J Mater Sci (2010) 45:2983–2990
DOI 10.1007/s10853-010-4297-7

Optical properties of aluminophosphate glasses containing silver, tin, and dysprosium

J. A. Jiménez · S. Lysenko · H. Liu

Received: 11 November 2009 / Accepted: 3 February 2010 / Published online: 17 February 2010

Abstract The spectroscopic properties of a Dy^{3+}-doped aluminophosphate glass containing silver and tin were reported. Different oxidation and aggregation states of silver were obtained by varying silver concentration and glass thermal history. The addition of silver and tin at the lowest concentration studied results in Dy^{3+} ions emission under nonresonant UV excitation in connection with the appearance of an excitation band around 270 nm, which is associated to isolated Ag^+ ions and twofold-coordinated Sn centers. The increase in silver and tin concentration leads to a broadening of aforementioned band and to the presence of charged silver dimers as evidenced by the appearance of an excitation band around 330 nm. The data indicated that light absorption might take place at ionic silver species and twofold-coordinated Sn centers, followed by energy transfer to Dy^{3+} ions. After heat treatment, ionic silver species were reduced to atomic Ag by tin with the subsequent formation of Ag nanoparticles (NPs) inside the dielectric host. A quenching effect in Dy^{3+} ions luminescence was shown with the presence of the Ag NPs, most notably for excitation of $^6H_{15/2} \rightarrow {}^4F_{9/2}, {}^4I_{15/2}, {}^4G_{11/2}$ transitions, which were in resonance with the dipole absorption mode of the particles. The silver NPs were believed to provide radiationless pathways for excitation energy loss in Dy^{3+} ions.

J. A. Jiménez
Department of Chemistry, University of Puerto Rico,
P.O. Box 9019, Mayagüez, PR 00681-9019, USA

S. Lysenko · H. Liu (✉)
Department of Physics, University of Puerto Rico,
P.O. Box 9016, Mayagüez, PR 00681-9016, USA
e-mail: huimin.liu@upr.edu

Introduction

A great deal of effort has been recently devoted to understanding the effect of noble metals on the spectroscopic properties of luminescent ions in a dielectric host in view of the prospective utility of these materials for the development of optoelectronic devices [1–12]. However, in spite of the work done, the conditions and mechanisms by which emission characteristics are enhanced by the presence of the metal remain controversial [5–12]. An important issue is related to which oxidation and aggregation state of the metal is liable for the improved luminescence of the emitting centers, namely charged metal species such as dimers vs. metallic nanoparticles (NPs). It was first reported by Malta et al. [13] that an enhanced photoluminescence (PL) for Eu^{3+} ions in glass containing silver NPs occurred due to the surface plasmon resonance (SPR) of the particles. The SPR is regarded as the collective excitation of the conduction band electrons which induces high electromagnetic fields in the metal particles resulting in the enhancement of several optical processes [14]. Hence, it was pointed out by Malta et al. [13] that long-range electromagnetic interactions associated with plasmon excitation were deemed significant in obtaining an enhanced PL. Hayakawa et al. [1] also carried out investigations on Ag/Eu co-doped glasses and observed PL enhancements ascribed in a similar manner to local field effects owing to the SPR of metal NPs. More recently, plasma oscillations in metallic NPs has also been suggested as accountable for the improved PL of rare-earth (RE) ions in glasses [3–5, 7, 12]. On the other hand, Strohhöfer and Polman [2] reported that silver served as a sensitizer for Er^{3+} ions in borosilicate glass, whereas no enhancement effect was ascribed to Ag NPs. They attributed the observed increase in emission intensity to energy transfer from silver pairs to Er^{3+} ions.

Martucci et al. [6] conducted a study on glass films co-doped with Ag and Er and also reported an energy transfer mechanism related to silver pairs and not to NPs. Likewise, the recent report from Matarelli et al. [9] shows agreement with an enhanced Er^{3+} ions PL owing to energy transfer processes originating at silver aggregates, mainly dimers. Furthermore, energy transfer from molecular-like noble metal particles to RE ions have been also reported recently by Trave et al. [8], and by Eichelbaum and Rademann [11].

With the aim of furthering the understanding of metal–RE interactions in a dielectric host, we recently studied the spectroscopic properties of Eu^{3+} ions in a melt-quenched aluminophosphate glass system containing silver and tin, in which isolated Ag^{+} ions were observed to enhance Eu^{3+} emission, whereas a quenching effect of europium ions PL showed with the presence of silver NPs [10]. The nature of energy transfer leading to the enhanced Eu^{3+} PL was further assessed along with the possible contribution to the PL quenching by chemical reduction of Eu^{3+} to Eu^{2+} by Sn^{2+} [15]. In the work reported herein, we present an extension of the study to investigate on the interactions involving ionic silver species including dimers, Ag NPs, and Dy^{3+} ions in the aluminophosphate glasses prepared by melting and heat treatment (HT) processes. The study not only becomes relevant owing to the significance of dysprosium ions for optical applications [16, 17] but also because of the importance of assessing the contribution of Ag and Sn species to material optical properties [15, 18–20]. The different oxidation and aggregation states of silver are obtained by varying the silver concentration and glass thermal history. It is observed that excitation of isolated Ag^{+} ions, silver pairs, and twofold-coordinated Sn centers leads to Dy^{3+} emission. On the other hand, thermal processing results in silver NPs formation within the matrix and a quenching effect on Dy^{3+} luminescence. Mechanisms likely operating are discussed.

