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Optical properties of photo-thermo-refractive glasses doped with terbium

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Abstract. In this study two types of photo-thermo-refractive glasses were investigated. First one was the classical photo-thermo-refractive glass doped with 0,007 mol.% Ce^{3+} co-doped with 1 mol.% Tb^{3+} and the second one did not contain any Ce^{3+} but only 1 mol.% Tb^{3+}. These types of glass were exposed to the mercury lamp using a cut-off filter that do not transmit wavelengths shorter than 350 nm. After the heat treatment such glasses did not show any plasmon resonance absorption peak. But in samples of photo-thermo-refractive glass without any Ce^{3+} but only containing Tb^{3+} plasmon resonance absorption peak corresponded to silver nanoparticles was appeared at 430 nm after mercury lamp exposure without filter and subsequent heat treatment.

Keywords: PTR glass, plasmon resonance, silver nanoparticles, terbium

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Оптические свойства фото-термо-рефрактивных стекол, активированных тербием

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Аннотация. В данной работе были исследованы два типа фото-термо-рефрактивных стекол. Первое представляло собой классическое фото-термо-рефрактивное стекло, легированное 0,007 мол.% Ce^{3+} с добавлением 1 мол.% Tb^{3+}. Второе содержало только 1 мол.% Tb^{3+}. Эти стекла подвергались воздействию ртутной лампы с использованием фильтра, не пропускающего длины волн короче 350 нм. После термообработки в таких стеклах не наблюдался пик поглощения плазмонного резонанса. Но в образцах фото-термо-рефрактивного стекла, содержащего только Tb^{3+} после облучения ртутной лампой без фильтра при последующей термической обработке появлялся пик плазмонного резонанса на 430 нм, соответствующий наночастицам серебра.

Ключевые слова: ФТР-стекло, плазмонный резонанс, наночастицы серебра, тербий

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Introduction

Photo-thermo-refractive (PTR) glasses are photosensitive glasses that are widely used in various optical schemes due to the possibility of recording volume Bragg gratings [1–2]. But for now, there is one significant drawback - the inability to record a hologram using visible light. Overcoming this obstacle will allow using cheaper and more affordable light sources for hologram recording [3] as well as open a new branch of holography for PTR glasses - image holography. Also, there will be possible to create complex holographic optical elements such as holographic lenses.

In this work classical PTR glasses co-doped with Tb_4O_7 as well as with replaced CeO_2 by Tb_4O_7 were studied. The choice of Tb^{3+} ions is explained by its energy levels which allow obtaining photo-electron in two stages. On the first stage UV exposure under 370 nm excite electron to $^5D_3$ level. From this energy level it relaxes to the lower metastable $^5D_4$ level and then, on the second stage, due to the excited state absorption (ESA) process, absorbs photon and excites to the $5d4f^7$ level which provides photoelectron to start a classical PTR photochemical process [4].

Materials and Methods

In this research PTR glasses with Na_2O-ZnO-Al_2O_3-SiO_2 matrix doped with photosensitizers such as Tb_4O_7 (1 mol.%), Sb_2O_3 (0,04 mol.%), Ag_2O (0,06 mol.%) and CeO_2 (0,007 mol.%) were studied. To find the value of glass transition temperature (T_g) the scanning calorimeter STA 449 F1 Jupiter (Netzsch) was used. The obtained T_g for the glasses under the study was around 490 °C. Absorption spectra in UV-vis regions were measured with Perkin Elmer Lambda 650 spectrophotometer.

The glass was melted in an electrical furnace in a quarts crucible at the temperature of 1480°C. Optical homogeneity was provided by platinum stirrer. After annealing in muffle furnace glass was cut in form of small plates 2 mm width which then were polished. Samples were UV irradiated with mercury lamp and then thermally treated in muffle furnace under 500 °C for 10 hours.

