Journal Pre-proof

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Please cite this article as: Y. Sgibnev, B. Asamoah, N. Nikoronov, S. Honkanen, Tunable photoluminescence of silver molecular clusters formed in Na$^+$-Ag$^+$ ion-exchanged antimony-doped photo-thermo-refractive glass matrix, *Journal of Luminescence* (2020), doi: https://doi.org/10.1016/j.jlumin.2020.117411.

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Tunable photoluminescence of silver molecular clusters formed in Na$^+$-Ag$^+$ ion-exchanged antimony-doped photo-thermo-refractive glass matrix

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Influence of Na$^+$-Ag$^+$ low-temperature ion exchange and subsequent heat treatment durations on the spectral-luminescent properties of silver molecular clusters formed in antimony-doped photo-thermo-refractive (PTR) glass matrix was studied. The ion exchange of PTR glass leads to long-wavelength shift of the ultra-violet (UV) edge of strong absorption. The shift magnitude is shown to linearly depend on the square root of the ion exchange duration. Increase in the ion exchange duration is shown to result in changing photoluminescent properties of silver molecular clusters, which allows the tuning of the emission color from cool and warm white to yellow and orange. Model for growth of silver molecular clusters in Na$^+$-Ag$^+$ ion-exchanged layers of the antimony-doped PTR glass matrix was proposed based on the observed changes in spectral-luminescent properties of the samples. The studied PTR glass samples doped with silver molecular clusters are characterized by photoluminescence quantum yield up to 57 %, which paves the wave for the development of solid-state light-emitting devices and spectral converters with tunable emission spectrum.

Introduction

Silver molecular clusters (SMCs) are of great interest for developing various luminescent devices thanks to their broadband and bright emission covering all visible range[1,2]. SMCs are subnanometer aggregates consisting of a few silver atoms and/or ions. Electronic and optical properties of nanoparticles are known to strongly depend on their size[3]. That is why properties of SMCs and silver nanoparticles (SNPs) differ significantly from each other. SMCs have molecule-like discrete set of energy levels and do not possess local surface plasmon resonance. Optical properties of SMCs stabilized in rare gas matrices at cryogenic temperatures are known since 1978 and well-studied[4–8]. Currently, absorption and photoluminescent properties of SMCs are studied in solutions[9,10], zeolites[11–13], and glasses[14–16].

Due to their high chemical and temperature stability, glasses doped with SMCs were already proposed as promising material for solid-state lighting[17], energy conversion[18], and flexible screen monitors[19]. Developing solid-state phosphors is now a hot topic to overcome low thermal stability of polymer/silicon with YAG:Ce^{3+} particles dispersed in it. Light emitting diode (LED) with a phosphor dispersed in inorganic glasses or glass–ceramics is a promising candidate for the realization of thermostable and long-lifetime white LEDs[20,21]. Recent researches show that white emission of SMCs dispersed in glass matrix can be used for developing white LEDs with chromaticity matching that of commercial LEDs based on YAG:Ce^{3+} yellow phosphor[17]. Another potential application of glasses doped with SMCs is photovoltaic, where glass with SMCs absorbing ultra-violet (UV) radiation and emitting visible light can be used as spectral converter to overcome poor spectral response in the UV and blue ranges for most of solar cells[18,22,23].

SMCs were stabilized and studied in phosphate[15], borosilicate[24], oxyfluoride[14], and silicate[16] glass matrices. Silicate glass based on photo-thermo-refractive (PTR) glass matrix doped with SMCs, however, possesses high absolute photoluminescence quantum yield (APLQY)[23,25]. PTR glass is a special multicomponent glass, whose refractive index can be varied upon UV irradiation and subsequent heat treatment (HT) due to growth of NaF nanocrystals in the UV irradiated areas[26,27]. The high transparency of PTR glass in a wide spectral range and the possibility to locally modify the refractive index has enabled its applications for the recording high-efficient volume Bragg gratings[28] used

as notch filters for wavelength selection[29] and stabilizers of laser sources[30]. Presence of sodium ions in PTR glass composition as one of the basic component allows the application of low-temperature ion exchange (IE) as the effective method of embedding silver ions. Low-temperature IE is based on substituting one kind of alkali cations (usually Na^+) in glass for another one (Li^+, K^+, Rb^+, Cs^+) or transition metal ions (Ag^+, Cu^+, Tl^+) from a corresponding salt melt at temperatures below the glass transition one[31,32]. In case of silicate glasses, the IE technique provides the possibility of obtaining silver concentration two orders of magnitude greater in comparison with a conventional glass synthesis.

