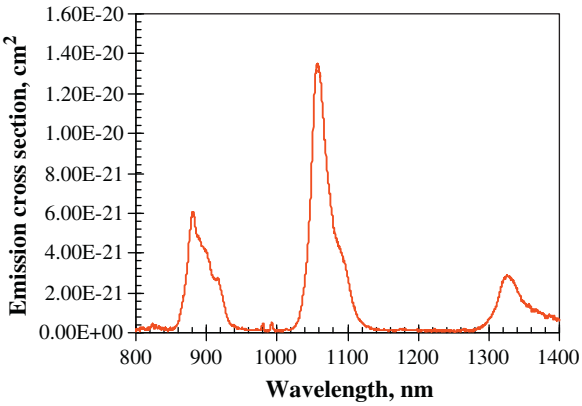

Fig. 7. Luminescence spectra of NdPTR glass exited with a xenon lamp radiation at $\lambda = 400$ nm.

Table 1
Refractive index change of NdPTR glass after irradiation and thermal treatment.

Dosage (J/cm^2)	1	5	10	20
Refractive index change (ppm)	65	225	250	264

opportunity for Nd ions to have fluorine ions in the nearest sites because absorption and luminescent spectra of Nd in fluoride glasses are shifted to shorter wavelengths compared to those in oxide glasses. The spectral width of the emission band at 1.06 μm is almost 30 nm which is typical for multicomponent silicate glasses.

3.5. Kinetics of luminescence in NdPTR glass

A typical example of the decay of Nd luminescence and its fit by an exponential function is shown Fig. 8. One can see a difference between exponential modeling and an experimental curve. This discrepancy could be caused by two factors. The first one is that the pulse rise time for the used measurement setup was about 10 μs. This means that no reliable data could be accumulated for initial decay time below 100 μs. The second factor is that we used 1 ms pulse duration for excitation of luminescence. In case of inhomogeneous distribution of lifetimes for different centers distributed in the glass matrix, the fast decaying centers with $\tau < 100$ μs would be underrepresented for such a long excitation pulses. However, those phenomena cold not affect significantly the estimation of radiation lifetime which is necessary for this research. The detailed study of Nd luminescence kinetics is a subject of a future study. For fitting we used the Forster Dexter model [8]

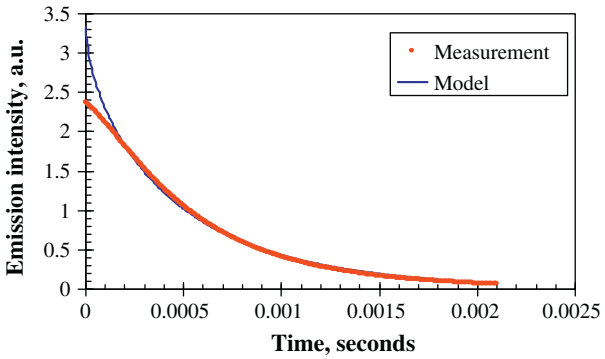

Fig. 8. Kinetics of NdPTR glass luminescence after excitation by a 1 ms pulse at 808 nm and fit by an exponential function.

and calculated the radiation lifetime of Nd luminescence. It is equal to ~700 μs for NdPTR glass and this is in accordance with what has been reported in the multiple literature sources for multicomponent silicate glasses.

3.6. Emission cross section of Nd

The emission cross section of Nd in PTR glass is calculated on the basis of luminescence spectrum and radiation lifetime and is shown in Fig. 7. One can see that the cross section at 1.06 μm is about 1.4×10^{-20} cm^2. This value is typical for best silicate laser glasses and, therefore, PTR glass doped with neodymium can be considered as a promising laser medium which provides an additional opportunity to record holograms in the volume of a gain element.

3.7. Testing of NdPTR glass

The samples of NdPTR glass were supplied to research groups at OptiGrate Corp., University of Central Florida (Orlando, FL, USA) and at Institute for Molecular Science (Okazaki, Japan). High efficiency volume Bragg gratings were recorded and lasing emission under pumping by flash lamps and diodes were successfully demonstrated [11].

4. Discussion

The study of Nd-doped PTR glass has shown that it possesses both luminescent and photosensitive properties. Let us consider if those values are suitable for creation of a complex medium that would provide an opportunity of fabrication a monolithic solid state laser. Absorption spectra of Nd in this glass are intermediate between oxide and fluoride glasses having SiO_2 as a glass former. Cross section of emission in PTR glass is of 1.4×10^{-20} cm^2. This value is typical for silicate laser glasses ranging from 0.9 to 3.6×10^{-20} cm^2 [7]. Absorption coefficient of PTR glass in the region of 1.06 μm is about 10^{-4} cm^{-1} which is several times less than that for the best laser glasses [12]. Scattering in pristine PTR glass is at the level of best optical materials. However, after thermal development is rises to the level of 10^{-3} cm^{-1}. This level of total losses for a laser material with the emission cross section of 1.4×10^{-20} cm^2 is acceptable for design of both large scale and portable lasers.

Photo-thermo-induced refractive index change in Nd-doped PTR glass is in the range of 200 ppm. This value is enough for recording of 100% diffraction efficiency volume Bragg gratings with thickness exceeding 5 mm that should operate in the range of 1 μm. It is important to note that the main idea of the use of volume Bragg gratings as components of laser resonators is to produce spectral locking and narrowing of laser emitters. It could be shown [13] that volume Bragg gratings with thickness above 5 mm would provide spectral narrowing of laser below 0.01 nm. Usually such narrow band laser could be produced by a combination of a number of different optical components with high spectral selectivity. The main result of the current research is that Nd-doped PTR glass possesses both spectral and photosensitive properties which provide an opportunity to make portable solid state lasers with extremely narrow spectral lines.

5. Conclusions

A new material, which combines properties of a phase photosensitive holographic medium and a laser gain medium, is created on the basis of photo-thermo-refractive (PTR) glass co-doped with neodymium. This glass shows photoinduced refractive index change up to 2.5×10^{-4}, luminescence lifetime of 700 μs, and

emission cross section at 1.06 μm of 1.4×10^{-20} cm^2. Volume Bragg gratings were recorded and laser operation was demonstrated in this glass.

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