Results and Discussion

First part of the study included only PTR glass with replaced CeO_2 by Tb_4O_7 (1 mol.%). Absorption spectra were measured before (initial), after UV irradiation to mercury lamp for 10 minutes and after heat treatment for 10 hours under the temperature of 500 °C. Results are presented in Fig. 1. To exclude contribution of heat treatment in the silver nanoparticles formation, the same glass plate sample was partly UV irradiated and fully heat treated in a furnace. It can be seen that in irradiated part of a sample (Tb 1 mol.%10H 500C UV) there is a broad plasmon

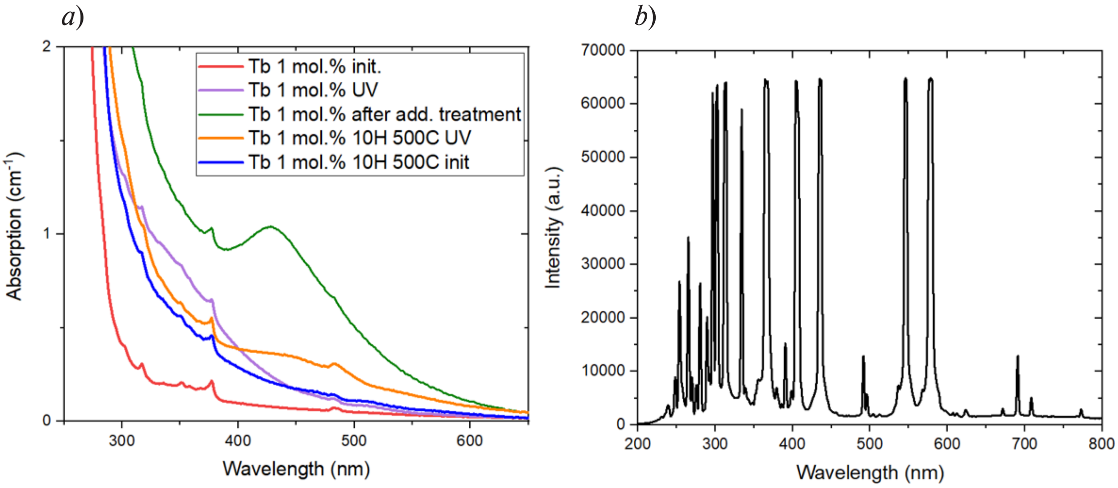

Fig. 1. Absorption spectra for Tb 1 mol.% (init), after UV irradiation (UV) and subsequent heat treatment (10H 500C UV) and after additional treatment (after add. treatment) (*a*) and spectrum of the mercury lamp (*b*)

resonance absorption peak correlated with silver nanoparticles in glass. For previously processed sample these stages were done twice which resulted in enhanced plasmon resonance absorption peak located at around 430 nm (Tb 1 mol.% after add. treatment).

From the mercury lamp spectrum (Fig. 1,*b*) it can be concluded that it has exactly the needed wavelength at around 365 nm to excite electron firstly from the ground state to $^5D_3$ and then at around 490 nm to excite further from $^5D_4$ level to $5d4f^7$ as was described above.

Second part of this study also included PTR glass co-doped with Ce^{3+} and Tb^{3+} ions. First, samples of this glass were UV-exposed and thermally treated under the same conditions as the one without Ce^{3+}. Results are presented in Fig. 2.

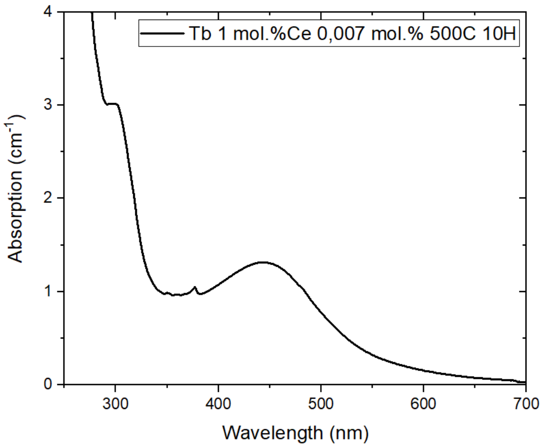

Fig. 2 Absorption spectra for the PTR glass co-doped with Ce^{3+} and Tb^{3+} ions that was UV exposed to mercury lamp and thermally treated for 10 hours under 500 °C

It can be clearly seen the plasmon resonance absorption peak at 445 nm corresponded to the silver nanoparticles. This result was expected because of the Ce^{3+} presence that initialize all photochemical processes under the UV lamp. Then it was used a filter to cut-off the wavelengths shorter than 350 nm. That was not let the Ce^{3+} ions release electrons because the absorption band is in the filtered band. For this purpose, C3C 21 glass from the standard catalog was used. Using this filter, two samples of PTR glass were irradiated: containing only Tb^{3+} and codoped with Ce^{3+}. Due to the fact that filter also partly cut-off needed band around 365 nm the time of the irradiation was increased from 10 minutes to 90 minutes. Absorption spectra after the heat treatment for 10 hours for 520 °C are presented in Fig. 3 as well as the spectrum of the lamp after filter.

