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Influence of Halides on the Luminescence of Silver Molecular Clusters in Photo-Thermo-Refractive Glasses

V.D. Dubrovin*, A.I. Ignatiev†, N.V. Nikonorov‡, A.I. Sidorov§

Saint-Petersburg National Research University of Information Technologies, Mechanics and Optics, 49, Kronverkskiy pr., 197101 Saint-Petersburg, Russia

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The luminescence spectra of silver molecular clusters in photo-thermo-refractive glasses are investigated in detail before and after the UV irradiation and also after the heat treatment of the samples. Also investigated are (I) the influence of halogens such as Cl and Br in glass matrix composition on the luminescence of silver molecular clusters in photo-thermo-refractive glasses and (II) the effect of temperature on the luminescence spectra and the integrated intensity of luminescence of photo-thermo-refractive glasses.

Keywords: Luminescence, Molecular Cluster, Silver, Photo-Thermo-Refractive Glass.

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1. INTRODUCTION

Luminescence glasses with neutral molecular clusters of silver are perspective for use as spectral converters radiation in solar energy and LED white light. Photo-thermo-refractive (PTR) glass [1, 2] other than the above applications, may be used for the optical recording and storage of information by allowing the local transformation of charged molecular clusters in neutral by UV irradiation. The aim of this work was to investigate the effect of NaCl and NaBr concentration on the spectral characteristics of silver's molecular clusters luminescence in PTR glasses.

2. OBJECT OF RESEARCH

In the work we investigated the Photo-thermo-refractive glasses based on the Na_2O-ZnO-Al_2O_3-SiO_2-NaF-NaHal (Hal being Cl or Br) and doped with photosensitive dopant of CeO_2 (0.007 mol.%), reductant dopant of Sb_2O_3 (0.04 mol.%) and also Ag_2O were synthesized. Two groups of samples denoted further by PTR(Cl) and PTR(Br) were prepared, NaHal in the group sample compositions being chosen to be NaCl(from 0 to 2.2 mol.%) or NaBr(from 0 to 1.5 mol.%), respectively. The Ag_2O content was taken, for the PTR(Cl) and PTR(Br) group samples, to be equal to 0.13 and 0.065 mol.% respectively. For synthesis, the reagent grade and chemically pure raw materials were used.

3. EXPEREMENTAL TECHNIQUE

The glass synthesis was conducted in Gero electric furnace with the air atmosphere using the platinum crucibles, the melts being homogenized with the platinum stirrer. It must be noted, that during synthesis Ce-ions partly change the valence state from IV to III, and Sb-ions – from III to V [3]. The glass transition temperature Tg was measured with STA6000 (Perkin-Elmer) differential scanning calorimeter, its magnitude being found to be 494 ^{O}C. Samples to be investigated were prepared in the form of plane-parallel plates 1.5-2.0 mm thick.

For the UV irradiation of PTR glass samples under study, a mercury lamp was used, one of the radiation maxima of the lamp coinciding practically in location (λ =305-315 nm) with the absorption maximum of Ce^{3+} ions. For heat-treating the samples, Heat treatment was carried out in a gradient furnace at different temperatures (250, 300, 350, 400 °C) with in 1h. For minimizing the effects of gradual heating and cooling, the samples were placed, at once, into the muffle furnace heated beforehand up to temperature required and, after a desired exposure, extracted from the hot furnace into air. For measuring the luminescence at a fixed excitation wavelength, EPP2000-UVN-SR (StellarNet) fiber spectrometer was used, the luminescence being excited by a semiconductor laser (λ = 405 nm).

4. RESULTS OF EXPERIMENTS

Fig. 1 shows the luminescence spectra of PTR glasses containing NaCl and NaBr, for different halides concentration after UV irradiation. The figure shows that PTR glasses containing no NaHal (Hal= Cl, Br) have relatively low broadband luminescence intensity in the spectral range of 475-800 nm. Comparison with literature data [4, 5, 6] allows to conclude that the main contribution to these luminescence bands (when luminescence excited by radiation with wave length 405 nm) making neutral molecular clusters Ag_2 and Ag_3. Increase of NaHal concentration leads to a significant increase in luminescence intensity. Thus, increasing the concentration of NaCl from 0 to 2 mol.% leads to an increase of luminescence intensity up to 6.3 times (at the peak). Increase of NaBr concentrations from 0 to 1.5 mol. % generally leads to an increase of luminescence intensity up to 2.7 times (at the

* dubrovinvictor@yandex.ru
† ignatiev@oi.ifmo.ru
‡ nikonorov@oi.ifmo.ru
§ aisidorov@qip.ru

peak). From fig.1 can be seen that the luminescence band maximum for PTR(Cl) accounts for λ = 530 nm, and for PTR(Br) – λ = 545 nm. At the same time the luminescence intensity of PTR(Br) glasses are higher than PTR(Cl) glasses at equal concentrations of NaHal and Ag_2O.