Experimental

Aluminophosphate glasses of the type P_2O_5:Al_2O_3:CaO:SrO:BaO were prepared by conventional melting and HT processes as described elsewhere [21]. Silver, tin, and/or dysprosium doping was done by adding Ag_2O, SnO, and/or Dy_2O_3 quantities in mol%, in relation to network former P_2O_5. Samples used in this study are referred to as: glass host (glass system without Ag_2O, SnO, and Dy_2O_3); Dy glass (2% Dy_2O_3); 4Ag/Sn glasses (4% of each Ag_2O and SnO); 4Ag/Sn–Dy glasses (4% of each Ag_2O and SnO, and 2% Dy_2O_3); and 6Ag/Sn–Dy glasses (6% of each Ag_2O and SnO, and 2% Dy_2O_3). The 4Ag/Sn–Dy and 6Ag/Sn–Dy glasses were subjected to HT to assess the dependence of optical properties on glass thermal history. Optical absorption measurements were employed in silver NP detection owing to SPR spectral features, and to detect UV absorption of dopants by using the glass host as reference in the dual-beam configuration of the instrument. Steady-state PL spectroscopy was performed in an ISA SPEX Fluoromax-2 spectrofluorometer. Unless otherwise specified, the spectra presented correspond to samples measured as glass slabs. To make possible the comparison of PL intensities, some samples were ground to powder and compressed into pellets for precise measurements in a sample holder with particular attention given to keep conditions constant during experiments. Laser-excited PL was carried out with a 20 ps Nd:YAG laser operating at 266 nm. Time-resolved spectra were recorded under pulsed excitation using a boxcar system for detection with a narrow time gate.

Results and discussion

Luminescence in glass before heat treatment

Figure 1 shows an overlay of the absorption and excitation spectra of the 4Ag/Sn–Dy glass before HT and the excitation spectrum of the Dy glass. The excitation spectra were obtained by monitoring emission of $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition in Dy^{3+} ions at 574 nm. The absorption spectrum of the 4Ag/Sn–Dy glass was obtained with the glass host as reference and shows an absorption band with a maximum around 275 nm. The excitation spectrum for the 4Ag/Sn–

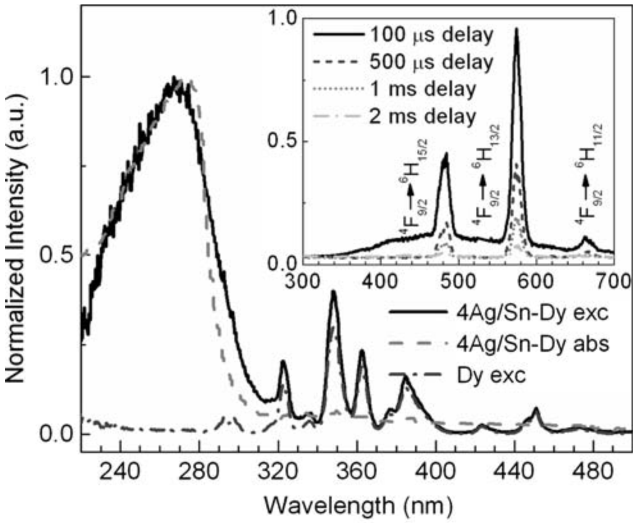

Fig. 1 Absorption (*abs*) and excitation (*exc*) spectra for 4Ag/Sn–Dy glass before HT, and excitation spectrum for Dy glass (emission monitored at 574 nm for both excitation spectra). The *inset* shows time-resolved spectra for 4Ag/Sn–Dy glass under pulsed laser excitation at 266 nm

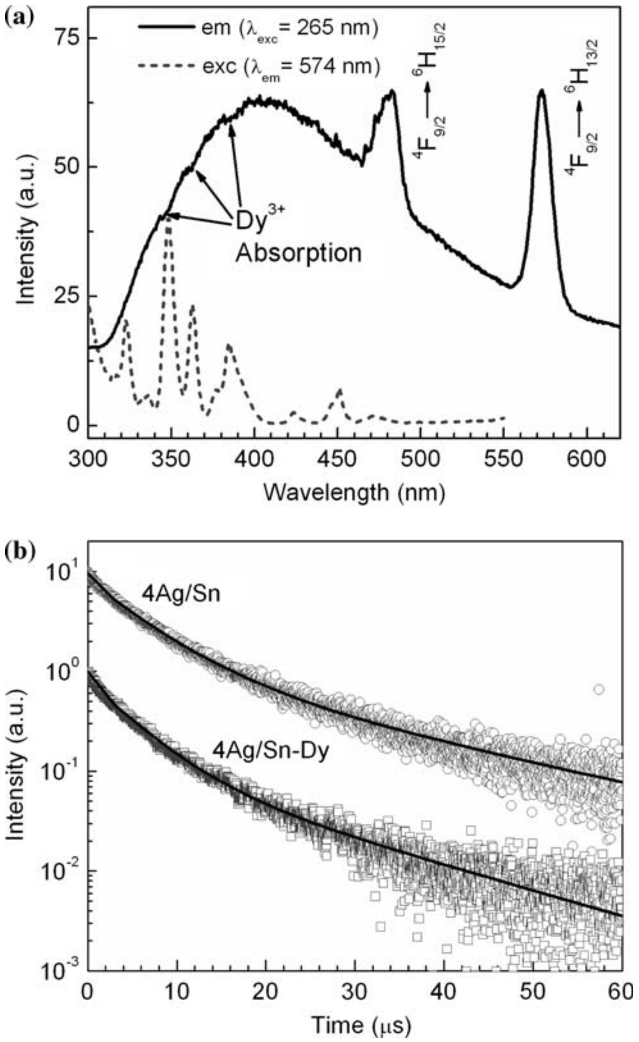

Fig. 2 **a** Emission (*em*) and excitation (*exc*) spectra for 4Ag/Sn–Dy glass. **b** Emission decays for 4Ag/Sn–Dy and 4Ag/Sn glasses collected at room temperature under laser excitation at 266 nm with detection wavelength set at 420 nm