The influence of the antimony content and HT parameters on the growth and spectral-luminescent properties of SMCs and SNPs in Na^+-Ag^+ ion-exchanged PTR glasses was studied in our previous paper[25]. The study revealed that SMCs formed in PTR glass matrix via the IE method are characterized by very broad and bright emission and APLQY up to 63%. Although IE technology is a well-established industrial process for the modification of glass properties, its role on the achievement of such high APLQY in PTR glasses has not been studied. The present study, therefore, focuses on the

investigation of the effect of Na^+-Ag^+ IE duration, as a key diffusion parameter, on the photoluminescent properties of SMCs in PTR glass matrix.

Experimental

A typical PTR glass matrix based on Na_2O–Al_2O_3–ZnO–SiO_2–F system, without photosensitive dopants such as cerium and silver, was used in this study. The PTR glass doped with 0.002 Sb_2O_3 (mol%) as a reducing agent for silver was synthesized in air atmosphere by melt-quench method in an electric furnace at 1500 °C in a platinum crucible with a mechanical stirrer. The glass transition temperature measured with the STA 449 FI Jupiter (Netzsch) differential scanning calorimeter at heating rate of 10 K/min was found to be 464±3 °C. The glass samples with thickness 0.9-1.0 mm were polished to optical quality for further investigation.

The silver ions were introduced into the synthesized glass via low-temperature Na^+-Ag^+ IE. For this purpose, PTR glass samples were immersed in a $95NaNO_3$:$5AgNO_3$ (mol %) mixed salt melt at 320 °C for different durations, from 5 min – 21 h (particularly 5min, 15 min, 30 min, 1h, 3h, 6h, 9h, 15h, and 21h). To promote the growth of SMCs, the ion-exchanged samples were then heat-treated in air atmosphere at 450 °C for 1 – 24 h.

Absorbance spectra of the samples were measured with the double-beam spectrophotometer Lambda 650 (Perkin Elmer) in 200 – 800 nm wavelength range. The registration of photoluminescence (PL) spectra excited by UV light at 350 nm and APLQY measurements were conducted inside the integrating sphere with PMA-12 Hamamatsu Photonic Multichannel Analyzer as the detector. All the measurements were carried out at room temperature.

The refractive index profiles of the ion-exchanged PTR glasses were calculated with the inverse Wentzel-Kramers-Brillouin method using the effective refractive indices of waveguide modes[33]. The latter were measured with the method of selective resonance excitation of waveguide modes through a prism coupler using a He-Ne laser (λ = 632.8 nm) as a source[34]. The measurement error of effective refractive indices was estimated to be $\pm 2 \times 10^{-4}$.

Results and Discussions

Na^+-Ag^+ IE has significant effect on the absorbance spectra of PTR glasses (Fig. 1a). The IE procedure causes a long-wavelength shift of the UV absorption edge. The shift is explained by absorption of the embedded silver ions that are characterized by strong absorption band at 225 nm in the PTR glass matrix[35]. That

is why the shift magnitude depends on the IE duration. Moreover, absorbance increment at a fixed wavelength was found to be linearly related to the square root of the IE time (Fig. 1b). The experimental points presented at the Fig. 1b were chosen so that absorbance magnitude was below 3, which is the upper limit of reliably recordable value with commercial UV-VIS spectrophotometers. Since the PTR glass matrix is transparent from 200 nm, absorbance amplitude of the ion-exchanged PTR glass samples at wavelengths greater 300 nm is determined by concentration of the introduced silver ions alone. The linear relation between absorbance increment and the square root of the IE time reveals that the integral concentration of silver ions depends on the IE time in the same way. Note that similar behaviour at different temperatures for the IE durations up to 3 h was reported by T. Ito in 1962[36].

One-dimensional IE diffusion in glass from infinite source is described by the second Fick's law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

where C is the concentration of invading ions, silver in our case, D – interdiffusion coefficient, t – time, and x – depth. The solution of equation (1) in case of semi-infinite medium and zero concentration of

the invading ions at initial moment ($C(x,t)_{t=0}=0$) is as follows[37]:

$$C(x,t) = C_0 \cdot erfc\left[\frac{x}{2\sqrt{Dt}}\right] \qquad (2)$$

where C_0 is the surface concentration and *erfc*– complementary error function. By integrating $C(x, t)$, one can find that the integral concentration of diffused ions is linearly proportional to the square root of the IE time. Thus, the linear dependence of absorbance increment on the square root of the IE time confirms linear diffusion (D is constant) of silver ions in the course of the Na^+-Ag^+ IE in PTR glass. Moreover, it proves that most of the silver introduced in the PTR glass remains in the ionic form at 320 °C even for the IE process lasting 21 h.