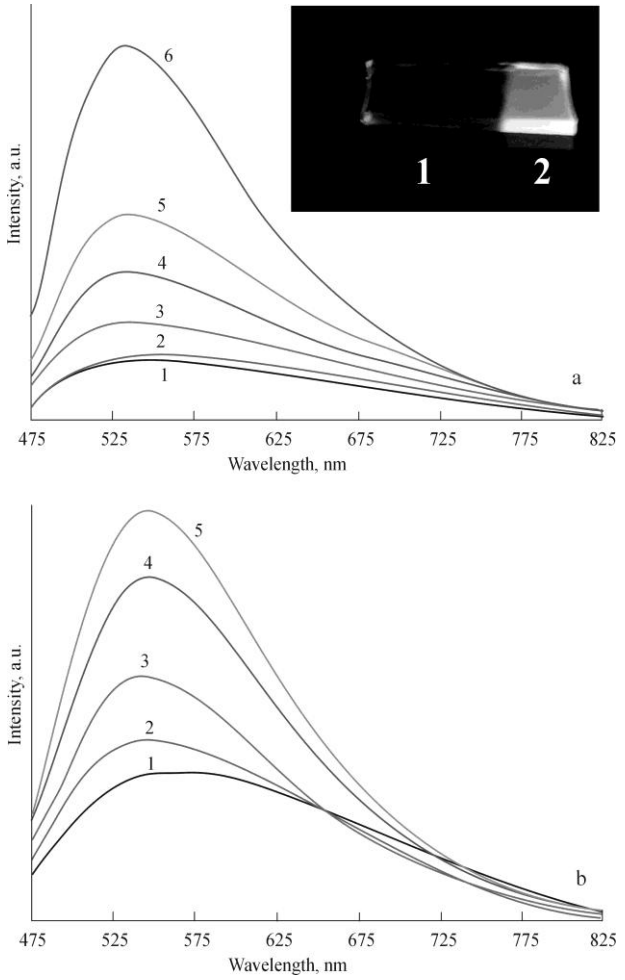

Fig. 1 – Luminescence spectra of PTR(Cl) (a) and PTR(Br) (b) glasses samples after the UV irradiation. a: 1 – 0 mol.%, 2 - 0.52, 3 – 0.74, 4 – 1, 5 – 1.46, 6 – 2. b: 1 – 0 mol.%, 2 – 0.25, 3 – 0.66, 4 – 1, 5 – 1.5. In the insert - photo of sample's luminescence without UV irradiation (1) and after UV irradiation (2)

Fig 2a shows the dependence of luminescence intensity at the maximum for PTR glasses from halide concentration after UV irradiation. It can be seen that PTR(Cl) glasses have a threshold concentration of halide which is equal to about 0.5 mol.% NaCl from which the luminescence intensity start to grow. For PTR(Br) threshold concentration doesn't exist or isn't more than 0.25 mol.% At concentrations of NaBr in PTR glass exceeding 1 mol. % increase in luminescence intensity is slowing. This is due to the fact that at such high concentrations in the glass NaBr can form nanocrystals AgBr already during its synthesis, which increase the absorption coefficient of glass and reduce the intensity of luminescence.

Fig. 2b shows the dependence of luminescence intensity at the maximum for PTR(Cl) and PTR(Br) glasses from halide concentration after UV irradiation and heat treatment at 400^{O}C for 1 hour. It can be seen that in PTR glasses the increase of NaCl concentration leads to increase of luminescence intensity after heat treatment by the law that is close to linear. In PTR(Br) glasses observed another picture: with increasing of halide concentration luminescence intensity is decreasing. Moreover, at concentrations greater than 1 mol.% of NaBr dependence attains saturation

Fig. 2c shows the dependence of luminescence intensity at the maximum for UV irradiated PTR glasses with 1.5 mol.% of NaHal from the heat treatment temperature. It can be seen that the heat treatment of glasses at temperatures greater than 200 ^{O}C leads to a significant increase in the luminescence intensity. However, for PTR(Br) glasses at heat treatment temperature above 350 ^{O}C begins luminescence quenching. Heat treatment of PTR(Cl) glasses, near glass transition temperature (494 ^{O}C), or at higher temperatures leads to luminescence quenching too.

