Spectral-luminescent Properties of Silver Clusters Formed in Ion-exchanged Antimony-doped Photo-thermo-refractive Glasses

Yevgeniy Sgibnev, Nikolay Nikonorov and Alexander Ignatiev
Department of Optical Information Technologies and Materials, ITMO University,
Birzhevaya line 4, 199034, St. Petersburg, Russian Federation

Keywords: Photo-thermo-refractive Glass, Ion Exchange, Silver Clusters, Silver Nanoparticles.

Abstract: Photo-thermo-refractive glasses are now attractive material for developing various elements and devices of photonics. Influence of antimony oxide content in the photo-thermo-refractive glass composition and subsequent heat treatment temperature on the spectral-luminescent properties of silver non-metal clusters and metal nanoparticles formed with low-temperature ion exchange method were studied. Silver clusters in ion-exchanged Sb-doped photo-thermo-refractive glasses reveal broadband and intense emission in the visible and near infrared ranges. Absolute quantum yield of luminescence reaches 63% (λ_{ex}=365 nm), which opens up new prospects for using such materials as phosphors for white LEDs and down-convertors for solar cells.

1 INTRODUCTION

Silver clusters, which are subnanosized aggregates consisting of several silver atoms and/or ions, in glasses are well known (Bourhis et al. 2013; Dubrovin et al. 2014) to have an intense broadband luminescence in the visible. Today glasses with luminescent silver clusters were proposed to be used as phosphors for white LEDs (A. S. Kuznetsov et al. 2013), luminescence down-shifting cover glasses for solar cells (Cattaruzza et al. 2015), and optical data storage media (Klyukin et al. 2014). However, low quantum efficiency of luminescence of silver clusters stabilized in various glass hosts, which does not exceed 35% at room temperature up to now (Sgibnev et al. 2016; Cattaruzza et al. 2015; Kuznetsov et al. 2012), limits their industrial applications.

Properties of some silver clusters well studied in solutions (Díez et al. 2012), zeolites (De Cremer et al. 2009), and solid rare gas matrices (Harbich et al. 1990; Félix et al. 1999). However, it is impossible in principle to grow a certain kind of silver clusters in glasses. Thereby, it should be remembered that different types of silver clusters with various structural and optical properties always coexist in a glass host.

At present, photo-thermo-refractive (PTR) glasses that are already used widely in photonics (Nikonorov et al. 2001) can be classified as polyfunctional materials combining, in themselves, the properties of several monofunctional materials such as the photorefractive, holographic, laser, plasmonic, photostructurable, and ion exchangeable ones. Bragg gratings based on PTR glasses are used as laser line narrowing and stabilizing filters, spectral and spatial filters, Raman filters, compressors for fs- and ps-lasers, spectral beam combiners, high power beam splitters, etc. (Andrusyak et al. 2009).

As known, PTR glass is multicomponent sodium-zinc-aluminosilicate one containing halogens (fluorine and bromine) and doped with antimony, cerium, and silver. Mechanisms of photochemical reactions and subsequent nanocrystallization in PTR glasses were studied in detail in (Dubrovin et al. 2016).

It should be noted that, owing to the low solubility of silver in silicate glasses (the order of 10^{19} cm^{-3} for soda-lime ones), the maximum possible silver oxide concentration in PTR glasses does not exceed 0.1% mol. However, thin layer with high concentration of silver can be easily formed with low-temperature ion exchange method. The ion exchange (IE) technology is known (Tervonen et al. 2011; Ramaswamy and Srivastava 1988) to be based on substituting one kind of alkali cations (usually

Sgibnev Y., Nikonorov N. and Ignatiev A.
Spectral-luminescent Properties of Silver Clusters Formed in Ion-exchanged Antimony-doped Photo-thermo-refractive Glasses.
DOI: 10.5220/0006212303730377

Na^+) in glass for another one (Li^+, K^+, Rb^+, Cs^+) or transition metal ions (Ag^+, Cu^+, Tl^+) from a salt melt.

As mentioned above, the PTR glass composition contain antimony that in the form of Sb^{3+} can act as a donor of electrons for silver ions. In this work, dependence of spectral-luminescent features of silver clusters and nanoparticles formed with low-temperature ion exchange in PTR glasses depending on antimony content was investigated. Moreover, influence of heat treatment temperature on the optical properties of silver clusters and nanoparticles was studied as well.