Dy glass shows a broad excitation band centered around 270 nm, which is not observed for the Dy glass. This result indicates that an intense 574-nm emission of Dy^{3+} ions can be obtained under nonresonant excitation for wavelengths near 270 nm for the 4Ag/Sn–Dy glass. It turns out that the excitation band appearing for the 4Ag/Sn–Dy glass resembles the difference absorption spectrum obtained between the same sample and the glass host as shown in Fig. 1, indicating that the species responsible for the absorption band are at the origin of an energy transfer process. Such type of absorption bands close to 270 nm have been observed in our previous works [10, 21] for Ag/Sn-doped glasses owing to contributions from both isolated Ag^{+} ions and twofold-coordinated Sn centers (will be also referred to herein as =Sn$^{\cdot\cdot}$ centers, where the two paired electrons are represented by "··", and the bond with two oxygen atoms by "="). Single Ag^{+} ions have been observed to contribute to the absorption band mainly around 270 nm owing to parity-forbidden transitions involving electron promotion from the $4d^{10}$ ground state to some levels in the $4d^9\,5s^1$ configuration [21]. The optically active =Sn$^{\cdot\cdot}$ centers, however, show a contribution to absorption around 255 nm due to electronic transitions from the ground singlet state to the first excited singlet state ($S_0 \rightarrow S_1$) [10, 20]. It therefore becomes evident that light absorption takes place at single Ag^{+} ions and/or =Sn$^{\cdot\cdot}$ centers followed by energy transfer to dysprosium, which results in populating the $^4F_{9/2}$ emitting state in Dy^{3+} ions. Such type of energy transfer between donor–acceptor pairs becomes evident in the time-resolved spectra presented in the inset of Fig. 1, which were obtained under pulsed laser excitation at 266 nm (near the top of aforementioned excitation band), for time delays of 100 μs, 500 μs, 1 ms, and 2 ms. At 100 μs of delay, a broadband emission is observed between 350 and 700 nm along with emission from dysprosium around 483, 574, and 662 nm, corresponding to $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^6H_{13/2}$, and $^6H_{11/2}$ transitions in Dy^{3+} ions, respectively. The broadband emission most likely contains contributions from both silver and tin, owing to $^3D_J \rightarrow {}^1S_0$ ($J = 3, 2, 1$) spin-forbidden transitions in Ag^{+} ions and electronic transitions from the first excited triplet state to the ground singlet state ($T_1 \rightarrow S_0$) in =Sn$^{\cdot\cdot}$ centers, both of which possess lifetimes in the microsecond time scale [15, 21]. After 500 μs of delay, the spectra mainly contain emission due to radiative relaxation of excited Dy^{3+} ions, which are longer-lived. Regarding the assessment of the energy transfer mechanism, e.g., radiative vs. nonradiative, let us consider data in Fig. 2. Shown in Fig. 2a is an overlay of emission and excitation spectra for the 4Ag/Sn–Dy glass. The emission spectrum recorded under 265 nm excitation is a broadband which shows dips corresponding to Dy^{3+} ions absorption as evidenced by the matching excitation peaks. This type of effect where band emission is suppressed only at the position of RE absorption lines is known to be characteristic of radiative energy transfer [22]. If the energy transfer process occurred through nonradiative mechanisms, the band emission would be suppressed uniformly, which is clearly not the present case. The decay curves shown in Fig. 2b, which were obtained for 4Ag/Sn and 4Ag/Sn–Dy glasses under excitation at 266 nm with emission monitored at 420 nm, support this assertion. If we consider that at this emission wavelength the luminescence can arise from both Ag^{+} ions and =Sn$^{\cdot\cdot}$ centers, a curve fitting should then reflect that behavior. Emission decays for Ag^{+} ions in glass have been previously studied and observed to follow a bi-exponential behavior with fast and slow components most likely corresponding to relaxation from upper and lower metastable states, respectively, as described in the framework of a four-level system [21]. It would be then expected that the decay curve involving both species, silver and tin, would have three components in accordance with a multi-exponential fitting appropriate for multiple states decaying at a particular wavelength. Hence, the decays in Fig. 2b were fitted to a tri-exponential function corresponding to the single-exponential decay from Sn-related centers [15] and to the bi-exponential behavior of Ag^+ ions [21]. The resulting estimated lifetimes for the 4Ag/Sn–Dy glass are 0.8, 4.8, and 17.1 μs. The lifetime of 4.8 μs would be related to tin since it is comparable to that reported for $=Sn^{\cdot\cdot}$ centers in the glass system [15]. The other two, 0.8 and 17.1 μs, can be thus related to single silver ions [21]. Similarly, for the 4Ag/Sn glass, lifetimes of 1.2 and 16.8 μs are estimated for silver ions, whereas a 5.3-μs lifetime is estimated in association with Sn. Indeed, from this assessment, the relaxation times estimated for Ag- and Sn-emitting species in the 4Ag/Sn–Dy glass are comparable to the ones obtained for the 4Ag/Sn glass, which is also consistent with a radiative energy transfer mechanism. If radiationless energy transfer occurred, the lifetimes of Ag and Sn as donor species would be significantly changed in the presence of Dy^{3+} ions as acceptors [22]. In fact, radiative energy transfer is likely in glass systems having a high metal solubility. Although some alumina was added as a less acid network former, the main constituent of the glass used in this study is phosphate. Such phosphate-based glass host supports large separations between doping species, making radiationless energy transfer among species less likely [23]. Furthermore, the metal solubility may be even increased due to the presence of Sn, which is known as a metalophilic agent [24]. Thus, the data appears consistent with recent results reported for Eu^{3+} ions in the same aluminophosphate glass system where the resonant radiative mechanism was observed to play an important role [15].