Heat treatment of the ion-exchanged PTR glass samples at 450 °C induces several processes: out diffusion of silver ions with subsequent formation of silver nanoparticles on the glass surface (i), migration of silver ions deeper into the glass (ii), reduction of silver ions to atoms (iii), and aggregation of isolated silver atoms into molecular clusters or nanoparticles (iv).

According to Yu. Kaganovskii et al, the process (i) takes place due to the interaction of embedded silver ions with water molecules from the atmosphere with subsequent thermal decomposition of silver oxide [38]:

$$\equiv Si - O - Ag^+ + \frac{1}{2}H_2O \leftrightarrow \equiv Si - O - H^+ + \frac{1}{2}Ag_2O$$

$$Ag_2O \rightarrow 2Ag^0 + O$$
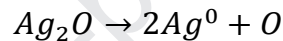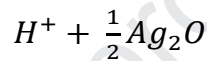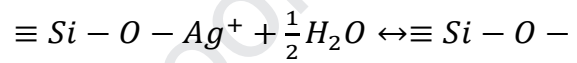
Formation of SNPs on the glass surface was observed in Na^+-Ag^+ ion-exchanged fluorophosphates, phosphate, and soda-lime silicate glasses during thermal treatment in reducing atmosphere [39–41]. The exact mechanisms governing growth of SNPs on the Na^+-Ag^+ ion-exchanged PTR glass surface during HT in air atmosphere will be studied in details in further researches.
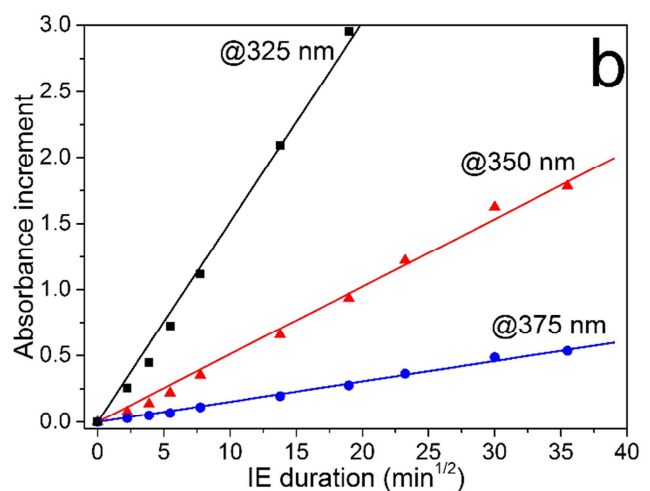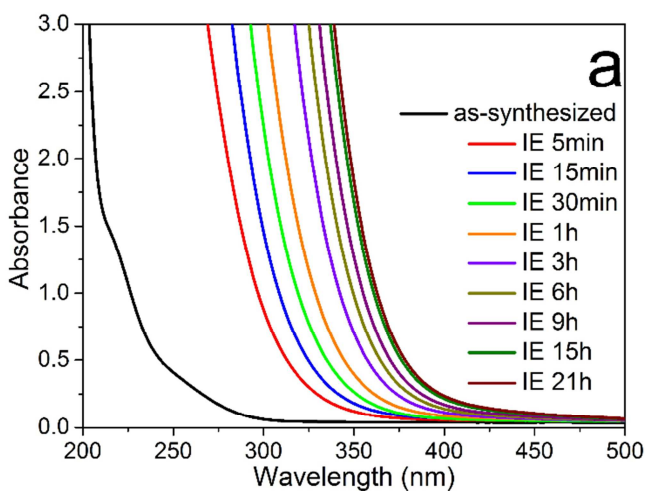
Fig. 1 Absorbance spectra of the glass samples ion-exchanged for different time (a), and absorbance increment for the ion-exchanged samples with respect to as-synthesized glass at different wavelengths (b).