2 EXPERIMENTAL

In order to investigate the effect of antimony ions alone on the formation of silver clusters and nanoparticles in PTR glasses, other dopants (such as silver and cerium oxides and also bromine) should be excluded from the glass compositions. Glass blocks of samples based on the $14Na_2O–3Al_2O_3–5ZnO–71.5SiO_2–6.5F$ (mol. %) matrix of typical PTR glasses doped with different concentrations of Sb_2O_3 were synthesized. Batch antimony oxide content of synthesized PTR matrix-based glass samples was 0, 0.002, 0.004, and 0.01 mol. %, (hereafter referred as GS0, GS2, GS4, and GS10, respectively). The glass synthesis was conducted in an electric furnace at 1500 °C in the air atmosphere using the platinum crucibles and mechanical stirrer. The glass transition temperature of the glasses measured with STA 449 F1 Jupiter (Netzsch) differential scanning calorimeter was found to be 464±3 °C. Planar polished samples 1 mm thick were prepared for further investigation.

Silver ions were incorporated into the above PTR matrix-based glass samples with ion exchange method. The samples were immersed in a bath with a melt of nitrate mixture $5AgNO_3/95NaNO_3$ (mol. %) at temperature T_{IE}=320 °C for 15 minutes. A gradient layer enriched by silver ions about 10 μm thick was formed due to replacing the Na^+ ions in glass by Ag^+ ones from a salt melt. The ion-exchanged samples were then heat-treated at different temperatures (250−500 °C) for 15 hours. The absorption spectra of the samples were recorded with double-beam spectrophotometer Lambda 650 (Perkin Elmer). The registration of emission spectra excited by UV light at 365 nm and absolute quantum yield measurements were carried out inside integrated sphere with Photonic Multichannel Analyzer (PMA-12, Hamamatsu) at room temperature. The measurement error for the absolute quantum yield (AQY) was ±1%.

3 RESULTS AND DISCUSSIONS

3.1 Influence of PTR Glass Composition

A long-wavelength shift of the UV edge of strong absorption with respect to its initial location was observed for all ion-exchanged glass samples. The shift results from the absorption envelope of Ag^+ ions with maximum around 225 nm caused by the interionic $4d^{10}→4d^95s^1$ transitions (Sgibnev et al. 2013). Weak luminescence assigned to different silver clusters were occurred in the visible range after the IE. In the course of the IE process, due to a great increase in the concentration of Ag^+ ions, chemical equilibrium of a reaction:

$$2Ag^+ + Sb^{3+} \leftrightarrow 2Ag^0 + Sb^{5+} \quad (1)$$

shifts to the right side in compliance with Le Chatelier principle (Jenkins 2008). Subsequent aggregation of silver atoms and ions through chemical reactions:

$$Ag^0 + Ag^+ \rightarrow Ag_2^+ \quad (2)$$

$$Ag^0 + Ag^0 \rightarrow Ag_2 \quad (3)$$

$$Ag^0 + Ag_2 \rightarrow Ag_3 \quad (4)$$

and similar ones results in formation of different non-metal silver clusters. Thus, growth of silver clusters takes place in the course of the IE and lead to occurrence of weak luminescence in the visible.

Increase in Sb^{3+} ions content in the PTR glass composition increases rate of the chemical reaction (1), i.e. rate of reducing silver ions Ag^+ to the atomic state Ag^0. Thereby, formation kinetics of silver clusters and nanoparticles is determined by concentration of reducing agent (Sb^{3+} ions) in the initial glass, which is proved experimentally by absorption spectra of PTR glass samples (Fig. 1).

Additional absorption bands were not observed in PTR glass sample GS0 with no antimony (i.e. silver remains in the GS0 glass in the ionic form). Absorption spectra of Sb-doped PTR glasses shows additional absorption bands centered at 350 and 420 nm. The long-wavelength band corresponds to the surface plasmon resonance (SPR) of silver nanoparticles (Schasfoort and Tudos 2008). The other one with maximum in the UV assigned to non-metal silver clusters (Ag_n, $n≥2$). Increase in antimony oxide content results in growth of the amplitude and changing relation of the bands.

