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High efficient luminescence of silver clusters in ion-exchanged antimony-doped photo-thermo-refractive glasses: Influence of antimony content and heat treatment parameters

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ABSTRACT

Photo-thermo-refractive glass is now promising material for developing various elements and devices of photonics. The effect of variations in the Sb_2O_3 concentration in the photo-thermo-refractive glass composition on the spectral-luminescent properties of silver clusters formed with the low-temperature ion exchange is studied for the first time. The effect of temperature and duration of subsequent heat treatment of ion-exchanged glasses is investigated in detail. Silver clusters in the glasses are shown to possess broadband luminescence in the visible and NIR. Luminescent silver clusters in Sb-doped photo-thermo-refractive glasses reveal the absolute quantum yield up to 63% ($\lambda_{ex} = 365$ nm), which can be used effectively for developing luminescent sensors, white LEDs, and down-convertors for solar cells.

1. Introduction

Today, silver nanostructures are of great interest for many applications in photonics due to their unique optical [1,2] nonlinear [3], and electrical [4] properties. Silver clusters (subnanosized aggregates consisting several silver atoms and/or ions) in glasses are well known [5–7] to have an intense broadband luminescence in the visible.

Glasses with luminescent silver clusters could find applications in solid-state lighting, energy conversion, and flexible screen monitors [8]. Most of the commercially available white LEDs combine a blue-emitting chip with an $Y_3Al_5O_{12}:Ce^{3+}$ yellow-emitting phosphor packed on the chip surface using epoxy resin or silicone [9,10]. However, heat emitted from the chip can cause degradation such resin or silicon that significantly reduce lifetime of the LED [11]. Therefore, LED with phosphor dispersed in inorganic glasses or glass–ceramics is a promising candidate for the realization of resin-free, high-temperature and long-lifetime white LED devices. Recently it was shown that Ag nanoclusters in oxyfluoride glass emit white light with chromaticity matching that of a commercial YAG:Ce^{3+} LED [12].

Another possible application field of glasses with luminescent silver clusters is solar cells. Classical theoretical efficiency limit of silicon solar cells is currently to be 29% [13], but detailed balance calculations show that the efficiency could be improved to approximately 38% by spectrum modification (down conversion, luminescence down-shifting, and up-conversion) [14]. Today cover glasses for solar cells are passive optical elements that are used for absorbing UV light and protecting the cell from dust and mechanical damage. Developing active cover glasses with silver clusters converting part of UV light into the visible range could enhance efficiency of solar cells. Luminescence down-shifting properties of silver ion-exchanged glasses were investigated in [15,16], however the authors have not observed improvements in Si and GaAs solar cells performance.

Properties of some silver clusters formed in solutions [11–13], zeolites [14,15], and solid rare gas matrices [16–19] have been well studied. Emission bands of silver clusters Ag_n (n = 1–4) stabilized in rare gas matrices are listed in Table 1. However, it is impossible, in principle, to grow a certain kind of silver clusters in glass. Thereby, it should be remembered that different types of silver clusters with various optical properties always coexist in a glass host.

Silver nanoparticles in glasses are characterized by absorption band around 410–420 nm related to surface plasmon resonance (SPR) [21]. Silver nanoparticles can be used to provide non-linear optical properties to glass [22] and formation of SERS-active silver films on glass surface [23]. A great number of articles are devoted to interaction of rare earth ions and silver nanoparticles. However, proper mechanism of the interaction is still not fully understood, both luminescent enhancement and quenching were observed [24–29].

At present, photo-thermo-refractive (PTR) glass, which is already used widely in photonics [30], can be classified as multifunctional material combining, in themselves, the properties of several monofunc-

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Table 1
Luminescent properties of silver clusters Ag_n (n = 1–4) stabilized in solid rare gas matrices.