Formation of SNPs on the PTR glass surface leads to additional absorbance and scattering of light. That is why silver nano-island film was removed mechanically by polishing the samples during several seconds after the HT for further optical study of the SMCs formed in the ion-exchanged samples. Diffusion of silver ions deeper into the PTR glass substrate during the HT results from concentration gradient of silver ions. Reducing of silver ions, process (iii), in the studied PTR glasses occurs through the following redox reaction:

$$2Ag^+ + Sb^{3+} \leftrightarrow 2Ag^0 + Sb^{5+} \tag{5}$$
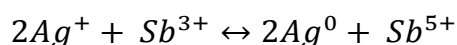
Chemical equilibrium of the redox reaction (5) shifts to the right side due to a high concentration of silver ions which exceeds that of the trivalent antimony ions by several orders. Further interaction of silver atoms and ions results in growth of various SMCs:

$$Ag^0 + Ag^+ \rightarrow Ag_2^+$$
$$Ag^0 + Ag^0 \rightarrow Ag_2$$
$$Ag^0 + Ag_2 \rightarrow Ag_3$$
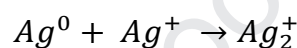
Presence of SMCs in the ion-exchanged and heat-treated samples manifests as a broad absorption in the range below 650 nm (Fig. 2a).
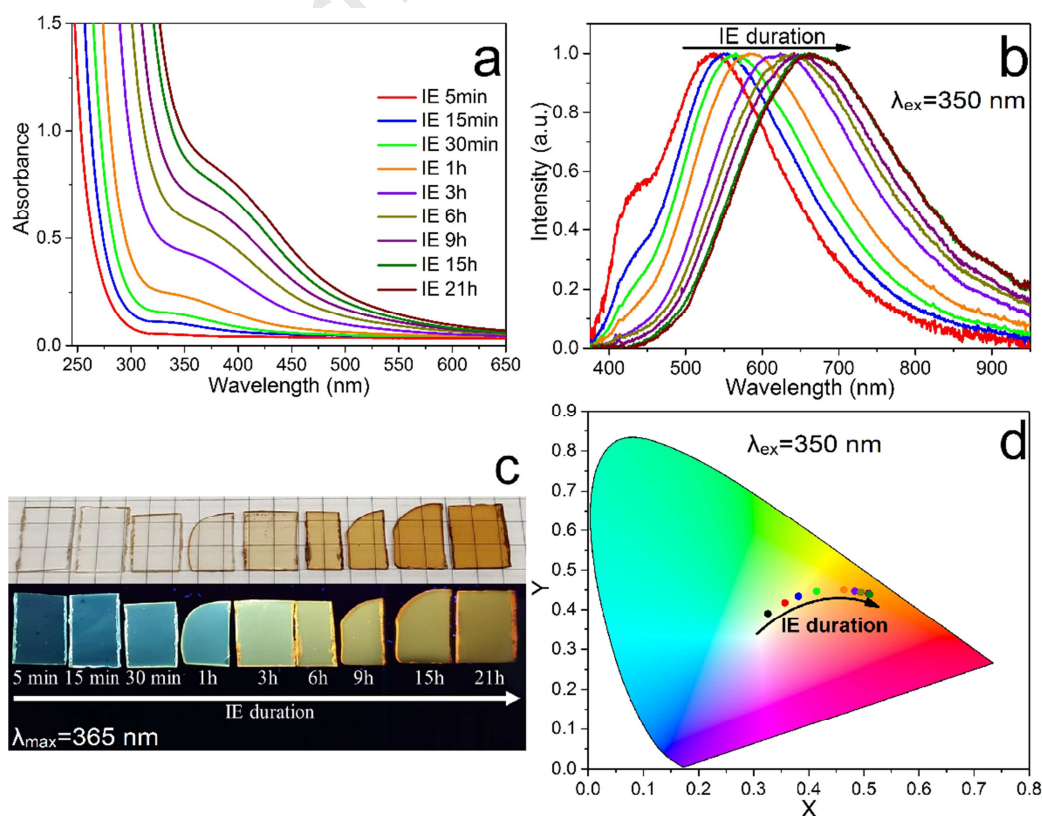
Fig. 2 Absorbance (a) and normalized PL (b) spectra under 350nm excitation the PTR glass samples after the IE and HT at 450 °C for 24h. Photo of the samples under daylight and UV mercury lamp with λ_{max}=365 nm (c), and CIE 1931 chromaticity diagram under 350 nm excitation (d).

SMCs in glass matrices are known to be characterized by absorption in the UV and blue ranges[15,22,42,43]. The amplitude of clusters-related absorption rises with increase in the IE time. Due to substantially overlapped band of silver ions and molecular clusters, it is difficult to reveal peak of SMCs absorption. Moreover, in case of Na^+-Ag^+ ion-exchanged glass, SMCs are growing in a layer with gradient of silver concentration, which should lead to formation of various Ag_n clusters, where n=2, 3, 4, etc. Thus, the observed broad absorption in the UV-VIS spectra is the envelope of absorption bands assigned to various SMCs. All samples after the IE and HT possess bright emission in the range of 400-950 nm under UV excitation at 350 nm (Fig. 2b). PL peak shifts to greater wavelengths with extension of the IE treatment. It should be noted that the shift occurs in the spectral region (from 535 to 660 nm), where absorbance of the studied samples differs insignificantly, and reabsorption of SMCs emission can be excluded from possible reasons of the emission peak shift. Thus, the shift is caused by variation of integral emission of SMCs in the ion-exchanged