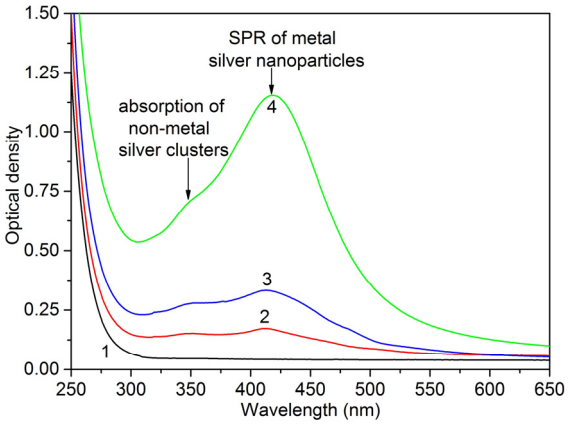

Figure 1: Optical density spectra of PTR glasses GS0-GS10 (1)-(4), respectively, after the IE and subsequent heat treatment at 500 °C.

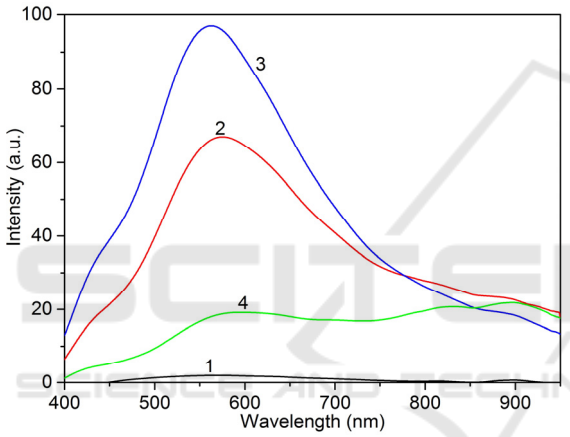

Figure 2: Emission spectra (λ_{ex} = 365 nm) of PTR glasses GS0-GS10 (1)-(4), respectively, after the IE and subsequent heat treatment at 500 °C.

Fig. 2 shows emission spectra of the PTR glasses after the IE and subsequent heat treatment at T=500 °C for 15 h. PTR glass GS0 demonstrates weak luminescence in the visible related to small amount of silver clusters formed by trapping electrons from glass impurities by silver ions. In Sb-doped PTR glasses intense and broadband luminescence of silver clusters in the range 400-950 nm was observed. Emission peak in the visible occurs around 560 nm and can be assigned to Ag_3 clusters that demonstrate emission bands peaked at 560 and 616 nm under 362 nm excitation in the solid argon matrix (Fedrigo et al. 1993). Luminescence in the visible quenches with increasing antimony oxide concentration. The luminescence quenching results from both decreasing amount of emitting centers due to transformation «cluster → nanoparticle» and absorption of the emission by silver nanoparticles.

3.2 Influence of the Heat Treatment Temperature

As it was shown in (Simo et al. 2012; Sgibnev et al. 2016) heat treatment temperature has a significant impact on properties of silver aggregates in ion-exchanged glasses.

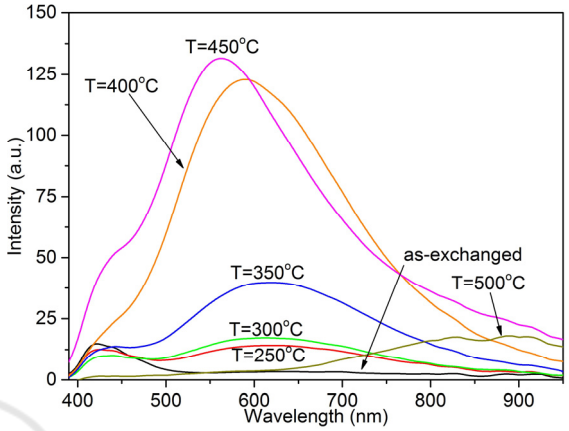

Figure 3: Emission spectra (λ_{ex}= 365 nm) of the ion-exchanged PTR matrix-based glass GS10 prior to any heat treatment and after the heat treatment at temperatures 250-500 °C (temperature values are indicated on the graph).