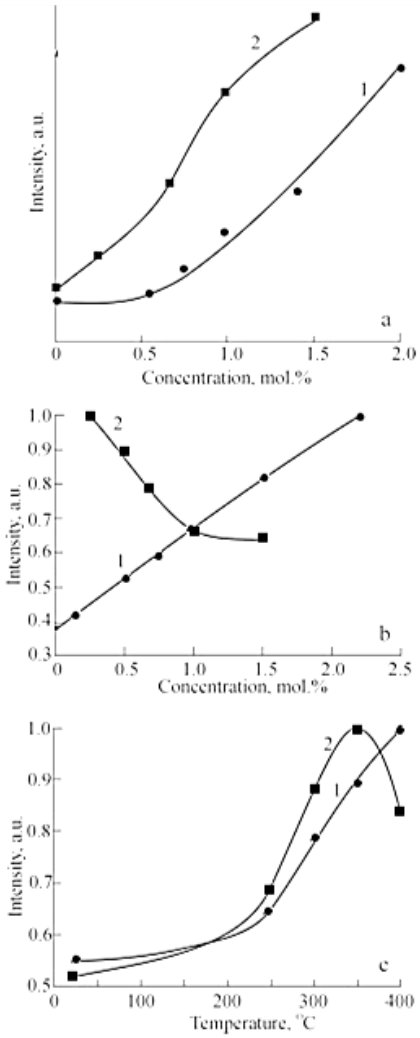

Fig. 2 – a – dependence of luminescent intensity for PTR(Cl) (curve 1) and PTR(Br) (curve 2) from halide concentration after UV irradiation. b – dependence of normalized luminescent intensity for PTR(Cl) (curve 1) and PTR(Br) (curve 2) from halide concentration after UV irradiation and heat treatment at 400 OC for 1h. c. - dependence of normalized luminescent intensity for PTR(Cl) (curve 1) and PTR(Br) (curve 2) from heat treatment temperature (1h) after UV irradiation (for 1.5 mol.%NaHal)

5. DISCUSSION AND CONCLUSION

In this way, increasing of halides concentration in silver contains glasses leads to increase of silver molecular clusters luminescence intensity. May be offered two mechanisms that give rise to similar effect. First of all increasing of halide concentration can lead to increase of inhomogeneities in the glass as ruptures of glass network. In this case the conditions for silver atoms diffusion during heat treatment and for silver neutral molecular clusters formation are improving, and consequently their concentration is increased. At this, in particular, indicate an increase of PTR glasses absorption coefficient in the spectral range 350-450 nm with increasing of halide concentration.

Secondly, the negative halogen ions in the glass can be attached to the positively charged molecular clusters of silver, forming a neutral molecular cluster like Ag_n-Hal. The possibility of formation a stable molecular clusters Ag_n-Cl (n = 2-7) by numerical simulations was demonstrated in paper [7]. As can be seen from the inset at Fig. 1a, translation of silver molecular clusters from charged to the neutral state significantly increases the luminescence intensity. Of the fact that in PTR glass, at least a part of molecular clusters has Agn-Hal form, indicates that the replacement of Cl ions to Br ions at the glass leads to a spectral shift of luminescence band and to change in its intensity. Increase of PTR glasses luminescence intensity with Br ions compared to PTR glasses containing Cl ions, may be due to the fact that the Agn-Br molecular clusters have more oscillator strength than Agn-Cl molecular clusters. Increasing of luminescence intensity with the increased of heat treatment temperature is caused by that the result of thermal diffusion of silver atoms and ions and halide ions are formed new molecular clusters, which leads to increase of their concentration. Luminescence quenching in glasses containing NaBr after heat treatment is associated with formation of silver bromide nanocrystals in glass which don't have luminescence bands in visible range, but increase the absorption coefficient. Luminescence quenching in glasses with NaCl after heat treatment at or near the glass transition temperature is due to the formation of silver nanocrystals in glass which don't have luminescence at PTR glasses. Since the silver molecular clusters are the centers of nucleation and growth of silver nanocrystals, such heat treatment leads to a decrease in the concentration of silver molecular clusters in glass or remove them altogether.

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