glasses. Visual changes in absorption and emission color with increase in the IE duration is shown in Fig. 2c. Under daylight, colorless samples become yellowish and even brownish with rising time of the IE treatment whereas UV-excited emission changes from cool white to warm white, yellow, and orange. Thus, emission of Na^+-Ag^+ ion-exchanged PTR glasses can be easily tuned in a wide range as shown by the CIE1931 chromaticity diagram in Fig. 2d. Color temperature of the SMCs emission in the samples drops from 6250 to 2300 K with increasing in the IE duration.

Heat treatment was found to differently affect the spectral-luminescent properties of the studied samples. Despite that similar changes are observed for all samples in the absorbance spectra, the behaviour of emission spectra varies significantly. As an example, absorbance spectra of the samples subjected to the IE for 15 minutes and 15 hours are shown in Fig. 3a and 3b, respectively.

A blue shift of the UV absorption edge and appearance of cluster-related bands are observed in the spectra with increase in the HT duration. As location of UV

absorption edge is governed by integral silver concentration in the ion-exchanged samples (see Fig. 1a), the blue shift is explained by lowering concentration of silver ions. The latter results from out diffusion to the glass surface and reduction of silver ions to atoms by trivalent antimony according to the redox reaction (5).
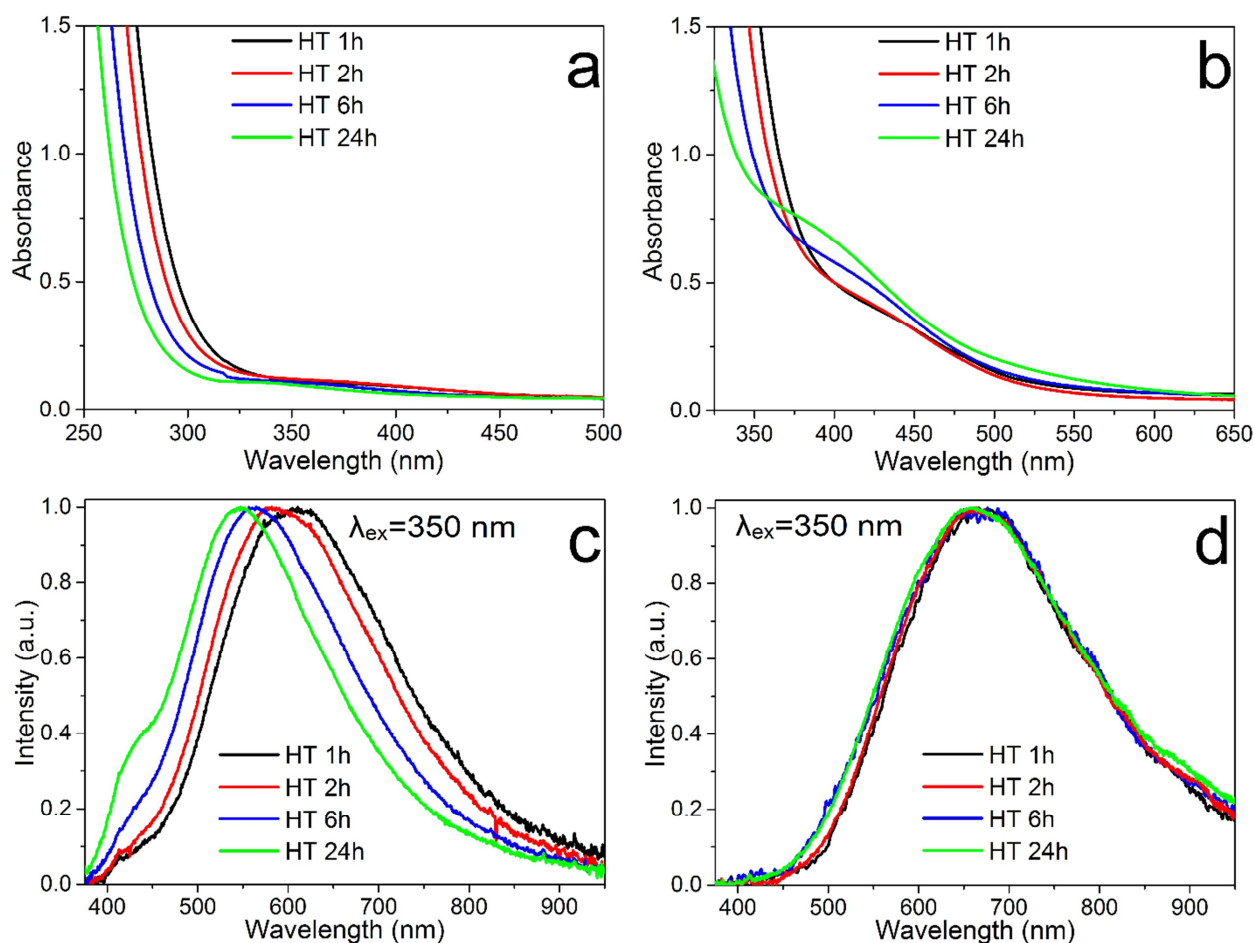