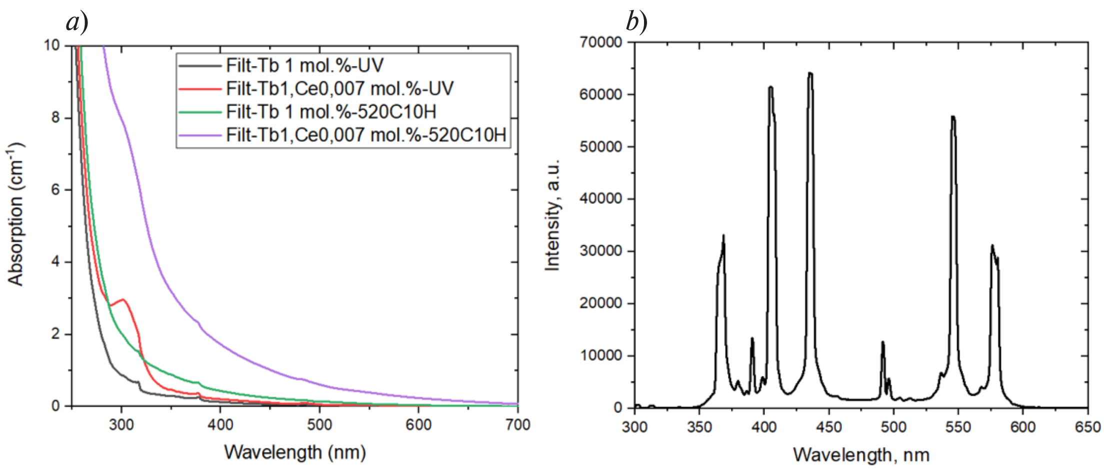

Fig. 3. Absorption spectra for Tb 1 mol.% and with or without 0,007 mol.% Ce^{3+} samples, after UV irradiation (UV) and subsequent heat treatment (520C10H) (*a*) and spectrum of the mercury lamp after using the cut-off filter (*b*)

It can be seen from the absorption spectra absence of any plasmon resonance absorption peak. It means that irradiation to the mercury lamp after the cut-off filter does not lead to the release any electron. However, the crystal formation can be noticed from the absorption spectra for samples with Tb 1 mol.% and 0.007 mol.% Ce^{3+}.

Observed effect can be explained from the fact that the most preferable irradiation wavelength intensity was decreased by the filter and electrons from the ground state of Tb^{3+} ions did not excite to the $^5D_3$ level and further also the dosage of needed wavelength for exciting electron from the $^5D_4$ level was not enough. But at the first part of the study when samples without Ce^{3+} were irradiated by mercury lamp there is a plasmon resonance absorption peak. That can be explained by the high intensity of UV irradiation wavelengths at around 300nm in the spectrum of not filtered lamp. It means that partly electrons were excited to the $5d4f^7$ level by these photons and energy of around 4.1 eV is enough for that process.

Conclusion

The absorption spectra of two types of PTR glass doped with Tb^{3+} ions and codoped with Ce^{3+} were measured before, after UV irradiation with a mercury lamp, and after heat treatment of irradiated glasses. In samples without Ce^{3+} there was a plasmon resonance absorption peak at the absorption spectra located at 430 nm which corresponds to the presence of silver nanoparticles in the studied PTR glass. At the same time in samples codoped with Ce^{3+} and Tb^{3+} and containing only Tb^{3+} after irradiation to the filtered spectrum of the mercury lamp and heat treatment did not appear any silver nanoparticles. It can be explained by the fact that only wavelengths shorter than 350 nm were influential in formation of nanoparticles in case of samples with Tb^{3+} ions irradiated by the mercury lamp without filter.

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