Fig. 3 clearly shows substantial effect of the heat treatment temperature on shape and intensity of the emission spectra of silver clusters formed in Sb-doped PTR glass. Shape of the emission spectra of the samples heat-treated at temperatures 250-350 °C remains unchanged, which evidences that concentration of silver clusters increases, while relation of different kinds of luminescent centers keeps constant. The emission maximum is located at 620 nm that coincides with emission of Ag_3 clusters (Fedrigo et al. 1993). Further rising heat treatment temperature up to 400 and 450 °C results in significant increase in luminescence intensity and blue shift of the emission peak. The blue shift can be assign to formation in glass host of Ag_4 clusters that in the argon matrix are characterized by the UV absorption bands at wavelengths up to 405 nm and the main emission band at 458 nm (Félix et al. 1999). Absorption of the luminescence of silver clusters by metal nanoparticles formed in the ion-exchanged layers after the heat treatment at 500 °C leads to changing emission color from yellowish white to deep red (Fig. 4). The NIR emission in PTR glasses can be assigned to large silver clusters Ag_n (n>4) remaining in the glass after heat treatment at 500 °C.

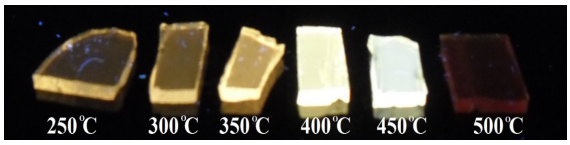

Figure 4: Photo of the PTR glass GS10 samples subjected to the IE and subsequent heat treatment at temperatures 250-500 °C.

Absolute quantum yield (AQY) allows to estimate efficiency of converting UV light in the visible range, that is why it is an important parameter for industrial applications of glasses with silver clusters as luminescence down shifting material or phosphor.

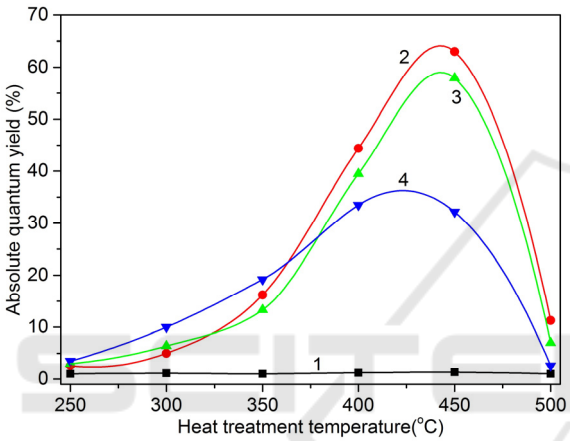

Figure 5: Dependence of AQY magnitudes for ion-exchanged PTR glasses GS0-GS10 (1)-(4), respectively, on the temperature of the subsequent heat treatment.

The AQY magnitudes of all as-exchanged and heat-treated at 250 °C glass samples do not exceed 4%. The subsequent heat treatment did not lead to any increase in the AQY magnitude for antimony-free GS0 glass (Fig. 5). Heat treatment of the Sb-doped PTR glass samples at 300 and 350 °C causes weak growth of AQY up to 6-9% and 12-18%, respectively. In the course of the heat treatment of antimony-doped samples at 400 and 450 °C the concentration of silver clusters increases dramatically and, hence, the AQY magnitudes increase as well. A strong enough AQY dependence on the antimony oxide concentration emerges at these temperatures. For example, the AQY magnitudes achieved after the heat treatment at 450 °C for 15 h are 63%, 59% and 32% for GS2, GS4, and GS10 glasses, respectively. A further increase in the heat treatment temperature up to 500 °C leads, for all Sb-doped ion-exchanged glass samples, to a decrease in their AQY magnitudes compared to those of samples heat-treated at 450 °C. This results from decreasing the amount of emitting centers and absorption the emission of silver clusters by silver nanoparticles.

Thus, heat treatment temperature determines color, intensity, and quantum yield of the luminescence of silver clusters dispersed in surface layers of ion-exchanged Sb-doped PTR glasses.

4 CONCLUSIONS

Influence of antimony oxide content in the PTR glass composition and subsequent heat treatment temperature on the spectral-luminescent properties of silver non-metal clusters and metal nanoparticles formed in the PTR glasses with low-temperature ion exchange method were studied. Antimony ions Sb^{3+} are the donor of electrons for silver ions Ag^{+} and play a key role in growth of silver luminescent clusters and plasmonic nanoparticles. Silver clusters in Sb-doped PTR glasses reveal broadband and intense emission in 400-950 nm range. Metal nanoparticles in ion-exchanged PTR glasses are formed only after subsequent heat treatment at temperature higher than the glass transition one and quench the luminescence. Absolute quantum yield magnitude of luminescence in Sb-doped PTR glasses with silver clusters can be as high as 63%. It opens up new prospects for using such materials as phosphors for white LEDs and down-convertors for solar cells.