Fig.3 Absorbance (a, b) and normalized PL (c, d) spectra under 350 nm excitation of the samples ion-exchanged for 15 min (a, c) and 15h (b, d) and heat-treated in air for 1, 2, 6, and 24h.

Analysis of PL spectra also reveals a blue shift of the emission maximum for the sample ion-exchanged for 15 minutes (Fig. 3c). On the other hand, the HT duration has almost no effect on PL spectra of the sample ion-exchanged for 15 hours (Fig. 3d).

Dependence of emission peak location on the IE duration for different HT durations is presented in Fig. 4. The blue shift of emission peak location at fixed IE time assumed to result from continued growth of SMCs induced by the further HT. This should lead to change in relation between

various emitting SMCs and, as a consequence, the emission spectra of the PTR glass samples. According to Simo et al. growth of SMCs and NPs in ion-exchanged glasses occurs by addition of silver monomers to already formed silver aggregates[42]. Thus, the growth of SMCs or SNPs lasts as long as there are neutral silver atoms in glass, i.e. in case of Sb-doped PTR glass matrix till chemical equilibrium is achieved in the redox reaction between silver and antimony ions.
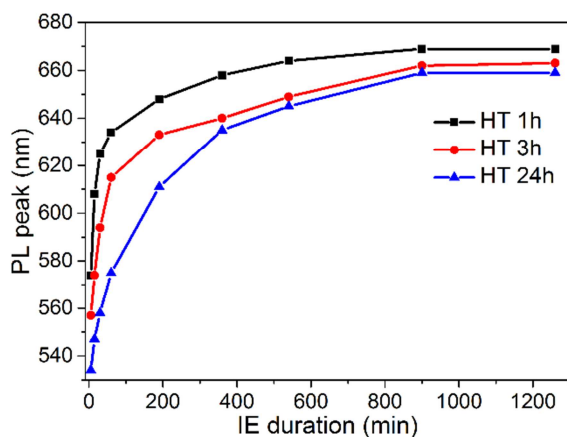

Fig. 4 PL peak vs the IE duration for the samples heat-treated for 1, 3, and 24 h.