The effect of increasing the concentration of silver and tin on the spectroscopic properties of the glass system shall now be assessed. Figure 3 shows excitation spectra obtained by monitoring emission at 574 nm for the Dy, 4Ag/Sn–Dy, and 6Ag/Sn–Dy glasses. It can be observed that increasing the concentration of silver and tin oxides to 6 mol% leads to a broader excitation band centered around 275 nm. It should be noted that in the 6Ag/Sn–Dy glass, the metal solubility may become increased relative to the 4Ag/Sn–Dy glass due to the increase in concentration of the metalophilic agent tin, and this may result in the shift of Ag^+ ions absorption to lower energy [20, 24]. In addition, a wider distribution of sites for single Ag^+ ions may be present in the amorphous host. Accordingly, the broad excitation band observed for the 6Ag/Sn–Dy glass may contain a significant contribution from single Ag^+ ions in association with inhomogeneous broadening. However, the increase in Ag concentration may also result in the formation of silver aggregates or molecular species which may also participate in energy transfer processes leading to Dy^{3+} ions emission. Co-existent charged silver dimers become evident from the excitation spectra presented in Fig. 4, which were obtained by monitoring emission at 375, 400, 425, 450, and 500 nm. Furthermore, the band observed around 275 nm is clearly connected with $4d^{10} \rightarrow 4d^9\,5s^1$ and $S_0 \rightarrow S_1$ transitions in Ag^+ ions and $=Sn^{\cdot\cdot}$ centers, respectively, the latter displaying its contribution to the high-energy wing. However, the appearance of the excitation band around 330 nm is indicative of PL originating at silver pairs [20, 25, 26]. It is observed that with the increase of detection wavelength from 375 to 500 nm, the excitation band is slightly shifted to longer

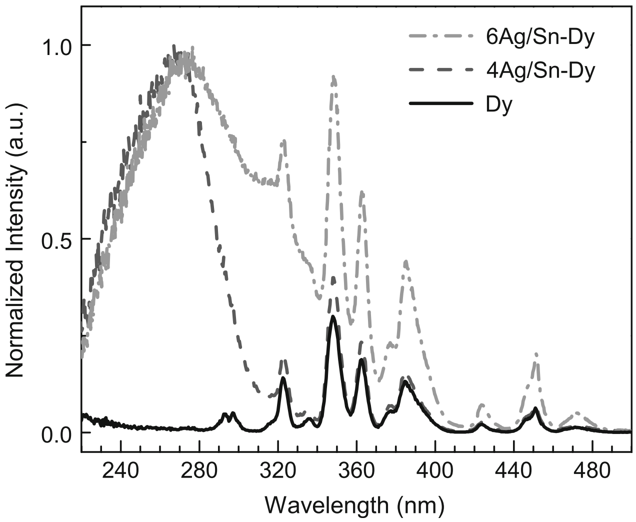

Fig. 3 Excitation spectra overlay for Dy, 4Ag/Sn–Dy, and 6Ag/Sn–Dy glasses before HT obtained by monitoring emission at 574 nm

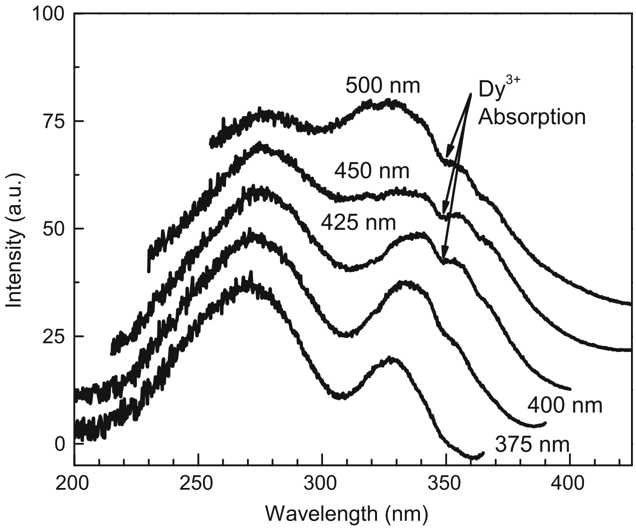

Fig. 4 Excitation spectra for 6Ag/Sn–Dy glass before HT obtained by monitoring emission at displayed wavelengths