ACKNOWLEDGEMENTS

Research was funded by Russian Science Foundation (Agreement #14-23-00136).

REFERENCES

Andrusyak, O. et al., 2009. Spectral Combining and Coherent Coupling of Lasers by Volume Bragg Gratings. *IEEE Journal on Selected Topics in Quantum Electronics*, 15(2), pp.344–353.

Bourhis, K. et al., 2013. Formation and thermo-assisted stabilization of luminescent silver clusters in photosensitive glasses. *Materials Research Bulletin*, 48(4), pp.1637–1644.

Cattaruzza, E. et al., 2015. $Ag^{+}\leftrightarrow Na^{+}$ ion exchanged silicate glasses for solar cells covering: Down-shifting properties. *Ceramics International*, 41(5), pp.7221–7226.

De Cremer, G. et al., 2009. Characterization of

fluorescence in heat-treated silver-exchanged zeolites. *Journal of the American Chemical Society*, 131(8), pp.3049–3056.

Díez, I. et al., 2012. Blue, green and red emissive silver nanoclusters formed in organic solvents. *Nanoscale*, 4(15), pp.4434–7.

Dubrovin, V.D. et al., 2014. Luminescence of silver molecular clusters in photo-thermo-refractive glasses. *Optical Materials*, 36(4), pp.753–759.

Dubrovin, V.D., Ignatiev, A.I. and Nikonorov, N. V., 2016. Chloride photo-thermo-refractive glasses. *Optical Materials Express*, 6(5), p.1701.

Fedrigo, S., Harbich, W. and Buttet, J., 1993. Optical response of Ag2, Ag3, Au2, and Au3 in argon matrices. *The Journal of Chemical Physics*, 99(1993), pp.5712–5717.

Félix, C. et al., 1999. Fluorescence and excitation spectra of Ag4 in an argon matrix. *Chemical Physics Letters*, 313(1-2), pp.105–109.

Harbich, W. et al., 1990. Deposition of mass selected silver clusters in rare gas matrices. *J. Chem. Phys.*, 93(12), pp.8535–8543.

Jenkins, H.D.B., 2008. *Chemical Thermodynamics at a Glance*, Blackwell Publishing, Oxford, 1st edition.

Klyukin, D. a et al., 2014. Luminescence quenching and recovering in photo-thermo-refractive silver-ion doped glasses. *Optical Materials*, 38, pp.233–237.

Kuznetsov, A. S. et al., 2013. Ag nanocluster functionalized glasses for efficient photonic conversion in light sources, solar cells and flexible screen monitors. *Nanoscale*, 5(21), pp.10065–75.

Kuznetsov, A. S. et al., 2012. Quantum yield of luminescence of Ag nanoclusters dispersed within transparent bulk glass vs. glass composition and temperature. *Applied Physics Letters*, 101(25).

Nikonorov, N. V. et al., 2001. Influence of Glass Composition on the Refractive Index Change upon Photothermoinduced Crystallization. *Glass Physics and Chemistry*, 27(3), pp.241–249.

Ramaswamy, R. V. and Srivastava, R., 1988. Ion-Exchanged Glass Waveguides: A Review. *Journal of Lightwave Technology*, 6(6), pp.984–1000.

Schasfoort, R.B.M. and Tudos, A.J., 2008. *Handbook of surface plasmon resonance*, RSC Publishing.

Sgibnev, E.M. et al., 2013. Effects of silver ion exchange and subsequent treatments on the UV-VIS spectra of silicate glasses. I. Undoped, CeO_2-doped, and (CeO_2 + Sb_2O_3)-codoped photo-thermo-refractive matrix glasses. *Journal of Non-Crystalline Solids*, 378, pp.213–226.

Sgibnev, Y.M., Nikonorov, N.V. and Ignatiev, A. I., 2016. Luminescence of silver clusters in ion-exchanged cerium-doped photo-thermo-refractive glasses. *Journal of Luminescence*, 176, pp. 292–297.

Simo, A. et al., 2012. Formation mechanism of silver nanoparticles stabilized in glassy matrices. *Journal of the American Chemical Society*, 134(45), pp.18824–18833.

Tervonen, A., West, B.R. and Honkanen, S., 2011. Ion-exchanged glass waveguide technology: a review. *Optical Engineering*, 50, p.71107.