Refractive index profiles of the samples ion-exchanged for 5-30 minutes reveal that silver ions are introduced into the PTR glass to the depth of up to 16 microns from each side (Fig. 5a). The calculated refractive index values at the surface of the PTR glass samples ion-exchanged for 5-30 minutes are in the range 1.5750 ± 0.0005, while the measured refractive index of the glass volume is 1.4934 ± 0.0002. These numbers and Lorentz-Lorenz equation was used to estimate amount of the silver on surface of the ion-exchanged PTR glass samples[32]. Concentration of silver ions was calculated to be around 4.75×10^{21} cm^{-3} that corresponds to 12.6mol% Ag$_2$O and 83% of initial Na$_2$O molar content in the studied PTR glass. Our result is in agreement with the literature data, Borsella et al. found that around 90% of sodium ions on the surface of soda-lime silicate glass were replaced by silver in the course of Na$^+$-Ag$^+$ IE for 30 minutes at 320 °C and AgNO$_3$ content in the salt melt equaled to 4 mol% [44]. It should be noted that measurement of refractive index profiles with the method of selective resonance excitation of waveguide modes of the samples ion-exchanged for more than 30 minutes is impossible due to very close location of the high order waveguide modes and intermodal interference.
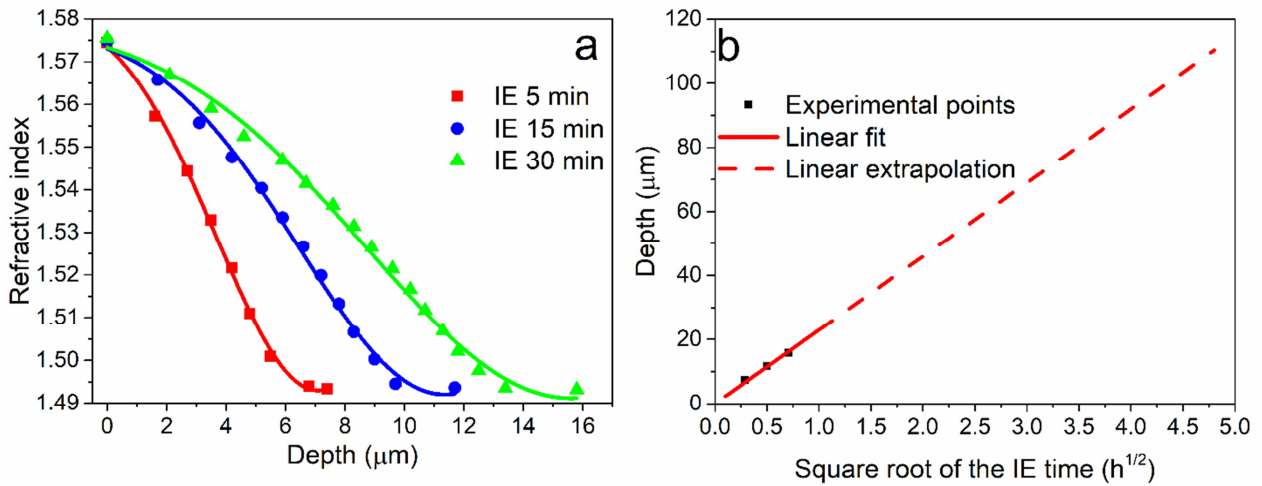
Fig. 5 Refractive index profiles for the samples ion-exchanged for 5, 15, and 30 minutes (a), and the diffusion depth dependence on the IE duration (b).

In case of Na^+-Ag^+ ion-exchanged silicate glass, the IE depth is known to depend on duration of the process (t_{IE}) as follows[45]:

$$h = \sqrt{D \cdot t_{IE}} \tag{7}$$

Linear relation of the IE depth and square root of the treatment duration is shown in Fig. 5b. According to the equation (7) and linear extrapolation, the thickness of silver-enriched layer of PTR glass after 21h of the IE reaches 100-110 microns from each side, which is already comparable to the thickness of glass samples itself (0.9-1 mm). During the subsequent HT of the samples at temperature close to the glass transition one, silver ions diffuse deeper into the glass dispersing in this way throughout the sample. It results in substantial extension of silver-enriched layer of the glass and lowering surface concentration of silver ions[46]. Silver ions diffused deeper into the glass can interact with trivalent antimony ions reducing to the atomic state. Thus, considering the small concentration of antimony ions in the glass, the limiting factor for growth of SMCs is finite number of electrons for reducing silver ions. The scheme of formation and growth of SMCs describing dependence of these processes on duration of the IE and HT is illustrated in Fig. 6.
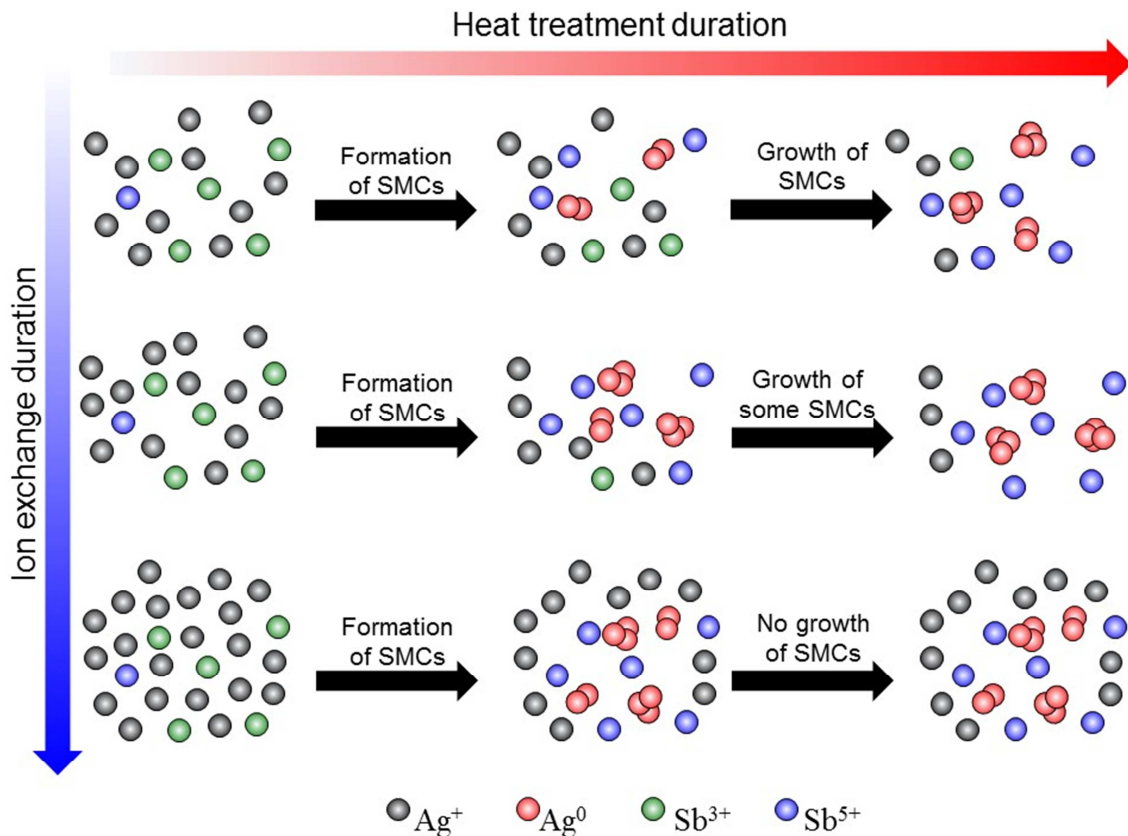
Heat treatment duration