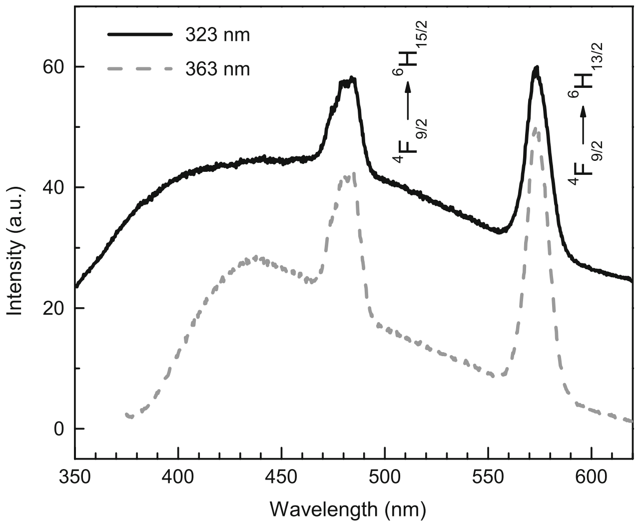

Fig. 5 Emission spectra for 6Ag/Sn–Dy glass before HT obtained under excitation at 323 and 363 nm

wavelengths at the beginning and eventually becomes broader. As reported in our previous works [20, 26], this is consistent with an overlapping behavior due to the presence of both Ag$^+$–Ag$^+$ and Ag$^+$–Ag^0 centers: Ag$^+$–Ag$^+$ pairs become more effectively excited at shorter wavelengths relative to Ag$^+$–Ag^0, whereas emission of Ag$^+$–Ag$^+$ shows at longer wavelengths in relation to Ag$^+$–Ag^0 pairs. Figure 5 shows spectra for the 6Ag/Sn–Dy glass before HT obtained under excitation at 323 and 363 nm, where emission of the two types of silver pairs can be observed along with Dy^{3+} ions emission. For instance, excitation close to the peak of the excitation band for the dimers but to the high-energy side at 323 nm leads to a broad emission band owing to both centers, where emission of Ag$^+$–Ag$^+$ pairs likely appears at longer wavelengths, e.g., 500 nm and longer, relative to that for the Ag$^+$–Ag^0 centers [20, 26]. Accordingly, under excitation at a longer wavelength to the low-energy side of the excitation band, namely at 363 nm, Ag$^+$–Ag^0 pairs PL shows around 430 nm, while the extension of inhomogeneous broadening toward the low-energy side in the spectrum suggests the presence of Ag$^+$–Ag$^+$ emission consistent with Ag$^+$–Ag^0 → Ag$^+$–Ag$^+$ energy transfer [20, 26]. Thus, the silver molecular dimers may also become energy donors to Dy^{3+} ions [2, 6, 9]. In fact, the dips observed around 350 nm in the excitation band associated to silver pairs in the spectra in Fig. 4 which correspond to absorption by Dy^{3+} ions suggest the radiative energy transfer process to be substantial [27].

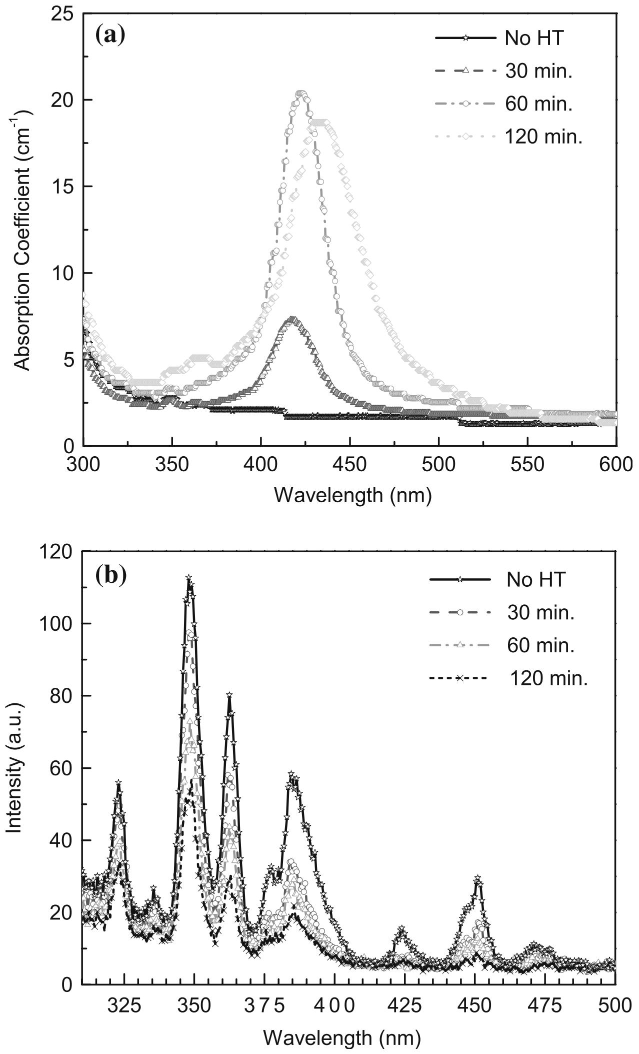

Fig. 6 **a** Optical absorption and **b** excitation spectra (samples measured as pellets with emission monitored at 574 nm) for 4Ag/Sn–Dy glass before and after HT at 570 °C for different holding times

Effect of heat treatment on glass spectral properties

We shall now consider the effect of thermal processing on the spectroscopic properties of the glasses. Absorption spectra for the 4Ag/Sn–Dy glasses before and after HT at 570 °C for different holding times are shown in Fig. 6a. Upon HT, a peak develops around 420 nm owing to the SPR absorption of silver NPs, which are formed due to reduction of Ag ions to the neutral state as 2Ag$^+$ + Sn^{2+} → 2Ag^0 + Sn^{4+} [21]. The observed SPR shift and broadening is suggestive of an increase in particle size [21, 28]. The presence of larger particles in the sample heat treated for 120 min is also evidenced by the appearance of an additional peak around 370 nm, which is attributed to the quadrupole resonance mode. In Fig. 6b, excitation spectra are presented for the 4Ag/Sn–Dy glass samples before and after HT, which were obtained by monitoring emission at 574 nm. Evidently, HT leads to a decrease in dysprosium ions emission with increasing holding time. In particular, it is observed that PL intensity is lowest for the sample heat treated for 120 min at wavelengths about

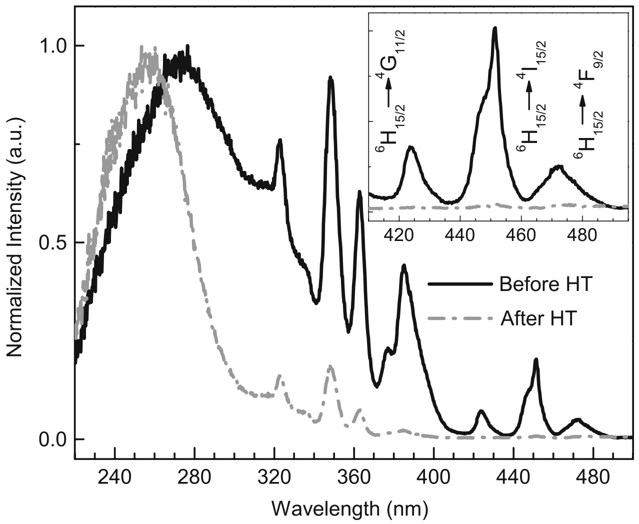

Fig. 7 Excitation spectra for 6Ag/Sn–Dy glass before and after HT at 520 °C for 1 h obtained by monitoring emission at 574 nm. The *inset* shows an enlargement in the region relevant to plasmon absorption in silver NPs; the vanishing of excitation peaks corresponding to $^6H_{15/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2}$, $^4G_{11/2}$ transitions is observed

350 nm and longer. In Fig. 7, excitation spectra are presented for the 6Ag/Sn–Dy glass before and after HT at 520 °C for 1 h, also obtained by monitoring emission at 574 nm. The inset shows an enlargement within 410 and 495 nm, a region relevant to SPR absorption of Ag NPs, where the vanishing of excitation peaks corresponding to $^6H_{15/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2}$, $^4G_{11/2}$ transitions is observed. In fact, no emission from Dy^{3+} could be recorded in our experiments by excitation of $^6H_{15/2} \rightarrow {}^4G_{11/2}$ transition at 424 nm for the glass heat treated at 520 °C for 1 h. For excitation at 323 and 363 nm, glass PL is shown as a function of thermal processing in Fig. 8a and b, respectively. The band emission associated with the silver pairs (vide supra) is observed to vanish with increasing HT temperature during isochronal processing, an expected result due to intensive chemical reduction of ionic Ag species to the neutral state by Sn and subsequent incorporation of the Ag atoms into non-luminescent Ag nanocrystals [20]. In fact, the sample heat treated for 1 h at 450 °C shows a dip around 420 nm (Fig. 8a) in association to absorption of luminescence by Ag NPs [21]. The chemical reduction process is also evident from the excitation spectra in Fig. 8c, where the excitation band between 300 and 375 nm related to silver pairs also vanishes with increasing HT temperature. Moreover, the excitation band associated with single Ag^+ ions and $=Sn^{\cdot\cdot}$ centers also evolves to a band centered around 250 nm. The latter excitation band can be also observed in Fig. 7 for the heat-treated glass. This result is indicative of depletion of the single silver ions due to conversion to the neutral state. The

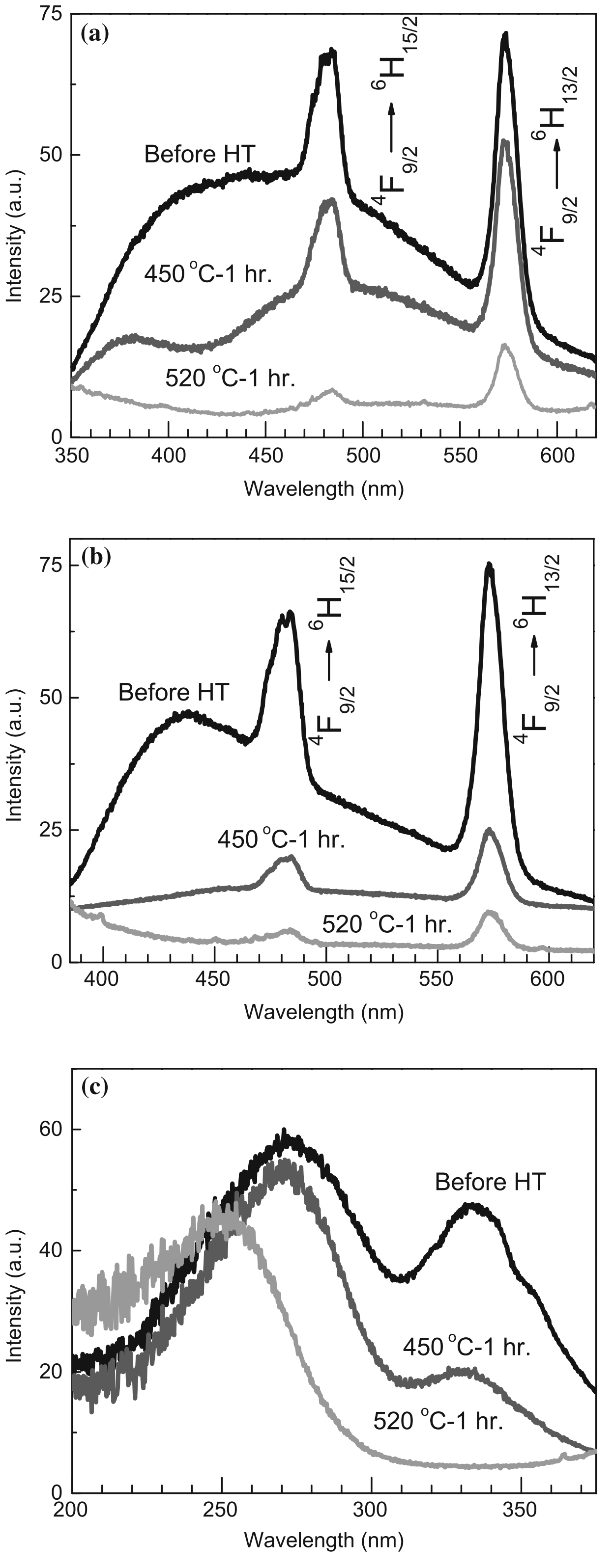

Fig. 8 Photoluminescence spectra for 6Ag/Sn–Dy glass before and after HT at 450 and 520 °C for 1 h. Panels **a** and **b** show emission spectra obtained under excitation at 323 and 363 nm, respectively. Panel **c** shows excitation spectra obtained by monitoring emission at 400 nm

excitation band remaining after HT at 520 °C for 1 h can be attributed to the $=\mathrm{Sn}^{\cdot\cdot}$ centers in agreement with their absorption features [10, 19, 20].

Concerning the observed diminution of dysprosium ions emission, it is expected that a smaller degree of enhancement associated to excitation of species participating in energy transfer would occur in correspondence to their depletion. However, it can be seen that the excitation spectra for the 4Ag/Sn–Dy glass in Fig. 6b considerably overlay plasmon absorption of Ag NPs in panel (a), whereas the region does not relate directly to excitation of ionic silver species present in the glass, namely the isolated silver ions. In addition, excitation spectra for the 6Ag/Sn–Dy in Fig. 7 show the vanishing of Dy^{3+} excitation peaks in the region within 410 and 495 nm, which lies in the range of dipole mode absorption of NPs and far from excitation of ionic silver species including pairs (vide supra). Thus, interpretation of results calls for consideration of Ag NPs influence on Dy^{3+} ions luminescence [10]. It has been considered by Hayakawa et al. [1] and Malta et al. [13] that an enhancement or quenching effect takes place for RE ions emission in glasses doped with metal NPs depending largely on particle volume fraction. Strohhöfer and Polman [2] also observed a diminution of PL intensity in samples containing Ag particles. Zhu [29] reported that with increasing gold NP content in solution phase, Dy^{3+} luminescence first increases and then decreases. In their theoretical treatment, Malta et al. [30] considered a competition between local field enhancement effects and quenching due to ion-to-particle energy transfer. An effective nonradiative energy transfer mechanism from a RE ion to particle plasmons was proposed to take place under resonant excitation conditions at high particle volume fractions. Our samples were 4 and 6% Ag_2O/SnO where HT conditions support increasing particle volume fractions of the order of $\sim 10^{-5}$ as estimated from the extent of the absorption coefficients. In fact, PL enhancements in Eu-doped silica glass were reported for volume fractions as low as $\sim 10^{-6}$ [1]. Accordingly, samples used in this study would be in the high particle volume fraction regime, where quenching effects may surpass any enhancement due to local field effects associated to NPs, particularly for the glass with higher concentrations of Ag and reducing agent Sn [10, 20]. The selective vanishing of excitation peaks in the heat-treated 6Ag/Sn–Dy glass which are in resonance with the dipole absorption mode of Ag NPs is clear evidence of the excitation energy transfer. Nonradiative energy transfer not only occurs through dipole modes in the NPs but also through higher order multipoles [31]. Thus, in the 4Ag/Sn–Dy glass sample heat treated for 120 min, the quadrupole resonance mode observed could also participate in the loss of excitation energy in Dy^{3+} ions by radiationless energy transfer for near-excitation wavelengths. Consistent with these results and interpretation is the recent report on X-ray photoelectron spectroscopy measurements of europium ions in the same glass system, which pointed out to ion-to-particle energy transfer as the origin of Eu^{3+} PL quenching after HT instead of a $Eu^{3+} \rightarrow Eu^{2+}$ reduction process [15].

Conclusions

Photoluminescence of Dy^{3+} ions in glass containing silver and tin was observed for nonresonant UV excitation close to 270 nm owing to energy transfer from single Ag^{+} ions and twofold-coordinated Sn atoms. With increasing concentration of silver, the formation of silver pairs was observed, which also contributed to Dy^{3+} ions luminescence. In terms of the energy transfer mechanism, consistent with previous results obtained for RE ions in phosphate-based glasses, it seems that an important channel for the transfer of excitation energy to dysprosium ions is the resonant radiative type. In this picture, light absorption would take place either at single silver ions, ionic silver pairs, or twofold-coordinated Sn centers, followed by emission of photons and subsequent reabsorption by Dy^{3+} ions. On the other hand, after HT, a decrease in Dy^{3+} ions emission intensity was observed with increasing holding time for excitation wavelengths relevant for silver NPs absorption. The increase in silver concentration resulted in a more pronounced luminescence quenching effect in connection with an increased particle volume fraction. The formation of small Ag particles is believed to be the main cause for the observed weakening of Dy^{3+} ions PL due to their likelihood to provide paths for the nonradiative loss of excitation energy in dysprosium ions through coupling with NP resonance modes. The present results are consistent with the model predicting a dominance of quenching effects over local field enhancements with increasing particle concentration.

Acknowledgements Financial support from the Alliance for Graduate Education and the Professoriate (AGEP) 2008-2009 Research Fellowship (Award # 0302696), the UPR-M DoE-SR 2008 Research Scholarship, and the Alfred P. Sloan Foundation Minority Ph.D. Program Scholarship is gratefully acknowledged.

References

1. Hayakawa T, Selvan ST, Nogami M (1999) J Non-Cryst Solids 259:16
2. Strohhöfer C, Polman A (2002) Appl Phys Lett 81:1414
3. Hayakawa T, Furuhashi K, Nogami M (2004) J Phys Chem B 108:11301
4. Naranjo LP, de Araújo CB, Malta OL, Santa Cruz PA, Kassab LRP (2005) Appl Phys Lett 87:241914

5. Fukushima M, Managaki N, Fujii M, Yanagi H, Hayashi S (2005) J Appl Phys 98:24316
6. Martucci A, De Nuntis M, Ribaudo A, Guglielmi M, Padovani S, Enrichi F, Mattei G, Mazzoldi P, Sada C, Trave E, Battaglin G, Gonella F, Borsella E, Falconieri M, Patrini M, Fick J (2005) Appl Phys A 80:557
7. Pivin JC, Sendova-Vassileva M, Lagarde G, Singh F, Podhorodecki A (2006) J Phys D Appl Phys 39:2955
8. Trave E, Mattei G, Mazzoldi P, Pellegrini G, Scian C, Maurizio C, Battaglin G (2006) Appl Phys Lett 89:151121
9. Matarelli M, Montagna M, Vishnubhatla K, Chiasera A, Ferrari M, Righini GC (2007) Phys Rev B 75:125102
10. Jiménez JA, Lysenko S, Liu H (2008) J Lumin 128:831
11. Eichelbaum M, Rademann K (2009) Adv Funct Mater 19:2045
12. Kassab LRP, Bomfim FA, Martinelli JR, Wetter NU, Neto JJ, de Araújo CB (2009) Appl Phys B 94:239
13. Malta OL, Santa-Cruz PA, De Sá GF, Auzel F (1985) J Lumin 33:261
14. Link S, El-Sayed MA (2003) Annu Rev Phys Chem 54:331
15. Jiménez JA, Lysenko S, Liu H, Fachini E, Cabrera CR (2010) J Lumin 130:163
16. Sardar DK, Bradley WM, Yow RM, Gruber JB, Zandi B (2004) J Lumin 106:195
17. Jayasimhadri M, Moorthy LR, Kojima K, Yamamoto K, Wada N, Wada N (2006) J Phys D Appl Phys 39:635
18. Peyser LA, Vinson AE, Bartko AP, Dickson RM (2001) Science 291:103
19. Cannizzo A, Leone M, Boscaino R, Paleari A, Chiodini N, Grandi S, Mustarelli P (2006) J Non-Cryst Solids 352:2082
20. Jiménez JA, Lysenko S, Liu H, Fachini E, Resto O, Cabrera CR (2009) J Lumin 129:1546
21. Jiménez JA, Lysenko S, Zhang G, Liu H (2007) J Mater Sci 42:1856. doi:10.1007/s10853-006-0898-6
22. Di Bartolo B (1968) Optical interactions in solids. Wiley, New York (Chap. 18)
23. Mattarelli M, Montagna M, Moser E, Vishnubhatla KC, Armellini C, Chiasera A, Ferrari M, Speranza G, Brenci M, Nunzi Conti G, Righini GC (2007) J Non-Cryst Solids 353:498
24. Weyl WA (1951) Coloured glasses. Society of Glass Technology, Sheffield, p 347, 406
25. Belharouak I, Weill F, Parent C, Le Flem G, Moine B (2001) J Non-Cryst Solids 293–295:649
26. Jiménez JA, Lysenko S, Liu H (2008) J Appl Phys 104:054313
27. Petit L, Griffin J, Carlie N, Jubera V, García M, Hernández FE, Richardson K (2007) Mater Lett 61:2879
28. Arnold GW, Borders JA (1977) J Appl Phys 48:1488
29. Zhu J (2005) Mater Lett 59:1413
30. Malta OL, Couto dos Santos MA (1990) Chem Phys Lett 174:13
31. Wokaun A, Lutz HP, King AP, Wild UP, Ernst RR (1983) J Chem Phys 79:509