Cluster	Emission bands	References
Ag_1	418, 425, 458, 490, 525	[17,18]
Ag_2	453, 479, 485, 506	[17,18]
Ag_3	380, 560, 608, 616, 625	[17–19]
Ag_4	458	[20]

tional materials such as the photorefractive, holographic, laser, plasmonic, photostructurable, and ion exchangeable ones. For example, the possibility of recording highly efficient phase volume holograms in the form of Bragg gratings was shown in [31]. 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. [32]. In [33], the possibility of drawing optical fibers from PTR glass and recording the Bragg gratings in the fibers are shown. Several papers [34–36] are devoted to doping PTR glasses with rare earth ions (ytterbium, erbium, and neodymium) and investigating their spectral, luminescent, and laser characteristics. Furthermore, the plasmonic, photostructurable, and ion exchangeable properties of the PTR glasses are described in [37–39].

Aluminosilicate glasses well-known to possess high transparency in wide spectral range, excellent mechanical strength and chemical durability [40–42].

PTR glass is multicomponent sodium-zinc-aluminosilicate one containing halogens (fluorine and bromine) and doped with antimony, cerium, and silver [30]. Cerium ions Ce^{3+} serves as the donor of photoelectrons that provides the sensitivity of the glass to the UV radiation. Antimony and, then, silver are the acceptors of photoelectrons. Mechanisms of photochemical reactions and subsequent nanocrystallization in PTR glasses were studied in detail in [43–45]. According to [43–45], the heat treatment at temperatures below the glass transition one (T_g) results in the fact that the antimony trapping center acts as the electron donor, i.e. it frees the previously trapped photoelectrons. The freed photoelectrons, in turn, are trapped by silver ions, thus forming the neutral Ag° states and small silver clusters [43]. This allows to form further the metal silver nanoparticles playing the role of nucleation centers. Furthermore, the heat treatment at temperatures above T_g leads to the formation of AgBr shell on the nanoparticle surfaces and, further, to the growth of NaF nanocrystals [44,46].

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 [47]), the maximum possible silver oxide concentration in PTR glasses does not exceed 0.1% mol. So, an increase in the Ag_2O content of PTR glass above this limit results in coloring the glass bulk due to the spontaneous formation of silver nanoparticles just in the course of glass synthesis. For some applications (for instance, optical, plasmonic, and luminescent waveguides and sensors), however, a thin layer with high concentration of silver in the glass surface region is required. Such layers can be easily formed by low-temperature ion exchange method. The ion exchange (IE) technology is known [48–53] to be based on substituting one kind of alkali cations (usually Na^+) in glass for another one (Li^+, K^+, Rb^+, Cs^+) or transition metal ion (Ag^+, Cu^+, Tl^+) from a salt melt.

The silver IE allows for reaching a high concentration of silver ions comparable to that of alkali ions in initial glasses. As reported in [54], for example, around 90% of sodium ions in silicate glass were replaced by silver ions at the glass surface in the course of silver IE for 30 min ($AgNO_3$ content in the salt melt being 4 mol% and T_{IE} being 320 °C).

In [55], the effect of doping soda-lime-silicate glass with 1 mol% of antimony oxide on the spectral and luminescent properties of the glass samples subjected to the silver IE was studied. The authors concluded that the silver ions incorporated into glass with IE method could be reduced by antimony Sb^{3+} ions down to the Ag° state. Emission band peaked at 615 nm was attributed to silver molecular clusters by the authors [55].

In [56] spectral-luminescent properties of silver clusters formed by ion exchange method in Ce-doped photo-thermo-refractive glasses were described. Silver clusters in that glasses reveal broad emission spectra, absolute quantum yield reached 32% that is comparable to maximal values for luminescence of silver clusters in silicate and oxyfluoride glasses at room temperature [12,15].

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 on antimony content was investigated for the first time. Influence of subsequent heat treatment parameters (temperature and duration) on the 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 (Table 2). 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 at heating rate 10 K/min 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 the 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 min. A gradient layer enriched by silver ions about 10 μm thick was formed by the replacement of 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) and durations (1–30 h). 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 conducted inside the 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 discussion

3.1. Effect of Sb_2O_3 content in PTR glass composition on growth and properties of silver clusters and nanoparticles

Additional absorption band in the UV peaked around 215 nm occurs

Table 2
Batch Sb_2O_3 content of PTR matrix-based glass samples investigated.

Glass	Batch Sb_2O_3 content, mol%
G1	0
G2	0.002
G3	0.004
G4	0.01