Ag^+ Ag^0 Sb^{3+} Sb^{5+}

Fig. 6 Schematic illustration for effect of the IE and HT durations on formation and growth of SMCs in the antimony-doped PTR glass matrix.

The dependence of APLQY on the IE and HT durations under 350 nm wavelength excitation is shown in Fig. 7. APLQY magnitude above 40% was observed for the samples ion-exchanged for 5-60 minutes with maximum reaching 55-57%. The samples ion-exchanged for longer durations are characterized by APLQY below 30%. Moreover, for these samples increase in the IE time causes lowering APLQY magnitude. The latter is explained by absorption of silver ions at excitation wavelength (see Fig. 2a)
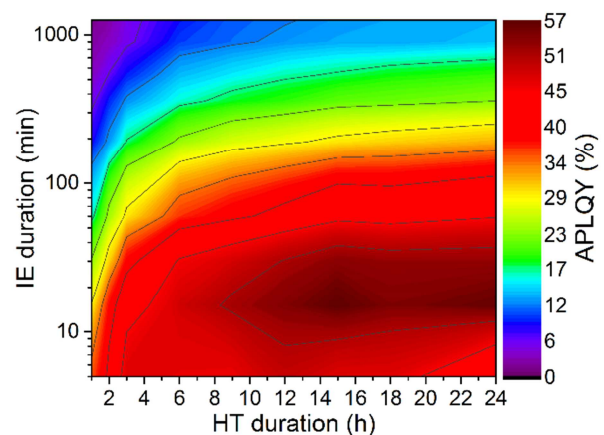

Fig. 7 The influence of the IE and HT durations on the APLQY magnitude of the studied samples.

Moreover, number of silver ions that remain in the ionic form inevitably increases with the IE time, because concentration of antimony ions reducing

silver ions is constant. APLQY values change insignificantly after the HT for 6 hours, which is related to kinetics of formation and growth of SMCs. Further HT does not lead to fall of the APLQY values that proves thermal stability of SMCs in the prepared glasses even at 450 °C.

Conclusions

In this work, the influence of the low temperature Na^+-Ag^+ IE and subsequent HT durations on the formation and spectral-luminescent properties of Sb-doped PTR glasses was studied. The IE duration was shown to have significant effect on absorbance and PL spectra, which allows the tuning of emission color in a wide range from cool and warm white to yellow and orange. The studied glasses doped with SMCs can find applications as phosphors for white LEDs with high thermal stability up to 450°C and chemical durability typical for silicate glasses. The presented technology might pave the way for a new class of lighting devices and spectral converters.

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Highlights

1. Influence of ion exchange duration on optical properties of photo-thermo-refractive glass with silver molecular clusters.

2. Tunable spectral luminescence of silver molecular clusters in glass matrix.

3. High temperature and chemically stable phosphor glass matrix for white LED application.

4. High absolute photoluminescence quantum yield of silver molecular clusters in glass matrix.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: